U.S. Patent No. 7,128,988
Declaration in Support of Petition for *Inter Partes* Review

UNITED STATES PATENT AND TRADEMARK OFFICE
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BEFORE THE PATENT TRIAL AND APPEAL BOARD
_____

TDK Corporation,
Petitioner

v.

Lambeth Magnetic Structures, LLC
Patent Owner

Patent No. 7,128,988
Issue Date: October 31, 2006
Title: MAGNETIC MATERIAL STRUCTURES,
DEVICES AND METHODS

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Inter Partes Review No. _____

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**DECLARATION OF DR. ROBERT SINCLAIR IN SUPPORT OF
PETITION FOR *INTER PARTES* REVIEW**

UNDER 35 U.S.C. §§ 311-319 AND 37 C.F.R. § 42.100 *et seq*.

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Exhibit List for Declaration of Dr. Robert Sinclair

Exhibit Description	Exhibit
PCT Publication No. WO 03/021579	A
Jin (U.S. Patent No. 5,998,048)	B
Kadau I (K. Kadau, R. Meyer, P. Entel, "Molecular-Dynamics Study of Thin Iron Films on Copper," Surface Review and Letters 6, 1, 35-43 (1999));	C
Pinarbashi (U.S. Patent No. 6,295,187)	D
P. Álvarez-Alonso, A. Pérez-Checa, I.R. Aseguinolaza, J. Alonso, A.V. Svalov, V.A. Chernenko, J.M. Barandiarán, "Fabrication of Patterned Ferromagnetic Shape Memory Thin Films," Key Engineering Materials, Vol. 644, pp. 219-22, May 2015.	E
Pierre Villars, Material Phases Data System (MPDS), CH-6354 Vitznau, Switzerland; SpringerMaterials; sd_0555891 (Springer-Verlag GmbH, Heidelberg, 2014), http://materials.springer.com/isp/crystallographic/docs/sd_0555891 originally accessed: 29-08-2015; copy dated 19_09_2015.	F
W. F. Smith "Principles of Materials Science and Engineering" McGraw-Hill, New York (1990, 1996), p. 94 et seq.;	G
Metals Handbook, Volume 8, American Society for Metals, p. 251 et seq. (1973)	H
L. J. Swartzendruber et al., J. of Phase Equilibria, vol. 12, pp. 288-312 (1991);	I
Curriculum Vitae of Dr. Robert Sinclair	J

1.   I, Robert Sinclair, Ph.D., submit the following declaration (the

"Declaration") in connection with the proceeding identified above.

I.   INTRODUCTION

2.   I have been retained by counsel for TDK Corporation ("TDK") as a

technical expert in connection with the proceeding identified above. I submit this

Declaration in support of Petitioner TDK's Petition for *Inter Partes* Review

("Petition") of United States Patent No. 7,128,988 ("the '988 patent") (Ex. 1001)

against Patent Owner Lambeth Magnetic Structures, LLC ("Lambeth"). All

"Ex. 10__" cites herein are to the Exhibits to the Petition. All "Ex. _" cites with

letters A through I herein are to Exhibits to this Declaration.

3.   I understand that Lambeth has filed a patent infringement lawsuit in

the U.S. District Court for the Western District of Pennsylvania alleging

infringement by Toshiba Corporation, Toshiba America Information Systems, Inc.,

Toshiba America Electronic Components, Inc., and Toshiba Of Canada, Ltd.

(collectively "Toshiba") of claims 1, 3, 6, 8, 11, 12, 17, 19, 23, 27, 28, and 29 (the

"asserted claims") of the '988 patent. *Lambeth Magnetic Structures*, *LLC v*.

Toshiba Corp., Civil Action No. 2:14-cv-01526-CB (W.D. Pa.).

4.   For the purposes of this Declaration, I will address the asserted claims

of the '988 patent and selected other claims of the '988 patent. I have omitted

from my analysis several claims that, in my view, cannot reasonably be asserted against Toshiba. However, inclusion of a claim in my analysis is not an indication that I believe it could reasonably be asserted against Toshiba. If, at any time in the future, additional claims are asserted by Lambeth against Toshiba, I reserve the right to amend or supplement this Declaration accordingly.

II.   BACKGROUND AND QUALIFICATIONS

5.   My curriculum vitae is attached (Ex. J). I am a professor of Materials Science and Engineering at Stanford University. At Stanford, I head a research group studying microelectronic and magnetic thin film microstructure. We primarily use transmission electron microscopy ("TEM") to image materials of interest at the atomic level. Doing so provides microstructural information necessary for the understanding of structural, electrical, and magnetic properties of those materials. We routinely examine materials of interest both to magnetic data storage and devices relating to that application.

6.   I joined the faculty of the Department of Materials Science and Engineering at Stanford in 1977. I have been a professor there ever since. I have also directed Stanford's Nanocharacterization Lab from 2002-2013. I became the Chair of the Department of Materials Science and Engineering in 2004 and served in that capacity until 2014. During the time I have been at Stanford, my research

has touched on various aspects of magnetic materials, materials used in the context of data storage, and thin film deposition.

7. Prior to being at Stanford, I held research positions at the University of Newcastle-upon-Tyne and the University of California, Berkeley. Before that, I received my B.S. and Ph.D. degrees in Materials Science from Cambridge University (UK).

8. I have authored around 250 refereed, scientific journal articles and over 200 conference proceedings in materials and physical science. Of these, I would estimate that approximately 30 percent directly or indirectly concern magnetic materials and/or thin film applications of magnetic materials. I have also authored six edited works and seven book chapters. Several of these touched upon some aspect of magnetic materials and/or thin film deposition.

9. For my research and work as an educator, I have received a number of awards. These awards include the Robert Lansing Hardy Gold Medal of the Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME), the Eli Franklin Burton Award of the Electron Microscopy Society of America, an Alfred P. Sloan Foundation Fellowship, and the Marcus E. Grossman Award of the American Society for Metals. I have also received two awards for Excellence in Undergraduate Teaching at Stanford, and most recently the Distinguished Scientist Award (Physical Sciences) of the

Microscopy Society of America in 2009, and the David M. Turnbull Lectureship of the Materials Research Society in 2012.

10.   In addition, I am very active in several professional societies. These societies include the Materials Research Society (MRS) and the Microscopy Society of America (MSA). I am also active in the organization of symposia and workshops on electron microscopy. Recent examples include the workshops on "Advanced and In Situ Microscopies of Functional Nanomaterials and Devices (IAMNano)" held in Krakow, Poland (2012), Rio de Janeiro, Brazil (2014), and Hamburg, Germany (2015) and the international conferences on "Remote Electron Microscopy and In Situ Studies," held at Stanford University (2008), Gothenburg, Sweden (2010), Pittsburgh, Pennsylvania (2011), and Lisbon, Portugal (2013). I have also organized numerous symposia at electron microscopy and materials research conferences and workshops. I was also invited to serve as Chair of the U.S. National Research Council's Committee on Smaller Facilities from 2003-2006, which is a rare responsibility on behalf of the National Academy of Sciences (NAS). This culminated in a 230 page report entitled "Midsize Facilities: Infrastructure for Materials Research" published by NAS in 2006.

11.   During my tenure at Stanford University, I have been actively involved in teaching and education, as well as scientific research, at both the undergraduate and graduate level. For instance, I have taught a course on

"Introduction to Materials Science" to undergraduates since 1977, which includes the structure and magnetic properties of materials and has involved approximately 3,000 students over the years. Likewise I have taught graduate courses on "Atomic Arrangements in Solids," "Nanocharacterization of Materials," and "Transmission Electron Microscopy."

12. I am being paid at an hourly rate for my work on this matter. I have no personal or financial stake or interest in the outcome of the present proceeding.

III. MATERIALS CONSIDERED

13. I have considered information from various sources in forming my opinions. Besides drawing from almost three decades of research and development in the area of distributed computing systems, I also have reviewed the following documents: (a) the '988 patent (Ex. 1001); (b) the prosecution file history of the '988 patent (including Ex. 1002); (c) PCT Publication No. WO 03/021579, the publication of international application, PCT /US02/27327, to which the '988 patent claims priority (Ex. A); (d) J. Shen, M. Klaua, P. Ohresser, H. Jenniches, J. Barthel, Ch. V. Mohan, J. Kirschner, "Structural and magnetic phase transitions of Fe on stepped Cu (111)," Phys. Rev. B 56, 17, 134-143 (1997) ("Shen") (Ex. 1011); (e) U.S. Patent No. 6,023,395 ("Dill") (Ex. 1009); (f) U.S. Patent No. 5,998,048 ("Jin") (Ex. B); (g) K. Kadau, R. Meyer, P. Entel,

"Molecular-Dynamics Study of Thin Iron Films on Copper," Surface Review and Letters 6, 1, 35-43 (1999) ("Kadau I") (Ex. C); (h) D.N. Lambeth, W. Yang, H. Gong, D.E. Laughlin, B. Lu, L.L. Lee, J. Zou, P.S. Harllee, "Magnetic Media Performance: Control Methods for Crystalline Texture and Orientation," Mat. Res. Soc. Symp. Proc. Vol. 517, 181 192 (1998) ("Lambeth I") (Ex. 1013); (i) U.S. Patent No. 5,862,022 ("Noguchi") (Ex. 1014); (j) U.S. Patent No. 6,295,187 ("Pinarbashi") (Ex. D); (k) U.S. Patent No. 5,465,185 ("Heim") (Ex. 1012); (l) TDK's Petition for *Inter Partes* Review of the '988 patent (the "Petition"), to which this Declaration is being submitted as Exhibit No. 1006; and (m) the other documents and references as cited herein. I reviewed the Petition in detail and agree with both its analysis and conclusions.

IV. LEGAL STANDARDS

14.   I have relied on instructions from counsel as to the applicable legal standards to use in arriving at my opinions in this Declaration.

15.   I have been informed and understand that patent claims are construed from the perspective of one of ordinary skill in the art at the time the claimed invention was made and that, during this proceeding, claims are to be given their broadest reasonable construction consistent with the specification.

16.   I have been informed and understand that a patent claim is invalid because of anticipation when every element of the claim is described in a single prior art reference, such that the elements are arranged as required by the claim. I have been informed and understand that the description of a claim element in a prior art reference can be express or inherent. For a prior art reference to describe a claim element inherently, the claim element must be necessarily present. Probabilities are not sufficient to establish inherency.

17.   I have also been informed and understand that the subject matter of a patent claim is obvious if the differences between the subject matter of the claim and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which the subject matter pertains. I have also been informed that the framework for determining obviousness involves considering the following factors: (i) the scope and content of the prior art; (ii) the differences between the prior art and the claimed subject matter; (iii) the level of ordinary skill in the art; and (iv) any objective evidence of non-obviousness.

18.   I further understand that the claimed subject matter would have been obvious to one of ordinary skill in the art if, for example, it results from the combination of known elements according to known methods to yield predictable results, the simple substitution of one known element for another to obtain

predictable results, the use of a known technique to improve similar devices in the same way, or the application of a known technique to a known device ready for improvement to yield predictable results. I have also been informed that the analysis of obviousness may include recourse to logic, judgment, and common sense available to the person of ordinary skill in the art that does not necessarily require explication in any reference. I understand that so-called "secondary considerations of non-obviousness," must be considered in an obviousness analysis. I understand that an analysis including these secondary considerations helps to prevent the forbidden use of hindsight in determining whether a patent claim is obvious. I understand that secondary considerations of non-obviousness include: (a) a long-felt but unresolved need for the invention; (b) commercial success of the invention; (c) copying of the invention; (d) praise and recognition of the invention by others; (e) licensing of the rights to the invention; and (f) unexpected results. In rendering my opinions, I followed these guidelines.

19. In my opinion, a person of ordinary skill in the art pertaining to the '988 patent at the relevant date would have an undergraduate degree in materials science, physics, or chemistry, and two to four years of experience in the design of magnetic materials. Relevant professional or practical experience or degrees in other subject areas where a person would gain experience with distributed computing systems may also suffice.

20.   Based on my education and experience in the field of materials science set forth above, I believe I am qualified to provide opinions about how one of ordinary skill in the art at the relevant time would have interpreted and understood the '988 patent and the prior art discussed herein.

V.   BRIEF OVERVIEW OF THE '988 PATENT

A.   Summary of the '988 Patent

21.   The '988 patent (Ex. 1001), titled "Magnetic Material Structures, Devices and Methods," issued from the national stage of International Patent Application No. PCT/US02/27327, which was filed on August 29, 2002. The '988 patent entered the national stage in the United States under 35 U.S.C. § 371 (c) on August 29, 2003. The '988 patent issued on October 31, 2006.

22.   The '988 patent is directed to "a structure to achieve uniaxial magnetocrystalline orientation via the use of the (110) texture of body centered cubic (bcc) or body centered cubic derivative crystal thin film structures."

(Ex. 1001, 12:58-13:2.)[1] In particular, the '988 patent describes "the invention" as "orientation control of bcc and bcc derivative materials." (Ex. 1001, 13:4-8.) "The invention" is applied in various devices to cause "good orientation, high magnetization, high permeability and low losses." (Ex. 1001, 13:4-8.)

23.   The '988 patent focuses on achieving "uniaxial [magnetic] anisotropy," which the '988 patent defines as the situation in which the "anisotropy energy density function only contains a single maximum and a single minimum" when the magnetization angle is rotated 180º. (Ex. 1001, 1:56-60.) The '988 patent explains that whether or not a thin magnetic film will exhibit uniaxial anisotropy is related to film structure, specifically to the presence and orientations of so-called crystallographic "variants." (*Id.*, 14:34-55.) Variants form as thin, crystal films grow epitaxially on a particular surface. (*Id.*) Different crystal variants tend to form during formation of the films in order to minimize the interfacial and surface energy of the newly forming film. It is possible to influence

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[1] The '988 patent uses the term "bcc-d" structure, which the '988 patent defines as "either a bcc or a bcc derivative crystal structure." (Ex. 1001, 14:66-67.) One of ordinary skill in the art would have understood this phrase to denote an elemental crystal having a bcc structure or a crystalline compound having a structure that is based on the bcc structure.

or determine the number and type of variants by controlling various parameters during the film deposition process. (*Id.*, 14:48-65.)

24. The inventor of the '988 patent purports to have discovered an entirely new system or set of six variants in a particular film growth regime, specifically the growth of bcc-d structured films on a (111) plane surface. (*Id.*, 14:49-53.) There is one important and allegedly unique advantage of the system. This six-variant system allegedly allows achieving uniaxial anisotropy by breaking the symmetry of the crystallographic variants. (*Id.*, 14:49-55.) The '988 patent asserts that prior known crystallographic variants for this materials system would not yield uniaxial anisotropy even where symmetry is broken.

B. '988 Patent Prosecution History

25. On August 29, 2003, Application No. 10/415,757 (the "'757 Application") (Ex. 1002) entered the national stage in the U.S. Patent and Trademark Office ("USPTO") under 35 U.S.C. § 371 (c). The original application had 65 total claims, including 8 independent claims. The Applicant canceled all claims and provided a new claim set via preliminary amendment on March 23, 2004. On September 8, 2005, the Examiner issued a restriction requirement with respect to those claims. In response to that requirement, on September 19, 2005, the Applicant chose to prosecute the claim set directed to "magnetic material[s] structure and magnetic device."

26.   On December 19, 2005, the USPTO issued a Non-Final Rejection rejecting claims 118-30, 134-37, and 140-58 based on 35 U.S.C. § 102 as being anticipated by or, in the alternative, under 35 U.S.C. § 103, as being obvious in view of Lambeth, et al. (U.S. Patent No. 6,248,416) ("Lambeth '416."). (Ex. 1003.) The Examiner also indicated that claims 131-33, 138, and 139 contained allowable subject matter and further rejected claim 157 under 35 U.S.C. § 112.

27.   On March 17, 2006, the Applicant responded to the Office Action. (Ex. 1004.) In the response, the Applicant amended claim 157 to overcome the rejection under 35 U.S.C. § 112. (*Id.*, p. 12.) The Applicant traversed the rejections under 35 U.S.C. § 102/103 by arguing that Lambeth '416 did not disclose uniaxial symmetry broken structure because Lambeth '416 relates to the growth of an (fcc) magnetic layer. (*Id.*, p. 14.) The Applicant argued that (fcc) magnetic structures cannot achieve such symmetry. (*Id.*) The Applicant further argued that, though Lambeth '416 "did disclose the use of a (111) template under a (110) bcc layer, . . . only 3 variants were found . . . [and such a] 3 variant system will not yield the desirable uniaxial symmetry broken magnetic properties of the present invention." (*Id.*) Applicant further made the statement that the "claimed substrate . . . is not considered by the Applicant to be novel." (*Id.*, p. 15.)

28. In response to Applicant's arguments, the Examiner issued a notice of allowance on July 28, 2006, of all pending claims directed toward the elected species. (Ex. 1005.) The only reasons given for allowance were that "Lambeth '416 fails to teach or suggest a uniaxial symmetry broken structure and a hexagonal (111) atomic template with a bcc-d magnetic layer (*see* Applicant's arguments in the response filed 3/17/06)." (*Id.*, p. 3.) The Applicant paid the issue fee on September 13, 2006, and the '757 Application issued as U.S. Patent No. 7,128,988 on October 31, 2006. The Applicant filed a Request for a Certificate of Correction on November 3, 2010, to add a priority claim to U.S. Provisional Application No. 60/315,920, filed on August 29, 2001. The Certificate Issued on December 7, 2010.

C.   '988 Patent Claims

29. Lambeth has asserted independent claims 1 and 27 and dependent claims 3, 6, 8, 11, 12, 17, 19, 23, 28, and 29 of the '988 patent against Toshiba. I understand the Petition challenges the patentability of claims 1-3, 6-19, 21-31, 34, 38, and 39. I address these claims below. Claim 1 is representative of the independent claims of the '988 patent.

1. [a] A magnetic material structure comprising:

a substrate;

[b] at least one bcc-d layer which is magnetic,

[c] forming a uniaxial

[d] symmetry broken structure; and

[e] at least one layer providing a (111) textured

[f] hexagonal atomic template disposed between said substrate and said bcc-d layer.

2. The magnetic material structure recited in claim 1, wherein said substrate is single crystal.

3. The magnetic material structure recited in claim 1, wherein a surface of said substrate is amorphous or polycrystalline.

6. The magnetic material structure recited in claim 1, wherein the layer providing said hexagonal atomic template is formed from a fcc-d or hcp crystalline material.

7. The magnetic material structure recited in claim 1, wherein the layer providing said hexagonal atomic template is magnetic.

8. The magnetic material structure recited in claim 1,

> wherein said bcc-d layer is epitaxially grown on said (111)
> textured hexagonal atomic template and has a (110) crystalline
> texture, and at least one crystalline grain of said (111) textured
> hexagonal atomic template has epitaxially grown thereon at
> least two and not more than four dominate (110) orientational
> variants.

9. The magnetic material structure according to claim 1, further comprising:

> a second layer providing a (111) textured hexagonal atomic
> template, wherein said second layer is magnetic.

10. The magnetic material structure according to claim 1, further comprising: a second bcc-d layer which is non-magnetic.

11. The magnetic material structure according to claim 1, further comprising: a second bcc-d layer which is magnetic.

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12. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer

wherein the crystalline orientation of the second bcc-d layer is epitaxially determined by said bcc-d layer.

13. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer; and a second layer providing a (111) textured hexagonal atomic template wherein said second layer providing a (111) textured hexagonal atomic template is disposed between said bcc-d layers.

14. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer, which is magnetic; and

at least one oxide layer between said bcc-d layers.

15. The magnetic material structure according to claim 1, further comprising:

a second and a third bcc-d layers which are non-magnetic;

a fourth bcc-d layer which is magnetic;

and at least one oxide layer between said second bcc-d layer and said third bcc-d layer

wherein said second and third bcc-d layers are disposed between said first and fourth bcc-d layers.

16. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer which is magnetic;

a second (111) textured hexagonal atomic template layer between said bcc-d layers; and

at least one oxide layer between said bcc-d layers.

17. The magnetic material structure recited in claim 1, wherein said bcc-d layer forming a uniaxial symmetry broken structure is composed of Fe or FeCo or an alloy of Fe or FeCo.

18. The magnetic material structure recited in claim 1, wherein said bcc-d layer forming a uniaxial symmetry broken structure is composed of an alloy of Fe or FeCo having one or more of the elements Al, B, Cr, C, Cu, Ni, N, Nb, Mo, V, Si, Ta, and Ti.

19. The magnetic material structure recited in claim 1, wherein the layer material forming said (111) textured hexagonal atomic template is composed of Ag, Al, Au, Cu, fcc-Co, fcc-CoCr, Ir, Ni, NiFe, Pt, Rh, Pd, hcp-Co, Gd, Re[,] Ru, Tb, Ti, or alloys of one of these materials combined with at least one element.

21. The magnetic material structure according to claim 1, further comprising:

    a coupling layer; and

    a second bcc-d layer which is magnetic

wherein the coupling layer material antiferromagnetically couples the bcc-d layers.

22. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer which is magnetic; and

a third bcc-d layer disposed between the bcc-d layers which are magnetic.

23. The magnetic material structure according to claim 1, further comprising:

a second bcc-d layer which is magnetic; and

a second (111) textured hexagonal atomic template layer

wherein said second (111) textured hexagonal atomic template is disposed between said bcc-d layers.

24. The magnetic material structure according to claim 1, further comprising:

at least one magnetic hcp Co alloy layer.

25. The magnetic material structure according to claim 1, further comprising:

at least one magnetic hcp Co alloy layer;

wherein said hcp Co alloy has a (1011) crystalline texture.

26. The magnetic material structure according to claim 1, wherein:

said substrate is a (111) crystalline textured single crystal; and

a surface of said single crystal provides a layer providing the (111) textured hexagonal atomic template

disposed between the bulk of said substrate and said at least one bcc-d layer.

27. A magnetic device having incorporated therein a magnetic material structure material comprising:

a substrate;

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at least one bcc-d layer which is magnetic,

forming a uniaxial

symmetry broken structure; and

at least one layer providing a (111) textured

hexagonal atomic template disposed between said substrate and

said bcc-d layer.

28. The magnetic device recited in claim 27, wherein the device is a
magnetic data storage system.

wherein the device is a magnetic data storage system.

29. The magnetic device recited in claim 27,

wherein the device is a data storage magnetic recording

transducer.

30. The magnetic device recited in claim 27, wherein the device is at

least one of:

an anisotropic magnetoresistive sensor; a spin valve magnetoresistive sensor; a magnetic tunnel junction magnetoresistive sensor and a data storage magnetic playback transducer.

31. The magnetic device recited in claim 27, wherein the device is at least one of:

a data storage magnetic recording media; a data storage magnetic recording media incorporating an oriented soft magnetic layer; and a data storage magnetic recording media incorporating an oriented hard magnetic layer.

34. The magnetic device recited in claim 27, wherein the device is at least one of:

an electronic circuit inductive component and an electronic circuit inductive transformer component.

38. The magnetic device according to claim 27, further comprising:

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at least one hard magnetic layer; wherein said at least one bcc-d

layer which is magnetic, forming a uniaxial symmetry broken

structure, is disposed between said (111) textured hexagonal

atomic template and said at least one hard magnetic layer.

39. The magnetic device according to claim 27, further comprising:

at least one hard magnetic layer; wherein said at least one hard

magnetic layer is disposed between said substrate and said at

least one bcc-d layer.

30. As discussed in ¶ 24, *supra*, and explored in more detail below, the

independent claim 1 system can be schematically represented as follows:

$\vdots$ To other layers

[1b] magnetic bcc-d layer:	(110)(bcc)
[1e] (111) textured hexagonal template:	(111)(fcc) or (0002)(hcp)

$\vdots$ To substrate [1a] and other layers

(Schematic A: Structure in claim 1 of the '988 patent.)

The '988 patent provides (111) (fcc) or (0002) (hcp) as two examples of the

claimed (111) textured hexagonal template. (Ex. 1001, 14:55-57.) Although the

'988 patent does not explicitly label (111)(fcc) and (0002)(hcp) as surface

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structures, one of ordinary skill in the art would have understood that to be the meaning.

D.   '988 Patent Filing Date

31.   The '988 patent is the national stage of International Patent Application No. PCT/US02/27327, which was filed on August 29, 2002, and properly designated in the United States for national stage entry. Application No. PCT/US02/27327 entered national stage in the United States one year later, on August 29, 2003. Therefore, I have been advised by counsel, under 35 U.S.C. § 371 (c), the '988 patent is entitled to the August 29, 2001 filing date of Provisional Application No. 60/315,920.

VI.   STATE OF THE ART

32.   Generally, and in the context of the '988 patent (Ex. 1001), "magnetic materials" are those that retain their own magnetic fields. The direction of the internal field is referred to as "magnetization" or "magnetization direction." The magnetic materials relevant to sensors, magnetic recording (*e.g*., read/write heads) and many other devices are generally in thin film form or stacks of thin films. They are typically grown onto a substrate by various vapor phase deposition techniques which include both physical vapor deposition (PVD) or chemical vapor deposition (CVD). Controlling the deposition processing can allow control of the

structure and magnetic properties of the resulting films, so long as structure/property relationships in the films are well-understood. Depending on the application, the thin film material can be employed while it remains on the substrate or can be removed from the substrate.

33.   Many magnetic devices employ the natural crystalline anisotropy associated with the crystal structure of the magnetic material. "Magnetic anisotropy" is a material's overall preference for a particular magnetization direction. A more anisotropic material will often have a greater preference. "Uniaxial anisotropy" is a severe form of anisotropy represented by a preference for a single axis such as the "easy magnetization axis." One such property could be the "easy" magnetization axis in which the material is more easily magnetized by an applied magnetic field in one specific crystallographic direction. When there is only one such axis, the "easy magnetization axis," the material is said to have "uniaxial anisotropy." As has been known for at least fifty years, magnetic anisotropy, and uniaxial anisotropy in particular, is advantageous in magnetic recording. Magnetic recording heads, for example, need to sustain magnetization in a particular direction, regardless of the influence of exterior magnetic fields. A write head incorporating a material with uniaxial anisotropy will not easily change its magnetization direction under the influence of local fields. (*See*, *e.g*., Ex. 1007, pp. 81-171.)

34.   Because of their very nature, crystalline materials have various symmetries associated with their structure, in which the atomic arrangements in separate but well-defined crystallographic orientations are identical resulting in identical magnetic or other physical or chemical properties. Materials with cubic symmetry such as (bcc), body-centered cubic structure, and (fcc), face-centered cubic structure, have the highest degree of symmetry of all known materials. There are exact interangular relationships between these "crystallographically equivalent" directions.

35.   The underlying substrate on which a thin film is grown, often referred to as a "template" or an "atomic template," will often dictate the film's structure and symmetry. In the absence of a template's "encouragement" to grow with a particular structure, a thin film will generally adopt the "natural" structure of the material the thin film comprises. As discussed above, so-called "body centered cubic" (bcc) and "face centered cubic" (fcc) structures are common among magnetic materials. It was well-known that when (bcc) structure phases grow in, or on, (fcc) structure phases that certain specific orientation relationships between the crystal structures are preferred. When the atoms in the two crystal phases have similar diameter (such as in (fcc) and (bcc) iron, (fcc) Ni, (fcc) Cu, (fcc) and (hcp) Co, (bcc) Cr and others) the most common orientation relationship is that described by G. Kurdjumov and G. Sachs (Z. Phys., vol. 64, p. 325 (1930)). In this case, the

closest packed planes and close packed directions are parallel. In crystallographic nomenclature this can be written as (fcc) (111) is parallel to (bcc) (110) for the close packed planes, and (fcc) [1$\bar{1}$0] is parallel to (bcc) [1$\bar{1}$1] for the close packed directions. As described in Shen, there are six possible (bcc) variants for each (fcc) close packed plane, "six kinds of atomic relationship between the bcc(110) and fcc(111) structure." (Ex. 1011, p. 137, ¶ 1; FIG. 4.) Shen describes these six variants as "KS domains," where "KS" stands for "Kurdjumov-Sachs." (*Id*.) One of ordinary skill in the art would have understood that these six crystallographic variants (KS domains) discussed by Shen in the (111)(fcc)/(110)(bcc) system are the same set of six crystallographic variants identified by the '988 patent. (Ex. 1001, 14:47-62.)

36. So-called crystallographic "variants" form naturally in films deposited on surfaces. The variants are crystals having the same structure, but different orientations relative to the atomic template on which the variants grow. Below is a schematic illustration of two crystallographic variants (A and B) each grown on the same atomic template, but having different orientations.
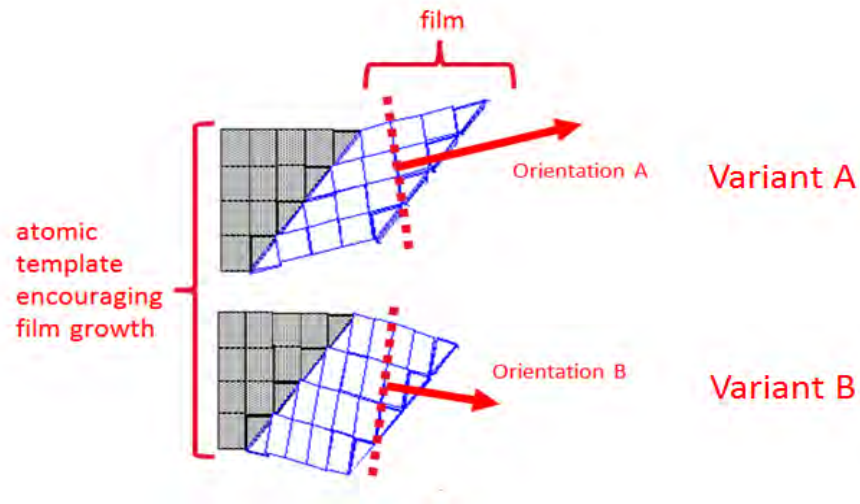
(Variant Growth Schematic adapted from Ex. E, pp. 219-22.)

37.   The orientation of a crystallographic variant can dictate its preferred magnetization direction. Moreover, variants forming on the same surface as part of a single film do not necessarily have the same preferred magnetization direction. When they do not, the presence of multiple, opposing variants may lessen or diminish the degree of magnetic anisotropy in the film. For this reason, increasing the volume fraction of certain variants over others has been a known way to increase magnetic anisotropy for decades. (*See*, *e.g*., Ex. 1008, p. 5777 (teaching enhancing anisotropy "by either nucleating favorable variants or increasing the volume fraction of the favorable variants.").) The '988 patent describes a "symmetry broken" structure in terms of crystallographic variants. (*See*, *e.g*., Ex. 1001, 23:37-41.) More specifically, the '988 patent describes a "symmetry broken" structure as one that does not include equal amounts of all variants in a

particular variant system, such as the six variant system found in (110)(bcc) films when grown on (111)(fcc) surfaces. (*Id.*) Therefore, one of ordinary skill in the art would have understood the meaning of ordinary meaning of a "symmetry broken" structure to be a structure with unequal volumes of crystallographic variants in either a three or six variant system.

38.   The highest degree of crystallographically preferred orientation is obtained when a single crystal thin film is grown epitaxially onto an underlying perfect single crystal substrate. The directionally determined properties of the thin film material are then determined by the crystallographic orientation of the thin film, as imposed by growth on the underlying substrate, and the crystallographic symmetry associated with specific directions normal to and within the thin film material.

39.   In many practical magnetic thin film sensors and related devices, the substrate is generally not a single crystal. It may be polycrystalline with random orientations, polycrystalline with preferred orientations, or even amorphous with no regular crystalline structure. Likewise, in many practical magnetic thin film sensors and related devices, an underlayer crystalline material is often grown first on the substrate to impart crystallographic preferred orientation on the subsequently grown magnetic thin film. It has been known for decades in materials science and physics that thin films can be grown under appropriate

conditions so that there is a preferred growth direction in the thin film (*i.e.*, perpendicular to the thin film plane) with its associated crystallographic symmetries. In the vast majority of cases, the thin films are polycrystalline with their crystal sizes determined by the growth conditions and with random orientations of the crystals "in plane."

40.   It has also been known for decades that there are specific growth methods whereby the random crystallographic orientations of the polycrystalline thin film material can be reduced to achieve preferred growth orientations, with associated anisotropic preferred magnetic properties. These include employing a stepped substrate or a substrate with polished grooves, depositing the thin film at an oblique angle to the substrate, depositing a magnetic thin film in an applied, defined magnetic field, etc. The degree of preferred orientation is dependent on the exact conditions used involving multiple parameters such as deposition rate, substrate temperature, background vacuum conditions, surface cleanliness and so on. A "preferred orientation" in plane is achieved under special combinations of circumstances and is very rarely, if ever, exactly perfect.

41.   Manipulation of structures of thin films used in magnetic device applications has been routine for decades. (Ex. 1001, 1:1-12:56.) In particular, it was well-understood in the art long before August 2001 that an "atomic template," *i.e.*, an underlying material surface as a structural scaffold, can be used to build,

grow, or deposit[2] an overlying layer that follows the crystalline structure of the template. (*Id.*) Influencing film structure is important, technologically, for a number of reasons, not the least of which is to improve magnetic properties of the grown film(s). (*Id.*; *see also* Ex. 1010, p. 9365.)

42. One very common film growth substrate is a hexagonally close packed (hcp) surface. "Close packed" means an arrangement of atoms in which the density is highest and the atoms are surrounded in the plane by the maximum number of neighbors (*i.e.*, six each), as shown in Shen's Fig. 4, reproduced in ¶ 49 below. Several kinds of hexagonally close-packed surface have been used for film growth, but one of the most common is (111)(fcc). (*See*, *e.g.*, Ex. 1010, p. 9375.) Using these surfaces as templates can be advantageous because their high atomic density, and other properties, facilitate known structural variations in thin films grown on their surfaces. For the purposes of growing thin films, different hexagonally close-packed surfaces provide equivalent or nearly equivalent surface templates. For example, film growth will likely not be very sensitive to differences between (111)(fcc) and (0002)(hcp) close packed surfaces, which both provide a (111) textured hexagonal close packed surface template.

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[2] Note that one of ordinary skill in the art would have used these terms somewhat interchangeably.

43.   The basic film structure of a (bcc) magnetic film grown on a

hexagonally close packed surface, such as (111)(fcc) or (0002)(hcp) is common for

reasons mentioned above. Moreover, some common ferromagnetic materials, such

as Fe, have a natural (bcc) structure at room temperature. (*See*, *e.g*., Ex. H, p. 251

et seq.; *see also* Ex. G, p. 94 *et seq.*) Other common magnetic materials, such as

Ni, have a natural (fcc) structure. When bcc materials form films on close-packed

surfaces, they tend to form a (110) orientation of the bcc crystalline structure, *i.e.*,

the closest packed bcc (110) plane lies on and parallel to the close packed fcc (111)

plane.

44.   Use of a hexagonal atomic template, such as (111)(fcc), for growing

magnetic thin films was well known long before the August 29, 2001 effective

filing date of the '988 patent. Moreover, as the '988 patent shows at least in

FIG. 3, crystallographic variants in this very system had been characterized before

2001. (Ex. 1001, 10:20-11:27; 11:33-12:54.) Also, their relationship to properties

such as magnetic anisotropy was understood before 2001.

VII.   ANALYSIS OF THE PRIOR ART

45.   There are a number of patents and publications that constitute prior art

to the '988 patent. The primary prior art references used in the invalidity grounds,

together with their filing date, are set forth in the table below. A description of these prior art references follows.

Ground	Reference(s)	Basis	Claims
1	Shen and Dill	35 U.S.C. §103	1 and 27
2	Dill and Shen	35 U.S.C. §103	1, 3, 6-11, 13-14, 17-19, 22, 24, 27-30, 34, and 38
3	Dill, Shen, and Heim	35 U.S.C. §103	12, 15, 16, 21, and 23
4	Dill, Shen, and Lambeth I	35 U.S.C. §103	2, 25, 26, and 31
5	Dill, Shen, and Noguchi	35 U.S.C. §103	39

46. As I discussed above, it is my understanding that, for the purposes of this proceeding, the earliest priority date that the '988 patent can claim is August 29, 2001. (*See* V(D) *supra*.)

47. In the following sections, I provide a brief summary of each of the prior art references in my analysis. Based on the filing dates and/or publication dates of the below-listed prior art, it is evident that each of them is prior art to the '988 patent.

A. J. Shen, M. Klaua, P. Ohresser, H. Jenniches, J. Barthel, Ch. V. Mohan, J. Kirschner, "Structural and magnetic phase transitions of Fe on stepped Cu (111)," Phys. Rev. B 56, 17 (1997) ("Shen")

48.   J. Shen et al. published a scientific paper in the journal Physical Review B titled "Structural and magnetic phase transitions of Fe on stepped Cu (111)" on November 1, 1997. Shen discloses that the (111)(fcc)/(bcc) system has symmetry breaking (dominance of two KS variants over the other four) (Ex. 1011, p. 137, ¶ 1; FIG. 4) and substantially increasing magnetization of the overlying layer. (*Id.*, p. 134, ¶ 4 (5).) In a (111)(fcc)/(bcc) material, there are six possible crystalline orientation variants. The '988 patent explains that "symmetry broken structure" means that the layer "do[es] not contain an equal amount of all six of the [possible] (110) textured bcc-d variants [*i.e.*, "KS domains"]." (Ex. 1001, 23:38-41.) This would also have been understood as the meaning by one of ordinary skill in the art. Shen discloses that symmetry breaking increases the magnetic field required to saturate the layer and contributes to uniaxial anisotropy, improving the magnetic properties of the bcc layer. (*Id.*, p. 139, left column.) Later, the '988 patent defines "the invention" as orientation control [*i.e.*, symmetry breaking] of bcc and bcc derivative materials," allowing "new devices to be constructed, which have… high magnetization…." (Ex. 1001, 13:2-8.)

49.   More specifically, Shen discloses the bi-layer materials system of
(bcc) Fe grown on Cu(111), *i.e.*, (111)(fcc)Cu /(bcc) Fe. (*See*, *e.g.*, Ex. 1011,
FIG. 1.)
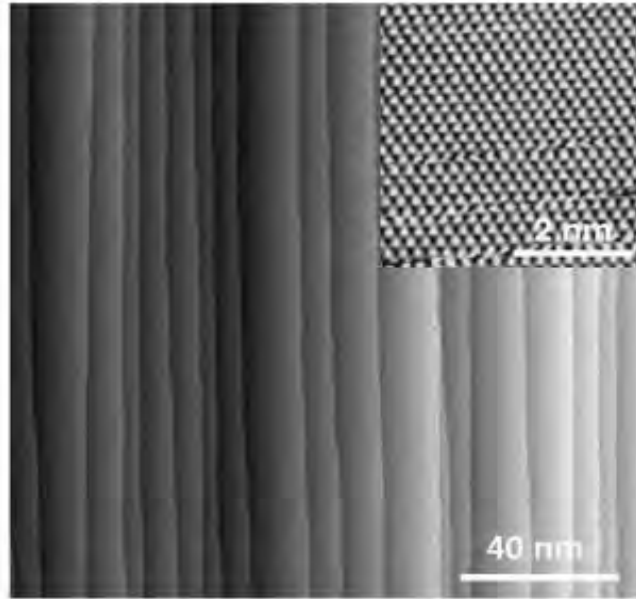
FIG. 1. STM topography image of a well-prepared Cu(111)
vicinal surface. The atomic steps are parallel and oriented along
(011) direction. The inset is an atomically resolved image (I,
$=0.25$ nA, $V_{bias}=10$ mV) recorded from a terrace showing the six-
fold symmetry of the Cu(111) surface.

(*Id.*, FIG. 1.)

50.   The Fe films were deposited in an MBE preparation chamber
(Ex. 1011, p. 135, ¶ 1) on top of the surface of the substrate which was cut at a
slight 1.2º miscut with respect to the (111) orientation (*id.*, p. 134, ¶ 2; p. 135, ¶ 2)
in order to form steps (*id.*, FIG. 1). The Fe films were grown epitaxially on the
(111)(fcc) surface, which has a hexagonal structure. Shen shows both epitaxial
growth and the hexagonal structure in FIG. 4.

FIG. 4. Demonstration of the Kurdjumov-Sachs superstructure. Upper left: LEED pattern of the 2.7-ML film at the beam energy of 90 eV. Upper right: Simulated LEED pattern of Fe bc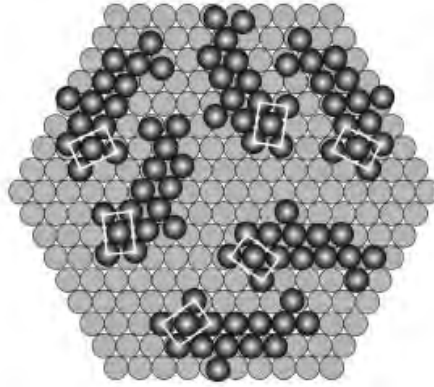c(110) on Cu(111) with Kurdjumov-Sachs orientation. Note the consistency between the experimental and the simulated LEED patterns. Bottom: real-space schematic view of the six KS domains on the Cu(111) substrate.

(*Id.*, FIG. 4.)

51. Therefore, Shen discloses the following structure:

[1b] Fe layer grown on Cu(111):	(110)(bcc)
[1e] Cu(111) surface:	(111)(fcc)

$\vdots$ To bulk Cu substrate [1a]

(Schematic B: Structure in Shen.) Shen discloses that both the structure and magnetic properties of the films depend on their thickness, which Shen reports in terms of "ML," or monolayers of Fe. (*See*, *e.g.*, *id.*, FIG. 2 and caption showing "morphological evolution" of the Fe overlayer "with increasing thickness.") Shen also discloses that the Fe films have a well-defined "easy magnetization axis." (*Id.*, pp. 138-39, ¶ 3.) Shen further reports that changes in properties relate to a change in Fe film structure with thickness, specifically a transition from (fcc) to bcc structure with increasing film thickness. (*Id.*, FIG. 3; p. 136, ¶ 1.)

52.   Shen explains that the morphological evolution of the Fe films, along with the fact that they are grown on steps of Cu(111) with a particular orientation (*i.e.*, along the <011> direction), results in breaking the symmetry of the Fe films. (*Id.*, p. 137, ¶ 1, emphasis added; *see also* FIG. 4.)   More particularly, Shen discloses that the "two [Kurdjumov-Sachs, or 'KS'] domain configurations [in the (bcc) ferromagnetic layer] which are parallel to the [Cu(111)] steps should be more favored as compared to the other four [KS] domains."   (*Id.*, p. 137, ¶ 1; FIG. 4.) Therefore, symmetry is broken because of a preference for two of the (bcc) ferromagnetic layer's six possible variants (*i.e.*, KS domains). The structural transition includes symmetry breaking and causes "[t]he magnetization of the transformed bcc Fe films [to sharply increase by] about four to five times larger than the extrapolated value from the low thickness fcc Fe films." (*Id.*, p. 134, ¶ 4 (5).)

B.   U.S. Patent No. 6,023,395 to Dill et al. ("Dill")

53.   Frederick Dill et al. filed a U.S. patent application titled "Magnetic Tunnel Junction Magnetoresistive Sensor With Instack Biasing" on May 29, 1998. This application issued as U.S. Patent No. 6,023,395 ("Dill") on February 8, 2000.

54.   Dill discloses embedding a (111)(fcc)/(bcc) layer structure, with a uniaxial (bcc) layer, in a multi-layer device, such as a magnetic tunnel junction (MTJ). (*See* ¶ 56, *infra*.) Dill discloses that adding this structure to the MTJ and

other similar devices is directed toward solving "the problem[]" of "developing a structure that generates an output signal that is both stable and linear with the magnetic field strength" and that can "maintain [the MTJ] in a single magnetic domain state" to prevent the domain walls from shifting positions. (Ex. 1009, 2:41-51.)

55.   Dill discloses a particular magnetic tunnel junction ("MTJ") magnetoresistive ("MR") read head in the form of a layer stack in FIG. 4A. (*Id.*, 5:26-28; FIG. 4A.):

FIG. 4A

(*Id.*, FIG. 4A.)

56.   Dill discloses two examples of an MR layer stack, schematically summarized in the following tables of layers:

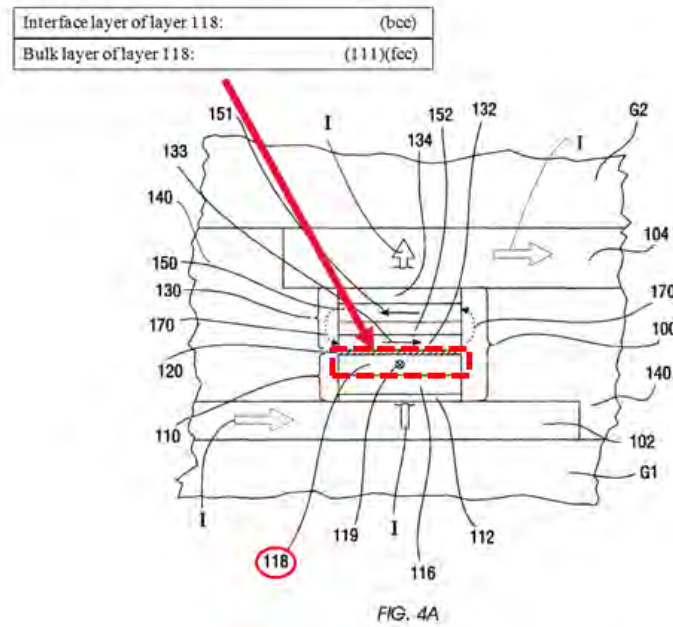| Example 1 from (Ex. 1009, 9:47-53; 8:29-57.)		
…various other layers…		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

Certain aspects of the above structure can be represented by the following simplified Schematic C:

⋮   To rest of layers in stack (FIG. 4A)

Interface layer of layer 118:	(bcc)
Bulk layer of layer 118:	(111)(fcc)

⋮   To layers 116, 112, and substrate (G1)

(Schematic C: Film structure for Dill, Example 1.)

Interface layer of layer 118: (bcc)
Bulk layer of layer 118: (111)(fcc)

FIG. 4A

(Ex. 1009, FIG. 4A, annotated.)

Example 2 from (Ex. 1009, 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	
Thin metal layer of 118:			
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

In Example 1, Dill discloses a $Ni_{81}Fe_{19}$ "template layer 112" that is "(111)…fcc"

material, that directs the (111) (fcc) crystalline growth of an overlying $Mn_{50}Fe_{50}$

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AF layer 116. (*Id.*, 8:35-47; FIG. 4A *supra*.) A "fixed layer" 118 near the middle of the layer stack, is grown onto AF layer 116. (*Id.*) In this example, layer 118 is divided into two layers, a lower "bulk" layer grown on (fcc) (111) layer 116 and an "interface" layer grown on the bulk layer. (*Id.*, 9:37-59.) In one example, the bulk layer is $Ni_{40}Fe_{60}$, and the interface layer is $Co_{30}Fe_{70}$ or $Co_{40}Fe_{60}$ (*id.*), making the bulk layer naturally (fcc) material and the interface layer naturally (bcc) material. (*See, e.g.*, Ex. F.) Also, one of ordinary skill in the art would have understood that the bulk and interface layers are both magnetic. Therefore, Dill discloses an (fcc)[bulk layer of layer 118]/(bcc)[interface layer of layer 118] structure embedded in a magnetic layer stack to form a magnetic device. Dill also discloses that the (fcc) structure of layer 118 is influenced by the structure of underlying (fcc) AF layer 116, and that the (fcc) structure of layer 116 is determined by (fcc)(111) "seed layer" 112. (*Id.*, 8:37-41; FIG. 4A.) Dill further discloses that uniaxial anisotropy is "induce[d]" in layer 118 by growing the layer under the influence of a magnetic field in the direction 119. (*Id.*, 10:47-52; FIG. 4A.) Dill discloses a number of different layer stacks and devices employing the (111)(fcc)/(bcc) structure discussed above. (*See*, *e.g., id.*, FIGs. 4A, 4B, and 6; *see also* Example 2 summarized above; *see also* magnetic layer variations and substitutions discussed from 5:22-7:52.) According to Dill, each of these

multilayer devices benefits from the ability of that structure to "provide[] a linear response to the magnetic fields from the recorded medium." (*Id.*, 3:2-4.)

C. U.S. Patent No. 5,465,185 ("Heim")

57. U.S. Patent No. 5,465,185 ("Heim") (Ex. 1012) issued on November 7, 1995. Heim discloses a magnetoresistive spin valve sensor with an improved pinned ferromagnetic layer and magnetic recording system using the sensor. (*Id.*, Title.) The structure includes a multi-film laminated pinned ferromagnetic layer (*id.*, Abstract) which "comprises a first $Ni_{81}Fe_{19}$ film 72 having a thickness of 30 Å formed directly on the copper spacer layer 65, a 5 Å ruthenium (Ru) film 73 deposited onto the first Ni-Fe film 72, and a second $Ni_{81}Fe_{19}$ film 74 of 30 Å thickness formed on the Ru film 73." (*Id.*, 5:19-23.) Heim discloses that separating layer 73 in this configuration is an "AF [antiferromagnetically] coupling film" that antiferromagnetically couples films 72 and 74. (*Id.*, 6:13-17.) Heim further discloses that the "AF coupling film" 73 can be comprised of a number of materials besides Ru, including Cr. (*Id.*, 7:3-10.)

D. D.N. Lambeth, W. Yang, H. Gong, D.E. Laughlin, B. Lu, L.L. Lee, J. Zou, P.S. Harllee, "Magnetic Media Performance: Control Methods for Crystalline Texture and Orientation," Mat. Res. Soc. Symp. Proc. Vol. 517, 181-192 (1998) ("Lambeth I")

58. David N. Lambeth et al. published a scientific paper in the Materials Research Society Proceedings titled "Magnetic Media Performance: Control

Methods for Crystalline Texture and Orientation" on April 15, 1998 ("Lambeth I").

Lambeth I provides "an overview of the guiding media design philosophy and

discuss[es] materials issues, multi-layered thin film material structures and

processing techniques which are used to control the microstructure and magnetic

properties of Co-alloy films." (Ex. 1013, Abstract.)

59.   More specifically, Lambeth I discloses particular methods for

controlling microstructure of magnetic films and devices/structures made with such

films. The disclosed methods include manipulating the "underlayer" structure of

deposited films in order to ensure a particular structure, phase composition, and

orientation of the resulting film. (*Id.*, p. 185, ¶ 1.) Lambeth I discloses that the

"choice of the underlayer texture upon which to perform epitaxial growth is

critical" in determining the orientation, crystalline quality, and grain size in

resulting films. (*Id.*) Lambeth I provides an overview of several relationships

between the structure of the underlayer and the structure and properties of the

resulting overlayer. (*See, e.g.*, *id.*, pp. 186-88.) In particular, Lambeth I discloses

that single crystalline underlayers, and/or underlayers with a particular

crystallographic orientation such as (111), can result in superior quality overlayer

films. (*Id.*, p. 188.)

E.   U.S. Patent No. 5,862,022 to Noguchi et al. ("Noguchi")

60.   Kiyoshi Noguchi et al. filed a U.S. patent application titled "Ferromagnetic Tunnel Junction, Magnetoresistive Element and Magnetic Head" on Sep. 19, 1997. This application issued as U.S. Patent No. 5,862,022 ("Noguchi") on January 19, 1999.

61.   Noguchi discloses a "ferromagnetic tunnel junction" comprising multiple configurations of magnetic layers (Ex. 1014, 12:53-67; Abstract; *see also*, *e.g.*, FIGs. 1, 6, 10, and 21.)
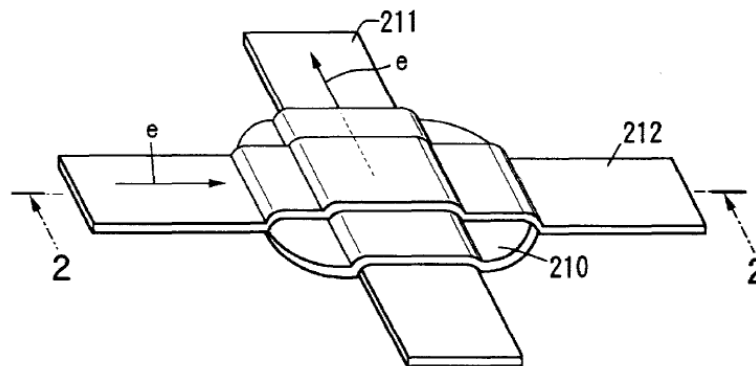

FIG. 1

(*Id.*, FIG. 1.)

62.   Noguchi's device shares similar goals and structure with the MTJ of Dill. For example, Noguchi discloses, like Dill, that tunneling junctions and layer stacks can be used in conjunction with magnetoresistive read heads (MRs). (*Id.*,

1:13-22.) Noguchi's MR includes ferromagnetic films and magnetic domain control films. (*Id.*, 12:53-67; FIGs. 6-8.) The magnetic domain control films "prevent a disturbing influence of an external magnetic field" (*id.*, 15:52-57) in the ferromagnetic films. Noguchi further discloses using the structure in a variety of other devices, including an "inductive magnetic conversion element." (*Id.*, 20:37-55.)

VIII. SHEN, ALONE OR IN COMBINATION WITH DILL, RENDERS OBVIOUS CLAIMS 1 AND 27 OF THE '988 PATENT

A. Claim Charts

63. The Petition sets forth claim charts (Petition, Sections VI(A) and (B)) citing disclosures in Shen and Dill that demonstrate how these prior art references render obvious claims 1 and 27 of the '988 patent. I fully agree with the claim charts. The following sections include additional analysis that demonstrates how Shen, alone or in combination with Dill, renders these claims obvious.

B. Shen, Alone or in Combination With Dill, Renders Obvious Claim 1

64. The preamble for claim 1 recites "[a] *magnetic material*." To the extent this preamble is a limitation, Shen discloses this limitation. For example, Shen discloses an Fe film ("magnetic material") deposited on a "copper

substrate."[3] (Ex. 1011, p. 135, ¶¶ 2-3.) Shen discloses that the Fe film is a

"magnetic" material. (*See*, *e.g.*, *id.*, Title; Abstract.)

65.   Claim 1 recites that the magnetic material comprises "*a substrate*."

Shen discloses that an Fe film is deposited on a "copper substrate." (*See*, *e.g.*, *id.*,

p. 135, ¶¶ 2-3.)

66.   Claim 1 recites "at least one *bcc-d layer which is magnetic*." Shen

discloses this limitation.

67.   Shen discloses that the Fe film has a "bcc(110)" structure. More

specifically, as the film thickness increases above a "critical thickness," the film

material changes from (fcc) to bcc structure. (*Id.*, Abstract; pp. 137-38, ¶ 2; FIG. 4

and caption; FIG. 5; p. 138, ¶¶ 1-3; p. 139, ¶ 2.) Shen presents experimental

results that confirm the bcc structure. (*See*, *e.g.*, *id.*, FIG. 3 and caption.) Shen

acknowledges that the Fe films are "magnetic," by discussing their "magnetic

properties" (*Id.*, p. 138, ¶ 3; p. 140, ¶ 3; p. 142, ¶ 3) and presenting experimental

results demonstrating "[t]he magnetization of both the (fcc) Fe films and the bcc Fe

films." (*Id.*, ¶ 1, FIG. 9 and caption.)

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[3] Shen uses the terms "copper substrate" and "Cu(111) substrate"

interchangeably. (*See*, *e.g.*, Ex. 1011, caption of FIG. 4.) Accordingly, I will do so

here as well.

68.   Claim 1 recites that the magnetic bcc-d layer "[forms] *a uniaxial structure*." The '988 patent describes "'uniaxial' anisotropy to exist if the anisotropy energy density function only contains a single maximum and a single minimum as the magnetization angle, θ, is rotated by 180 degrees from a physical axis" (Ex. 1001, 1:56-60), which a person of ordinary skill in the art would have understood to be demonstrated if the material has one easy magnetization axis. Shen discloses this limitation.

69.   Shen consistently refers to the easy axis in the disclosed films as singular. For example, Shen discloses that the (fcc) to (bcc) structural transition observed in the Fe films caused "the easy magnetization direction [to switch] from perpendicular to in plane." (Ex. 1011, p. 139; *also, id.*, pp. 140-41, ¶ 3, "The film thus may have a[n] in-plane easy magnetization axis . . ."). In other words, Shen discloses that in this example the Fe films, whether they have (fcc) or bcc structure, are uniaxial in that they have a single, easy magnetization direction. Shen confirms this by referring to "a" or "the" easy axis in both the (fcc) films and the (bcc) films. (Ex. 1011, Abstract; p. 139, top of right column.)

70.   Shen explained that, though the bcc Fe layers have an easy magnetization axis and the easy axis is in the plane of the Fe layer, Shen's available equipment was not able to measure the specific direction of the axis in the layer plane, other than to say that it is not in the direction of the substrate steps.

(Ex. 1011, p. 139, ¶ 1.) Even if Shen was unable, for technical reasons, to establish the specific direction of the easy axis, one of ordinary skill in the art would still have understood from the disclosure above that Shen discloses that the Fe films have a preferred easy axis and, therefore, they have uniaxial anisotropy.

72. Dill also discloses a magnetic device with a bcc magnetic layer that is uniaxial. Dill further discloses that operation of the magnetic device can be improved by predetermining and "induc[ing]" that direction to cooperate with operation of the device. Specifically, as discussed in ¶ 56 *supra*, Dill discloses a fixed layer 118 that is bcc and magnetic and also discloses inducing uniaxial anisotropy in the layer. And Dill discloses a method for inducing this uniaxial anisotropy. In fact, the very method Dill discloses is identified by the '988 patent as a method "[to] achieve a single uniaxial anisotropy." (Ex. 1001, 4:60-65.) Moreover, one of ordinary skill in the art would have recognized this method as achieving uniaxial anisotropy.

72. It would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to modify Shen's (bcc) Fe layer (Ex. 1001, FIG. 4) by using Dill's method to form a predetermined uniaxial structure.

73. Specifically, Shen discloses a magnetic film structure of Cu(111)/(bcc) Fe, where the (bcc) Fe layer is grown on Cu(111) and has an easy

magnetization axis. (Ex. 1011, FIG. 4; pp. 140-41, ¶ 3.) Dill discloses growing ferromagnetic layer 118 in the presence of a magnetic field to induce an easy magnetization axis aligned in the direction of an applied field. (Ex. 1009, 10:47-10:52.) Dill further indicates that inducing uniaxial anisotropy this way may be "beneficial." (*Id.*) Although Dill does not explicitly describe the benefit, one of ordinary skill in the art would have understood that the benefit is to create a more reliable magnetization along a particular direction that will be less easily changed under the influence of external magnetic fields.

74. Applying a field to induce uniaxial anisotropy during the growth of Shen's (bcc) Fe layer would be straight-forward and predictable. Shen's (bcc) Fe layer is uniaxial and grown on an (fcc) Cu(111) substrate (*see*, *e.g*., Ex. 1011, pp. 138-39, ¶ 3). Similarly, Dill's ferromagnetic layer 118 is grown on layer 116 (Ex. 1009, 8:37-41), which is fcc(111).

75. Therefore, a person of ordinary skill in the art would have been able to modify Shen's (bcc) Fe layer (Shen, FIG. 4) by growing it in a magnetic field such that it has a uniaxial structure, as disclosed by Dill.

76. Claim 1 recites that the bcc-d layer forms a "***symmetry broken structure***." Shen discloses this limitation.

77. As discussed in ¶ 48, *supra*, the '988 patent explains that "symmetry broken structure" means that the layer "do[es] not contain an equal amount of all

six of the possible (110) textured bcc-d variants [*i.e*., "KS domains"]." (Ex. 1001, 23:38-41) This would also have been understood as the meaning by one of ordinary skill in the art. Shen discloses that the Fe films have a symmetry broken structure (dominance of two crystalline variants) (Ex. 1011, p. 134, ¶ 4 (5)) and have improved magnetic properties (*see* ¶ 48, *supra*). Further, Shen discloses a method of breaking the symmetry by enhancing certain variants and minimizing others in the (bcc) layer. (*See* ¶¶ 51-52, *supra*.)

78.   Specifically, Shen discloses that when the (bcc) Fe layer is grown on the Cu(111) substrate, there are six crystallographic variants of the (bcc) Fe that might possibly grow. These variants are referred to as "Kurdjumov-Sachs domains" or "KS domains." However, Shen discloses that two of the six variants were preferentially grown on the stepped (111) surface [*i.e*., symmetry was broken in the Fe layer]. (Ex. 1011, p. 137, right column; FIG. 4.)

> [T]he STM images have shown that there are more domains elongated along the step direction than the other two <011> directions. . . . The two domain configurations which are parallel to the [substrate] steps should be more favored as compared to the other four domains.

(*Id.*, p. 137; FIGs. 2(f)-(g) and 4.)[4] Shen discloses that symmetry breaking increases the magnetic field required to saturate the layer and contributes to the uniaxial anisotropy, improving the magnetic properties of the bcc layer. (*Id.*, p. 139, left column.) Shen also discloses that the structural transition from (fcc) to (bcc) in the Fe films results in a "four to five times" increase in magnetization of the Fe films. (Ex. 1011, p. 134, ¶ 4 (5); *see also* pp. 140-41, ¶ 3; p. 137, ¶ 2.)

79.   Claim 1 recites "at least one *layer providing a (111) textured hexagonal template*." Shen discloses this limitation.

80.   For example, Shen discloses that the copper substrate, "Cu(111)," has a (111) texture. Shen consistently and repeatedly refers to the (111) texture of the Cu(111) surface. (*See*, *e.g.*, Ex. 1011, p. 135, ¶¶ 2-3; Abstract; FIGs. 1, 2, and 3.) A topographic image of the "Cu(111)" surface shows that the surface provides a hexagonal template. (*Id.*, FIG. 1 and caption, reproduced above in ¶ 49.) Shen shows the same surface schematically in a "real-space schematic view of the six KS domains on the Cu(111) substrate." (*Id.*, FIG. 4, *infra*, and caption.)

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[4] Shen acknowledges that the dominance of the two particular KS domains should also, "in principle," give different spot intensities in the measured LEED pattern, but the actual LEED data has insufficient resolution to show this definitively. (Ex. 1011, p.137, right column; FIG. 4, upper left.)

81.   I have annotated a part of that figure below in order to show the hexagonal pattern.
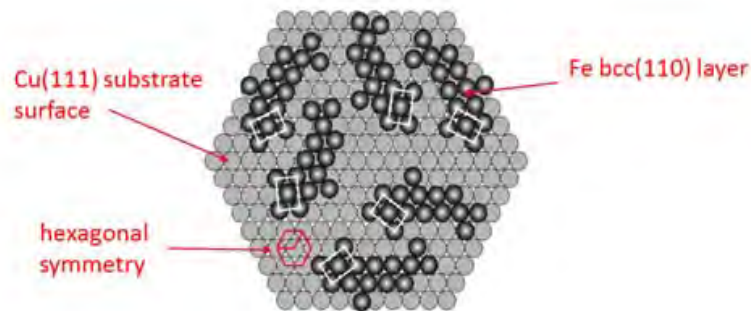
(Ex. 1011, FIG. 4, annotated.)

82.   Moreover, one of ordinary skill in the art would have understood that (111) texture in (fcc) material would have a hexagonal structure. (*See*, *e.g.*, Ex. G, p. 94 *et seq*.) In fact, the '988 patent indicates that (111) (fcc) is one example of a "(111) textured hexagonal atomic template." (Ex. 1001, 14:55-58.)

83.   Shen discloses that the Cu(111) substrate is fcc. For example, Shen explains that, when the Fe layer grown on Cu(111) is relatively thin, the films "adopt the fcc ***structure from the*** [Cu(111)] ***substrate***." (Ex. 1011, Abstract, emphasis added.) Shen also refers to the (fcc) structure of the Cu(111) substrate numerous times throughout the text. (*See*, *e.g.*, Ex. 1011, p. 136, ¶ 1; p. 137, ¶¶ 1-2.)

84.   Claim 1 recites that ***the template is "disposed between said substrate and said bcc-d layer*****.**" Shen discloses this limitation. The '988 patent explains

that a "layer…disposed between said substrate and said bcc-d layer" could be the top surface of the substrate. For example, dependent claim 26 recites "[the] surface of said single crystal provides a layer providing the (111) textured hexagonal atomic template disposed between the bulk of said substrate and said at least one bcc-d layer."

85. Shen discloses that the top surface of the Cu(111) substrate provides the (111) textured hexagonal atomic template. (*See* ¶¶ 18-21, *supra*.)

86. Finally, by disclosing that the layer stack is (fcc) Cu(111)/bcc Fe (110), Shen discloses that the surface of the Cu(111) substrate is disposed between the underlying body of the substrate and the overlying bcc-d Fe layer.

C. Shen, Alone or in Combination With Dill, Renders Obvious Claim 27

87. Claim 27 of the '988 patent is identical to claim 1, apart from the additional limitation that the magnetic material structure must be incorporated into a "***magnetic device***." As discussed in VIII(B) *supra*, Shen, alone or in combination with Dill, discloses all the limitations of claim 1. Shen also discloses the additional limitation of claim 27 that the magnetic structure can be incorporated into a "magnetic device."

88. The '988 patent defines a "magnetic device" broadly in a way that one of ordinary skill in the art would have understood to encompass a layered structure of at least one magnetic material. For example, the '988 patent refers to "magnetic

media" as a "device," even though the medium is nothing more than layers of magnetic material with a "preferred orientation ratio." (Ex. 1001, 32:32-47.) Therefore, because Shen discloses a magnetic material bi-layer with a preferred orientation (*i.e.*, a net orientation preference in the direction of <110> steps of Cu(111)) (Ex. 1011, p. 137, ¶ 1; FIG. 4.), the Cu(111)/Fe(bcc) bi-layer of Shen is a "magnetic device."

IX. DILL, IN COMBINATION WITH SHEN ALONE OR IN FURTHER COMBINATION WITH HEIM, RENDERS OBVIOUS CLAIMS 1, 3, 6-19, 21-24, 27-30, 34 AND 38 OF THE '988 PATENT

A. Claim Charts

89. The Petition sets forth claim charts (Petition, Sections VI(B) and (C)) citing disclosures in Dill and Shen that demonstrate how the combination of Dill and Shen alone, or in further combination with Heim, renders obvious claims 1, 3, 6-19, 21-24, 27-30, 34 and 38 of the '988 patent. I fully agree with the claim charts. The following sections include additional analysis that demonstrates how the combination of Dill and Shen alone, or in further combination with Heim, renders these claims obvious.

B. Dill in Combination With Shen Renders Obvious Claim 1

90. For at least the following reasons, Dill in combination with Shen renders obvious claim 1 of the '988 patent.

91.   The preamble for claim 1 recites "[a] *magnetic material*." To the extent this preamble is a limitation, Dill discloses this limitation.

92.   For example, Dill discloses a magnetic tunnel junction ("MTJ") magnetoresistive ("MR") read head ("magnetic material") that includes a magnetic layer stack on a substrate. (Ex. 1009, 5:26-31; FIG. 4A.) One of ordinary skill in the art would readily have understood that an MTJ read head includes "magnetic material."

93.   As discussed in ¶ 56, *supra*, Dill discloses two examples of an MR layer stack, schematically summarized in the following tables of layers:

Example 1 from (Ex. 1009, 9:47-53; 8:29-57.)		
…various other layers…		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

Example 2 from (Ex. 1009, 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	
Thin metal layer of 118:			
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

94. Claim 1 recites that the magnetic material comprises "*a substrate*." Dill discloses that the MTJ includes a "G1 alumina layer as the substrate." (*See, e.g., id.*, 10:29-32; Example 1 or Example 2 above.)

95. Claim 1 recites "at least one *bcc-d layer which is magnetic*." Dill discloses this limitation.

96. In Example 1, as schematically represented above, layer 118 has two layers: 1) a lower, bulk layer (hereinafter, the "bulk layer of layer 118" or "bulk layer of 118") and 2) an upper, interface layer (hereinafter, the "interface layer of layer 118" or "interface layer of 118") grown thereon. (*Id.*, 9:47-59.) The interface layer of 118 is $Co_{30}Fe_{70}$ or $Co_{40}Fe_{60}$. (*Id.*) One of ordinary skill in the art would have known that the natural crystal structure of the interface material is bcc

and magnetic. (*See*, *e.g*., Ex. H, p. 251 *et seq*.; Ex. G, p. 94 *et seq*.; Ex. F.) The bulk layer of layer 118 is $Ni_{40}Fe_{60}$. (Ex. 1009, 9:47-59.) This material naturally has (fcc) structure and is magnetic.

97. In Example 2, as schematically represented above, layer 118 is comprised of a thin metal layer separating two ferromagnetic layers, a lower layer of 118 and an upper layer of 118. (*Id.*, 9:65-10:4.) Each ferromagnetic layer is comprised of "Ni, Co, Ni-Fe alloys, Co-Fe alloys, or Ni-Fe-Co ternary alloys" (*id.*) such as the $Co_{30}Fe_{70}$ or $Co_{40}Fe_{60}$ discussed above, which as discussed in ¶ 96 *supra* is (bcc) material.

98. Claim 1 of the '988 patent recites that the bcc-d layer "form[s] *a uniaxial … structure*." Dill discloses this limitation.

99. Dill discloses that layer 118 is "grown in a [magnetic] field oriented along [a particular] direction 119 in FIG 4A," "to induce in the fixed [layer] 118, sensing [layer] 132 and biasing [layer] 150 …appropriate magnetic anisotropies." (Ex. 1009, 10:47-10:59.) FIG 4A shows the field direction 119 used to induce uniaxial anisotropy in layer 118:
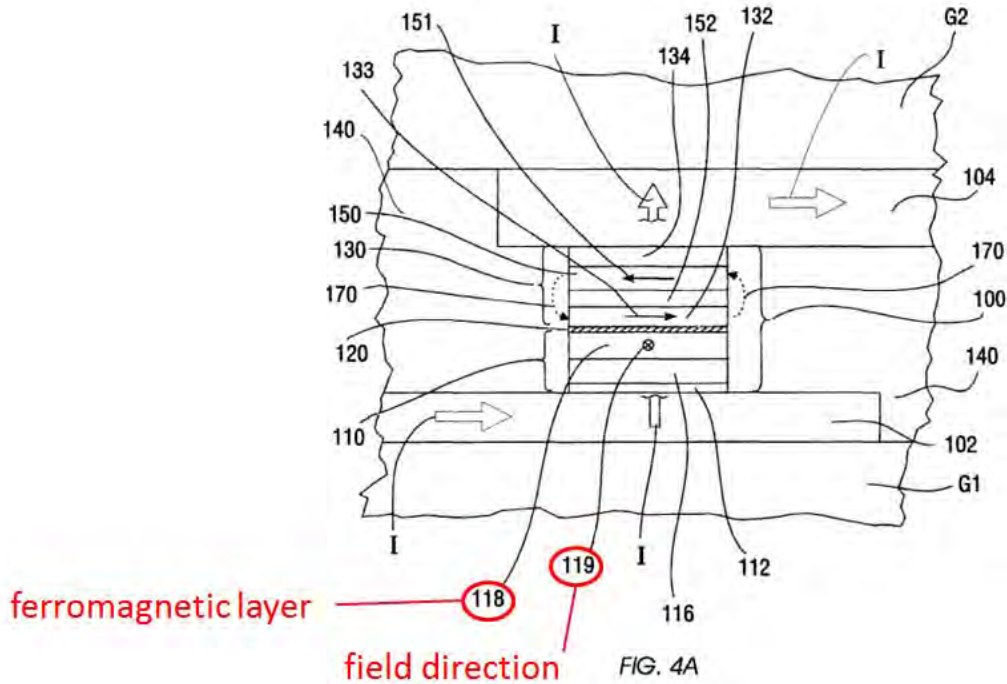
(Ex. 1009, FIG. 4A, annotated.)

100. One of ordinary skill in the art would readily have understood that growing ferromagnetic layer 118 under the influence of such a field "to induce in the fixed [layer] 118 … [an] appropriate magnetic anisotrop[y]" creates a preferred uniaxial magnetic anisotropy in the interface layer of 118. In fact, the '988 patent recognizes "depos[iting a magnetic film] in the presence of an applied magnetic field" as one way of "achiev[ing] a single uniaxial anisotropy" in the film by ensuring that the film's "resulting single magnetic easy axis is aligned along the applied magnetic field." (Ex. 1001, 4:60-65, "Background of the Invention" discussing the prior art.) Similarly, U.S. Patent No. 5,998,048 to Jin (Ex. B) ("Jin") discloses applying "magnetic fields during the deposition of the films

comprising Co-Fe-Cr-N to induce magnetic anisotropy" through "preferential ordering of atoms to form an easy direction of magnetization." (Ex. B, 5:48-65; 11:1-9.)

101. Dill discloses that, in Example 1, ferromagnetic layer 118 is also exchanged coupled, in the same direction as the easy axis (*i.e.*, in the direction of applied field 119). (Ex. 1009, 11:62-12:15.) However, one of ordinary skill in the art would have known that exchange coupling and uniaxial anisotropy can coexist, and, in fact, complement one another, in the same layer. In addition to Dill, another example of providing exchange coupling as a complement to uniaxial anisotropy to ensure magnetization along a particular direction is disclosed by U.S. Patent No. 6,295,187 to Pinarbashi (Ex. D). More specifically, Pinarbashi provides a "highly stabilized pinned layer structure" by simultaneously exchange coupling and pinning with stress induced uniaxial anisotropy. Pinarbashi discloses that, when temperature effects degrade the pinning strength, the stress induced uniaxial anisotropy "maintains the orientation of the magnetic moment of the AP pinned layer" in the desired direction. (Ex. D, 1:3-30.)

102. Claim 1 recites that the "bcc-d layer which is magnetic" forms a "*symmetry broken structure*." Dill in combination with Shen discloses this limitation.

103.   As shown in Example 1 above, Dill discloses that the following layers are grown in sequence: (111) (fcc) template layer 112, (111) (fcc) layer 116, (111) (fcc) bulk layer of 118, and (bcc) interface layer of 118. (*Id.*, 8:37-41; 9:37-59; FIG. 4A; *see also* ¶¶ 107-13, *infra*). Particularly, the (bcc) interface layer of 118 is grown on a "bulk [$Ni_{40}Fe_{60}$] layer" that is (111) (fcc). (Ex. 1009, 8:29-57; 9:37-59).

104.   As discussed in ¶ 48, *supra*, Shen discloses a bcc layer (disposed onto a (111) (fcc) layer) that has broken symmetry. Shen also discloses that the magnetic properties of the bcc layer are improved. (*See* ¶ 48, *supra*.) It would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to use Dill's (111)(fcc) bulk layer of layer 118 / (bcc) interface layer of layer 118 to form broken symmetry in the interface layer to improve the magnetic properties of the interface layer. (*See* ¶¶ 48-52, *supra*.) For example, one of ordinary skill in the art would have known Shen's teaching that creating the disclosed symmetry broken layer would increase the magnetic field required to saturate the layer and would contribute to magnetic anisotropy. (*Id.*) One of ordinary skill in the art would have also understood that the structural transition from (fcc) to (bcc) in the Fe films dramatically increases the magnetization of the layer. (*Id*.)

105. Specifically, Shen discloses a magnetic material layered structure formed by growing a (bcc) magnetic layer on a stepped (111) (fcc) surface. (Ex. 1011, FIG. 4; FIG. 5; p. 138, ¶¶ 1-2; p. 139, ¶ 2.) Shen discloses that the (bcc) films have broken symmetry because two of the six possible crystallographic variants are favored in the growth. (Ex. 1011, p. 137, ¶ 1; FIG. 1.)

106. Dill's (bcc) interface layer of 118 was grown onto the (fcc) bulk layer of 118, to form the (111)(fcc)/(bcc) structure as disclosed by Shen.[5] (Ex. 1009, FIG. 4A; Ex. 1011, FIGs. 2 and 4.) Shen discloses that broken symmetry is formed in such a (111)(fcc)/(bcc) structure. (Ex. 1011, p. 134, ¶ 4; p. 137, ¶ 1.) Also in Dill's Example 2 (*see* ¶ 96, *supra*), the (bcc) lower ferromagnetic layer of 118 was grown onto the (111)(fcc) AF layer 116,[6] a (111)(fcc)/(bcc) structure. It would have been obvious to use the teaching of Shen to form broken symmetry in the (bcc) layers of Dill's examples in order to gain improvement in magnetic properties as discussed in ¶ 104, *supra*.

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[5] Note that here and in the Petition, the (111)(fcc)/(bcc) structure formed according to the teachings of Shen discussed *supra* is referred to as "Shen's symmetry broken (111)(fcc)/(bcc) structure."

[6] I say "*lower* ferromagnetic layer" here because it is the lower of the two ferromagnetic layers of 118, not because it is lower than AF layer 116.

107. Claim 1 recites "at least one *layer providing a (111) textured hexagonal template*." As discussed in ¶ 56, *supra*, Dill discloses that layers 112, 116, and bulk layer of 118 are all (111) textured hexagonal templates.

108. In Example 1, the "template layer 112" is "fcc (111) $Ni_{81}Fe_{19}$." (Ex. 1009, 8:37-41.) Because layer 112 is (111) textured fcc, it has a hexagonal texture and is a "(111) textured hexagonal atomic template," according to the definition provided by the '988 patent. (Ex. 1001, 14:55-58.) Dill discloses that layer 116 is grown directly on layer 112, and layer 112 "encourages" the growth of AF layer 116 by providing the template for layer 116. (Ex. 1009, 8:29-57.) Dill further discloses that the antiferromagnetic ("AF") layer 116 is $Mn_{50}Fe_{50}$. (*Id.*) One of ordinary skill in the art would have understood that $Mn_{50}Fe_{50}$ is naturally (fcc). Because (fcc) layer 116 is grown directly on layer 112, one of ordinary skill in the art would have understood that the (fcc) (111) hexagonal texture of template layer 112 is imparted to layer 116. Moreover, because the bulk layer of layer 118 is $Ni_{40}Fe_{60}$ and grown on (fcc) layer 116, one of ordinary skill would have understood that the bulk layer of layer 118 also has a (111) (fcc) textured hexagonal atomic template. (¶ 56 *supra*; Ex. 1009, 8:29-57; 9:37-59.)

109. In Example 1, layers 112 and 116 and the bulk layer of 118 each provide a (111) textured hexagonal atomic template.

Example 1 from (Ex. 1009, 9:47-53; 8:29-57.)		
…various other layers…		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

110.   This is because, as shown above, each of the layers has an (111)(fcc) structure as a result of being grown in seed layer 112 which Dill explicitly discloses as having such a structure. (*See* Ex. 1009, 8:37-41.)

111.   In Example 2 discussed in ¶¶ 108-09, AF layer 116 provides an fcc (111) hexagonal atomic template to the (bcc) lower layer of 118. (*Id.*)

Example 2 from (Ex. 1009, 9:65-10:3; 9:47-53; 8:29-57.)		
…various other layers…		
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	
Thin metal layer of 118:		
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

112. Claim 1 recites that *the template is "disposed between said substrate and said bcc-d layer*." Dill's Example 1 shows this limitation, with the bulk layer of 118 disposed between the interface layer of 118 and the substrate, and Example 2 shows this limitation with AF layer 116 disposed between the lower layer of 118 and the substrate. (*See* Ex. 1009, FIG. 4A.)

C.   Dill in Combination With Shen Renders Obvious Claim 3

113. Claim 3 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein a surface of said *substrate is amorphous or polycrystalline*." The combination of Dill and Shen renders obvious this limitation.

114. Dill discloses depositing the MTJ MR layers on a layer of Au metal that is deposited on the surface of an "alumina substrate" (Ex. 1009, 8:43-48). Although Dill does not explicitly disclose that the Al_2O_3 layer is polycrystalline, one of ordinary skill in the art would have understood the Al_2O_3 substrate is polycrystalline because Dill's reference to the Al_2O_3 substrate as an "alumina" substrate would have been understood as polycrystalline. Moreover, one of ordinary skill in the art would have understood that the Au metal is deposited onto the polycrystalline Al_2O_3 layer and that this would naturally create a polycrystalline Au surface.

D. Dill in Combination With Shen Renders Obvious Claim 6

115. Claim 6 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein the ***layer providing said hexagonal atomic template is formed from a fcc-d or hcp crystalline material***." Dill discloses this limitation.

116. As discussed above and shown in Example 1, Dill's layers 112 and 116 each has (fcc) structure and provides a (111) textured hexagonal atomic template. Specifically, Dill discloses that "template layer 112" is "(111)… (fcc) $Ni_{81} Fe_{19}$," and because AF layer 116 is $Mn_{50}Fe_{50}$ grown on layer 112, the crystalline structure of AF layer 116 is "encourage[d]" by underlying layer 112. Because layer 116 is grown on (111)(fcc) layer 112, one of ordinary skill in the art would have known that layer 116's structure is also (111)(fcc). (Ex. 1009, 8:29-57; *see also*, *e.g.*, Ex. H, p. 251 *et seq.*; Ex. I, pp. 288-312; Ex. G, p. 94 *et seq.*)

E. Dill in Combination With Shen Renders Obvious Claim 7

117. Claim 7 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein ***the layer providing said hexagonal atomic template is magnetic***." Dill discloses this limitation.

118. As discussed in IX(B) and IX(D) *supra* and shown in Example 1, the bulk layer of layer 118 is $Ni_{40}Fe_{60}$, grown onto (111)(fcc) AF layer 116 and

"provid[es] said hexagonal atomic template." (Ex. 1009, 9:47-53; 8:29-57.)

$Ni_{40}Fe_{60}$ is magnetic material. Therefore the bulk layer of 118 is "magnetic." (*See, e.g.*, Ex. 1009, 7:65; 9:65-67; 8:29-57; 9:37-10:4.)

F.   Dill in Combination With Shen Renders Obvious Claim 8

119.   Claim 8 of the '988 patent recites "wherein said ***bcc-d layer*** [of claim 1] ***is epitaxially grown on said (111) textured hexagonal atomic template***." The combination of Dill and Shen discloses this limitation.

120.   As discussed in IX(B) *supra*, Dill discloses that the bulk layer of 118 provides a (111) textured hexagonal atomic template to the (bcc) interface layer of 118, which is grown thereon. (Ex. 1009, 8:29-57; 9:37-57.) One of ordinary skill in the art would have known that in this context, the term "grown on" (*id.*, 8:46) means epitaxially grown on, with layers 112 and 116, the bulk layer of 118, and the interface layer of 118 epitaxially grown on their respective underlayers. For the same reason, one of ordinary skill in the art would also have understood that the lower ferromagnetic layer of layer 118 is epitaxially grown on layer 116.

121.   Even if Dill does not explicitly disclose that the (bcc) interface layer of 118 was epitaxially grown on the (111) (fcc) bulk layer of 118 or that the (bcc) lower ferromagnetic layer of layer 118 was epitaxially grown on layer 116, Shen discloses that such epitaxial growth is part of forming Shen's symmetry broken (111)(fcc)/(bcc) structure discussed in IX(B) *supra*. Specifically, Shen discloses

growing the bcc Fe(110) layer on the Cu(111) substrate and shows that this is epitaxial growth in FIG. 4. (Ex. 1011, pp. 136-37; FIG. 4.)

122. Claim 8 also recites that "*the bcc-d layer…has a (110) crystalline texture*." Dill does not explicitly disclose the crystalline texture of the interface layer of 118. However, as discussed in ¶¶ 102-06, *supra*, it would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to combine the teachings of Shen and Dill to improve the magnetic properties of Dill's (bcc) interface layer of 118 (*see also* ¶¶ 48-52, *supra*). Shen discloses that Shen's symmetry broken (111)(fcc)/(bcc) structure formed a (110) structure in the (bcc) layer. (*See*, *e.g*., Ex. 1011, FIG. 4.)

123. More specifically, Shen discloses that when the bcc layer is more than 2 or 3 ML (atomic monolayers) thick, the bcc layer in the (111) (fcc)/(bcc) structure forms a (110) crystalline texture. (*Id.*, pp. 140-41, ¶ 3.) Likewise, Dill discloses an example in which the interface layer of layer 118 is 2 nm thick. (Ex. 1009, 9:53-54.) An atomic monolayer is on order of 0.2 nm thick. Therefore, the exemplary interface layer portion of layer 118 is approximately 10 ML thick.

124. Therefore, one of ordinary skill in the art would have understood from Dill that the interface layer of layer 118 forms a (110) crystalline texture.

125. Claim 8 also recites "at least *one crystalline grain of said (111) textured hexagonal atomic template has epitaxially grown thereon at least two*

and not more than four dominate (110) orientational variants." Dill does not explicitly disclose the number of orientational variants in the interface layer of 118 after it is grown on the bulk layer of 118.

126.   However, as discussed in IX(B) *supra*, Dill discloses the following (111)(fcc)/(bcc) structure: (fcc) (111) bulk layer of 118/(bcc) interface layer of 118. As discussed in VIII(B) *supra*, Shen grows a (bcc) ferromagnetic layer onto a stepped (111)(fcc) layer to form a (110) crystalline texture in the top bcc layer with two dominant growth orientational variants. (Ex. 1011, pp. 136-37; FIG. 4.) Therefore, the combination of Dill and Shen discussed in IX(B) *supra* discloses an interface layer of 118 grown on the bulk layer of 118, to cause broken symmetry (*see* X(B) *supra*), to form a (bcc) film with two dominant (110) orientational variants. To the extent that growing the layers of Dill according to the disclosure in Shen does not provide such variants, it would have been obvious to grow the interface layer of layer 118 to provide the variants as disclosed in Shen to improve magnetic properties in the interface layer of layer 118. (*See* X(B) *supra*.)

G.   Dill in Combination With Shen Renders Obvious Claim 9

127.   Claim 9 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second layer providing a (111) textured hexagonal atomic template*, wherein said second layer is *magnetic*." Dill discloses this limitation, as summarized in Example 1 (below)

Example 1 from (Ex. 1009, 9:47-53; 8:29-57.)		
…various other layers…		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

128.   Template layer 112 is "a second layer providing a (111) textured hexagonal atomic template" that is magnetic. This is because layer 112 is (fcc) $Ni_{81}Fe_{19}$ and has a (111) structure (Ex. 1009, 8:29-57), which the '988 patent defines as a (111) textured hexagonal template (Ex. 1001, 14:55-58.) Moreover, one of ordinary skill in the art would have known layer 112 to be a hexagonal, magnetic template, at least because of layer 112's (111)(fcc) structure and because both Ni and Fe, and their alloys, are magnetic. Alternatively, Dill discloses a "sensing ferromagnetic layer 132" that is $Ni_{81}Fe_{19}$, which provides a (111) textured hexagonal atomic template to (bcc) Cr spacer layer 152. (*See*, *e.g.*, Ex. 1009, 8:50-53; FIG. 4A.) One of ordinary skill in the art would have known that $Ni_{81}Fe_{19}$ has an (fcc) structure and is magnetic.

H. Dill in Combination With Shen Renders Obvious Claim 10

129. Claim 10 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer which is non-magnetic*." Dill discloses this limitation, as summarized in Example 1.

Example 1 from (Ex. 1009, 9:47-53; 8:29-57.)		
…various other layers…		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	second (111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

130. For example, Dill discloses a spacer layer 152 that is made of chromium (Cr) metal. (Ex. 1009, 8:50-57.) The '988 patent indicates that Cr is a "non-magnetic bcc [material]." (Ex. 1001, 10:57-60.)

I. Dill in Combination With Shen Renders Obvious Claim 11

131. Claim 11 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer which is magnetic*." Dill discloses this limitation in an alternate of Example 1.

Example 1 from (Ex. 1009, 9:37-53; 8:29-57.)		
…various other layers…		
Bulk layer of sensing layer 132:		
Interface layer of 132:	$Co_{(40)}Fe_{(60)}$ (bcc)	"second bcc-d layer which is magnetic"
Tunnel barrier 120:	Al_2O_3	
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

132. Dill discloses an exemplary "alternative sensing ferromagnetic layer 132" "comprised of a thin Co or $Co_{(100-x)}Fe_{(x)}$ or $Ni_{(100-x)}Fe_x$ (x is approximately 60) layer at the interface between the sensing ferromagnetic layer 132 and the tunnel barrier layer 120." (Ex. 1009, 9:37-41; FIG.4A.) Because "x is approximately 60," the composition of this interface layer is approximately $Co_{40}Fe_{60}$, an Fe-rich alloy of FeCo. One of ordinary skill in the art would have understood that the layer has the (bcc) structure. (*See, e.g*., Ex. F.) And with both Co and Fe being magnetic, one of ordinary skill in the art would have understood that their alloys are also magnetic.

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J. Dill in Combination With Shen and Heim Renders Obvious Claim 12

133. Claim 12 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: **a second bcc-d layer . . . .**" Dill discloses this limitation as summarized in Example 2.

Example 2 from (Ex. 1009, 8:14-22; 10:57-60; 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	
Thin metal layer of 118:	Cr	(bcc)	"second bcc-d layer"
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

134. As discussed in ¶ 97 *supra* and shown in Example 2, Dill discloses an alternative example of layer 118 that includes two ferromagnetic layers of (bcc) $Co_{30}Fe_{70}$ "separated by a thin metallic layer, which results in antiferromagnetic coupling of the two ferromagnetic layers." (Ex. 1009, 9:65-10:4.) One of ordinary skill in the art would have known that, in this example, the spacer layer must be non-magnetic in order to allow AF coupling of the ferromagnetic layers.

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135. Dill does not explicitly specify the spacer layer in this example of layer 118, but Dill discloses that the thin metal layer is non-magnetic metal that separates and couples two ferromagnetic layers. Dill cites Heim as providing further information about the "type of laminated fixed layer" of layer 118, including the above-mentioned thin metal layer. (Ex. 1009, 9:60-10:4.) Because Dill cites Heim for the laminate structure and because Heim discloses the same ferromagnetic structure as disclosed in Dill, it would have been obvious for a person of ordinary skill to use this information from Heim, including that the thin layer can be Cr. (Ex. 1012, 7:3-10.) Similarly, Dill discloses another non-magnetic metal spacer layer 152 that separates and couples the ferromagnetic sensing layer 132 and its ferromagnetic bias layer 150. (Ex. 1009, 8:14-22.) The non-magnetic spacer layer between layers 132 and 150 is chromium. Dill discloses that Cr layer 152 couples layers 150 and 132 to "maintain a generally single domain state" in film 132. (Ex. 1009, 8:14-22.) Also, the '988 patent explains that Cr is an example of what is claimed as a "non-magnetic bcc [material]." (Ex. 1001, 10:57-60.)

136. In this example, the first ferromagnetic film of layer 118 is the claimed first "bcc-d layer," and the Cr spacer of layer 118 is the claimed "second bcc-d layer." Alternatively, the "second bcc-d layer" is the second ferromagnetic film of layer 118, grown onto the Cr spacer of layer 118.

137. Claim 12 of the '988 patent further recites "wherein *the crystalline orientation of the second bcc-d layer is epitaxially determined by said [first] bcc-d layer*." Dill discloses this limitation.

138. As discussed in ¶¶ 135-36, *supra*, the chromium spacer and both ferromagnetic films of layer 118 have a (bcc) structure, and one of ordinary skill in the art would have known that the Cr spacer layer would grow epitaxially on and have its crystalline orientation epitaxially determined by the lower ferromagnetic film. Because the upper ferromagnetic film is grown on the Cr thin metal layer, one of ordinary skill in the art would have known that its structure would be determined by the thin metal layer and, therefore, also epitaxially determined by the lower ferromagnetic film (first bcc-d layer). Therefore, it would have been obvious to one of ordinary skill in the art to have a second bcc-d layer (the Cr spacer layer of layer 118 or the upper ferromagnetic film of 118) whose bcc-d crystalline orientation is epitaxially determined by the first bcc-d layer (lower ferromagnetic film).

K. Dill in Combination With Shen Renders Obvious Claim 13

139. Claim 13 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer*." Dill discloses this limitation as summarized in Example 1.

Example 1 from (Ex. 1009, 8:51-52; 9:41-42; 9:47-53; 8:29-57.)			
…various other layers…			
Spacer layer 152:	Cr	(bcc)	"second bcc-d layer"
Bulk layer of sensing layer 132:	$Ni_{81}Fe_{19}$	(fcc)	second "(111)…hexagonal atomic template"
Interface layer of 132:	$Co_{(40)}Fe_{(60)}$ (bcc)		
Tunnel barrier 120:	Al_2O_3		
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)		"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)		"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)		(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)		(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

140. For example, Dill discloses a layer 152 that is made of chromium (Cr) metal. (Ex. 1009, 8:50-57.) The '988 patent indicates that Cr is an example of what is claimed as a "non-magnetic bcc [material]." (Ex. 1001, 10:57-60.) Therefore, layer 152 is the claimed "second bcc-d layer."

141. Claim 13 of the '988 patent further recites "*a second layer providing a (111) textured hexagonal atomic template*." Dill discloses this limitation.

142. For example, Dill discloses that sensing layer 132 is $Ni_{81}Fe_{19}$. (Ex. 1009, 8:51-52; 9:41-42.) One of ordinary skill in the art would have known that $Ni_{81}Fe_{19}$ naturally has an (fcc) structure and is magnetic. (*See*, *e.g.*, Ex. H, p. 251 *et seq.*; Ex. I, pp. 288-312; Ex. G, p. 94 *et seq.*) In addition, one of ordinary skill in the art would also have known that this particular composition, $Ni_{81}Fe_{19}$,

would naturally form a (111)(fcc) structure. (*Id.*) Therefore, alternative sensing layer 132 would be the claimed "second layer providing a (111) textured hexagonal template."

143. Claim 13 of the '988 patent further recites "wherein said *second layer providing a (111) textured hexagonal atomic template is disposed between said bcc-d layers*." Dill discloses this limitation.

144. Example 1 summarized above shows that layer 132 (the "second layer providing a (111) textured hexagonal atomic template") is located between layer 152 (the "second bcc-d layer") and layer 118 (the first "bcc-d layer").

145. Moreover, FIG. 4A shows that layer 132 is disposed between layers 118 and 152.

L.   Dill in Combination With Shen Renders Obvious Claim 14

146. Claim 14 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer*, *which is magnetic*." Dill discloses this limitation as summarized in Example 1.

Example 1 from (Ex. 1009, 8:51-52; 9:41-42; 9:47-53; 8:29-57.)		
…various other layers…		
Spacer layer 152:	Cr (bcc)	
Bulk layer of sensing layer 132:	$Ni_{(81)}Fe_{(19)}$ (fcc)	
Interface layer of 132:	$Co_{(40)}Fe_{(60)}$ (bcc)	"second bcc-d layer, which is magnetic"
Tunnel barrier 120:	Al_2O_3	"oxide layer between"
Interface layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
Bulk layer of layer 118:	$Ni_{(40)}Fe_{(60)}$ (fcc)	"[first] (111)…hexagonal atomic template"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	(111)…hexagonal atomic template
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

147.   For example, Dill discloses an alternative sensing layer 132 that includes an interface layer of 132 that is $Co_{(40)}Fe_{(60)}$. (Ex. 1009, 9:37 41.) One of ordinary skill in the art would have known that both Co and Fe are magnetic, as are their alloys. Therefore, one of ordinary skill in the art would have known this layer to be magnetic. As shown in the phase diagram for this material, one of ordinary skill in the art would have understood that the natural state of $Co_{(40)}Fe_{(60)}$ is bcc. (*See*, *e.g.*, Ex. H, p. 251 *et seq.*; Ex. I, pp. 288-312; Ex. G, p. 94 *et seq.*)

148.   Claim 14 further recites "***at least one oxide layer between said bcc-d layers***." Dill discloses this limitation.

149. For example, Dill discloses a "tunnel barrier layer 120" ("at least one oxide layer between said bcc-d layers") that is comprised of the oxide Al_2O_3. (Ex. 1009, 8:49-51.) As shown at least in Example 1 above, tunnel barrier 120 is disposed between ferromagnetic fixed layer 118 (which includes the first bcc-d layer) and layer 132 (which includes the second bcc-d layer). This is also shown in FIG. 4A of Dill. (Ex. 1009, FIG. 4A.)

M. Dill in Combination With Shen and Heim Renders Obvious Claim 15

150. Claim 15 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second and a third bcc-d layers which are non-magnetic*." Dill discloses this limitation as summarized in Example 2.

Example 2 from (Ex. 1009, 13:35-38; 9:65-10:3; 9:47-53; 8:29-57.)		
Cap layer 134:	Cr (bcc)	
Top layer of 150:	$Co_{(30)}Fe_{(70)}$ (bcc)	
Thin metal layer of 150:		
Bottom layer of 150:	$Co_{(30)}Fe_{(70)}$ (bcc)	"fourth bcc-d layer which is magnetic"
Spacer layer 152:	Cr (bcc)	"third bcc-d layer" which is non-magnetic
Sensing layer 132:	$Co_{(40)}Fe_{(60)}$ (bcc)	
Tunnel barrier 120:	Al_2O_3	"oxide layer between"
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	
Thin metal layer of 118:	Cr (bcc)	second bcc-d layer which is non-magnetic
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

151. As discussed in ¶¶ 96-97, 134-35 and shown in Example 2 above, Dill

discloses that an alternative example of layer 118 includes two ferromagnetic

layers of (bcc) $Co_{30}Fe_{70}$ "separated by a thin metallic [spacer] layer" (Ex. 1009,

9:65-10:4), where it would have been obvious for the spacer layer to be Cr (*id.*; *see*

also Ex. 1012, 7:3-10), which is non-magnetic and (bcc) (Ex. 1001, 10:57-60).

(*See* ¶¶ 134-35, *supra*.) Because the film is "thin" and has a natural (bcc)

structure, one of ordinary skill would have understood that it would conform to the

(bcc) crystalline structure of the underlying $Co_{30}Fe_{70}$ layer. In this example, the lower ferromagnetic film of layer 118 is the claimed *first* "*bcc-d layer*" and the Cr spacer of layer 118 is the claimed "*second bcc-d layer*…which [is] non-magnetic."

152. Similarly, Dill also discloses a layer 152 that is made of chromium (Cr) metal. (Ex. 1009, 8:50-57.) As discussed above, one of ordinary skill in the art would have known that Cr is a (bcc) material that is non-magnetic, and the '988 patent indicates as much. Therefore, layer 152 is the claimed "*third bcc-d layer*…which [is] non-magnetic."

153. Claim 15 further recites "*a fourth bcc-d layer which is magnetic*." Dill discloses this limitation.

154. For example, Dill first discloses a "biasing ferromagnetic layer 150" that is a single ferromagnetic layer located over the sensing layer 132. (Ex. 1009, 8:51-54.) Dill then discloses an improved layer 150 that "secures the magnetic moment" of layer 150 (Ex. 1009, 13:8-11) by forming layer 150 from "a bilayer of a ferromagnetic layer of permalloy covered with an antiferromagnetic layer of FeMn." (Ex. 1009, 13:35-38.) Dill also discloses a tri-layer laminate structure (for layer 118) that will "increase[] further" the stability of one of the ferromagnetic layers. (Ex. 1009, 9:65-10:4, emphasis added.) As discussed in ¶ 134 *supra*, in this example the laminate structure includes two (bcc) ferromagnetic layers separated by a thin metal layer. It would have been obvious to one of ordinary

skill in the art to apply the "further" increased stability of the layer laminate structure (for layer 118) to the merely increased stability of layer 150 to form a tri-layer laminate layer 150, like the tri-layer laminate layer 118. In this case, as shown in Example 2 above, layer 150 would be a laminate of a $Co_{(30)}Fe_{(70)}$ layer / a thin metal layer / a $Co_{(30)}Fe_{(70)}$ layer.

155. The lower ferromagnetic layer of layer 150 is $Co_{(30)}Fe_{(70)}$ which is naturally (bcc) and magnetic. The layer is grown directly on the Cr spacer layer 152, which is also naturally (bcc). Therefore, one of ordinary skill in the art would have known that it is natural that the lower ferromagnetic layer of layer 150 is (bcc) and that Dill discloses the "fourth bcc-d layer which is magnetic" limitation.

156. Claim 15 further recites "*at least one oxide layer between said second bcc-d layer and said third bcc-d layer*." Dill discloses this limitation.

157. Dill discloses a "tunnel barrier layer 120" that is comprises of the oxide Al_2O_3. (Ex. 1009, 8:49-51.) As summarized in Example 2 above, tunnel barrier 120 is disposed between layer 118 (that includes the second "bcc-d [layer] which [is] non-magnetic") and layer 152 (the third "bcc-d [layer] which [is] non-magnetic").

158.   Claim 15 further recites "wherein said *second and third bcc-d layers are disposed between said first and fourth bcc-d layers*." Dill discloses this limitation.

159.   As summarized in Example 2 above, the Cr thin metal layer of layer 118 ("second…bcc-d layer") and Cr layer 152 ("third bcc-d layer") are located between the lower ferromagnetic layer of layer 118 ("first…bcc-d layer") and the lower ferromagnetic layer of layer 150 ("fourth bcc-d layer"). This is also shown explicitly in FIG. 4A of Dill. (Ex. 1009, FIG. 4A.)

N.   Dill in Combination With Shen and Heim Renders Obvious Claim 16

160.   Claim 16 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer which is magnetic*." Dill discloses this limitation as summarized in Example 2.

Example 2 from (Ex. 1009, 9:37-41; 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Sensing layer 132:			
Interface layer of 132	$Co_{(40)}Fe_{(60)}$	(bcc)	"second bcc-d layer which is magnetic"
Tunnel barrier 120:	Al_2O_3		"oxide layer between"
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	
Thin metal layer of 118:	Ru	(hcp)	second (111)…hexagonal atomic template
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

161.   For example, Dill discloses an alternative sensing layer that includes an interface layer of layer 132 that is bcc and magnetic. (Ex. 1009, 9:37-41.) With "x [being] approximately 60," the interface layer of layer 132 is $Co_{(40)}Fe_{(60)}$ (*id.*), because both Co and Fe are magnetic, as are their alloys, one of ordinary skill in the art would have known this layer to be magnetic. One of ordinary skill in the art would have understood that the natural state of $Co_{(40)}Fe_{(60)}$ is bcc. (*See*, *e.g.*, Ex. F.)

162.   Claim 16 further recites "***a second (111) textured hexagonal atomic template layer between said bcc-d layers***." Dill discloses this feature.

163. In the example discussed in ¶ 97, *supra*, layer 118 comprises a thin metal layer separating two (bcc) layers of $Co_{30}Fe_{70}$. (Ex. 1009, 9:47-53; 9:65-10:4.) Dill cites Heim as providing further information about the "type of laminated fixed layer" of layer 118, including the above-mentioned thin metal layer. (Ex. 1009, 9:60-10:4.)   Because Dill cites Heim for the laminate structure and because Heim discloses the same ferromagnetic structure as disclosed in Dill, it would have been obvious for a person of ordinary skill to use this information from Heim, including that the thin layer can be Ru. (Ex. 1012, 5:16-27; *see also* ¶ 135, *supra*.)   One of ordinary skill in the art would have known from the relevant phase diagram that the natural structure of Ru grown on a (bcc) surface is (hcp) that provides a (111) hexagonal atomic template. (*See*, *e.g*., Ex. G, p. 94 *et seq*.) Therefore, in this example the metal layer of 118 is "a second (111) textured hexagonal atomic template layer."

164. Because the Ru thin metal layer of layer 118 separates the two ferromagnetic layers of layer 118, it is disposed above the lower ferromagnetic layer of layer 118 (the first "bcc-d layer"). As summarized for Example 2 above, the Ru thin metal layer of layer 118 ("second layer providing a (111) textured hexagonal atomic template") is disposed below the $Co_{(40)}Fe_{(60)}$ interface layer of layer 132 (the "second bcc-d layer"). The metal layer of 118 is located between

the lower ferromagnetic layer of layer 118 (the first "bcc-d layer") and the
interface layer of layer 132 (the "second bcc-d layer").

165.   Claim 16 further recites "at least one *oxide layer between said bcc-d
layers*." Dill discloses this limitation.

166.   Dill discloses an Al_2O_3 "tunnel barrier layer 120." (Ex. 1009,
8:49-51.) As summarized for Example 2 above, tunnel barrier 120 is disposed
between biasing layer 150 (with the "second bcc-d layer which is magnetic") and
fixed layer 118 (with the first "bcc-d layer which is magnetic").

167.   FIG. 4A further shows that layer 120 is disposed between layers 150
and 118.

O.   Dill in Combination With Shen Renders Obvious Claim 17

168.   Claim 17 of the '988 patent recites: "The magnetic material structure
recited in claim 1, wherein said *bcc-d layer forming a uniaxial symmetry broken
structure is composed of Fe or FeCo or an alloy of Fe or FeCo*." Dill in
combination with Shen discloses this limitation.

169.   For example, as discussed in IX(B) *supra*, Dill in combination with
Shen discloses in Example 1 that the interface layer of layer 118 is (bcc) and
provides a uniaxial symmetry broken structure (first "bcc-d layer"). Also, the

interface layer is $Co_{(100-x)}Fe_{(x)}$ (x is approximately 60). (Ex. 1009, 9:47-59.)

Therefore, the interface layer is "an alloy of Fe or FeCo" as claimed.

P. Dill in Combination With Shen Renders Obvious Claim 18

170. Claim 18 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein said ***bcc-d layer forming a uniaxial symmetry broken structure is composed of an alloy of Fe or FeCo having one or more of the elements Al*, *B*, *Cr*, *C*, *Cu*, *Ni*, *N*, *Nb*, *Mo*, *V*, *Si*, *Ta*, *and Ti***." Dill discloses this limitation.

171. For example, as discussed in IX(B) *supra*, Dill discloses in Example 2 that the layer 118 "can be ... form[ed] from a lamination of two ferromagnetic layers, such as Ni, Co, Ni-Fe alloys, Co-Fe alloys, or Ni-Fe-Co ternary alloys, separated by a thin metallic layer ...." (*See* ¶¶ 56, 93, 108-09, 111, *supra*; *see also* Ex. 1009, 9:65-10:3; 9:47-53; 8:29-57.) As discussed above, the lower ferromagnetic layer provides a uniaxial symmetry broken structure (first "bcc-d layer"). (*Id.*) The same layer can contain Ni and, therefore, is "an alloy of Fe … having … Ni" as claimed. (*Id.*)

Q. Dill in Combination With Shen Renders Obvious Claim 19

172. Claim 19 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein ***the layer material forming said (111) textured***

hexagonal atomic template is composed of Ag, *Al*, *Au*, *Cu*, *fcc-Co*, *fcc-CoCr*, *Ir*, *Ni*, *NiFe*, *Pt*, *Rh*, *Pd*, *hcp-Co*, *Gd*, *Re*, *Ru*, *Tb*, *Ti*, *or alloys* of one of these materials combined with at least one element." Dill discloses this limitation.

173.   For example, as discussed in IX(B) *supra*, Dill discloses in Example 1 that the bulk layer of layer 118 "form[s] said (111) textured hexagonal atomic template" and is composed of $Ni_{(100-x)}Fe_{(x)}$ (x is approximately 60), which is an alloy of Fe and Ni as claimed.

R.   Dill in Combination With Shen and Heim Renders Obvious Claim 21

174.   Claim 21 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a coupling layer*." Dill discloses this limitation, as summarized for Example 2 below.

Example 2 from (Ex. 1009, 9:37-41; 9:65-10:3; 9:47-53; 8:29-57.)		
…various other layers…		
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"second bcc-d layer which is magnetic"
Thin metal layer of 118:	Ru (hcp)	"coupling layer" and AF coupling
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$ (bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$ (fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$ (fcc)	(111)…hexagonal atomic template
…various other layers…		
Substrate G1:	Al_2O_3	

175.   Dill discloses that fixed layer 118 ("bcc-d layer which is magnetic") can be formed "from a lamination of two ferromagnetic layers [*i.e.*, a first and a second bcc-d layer]" that are separated by a "thin metallic layer" ("coupling layer") "which results in antiferromagnetic coupling of the two ferromagnetic layers." (Ex. 1009, 9:60-10:3.)

176.   Claim 21 further recites "*a second bcc-d layer which is magnetic*." Dill discloses this limitation.

177.   For example, Dill discloses that fixed layer 118 ("bcc-d layer which is magnetic") can be formed "from a lamination of two ferromagnetic layers [*i.e.*, a first and a second bcc-d layer], such as Ni, Co, Ni-Fe alloys, Co-Fe alloys, or Ni-Fe-Co ternary alloys." (Ex. 1009, 9:60-10:3.) One of ordinary skill in the art would have known that at least Fe and some of its alloys are (bcc) and magnetic. (*See*, *e.g.*, Ex. H, p. 251 *et seq.*; Ex. G, p. 94 *et seq.*)

178.   Claim 21 further recites "wherein the coupling layer material *antiferromagnetically couples the bcc-d layers*." Dill discloses this limitation.

179.   For example, Dill discloses that the "thin metallic layer" ("coupling layer") "results in antiferromagnetic coupling of the two ferromagnetic layers [*i.e.*, a first and a second bcc-d layer]." (Ex. 1009, 9:60-10:3.)

S. Dill in Combination With Shen Renders Obvious Claim 22

180. Claim 22 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer which is magnetic*." Dill discloses this limitation as shown in the summary of Example 2 below.

Example 2 from (Ex. 1009, 9:37-41; 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Sensing layer 132:			
Interface layer of 132	$Co_{(40)}Fe_{(60)}$	(bcc)	"second bcc-d layer which is magnetic"
Tunnel barrier 120:	Al_2O_3		
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"third bcc-d layer…between"
Thin metal layer of 118:		(hcp)	
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

181. For example, Dill discloses an alternative ferromagnetic sensing layer that includes an interface layer of layer 132 that is bcc and magnetic. (Ex. 1009, 9:37-41.) With "x [being] approximately 60," the interface layer of layer 132 is $Co_{(40)}Fe_{(60)}$, which one of ordinary skill in the art would have understood to be bcc (*id.*) and magnetic ("second bcc-d layer which is magnetic") in its normal state.

182. Claim 22 further recites "*a third bcc-d layer disposed between the bcc-d layers which are magnetic*." Dill discloses this feature.

183. Dill discloses an example of layer 118 has a lower ferromagnetic layer of 118 ("[first] bcc-d layer") and an upper ferromagnetic layer of 118 ("third bcc-d layer"), separated by a metallic layer. (Ex. 1009, 9:65-10:4.)

184. As summarized for Example 2 above, the upper ferromagnetic layer of 118 ("third bcc-d layer") is disposed between the lower ferromagnetic layer of 118 ("[first] bcc-d layer which is magnetic") and the layer added to layer 132 ("second bcc-d layer which is magnetic").

T.   Dill in Combination With Shen and Heim Renders Obvious Claim 23

185. Claim 23 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: *a second bcc-d layer which is magnetic;* and *a second (111) textured hexagonal atomic template layer*." Dill discloses this limitation as summarized for Example 2 below:

Example 2 from (Ex. 1009, 9:37-41; 9:65-10:3; 9:47-53; 8:29-57.)			
…various other layers…			
Upper layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"second bcc-d layer"
Thin metal layer of 118:	Ru	(hcp)	second (111)…hexagonal atomic template
Lower layer of layer 118:	$Co_{(30)}Fe_{(70)}$	(bcc)	"[first] bcc-d layer which is magnetic"
AF layer 116:	$Mn_{(50)}Fe_{(50)}$	(fcc)	"[first] (111)…hexagonal atomic template"
Template layer 112:	$Ni_{(81)}Fe_{(19)}$	(fcc)	(111)…hexagonal atomic template
…various other layers…			
Substrate G1:	Al_2O_3		

186.　See, in particular, the "upper layer of layer 118" and the "thin metal layer of 118" *supra*.

187.　More specifically, as discussed in IX(B) *supra*, Dill discloses the example of lower ferromagnetic layer of 118 and the upper ferromagnetic layer of 118 that are $Co_{30}Fe_{70}$ and are naturally bcc materials and magnetic (the "[first] bcc-d layer which is magnetic" and the "second bcc-d layer which is magnetic," respectively), and intervening metal layer of 118 is Ru and in this example naturally provides a "second (111) textured hexagonal atomic template."

188.　Claim 23 further recites "wherein said *second (111) textured hexagonal atomic template is disposed between said bcc-d layers*." Dill discloses this limitation.

189. As shown in the summary for Example 2 above, the Ru metal layer of layer 118 ("second (111) textured hexagonal atomic template layer") is disposed below the $Co_{(30)}Fe_{(70)}$ upper layer of layer 118(the "second bcc-d layer").

190. Because the Ru thin metal layer of layer 118 separates the two ferromagnetic layers of layer 118, it is disposed above the interface layer of layer 118 (the first "bcc-d layer").

191. This is further shown in the summary for Example 2 above.

U. Dill in Combination With Shen Renders Obvious Claim 24

192. Claim 24 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: at least *one magnetic hcp Co alloy layer*." Dill discloses this limitation. For example, Dill discloses an example in which layer 150 is $Co_{75}Pt_{13}Cr_{12}$, which one of ordinary skill in the art would have understood has an hcp crystalline structure and is magnetic. (Ex. 1009, 8:52-53; *see*, *e.g.*, Ex. G, p. 94 *et seq*.)

V. Dill in Combination With Shen Renders Obvious Claim 27

193. Claim 27 of the '988 patent is identical to claim 1, apart from the additional limitation that the magnetic material structure must be incorporated into a "*magnetic device*." As discussed in IX(B) *supra*, the combination of Dill and Shen discloses all the limitations of claim 1. Dill also discloses the additional

limitation of claim 27 that the magnetic structure must be incorporated into a "magnetic device."

194. For example, Dill discloses a magnetic tunnel junction ("MTJ") magnetoresistive ("MR") read head (i.e., a "magnetic device") in the form of a layer stack that includes a "gap layer G1 substrate" ("substrate"). (Ex. 1009, 5:26-31; FIG. 4A.) One of ordinary skill in the art would readily have understood that an MTJ and an MR read head are devices that both incorporate or include at least one "magnetic material."

W.   Dill in Combination With Shen Renders Obvious Claim 28

195. Claim 28 recites: "The magnetic device recited in claim 27, wherein the device is *a magnetic data storage system*." Dill discloses this limitation.

196. For example, Dill discloses that the MTJ of the invention could be used in "heads for magnetic recording systems." (Ex. 1009, 1:41-43.)

X.   Dill in Combination With Shen Renders Obvious Claim 29

197. Claim 29 of the '988 patent recites: "The magnetic device recited in claim 27, wherein the device is *a data storage magnetic recording transducer*." Dill discloses this limitation.

198. For example, Dill discloses that the magnetic film structure is used in "heads for magnetic recording systems" (Ex. 1009, 1:41-43) and, more

specifically, in an "MR read head" of a "read/write . . . transducer" that also includes an "inductive write head." (*See*, *e.g.*, Ex. 1009, 4:22-25; 5:23-25.)

Y.   Dill in Combination With Shen Renders Obvious Claim 30

199. Claim 30 of the '988 patent recites: "The magnetic device recited in claim 27, wherein the device is at least one of: an anisotropic magnetoresistive sensor; a spin valve magnetoresistive sensor; a *magnetic tunnel junction magnetoresistive sensor* and a data storage magnetic playback transducer." Dill discloses this limitation.

200. For example, Dill is entitled "Magnetic Tunnel Junction Magnetoresistive Sensor . . . " and discloses that the device in FIG. 4A is a magnetic tunnel junction ("MTJ") for a magnetic read head (i.e., a magnetic data storage system). (Ex. 1009, Title; 3:57-59; 3:7-41; Abstract; *see also* 7:53-56.)

Z.   Dill in Combination With Shen Renders Obvious Claim 34

201. Claim 34 of the '988 patent recites: "The magnetic device recited in claim 27, wherein *the device is* at least one of: an electronic circuit inductive component and an *electronic circuit inductive transformer component*." The combination of Dill with Shen discloses this limitation. Dill discloses that the magnetic film structure is used in "heads for magnetic recording systems" (Ex. 1009, 1:41-43.) and, more specifically, in an "MR read head" of a "read/write

. . . transducer" that also includes an "inductive write head." (*See*, *e.g*., Ex. 1009, 4:22-25; 5:23-25.)

AA.   Dill in Combination With Shen Renders Obvious Claim 38

202.   Claim 38 of the '988 patent recites: "The magnetic device according to claim 27, further comprising: at least *one hard magnetic layer*." The combination of Dill with Shen discloses this limitation.

203.   For example, Dill discloses an example in which bias layer 150 is $Co_{75}Pt_{13}Cr_{12}$. (Ex. 1009, 8:52-53.) One of ordinary skill in the art would have understood that this material is magnetically hard.

204.   Claim 38 further recites "wherein said at least one *bcc-d layer* which is magnetic, forming a uniaxial symmetry broken structure, is *disposed between* said *(111) textured hexagonal atomic template* and said at least one *hard magnetic layer*." Dill discloses this limitation.

205.   As discussed in ¶¶ 95-105 *supra*, Dill discloses that the interface layer of layer 118 is a bcc-d layer which is magnetic, forming a uniaxial symmetry broken structure. As discussed in IX(B) *supra*, Dill discloses that the interface layer of 118 in Example 1 is **grown onto** the bulk layer of 118, which provides a (111) textured hexagonal atomic template to the interface layer of 118. As shown in FIG. 4A, Dill discloses that the interface layer of 118 is **disposed beneath** bias layer 150. Therefore, the interface layer of 118 ("bcc-d layer which is

magnetic…broken symmetry structure") is *disposed between* the bulk layer of 119 (the "(111) textured hexagonal atomic template") and bias layer 150 (the "hard magnetic layer").

X. DILL IN COMBINATION WITH SHEN AND LAMBETH I RENDERS OBVIOUS CLAIMS 2, 25, 26, AND 31 OF THE '988 PATENT

A. Claim Chart

206. The Petition sets forth a claim chart (Petition, Section VI(D)) citing disclosures in Dill, Shen, and Lambeth I that demonstrate how this combination of prior art references renders obvious the above-referenced claims. I fully agree with the claim chart. The following sections include additional analysis that demonstrates how the combination renders obvious each of these claims.

B. Dill in Combination With Shen and Lambeth I Renders Obvious Claim 2

207. Claim 2 of the '988 patent recites: "The magnetic material structure recited in claim 1, wherein said substrate is *single crystal*." The combination of Dill and Shen with Lambeth I renders obvious this limitation.

208. Dill discloses depositing the MTJ MR layers on the surface of an "alumina…substrate." (Ex. 1009, 10:19-34.) Even if Dill does not teach or suggest that the substrate is single crystal, Lambeth I does.

209. Lambeth I discloses the advantages of using a single crystal substrate to control crystalline texture and orientation when growing magnetic thin films. (Ex. 1013, Title; Abstract.) Specifically, Lambeth I discloses that "utilizing single crystal Si as a substrate" to grow magnetic films on top of "fcc metals," including those of Au metal as used by Dill, "with a very high degree of epitaxy." (*Id.*, p. 189.) Lambeth I discloses that this "maximize[s] the coercivity" and "minimize[s] the media noise . . . [and helps] to control the easy axes orientations." (*Id.*) Lambeth I further discloses that the "fcc" metal films can "easily be used to epitaxially grow other quasi-single crystal films of similar or differing crystalline structure," and gives the example of magnetic films of Co metal. (*Id.*, pp. 189-90.)

210. It would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to grow Dill's magnetic structure on a single crystalline material, according to Lambeth I.

211. Dill discloses growing a magnetic layer stack on a substrate. (Ex. 1009, 5:26-28.) Similarly, Lambeth I discloses forming magnetic structures, including multilayer structures, on a substrate. (Ex. 1013, p. 190, ¶ 1; FIG. 5.)

212. Growing Dill's multilayer structures on a single crystal substrate would be straightforward and predictable. One of ordinary still in the art would have known that layer stacks can be grown on single crystal surfaces.

213. Therefore, it would have been obvious to a person of ordinary skill in the art to try growing Dill's layered structure on a single crystal surface, as disclosed by Lambeth I to "maximize the coercivity and . . . minimize the media noise . . . [and help] to control the easy axes orientations." (Ex. 1013, p. 189.)

C. Dill in Combination With Shen and Lambeth I Renders Obvious Claim 25

214. Claim 25 of the '988 patent recites: "The magnetic material structure according to claim 1, further comprising: at least one *magnetic hcp Co alloy layer*." Dill discloses this limitation.

215. As discussed in IX(U) *supra*, Dill discloses an example in which layer 150 is $Co_{75}Pt_{13}Cr_{12}$, which one of ordinary skill in the art would have understood has an hcp crystalline structure and is magnetic. (Ex. 1009, 8:52-53.)

216. Claim 25 also recites "wherein said *hcp Co alloy has a (1011) crystalline texture*."

217. Lambeth I discloses that the anisotropy of Co magnetic layers can be improved by growing selected crystalline textures, such as the (1011) texture. (Ex. 1013, p. 189, ¶ 1; p. 190.) Therefore, Lambeth I discloses a "magnetic hcp Co alloy layer" with "a (1011) crystalline texture."

218. It would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to grow Dill's Co-alloy of

layer 150, a "magnetic hcp Co alloy layer," to have "a (1011) crystalline texture," according to Lambeth I.

219. Dill discloses growing a magnetic layer stack on a substrate. (Ex. 1009, 5:26-28.) Similarly, Lambeth I discloses forming magnetic structures, including multilayer structures, on a substrate. (Ex. 1013, p. 190, ¶ 1; FIG. 5.) Because of the similarity in structures, growing Dill's Co-containing interface layer to achieve the (1011) texture according to Lambeth I would be straightforward and predictable.

220. Therefore, a person of ordinary skill would grow Dill's Co-containing interface layer of layer 118, a "magnetic hcp Co alloy layer" to have "a (1011) crystalline texture," according to Lambeth I. Doing so would "grow Co-alloy and underlayer crystalline grains of considerable perfection and appropriate texture to avoid compromising the crystalline [magnetic] anisotropy." (Ex. 1013, p. 189.)

D. Dill in Combination With Shen and Lambeth I Renders Obvious Claim 26

221. Claim 26 of the '988 patent recites: "The magnetic material structure according to claim 1, wherein: said *substrate is a (111) crystalline textured single crystal; and a surface of said single crystal provides a layer providing the (111) textured hexagonal atomic template*." Dill in combination with Shen and Lambeth I discloses this limitation.

222. Dill discloses depositing the MTJ MR layers on the surface of an "alumina…substrate" (Ex. 1009, 10:19-34), which is not a single crystal, that has been coated with Au metal (*id.*, 8:43-48). However, it would have been obvious in view of Lambeth I to grow Dill's multilayer structures on a single crystal. (*See* X(B) *supra*.)

223. Lambeth I discloses that the substrate can be a single crystal with a (111) surface. (Ex. 1013, p. 190, ¶ 1; FIG. 5 and caption.) Lambeth I further discloses that the single crystal Si structure provides a system "to control the easy axes orientations" to maximize the coercivity and minimize the noise in the film. (*Id.*, p. 189, ¶ 1.) One of ordinary skill in the art would have known that a Si (111) surface provides a (111) textured hexagonal atomic template. For these reasons, it would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to try growing Dill's layer stack on Lambeth I's single crystal Si(111).

224. Dill discloses growing a magnetic layer stack on a substrate. (Ex. 1009, 5:26-28.) Similarly, Lambeth I discloses forming magnetic structures, including multilayer structures, on a substrate. (Ex. 1013, p. 190, ¶ 1; FIG. 5.) Because of the similarity in structures, growing Dill's layer stack on a single crystal (111) surfaced substrate would be straightforward and predictable.

225.   The next limitation of claim 26 is that the template is "*disposed*

between the bulk of said substrate and said at least one bcc-d layer." Dill

discloses this feature.

226.   Dill discloses that the surface of the substrate G1 on which

antiferromagnetic layer 116 ("layer providing the (111) texture") is provided is

disposed between the bulk of the substrate (G1) and the ferromagnetic layer 118

("bcc-d layer which is magnetic"). (*See*, *e.g.*, Ex. 1009, FIG. 4A.)

FIG. 4A

(Ex. 1009, FIG. 4A, annotated.)

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E. Dill in Combination With Shen and Lambeth I Renders Obvious Claim 31

227. Claim 31 recites: "The magnetic device recited in claim 27, wherein the device is at least one of a *data storage magnetic recording media*; a data storage magnetic recording media incorporating an oriented soft magnetic layer; and a data storage magnetic recording media incorporating an oriented hard magnetic layer." The combination of Dill and Lambeth I discloses this limitation.

228. As discussed above in Sections VIII(B) and (C), Shen in combination with Dill discloses a multi-layer device with broken symmetry and improved magnetic properties. However, neither Shen nor Dill explicitly discloses that the layered device can be used as data storage media.

229. Lambeth I discloses controlling growth and texture in magnetic film structures (Ex. 1013, Title; Abstract) for use in "Magnetic Media" (*id.*). Lambeth I discloses the relationship between "media thin film microstructure" and "microstructural properties" in media performance. (*Id.*, p. 182.)

230. Therefore, Lambeth I discloses "recording magnetic media" for which the "media thin film microstructure" can improve the "achievable areal recording density" and "media signal to noise ratio." (*Id.*)

231. It would have been obvious to a person of ordinary skill in the art at the time of the effective filing date of the '988 patent to apply Shen's

(111)(fcc)/(bcc) structure and broken symmetry (Ex. 1011, FIG. 4) to improve

magnetic properties in the "recording magnetic media" disclosed by Lambeth I.

232.   Shen discloses breaking symmetry in multi-layered, magnetic

structures deposited on a substrate. (Ex. 1011, FIG. 4.) Lambeth I discloses

forming magnetic structures, including multilayer structures, on a substrate.

(Ex. 1013, p. 190, ¶ 1; FIG. 5.) Because of the similarity in structures, applying

Shen's teachings to Lambeth I's magnetic media would be obvious,

straightforward and predictable.

XI.   DILL IN COMBINATION WITH SHEN AND NOGUCHI RENDERS OBVIOUS CLAIM 39 OF THE '988 PATENT

A.   Claim Chart

233.   The Petition sets forth a claim chart (Petition, Section VI(E)) citing

disclosures in Dill, Shen, and Noguchi that demonstrate how this combination of

prior art references renders obvious claim 39. I fully agree with the claim chart.

The following sections include additional analysis that demonstrates how the

combination renders obvious that claim.

B.   Dill in Combination With Shen and Noguchi Renders Obvious Claim 39

234.   Claim 39 of the '988 patent recites: "The magnetic device according

to claim 27, further comprising: at least one *hard magnetic layer…disposed*

between said substrate and said…bcc-d layer." The combination of Dill with

Shen and Noguchi discloses this limitation.

235. Even if Dill does not disclose the claimed hard magnetic layer, it

would be obvious to add the hard magnetic layer of Noguchi to Dill. Like Dill,

Noguchi discloses forming an "MR element" ("magnetic material"), including

"ferromagnetic tunnel junction 21" and a substrate 4 ("substrate"). (Ex. 1014,

14:55-15:10; FIGs. 6-8.) The MR includes first ferromagnetic film 211 and

magnetic domain control films 214 and 215 ("hard magnetic layer"). (*Id*.,

12:53-67; FIGs. 6-8.) Noguchi discloses that using such hard magnetic films

"prevent[s] a disturbing influence of an external magnetic field" (*id*., 15:52-57) and

that they may be provided to "ferromagnetic film 211." (*Id*., 15:46-48.)

Therefore, it would have been obvious to a person of ordinary skill in the art at the

time of the effective filing date of the '988 patent to use the "hard magnetic layer"

(214 and 215), as taught by Noguchi, in Dill's magnetic layered structure

(FIG. 4A). Because of the similarity in structure and function, applying Noguchi's

"hard magnetic layer" (214 and 215) to Dill's magnetic layered structure (FIG. 4A)

would be straightforward and predictable.

236. In FIG. 12, Noguchi shows magnetic domain control films 214 and

215 disposed between the substrate 4 and ferromagnetic layer 211:
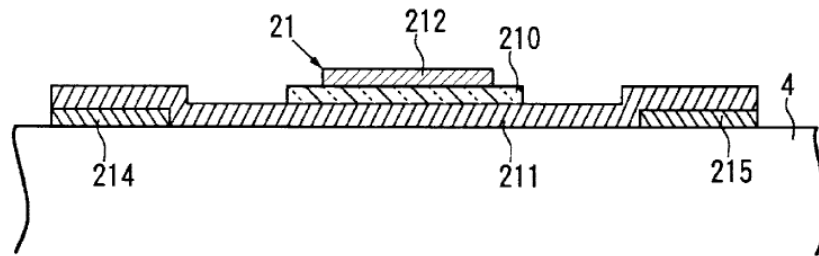
FIG. 12

(Ex. 1014, FIG. 12.)

237. Because Noguchi discloses disposing magnetic domain control films 214 and 215 ("hard magnetic layer") between (bcc) first ferromagnetic film 211 and substrate 4, it would have been obvious to place the magnetic domain control films 214 and 215 ("hard magnetic layer") between Dill's (bcc) bulk layer of 118 ("bcc d layer which is magnetic, forming a uniaxial symmetry broken structure") and the substrate G1. Doing so would have "prevent[ed] a disturbing influence of an external magnetic field." (Ex. 1014, 15:52-57.)

XII. CONCLUSION

238. For at least the preceding reasons, I believe that each of claims 1-3, 6-19, 21-31, 34, 38, and 39 of the '988 patent is invalid pursuant to 35 U.S.C. §§ 102 and/or 103.

239. I may testify about any of the preceding topics at a deposition or hearing.

240. I reserve the right to respond to any declarations that are submitted by Lambeth's expert witnesses or to any testimony by Lambeth's fact or expert witnesses, whether at deposition or at trial.

Robert L 10.5.15

Robert Sinclair, Ph.D.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) **Title:** MAGNETIC MATERIAL STRUCTURES, DEVICES AND METHODS

(57) **Abstract:** A thin film magnetic structure, magnetic devices, and method of producing the same, wherein (110) textured, symmetry broken body centered cubic or body centered cubic derivative crystalline structures epitaxially grown on hexagonal shaped templates, in the presence of a symmetry breaking mechanism is provided to promote oriented uniaxial magnetic properties from a series of successively deposited film layers, result in new oriented magnetic layer structures and microstructures and thus improved magnetic devices and device performance.

Magnetic Material Structures, Devices And Methods
BACKGROUND OF THE INVENTION
1. <u>Field of the Invention</u>

This invention is directed to magnetic material
5 structures, methods for making magnetic material structures
and devices made from magnetic material structures.

2. Description of the Prior Art

As the home, office, transportation system, business
10 place and factory become more automated and electronically
connected, and as electronic devices and appliances such as
computers, communication devices, wireless communication
devices, electronic games, entertainment systems, personal
data assistants, transportation vehicles, manufacturing
15 tools, shop tools, and home appliances become more
sophisticated there is, and will be, an ever-increasing
demand for higher performance and low cost electronic
circuits, sensors, transducers, data storage systems and
other magnetic devices which employ magnetic thin film
20 materials. In order for these devices to remain
competitive in the market place each product generation
must be higher performing, unobtrusive and, usually, less
expensive than the previous. Hence there are ever
increasing demands for technical improvements in the
25 materials and structure of these devices.

For all of these applications the magnetic material
has an improved performance if the magnetic properties can
be better controlled during the construction. Two familiar
properties, which are sometimes considered to be intrinsic
30 magnetic properties, are the saturation magnetization, M_s,
and the magnetocrystalline anisotropy energy density
constants (usually denoted by a subscripted K symbol). The
meaning of magnetic anisotropy energy is that the
magnetization would have a preferred direction, or
35 directions, of orientation. That is, the energy of the
system is minimal when the magnetization vector points
along certain directions. These directions are referred to
as the magnetic easy axes while the magnetic hard axes

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coincide with magnetic orientations where the energy is maximized. However, it should be noted that the magnetic anisotropy is not actually an intrinsic property in the sense that the materials are commonly not made perfectly. 5 Nevertheless, good performance in device applications is almost always dependent upon there being a single preferred magnetic orientation or anisotropy direction and so in the manufacturing process one strives to achieve a desired uniaxial anisotropy. An objective of the present invention 10 is to provide new mechanisms for controlling the magnetocrystalline anisotropy of thin magnetic films. By doing so the performance of almost all magnetic devices are envisioned to be improved.

In general the anisotropy energy is a function of the 15 orientation of the magnetization vector with respect to a given physical axis. Here, we define a "uniaxial" anisotropy to exist if the anisotropy energy density function only contains a single maximum and a single minimum as the magnetization angle, θ, is rotated by 180 20 degrees from a physical axis. Likewise we define an "ideal uniaxial" anisotropy energy to exist if the energy equation has only a $\sin^2(\theta)$ or $\cos^2(\theta)$ dependence. Materials and device processing to achieve a desired orientation or anisotropy is commonly difficult and sometimes impossible, 25 perhaps because heretofore the mechanism for achieving anisotropic orientation has not been well understood. Furthermore, uniform control of the orientation of the magnetic anisotropy is often difficult to achieve and maintain in a manufacturing process where many different 30 desired material properties must be obtained simultaneously.

Background for Oriented Soft Magnetic Films

35   In magnetic devices, for example, such as sensors, transducers, transformers, inductors, signal mixers, flux concentrators, recording media keepers, data recording and playback transducers it is common that the magnetic

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response to a driving field possess high sensitivity and at
the same time, low coercivity (Hc). Or stated simply, the
material possesses essentially non-hysteretic behavior.
For this type of behavior the device is constructed so that
5   the applied field is directed along the hard magnetic axis
of a uniaxial magnetic material. This results in the
minimization of coercivity and hysteric effects, which are
many times associated with magnetic domain wall motion of
materialsthat are multi-axial. For example, a material,
10   which has bi-axial anisotropy, will have two easy and two
hard magnetic axes and will exhibit hystersis and losses.
In many of these applications a linear, or near linear
response is also advantageous, while in other applications,
such as signal mixers, a controlled non-linear response is
15   desire. To obtain a linear magnetic response, requires
both applying a field along the magnetic hard axis and that
the anisotropy energy density function not only be
uniaxial, but that it also have simple $\sin^2(\theta)$ or negative
$\cos^2(\theta)$ dependence, where, θ, is the angle measured between
20   the magnetization vector direction and the physically
determined magnetic easy axis. Since there is the
mathematical identity, $\sin^2(\theta) = 1 - \cos^2(\theta)$, and since the
origin in the energy function is arbitrarily defined the
use of $\sin^2(\theta)$ or $-\cos^2(\theta)$ yield equivalent physical
25   behavior. Item [1] of Figure 1 illustrates the squared
sinusoidal anisotropy energy density curve shape versus the
angle of the magnetization vector with respect to the easy
axis located at zero degrees. Figure 2 illustrates the
response of the components of the magnetization, M_x and M_y,
30   as a function of applied field, $H_x = H_a$, along the hard
magnetic axis direction, x. The linear curve kinks only at
the point [2] where the magnetization becomes saturated, or
fully aligned with the applied field. For this special
uniaxial anisotropy this occurs at the applied field value
35   of H_k along the x direction, which is known as the
anisotropy field. These response curves are sometimes
referred to as hysteresis loops even though they exhibit no

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hystersis. It is the shape of the $\sin^2(\theta)$ energy function that causes the response, M_x, along the hard axis to be linear and to be fully reversible. M_y is the response in the y direction to an applied field in the x direction.

5   The curve shape shown is quadratic for applied field magnitudes less than H_k, where M_y is zero for larger magnitude fields. The quadratic behavior is necessary for linear M_x since $M_s^2 = M_x^2 + M_y^2$, where M_s is the total, constant, saturation magnetization vector magnitude. If

10   the anisotropy energy is uniaxial, but is not governed by the, ideal, $\sin^2(\theta)$ functional form then the magnetic response is not linear. However, heretofore, the applicant knows of no real material examples exhibiting both a uniaxial energy curve and a non-linear M_x versus H_x

15   behavior.

Materials exhibiting the $\sin^2(\theta)$ energy density functional form are often referred to as having Stoner-Wohlfarth behavior after the famous ideal uniaxial single domain magnetization theory. However, thin films are

20   commonly multi-domain even though they might exhibit the $\sin^2(\theta)$ functional energy form on a localized basis. Unless the hard axis direction is the same at all points in a sample and the applied driving field is exactly parallel to the hard axis then domain wall motion can commonly be

25   observed. This motion results in coercivity mechanisms and hysteretic energy losses. The lossless behavior of samples represented by Figure 2 is due to the magnetization rotating in response to the applied field rather than a response via domain wall motion. Multi-axis anisotropy

30   materials always switch via wall motion and so suffer losses.

It is also well known that, for soft uniaxial thin films, by first applying a field along the easy axis, and then by keeping a constant bias field in this direction, to

35   eliminate 180 degree domain walls, one can force all of the material to appear to be single domain as the hard axis is then driven. Hence, because of this bias field, $H_b = H_y$, in

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the easy axis direction the application of any finite H_x field along the hard axis can never quite drive the magnetization vector completely to the energy maximum [3] and the response will always be reversible and so lossless.

5   This is not the case for materials with multiple anisotropy axes. For uniaxial materials the rotational response is key to many sensor devices and it is common in various forms of magnetoresistive sensors to provide a bias field along the easy axis by either applying a small field or by exchange

10   coupling the magnetic sensor material to a hard magnetic material that has been so oriented to provide an effective bias field.

      For some sensor applications, such as anti-theft devices, and special electronic mixing circuit devices,

15   soft, low loss, magnetic properties are desired simultaneously with a specific non-linear response. In these applications, the driving field has historically, and most commonly, been directed along an easy axis or in the direction of the lowest magnetic anisotropy energy. In

20   this direction magnetic domain wall motion is usually significant. This domain wall motion commonly results in a highly non-linear response or even in strong hysteretic behavior.

      Certain anti-theft, article surveillance, article

25   identification or inventory control devices rely upon detecting harmonic signals, which are generated by this non-linear behavior or upon materials being driven in to saturation. One of many examples, of this type of surveillance system and tag is described in U.S. Patent No.

30   3,747,086. This type of tag response has also been disclosed as enabling multiple bits of information to identify objects in U. S. Patent No. 5,538,803   Other article tag devices are based upon the magnetoelastic effect and mechanical resonance, where coupling exist

35   between the magnetization and the mechanical strain in the material. An example, of this type of tag is disclosed in U.S. Patent No. 4,510,489. In these later devices it is desirable to drive the magnetization towards a hard axis so

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that rotation of the magnetization dominates and magnetic
hysteretic losses are minimized. By using this mode, and
by using the field to drive the device at its mechanical
resonance frequency significant amounts of energy can be
5   stored in the device. Hence, even after the drive field
has been removed the mechanical vibration continues, the
magnetoelastic properties are then used to invert the
process to transmit a magnetic field as the mechanical
stress causes the magnetization vector direction to
10 rotationally oscillate synchronously with the mechanical
vibration. This time dependent magnetic dipole radiates a
magnetic field at the distinct resonance frequency, which
can be detected to verify the tag's existence. Uniaxial
anisotropy is needed in such a device to achieve low
15 losses. Due to the magnetoelastic coupling between the
mechanical strain and the magnetic moment orientation the
fundamental of the mechanical resonance frequency is
emitted as an oscillating magnetic dipole field. However,
if the uniaxial anisotropy is non-ideal and results in a
20 non-linear response then the harmonics would also be
available for detection in the presence of a drive signal.
This is advantageous, but there have never been available
materials from which to form such a device before.
    Likewise, in analog mixer circuit devices a non-linear
25 response is desired. When two separate sinusoidal signals
are simultaneously imposed on a nonlinear circuit device
component a multiplication process results in a beating of
the two signals. This results in additional harmonics at
the sum and difference frequencies of the initial signals.
30 Hence, the information contained in a modulated carrier
frequency signal can be shifted to a beat frequency.
Typically this is done to shift the information carrying
bandwidth to a higher carrier frequency bandwidth
(modulation) or bring the information carrying bandwidth
35 signal back down to a bandwidth located near, or nearer to,
zero frequency for demodulation. These techniques of
frequency shifting are common to telecommunication and
signal processing and in many other signal processing

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applications. The non-linear circuit response, circuit components, and circuit implementation used to perform these signal mixing processes are described in many electrical engineering circuit textbooks. Two example texts are "Electronic Communications Techniques" by P. H. Young and "Physics of Semiconductor Devices" by S. M. Sze. Ideally the non-linear device used to mix the signals is efficient, low loss, and low noise. Usually non-linear Silicon active devices are used for this. In the past when magnetic devices were used for this application domain wall motion caused both losses to the signal and induced noise. A magnetic material with non-linear response that operates by low loss magnetization rotation rather than by domain wall motion is very desirable.

For most all transducer and sensor applications, which require low anisotropy values in order to provide large sensitivity, the use of cubic crystalline materials are common. However, due to the three fold crystalline symmetry of cubic materials, achieving a single axis of anisotropy energy density, which is almost always essential to obtaining the desired low loss, low noise, magnetic properties, is difficult. Thin, or thick, film materials are commonly employed. For example many devices, such as data storage playback transducers or field transducers, commonly utilize face centered cubic, fcc, thin film crystalline materials. Should these materials be prepared with a (001) crystalline texture the anisotropy energy, as a function of angle in the film plane is bi-axial, has multiple easy and hard axes in the film plane yielding a non-linear and hysteretic magnetic response resulting in noisy signals. Hence, a (111) crystalline texture is desired, where it can be mathematically shown for the case of the magnetization being confined to the (111) texture plane, that due to the crystalline three fold symmetry of the projection of the {111} crystalline directions into the film plane, the cubic material will possess no net first order anisotropy energy density. Even for only moderate saturation magnetization thin films, the magnetization is

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essentially confined to the film plane by the demagnetization forces associated with the planar film shape.

To achieve a single uniaxial anisotropy in a cubic
5   material with (111) texture the material is usually subjected to a thermal treatment, or is deposited directly, in the presence of an applied magnetic field. The resulting single magnetic easy axis is aligned along the applied magnetic field, while the hard axis is
10 perpendicular to this applied field. Furthermore the M_x versus H_x response function is a linear response. While the mechanism for the cause of this induced magnetic anisotropy is not well understood it is often argued that an atomic pair ordering mechanism occurs to break the
15 symmetry of the directions in the (111) plane for each grain of the material. That is, on a local scale inside each grain, pairs of atoms align along the applied field during the deposition, or the annealing process, to reduce the magnetic field energy. Interestingly, annealing in a
20 field of different orientation can often alter this induced anisotropy direction demonstrating that the orientation inducing mechanism is reversible. It is believed that this localized ordering allows fcc materials such as the NiFe alloys, permalloy, to have a small induced uniaxial
25 anisotropy. Magnetic thin film body centered cubic, bcc, or bcc derivative materials, such as Fe, FeCo, FeAl, and similar compositions, are seldom used in such applications because the required (111) crystalline texture never develops during deposition of the bcc symmetric crystals.
30   It is well understood that during the growth of thin metal films certain texture orientations tend to appear. These are driven by the minimization of surface energy and surface bonding considerations and are modified by surface mobility issues, which can be somewhat controlled by
35 substrate and processing conditions. One simple rule of thumb is that the film surface energy is minimized when the atomic surface configuration is the most closely packed. For a fcc crystal the atoms in the surface are most closely

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packed in the (111) plane and so this texture is the most
likely. The (001) texture is less energetically likely,
but is possible where as the high surface energy (110)
texture never seems to occur. On the other hand, for a bcc
5   crystal the atomic surface most closely packed is the (110)
texture and this commonly appears, the (001) texture is the
next lowest energy and is sometimes induced, but the high
surface energy (111) texture never seems to occur. Hence,
for fcc crystals we refer to the (111) texture as being
10   natural where as for the bcc crystal we refer to the (110)
texture as being naturally occurring. If a low surface
energy substrate is chosen, such as an amorphous metal,
which tends to wet to the depositing material, the fcc
(111) texture and the bcc (110) texture naturally occur. On
15   the other hand, if the substrate is non-wetting, such as an
oxidized surface where the depositing material tends to
bond to the oxygen atoms to limit the atomic surface
mobility, then it is common to see limited orientation in
the deposited films or at best a set of mixed textures.
20   The fcc crystal tends to form only weak (111) and
(001) textures while the bcc crystal tends to form only weak
(110) and (001) textures. For magnetic cubic crystalline
thin film grains with (110) or (001) texture there are
multiple easy or hard axes in the film plane of the grain.
25   In addition, because each grain has a random in-plane
orientation relative to other grains, these polycrystalline
magnetic materials result in an ensemble of grains with
multiple, random, anisotropy axes. These materials yield
both a non-linear response, as well as, high coercivity
30   associated with losses and noise. Hence, bcc or bcc
derivative materials, which almost always grow with (110)
or (001) texture, are seldom used for devices. For this
reason the high saturation magnetization value of bcc
materials have largely been unavailable to the device
35   designer who wishes to avoid domain wall motion.

One need only consult the very authoritative text,
"Physics of Ferromagnetism, 2nd Edition" by Soshin
Chikazumi, pages 299-309, on thermally induced anisotropy

of permalloy to see that the degree of understanding of the
cause of uniaxial anisotropy in cubic materials is poor.
Professor Chikazumi details the literature on the subject
and notes that one theory attempts to explain this
5   "phenomena in terms of "directional order," or an
anisotropic distribution of different atomic pairs such as
Ni-Ni, Fe-Fe, or Ni-Fe." The logic is that the atomic
spacing between the Ni-Fe pair is smaller than the other
possible pairs and so a lattice distortion results from the
10   atomic pairing. A magneto-crystalline uniaxial anisotropy
is then proposed to result from the magneto-elastic energy
associated with the resulting lattice distortion.
Professor Chiakazumi also outlines a second theory in which
it is "assumed that ordering occurred by the growth of
15   distinct volumes of the ordered phase, and explains the
induced anisotropy as the result of shape anisotropy of the
second phase." Geometrical grain shapes, other than
spherical, could generate considerable shape anisotropy
energy. It should be pointed out however, that no physical
20   evidence supporting either of these theories has been
provided.
      Shape anisotropy is an intellectually comforting
explanation, as this phenomenon is quite observable in
elongated magnetic particles such as used in magnetic
25   particulate data storage tapes and bar shaped permanent
magnets. In these, the magnetic easy axis is aligned with
the longer dimension. However, while Professor Chiakazumi
illustrates that a rather complex pair ordering model with
dipole-dipole interactions proposed by Neel can be used to
30   qualitatively explain field induced anisotropy, there is no
quantitative agreement and he comments "The reasons why
quantitative agreement is not obtained may lie in the
approximate estimates of various quantities and in failure
to attain complete thermal equilibrium." Nevertheless, he
35   comments regarding the texture of the materials that
"magnetic annealing is most effective for, <111> annealing,
less effective for <110>, and least effective for <100>."
In this statement he is referring to the parallel

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orientation of the applied field and the crystalline directions during the annealing process.

Very recently a publication; "Soft High Saturation Magnetization $(Fe_{0.7}Co_{0.3})_{1-x}N_x$ Thin Films For Inductive Write
5   Heads," IEEE Transactions On Magnetics, Vol. 36, No. 5, September 2000, by N. X. Sun and S. X. Wang, claimed to achieve orientation of the bcc like material during deposition in an applied magnetic field. The publication appears to indicate that the Nitrogen content was
10   necessary, induced strain into the films, and created a small grain structure as it shifted the angle of, and broadened, the (110) x-ray diffraction peak. They also indicated that a "significant amount" of a second crystalline magnetic phase, Fe_4N, appeared in the films. As
15   Chikazumi suggests perhaps this anisotropy behavior is due to the strain or shape or pair ordering associated with the second phase. It is interesting to note that they obtained this orientation on an oxidized Si (100) textured substrate and by the applicant's standards the FeCoN (110) texture is
20   weak. They went on to indicate that by sandwiching the FeCoN film between two permalloy films the hard axis coercivity could be decreased, but they did not indicate or offer any evidence that the orientation of the FeCoN film was improved by depositing upon the permalloy. In fact, a
25   comparison of hard axis hystersis loops for films prepared with and without the permalloy films indicate similar anisotropy fields necessary to saturate the magnetization. This would indicate that the permalloy layer did not improve the orientation in their structure.
30

Background For Orientation with Hard Magnetic Films

It should be noted that unlike field sensing and energy transforming devices that usually require soft
35   magnetic materials, devices such as magnetic recording media and permanent magnets demand higher uniaxial anisotropy energy in order to achieve high coercivity Hc, and a preferred orientation in order to achieve a high

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remnance value. For motors or actuators this directly affects the amount of work that a device can deliver while for recording media it directly affects the output signal level and signal pulse width, or flux transition width,

5   and, hence, the recording density. Even in some of these hard magnet applications it is desirable to incorporate soft magnetic materials to enhance overall performance. For example, perpendicular thin film recording media has long been discussed as a future replacement for

10 longitudinal thin film media. However, in order for a recording system to function properly it is desirable that a soft magnetic keeper layer, or underlayer, be placed on the opposite side of the perpendicular hard magnetic recording layer from the recording head. This soft layer

15 then provides a flux return path, or flux concentrator, for the recording head fields, as well as, a flux closure path for stabilizing the recorded bits against demagnetization energies after the head is removed. The former enables recording heads to function with higher coercivity media

20 and with better resolution, while the later provides improved stability to the recorded patterns by eliminating a portion of the self-demagnetization energy associated with perpendicular recording. In longitudinal recording media a soft magnetic layer would also improve the

25 stability of the recorded patterns by reducing the self-demagnetization energy of the hard recording layer. However, heretofore, no soft magnetic underlayer has been found to be a satisfactory keeper layer for either perpendicular or longitudinal media as no good method of

30 controlled the anisotropy orientation has been available. Soft magnetic underlayers, without a uniform and controlled anisotropy direction, results in domain wall induced media noise via domain wall motion Barkhausen phenomena. As the magnetic head passes over the media data it effectively

35 shorts out the stray media bit fringe fields causing the magnetic patterns in the soft magnetic underlayers to relax to new positions. If there are significatn domain walls involved in this process they commonly break loose from

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localized pinning defects causing sudden changes in their
magnetic configuration.   This Barkhausen phenomena causes
noise signals to appear in the data playback head.   For
either perpendicular or longitudinal hard disk recording,
5   where the recorded bit or flux patterns have been wider
across the recorded track than the bit length, the desired
anisotropy configuration for the soft layer is for the hard
magnetic axis to be along the recorded track so that the
easy axis lies across the track direction.   Hence, for a
10   traditional hard disk system this implies that the easy
axis of the soft film should be directed radially, while
the hard axis is directed circumferentially.   Since the
easy axis of the soft magnetic layer of this configuration
is at 90 degrees to the fields produced by the flux
15   transitions of the hard recording layer, the magnetization
vector of the soft magnetic layer rotates by spin rotation
and the noise generating domain wall motion is avoided.
Having a uniaxial soft magnetic underlayer with radial
orientation will solve a long-standing technical problem.
20   As data storage areal densities are pushed forward,
magnetic grain sizes have been reduced to the extent that
the magnetic recorded state is near the thermal stability
limit.   Hence, even longitudinal recording stability and
the transition length also benefit from the use of a soft
25   magnetic underlayer to reduce the bit transition
demagnetizing effects.   Again, because of domain wall
motion generates noise the ideal orientation of the soft
underlayer easy axis should be radial to minimize the
potential for domain wall noise. Similarly, anisotropy
30   orientation control can benefit magnetic tape and x-y
addressable data storage systems by providing a keeper
layer wherein the magnetization vector is rotated by spin
rotation and domain wall motion is minimized. This
invention, of oriented soft magnetic materials, represents
35   a significantly improving future magnetic media.

Background For Hard Magnetic Film Orientation

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Modern hard disk longitudinal media consists of a polycrystalline thin film composed essentially of uniaxial grains randomly oriented in the substrate plane. Playback by averaging the signals from the randomly oriented grains results in an isotropic response around the disk radius. This orientation randomness has been necessary to avoid the twice around modulation during disk rotation of a non-isotropic media. By mechanically grooving the disk surface prior to deposition of the thin film layers some small amount of orientation along the circumferential direction is sometimes observed. However, the orientation ratio, OR, of the hard magnetic remanence along the track to the radial remanence is seldom more than 1.2 and more often typically less than 1.1 and has been decreasing as substrates have been made smoother and media films made thinner to enable higher areal recording densities. Likewise, the ratio of the coercivities in the two directions is also sometimes referred to as the orientation ratio, OR, and its maximum value is also typically similar to that of the magnetic remanence ratios. The origin of this hard magnetic material orientation has been in dispute for several years. While it has been argued by some that it originates from a slight preference of the c-axis of the hexagonal close packed, hcp, cobalt alloy to lie along the grooved direction, it has also been shown to diminish or vanish if the disk is thermally cycled before media deposition, but after the mechanical grooving. This latter phenomenon has resulted in some arguing that the orientational origin is due to a thermal stress development between the substrate and the film layers as the substrate stress associated with the grooves relaxes from the heat used, or generated, during the deposition. In US Patent 5,989,674, Marinero et al. outlines several patents and publications claiming to reveal the cause of media orientation and then invokes stress, shape and even crystalline orientation to claim a cause for orientation during the deposition of an hcp cobalt alloy on a mechanically grooved substrate. Others had claimed to

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achieve small orientation ratios by deposition of the media
materials at an oblique angle to the disk surface. See for
example, U.S. Patent No. 4,776,938. While this approach has
shown some effect it has not resulted in a significantly
5   improved OR over grooved substrates and the deposition
methods described are significantly inefficient in the
deposition of material. Furthermore, the crystallographic
origin of this orientation effect has also never been
clearly stated or proven and it is possible that it is due
10   to particle shape effects. In spite of it's the patent
description a number of years ago the method is not a
technology that is currently used in production.

     Nevertheless, from wherever the orientation
originates, it has been proven to be beneficial to magnetic
15   recording for achieving higher resolution and shorter
magnetic flux transition lengths and better thermal
stability. There is little doubt that a greater degree of
this orientation is of benefit to future hard disk data
storage systems. Likewise, in particulate tape the
20   individual acicular magnetic particles are commonly
oriented physically during the wet coating process to have
their long axis, and hence their easy magnetic axes, to lie
along the track direction. This results in a higher signal
level, shorter transition length, and higher recording
25   densities. It is an interesting observation, that for best
performance, the easy axis orientation of the hard magnetic
media layer, whether longitudinal or perpendicular media,
should be along the applied head field direction, while the
easy axis orientation of an associated soft keeper layer
30   should be across the recording track, perpendicular to the
applied head field direction for longitudinal media; in
order to enjoy the benefits of magnetic moment rotation
instead of domain wall motion to avoid the Barkhausen noise
phenomena of the soft keeper layer.
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          Background for epitaxial thin film growth

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One of the most often sited concepts is that thin films prefer to grow with the atoms arranged on the thin film surface to minimize the atomic bonding energy. This implies that the most stable atomic crystalline surface

5   grows when the surface atoms form the densest arrangement consistent with the crystalline structure. This means that for the fcc lattice, and fcc derivatives, the (111) texture develops in a thin film because the atoms are the most closely packed on this crystalline plane. The next most

10   commonly occurring texture would be the (001) while the (110) texture would be seen only rarely. On the other hand for the bcc, and bcc derivatives, the (110) texture preferentially develops, as it is the most closely packed crystalline plane. The next most commonly occurring

15   texture is the (001), while the (111) texture is never observed. In rare instances, such as described in U.S. Patent No. 5,693,426 it was found that for some materials the B2, bcc derivative, crystalline structure may form a (112) texture if deposited under the correct conditions.

20   However, even the B2 crystal will easily form the (110) texture on non-oxidized surfaces, where the initially deposited atoms have high surface mobility during the film growth. Likewise, for hexagonal close packed (hcp) crystals the (0002) texture is the most closely packed and

25   most commonly develops.

Likewise, there are several publications describing the epitaxial relationships, which prevail when a second crystalline material is deposited directly upon an underlayer. U.S. Patent No. 6,248,416 discusses a number of

30   these. Assuming that the atomic lattice spacing of the first material and the second material sufficiently match a number of second layer texture following relationships to the first layer texture have been found. However, if the atomic lattice matching is not sufficient then epitaxial

35   growth does not occur. For example, U.S. Patent No. 6,248,416, which is incorporated herein by reference, Lambeth et al. have discussed, non-ferromagnetic, Cr

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textures grown as quasi-epitaxial single crystal thin films
on clean, non-oxidized, single crystal Si substrates.

The textures developed on these substrates are
extremely strong indicating a high degree of order and
5   single orientation.   In this patent, and in other
publications, it has been shown that two different fcc
materials can epitaxially grow upon each other with the
same texture. Likewise, two different bcc materials can
epitaxially grow upon each other with the same texture.
10 Likewise, two different hcp materials can epitaxially grow
upon each other with the same texture. More interesting,
however, is the case when one crystalline material class is
deposited upon a different crystalline material class. Not
only is crystalline texture induced into the second layer
15 by the epitaxial growth on the first layer, the texture,
and the in-plane orientation of the second layer is
determined by the first layer texture and orientation. For
example, U. S. Patent 6,248,416 shows that a clean Si (001)
single crystal can induce fcc Ag (001) texture and if bcc
20 Cr is grown on this then (001) texture results.   The
authors then showed that hcp Co (11$\underline{2}$0) texture grows on the
Cr (001) texture and that the possible c-axes orientations
is predetermined, to be only two possible directions, by
the crystalline directions of the single crystal Si wafer.
25 Likewise, they showed that if a Si (110) textured single
crystal is used as the substrate then the highly unusual
fcc Ag (110) texture develops and on this, the unusual bcc
Cr (112) texture, develops. Co (10$\underline{1}$0) texture is induced by
this Cr surface and the in-plane single Co c-axis lies
30 parallel to the Cr <110> direction.   Another epitaxial
texture relationship described in U. S. Patent 6,248,416 is
noted. If the initial single crystal Si substrate is (111)
the epitaxial fcc Ag will be (111) textured and oriented in
the plane in the same directions as the Si crystal.   If
35 another fcc, such as Cu or Ni, is deposited upon this then
it too will be epitaxial and so carry the (111) texture and
orientation. Each of these textures is strongly oriented
because the layer below it is strongly oriented and one can

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continue the epitaxial growth of one layer on the next.
They also described how this structure, with the use of a
Ti layer can be used to grow hard magnetic perpendicular Co
(0002) texture films. They did not describe how Cr would
5   grow on these (111) texture fcc layers or the Co (0002)
textured layer. Nevertheless in separate publications H.
Gong et al, (H. Gong, W. Yang, M. Rao, D.E. Laughlin and
D.N. Lambeth, "Epitaxial growth of quad-crystal Co-alloy
magnetic recording media," *IEEE Transactions on Magnetics,*
10   35(5), 1999, pp.2676-2663), as well as, G. Zangari et al (
G. Zangari, B. Lu, D. E. Laughlin and D. N. Lambeth,
"Structure and Magnetic Properties of Sm-Co Thin Films on
Cr/Ag/Si Templates," *Journal of Applied Physics,* Vol. 85
(8), April 15, 1999, pp. 5759-5761), noted that upon the
15   (111) single crystal Si substrate and subsequent epitaxial
(111) textured fcc layers when a bcc Cr was deposited a
strong Cr (110) texture resulted. However, the atomic
arrangement of the. (110) bcc crystalline plane is
rectangular while the fcc atomic arrangement of the (111)
20   crystalline plane has hexagonal symmetry. Gong et al
notes, as does Zangari et al, that there are three possible
ways (variants) for the bcc Cr (110) plane to orient on
this atomic hexagonally arrange surface. These crystalline
planes and crystalline directions are illustrated in Figure
25   3. These three orientations correspond to when the <001>
directions of the (110) textured Cr lie exactly parallel to
the <110>, or perpendicular to the <112>, directions of the
hexagonal atomic lattice plane of the (111) textured fcc.
They summarized these three Cr (110) orientational variant
30   relationships with the fcc underlayer via the following
notation:

         Cr(110)[001] || Ag(111)[1$\bar{1}$0] || Si(111)[1$\bar{1}$0],
         Cr(110)[001] || Ag(111)[10$\bar{1}$] || Si(111)[10$\bar{1}$],
35   Cr(110)[001] || Ag(111)[01$\bar{1}$] || Si(111)[01$\bar{1}$].

Their publications, as well as U. S. Patent 6,248,416, were
focused upon hard hcp and soft fcc magnetic structures that
40   could be grown and they show no evidence of working with

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anything but non-magnetic bcc materials such as Cr. Upon
each of these three Cr variants four possible hcp Co (10$\underline{1}$1)
quad-crystal variants were obtained. This Co layer then
contains grains with four possible easy axes directions

5   when grown on each Cr variant. As a result, the Co quad-
crystal structure consists of grains, each with one of
twelve possible easy axis directions. There are four Co
orientational possibilities for each of the three possible
Cr variants.

10   Figure 3 illustrates the positions of the three bcc Cr
(110) orientational variants [4] relative to the fcc (111)
epitaxial template [5]. Example <001> bcc directions and
an example <112> fcc direction are shown along with other
relevant crystallographic directions. Hence, the public

15   literature, states that there are three possible Cr
variants that can grow on the (111) fcc textured substrate.
The same result would apply to any size single crystal
provided it is (111) textured fcc and the lattice constants
are sufficiently matched to induce the epitaxial growth.

20   Hence, since polycrystalline fcc films, grown on a non-
single crystal substrate, with strong (111) texture,
contain a large number of single crystal grains, one could
obtain the same result for each individual grain. However,
if the grain were small enough, it is possible that only

25   one or two of the three possible bcc (110) textured
orientational variants might grow on a given grain, but it
is also possible, depending upon the deposition processing
conditions, that all three variants could coexist on a
single fcc (111) textured grain. Furthermore, since the

30   probability of growth for each variant is equal then a
sufficiently large sample will contain an equal volume of
each variant and a magnetic material will appear to have
symmetrical orientational magnetic properties. This would
be true if the epitaxial growth occurred on a single

35   crystal substrate or if the final film were polycrystalline
and had been grown on a non-single crystal substrate.

These effect will now be explained in terms of the
anisotropy energy density.

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Magnetic Anisotropy Energy of (110) Textured Thin Films

5   To understand the magnetic properties of (110) textured magnetic bcc materials grown on a (111) texture fcc substate we consider the expression for the cubic magnetocrystalline anisotropy energy when the magnetization is confined to the thin film plane of a single crystal of

10   cubic material. Consider the in-plane unit cell atomic surface [6] of a single variant of the (110) textured film grown in Figure 3. Figure 4 shows the magnetocrysalline energy plotted, where the magnetization is confined to the (110) crystalline plane, as a function of angle for this

15   single variant for $K_1 > 0$ and $K_2 = 0$. The magnetocrystalline energy density is given by $E_{110}(\theta)$ (See "Physics of Ferromagnetism, 2nd Edition" by Soshin Chikazumi, pages 249-256), where:

20     $$E_{110}(\theta) = K_1\{(1/4)\sin^4(\theta) + \sin^2(\theta)\cos^2(\theta)\} +$$
$$K_2\{(1/4)\ \sin^4(\theta)\cos^2(\theta)\} + \text{higher } K \text{ terms.}$$

Or when expanded into the harmonics of θ,

25     $$E_{110}(\theta) = (1/32)K_1\{7- 4\cos(2\theta) -3\cos(4\theta)\} +$$
$$(1/128)K_2\{2-\cos(2\theta)-2\cos(4\theta)-\cos(6\theta)\},$$

where θ is the magnetization vector direction measured from the <100> bcc direction in the film plane, and K_1 and

30   K_2 are the first and second order magnetocrystalline anisotropy energy density constants, respectively. The higher order energy terms are usually much smaller and are neglected here.

       For pure Fe, K_1 is often quoted to be about $+4.7 \times 10^5$

35   erg/cc, but can be tailored by chemical additions. On the other hand the disordered bcc form of $Co_{50}Fe_{50}$ is believed to be about -1.5×10^5 erg/cc while the ordered bcc

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derivative, B2, form of $Co_{50}Fe_{50}$ is about zero. Interestingly, the K_1 value for both the ordered and disordered alloys are about the same when the Co atomic percent is 35% or less. $K_1 \sim +1 \times 10^5$ erg/cc for $Co_{35}Fe_{65}$

5   and approaches the Fe value for Co content of less than 25%. This alloy is of particular interest due to its very high M_s value and interesting anisotropy properties as a function of composition. See "Modern Magnetic Materials Principles and Applications" by R. C. O'Handley, pages 190,

10 192 for anisotropy constants and page 145 for saturation magnetization values. The higher order anisotropy constants, such as K_2, are less well known, but are usually smaller in magnitude and are weighted less heavily in the energy expression. Only in cases where the role of K_1

15 tends to vanish do the K_2 terms seem to play a significant role in these calculations. In the description of variant sets which will follow below, it is important to note the 2θ harmonics will play a dominate role while the 4θ harmonic tends to cancel out. Furthermore, the 6θ harmonic

20 of the second order anisotropy energy term is weighted significantly less than the 2θ or 4θ harmonic. Hence, in most cases the effect of this 6θ harmonic can be neglected. While one skill in the field of magnetism will understand that the higher order anisotropy energy densities may play

25 a small role in this invention, for simplicity of explanation they will be neglected in the following derivations.

While the smallest energy minimum for the function $(K_1>0)$ is at the in-plane <100> direction there are two

30 equal maximums along the in-plane <111> directions [7]. Hence, there is a localized minimum [8] located between the two <111> directions and directed along the <110> direction. Hence, this texture does not yield uniaxial behavior and is subject to domain wall motion resulting in

35 highly non-linear switching for all directions of applied field when the sample is driven near to saturation. There is a reasonably a large region of monotonic behavior on

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this energy curve where the response conceivably could be reversible and low loss if the magnetic configuration was single domain orientation. Conceptually if the magnetization is initially all pointed along the <001>
5   direction and then is rotated toward one of the in-plane <111> hard axes by an applied field the process could be reversible, hence lossless, until the magnetization approached the hard axis. However, as the magnetization crossed the in-plane <111> direction it would then abruptly
10 jump towards the localized energy minimum at the in-plane <110> direction. This jump is not reversible and so represents a lossy process. Since a 90-degree domain almost always wall exists, or forms, between the magnetization pointing along the in-plane <001> and <110> directions then
15 wall motion dominates any possible rotational mechanism. Grain boundaries or defects in the film structure would cause localized wall motion jumps, again resulting in loss mechanisms.

      In the 0 to 180 degree region of the energy plot,
20 Figure 4, we see, for the case of $K_1>0$, the one minimum [9], two maximums [7], and a localized minimum [8] corresponding to the single <100>, two <111> and single <110> directions, respectively, of variant [6] of Figure 3. These extremes would invert if the $K_1<0$. Clearly, this
25 curve does not satisfy our definition for a uniaxial magnetic material.

                        SUMMARY OF THE INVENTION

30   The present invention is directed generally to oriented thin film magnetic materials and devices including magnetic sensors, transducers, electronic circuit components, recording heads, recording media, and data storage systems, incorporating the said, thin film oriented
35 magnetic materials and, more particularly, crystallographically oriented thin film materials and oriented magnetic layer structures utilizing materials such as iron, nickel, and cobalt, and alloys of the same. In

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particular, this invention deals with a structure to achieve uniaxial magnetocrystalline orientation via the use of the (110) texture of body centered cubic (bcc) or body centered cubic derivative crystal thin film structures. In
5   general, the bcc or bcc derivative materials have higher saturation magnetizations than face centered cubic and the invention of orientation control of bcc and bcc derivative materials allows new devices to be constructed, which have good orientation, high magnetization, high permeability and
10   low losses. These devices are used to detect or determine magnetic fields, store and retrieve data, and to transform energy or perform electronic signal processing. Improved magnetic properties or orientation of the magnetic properties of the materials when used in such devices
15   result in better technical performance or allows for the construction of smaller, faster or less expensive systems. In most existing magnetic devices, with designs utilizing traditional magnetic materials structures, the performance is significantly improved by simply replacing the
20   traditional magnetic material structure with the new structure described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

25   The advantages of the present invention can be better understood by reference to the drawings in which:

         Figure 1 shows a plot of the magnetic anisotropy energy density for the uniaxial Stoner-Wohlfarth model.
30
         Figure 2 shows the magnetic hard axis response function, M_x, to an applied field along the hard axis, H_x, for the uniaxial Stoner-Wohlfarth model; and the magnetic easy axis response function, M_y, to an applied field along
35   the hard axis, H_x, for the uniaxial Stoner-Wohlfarth model.

         Figure 3 shows an illustration of the historical three orientational variant arrangement of the (110) crystal

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plane of a bcc crystal in comparison to the atomic arrangement of the (111) crystal plane of an fcc crystal.

5   Figure 4 shows a plot of the magnetic anisotropy energy density versus magnetization direction in the plane for the (110) texture plane of a cubic crystal, where the first order anisotropy energy density constant, K_1, is positive.

10   Figure 5 shows an illustration of two of the six possible orientational variants of the (110) crystal plane of a bcc-d crystal in comparison to the atomic arrangement of the (111) crystal plane of a hexagonal lattice template crystal.

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Figure 6 shows a plot of the magnetic anisotropy energy density versus the in-plane magnetization direction for the specific case of three (b1, b2, and c1) coupled (110) variants, of the six bcc-d (110) textured variants

20   when K1 > 0 and δ = 7.5 degrees. Only one energy minimum and one energy maximum per 180 rotation occurs.

Figure 7 shows a plot of the magnetic anisotropy energy density versus the in-plane magnetization direction

25   for the specific case of two (a1 and c2) coupled (110) variants, of the six possible bcc-d (110) textured variants when K1 > 0 and δ = 5.26 degrees. Only one energy minimum and one energy maximum per 180 rotation occurs.

30   Figure 8 shows a plot of the magnetic anisotropy energy density versus the in-plane magnetization direction for the specific case of four (a2, b1, b2 and c1) coupled (110) variants, of the six possible bcc-d (110) textured variants when K1 > 0 and d = 5.26 degrees. Only one energy

35   minimum and one energy maximum per 180 rotation occurs.

Figure 9 shows the magnetic hard axis response function, M_x, and the magnetic easy axis response function,

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M_y, for an applied field along the hard axis, H_x, for the coupled variant pair (a1 and c2) when K1 >0 and δ = 5.264 degrees.

5   Figure 10 shows a plot of the magnetic anisotropy energy density versus the in-plane magnetization direction for the specific case of three (b1, b2, and c1) coupled (110) variants, of the possible six bcc-d (110) textured variants when K1 > 0 and δ = 5.264 degrees.   Only one
10   energy minimum and one energy maximum per 180 rotation occurs.

      Figure 11 shows a plot of the magnetic anisotropy energy density versus the in-plane magnetization direction
15   for the specific case of two (a1 and b2) coupled (110) variants, of the six possible bcc-d (110) textured variants when K1 > 0 and δ = 5.264 degrees.   Two energy minimums and two energy maximums per 180 rotation occurs.

20   Figure 12 shows a sketch of the coordinate system for defining the angle of atomic motion during angle of incidence deposition.   The substrate plane is x-y and the depositing materials arrive along r.   The angle of deposition, ω, is defined as the angle between the z-axis
25   and r vector.

      Figure 13 is a schematic illustration of a new sputtering cathode geometry relative to a disk surface for angle of incidence deposition.
30

      Figure 14 is X-ray pole figure data demonstrating the existence of six bcc-d (110) textured variants with δ = 5.264 where variant a1 and c2 dominate the other four variants to produce a symmetry broken structure.   Also
35   shown are the three Ag (220) peaks.   The sample was produced using angle of incidence deposition.

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Figure 15 shows the uniaxial magnetic hard axis response, M_x, function, and easy axis response function, M_y, data to an applied field along the hard axis, H_x, for an Fe ($K_1 > 0$) sample prepared with the easy axis along the

5   hexagonal template <112> direction. The symmetry breaking mechanism was an applied magnetic field along the <112> direction.

Detailed Description Of The Preferred Embodiments

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The material structures of the invention can be embodied in both magnetically hard and soft magnetic devices including magnetic field sensors, transducers, electronic circuit components, magnetic solid state memory,

15   antitheft devices, recording heads, recording media, and data storage systems, incorporating the said, thin film oriented magnetic materials and, more particularly, crystallographically oriented thin film materials and oriented magnetic layer structures utilizing materials such

20   as iron, nickel, and cobalt, and alloys of the same. These structures are especially useful where the embodiment of the device requires special magnetic orientation, specific linear or non-linear response, or a low loss response.

By carefully controlling the epitaxial growth

25   conditions of (110) crystalline textured bcc or bcc derivative thin film materials on highly oriented (111) hexagonal atomic templates the applicant has invented a new set of six crystalline variants with special orientational relationships. By the selection and the growth of a very

30   special exchange coupled subset of these six orientational variants a symmetry broken uniaxial magnetic thin film is obtained. The (111) textured fcc, (111) textured fcc derivative, or an (0002) textured hcp crystals are examples of the (111) textured hexagonal atomic template. In each

35   of these cases the atoms of the template are close packed. When a highly oriented (111) hexagonal template is available a highly oriented bcc or bcc derivative (110) texture structure can be epitaxially grown. With the combination of being highly oriented and the use of special

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processing techniques the six new variants can be
constructed. Since under many circumstances the bcc and
the bcc derivative materials form a single class of
behavior, we shall consider the notation "bcc-d" to
5   represent either a bcc or a bcc derivative crystal
structure. Likewise, the notation "fcc-d" shall be used to
represent either an fcc or fcc derivative crystal
structure. For example, here materials with the NaCl
prototype structure are considered to be a fcc derivative
10   as there is a close packed hexagonal pattern of atoms in
the (111) plane. The (111) plane of atoms of these fcc-d
and (0002) plane of hcp crystals are always close packed
and so are different from the (111) atomic crystal planes
of many fcc Bravais lattices, which are not close packed.
15   For example, the Si, diamond structure, substrate is a
member of the fcc Bravais lattice F3dm space group.
Likewise, the C15 (Strukturbericht designation) is a member
of the F3dm group, which does not have a close packed (111)
plane. From Figure 3 one can see that there are three
20   hexagonal template <110> directions similar to [10]. It
was found that, by carefully controlling the epitaxial film
growth conditions, a strongly (110) textured bcc-d crystal
could be made to grow with one of its <111> directions
parallel to the hexagonal template <110> directions. This
25   orientation is different than was obtained by the
processing of Gong and Zangari. In our processing the bcc-d
<110> directions are no longer parallel to the hexagonal
template <112> directions.

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Before discussing the new 6 crystalline (110) textured
bcc-d variant system it is worthwhile to further analyze
the 3 crystalline (110) textured variant system.   The
5   energy expression for the single variant, $E_{110}(\theta)$ was given
earlier and discussed in the context of Figure 4.   It is
important to point out that if there were two dominate
variants of this (110) textured bcc on the same (111)
textured fcc crystal surface and if they were magnetically
10   coupled by being in contact or via another magnetic
material being in contact with each of them then the
magnetization vector of each of the variants would tend to
move or rotate together.   Likewise, if there were all three
variants, as illustrated by [4] in Figure 3 and espoused
15   for Cr, in both the Gong and Zangari literature, and the
three variants were magnetically coupled the magnetization
of each would tend to move with the others. Of course Cr
has no magnetic moment and so neither Gong nor Zangari
discussed this. The anisotropy energy density equation for
20   equal amounts of each of these three crystalline variants,
with the magnetization rotating together would be written
as the sum of each of the variants:

$$E_3{}'(\theta) = \{E_{110}(\theta) + E_{110}(\theta - 60) + E_{110}(\theta - 120)\}/3.$$

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Here θ is the angle of the magnetization vector with
respect to the <100> direction of the original single
variant [6].   Because the underlayer in-plane fcc <112>
directions are at 60 degree intervals, the two other bcc
30   (110) texture variant easy axes are located at 60 degree
intervals with respect to the first.   By simple
trigonometry it can be shown that the sum of the energy of
these three variants is a constant of $(7/32)K1$ and has no θ
dependence.   Hence, there are no net anisotropy directions.
35   However, in actual materials, since domain walls can form,
the localized anisotropy of each variant, in combination

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with material defects, results in a significant coercivity and lossy behavior.

Because the reference point in any energy calculation is arbitrarily chosen one can always add a constant to the energy function without changing the predicted physical behavior. Also, since the combined energy in the three variant case just discussed is a constant, it is obvious that if there were only two coupled variants the energy function would be simply proportional to the negative of the single variant case. Writing this statement mathematically:

$$\{E_{110}(\theta) + E_{110}(\theta - 60) + E_{110}(\theta - 120)\}/3 = 7/32.$$

Hence, for a material with only two variants

$$E_2'(\theta) = \{E_{110}(\theta - 60) + E_{110}(\theta - 120)\}/2 = 21/64 - E_{110}(\theta)/2.$$

Therefore, after normalizing the energy density by the appropriate unit volume of material, the energy curve of the two, coupled variants is simply 1/2 the inverted energy curve of the single variant of the same total unit volume of material. The curve shape and energy minimums and maximums interchange position and so the hard axes and easy axes directions would interchange. Any localized easy axis or energy minimum, such as [8], would become a localized hard axis or energy maximum. Recall that the constant in the energy expressions is arbitrary and has no effect on the physical response so it can be considered to be equal to zero in any analysis. Hence, the response of a magnetically coupled pair of these variants appears as a single variant material with a change in sign of the K_1 value and a decrease in the amplitude of the differences in the energy extremes by a factor of 1/2. Hence, whether the material of a (110) textured cubic magnetic material is composed of a single variant, two coupled variants or three coupled variants the magnetocrystalline anisotropy energy density function does not yield uniaxial behavior, but a

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form of bi-axial behavior. Therefore, when there are three possible variants of bcc magnetic material located at 60 degree intervals, as advocated for the non-magnetic bcc Cr by Gong et al and Zangari et al, and whether a (110)
5   textured cubic magnetic film is polycrystalline or is epitaxially grown on a single crystal, it cannot possess uniaxial behavior. Hence, the M versus H response function will have coercivity and lossy behavior. Furthermore, uniaxial behavior cannot be obtained even if the volumes of
10   each of the three variants are arbitrarily selected. When the volumes of the three variants are not equal we herein refer to the sample as being "symmetry broken."

It is also clear that should all three variants be present, but that either one or more than one be of more
15   volume than the others then the energy properties of the larger volume variants will be dominate. To clarify this, simply consider the case of Figure 3 where 6 has a volume fraction of 1/2 while the other two equal volume variants have a volume fraction of 1/4 each. Then 1/2 of the volume
20   of 6 is equal to the volume of each of the other two. So the energy terms from these three quarters of the total volume would be equally portioned and sum to a constant. This then would leave the remaining 1/2 of variant 6 to provide an energy curve of the shape of Figure 4. Hence,
25   we herein referred to the larger volume variants as being "dominate."

It is important to note that nowhere in U. S. Patent 6,248,416 or in Gong et al or Zangari et al, was the use of any magnetic bcc or bcc derivative thin film discussed.
30   Nor were magnetic bcc or bcc derivative materials investigate or advocated as the magnetic layer. If they had been investigated, and found to have the same three variant crystalline orientational relationships that were found for bcc (110) Cr when placed on a (111) fcc layer,
35   the magnetic properties would have had to have been lossy and to have significant coercivity. Furthermore, they never suggested that they obtained a sample situation where the volumes of each of the variants were not equal. Hence,

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at no time did they discuss a symmetry broken variant system nor a dominate variant system.

Likewise it is important to note that in their discussion of FeCoN thin films Sun and Wang provided no evidence regarding any (110) textured variants. Furthermore, they offered no explanation for the anisotropy the observed and because their anisotropy fields appeared to be the same whether or not permalloy was placed under their CoFeN film their results were not dependent upon on any ordered variant structure. Furthermore, their results showed a strained lattice and a significant Fe_4N second phase indicating a possible anisotropy mechanism associated with strain or shape effects as discussed by Chikazumi.

It is well known that crystallographic twinning can form at the (112) planes of the bcc-d. These (112) planes contain both a <110> and a <111> direction. Hence a pair of bcc-d twins can form with an interface along the plane containing the thin film surface normal and containing one of the hexagonal template <110> directions. In this arrangement the hexagonal template <110> directions coincides with one of the bcc-d <111> directions. Hence, for bcc-d (110) texture films that have grown with a <111> direction parallel to a hexagonal template <110> direction, there are two possible variants. Since there are three possible hexagonal template <110> directions, then there three possible sets of twins. Hence, we are lead to the concept that there are 6 possible bcc-d variants that could be grown. However these variants do not have to be in a twinned configuration to exist. For clarity, only two of these six possible variants are shown in Figure 5. The other four variants can be constructed by rotating the positions of these two by 60 and 120 degrees. This sketch is meant to be illustrative in showing the orientation of the variants and it is to be understood that a single variant would extend over a considerable some of atomic distances.

The angle formed between the bcc-d <111> direction and the bcc-d <100> direction is given by $arctan(\sqrt{2}) = 54.736$

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degrees. Likewise, the angle between the <111> direction and the <110> direction is arctan $(1/\sqrt{2})$ = 35.264 degrees. The sum of these two angles is of course 90 degrees and forms the angle between the <100> and <110> directions.

5   The importance of this 54.736 degree angle value is that it differs from the 60 degree interval of the <110> directions of the hexagonal template by 5.264 degrees. In contrast to the three variants observed by Gong and Zangari, the <100> directions of the proposed six bcc-d variants do not lie

10   parallel to any of the hexagonal template <110> directions. Furthermore, where as for the Gong and Zangari symmetrical arrangement where none of the <111> bcc directions lie parallel to the hexagonal template <110> directions, for our new variants one of the bcc-d <111> directions lies

15   parallel to one of the hexagonal template <110> directions and the bcc-d <100> direction does not lie parallel to the <110> hexagonal template. Hence, for a coordinate system where θ = 0 at the hexagonal template direction [110], the bcc-d variant crystal <100> directions and easy magnetic

20   axis ($K_1 > 0$) lie at angles of β_i = $0 \pm \delta, 60 \pm \delta$ and $120 \pm \delta$ degrees where δ = $60-\arctan(\sqrt{2})$ = 5.264 degrees. In Figure 5, it is also important to note the orientation of the two <111> directions of each of the two the bcc-d variants. They match the 60 and 120 degree hexagonal template <110>

25   directions, but near the 0 degree axis they differ from the <110> axis by + and - 2δ. When exchange coupled this variant pair will be represented by an energy function $E_{2\text{-}alc2}(\theta)$ in the discussion below.

        For a (110) textured bcc-d crystalline structure

30   containing six equally occurring magnetically coupled variant volumes the anisotropy energy density function is written as:

        $E_6(\theta)$ = $\{E_{110}(\theta \pm \delta) + E_{110}(\theta - 60 \pm \delta) + E_{110}(\theta - 120 \pm \delta)\}/6$,

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        where the + and - signs are to represent two functions for each angle in this expression. As before, it can be

mathematically shown that the total anisotropy energy of this symmetrically balanced arrangement of six variants, six E_{110} energy terms, has no angular dependence and so the anisotropy energy density function is a constant, $K_1(7/32)$.

5   However, of particular interest here are the cases when only an odd or even numbers of particular variants are coupled. It is important to consider that any one or more of the six variants could possibly grow on a hexagonal template and it is not a requirement that they appear in twin pairs or of a balanced, equal amounts of material.

10   However, for clarity, during the discussion of the next few paragraphs we will consider the amounts of material in each variant of a coupled group of variants to be balanced to be equal. That is to say, for example, if there are only three variants coupled together we shall assume that the

15   volume of each of the three is equal.

     If there is only one of the six variant then the energy density function simply reduces to that of $E_{110}(\theta)$ shifted by the particular variant offset angle

20   β_i. Likewise, if there are five of the six variants then, similarly to the earlier logic and ignoring the unimportant energy constant offset or origin, the resulting normalized energy density function is negative 1/5th the energy function peak to peak value of the missing variant. As

25   shown in Figure 4, since the $E_{110}(\theta)$ function has two maximums, one minimum and a localized minimum (for $K_1>0$, or two minimums, one maximum and a localized maximum for $K_1<0$), these two possible sets of coupled variants yield energy functions that do not represent uniaxial magnetic

30   material behavior. There are three other possible sets of numbers of coupled variants; two, three, and four variants per combination. However, there is more than one way to form each of these, as there are six variants to choose from. Here, we continue to consider each of the variants

35   in a set to be balanced or of equal volume of material.

     As stated before there are six possible bcc-d variants each with a single crystalline <100> direction in the plane (and easy magnetic axis when $K_1 > 0$) lying at one of the

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six angles β_i = +0 ± δ, +60 ± δ and +120 ± δ degrees. We shall
denote these six possible variants by the names: a1(60+δ),
a2(60-δ), b1(0+δ), b2(0-δ), c1(120+δ), and c2(120-δ), where
the angle in the corresponding parenthesis represents the
5   angular location of the bcc-d <100> direction for the given
variant relative to the <110> direction [10] of the
hexagonal template. We see that, for example, the a1 and
a2 variants are located at, or deviate by, +δ and -
δ degrees, respectively, from the 60 degree position of the
10 <110> direction of the hexagonal template.

Special Case: δ = 7.5 Degrees

Before discussing the energy density curves for the
15 various other combinations of variants it is informative to
consider three particular sets of two couple variants of
the possible fifteen cases of pairs. However, we now
consider the special case when the deviation angle of the
variant, δ, is not equal to 60-arctan($\sqrt{2}$)= 5.264 degrees,
20 but is exactly equal to 7.5 degrees. The three particular
sets of energy density functions of interest are written
as:

$E_{2\_b1a2}{}''(\theta)$ = {$E_{110}(\theta-0-7.5)$ + $E_{110}(\theta-60+7.5)$}/2,

25 $\qquad$ $E_{2\_a1c2}{}''(\theta)$ = {$E_{110}(\theta-60-7.5)$ + $E_{110}(\theta-120+7.5)$}/2, and

$E_{2\_c1b2}{}''(\theta)$ = {$E_{110}(\theta-120-7.5)$ + $E_{110}(\theta-0+7.5)$}/2.

The subscripted energy function notation, for example,
$E_{2-b1a2}{}''(\theta)$ represents the two variants b1 and a2 coupled as
30 a pair. The quotation mark, '', is used to denote this
special δ = 7.5 degree case. We see that in each of these
three cases the coupled variants are phase shifted by
exactly 45 degrees from each other. It can easy be shown,
by trigonometry for this particular δ=7.5 degree angle,
35 that for each of these pairs, which are separated by 45

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degrees phase angle, the only dependence on θ is of the form of $\cos^2(\theta)$. In particular, it can be shown that:

$$E_{2\_b1a2}"(\theta) = (K_1/64)\{14-8\cos(45)+16\cos(45)\cos^2(\theta+60)\},$$

5          $$E_{2\_a1c2}"(\theta) = (K_1/64)\{14-8\cos(45)+16\cos(45)\cos^2(\theta)\}, \text{ and}$$

$$E_{2\_c1b2}"(\theta) = (K_1/64)\{14-8\cos(45)+16\cos(45)\cos^2(\theta-60)\}.$$

$E_{2\_a1c2}"(\theta)$, for example, represents a coupled pair of variants that has a Stoner-Wohlfarth hard axis at zero
10   degrees and easy axis at 90 degrees, while the individual variants have their easy axes (<100> directions for K1>0) angled at +67.5 and 112.5 degrees. In other words, each of these paired variants result in an energy function that is of the same functional form as the uniaxial Stoner-
15   Wohlfarth model with an easy axis (K1>0) angle located half between the easy axis directions of the two individual variant easy axis locations. This Stoner-Wohlfarth behavior only occurs because of the coupling of the two variants and their specific $60 - 2\delta = 45$ degree orientation
20   with respect to each other. It is also clear that if the anisotropy energy density constant K1 <0 the direction of the resulting easy and hard axes of the coupled pair of variants invert.

Each of these paired variants not only results in a
25   uniaxial energy function, but, as discussed earlier for figure 2, in a zero loss hard axis driven M_x versus H_x response function and a non-linear, quadratic M_y vers H_x response function. (To a reasonable approximation this will turn out to also be the case for $\delta = 60-\arctan(\sqrt{2}) =$
30   5.264 degrees.) Each of these three coupled pairs ($\delta = 7.5$) represents an ideal way to construct an ideal uniaxial response from a (110) textured bcc-d magnetic material. As before, because the sum of the energy functions of all six possible variants is equal to a constant, $K_1(7/32)$, then in
35   each of these three paired variant cases the sum of the remaining four variant energy functions is equal to -1/4 of

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the sum of the paired variants. Hence, there are three
particular sets of four coupled variants that sum to yield
a Stoner-Wohlfarth type energy function, however because of
the negative sign, its hard and easy axes are rotated by 90
5   degrees relative to the corresponding coupled pair and the
peak to peak energy amplitude swing is 1/2 that of the
coupled pair case. Hence, these three sets of four coupled
variants result in, a Stoner-Wohlfarth, linear and lossless
M versus H response functions when driven along the net
10   hard axis. From a notation standpoint we should state that
the coupled variants represented by the energy function $E_{2\text{-}b1a2}''(\theta)$ and corresponding $E_{4\text{-}a1b2c1c2}''(\theta)$ are complements.
After all, similarly to before

15        $E_6''(\theta) = \{ 2E_{2\_a1c2}''(\theta)$ $+$

$4E_{4\_b1a2b1c2}''(\theta) \}/6 = K_1(7/32) = constant.$

It should also be noted that there are twelve other
possible combinations of pairs of coupled variants and that
20   none of them yield a uniaxial energy function. Some are
worst than others in terms of the depth of the localized
energy minimum. Likewise, the corresponding twelve other
possible complementary foursomes of coupled variants cannot
yield uniaxial behavior, because they can be written in
25   terms of the non-uniaxial coupled pairs of crystallographic
variants. This analysis now only leaves the twenty
possibilities for sets of three coupled variants to be
considered. By similar logic as used before, ten of them
are complements (negatives) of the other ten. Fourteen of
30   them have either double minimums or maximums and localized
extremes. The other six satisfy the definition of uniaxial
anisotropy energy functions, but each does contain a wavy
portion[11] of the energy curve located about midway
between, and only on one side of, the single minimum and
35   the single maximum. A response curve when driven at an
angle between this wavy portion and the hard axis would be
nearly lossless, but non-linear over large portions of the
response curve. If driven along an angle constrained to the

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smooth part of the curve near the hard axis [12] the response would be lossless and more linear over just this portion of the drive. A representative plot of one of these six energy curves, $E_{2\_a1b2}''(\theta)$, is shown in Figure 6.

5   In summary, not including the previously discussed six singular variants and the null case of all six, there are fifty six possible combinations of equally weighted variants. Hence, when the variant phase angle is set to 7.5 degrees, there are six possible balanced variant

10   combinations that will yield exact Stoner-Wohlfarth like energy curves and corresonding M versus H response functions, plus there are six possible balanced variant combinations that will yield uniaxial, but wavy energy density functions. All others yield non-uniaxial behavior.

15   For completeness, we briefly consider the effect of higher order anisotropy energy terms. An energy expression example, for the uniaxial case of a coupled pair of variants, when the second order anisotropy energy density constant, K_2, is non-zero, is given by:

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$$E_{2\_a1c2}''(\theta) = (K_1/64)\{14-8\cos(45)+16\cos(45)\cos^2(\theta)\} +$$
$$(K_2/64)\{1-\cos(45)/2+\cos(45)\cos^2(\theta)+\cos(45)\cos(6\theta)/2.$$

We investigated this function and found that the

25   effect of the 6θ harmonic is of most significance to the uniaxial behavior when the magnitude of K_2 is comparable to or larger than the magnitude of K_1. However, for many materials this is not the case and in most cases $K2$ is so insignificant that it is unknown. For example, for iron,

30   it is sometimes reported that $|K_1/K_2|>5$, but in some publications it is unmeasurable. Nevertheless, if needed, a similar analysis could be conducted including K_2.

Special Case: $\delta = 5.264$ Degrees

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We now return to the case where the variant phase angle δ, is given by $60-\arctan(\sqrt{2})= 5.264$ degrees. The

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5.264 degree phase angle is not largely different from the 7.5 degree value and the resulting energy curves for the same combinations of variants, but using 5.264 degree phase shifts, are similar to the special 7.5 degree cases just
5   discussed. Uniaxial energy density curves are obtained for the same three sets of pairs of variants as observed before, but using the smaller δ value:

$$E_{2\_b1a2}(\theta) = \{E_{110}(\theta-0-5.264)+ E_{110}(\theta-60+5.264)\}/2,$$
10   $$E_{2\_a1c2}(\theta) = \{E_{110}(\theta-60-5.264)+ E_{110}(\theta-120+5.264)\}/2, \text{and}$$
$$E_{2\_c1b2}(\theta) = \{E_{110}(\theta-120-5.264)+ E_{110}(\theta-0+5.264)\}/2.$$

We also note that each of these energy functions, or variant pairs, is the same if simply phase shifted by 60
15   degrees on the hexagonal atomic template,

$$E_{2\_b1a2}(\theta) = E_{2\_a1c2}(\theta+60) = E_{2\_c1b2}(\theta+120).$$

Likewise there are three sets of corresponding;
20   complementary variant foursomes that yield similar, but inverted and reduced amplitude differences, energy curves. Furthermore, each of these energy functions, or variant foursomes, is the same if simply phase shifted by 60 degrees on the hexagonal atomic template.
25   As an example of the functional shape we use $K_1=1$, $K_2=0$ and plot in Figure 7 the anisotropy energy density function for:
$$E_{2\_a1c2}(\theta) = \{E_{110}(\theta-60-5.264)+ E_{110}(\theta-120+5.264)\}/2.$$

30   And, in Figure 8 is plotted the anisotropy energy density function for the complement coupled variant set, corresponding to the foursome variant combination:

$$E_{4-b1a2c1b2}(\theta) = \{E_{110}(\theta-0-5.264)+ E_{110}(\theta-60+5.264)+$$
35   $$E_{110}(\theta-120-5.264)+ E_{110}(\theta-0+5.264)\}/4.$$

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As discussed earlier, ignoring the additive constant, the anisotropy energy density function of Figure 8 has a peak to peak difference of is just -1/2 the amplitude difference of the energy density function represented in

5   Figure 7.   While these functions are very similar to the $\sin^2(\theta)$ or the $\cos^2(\theta)$ dependence of the Stoner-Wohlfarth model the curvature around the maximum and the minimum can be seen to differ. They are uniaxial in behavior, but the hard axis magnetic response function is somewhat non-

10   linear, but free of lossy processes. The curve shape at the extremes invert, and so the easy and hard axes deviations, from the Stoner-Wohlfarth model, interchange, when $K_1 < 0$.

The M_x [13] versus H_x and the M_y [14] versus H_x response curves corresponding to $E_{2-a1c2}(\theta)$ are plotted in

15   Figure 9.   The M_x versus H_x curve (solid) shows the non-linearity resulting from δ not exactly equaling 7.5 degrees. However it represents a lossless response. The M_y response curve shows similarity to the quadratic behavior of the Stoner-Wohlfarth response.   For

20   completeness, Figure 10 is provided to show the $E_{2-b1b2}(\theta)$ coupled variant energy curve for $\delta = 5.264$ degrees, which is analogous to that of Figure 6 where $\delta = 7.5$ degrees. The curve is almost flat on the right side of the maximum. However, it still represents a uniaxial material.   From

25   these comparisons we can see that for $\delta = 5.264$ degrees there are also 12 possible uniaxial coupled variant sets.

If portions of a film are constructed from a coupled variant pair, for example $E_{2-a1c2}(\theta)$, and other portions of the film are constructed from a coupled variant foursome,

30   for example $E_{4\_b1a2c1b2}(\theta+90)$, rotated 90 degrees then they both have a common easy and hard axis. The two film portions must not be strongly coupled so that the two separate coupled variant sets function independently. Then the two non-linear response functions can average to yield

35   a net response function that is nearly linear. However we have found that the response of physical samples may

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contain some waviness. It is important to realize that to
achieve the rotation of the foursome the templates for the
two portions of the material need to be rotated relative to
each other by 90 degrees so that the hard axes of the two
5   material portions coincide.   Of course because the
hexagonal template repeats very 60 degrees of rotational it
implies that the template actually only needs to be rotated
30 degrees to be equivalent to a 90 degree shift. This is
because the symmetry breaking mechanism is common for both
10 variant sets. Of course it is obvious that other variant
sets, perhaps not balanced, can occur for template
orientations between the 0 and 30 degree directions and may
yield near linear behavior. This concept, of utilizing
more than one group of different sets of coupled variants
15 in a single sample, is very powerful as it enables the
development of nearly linear magnetic response functions
even for polycrystalline (110) textured. bcc-d films
epitaxially grown on polycrystalline, randomly oriented,
(111) hexagonal atomic templates. This means that even
20 though a single crystal substrate will yield the best and
most easily understood performance, having a single crystal
is not a requirement to achieve the near linear and low
loss magnetic response function. The requirement is only
that each group of coupled variants be selected and placed
25 upon an appropriately rotated polycrystalline grain
template so as to produce a nearly common hard magnetic
axis for the entire sample. When a non-single crystalline
substrate is used for the deposition of a highly (111)
textured polycrystalline hexagonal atomic template the
30 films will consist of individual grains with random in-
plane orientation. The technique to obtaining the same
easy and hard magnetic axis behavior across an entire
polycrystalline sample is to induce the appropriate (110)
textured bcc-b coupled uniaxial variant set for each of the
35 randomly oriented hexagonal templates. The method of
achieving this is to provide an energetically driven growth
process that preferentially selects the appropriate coupled
variant set for each hexagonal template orientation being

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use.   In the experimental results that are to follow we
have used both a magnetic field applied along the desired
easy axis direction during magnetic variant film deposition
or angular vacuum vapor deposition of the bcc-d material to
5   select a direction for the crystallographic orientation
growth. Deposition in an applied field was found to yield
superior uniaxial behavior. However, unique subsets of the
many variant sets were obtained in both cases.   These
methods result in a controlled uniaxial behavior for the
10   ·magnetic film.   Other methods of supplying an energetically
favored crystallographic growth direction may include
chemical plating in an applied magnetic field, chemical
plating from a bath solution which flows along the
substrate in a particular direction, deposition on a miss
15   cut single crystal substrate, and deposition upon a
strained, or distorted hexagonal template.

        We believe that just as there is a preference for the
formation of lowest energy atomic arrangements that can
cause preferred crystalline textures, there is a similar
20   mechanism in the symmetry breaking mechanisms to cause
orientation in of the crystalline directions in the film
plane.   In particular, on a surface the resulting texture
is usually the most close packed atomic arrangement.
Hence, for angle depositions of bcc-d materials one would
25   expect the <111> directions to tend to align with the
direction of the depositing material.   Furthermore, it has
been found that since there are two <111> directions in the
bcc-d (110) texture plane and multiple , <110> hexagonal
template directions there is some latitude as to whether
30   one of the <111> directions align exactly with the <110>
template direction parallel to the deposition direction or
that it align with one of the <110> directions at + or - 60
degrees.   The later is usually the case for unaxial
materials. Also, the energies of film formation must be
35   just balanced against the surface bonding energies
otherwise this symmetry breaking will not occur.   Likewise,
we have found that unless the processing conditions are
just right not only will the variants not be symmetry

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broken, but the variant set will be the three variants discussed by Gong and Zangari rather than the six new ones. By adjusting these competing energies the desired film structure can be obtained. Adjustment parameters include

5   deposition rate, substrate temperature, vacuum quality against film oxidation, and hexagonal template atomic spacing and material composition. We have found that it is not necessary to achieve magnetic coupling between variants to achieve a symmetry broken structure. However, in order

10 to achieve a uniaxial magnetic behavior the appropriate set of variants must be exchange coupled. The exchange coupling may be directly between the individual touching variants when their size and spacing is such that the exchange length is comparable or not to small compared to

15 variant grain size. However, more preferred is to place a magnetic hexagonal template material directly in contact with the magnetic bcc-d film to assist the exchange coupling via the hexagonal shaped layer. Furthermore, while it has been observed that the hexagonal magnetic

20 exchange coupling layer may be place either under or on top of the magnetic bcc-d layer it is most preferred to place it under the films and so also use it as the as the hexagonal atomic template. It is also viable to build multple alternating layers of hexagonal templates and bcc-d

25 magnetic layers.

To illustrate that not all variant sets yield a uniaxial energy function a three variant set, $E_{3-b1b2c1}$, example is plotted in Figure 11. Clearly this is not uniaxial, but bi-axial behavior.

30 Clearly there are a large number of possible ways of coupling sets of variants to achieve a lossless magnetization response function. For epitaxial growth on single crystal substrates the resulting hard and easy axes are correlated to the substrate directions. However, for

35 polycrystalline substrates the epitaxially grown films contain multiple variant sets corresponding to the crystalline orientations of the individual hexagonal template grains. The appropriate set of couple variants

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are selected for the particular orientated polycrystalline
hexagonal template via processing conditions and symmetry
breaking mechanism. These coupled variant sets do not have
to be equally weighted in volume in the sample. Also key,
5   for used of both random in-plane oriented polycrystalline
hexagonal template films, and for single crystalline
substrates is the concept that the variants of the selected
coupled set be sufficiently strongly magnetically coupled
so that the magnetization vector of each of the variants of
10   the set rotates together. The coupling is most likely via
magnetic exchange coupling. Hence, we adopt the phrase
"uniaxial symmetry broken" to denote the crystallographic
characteristics of these uniaxial and nearly uniaxial, bcc-
d materials, which have low coercivity and, so, low loss
15   magnetic properties. A crystallographically "symmetry
broken" material is defined to exit when individual,
variant sets do not contain an equal amount of all six of
the (110) textured bcc-d variants. We use the phrase
"symmetry breaking mechanism" to describe the energic
20   process by which a "symmetry broken" crystalline structure
is obtained. Because of the conceptual complexity and
multiplicity of these systems, we have only discussed at
lenght the cases where the variants of a coupled set of
variants are equally weighted (balanced) in volume of
25   material. This does not have to be the situation and other
interesting energy functions and response curves can be
obtained for these cases. One trivial, but important case
can be envisioned by considering a film composed of the six
coupled variants. If the volume of each variant is equal
30   then, as noted before, the energy density function is a
constant and has no θ dependence. However, if two of the
six variants are of different volume than the other four
then uniaxial behavior can result. Consider the simple
case when the two variants with different volumes of
35   material are selected as one of the three Stoner-Wohlfarth
variant pairs ($E_2^{\setminus}(\theta)$ or $E_2(\theta)$). If the quantity of
material for this pair is slightly greater than the other
four variants then this would break the symmetry and

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uniaxial behavior would result. However, the energy density difference between the minimum and the maximum would be decreased by the relative difference in volume of materials. For example, of the six couple variants suppose

5   that each of variants of the Stoner-Wohlfarth like coupled pair occupied 30% of the total volume and each of the other four variants occupied 10% of the total volume. Then this would result in a minimum to maximum energy difference equal to 40% of what would be obtained when all the

10 material was in just the Stoner-Wohlfarth like pair. Hence, the magnetic response function would be more sensitive to the applied field as the minimum to maximum energy difference would be smaller for the total magnetic volume. This represents a method of adjusting the slope,

15 also called the magnetic relative permeability, of the magnetic response function.

        In many magnetic devices it is advantageous to have multiple thin film layers. Many times they need to magnetically or electronically interact and so there needs

20 to be specifically anisotropy orientational relationships between them. For example, to minimize noise signal it is extremely useful to apply a controlling force along the easy axis of a magnetoresistive sensor in order to stabilize the device against the formation or motion of

25 magnetic domain walls in the sensor material. This is sometimes accomplished by placing a hard magnetic material at the ends of a rectangular shaped device to provide a small magnetostatic field or to exchange couple to the soft film. Likewise, in these devices there is a need to bias

30 the magnetization into a partially rotated state. This allows the magnetization to swing both positive and negative toward the hard axis and tends to avoid signal clipping or extreme non-linearities. In this anisotropic magneto resistance device the signal resistance varies with

35 the orientation angle of the magnetization relative to the current flow direction. Hence, a second layer of controlled hardness or anisotropy, when placed in contact or proximity of the first layer, can provide these

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stabilizing or orienting effects.   Likewise, in a spin
valve or magnetic tunnel junction type magnetoresistive
sensor the electron spin transport across an interface
between the two stacked magnetic layers is effected via the
5   relative orientation of the two magnetic layers.   R. C.
O'Handley's text, "Modern Magnetic Materials and Principles
and Applications" discusses the structures and mechanisms
of these magnetoresistive effects as well as other magnetic
applications.   This technology is now well developed for
10   field sensors, magnetic data storage playback heads and is
rapidly being developed for Magnetic Random Access Memory
(MRAM).   When the magnetization of the two magnetic layers
is aligned the electrical resistance is minimized as spin
transport across the interface is enabled or enhanced.   For
15   example, sensing an external field is accomplished by
pinning one layer against rotation while leaving the other
free to rotate or designing a structure where the two films
are antiparallel and both of them are allowed to rotate
toward a common direction as the applied field is
20   increased.   When the two layers are not aligned the
available conduction spin states are not common and the
conductivity is minimized.   In these types of devices a
variety of orientation geometries have been discuss in the
literature, but for all of these the signal always depends
25   upon the field induced magnetization orientation changes
between the stacked magnetic layers.   In some device
geometries there are multiple magnetic layers, more than
two, and the magnetoresistance effect is determined via the
conduction between the multiple film interfaces.   Hence the
30   signal determining applied field or magnetic state is
determined by the field induced angle difference between
the pairs oflayers. Clearly, the incorporation of layers in
which the anisotropy can be better controlled is essential
to improving these types of devices. The uniaxial symmetry
35   broken magnetic layer technology invented, and discussed
here, is of considerable value for each of these devices.
A third, hard magnetic layer structure, antiferromagnetic,
or synthetic antiferromagnetic layer constructed from hard

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magnetic layers can be used to pin or exchange couple to one or more of the sensor magnetic layers. Control of the anisotropy of this layer is likewise of value in the device designs. By choosing the composition of two layers to have

5   differing anisotropy constants one layer essentially appears hard to rotate while the layer with the lower anisotropy constant can appear to be magnetically softer and freer to rotate. Later in this application, we will discuss another method of using the uniaxial symmetry

10 broken technology to orient hard disk magnetic media. This same approach can also be used to create or orient these hard or antiferromagnetic layer structures.

A new integrated circuit technology is emerging based upon the spin transport process and upon the orientation of

15 magnetic layers similar to those just discuss. This technology is sometimes referred to as spintronics. The most simple of these concepts is a magnetic spin transistor whose conduction is a function of magnetic spins injected into a current controlling junction region. The current

20 controlling concept is analogous to the carrier control or field control produced in a bipolar or field effect transistor. However, for spintronics, the orientation of a magnetic moment in the junction region of the device determines the spin dependent injection of the electronic

25 carriers. Hence, control of the orientation and the magnetic state of these layers is essential. It is envisioned that transistors can be constructed as well as electronic logic and state devices. Furthermore, because with proper design magnetic states can remain after

30 electrical power is removed, it is envisioned that these devices can possess memory functionality. These future electronic devices may come in unforeseen designs and functionallity, but one aspect is assured. Control of the anisotropy energy density and anisotropy orientation will

35 be critical. The uniaxial symmetry broken mechanism can provide a methodology for controlling these angles and magnetic states.

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Other magnetic circuit components, which can benefit from improved anisotropy control, include inductive properties. These are envisioned to include small traditional inductor geometries of magnetic materials in
5 proximity of current carrying conductors. The permeability of the magnetic materials enable the additional storage of energy and so can be used to manipulate signal waveforms as in filters or to transfer or convert power to alternative voltage or current levels. Thin film structures would be
10 especially useful at the microcircuit scale where high frequencies would normally eliminated the use of bulk magnetic materials. Both inductors and transformers are envisioned where serpentine pathways of layers of conductors and magnetic materials would be used to form the
15 magnetic devices. The design needs to incorporate a considerable degree of magnetic flux path closure in order to achieve a reasonably high extrinsic permeability and, hence, efficiency. For linear signal transfer a near linear magnetic response is desirable, whereas for power transfer
20 this is not as critical an issue. On the other hand, an analog signal mixer, as is commonly employed in radio communication, requires a non-linear response, which can be obtained from a uniaxial material via the easy axis response to a hard axis drive field in the presence of a
25 bias field along the easy axis. However, important to each of these devices is that the magnetic losses be minimal. Otherwise the devices inject noise into the signal, tend to over heat as energy is dissipated in each cycle, and possess a limited frequency response. Clearly the uniaxial
30 symmetry broken mechanism can provide a methodology for controlling the magnetic anisotropy and orientation and so enable these desirable device attributes.

Another magnetic field sensor, which utilizes the non-linear response function and benefits tremendously from a
35 lossless process and high frequency operation, is known as the fluxgate. Fluxgates are commonly used to sense the earth's field and are extensively used in the well drilling process to monitor direction of the drilling process. This

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is especially important for deep well drilling such as in
the oil industry where the cost of pulling the drill is
quit significant. Having a robust field sensor to provide
information for avoiding hitting certain materials is quite
5   valuable. There are a number of physical designs for these
devices. However, they all work on the simple concept of
driving one magnetic axis and inductively measuring the
time rate of change of the magnetization induced by the
external magnetic field along an orthogonal axis. A non-
10 linear response yields a signal, which is proportional to
both the external field and drive frequency; and, is a
second harmonic to the drive field frequency. Since the
response is proportional to the drive frequency, the signal
amplitude, for a small applied field, can be increase
15 considerably via the use of a high frequency drive.
However, if the material has losses the drive frequency is
limited and if the losses are due to the Barkhausen
phenomena associated with domain wall motion then the
measurement sensitivity is also noise limited. If the
20 magnetic material has a lossless uniaxial response, as
obtained by a uniaxial symmetry broken structure, then
device can be operated to higher frequencies and with
better sensitivity to external fields.

        Another family of magnetic devices can be used for
25 article surveillance and article identification and are
commonly referred to as tags. Some of these devices
operate on the principle of non-linear response and others
operate on the principles of linear response employing
energy storage for later radiation. The control of the
30 anisotropy energy density and direction is essential in
each. The non-linear response devices typically allow the
switching of the magnetic state abruptly via wall motion,
which generated large amounts of harmonics of the driving
field, which are then detected via picked up via
35 electromagnetic sensing   antennas. In the simplest
manifestation the non-liear response tag is simply a strip
of very soft magnetic material with a uniaxial anisotropy

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direction. This is easily produced utilizing our uniaxial symmetry broken material structures.

The linear tags work on the principle of coupling the magnetization orientation to the mechanical resonance of acoustic vibrations in the tag. This is done via the magnetoelastic properties, which is a complement property to magnetostriction, of the materials. For these materials a large magnetostriction coefficient is desired. When the magnetization is rotated away from the easy axis by a drive field along the hard axis the material either elongates or contracts depending upon the coefficient sign. This shape change is equivalent to an acoustic wave traveling along the tag. When the acoustic wave reaches the end of the material it tends to reflect backwards. Hence, if the tag is driven with magnetic field that oscillates with a period corresponding to the acoustic transit time between the ends of the tag, resonance is obtained. Likewise, if the drive field is fixed the length of the tag can be adjusted to match. For bulk material devices, where there is no substrate, the acoustic properties are determined by the acoustic properties of the magnetic material. However, if the magnetic material is laminated with another material or deposited upon a substrate then the acoustic propagation properties are determined by the combined properties of the magnetic material and the laminate or substrate. However, the acoustic resonance condition, of the combined set of materials, must still be matched to the magnetic field driving frequency. Tag detection occurs after the magnetic drive field is discontinued. Due to the acoustic resonance the tag continues to elongate and contract at the mechanical resonance frequency. Via magnetostrictive coupling to the acoustic vibrations the magnetization vector oscillates at the mechanical frequency, generating a magnetic field at the very specific mechanical resonance frequency, which can be detected by the detection antennas. As with the magnetoresistive field sensors the magnetoelastic tag device works best if a DC bias field is employed to tilt the magnetization from the easy axis. In

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this manner the magnetization vector oscillates about the
bias point, which avoid frequency doubling and improves
efficiency and sensitivity. For thin films, deposited on
thin Si substrates, or very then substrates etched from Si
5   structures, the high mechanical Q of the Si further
improves the mechanical resonance process. A multitude of
resonance frequencies can be utilized if substrates of
different lengths are employed.   The Micro-Electro-
Mechanical structure, MEMS technology, is ideally suited to
10   be incorporated in such a device when a multitude of unique
tags are desired. Resonance beams of various lengths can
be micro-machined on to a single substrate for a single
device. The magnetoelastic material deposited on to all of
the beams. Just as with electronic circuit technology many
15   of these devices can be processed on a Si wafer in
parallel. When this device is driven by an oscillating
magnetic field only those beams with the length
corresponding to the driving field frequency vibrate and
store energy. By sweeping the drive frequency and then
20   electronically listening via an antenna for the radiated
magnetic field response each of the beams sequentially, or
by applying an impulse field and then observing the various
response frequencies, a very unique signal signature can be
obtained. Various acoustical MEMS structures can be
25   designed to allow a generic MEMS structure, which can be
programmed after the devices are constructed. For example,
via mechanical dampening of predetermined beams of specific
lengths of a given device, a unique signal signature can be
obtained. Hence, from a single MEMS processed Si substrate
30   thousands of unique tag devices can be constructed. Hence,
it is conceivable to label each product with unique tag
device, each with a unique signal signature. Critical to
any of these devices for operation is the control and
orientation of the uniaxial magnetic anisotropy energy.
35   The unaxial symmetry broken magnetic material structure is
ideal for this application.
     Also, as discussed earlier, in hard disk media it is
potentially valuable to have a soft keeper layer in close

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proximity to the hard media layer. By using a uniaxial material and controlling the orientation of this layer relative to the recording track, and to the preferred direction of the hard memory layer, can yield improved

5   areal densities via improved media noise, SNR, PW50, thermal stability, and overwrite properties. We have also found that the use of the orientation determining bcc-d variants as an underlayer can result in some control of the orientation of the hard magnetic layer.

10   By investigating the epitaxial growth of various film stacks on single crystal substrates we have found that there are some unique epitaxial relationships that have heretofore not been invented or utilized, as well as, some which enable unique characteristics when combined with the

15   newly invented coupled variant structures.

        We investigated three Si crystal substrate texture orientations, (100), (110), and (111) by first depositing epitaxial Ag on to these cleaned surfaces. Some epitaxial relationships are already known from U. S. Patent

20   6,248,416, Heng, Zangari, and similar publications where, for example, the growth of Cu(fcc) on Ag(fcc); permalloy(fcc) on Ag(fcc) or Cu(fcc); Co(fcc) on Cu(fcc) or permalloy(fcc); Cr(bcc) on Ag(fcc); Ti(hcp) on Ag(fcc); or Co(hcp) on Cr(bcc) or Ti(hcp) were studied extensively.

25   However, nowhere in these works was any evidence presented of depositing bcc-b magnetic materials nor of the observation of any symmetry broken structures disclosed. We have observed symmetry broken structures by applying symmetry breaking methods and controlling the deposition

30   process conditions. For example, we have used both deposition in an applied field and deposition at an angle on highly oriented hexagonal templates to obtain highly textured symmetry broken iron, iron compounds and iron alloys.

35   Also, we have found, as has been disclosed in the literature, that we can epitaxially grow one bcc-d on another and again on another while maintain the strong texture and orientational relationships between each of the

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bcc-d on each of the three Si crystalline textures, <100>, <111>, and <110>. There are also other relationships. Epitaxial fcc Ag, Au or Al always forms the same texture as the Si substrate surface. On this fcc-d substrate, a
5 number of epitaxial relationships can be obtained for the following layers. Upon these layers yet other epitaxial relationships are formed. When a bcc-d is grown on another bcc-d the same texture results. When fcc-d is grown on fcc-d the same texture results. However, when bcc-d materials
10 are epitaxially grown upon, denoted by "/", fcc-d materials of a give texture the following texture relationships result:

          bcc-d texture/fcc-d texture
          (100)/(100)
15   (110)/(111)
          (112)/(110).

When fcc-d materials are epitaxially grown on bcc-d the following texture relationships result:

          fcc-d texture/bcc-d texture
20   (100)/(100)
          (111)/(110)
          (110)/(112).

When hcp materials, such as Co alloys, are epitaxially grown on bcc-d the following relationships result:

25   hcp texture/bcc-d texture
          (11$\underline{2}$0)/(100)
          (10$\underline{1}$1)/(110)
          (10$\underline{1}$0)/(112).

When Ti is epitaxially grown on fcc the resulting Ti is hcp
30 and the following texture relationship can resulted:

          hcp Ti texture/fcc texture
          (0002)/(111).

However, the bulk phase diagrams of Co alloys show both an hcp phase at low temperatures and an fcc phase at somewhat
35 higher, but not extreme, temperatures and so it is possible to grow either hcp or fcc Co. When grown on an fcc underlayer we found the epitaxial Co to most commonly form the fcc phase and texture of the underlayer. Hence, it

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behaved just as other fcc-d materials deposited upon fcc-d
templates. However, when formed on bcc-d it formed the hcp
phase and the texture relationships noted above resulted.
When Co is epitaxially grown on another hcp it is hcp and

5   has the same texture and orientation as the underlayer hcp.

      In each of these cases, except for the case of the six
bcc-d variant structures under discussion, the in-plane
orientational relationships were as denoted in U. S. Patent
6,248,416, and publications by Heng and by Zangari.

10   However, we have invented some new relationships involving
oxides, which enable the construction of new devices. For
the three fcc metals, Cr, Fe, and Al; and for selected
alloys of these, we have found that the surface of the
metals can be formed as oxides and then when the same metal

15   is then deposited upon this surface oxide the second metal
layer sometimes epitaxially grows and assumes the texture
and in-plane orientation nearly as though the first metal
layer had not been oxidized. This statement was found to be
true for all three of the Si substrate textures

20   investigate. However, the Si(111) is the most stable agains
oxidation followed by Si(100) followed by the least stable
S(110). And so when growing epitaxial films, by our current
techniques, usually the films that develop on Si(111) are
of the highest quality and their resulting textures of the

25   following layers are also of higher quality. Hence, they
are also the easiest to analyize. Because of the high
degree of texture and lack of large angle grain boundaries,
when these metals are exposed to oxygen they appear to
passivate uniformly with a thin oxide layer and then cease

30   to be consumed into oxides. It is estimated that even for
a reasonable exposure to atmospheric conditions the oxides
can be as thin as 1 to 3 nanometers, but could also be
grown thicker by direct epitaxial oxide deposition or with
the addition of heat or moisture during a post deposition

35   exposure to oxygen. While extremely thin and difficult to
measure each of these oxides may form the rhombohedral
corundum crystalline phase commonly designate as prototype
α-Al$_2$O$_3$. Interestingly enough α-Cr$_2$O$_3$ and α-Fe$_2$O$_3$ form a

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continuous solid solution. It was found that when the first metal was a Cr alloy, then oxidized, and the second metal was Fe, that the second metal formed, to a limited degree, the same texture and orientation as the first. The same

5   was true when the Fe was the first metal and the Cr was the second. However, when the Fe was oxidized on its surface many of its magnetic properties were degraded. In addition, there are many additional elements that can be added to Cr, Fe, or Al and then be oxidized into the same crystal

10   structure. For example, both α-V$_2$O$_3$ and α-Ti$_2$O$_3$ phases exist. The α-V$_2$O$_3$ forms a solid solution with α-Fe$_2$O$_3$. Also limited amounts of Al can be added to Fe and the α-Al$_2$O$_3$ crystalline structure still results when oxidize. Likewise, it is known that FeTiO$_3$, MnTiO$_3$, CoTiO$_3$, NiTiO$_3$

15   can be added to α-Fe$_2$O$_3$. There are a large number of other metals that in small quantities can be added to the Cr, Fe, or Al and when oxidized still result in the α-Al$_2$O$_3$ structure. However, it should be recalled that in our samples the oxide is very thin and it was difficult to

20   determine the exact crystal structure. It is possible that more than one oxide structure can pass the texture and orientation of the first metal layer to the second. Fe and Cr both also form the cubic spinel structure, A$_1$B$_2$O$_4$, and there are many transition metals, and combinations of

25   metals, that can be added to these to still form the spinel. There is also the possibility that the oxides formed are more than one crystal structure. CrO$_2$ is a tantalizing possibility as its nearly half filled conduction band is essentially half filed with a single

30   magnetic spin orientation and so holds tremendous potential in a spin valve or tunneling structure. The corundum, however, is an excellent candidate for the oxide due to its stability and is commonly known to form on Fe, Cr and Al metal surfaces. While amorphous oxides also form, it is

35   hard to believe that the strong texture could be passed from one metal to the other via an amorphous oxide.

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Furthermore, for the <110> bcc-d texture, we have found that the texture of the six variants discussed propagates the variant crystalline orientations if one bcc-d is place directly on another metallic bcc-d or if it was placed upon the oxidized surface as just discussed. Hence, it is possible to develop a first symmetry broken uniaxial bcc-d layer, epitaxially grow a second symmetry broken bcc-d layer, oxidize it, and then grow yet another bcc-d layer on the oxide with the same texture as the first bcc-d. Some interesting magnetic arrangements can be constructed from these layer-to-layer texture relationships. If the two variant sets that have been epitaxially grown on top of one another, and have anisotropy energy constants of the same sign, then the easy axes are aligned. However, an interesting case arises if one layer has a positive and the other a negative anisotropy energy density constant. This results in the two layers having easy axes at 90 degrees to one another. This means that one orientation can be induced by the symmetry breaking mechanism and then by using a bcc-d with the opposite anisotropy constant sign the easy axes of the second layer is rotated 90 degrees with respect to the first bcc-d layer even without the use of a process that would normally be required to break the symmetry of the second bcc-d film. Furthermore, the thickness of a non-magnetic bcc-d layer, which can be placed between these two magnetic layers, can be used to adjust the magnetic exchange coupling between the layers. This can be adjusted from being strong to weak as this non-magnetic layer is made thicker. . Adjusting this non-magnetic layer thickness and the thickness-saturation magnetization product of each of the two magnetic layers adjusts both the angle between the magnetization vectors and the in-plane orientation of the two magnetic layers. Hence, because exchange coupling strength between the two magnetic bcc-d layers a can be controlled by selecting the coupling material or by controlling the coupling layer thickness the net magnetic easy axis orientation of the coupled film structure can be selected. These features are

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useful in a variety of magnetic device designs as they
allow the angle between the two magnetic layers, as well as
the stiffness to changes in the angle, to be varied
without the use of an additional hard or anti-ferromagnetic
5   layer.   This type of behavior is of use in device
construction such as spin valves or spend dependent
tunneling devices.

     We also found that a strong (111) fcc-d texture
develops when grown on the six variants of the bcc-d.
10   Furthermore, the in-plane orientation assumes the same
direction as the underlying hexagonal (hex) template.
Hence, a layer structure such as

     bcc-d(110)/fcc-d(111)/bcc-d(110)/hex(111)/Ag(111)/Si(111)

15

is viable, where either, or both, of the bcc-d. layers are
symmetry broken by the use of the symmetry breaking
mechanism.   (Here we use the notation that the film on the
left of the "/" is deposited after the film on the right of
20   the "/".   From the tilt angle of the "/" it is easy to
recall which layer is on top.) Of course this approach also
applies when the substrate is polycrystalline via the grain
orientation averaging process.   Furthermore, when both
layers are made uniaxial, the easy axes of the two magnetic
25   bcc-d layers can be adjusted relative to each other by
using the symmetry breaking mechanism at different angles
for each layer.   In another, example, a multiple layer
epitaxial uniaxial layer structure can be formed as

30   bcc-d/Cr/O/Cr/bcc-d/hex(111)/substrate.

Again, here, the "/" symbol denotes a layer change, while
the "O" layer represents the exposure of the prior film
surface to oxygen or air. The bcc-d layers are magnetic,
35   (110) textured, and symmetry broken.   This Chromium example
represents a non-magnetic bcc-d material that is
epitaxially grown on the magnetic bcc-d layer and allows an
oxide layer that does not contact the magnetic layer. This

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structure allows the two magnetic layers to be electrically insulated from each other via the oxide layer and yet uniaxial behavior is obtained by utilizing the symmetry broken structure. Implied in this structure, but not
5   shown, are the variant exchange coupling materials or layers. For example a magnetic hex (111) layer. In fact, it is not uncommon that the hex (111) layer structure is composed of more that one layer. Likewise, an fcc-d magnetic variant coupling layer, such as NiFe, can be
10   placed on top of the final bcc-d layer.
        For very thin oxide layers spin dependent electrical tunnel conduction devices have been constructed as a large effect magnetic field sensor. These devices, just as with the spin valve device, rely upon the electronic transport
15   being sensitive to the relative orientation of two magnetic layers. However, in tunneling devices the current is directed perpendicular to the film plane and tunneling must occur through the oxide. Traditionally, these are usually constructed from fcc Co or permalloy magnetic layers with
20   an Al oxide insulator layer. The use of an Al oxide as the insulator is widely published upon. However, deposition of the oxide has been hard to control and oxidation of a deposited, very thin polycrystalline Al oxide layer usually results in conduction pin holes. Sometimes the Al has been
25   deposited as a metal and then post oxidized, but because of the limited quality of the underlying metal texture uniformity of the polycrystalline oxide is still a problem. The oxide layer thickness should only be about 1 to 2 nanometers in order for the tunneling energy barrier to be
30   a reasonable value. Clearly the highly oriented films used to make the oxide structure listed above, where the Al is used to replace, or in addition to, the first Cr layer would benefit the spin dependent tunneling device. This is especially true when constructed upon the single crystal Si
35   substrate. The uniaxial properties of the symmetry broken structure enable a considerably simpler device or construction process to be developed.

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Yet another, example, of a multiple epitaxial set of
layers allows both an oxide insulator, O to separate a
conductor, such as fcc Ag or Cu, from the two magnetic
layers

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bcc-d/Cr/O/Cr/Ag/Cr/O/Cr/bcc-d/hex(111)/substrate.

For brevity, the texture and orientation relationships are
not shown, but are understood to exist as discussed above.
10   When the Ag conductor carries a current, the two magnetic
bcc-d layers guide the magnetic flux generated in a close
path around the conductor (e.g. Ag). In this configuration
each or both magnetic layers may be uniaxial with
anisotropy directions equal or different. Providing the
15   relative magnetic permeability is greater than one and that
lithographically defined current paths have been
constructed this represents a compact electronic thin film
inductor; and with the use of additional conductors and
magnetic layers multiple turn electronic transformers can
20   be constructed. Inductance is proportional to the magnetic
relative permeability. We have found that relative
permeabilities exceeding 10 are quite viable and in some
structures exceeded several hundred in our uniaxial,
symmetry broken bcc-d film structures. Furthermore, for
25   thin metallic magnetic films the maximum operational
frequency is either determined by the ferromagnetic
resonance frequency or by eddy currents, if the structures
are made thick. Our modeling indicates the it is quite
reasonable to expect operational frequencies of a few
30   Gigahertz using Fe or Fe alloys. For uniaxial materials
the resonance frequency is proportional to the root of the
cross product of the saturation magnetization, M_s, and the
anisotropy field, H_K. For linear uniaxial materials $H_K =
2K_u/M_s$. Hence, the ferromagnetic resonance frequency is
35   proportional to the anisotropy energy density, while the
permeability is related to the inverse of this. For
thicker films where the operational frequency might be
limited by eddy currents, making chemical additions of only

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a few percent of secondary materials, such as Si, N, C, or Al to Fe or FeCo can increase the resistivity substantially. For example 3% Si by weight in Fe results in a 5 fold decrease in conductivity. The penetration depth, or skin depth, of eddy currents is inversely proportional to the square root of the inverse permeability-conductivity-frequency product. Our estimates indicate that for the proposed geometry that the thickness of the magnetic layer will have to approach one or microns before the eddy currents limit the operational frequency. Hence, inductors, transformers, and sensors made utilizing these symmetry broken material structures should function in the Giga Hertz range.

It should be stated again that due to the variety of symmetry broken coupled variant sets and the fact that epitaxial growth should be viewed as happening on each individual grain of a polycrystalline material these texture relationships and the device concepts apply to both polycrystalline film structures and single crystal structures prepared on single crystal substrates such as Si. Likewise, other single crystal substrates can be used to produce the uniaxial symmetry broken thin film structures with exceptionally strong texture orientation, such as the commonly available Ge anb GaAs, can be used provided that the texture is chosen to present the hex (111) template and that epitaxial thin film grown is obtained.

Yet another example of a device that can benefit from the symmetry broken structure is the growth of magnetic recording media. Here the hard magnetic layer is usually composed of hcp Co alloys such as CoCrTa, CoCrPt, CoCrPtTa, CoCrPtB, CoCrPtCuB and the like. In each of these the desired crystal structure is hcp to enable a high anisotropy energy density constant. Traditionally, hcp Co is grown on Cr or Cr alloy underlayers to control the crystalline texture and disk substrate is mechanically textured (scratched) along the recording direction to achieve a preferred orientation ratio to be greater than

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one, when compared to that perpendicular to the recording direction. Having a hard disk recording media oriented preferential along the recording direction results in a higher coercivity and better thermal stability. It is well

5 documented that upon a Cr (110) textured underlayer hcp Co alloys develop (10$\underline{1}$1) crystalline texture. The texture is referred to as the Co alloy quad-crystal because there are four possible c-axis orientations on a single crystal Cr grain with (110) texture. This is not the ideal hcp

10 texture because the hcp c axis, which is the magnetic easy axis, is tilted in or out of the film plane by about 28 degrees. Nevertheless, this texture has been used extensively for media and if it were oriented along the recording field direction it would be of considerable

15 benefit. Because of the demagnetization field of thin films the magnetization vector lies in the projection of the c-axis into the plane of the film. This then reduces the possible number of in-plane projections of c-axis orientations on a single Cr (110) textured crystallite to

20 two. They are at angles of + and - the arctan$(1/\sqrt{2})$ = 35.26 degrees with respect to the bcc-d <100> directions. If one considers the bcc-d coupled variant pairs as template underlayers for epitaxial Co alloy growth then the symmetry broken films provide a template with preferred

25 direction for the Co alloy to grow upon. This technique of selecting a textured and oriented underlayer provides a pathway to achieve hard disk oriented media. Consider, the coupled variant pair, $E_{2-a1c2}(\theta)$. This symmetry broken coupled variant pair has the its <111> crystal lattice

30 directions, that are parallel to the (111) hexagonal template <110> directions, along the θ = 60 and 120 directions. From Figure 5 it is easy to see the <100> directions of the two bcc-d cells. When a Co alloy quad-crystal is grown, the projection of the c-axis is

35 approximately at +40.3 or -40.3 degrees with respect to the bcc-d <100> direction.

Table 1 lists all of the possible quadcrystal structure Co alloy in-plane easy axes directions when grown

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on all of the six possible bcc-d variants discussed.   An
ideal, hcp c/a = $2\sqrt{(2/3)} = 1.63$, crystalline unit cell was
assumed for these angle calculations.   As an example to
understanding the calculations in Table 1 consider the
5   first variant, a_1. The <100> direction is listed as 65.26
degrees in Figure 5. Hence, the two in-plane Co c-axis
projections would be at approximately 105.6 and 25.0
corresponding to the + and - entries in the first row of
Table 1. Considering only the two variants of the symmetry
10   broken E_{2_a1c2} coupled variant of Figure 5 one can predict
the Co alloy magnetocrystalline anisotropy directions which
will be selected from those of Table 1..   These two bcc-d
variants, whether coupled or not, would induce the eight
possible Co alloy variants associated with obtaining two
15   quadcrystals.   There would be four for each of the two a1
and c2 bcc-d variants.   However, because the out of plane
demagnetization forces would drive the magnetization vector
into the thin film plane, the four c-axes projections in
the film plane would be 105.6 and 25 degrees for a_1 and 155
20   and 74.4 degrees for c_2.   Since the later two are closer to
the 90 degree direction than the first two are to the 0
degree direction the net coercivity along the 90 degree
direction is higher than that along the 0 degree position.
Clearly, the recording tract should be oriented along the
25   90 degree direction to obtain an magnetic orientation ratio
greater than one.   Unlike the soft magnetic films it is
desireable, for good SNR, that the four possible hcp cobalt
orientations be individual grains, which are decoupled.
For this reason it is best if a non-magnetic symmetry
30   broken bcc-d provide the template for the Co alloy to grow.
However, a magnetic bcc-d symmetry broken template can
first be grown and then the non-magnetic variant template
can be epitaxially grown on this.   As discussed earlier,
while not necessary in all media structures it may also be
35   desirable to have a soft magnetic keeper layer below the
oriented hard magnetic layer. The ideal easy axis direction
for the keeper would be perpendicular to the recording
track so that the stray fields from the recorded bits drive

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the keeper layer magnetization along its hard axis. However, the easy axis for the $E2-alc2$ example is also at the 90 degree position. As discussed earlier however, it is easily reoriented to the 0 degree position by choosing a
5   material with a K_1 < 0. Due to the manufacturing constrains of a circular disk, the preferred symmetry breaking method is to deposit the bcc-d material radially on the round disk surface and at an angle relative to the substrate normal. Our findings are that a symmetry broken structure can be
10   obtained even for polycrystalline films provided the (111) hexagonal template is highly textured and the deposition angle with respect to the substrate normal is constrained to be within 15 $\leq$ Ω $\leq$ 75 degrees from the normal. The incident angle is shown in Figure 12, where the arriving
15   bcc-d material travels along -r, which is at an angle Ω with respect to a normal (z) to the substrate plane (x-y). When the deposition material arrives at grazing angle, 75 degrees, the efficiency of deposit decrease, but the symmetry breaking method is very effective. When the
20   deposition angle is near the normal, 15 degrees, the deposition efficiency is superior but the symmetry breaking tends to diminish. The application of a magnetic field is also very effective symmetry breaking method, but a bcc-d layer with K1 > 0 and a field directed along the track
25   direction to achieve the $E2\_alc2$ are required. Due to the standard manufacturing process of simultaneous deposition of materials on both sides of the disk a radially directed or circumferentially directed field is not very conducive to incorporation in to modern hard disk media manufacturing
30   process.

Table 1

Variant name	bcc-d <100> direction angle relative to template, θ=0, <110> direction.	Two in-plane projected QuadCrystal projected c-axes angles relative to template <110> direction, θ=0.	
		+	-
a1	65.264	100.529	30.000
a2	54.736	90.000	19.471

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b1	5.264	40.529	-30.000
b2	-5.264	30.000	-40.529
c1	125.264	160.529	90.000
c2	114.736	150.000	79.471

Also, we found that by first depositing a metal
5   wetting layer on a typical hard disk substrate surface that
strong (111) texture could be obtain. The increased atomic
surface mobility provided by the wetting layer allows the
close packed texture to form from a hexagonal template
material such as fcc Ag, Cu, Ni, NiFe or even a hcp Co
10 alloy. A non-magnetic Co alloy of $Co_{1-x}Cr_x$, where
$25_{at\%} > x > 50_{at\%}$ is preferred if exchange coupling of the bcc-d
is not desired. It was found that a deposited amorphous
metallic layer provided an excellent wetting layer.

In particular, in any application where a wet layer
15 was desired, a amorphous compositions of NiP or materials
that under bulk material equilibrium conditions would form
C15 or C14 crystal structures seem to form excelled
amorphous wetting layers when vacuum deposited. Examples
of the C15 and C14 structures are $Cr_{1-x}Ta_x$ and $Cr_{1-x}Nb_x$, or
20 $Fe_{1-x}Ta_x$ and $Fe_{1-x}Nb_x$ where $55 < x < 75$ atomic percent. It is
noteworthy that in the Cr-Ta alloys the equilibrium phase
diagram shows a high temperature to low temperature phase
transition from a crystal structure of C14 to C15. It is
believed by the author that the pairing of these complex
25 equilibrium crystal structure enhance the propensity for an
amorphous film to form in the non-equilibrium thin film
deposition process. In each hexagonal atomic template
material case, fcc-d or hcp, the use of these amorphous
layers resulted in strong, (111) or (0002), texture
30 respectively. In the case of these two C15 materials it
was found that they could be exposed to oxygen and a
reasonably strong texture still developed. Hence, the
grain sizes of the hexagonal template layer and following
layers could be made smaller in a process controlled
35 manner.

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While a cylindrical geometry is not needed for magnetic media that is not to be used in a disk format, it is needed for modern hard disk media. In order to achieve uniform and symmetric deposition, with preferred magnetic
5   orientation around a disk substrate structure, a new vacuum sputtering cathode was devised. Figure 13 illustrates a cross-sectional view of a rod shaped sputtering target [15] composed of bcc-d material for deposition on to a disk substrate. A shield [16] and magnets [17] to facilitate a
10   sputtering plasma at low Ar gas pressures surround the target. A disk substrate [18] is held on axis with the sputtering target, but at a distance to cause the sputtered material [27] to arrive at the disk surface along a radial direction and at an angle of incidence. Ar gas is
15   introduced into the vacuum chamber via a pathway [26] between the target and a water cooled shield. This concentrates the sputtering gas [25] in the vicinity of the sputtering target and minimizes it in the vicinity of the disk substrate. The sputtering gas also provides a cooling
20   mechanism to transfer heat from the target to the water cooled shield. A low gas pressure is desired to enable a scattering mean free path of the sputtered material to be comparable to, or longer than, the distance from the target to the disk substrate. This prevents the randomization of
25   the direction of the sputtered material by avoiding gaseous collisions. Sputtering wears the target in a predefined and somewhat conical shape causing a deposition path from the target to the disk at the desired range of incident angles between 15 and 75 degrees. However, it has been
30   found that a more narrow angle distribution centered about 45 degrees is preferred. The target rod diameter is small compared to the desired inside disk recording diameter and so the material leaving the target essentially follows a radial path toward the disk at all locations on the disk
35   surface. In combination with the target surface profile shape, the disk to target distance is adjusted to set the deposition angle. To avoid non-uniformity produced by the magnetic fields of the sputtering cathode magnets the

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magnet structure may be rotated around the target rod during the deposition process. While not needed for this current work it is envisioned that the target wears smoothly to a somewhat conical point allowing the target to
5   be advanced, relative to the magnets, toward the disk center along a normal path from the disk surface and center during the deposition of any one disk. This allows for adjustment of the deposition angle and deposition rate at various positions along the radius of the disk. Likewise,
10   the advancement of the overall position of the target relative to the magnets allows for continuous replacement of the worn target. This allows deposition on to many disks before the vacuum must be opened to replace the consumed targets. An interesting benefit arises from
15   spinning the sputtering magnets around the target. The magnetic fields from the magnets can be so arranged to provide a small, but non-negligible, magnetic field at the disk surface directed around the circumference of the disk. This directionally provides, a second symmetry breaking
20   mechanism, in addition to the deposition at an angle, an energy mechanism of deposition in a magnetic field to help promote bcc-d orientation of the magnetic material. For magnetic bcc-d material with K1>0 the promoted easy axis from both symmetry breaking mechanism coincides.
25   Methods and structures to obtain an oriented hard Co alloy using the symmetry broken structures have been invented. It is also clear that these can be used to pin, via exchange coupling, the soft magnetic layers in many of the magnetic devices utilizing a soft magnetic layer.
30   To further confirm the information already described in this invention description a selected set of physically constructed materials and the analysis of these materials will be described in more detail.
          A large number of thin film sample structures were
35   fabricated and analyzed. Four types of substrates were initially utilized: Si(111), Si(110), Si(100) and glass. The substrates were carefully cleaned via intensive washing with solvents such as acetone, toluene, and isopropyl

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alcohol and then washed with detergent and hot water. They
were then rinsed extensively with distilled water,
isopropyl alcohol, distilled water and were blown dry.
This removed all organic residues, water and most
5   extraneous metals from the substrates. The Si substrates
were then etched for approximately 30 seconds in 49%
Hydrofluoric acid and blown dry. The substrates were
attached to a carrier and were quickly introduced into the
vacuum system via a load lock system. The HF etch of the
10   Si is well known to leave a residual hydrogen bonding on
the Si surface and temporarily prevent oxidation. The
vacuum deposition system was both cryogenically and turbo-
molecularly pumped. A vacuum base pressure of 1×10^{-7} Torr
or better was commonly obtained. Via a vacuum manipulator,
15   the substrate carrier was attached to one of three heated
carrier positions to await thin film deposition.

The substrate carrier mount facilitated approximately
a 7-inch radius planetary motion in a vertical plane.
There were three possible positions for the substrate
20   carriers to be mounted; two on the planetary circle and one
in the center on the planetary axis. Four magnetron
sputtering target positions allowed up to four different
materials to be deposited at various angles of deposition,
each multiple times if needed, during one deposition
25   sequence. Three targets were arranged along the edge of an
approximately 7-inch radius circle, which was aligned with
the planetary positions of the substrate carrier positions.
In this manner the three targets and the two concentric
substrate holders could be brought into alignment to face
30   each other for normal angle deposition or the substrates
could be rotated into any arbitrary position on the
planetary circle for angular deposition. For example, one
target could be located at the equivalent position of three
AM on the face of an imaginary clock and the substrate
35   carrier, which was spaced an adjustable distance along the
normal to the planetary plane, could be rotated to any
position on the opposing imaginary clock face. The
substrate carrier could be move away or toward the targets

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over approximately a 7-inch swing, with a minimum spacing
of less than 2 inches. The fourth target was located at the
center of the planetary motion axis and in a plane with the
other targets.   Likewise, the third substrate carrier
5   position was located at the planetary center in the
substrate carrier plane. The carriers could be moved from
a planetary position to the center and back via the
mechanical manipulator in a time frame of less than one
minute allowing layer to layer epitaxial growth.
10   The one and two inch diameter targets were usually
small compared to the distance between the targets and the
substrates.   In a similar manner to that discussed for
Figure 13, the Argon gas was introduced at the target
surface allow a plasma while increasing the mean free path
15   length in the rest of the chamber, and so to limit
scattering, of the depositing material. A secondary gas
flow such as N or H could also be introduced via the same
path or another to allow interaction with the deposited
layers. Each substrate carrier position was independently
20   heated and monitored and the temperature could be varied
from room temperature to about 350 degrees C. Except when
experiments were performed on multiple substrate textures
simultaneously, the temperature was selected to optimize
the process for the particular single crystal substrate
25   texture chosen. The substrates were heated prior to and
during the deposition and to a limited degree the
temperature could be changed as each layer was deposited.
The sputtering cathodes were DC powered with up to 500
watts available. The physical dimensions when a bcc-d was
30   deposited from the center cathode to a substrate that was
on the planetary circle allowed angles of deposition
ranging from 75 to 33 degrees measured from the substrate
normal. For smaller angles the substrate was mounted at 45
degrees to the substrate carrier and then the target to
35   carrier angle was adjusted. Also, under some circumstances
deposition at smaller angles could be accomplished by using
a target and substrate position both on the planetary
circle, but with the substrate rotated relative to the

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target. Of course the distance between the target and the
substrate could also be adjusted, but this did create a
potential difference in deposition rate.

5   While a large number of deposition conditions were
investigated it was soon found that working with layers
that were 20 to 100 nm thick facilitated easier optical,
magnetic and microstructure analysis. Hence, most of the
bcc-d films were prepared at 20 nm to 200nm thickness.
Most of the Ag layers on Si substrates were 40 nm thick and
10   sometimes a second Ag or Cr layer or both was deposited as
a final capping layer to prevent corrosion of the magnetic
layers. Hexagonal template thickness varied and could be
as thin as 1 nm and were made as thick as 40 nm. Typically
a magnetic exchange coupling hexagonal template was kept
15   minimally thick, 1 to 5 nm so that the bulk magnetic
properties were not significant compared to the bcc-d
magnetic properties. This facilitated easier
interpretation of the magnetic data.

Commonly investigated materials included: Ag, Cu, Ni,
20   NiFe, Al, Co and CoCrTa, which are fcc; Cr, Fe, Nb, NiAl,
FeCo, which are all bcc-d, and Ti and CoCrTa, which are
hcp.

Other bcc-d materials, which may be used to alloy with
Fe or FeCo include W, Mo, V, Cr, Ti, Ta, Si, Al, N, Cu and
25   B. Other fcc-d materials, which may be used include CoCr,
Au, Pt, Rh, Pd, and Ir, while other hcp materials, which
may be used includes Re, Ru, Gd, Ti and Tb . The materials
of choice are chosen for there chemical, magnetic, or
lattice matching properties. Considerable flexibility in
30   atomic lattice constant is sometimes desirable to achiever
epitaxial growth.

The following example notation will be used to
designate the sequence of film layers that were prepare:

35   bcc/hcp/bcc-d/bcc-d<55,<xyz>/hex/fcc/Sub(tex).

Again, the notation is that the film on the left of the "/"
is deposited after the film on the right of the "/". From

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the tilt angle of the "/" it is easy to recall which layer is on top. The "tex" symbol represents the single crystal substrate texture used. The <55 represents the angle that the bcc-d is deposited and the number specifies the angle

5   from the film normal. In general when used, the < symbol represents that a symmetry breaking mechanism is being employed. Likewise, if a magnetic field, H_a, is used to break the symmetry then the field is applied along the hexagonal crystal direction <xyz>. Likewise, when an angle

10   of deposition is used to break the symmetry the in-plane direction of deposition material is also denoted to follow the <xyz> crystal direction.

Hence, as written in the example expression immediately above, fcc would be first deposited on the

15   substrate at a normal angle, then the hexagonal template would be deposited at a normal angle, then at an angle to the plane normal of 55 degrees and parallel to the hex template <xyz> direction the bcc-d would be deposited. Then a second bcc-d would be deposited, then an hcp would

20   be deposited and finally a bcc would be deposited last. If a surface was oxidized by exposure or an oxide was deposited then we would write that layer as a "O".

U. S. Patent 6,248,416 and the Gong and Zangari publications demonstrated that the textures and epitaxial

25   relationships mentioned earlier could be grown on Si. This invention relates to the growth of six bcc-d variants rather than three, as was found by U. S. Patent 6,248,416 and Gong and Zangari, the exchange coupling of the variants, and in the symmetry breaking of the coupled

30   variant sets so that they do not have equal variant volume weighting. That is, to obtain symmetry breaking, the three variants, in the Gong and Zangari publications, or the six variants, as describe here, are not balanced.

We first investigate the epitaxial growth of the bcc-d

35   textures even though the surface of the first metal, when exposed to air, has formed an oxide. The key for this aspect of this invention to be assured is that the underlying crystallinity of the film exhibits extremely

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uniform oriented texture and, while we do not address it here with physical evidence, we believe this leads to the underlying film being very dense.   When a film has extremely high texture, then for some textures the grain
5   boundaries are of low angle or there is little space between the grains.   This assures that the film surface tends to passivate rather than oxidize down the grain boundaries to force the film from the substrate via expansion. This is extremely important for polycrystalline
10   materials like Fe, which tend to oxidize badly.

   First we provide a perspective for the degree of texture obtained by observing a θ–2θ x-ray diffraction scan of a conventional polycrystalline film structure:

15   Hcp-CoCr$_{12}$Ta$_2$/Cr/glass

   This is a classic, but simple structure sometimes sputtered for hard disk media.   Upon examination of the X-ray scan we found that two peaks exist.   Cr(110) had a peak
20   height of about 150 counts and the resulting Co-alloy quad-crystal (10$\underline{1}$1) peak height of 25 counts and a uni-crystal (10$\underline{1}$0) peak height of 40 counts resulted.   The base line was rather noisy and there were no other discernable peaks. We use the same scan time and X-ray anode current and
25   voltage for all of the θ–2θ X-ray diffraction scan examples to be discussed.

   Four samples were made simultaneously each with a different substrate: glass, Si(100), Si(110), Si(111) where the Si was cleaned and HF treated as mentioned before.
30   They were introduced into the vacuum system and quickly heated to approximately 165 degrees C before the first Ag deposition was made. The layer composition was:

   Hcp-CoCr$_{12}$Ta$_2$(58nm)/Fe(37nm)<45/O/Fe(37nm)<45/Ag(40nm)/sub
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   Where the value given in the parenthesis is the nominal film thickness in nanometers.   There was an oxidation exposure step in the process.   This required that

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after the first two film depositions the sample be briefly
removed from the vacuum system. In the following table the
entries are listed as (X-ray counts)/(X-ray texture)

99C15-19-2: CoCr$_{12}$Ta$_2$(58nm)/Fe(37nm)<45/O/Fe(37nm)<45/Ag(40nm)/sub			
CoCr$_{12}$Ta$_2$(58nm)/	Fe(37nm)/	Ag(40nm)	Substrate
50/(10$\underline{1}$1)	200/(110)	600/(111)	glass
1450/(11$\underline{2}$0)	3500/(100)	1.6x10^4/(100)	Si(100)
1600/(10$\underline{1}$0)	1400/(112)	9000/(110)	Si(110)
600/(10$\underline{1}$1)	1.4x10^4/(110)	>10^5/(111)	Si(111)

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        Other than from the single crystal substrate or second
order diffraction peaks there were no other diffraction
peaks observed indicating the strong singular texture
orientation of each layer. The textures behaved just as
10   predicted and discussed earlier. These results confirm
that bcc-d Fe grows with the same textures as Cr when
deposited on a hexagonal template or each of the other
single crystal textures. Since the second layer Fe would
have had the same peaks as the first, the absence of any
15   additional peaks, along with the strength of the peaks, is
a good indicator that the texture, even when the second
layer of Fe is grown on the oxidized surface is identical
to the that of the first layer. However, since the peaks
would collinear with the first film peaks there remains the
20   question whether as to whether or not there are any second
layer peaks at all. The hcp-Co alloy peaks and their
strength compared to those on glass tell us that epitaxial
growth of the second layer of Fe on the Fe-O was very good
and provided an excellent template for the Co alloy film
25   growth. This to confirms the texture of the second Fe
layer is identical to that of the first layer of the Fe.
The epitaxial growth over the oxide is confirmed for all of
these textures, including the use of glass as a substrate.

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This later case is largely due to the excellent texture of the Ag(111) on the glass. In separated experiments the strength of the Ag(111) texture has been seen to improve several fold over the value of that directly on glass when
5   a wetting layer of amorphous $Cr_{35}Ta$ was deposited upon the glass prior to the Ag. It also should be stated that the lattice match between Cr or Fe, which has virtually the same atomic lattice spaceing, and Ag is not particularly good. Since another hexagonal template material (fcc-d or
10 hcp) could epitaxially grown on Ag better than the bcc-d we investigate this. Hexagonal templates of Cu, Ni, NiFe, and a combination layer fcc-Co on top of Cu, when place upon the Ag templates were all found to produce a stronger Fe or Cr texture.
15   To further investigate the oxide located between two different materials the following film structures were constructed:

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99C15-19-3:				
$CoCr_{12}Ta_2$(58nm)/Cr(40nm)/O/Fe(37)<45/Ag(40nm)/sub				
$CoCr_{12}Ta_2$(58nm)/	Cr(40nm)/	Fe(37nm)/	Ag(40nm)	Substrate
50/(10$\underline{1}$0) 25/(11$\underline{2}$0)	50/(100)	250/(110)	>600/(111)	glass
1450/(11$\underline{2}$0)	2900/(100)	1900/(100)	1.8×10^4/(100)	Si(100)
75/(10$\underline{1}$0) 30/(11$\underline{2}$0)	750/(112)	700/(112)	1.3×10^5/(110)	Si(110)
40/(11$\underline{2}$0)	30/(100)	6500/(110)	1.2×10^5/(111)	Si(111)

From this table we can see that for Si(100) epitaxy over the oxide was excellent, however there does not appear
5   to be much, if any, epitaxy via the oxide when Si(111) is used.   It appears the the Cr epitaxy on the Fe-O was quite good for the Si(110) however the Co texture was not particularly impressive.   To within experimental error the time and temperatures used to prepare this sample were the
10   same as were used on the Fe-O-Fe samples (99C15-19-2) discussed just before this one.

The roles of Cr and Fe were interchange and the experiment repeated.

99C15-19-4:				
$CoCr_{12}Ta_2$(58nm)/Fe(37nm)/O/Cr(40)<45/Ag(40nm)/sub				
$CoCr_{12}Ta_2$(58nm)	Fe(37nm)/	Cr(40nm)/	Ag(40nm)	Substrate
35/(11$\underline{2}$0)	25/(100)	150/(110)	300/(111)	glass
1800/(11$\underline{2}$0)	1600/(100)	4000/(100)	1.1×10^4/(100)	Si(100)
60/(10$\underline{1}$0) 20/(11$\underline{2}$0)	?/(112)	1350/(112)	5000/(110)	Si(110)
100/(10$\underline{1}$1)	?/(110)	3.1×10^4/(110)	8.5×10^4/(111)	Si(111)

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Here we see that the Cr grew highly textured on the Ag and the Fe(100) grew well on the Cr-O. However it is not clear if much of the Fe (112) grew as the peak was broad and the Cr and Fe peaks lie extremely close together and

5   would be difficult to observe. It appears that there was some enhanced epitaxial growth of the Fe(110), but it was difficult to discern as the Cr(110) was over whelming. Nevertheless the Co (10$\underline{1}$1) peak was the only one present. In the Si(110) case the fact that any Co (10$\underline{1}$0) texture

10   appeared is strong evidence that some of the Fe was (112) texture.

Overall we see that for the particular deposition temperature, deposition rate, and in general these particular processing conditions it was found that Fe/O/Fe

15   epitaxially grew for all three of the Si textures. We found similar results for Cr/O/Cr. For the Cr/O/Fe/Ag/Si it appears that Cr(100) texture grew well and the Cr(112) texture grew somewhat. The Cr(110) texture did not grow well. Hence, it appears the bcc-d epitaxially grows well

20   on the oxide of itself. Also the bcc-d (100) texture appears to grow well even on other members. The (110) and the (111) textures grow, but not as enthusiastically. We varied the processing temperature for the deposition of Ag on Si and found that the ideal temperature varied

25   considerably with the Si orientation. The processing latitude was even more dramatic. Si(111) substrates could be processed at higher temperatures before it oxidized and this improved some of the later depositions. The Si(100) textured substrate had the next broadest process

30   temperature range and the Si(110) substrate had the narrowest and least tolerable process temperature range. This is logical as this surface is the most unstable for an fcc Bravais lattice or for an fcc-d lattice. Each substrate texture had its own optimum temperature and

35   temperature range and the particular temperature was dependent upon the deposition rate and humidity during the time interval just prior to placing the substrate in the vacuum system. We found the HF etched Si surface quality

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to be very dependent upon the environment prior to the Si
reaching the vacuum system. Hence, optimizing all of the
conditions simultaneously were difficult, but when it was
done the results showed that epitaxial growth through the
5 oxide on the other Si textures is significantly improved.
Fortunately the (111) surface is the most stable for the
hexagonal template materials and this allowed for larger
latitude of temperature and deposition rate. This allows
the optimization of the temperature for the oxide to be
10 grown for each material combination.

Evidence of the six variant structures is demonstrated
next. In fact, the E_{2-a1c2} variant set is shown. The
following film structure was made by angle of incident
deposition. Two samples were prepared simultaneously, but
15 with slightly different angles of deposition, different
thicknesses, but most importantly at different angles
relative to the template lattice plane direction. This was
accomplished by mounting two substrates on the same
carrier, but at different hex template angles. The
20 deposition direction was along the <110> for sample 0909-6
and along the <112> template direction for sample 0909-5.
The structure is defined here:

Sample name: 0909-6
25 Ag(200nm)/Cr(40nm)/Fe(37nm)<45<110>/Cu(10nm)/Ag(40nm)/Si(11
1)
Sample name: 0909-5
Ag(200nm)/Cr(40nm)/Fe(60nm)<55<112>/Cu(10nm)/Ag(40nm)/Si(11
1)
30

It should be pointed out that the Cu hexagonal
template is non-magnetic and so does not provide the
exchange coupling needed to cause uniaxial M-H curves.
Nevertheless, it is shown below that the needed variant
35 pair was obtained. If the Cu were replaced with fcc-Co, Ni
or NiFe, or if the Ni or NiFe were deposited on top of the
Fe then the coupled pair would be exchange coupled. In
this example, the final thick Ag and Cr layers were applied
to avoid the possibility of corrosion of the Fe after the

75

sample was made. It was found that these layers, especially the Cr was very effective at preventing corrosion. The sample was stored for one year without obvious corrosion of the Fe. We conclude this based upon

5   the fact that while Fe magnetic properties are very sensitive to oxidation they did not change. The protective Ag layer did discolor some.

A X-ray pole figure analysis was performed. This test allows one to rotate the sample while setting the x-ray

10   diffraction angle to a specific reflection plane. The Fe is (110) textured so the (100) planes are tilted at 45 degrees to the surface of the film. The sample was tilted to 45 degrees and then θ–2θ was set to reflect from the (100) crystal planes. The sample was then rotated through

15   360 degrees and the signal was monitored. According to Figure 3, as espoused by Gong and Zangari, if there are only three possible variants then there should be three peaks observed for each 180 degrees of rotation and they would be equally spaced at 60 degree intervals. These

20   would repeat during the second 180 of rotation. However, if there are six variants as advocated in this invention then Figure 5 is of relevance and six peaks would be seen per 180 degrees of rotation; and 12 would be seen during the full 360 degree rotation. If the variants are equally

25   weighted by volume of material and the substrate were perfectly cut then all the variants of the set would be seen. We have observed both types of sets. Hence, not all samples have the potential of being represented by the energy equations associated with the six variant set. The

30   Gong and Zangari three variant set is the most commonly observed as the energy mechanism for rotating the crystal planes and then splitting the diffraction peaks is non-trivial to accomplish. Figure 14 shows the pole figure analysis for sample 0909-6. Careful analysis of the data

35   shows the peak height of the a1 and the c2 variants are more than a factor of two higher than any of the other variant diffraction peaks. However, the relevant quantity of measure is the area under the peak curve and this is a

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very time consuming and difficult measurement, but shows a
considerable larger fraction of material being in these two
variants. In theory the scan should only show the Fe(100)
diffraction peaks as the θ–2θ angle was set specifically
5   for this crystal plane. However there is a Ag (220)
diffraction line near by and because the peak is so very
strong the tails of these six peaks also show. Likewise,
there is slight evidence of the very strong Si(400) peak.
The angle between pairs of the six bcc-d variants was
10   experimentally determined to be $2\delta = 2(5.26)$ degrees, as
discussed at length earlier. However the angle between the
peaks in the pole Figure 14 is smaller because of the
coordinate frame rotations required to go from the (110)
and (100) planes. In the figure the spread between any
15   pair of peaks should be ~2(3.74)= 7.5 degrees. This is
exactly what is observed. This data is strong evidence of
both the six variant concepts and of the symmetry breaking
mechanism.   For sample 0909-5 where the deposition
direction projection was the <112> direction along the
20   hexagonal template the results were not as clearly defined.
It appeared that there were again two dominant variants of
the six.   However they were represented by $E_{2\text{-}a1b2}$. For
reference, the pole figure peaks for these variants, a1 and
b2, along with the other four, are also noted on Figure 14
25   while the corresponding bi-crystal energy curve for $E_{2\text{-}a1b2}$
was illustrated in Figure 11. Clearly, even if magnetically
coupled, this variant pair does not yield uniaxial behavior
at all.   Hence, angle of incident deposition along the
<112> template direction yields and entirely different
30   result. In summary, when deposited onto a (111) textured
single crystal substrate and using angle of deposition
along the directions just described as a symmetry breaking
mechanism, then one set of variants yields uniaxial
behavior and the other set does not.   To achieve uniaxial
35   behavior via the symmetry breaking method requires proper
orientation of the template and deposition direction.
However, in both orientation cases the variant symmetry was
broken.

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It was found that even when a hexagonal template of non-magnetic material was employed it was possible to have exchange coupled variants and to obtain the uniaxial symmetry broken behavior. Samples of structure just as

5   described when processed at different deposition rates and temperatures yielded different grain sizes and magnetic exchange between them was possible. It was also found that deposition at an angle could result in grain morphologies, which possessed particle shape anisotropy. However, by

10 studying the films deposited along both the <112> and <110> hexagonal template directions it was found that the symmetry breaking process and uniaxial behavior caused by the crystalline orientation still existed along with the anisotropy associated with grain shape effects. Using the

15 proper, strongly textured and matched atomic lattice spacing, hexagonal template to induce good epitaxial growth significantly helped to minimize particle shape effects.

    A similar set of experiments was conducted with a magnetic hexagonal template and an applied field. That is,

20 rather than using the angle of incident deposition as the symmetry breaking mechanism, a magnetic field was used. Ni was used at the hexagonal template and placing permanent magnets on the substrate carrier in the vicinity of the substrates generated an applied field in the 100 Oe range.

25 The sample structure was:

Ag(200nm)/Cr(40nm)/Fe(50nm)<45/Ni(5nm)/Ag(40nm)/Si(111)

    The resulting variant set for the case when the field

30 was applied generally along the hexagonal template <112> direction was E_{2-a1c2}, whereas, if the field were applied generally along the <111> direction then one of the complement four-element variant sets with uniaxial behavior was selected. However, it was difficult to observe by x-

35 ray pole figure measurement techniques, exactly which set of four variants dominated. Nevertheless, from the magnetic response it was determined to be one of the symmetry broken uniaxial sets. Hence, unlike the angle of

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incident deposition technique, when the symmetry is broken using a magnetic field mechanism, uniaxial behavior is obtain when the field is directed along either of the hexagonal template crystal directions; <110> or <112>.

5   While the hard axis permeability, when the symmetry breaking field was along the <110> direction, which caused the four variant set to appear, should have been higher than for the two variant set it was difficult to say this was the case. The coercivity was higher and the uniaxial

10 magnetic response function was not as ideal.   These magnetic effects indicate the greater difficulty in preparing the four variant set where the processing latitude is more sever. The magnitude of the applied field varied over some of the samples prepared and very small, ~

15 1.5 to 2 mm, size segments of the samples were studied for their individual magnetic properties.   Hence, these segments represent individual samples prepared with various applied magnetic field magnitude and direction. From these measurements it was estimated that the magnetic field

20 symmetry breaking mechanism was causing an observable degree of symmetry breaking for fields as small as 10 Oe. It should be mentioned that the applicant became concerned that the earth's magnetic field or some other stray magnetic field might be influencing the findings. The stray

25 fields were measured in the vicinity of the substrate carrier and found to be less than or approximately one Oe, which was comparable to the measured earth's magnetic field intensity. Nevertheless, experiments were conducted where the sample substrate was mounted to a sample carrier

30 containing the applied field magnets. Then during the deposition process the substrate carrier and, hence, the applied field magnets and sample were rotated together. This provided a constant applied field while the rotation provided an averaging mechanism for any stray applied

35 fields. Likewise, a similar experiment was carried out with out any applied field, but employing the angle of incidence symmetry breaking technique.   For both symmetry breaking techniques the magnetic results were found to be unchanged

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from samples prepared without the rotation process. Hence, applicant was convinced that stray fields were not playing any significant role in the experimental results.

5   We anticipate that achieving the four variant uniaxial results would be much easier to obtain if we had a better vacuum system and did not have to passivate the Si via H bonding from the HF-etching technique. It is well known that the silicon oxide sublimes from Si at about 850 degrees C leaving behind a clean Si surface. If the process

10   were preformed in an ultra high vacuum system a cleaner substrate would be available for the initial Ag deposition. We anticipate this would result in higher quality films and film structures and better control of the overall process.

       Magnetic response curve measurements were made for

15   these samples.   Because the magnetic field from the permanent magnets was not perfectly uniform over the sample the symmetry breaking mechanism was not perfectly aligned with the hexagonal template <112> direction. Nevertheless, it was estimated that the field direction did not vary by

20   more than 10 degrees over the measured sample and it was in much better alignment over the majority of the sample. This was sufficiently aligned to demonstrate the symmetry breaking mechanisms via the magnetic response curves. Figure 15 shows the M_x and M_y versus H_x response of one of

25   the two variant exchange coupled, uniaxial symmetry broken samples using the structure:

       Sample name: LS1425_2cx
       Ag(200nm)/Cr(40nm)/Fe(50nm)<H<112>/Ni(5nm)/Ag(40nm)/Si(11

30   1)

       The coercivity of the Ni alone was measured and found to be comparable to the 10 Oe observed for the hard axis loop of this sample. Hence, it is observed that exchange

35   coupling the film variants is not sufficient to achieve a low coercivity. The exchange coupling layer must also be magnetically soft. Permalloy, a well known soft NiFe alloy was substituted for the Ni and the coercivity was found to

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drop to less than 1.0 Oe. However, interestingly, even
using the Ni template the sample exhibited lossless
behavior if high drive fields were not used to drive the
sample all the way to saturation. In a separate measurement
5   from Figure 15, the sample was first driven along the easy
axis to remove most of the domain walls and then driven
along the hard axis, but only to approximately 80% of the
field needed to saturate the sample. This minor loop
response showed coercivities of less than one Oe, which was
10   approximately the resolution limit of the measurement
instrument. Figure 15 clearly shows a non-linear uniaxial
type of response function when the sample was driven into
saturation and uniaxial result similar to the ideal of
Figure 2. This statement applies both to the narrow hard
15   axis loop, M_x vs. H_x [19] and the somewhat quadratic M_y easy
axis [20] response. The hard axis loop, M_x, illustrates
the potential near linear behavior, while the M_y response
illustrates the non-linear response.

Other, similar composition and layer structured,
20   samples made by angle of incident deposition showed no
measurable coercivity or losses for the minor hard axis
loop. In these cases permeabilities ranging from 80 to over
1000 were observed.

Hard disk media samples were prepared using a
25   production hard disk media vacuum system, but by a similar,
but less ideal than previously described, angle of
incidence deposition technique. The source bcc-d material
was delivered in a radial pattern over the entire disk at
angles varying over the surface of the disk. This was
30   accomplished by depositing from a standard sputtering
target but by masking a large portion of the disk with a
circular mask with a hole in the center. Hence, the
sputtered material exited the hole at an incident angle and
essentially radially. Several samples were prepared with
35   layer constructions made as follows:

LSSDK-0505-1
Cr(40nm)/Fe(40nm)<~45/Cu(20nm)/Cr$_{35}$Ta(20nm)/glass-ceramic

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and

LSSDK—0505-2

CoCrPt(20nm)/Cr(40nm)<~45/Cu(20nm)/$Cr_{35}Ta$(20nm)/glass-ceramic

5   The magnetic properties of the first sample (Fe)
exhibit anisotropic behavior with an OR of greater than one
and provided confidence to proceed with sample 0505-2. The
Fe was changed to Cr so as to not obscure the magnetic
results of the harder CoCrPt alloy with the properties soft
10   Fe. Of the samples prepared OR ranging from 1.05 to 1.15
were obtained when dividing the circumferential coercivity
by the radial. This is as desired, and the over all
coercivity was in the range of 2500 Oe. Because of the
polycrystalline hexagonal template layer and the mixed
15   amorphous and ceramic substrate has a very large
interfering set of diffraction peaks no X-ray data was
taken.

        Those of ordinary skill in the art will appreciate
that a number of modifications and variations can be made
20   to specific aspects of the material structures, devices,
method and apparatus of the present invention without
departing from the scope of the present invention. Such
modifications and variations are intended to be covered by
the foregoing specification and the following claims.

25

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1.   A magnetic material structure comprising:
      a substrate;
      at least one bcc-d magnetic layer forming a symmetry broken structure; and
5   at least one layer providing a (111) textured hexagonal atomic template disposed between said substrate and said symmetry broken bcc-d material structure.

2.   A magnetic material structure comprising:
10   a substrate;
      at least one bcc-d magnetic layer forming a uniaxial symmetry broken structure; and
      at least one layer providing a (111) textured hexagonal atomic template disposed between said substrate
15   and said symmetry broken bcc-d material structure.

3.   The magnetic material structure recited in claim 2 wherein said substrate is single crystal.

20   4.   The magnetic material structure recited in claim 2 wherein said substrate surface is amorphous or polycrystalline.

5.   The magnetic material structure recited in claim 4
25   wherein said amorphous surface is formed from an alloy of NiP, Cr_xTa_{1-x}, Cr_xNb_{1-x}, Fe_xTa_{1-x}, or Fe_xNb_{1-x} and $55<x<75$.

6.   The magnetic material structure recited in claim 4 wherein said amorphous surface is oxidized and is formed
30   from Cr_xTa_{1-x}, Cr_xNb_{1-x}, Fe_xTa_{1-x}, or Fe_xNb_{1-x} and $55<x<75$.

7.   The magnetic material structure recited in claim 2 wherein the layer forming said hexagonal atomic template is formed from a fcc-d or hcp crystalline material.
35
8.   The magnetic material structure recited in claim 2 wherein the layer forming said hexagonal atomic template is magnetic.

83

9.   The magnetic material structure according to claim 2
further comprising
        at least one second magnetic layer wherein the second
5   layer forms a hexagonal atomic surface.

10.   The magnetic material structure according to claim 2
further comprising   .
        at least one second bcc-d layer.
10

11.   The magnetic material structure according to claim 2
further comprising
        at least one second magnetic bcc-d layer.

15   12.   The magnetic material structure according to claim 2
further comprising   .
        at least   one second   bcc-d   layer wherein   the
crystalline orientation of the second layer is epitaxially
determined by the first bcc-d layer.
20

13.   The magnetic material structure according to claim 2
further comprising
        at least one second bcc-d layer; and
        at least one second hexagonal (111) template wherein
25   said hexagonal template is disposed between the first bcc-d
layer and the second bcc-d layer.

14.   The magnetic material structure according to claim 2
further comprising
30   at least one second magnetic bcc-d layer; and
        at least one oxide layer between said first bcc-d
layer and said second bcc-d layer.

15.   The magnetic material structure according to claim 2
35 further comprising   .
        at least one second and third non-magnetic bcc-d
layers;
        at least one fourth magnetic bcc-d layer; and

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at least one oxide layer between said second non-magnetic bcc-d layer and said third non-magnetic bcc-d layer wherein second and third non-magnetic layers are disposed between said first and fourth magnetic bcc-d
5   layers.

16. The magnetic material structure according to claim 2 further comprising
at least one second and third non-magnetic hexagonal
10   template layers;
at least one fourth magnetic bcc-d layer; and
at least one oxide layer between said second non-magnetic layer and said third non-magnetic layer wherein second and third non-magnetic layers are disposed between
15   said first and fourth magnetic bcc-d layers.

17. The magnetic material structure recited in claim 2 wherein said symmetry broken bcc-d is composed of Fe or FeCo or an alloy of Fe or FeCo.
20

18. The magnetic material structure recited in claim 2 wherein said symmetry broken bcc-d is composed of an alloy of Fe or FeCo and one or more of the elements Cr, Si, N, C, Cu, Nb, and Al.
25

19. The magnetic material structure recited in claim 2 wherein said symmetry broken bcc-d is composed of an alloy of Fe or FeCo and one or more of the elements Al, B, Cr, C, Cu, Ni, N, Nb, Mo, V, Si, Ta, Ti and Nb.
30

20. The magnetic material structure recited in claim 2 wherein the layer material forming said hexagonal atomic template is composed of Ag, Cu, Ni, fcc-Co, NiFe, Al, hcp-Co, or Ti, or their alloys.
35

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21. The magnetic material structure recited in claim 1 wherein the layer material forming said hexagonal atomic template is composed of Ag, Al, Au, Cu, fcc-Co, fcc-CoCr, Ir, Ni, NiFe, Pt, Rh, Pd, hcp-Co, Gd, Re Ru, Tb, or Ti, or
5 their alloys

22. The magnetic material structure according to claim 2, further comprising
    at least one second bcc-d layer; wherein first and
10 second bcc-d layers are magnetic with anisotropy energy density constants of opposite sign.

23. The magnetic material structure according to claim 2, further comprising
15   at least one second bcc-d layer;
        at least one third bcc-d layer;
        wherein first and third bcc-d layers are magnetic and second bcc-d layer material is antiferromagnetic.

20 24. The magnetic material structure according to claim 2 further comprising
        at least one second magnetic symmetry broken bcc-d layer; and
        at least one second hexagonal (111) template wherein
25 said second hexagonal template is disposed between the first bcc-d layer and the second bcc-d layer.

25. The magnetic material structure according to claim 2 further comprising
30   at least one Co alloy magnetic hcp layer; wherein Co alloy has a (10$\underline{1}$1) crystalline texture.

26. A magnetic material structure comprising:
        a (111) textured single crystal substrate; and
35   at least one bcc-d magnetic layer forming a uniaxial symmetry broken structure; wherein the bcc-d magnetic layer is disposed upon the (111) textured substrate.

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27. A magnetic material structure comprising:
     at least one (111) textured hexagonal atomic template;
and
     at least one (110) textured bcc-d magnetic layer
5   forming a symmetry broken structure disposed upon said
(111) textured hexagonal atomic template.

28. A magnetic device incorporating therein the magnetic
material structure of claims 1, 2, 26 or 27.
10

29. The magnetic device recited in claim 24 wherein the
device is a magnetic data storage system.

30. The magnetic device recited in claim 24 wherein the
15 device is a data storage magnetic recording transducer.

31. The magnetic device recited in claim 24 wherein the
device is a data storage magnetic playback transducer.

20 32. The magnetic device recited in claim 24 wherein the
device is a data storage magnetic recording media.

33. The magnetic device recited in claim 24 wherein the
device is a data storage magnetic recording media
25 incorporating an oriented soft magnetic layer.

34. The magnetic device recited in claim 24 wherein the
device is data storage magnetic recording media
incorporating an oriented hard magnetic layer.
30

35. The magnetic device recited in claim 24 wherein the
device is a data storage magnetic random access memory.

36. The magnetic device recited in claim 24 wherein the
35 device is an article surveillance tag.

37. The magnetic device recited in claim 24 wherein the
device is a magnetoelastic article surveillance tag.

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38. The magnetic device recited in claim 24 wherein the device is a magnetoelastic multiple harmonic generating article surveillance tag.

5

39. The magnetic device recited in claim 24 wherein the device is a non-linear response multiple harmonic generating article surveillance tag.

10   40. The magnetic device recited in claim 24 wherein the device is an electronic circuit inductive component.

41. The magnetic device recited in claim 24 wherein the device is a signal mixing electronic circuit component.

15

42. The magnetic device recited in claim 24 wherein the device is a magnetic fluxgate sensor.

43. The magnetic device recited in claim 24 wherein the
20   device is a anisotropic magnetoresistive sensor.

44. The magnetic device recited in claim 24 wherein the device is a spin valve magnetoresistive sensor.

25   45. The magnetic device recited in claim 24 wherein the device is a magnetic tunnel junction magnetoresistive sensor.

46. The magnetic device recited in claim 24 wherein the
30   device is an electronic circuit inductive transformer component.

47. The magnetic device recited in claim 24 wherein the device is an electronic spin tunneling digital logic
35   circuit component.

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48. An magnetic recording media device comprising;
    substrate;
    at least one hard magnetic recording layer;
    at least one (111) textured hexagonal atomic template;

5 and
    a soft magnetic keeper layer composed of at least one
bcc-d magnetic layer forming a uniaxial symmetry broken
structure disposed between said hexagonal atomic template
and said hard magnetic recording layer.

10

49. An magnetic recording media device comprising;
    substrate;
    at least one (111) textured hexagonal atomic template;
    at least one symmetry broken (110) textured bcc-d

15 layer; and
    at least one oriented hard magnetic recording layer;
where in said bcc-d layer is disposed between said hard
magnetic layer and said hexagonal atomic template and said
hexagonal atomic template is disposed between said bcc-d

20 layer and said substrate.

50. An apparatus for depositing a disk media layer
structure comprising;
    a rod shaped sputtering target of diameter smaller

25 than the inside disk recording diameter;
    a shield and permanent magnet structure surrounding
said sputtering target;
    a gas pathway between said sputtering target and said
shield; and

30   a gas exit near one end of the sputtering target;
    wherein the apparatus delivers vacuum disposed
material symmetrically from near an end surface of said
target rod in a generally radial direction to the hard disk
media substrate at an angle of incidence angle of between

35 15 and 75 degrees.

51. An apparatus recited in claim 50

wherein said disk media layer structure is an oriented soft magnetic keeper layer.

52.   An apparatus recited in claim 50
5   wherein said disk media layer structure is an oriented media underlayer.

53.   A method of producing a symmetry broken bcc-d structure comprising:
10   providing a (111) textured hexagonal atomic template;
        providing at least one bcc-d layer;
        depositing a bcc-d crystalline material on said (111) textured hexagonal atomic template while employing at least one symmetry breaking mechanism;
15   forming a bcc-d (110) crystalline textured film; and
        forming a symmetry broken crystalline structure containing at least one dominate (110) orientational variant and not more than five dominate variants.

20   54. A method of producing a symmetry broken bcc-d structure recited in claim 53, wherein
        at least one said dominate (110) orientational variant has a <111> crystalline direction in the plane of the said texture at approximately +5.26 or -5.26 degrees relative a
25   <110> direction of the said (111) textured hexagonal atomic template in the plane of the template.

55.   A method of producing a symmetry broken bcc-d structure recited in claim 53, wherein
30   said symmetry breaking mechanism is deposition of said bcc-d material upon said (111) textured hexagonal atomic template at an angle of incidence angle between 15 and 75 degrees.

35   56.   A method of producing a symmetry broken bcc-d structure recited in claim 55, wherein
        said angle of incidence is directed generally along the (111) textured template <110> direction.

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57. A method of producing a symmetry broken bcc-d structure recited in claim 53, wherein
        said symmetry breaking mechanism is deposition of said
5   bcc-d material upon said (111) textured hexagonal atomic template in an applied magnetic field.

58. A method of producing a symmetry broken bcc-d structure recited in claim 57, wherein
10   said applied magnetic field is directed generally along the (111) textured template <112> direction.

59. A method of producing a symmetry broken bcc-d structure recited in claim 57, wherein
15   said applied magnetic field is directed generally along the (111) textured template <111> direction.

60. A method of producing a symmetry broken bcc-d structure recited in claim 57, wherein
20   said applied magnetic field is of magnitude 10 Oe or greater.

61. A method of producing a symmetry broken bcc-d structure recited in claim 53, further comprising:
25   providing at least one second thin film bcc-d material; and
        forming at least one second symmetry broken bcc-d crystalline structure containing at least one dominate (110) orientational variant and not more than five dominate
30   variants.

62. A method of producing a symmetry broken bcc-d structure recited in claim 61, wherein
        said first and said second bcc-d materials have
35   anisotropy energy density constants of opposite sign.

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63. A method of producing a symmetry broken bcc-d structure recited in claim 61, wherein

    said first and said second bcc-d materials have anisotropy energy density constants of the same sign.

5

64. A method of producing a symmetry broken bcc-d structure recited in claim 61, further comprising:

    forming at least one oxide layer between said first bcc-d layer and said second bcc-d layer, to form an

10 electrical insulation barrier.

65. A method of producing a symmetry broken bcc-d structure recited in claim 61, further comprising:

    forming at least one second (111) textured hexagonal

15 atomic template between said first bcc-d layer and said second bcc-d layer.

20

25

Figure 1

θ
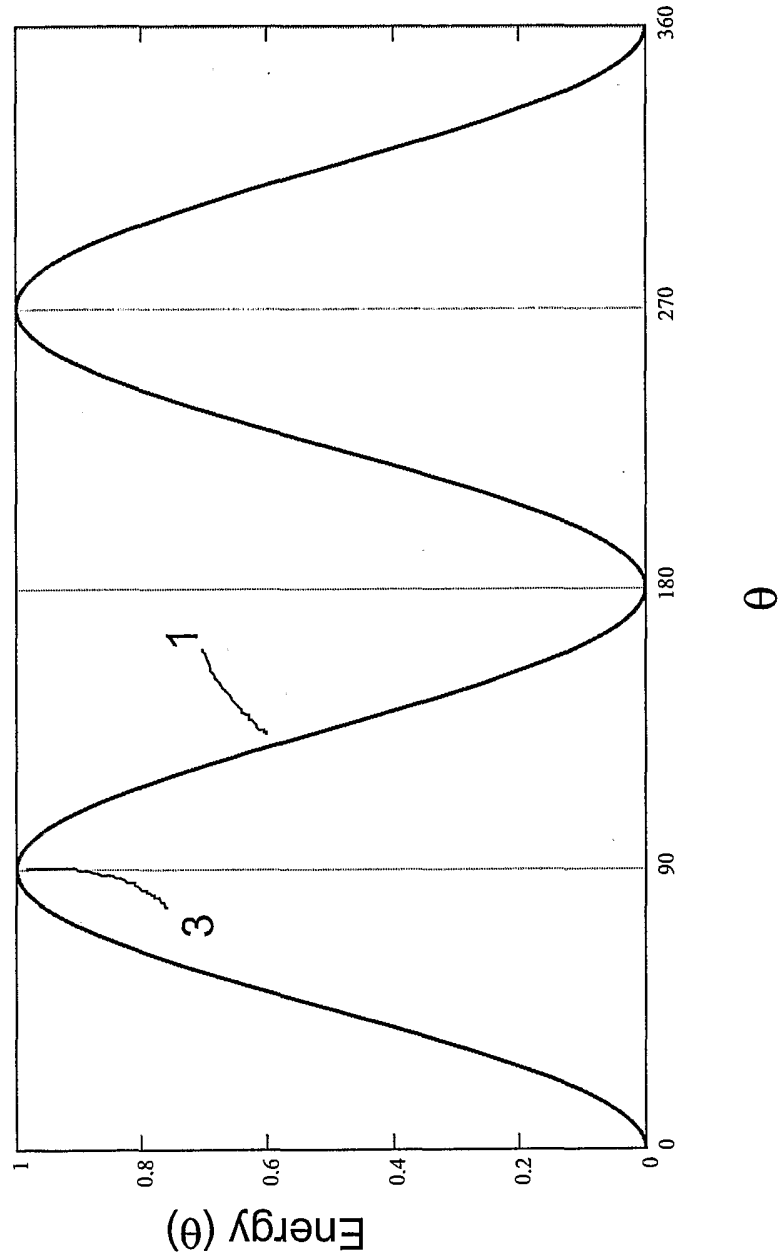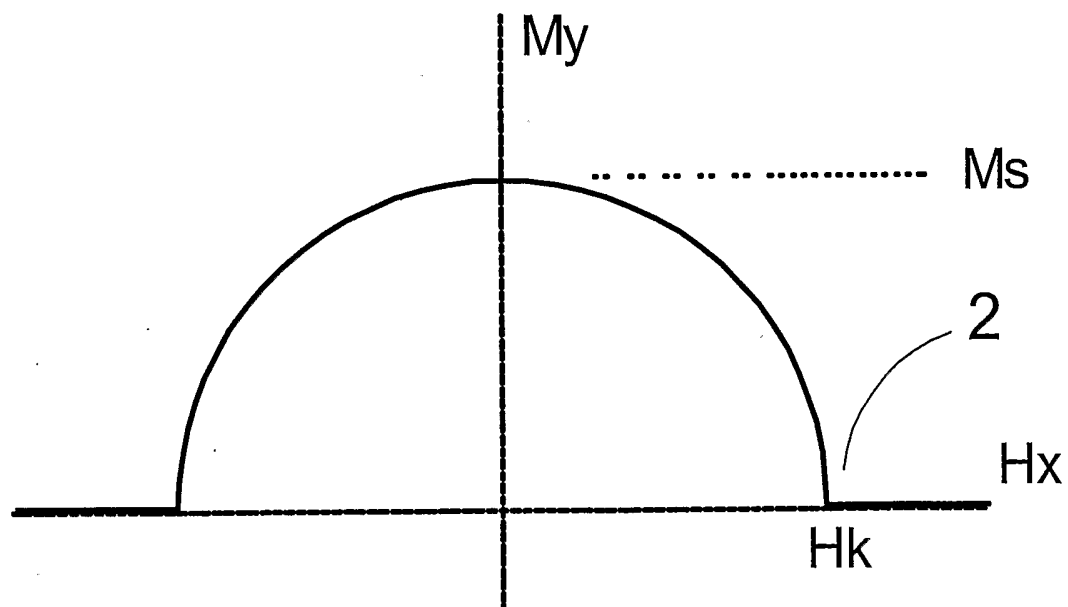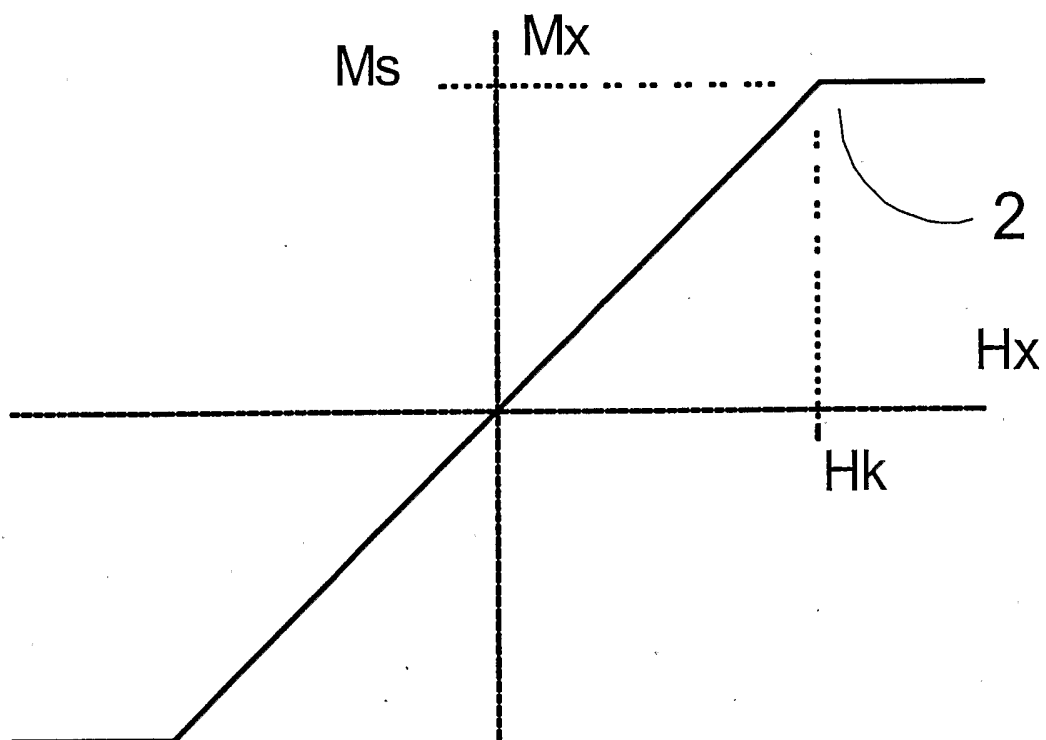
PRIOR ART
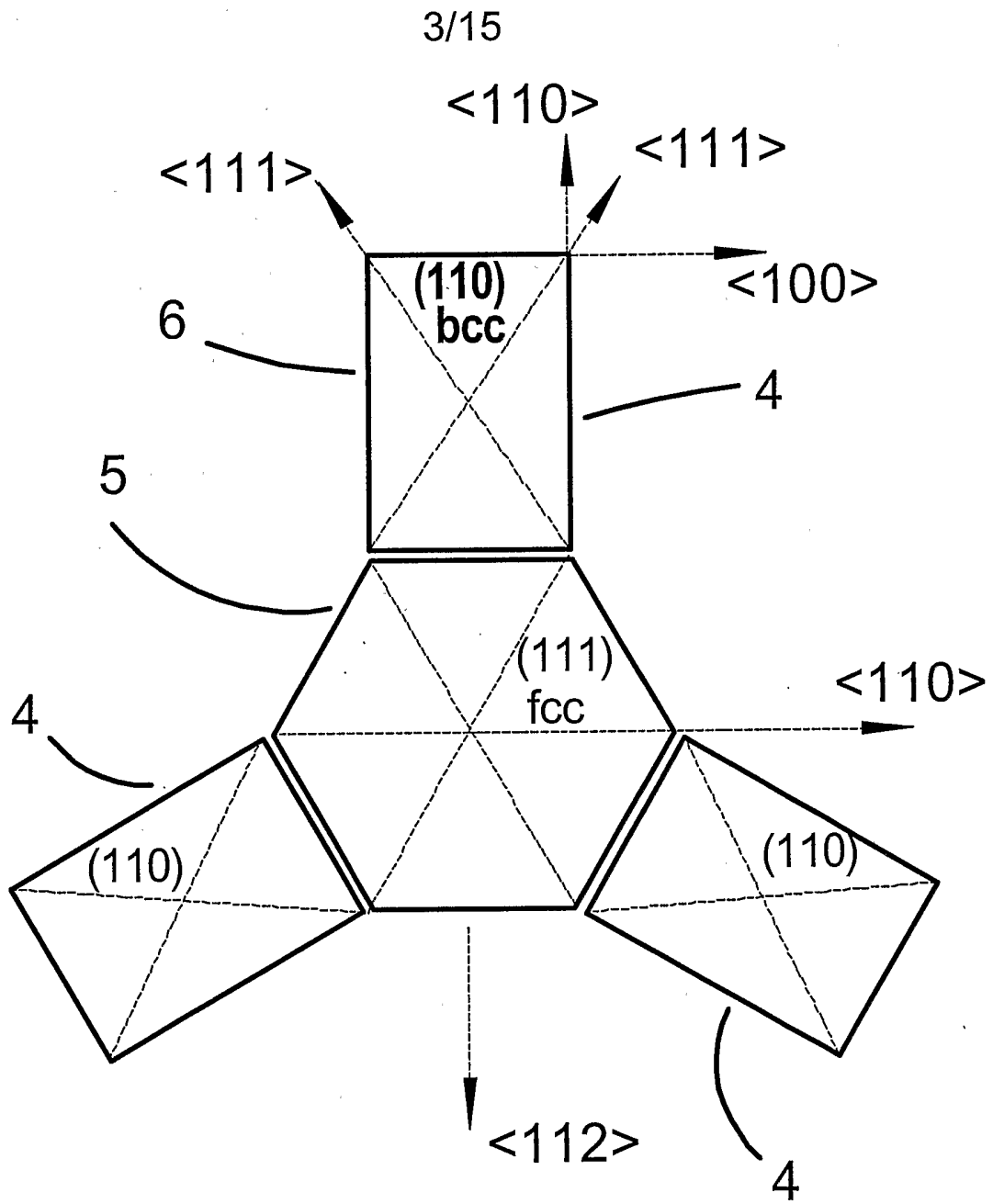
Figure 2

PRIOR ART

Figure 3

PRIOR ART

Figure 4
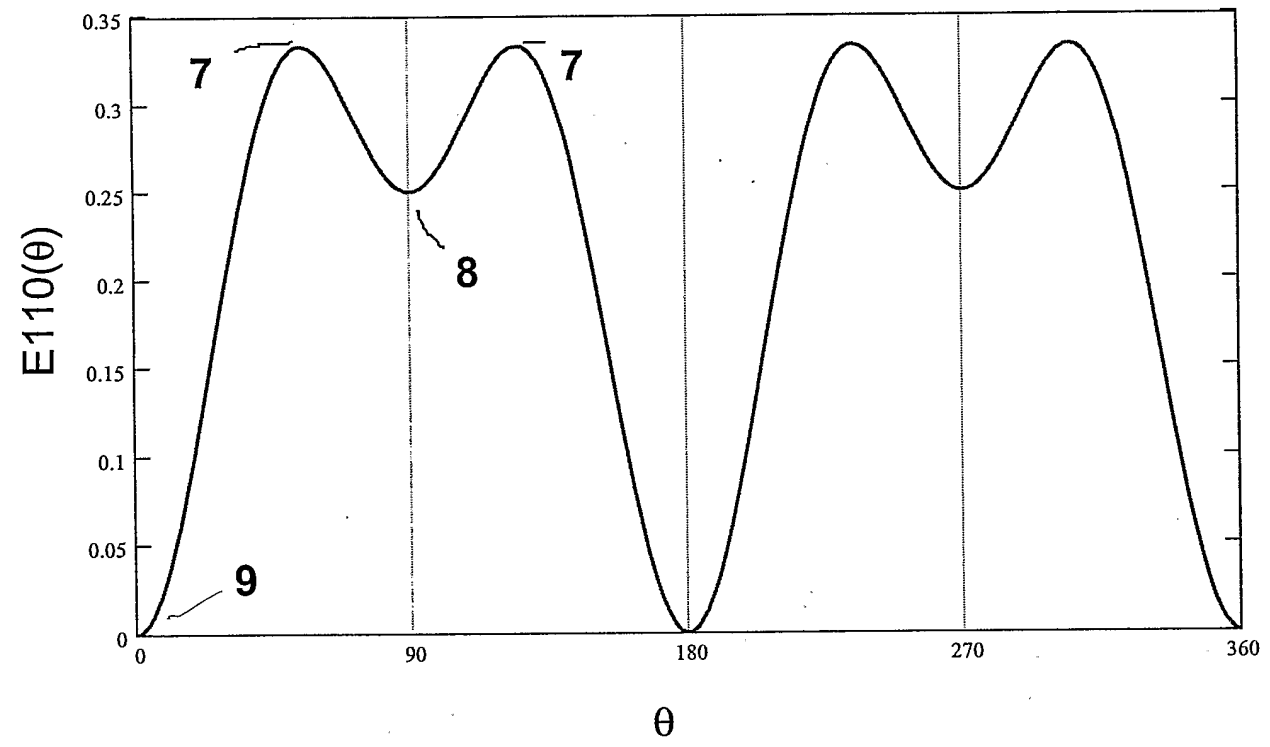
5/15
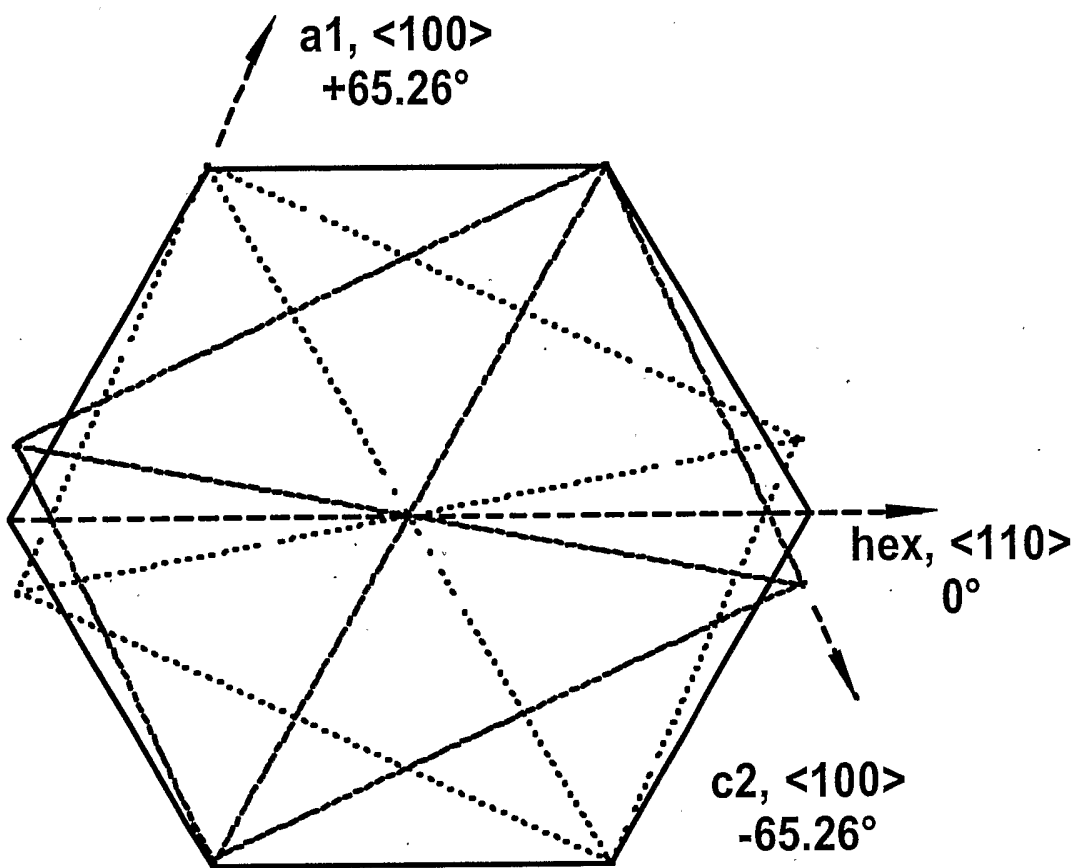
Figure 5

6/15

Figure 6
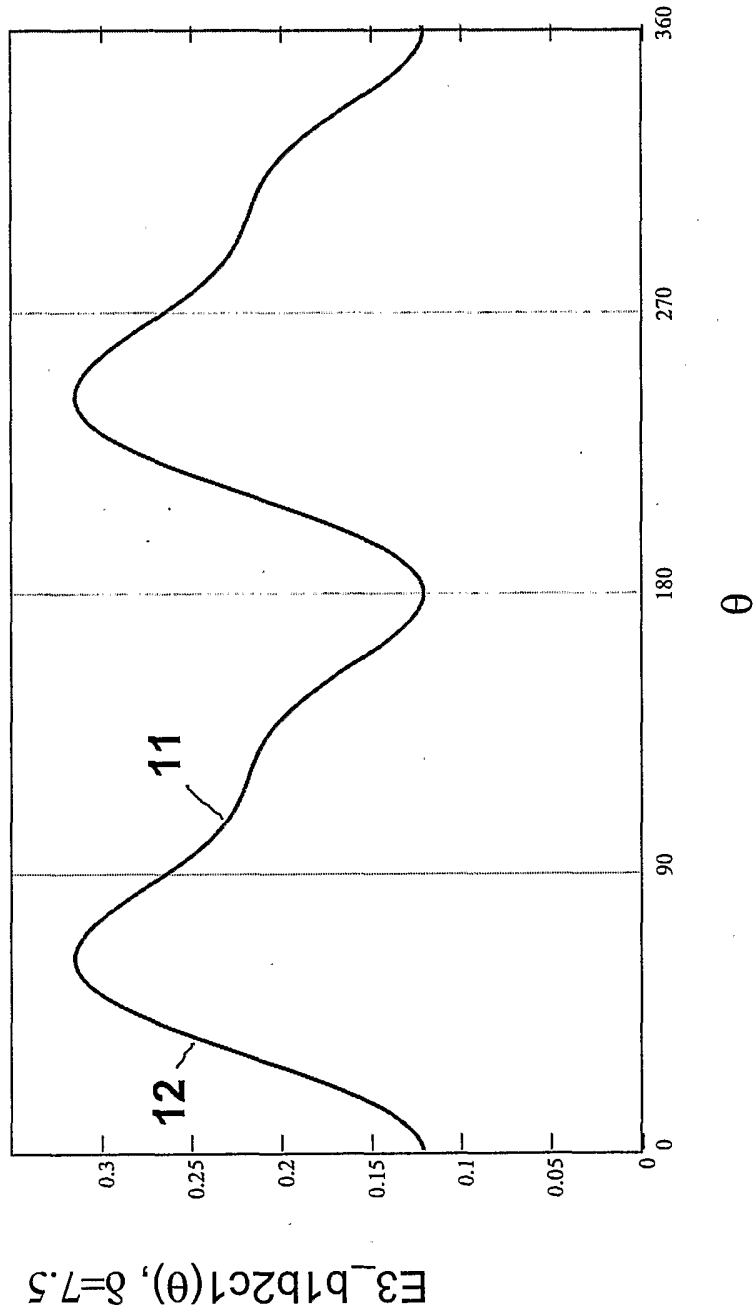
7/15

Figure 7
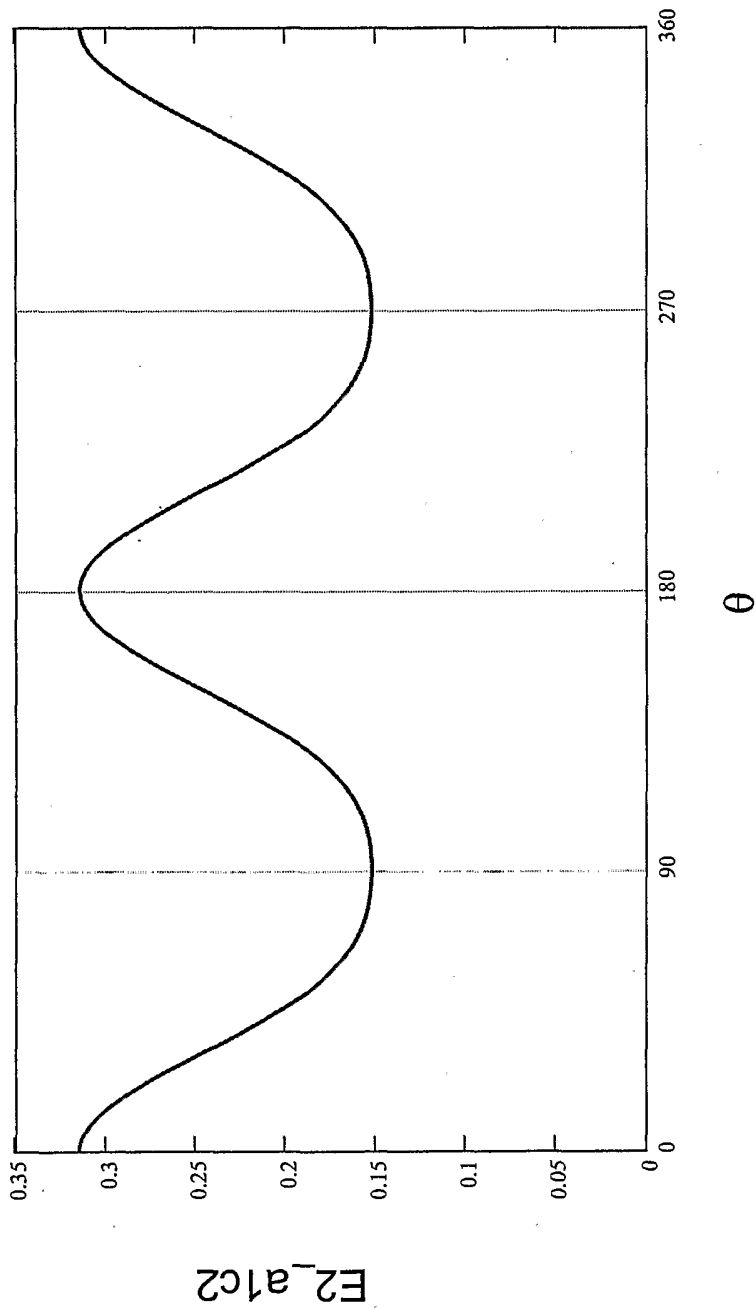
8/15

Figure 8
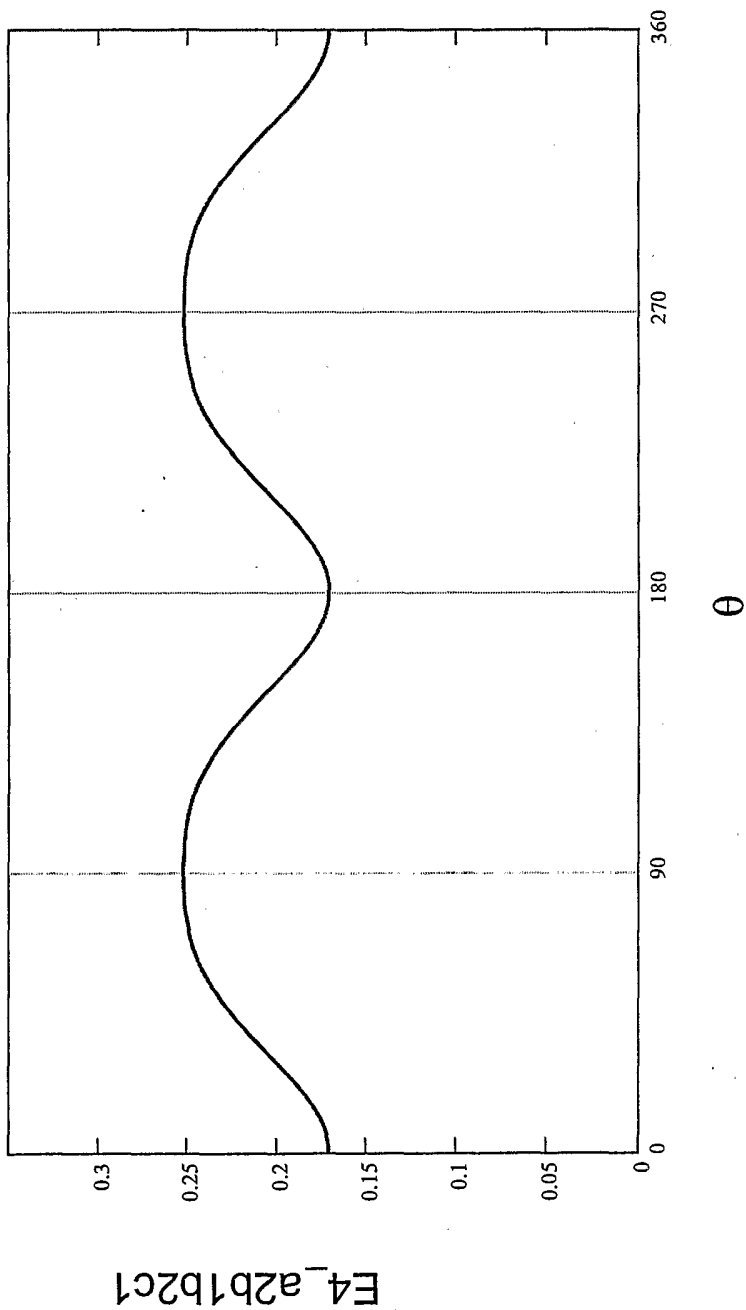
9/15

Normalized Magnetization Vs. Hard Axis Field, Hx
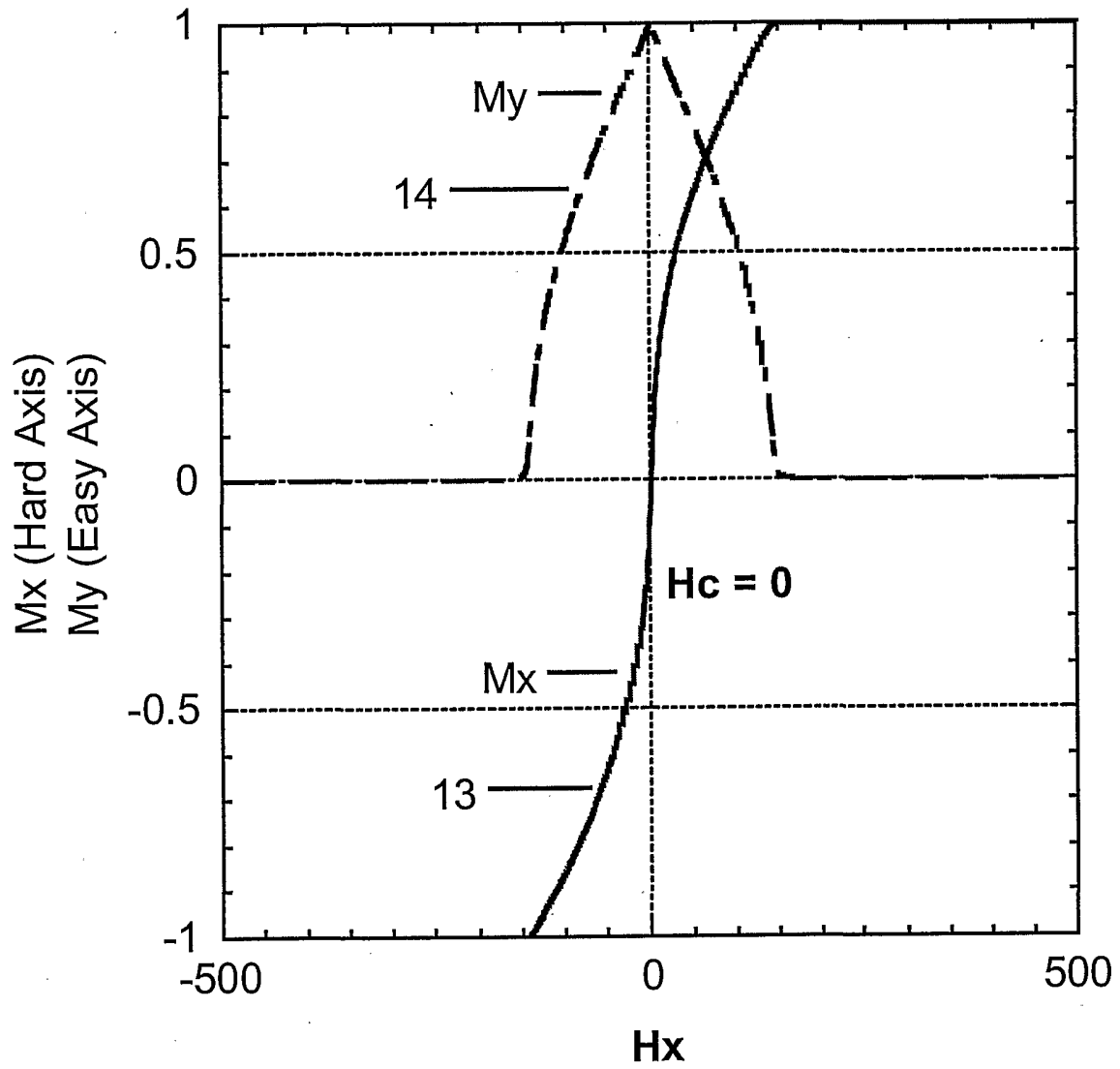
Figure 9

10/15

Figure 10

$E3\_b1b2c1(\theta),\ \delta=5.26$

θ

Figure 11

Figure 12

13/15
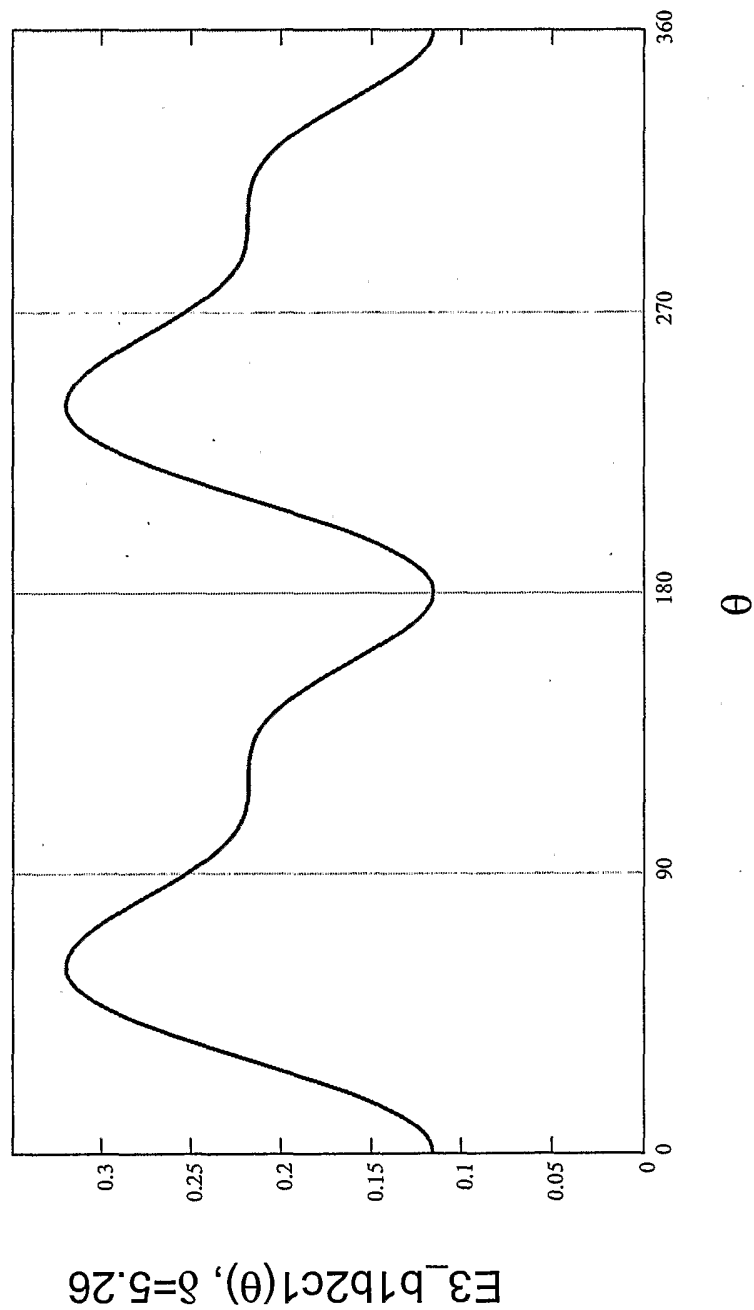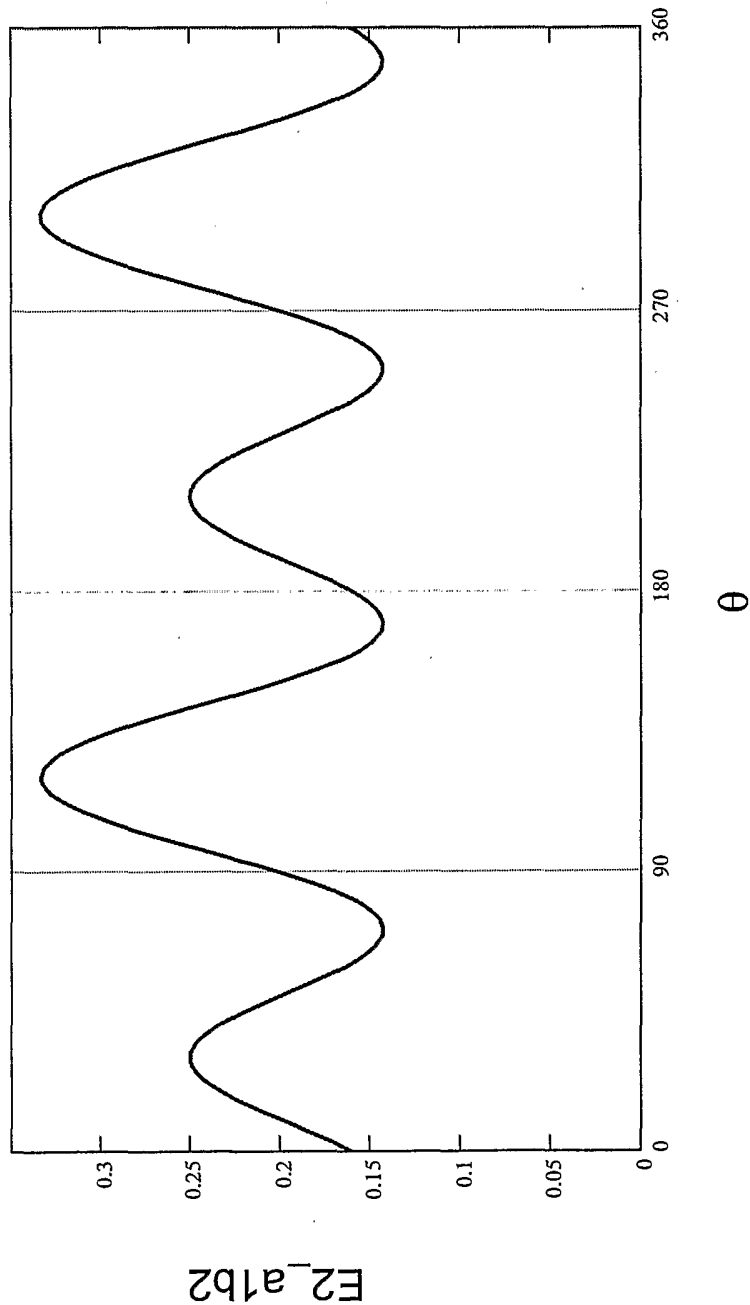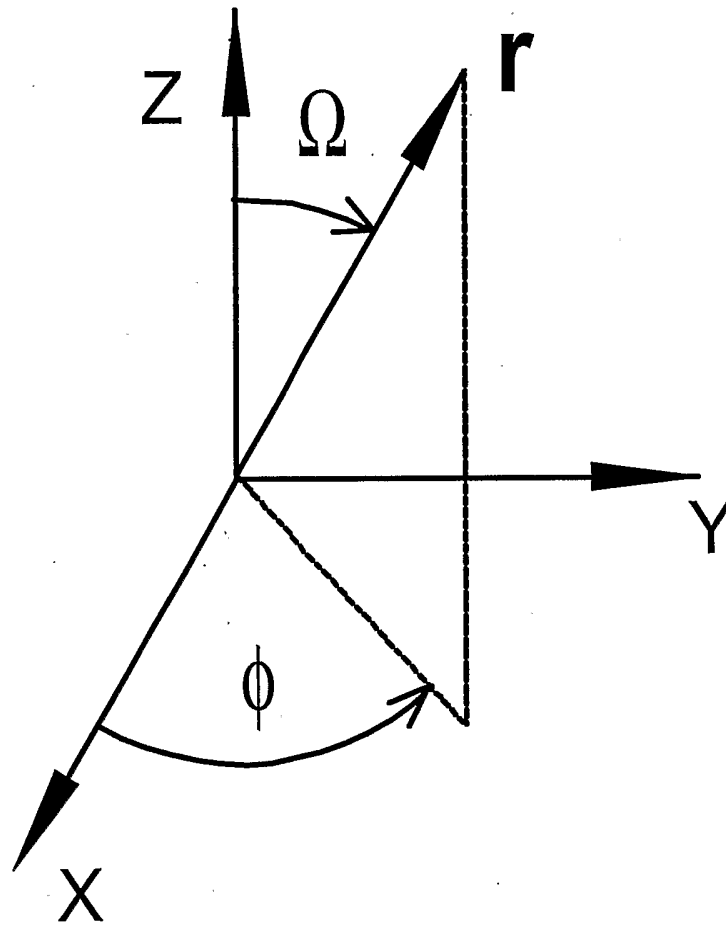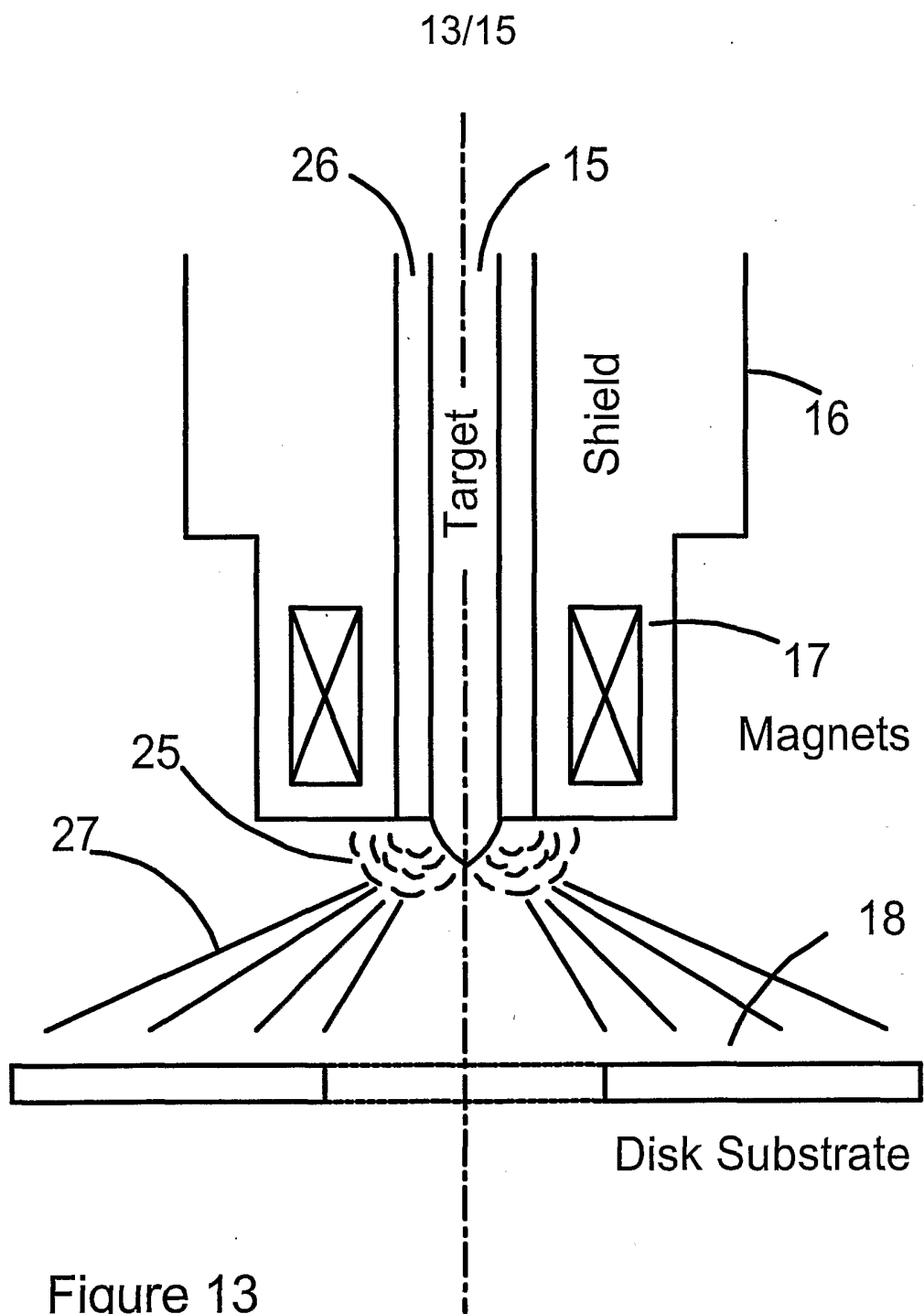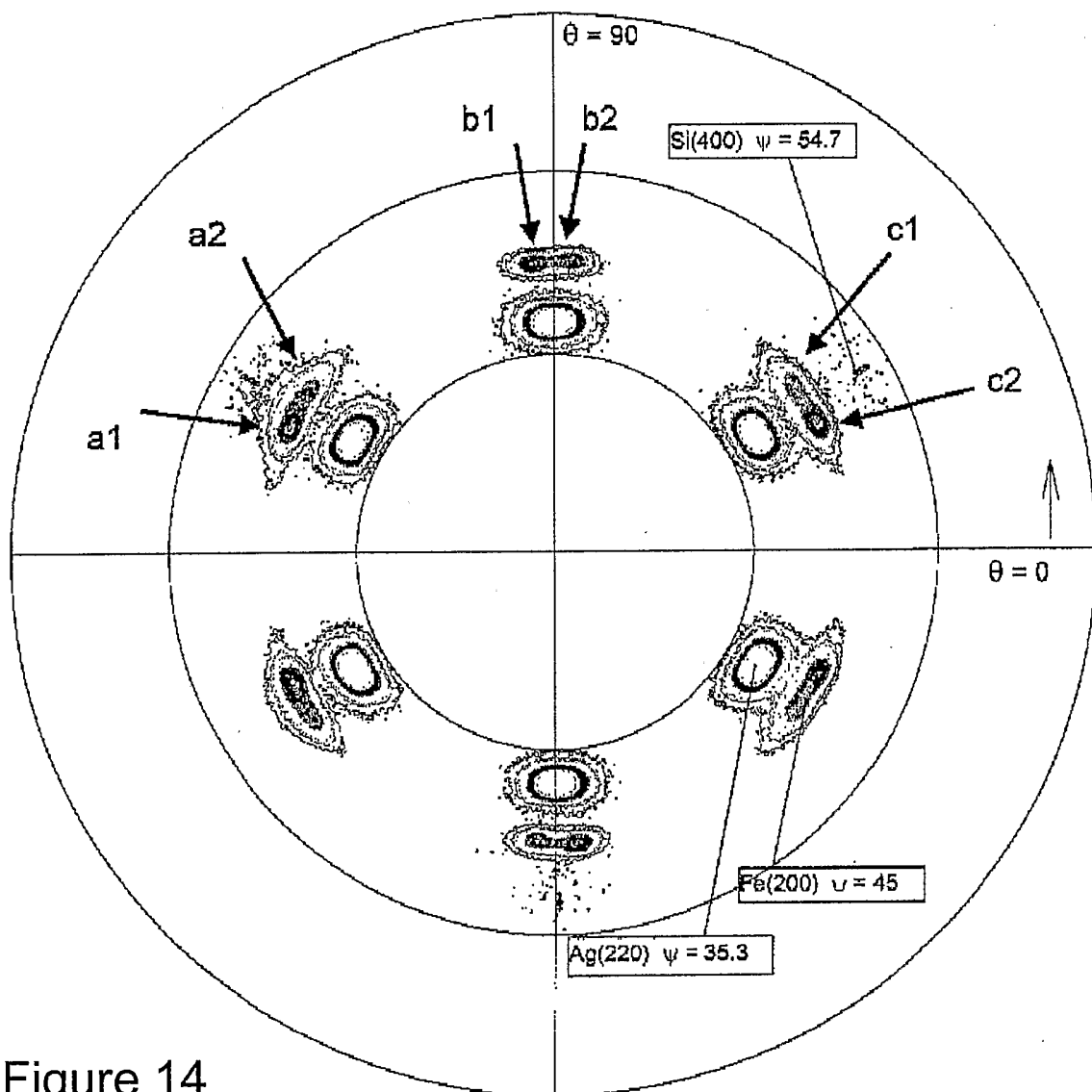
Figure 13

Figure 14

Normalized Magnetizations Vs. Hard Axis Field, Hx (Oe)
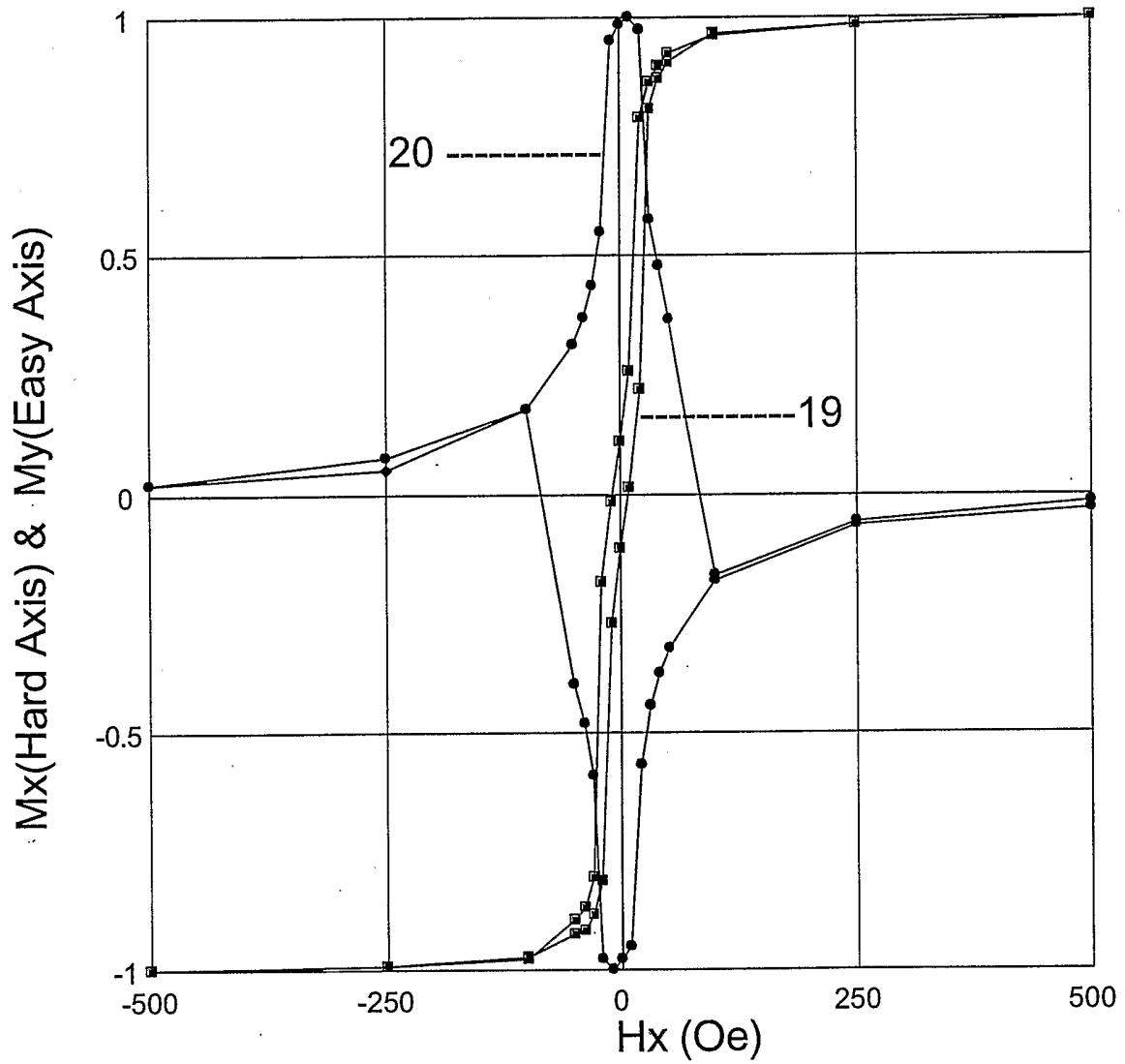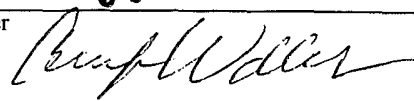
Figure 15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/27327

A.	CLASSIFICATION OF SUBJECT MATTER
IPC(7)	: G11B 5/64, 5/66, 5/667, 5/673
US CL	: 428/668, 694TS, 694TM

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
        U.S. : 428/668, 694TS, 694TM

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99/24973 (LAMBETH et al) 20 May 1999 (20.05.1999), pages 15 - 17, 22, 34, 35 41, 44, 51 and 53.	1-12, 17-21, 25-28, 48-61 and 63
Y	US 6,248,416 B1 (LAMBETH et al) 19 June 2001 (19.06.2001), columns 13, 20, 21 and 27.	21-12, 17-21, 25-28, 48-61 and 63
Y	US 6,146,776 A (FUKUZAWA et al) 14 November 2000 (14.11.2000), column 8, lines 32 - 49 and Figures.	1-65
Y	JP 08-204253 A (FUJIKATA et al) 9 August 1996 (09.08.1996), Entire Derwent Abstract Translation.	1-65
Y	US 6,097,579 (GILL) 01 August 2000 (01.08.2000), columns 1, 2, 6 and 8, and Figures.	13-16, 23, 24, 29-47, 61 and 63-65
Y	US 6,262,869 B1 (LIN et al) 17 July 2001 (17.07.2001), columns 3 and 9, and Figures.	13-16, 23, 24, 29-47, 61 and 63-65

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 November 2002 (04.11.2002)	**06 DEC 2002**
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Kevin Bernatz Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/27327

Box I   Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐   Claim Nos.:
      because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐   Claim Nos.:
      because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐   Claim Nos.:
      because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐   As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐   As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐   As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐   No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐   The additional search fees were accompanied by the applicant's protest.
                          ☐   No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)) (July 1998)

[54] **ARTICLE COMPRISING ANISOTROPIC CO–FE–CR–N SOFT MAGNETIC THIN FILMS**

[75] Inventors: **Sungho Jin**, Millington; **Timothy J. Klemmer**, Watchung; **Thomas Henry Tiefel, deceased**, late of North Plainfield, by Linda J. Tiefel, administratrix; **Robert Bruce Van Dover**, Maplewood; **Wei Zhu**, Warren, all of N.J.

[73] Assignee: **Lucent Technologies Inc.**, Murray Hill, N.J.

[21] Appl. No.: **09/033,204**

[22] Filed: **Mar. 2, 1998**

[51] **Int. Cl.**^{6} **G11B 5/66**
[52] **U.S. Cl.** .... **428/694 T**; 428/694 TS; 428/694 TM; 428/900; 427/128; 427/129; 427/130; 427/131; 204/192.2
[58] **Field of Search** .... 478/694 T, 694 TS, 478/694 TM, 900; 427/128–131; 204/192.2

[56] **References Cited**

U.S. PATENT DOCUMENTS

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Masato Mino, Toshiaki Yachi, Aiko Tago, Keiichi Yanagisawa and Kazuhikio Sakakibara, "A New Planar Microtransformer for Use in Micro Switchcing Converters", *IEEE Transactions on Magnetics*, vol. 28, No. 4, Jul. 1992, pp. 1969–1973.
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G. Qiu, E. Haftek and J. A. Bernard, "Magnetic Properties and Crystal Structure of High Moment FeTaN Materials For Thin–Film Recording Heads,"*J. App. Phys.* 73 (10), May 1993, pp. 6573–6575.
Book, *Magnetic Materials*, by R. S. Tebble and D. J. Craik, publisher, Wiley–Interscience, a division of John Wiley & Sons Ltd., London, New York, Sydney, Toronto 1969.
Book, *Magnetic Thin Films*, by Ronald F. Soohoo, Associate Professor, Division of Engineering and Applied Science, The California Institute of Tecnology, publisher, Harper & Row, New York, Evanston and London, 1965.
Book, *Thin Ferromagnetic Films*, by M. Prutton, publisher, Washington Butterworths, 1964.

Primary Examiner—Leszek Kiliman
Attorney, Agent, or Firm—John M. Harman

[57] **ABSTRACT**

The invention is embodied in an anisotropic, soft magnetic thin film article comprising a cobalt-iron-chromium-nitrogen (Co—Fe—Cr—N) alloy. The thin film is formed such that the alloy has a relatively high saturation magnetization ($4\pi M_s$), e.g., greater than approximately 8 kilogauss (kG), a relatively low coercivity (H_c), e.g., less than approximately 2.0 oersteds (Oe), a relatively high squareness ratio (M_r/M_s), e.g., greater than approximately 0.90, and a relatively high anisotropy field (H_k), e.g., greater than approximately 20 Oe, in an as-deposited condition or, alternatively, with a relatively low temperature treatment, e.g., below approximately 300° Celsius. The inventive films are suitable for use in electromagnetic devices, e.g., in microtransformer cores, inductor cores and in magnetic read-write heads.

21 Claims, 5 Drawing Sheets

PROVIDE TARGET FOR THIN FILM DEPOSITION — 110

PROVIDE SUBSTRATE FOR MAGNETIC FILM DEPOSITION — 120

DEPOSIT Co–Fe–Cr–N BASED FILMS BY REACTIVE SPUTTERING — 130

ASSEMBLE THE MAGNETIC THIN FILM INTO MAGNETO ELECTRIC DEVICES — 140

FIG. 1

```
                                                          ┌110
┌────────────────────────────────────────────────────────┐
│        PROVIDE  TARGET  FOR  THIN  FILM  DEPOSITION      │
└────────────────────────────────────────────────────────┘
                            │                             ┌120
┌────────────────────────────────────────────────────────┐
│      PROVIDE  SUBSTRATE  FOR  MAGNETIC  FILM  DEPOSITION │
└────────────────────────────────────────────────────────┘
                            │                             ┌130
┌────────────────────────────────────────────────────────┐
│   DEPOSIT  Co-Fe-Cr-N  BASED  FILMS  BY  REACTIVE  SPUTTERING │
└────────────────────────────────────────────────────────┘
                            │                             ┌140
┌────────────────────────────────────────────────────────┐
│ ASSEMBLE  THE  MAGNETIC  THIN  FILM  INTO  MAGNETO  ELECTRIC  DEVICES │
└────────────────────────────────────────────────────────┘
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FIG. 2A

FIG. 2B

FIG. 3A

FIG. 3B

FIG. 3C
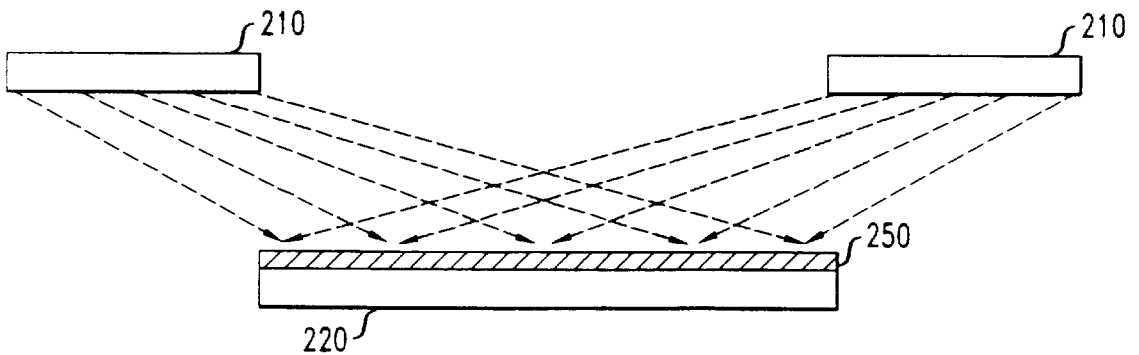
FIG. 4
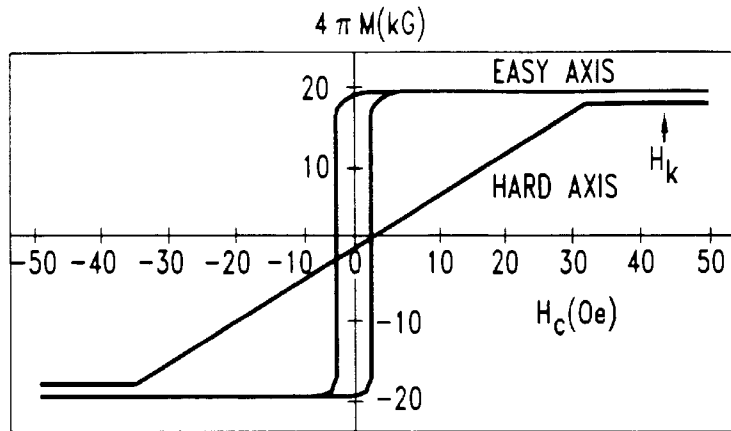
FIG. 5
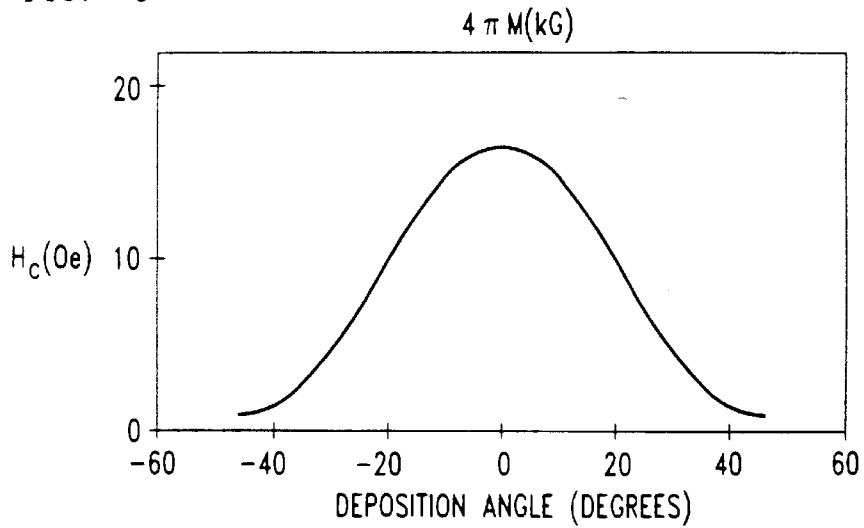
FIG. 6
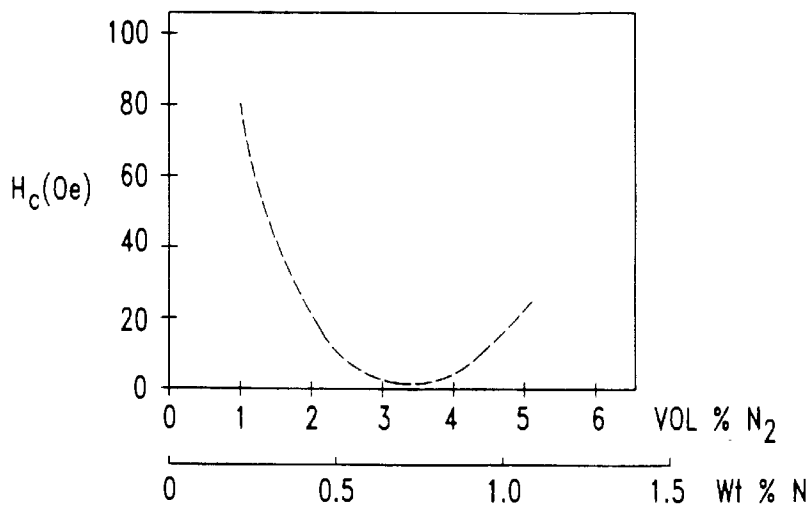
FIG. 7A
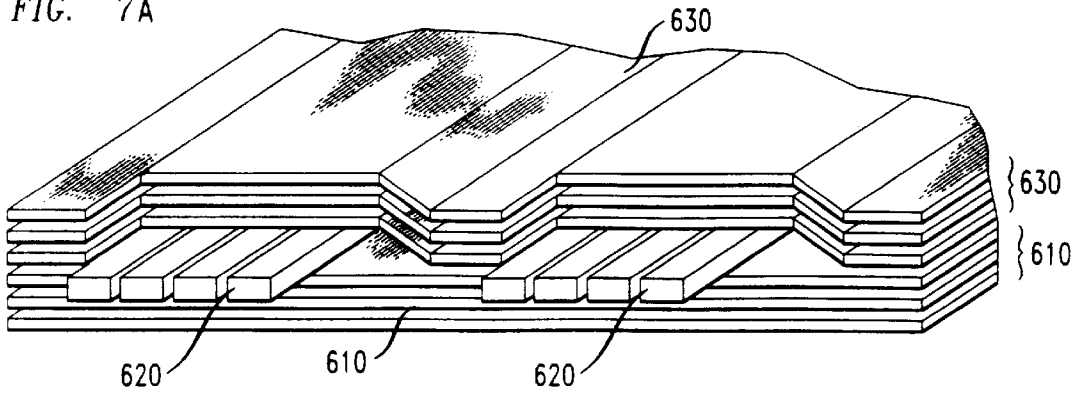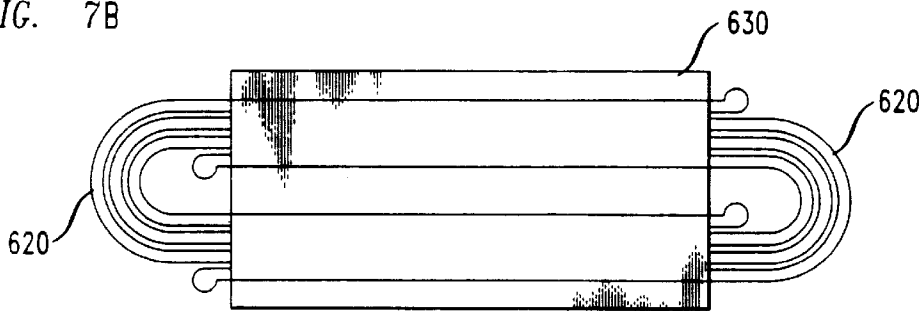
630

630

610

620   610   620

FIG. 7B

630

620

620

FIG. 8A

730

710

730

720   710

FIG. 8B

730

730

730

730   720

730

FIG. 9A

840

810

830

820

FIG. 9B

810

850

820

1
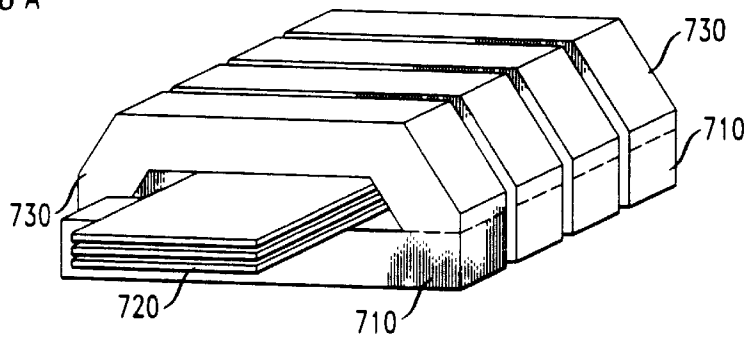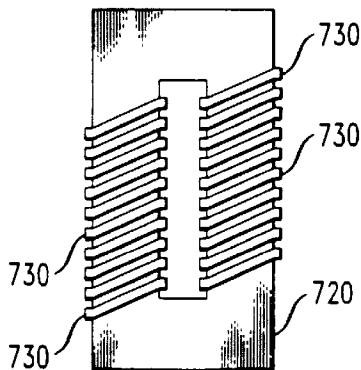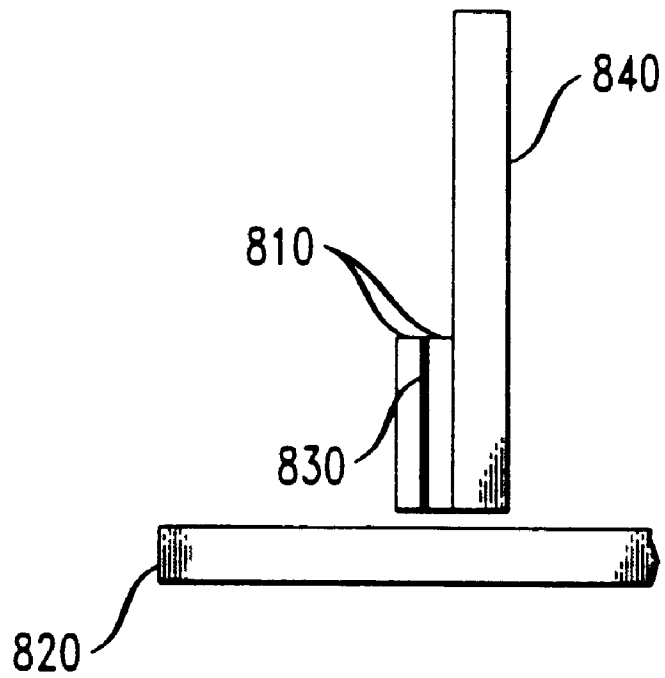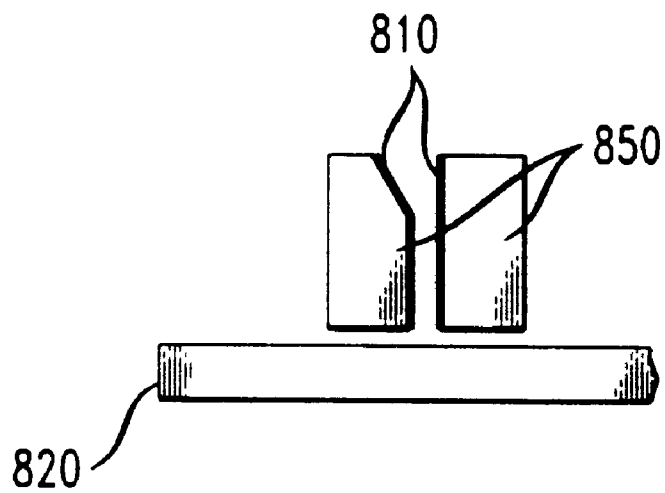
ARTICLE COMPRISING ANISOTROPIC CO–FE–CR–N SOFT MAGNETIC THIN FILMS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to thin films of magnetically soft alloys. More particularly, the invention relates to articles comprising these alloys and methods for making such articles.

2. Description of the Related Art

Thin film soft magnetic materials are useful in modern, high-frequency, electromagnetic devices, e.g., as a field-amplifying component in the read-write head of magnetic disk memories in computers or as a core in microtransformers and inductors. Among the desired properties of these films are relatively high saturation magnetization ($4\pi M_s$), low coercivity (H_c), high permeability, high electrical resistivity and high corrosion resistance. Various applications of soft magnetic thin films are described, e.g., in books *Magnetic Thin Films* by R. F. Soohoo, Harper and Row, 1965; *Thin Ferromagnetic Films* by M. Prutton, Butterworth, 1964; and in articles such as C. R. Sullivan and S. R. Sanders, IEEE Trans. on Power Electronics, Proc. 24th Annual Power Electronics Specialists Conf., p. 33–40, June 1993; and T. Yachi et al., IEEE Trans. Magn. 28, 1969–1973 (1992).

Among conventional soft magnetic thin films, nickel-iron (Ni—Fe) based films such as 80% Ni-20% Fe (permalloy) are useful because of their favorable magnetic properties and zero magnetostriction characteristics. Iron-based films such as iron-tantalum (Fe—Ta), iron-zirconium (Fe—Zr) and iron-hafnium (Fe—Hf) alloys generally exhibit saturation magnetizations ($4\pi M_s$) of approximately 15–20 kilogauss (kG) as compared to approximately 10 kG for the 80% Ni permalloy films (see, e.g., N. Kataoka et al., Japanese J. Appl. Phys. 28, L462–L464, 1989, Trans. Jap. Inst. Metals 31, 429, 1990). However, iron-based films exhibit poorer soft magnetic properties and require post-deposition heat treatment.

To obtain improved soft magnetic properties, nitrogen-containing films of these iron-based alloys such as iron-tantalum-nitrogen (Fe—Ta—N) have been prepared. See, e.g., E. Haftek et al., IEEE Trans. Magn. 30, 3915–3917 (1994); N. Ishiwata et al., J. Appl. Phys. 69, 5616 (1991); J. Lin et al., IEEE Trans. Magn. 30, 3912–3914 (1994); and G. Qiu et al., J. Appl. Phys. 73, 6573 (1993). However, although desirable magnetic softness, e.g., a coercivity (H_c) of less than approximately 2 oersteds (Oe) (for microtransformer applications), is obtainable in these nitrogen-containing films, it is apparent from the aforementioned articles that such desirable soft magnetic properties are difficult to obtain in an as-deposited form, but are possible after post-deposition heat treatment at high temperatures.

However, such heat treatment of deposited films is an additional processing step that needs to be avoided if possible, not only from a manufacturing cost point of view but also because of the complications of having to expose various other components and materials in the devices to high temperatures. Therefore, it is desirable for the required soft magnetic properties in the films to be obtained in the as-deposited condition, or at worst, with a very low temperature heat treatment below approximately 150° Celsius.

Desirable high-frequency properties for soft magnetic films include relatively high permeability and low power loss. There are several sources of loss in ferromagnetic materials, including hysteresis loss, eddy current loss and ferromagnetic resonance (FMR) loss.

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Hysteresis loss is reduced or minimized, e.g., by avoiding magnetic domain wall displacement, such as by performing alternating current (AC) operation of the magnetic films in the magnetically hard-axis so that magnetization only by spin rotation is used. Such mode of operation is accomplished most conveniently by providing a strong anisotropy (H_k) and a square magnetic hysteresis (M-H) loop. For example, see co-pending application Ser. No. 08/595,543, filed Feb. 2, 1996 now U.S. Pat. No. 5,780,175 and assigned to the assignee of the present invention.

Eddy current loss increases in proportion to the square of the operating frequency, and thus plays an important role in the high-frequency applications. Eddy current loss is reduced, e.g., by increasing the field penetration depth (skin depth) with relatively high electrical resistance in the magnetic material, either by using a thin film configuration or by selecting relatively high resistivity materials.

The occurrence of ferromagnetic resonance (FMR) in high-frequency ranges such as approximately 10 megahertz (MHz) or greater in most of the soft magnetic materials generally causes the magnetic permeability to drop off and the magnetic loss to increase by orders of magnitude, often spanning a frequency range from approximately 1–2 orders of magnitude. Such behavior is conventional for Ni—Zn ferrites. For example, see generally R. S. Tebble and D. J. Craik, *Magnetic Materials* (Wiley, New York, 1969), p. 598.

Ferromagnetic resonance (FMR) occurs when the frequency of the applied AC field matches the characteristic precession frequency of spins in the magnetic material. This precession frequency, fr, is determined by the total anisotropy field (H_k) experienced by the spins. For a thin film, for which the demagnetizing field (H_d) along the z direction is approximately equal to the saturation magnetization ($4\pi M_s$), the FMR frequency is expressed as

$$f_r = 2\pi\gamma \cdot (H_k \cdot 4\pi M_s)^{1/2},$$

where γ is the gyromagnetic constant ($2\pi\gamma = 2.8$ MHz/Oe), and H_k is the in-plane anisotropy field. This relation applies for the case when the AC field is applied in the plane of the film perpendicular to the easy-axis. In order to raise the FMR frequency so that ferromagnetic resonance does not interfere with the high-frequency operation of the magnetic materials, a higher anisotropy field (H_k) and higher saturation magnetization ($4\pi M_s$) are needed. Typically, values of the anisotropy field (H_k) up to approximately 10–15 oersteds (Oe) are obtainable, but anisotropy fields (H_k) higher than 15 Oe in soft magnetic films generally are difficult to obtain. However, in high-frequency applications such as in wireless cellular communications, magnetic films with FMR frequencies of at least approximately 1 gigahertz (GHz) are desired.

Therefore, it is desirable to have soft magnetic thin films with greater saturation magnetization ($4\pi M_s$) and greater anisotropy fields (H_k) than conventional soft magnetic thin films.

SUMMARY OF THE INVENTION

The invention is embodied in anisotropic, soft magnetic thin films comprising a cobalt-iron-chromium-nitrogen (Co—Fe—Cr—N) alloy and methods for making them. The thin films are formed such that the alloy has a relatively high saturation magnetization ($4\pi M_s$), e.g., greater than approximately 8 kilogauss (kG), a relatively low coercivity (H_c), e.g., less than approximately 2.0 oersteds (Oe), a relatively

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high squareness ratio (M_r/M_s), e.g., greater than approximately 0.90, and a relatively high anisotropy field (H_k), e.g., greater than approximately 20 Oe. The soft magnetic properties are obtained in an as-deposited condition or, alternatively, with a relatively low temperature treatment, e.g., below approximately 300° Celsius. Thin films according to embodiments of the invention are suitable for use, e.g., in electromagnetic devices such as in microtransformer cores, inductor cores and in magnetic read-write heads.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a simplified block diagram of a method for making soft magnetic thin films comprising Co—Fe—Cr—N according to embodiments of the invention;

FIGS. 2a–b are diagrams showing various configurations of depositing thin films in the presence of an applied magnetic field according to embodiments of the invention;

FIGS. 3a–c are diagrams showing various configurations of oblique angle thin film deposition in the absence of an applied magnetic field according to embodiments of the invention;

FIG. 4 is a graphical diagram of the magnetic hysteresis (M-H) loops along the easy and hard-axis direction of magnetization of as-deposited Co—Fe—Cr—N alloy films according to embodiments of the invention;

FIG. 5 is a graphical diagram illustrating magnetic coercivity, H_c, as a function of film deposition angle for Co—Fe—Cr—N films according to an embodiments of the invention;

FIG. 6 is a graphical diagram of magnetic coercivity, H_c, as a function of nitrogen flow rate in an argon (Ar) carrier gas during a reactive sputtering process for Co—Fe—Cr—N alloy films according to embodiments of the invention;

FIGS. 7a–b are perspective and top views, respectively, of a pot-core type microtransformer comprising Co—Fe—Cr—N films according to embodiments of the invention;

FIGS. 8a–b are perspective and top views, respectively, of a toroid type microtransformer comprising Co—Fe—Cr—N films according to embodiments of the invention; and

FIGS. 9a–b are side, cross-sectional views of a magnetic recording head comprising Co—Fe—Cr—N films according to embodiments of the invention.

It is to be understood that the drawings are to illustrate the concepts of the invention and are not to scale.

DETAILED DESCRIPTION

FIG. 1 is a simplified block diagram of a method for making soft magnetic thin films comprising cobalt-iron-chromium-nitrogen (Co—Fe—Cr—N) in accordance with embodiments of the invention. A first step 110 is to provide an alloy target or targets from which the inventive magnetic thin films are to be deposited, e.g., by chemical or physical deposition such as by sputtering, evaporation, molecular beam epitaxial growth, ion beam deposition and laser ablation.

For example, deposition by sputtering is amenable to large-scale industrial manufacturing. The sputtering target (shown as 210 in FIG. 2a), which typically is in the form of a round plate, in one embodiment, has an alloy composition similar to the desired film composition and, in another embodiment, has composite sections of different metals or alloys on the target surface to be sputtered away. Alternatively, the film deposition is accomplished by using multiple targets, e.g., by co-sputtering from two or more

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targets with different compositions chosen so that the final composition of the deposited film on the substrate corresponds to the desired composition. For example, as will be discussed in greater detail hereinbelow, in data shown in FIG. 6, co-sputtering with two targets was used, e.g., a Co-9.6%Fe-4.4%Cr (in weight %) target on one side and a Fe-4.5%Cr target on the other side separated by approximately 6 inches.

According to one embodiment of the invention, diode sputtering or triode sputtering is used for deposition of the inventive films. Triode sputtering often is used instead of diode sputtering because triode sputtering uses lower bias voltage and lower argon (Ar) pressure, thus allowing easier control of the sputter deposition and the formation of desired nanocrystalline microstructure in the inventive soft magnetic films comprising Co—Fe—Cr—N.

According to another embodiment of the invention, nitrogen (N) is incorporated into the alloy film by reactive deposition, i.e., by continuously supplying a specific partial pressure of nitrogen gas in the background Ar gas carrier during the sputtering process. The nitrogen atoms are believed to go into the thin film structure both by reaction with one or more of the metallic elements in the form of a nitride, such as Cr-nitride or Fe-nitride, and/or by dissolution in the form of interstitial solute atoms in the alloy crystal lattice.

According to another embodiment of the invention, nitrogen is supplied by alloying it directly into the sputtering targets or by adding it to the films after deposition, e.g., by ion implantation. Accordingly, thin films of inventive alloys, prepared by any suitable technique, are subjected to nitrogen implantation with appropriate doses and processing temperatures.

In the case of using a single alloy target for sputtering, the composition of the target according to embodiments of the invention is, e.g., cobalt (Co) within the range from approximately 10–90 weight %, typically within the range from approximately 20–80 weight %, more typically within the range from approximately 30–60 weight %, iron (Fe) within the range from approximately 10–90 weight %, typically within the range from approximately 20–80 weight %, more typically within the range from approximately 30–60 weight %, chromium (Cr) in the range from approximately 0–15 weight %, typically within the range from approximately 1.0–12.0 weight % and more typically within the range from approximately 1.5–8.0 weight %. If nitrogen (N) is to be added to the sputtering target, the alloy target includes nitrogen within the range from approximately 0–10 weight %, depending on the concentration of the nitrogen gas used during the sputtering.

The next step 120 is to provide a substrate onto which one or more soft magnetic films according to embodiments of the invention are to be deposited. A clean and smooth non-magnetic substrate surface is desired, e.g., for microtransformer-type applications. Substrate materials include, e.g., semiconductors such as silicon (Si) and gallium-arsenide (Ga—As), and other materials such as glass, quartz, ceramic, polymer and polyimide. A silicon substrate is convenient if other semiconductor electronic integrated circuit (IC) circuitry and interconnection features are to be integrated on portions of the same substrate. The IC circuits are fabricated, e.g., either before or after the deposition of the soft magnetic films.

For use in microtransformer or inductor applications, especially for high-frequency devices (e.g., f=1–1000 megahertz or greater), Co—Fe—Cr—N thin films according to

embodiments of the invention are formed, e.g., into a multilayer, patterned Configuration with dielectric spacer layers, such as spin-coated or spray-coated and optionally photolithographically patterned polyimide films, interleaved therebetween. Alternatively, the thin films are formed by vacuum or CVD deposition of dielectric films such as aluminum oxide (Al_2O_3), aluminum nitride (AlN), silicon dioxide (SiO_2) and yttrium oxide (Y_2O_3). The multilayer configuration of magnetic thin films according to embodiments of the invention provides high electrical resistance for the film layers so as to reduce eddy current loss, e.g., during high-frequency operation.

In such multilayer arrangement, typically more than one substrate material is involved. For example, after depositing the first magnetic layer comprising Co—Fe—Cr—N on, e.g., a silicon (Si) substrate, a polyimide insulation layer is deposited on the first magnetic layer and thus becomes the next substrate for the remaining magnetic layers. Also, because the magnetic properties of alloys and compounds often are influenced by crystallographic texture and lattice parameters, it is possible to choose the substrate material to provide epitaxial growth with accompanying lattice parameter modifications, to induce growth texture (such as a columnar structure) or to induce desired degrees of crystallization.

The next step **130** is to deposit thin films comprising Co—Fe—Cr—N, e.g., by reactive sputtering in a nitrogen-containing atmosphere. According to embodiments of the invention, the amount of nitrogen used is within the range from approximately 0.2–30.0% in volume in argon (Ar), and often within the range from approximately 0.5–10.0% in volume with a total (Ar+N_2) gas pressure of approximately 10^{-2} to 10^{-4} Torr. The sputtering target(s) is subjected to a bias voltage in the range from approximately 20–500 volts, typically within the range from approximately 50–200 volts.

For microtransformer or inductor applications involving multilayer deposition and temperature-sensitive dielectric spacer layers such as polyimide, the substrate temperature typically is kept at or near ambient temperature. Alternatively, the substrate temperature is kept below approximately 150° Celsius (a temperature above which many polymers or polyimides begin to suffer damage with undesirable chemical or structural changes). For other device applications in which temperature-degradable materials are not involved, higher substrate temperatures generally are used.

Other embodiments of the present invention use one or more magnetic fields during the deposition of the films comprising Co—Fe—Cr—N to induce magnetic anisotropy in the desired direction. Since the inventive films have soft magnetic properties, a relatively low field is applied to introduce preferential ordering of atoms to form an easy direction of magnetization for higher permeability, lower coercivity (H_c), and a more square magnetic hysteresis (M-H) loop shape. The magnitude of the applied field is within the range from approximately 2–5000 oersteds (Oe), typically within the range from approximately 10–500 Oe. Since the deposition temperature for the inventive films often is near ambient temperature, the magnetic fields are applied conveniently, e.g., by placing one or more electromagnets or permanent magnets near the substrate. Such is done without fear of solenoid wire insulation damage or loss of magnetism in permanent magnets upon heating toward or above the Curie temperature.

In the case of magnetron sputtering, the stray magnet field itself in the deposition system is used conveniently to induce

anisotropy. As shown in FIGS. 2*a–b,* if an additional field is to be applied, one or more permanent magnets is used because of the relative simplicity of placing magnets either on the sides of or beneath substrate **220** during the deposition. Various permanent magnets **240** are acceptable, including those made of relatively high coercivity materials samarium-cobalt (Sm—Co), neodymium—iron— boron (Nd—Fe—B), barium-ferrite and iron-chromium-cobalt (Fe—Cr—Co), all of which reduce self-demagnetization in small or short magnet configurations. Multiple magnet arrays, such as shown in FIG. **2***b,* generally provide a stronger field to the substrate regions between the magnets than, e.g., the magnet arrangement shown in FIG. **2***a.* If a relatively uniform in-plane field is desirable over the substrate area, it is possible to replace the small magnets shown in FIG. **2***a* with a single magnet having a size comparable to that of the substrate.

In the case of multilayer deposition, the thickness of the layers comprising Co—Fe—Cr—N are within the range, e.g., from approximately 0.001–10.0 microns, typically within the range from approximately 0.01–2.0 microns. Higher frequency operations generally require thinner magnetic films to reduce eddy current loss. The insulating (dielectric) spacers, such as nitride or oxide ceramic films or plastic or polyimide films formed between the magnetic layers, typically are within the range from approximately 0.001–1.0 microns. The number of magnetic layers in use depends on the total amount of magnetic flux required and the thickness of each layer, but typically is between approximately 1–1000 layers.

The composition of the inventive films include, e.g., cobalt (Co) within the range from approximately 10–90 weight %, typically within the range from approximately 20–80 weight %, more typically within the range from approximately 30–60 weight %; iron (Fe) within the range from approximately 10–90 weight %, typically within the range from approximately 20–80 weight %, more typically within the range from approximately 30–60 weight % balance; chromium (Cr) within the range from approximately 0–15.0 weight %, typically within the range from approximately 1.0–12.0 weight %, and more typically within the range from approximately 1.5–8.0 weight %; and nitrogen (N) in the range from approximately 0.1–10 weight %, typically within the range from approximately 0.2–8 weight %, more typically in the range from approximately 0.3–5.0 weight %. Also, the inventive films may contain one or more impurity elements such as copper (Cu), nickel (Ni), tantalum (Ta), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), molybdenum (Mo), niobium (Nb) and tungsten (W), cerium (Ce), yttrium (Y), lanthanum (La), carbon (C), aluminum (Al) and silicon (Si), with individual element amounts of less than approximately 1 weight % and typically less than approximately 0.5 weight %, and with total element amounts less than approximately 3 weight % and typically less than approximately 0.5 weight %.

Structurally, the inventive film includes a nanocrystalline or near-amorphous structure with an average crystallite size (grain-size), e.g., of less than approximately 1000 angstroms (Å), typically less than approximately 500 Å, and more typically less than approximately 200 Å. Also, the inventive film exhibits suitable soft magnetic properties in the as-deposited condition without having to undergo post-deposition heat treatment. For example, the coercivity (H_c) of the inventive films often is less than approximately 5 oersteds (Oe), and typically less than approximately 2 Oe. Also, the saturation ($4\pi M_s$) often is greater than approximately 12 kilogauss (kG), typically greater than approximately 15 kG, and more typically greater than approximately 18 kG.

The inventive films also exhibit squareness ratios (M_r/M_s), e.g., of at least approximately 0.90 and typically greater than approximately 0.95. Also, the anisotropy field (H_k) often is at least approximately 15 Oe, typically greater than approximately 30 Oe, and more typically greater than approximately 50 Oe.

Some of the processing and properties of the inventive films are described in the examples given below.

EXAMPLE 1

Thin films comprising the inventive Co—Fe—Cr—N alloy were deposited on 4 inch diameter (100) Si wafer substrates by triode DC magnetron sputtering, using the co-sputtering process illustrated generally in FIG. 3c, with two 2.25 inch diameter targets having approximate compositions of 86%Co-9.5%Fe-4.5%Cr (in weight %) and 95.5%Fe-4.5%Cr, respectively, and using a reactive process in a nitrogen-containing atmosphere. The sputtering chamber first was pumped down to approximately 2×10^{-7} Torr, and then the reactive sputtering was performed under a gas atmosphere with an initial pressure (Ar+N$_2$) of approximately 5×10^{-3} Torr and a gas flow rate of approximately 50 cubic centimeters per minute. The amount of nitrogen in the argon gas was approximately 2.5% in volume, which resulted in a nitrogen content in the deposited film of approximately 0.6 weight %. A bias voltage of approximately 140 volts was applied to both targets. The Si substrate was kept at ambient temperature during sputtering. The rate of sputter deposition was approximately 100 Å per minute. The films were approximately 1000 Å thick.

The magnetic hysteresis (M-H) loops were measured using a Vibrating Sample Magnetomer (VSM). The M-H loops were measured as a function of the in-plane orientation to determine the direction of easy and hard magnetization. Because the co-sputtering process targets are placed approximately 6 inches apart, the deposited Co—Fe—Cr—N films have a concentration gradient from one end to the other (e.g., from the Co-rich end to the Fe-rich end). Small samples, each approximately 0.125 inch square, were cut from various locations of the substrate to represent a spectrum of the gradient composition. Table 1 shows the easy-axis magnetic properties of some selected samples cut from the Si wafer. The approximate compositions also are given in the table.

TABLE 1

Magnetic Properties of Co-Sputtered Co—Fe—Cr—N Films in the As-Deposited Condition							
Composition (wt %)				$4\pi M_s$	Squareness	H_c	H_k
Co	Fe	Cr	N	(kilogauss)	(M_r/M_s)	(Oe)	(Oe)
83.6	10.6	4.5	1.3	14.8	0.98	6.6	32
54.0	40.2	4.5	1.3	16.2	0.98	2.9	80
42.7	51.5	4.5	1.3	19.3	0.99	1.9	73
36.5	57.7	4.5	1.3	18.6	0.97	3.1	68
14.9	79.3	4.5	1.3	17.2	0.95	3.2	72
2.7	91.5	4.5	1.3	16.2	0.97	2.7	57

As is evident from Table 1, thin films according to embodiments of the invention exhibit, in the as-deposited condition, advantageous soft magnetic properties with relatively square M-H loops, high saturation magnetization ($4\pi M_s$), low coercivity (H_c) and high anisotropy fields (H_k). Of particular interest is the thin film with an estimated composition of approximately 42.7%Co-51.5%Fe-4.5%Cr-1.3%N in weight %.

EXAMPLE 2

A thin film comprising the inventive Co—Fe—Cr—N alloy, e.g., with a composition of 49.7%Co-44.5%Fe-4.5Cr-1.3%N (in weight %) was deposited on a silicon (Si) substrate from a single alloy target by triode magnetron sputtering. The nitrogen content in the argon gas was approximately 2.5% in volume. The mixed gas was blown directly onto the substrate at a distance of approximately 1 inch. A bias voltage of approximately 140 volts was applied to the single alloy target. The substrate was kept at ambient temperature. The rate of deposition was approximately 100 Å per minute. The film thickness was approximately 1000 Å.

Referring now to FIG. 4, magnetic hysteresis (M-H) loops along the in-plane easy-axis and the hard-axis of the thin film are shown. The easy-axis M-H loop exhibits advantageous soft magnetic properties of the film in the as-deposited condition. For example, such advantageous properties include a relatively high saturation magnetization ($4\pi M_s$) of approximately 19 kG, a relatively low coercivity (H_c) of approximately 0.87 Oe, and a relatively high squareness ratio (M_r/M_s) of approximately 0.98. The hard-axis loop, obtained in a 90° rotated direction, exhibits an advantageously closed loop and an anisotropy field (H_k) of approximately 35 Oe. The ferromagnetic resonance (FMR) frequency is estimated to be approximately 2.2 gigahertz (GHz).

It should be noted that the alloy films according to embodiments of the invention have relatively well-defined easy-axis and hard-axis orientations, typically both in-plane and approximately 90 degrees apart. For minimal power loss in high-frequency applications, it is advantageous to have the hard-axis loop as closed as possible and with a coercivity (H_c) along the hard-axis of less than approximately 5 Oe, typically less than approximately 2 Oe, and more typically less than approximately 1 Oe, and with the remanent induction as close to zero as possible, with a squareness ratio (M_r/M_s), typically less than approximately 0.1 and typically less than 0.02.

EXAMPLE 3

A film comprising the inventive Co—Fe—Cr—N alloy and having a thickness of approximately 1000 Å was deposited on a silicon (Si) substrate using a diode sputtering system. The target-to-substrate incident angle was tilted to be approximately 45 degrees. The nitrogen gas content in argon was at approximately 17 volume %. The mixed gas was fed into the deposition chamber with a distance to the substrate of approximately 6 inches. The resultant film in the as-deposited condition yielded advantageously highly anisotropic, magnetic properties, e.g., an anisotropy field (H_k) of approximately 230 Oe, a saturation magnetization ($4\pi M_s$) of approximately 10 kG, a squareness ratio (M_r/M_s) of approximately 0.97, and a coercivity (H_c) of approximately 18 Oe. The ferromagnetic resonance frequency of this film is estimated to be approximately 4.2 GHz.

It is evident from the Examples 1–3 described above that advantageously highly anisotropic, soft magnetic properties are obtainable in the as-deposited condition for films according to embodiments of the invention prepared by either co-sputtering or single alloy sputtering. Such combinations of relatively high saturation magnetization ($4\pi M_s$), low coercivity (H_c), high squareness ratios (M_r/M_s) and high anisotropy fields (H_k) are advantageous for use in many electromagnetic devices, such as in microtransformers, recording heads and high-frequency telecommunication devices.

The advantageous squareness ratio of the loop, the strong anisotropy and the unusually high anisotropy field values in films according to embodiments of the invention are believed to be the result of the inventive alloys and the unique processing procedures employed. The addition of chromium (Cr), especially in combination with oblique incident film deposition, appears to be advantageous in enhancing the magnetic anisotropy and electrical resistivity. Also, the presence of Cr is believed to help the formation of desirable nanocrystalline structure and microstructural texture for strong in-plane anisotropy fields. Such presence also is believed to improve soft magnetic properties, e.g., a lower coercivity (H_c), by reducing magnetocrystalline anisotropy or magnetostriction.

Furthermore, according to embodiments of the invention, increasing the angle of sputter deposition during the formation of the invention alloys advantageously improves their magnetic properties. For purposes of discussion herein, the terms "angle of sputter deposition" or "sputter deposition angle" or "deposition angle" are intended to include the angle at which the sputtered atoms arrive at and impinge on the substrate.

For example, FIG. 3 illustrates various deposition angle configurations according to embodiments of the invention. In FIG. 3a, a target 210 is centered above a substrate 220. In this configuration, the portion of a film 250 near the periphery of the substrate is deposited with a greater inclined angle than the portion of film 250 deposited near the center of the substrate. The angular difference affects the magnetic properties of the film, e.g., as shown in FIG. 5. The plot in FIG. 5 was derived from a film having a thickness of approximately 1000 Å, with a composition of Co-45%Fe-4.5%Cr-0.6%N (weight percent). For an angular difference of approximately 45 degrees, an advantageously low coercivity value (H_c) of approximately 2 Oe or less is achieved, while for an angular difference of approximately 0 degrees, a disadvantageously high coercivity value (H_c) of approximately 18 Oe occurs.

To keep a sufficiently high deposition angle, the target and the substrate should be laterally displaced, e.g., as shown in FIG. 3b. In the case of co-sputtering, two or more targets may be placed laterally away from the substrate position, e.g., as shown in FIG. 3c. According to embodiments of the invention, sputter deposition angles of at least approximately 10 degrees should be maintained. Alternatively, maintaining sputter deposition angles of at least approximately 20 degrees or even at least approximately 40 degrees are advantageous.

Referring now to FIG. 6, the magnetic coercivity, H_c, of the inventive films comprising Co—Fe—Cr—N as a function of nitrogen content (in volume %) in the Ar gas sputtering atmosphere is shown. The coercivity value, H_c, of the films depends on the nitrogen content, with the lowest coercivity often being obtained by sputtering at a nitrogen gas content of approximately 2.5 volume %, which corresponds to approximately 0.6 weight % nitrogen atoms in the film. An insufficient nitrogen content is ineffective for preventing grain growth of the alloy matrix and results in an increased coercivity value. However, a nitrogen content too great (e.g., more than approximately 5 weight %) reduces the saturation magnetization ($4\pi M_s$) and also increases the coercivity. Thus, there appears to be a moderate, optimal range of nitrogen content for a given alloy composition.

The addition of Cr to a Co—Fe—N alloy film improves the soft magnetic properties of the film. Such improvements include, e.g., a lower coercivity (H_c), a more square mag-

netic hysteresis (M-H) loop, and a higher anisotropy field (H_k) in the as-deposited condition. Also, such additions reduce or eliminate the need for post-deposition heat-treatment.

According to an alternative embodiment of the invention, the inventive films are given a low-temperature heat treatment to further improve the soft magnetic properties. To reduce the damage to insulating layers such as polyimide, heat treatment temperatures below approximately 300° Celsius and typically below approximately 150° Celsius are used. Also, to reduce surface oxidation during the heat treatment, a vacuum atmosphere of greater than approximately 10^{-4} Torr is used. However, a vacuum atmosphere less than approximately 10^{-4} Torr is used, e.g., if the top surface of the film is protected by oxidation-resistant coatings such as Cr, Al, oxide, or nitride films.

According to another embodiment of the invention, the inventive films are formed as a composite structure with a different type of magnetic layer. For example, the composite structure has one or more exchange bias films made of, e.g., one or more antiferromagnetic, ferromagnetic or ferrimagnetic materials, that are added directly on the surface of the soft magnetic film. For example, a thin film of Fe-50% manganese antiferromagnetic alloy is added onto some or all of the soft magnetic layers comprising Co—Fe—Cr—N to shift the magnetic hysteresis (M-H) loop by more than the coercivity of the soft magnetic film (i.e., by at least approximately 2 Oe). Also, the thin film of Fe-50% manganese antiferromagnetic alloy is added to allow for high-frequency operation (e.g., approximately 0.1–10 GHz) of the soft magnetic films in the internal bias-field mode with minimal magnetic domain wall motion.

Some of the inventive Co—Fe—Cr—N films exhibit highly square, easy-axis loop characteristics in combination with closed, hard-axis loop shapes and relatively high, easy-axis coercivity, e.g., greater than approximately 10–30 Oe. Such high coercivity is desirable in operations that are free of domain-wall motion because the high coercivity provides the stability of easy-axis saturation against stray fields and thus makes it unnecessary to add anitiferromagnetic bias films.

The last step 140 in FIG. 1 is to assemble the magnetic thin film within electromagnetic devices such as microtransformers, saturable transformers, inductors and recording heads. Step 140 comprises appropriately sizing the substrate (which contains a deposited and optionally patterned single layer, multilayer or composite-structured magnetic film), adding appropriate interconnection and conductor circuitry if needed, and assembling the film within the electromagnetic devices.

Referring now to FIGS. 7a–b, various views of a pot-core type microtransformer comprising the inventive films comprising Co—Fe—Cr—N are shown. To form such transformer, a multiplicity of soft magnetic film layers 610 (laminations with polyimide or other insulating layers there between) first is deposited, then a patterned conductor layer 620 (e.g., containing Cu lines) is added above magnetic film layers 610, and then more magnetic film laminations 630 are deposited, as shown.

FIGS. 8a–b show various views of a toroidal microtransformer according to an embodiment of the invention. Here, a conductor layer 710 in the form of parallel segments first is prepared, then a magnetic film lamination 720 comprising Co—Fe—Cr—N is deposited thereon, and then a top conductor layer 730 in the form of parallel segments is added for connection with segments of conductor layer 710 to form the toroidal winding configuration as shown.

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For certain applications, films comprising Co—Fe—Cr—N are deposited in such a way that the easy-axis of magnetization coincides with the direction of the applied field from the windings. For very high-frequency applications (e.g., frequencies of approximately 10 MHz or greater), magnetization switching by domain wall motion typically is not desired and hence the magnetically hard direction is used so that coherent spin rotation mode is operational.

For this reason, in-plane uniaxial magnetic anisotropy and the accompanying square magnetic hysteresis (M-H) loop shape typically is used. The uniaxial anisotropy, which is induced, e.g., by thin film deposition in the presence of magnetic fields, is defined, e.g., in terms of the anisotropy field (H_k), which is represented by the field in which the hard-axis magnetization loop reaches saturation. See, for example, FIG. 4, which is discussed hereinabove.

According to embodiments of the invention, anisotropy fields (H_k) in the inventive films are advantageously high, e.g., in the range from approximately 15–200 Oe and typically in the range from approximately 30–100 Oe. However, too high of an anisotropy field, e.g., greater than approximately 500 Oe, reduces the high-frequency permeability, which is proportional to the saturation magnetization divided by the anisotropy field value ($4\pi M_s/H_k$) in the hard-axis operation. Also, too low of an anisotropy field, e.g., less than approximately 10 Oe, causes the ferromagnetic resonance frequency to be reduced and to interfere with operating frequency ranges. Therefore, too much magnetic softness (i.e., a very low anisotropy value) typically is disadvantageous for high-frequency operation of devices comprising the inventive films.

A relatively high "squareness" of the magnetic hysteresis (M-H) loop in the easy-axis direction is advantageous for high-frequency applications (e.g., greater than 0.5 GHz), as devices comprising the inventive films advantageously are saturated essentially into a single domain state along the easy-axis, and then are operated in a high-frequency alternating current (AC) mode in the hard-axis direction to reduce or minimize the domain wall motion. In this manner, devices with the inventive films comprising Co—Fe—Cr—N have a "squareness" (as defined by the ratio of the remanent magnetization, M_r, to the saturation magnetization, M_s) of at least 0.90 and typically at least 0.95.

FIGS. 9a–b show cross-sectional views of electromagnetic devices having embodiments of the invention incorporated therein. A cross-sectional view of a recording read-write head comprising an embodiment of the inventive film is illustrated in FIG. 9a. The soft magnetic film **810** serves to amplify the magnetic signal from the recorded magnetic memory bit information in the magnetic disk or tape **820** such that the inductive sense coil or magnetoresistive sensor **830** generates a higher output signal. Shown also is the substrate **840** upon which soft magnetic film **810** is formed.

Alternatively, as shown in FIG. 9b, the inventive film is used as the high-magnetization material in the metal-in-gap (MIG) type head configuration. In this embodiment, the head **850** is made of, e.g., ferrite.

It will be apparent to those skilled in the art that many changes and substitutions can be made to the thin films and their incorporation into the electromagnetic devices herein described without departing from the spirit and scope of the invention as defined by the appended claims.

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What is claimed is:

1. An article, comprising:

a non-magnetic substrate; and

an anisotropic, magnetically soft film supported by said substrate, said film including an alloy of cobalt-iron-chromium-nitrogen (Co—Fe—Cr—N) and having a saturation magnetization ($4\pi M_s$) of at least approximately 8 kilogauss (kG), an anisotropy field (H_k) within the range from approximately 15 to 300 oersteds (Oe) and a magnetic hysteresis (M-H) loop squareness ratio (remanent magnetization, M_r, to saturation magnetization, M_s) of at least approximately 0.90, wherein said alloy contains, by atomic percentage, at least approximately 15% cobalt (Co), and wherein said article has been heat treated at a temperature of no more than approximately 150° Celsius.

2. The article as recited in claim 1, wherein said film has an anisotropy field (H_k) greater than approximately 50 Oe, and has a ferromagnetic resonance (FMR) frequency greater than approximately 1 gigahertz (GHz).

3. The article as recited in claim 1, wherein said Co—Fe—Cr—N alloy includes chromium (Cr) within the range from approximately 0 to 15 weight %.

4. The article as recited in claim 1, wherein said Co—Fe—Cr—N alloy contains cobalt (Co) within the range from approximately 20 to 80 weight %, iron (Fe) within the range from approximately 20 to 80 weight %, chromium (Cr) within the range from approximately 1 to 12 weight %, and nitrogen (N) within the range from approximately 0.2 to 8.0 weight %.

5. The article as recited in claim 1, wherein said film further comprises a plurality of thin film layers and wherein said article further comprises a corresponding plurality of dielectric spacer layers formed between said thin film layers in such a way that a multilayer structure is formed.

6. The article as recited in claim 5, wherein said plurality of dielectric spacer layers further comprises polyimide or ceramic insulators.

7. The article as recited in claim 1, wherein said film is formed on said substrate in such a way that the average grain structure size of said film is less than approximately 500 angstroms (Å).

8. The article as recited in claim 1, further comprising one or more exchange bias films formed on said film, said exchange bias films selected from a group consisting of antiferromagnetic, ferromagnetic and ferrimagnetic material.

9. The article as recited in claim 1, wherein said article is part of an electromagnetic device selected from a group consisting of a microtransformer, an inductor and a magnetic read-write head.

10. The article as recited in claim 1, wherein said article is for use at an operating frequency of at least approximately 10 megahertz (MHz), and wherein said film is saturated along an easy-axis of magnetization into a single domain state and then operated in an alternating current (AC) field along a hard-axis of magnetization.

11. The article as recited in claim 1, wherein said film has an easy-axis coercive force of at least approximately 30 oersteds (Oe).

12. A method for making a magnetically soft thin film article, said method comprising the steps of:

providing a non-magnetic substrate; and

depositing at least one anisotropic, magnetically soft thin film in such a way that said non-magnetic substrate supports said film, said film including an alloy of cobalt-iron-chromium-nitrogen (Co—Fe—Cr—N) and

having a saturation magnetization ($4\pi M_s$) of at least approximately 8 kilogauss (kG), an anisotropy field (H_k) within the range from approximately 15 to 300 oersteds (Oe) and a magnetic hysteresis (M-H) loop squareness ratio (remanent magnetization, M_r, to saturation magnetization, M_s) of at least approximately 0.90, wherein said alloy contains, by atomic percentage, at least approximately 15% cobalt (Co), and wherein said article has been heat treated at a temperature of no more than approximately 150° Celsius.

13. The method as recited in claim 12, wherein said Co—Fe—Cr—N alloy includes chromium (Cr) within the range from approximately 0 to 15 weight %.

14. The method as recited in claim 12, wherein the Co—Fe—Cr—N alloy contains cobalt (Co) within the range from approximately 30 to 60 weight %, iron (Fe) within the range from approximately 30 to 60 weight %, chromium (Cr) within the range from approximately 1 to 12 weight %, and nitrogen (N) within the range from approximately 0.7 to 5.0 weight %.

15. The method as recited in claim 12, wherein said depositing step is selected from the group consisting of sputtering, evaporation, molecular beam epitaxial growth, ion beam deposition and laser ablation.

16. The method as recited in claim 12, wherein said forming step further comprises depositing the elements of

said alloy without nitrogen on said substrate, and then adding nitrogen to said alloy by ion implantation.

17. The method as recited in claim 12, wherein said forming step further comprises sputter-depositing said magnetically soft thin film on said substrate with a deposition angle of at least approximately 10 degrees.

18. The method as recited in claim 12, wherein said forming step further comprises sputter-depositing said magnetically soft thin film on said substrate at ambient temperature and in the presence of an applied magnetic field having a strength greater than approximately 2.0 oersteds (Oe).

19. The method as recited in claim 12, further comprising, after said depositing step, the step of heat treating said magnetically soft thin film below a temperature of approximately 150° Celsius.

20. The method as recited in claim 12, wherein said depositing step further comprises depositing a plurality of magnetically soft thin film layers interleaved with corresponding plurality of dielectric spacer layers.

21. The method as recited in claim 12, further comprising the step of incorporating said magnetically soft thin film into an electromagnetic device selected from the group consisting of a microtransformer core, an inductor core, and a magnetic read-write head.

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MOLECULAR-DYNAMICS STUDY OF THIN IRON FILMS ON COPPER

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We have studied the structural stability of thin γ-iron films on Cu(001) and Cu(111) substrates using molecular-dynamics simulations in combination with a semiempirical model. Experimentally, the stability of such films has turned out to depend on (growth) temperature and film thickness. On increasing the thickness or decreasing the temperature the films undergo a structural change to the bcc structure, which is well reproduced by our simulations. An analysis of the local atomic environment of the films after the structural transformation shows that, especially on Cu(001), only parts of the film accomplish the transformation into the bcc structure. Considerations of the atomic displacements during the transformation allow us to give an explanation of the different stability of the films on Cu(001) and Cu(111) as well as the observed orientational relationships.

1. Introduction

The structural and magnetic properties of thin films usually differ from those of the corresponding bulk materials. This allows the study of systems under conditions which cannot be realized by bulk systems. A well-known example of this is the stabilization of fcc (γ-)iron on a copper substrate.

Bulk γ-Fe is only stable between 1184 and 1666 K, while at lower temperatures the stable phase is bcc (α-)iron.[1] Despite this, numerous experimental investigations have shown that it is possible to grow thin γ-Fe films epitaxially on Cu(001) or Cu(111) surfaces at room temperature.[2–11] The structural and magnetic properties of such films are still under discussion, due to the complex magnetic behavior of γ-Fe. Nevertheless, there is much experimental evidence that in the case of Fe on Cu(001) three different growth regimes have to be distinguished.[4,8] Films with a thickness of less than approximately five monolayers (ML) grown near or below room temperature show an fct-like structure with complex superstructures and a high-moment ferromagnetic state.[9,12] In the region of ≈ 5–10 ML a layer-by-layer growth of nearly isotropic fcc-Fe films is observed for growth at room temperature. In this regime the films show an antiferromagnetic layer-coupling in the interior of the films[13] and a ferromagnetic coupling of the surface layers.[4,8,12] Above a thickness of about 10 ML the fcc structure transforms into a twinned bcc structure.[7] Many different values for the maximum thickness of stable γ-Fe films on Cu(001) have been reported. The reason for these discrepancies is that the onset of the structural transformation depends on several parameters. It has been shown that lower growth temperatures lead to a lower critical thickness of the films, while a higher background pressure (for example by CO molecules) stabilizes the fcc structure. Moreover, subsequent cooling of γ-Fe films grown at room temperature might lead to the formation of the bcc structure as well as mild

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sputtering does.[7] The maximum thickness of isotropic γ-Fe films on Cu(111) surfaces is significantly lower than on Cu(001). Values between 2.3 and 6 ML have been observed.[3,10,11] Films thicker than these values undergo a structural transformation to the bcc structure similar to the case of Fe/Cu(001).

In this paper we focus on the stability of γ-Fe films on Cu(001) and Cu(111) surfaces. We have not looked at the differences between the first two growth regimes of Fe/Cu(001). These differences are certainly connected with changes in the magnetic structure of the films, which are beyond the scope of the model used in our computations. The rest of this paper is organized as follows. In the next section we give a short description of the model and the computational methods used in our calculations. The results obtained from computer simulations of Fe films on Cu(001) and Cu(111) are presented in Sec. 3. Finally, a short summary of the results is given in Sec 4.

2.   Computational Methods

In this study we used the method of molecular-dynamics (MD) simulations to investigate the structural stability of thin iron films on copper substrates. MD simulations have turned out to be a useful tool in the study of equilibrium and nonequilibrium phenomena of solids, like thermal properties, crack propagation, the contact mechanism, structural transformations, surface phonons, and many others.

Any kind of atomistic computer simulation requires a reliable model for the description of the interactions between the atoms. In our simulations we have made use of a model based on the embedded-atom method (EAM) of Daw and Baskes,[14,15] since this method is able to give a better description of the elastic properties of metals than ordinary pair potentials do. Within our simulations the energy of the system is written as

$$E = \sum_i F_{\alpha_i}(\rho_i) + \sum_i \sum_{j \neq i} \frac{Z_{\alpha_i}(r_{ij}) Z_{\alpha_j}(r_{ij})}{r_{ij}}, \quad (1)$$

where the indices i and j denote individual atoms; α_i, α_j = Fe, Cu refer to the species of the corresponding atoms, and r_{ij} is the separation of atoms i and j. The function F_{α_i} represents the embedding energy of atom i depending on the background charge density

$$\rho_i = \sum_{j \neq i} \rho_{\alpha_j}^{at}(r_{ij}), \quad (2)$$

which is superposition of the contributions $\rho_{\alpha_j}^{at}$ of all atoms j except i. The second term of Eq. (1) is a screened Coulomb potential with the effective charges Z_{α_i}.

The functions F_{α_i} and Z_{α_i} are cubic spline functions which have been fitted empirically to the properties of pure iron and copper. In the case of iron we fitted these functions using the experimental data of the lattice constant, cohesive energy, vacancy formation energy, elastic constants and some phonon frequencies of α-Fe. Details of these calculations and the parameters of the resulting functions can be found in Ref. 16. It has to be noted that this EAM potential is based on the data of ferromagnetic α-Fe only. As a consequence, this potential is best suited for a description of the high-moment ferromagnetic state of γ-Fe.[17] Nevertheless, this model has successfully been applied in simulations of the bcc-to-fcc transformation in iron–nickel alloys and should therefore also be suitable within the context of this work. For copper we used the functions of Gui et al.,[18] which were obtained by a fit to the experimental data of the lattice constant, cohesive energy, vacancy formation energy and elastic constants of copper. In both cases the atomic contributions to the background charge density $\rho_{\alpha_j}^{at}$ are calculated with the help of the wave functions of the valence electrons in free atoms tabulated by Clementi and Roetti.[19]

In an atomistic MD simulation of a solid, the classical equations of motions of the atoms are numerically integrated and thermodynamical averages are calculated from the resulting trajectories.[20] For the integration of the equations of motions we adopted the velocity Verlet algorithm (see, for example, Ref. 20) with a time increment of 1.5 fs and the Nosé–Hoover thermostat method, which leads to a canonical distribution of the atomic configurations.[21] Artificial surface effects have been minimized through the use of periodic boundary conditions in the directions perpendicular to the film normal, while changes in the size and shape of the simulation cell were allowed using the scheme of Parrinello and Rahman.[22]

The initial configurations of our simulations consisted of regular arrangements of atoms on a perfect fcc lattice with randomly chosen velocities

according to the Maxwell–Boltzmann distribution. The following geometries have been used: 7 ML Fe on Cu(001), 15 ML Fe on Cu(001), 6 ML Fe on Cu(111) and 14 ML Fe on Cu(111). Since every real film inevitably contains a number of defects, we introduced about 2 % of vacancies into the systems. This high concentration was chosen in order to guarantee a significant number of vacancies in the simulation box and to emulate the effect of other defects like dislocations and grain boundaries. The influence of these defects has been studied by additional simulations of defect-free films in the case of Fe/Cu(001). The total size of the configurations was about 21^3 lattice constants, containing approximately 37 000 atoms. The surface normal was oriented along the z-axis of the simulation cell. Actually, our systems contained two free surfaces: one iron surface at the top of the system and one copper surface at the bottom. However, we have studied only the iron surface except for the relaxation of the interlayer spacing, which we have analyzed at both surfaces as well as in the vicinity of the Fe/Cu interface. In order to check for finite-size effects, additional simulations have been carried out using configurations with a lateral size of 10, 15, 30 and 40 lattice constants.

At the beginning of the simulation runs the initial configurations had to be equilibrated at the desired temperature. In order to do this, we simulated the systems over a period of 500 simulation steps and rescaled the instantaneous temperature of the systems at every 50th step. Afterwards the normal parts of the simulation runs began, which consisted of a sequence of successive short simulations with a length of 300 time steps. From the mean positions of the atoms during these runs we calculated the percentage of iron atoms with a local bcc environment. The simulation runs ended when no significant change of this value was observed for a longer period. The structure of the local environment of an atom was determined by the following procedure. An atom was assumed to have a bcc environment if the standard deviation of the distance of its ten nearest neighbors was larger than $0.02\,a_B$. Here we make use of the fact that the first nearest-neighbor shell of the bcc lattice contains only eight atoms while the fcc lattice has a coordination number of 12. Therefore, the 12 nearest neighbors of an atom in an fcc environment all belong to the same neighbor shell, whereas in a bcc environment two different neighbor shells are involved. Two

points have to be noted. First, our method for the determination of the local environment of an atom fails in the case of a surface atom due to the different coordination of these atoms. Therefore, we have discarded the surface atoms in the calculation of the percentage of bcc iron. Second, it is rather important that we have used mean atomic positions averaged over 300 simulation steps. If one uses the actual positions of the atoms at one time, thermal fluctuations lead to a much broader distribution of the neighbor separations, making it impossible to distinguish between local crystal structures. Problems arise from the diffusion of atoms in the case of the presence of vacancies. If an atom moves into the position of a neighboring vacancy, the mean position of this atom calculated during the hopping process is almost meaningless. This might lead to a slight overestimation of the fraction of atoms with a bcc environment. However, since such processes are rather rare, the resulting error is small and should not influence the observed general tendencies.

3. Results

3.1. *Fe on Cu(001)*

The interatomic potentials we used in our simulations have only been constructed on the basis of bulk properties of iron and copper. Therefore, it seemed appropriate to check the reliability of the EAM model in the context of surface phenomena. In order to do this, we compared the interlayer distances near the surface predicted by the model with experimental results. As will be discussed below, simulations of the configurations with 7 and 15 ML Fe/Cu(001) without vacancies showed no structural change at 300 K. From these simulations we derived an inward relaxation of the first copper layer by 3%. This is somewhat larger than the experimental values, which are in the range of 1–2%, but compares well with the results of other interatomic potentials (see Ref. 23 and references therein). At the iron surface we found an inward relaxation of the outermost layer by nearly 7%. In this case the experimentally observed value depends on the magnetic structure of the film. Wuttig *et al.* report an inward relaxation of 2% for a 5 ML film, whereas they found a considerable outward relaxation in films with 6–11 ML Fe/Cu(001).[7] This difference is caused by the antiferromagnetic coupling in the interior of
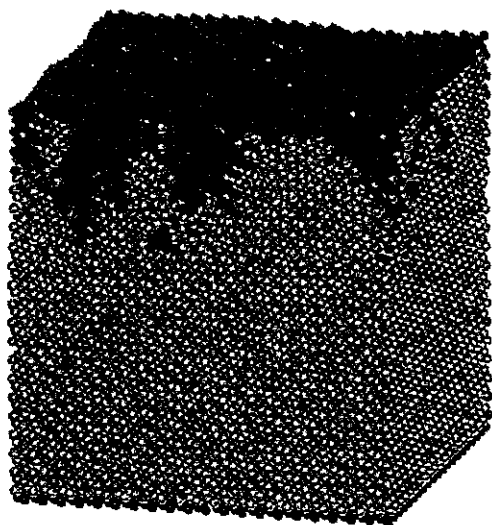
Fig. 1.   Resulting configuration of 15 ML Fe/Cu(001) with 2% vacancies after a simulation time of 13.5 ps. The blue atom indicates a local bcc environment, while atoms with an fcc environment are drawn in orange.
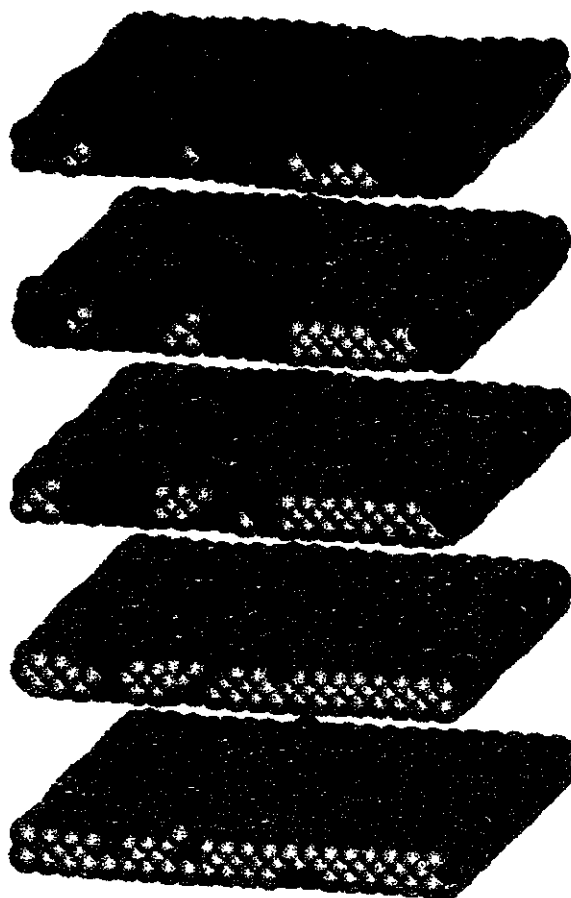
Fig. 2.   Iron film from Fig. 1 drawn slicewise.

the thicker films, which reduces the layer separation of the deeper layers. Again, it turns out that the EAM model is best suited for a description of ferromagnetic γ-Fe. The large value of the relaxation we find is a consequence of the fact that the EAM model predicts rather low elastic constants for γ-Fe at low temperatures.[17] In addition to the relaxation of the surface layers, we also studied the interlayer distances near the iron–copper interface in our systems. Here we find a pronounced increase of the separation of the first two iron layers by 6%. Although this effect might be an artifact of the short interaction range of the repulsive pair potentials in the EAM model, it would be interesting to check this result experimentally.

The main subject of this work is the investigation of the structural stability of iron films on copper substrates. Figure 1 shows the resulting (stable) configuration of the system with 15 ML Fe/Cu(001) and 2% vacancies after simulation over a period of 13.5 ps. The blue color indicates atoms with a local bcc environment, while atoms with an fcc environment are drawn in orange. From this figure it is clearly visible that not all of the iron atoms transformed into the bcc structure and that the amount of bcc iron decreases in the interior of the film. The resulting complicated domain structure consisting of channels of α-Fe going down from the surface can be seen in detail in Fig. 2, where the iron film is shown slicewise. The fact that only a part of the film transformed into the bcc structure has also been observed in experiments.[24] However, to the best of our knowledge no experiments have so far revealed the topology of the resulting domain structure.

In Figs. 3 and 4 the surface structures of the initial configuration and the transformed film are compared.   While in Fig. 3 the regular square structure of the fcc unit cells can be seen, the stretched hexagons drawn in Fig. 4 are characteristic of $(110)_{bcc}$ planes. The occurrence of two different orientations of the hexagons is a consequence of the fact that the transformed film possesses a twin structure with $(\bar{1}12)$ twinning planes and $[1\bar{1}1]$ shear directions.   This twin system is rather typical of the bcc structure.[25] The formation of twin variants reduces the atomic movement necessary for accomplishing the structural transformation. Without the twinning plane the transformation of fcc into bcc would require a macroscopic deformation of the
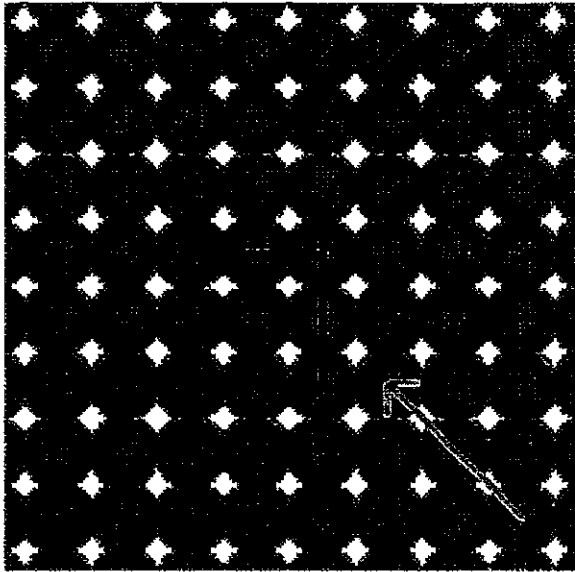
Fig. 3. Surface of the initial configuration of the system in Fig. 1. The dark arrow indicates the $[010]_{fcc}$ direction, the light arrow $[\bar{1}10]_{fcc}$.
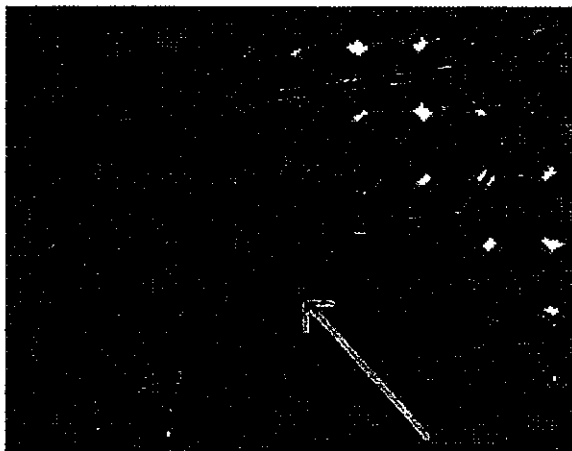
Fig. 4. Surface of the system in Fig. 1. The distorted hexagons are typical of $(110)_{bcc}$. The dark arrow indicates the $[001]_{bcc}$ direction, the light arrow $[1\bar{1}1]_{bcc}$.

iron film, which is rather unfavorable since the copper substrate retains its fcc structure. We generally find from our simulations a separation of 5–10 $(\bar{1}12)_{bcc}$ planes between the twinning planes. The same width has been found in simulations of systems with lateral sizes of 10, 15, 30 and 40 lattice constants. This shows that the width of the stripes is not influenced by finite-size effects, but is determined by the transformation process and elastic energies. If one compares Figs. 3 and 4, one can see that the
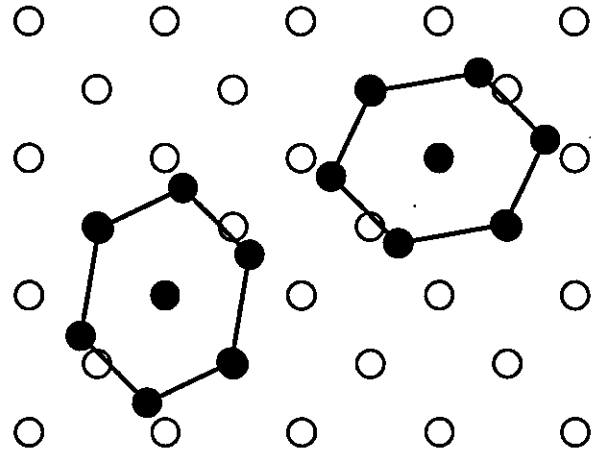
Fig. 5. Formation of $(110)_{bcc}$ hexagons (full circles) in Pitsch orientation from a $(001)_{fcc}$ plane (open circles).

close-packed $[110]_{fcc}$ direction is transformed into the $[1\bar{1}1]_{bcc}$ direction without any rotation. This orientational relationship combined with the plane condition $(001)_{fcc} \parallel (110)_{bcc}$, given by the film geometry, is called the Pitsch orientation.[26] It has experimentally been observed by Wuttig *et al.*[7] in their scanning-tunneling-microscopy investigations of Fe/Cu(001). These authors also report the formation of twin variants similar to those we find in our simulations. The orientational relationships are further illustrated by Fig. 5, which schematically shows two variants of the distorted hexagons of the $(001)_{bcc}$ planes in comparison to the $(001)_{fcc}$ planes. The lattice constants have been chosen in such a manner that the atomic volumes of the two structures are equal, which nearly meets the situation of bcc iron and fcc copper. From Fig. 5 it can be seen that two other crystallographically equivalent variants of the bcc structure could be formed. However, due to the finite size of the systems, only two variants occurred simultaneously in the simulations.

The amount of iron atoms transformed from fcc into bcc, which we found in our simulations, depends both on temperature and on the thickness of the film. In Table 1 we present the results which we obtained from simulations of Fe films on Cu(001) with 2% vacancies at 50 and 300 K. The fcc structure remained more or less stable in both films at the higher temperature (the small fractions of α-Fe we observed are probably artefacts of diffusion processes), whereas at 50 K both films partially transformed into the

Table 1. Percentage of iron
transformed from fcc into bcc
in a Fe/Cu(001) film with 2%
vacancies after a simulation
time of 9 ps.

ML Fe	50 K	300 K
7	13.68%	0.49%
15	43.28%	0.03%

Table 2. Percentage of iron
transformed from fcc into bcc
in a Fe/Cu(001) film without
vacancies after a simulation
time of 9 ps.

ML Fe	50 K ·	300 K
7	1.32%	0.00%
15	17.93%	0.00%

bcc structure, with the thicker film showing a significantly higher amount of α-Fe. This behavior reflects the experimental observation that the fcc structure of Fe/Cu(001) gets more and more unstable with increasing film thickness and/or decreasing temperature. However, some differences between our simulations and experimental results have to be noted. In contrast to our simulations, most experimental investigations did not show a stable fcc structure in films with a thickness of 15 ML Fe/Cu(001) at room temperature. Different results are probably related to higher background pressures. This discrepancy is probably caused by the permanent perturbation of the surface and the unavoidable presence of surface steps under experimental conditions. The neglect of these effects might artificially stabilize the fcc structure in the simulation. So far the small fraction of α-Fe we found in the thin film at 50 K has also not been observed in experiments. The corresponding bcc regions appear directly at the surface of the film. It is, therefore, likely that they are connected with the wrong interlayer relaxation at the surface and are caused by the insufficient treatment of magnetic effects by our model.

So far we have presented only results obtained from configurations containing 2% vacancies. Simulations using configurations without defects yielded somewhat different results. In Table 2 the amount of transformed iron atoms in these films is reported. From this table it can be seen that the amount of transformed iron atoms in these perfect films is strongly reduced with respect to Table 1. More serious than this difference in the amount of transformed iron, however, is the fact that the orientational relationship, which we observed in the films with defects, does not hold for the perfect films. While still the $(001)_{fcc}$ planes are transformed into $(110)_{bcc}$ planes, i.e. $(001)_{fcc} \parallel (110)_{bcc}$, the relationship $[100]_{fcc} \parallel$

$[1\bar{1}0]_{bcc}$ holds instead of $[110]_{fcc} \parallel [1\bar{1}1]_{bcc}$. These orientational relationships correspond exactly to the well known purely distortive Bain transformation. A schematic view of both possible variants is given in Fig. 6. However, we did not observe the formation of a twinned structure, but instead growth of symmetrically arranged isolated islands of α-Fe within the matrix of γ-Fe.

An explanation of the different transformation behavior of films with and without defects might be given by the total displacement of the atoms during the transformation. The energy of the interface between a region of α-Fe and the copper substrates or the surrounding γ-Fe matrix should be approximately proportional to the square of the displacement (misfit) of the atoms. The sum of the squared displacements of the atoms of one hexagon in Fig. 5 is 0.24 in terms of the fcc lattice constant, while in Fig. 6 it is only 0.14 (the sum of the absolute values of the displacements are 1.02 and 0.89 fcc lattice constants, respectively). Therefore, it is clear that
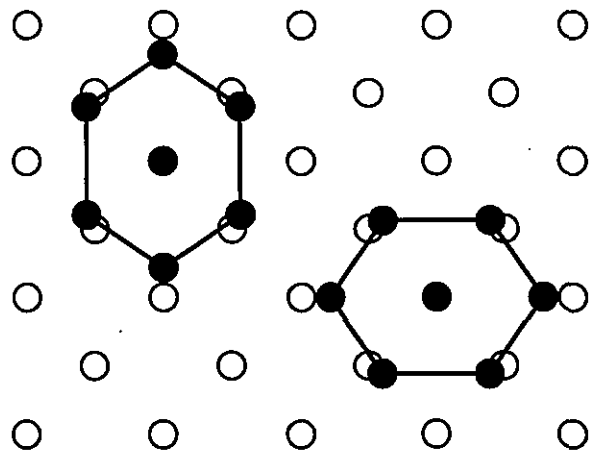
Fig. 6.   Formation of $(110)_{bcc}$ hexagons (full circles) in Bain orientation from a $(001)_{fcc}$ plane (open circles).

the system without vacancies prefers the transformation according to Fig. 6. However, what is then the reason for the different behavior of Fe/Cu(001) with defects? The vacancies give the system much more freedom to shield the elastic stress originating from the interface. Thus, the influence of other factors on the transformation path might grow due to the presence of defects. An important difference between the Pitsch orientation and the Bain orientation is the fact that the Pitsch orientation is a shearlike transformation while the Bain transformation is purely distortive. Hence the Pitsch orientation might be realized in systems with defects due to a lower activation energy along the transformations path. Another advantage of the Pitsch orientation is that it leads to the formation of long homogeneous stripes. The resulting twin structure requires much less interface energy between the different variants of α-Fe than the spotlike islands formed in the case of the Bain transformation.

Our explanation of the transformation behavior given above is supported by simulations of Fe/Ni(001),[27] similar to the simulations presented in this work. In these simulations the Bain orientation occurs only as an intermediate phenomenon during the precipitation of the transformation. With an increasing amount of α-Fe, more and more regions of the system switch to the Pitsch orientation. After the transformation is completed, only this orientation is present, regardless of the presence of vacancies. On the Ni substrate the sum of the squared displacements of the atoms at the interface gives values of 0.21 and 0.12 for the Pitsch and the Bain orientation, respectively (the same units as before). Thus, according to our arguments, the realization of the Pitsch orientation on the nickel substrate requires less energy than on the copper substrate and can even be realized without the help of the vacancies.

3.2. Fe on Cu(111)

From simulations of Fe/Cu(111) films containing 2% vacancies we found that γ-Fe is generally less stable on this surface than on Cu(001). The amount of iron transformed into the bcc structure in these films is presented in Table 3. The presence of small amounts of α-Fe at 300 K and in the thin film at 50 K should have the same reasons as in the case of Fe/Cu(001),

Table 3. Percentage of iron transformed from fcc into bcc in a Fe/Cu(111) film with 2% vacancies after a simulation time of 9 ps.

ML Fe	50 K	300 K
6	8.43%	1.10%
14	91.673%	1.46%

which have already been discussed. The orientational relationships we observed in these simulations are $(111)_{fcc} \parallel (110)_{bcc}$ and $[1\bar{1}0]_{fcc} \parallel [1\bar{1}1]_{bcc}$, which is the Kurdjumov–Sachs orientation. This is in accordance with experimental observations.[3,10,11] As in the case of Fe/Cu(001) (with defects), the structural transformation in the simulations of Fe/Cu(111) led to the formation of two variants of the bcc structure forming a twin system. Here, too, the finite size of the system prohibited the formation of all crystallographically equivalent variants. In Fig. 7 we show the formation of the distorted hexagon of the $(110)_{bcc}$ planes in comparison to a $(111)_{fcc}$ plane. As before, the lattice constants have been chosen in order to get the same atomic volume in the two structures. The sum of the squared displacements of the atoms of one hexagon in Fig. 7 is 0.06 in terms of
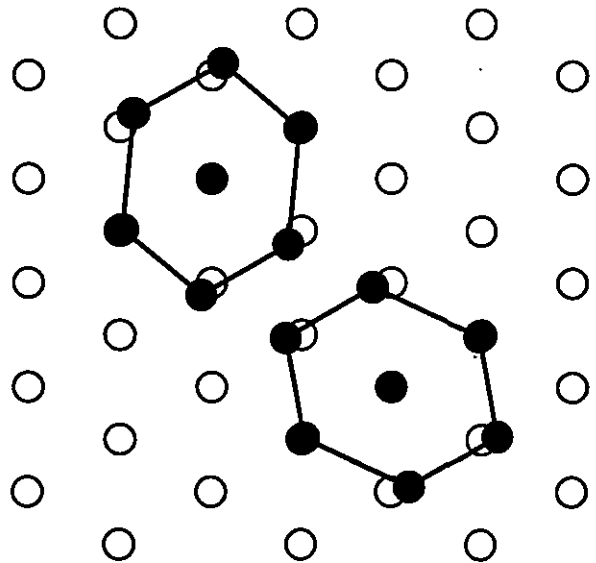
Fig. 7. Formation of $(110)_{bcc}$ hexagons (full circles) in Kurdjumov–Sachs orientation from a $(111)_{fcc}$ plane (open circles).

the fcc lattice constant (the sum of the absolute displacements is 0.52 fcc lattice constants). These values are significantly lower than in the case of Fe/Cu(001). Therefore, according to the arguments given above, the stronger tendencies of Fe/Cu(111) to accomplish the structural transformation can be explained by a lower interface energy.

4.   Summary and Conclusions

We have done MD simulations of thin films of iron on Cu(001) and Cu(111) substrates using a semiempirical EAM model. In these simulations we were able to reproduce the basic properties of the experimentally observed structural transformation from γ-Fe into α-Fe in such films. In particular, we found a growing tendency of the films to undergo the transformation with increasing film thickness and decreasing temperature. Minor differences between experimental results and our simulations can be explained by the neglect of the growth process during the simulations and the insufficient treatment of magnetism by the EAM model in our calculations.

We have analyzed the local atomic environment of configurations resulting from simulations of Fe/Cu(001). This analysis revealed that actually only a part of the iron atoms transformed into the bcc structure. A visualization of the atomic configuration showed that the amount of α-iron is highest near the surface of the film and decreases in its interior. In these simulations the experimentally observed Pitsch orientation was realized as long as defects (vacancies) were present in the system. During the transformation, stripes of two crystallographically equivalent variants of the bcc structure were formed, which are separated by twinning boundaries. Experimentally, a similar structure has been found in STM investigations.[7] In contrast to this, simulations of perfect films without vacancies led to different results. In this case the structural transformation was accomplished by a purely distortive Bain transformation and no twin system was formed. This emphasizes the influence of defects on the properties of structural transformations.

Simulations of Fe/Cu(111) showed a significantly reduced stability of the fcc structure in comparison to the simulations of Fe/Cu(001). In these films the bcc structure grew in the Kurdjumov–Sachs orientation and again the formation of a twin system was observed. It is rather remarkable that the simulations of thin films on both substrates revealed the experimentally observed orientational relationships.

The different transformation paths realized in our simulations can be explained in a hand-waving manner by considerations of the total displacement of the atoms during the transformation. From this we conclude that especially the energy required by the formation of an interface between α-iron and the substrate is rather crucial for the structural stability of the films. The films remain stable until this interface energy is balanced by the structural energy difference between α- and γ-Fe growing with increasing film thickness and decreasing temperature.

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(12) **United States Patent**
Pinarbasi

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(45) **Date of Patent:** **Sep. 25, 2001**

(54) **SPIN VALVE SENSOR WITH STABLE ANTIPARALLEL PINNED LAYER STRUCTURE EXCHANGE COUPLED TO A NICKEL OXIDE PINNING LAYER**

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(52) **U.S. Cl.** **360/324.11**; 360/314
(58) **Field of Search** 360/324–327

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(57) **ABSTRACT**

A spin valve sensor has a pinned layer structure that has a net positive stress induced uniaxial anisotropy that promotes a pinning of the pinned layer structure in a pinned direction for stabilizing the pinning of the pinned layer structure at high temperatures near to a blocking temperature of a pinning layer which is exchange coupled to the pinned layer.

32 Claims, 9 Drawing Sheets

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 10

FIG. 8

FIG. 9

FIG. 11
(ABS)

FIG. 12

COMPRESSION

226

CAP   30Å   Ta

I_S

(AFM)

306

AP1
214

(I)   5Å   NiFe

⊙   15 – 20Å   HIGH + MS

5Å   Co or CoFe

8Å   Ru or Rh

5Å   Co or CoFe

AP2
218

⊗   10 – 20Å   HIGH + MS

10 – 20Å   Co or CoFe

308   (S)   24Å   Cu

210   15Å   CoFe

(F)   60Å   NiFe

(I)   10Å   Ta

(G1)

ea

ea

300

208

222

234

220

232

228

230

240

236

242

238

202

207

206

302

304

AP PINNED LAYER
STRUCTURE 204

FIG. 13

5Å Co or CoFe	242
15–20Å $Ni_{45}Fe_{55}$ (+MS)	220
5Å $Ni_{80}Fe_{20}$	234
(AFM) 425Å NiO	222

AP1 214

FIG. 14

5Å Co or CoFe	242
15–20Å NiFeNb (+MS)	220
5Å $Ni_{80}Fe_{20}$	234
(AFM) 425Å NiO	222

AP1 214

FIG. 15

5Å Co or CoFe	242
15–20Å $Ni_{50}Co_{50}$ (+MS)	220
5Å $Ni_{80}Fe_{20}$	234
(AFM) 425Å NiO	222

AP1 214

FIG. 16

FIG. 17

1

SPIN VALVE SENSOR WITH STABLE ANTIPARALLEL PINNED LAYER STRUCTURE EXCHANGE COUPLED TO A NICKEL OXIDE PINNING LAYER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a spin valve sensor with a stable antiparallel pinned layer structure exchange coupled to a nickel oxide pinning layer and, more particularly, to an antiparallel pinned layer structure which has at least first and second antiparallel pinned layers wherein at least one of the antiparallel pinned layers includes a thin film that has positive magnetostriction.

2. Description of the Related Art

A high performance read head employs a spin valve sensor for sensing magnetic fields on a moving magnetic medium, such as a rotating magnetic disk or a linearly moving magnetic tape. The sensor includes a nonmagnetic electrically conductive first spacer layer sandwiched between a ferromagnetic pinned layer and a ferromagnetic free layer. An antiferromagnetic pinning layer interfaces the pinned layer for pinning the magnetic moment of the pinned layer 90° to an air bearing surface (ABS) which is an exposed surface of the sensor that faces the magnetic medium. First and second leads are connected to the spin valve sensor for conducting a sense current therethrough. The magnetic moment of the free layer is free to rotate in positive and negative directions from a quiescent or bias point position in response to positive and negative magnetic fields from a moving magnetic medium. The quiescent position is the position of the magnetic moment of the free layer when the sense current is conducted through the sensor without magnetic field signals from a rotating magnetic disk. The quiescent position of the magnetic moment of the free layer is preferably parallel to the ABS. If the quiescent position of the magnetic moment is not parallel to the ABS the positive and negative responses of the free layer will not be equal which results in read signal asymmetry which is discussed in more detail hereinbelow.

The thickness of the spacer layer is chosen so that shunting of the sense current through the sensor and a magnetic coupling between the free and pinned layers are minimized. This thickness is less than the mean free path of electrons conducted through the sensor. With this arrangement, a portion of the conduction electrons are scattered by the interfaces of the spacer layer with the pinned and free layers. When the magnetic moments of the pinned and free layers are parallel with respect to one another scattering is minimal and when their magnetic moments are antiparallel scattering is maximized. An increase in scattering of conduction electrons increases the resistance of the spin valve sensor and a decrease in scattering of the conduction electrons decreases the resistance of the spin valve sensor. Changes in resistance of the spin valve sensor is a function of $\cos \theta$, where θ is the angle between the magnetic moments of the pinned and free layers. This resistance, which changes due to changes in scattering of conduction electrons, is referred to in the art as magnetoresistance (MR). A spin valve sensor has a significantly higher magnetoresistive (MR) coefficient than an anisotropic magnetoresistive (AMR) sensor. For this reason it is sometimes referred to as a giant magnetoresistive (GMR) sensor. Magnetoresistive coefficient is dr/R where dr is the difference in resistance between minimum resistance, where the magnetic moments of the free and pinned layers are parallel, and

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maximum resistance, where the magnetic moments of the free and pinned layers are antiparallel, and R is the minimum resistance, where the magnetic moments of the free and pinned layers are parallel.

When a spin valve sensor employs a single pinned layer it is referred to as a simple spin valve. Another type of spin valve sensor is an antiparallel (AP) pinned spin valve sensor. The AP pinned spin valve sensor differs from the simple spin valve sensor in that an AP pinned structure has multiple thin film layers instead of a single pinned layer. The AP pinned structure has an AP coupling layer sandwiched between first and second ferromagnetic pinned layers. The first pinned layer has its magnetic moment oriented in a first direction by exchange coupling to the antiferromagnetic pinning layer. The second pinned layer is immediately adjacent to the spacer layer and is antiparallel coupled to the first pinned layer because of the minimal thickness (in the order of 8 Å) of the AP coupling film. Accordingly, the magnetic moment of the second pinned layer is oriented in a second direction that is antiparallel to the direction of the magnetic moment of the first pinned layer.

The AP pinned structure is preferred over the single pinned layer because the magnetic moments of the first and second pinned layers of the AP pinned structure subtractively combine to provide a net magnetic moment that is less than the magnetic moment of the single pinned layer. The direction of the net moment is determined by the thicker of the first and second pinned layers. A reduced net magnetic moment equates to a reduced demagnetization (demag) field from the AP pinned structure. Since the antiferromagnetic exchange coupling is inversely proportional to the net pinning moment, this increases exchange coupling between the first pinned layer and the pinning layer. The AP pinned spin valve sensor is described in commonly assigned U.S. Pat. No. 5,465,185 to Heim and Parkin which is incorporated by reference herein.

The first and second pinned layers of the AP pinned structure are typically made of cobalt (Co). Unfortunately, cobalt has high coercivity, high magnetostriction and low resistance. When the first and second pinned layers of the AP pinned structure are formed they are sputter deposited in the presence of a magnetic field that is oriented perpendicular to the ABS. This sets the easy axis (e.a.) of the pinned layers perpendicular to the ABS. During a subsequent making of the magnetic head, the AP pinned structure is subjected to magnetic fields that are directed parallel to the ABS. These fields can cause the magnetic moment of the first pinned layer to switch from a desirable first direction perpendicular to the ABS to an undesirable second direction which is not perpendicular to the ABS. The same occurs to the second pinned layer of the AP pinned structure. If the coercivity of the first pinned layer of the AP pinned structure is higher than the exchange coupling between the first pinned layer and the pinning layer the exchange coupling will not return the magnetic moment of the first pinned layer to its original direction. This ruins the read head. This problem can occur during operation of the magnetic head in a disk drive when a magnetic field stronger than the exchange field of the first pinned layer of the AP pinned structure is exerted on the read head.

Efforts continue to increase the MR coefficient (dr/R) of GMR heads. An increase in the MR coefficient equates to higher bit density (bits/square inch of the rotating magnetic disk) read by the read head. When these efforts are undertaken it is important that the coercivity (H_C) of the pinned layer next to the pinning layer not exceed the exchange coupling field therebetween.

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SUMMARY OF THE INVENTION

The present invention provides a highly stabilized antiparallel (AP) pinned layer structure which is exchange coupled to a nickel oxide (NiO) pinning layer. At least one of the AP pinned layers includes a thin film composed of a material that has a positive magnetostriction. In an embodiment of the invention, where only one of the AP pinned layers has a thin film composed of a material having positive magnetostriction, the AP pinned layer structure is exchange coupled to the nickel oxide (NiO) pinning layer. With this arrangement the AP pinned layer that is exchange coupled to the nickel oxide (NiO) pinning layer has a stress induced uniaxial anisotropy which is oriented perpendicular to the surface planes of the layers of the spin valve sensor. This uniaxial anisotropy promotes a pinning of the magnetic moment of the AP pinned layer perpendicular to the planes of the layers caused by the exchange coupling of the AP pinned layer to the nickel oxide (NiO) pinning layer. The stress induced uniaxial anisotropy of the AP pinned layer is in the same direction as the orientation of the magnetic moment of the AP pinned layer due to the exchange coupling with the nickel oxide pinning layer. Accordingly, when the pinning strengths of the nickel oxide (NiO) pinning layer is degraded in a magnetic disk drive with operating temperatures as high as 150° C. the stress induced anisotropy, due to the positive magnetostriction of the film in the AP pinned layer exchange coupled to the nickel oxide (NiO) pinning layer, maintains the orientation of the magnetic moment of the AP pinned layer perpendicular to the planes of the layers of the spin valve sensor.

In my investigation I found that when the positive magnetostriction film of the AP pinned layer interfaces the AP coupling layer, which is typically ruthenium (Ru), the performance of the spin valve sensor is degraded. This has been overcome by providing the AP pinned layer with a thin film of cobalt (Co) or cobalt iron (CoFe) between the positive magnetostriction thin film and the ruthenium (Ru) AP coupling layer. I further found that when the positive magnetostriction thin film is a material other than nickel iron (NiFe) the performance of the spin valve sensor is degraded when the positive magnetostriction thin film interfaces the nickel oxide (NiO) pinning layer. This problem has been overcome by providing the AP pinned layer with a nickel iron (NiFe) thin film between the positive magnetostriction thin film and the nickel oxide (NiO) pinning layer.

In a preferred embodiment the second AP pinned layer, which interfaces the spacer layer, also includes a thin film layer that has positive magnetostriction. This further supports pinning of the first AP pinned layer by antiparallel exchange coupling between the first and second AP pinned layers. In the same manner as the first AP pinned layer the second AP pinned layer may include a thin film of cobalt (Co) or cobalt iron (CoFe) between the positive magnetostriction thin film and the AP coupling layer of ruthenium (Ru). I have further enhanced the performance of the spin valve sensor by providing the second AP pinned layer with a third thin film which distinguishes it from the first AP pinned layer. The second AP pinned layer may be provided with a thin film of cobalt (Co) or cobalt iron (CoFe) between the positive magnetostriction thin film and the copper (Cu) spacer layer. The preferred AP pinned layer structure includes all of the thin films, as described hereinabove, exchange coupled to a nickel oxide (NiO) pinning layer. However, in a broad aspect of the invention only one of the AP pinned layers has a positive magnetostriction thin film, with or without the other thin films, exchange coupled to

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pinning layers which may be composed of antiferromagnetic materials other than nickel oxide (NiO). The above arrangement may be applied to either a top or a bottom spin valve sensor wherein the pinning layer is at the bottom or at the top respectively of the spin valve sensor. Further, the present invention applies to a single pinned layer structure which includes a positive magnetostriction thin film and a thin film of cobalt (Co) or cobalt iron (CoFe) located between the positive magnetostriction thin film and the copper (Cu) spacer layer. This single pinned layer structure may further include a thin film of nickel iron (NiFe) between the positive magnetostriction thin film and the nickel oxide (NiO) pinning layer when the positive magnetostriction thin film is composed of a material other than nickel iron (NiFe).

An object of the present invention is to provide an antiparallel (AP) pinned layer structure which has a net positive stress induced uniaxial anisotropy that supplements a pinning field between the pinned layer structure and a pinning layer.

Another object is to provide a highly stable antiparallel pinned layer structure that is exchange coupled to a nickel oxide (NiO) pinning layer during operating temperatures of the AP pinned layer structure in a magnetic disk drive.

A further object is to provide one or both of the AP pinned layers of an AP pinned layer structure with a thin film composed of a positive magnetostriction material.

Other objects and attendant advantages of the invention will be appreciated upon reading the following description taken together with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plan view of an exemplary magnetic disk drive;

FIG. 2 is an end view of a slider with a magnetic head of the disk drive as seen in plane 2—2;

FIG. 3 is an elevation view of the magnetic disk drive wherein multiple disks and magnetic heads are employed;

FIG. 4 is an isometric illustration of an exemplary suspension system for supporting the slider and magnetic head;

FIG. 5 is an ABS view of the magnetic head taken along plane 5—5 of FIG. 2;

FIG. 6 is a partial view of the slider and a piggyback magnetic head as seen in plane 6—6 of FIG. 2;

FIG. 7 is a partial view of the slider and a merged magnetic head as seen in plane 7—7 of FIG. 2;

FIG. 8 is a partial ABS view of the slider taken along plane 8—8 of FIG. 6 to show the read and write elements of the piggyback magnetic head;

FIG. 9 is a partial ABS view of the slider taken along plane 9—9 of FIG. 7 to show the read and write elements of the merged magnetic head;

FIG. 10 is a view taken along plane 10—10 of FIGS. 6 or 7 with all material above the coil layer and leads removed;

FIG. 11 is an isometric ABS illustration of a read head which employs an AP pinned spin valve (SV) sensor;

FIG. 12 is an ABS illustration of the present AP pinned structure in a bottom spin valve sensor;

FIG. 13 is an ABS illustration of the present AP pinned layer structure in a top spin valve sensor;

FIG. 14 is an ABS illustration of the first AP pinned layer with a positive magnetostriction thin film of $Ni_{45}Fe_{55}$;

FIG. 15 is an ABS illustration of the first AP pinned layer with a positive magnetostriction thin film composed of nickel iron niobium (NiFeNb);

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FIG. **16** is an ABS illustration of a first AP pinned layer with a positive magnetostriction thin film composed of nickel cobalt ($Ni_{50}Co_{50}$); and

FIG. **17** is an ABS illustration of a single pinned layer structure having a positive magnetostriction thin film in a spin valve sensor.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

MAGNETIC DISK DRIVE

Referring now to the drawings wherein like reference numerals designate like or similar parts throughout the several views, FIGS. **1–3** illustrate a magnetic disk drive **30**. The drive **30** includes a spindle motor **32** that supports and rotates a magnetic disk **34**. The spindle **32** is rotated by a motor **36** that is controlled by a motor controller **38**. A slider **42** with a combined read and write magnetic head **40** is supported by a suspension **44** and actuator arm **46** which is selectively rotatably positioned by an actuator **47**. A plurality of disks, sliders and suspensions may be employed in a large capacity direct access storage device (DASD) as shown in FIG. **3**. The suspension **44** and actuator arm **46** position the slider **42** so that the magnetic head **40** is in a transducing relationship with a surface of the magnetic disk **34**. When the disk **34** is rotated by the motor **36** the slider is supported on a thin (typically, 0.05 μm) cushion of air (air bearing) between the surface of the disk **34** and the air bearing surface (ABS) **48**. The magnetic head **40** may then be employed for writing information to multiple circular tracks on the surface of the disk **34**, as well as for reading information therefrom. Processing circuitry **50** exchanges signals, representing such information, with the head **40**, provides motor drive signals for rotating the magnetic disk **34**, and provides control signals to the actuator **47** for moving the slider to various tracks. In FIG. **4** the slider **42** is shown mounted to a suspension **44**. The components described hereinabove may be mounted on a frame **54** of a housing, as shown in FIG. **3**.

FIG. **5** is an ABS view of the slider **42** and the magnetic head **40**. The slider has a center rail **56** that supports the magnetic head **40**, and side rails **58** and **60**. The rails **56, 58** and **60** extend from a cross rail **62**. With respect to rotation of the magnetic disk **34**, the cross rail **62** is at a leading edge **64** of the slider and the magnetic head **40** is at a trailing edge **66** of the slider.

FIG. **6** is a side cross-sectional elevation view of a piggyback magnetic head **40**, which includes a write head portion **70** and a read head portion **72**, the read head portion employing a spin valve sensor **74** of the present invention. FIG. **8** is an ABS view of FIG. **6**. The spin valve sensor **74** is sandwiched between nonmagnetic electrically insulative first and second read gap layers **76** and **78**, and the read gap layers are sandwiched between ferromagnetic first and second shield layers **80** and **82**. In response to external magnetic fields, the resistance of the spin valve sensor **74** changes. A sense current I_s conducted through the sensor causes these resistance changes to be manifested as potential changes. These potential changes are then processed as readback signals by the processing circuitry **50** shown in FIG. **3**.

The write head portion **70** of the magnetic head **40** includes a coil layer **84** sandwiched between first and second insulation layers **86** and **88**. A third insulation layer **90** may be employed for planarizing the head to eliminate ripples in the second insulation layer caused by the coil layer **84**. The first, second and third insulation layers are referred to in the

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art as an "insulation stack". The coil layer **84** and the first, second and third insulation layers **86, 88** and **90** are sandwiched between first and second pole piece layers **92** and **94**. The first and second pole piece layers **92** and **94** are magnetically coupled at a back gap **96** and have first and second pole tips **98** and **100** which are separated by a write gap layer **102** at the ABS. An insulation layer **103** is located between the second shield layer **82** and the first pole piece layer **92**. Since the second shield layer **82** and the first pole piece layer **92** are separate layers this head is known as a piggyback head. As shown in FIGS. **2** and **4**, first and second solder connections **104** and **106** connect leads from the spin valve sensor **74** to leads **112** and **114** on the suspension **44**, and third and fourth solder connections **116** and **118** connect leads **120** and **122** from the coil **84** (see FIG. **8**) to leads **124** and **126** on the suspension.

FIGS. **7** and **9** are the same as FIGS. **6** and **8** except the second shield layer **82** and the first pole piece layer **92** are a common layer. This type of head is known as a merged magnetic head. The insulation layer **103** of the piggyback head in FIGS. **6** and **8** is omitted.

FIG. **11** is an isometric ABS illustration of the read head **72** shown in FIGS. **6** or **8**. The read head **72** includes the present spin valve sensor **130** which is located on an antiferromagnetic (AFM) pinning layer **132**. A ferromagnetic pinned layer in the spin valve sensor **130**, which is to be described hereinafter, has a magnetic moment that is pinned by the magnetic spins of the pinning layer **132**. The AFM pinning layer may be 425 Å of nickel oxide (NiO). First and second hard bias and lead layers **134** and **136** are connected to first and second side edges **138** and **140** of the spin valve sensor. This connection is known in the art as a contiguous junction and is fully described in commonly assigned U.S. Pat. No. 5,018,037 which is incorporated by reference herein. The first hard bias and lead layers **134** include a first hard bias layer **140** and a first lead layer **142** and the second hard bias and lead layers **136** include a second hard bias layer **144** and a second lead layer **146**. The hard bias layers **140** and **144** cause magnetic fields to extend longitudinally through the spin valve sensor **130** for stabilizing the magnetic domains therein. The AFM pinning layer **132**, the spin valve sensor **130** and the first and second hard bias and lead layers **134** and **136** are located between nonmagnetic electrically insulative first and second read gap layers **148** and **150**. The first and second read gap layers **148** and **150** are, in turn, located between ferromagnetic first and second shield layers **152** and **154**.

THE PRESENT INVENTION

FIG. **12** shows an ABS illustration of a preferred embodiment **200** of the present spin valve sensor. The spin valve sensor **200** includes a spacer layer (S) **202** which is located between an antiparallel (AP) pinned layer structure **204** and a free layer structure (F) which may include films **206** and **207**. On top of the free layer **206** is a cap layer **208** for protecting the free layer from subsequent formations of layers of the read head. The free layer structure **206** and **207** has a magnetic moment **210** which is directed parallel to the ABS in a quiescent state (no signal field), either from right to left or from left to right, as shown in FIG. **12**. The AP pinned layer structure **204** has a magnetic moment **212** which is pinned perpendicular to the ABS, either away from the ABS or toward the ABS, as shown in FIG. **12**. When a signal field from a track of a rotating magnetic disk rotates the magnetic moment **210** upwardly the magnetic moments **210** and **212** become more antiparallel, which increases the resistance of the spin valve sensor and when the signal field

from the track of a rotating magnetic disk rotates the magnetic moment 210 downwardly the magnetic moments 210 and 212 become more parallel, which decreases the resistance of the spin valve sensor. In a sense current I_s circuit these resistance changes are manifested as potential changes which are processed as playback signals by the processing circuitry shown in FIG. 3.

The AP pinned layer structure 204 may include first and second AP pinned layers (AP1) and (AP2) 214 and 218. The first AP pinned layer 214 includes a first thin film 220 which is composed of a material that has a positive magnetostriction (+MS). The first AP pinned layer 214 is exchange coupled to an antiferromagnetic pinning layer 222, which is composed of nickel oxide, which pins a magnetic moment 224 of the positive magnetostriction first thin film 220 perpendicular to and away from the ABS, as shown in FIG. 12.

In prior art AP pinned layers, which do not employ a positive magnetostriction thin film 220, the pinning of the magnetic moment 224 is not stable when the read sensor reaches operating temperatures as high as 150° C. in a magnetic disk drive. While a blocking temperature of the nickel oxide (NiO) pinning layer 222 is 215°–225° C., there is a blocking temperature distribution where magnetic spins of the pinning layer are free to rotate below the blocking temperature. Blocking temperature is the temperature at which all of the magnetic spins of the pinned layer are no longer pinned by the pinning layer. Unfortunately, there is a percentage of the blocking temperature distribution that is at and below 150° C. which means that a percentage of the magnetic spins of the pinning layer are free to rotate at these temperatures. This causes the pinning strengths between the pinning layer 222 and the first AP pinned layer 214 to be degraded allowing extraneous fields to relocate the magnetic moment 224 in an orientation that is not perpendicular to the ABS. If the coercivity (H_C) of the first AP pinned layer 214 is greater than the pinning strength, the pinning layer 222 will not have sufficient pinning strength to bring the magnetic moment 224 back to its perpendicular orientation, as shown in FIG. 12.

By providing the first AP pinned layer 214 with the positive magnetostriction thin film 220 the first AP pinned layer 214 has a stress induced uniaxial anisotropy which supports the pinning of the magnetic moment 224 in its orientation shown in FIG. 12. This is made possible due to the fact that after lapping the magnetic head structure the layers of the spin valve sensor 200 are in compression parallel to the ABS. This is exemplified at 226 for the top cap layer 226 and is the same for the layers therebelow, including the AP pinned layer structure 204. Because of the compression, the positive magnetostriction of the thin film 220 causes the easy axis 228 of the positive magnetostriction thin film 220 to be perpendicular to the ABS. Accordingly, when the pinning layer 222 pins the magnetic moment 224 perpendicular to and away from the ABS there is a stress induced uniaxial anisotropy which is oriented in the same direction. If the pinning layer 222 pins the thin film layer 220 perpendicular to and toward the ABS the stress induced anisotropy would be in the same direction, namely perpendicular to and toward the ABS. The stress induced uniaxial anisotropy finds its orientation when the magnetic spins of the pinning layer 222 are reset by applying a magnetic field to the first AP pinned layer which orients the magnetic moment of the thin film 220 perpendicular to and away from the ABS, as shown in FIG. 12.

The AP pinned layer structure 214, 224 includes an antiparallel (AP) coupling layer 230 which is located

between the first and second AP pinned layers 214 and 218. I found that when the positive magnetostriction thin film 220 interfaces the AP coupling layer 230, which is typically composed of ruthenium (Ru), that the performance of the spin valve sensor is degraded. I have overcome this problem by providing a thin film of cobalt (Co) or cobalt iron (CoFe) between the positive magnetostriction thin film 220 and the AP coupling layer 230. Further, I found that when the positive magnetostriction layer 220 interfaces the nickel oxide (NiO) pinning layer 222 that the performance of the spin valve sensor is degraded. I have overcome this problem by providing the first AP pinned layer 214 with a nickel iron (NiFe) thin film 234 which is located between the positive magnetostriction thin film 220 and the pinning layer 222.

In a preferred embodiment the second AP pinned layer 218 also includes a positive magnetostriction thin film 236. Because of the positive magnetostriction of the thin film 236 this thin film also has an easy axis 238 which is oriented perpendicular to the ABS. By antiparallel coupling between the first and second AP pinned layers 214 and 218 the magnetic moment 212 of the positive magnetostriction thin film 236 is oriented perpendicular to toward the ABS, as shown in FIG. 12. This causes a stress induced uniaxial anisotropy which is oriented in the same direction for supporting the orientation of the magnetic moment 212 perpendicular to and toward the ABS. It should be noted that because of antiparallel coupling between the first and second AP pinned layers 214 and 218 the stress induced uniaxial anisotropy of the second AP pinned layer 218 will additionally support the orientation of the magnetic moment 224 of the positive magnetostriction film 220 perpendicular to and away from the ABS. This is particularly important when the spin valve sensor reaches operating temperatures of the disk drive which reduces the pinning strength between the nickel oxide (NiO) pinning layer 222 and the positive magnetostriction thin film 220. Accordingly, the present AP pinned layer structure 224 is highly stabilized by employing a positive magnetostriction thin film in each of the first and second AP pinned layers 214 and 218.

For the same reason as explained for the first AP pinned layer 214 a thin film of cobalt (Co) or cobalt iron (CoFe) 240 is provided between the positive magnetostriction thin film 236 and the AP coupling layer 230 for improving the performance of the spin valve sensor. In a preferred embodiment the second AP pinned layer 218 includes a third thin film which differs from the thin film 234 employed in the first AP pinned layer 214. The thin film 242 in the second AP pinned layer is located between the positive magnetostriction thin film 236 and the copper (Cu) spacer layer 202. I found that the thin film 242 further increases the performance of the spin valve sensor. In a preferred embodiment the AP pinned layer 204 includes all of the thin films as described hereinabove.

Preferred thicknesses and materials for the layers and thin films are 425 Å of nickel oxide (NiO) for the pinning layer 222, 5 Å of nickel iron (NiFe) for the thin film 234, 15 Å to 20 Å of a positive magnetostriction material for the thin film 220, 5 Å of cobalt (Co) or cobalt iron (CoFe) for the thin film 232, 8 Å of ruthenium (Ru) for the AP coupling layer 230, 5 Å of cobalt (Co) or cobalt iron (CoFe), for the thin film 240 10–20 Å of a positive magnetostriction material for the thin film 236, 10–20 Å of cobalt (Co) or cobalt iron (CoFe) for the thin film 242, 24 Å of copper (Cu) for the spacer layer 202, 60 Å of nickel iron (NiFe) for the free layer film 206 and 15 Å of cobalt iron (CoFe) for the free layer film 207 and 30 Å of tantalum (Ta) for the cap 208. It should be understood that the magnetic moments of the thin films 234

and **232** will be oriented in the same direction as the magnetic moment **224**, and that the magnetic moments of the thin films **240** and **242** will be oriented in the same direction as the magnetic moment **212**. The thickness of the first AP pinned layer **214** may be greater or less than the thickness of the second AP pinned layer **218**. It should be noted that the pinning layer **222** is below the other layers of the spin valve sensor. This means that the layers of the spin valve sensor are formed on top of and after the formation of the pinning layer **222**. This type of spin valve sensor is known in the art as a bottom spin valve sensor since the pinning layer is located at the bottom of the sensor.

FIG. **13** shows an ABS illustration of another preferred embodiment **300** of the present invention which is the same as the embodiment **200** shown in FIG. **12**, except the AP pinned layer structure **204** is turned upside down, the spacer layer **202** and the free layer structure **206** and **207** are located below the AP pinned layer structure **204**, a seed layer, such as a tantalum (Ta) layer **302** 10 Å–30 Å thick, is provided between the free layer **206** and **207** and a first gap layer (G1) **304** and an antiferromagnetic (AFM) pinning layer **222**, which may be nickel oxide (NiO), is located above the AP pinned layer structure **204**. A further difference is that the magnetic moment **306** of the first AP pinned layer is perpendicular to and toward the ABS and the magnetic moment **308** of the second AP pinned layer is perpendicular and away from the ABS, as shown in FIG. **13**. Because of the compression **226** the easy axis **228** and **238** of the positive magnetostriction thin films will be oriented perpendicular to the ABS so that when the magnetic spins of the pinning layer **222** are oriented perpendicular to and toward the ABS the positive magnetostriction thin films **220** will be a stress induced uniaxial anisotropy supporting the magnetic moment **306** in a direction perpendicular to and toward the ABS and the positive magnetostriction thin film **236** will have a stress induced uniaxial anisotropy that supports the orientation of the magnetic moment **308** in a direction perpendicular to and away from the ABS. The pinning layer **222** may be composed of an antiferromagnetic material other than nickel oxide (NiO), such as alpha iron oxide (αFe_2O_3), nickel manganese (NiMn), iron manganese (FeMn), platinum manganese (PtMn) or iridium manganese (IrMn). In a preferred embodiment, however, the pinning layer **222** is nickel oxide (NiO). Since the pinning layer **222** is located at the top of the spin valve sensor in FIG. **13**, this type of spin valve sensor is known in the art as a top spin valve sensor.

Various thin film layers for the first AP pinned layer **214** in either of the spin valves **200** or **300** in FIGS. **12** and **13** are shown in FIGS. **14, 15** and **16**. In each of the embodiments shown in FIGS. **14, 15** and **16** a thin film layer of nickel iron ($Ni_{80}Fe_{20}$) **234** 5 Å thick is employed between the positive magnetostriction thin film **220** and the nickel oxide (NiO) pinning layer **222**. Further, in each of the embodiments shown in FIGS. **14, 15** and **16** a thin film of cobalt (Co) or cobalt iron (CoFe) is employed between the positive magnetostriction thin film **220** and the AP coupling layer **230** of ruthenium (Ru). The difference between the embodiments in FIGS. **14, 15** and **16** is the material used for the positive magnetostriction thin film **220**. In the embodiment shown in FIG. **14** the positive magnetostriction thin film **220** is 15 Å to 20 Å of nickel iron ($Ni_{45}Fe_{55}$), the positive magnetostriction **220** in the embodiment in FIG. **15** is 15 Å to 20 Å of nickel iron niobium (NiFeNb) and the positive magnetostriction thin film **220** in FIG. **16** is 15 Å to 20 Å of nickel cobalt ($Ni_{50}Co_{50}$). Each of these materials for the thin film **220** has a positive magnetostriction. The nickel

iron ($Ni_{45}Fe_5$) has a magnetostriction of $+5\times10^{-5}$, the nickel iron niobium (NiFeNb) has a magnetostriction of $+4\times10^{-5}$ and the nickel cobalt ($Ni_{50}Co_{50}$) has a magnetostriction of $+1$–10×10^{-5}. As a comparison, nickel iron ($Ni_{80}Fe_{20}$) has substantially zero magnetostriction. In regard to the second AP pinned layer **218** in either of the embodiments **200** or **300** in FIGS. **12** and **13**, the materials of the thin films may be identical as that shown for the first AP pinned layer **214** in FIGS. **14, 15** and **16**, except the thin film of cobalt (Co) or cobalt iron (CoFe) **242** shown in FIGS. **12** and **13** is substituted for the nickel iron ($Ni_{80}Fe_{20}$) thin film **234** in FIGS. **14, 15** and **16**.

It has been found that when the positive magnetostriction layer **220** interfaces the ruthenium (Ru) AP coupling layer **230** the strength of the antiparallel coupling between the first and second AP pinned layers **214** and **218** is degraded. I found that when the positive magnetostriction thin film **220** is cobalt iron (CoFe) it has a high coercivity (H_C) when it interfaces the nickel oxide (NiO) pinning layer **222**. This coercivity (H_C) can easily exceed the pinning strength of the pinning layer **222** so that during operating temperatures the magnetic moment **224** of the thin film **220** can be switched from its orientation shown in FIGS. **12** and **13** and remain at the switched position even after termination of the operating temperature because the coercivity (H_C) of the thin film **220** exceeds the pinning strength of the pinning layer **222**. However, if the material of the thin film **220** is nickel iron ($Ni_{45}Fe_{55}$) it can interface the nickel oxide (NiO) pinning layer **222** which obviates the need for the nickel iron (NiFe) thin film **234**.

FIG. **17** is an ABS illustration of another embodiment **400** of the spin valve sensor. This spin valve sensor differs from the embodiments **200** and **300** in that the pinned layer structure **402** is a single pinned layer structure instead of an AP pinned layer structure. A spacer layer **404** is located between the pinned layer structure **402** and the free layer **406**. A cap layer **408** is located on the free layer **406** for its protection from subsequent processing steps. The AP pinned layer **402** has a magnetic moment **410** which is pinned perpendicular to and toward the ABS or away from the ABS, as shown in FIG. **17**. The sense current I_S is directed from left to right so as to support the pinning of the magnetic moment **410** in the direction shown.

The pinned layer structure **402** includes a positive magnetostriction (+MS) thin film **412** which has an easy axis **414** oriented perpendicular to the ABS because of the compression **416** which is manifested in the pinned layer structure **402**. The pinned layer structure **402** includes a thin film **416** of nickel iron (NiFe) between the positive magnetostriction thin film **412** and a nickel oxide (NiO) pinning layer **418**. I found this thin film **416** to be necessary when the positive magnetostriction thin film **412** is cobalt iron (CoFe) so as to reduce its coercivity (H_C) below the pinning strength of the pinning layer **418**, as discussed hereinabove. Further, I have provided a thin film **420** of cobalt (Co) or cobalt iron (CoFe) between the positive magnetostriction thin film **412** and the copper (Cu) spacer layer **404** for enhancing the performance of the spin valve sensor. The thicknesses of the layers and thin films of the embodiment **400** are the same as the equivalent layers in the embodiments **200** and **300**.

Clearly, other embodiments and modifications of this invention will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, this invention is to be limited only by following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying drawings.

I claim:

1. A magnetic read head having an air bearing surface (ABS) comprising:

a spin valve sensor that includes:

a ferromagnetic free layer structure having a magnetic moment that is free to rotate from a first direction in response to signal fields from a moving magnetic medium;

a ferromagnetic antiparallel (AP) pinned layer structure;

an antiferromagnetic (AFM) pinning layer exchange coupled to the AP pinned layer structure for pinning a magnetic moment of the AP pinned layer structure in a second direction;

a nonmagnetic conductive spacer layer located between the free layer structure and the AP pinned layer structure;

the (AP) pinned layer structure including:

first and second antiparallel (AP) pinned layers;

an antiparallel (AP) coupling layer between the first and second AP pinned layers;

the first AP pinned layers including a first pinned film that has a positive magnetostriction and a second pinned film that is composed of cobalt (Co) or cobalt iron (CoFe); and

the second pinned film being located between and interfacing each of the first pinned film and the AP coupling layer.

2. A magnetic read head as claimed in claim 1 including:

nonmagnetic conductive first and second lead layers electrically connected to the spin valve sensor;

nonmagnetic nonconductive first and second read gap layers;

the spin valve sensor and the first and second lead layers being located between the first and second read gap layers; and

ferromagnetic first and second shield layers; and

the first and second read gap layers being located between the first and second shield layers.

3. A magnetic read head as claimed in claim 2 wherein the pinning layer is nickel oxide (NiO), the first pinned film is $Ni_{45}Fe_{55}$ and the first pinned film is interfaces the pinning layer.

4. A magnetic read as claimed in claim 2 including:

the pinning layer being nickel oxide (NiO); and

the first AP pinned layer including a third film of nickel iron which is located between and interfaces each of the pinning layer and the first pinned film.

5. A magnetic read head as claimed in claim 4 wherein the first pinned film is nickel iron niobium (NiFeNb).

6. A magnetic read head as claimed in claim 4 wherein the first pinned film is nickel cobalt ($Ni_{50}Co_{50}$).

7. A magnetic read head as claimed in claim 4 wherein the second AP pinned layer has a first pinned film with a positive magnetostriction and a second pinned film of cobalt (Co) or cobalt iron (CoFe) which is located between and interfaces the first pinned film and the spacer layer.

8. A magnetic read head as claimed in claim 7 wherein the first pinned film of the second AP pinned layer is nickel iron ($Ni_{45}Fe_{55}$).

9. A magnetic read head as claimed in claim 7 wherein the first pinned film of the second AP pinned layer is nickel iron niobium (NiFeNb).

10. A magnetic read head as claimed in claim 7 wherein the first pinned film of the second AP pinned layer is nickel cobalt $Ni_{50}Co_{50}$).

11. A magnetic read head as claimed in claim 7 including:

the second AP pinned layer including a third pinned film composed of cobalt (Co) or cobalt iron (CoFe); and

the third film of being located between and interfacing each of the AP coupling layer and the first pinned film of the second AP pinned layer.

12. A magnetic head assembly having a read head and a write head and an air bearing surface (ABS) comprising:

the write head including:

first and second pole piece layers;

each of the first and second pole piece layers having a yoke portion located between a pole tip portion and a back gap portion;

a nonmagnetic write gap layer located between the pole tip portions of the first and second pole piece layers;

an insulation stack with at least one coil layer embedded therein located between the yoke portions of the first and second pole piece layers; and

the first and second pole piece layers being connected at their back gaps portions; and

the read head including:

a spin valve sensor;

first and second lead layers electrically connected to the spin valve sensor;

nonmagnetic nonconductive first and second read gap layers;

the spin valve sensor and the first and second lead layers being located between the first and second read gap layers;

the spin valve sensor including:

a ferromagnetic free layer structure having a magnetic moment that is free to rotate from a first direction in response to signal fields from a moving magnetic medium;

a ferromagnetic antiparallel (AP) pinned layer structure;

an antiferromagnetic (AFM) pinning layer exchange coupled to the AP pinned layer structure for pinning a magnetic moment of the AP pinned layer structure in a second direction;

a nonmagnetic conductive spacer layer located between the free layer structure and the AP pinned layer structure;

the (AP) pinned layer structure including:

first and second antiparallel (AP) pinned layers;

an antiparallel (AP) coupling layer between the first and second AP pinned layers; and

the first AP pinned layers including a first pinned film that has a positive magnetostriction and a second pinned film that is composed of cobalt (Co) or cobalt iron (CoFe); and

the second pinned film being located between and interfacing each of the first pinned film and the AP coupling layer.

13. A magnetic head assembly as claimed in claim 12 including:

the read head further including:

a ferromagnetic second shield layer;

a nonmagnetic electrically insulative separation layer; and

the separation layer being located between the second shield layer and the first pole piece layer.

14. A magnetic head assembly as claimed in claim 12 including:

the pinning layer being nickel oxide (NiO); and

the first AP pinned layer including a third film of nickel iron which is located between and interfaces each of the pinning layer and the first pinned film.

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15. A magnetic head assembly as claimed in claim **12** wherein the second AP pinned layer has a first pinned film with a positive magnetostriction and a second pinned film of cobalt (Co) or cobalt iron (CoFe) which is located between and interfaces the first pinned film and the spacer layer.

16. A magnetic head assembly as claimed in claim **15** including:

the second AP pinned layer including a third pinned film composed of cobalt (Co) or cobalt iron (CoFe); and

the third film of the second AP pinned layer being located between and interfacing each of the AP coupling layer and the first pinned film of the second AP pinned layer.

17. A magnetic head assembly as claimed in claim **16** including:

the pinning, layer being nickel oxide (NiO); and

the first AP pinned layer including a third film of nickel iron which is located between and interfaces each of the pinning layer and the first pinned film.

18. A magnetic head assembly as claimed in claim **17** wherein the first pinned film of each of the first and second AP pinned layers is nickel iron niobium (NiFeNb).

19. A magnetic head assembly as claimed in claim **17** wherein the first pinned film of each of the first and second AP pinned layers is nickel cobalt (NiCo).

20. A magnetic disk drive having at least one slider that has an air bearing surface (ABS), the slider supporting at least one magnetic head assembly that includes a read head and a write head, the disk drive comprising:

the write head including:

first and second pole piece layers;

each of the first and second pole piece layers having a yoke portion located between a pole tip portion and a back gap portion;

a nonmagnetic write gap layer located between the pole tip portions of the first and second pole piece layers;

an insulation stack with at least one coil layer embedded therein located between the yoke portions of the first and second pole piece layers; and

the first and second pole piece layers being connected at their back gaps portions; and

the read head having a spin valve sensor that includes:

a ferromagnetic free layer structure having a magnetic moment that is free to rotate from a first direction in response to signal fields from a moving magnetic medium;

a ferromagnetic antiparallel (AP) pinned layer structure;

an antiferromagnetic (AFM) pinning layer exchange coupled to the AP pinned layer structure for pinning a magnetic moment of the AP pinned layer structure in a second direction;

a nonmagnetic conductive spacer layer located between the free layer structure and the AP pinned layer structure;

the (AP) pinned layer structure including:

first and second antiparallel (AP) pinned layers;

an antiparallel (AP) coupling layer between the first and second AP pinned layers;

the first AP pinned layers including a first pinned film that has a positive magnetostriction and a second pinned film that is composed of cobalt (Co) or cobalt iron (CoFe); and

the second pinned film being located between and interfacing each of the first pinned film and the AP coupling layer;

the read head further including:

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nonmagnetic conductive first and second lead layers electrically connected to the spin valve sensor;

nonmagnetic nonconductive first and second read gap layers;

the spin valve sensor and the first and second lead layers being located between the first and second read gap layers;

a ferromagnetic first shield layer; and

the first and second read gap layers being located between the first shield layer and the first pole piece layer; and

a housing;

a magnetic disk rotatably supported in the housing;

a support mounted in the housing for supporting the magnetic head assembly with its ABS facing the magnetic disk so that the magnetic head assembly is in a transducing relationship with the magnetic disk;

a spindle motor for rotating the magnetic disk;

an actuator connected to the support for moving the magnetic head assembly to multiple positions with respect to said magnetic disk; and

a processor connected to the magnetic head assembly to the means for rotating the magnetic disk and to the positioning means for exchanging signals with the magnetic head assembly, for controlling movement of the magnetic disk and for controlling the position of the magnetic head assembly.

21. A magnetic disk drive as claimed in claim **20** including:

the read head further including:

a ferromagnetic second shield layer;

a nonmagnetic electrically insulative separation layer; and

the separation layer being located between the second shield layer the first pole piece layer.

22. A magnetic disk drive as claimed in claim **20** wherein the pinning layer is nickel oxide (NiO), the first film is nickel iron ($Ni_{45}Fe_{55}$) and the first pinned film interfaces the pinning layer.

23. A magnetic disk drive as claimed in claim **20** including:

the pinning layer being nickel oxide (NiO); and

the first AP pinned layer including a third film of nickel iron which is located between and interfaces each of the pinning, layer and the first pinned film.

24. A magnetic disk drive as claimed in claim **23** wherein the second AP pinned layer has a first pinned film with a positive magnetostriction and a second pinned film of cobalt (Co) or cobalt iron (CoFe) which is located between and interfaces the first pinned film and the spacer layer.

25. A magnetic disk drive as claimed in claim **4** including:

the second AP pinned layers including a third pinned film composed of cobalt (Co) or cobalt iron (CoFe); and

the third film of the second AP pinned layer being located between and interfacing each of the AP coupling layer and the first pinned film of the second AP pinned layer.

26. A magnetic disk drive as claimed in claim **25** wherein the first pinned film of each of the first and second AP pinned layers is nickel iron niobium (NiFeNb).

27. A magnetic disk drive as claimed in claim **26** wherein the first pinned film of each of the first and second AP pinned layers is nickel cobalt (NiCo).

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28. A magnetic read head having an air bearing surface (ABS) comprising:

a spin valve sensor that includes:

a ferromagnetic free layer structure having a magnetic moment that is free to rotate from a first direction in response to signal fields from a moving magnetic medium;

a ferromagnetic pinned layer structure;

an antiferromagnetic (AFM) pinning layer exchange coupled to the pinned layer structure for pinning a magnetic moment of the pinned layer structure in a second direction;

a nonmagnetic conductive spacer layer located between the free layer structure and the pinned layer structure; and

the first pinned film having a positive magnetostriction and the second pinned film being cobalt (Co) or cobalt iron (CoFe) and being located between the first pinned film and spacer layer.

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29. A magnetic read head as claimed in claim **28** including:

nonmagnetic conductive first and second lead layers electrically connected to the spin valve sensor;

nonmagnetic nonconductive first and second read gap layers;

the spin valve sensor and the first and second lead layers being located between the first and second read gap layers; and

ferromagnetic first and second shield layers; and

the first and second read gap layers being located between the first and second shield layers.

30. A magnetic read head as claimed in claim **29** wherein the first pinned film is substantially nickel iron ($Ni_{45}Fe_{55}$).

31. A magnetic read head as claimed in claim **29** wherein the first pinned film is nickel iron niobium (NiFeNb).

32. A magnetic read head as claimed in claim **29** wherein the first pinned film is substantially nickel cobalt ($Ni_{50}Co_{50}$).

* * * * *

Fabrication of patterned ferromagnetic shape memory thin films

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Abstract. We report two possible routes of fabrication of large surfaces of ferromagnetic shape memory antidots with tunable pore size and center-to-center distances. By using the drop coating method, we have prepared a large area of 2D arrays (typically $1cm^2$) of polystyrene spheres (PS) ($1.4\pm0.1\mu m$ diameter) on a Si substrate. We have used reactive ion etching with a gas mixture of O_2 (12sccm) and Ar (5sccm) to reduce the diameter of the PS spheres whereby controlling the size of pores. The film deposition was performed on a substrate heated at 500ºC (route 1) and at room temperature with subsequent annealing in a furnace at 500ºC for 4 hours (route 2). Route 1 proved to be promising but more work is needed to optimize it. The antidots of Ni-Mn-Ga obtained along route 2 are ferromagnetic with a Curie temperature ~100ºC, and a spread martensitic transformation (between -100ºC and -30ºC).

Introduction

Ferromagnetic shape memory alloy (FSMA) thin films have been the subject of intense research because of the interesting underlying physics and high potential for applications [1]. FSMAs exhibit a magnetic-field-activated giant recoverable strain of about 10% together with pronounced mechanical/electrical/magnetic/caloric properties, making them very suitable for the use in sensing/actuating devices [2-4]. When in thin film form, these properties can be affected by several parameters, including the composition, internal stress, thermal treatment, morphology and thickness of the thin films [5,6].

It is also well known that a material will exhibit a different behaviour when reduced to the nanoscale, a fact that has opened new opportunities in the field of sensors and actuators. For example, free-standing nanofabricated thin films of Ni-Mn-Ga FSMAs have attracted great interest due to their actuation capabilities related to the thermoelastic and magnetomechanical coupling effects [7–9]. In this sense, the abilities of micro- and nano-fabrication of FSMAs and downscaling of their functional properties are crucial for implementation in devices like microelectromechanical systems (MEMS). In general, two different approaches have been developed to fabricate micro/nanostructured materials: "top-down" [e.g., reactive ion etching (RIE)] and "bottom-up" (e.g., film sputter deposition). A particularly interesting technique to fabricate these materials is the Sphere Lithography, which combines characteristics of both approaches to improve the quality of the patterned structures. This technique is based on a two-step process [10]: a) the fabrication of a periodic array of the self-assembled polystyrene (PS) spheres on the substrate, which acts as a mask for b) the deposition of the material of interest.

In this work, we present two procedures based on the sphere lithography to fabricate antidot-patterned thin films of Ni-Mn-Ga.

Experimental Procedure

Previous studies have shown that the deposition temperature is a determining factor to achieve the appropriate structural and magnetic order of Ni-Mn-Ga films [4]. Due to the degradation of the spheres above 70ºC, we propose two routes to fabricate Ni-Mn-Ga patterned films that overcome the temperature limitation. A sketch of both procedures is shown in Fig.1(a). The routes start with two common steps: (a) the formation of a template by depositing a single layer of PS spheres (1.3±0.1µm diameter, see inset in Fig.1(b), obtained by dispersion polymerization [11]), on the surface of a Si wafer using the drop-coating method [12]; and (b) reduction of the PS spheres [0.9 ±0.1µm diameter, see inset in Fig.1(c)] by a RIE process, working under the conditions presented in Table 1.
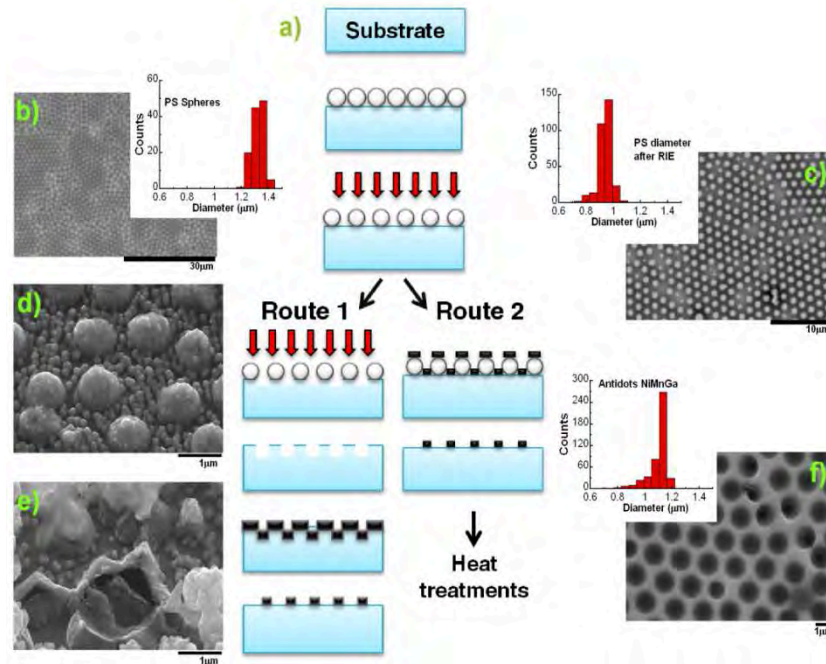
Figure1. a) Scheme of the two routes used to fabricate Ni-Mn-Ga antidots. Red arrows denote the RIE treatment, Ni-Mn-Ga film is sketched by black color. SEM micrograph of the PS spheres (b), PS spheres after RIE (c), Si pillars covered by Ni-Mn-Ga (d), collapse of the pillars after KOH etch (e), and antidot-patterned Ni-Mn-Ga film obtained by route 2 (f). Insets: histograms for the diameters of the PS spheres before and after RIE, and of the Ni-Mn-Ga antidots.

Table 1. Conditions for the reactive ion etching of the different layers.

	Gas flow (sccm)	ICP/RF power (W)	Pressure (Torr)	Temperature (ºC)	Time (min)
PS spheres	O_2:12/Ar:5	0/100	0.1	20	3
SiO_2	SF_6:30	150/150	0.1	10	0.3
Si	CHF_3:10	0/50	0.02	10	15

To avoid a heat-induced degradation of PS, route 1 uses the Si wafer as a sacrificial layer. Thus, the following steps are taken: (1c) without removing the spheres, we fabricate Si dots by a selective etching of the wafer by RIE (see conditions in Table 1); (1d) then the PS spheres are removed; and (1e) Ni-Mn-Ga is deposited at 500ºC by DC magnetron sputtering (Pfeiffer vacuum classic 500 station), using the parameters shown in Table 2. Finally, to remove the Si dots, the samples were (1f) subjected to a wet etching with a solution of 20% KOH at different temperatures, between 60 and 100ºC, during 1 to 10min.

On the other hand, route 2 comprises: (2c) a deposition of Ni-Mn-Ga alloy at room temperature under the conditions summarized in Table 2; and (2d) a removal of the PS spheres with Tetrahydrofuran. Due to the low crystallinity of the as-deposited samples, they show neither a martensitic transformation nor a ferro-to-paramagnetic transition, and hence, the samples must be annealed at 500ºC during 4h under vacuum (10^{-5}Torr) after deposition. In addition to the patterned samples, continuous 500nm thick Ni-Mn-Ga films have been deposited onto non-patterned substrates using the deposition conditions and heat treatments of route 2 to contrast their properties with the patterned analogs.

Table 2. Parameters of the sputter deposition of Ni-Mn-Ga thin films in both procedures.

Route	Distance Target-Substrate (cm)	RF power (W)	Pressure (Torr)	Temperature (ºC)	Time (min)
1	9	150	$2.0 \cdot 10^{-2}$	500	5
2	9	150	$2.0 \cdot 10^{-2}$	20	10

The structural and compositional characterization of the samples was carried out by a scanning electron microscopy (SEM) (Hitachi TM 3000) and energy dispersive X-ray spectroscopy. An atomic force microscope (Nanotec DSP Classic) was used to determine the films surface profile. The temperature dependences of the magnetization M(T) and resistivity were measured by a vibrating sample magnetometer and four-probe method, respectively.

Results

The deposition of a 250nm-thick Ni-Mn-Ga film by route 1 led to an additional sidewall deposition alongside the Si dots [see Fig.1(d)], hindering their elimination by wet etching –only a few percent of the Si pillars were eliminated, provoking the collapse of the Ni-Mn-Ga layer, as shown in Fig. 1(e). This issue was attributed to an excessive Ni-Mn-Ga/Si dot thickness ratio and could be further overcome by the optimization of the film thickness. An antidot-patterned $Ni_{50}Mn_{27}Ga_{23}$ (at.%) thin film was successfully obtained through route 2, as demonstrated by SEM in Fig.1(f). The antidots present a narrow diameter distribution with a mean value of around 1.1±0.1µm [see inset in Fig.1(f)] and they are arranged in hexagonal-type close packing forming coherent domains of about 15µm of length. The dots have a height of about 500nm and diameter of around 1µm.

The results of the magnetic and electric measurements are shown in Fig. 2 for the previously cited patterned film and two continuous films deposited on unpatterned substrates at 500ºC ($Ni_{48}Mn_{32}Ga_{20}$) and at 20ºC with subsequent post-annealing ($Ni_{50}Mn_{27}Ga_{23}$). The continuous film deposited at high temperature displays a Curie temperature [defined as the inflexion point of the M(T) curve] at ~100ºC with a sharp magnetization drop, evidencing a high atomic ordering. It also exhibits the martensitic transformation in a broad interval between -50ºC and 50ºC, which could be a result of a wide stress distribution in the film. The continuous film deposited at room temperature and annealed at 500ºC presents a Curie temperature of about 50ºC, far below the expected from its composition (~100ºC), while the martensitic transformation does not appear in the studied temperature interval. The reason of those features could be the partial crystal lattice disorder that remains from the room temperature deposition, even after heat treatment [4]. In the patterned film, the Curie temperature appears at about 100ºC, although a coexistence of the ordered and less-ordered phases could be inferred from the multiple magnetization drops from 25ºC to 100ºC. A hint of the martensitic transformation is manifested below -30ºC. The value of the Curie temperature and the occurrence of the martensitic transformation indicate that, in this case, the $L2_1$ atomic ordering degree is much higher than in the continuous film. The diffusion assisted higher atomic ordering during annealing in this case could be promoted by the enhanced amount and mobility of crystal defects due to the antidot boundaries.
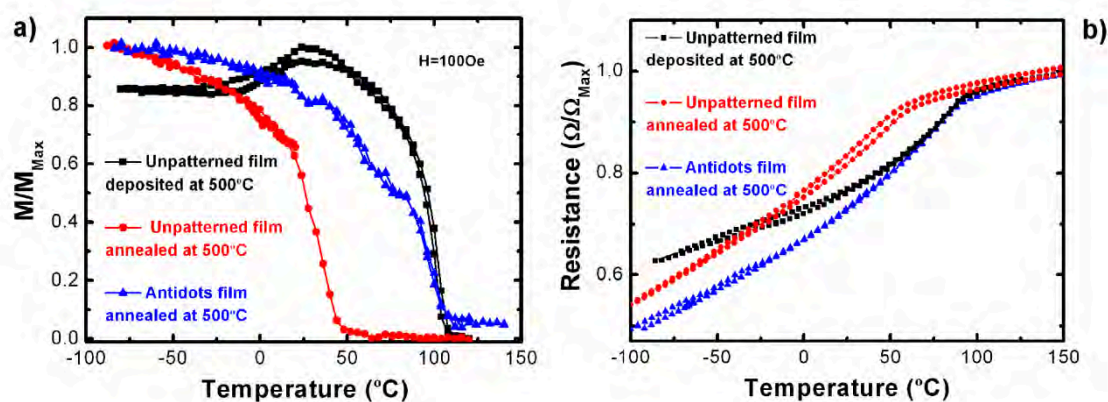
Figure 2. a) Normalized magnetization at H=100Oe and b) normalized electrical resistance as a function of temperature, evidencing the Curie and martensitic transformation temperatures.

Summary

Two ways for Ni-Mn-Ga thin film micropatterning have been developed by using self-assembled polystyrene spheres and reactive ion etching. The process allows tailoring the dimensions of the pattern, giving rise to different properties of the FSMA film. The patterned films have shown functional features like ferromagnetism and martensitic transformation, making them interesting for microdevices. The lattice ordering is incomplete in thin films deposited at room temperature with subsequent annealing. Further efforts will be focused on the elaboration of a route in which high-temperature deposition would be employed using the sacrificial layer method.

Acknowledgement

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Inorganic Solid Phases

$Fe_{60}Co_{40}$ ($Fe_{0.7}Co_{0.3}$ ht) Crystal Structure

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General Information

- **Phase Label(s):** $Fe_{0.7}Co_{0.3}$ ht
- **Structure Class(es):** b.c.c. atom arrangement
- **Classification by Properties:** ferromagnet FM, hard magnet, metal
- **Mineral Name(s):** –
- **Pearson Symbol:** cI2
- **Space Group:** 229

- **Phase Prototype:** W
- **Measurement Detail(s):** Debye-Scherrer film (determination of cell and structural parameters), X-rays, Mo Kα (determination of cell and structural parameters), T = 298 K (determination of cell and structural parameters)
- **Phase Class(es):** –
- **Compound Class(es):** intermetallic
- **Interpretation Detail(s):** cell parameters determined and type with fixed coordinates assigned; composition dependence studied
- **Sample Detail(s):** powder (determination of cell and structural parameters)

Substance Summary

- **Standard Formula:** $Fe_{0.6}Co_{0.4}$
- **Alphabetic Formula:** $Co_{0.4}Fe_{0.6}$
- **Published Formula:** $Fe_{60}Co_{40}$
- **Refined Formula:** $Co_{0.40}Fe_{0.60}$
- **Wyckoff Sequence:** 229,a
- **Z Formula Units:** 2
- **Density:** $\rho = 8.09\ Mg \cdot m^{-3}$

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Cell Parameters

Cell Parameters	Published Data	Unit Cell	Standardized I Niggli
Space Group	–	–	–
a	–	–	–
b	–	–	–
c	–	–	–
α	–	–	–
β	–	–	–
γ	–	–	–
a/b	–	–	–
b/c	–	–	–

c/a   –   –   –

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Atom Coordinates

Standardized

Site	Element	**Wyckoff Symbol**	Symmetry	X	Y	Z	Occupation
–	–	–	–	–	–	–	–

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Published

Site	Element	**Wyckoff Symbol**	Symmetry	X	Y	Z
_	_	_	_	_	_	_

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Experimental Details

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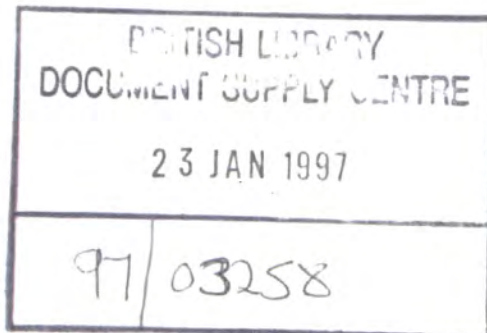
William F. Smith

Professor of Engineering
University of Central Florida

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Polymer-matrix composite tube being filament-braided with aramid fibers and an epoxy matrix. Computerized braiding machines fabricate these tubes for critical applications in the medical, electrical, automotive, and aerospace industries. (*Courtesy of Polygon Company, Walkerton, Ind.*)

3

Crystal Structures and Crystal Geometry

3.1 THE SPACE LATTICE AND UNIT CELLS

The physical structure of solid materials of engineering importance depends mainly on the arrangements of the atoms, ions, or molecules which make up the solid and the bonding forces between them. If the atoms or ions of a solid are arranged in a pattern that repeats itself in three dimensions, they form a solid which is said to have a *crystal structure* and is referred to as a *crystalline solid* or *crystalline material.* Examples of crystalline materials are metals, alloys, and some ceramic materials.

Atomic arrangements in crystalline solids can be described by referring the atoms to the points of intersection of a network of lines in three dimensions. Such a network is called a *space lattice* (Fig. 3.1a) and can be described as an infinite three-dimensional array of points. Each point in the space lattice has identical surroundings. In an ideal crystal the grouping of lattice points about any given point are identical with the grouping about any other lattice point in the crystal lattice. Each space lattice can thus be described by specifying the atom positions in a repeating *unit cell,* such as the one heavily

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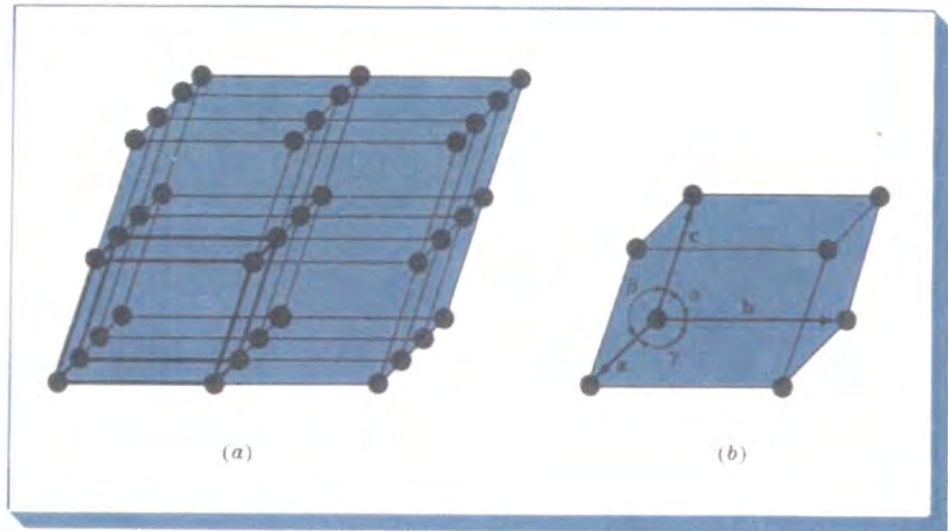
outlined in Fig. 3.1a. The size and shape of the unit cell can be described by
three lattice vectors **a, b,** and **c,** originating from one corner of the unit cell
(Fig. 3.1b). The axial lengths a, b, and c and the interaxial angles α, β, and γ
are the *lattice constants* of the unit cell.

3.2 CRYSTAL SYSTEMS AND BRAVAIS LATTICES

By assigning specific values for axial lengths and interaxial angles, unit cells
of different types can be constructed. Crystallographers have shown that only
seven different types of unit cells are necessary to create all point lattices.
These crystal systems are listed in Table 3.1.

Many of the seven crystal systems have variations of the basic unit cell.
A. J. Bravais[1] showed that 14 standard unit cells could describe all possible
lattice networks. These Bravais lattices are illustrated in Fig. 3.2. There are four
basic types of unit cells: (1) simple, (2) body-centered, (3) face-centered, and
(4) base-centered.

In the cubic system there are three types of unit cells: simple cubic, body-
centered cubic, and face-centered cubic. In the orthorhombic system all four
types are represented. In the tetragonal system there are only two: simple and
body-centered. The face-centered tetragonal unit cell appears to be missing
but can be constructed from four body-centered tetragonal unit cells. The

---

[1] August Bravais (1811–1863) French crystallographer who derived the 14 possible
arrangements of points in space
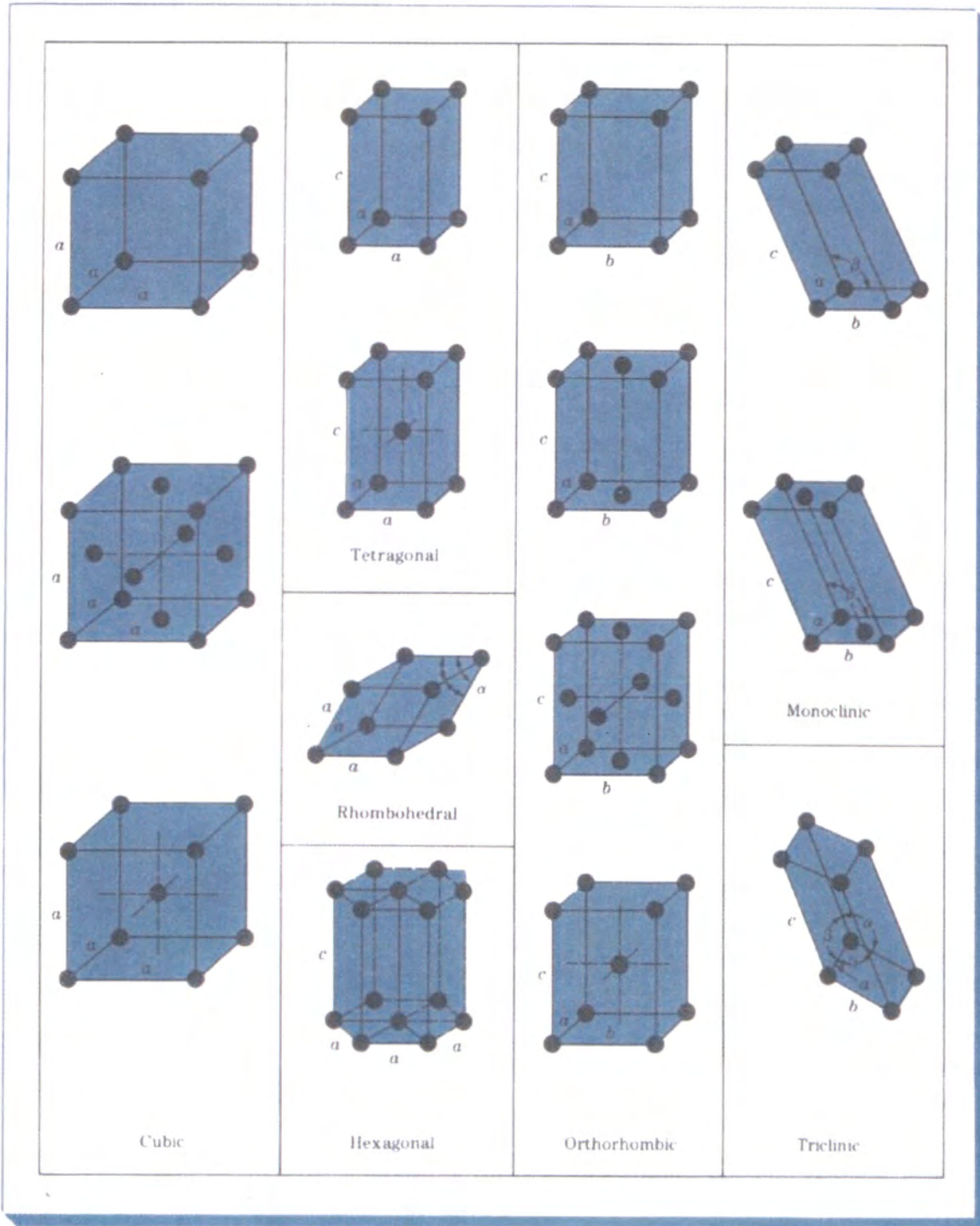
FIGURE 3.2 The 14 Bravais conventional unit cells grouped according to crystal system. The dots indicate lattice points that, when located on faces or at corners, are shared by other identical lattice unit cells. (*After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I "Structure," Wiley, 1964, p. 47.*)

TABLE 3.1   Classification of Space Lattices by Crystal System

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90°$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90°$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90°$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90°,$ $\gamma = 120°$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90° \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple triclinic

monoclinic system has simple and base-centered unit cells, and the rhombohedral, hexagonal, and triclinic systems have only one simple type of unit cell.

3.3 PRINCIPAL METALLIC CRYSTAL STRUCTURES

In this chapter the principal crystal structures of elemental metals will be discussed in detail. In Chap. 10 the principal ionic and covalent crystal structures which occur in ceramic materials will be treated.

Most elemental metals (about 90 percent) crystallize upon solidification into three densely packed crystal structures: *body-centered cubic (BCC)* (Fig. 3.3*a*), *face-centered cubic (FCC)* (Fig. 3.3*b*) and *hexagonal close-packed (HCP)* (Fig. 3.3*c*). The HCP structure is a denser modification of the simple hexagonal crystal structure shown in Fig. 3.2. Most metals crystallize in these dense-packed structures because energy is released as the atoms come closer together and bond more tightly with each other. Thus, the densely packed structures are in lower and more stable energy arrangements.
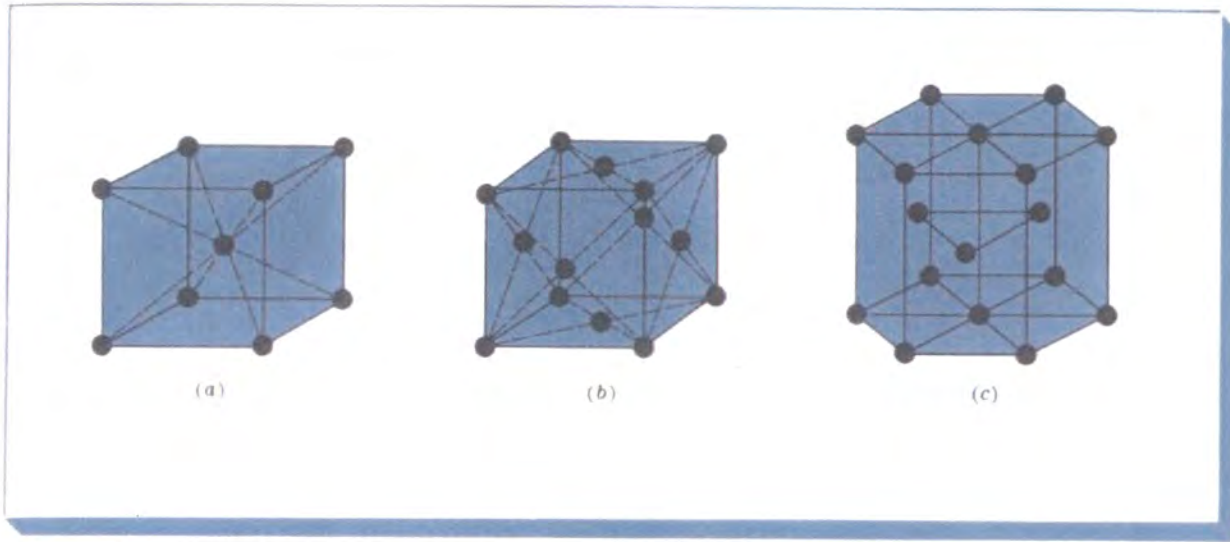
FIGURE 3.3 Principal metal crystal structure unit cells: (a) body-centered cubic, (b) face-centered cubic, (c) hexagonal close-packed.

The extremely small size of the unit cells of crystalline metals which are shown in Fig. 3.3 should be emphasized. The cube side of the unit cell of body-centered cubic iron, for example, at room temperature is equal to 0.287×10^{-9} m, or 0.287 nanometer (nm).[1] Therefore, if unit cells of pure iron are lined up side by side, in 1 mm there will be

$$1 \text{ mm} \times \frac{1 \text{ unit cell}}{0.287 \text{ nm} \times 10^{-6} \text{ mm/nm}} = 3.48 \times 10^{6} \text{ unit cells!}$$

Let us now examine in detail the arrangement of the atoms in the three principal crystal structure unit cells. Although an approximation, we shall consider atoms in these crystal structures to be hard spheres. The distance between the atoms (interatomic distance) in crystal structures can be determined experimentally by x-ray diffraction analysis.[2] For example, the interatomic distance between two aluminum atoms in a piece of pure aluminum at 20°C is 0.2862 nm. The radius of the aluminum atom in the aluminum metal is assumed to be half the interatomic distance, or 0.143 nm. The atomic radii of selected metals are listed in Tables 3.2 to 3.4.

Body-Centered Cubic (BCC) Crystal Structure

First, consider the atomic-site unit cell for the BCC crystal structure shown in Fig. 3.4a. In this unit cell the solid spheres represent the centers where atoms are located and clearly indicate their relative positions. If we represent the

---

[1] 1 nanometer = 10^{-9} meter
[2] Some of the principles of x-ray diffraction analysis will be studied in Sec. 3.11.

(a)　　　　　(b)　　　　　(c)
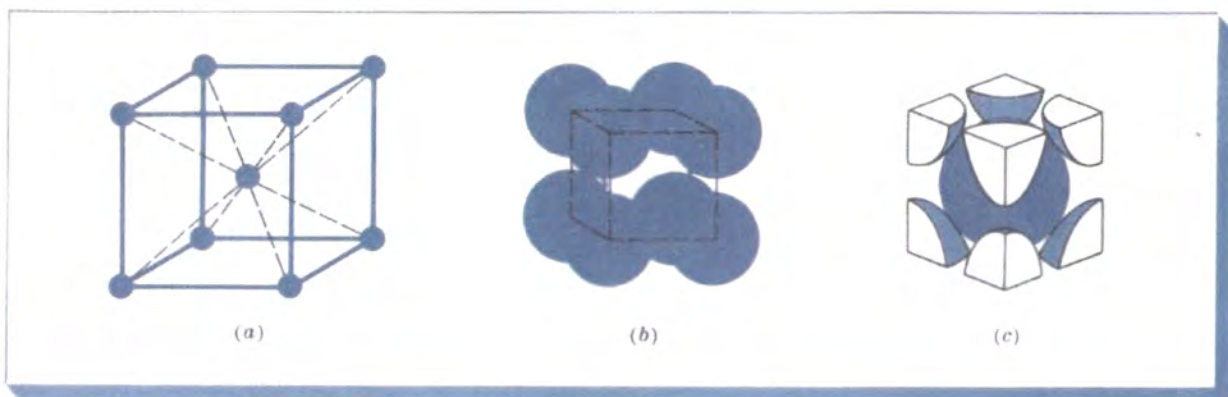
FIGURE 3.4 BCC unit cells: (a) atomic-site unit cell, (b) hard-sphere unit cell, and (c) isolated unit cell.

atoms in this cell as hard spheres, then the unit cell appears as shown in Fig. 3.4b. In this unit cell we see that the central atom is surrounded by eight nearest neighbors and is said to have a coordination number of 8.

If we isolate a single hard-sphere unit cell, we obtain the model shown in Fig. 3.4c. Each of these cells has the equivalent of two atoms per unit cell. One complete atom is located at the center of the unit cell, and an eighth of a sphere is located at each corner of the cell, making the equivalent of another atom. Thus there is a total of 1 (at the center) + 8 × ⅛ (at the corners) = 2
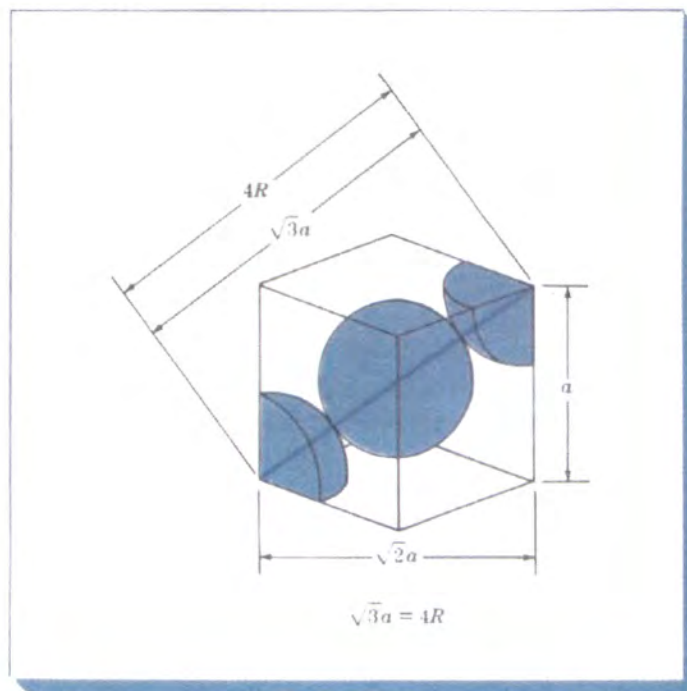
FIGURE 3.5 BCC unit cell showing relationship between the lattice constant a and the atomic radius R

atoms per unit cell. The atoms in the BCC unit cell contact each other across the cube diagonal, as indicated in Fig. 3.5, so that the relationship between the length of the cube side a and the atomic radius R is

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

Example Problem 3.1

Iron at 20°C is BCC with atoms of atomic radius 0.124 nm. Calculate the lattice constant a for the cube edge of the iron unit cell.

Solution:

From Fig. 3.5 it is seen that the atoms in the BCC unit cell touch across the cube diagonals. Thus, if a is the length of the cube edge, then

$$\sqrt{3}a = 4R \tag{3.1}$$

where R is the radius of the iron atom. Therefore

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124 \text{ nm})}{\sqrt{3}} = 0.2864 \text{ nm} \blacktriangleleft$$

TABLE 3.2   Selected Metals Which Have the BCC Crystal Structure at Room Temperature (20°C) and Their Lattice Constants and Atomic Radii

Metal	Lattice constant a, nm	Atomic radius R,* nm
Chromium	0.289	0.125
Iron	0.287	0.124
Molybdenum	0.315	0.136
Potassium	0.533	0.231
Sodium	0.429	0.186
Tantalum	0.330	0.143
Tungsten	0.316	0.137
Vanadium	0.304	0.132

*Calculated from lattice constants by using Eq. (3.1), $R = \sqrt{3}a/4$

If the atoms in the BCC unit cell are considered to be spherical, an atomic packing factor (APF) can be calculated by using the equation

$$\text{Atomic packing factor (APF)} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}} \quad (3.2)$$

Using this equation, the APF for the BCC unit cell (Fig. 3.3a) is calculated to be 68 percent (see Example Problem 3.2). That is, 68 percent of the volume of the BCC unit cell is occupied by atoms and the remaining 32 percent is empty space. The BCC crystal structure is *not* a close-packed structure since the atoms could be packed closer together. Many metals such as iron, chromium, tungsten, molybdenum, and vanadium have the BCC crystal structure at room temperature. Table 3.2 lists the lattice constants and atomic radii of selected BCC metals.

Example Problem 3.2

Calculate the atomic packing factor (APF) for the BCC unit cell, assuming the atoms to be hard spheres.

Solution:

$$\text{APF} = \frac{\text{volume of atoms in BCC unit cell}}{\text{volume of BCC unit cell}} \quad (3.2)$$

Since there are two atoms per BCC unit cell, the volume of atoms in the unit cell of radius R is

$$V_{\text{atoms}} = (2)(\tfrac{4}{3}\pi R^3) = 8.373R^3$$

The volume of the BCC unit cell is

$$V_{\text{unit cell}} = a^3$$

where a is the lattice constant. The relationship between a and R is obtained from Fig. 3.5, which shows that the atoms in the BCC unit cell touch each other across the cubic diagonal. Thus

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \quad (3.1)$$

Thus

$$V_{\text{unit cell}} = a^3 = 12.32R^3$$

The atomic packing factor for the BCC unit cell is, therefore,

$$APF = \frac{V_{atoms}/\text{unit cell}}{V_{unit\ cell}} = \frac{8.373R^3}{12.32R^3} = 0.68 \blacktriangleleft$$

Face-Centered Cubic (FCC) Crystal Structure

Consider next the FCC lattice-point unit cell of Fig. 3.6a. In this unit cell there is one lattice point at each corner of the cube and one at the center of each cube face. The hard-sphere model of Fig. 3.6b indicates that the atoms in the FCC crystal structure are packed as close together as possible. The APF for this close-packed structure is 0.74 as compared to 0.68 for the BCC structure which is not close-packed.

The FCC unit cell as shown in Fig. 3.6c has the equivalent of four atoms per unit cell. The eight corner octants account for one atom ($8 \times \frac{1}{8} = 1$), and the six half-atoms on the cube faces contribute another three atoms, making a total of four atoms per unit cell. The atoms in the FCC unit cell contact each other across the cubic face diagonal, as indicated in Fig. 3.7, so that the relationship between the length of the cube side a and the atomic radius R is

$$\sqrt{2}a = 4R \qquad \text{or} \qquad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

The APF for the FCC crystal structure is 0.74, which is greater than the 0.68 factor for the BCC structure. The APF of 0.74 is for the closest packing possible of "spherical atoms." Many metals such as aluminum, copper, lead, nickel, and iron at elevated temperatures (912 to 1394°C) crystallize with the FCC crystal structure. Table 3.3 lists the lattice constants and atomic radii for some selected FCC metals.
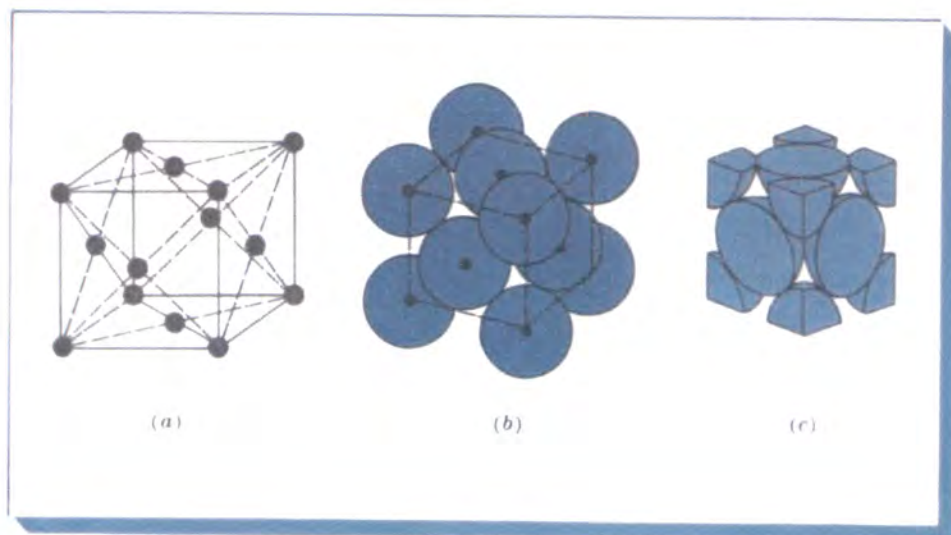
FIGURE 3.6 FCC unit cells: (a) atomic-site unit cell, (b) hard-sphere unit cell, and (c) isolated unit cell.

(a)   (b)   (c)
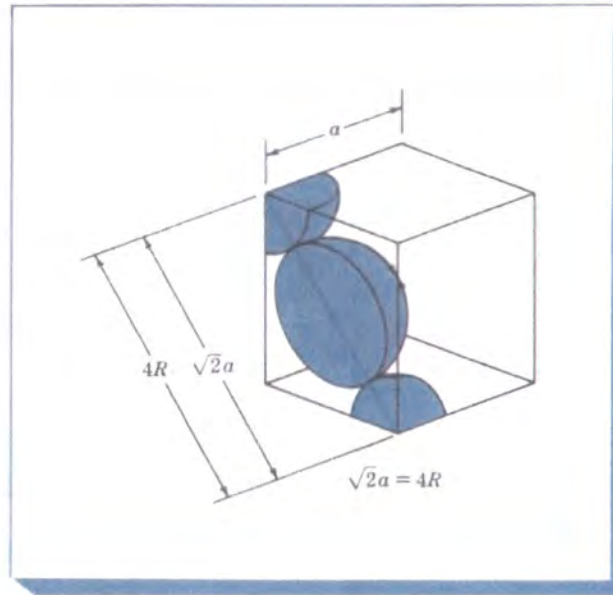
FIGURE 3.7 FCC unit cell showing relationship between the lattice constant a and atomic radius R. Since the atoms touch across the face diagonals $\sqrt{2}a = 4R$.

TABLE 3.3   **Selected Metals Which Have the FCC Crystal Structure at Room Temperature (20°C) and Their Lattice Constants and Atomic Radii**

Metal	Lattice constant a, nm	Atomic radius R,* nm
Aluminum	0.405	0.143
Copper	0.3615	0.128
Gold	0.408	0.144
Lead	0.495	0.175
Nickel	0.352	0.125
Platinum	0.393	0.139
Silver	0.409	0.144

*Calculated from lattice constants by using Eq. (3.3), $R = \sqrt{2}a/4$

Hexagonal Close-Packed (HCP) Crystal Structure

The third common metallic crystal structure is the HCP structure shown in Fig. 3.8. Metals do not crystallize into the simple hexagonal crystal structure shown in Fig. 3.2 because the APF is too low. The atoms can attain a lower energy and a more stable condition by forming the HCP structure of Fig. 3.8. The APF of the HCP crystal structure is 0.74, the same as that for the FCC crystal structure since in both structures the atoms are packed as tightly as possible. In both
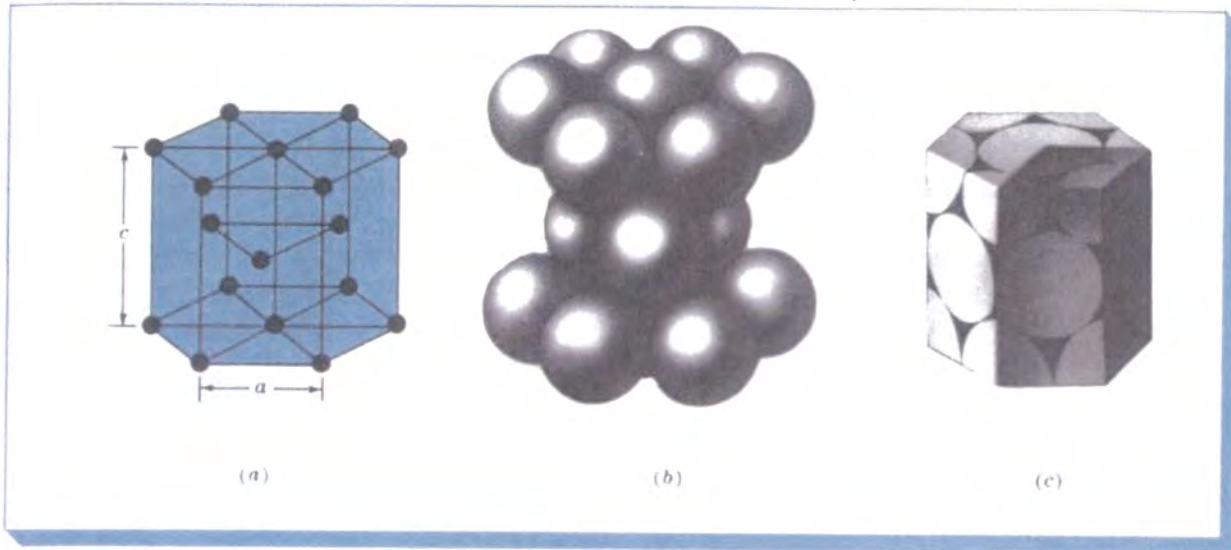
FIGURE 3.8 HCP unit cells: (a) atomic-site unit cell, (b) hard-sphere unit cell, and (c) isolated unit cell. [(b) and (c) After F. M. Miller, "Chemistry, Structure and Dynamics," McGraw-Hill, 1984, p. 296.]

the HCP and FCC crystal structures each atom is surrounded by 12 other atoms, and thus both structures have a coordination number of 12. The differences in the atomic packing in FCC and HCP crystal structures will be discussed in Sec. 3.8.

The isolated HCP unit cell is shown in Fig. 3.8c and has the equivalent of six atoms per unit cell. Three atoms form a triangle in the middle layer, as indicated by the atomic sites in Fig. 3.8a. There are six $\frac{1}{6}$-atom sections on both the top and bottom layers, making an equivalent of two more atoms $(2 \times 6 \times \frac{1}{6} = 2)$. Finally, there is one-half an atom in the center of both the

TABLE 3.4   Selected Metals Which Have the HCP Crystal Structure at Room Temperature (20°C) and Their Lattice Constants, Atomic Radii, and c/a Ratios

Metal	Lattice constants, nm		Atomic radius R, nm	c/a ratio	% deviation from ideality
	a	c			
Cadmium	0.2973	0.5618	0.149	1.890	+15.7
Zinc	0.2665	0.4947	0.133	1.856	+13.6
Ideal HCP				1.633	0
Magnesium	0.3209	0.5209	0.160	1.623	-0.66
Cobalt	0.2507	0.4069	0.125	1.623	-0.66
Zirconium	0.3231	0.5148	0.160	1.593	-2.45
Titanium	0.2950	0.4683	0.147	1.587	-2.81
Beryllium	0.2286	0.3584	0.113	1.568	-3.98

top and bottom layers, making the equivalent of one more atom. The total number of atoms in the HCP crystal structure unit cell is thus 3 + 2 + 1 = 6.

The ratio of the height c of the hexagonal prism of the HCP crystal structure to its basal side a is called the *c/a ratio* (Fig. 3.8a). The *c/a ratio* for an ideal HCP crystal structure consisting of uniform spheres packed as tightly together as possible is 1.633. Table 3.4 on page 79 lists some important HCP metals and their *c/a* ratios. Of the metals listed, cadmium and zinc have *c/a* ratios higher than ideality, which indicates that the atoms in these structures are slightly elongated along the *c* axis of the HCP unit cell. The metals magnesium, cobalt, zirconium, titanium, and beryllium have *c/a* ratios less than the ideal ratio. Therefore, in these metals the atoms are slightly compressed in the direction along the *c* axis. Thus, for the HCP metals listed in Table 3.4 there is a certain amount of deviation from the ideal hard-sphere model.

Example Problem 3.3

Calculate the volume of the zinc crystal structure unit cell by using the following data: pure zinc has the HCP crystal structure with lattice constants $a = 0.2665$ nm and $c = 0.4947$ nm.

Solution:

FIGURE 3.9 Diagrams for calculating the volume of an HCP unit cell. (a) HCP unit cell. (b) Base of HCP unit cell. (c) Triangle ABC removed from base of unit cell.

The volume of the zinc HCP unit cell can be obtained by determining the area of the base of the unit cell and then multiplying this by its height (Fig. 3.9).

The area of the base of the unit cell is area *ABDEFG* of Fig. 3.9a and b. This total area consists of the areas of six equilateral triangles of area *ABC* of Fig. 3.9b. From Fig. 3.9c,

(a)   (b)   (c)
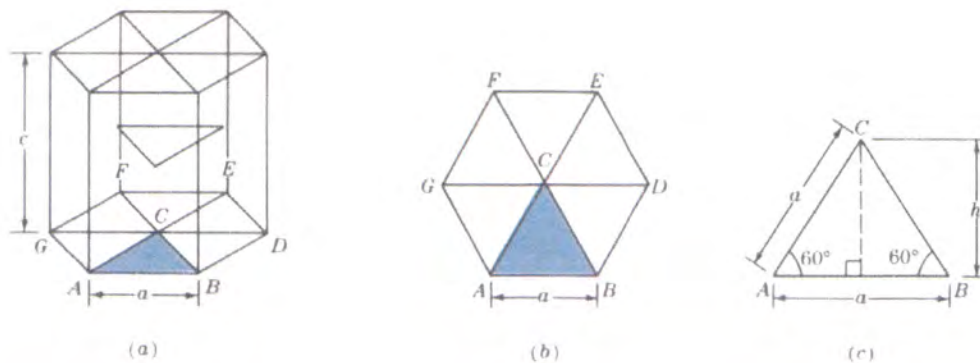
$$\text{Area of triangle } ABC = \tfrac{1}{2}(\text{base})(\text{height})$$

$$= \tfrac{1}{2}(a)(a \sin 60°) = \tfrac{1}{2}a^2 \sin 60°$$

From Fig. 3.9b,

$$\text{Total area of HCP base} = (6)(\tfrac{1}{2}a^2 \sin 60°)$$

$$= 3a^2 \sin 60°$$

From Fig. 3.9a,

$$\text{Volume of zinc HCP unit cell} = (3a^2 \sin 60°)(c)$$

$$= (3)(0.2665 \text{ nm})^2(0.8660)(0.4947 \text{ nm})$$

$$= 0.0913 \text{ nm}^3 \blacktriangleleft$$

3.4 ATOM POSITIONS IN CUBIC UNIT CELLS

To locate atom positions in cubic unit cells, we use rectangular x, y, and z axes. In crystallography the positive x axis is usually the direction coming out of the paper, the positive y axis is the direction to the right of the paper, and the positive z axis is the direction to the top (Fig. 3.10). Negative directions are opposite to those just described.
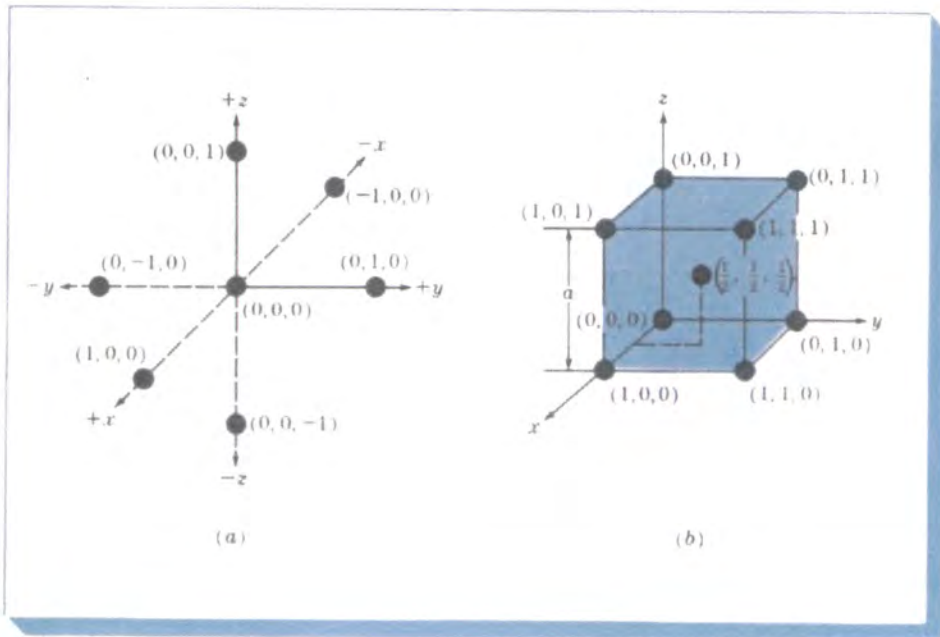
FIGURE 3.10 (a) Rectangular x, y, and z axes for locating atom positions in cubic unit cells. (b) Atom positions in a BCC unit cell.

Atom positions in unit cells are located by using unit distances along the x, y. and z axes, as indicated in Fig. 3.10a. For example, the position coordinates for the atoms in the BCC unit cell are shown in Fig. 3.10b. The atom positions for the eight corner atoms of the BCC unit cell are

$$(0, 0, 0) \quad (1, 0, 0) \quad (0, 1, 0) \quad (0, 0, 1)$$
$$(1, 1, 1) \quad (1, 1, 0) \quad (1, 0, 1) \quad (0, 1, 1)$$

The center atom in the BCC unit cell has the position coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For simplicity sometimes only two atom positions in the BCC unit cell are specified which are $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The remaining atom positions of the BCC unit cell are assumed to be understood. In the same way the atom positions in the FCC unit cell can be located.

3.5   DIRECTIONS IN CUBIC UNIT CELLS

Frequently it is necessary to refer to specific directions in crystal lattices. This is especially important for metals and alloys that have properties which vary with crystallographic orientation. *For cubic crystals the crystallographic direction indices are the vector components of the direction resolved along each of the coordinate axes and reduced to the smallest integers.*

To diagrammatically indicate a direction in a cubic unit cell, we draw a direction vector from an origin which is usually a corner of the cubic cell until it emerges from the cube surface (Fig. 3.11). The position coordinates of the unit cell where the direction vector emerges from the cube surface after being converted to integers are the direction indices. The direction indices are enclosed by square brackets with no separating commas.

For example, the position coordinates of the direction vector *OR* in Fig.

FIGURE 3.11 Some directions in cubic unit cells.
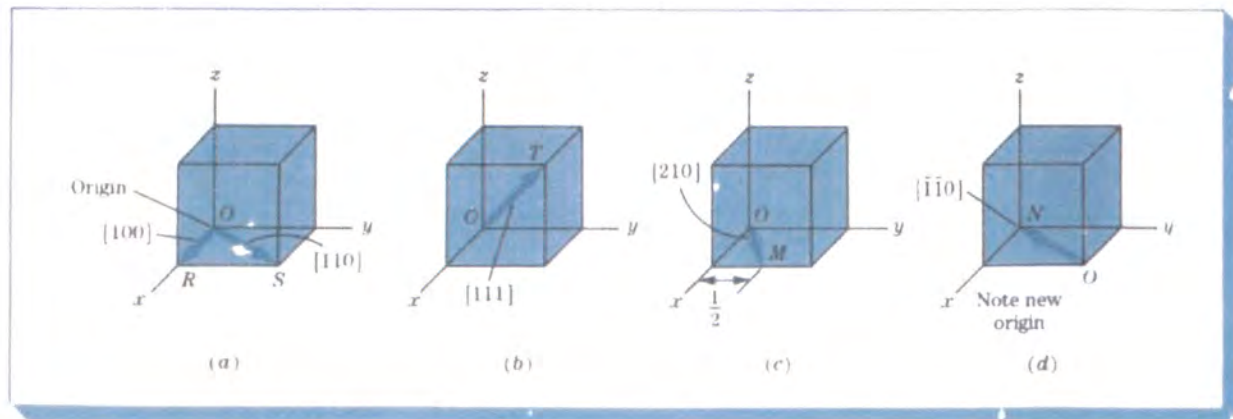
3.11*a* where it emerges from the cube surface are (1, 0, 0), and so the direction indices for the direction vector *OR* are [100]. The position coordinates of the direction vector *OS* (Fig. 3.11*a*) are (1, 1, 0), and so the direction indices for *OS* are [110]. The position coordinates for the direction vector *OT* (Fig. 3.11*b*) are (1, 1, 1), and so the direction indices of *OT* are [111].

The position coordinates of the direction vector *OM* (Fig. 3.11*c*) are $(1, \frac{1}{2}, 0)$, and since the direction vectors must be integers, these position coordinates must be multiplied by 2 to obtain integers. Thus, the direction indices of *OM* become $2(1, \frac{1}{2}, 0) = [210]$. The position coordinates of the vector *ON* (Fig. 3.11*d*) are $(-1, -1, 0)$. A negative direction index is written with a bar over the index. Thus, the direction indices for the vector *ON* are $[\bar{1}\bar{1}0]$. Note that to draw the direction *ON* inside the cube the origin of the direction vector had to be moved to the front lower-right corner of the unit cube (Fig. 3.11*d*). Further examples of cubic direction vectors are given in Example Problem 3.4.

The letters *u, v, w* are used in a general sense for the direction indices in the *x, y,* and *z* directions, respectively, and are written as [*uvw*]. It is also important to note that *all parallel direction vectors have the same direction indices.*

Directions are said to be *crystallographically equivalent* if the atom spacing along each direction is the same. For example, the following cubic edge directions are crystallographic equivalent directions:

$$[100], [010], [001], [0\bar{1}0], [00\bar{1}], [\bar{1}00] \equiv \langle 100 \rangle$$

Equivalent directions are called *indices of a family or form.* The notation $\langle 100 \rangle$ is used to indicate cubic edge directions collectively. Other directions of a form are the cubic body diagonals $\langle 111 \rangle$ and the cubic face diagonals $\langle 110 \rangle$.

Example Problem 3.4

Draw the following direction vectors in cubic unit cells:
(*a*) [100] and [110]   (*b*) [112]   (*c*) [$\bar{1}$10]   (*d*) [$\bar{3}2\bar{1}$]

Solution:

(*a*) The position coordinates for the [100] direction are (1, 0, 0) (Fig. 3.12*a*). The position coordinates for the [110] direction are (1, 1, 0) (Fig. 3.12*a*).
(*b*) The position coordinates for the [112] direction are obtained by dividing the direction indices by 2 so that they will lie within the unit cube. Thus they are $(\frac{1}{2}, \frac{1}{2}, 1)$ (Fig. 3.12*b*).
(*c*) The position coordinates for the [$\bar{1}$10] direction are $(-1, 1, 0)$ (Fig. 3.12*c*). Note that the origin for the direction vector must be moved to the lower left front corner of the cube.
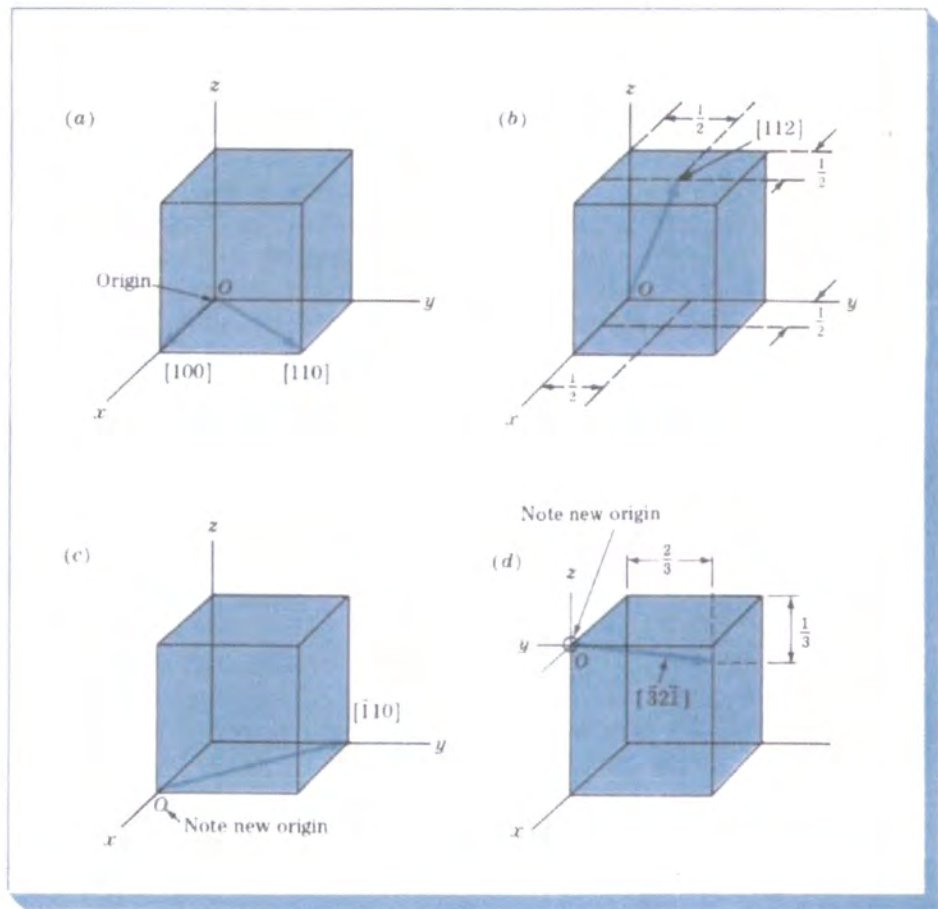
FIGURE 3.12 Direction vectors in cubic unit cells.

(*d*) The position coordinates for the [$\bar{3}2\bar{1}$] direction are obtained by first dividing all the indices by 3, the largest index. This gives -1, $\frac{2}{3}$, $-\frac{1}{3}$ for the position coordinates of the exit point of the direction [$\bar{3}2\bar{1}$] which are shown in Fig. 3.12*d*.

Example Problem 3.5

Determine the direction indices of the cubic direction shown in Fig. EP3.5*a*.

Solution:

Parallel directions have the same direction indices, and so we move the direction vector in a parallel manner until its tail reaches the nearest corner of the cube, still keeping the vector within the cube. Thus, in this case, the upper left front corner becomes the new origin for the direction vector (Fig. EP3.5*b*). We can now determine the position coordinates where the direction vector leaves the unit cube. These are $x = -1$, $y = $
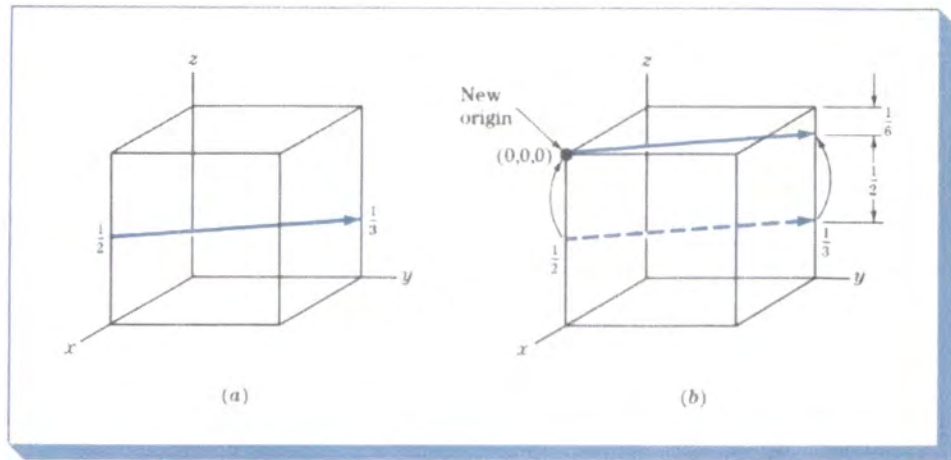
FIGURE EP3.5

$+1$, and $z = -\frac{1}{6}$. The position coordinates of the direction where it leaves the unit cube are thus $(-1, +1, -\frac{1}{6})$. The direction indices for this direction are, after clearing the fraction $6x$, $(-1, +1, -\frac{1}{6})$, or $[\bar{6}6\bar{1}]$.

Example Problem 3.6

Determine the direction indices of the cubic direction between the position coordinates $(\frac{3}{4}, 0, \frac{1}{4})$ and $(\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$.

Solution:

First we locate the origin and termination points of the direction vector in a unit cube, as shown in Fig. EP3.6. The fraction vector components for this direction are
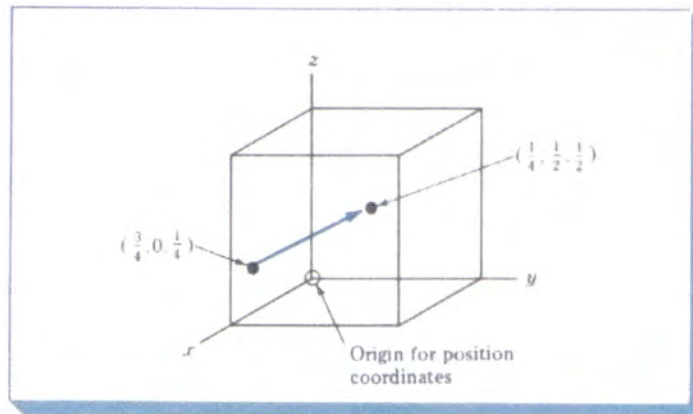
FIGURE EP3.6

$$x = -(\tfrac{3}{4} - \tfrac{1}{4}) = -\tfrac{1}{2}$$

$$y = (\tfrac{1}{2} - 0) = \tfrac{1}{2}$$

$$z = (\tfrac{1}{2} - \tfrac{1}{4}) = \tfrac{1}{4}$$

Thus, the vector direction has fractional vector components of $-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{4}$. The direction indices will be in the same ratio as their fractional components. By multiplying the fraction vector components by 4, we obtain $[\bar{2}21]$ for the direction indices of this vector direction.

3.6 MILLER INDICES FOR CRYSTALLOGRAPHIC PLANES IN CUBIC UNIT CELLS

Sometimes it is necessary to refer to specific lattice planes of atoms within a crystal structure, or it may be of interest to know the crystallographic orientation of a plane or group of planes in a crystal lattice. To identify crystal planes in cubic crystal structures, the *Miller*[1] *notation system* is used. The *Miller indices of a crystal plane* are defined as the *reciprocals of the fractional intercepts (with fractions cleared) which the plane makes with the crystallographic x, y, and z axes of the three nonparallel edges of the cubic unit cell.* The cube edges of the unit cell represent unit lengths, and the intercepts of the lattice planes are measured in terms of these unit lengths.

The procedure for determining the Miller indices for a cubic crystal plane is as follows:

1. Choose a plane that does *not* pass through the origin at $(0, 0, 0)$.
2. Determine the intercepts of the plane in terms of the crystallographic x, y, and z axes for a unit cube. These intercepts may be fractions.
3. Form the reciprocals of these intercepts.
4. Clear fractions and determine the *smallest* set of whole numbers which are in the same ratio as the intercepts. These whole numbers are the Miller indices of the crystallographic plane and are enclosed in parentheses without the use of commas. The notation (hkl) is used to indicate Miller indices in a general sense, where h, k, and l are the Miller indices of a cubic crystal plane for the x, y, and z axes, respectively.

Figure 3.13 shows three of the most important crystallographic planes of cubic crystal structures. Let us first consider the shaded crystal plane in Fig. 3.13a, which has the intercepts 1, ∞, ∞ for the x, y, and z axes, respectively.

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[1] William Hallowes Miller (1801–1880) English crystallographer who published a "Treatise on Crystallography" in 1839, using crystallographic reference axes which were parallel to the crystal edges and using reciprocal indices.
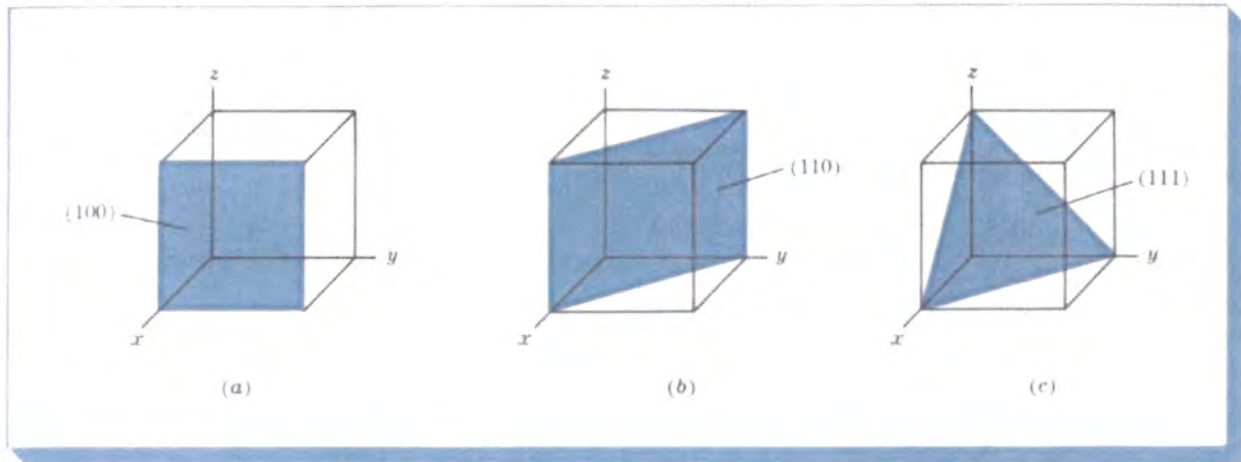
FIGURE 3.13 Miller indices of some important cubic crystal planes. (a) (100), (b) (110), and (c) (111).

We take the reciprocals of these intercepts to obtain the Miller indices, which are therefore 1, 0, 0. Since these numbers do not involve fractions, the Miller indices for this plane are (100), which is read as the one-zero-zero plane. Next let us consider the second plane shown in Fig. 3.13b. The intercepts of this plane are 1, 1, ∞. Since the reciprocals of these numbers are 1, 1, 0, which do not involve fractions, the Miller indices of this plane are (110). Finally, the third plane (Fig. 3.13c) has the intercepts 1, 1, 1, which give the Miller indices (111) for this plane.

Consider now the cubic crystal plane shown in Fig. 3.14 which has the intercepts $\frac{1}{3}$, $\frac{2}{3}$, 1. The reciprocals of these intercepts are 3, $\frac{3}{2}$, 1. Since fractional
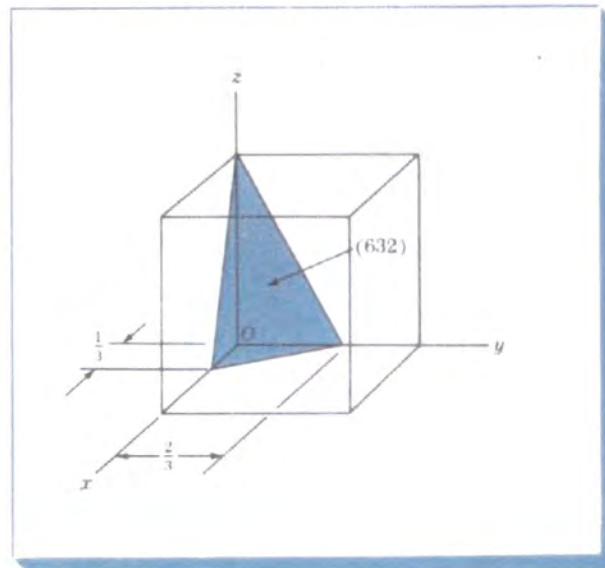
FIGURE 3.14 Cubic crystal plane (632) which has fractional intercepts

intercepts are not allowed, these fractional intercepts must be multiplied by 2 to clear the ⅔ fraction. Thus, the reciprocal intercepts become 6, 3, 2 and the Miller indices are (632). Further examples of cubic crystal planes are shown in Example Problem 3.7.

If the crystal plane being considered passes through the origin so that one or more intercepts are zero, the plane must be moved to an equivalent position in the same unit cell and the plane must remain parallel to the original plane. This is possible because all equispaced parallel planes are indicated by the same Miller indices.

If sets of equivalent lattice planes are related by the symmetry of the crystal system, they are called *planes of a family or form*, and the indices of one plane of the family are enclosed in braces as $\{hkl\}$ to represent the indices of a family of symmetrical planes. For example, the Miller indices of the cubic surface planes (100), (010), and (001) are designated collectively as a family or form by the notation $\{100\}$.

Example Problem 3.7

Draw the following crystallographic planes in cubic unit cells:
(a) (101)   (b) (1$\bar{1}$0)   (c) (221)
(d) Draw a (110) plane in a BCC atomic-site unit cell, and list the position coordinates of the atoms whose centers are intersected by this plane.

Solutions:

(a)

(b)   Note new origin

(c)

(d)
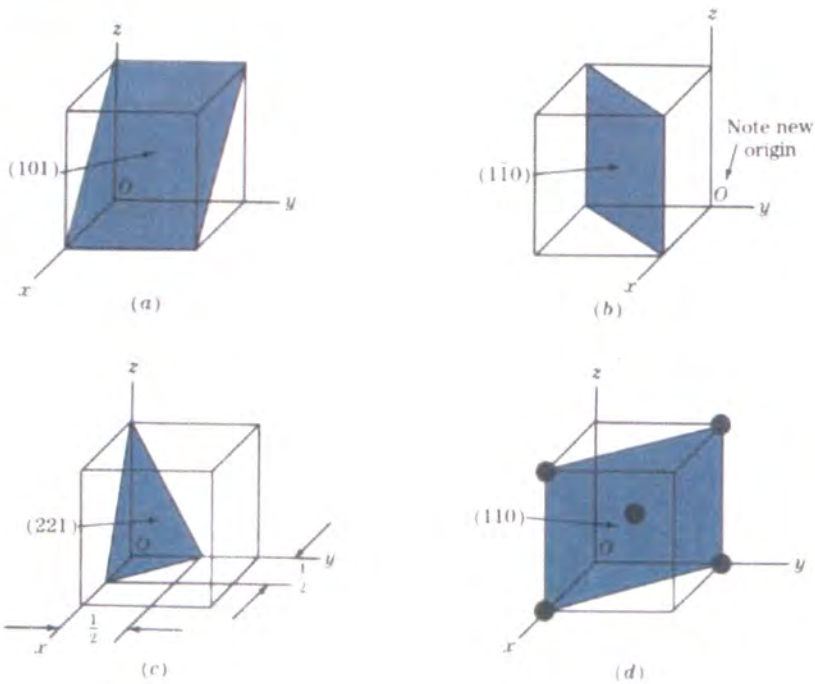
(a) First determine the reciprocals of the Miller indices of the (101) plane. These are 1, ∞, 1. The (101) plane must pass through a unit cube at intercepts $x = 1$ and $z = 1$ and be parallel to the y axis.

(b) First determine the reciprocals of the Miller indices of the ($1\bar{1}0$) plane. These are 1, -1, ∞. The ($1\bar{1}0$) plane must pass through a unit cube at intercepts $x = 1$ and $y = -1$ and be parallel to the z axis. Note that the origin of axes must be moved to the lower right back side of the cube.

(c) First determine the reciprocals of the Miller indices of the (221) plane. These are $\frac{1}{2}$, $\frac{1}{2}$, 1. The (221) plane must pass through a unit cube at intercepts $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = 1$.

(d) Atom positions whose centers are intersected by the (110) plane are (1, 0, 0), (0, 1, 0), (1, 0, 1), (0, 1, 1), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). These positions are indicated by the solid circles.

An important relationship for the cubic system, and *only the cubic system*, is that the direction indices of a direction *perpendicular* to a crystal plane are the same as the Miller indices of that plane. For example, the [100] direction is perpendicular to the (100) crystal plane.

In cubic crystal structures the *interplanar spacing* between two closest parallel planes with the same Miller indices is designated d_{hkl}, where h, k, and l are the Miller indices of the planes. This spacing represents the distance from a selected origin containing one plane and another parallel plane with the
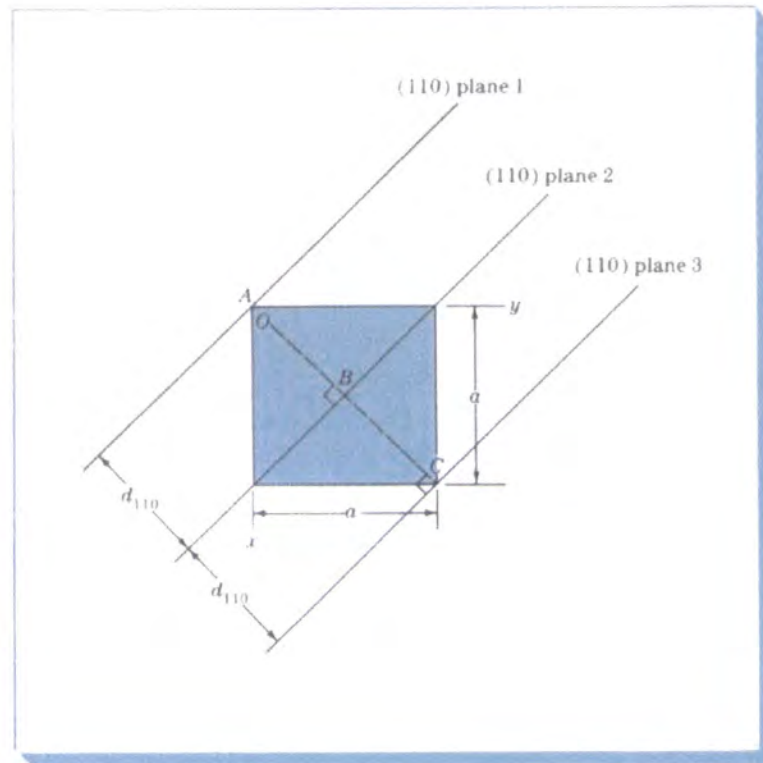
FIGURE 3.15 Top view of cubic unit cell showing the distance between (110) crystal planes. d_{110}.

same indices which is closest to it. For example, the distance between (110) planes 1 and 2, d_{110}, in Fig. 3.15 on page 89 is AB. Also, the distance between (110) planes 2 and 3 is d_{110} and is length BC in Fig. 3.15. From simple geometry, it can be shown that for cubic crystal structures

$$ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.4} $$

where d_{hkl} = interplanar spacing between parallel closest planes with Miller
indices h, k, and l
a = lattice constant (edge of unit cube)
h, k, l = Miller indices of cubic planes being considered

Example Problem 3.8

Determine the Miller indices of the cubic crystallographic plane shown in Fig. EP3.8a.

Solution:

First, transpose the plane parallel to the z axis $\frac{1}{4}$ unit to the right along the y axis as shown in Fig. EP3.8b so that the plane intersects the x axis at a unit distance from the new origin located at the lower-right back corner of the cube. The new intercepts of the transposed plane with the coordinate axes are now $(+1, -\frac{5}{12}, \infty)$. Next, we take the reciprocals of these intercepts to give $(1, -\frac{12}{5}, 0)$. Finally, we clear the $\frac{12}{5}$ fraction to obtain $(5\overline{1}20)$ for the Miller indices of this plane.
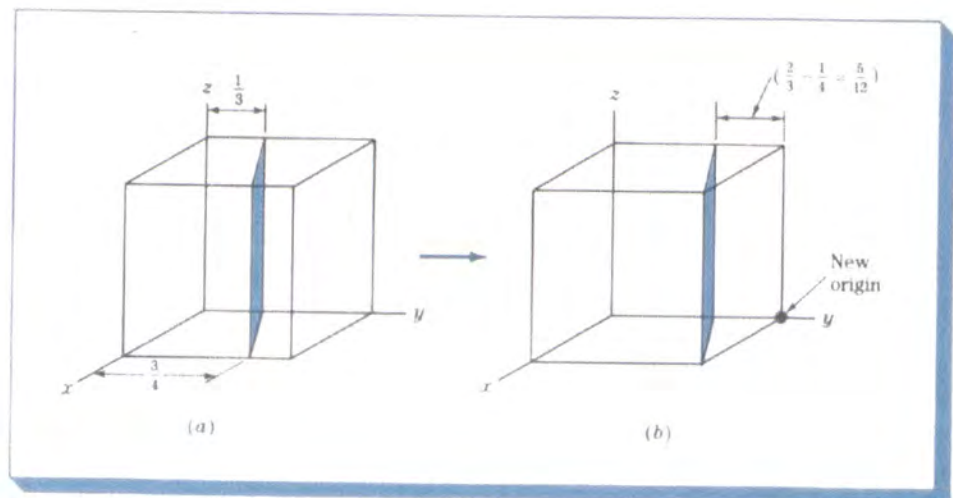
FIGURE EP3.8

Example Problem 3.9

Determine the Miller indices of the cubic crystal plane which intersects the position coordinates $(1, \frac{1}{4}, 0)$, $(1, 1, \frac{1}{2})$, $(\frac{3}{4}, 1, \frac{1}{4})$, and all coordinate axes.

Solution:

First, we locate the three position coordinates as indicated in Fig. EP3.9 at A, B, and C. Next, we join A and B and extend AB to D and then join A and C. Finally, we join A to C to complete plane ACD. The origin for this plane in the cube can be chosen at E, which gives axial intercepts for plane ACD at $x = -\frac{1}{2}$, $y = -\frac{3}{4}$, and $z = \frac{1}{2}$. The reciprocals of these axial intercepts are -2, $-\frac{4}{3}$, and 2. Multiplying these intercepts by 3 clears the fraction, giving Miller indices for the plane of $(\bar{6}\bar{4}6)$.
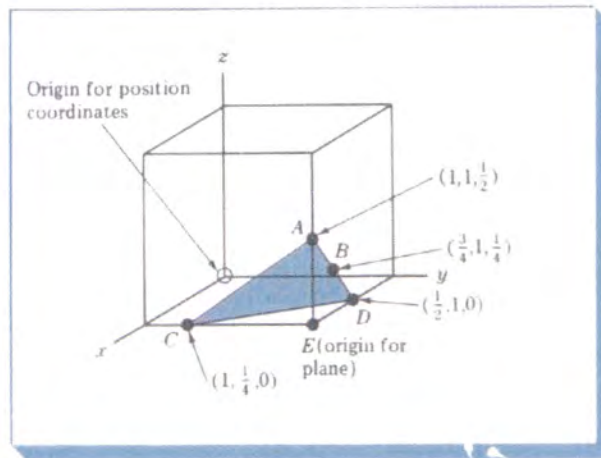
FIGURE EP3.9

Example Problem 3.10

Copper has an FCC crystal structure and a unit cell with a lattice constant of 0.361 nm. What is its interplanar spacing d_{220}?

Solution:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.361 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.128 \text{ nm} \blacktriangleleft$$

3.7 CRYSTALLOGRAPHIC PLANES AND DIRECTIONS IN HEXAGONAL UNIT CELLS

Indices for Crystal Planes in HCP Unit Cells

Crystal planes in HCP unit cells are commonly identified by using four indices instead of three. The HCP crystal plane indices, called *Miller-Bravais indices*, are denoted by the letters h, k, i, and l and are enclosed in parentheses as ($hkil$). These four-digit hexagonal indices are based on a coordinate system with four axes, as shown in Fig. 3.16 in an HCP unit cell. There are three basal axes, a_1, a_2, and a_3, which make 120° with each other. The fourth axis or c axis is the vertical axis located at the center of the unit cell. The a unit of measurement along the a_1, a_2, and a_3 axes is the distance between the atoms along these axes and is indicated in Fig. 3.16. The unit of measurement along the c axis is the height of the unit cell. The reciprocals of the intercepts that a crystal plane makes with the a_1, a_2, and a_3 axes give the h, k, and i indices, while the reciprocal of the intercept with the c axis gives the l index.

Basal planes   The basal planes of the HCP unit cell are very important planes for this unit cell and are indicated in Fig. 3.17a. Since the basal plane on the top of the HCP unit cell in Fig. 3.17a is parallel to the a_1, a_2, and a_3 axes, the intercepts of this plane with these axes will all be infinite. Thus, $a_1 = \infty$, $a_2 = \infty$, and $a_3 = \infty$. The c axis, however, is unity since the top basal plane intersects the c axis at unit distance. Taking the reciprocals of these intercepts gives the Miller-Bravais indices for the HCP basal plane. Thus $h = 0$, $k = 0$, $i = 0$, and $l = 1$. The HCP basal plane is, therefore, a zero-zero-zero-one or (0001) plane.
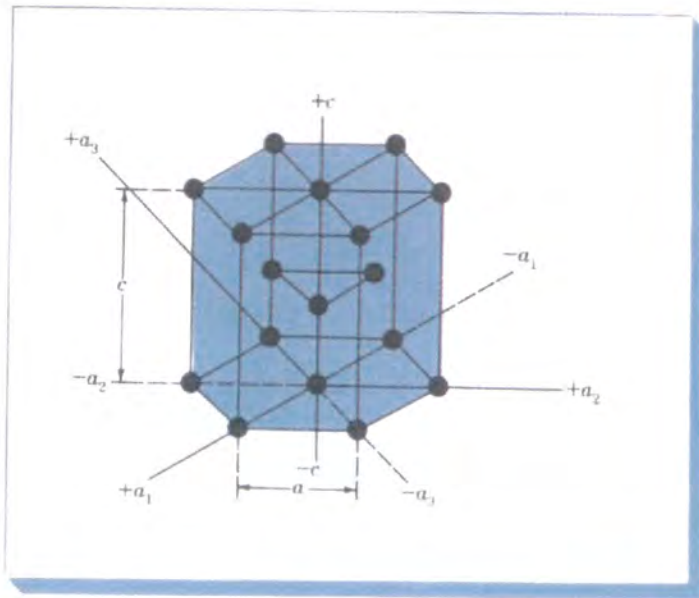
FIGURE 3.16 The four coordinate axes (a_1, a_2, a_3, and c) of the HCP crystal structure unit cell
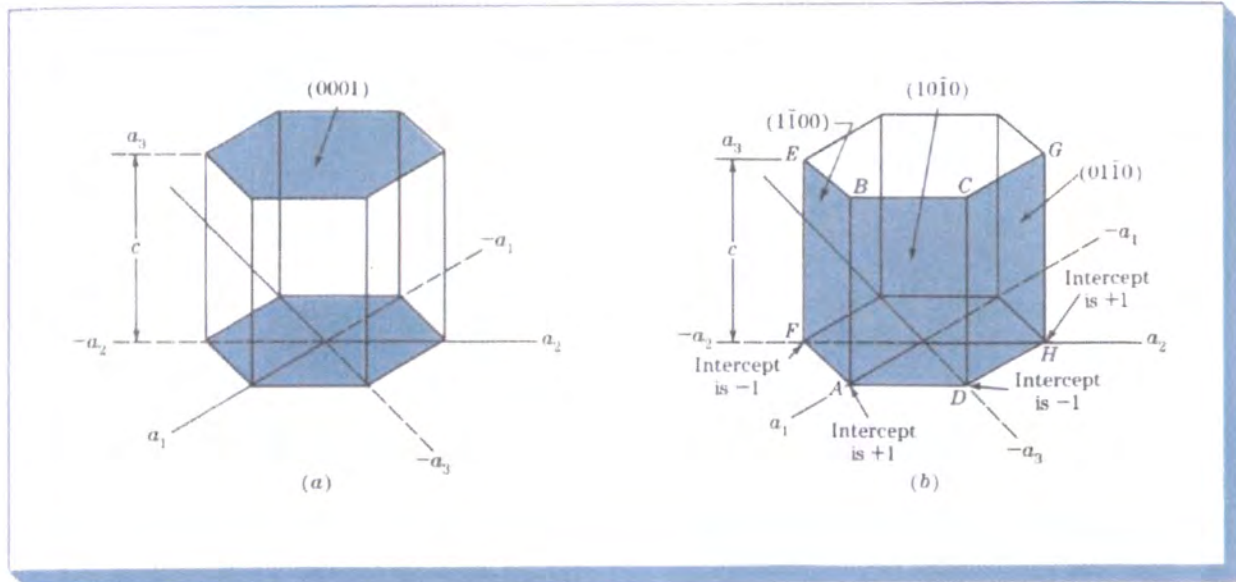
FIGURE 3.17 Miller-Bravais indices of hexagonal crystal planes: (a) basal planes, and (b) prism planes.

Prism planes Using the same method, the intercepts of the front prism plane (ABCD) of Fig. 3.17b are $a_1 = +1$, $a_2 = \infty$, $a_3 = -1$, and $c = \infty$. Taking the reciprocals of these intercepts gives $h = 1$, $k = 0$, $i = -1$, and $l = 0$, or the $(10\bar{1}0)$ plane. Similarly, the *ABEF* prism plane of Fig. 3.17b has the indices $(1\bar{1}00)$ and the *DCGH* plane the indices $(01\bar{1}0)$. All HCP prism planes can be identified collectively as the $\{10\bar{1}0\}$ family of planes.

Sometimes HCP planes are identified only by three indices (*hkl*) since $h + k = -i$. However, the (*hkil*) indices are used more commonly because they reveal the hexagonal symmetry of the HCP unit cell.
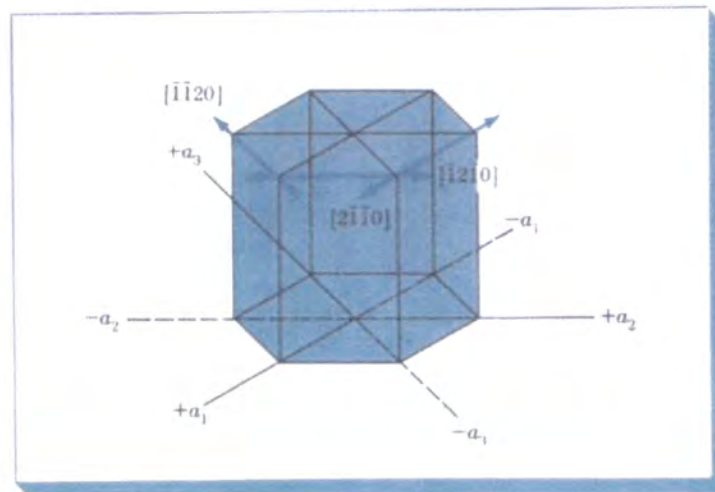
FIGURE 3.18 Some important directions in HCP unit cells.

Direction Indices in HCP Unit Cells

Directions in HCP unit cells are also usually indicated by four indices u, v, t, and w enclosed by square brackets as $[uvtw]$. The u, v, and t indices are lattice vectors in the a_1, a_2, and a_3 directions, respectively (Fig. 3.16), and the w index is a lattice vector in the c direction. To maintain uniformity for both HCP indices for planes and directions, it has been agreed that $u + v = -t$ for directions also, leading to a cumbersome method of designating directions whose method of determination is beyond the scope of this book. Some of the important directions in HCP unit cells are indicated in Fig. 3.18.

3.8 COMPARISON OF FCC, HCP, AND BCC CRYSTAL STRUCTURES

Face-Centered Cubic and Hexagonal Close-Packed Crystal Structures

As previously pointed out, both the HCP and FCC crystal structures are close-packed structures. That is, their atoms which are considered approximate "spheres" are packed together as closely as possible so that an atomic packing factor of 0.74 is attained.[1] The (111) planes of the FCC crystal structure shown

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[1] As pointed out in Sec. 3.3, the atoms in the HCP structure deviate to varying degrees from ideality. In some HCP metals the atoms are elongated along the c axis, and in other cases they are compressed along the c axis (see Table 3.4)

FIGURE 3.19 Comparison of the (a) FCC crystal structure showing the close-packed (111) planes, and (b) the HCP crystal structure showing the close-packed (0001) planes. (*After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I, "Structure," Wiley, 1964, p. 51.*)

(a)   (b)
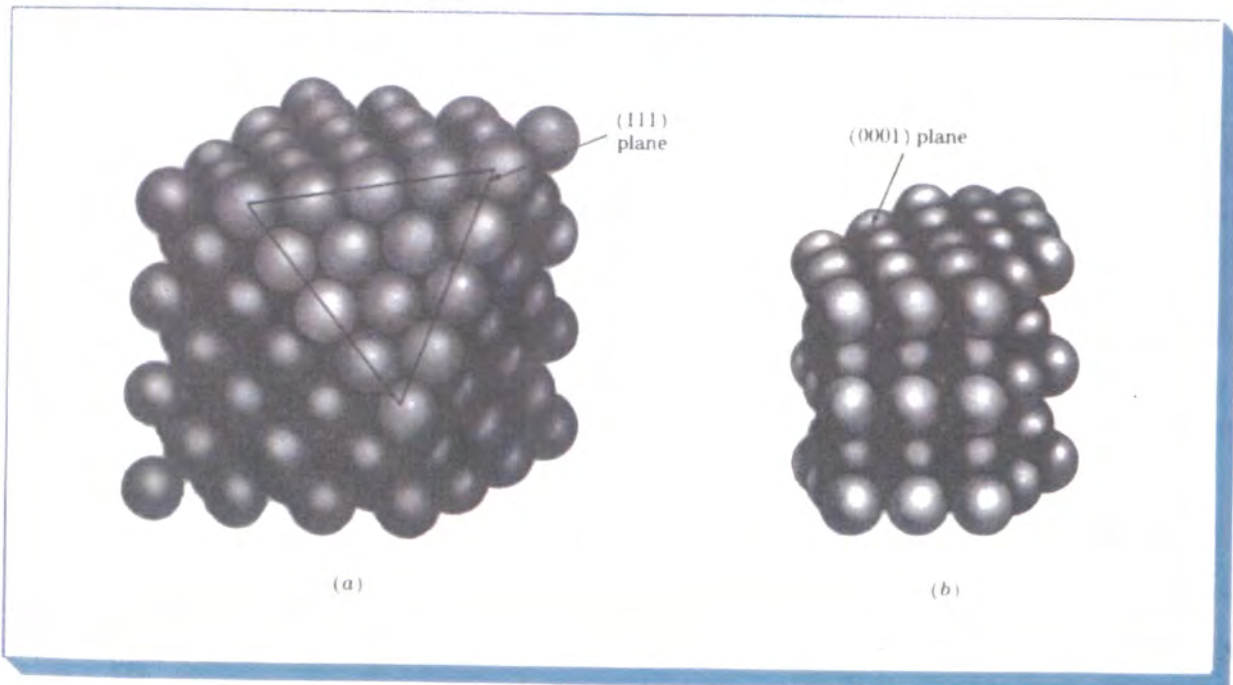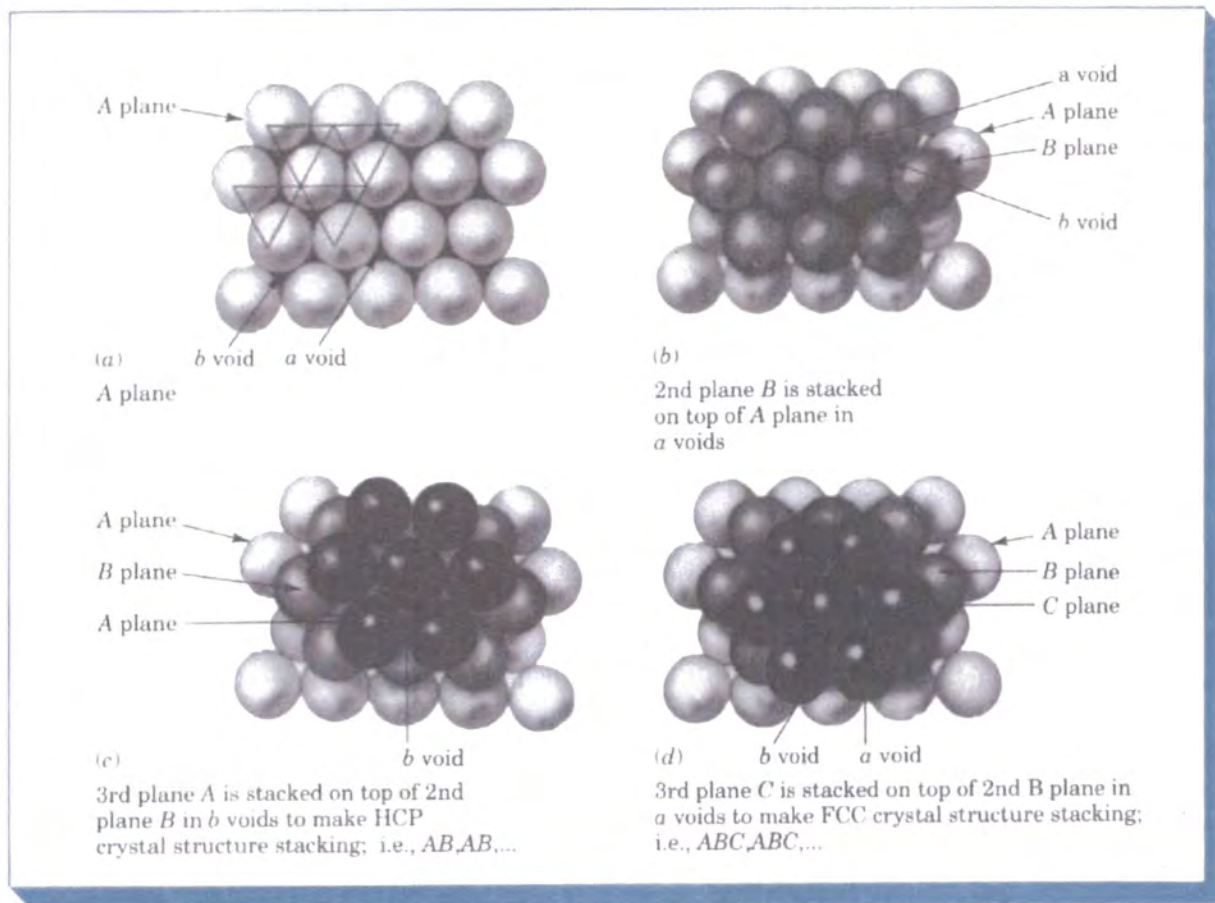
FIGURE 3.20 Formation of HCP and FCC crystal structures by changing the stacking of close-packed planes of atoms. (a) A plane containing a- and b-type voids between the atoms. (b) B plane is stacked on top of A plane in a voids. (c) Third plane: Another A plane is stacked on top of the b voids of B plane to make HCP crystal structure stacking. i.e., ABAB.... (d) Third plane (alternate): a C plane is stacked on the a voids of B plane to make an FCC stacked crystal structure: ABCABC....

in Fig. 3.19a have the identical packing arrangement as the (0001) planes of the HCP crystal structure shown in Fig. 3.19b. However, the three-dimensional FCC and HCP crystal structures are not identical because there is a difference in the stacking arrangement of their atomic planes, which can best be described by considering the stacking of hard spheres representing atoms. As a useful analogy, one can imagine the stacking of planes of equal-sized marbles on top of each other, minimizing the space between the marbles.

Consider first a plane of close-packed atoms designated the A plane, as shown in Fig. 3.20a. Note that there are two different types of empty spaces or voids between the atoms. The voids pointing to the top of the page are designated a voids and those pointing to the bottom of the page, b voids. A second plane of atoms can be placed over the a or b voids and the same three-dimensional structure will be produced. Let us place plane B over the a voids,

as shown in Fig. 3.20*b*. Now if a third plane of atoms is placed over plane *B* to form a closest-packed structure, it is possible to form two different close-packed structures. One possibility is to place the atoms of the third plane in the *b* voids of the *B* plane. Then the atoms of this third plane will lie directly over those of the *A* plane and thus can be designated another *A* plane (Fig. 3.20*c*). If subsequent planes of atoms are placed in this same alternating stacking arrangement, then the stacking sequence of the three-dimensional structure produced can be denoted by *ABABAB*.... Such a stacking sequence leads to the HCP crystal structure (Fig. 3.19*b*).

The second possibility for forming a simple close-packed structure is to place the third plane in the *a* voids of plane *B* (Fig. 3.20*d*). This third plane is designated the *C* plane since its atoms lie neither directly above those of the *B* plane nor of the *A* plane. The stacking sequence in this close-packed structure is thus designated *ABCABCABC* ... and leads to the FCC structure shown in Fig. 3.19*a*.

Body-Centered Cubic Crystal Structure   The BCC structure is not a close-packed structure and hence does not have close-packed planes like the {111} planes in the FCC structure and the {0001} planes in the HCP structure. The most densely packed planes in the BCC structure are the {110} family of planes of which the (110) plane is shown in Fig. 3.21*b*. The atoms, however, in the BCC structure do have close-packed directions along the cube diagonals, which are the ⟨111⟩ directions.

FIGURE 3.21 BCC crystal structure showing (*a*) the (100) plane and (*b*) a section of the (110) plane. Note that this is not a close-packed structure but that diagonals are close-packed directions. [(*a*) After W. G. Moffatt, G. W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p. 51.]
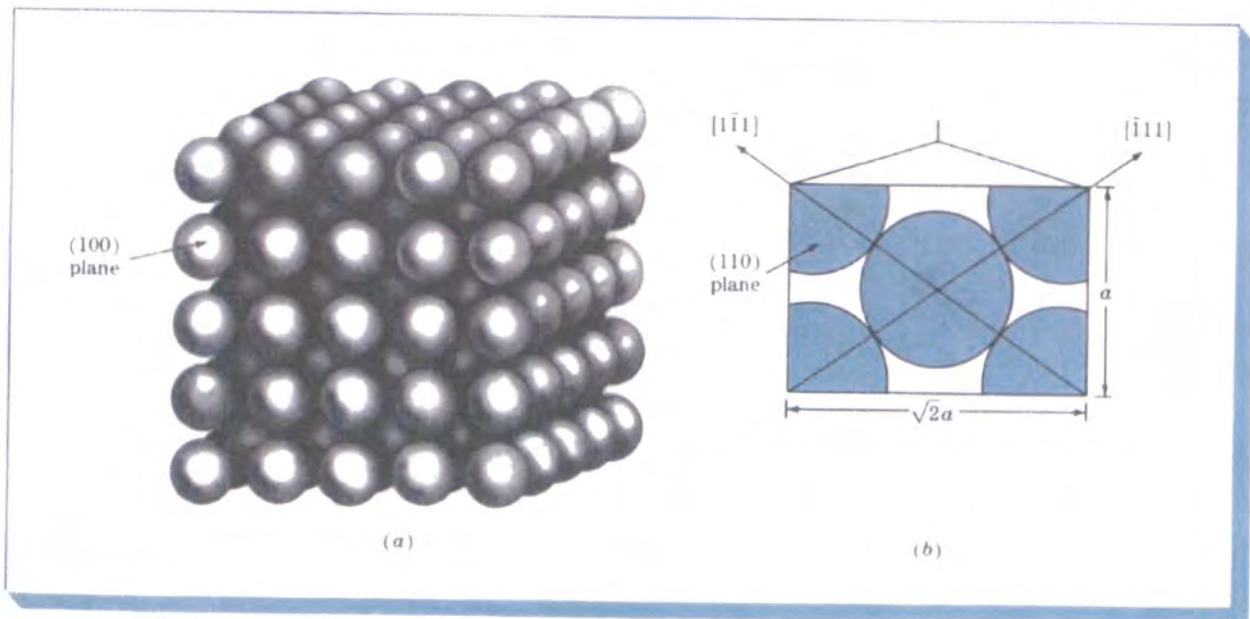
3.9 VOLUME, PLANAR, AND LINEAR DENSITY UNIT-CELL CALCULATIONS

Volume Density   Using the hard-sphere atomic model for the crystal structure unit cell of a metal and a value for the atomic radius of the metal obtained from x-ray diffraction analysis, a value for the volume density of a metal can be obtained by using the equation

$$\text{Volume density of metal} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \tag{3.5}$$

In Example Problem 3.11 a value of 8.98 Mg/m^3 (8.98 g/cm^3) is obtained for the density of copper. The handbook experimental value for the density of copper is 8.96 Mg/m^3 (8.96 g/cm^3). The slightly lower density of the experimental value could be attributed to the absence of atoms at some atomic sites (vacancies), line defects, and mismatch where grains meet (grain boundaries). These crystalline defects are discussed in Chap. 4. Another cause of the discrepancy could also be due to the atoms not being perfect spheres.

Example Problem 3.11

Copper has an FCC crystal structure and an atomic radius of 0.1278 nm. Assuming the atoms to be hard spheres which touch each other along the face diagonals of the FCC unit cell as shown in Fig. 3.7, calculate a theoretical value for the density of copper in megagrams per cubic meter. The atomic mass of copper is 63.54 g/mol.

Solution:

For the FCC unit cell, $\sqrt{2}a = 4R$, where a is the lattice constant of the unit cell and R is the atomic radius of the copper atom. Thus

$$a = \frac{4R}{\sqrt{2}} = \frac{(4)(0.1278 \text{ nm})}{\sqrt{2}} = 0.361 \text{ nm}$$

$$\text{Volume density of copper} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \tag{3.5}$$

In the FCC unit cell there are four atoms/unit cell. Each copper atom has a mass of (63.54 g/mol)/(6.02 $\times$ 10^{23} atoms/mol). Thus the mass m of Cu atoms in the FCC unit cell is

$$m = \frac{(4 \text{ atoms})(63.54 \text{ g/mol})}{6.02 \times 10^{23} \text{ atoms/mol}} \left(\frac{10^{-6} \text{ Mg}}{\text{g}} \right) = 4.22 \times 10^{-28} \text{ Mg}$$

The volume V of the Cu unit cell is

$$V = a^3 = \left(0.361 \text{ nm} \times \frac{10^{-9} \text{ m}}{\text{nm}} \right)^3 = 4.70 \times 10^{-29} \text{ m}^3$$

Thus the density of copper is

$$\rho_v = \frac{m}{V} = \frac{4.22 \times 10^{-28} \text{ Mg}}{4.70 \times 10^{-29} \text{ m}^3} = 8.98 \text{ Mg/m}^3 \qquad (8.98 \text{ g/cm}^3) \blacktriangleleft$$

Planar Atomic Density Sometimes it is important to determine the atomic densities on various crystal planes. To do this a quantity called the *planar atomic density* is calculated by using the relationship

Planar atomic density $= \rho_p$

$$= \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}}$$

(3.6)

For convenience the area of a plane which intersects a unit cell is usually used in these calculations, as shown, for example, in Fig. 3.22 for the (110) plane in a BCC unit cell. In order for an atom area to be counted in this calculation, the plane of interest must intersect the center of an atom. In Example Problem 3.12 the (110) plane intersects the centers of five atoms, but the equivalent of only two atoms is counted since only one-quarter of each of the four corner atoms is included in the area inside the unit cell. Figure 3.22A shows area occupied by atoms on a planar section of an (111) plane in the FCC lattice.
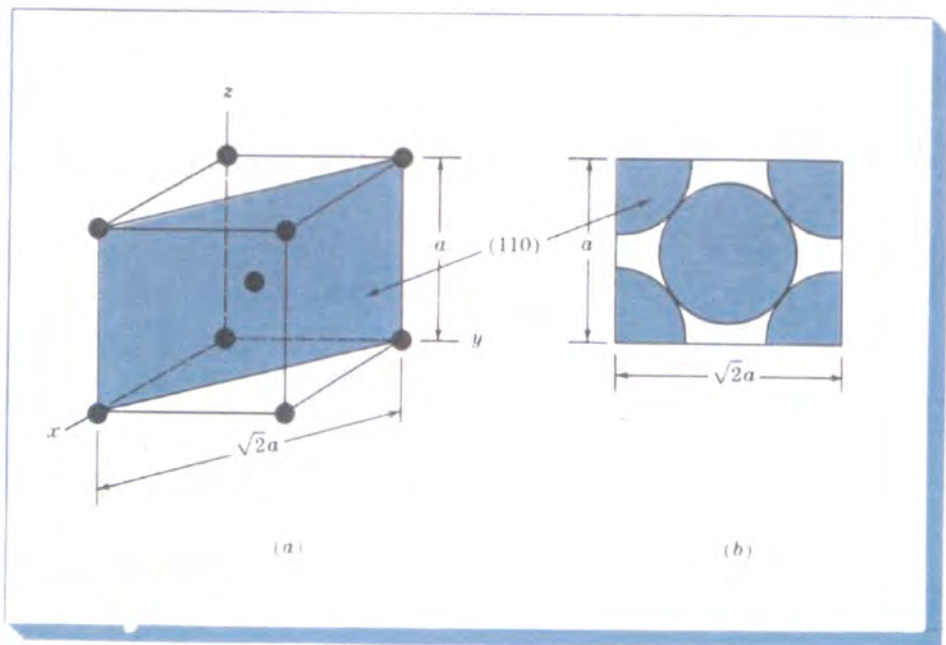
FIGURE 3.22 (a) A BCC atomic-site unit cell showing a shaded (110) plane. (b) Areas of atoms in BCC unit cell cut by the (110) plane.
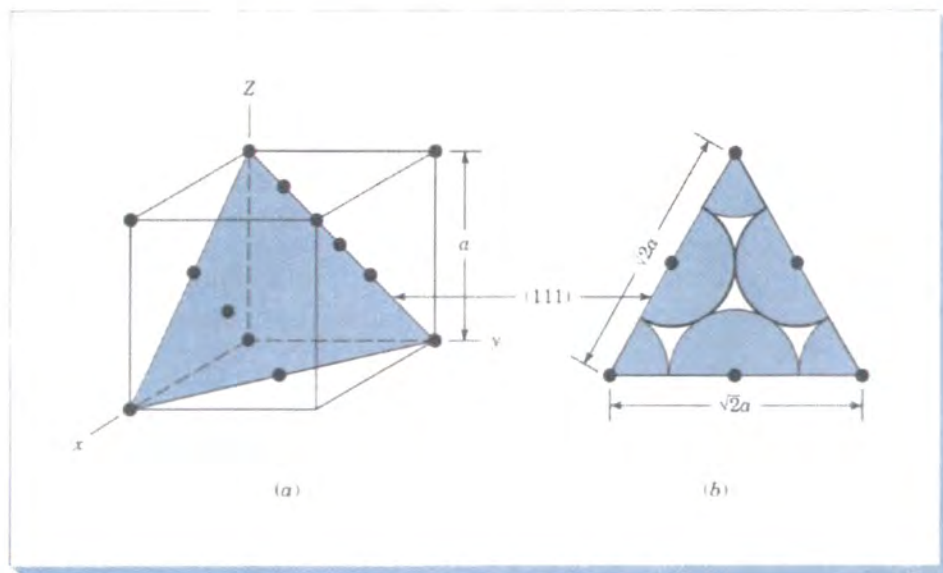
FIGURE 3.22A (a) An FCC atomic-site unit cell showing a shaded (111) plane. (b) Areas of atoms in FCC unit cell cut by the (111) plane.

Example Problem 3.12

Calculate the planar atomic density ρ_p on the (110) plane of the α iron BCC lattice in atoms per square millimeter. The lattice constant of α iron is 0.287 nm.

Solution:

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \quad (3.6)$$

The equivalent number of atoms intersected by the (110) plane in terms of the surface area inside the BCC unit cell is shown in Fig. 3.22 and is

$$1 \text{ atom at center} + 4 \times \tfrac{1}{4} \text{ atoms at four corners of plane} = 2 \text{ atoms}$$

The area intersected by the (110) plane inside the unit cell (selected area) is

$$(\sqrt{2}a)(a) = \sqrt{2}a^2$$

Thus the planar atomic density is

$$\rho_p = \frac{2 \text{ atoms}}{\sqrt{2}(0.287 \text{ nm})^2} = \frac{17.2 \text{ atoms}}{\text{nm}^2}$$

$$= \frac{17.2 \text{ atoms}}{\text{nm}^2} \times \frac{10^{12} \text{ nm}^2}{\text{mm}^2}$$

$$= 1.72 \times 10^{13} \text{ atoms/mm}^2 \blacktriangleleft$$

Linear Atomic Density   Sometimes it is important to determine the atomic densities in various directions in crystal structures. To do this a quantity called the *linear atomic density* is calculated by using the relationship

Linear atomic density = ρ_l

$$= \frac{\text{no. of atomic diam. intersected by selected length of line in direction of interest}}{\text{selected length of line}} \qquad (3.7)$$

Example Problem 3.13 shows how the linear atomic density can be calculated in the [110] direction in a pure copper crystal lattice.

Example Problem 3.13

Calculate the linear atomic density ρ_l in the [110] direction in the copper crystal lattice in atoms per millimeter. Copper is FCC and has a lattice constant of 0.361 nm.

Solution:

The atoms whose centers the [110] direction intersects are shown in Fig. 3.23. We shall select the length of the line to be the length of the face diagonal of the FCC unit cell, which is $\sqrt{2}a$. The number of atomic diameters intersected by this length of line are $\frac{1}{2} + 1 + \frac{1}{2} = 2$ atoms. Thus using Eq. (3.7), the linear atomic density is

$$\rho_l = \frac{2 \text{ atoms}}{\sqrt{2}a} = \frac{2 \text{ atoms}}{\sqrt{2}(0.361 \text{ nm})} = \frac{3.92 \text{ atoms}}{\text{nm}}$$

$$= \frac{3.92 \text{ atoms}}{\text{nm}} \times \frac{10^6 \text{ nm}}{\text{mm}}$$

$$= 3.92 \times 10^6 \text{ atoms/mm} \blacktriangleleft$$
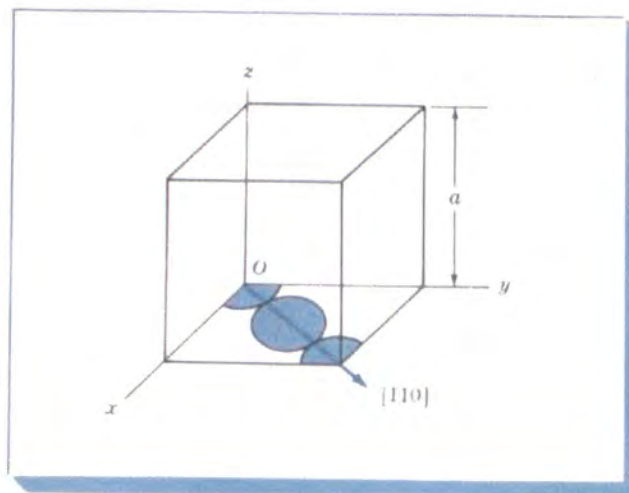
FIGURE 3.23 Diagram for calculating the atomic linear density in the [110] direction in an FCC unit cell.

3.10 POLYMORPHISM OR ALLOTROPY

Many elements and compounds exist in more than one crystalline form under different conditions of temperature and pressure. This phenomenon is termed *polymorphism*, or *allotropy*. Many industrially important metals such as iron, titanium, and cobalt undergo allotropic transformations at elevated temperatures at atmospheric pressure. Table 3.5 lists some selected metals which show allotropic transformations and the structure changes which occur.

Iron exists in both BCC and FCC crystal structures over the temperature range from room temperature to its melting point at 1539°C, as shown in Fig. 3.24. Alpha (α) iron exists from -273 to 912°C and has the BCC crystal structure.

TABLE 3.5   Allotropic Crystalline Forms of Some Metals

Metal	Crystal structure at room temperature	At other temperatures
Ca	FCC	BCC (>447°C)
Co	HCP	FCC (>427°C)
Hf	HCP	BCC (>1742°C)
Fe	BCC	FCC (912–1394°C)
		BCC (>1394°C)
Li	BCC	HCP (< −193°C)
Na	BCC	HCP (< −233°C)
Tl	HCP	BCC (>234°C)
Ti	HCP	BCC (>883°C)
Y	HCP	BCC (>1481°C)
Zr	HCP	BCC (>872°C)
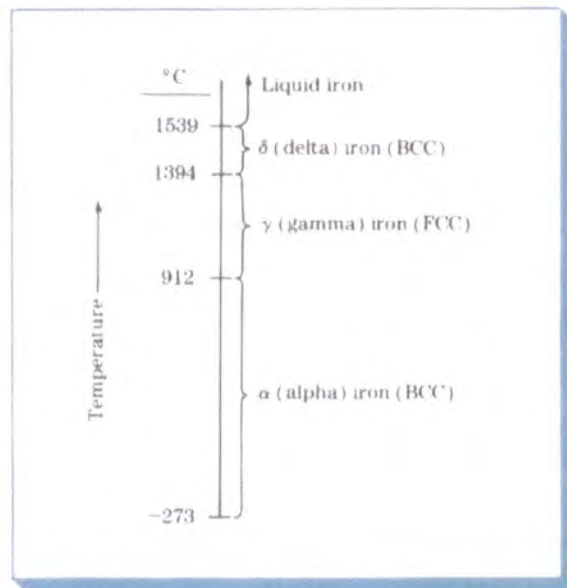
FIGURE 3.24 Allotropic crystalline forms of iron over temperature ranges at atmospheric pressure.

Gamma (γ) iron exists from 912 to 1394°C and has the FCC crystal structure. Delta (δ) iron exists from 1394 to 1539°C, which is the melting point of iron. The crystal structure of δ iron is also BCC but with a larger lattice constant than α iron.

Example Problem 3.14

Calculate the theoretical volume change accompanying a polymorphic transformation in a pure metal from the FCC to BCC crystal structure. Assume the hard-sphere atomic model and that there is no change in atomic volume before and after the transformation.

Solution:

In the FCC crystal structure unit cell, the atoms are in contact along the face diagonal of the unit cell, as shown in Fig. 3.7. Hence

$$\sqrt{2}a = 4R \qquad \text{or} \qquad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

In the BCC crystal structure unit cell, the atoms are in contact along the body diagonal of the unit cell as shown in Fig. 3.5. Hence

$$\sqrt{3}a = 4R \qquad \text{or} \qquad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

The volume per atom for the FCC crystal lattice, since it has four atoms per unit cell, is

$$V_{FCC} = \frac{a^3}{4} = \left(\frac{4R}{\sqrt{2}}\right)^3 \left(\frac{1}{4}\right) = 5.66R^3$$

The volume per atom for the BCC crystal lattice, since it has two atoms per unit cell, is

$$V_{BCC} = \frac{a^3}{2} = \left(\frac{4R}{\sqrt{3}}\right)^3 \left(\frac{1}{2}\right) = 6.16R^3$$

The change in volume associated with the transformation from the FCC to BCC crystal structure, assuming no change in atomic radius, is

$$\frac{\Delta V}{V_{FCC}} = \frac{V_{BCC} - V_{FCC}}{V_{FCC}}$$

$$= \left(\frac{6.16R^3 - 5.66R^3}{5.66R^3}\right) 100\% = +8.8\% \blacktriangleleft$$

3.11   CRYSTAL STRUCTURE ANALYSIS

Our present knowledge of crystal structures has been obtained mainly by x-ray diffraction techniques which utilize x-rays about the same wavelength as the distance between crystal lattice planes. However, before discussing the manner in which x-rays are diffracted in crystals, let us consider how x-rays are produced for experimental purposes.

X-Ray Sources

X-rays used for diffraction are electromagnetic waves with wavelengths in the range 0.05 to 0.25 nm (0.5 to 2.5 Å). By comparison the wavelength of visible light is of the order of 600 nm (6000 Å). In order to produce x-rays for diffraction purposes, a voltage of about 35 kV is necessary and is applied between a cathode and an anode target metal, both of which are contained in a vacuum, as shown in Fig. 3.25. When the tungsten filament of the cathode is heated, electrons are released by thermionic emission and accelerated through the vacuum by the large voltage difference between the cathode and anode, thereby gaining kinetic energy. When the electrons strike the target metal (e.g., molybdenum), x-rays are given off. However, most of the kinetic energy (about 98 percent) is converted into heat, so the target metal must be cooled externally.

The x-ray spectrum emitted at 35 kV using a molybdenum target is shown in Fig. 3.26. The spectrum shows continuous x-ray radiation in the wavelength range from about 0.2 to 1.4 Å (0.02 to 0.14 nm) and two spikes of characteristic radiation which are designated the K_α and K_β lines. The wavelengths of the K_α and K_β lines are characteristic for an element. For molybdenum, the K_α line occurs at a wavelength of about 0.7 Å (0.07 nm). The origin of the characteristic

FIGURE 3.25 Schematic diagram of the cross section of a sealed-off filament x-ray tube (*After B. D. Cullity, "Elements of X-Ray Diffraction," 2d ed., Addison-Wesley, 1978, p. 23.*)
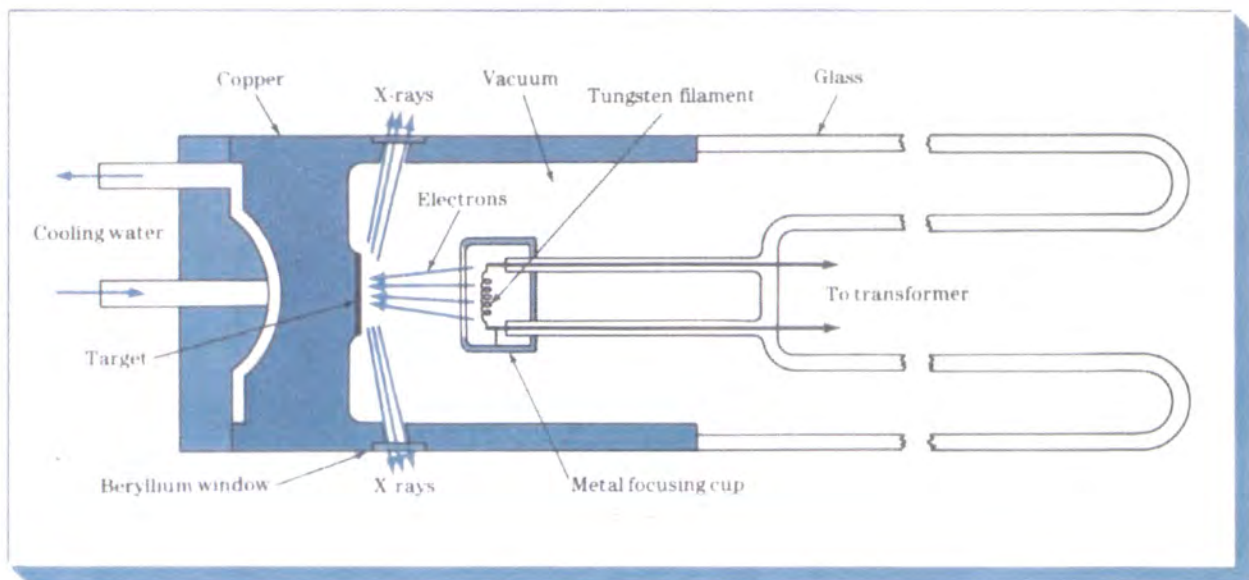
FIGURE 3.26 X-ray emission spectrum produced when molybdenum metal is used as the target metal in an x-ray tube operating at 35 kV.
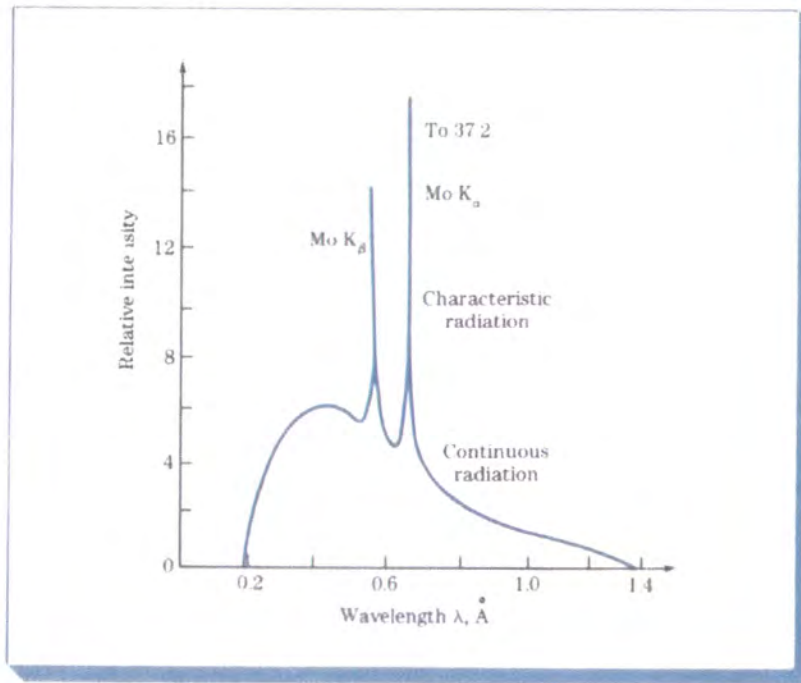
radiation is explained as follows. First, K electrons (electrons in the $n = 1$ shell) are knocked out of the atom by highly energetic electrons bombarding the target, leaving excited atoms. Next, some electrons in higher shells (that is, $n = 2$ or 3) drop down to lower energy levels to replace the lost K electrons, emitting energy of a characteristic wavelength. The transition of electrons from

FIGURE 3.27 Energy levels of electrons in molybdenum showing the origin of K_α and K_β radiation.
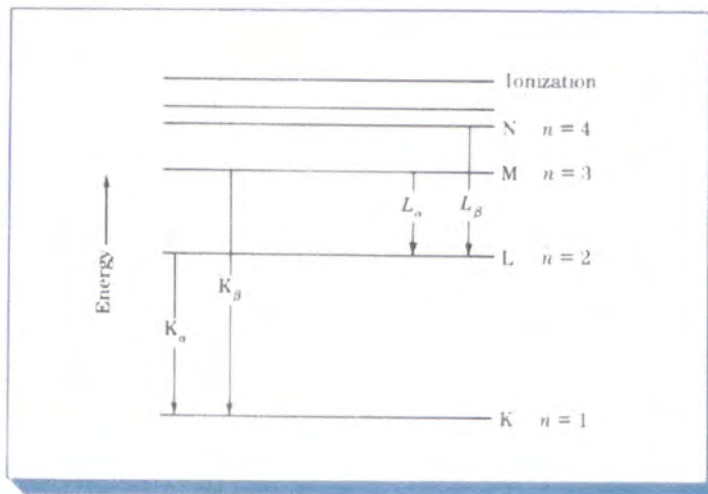
the L ($n = 2$) shell to the K ($n = 1$) shell creates energy of the wavelength of the K_α line, as indicated in Fig. 3.27.

X-Ray Diffraction Since the wavelengths of some x-rays are about equal to the distance between planes of atoms in crystalline solids, reinforced diffraction peaks of radiation of varying intensities can be produced when a beam of x-rays strikes a crystalline solid. However, before considering the application of x-ray diffraction techniques to crystal structure analysis, let us examine the geometric conditions necessary to produce diffracted or reinforced beams of reflected x-rays.

Consider a monochromatic (single-wavelength) beam of x-rays to be incident on a crystal, as shown in Fig. 3.28. For simplification let us allow the crystal planes of atomic scattering centers to be replaced by crystal planes which act as mirrors in reflecting the incident x-ray beam. In Fig. 3.28 the horizontal lines represent a set of parallel crystal planes with Miller indices (*hkl*). When an incident beam of monochromatic x-rays of wavelength λ strikes this set of planes at an angle such that the wave patterns of the beam leaving the various planes are *not in phase, no reinforced beam will be produced* (Fig. 3.28*a*). Thus destructive interference occurs. If the reflected wave patterns of the beam leaving the various planes are in phase, then reinforcement of the beam or constructive interference occurs (Fig. 3.28*b*).

Let us now consider incident x-rays 1 and 2 as indicated in Fig. 3.28*c*. For these rays to be in phase, the extra distance of travel of ray 2 is equal to *MP* + *PN*, which must be an integral number of wavelengths λ. Thus

$$n\lambda = MP + PN \tag{3.8}$$

where $n = 1, 2, 3, \ldots$ and is called the *order of the diffraction*. Since both *MP* and *PN* equal $d_{hkl} \sin \theta$, where d_{hkl} is the interplanar spacing of the crystal planes of indices (*hkl*), the condition for constructive interference (i.e., the production of a diffraction peak of intense radiation) must be

$$n\lambda = 2d_{hkl} \sin \theta \tag{3.9}$$

This equation, known as *Bragg's law*,[1] gives the relationship among the angular positions of the reinforced diffracted beams in terms of the wavelength λ of the incoming x-ray radiation and of the interplanar spacings d_{hkl} of the crystal planes. In most cases, the first order of diffraction where $n = 1$ is used, and so for this case Bragg's law takes the form

$$\lambda = 2d_{hkl} \sin \theta \tag{3.10}$$

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[1] William Henry Bragg (1862–1942) English physicist who worked in x-ray crystallography.
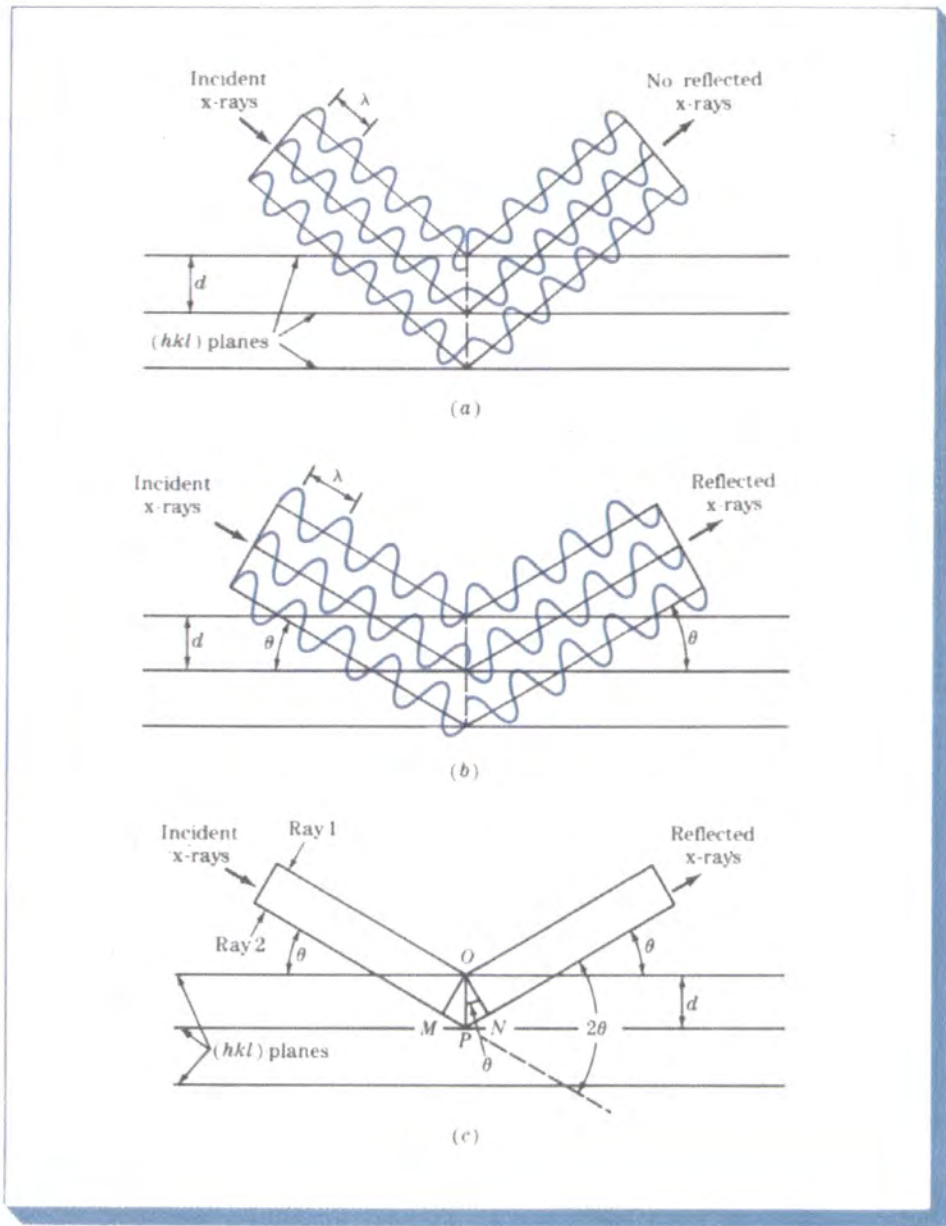
FIGURE 3.28 The reflection of an x-ray beam by the (*hkl*) planes of a crystal. (*a*) No reflected beam is produced at an arbitrary angle of incidence. (*b*) At the Bragg angle *θ*, the reflected rays are in phase and reinforce one another. (*c*) Similar to (*b*) except that the wave representation has been omitted. (*After A. G. Guy and J. J. Hren, "Elements of Physical Metallurgy," 3d ed., Addison-Wesley, 1974, p. 201.*)

Example Problem 3.15

A sample of BCC iron was placed in an x-ray diffractometer using incoming x-rays with a wavelength $\lambda = 0.1541$ nm. Diffraction from the {110} planes was obtained at $2\theta = 44.704°$. Calculate a value for the lattice constant a of BCC iron. (Assume first-order diffraction with $n = 1$.)

Solution:

$$2\theta = 44.704° \qquad \theta = 22.35°$$

$$\lambda = 2d_{hkl} \sin \theta \tag{3.10}$$

$$d_{110} = \frac{\lambda}{2 \sin \theta} = \frac{0.1541 \text{ nm}}{2(\sin 22.35°)}$$

$$= \frac{0.1541 \text{ nm}}{2(0.3803)} = 0.2026 \text{ nm}$$

Rearranging Eq. (3.4) gives

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$

Thus

$$a \text{ (Fe)} = d_{110}\sqrt{1^2 + 1^2 + 0^2}$$

$$= (0.2026 \text{ nm})(1.414) = 0.287 \text{ nm} \blacktriangleleft$$

X-Ray Diffraction Analysis of Crystal Structures

The powder method of x-ray diffraction analysis   The most commonly used x-ray diffraction technique is the *powder method*. In this technique a powdered specimen is utilized so that there will be a random orientation of many crystals to ensure that some of the particles will be oriented in the x-ray beam to satisfy the diffraction conditions of Bragg's law. Modern x-ray crystal analysis uses an x-ray diffractometer which has a radiation counter to detect the angle and intensity of the diffracted beam (Fig. 3.29). A recorder automatically plots the intensity of the diffracted beam as the counter moves on a goniometer[1] circle (Fig. 3.30) which is in synchronization with the specimen over a range of 2θ values. Figure 3.31 shows an x-ray diffraction recorder chart for the intensity of the diffracted beam vs. the diffraction angles 2θ for a powdered pure-metal specimen. In this way both the angles of the diffracted beams and their intensities can be recorded at one time. Sometimes a powder camera with an enclosed filmstrip is used instead of the diffractometer, but this method is much slower and in most cases less convenient.

[1] A goniometer is an instrument for measuring angles
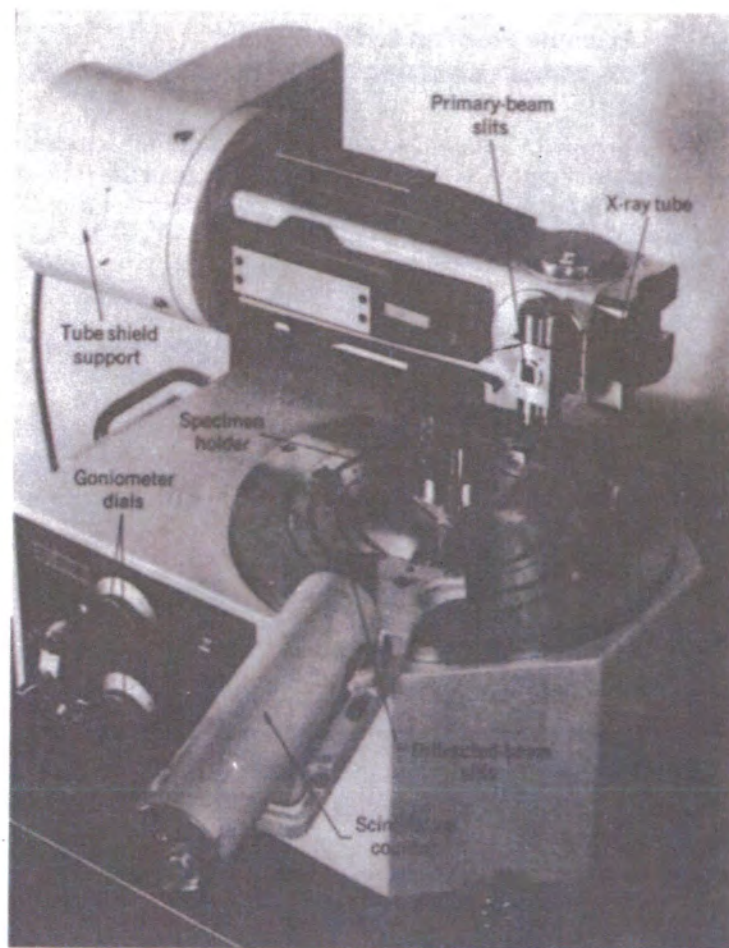
FIGURE 3.29 An x-ray diffractometer (with x-radiation shields removed). (*Philips Electronic Instruments, Inc.*)

Diffraction conditions for cubic unit cells X-ray diffraction techniques enable the structures of crystalline solids to be determined. The interpretation of x-ray diffraction data for most crystalline substances is complex and beyond the scope of this book, and so only the simple case of diffraction in pure cubic metals will be considered. The analysis of x-ray diffraction data for cubic unit cells can be simplified by combining Eq. (3.4),

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

with the Bragg equation $\lambda = 2d \sin \theta$, giving

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \tag{3.11}$$
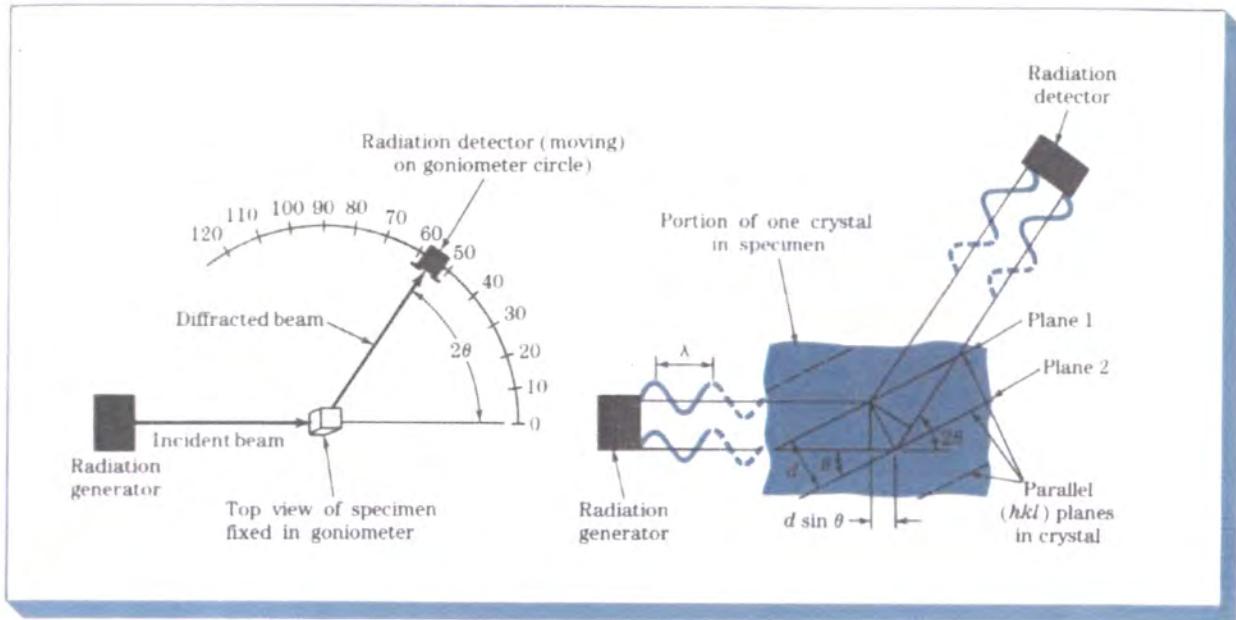
FIGURE 3.30 Schematic illustration of the diffractometer method of crystal analysis and of the conditions necessary for diffraction. (*After A. G. Guy, "Essentials of Materials Science," McGraw-Hill, 1976.*)

FIGURE 3.31 Record of the diffraction angles for a tungsten sample obtained by the use of a diffractometer with copper radiation. (*After A. G. Guy and J. J. Hren, "Elements of Physical Metallurgy," 3d ed., Addison-Wesley, 1974, p. 208.*)
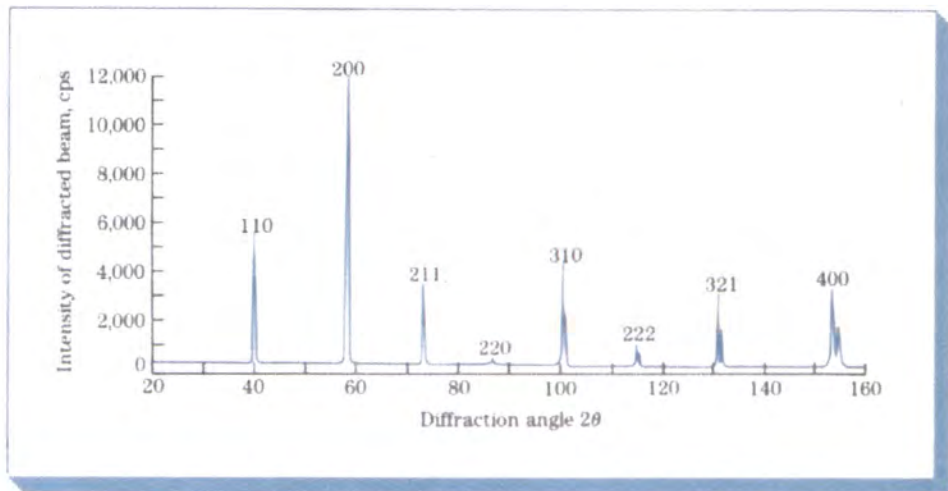
This equation can be used along with x-ray diffraction data to determine if a cubic crystal structure is body-centered or face-centered cubic. The rest of this subsection will describe how this is done.

To use Eq. (3.11) for diffraction analysis, we must know which crystal planes are the diffracting planes for each type of crystal structure. For the

simple cubic lattice, reflections from all (*hkl*) planes are possible. However, for the BCC structure diffraction occurs only on planes whose Miller indices when added together ($h + k + l$) total to an even number (Table 3.6). Thus, for the BCC crystal structure the principal diffracting planes are {110}, {200}, {211}, etc., which are listed in Table 3.7. In the case of the FCC crystal structure, the principal diffracting planes are those whose Miller indices are either all even or all odd (zero is considered even). Thus, for the FCC crystal structure the diffracting planes are {111}, {200}, {220}, etc., which are listed in Table 3.7.

Interpreting experimental x-ray diffraction data for metals with cubic crystal structures We can use x-ray diffractometer data to determine crystal structures. A simple case to illustrate how this analysis can be used is to distinguish between the BCC and FCC crystal structures of a cubic metal. Let us assume that we have a metal which has either a BCC or an FCC crystal structure and that we are able to identify the principal diffracting planes and their corresponding 2θ values, as indicated for the metal tungsten in Fig. 3.31.

TABLE 3.6   Rules for Determining the Diffracting (*hkl*) Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	($h + k + l$) = even	($h + k + l$) = odd
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

TABLE 3.7   Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes (*hkl*)	$h^2 + k^2 + l^2$	Sum $\Sigma(h^2 + k^2 + l^2)$	Cubic diffracting planes (*hkl*) FCC	Cubic diffracting planes (*hkl*) BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2		110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6		211
. . .		7		
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10		310

By squaring both sides of Eq. (3.11) and solving for $\sin^2 \theta$, we obtain

$$\sin^2 \theta = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2} \tag{3.12}$$

From x-ray diffraction data we can obtain experimental values of 2θ for a series of principal diffracting $\{hkl\}$ planes. Since the wavelength of the incoming radiation and the lattice constant a are both constants, we can eliminate these quantities by forming the ratio of two $\sin^2 \theta$ values as

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2} \tag{3.13}$$

where θ_A and θ_B are two diffracting angles associated with the principal diffracting planes $\{h_A k_A l_A\}$ and $\{h_B k_B l_B\}$, respectively.

Using Eq. (3.13) and the Miller indices of the first two sets of principal diffracting planes listed in Table 3.7 for BCC and FCC crystal structures, we can determine values for the $\sin^2 \theta$ ratios for both BCC and FCC structures.

For the BCC crystal structure the first two sets of principal diffracting planes are the $\{110\}$ and $\{200\}$ planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. (3.13) gives

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{1^2 + 1^2 + 0^2}{2^2 + 0^2 + 0^2} = 0.5 \tag{3.14}$$

Thus, if the crystal structure of the unknown cubic metal is BCC, the ratio of the $\sin^2 \theta$ values which correspond to the first two principal diffracting planes will be 0.5.

For the FCC crystal structure the first two sets of principal diffracting planes are the $\{111\}$ and $\{200\}$ planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. (3.13) gives

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{1^2 + 1^2 + 1^2}{2^2 + 0^2 + 0^2} = 0.75 \tag{3.15}$$

Thus, if the crystal structure of the unknown cubic metal is FCC, the ratio of the $\sin^2 \theta$ values which correspond to the first two principal diffracting planes will be 0.75.

Example Problem 3.16 uses Eq. (3.13) and experimental x-ray diffraction data for the 2θ values for the principal diffracting planes to determine whether an unknown cubic metal is BCC or FCC. X-ray diffraction analysis is usually much more complicated than Example Problem 3.16, but the principles used are the same. Both experimental and theoretical x-ray diffraction analysis has been and continues to be used for the determination of the crystal structure of materials.

Example Problem 3.16

An x-ray diffractometer recorder chart for an element which has either the BCC or the FCC crystal structure shows diffraction peaks at the following 2θ angles: 40, 58, 73, 86.8, 100.4, and 114.7. The wavelength of the incoming x-ray used was 0.154 nm.

(a) Determine the cubic structure of the element.
(b) Determine the lattice constant of the element.
(c) Identify the element.

Solution:

(a) *Determination of the crystal structure of the element.* First, the $\sin^2 \theta$ values are calculated from the 2θ diffraction angles.

2θ, deg	θ, deg	$\sin \theta$	$\sin^2 \theta$
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903
114.7	57.35	0.8420	0.7090

Next the ratio of the $\sin^2 \theta$ values of the first and second angles is calculated:

$$\frac{\sin^2 \theta}{\sin^2 \theta} = \frac{0.117}{0.235} = 0.498 \approx 0.5$$

The crystal structure is BCC since this ratio is ≈ 0.5. If the ratio had been ≈ 0.75, the structure would have been FCC.

(b) *Determination of the lattice constant.* Rearranging Eq. (3.12) and solving for a^2 gives

$$a^2 = \frac{\lambda^2}{4} \frac{h^2 + k^2 + l^2}{\sin^2 \theta} \tag{3.16}$$

or

$$a = \frac{\lambda}{2} \sqrt{\frac{h^2 + k^2 + l^2}{\sin^2 \theta}} \tag{3.17}$$

Substituting into Eq. (3.17) $h = 1$, $k = 1$, and $l = 0$ for the h, k, l Miller indices of the first set of principal diffracting planes for the BCC crystal structure, which are the {110} planes, the corresponding value for $\sin^2 \theta$, which is 0.117, and 0.154 nm for λ, the incoming radiation, gives

$$a = \frac{0.154 \text{ nm}}{2} \sqrt{\frac{1^2 + 1^2 + 0^2}{0.117}} = 0.318 \text{ nm} \blacktriangleleft$$

(c) *Identification of the element.* The element is tungsten since this element has a lattice constant of 0.316 nm and is BCC.

SUMMARY

Atomic arrangements in crystalline solids can be described by a network of lines called a *space lattice.* Each space lattice can be described by specifying the atom positions in a repeating *unit cell.* There are seven crystal systems based on the geometry of the axial lengths and interaxial angles of the unit cells. These seven systems have a total of 14 sublattices (unit cells) based on the internal arrangements of atomic sites within the unit cells.

In metals the most common crystal structure unit cells are: *body-centered cubic* (BCC), *face-centered cubic* (FCC), and *hexagonal close-packed* (HCP) (which is a dense variation of the simple hexagonal structure).

Crystal directions in cubic crystals are the vector components of the directions resolved along each of the component axes and reduced to smallest integers. They are indicated as $[uvw]$. Families of directions are indexed by the direction indices enclosed by pointed brackets as $\langle uvw \rangle$. *Crystal planes* in cubic crystals are indexed by the reciprocals of the axial intercepts of the plane (followed by the elimination of fractions) as (hkl). Cubic crystal planes of a form (family) are indexed with braces as $\{hkl\}$. Crystal planes in hexagonal crystals are commonly indexed by four indices h, k, i, and l enclosed in parentheses as $(hkil)$. These indices are the reciprocals of the intercepts of the plane on the a_1, a_2, a_3, and c axes of the hexagonal crystal structure unit cell. Crystal directions in hexagonal crystals are the vector components of the direction resolved along each of the four coordinate axes and reduced to smallest integers as $[uvtw]$.

Using the hard-sphere model for atoms, calculations can be made for the volume, planar, and linear density of atoms in unit cells. Planes in which atoms are packed as tightly as possible are called *close-packed planes,* and directions in which atoms are in closest contact are called *close-packed directions.* Atomic packing factors for different crystal structures can also be determined by assuming the hard-sphere atomic model. Some metals have different crystal structures at different ranges of temperature and pressure, a phenomenon called *polymorphism.*

Crystal structures of crystalline solids can be determined by using x-ray diffraction analysis techniques. X-rays are diffracted in crystals when the *Bragg's law* ($n\lambda = 2d \sin \theta$) conditions are satisfied. By using the x-ray diffractometer and the *powder method,* the crystal structure of many crystalline solids can be determined.

DEFINITIONS

Sec. 3.1

Crystal: a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.

Crystal structure: a regular three-dimensional pattern of atoms or ions in space.

Space lattice: a three-dimensional array of points each of which has identical surroundings.

Lattice point: one point in an array in which all the points have identical surroundings.

Unit cell: a convenient repeating unit of a space lattice. The axial lengths and axial angles are the lattice constants of the unit cell.

Sec. 3.3

Body-centered cubic (BCC) unit cell: a unit cell with an atomic packing arrangement in which one atom is in contact with eight identical atoms located at the corners of an imaginary cube.

Face-centered cubic (FCC) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central atom. The stacking sequence of layers of close-packed planes in the FCC crystal structure is *ABCABC.* . . .

Hexagonal close-packed (HCP) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central identical atom. The stacking sequence of layers of close-packed planes in the HCP crystal structure is *ABABAB.* . . .

Atomic packing factor (APF): the volume of atoms in a selected unit cell divided by the volume of the unit cell.

Sec. 3.5

Indices of direction in a cubic crystal: a direction in a cubic unit cell is indicated by a vector drawn from the origin at one point in a unit cell through the surface of the unit cell; the position coordinates (x, y, and z) of the vector where it leaves the surface of the unit cell (with fractions cleared) are the indices of direction. These indices, designated u, v, and w are enclosed in brackets as $[uvw]$. Negative indices are indicated by a bar over the index.

Sec. 3.6

Indices for cubic crystal planes (Miller indices): the reciprocals of the intercepts (with fractions cleared) of a crystal plane with the x, y, and z axes of a unit cube are called the Miller indices of that plane. They are designated h, k, and l for the x, y, and z axes, respectively, and are enclosed in parentheses as (hkl). Note that the selected crystal plane must *not* pass through the origin of the x, y, and z axes.

Sec. 3.9

Volume density ρ_v: mass per unit volume; this quantity is usually expressed in Mg/m^3 or g/cm^3.

Plan r density ρ_p: the equivalent number of atoms whose centers are intersected by a selected area divided by the selected area.

Linear density ρ_l: the number of atoms whose centers lie on a specific direction on a specific length of line in a unit cube.

Sec. 3.10

Polymorphism (as pertains to metals): the ability of a metal to exist in two or more crystal structures. For example, iron can have a BCC or an FCC crystal structure, depending on the temperature.

PROBLEMS

3.1.1   Define a crystalline solid.

3.1.2   Define a crystal structure. Give examples of materials which have crystal structures.

3.1.3   Define a space lattice.

3.1.4   Define a unit cell of a space lattice. What lattice constants define a unit cell?

3.2.1   What are the 14 Bravais unit cells?

3.3.1   What are the three most common metal crystal structures? List five metals which have each of these crystal structures.

3.3.2   How many atoms per unit cell are there in the BCC crystal structure?

3.3.3   What is the coordination number for the atoms in the BCC crystal structure?

3.3.4   What is the relationship between the length of the side a of the BCC unit cell and the radius of its atoms?

3.3.5   Potassium at 20°C is BCC and has an atomic radius of 0.238 nm. Calculate a value for its lattice constant a in nanometers.

3.3.6   Tungsten at 20°C is BCC and has an atomic radius of 0.141 nm. Calculate a value for its lattice constant a in nanometers.

3.3.7   Tantalum at 20°C is BCC and has a lattice constant of 0.33026 nm. Calculate a value for the atomic radius of a tungsten atom in nanometers.

3.3.8   Barium at 20°C is BCC and has a lattice constant of 0.5019 nm. Calculate a value for the atomic radius of a chromium atom in nanometers.

3.3.9   How many atoms per unit cell are there in the FCC crystal structure?

3.3.10 What is the coordination number for the atoms in the FCC crystal structure?

3.3.11 Copper is FCC and has a lattice constant of 0.3615 nm. Calculate a value for the atomic radius of a copper atom in nanometers.

3.3.12 Calcium is FCC and has a lattice constant of 0.5582 nm. Calculate a value for the atomic radius of an aluminum atom in nanometers.

3.3.13 Iridium is FCC and has an atomic radius of 0.135 nm. Calculate a value for its lattice constant a in nanometers.

3.3.14 Aluminum is FCC and has an atomic radius of 0.143 nm. Calculate a value for its lattice constant a in nanometers.

3.3.15 Calculate the atomic packing factor for the FCC structure.

3.3.16 How many atoms per unit cell are there in the HCP crystal structure?

3.3.17 What is the coordination number for the atoms in the HCP crystal structure?

3.3.18 What is the ideal c/a ratio for HCP metals?

3.3.19 Of the following HCP metals, which have higher or lower c/a ratios than the ideal ratio: Zr, Ti, Zn, Mg, Co, Cd, and Be?

3.3.20 Calculate the volume in cubic nanometers of the beryllium crystal structure unit cell. Beryllium is HCP at 20°C with $a = 0.22856$ nm and $c = 0.35832$ nm.

3.3.21 Magnesium at 20°C is HCP. The height c of its unit cell is 0.52105 nm and its c/a ratio is 1.623. Calculate a value for its lattice constant a in nanometers.

3.3.22 Cadmium at 20°C is HCP. Using a value of 0.148 nm for the atomic radius of cadmium atoms, calculate a value for its unit-cell volume. Assume a packing factor of 0.74.

3.4.1   How are atomic positions located in cubic unit cells?

3.4.2   List the atom positions for the eight corner and six face-centered atoms of the FCC unit cell.

3.5.1   How are the indices for a crystallographic direction in a cubic unit cell determined?

3.5.2   Draw the following directions in a BCC unit cell and list the position coordinates of the atoms whose centers are intersected by the direction vector:
(a) [100]   (b) [110]   (c) [111]

3.5.3   Draw direction vectors in unit cubes for the following cubic directions:
(a) $[1\bar{1}\bar{1}]$ (b) $[1\bar{1}0]$ (c) $[\bar{1}2\bar{1}1]$ (d) $[\bar{1}\bar{1}3]$

3.5.4   Draw direction vectors in unit cubes for the following cubic directions:
(a) $[1\bar{2}1]$ (d) $[20\bar{1}]$ (g) $[\bar{2}21]$ (j) $[20\bar{3}]$
(b) $[21\bar{2}]$ (e) $[10\bar{2}]$ (h) $[\bar{3}23]$ (k) $[1\bar{2}2]$
(c) $[3\bar{2}1]$ (f) $[2\bar{3}3]$ (i) $[1\bar{2}3]$ (l) $[\bar{2}\bar{2}3]$

3.5.5   What are the indices of the directions shown in the unit cubes of Fig. P3.5.5?
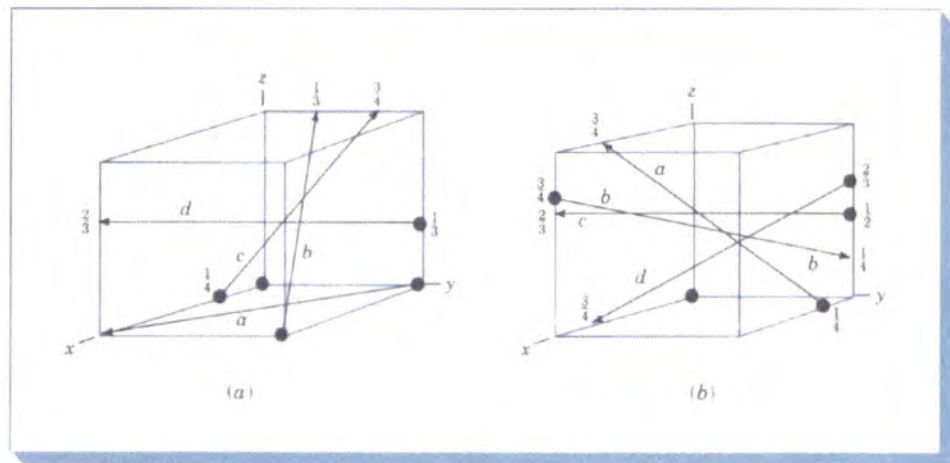
FIGURE P3.5.5

3.5.6   A direction vector passes through a unit cube from the $(\frac{1}{4}, 0, \frac{1}{4})$ to the $(1, \frac{3}{4}, 1)$ positions. What are its direction indices?

3.5.7   A direction vector passes through a unit cube from the $(\frac{1}{4}, \frac{3}{4}, 0)$ to the $(\frac{1}{2}, \frac{1}{4}, 0)$ positions. What are its direction indices?

3.5.8   What are the crystallographic directions of a family or form? What generalized notation is used to indicate them?

3.5.9   What are the directions of the ⟨100⟩ family or form for a unit cube?

3.5.10 What are the directions of the ⟨111⟩ family or form for a unit cube?

3.5.11 What ⟨110⟩-type directions lie on the (111) plane of a cubic unit cell?

3.5.12 What ⟨111⟩-type directions lie on the (110) plane of a cubic unit cell?

3.6.1   How are the Miller indices for a crystallographic plane in a cubic unit cell determined? What generalized notation is used to indicate them?

3.6.2 Draw in unit cubes the crystal planes which have the following Miller indices:

(a) $(21\bar{3})$ (d) $(\bar{3}\bar{3}1)$ (g) $(1\bar{2}0)$ (j) $(12\bar{2})$

(b) $(21\bar{2})$ (e) $(\bar{3}1\bar{2})$ (h) $(23\bar{2})$ (k) $(1\bar{3}3)$

(c) $(\bar{3}\bar{2}1)$ (f) $(20\bar{3})$ (i) $(\bar{3}32)$ (l) $(2\bar{2}3)$

3.6.3 What are the Miller indices of the cubic crystallographic planes shown in Fig. P3.6.3?

3.6.4 What is the notation used to indicate a family or form of cubic crystallographic planes?

3.6.5 What are the {100} family of planes of the cubic system?

3.6.6 Draw the following crystallographic planes in a BCC unit cell and list the position of the atoms whose centers are intersected by each of the planes:

(a) (100)   (b) (110)   (c) (111)

3.6.7 Draw the following crystallographic planes in an FCC unit cell and list the position coordinates of the atoms whose centers are intersected by each of the planes:

(a) (100)   (b) (110)   (c) (111)
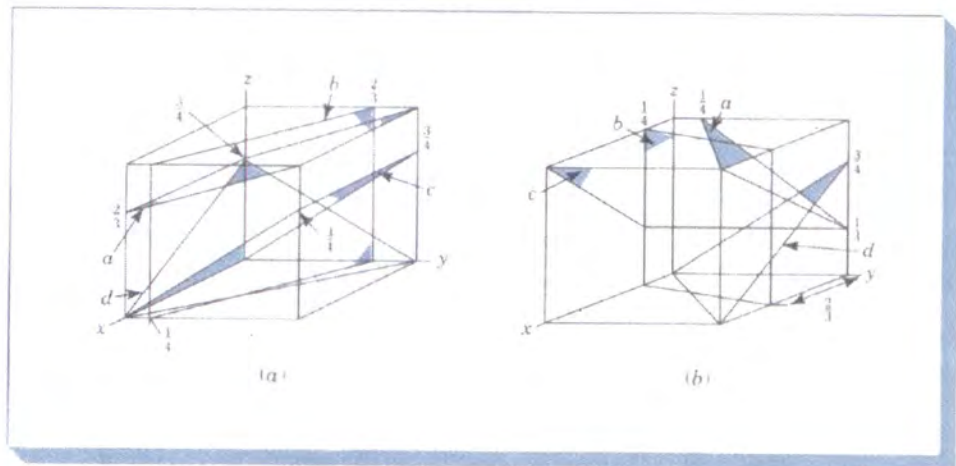
FIGURE P3.6.3

3.6.8 A cubic plane has the following axial intercepts: $a = \frac{1}{3}, b = -\frac{2}{3}, c = \frac{1}{2}$. What are the Miller indices of this plane?

3.6.9 A cubic plane has the following axial intercepts: $a = -\frac{1}{2}, b = \frac{1}{2}, c = \frac{2}{3}$. What are the Miller indices of this plane?

3.6.10 A cubic plane has the following axial intercepts: $a = 1, b = \frac{2}{3}, c = -\frac{1}{2}$. What are the Miller indices of this plane?

3.6.11 Determine the Miller indices of the cubic crystal plane which intersects the following position coordinates: $(1, 0, 0); (1, \frac{1}{2}, \frac{1}{4}); (\frac{1}{2}, \frac{1}{2}, 0)$

3.6.12 Determine the Miller indices of the cubic crystal plane which intersects the following position coordinates: $(\frac{1}{2}, 0, \frac{1}{2}); (0, 0, 1); (1, 1, 1)$

3.6.13 Determine the Miller indices of the cubic crystal plane which intersects the following position coordinates: $(1, \frac{1}{2}, 1); (\frac{1}{2}, 0, \frac{3}{4}); (1, 0, \frac{1}{2})$

3.6.14 Determine the Miller indices of the cubic crystal plane which intersects the following position coordinates: $(0, 0, \frac{1}{2}); (1, 0, 0); (\frac{1}{2}, \frac{1}{4}, 0)$

3.6.15 Nickel is FCC and has a lattice constant of 0.35236 nm. Calculate the following interplanar spacings in nm.

(a) d_{111} (b) d_{200} (c) d_{220}

3.6.16 Molybdenum is BCC and has a lattice constant of 0.31468 nm. Calculate the following interplanar spacings in nm.

(a) d_{110} (b) d_{220} (c) d_{310}

3.6.17 The d_{321} interplanar spacing in a BCC metal is 0.084165 nm. (a) What is its lattice constant "a"? (b) What is the atomic radius of the metal? (c) What could this metal be based on its lattice constant "a"?

3.6.18 The d_{222} interplanar spacing in an FCC metal is 0.11327 nm. (a) What is its lattice constant "a"? (b) What is the atomic radius of the metal? (c) What could this metal be based on its lattice constant "a"?

3.7.1 How are crystallographic planes indicated in HCP unit cells?

3.7.2 What notation is used to describe HCP crystal planes?

3.7.3 Draw the hexagonal crystal planes whose Miller-Bravais indices are:

(a) $(10\bar{1}1)$ (d) $(1\bar{2}12)$ (g) $(\bar{1}2\bar{1}2)$ (j) $(\bar{1}100)$
(b) $(01\bar{1}1)$ (e) $(21\bar{1}1)$ (h) $(2\bar{2}00)$ (k) $(\bar{2}111)$
(c) $(\bar{1}2\bar{1}0)$ (f) $(1\bar{1}01)$ (i) $(10\bar{1}2)$ (l) $(\bar{1}012)$

3.7.4 Determine the Miller-Bravais indices of the hexagonal crystal planes in Fig. P3.7.4.
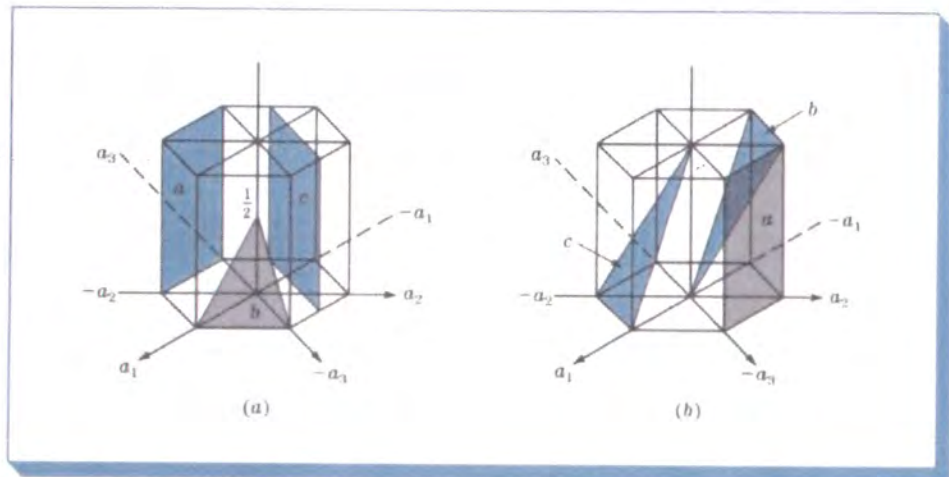
FIGURE P3.7.4

3.8.1 What is the difference in the stacking arrangement of close-packed planes in (a) the HCP crystal structure and (b) the FCC crystal structure?

3.8.2 What are the densest-packed planes in (a) the FCC structure and (b) the HCP structure?

3.8.3 What are the closest-packed directions in (a) the FCC structure and (b) the HCP structure?

3.9.1 The lattice constant for BCC niobium at 20°C is 0.33007 nm, and its density is 8.60 g/cm³. Calculate a value for its atomic mass.

3.9.2 Calculate a value for the density of FCC silver in grams per cubic centimeters from its lattice constant a of 0.40856 nm and its atomic mass of 107.87 g/mol.

3.9.3   Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in BCC tungsten, which has a lattice constant of 0.31648 nm: (a) (100), (b) (110), (c) (111).

3.9.4   Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in FCC nickel, which has a lattice constant of 0.35236 nm: (a) (100), (b) (110), (c) (111).

3.9.5   Calculate the planar atomic density in atoms per square millimeter for the (0001) plane in HCP cobalt, which has an a constant of 0.2506 nm and a c constant of 0.4069 nm.

3.9.6   Calculate the linear atomic density in atoms per millimeter for the following directions in BCC tantalum, which has a lattice constant of 0.33026 nm: (a) [100], (b) [110], (c) [111].

3.9.7   Calculate the linear atomic density in atoms per millimeter for the following directions in FCC platinum, which has a lattice constant of 0.39239 nm: (a) [100], (b) [110], (c) [111].

3.10.1   What is polymorphism with respect to metals?

3.10.2   Titanium goes through a polymorphic change from BCC to HCP crystal structure upon cooling through 882°C. Calculate the percentage change in volume when the crystal structure changes from BCC to HCP. The lattice constant a of the BCC unit cell at 882°C is 0.332 nm, and the HCP unit cell has $a = 0.2950$ nm and $c = 0.4683$ nm.

3.10.3   Pure iron goes through a polymorphic change from BCC to FCC upon heating through 912°C. Calculate the volume change associated with the change in crystal structure from BCC to FCC if at 912°C the BCC unit cell has a lattice constant $a = 0.293$ nm and the FCC unit cell $a = 0.363$ nm.

3.11.1   What are x-rays, and how are they produced?

3.11.2   Draw a schematic diagram of an x-ray tube used for x-ray diffraction, and indicate on it the path of the electrons and x-rays.

3.11.3   What is the characteristic x-ray radiation? What is its origin?

3.11.4   Distinguish between destructive interference and constructive interference of reflected x-ray beams through crystals.

3.11.5   Derive Bragg's law by using the simple case of incident x-ray beams being diffracted by parallel planes in a crystal.

3.11.6   A sample of BCC metal was placed in an x-ray diffractometer using x-rays with a wavelength of $\lambda = 0.1541$ nm. Diffraction from the {310} planes was obtained at $2\theta = 101.502°$. Calculate a value for the lattice constant a for this BCC elemental metal. (Assume first-order diffraction, $n = 1$.)

3.11.7   X-rays of an unknown wavelength are diffracted by a nickel sample. The 2θ angle was 102.072° for the {220} planes. What is the wavelength of the x-rays used? (The lattice constant of nickel = 0.352236 nm; assume first-order diffraction, $n = 1$.)

*3.11.8   An x-ray diffractometer recorder chart for an element which has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 38.184°, 44.392°, 64.576°, and 77.547°. (Wavelength of the incoming radiation was 0.154056 nm.)
    (a) Determine the crystal structure of the element.
    (b) Determine the lattice constant of the element.
    (c) Identify the element.

*3.11.9 An x-ray diffractometer recorder chart for an element which has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: $25.062°$, $35.698°$, $44.116°$, and $51.405°$. (Wavelength λ of the incoming radiation was 0.154056 nm.).

(a) Determine the crystal structure of the element

(b) Determine the lattice constant of the element.

(c) Identify the element.

*3.11.10 An x-ray diffractometer recorder chart for an element which has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: $38.116°$, $44.277°$, $64.426°$, and $77.472°$. (Wavelength of the incoming radiation was 0.154056 nm.)

(a) Determine the crystal structure of the element.

(b) Determine the lattice constant of the element.

(c) Identify the element.

*3.11.11 An x-ray diffractometer recorder chart for an element which has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: $40.113°$, $46.659°$, $68.080°$, and $82.090°$. (Wavelength λ of the incoming radiation was 0.154056 nm.)

(a) Determine the crystal structure of the element.

(b) Determine the lattice constant of the element.

(c) Identify the element.

*Data from International Centre for Diffraction Data

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AMERICAN SOCIETY FOR METALS

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CONSTITUTION OF BINARY ALLOYS

By DONALD T. HAWKINS and RALPH HULTGREN*

CONTENTS

Introduction

THIS SECTION presents phase diagrams for 434 binary alloy systems, selected to serve the largest number of industrial metallurgists. Many of the diagrams were provided by contributors familiar experimentally with the systems; the remainder were selected by the authors from the literature. The contributor's name or initials appear at the lower left of each diagram. Contributors other than the authors are listed at the bottom of this page.

The phase diagrams are in the alphabetical order of the chemical symbols of the components. The symbol for the more important component is on the left side of the diagram. Intermetallic

*Dr. Hawkins is Information Scientist, Bell Laboratories, Murray Hill, N. J. (formerly, Research Metallurgist, Lawrence Berkeley Laboratory, University of California). Dr. Hultgren is Professor Emeritus – Metallurgy, Dept. of Materials Science and Engineering, Lawrence Berkeley Laboratory, University of California. †For a discussion of the 1948 and 1968 temperature scales, see T. B. Douglas, *J Res Nat Bur Std*, Vol 73A (1969), p 451-470.

phases are designated by consecutive Greek letters, left to right, except for phases having other generally accepted designations, such as the sigma phase. Terminal solid solutions are identified by the symbol for the element, in parentheses, instead of by Greek letters.

The diagrams are plotted in weight percentages; however, atomic percentage is shown at the top of each diagram. Temperature is plotted in degrees Centigrade; degrees Fahrenheit are also indicated. All temperatures were corrected to the 1968 International Practical Temperature Scale.† Known temperatures are indicated in Centigrade with a degree sign; known compositions, by numbers (usually with no per cent signs). All constructions agree with the general laws of phase equilibria. Many regions are shown in detail on an enlarged scale.

Dashed lines on the diagrams signify doubt as to the position of the line in question. A dotted line signifies the Curie and Néel magnetic transformation

temperatures. Notes and references for each alloy system in the diagrams, as well as for 18 systems for which no diagrams are shown, are presented in the section that begins on page 339. Crystal structures of intermediate phases of many systems are tabulated with the notes, and are collated into the table that begins on page 243. Crystal structures of the elements are given in the table on page 242.

Melting points and transformation temperatures of the pure elements are in accordance with the tables on the back endpapers in this volume.

Many diagrams here were adopted from those published by M. Hansen, and in the supplements by R. P. Elliott and F. A. Shunk (see general references 3, 4 and 5 in the list on page 339).

We are grateful to the contributors of diagrams and data, to Stephen S. Vogt and David K. Mullin, who assisted with plotting and calculations, and to Leo Brewer, who provided some of the references and crystal structures.

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Ag-Al　Silver-Aluminum

°C

Atomic Percentage Aluminum

L. A. Willey

Weight Percentage Aluminum

Ag-Bi　Silver-Bismuth

°C

Atomic Percentage Bismuth

G. H. S.

Weight Percentage Bismuth

Ag-Au　Silver-Gold

°C

Atomic Percentage Gold

Donold T. Hawkins

Weight Percentage Gold

Ag-Cd　Silver-Cadmium

°C

Atomic Percentage Codmium

G. H. S.

Weight Percentage Cadmium

Ag-Be　Silver-Beryllium

°C

Atomic Percentage Beryllium

George H. Sistare
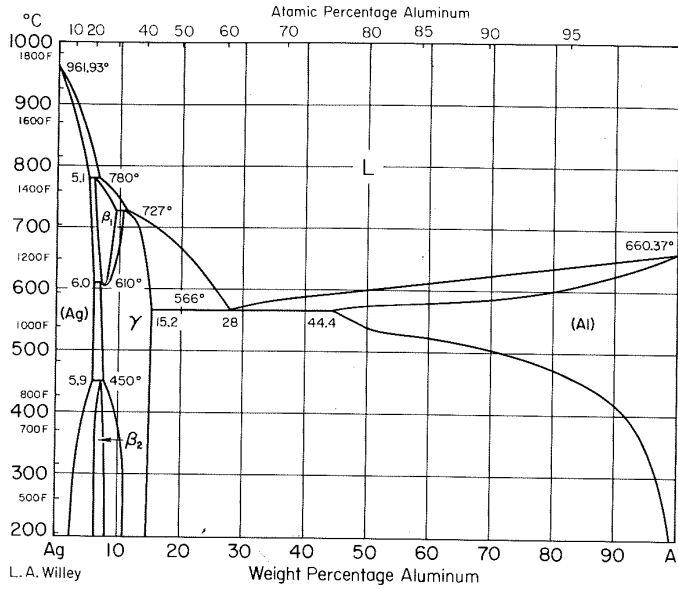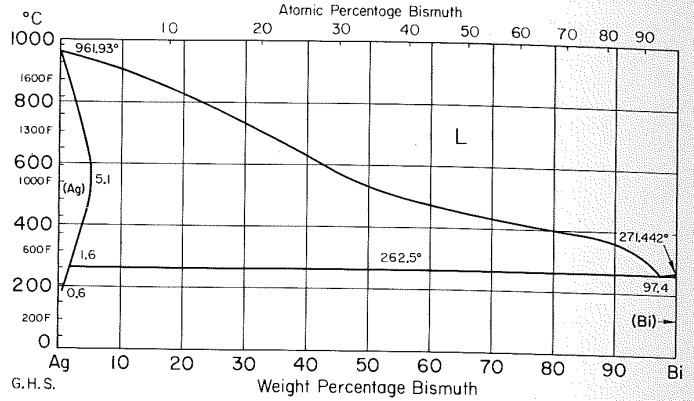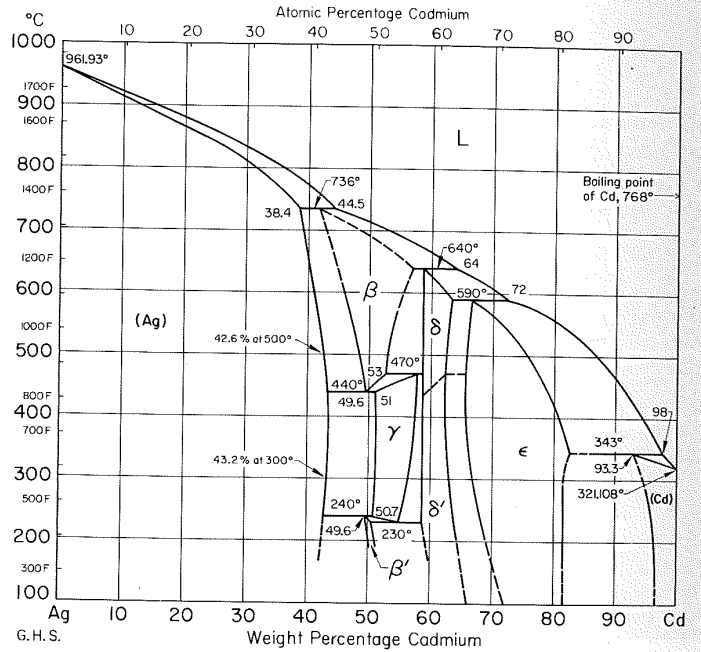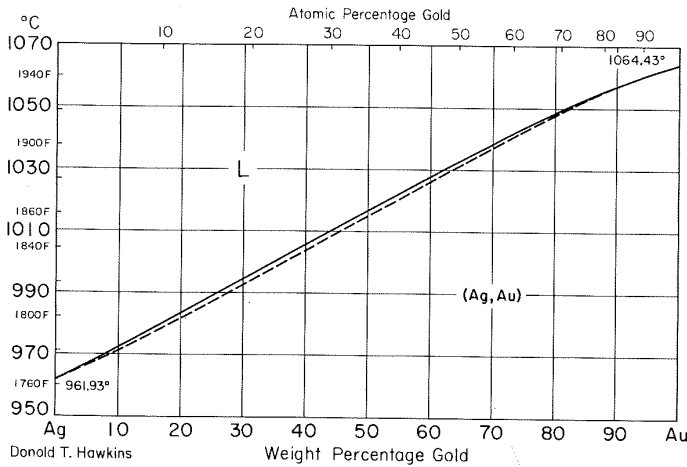
Weight Percentage Beryllium

Ag-Cr　Silver-Chromium

°C

Atomic Percentage Chromium

G. H. S.

Weight Percentage Chromium

Ag-Cu   Silver-Copper

°C
Atomic Percentage Silver
10 20 30 40 50 60 70 80 90

1100 1084.5°

L

961.93°

(Cu)

780°

7.9   71.9   91.2

(Ag)

Cu 10 20 30 40 50 60 70 80 90 Ag

Weight Percentage Silver

J. C. Chaston

Ag-Hg   Silver-Mercury

°C
Atomic Percentage Mercury
10 20 30 40 50 60 70 80 90

1000 961.93°

L

(Ag)

Boiling point of Hg, 357°

52.4   276°

127°

β   γ

-38,862°

-38.9°

(Hg)

Ag 10 20 30 40 50 60 70 80 90 Hg

Weight Percentage Mercury

G. H. S.

Ag-Ga   Silver-Gallium

°C
Atomic Percentage Gallium
10 20 30 40 50 60 70 80 90

1000 961.93°

L

611°
13

(Ag)

β   γ

~425°

12,2   380°

β'

~375°

326°

8.0

δ

25°   29.75°
~95.5
(Ga)

Ag 10 20 30 40 50 60 70 80 90 Ga

Weight Percentage Gallium

George H. Sistare

Ag-In   Silver-Indium

°C
Atomic Percentage Indium
10 20 30 40 50 60 70 80 90

1000 961.93°

L

695°
670°   660°

β

(Ag)

γ

187°

205°

166°

α'   δ   ε   144°   (In)   97

156.634°

Ag 10 20 30 40 50 60 70 80 90 In

Weight Percentage Indium

Donald T. Hawkins

Ag-Ge   Silver-Germanium

°C
Atomic Percentage Germanium
10 20 30 40 50 60 70 80 90

000 961.93°

L

938.3°

(Ag) 6.7

19   651°

(Ge)

Ag 10 20 30 40 50 60 70 80 90 Ge

Weight Percentage Germanium

G. H. S.

Ag-Li   Silver-Lithium

°C
Atomic Percentage Lithium
10 40 60 70 80 85 90 93 95 97 98 99

500

(Ag) 330°   317°
11.8

9.3

β

L

201°,11%

164°

γ   180.5°

154°   145.5°

6.2
7.5
5.3   15   17

δ   ε   (Li)

Ag 10 20 30 40 50 60 70 80 90 Li

Weight Percentage Lithium

G. H. S.

Ag-Mg Silver-Magnesium

George H. Sistare

Ag-Ni Silver-Nickel

G.H.S.

Ag-Mn Silver-Manganese

G.H.S.

Ag-O Silver-Oxygen

J. C. Choston

J.C.C.
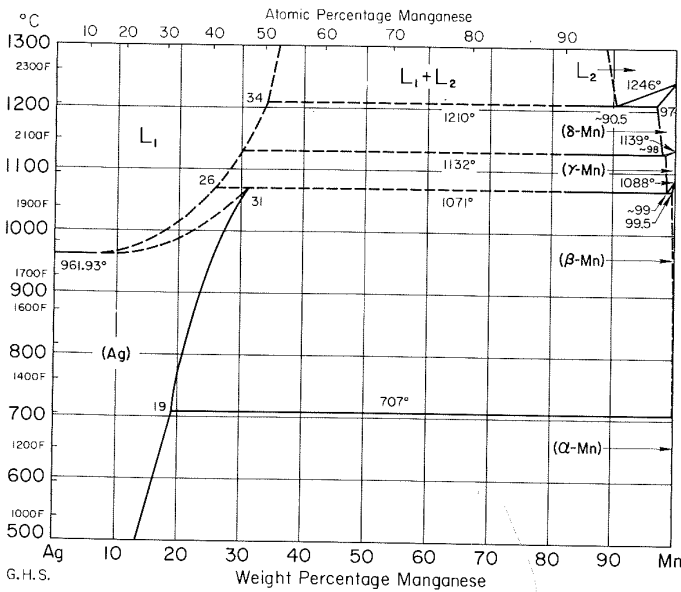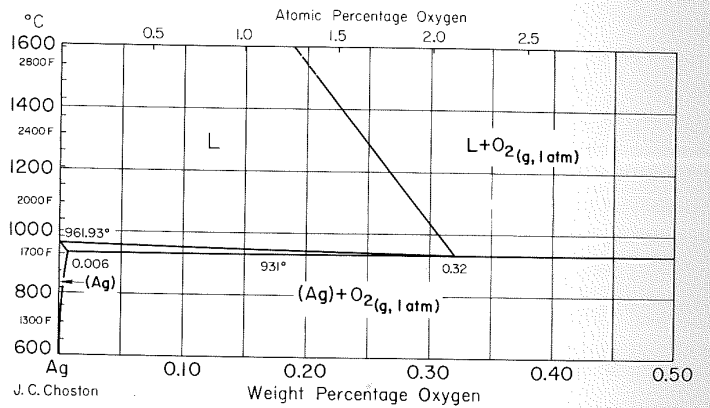
Ag-Na Silver-Sodium

G.H.S.

Ag-P   Silver-Phosphorus

Atomic Percentage Phosphorus

George H. Sistare

Ag-Pb   Silver-Lead

C. DiMartini

Weight Percentage Silver

Ag-Pd   Silver-Palladium

A. S. Darling   Weight Percentage Silver

Ag-Pt   Silver-Platinum

G.H.S.   Weight Percentage Silver
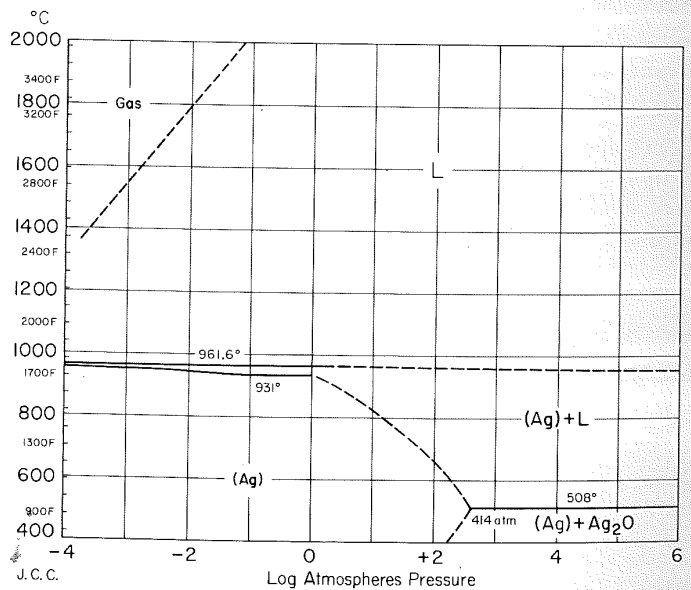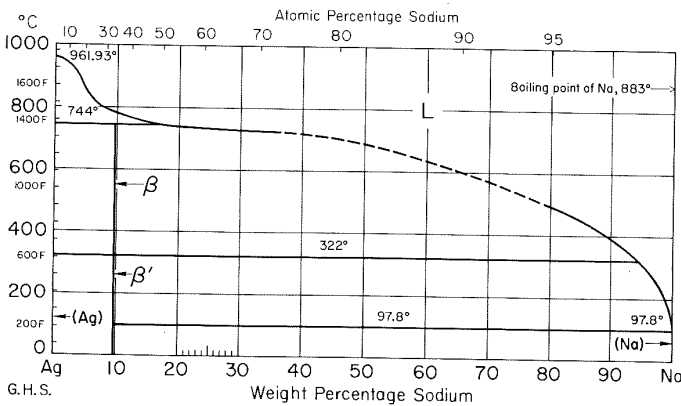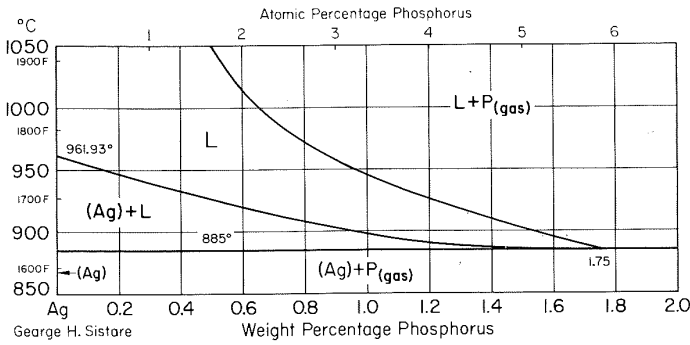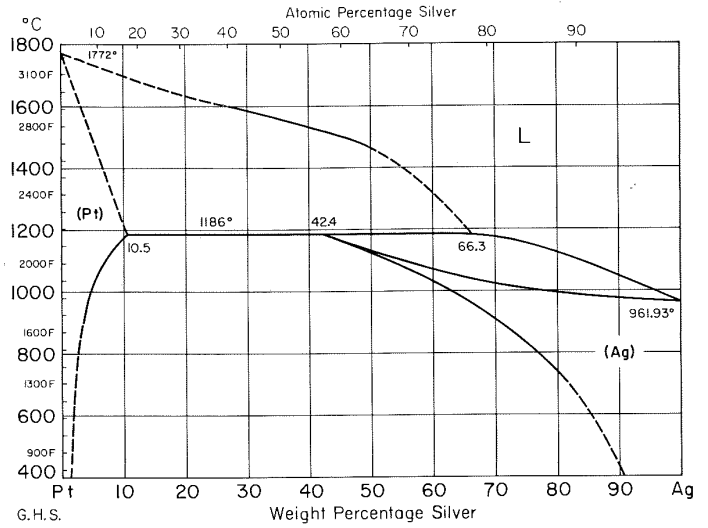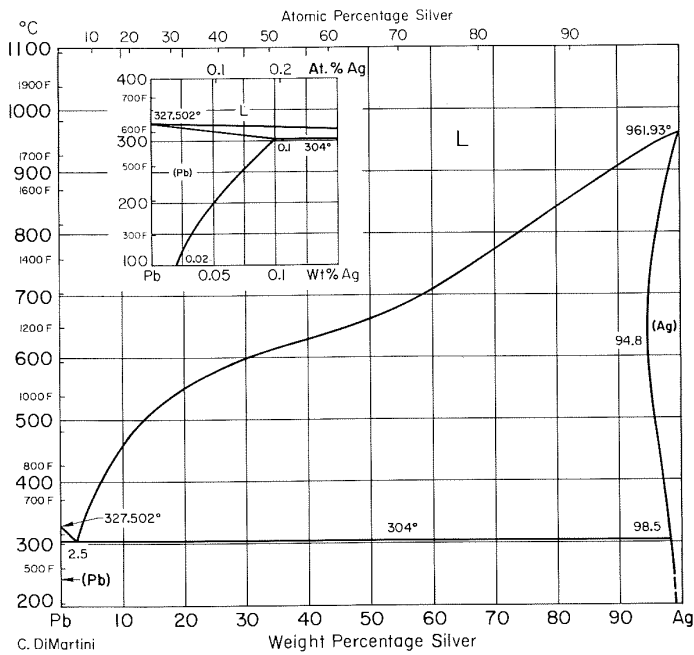
Ag-Rh   Silver-Rhodium
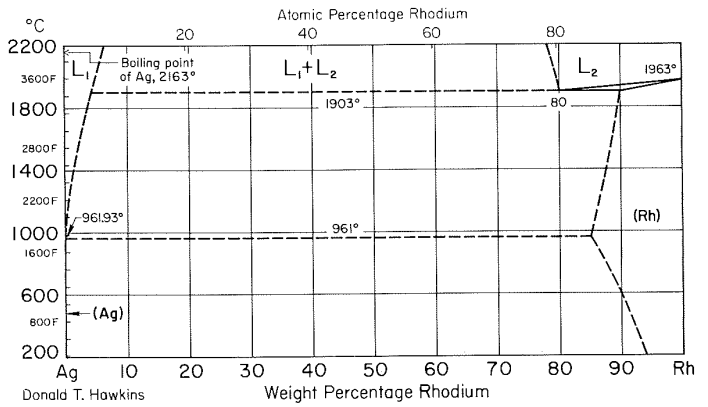
Donald T. Hawkins   Weight Percentage Rhodium

Ag-Sb   Silver-Antimony
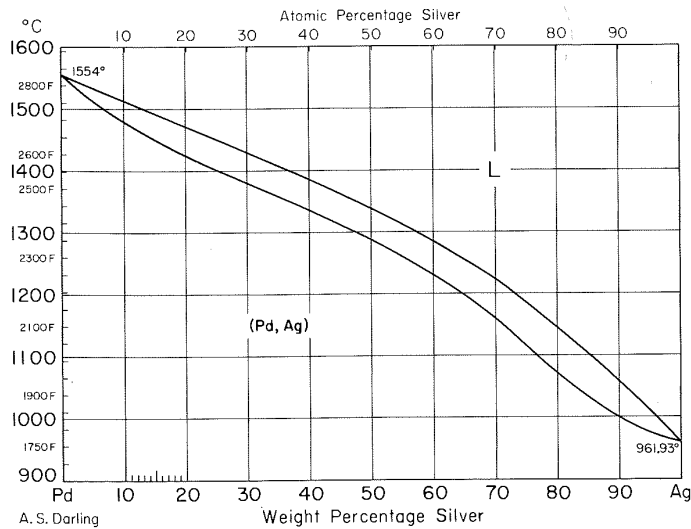
G.H.S.   Weight Percentage Antimony

Ag-Si   Silver-Silicon

Donald T. Hawkins

Ag-Sn   Silver-Tin

George H. Sistare

Ag-Ti   Silver-Titanium

G.H.S.

Ag-Zn   Silver-Zinc

G.H.S.
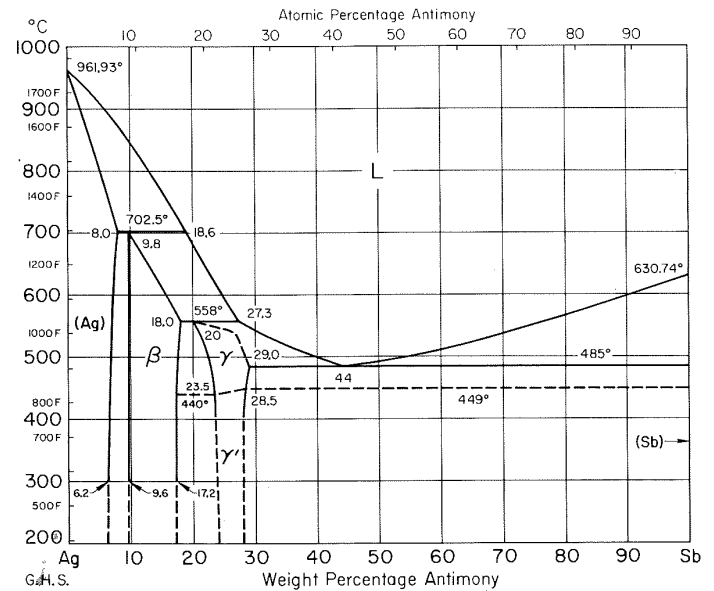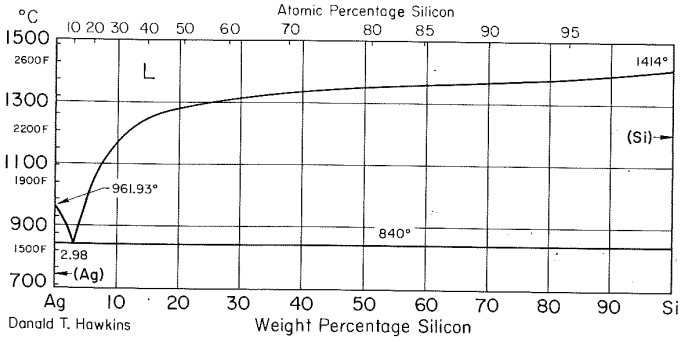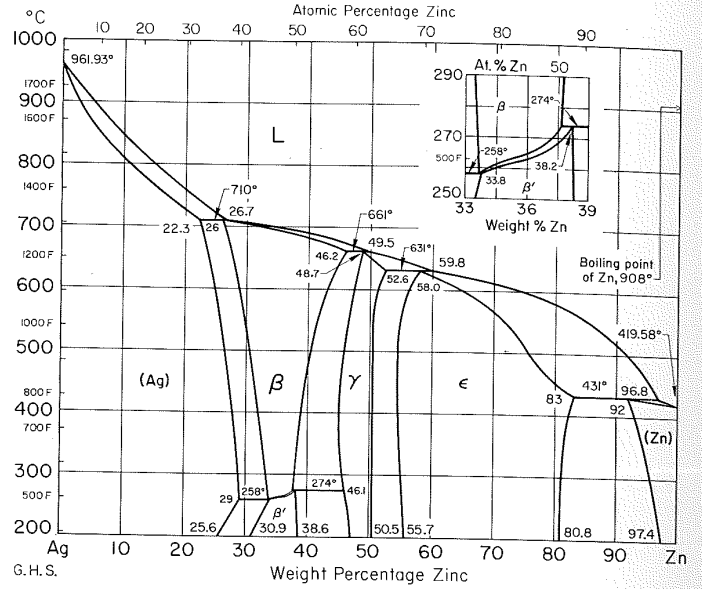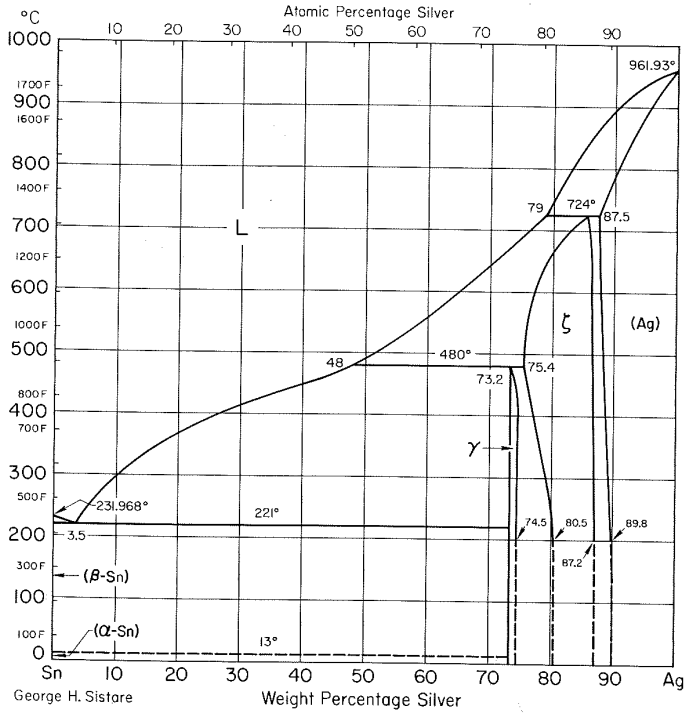
Ag-Zr   Silver-Zirconium

G.H.S

Al-Au   Aluminum-Gold

L. A. Willey

Al-B   Aluminum-Boron

°C
Atomic Percentage Boron
10 20 30 40 50 60 70 80 90

1400
2400F
~1.0
~1350°
γ_1
1200
2000F
L
1000
1600F
~850°
(B)→
800
0.1
660.37°
-0.022   659.9°
1200F
β
γ_2
600
(Al)

Al   10   20   30   40   50   60   70   80   90   B

L. A. Willey   Weight Percentage Boron

°C
Atomic Percentage Boron
0.4   0.8   1.2   1.6   2.0   2.4

900
1600F
0.1
~850°
800
1400F
L
700
660.37°
1200F
0.022   659.9°
600
(Al)

Al   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8   0.9   1.0
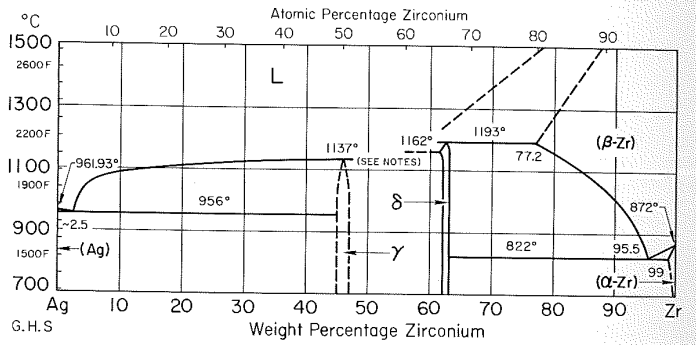
L.A.W.   Weight Percentage Boron
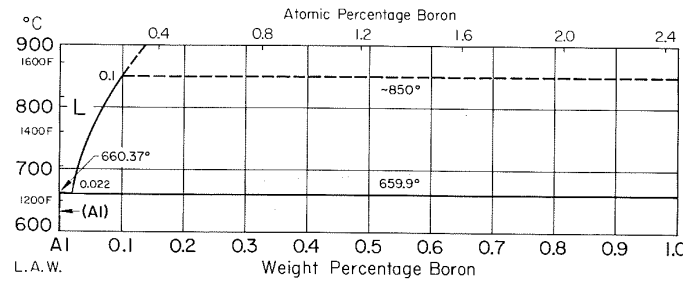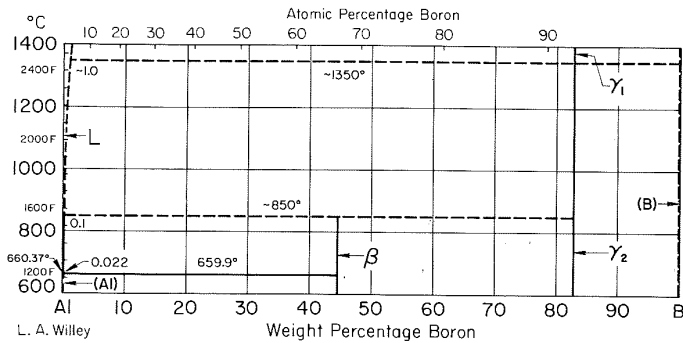
Al-Be   Aluminum-Beryllium

°C
Atomic Percentage Beryllium
10 20 30 40 50 60 70 80 85 90   95

1400
2400F
1289°
1200
2000F
L
1256°
(β-Be)
1000
1600F
800
660.37°
1200F
0.87   645°   ~99.95
600
0.06
900F
(Al)   (α-Be)→
400

Al   10   20   30   40   50   60   70   80   90   Be

L. A. W.   Weight Percentage Beryllium

Al-Bi   Aluminum-Bismuth

°C
Atomic Percentage Bismuth
2   4   6   8   10   15   20   30   40   60   90

1300
2300F
L_2
1100
1900F
L_1
L_1+L_2
900
1500F
660.37°
700
1200F
657°
3.4   98.1
500
800F
(Al)
300
270°   271.442°
400F
(Bi)→
100

Al   10   20   30   40   50   60   70   80   90   Bi

L. A. W.   Weight Percentage Bismuth
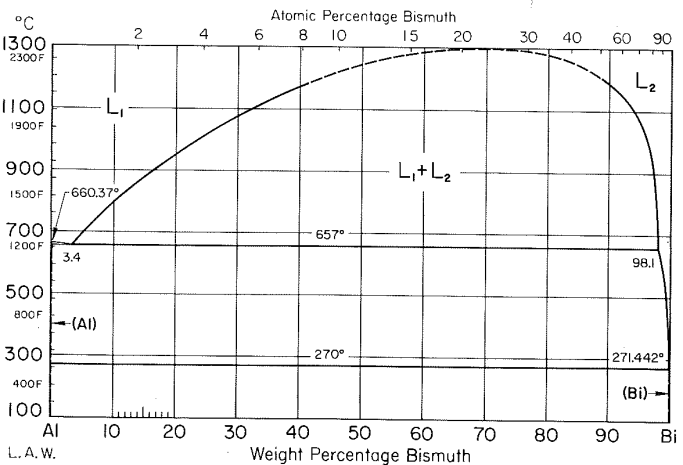
Al-C   Aluminum-Carbon

See Notes.

Al-Ca   Aluminum-Calcium

°C
Atomic Percentage Calcium
10   20   30   40   50   60   70   80   90

1200
2100F
1100
1079°
1900F
1000
L
1700F
900
1600F
840°
800
1400F
700
700°
660.37°   14
1200F
616°
600
7.6
1000F
<0.001   545°   73
500
(Al) γ→ δ→   447°   (β-Ca)
800F
400
700F
(α-Ca)→
300

Al   10   20   30   40   50   60   70   80   90   Ca

L. A. W.   Weight Percentage Calcium
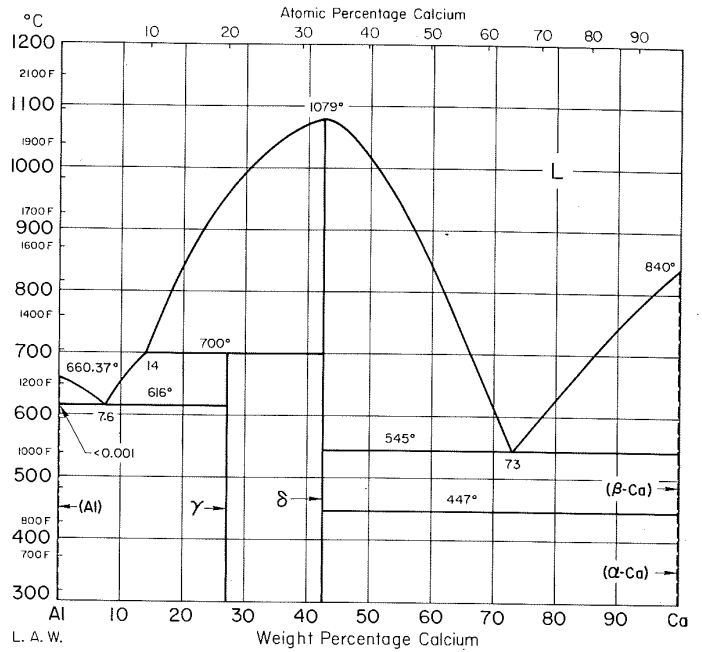
Al-Cb   Aluminum-Columbium

°C
Atomic Percentage Columbium
5   10   15   20   30   40   50   60   70   90

2600
4600F
Boiling point of Al, 2520°
2471°
2400
4200F
2200
L
3800F
2000
91.2
3400F
1963°,88%   92
1800
1873°,85.5%   88   (Cb)
3100F
87.3 δ
1600
1607°
2800F
1552° σ
1400
53.4   71.5   83
2400F
1200
2000F
0.75% at 1100°
1000
1600F
0.15% at 900°
800
0.01
660.37°
1200F
661.6°
600
0.22
900F
(Al) β→
400
500F
200

Al   10   20   30   40   50   60   70   80   90   Cb

L. A. W.   Weight Percentage Columbium

Al-Cd　Aluminum-Cadmium

L. A. Willey

Al-Co　Aluminum-Cobalt

L.A.W.
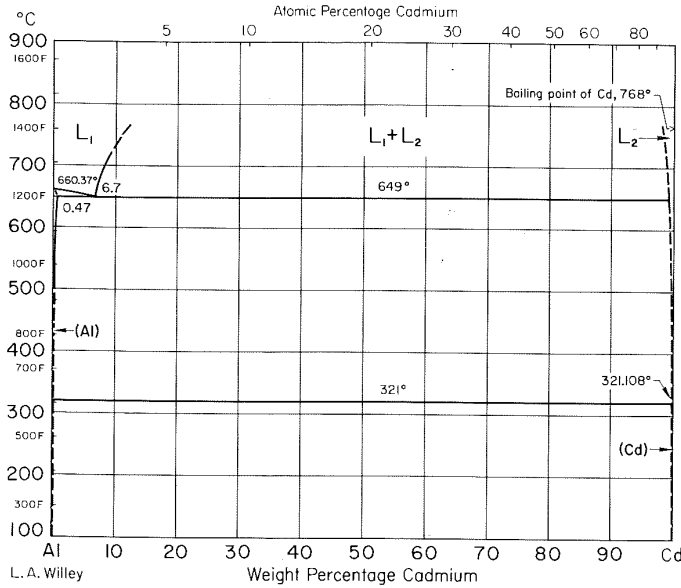
Al-Cr　Aluminum-Chromium

L.A.W.

L.A.W.
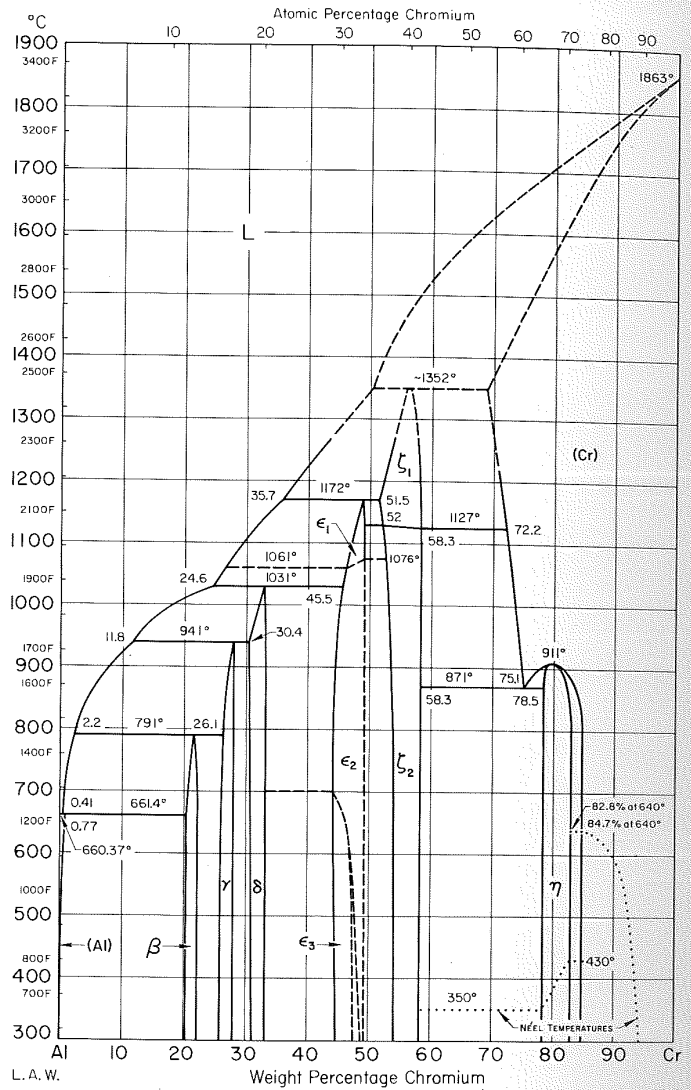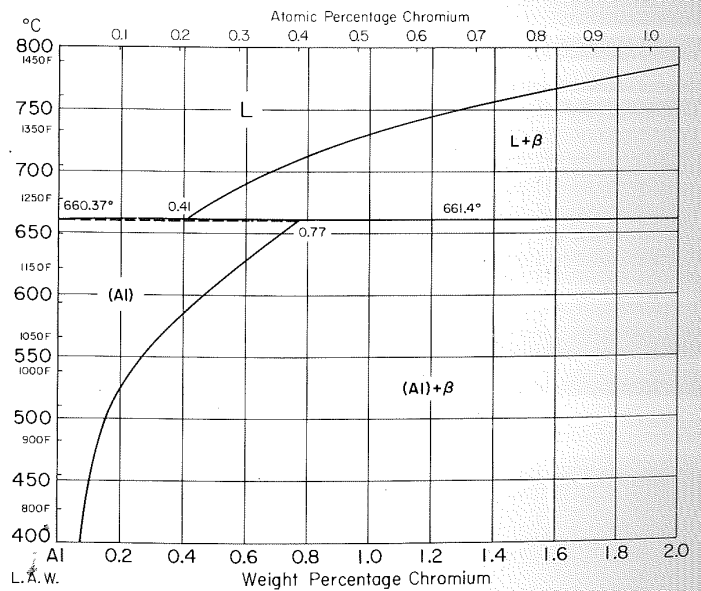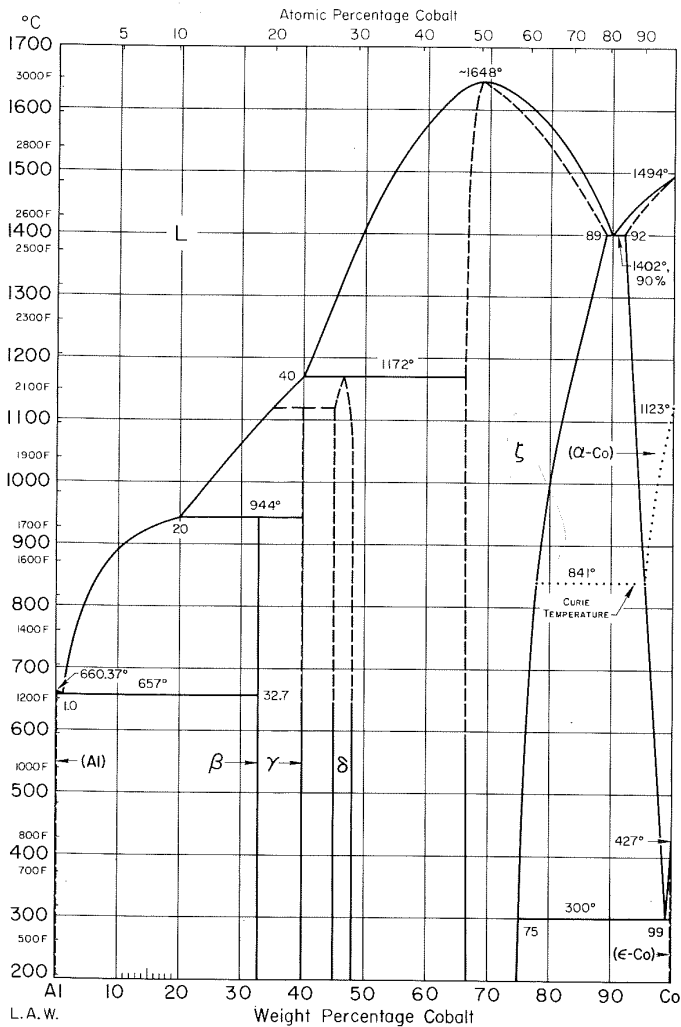
Al-Cu   Aluminum-Copper

L.A. Willey

L.A.W.

Al-Fe   Aluminum-Iron

L.A. Willey

Al-Ga   Aluminum-Gallium

L.A.W.

Al-Ge   Aluminum-Germanium

L.A.W.

L.A.W.

Al-H   Aluminum-Hydrogen
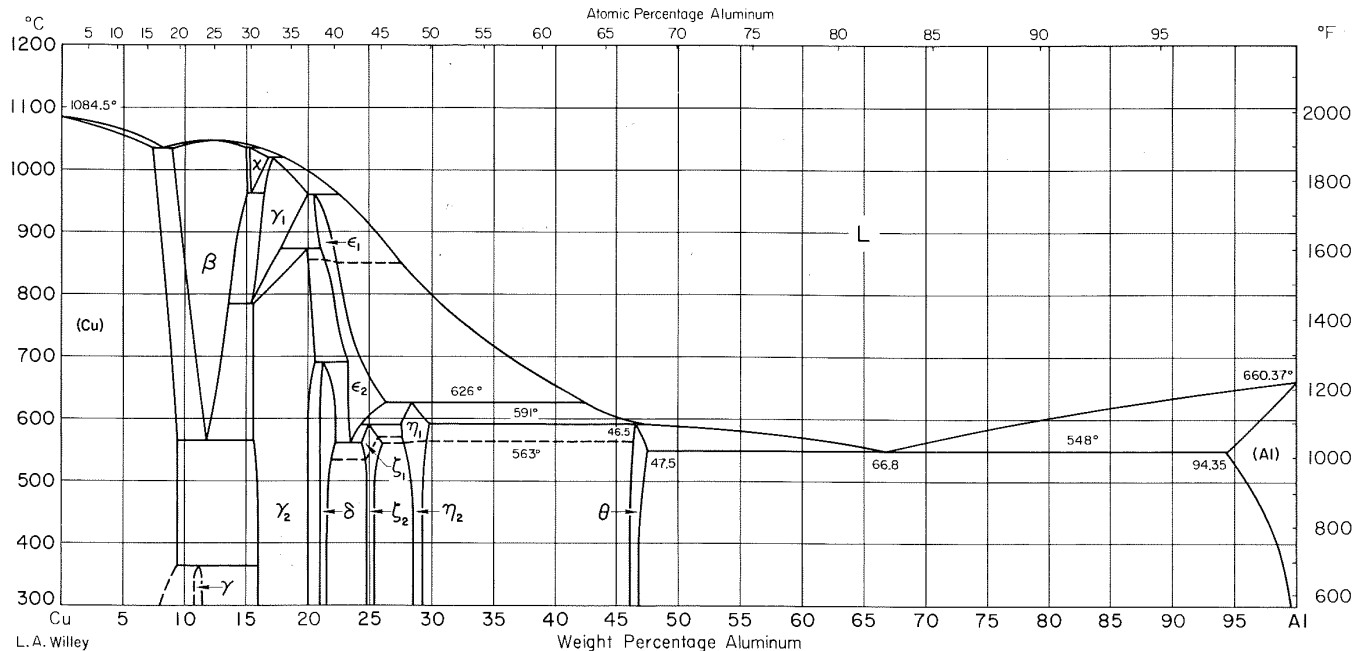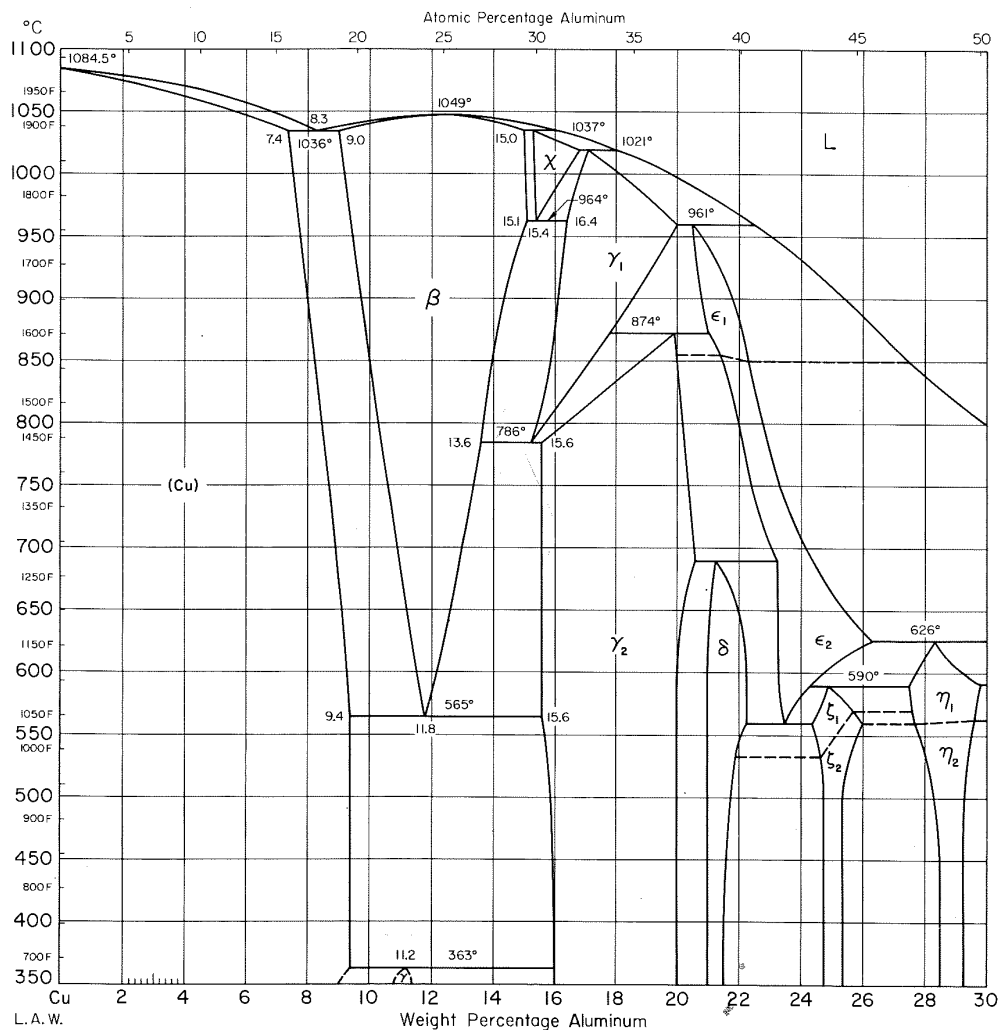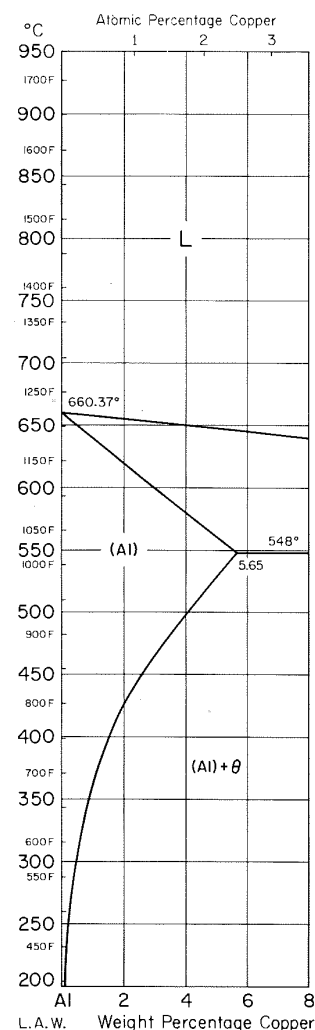
See Notes.

Al-Hf   Aluminum-Hafnium

L.A.Willey
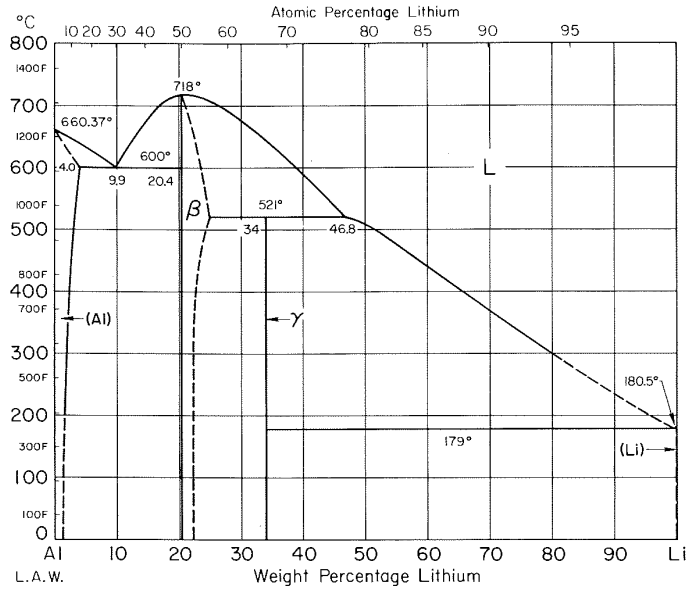
Al-Hg   Aluminum-Mercury

L.A.W.

Al-In   Aluminum-Indium

L.A.W.

Al-Li   Aluminum-Lithium

L.A.W.
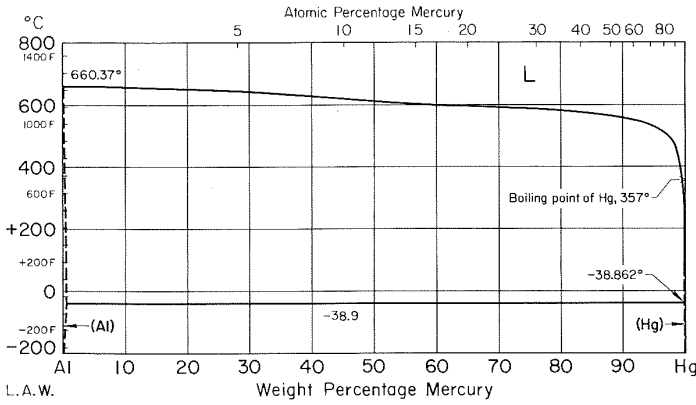
Al-Mg   Aluminum-Magnesium

L.A.W.
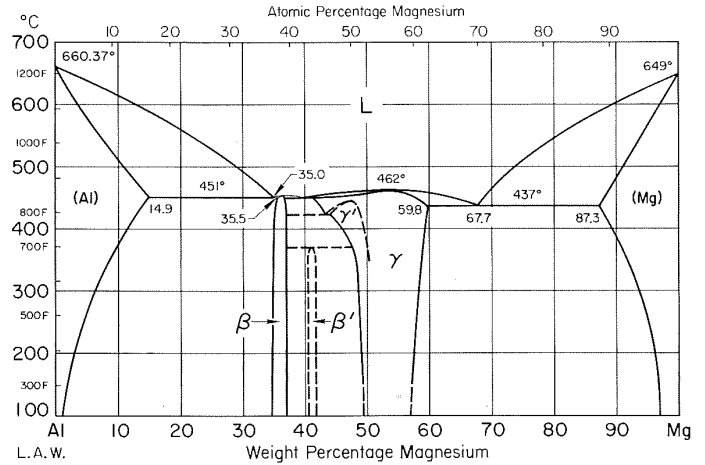
L.A.W.   Weight Percentage Magnesium
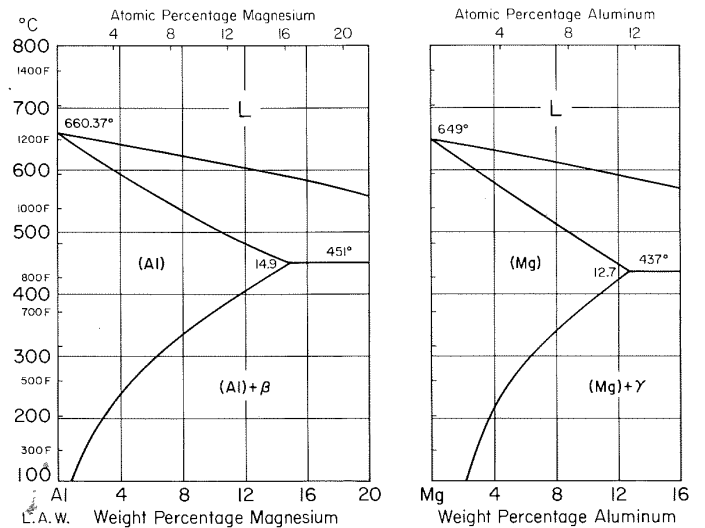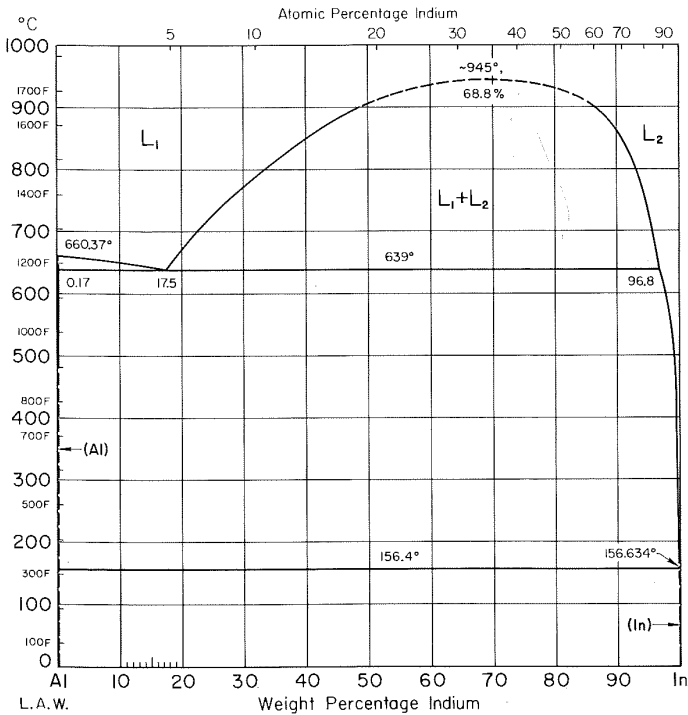
Al-Mn   Aluminum-Manganese

L. A. Willey

L.A.W.
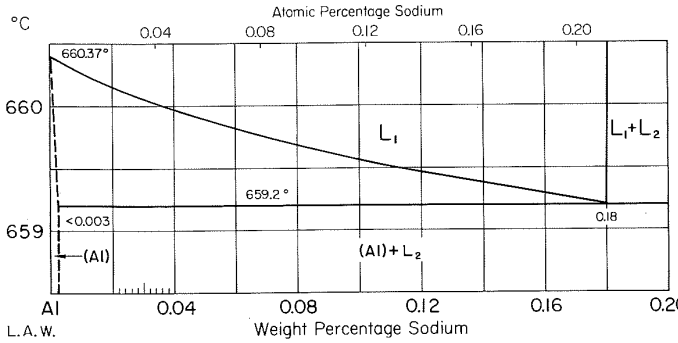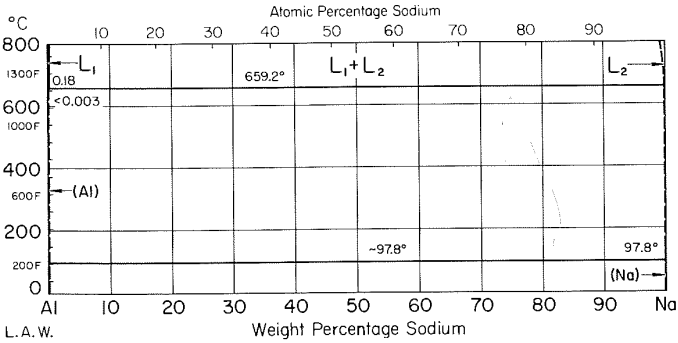
Al-Ni   Aluminum-Nickel

L.A.W.

Al-Na   Aluminum-Sodium

L.A.W.

L.A.W.

L.A.W.
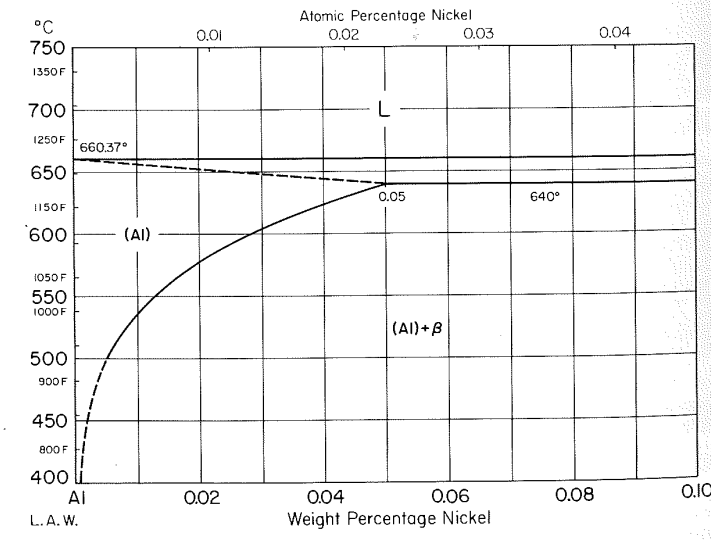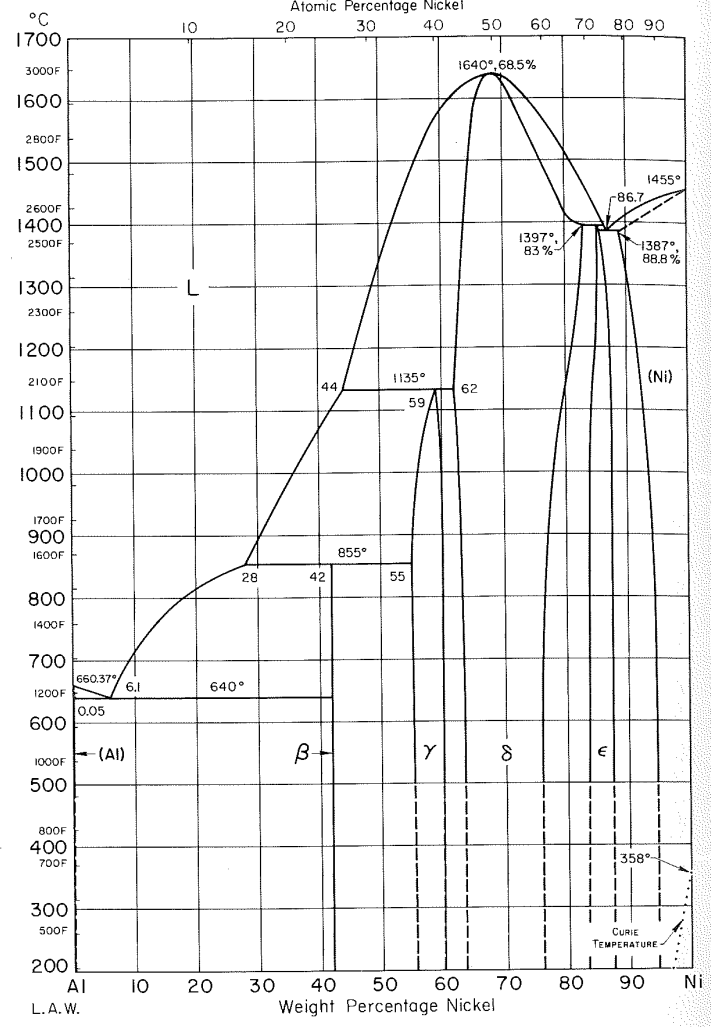
Al-O   Aluminum-Oxygen

See Notes.

Al-Pb   Aluminum-Lead

L. A. Willey
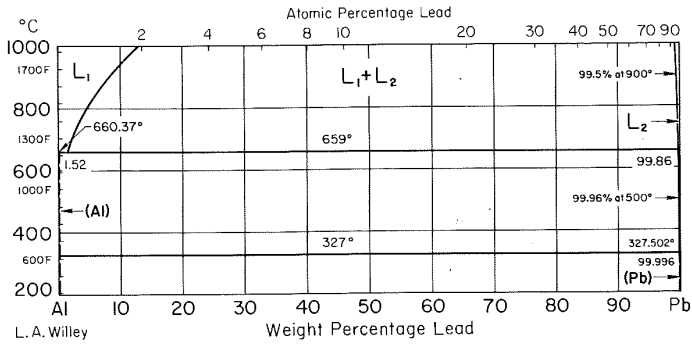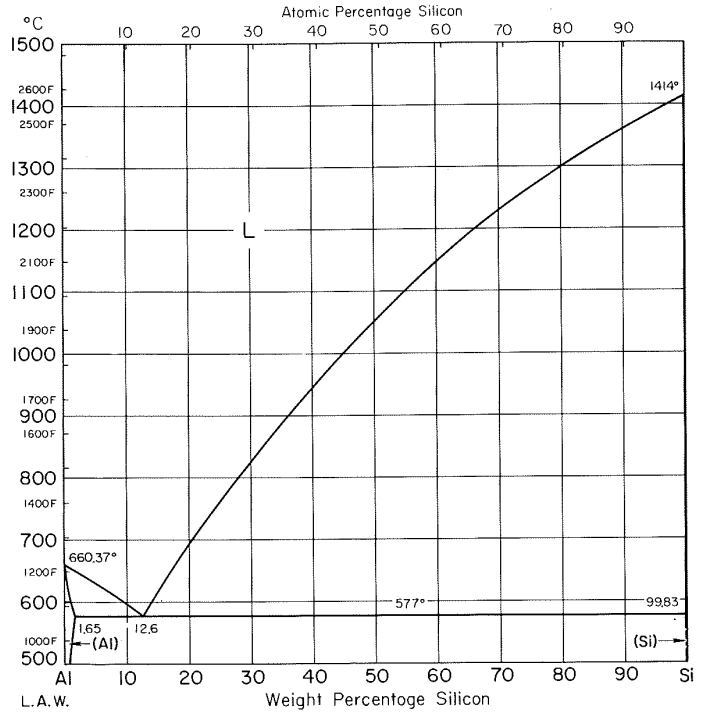
Al-Pu   Aluminum-Plutonium

F. H. Ellinger

Al-Sb   Aluminum-Antimony

L. A. W.

Al-Si   Aluminum-Silicon

L. A. W.

L. A. W.

Al-Sn   Aluminum-Tin

L. A. W.

Al-Ta   Aluminum-Tantalum

L. A. Willey

Al-Ti   Aluminum-Titanium

Harold Margolin

L. A. W.

Al-U   Aluminum-Uranium

L. A. W.

Al-V   Aluminum-Vanadium

L. A. W.

Al-W   Aluminum-Tungsten

Atomic Percentage Tungsten

°C

1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600

L

1652°
98.3

θ

1422°?

1345° η   1336°   1318°
1327°
1302°   97.8
ζ

871°
ε
(W)

660.37°
697°
660.5°
0.16
(Al)   β?   γ   δ

Al   10   20   30   40   50   60   70   80   90   W
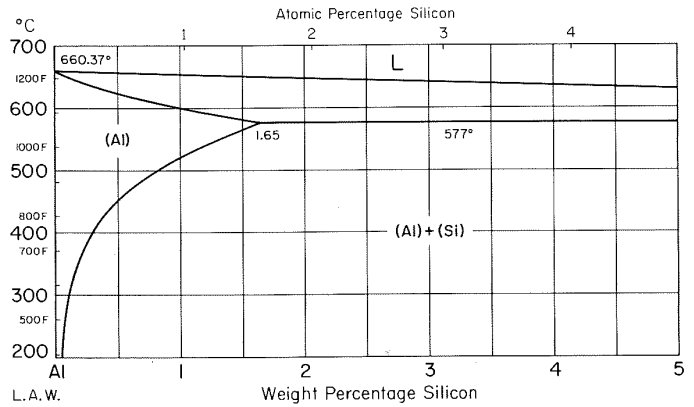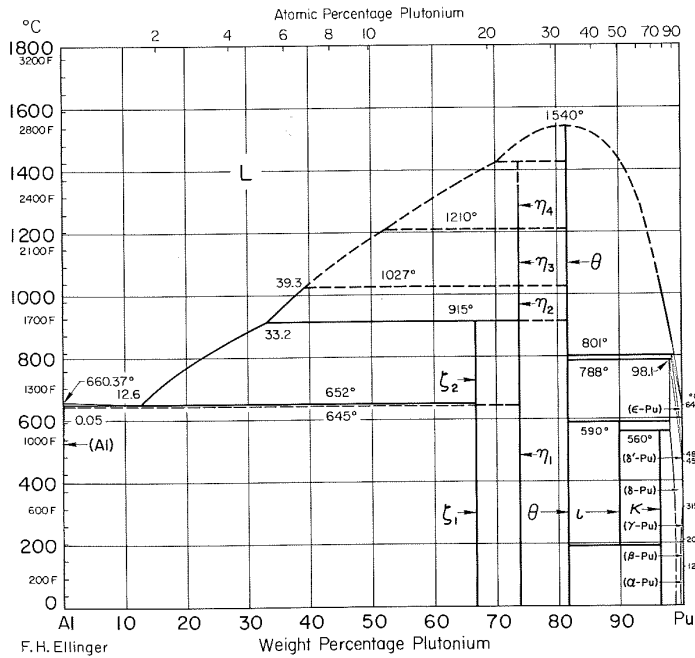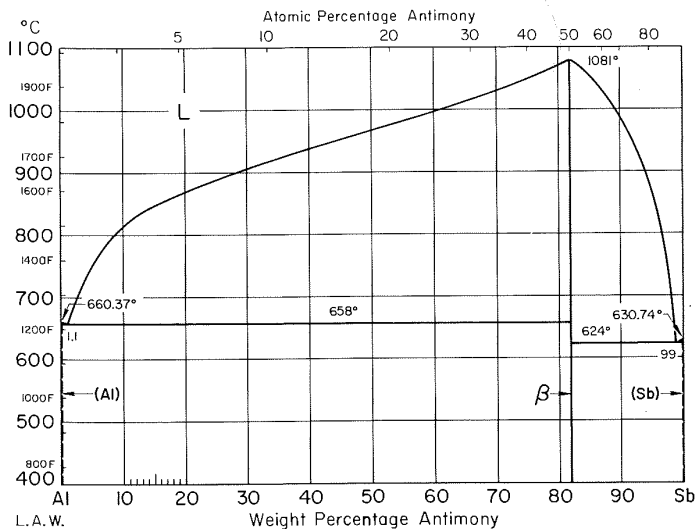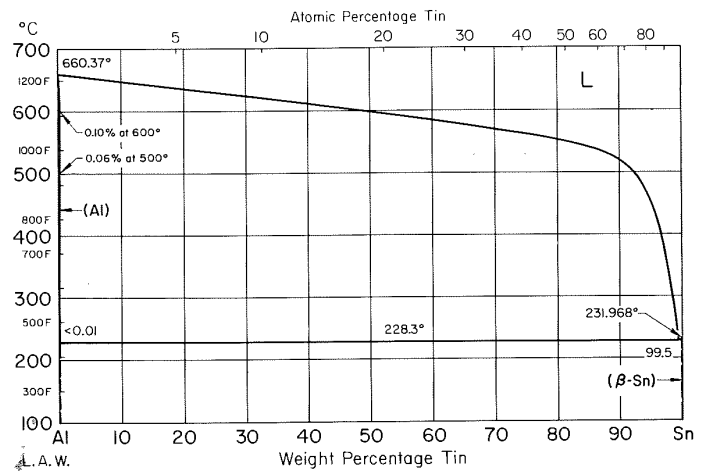
L.A. Willey   Weight Percentage Tungsten
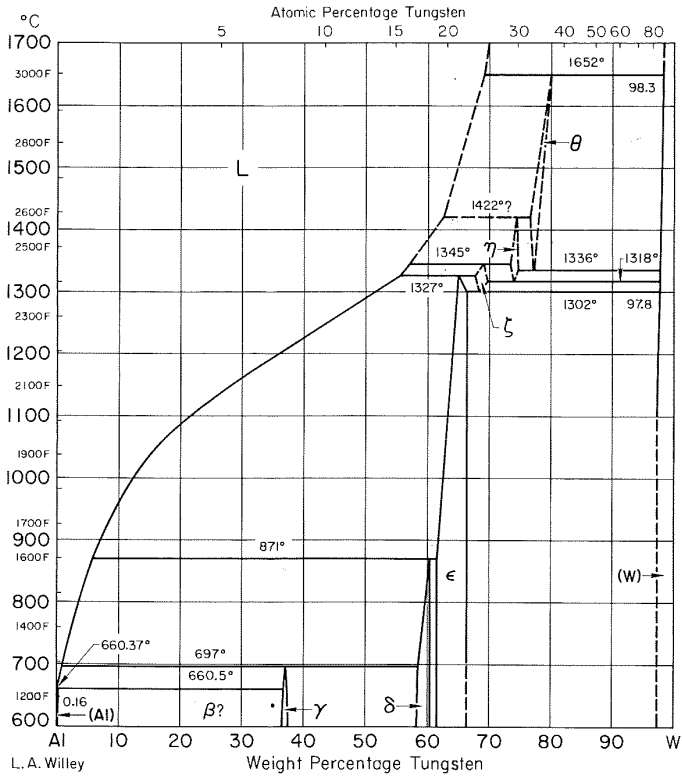
Al-Zr   Aluminum-Zirconium

Atomic Percentage Zirconium

°C

1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600

L

1865°
1647°
1582°   1592°
1492°
55
1482°   1532°
78
1397°   1352°, 90.5%
89
1252°   1252° (β-Zr)
θ
976°
941°
96.5
96.8
872°
660.37°
0.11   660.7°
0.28
(Al)   β   γ   δ   ε   η   ι   κ
ζ
(α-Zr)

Al   10   20   30   40   50   60   70   80   90   Zr

L.A.W.   Weight Percentage Zirconium

Al-Zn   Aluminum-Zinc

Atomic Percentage Zinc

°C

700
600
500
400
300
200
100

660.37°
(Al)
L
419.58°
382°
82.8
353°, 61.3%
95
99
275°
78
99.4
31.6
(Zn)

Al   10   20   30   40   50   60   70   80   90   Zn

L.A.W.   Weight Percentage Zinc

Atomic Percentage Zinc

°C

500
400
300
200
100

L
419.58°
95
382°
(Al)+(Zn)
99
(Zn)
275°
99.4
(Al)+(Zn)

95   95.5   96   96.5   97   97.5   98   98.5   99   99.5   Zn

L.A.W.   Weight Percentage Zinc

Atomic Percentage Zirconium

°C

900
800
700
600

L
L+β
660.37°
0.11   660.7°
0.28
(Al)   (Al)+β

Al   0.2   0.4   0.6   0.8   1.0   1.2   1.4   1.6   1.8   2.0

L.A.W.   Weight Percentage Zirconium

As-Cu   Arsenic-Copper

Atomic Percentage Arsenic

°C

1100
900
700
500
300
100

1084.5°
L
827°
Extrapolated melting point of As, 809°
685°
710°
6.77
21.0
600°
Sublimation point (at 1 atm) of As, 603°
(Cu)
50.1
γ   δ
395°
7.8
325±25°
β
(As)

Cu   10   20   30   40   50   60   70   80   90   As

Donald T. Hawkins   Weight Percentage Arsenic

As-Fe   Arsenic-Iron

Donald T. Hawkins

As-In   Arsenic-Indium

M. B. Panish and M. Ilegems

As-Ni   Arsenic-Nickel

See Notes.

As-Pb   Arsenic-Lead

C. DiMartini

Au-Bi   Gold-Bismuth

D.T.H.

Au-Cd   Gold-Cadmium

George H. Sistare

Au-Co   Gold-Cobalt

J. C. Chaston

Au-Cr   Gold-Chromium

J. C. Chaston

Au-Cu   Gold-Copper

Donald T. Hawkins

Au-Fe   Gold-Iron

D.T.H.

Au-Ge   Gold-Germanium

J.C.C.

Au-In   Gold-Indium

J.C.C.

Au-Ni   Gold-Nickel

J.C.C.

Au-Pb   Gold-Lead

Donald T. Hawkins

Au-Pd   Gold-Palladium

W. G. Bugden

Au-Pt   Gold-Platinum

A. S. Dorling

Au-Rh   Gold-Rhodium

G. L. Selman

Au-Sb   Gold-Antimony

George H. Sistare

Au-Si   Gold-Silicon

J. C. Chaston

Au-Sn Gold-Tin

J. C. Chaston

Au-Ti Gold-Titanium

See Notes.

Au-U Gold-Uranium

George H. Sistare

Au-V Gold-Vanadium

J. C. C.

Au-Zn Gold-Zinc

G. H. S.
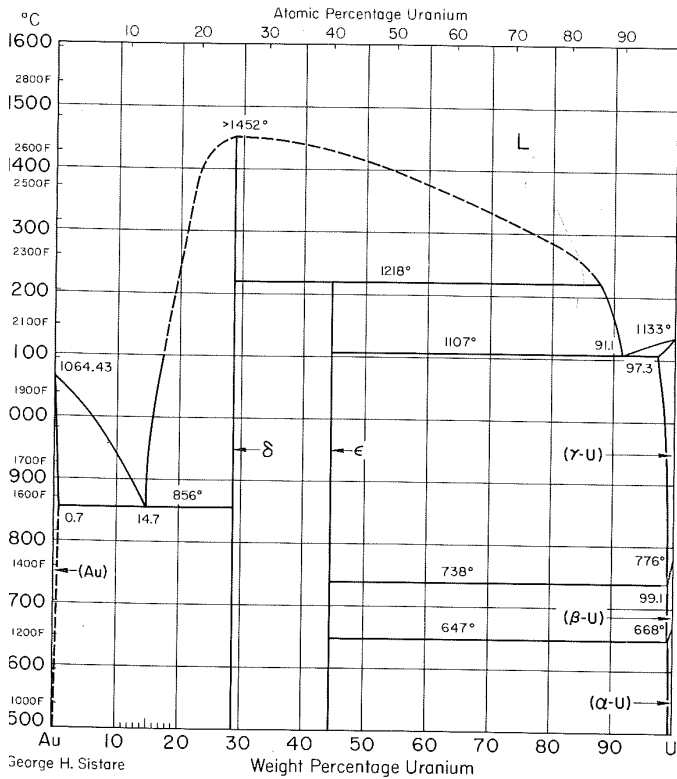
Au-Zr Gold-Zirconium

See Notes.

B-Cr Boron-Chromium

Donald T. Hawkins

B-Cu　Boron-Copper

Atomic Percentage Boron

°C

L

1084.5°

1014°　　99.5

(Cu) 0.53　　47.4　　　(B)

Cu　10　20　30　40　50　60　70　80　90　B

Robert C. Ruhl　　Weight Percentage Boron

B-Fe　Boron-Iron

Atomic Percentage Boron

°C

L

~2103°

1983°

78.6

1652°

1502°

1538°

(δ-Fe)　25.6

1394°, 1.5%　1391°

ζ'

(γ-Fe)

3.8　1137°

1161°　　　η　　(B)

913°

~912°　Curie Temperature

(α-Fe)　770°　ε　ζ

(γ-Fe)

912°

0.002　913°

0.001

770°

(α-Fe)

Curie Temperature

Fe　0.008　0.016　0.024

Weight % B

Fe　10　20　30　40　50　60　70　80　90　B

A. R. Marder　　Weight Percentage Boron

B-Hf　Boron-Hafnium

Atomic Percentage Hafnium

°C

3367°, 89.25%

L

L

~2103°　2027°

2231°

94.5

(B)

1795°

γ　δ

B　10　20　30　40　50　60　70　80　90　Hf

D.T.H.　　Weight Percentage Hafnium

°C

Atomic % Hafnium

γ+L

2097°　94.5

δ

γ+δ

1872°

1795°

(β-Hf)

99.1　1742°

2231°

L

(α-Hf)

D.T.H.　Weight % Hafnium　94　95　96　97　98　99　Hf

B-Pd　Boron-Palladium

Atomic Percentage Boron

°C

Atomic % B

1100

L

~2.6

700

α(Pd)　β　γ　γ+(B)

α₁　α₁+α₂　α₂　α'

300　Pd　0.5　1　1.5　2　2.5　3　3.5　4　4.5

Weight % B

L

1554°　　　　　　　　　　~2103°

~1021°

(B)

γ+(B)

SEE DETAIL ABOVE

Pd　10　20　30　40　50　60　70　80　90　B

A. S. Darling　　Weight Percentage Boron

B-Ti　Boron-Titanium

Atomic Percentage Titanium

°C

L

3232°, 69.5%

L

~2103°　2083°

2194°　86.0

8.3

(B)

γ　δ　(β-Ti)

98.3

1672°

1542°

883°

881°

(α-Ti)

B　10　20　30　40　50　60　70　80　90　Ti

D.T.H.　　Weight Percentage Titanium

B-Zr　Boron-Zirconium

Atomic Percentage Zirconium

°C

3252°, 81.3%

L

45.5　2254°

~2103°　2003°　51.0

14.7　　γ

1713°　48.4

(B)

δ　(β-Zr)

1865°

1663°　98.4

881°

872°

(α-Zr)

B　10　20　30　40　50　60　70　80　90　Zr

D.T.H.　　Weight Percentage Zirconium

Ba-Pb   Barium-Lead

C. DiMartini
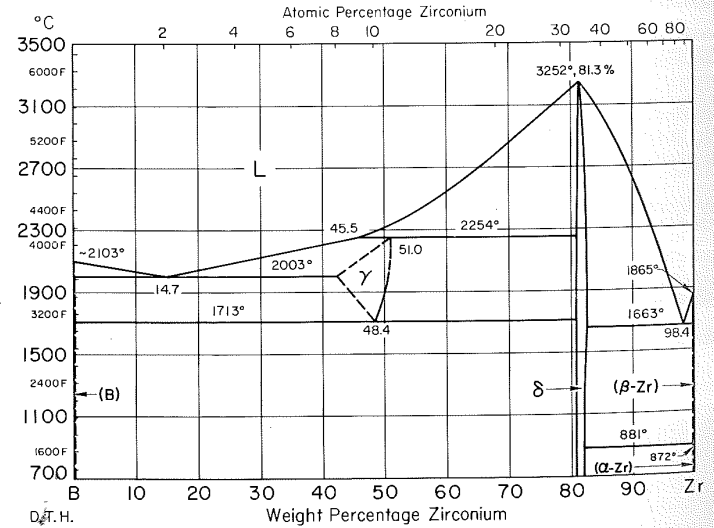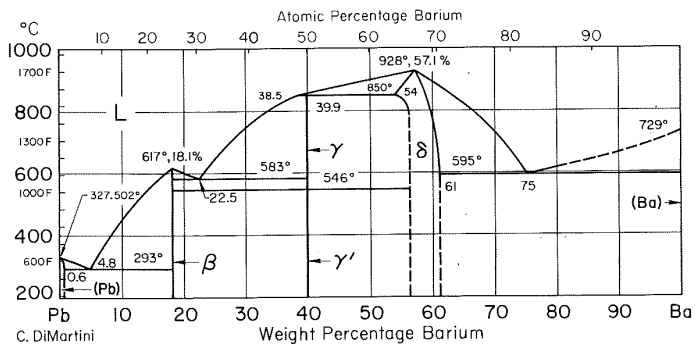
Be-Fe   Beryllium-Iron

D.T.H.
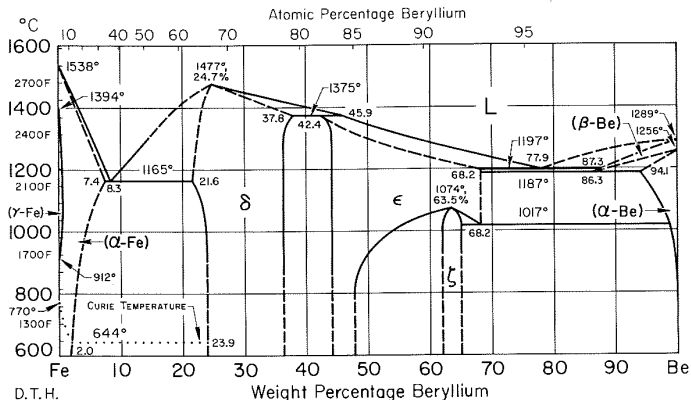
Be-Cu   Beryllium-Copper

Donald T. Hawkins
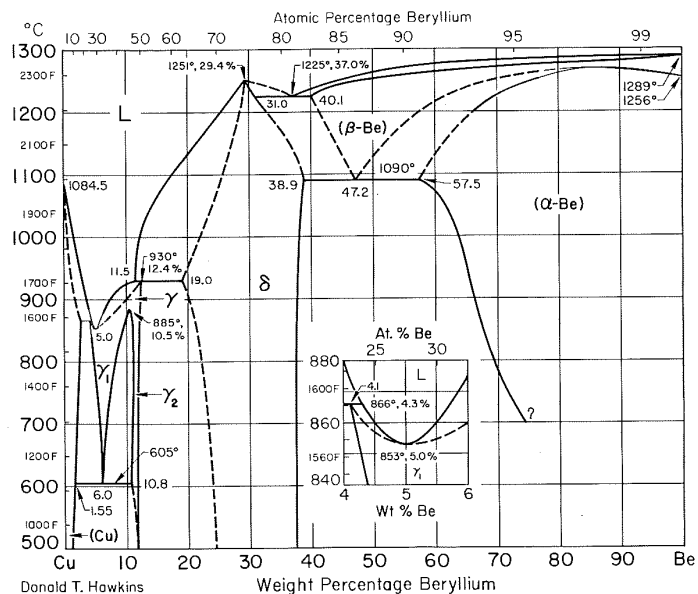
Be-Hf   Beryllium-Hafnium

See Notes.

Be-Ni   Beryllium-Nickel

D.T.H.
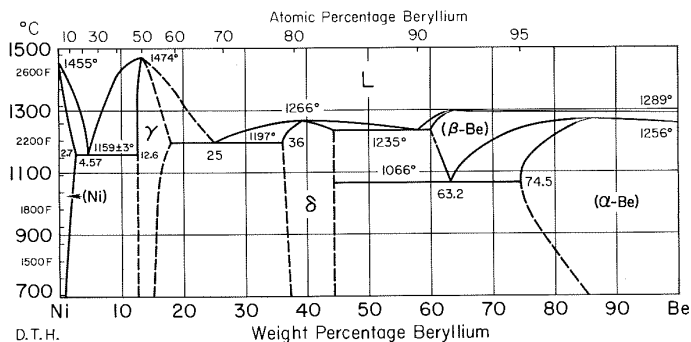
Be-Pu   Beryllium-Plutonium

D.T.H.

Ralph Hultgren
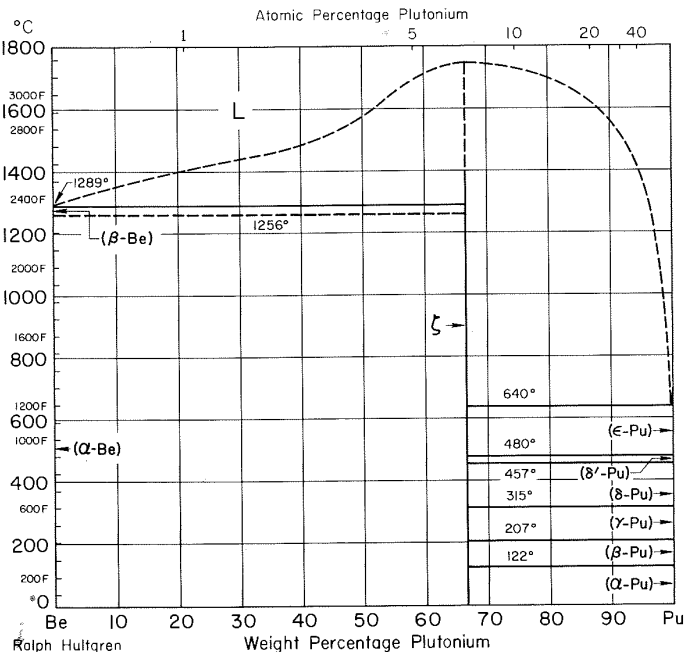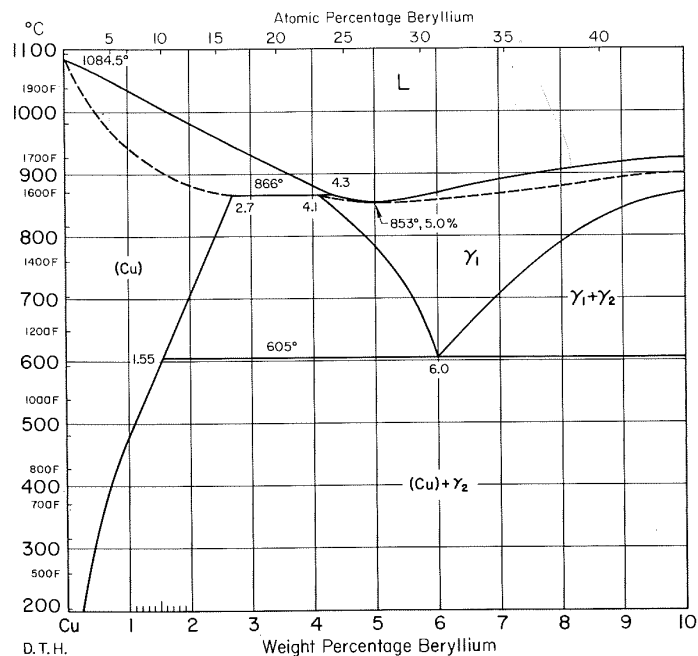
Be-Ti   Beryllium-Titanium

Atomic Percentage Titanium

Ralph Hultgren   Weight Percentage Titanium

Bi-Ce   Bismuth-Cerium

Atomic Percentage Cerium
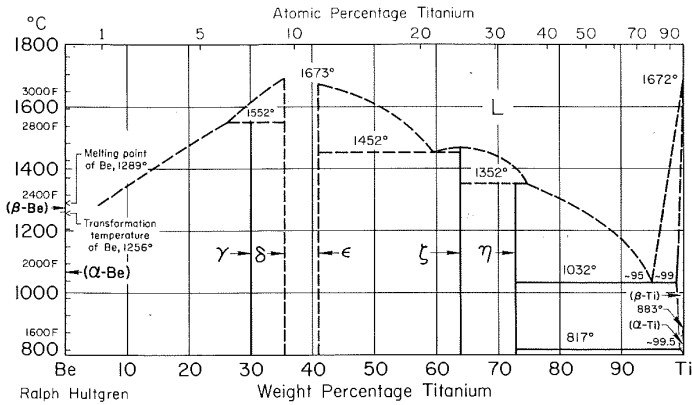
R. H.   Weight Percentage Cerium

Be-U   Beryllium-Uranium

Atomic Percentage Uronium
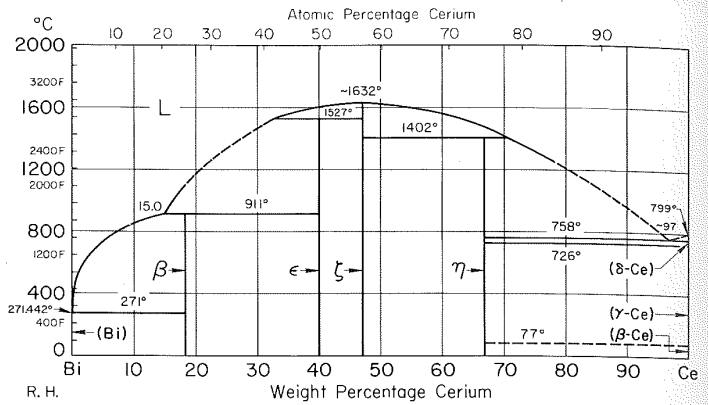
Donald T. Hawkins   Weight Percentage Uranium

Bi-Cu   Bismuth-Copper

Atomic Percentage Bismuth

D.T.H.   Weight Percentage Bismuth
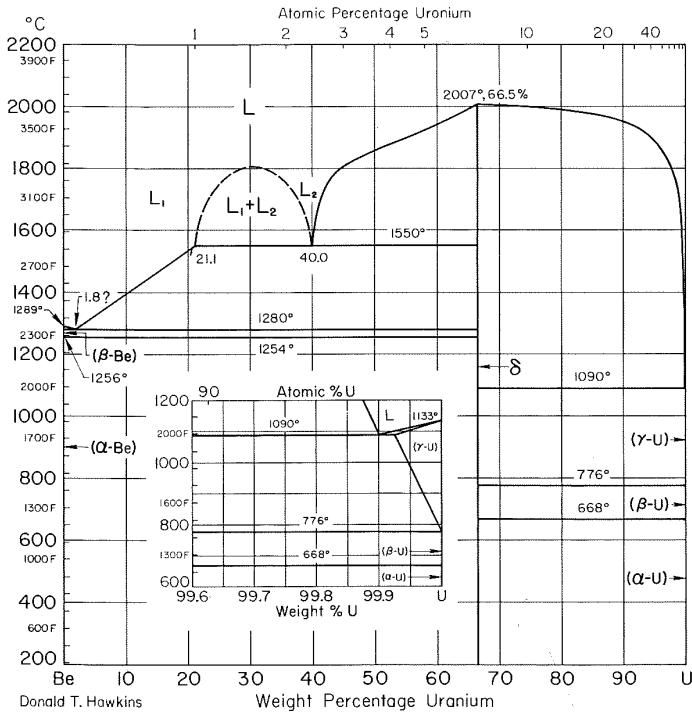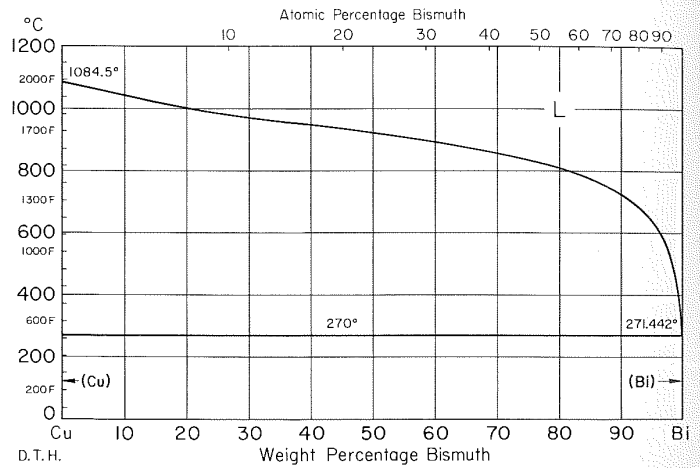
Bi-Fe   Bismuth-Iron

See Notes.

Bi-In   Bismuth-Indium

Atomic Percentage Indium

D.T.H.   Weight Percentage Indium
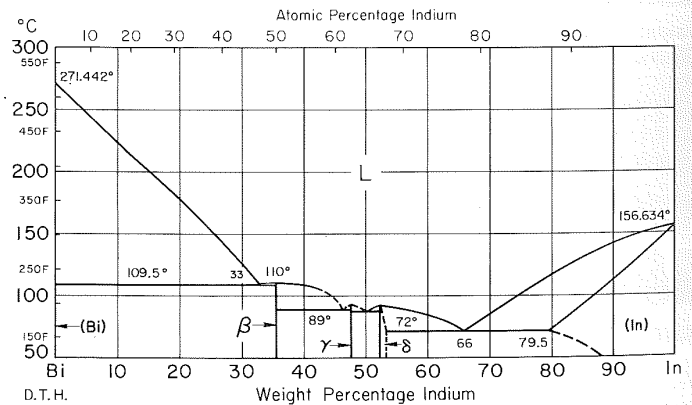
Be-Zr   Beryllium-Zirconium

See Notes.

Bi-Cd   Bismuth-Cadmium

Atomic Percentage Cadmium

D.T.H.   Weight Percentage Cadmium
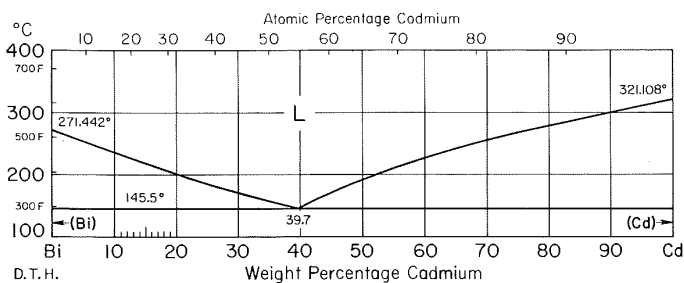
Bi-Li   Bismuth-Lithium

See Notes.

Bi-Mg   Bismuth-Magnesium

Donald T. Hawkins

Bi-Pb   Bismuth-Lead

D.T.H.

Bi-Sb   Bismuth-Antimony

D.T.H.

Bi-Sn   Bismuth-Tin

D.T.H.
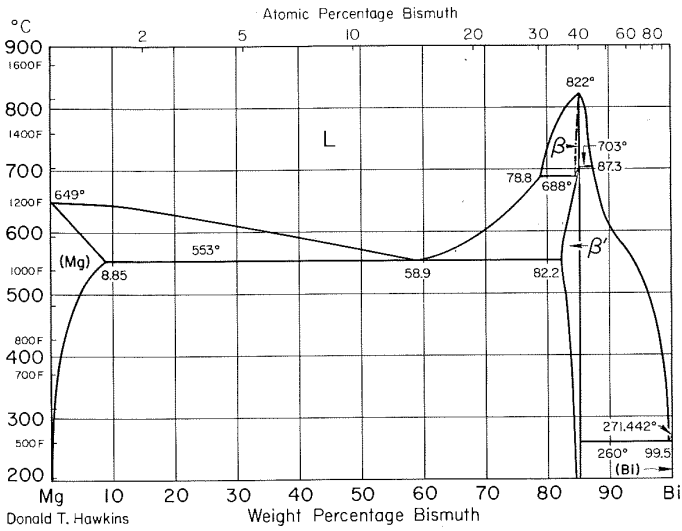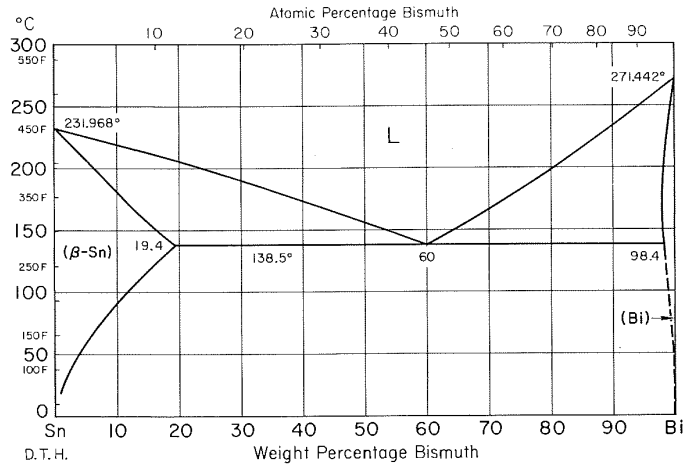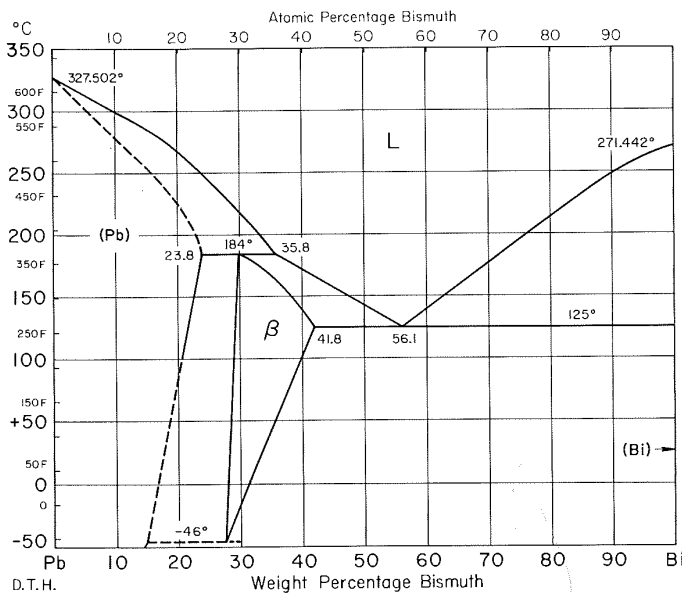
Bi-Te   Bismuth-Tellurium

Ralph Hultgren
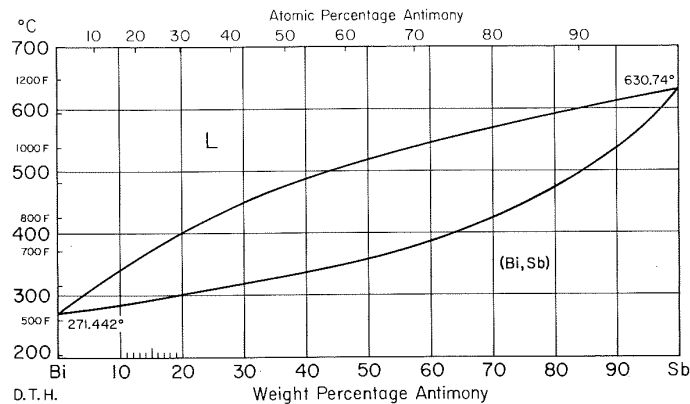
Bi-U   Bismuth-Uranium

D.T.H
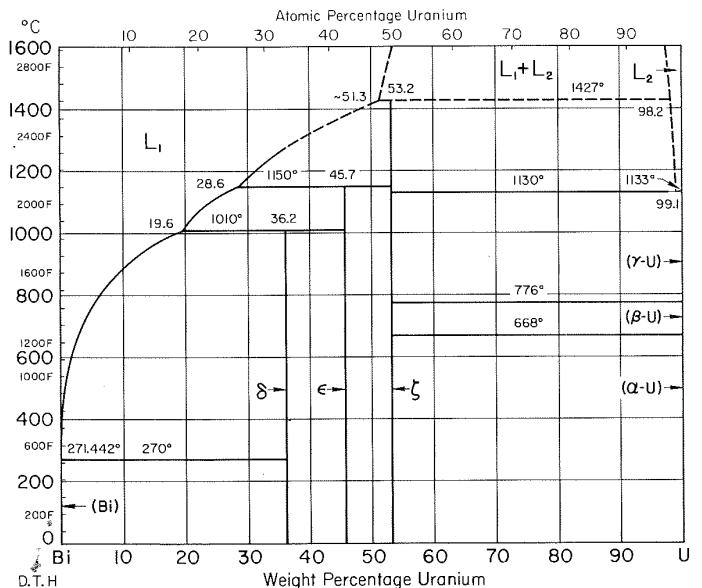
Bi-Zn   Bismuth-Zinc
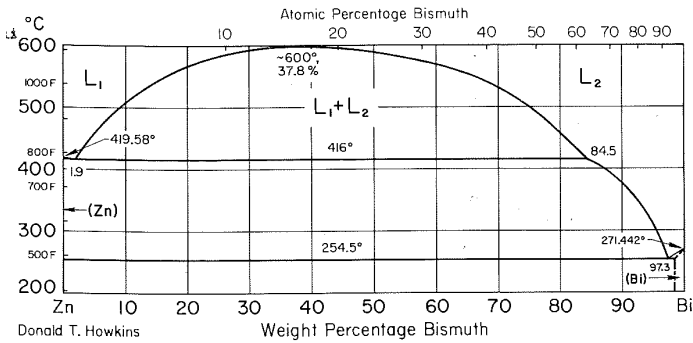
Donald T. Howkins
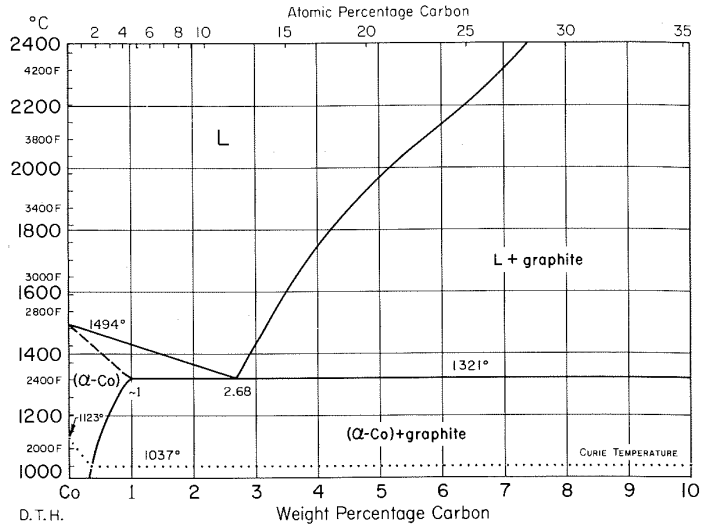
Bi-Zr   Bismuth-Zirconium

D. T. H.
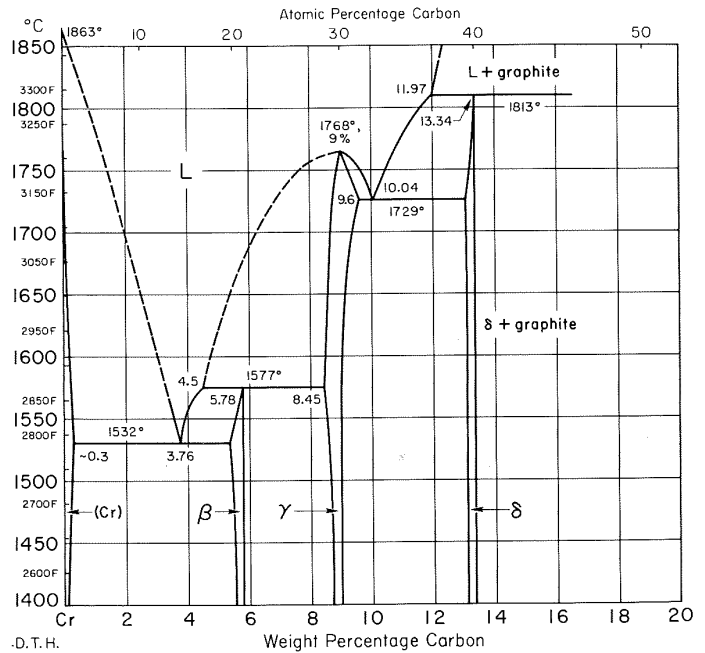
C-Cb   Carbon-Columbium

E. K. Storms

C-Co   Carbon-Cobalt

D. T. H.

C-Cr   Carbon-Chromium

.D.T.H.
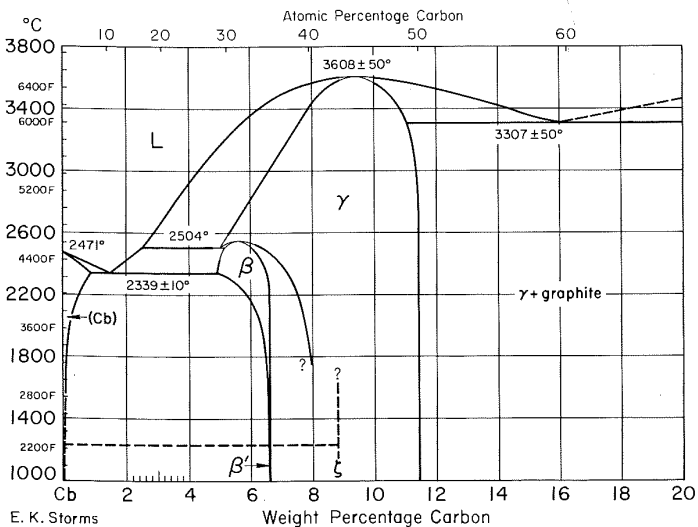
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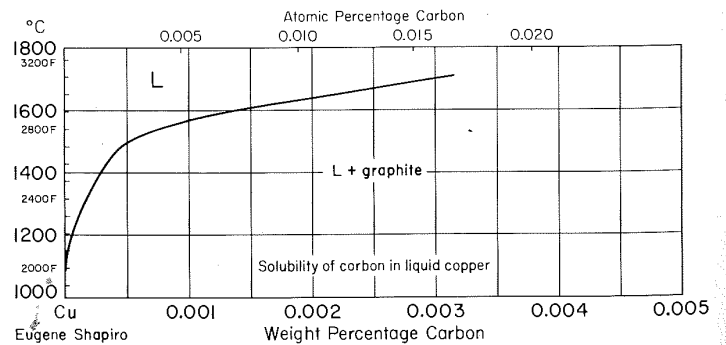
Eugene Shapiro

C-Fe   Carbon-Iron

Atomic Percentage Carbon

Gas

$P_{Fe}=1$ atm

Boiling point

$P_{Fe}=0.1$ atm

L

$P_{Fe}=0.01$ atm

Solubility of graphite in liquid Fe

2880°

2420°

2083°

1538°

1495°

(δ-Fe)

1394°

(γ-Fe)
Austenite

2.08

2.11

1154°

1148°

4.26

4.30

1227°

6.69

Cementite
(Fe₃C)→

912°

0.68

770°

0.77

738°

727°

(α-Fe)
Ferrite

230°

?

X(Fe₂.₂C)→

Cementite (Fe₃C) liquidus (calculated)
Iron-X carbide (Fe₂.₂C) transformation
(calculated)
Iron-cementite (Fe₃C) equilibrium diagram
(experimental)
Iron-graphite equilibrium diagram
(experimental), except where coincident
with iron-cementite (Fe₃C) diagram
Uncertain region of cementite (Fe₃C)
Curie temperature of ferrite

John Chipman

Weight Percentage Carbon

Phase Diagrams of Binary Alloy Systems

C-Fe   Carbon-Iron

John Chipman

J.C.

J.C.

Two-phase fields involving graphite or iron carbide
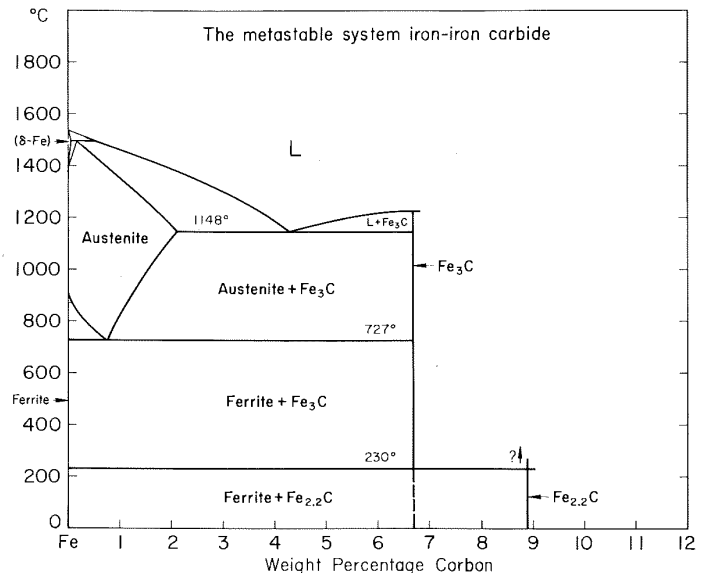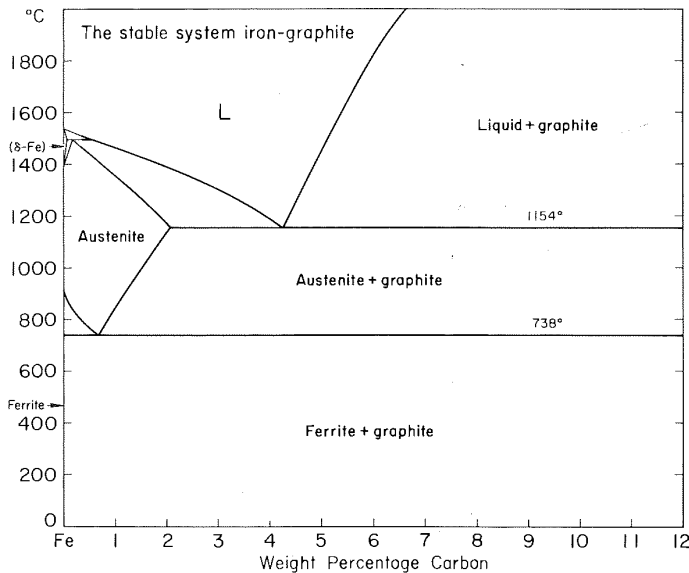
C-Fe (Carbon-Iron)

By JOHN CHIPMAN

The diagrams and tables are from a review by Chipman (1). Many iron carbides have been reported, but only those that have been studied under stable or metastable equilibrium conditions are considered here.

The major lines of the diagrams are based on direct observations and are drawn to conform to the known thermodynamic properties of iron, from Orr and Chipman (2), and to experimentally determined activity coefficients. Lines showing composition-temperature relations at several pressures were calculated from (a) the known vapor pressure of liquid iron, from Hultgren et al (3); and (b) the activity of iron in liquid-iron-plus-carbon solution, from Chipman (1) and Syu et al (4). The liquidus curve for cementite (Fe₃C) has never been observed but was calculated by Chipman (1, 5) from the free energy of cementite and from that of the equilibrium liquid as extrapolated into the metastable range below the graphite liquidus.

Crystal-structure data are given in the notes for the C-Fe system, on page 350 in this volume.

The Austenite Field. The properties and boundary lines of the face-centered cubic austenite (γ-Fe) solid-solution area are well known. The activity of carbon as a function of temperature and composition has been determined by many observers, chiefly through studies of the equilibria: C (in Fe) + 2H₂ = CH₂ and C (in Fe) + CO₂ = 2CO. The earlier investigations of the latter reaction, by Dünwald and Wagner (6) and by Smith (7), are in agreement with the more recent work of Scheil et al (8) — except at the highest carbon concentrations — and of Ban-ya et al (9). Studies of the former reaction have been subject to errors, especially at low carbon levels, because of the reaction of methane with residual gas impurities. These errors may have caused the differences observed by Smith (7) between activity coefficients determined by the two equilibria. Studies based on the latter reaction were subject to similar but generally smaller errors, which increased with increasing temperature and carbon content.

The solubility of graphite in austenite (γ-Fe) was calculated from the data on activity of carbon in austenite, using the equations presented by Chipman (1). These solubility values are in rather good agreement with the direct measurements of Wells (10) and of Gurry (11) and with a downward extrapolation of the solidus line of Benz and Elliott (12) to the eutectic temperature. Average values of these three determinations are listed in Table 1.

The (γ-Fe)-Liquid Equilibrium. The austenite solidus line of Benz and Elliott and a portion of the austenite liquidus line of Buckley and Hume-Rothery (13) are shown in the diagram. The solidus line was given a slight inflection with downward curvature near its lower end to conform to the data of Ban-ya

Table 1. Solubility of Graphite and Cementite in γ-Fe (Austenite)

Temperature		Graphite		Cementite	
C	F	C:Fe(a)	C, wt %	C:Fe(a)	C, wt %
727(b)	1341	...	...	0.0356	0.77
738(c)	1360	0.0320	0.68	...	...
800	1472	0.0408	0.87	0.0442	0.94
900	1652	0.0561	1.19	0.0580	1.22
1000	1832	0.0725	1.53	0.0730	1.55
1100	2012	0.0896	1.89	0.0910	1.92
1148(d)	2098	...	...	0.1000	2.11
1154(e)	2109	0.0990	2.08	...	...

(a) Ratio of number of carbon atoms to number of iron atoms. (b) Cementite eutectoid. (c) Graphite eutectoid. (d) Cementite eutectic. (e) Graphite eutectic.

Table 2. Solid-Liquid Equilibria for γ-Fe

Temperature		γ-Fe Solidus		Liquidus	
C	F	C:Fe(a)	C, wt %	C:Fe(a)	C, wt %
1148(b)	2098	0.1000	2.11	0.2092	4.30
1154(c)	2109	0.0900	2.08	0.2072	4.26
1200	2192	0.0877	1.85	0.1906	3.93
1250	2282	0.0718	1.59	0.1689	3.50
1300	2372	0.0613	1.30	0.1450	3.02
1350	2462	0.0475	1.01	0.1179	2.47
1400	2552	0.0333	0.71	0.0891	1.88
1450	2642	0.0196	0.42	0.0570	1.21
1495(d)	2723	0.0079	0.17	0.0248	0.53
1527(e)	2781	0.0000	0.00	0.0000	0.00
1538(f)	2800	...	...	...	...

(a) Ratio of number of carbon atoms to number of iron atoms. (b) Cementite eutectic. (c) Graphite eutectic. (d) Peritectic. (e) Metastable melting point of γ-Fe. (f) Melting point of δ-Fe.

et al. Both lines are superior in accuracy to those of earlier investigators and are supported by data of Adcock (14). When the liquidus and solidus lines are extended, as shown by Chipman (1), they intersect at the metastable melting point of γ-Fe (1527 C; 2781 F) as calculated by Orr and Chipman. Values from the curves in their entirety are listed in Table 2.

The Liquid Phase. The best data on the activity of carbon in liquid Fe-C alloys were determined by Richardson and Dennis (15) at 1560, 1660 and 1760 C (2840, 3020 and 3200 F), using the equilibrium: C (in Fe) + CO₂ = 2CO. For lower temperatures, Chipman (1) used the activity of carbon in austenite at points along the solidus to determine the activity coefficient in the liquid for compositions along the liquidus.

The solubility of graphite in liquid iron has been measured by many investigators. Up to 1800 C (3272 F), excellent agreement is found among Ruer and Biren (16), Chipman et al (17) and Kitchener et al (18). Data for temperatures up to 2500 C (4532 F) were reported by Ruer and Biren, for up to 2875 C (5207 F) by Cahill et al (19), and for 2050 to 2375 C (3722 to 4307 F) by Vertman et al (20). Interpolated data and estimates of probable accuracy are given in Table 3. The

Table 3. Solubility of Graphite in Liquid Iron

Temperature C	F		C, wt %	Temperature C	F		C, wt %
1154	2109	....	4.26 ± 0.02	2100	3812	....	7.05 ± 0.2
1200	2192	....	4.37	2200	3992	....	7.56 ± 0.3
1300	2372	....	4.63	2300	4172	....	8.10
1400	2552	....	4.88	2400	4352	....	8.68
1500	2732	....	5.14	2500	4532	....	9.28 ± 0.4
1600	2912	....	5.40 ± 0.03	2600	4712	....	9.87
1700	3092	....	5.66	2700	4892	....	10.50
1800	3272	....	5.94 ± 0.05	2800	5072	....	11.12
1900	3452	....	6.26 ± 0.10	2900	5252	....	11.75 ± 0.5
2000	3632	....	6.63 ± 0.10				

Table 4. Solubility of Graphite, Fe₃C and Fe₂.₂C in α-Fe (Ferrite)

Tempera- ture C	F	Solubility, ppm — Graph- ite(a)	Fe₃C(b)	Fe₂.₂C(c)	Tempera- ture C	F	Solubility, ppm — Graph- ite(a)	Fe₃C(b)	Fe₂.₂C(c)
738	1360	. 206	...	...	500	932	. 4.3	13	...
727	1341	. ...	218	...	450	842	. 1.35	5.7	...
700	1292	. 127	160	...	400	752	. 0.37	2.3	...
650	1202	. 63	102	...	350	662	. 0.081	0.75	1.3
600	1112	. 28	57	...	300	572	. 0.013	0.21	0.30
550	1022	. 11.7	28	...	250	482	. ...	0.045	0.050
					200	392	. ...	0.007	0.0055

(a) Data derived from equation in Chipman (1). (b) Calculated from observed value at 727 C (1341 F) and free energy of formation. (c) From free energy of formation.

selected eutectic at 1154 C (2109 F) and 4.24 to 4.28 wt % C has been confirmed by Ruth and Turpin (21).

The δ Phase and Peritectic. The δ-Fe region is shown on the diagram with the peritectic at 1495 C (2723 F), as recommended by Buckley and Hume-Rothery. The liquidus of δ-Fe phase is shown as a straight line from the melting point to 0.53 wt % C at the peritectic. The compositions of the peritectic are: δ-Fe, 0.09 wt % C; γ-Fe, 0.17 wt % C; liquid, 0.53 wt % C. Compositions of δ-Fe and liquid at the peritectic are averages of several published values that have been selected to agree with the heat effects at 1394 C (2541 F), and at the melting point, from Orr and Chipman, and with the activity of iron in the δ-Fe and liquid solutions from Chipman (5) and Syu et al.

The α-γ Equilibrium. The (γ-Fe)-(α-Fe + γ-Fe) phase boundary is based almost entirely on the data of Mehl and Wells (22), corrected by 1 C (1.8 F) at the pure iron end with negligible correction at the eutectoid end. The intersections of Chipman's solubility lines (1) place the Fe-graphite eutectoid at 738 C (1360 F) and 0.68 wt % C, and the Fe-cementite eutectoid at 727 C (1341 F) and 0.77 wt % C. The latter temperature agrees with Smith and Darken (23) and is 4 C (7 F) higher than that of Mehl and Wells.

The (α-Fe)-(α-Fe + γ-Fe) phase boundary, which is based on data at 800 and 750 C (1472 and 1382 F) by Smith (7), is extrapolated to 0.0206 and 0.0218 wt % C at the graphite and cementite eutectoid temperatures.

Solubility of Graphite in α-Fe. The activity of carbon in body-centered-cubic α-Fe was determined by Smith (7, 24) and Swartz (25) at 590 to 800 C (1094 to 1472 F). The activity in body-centered-cubic δ-Fe at the peritectic temperature (1495 C; 2723 F) is known from the activity in the γ-Fe and liquid phases. These activity data, and the activity of carbon at the peritectic temperature, were used to calculate the values for the solubility of graphite in α-Fe that are given in Table 4.

The Iron Carbides. Numerous carbides of iron are reported, ranging in composition from FeC to Fe₄C. Only two of these have been studied under metastable equilibrium conditions, and it is only for these two that thermodynamic data are available.

Cementite, sometimes called θ carbide, is usually assigned the formula Fe₃C, but its exact conformance to the stoichiometric composition has not been proved. A slight iron deficiency above 800 C (1472 F) was suggested by Benz et al (26). Several observers have reported variations in composition and in the lattice parameter.

The existence of Fe₂C was suggested by Glud et al (27). An x-ray diffraction pattern by Hofmann and Groll (28) for iron carburized at temperatures below 400 C (752 F) showed an unknown carbide and Fe₃C; in iron carburized above 400 C (752 F), only Fe₃C was found. Experiments using a hydrogen-reduction method for determination of carbidic and free carbon contents showed that when iron was carburized with CO at 225 C (437 F), the product contained 9.7 wt % C, the carbon content of Fe₂C. At higher temperatures, a mixture of Fe₂C and Fe₃C was formed; at 400 C (752 F) and above, only Fe₃C was formed. The x-ray diffraction pattern for the new carbide

was determined by Hägg (29). This carbide is frequently called Hägg or χ carbide and has a slightly variable composition approximating Fe₂.₂C.

The solubilities of Fe₃C and Fe₂.₂C in α-Fe (ferrite) are given in Table 4.

Cementite (θ Carbide). The (γ-Fe)-(γ-Fe + cementite) phase boundary is from Ban-ya et al, and is based on the direct measurements of solubility by Smith (30) and on the CO-CO₂ equilibrium measurements by Scheil et al. The Fe₃C liquidus line and the melting point (1227 C; 2241 F) were calculated by Chipman (1). Values from the phase boundary are listed in Table 1.

The solubility of cementite in α-Fe (ferrite) was calculated from the free energy of formation of cementite as determined by the gas-solid equilibrium studies of Scheil et al. Within the temperature range shown in the diagram, the result is in fair agreement with studies by Swartz of the solubility of stress-free cementite using internal-friction methods.

Hägg (χ) Carbide. The carbide prepared by Browning et al (31) by treatment of hydrogen-reduced iron with butane at 275 C (527 F) was identified by its diffraction pattern as the same as that prepared by Hägg at 225 C (437 F). Both observers found that this carbide was converted to Fe₃C by heating to 500 C (932 F). The structure was listed as orthorhombic with the added notation that a monoclinic or triclinic structure was not excluded. Recent studies show a monoclinic structure isotypic with Mn₅C₂. The χ carbide is represented by the formula Fe₂.₂C (or Fe₅C₂) and has a Curie temperature of 247 C (477 F).

The transformation indicated on the diagram at 230 C (446 F) is uncertain but is based on observations of gas equilibria with the respective carbides by Browning et al. Below a temperature estimated at 230 to 350 C (446 to 662 F), χ carbide is more stable than cementite.

The ε carbide occurs as a transition phase in the tempering and aging of steel. It has not been isolated, and its thermodynamic properties are unknown. Hofer (32) described it as close-packed hexagonal with a Curie temperature of 370 C (698 F) and a variable composition — commonly about Fe₂.₄C.

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C-Mn   Carbon-Manganese

Atomic Percentage Carbon

Donald T. Hawkins   Weight Percentage Carbon

C-Mo   Carbon-Molybdenum

Atomic Percentage Carbon

E. K. Storms   Weight Percentage Carbon

C-Ni   Carbon Nickel

Atomic Percentage Carbon

D.T.H.   Weight Percentage Carbon

C-Ta   Carbon-Tantalum

Atomic Percentage Carbon

D.T.H.   Weight Percentage Carbon
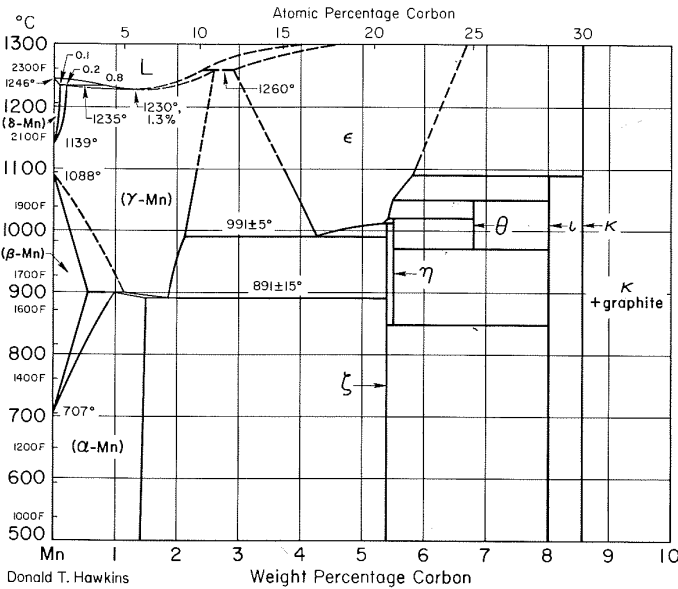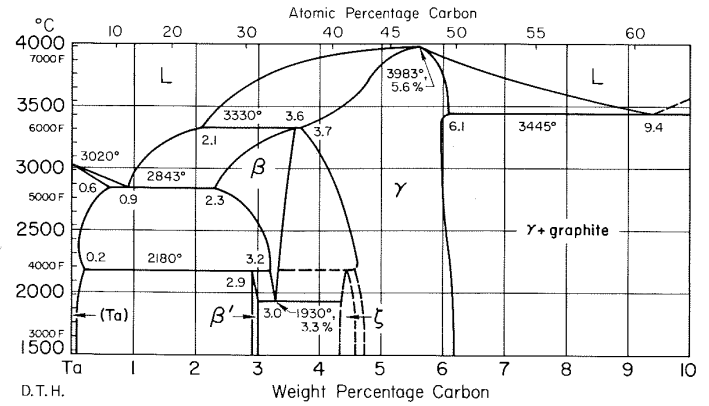
C-Ti   Carbon-Titanium

Atomic Percentage Carbon

D.T.H.   Weight Percentage Carbon

C-U   Carbon-Uranium

Atomic Percentage Carbon

E. K. S.   Weight Percentage Carbon
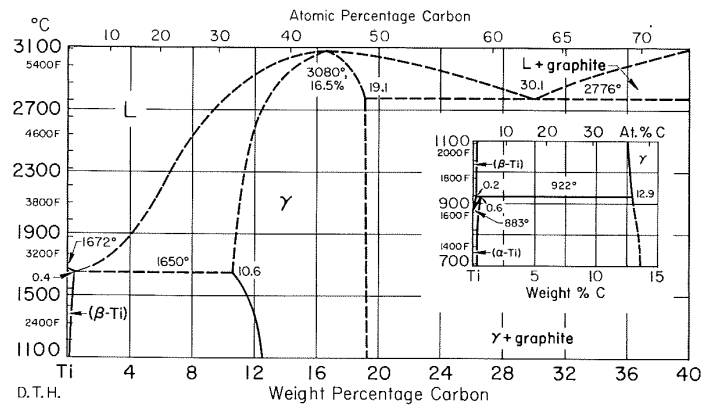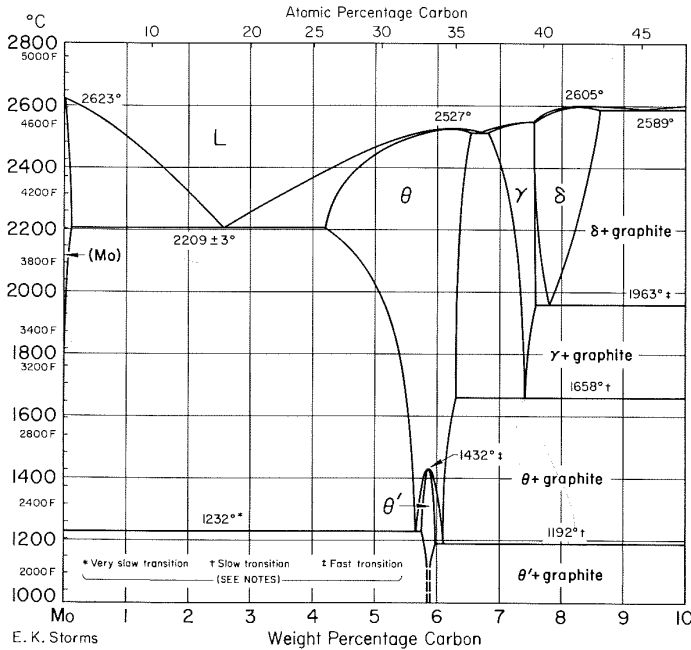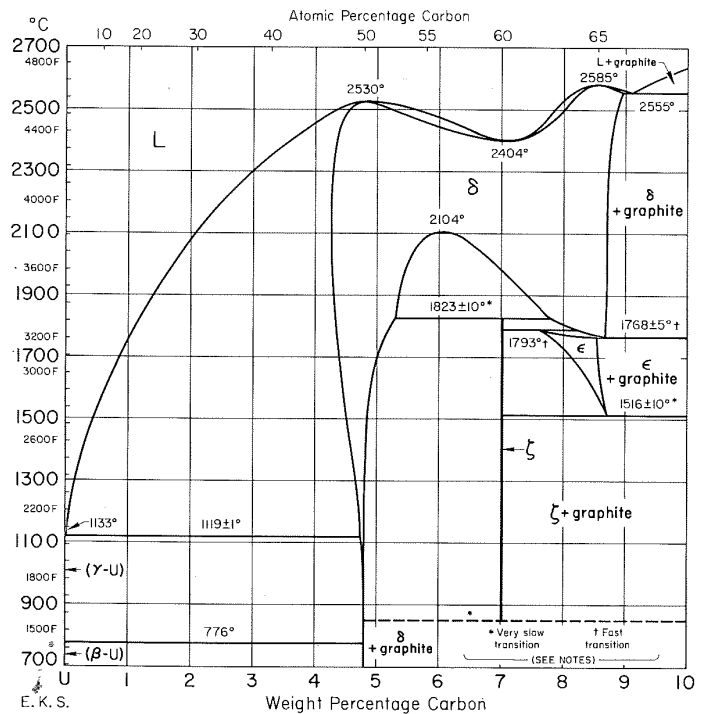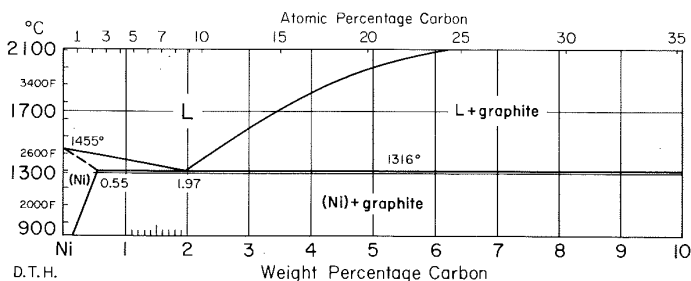
C-V   Carbon-Vanadium

E. K. Storms

C-W   Carbon-Tungsten

E. K. S.
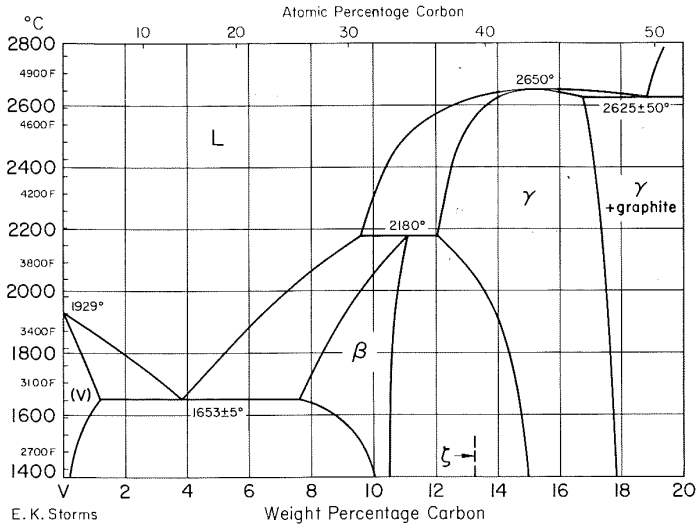
C-Zr   Carbon-Zirconium

E. K. S.

Ca-Cu   Calcium-Copper
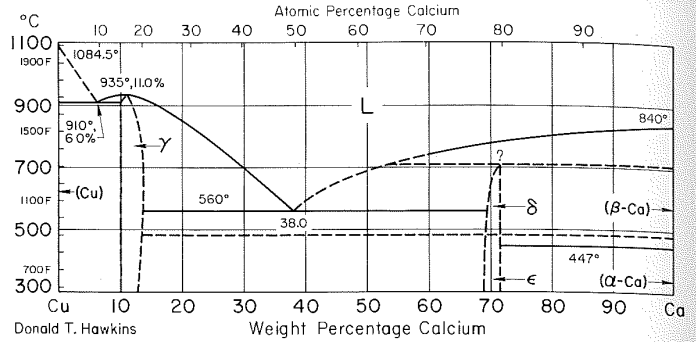
Donald T. Hawkins

Ca-Mg   Calcium-Magnesium

D. T. H.
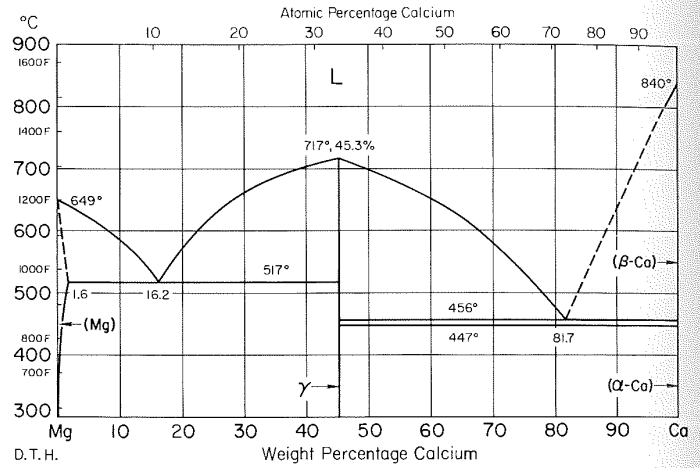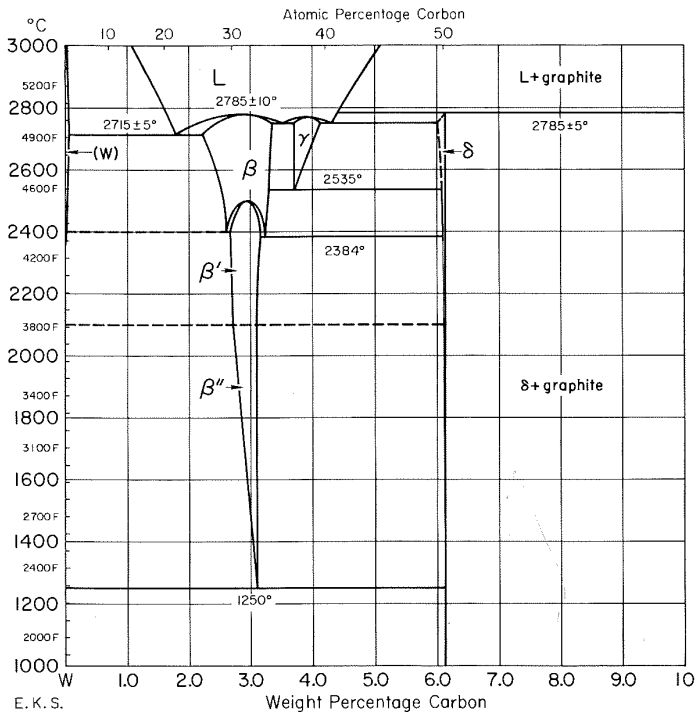
Ca-Pb   Calcium-Lead

C. DiMartini

Ca-Sn   Calcium-Tin
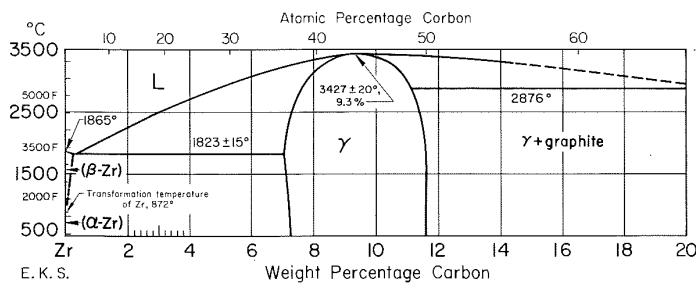
Donald T. Hawkins

Ca-Sr   Calcium-Strontium
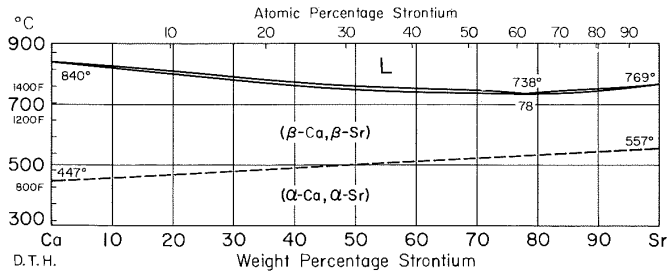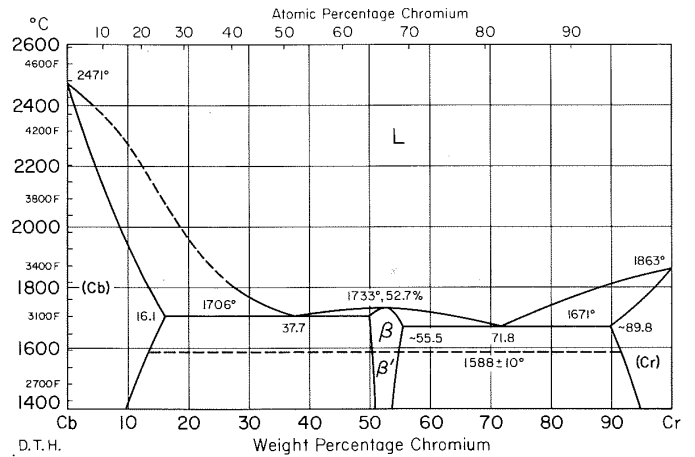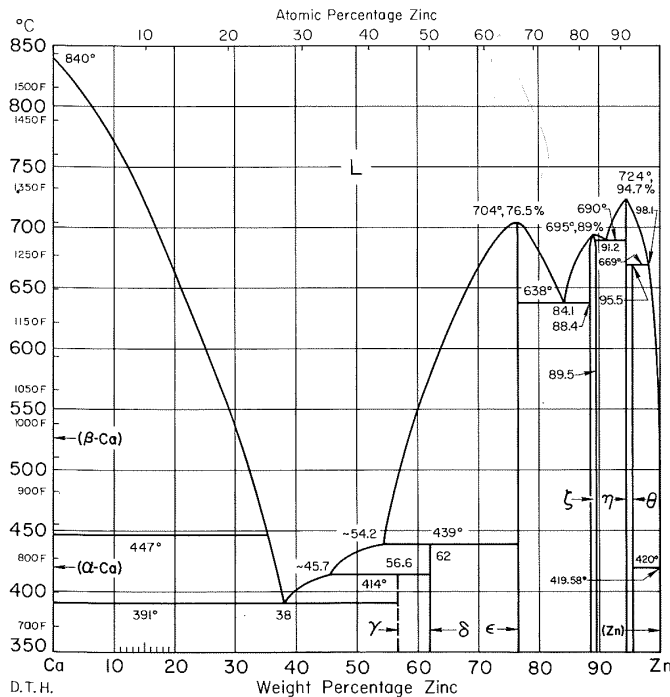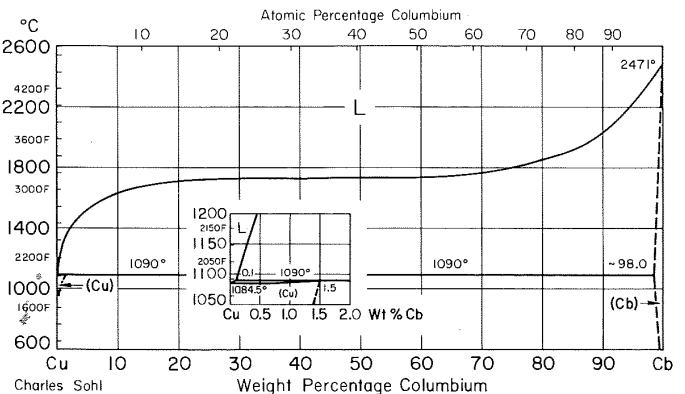
D.T.H.

Ca-Zn   Calcium-Zinc

D.T.H.

Cb-Co   Columbium-Cobalt

D.T.H.

Cb-Cr   Columbium-Chromium

D.T.H.

Cb-Cu   Columbium-Copper

Charles Sohl

Cb-Fe Columbium-Iron

L. R. Woodyatt

L. R. W.

Cb-Hf Columbium-Hafnium

Donald T. Howkins

Cb-Ir Columbium-Iridium

D. T. H.

Cb-Mo Columbium-Molybdenum

D. T. H.

Cb-Ni Columbium-Nickel

D. T. H.
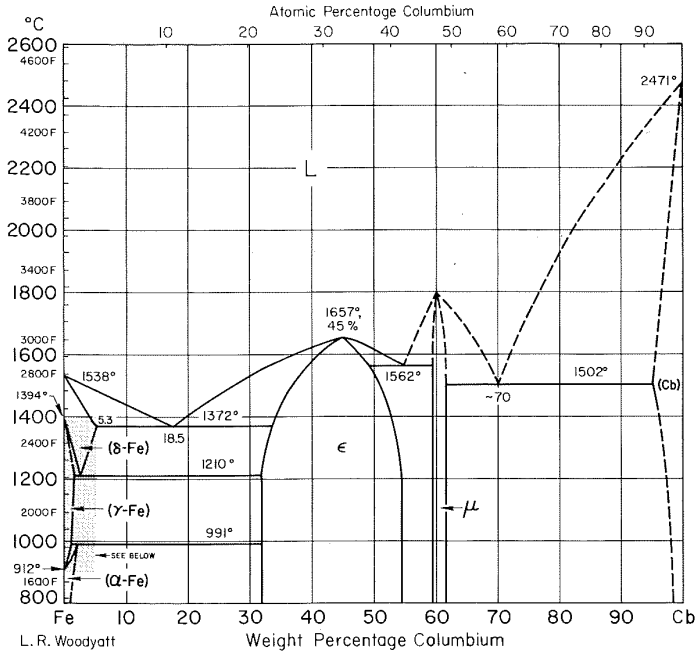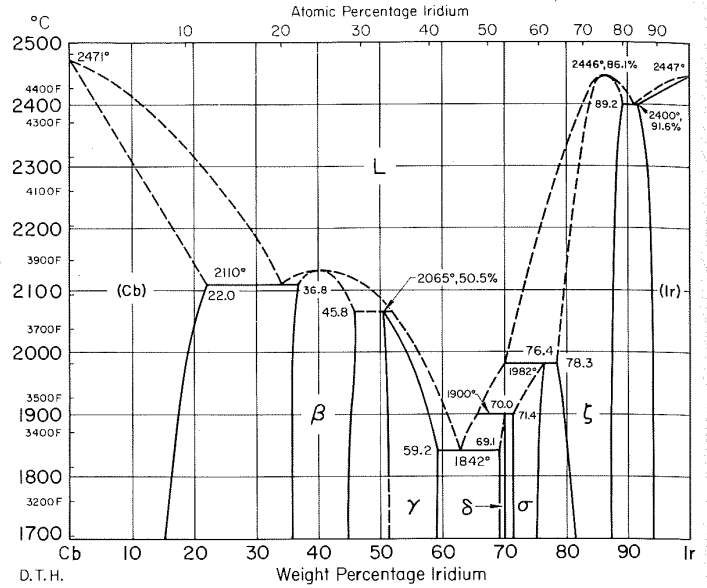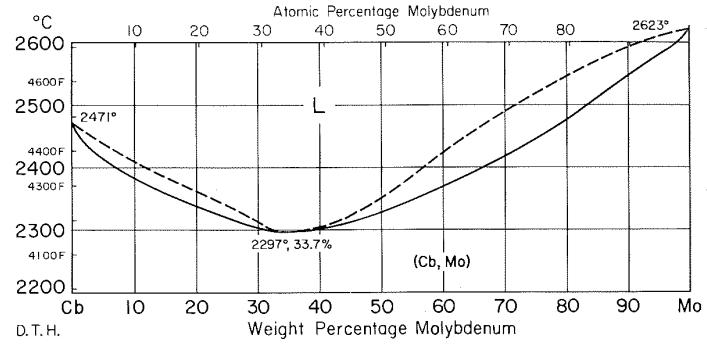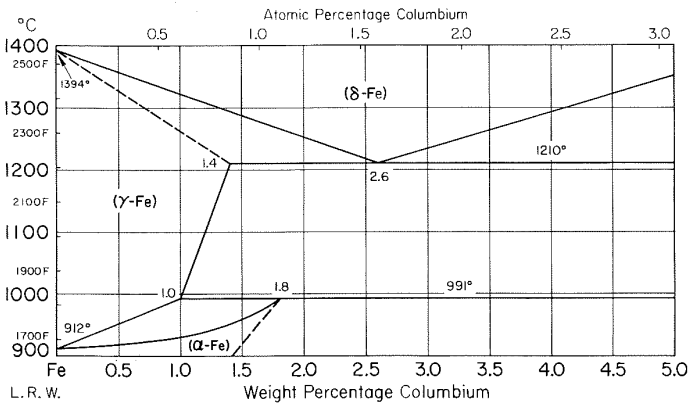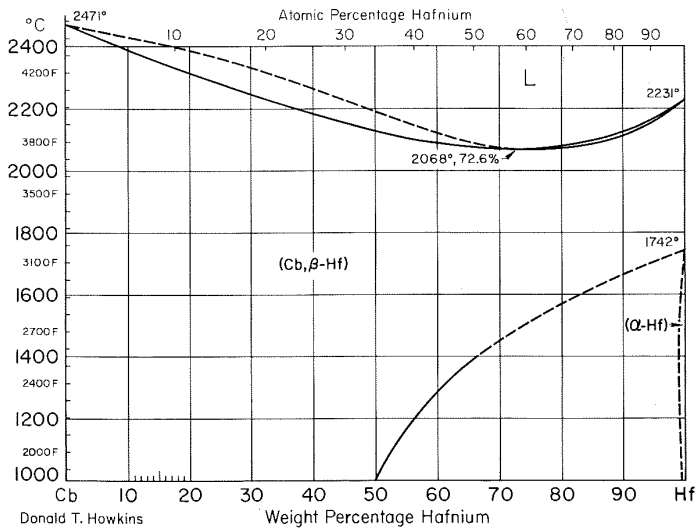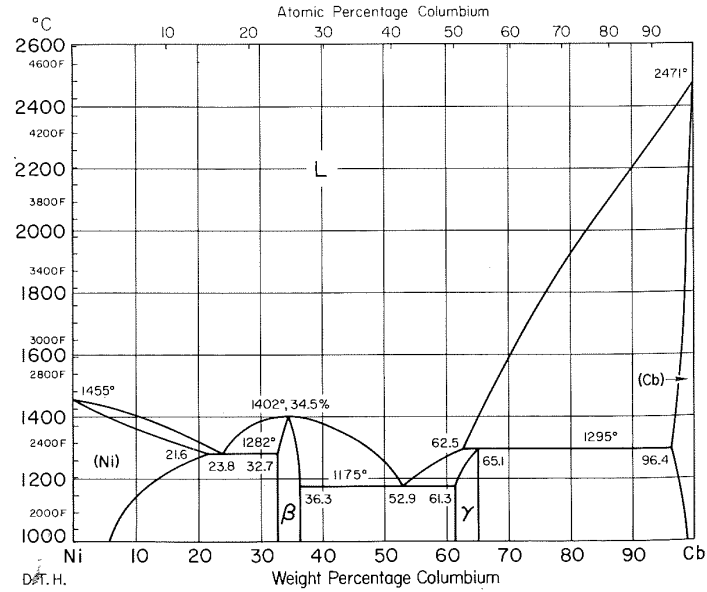
Cb-Pd Columbium-Palladium

°C
Atomic Percentage Columbium
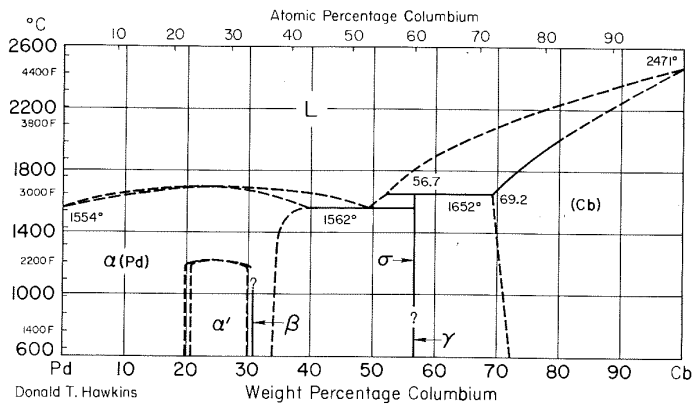
Donald T. Hawkins
Weight Percentage Columbium
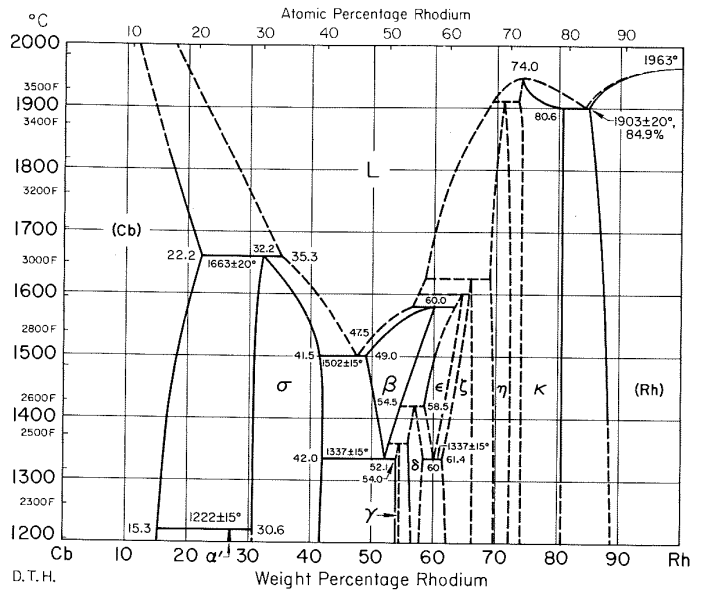
Cb-Pt Columbium-Platinum

°C
Atomic Percentage Columbium

D.T.H.
Weight Percentage Columbium

Cb-Re Columbium-Rhenium

°C
Atomic Percentage Rhenium

A. G. Knapton
Weight Percentage Rhenium

Cb-Rh Columbium-Rhodium

°C
Atomic Percentage Rhodium

D.T.H.
Weight Percentage Rhodium
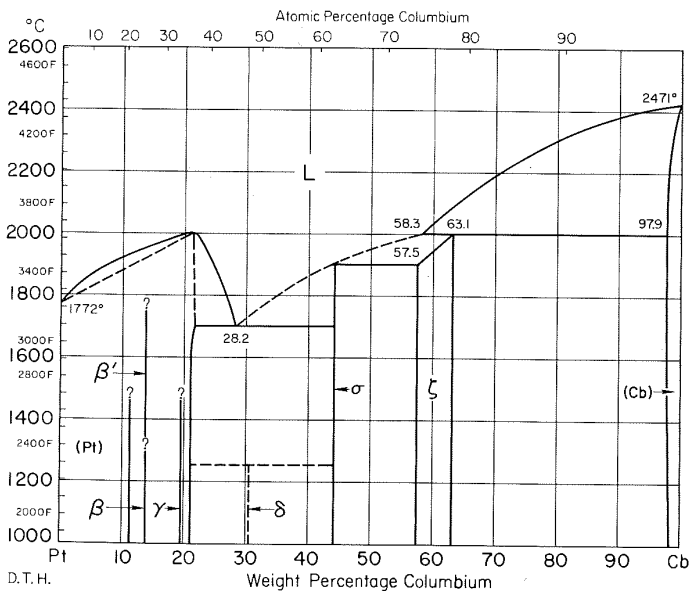
Cb-Ru Columbium-Ruthenium

°C
Atomic Percentage Ruthenium

D.T.H.
Weight Percentage Ruthenium

Cb-Si Columbium-Silicon

°C
Atomic Percentage Silicon

A. G. K.
Weight Percentage Silicon
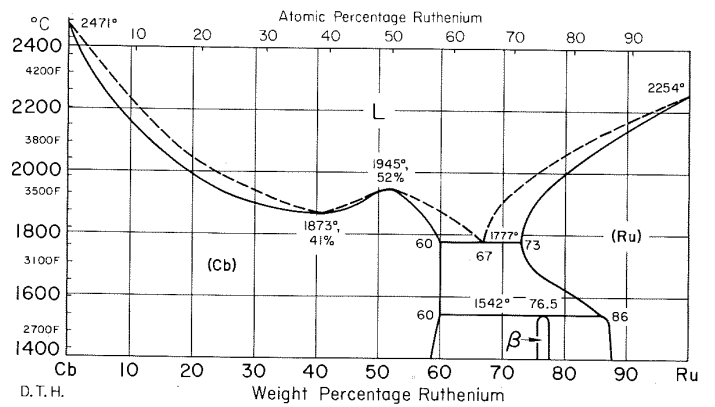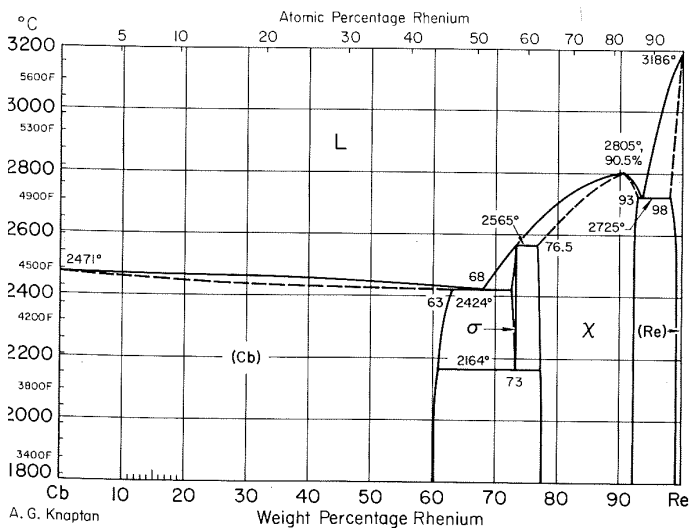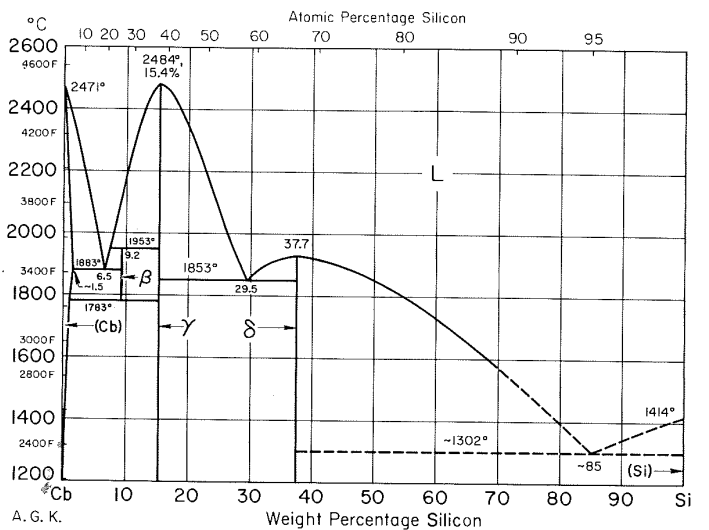
Cb-Sn   Columbium-Tin

Donald T. Hawkins
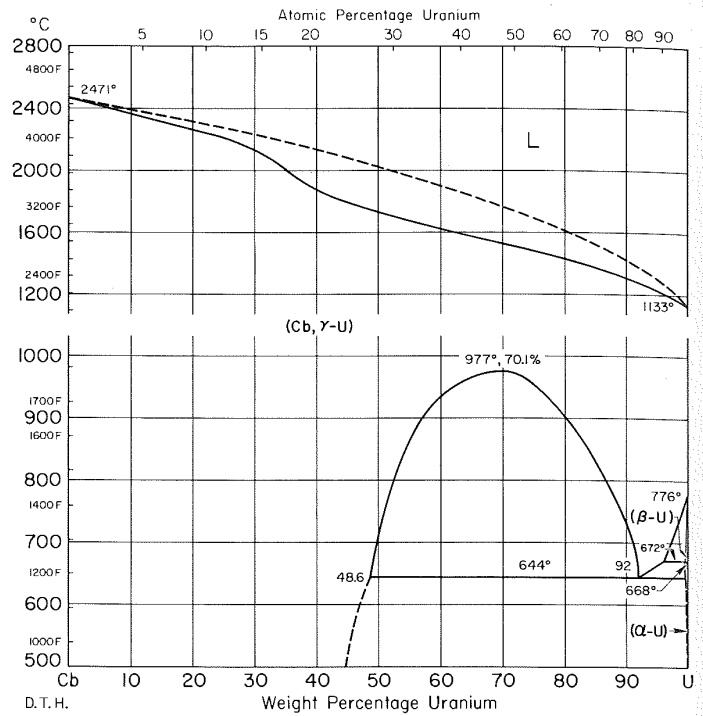
Cb-Ta   Columbium-Tantalum

D.T.H.

Cb-Ti   Columbium-Titanium

A. G. Knopton

Cb-U   Columbium-Uranium

D.T.H.
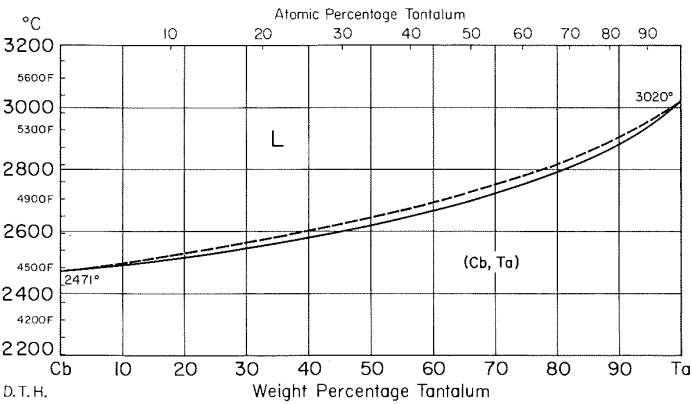
Cb-V   Columbium-Vanadium

D.T.H.

Cb-W   Columbium-Tungsten

D.T.H.

Cb-Zn   Columbium-Zinc

Ralph Hultgren

Cb-Zr   Columbium-Zirconium

A. G. Knapton

Cd-Cu   Cadmium-Copper

Donald T. Hawkins

Cd-Fe   Cadmium-Iron

See Notes.

Cd-Ga   Cadmium-Gallium

R. H.

Cd-Hg   Cadmium-Mercury

D. T. H.

Cd-In   Cadmium-Indium

D. T. H.

Cd-Mg   Cadmium-Magnesium

Donold T. Hawkins

Cd-Ni   Cadmium-Nickel

D.T.H.

Cd-Pb   Cadmium-Lead

D.T.H.
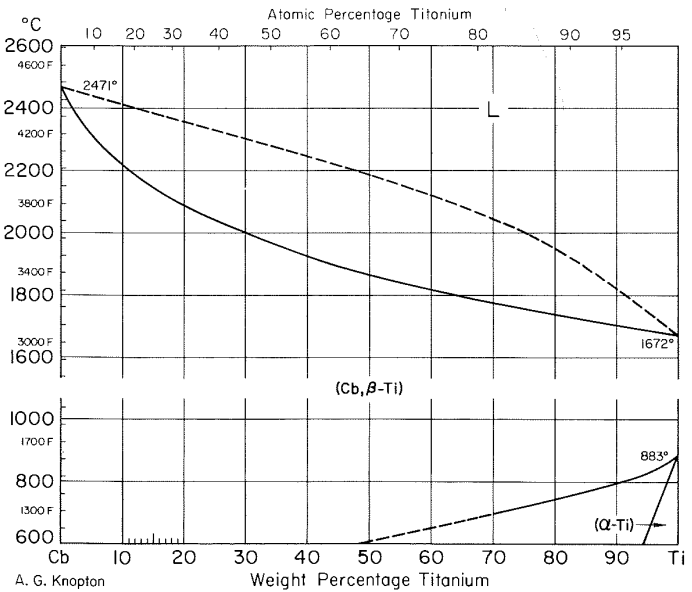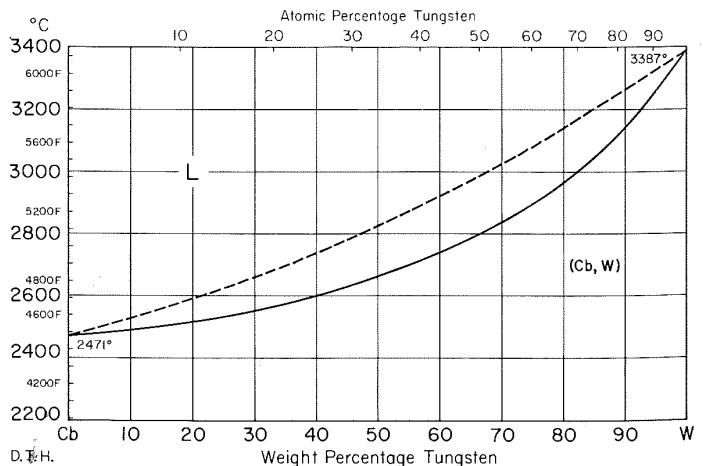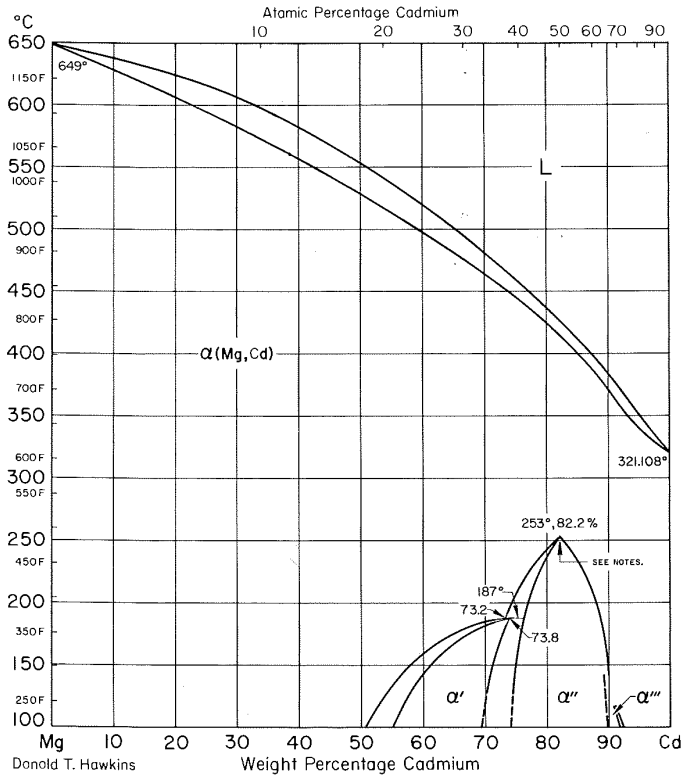
Cd-Pu   Cadmium-Plutonium

Ralph Hultgren

Cd-Sb   Cadmium-Antimony

D.T.H.

Cd-Sn   Cadmium-Tin

D.T.H.

Cd-Te   Cadmium-Tellurium

Ralph Hultgren

Cd-Zn   Cadmium-Zinc

J. W. Simpson and W. Showak

Ce-Mg   Cerium-Magnesium

Donald T. Howkins

Co-Cr   Cobalt-Chromium

D. T. H.

Co-Cu   Cobalt-Copper

D. T. H.

Co-Fe   Cobalt-Iron

Theodore E. Torok

Co-Mg   Cobalt-Magnesium

Donald T. Hawkins

Co-Ni   Cobalt-Nickel

D.T.H.

Co-Mn   Cobalt-Manganese

D.T.H.

Co-Pb   Cobalt-Lead

D.T.H.

Co-Pd   Cobalt-Palladium

D.T.H.

Co-Mo   Cobalt-Molybdenum

D.T.H.

Co-Pt Cobalt-Platinum

Atomic Percentage Cobalt

L

α(Pt,α-Co)

1772°

~1472°

1494°

1123°

Curie Temperature

834±2°

α'

α''

(ε-Co)

427°

°C / °F axis: 1800/3100F, 1600/2800F, 1400/2400F, 1200/2000F, 1000, 800/1600F, 600/1200F 1000F, 400/600F, 200

Pt 10 20 30 40 50 60 70 80 90 Co

Weight Percentage Cobalt

A.S. Darling

Co-Re Cobalt-Rhenium

Atomic Percentage Rhenium

3186°

Boiling point of Co, 2934°

L

1494°

~1502°

(α-Co)

(ε-Co,Re)

1123° (Curie Temperature)

Co 10 20 30 40 50 60 70 80 90 Re

Weight Percentage Rhenium

Donald T. Hawkins

Co-Pu Cobalt-Plutonium

Atomic Percentage Plutonium

1494°

L

1212°

1123°

1232°

1171°

Curie Temperature

(α-Co)

ζ

η

605°

640°

(ε-Pu)

442°

406°

Transformation temperature of Co, 427°

(ε-Co)

θ

(δ-Pu)

ι

395°

χ

320°

315°

λ

(γ-Pu)

220°

207°

(β-Pu)

150°

122°

(α-Pu)

Atomic % Pu
98.0   99.0

(ε-Pu)

480°

(δ'-Pu)

457°

(δ-Pu)

406°

99.44

414°

99.2 99.4 99.6 99.8 Pu

Weight % Pu

Co 10 20 30 40 50 60 70 80 90 Pu

Weight Percentage Plutonium

J.C. Chaston

Co-Ti Cobalt-Titanium

Atomic Percentage Titanium

1672°

1494°

L

1230°   1250°   39.5

9.1

13.4

1200°

1170°

1123°

48.8   1050°   62.3   69.8

1015°

62.3   73.3   82.9

(β-Ti)

(α-Co)   γ   δ   ε   ζ   η

Curie Temperature

883°

680°

62.0

90.1

(α-Ti)

Co 10 20 30 40 50 60 70 80 90 Ti

Weight Percentage Titanium

D.T.H.

Co-V   Cobalt-Vanadium

Donald T. Howkins

Co-W   Cobalt-Tungsten

D. T. H.

Co-Zn   Cobalt-Zinc

J. C. Choston

Co-Zr   Cobalt-Zirconium

D.T.H.

Cr-Cu   Chromium-Copper

S. Friedman

S.F.

Cr-Fe   Chromium-Iron

M. V. Rao

Cr-Ni   Chromium-Nickel

D. T. H.

Cr-Mn   Chromium-Manganese

Donald T. Howkins

Cr-Os   Chromium-Osmium

J. C. Chaston

Cr-Pd   Chromium-Palladium

D. T. H.

Cr-Mo   Chromium-Molybdenum

D. T. H.

Cr-Pt   Chromium-Platinum

Atomic Percentage Chromium

°C

Richard M. Waterstrat   Weight Percentage Chromium

Cr-Ti   Chromium-Titanium

Atomic Percentage Titanium

°C

Ralph Hultgren   Weight Percentage Titanium

Cr-Si   Chromium-Silicon

Atomic Percentage Silicon

°C

Donald T. Hawkins   Weight Percentage Silicon

Cr-V   Chromium-Vanadium

Atomic Percentage Vanadium

°C

D.T.H.   Weight Percentage Vanadium

Cr-Ta   Chromium-Tantalum

Atomic Percentage Tantalum

°C

D.T.H.   Weight Percentage Tantalum

Cr-W   Chromium-Tungsten

Atomic Percentage Tungsten

°C

D.T.H.   Weight Percentage Tungsten

Cr-Zr   Chromium-Zirconium

Atomic Percentage Zirconium

Donald T. Hawkins   Weight Percentage Zirconium

Cs-K   Cesium-Potassium

Atomic Percentage Potassium

Ralph Hultgren   Weight Percentage Potassium

Cu-Fe   Copper-Iron

Atomic Percentage Copper

Robert E. Johnson   Weight Percentage Copper

Cu-Ga   Copper-Gallium

Atomic Percentage Gallium

Atomic % Ga

Weight % Ga

Warren Smith   Weight Percentage Gallium

Cu-Ge   Copper-Germanium

Atomic Percentage Germanium

R. H.   Weight Percentage Germanium

Cu-H   Copper-Hydrogen

Atomic Percentage Hydrogen

Solubility at 1 atmosphere pressure

Dennis Bishop   Weight Percentage Hydrogen

Cu-In Copper-Indium

Atomic Percentage Indium

°C
1100
1900F
1000
1700F
900
1600F
800
1400F
700
1200F
600
1000F
500
800F
400
700F
300
500F
200
300F
100

1084.5°

677°, 41.0%
710° 28.4 33.3
16.7
(Cu)   β   36.6, 38.2
682°, 43.0%
667°, 46.6%
50.4
617°   γ   45.1
18.2 31.1   42.4
574°   630°, 43.6%   613°, 44.3%
48.2
55.6
53.6
310°   96.0
δ   ε   ζ
56.7   153°   156.634°
99.3
(In)

Cu 10 20 30 40 50 60 70 80 90 In

Derek Tyler

Weight Percentage Indium

Cu-Ir Copper-Iridium

Atomic Percentage Iridium

°C
2300
4000F
1900
3200F
1500
2400F
1100
1600F
700

2447°

L

II
21
1142°   99
1084.5°
(Cu)
(Ir)

Cu 10 20 30 40 50 60 70 80 90 Ir

J. C. Chaston

Weight Percentage Iridium

Cu-Li Copper-Lithium

Atomic Percentage Lithium

°C
1200
2000F
1000
1600F
800
1200F
600
1000F
400
600F
200
200F
0

1084.5°

L

(Cu)
-2.7
179°   180.5°
(Li)

Cu 10 20 30 40 50 60 70 80 90 Li

Robert C. Ruhl

Weight Percentage Lithium

Cu-Mg Copper-Magnesium

Atomic Percentage Copper

°C
1100
1900F
900
1500F
700
1100F
500
700F
300

1084.5°
L
820°
722°
90.3
96.7
649°
0.61   485°   568°   552°
30.7   65.4
(Mg)   β   γ   (Cu)

Mg 10 20 30 40 50 60 70 80 90 Cu

R. N. Caron

Weight Percentage Copper

Cu-Mn Copper-Manganese

Atomic Percentage Manganese

°C
1300
2300F
1200
2100F
1100
1900F
1000
1700F
900
1600F
800
1400F
700
1200F
600
1000F
500
800F
400
700F
300

1246°
1084.5°
L
85.8 (δ-Mn)
1099°   1139°
86.8   1088°
871°
~33.7
γ(Cu, γ-Mn)   (β-Mn)   707°
(α-Mn)
?
γ'   γ''

Cu 10 20 30 40 50 60 70 80 90 Mn

Richard D. Lanam

Weight Percentage Manganese

Cu-Ni Copper-Nickel

Atomic Percentage Nickel

°C
1500
2600F
1400
2500F
1300
2300F
1200
2100F
1100
1900F
300
500F
200

1455°
L
1084.5°
α(Cu, Ni)
322°   358°
α₁
CURIE TEMPERATURE
α₁+α₂   α₂

Cu 10 20 30 40 50 60 70 80 90 Ni

Avinash D. Kulkarni

Weight Percentage Nickel

Cu-O   Copper-Oxygen

°C

Atomic Percentage Oxygen

L_1

L_2

$P_{O_2}=10^{-4}$ atm

$P_{O_2}=10^{-5}$ atm

$P_{O_2}=0.035$ atm

$P_{O_2}=10^{-3}$ atm

$P_{O_2}=0.01$ atm

$P_{O_2}=0.1$ atm

L_1+L_2

$1231°$

$P_{O_2}=0.2$ atm

$L+O_{2(g,1atm)}$

2.1

1218°

10.3

$P_{O_2}=10^{-4}$ atm

$P_{O_2}=1.0$ atm

$P_{O_2}=10^{-5}$ atm

14.4

1125°

$P_{O_2}=0.43$ atm

β (Cu$_2$O)

1092°

14.0

1066°

0.39

$P_{O_2}=10^{-6}$ atm

γ (CuO)

$P_{O_2}=0.1$ atm

$P_{O_2}=10^{-8}$ atm

$\gamma+O_{2(g,1atm)}$

(Cu)

$P_{O_2}=0.01$ atm

$P_{O_2}=10^{-10}$ atm

$P_{O_2}=10^{-3}$ atm

$P_{O_2}=10^{-4}$ atm

$P_{O_2}=10^{-12}$ atm

$P_{O_2}=10^{-6}$ atm

1084.5°

Robert E. Johnson

Weight Percentage Oxygen

°C   Atomic Percentage Oxygen

1084.5°

L_1

(Cu)+L_1

1066°

(Cu)

(Cu)+β

F. N. Rhines   Weight Percentage Oxygen

Temperature, °F

Pressure, atm

Cu+Cu$_2$O+L_1 Cu$_2$O+L_2

CuO+Cu$_2$O+L_2 Cu$_2$O+L_1+L_2

Cu+L_1 O$_2$+CuO+L_2

O$_2$+CuO+Cu$_2$O   O$_2$+L_2+Cu$_2$O

Q_3

O$_2$+L_1+L_2 O$_2$+L_1

M

Q_2

O$_2$+Cu+L_1 Q_1

T O$_2$+L_1+Cu$_2$O

O$_2$+Cu+Cu$_2$O

O$_2$+Cu

Approximate representation

F. N. R.   Temperature, °C

Cu-P Copper-Phosphorus

Atomic Percentage Phosphorus

Eugene Shapiro

Weight Percentage Phosphorus

Cu-Pr Copper-Praseodymium

Atomic Percentage Praseodymium

E. S.

Weight Percentage Praseodymium

Cu-Pb Copper-Lead

Atomic Percentage Lead

Robert E. Johnson

Weight Percentage Lead

Cu-Pt Copper-Platinum

Atomic Percentage Copper

Dennis Bishop

Weight Percentage Copper

Cu-Pd Copper-Palladium

Atomic Percentage Copper

S. Friedman

Weight Percentage Copper

Cu-Pu Copper-Plutonium

Atomic Percentage Plutonium

Philip A. Tucker   Weight Percentage Plutonium

Cu-Rh   Copper-Rhodium

Atomic Percentage Rhodium

°C
2200
3800F
1963°
L
1800
3000F
1400
2200F
1000
1084.5°
α(Cu,Rh)
1400F
α₁
α₁+α₂
α₂
600

Cu 10 20 30 40 50 60 70 80 90 Rh
Weight Percentage Rhodium

J. C. Chaston

Cu-S   Copper-Sulfur

Atomic Percentage Sulfur

°C
1200
L₁
1084.5°
1107°   L₁+L₂   L₂
1068°   19.80
1000
L₂+L₃
L₃
SEE DETAIL BELOW
1600F
~26
814°
800
22.3
(Cu)
δ
1200F
600
20.15
507°
1000F
435°
22.5
400
600F
β
ε
200
200F
103.5°
76°
115°
115.21°
(β-S)
SEE DETAIL BELOW
33.54
Transformation temperature of S,95.39°
(α-S)
0

Cu 10 20 30 40 50 60 70 80 90 S
Weight Percentage Sulfur

H. H. Kellogg

Atomic Percentage Sulfur

°C
1200
2100F
L₁
1084.5°
0.95
L₁+L₂
1107°
1131°, 20.24%
1100
19.80
L₂
1900F
0.84
1068°
1000
20.18% at 950°
δ
1700F
(Cu)
900

Cu 5 10 15 20 25
Weight Percentage Sulfur

H. H. K

Atomic Percentage Sulfur

°C
600
32 33 34 35 36 37 38
δ+L₃
1000F
500
22.5
507°
800F
435°
400
700F
δ
δ+ε
300
500F
200
300F
21.50
21.52
21.61
100
103.5°
β
20.25
93°
76°
100F
β'
20.21
92°
83°
δ'
δ'+ε
0
γ
20.47
22.23
19 20 21 22 23 24
Weight Percentage Sulfur

H. H. K.

Cu-Sb   Copper-Antimony

Atomic Percentage Antimony

°C
1100
1084.5°
1900F
1000
1700F
900
L
1600F
800
1400F
700
684°
630.74°
1200F
(Cu)
645°
31 31.5
586°
62
600
11
586°
526°
1000F
β
500
488°
76
26
800F
γ
ε
η
400
400°
700F
δ
ζ
(Sb)
300
500F
200
300F
100

Cu 10 20 30 40 50 60 70 80 90 Sb
Weight Percentage Antimony

R. N. Caron

Atomic Percentage Antimony

°C
550
14 16 18 20 22 24 26
1000F
β
500
488°
900F
26
462°
31
445°
450
435°
800F
γ
400°
ε
400
390°
700F
360°
350
ζ
600F
δ
300
550F
260°
250
450F
200
22 24 26 28 30 32 34 36 38 40 42
Weight Percentage Antimony

R.N.C.

Cu-Se   Copper-Selenium

Atomic Percentage Selenium

°C
1150
10 20 30 40
1149±5°
2050F
L
1100
1107°
0.010 0.025 0.030
1400
2400F
L
1950F
1063°
1200
1050
2.2
38.22
40.7% at 1063°
1084.5°
2000F
1000
1063°
1900F
(Cu)
β
1600F
1000
1800F
(Cu)
800
950
1400F
600

Cu 10 20 30 40 50   Cu 0.02 0.04 0.06
Weight Percentage Selenium

Richard D. Lanam

Cu-Si   Copper-Silicon

Donald T. Hawkins

D.T.H.

D.T.H. Weight Percentage Copper

Cu-Sn Copper-Tin

Robert E. Johnson

Cu-Te　Copper-Tellurium

Atomic Percentage Tellurium

°C 1200 · 2100F · 1100 · 1900F · 1000 · 1700F · 900 · 1600F · 800 · 1400F · 700 · 1200F · 600 · 1000F · 500 · 800F · 400 · 700F · 300 · 500F · 200

L_1　L_1+L_2　L_2 1127°
1084.5°　1052°　SEE DETAIL
8.3　1051°　46.3
(Cu)
β →
630°
555°
γ
β'　δ
449.57°
360°　367°
305°　340°
β"
β'''　γ'
δ'　ε
(Te) →

Cu 10 20 30 40 50 60 70 80 90 Te
Charles Sohl　Weight Percentage Tellurium

Schematic
L_2
L_1+L_2
1052°
(Cu)+L_2　$L_2+β$
1051°　46.3
(Cu)+β
Wt % Te

Boiling point of Te, 989°

Cu-Th　Copper-Thorium

Atomic Percentage Thorium

°C 1800 · 3000F · 1600 · 2800F · 1400 · 2400F · 1200 · 2000F · 1000 · 1600F · 800

1758°
(β-Th)
1365°
L
1084.5°
?
?
(Cu)　936°
976°　? ~951°　1038°
γ　δ　ε　ζ　η　(α-Th)

Cu 10 20 30 40 50 60 70 80 90 Th
Ralph Hultgren　Weight Percentage Thorium

Cu-Ti　Copper-Titanium

Atomic Percentage Titanium

°C 1200 · 2100F · 1100 · 1900F · 1000 · 1700F · 900 · 1600F · 800 · 1400F · 700

L
1084.5°
(β-Ti)
981°　991°
31　936°　961°　?
4.7　896°　237°　896°　50　83.2
18.5　22　883°
881°　?　?
799°　98.5
(Cu)　γ　δ　ε　ζ　η　93 (α-Ti)

Cu 10 20 30 40 50 60 70 80 90 Ti
J. Crane　Weight Percentage Titanium

Cu-Tl　Copper-Thallium

Atomic Percentage Thallium

°C 1300 · 2200F · 1100 · 1800F · 900 · 1400F · 700 · 1200F · 500 · 800F · 300 · 400F · 100

L
1084.5°
(Cu)
~0.9　35.3　968°　94.0
~304°　304°
(β-Tl)
234°　(α-Tl)

L
1084.5°　968°
~0.9
(Cu)
Cu 1.0 Wt%Tl

Cu 10 20 30 40 50 60 70 80 90 Tl
S. Friedman　Weight Percentage Thallium

Cu-U　Copper-Uranium

Atomic Percentage Uranium

°C 1300 · 2200F · 1100 · 1900F · 900 · 1500F · 700 · 1100F · 500

L_1　L_1+L_2　L_2
1084.5°　~52　1081°　1133°　~98.5
950°　1053°　(γ-U)
24.5
(Cu)　δ　776°　(β-U)
668°　(α-U)

Cu 10 20 30 40 50 60 70 80 90 U
Warren Smith　Weight Percentage Uranium

Cu-V　Copper-Vanadium

Atomic Percentage Vanadium

°C 2000 · 3400F · 1600 · 2600F · 1200 · 1084.5° · 1800F · 800

L_1　L_2　1929°
1532°　1250　1532°
3.2　1150　83.6　90.2
1122°　0.32　1122°　1122°
(Cu)　1050　(V)
0.64
1084.5°
(Cu)
Cu 0.5 Wt%V

Cu 10 20 30 40 50 60 70 80 90 V
Richard D. Lanam　Weight Percentage Vanadium

Cu-Y　Copper-Yttrium

Atomic Percentage Yttrium

°C 1400 · 2400F · 1200 · 2000F · 1000 · 1600F · 800 · 1400F · 600

1528°
(β-Y)　1481°
L
1084.5°　(α-Y)
931±20°　986±15°　936±15°　936±15°
16.7
891±10°,　841±15°,　831±15°,
12.5%　35.0%　50.0%
761±15°,
73.7%
(Cu)　γ　δ　ε　ζ

Cu 10 20 30 40 50 60 70 80 90 Y
C. S.　Weight Percentage Yttrium

Cu-Zn   Copper-Zinc

Atomic Percentage Zinc

Donald T. Hawkins

Weight Percentage Zinc

Cu-Zr   Copper-Zirconium

Stanley Shapiro

Fe-H   Iron-Hydrogen

Carl A. Zapffe

Fe-C   Iron-Carbon

See "C-Fe Carbon-Iron".

Fe-Ge   Iron-Germanium

Donald T. Howkins

Fe-Hf   Iron-Hafnium

A.R. Marder
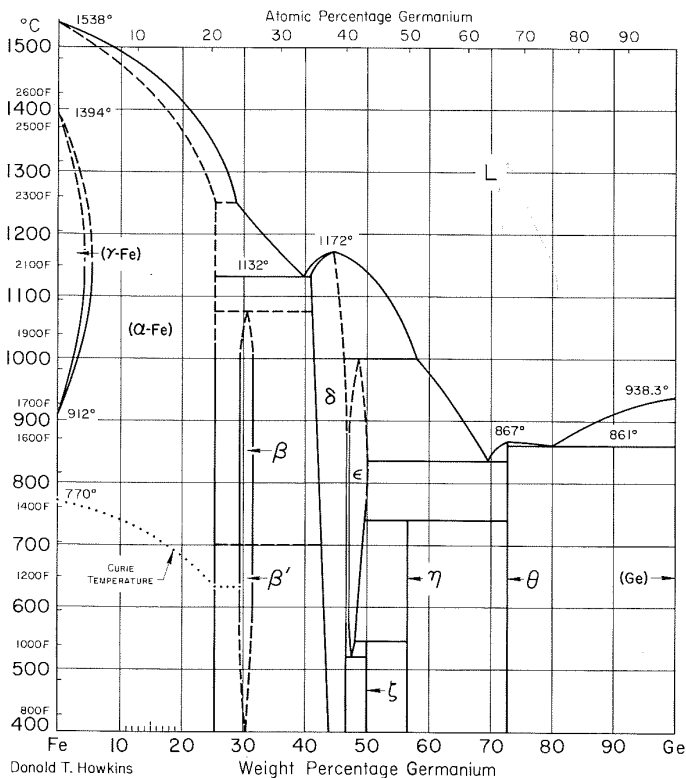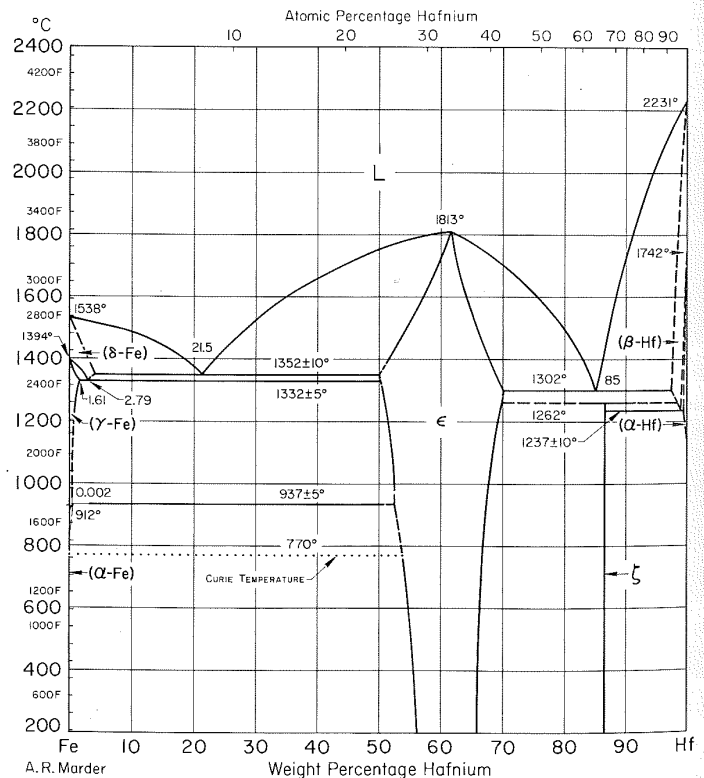
Fe-Hg   Iron-Mercury

See Notes.

Fe-Ir   Iron-Iridium
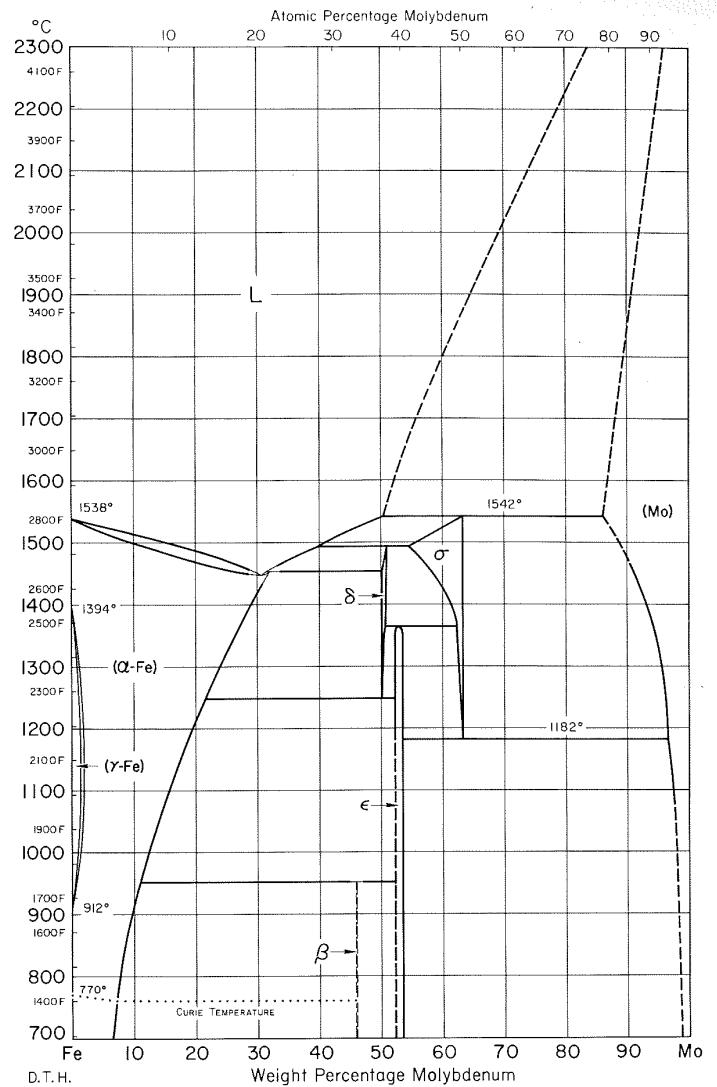
Donald T. Hawkins

Fe-K   Iron-Potassium
Fe-Li   Iron-Lithium
Fe-Mg   Iron-Magnesium

See Notes.

Fe-Mn   Iron-Manganese

Malcolm J. Roberts

Fe-Mo   Iron-Molybdenum

D.T.H.

Fe-N   Iron-Nitrogen

D.T.H.
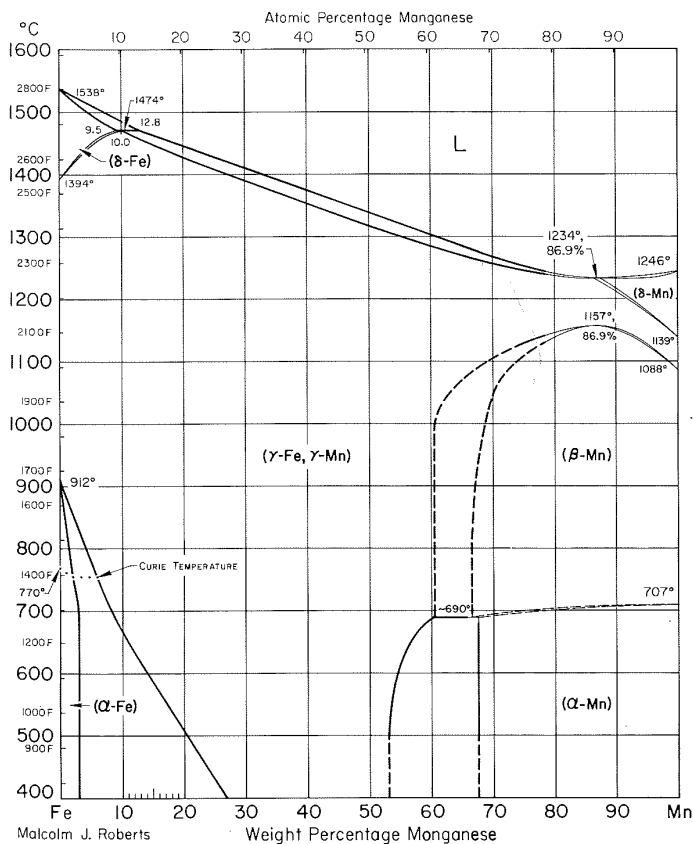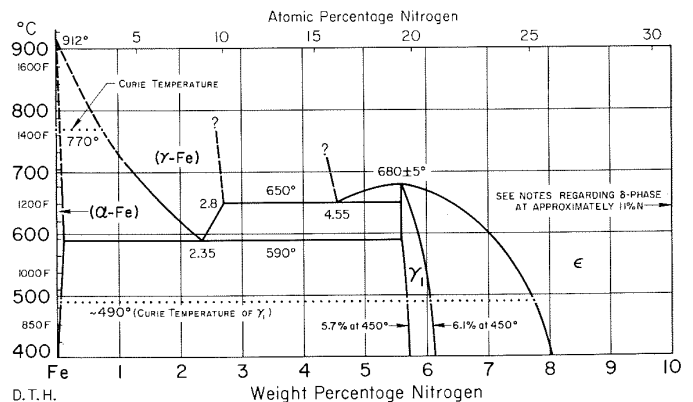
Fe-Na   Iron-Sodium

See Notes.

Fe-Ni　Iron-Nickel

J. I. Goldstein
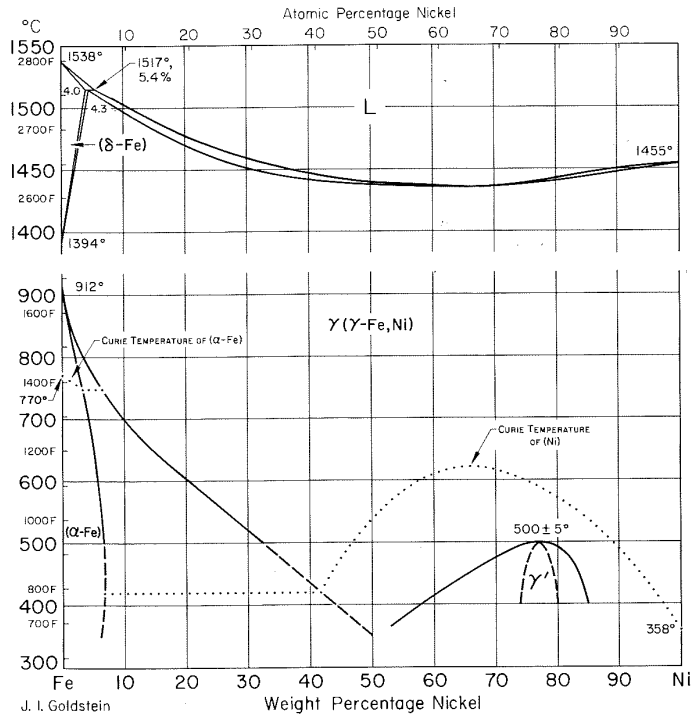
Fe-P　Iron-Phosphorus

Donald T. Hawkins

Fe-O　Iron-Oxygen

Sudhir K. Sharma
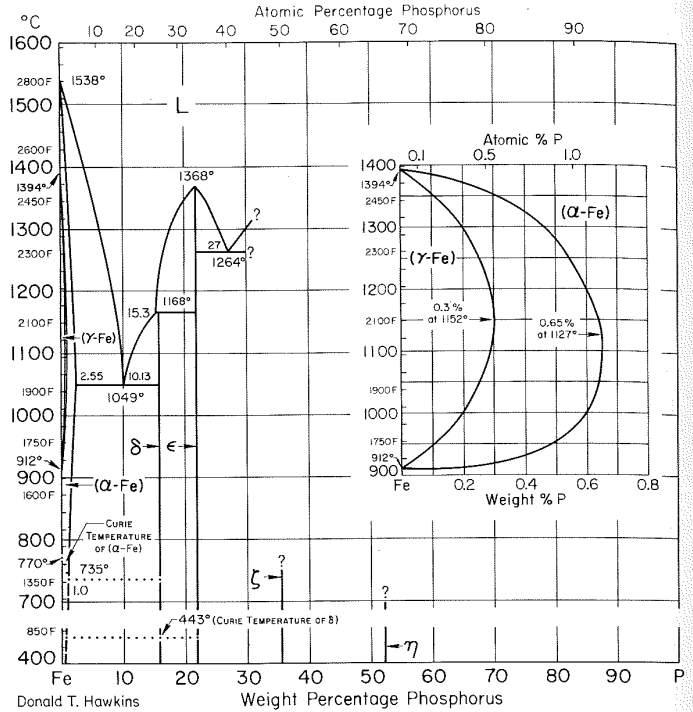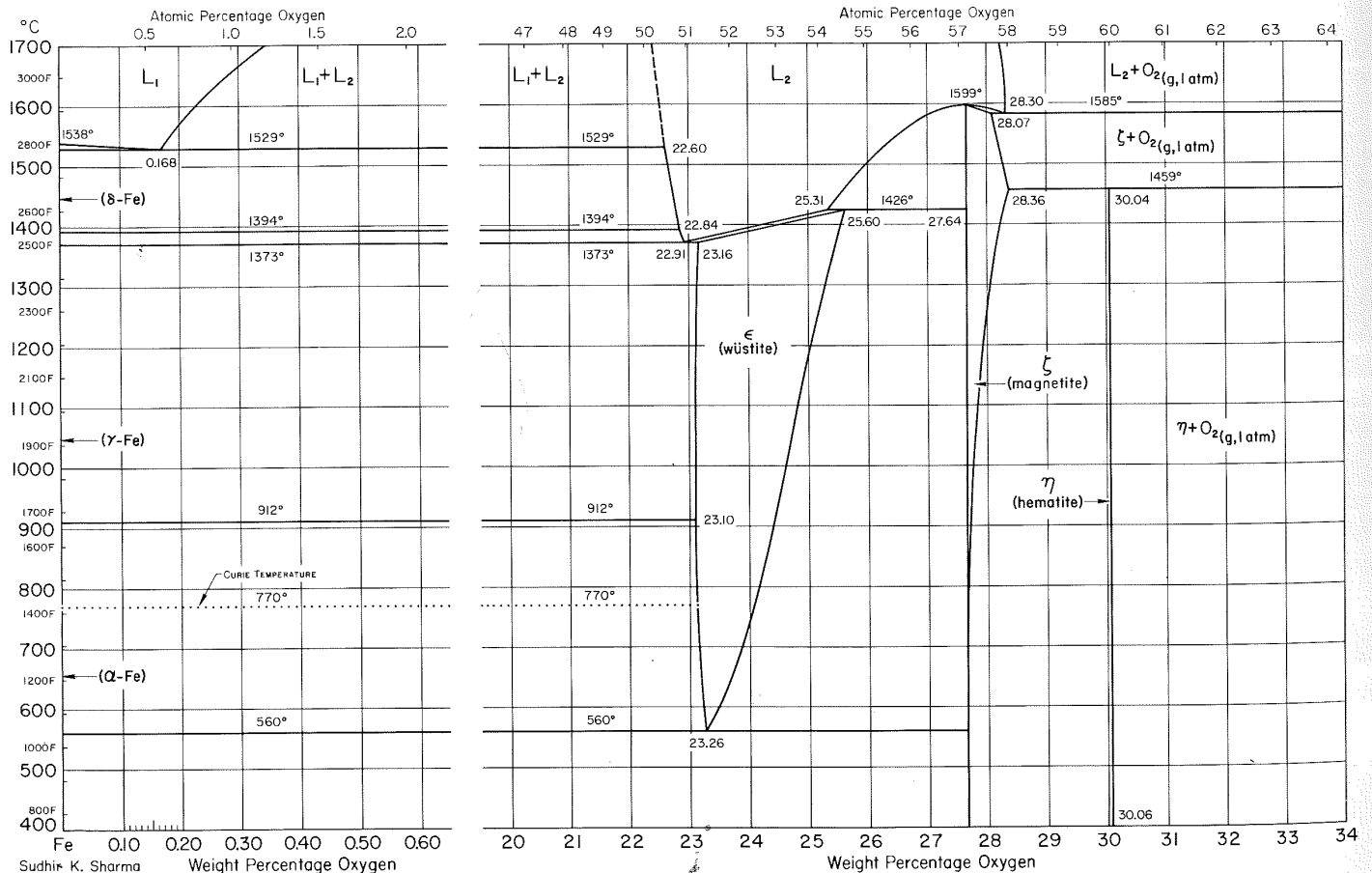
Fe-Pb   Iron-Lead
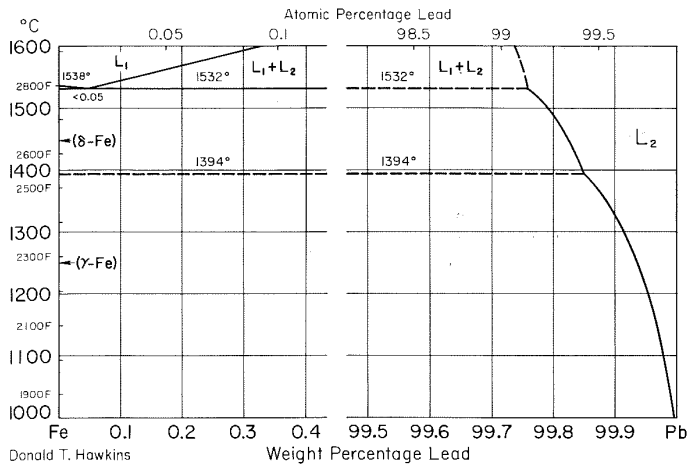
Donald T. Hawkins
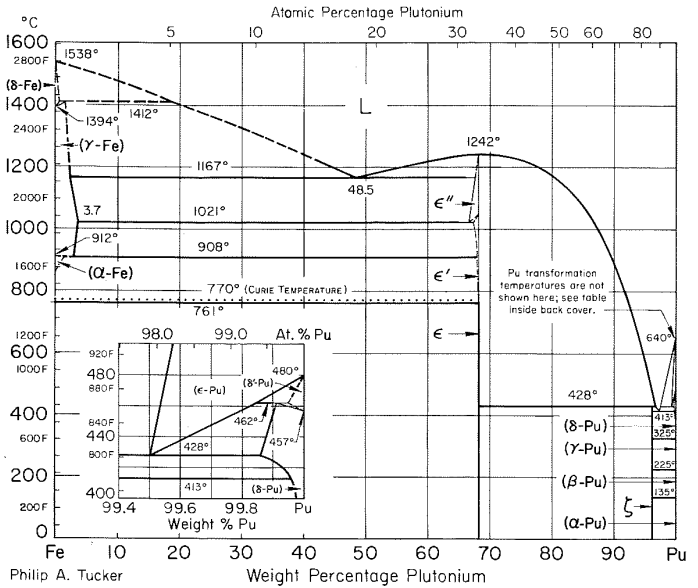
Fe-Pd   Iron-Palladium

D.T.H.
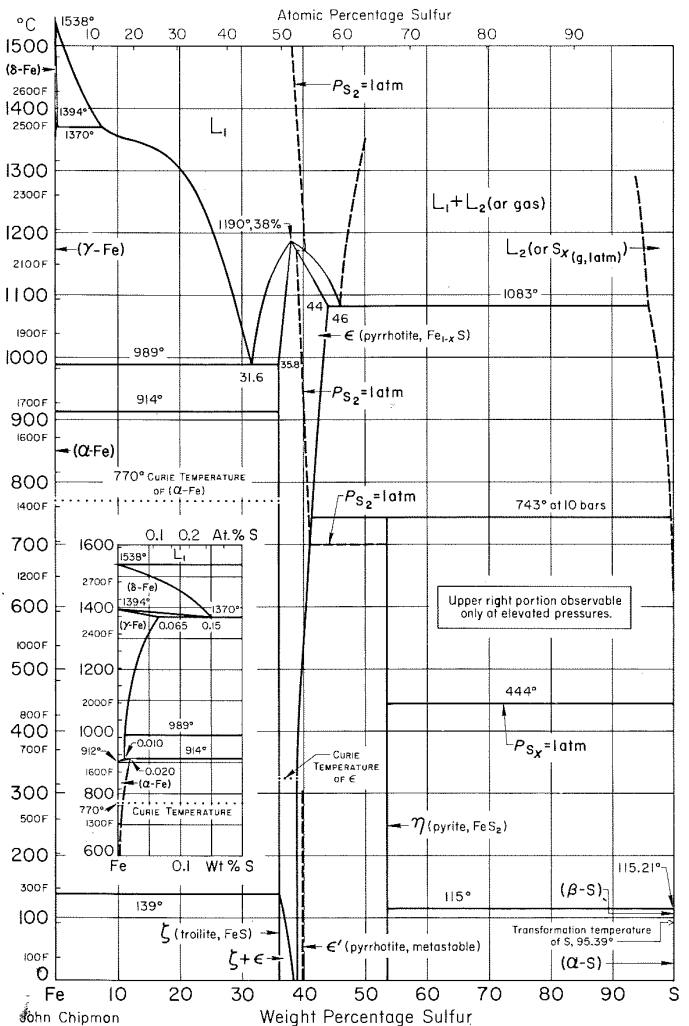
Fe-Pt   Iron-Platinum

D.T.H.

Fe-Pu   Iron-Plutonium

Philip A. Tucker

Fe-S   Iron-Sulfur

John Chipman
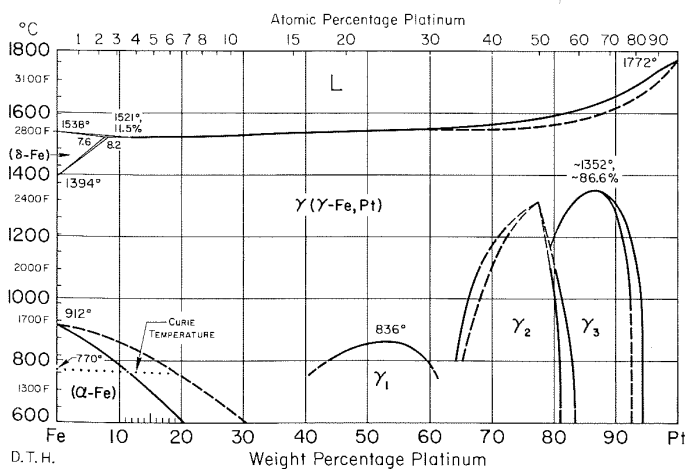
Fe-Sb   Iron-Antimony

Donald T. Hawkins
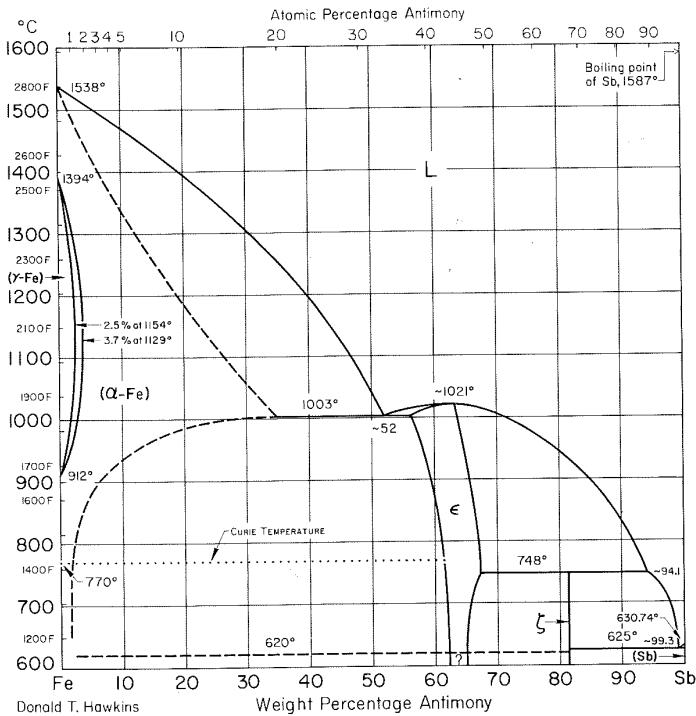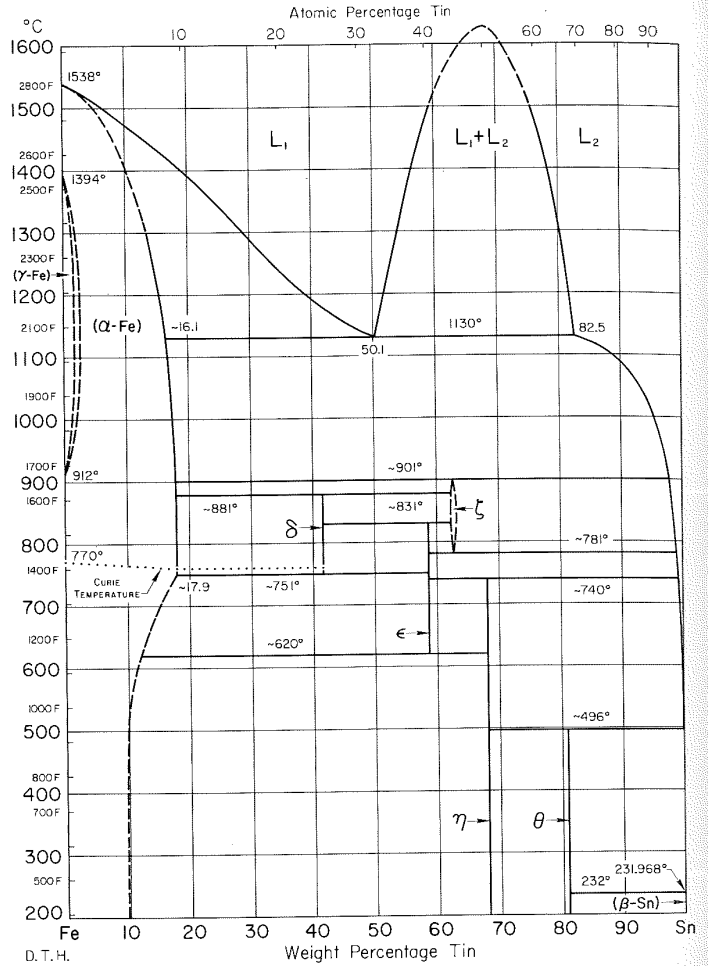
Fe-Se   Iron-Selenium

See Notes.

Fe-Si   Iron-Silicon

John Chipman

Fe-Sn   Iron-Tin

D. T. H.
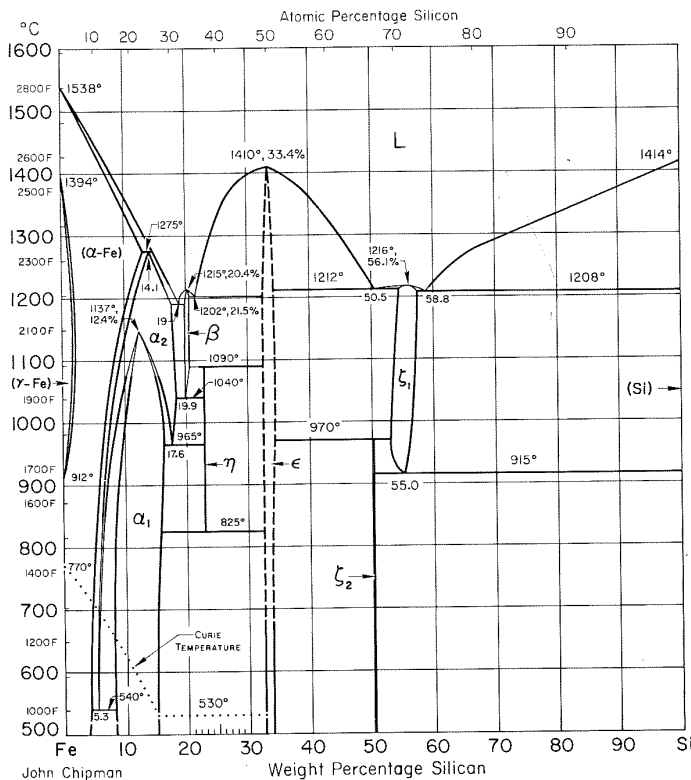
Fe-Ta   Iron-Tantalum

Halle Abrams
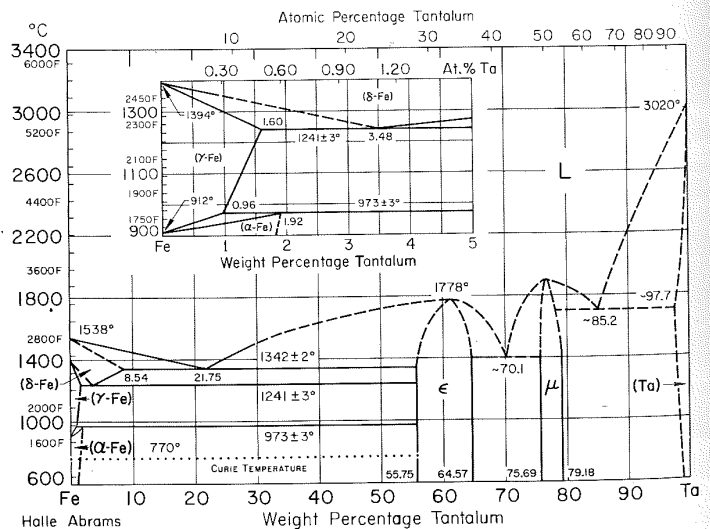
Fe-Te   Iron-Tellurium

See Notes.

Fe-Ti　Iron-Titanium

P. K. Rohatgi

Fe-V　Iron-Vanadium

E. C. Oren

Fe-U　Iron-Uranium

Donald T. Hawkins

Fe-W　Iron-Tungsten

E. T. Stephenson

Fe-Zn   Iron-Zinc

Atomic Percentage Zinc

°C

L

(γ-Fe)

(α-Fe)

Boiling point of Zn, 908°

912°

801°, 5.0%

770°

46   783°   74.0   92.6

CURIE TEMPERATURE

18.B

622°

80.0   672°   91.0

79.2   640°   88.6

ε

δ

ε₁

530°

ζ

72   79   419.58°   419.4°

Fe 10 20 30 40 50 60 70 80 90 Zn

J. W. Simpson and W. Showak   Weight Percentage Zinc

Atomic Percentage Iron

°C

L

783°

7.4

3.0   672°   9.0

620°

7.5   8.5

ε   10.0

1.1

0.25   530°

6.1   6.9

ε₁

419.58°

419.4°

0.015

5.5

ζ

(Zn)

420

419.58°   L   0.015

(Zn)   0.008   419.4°

419

Zn   0.005   0.010   Wt % Fe

6.0   6.2   7.0

Zn 1 2 3 4 5 6 7 8 9 10

J. W. S. and W. S.   Weight Percentage Iron

Fe-Zr   Iron-Zirconium

Atomic Percentage Zirconium

°C

1647°

1538°

(δ-Fe)

1482°

1394°

1308°   1306°

11.7   13.6

(γ-Fe)

ε   ζ

L

(β-Zr)

912°   926°

0.8

η

948±5°

85   95.75

872°

796±5°, 97.8%

θ

99.98

(α-Zr)

CURIE TEMPERATURE 770°

(α-Fe)

Fe 10 20 30 40 50 60 70 80 90 Zr

B. L. Bramfitt   Weight Percentage Zirconium

Ga-Mg   Gallium-Magnesium

Atomic Percentage Magnesium

°C

649°

L

470°

450°

425°

(Mg)

365°

285°

β

γ   δ   ε   ζ

29.75°

(Ga)

Ga 10 20 30 40 50 60 70 80 90 Mg

Ralph Hultgren   Weight Percentage Magnesium

Ga-Sb   Gallium-Antimony

Atomic Percentage Antimony

°C

L

709.6°

630.74°

588.5°   93.02

β

(Sb)

29.75°

(Ga)

29.7°   63.61

Ga 10 20 30 40 50 60 70 80 90 Sb
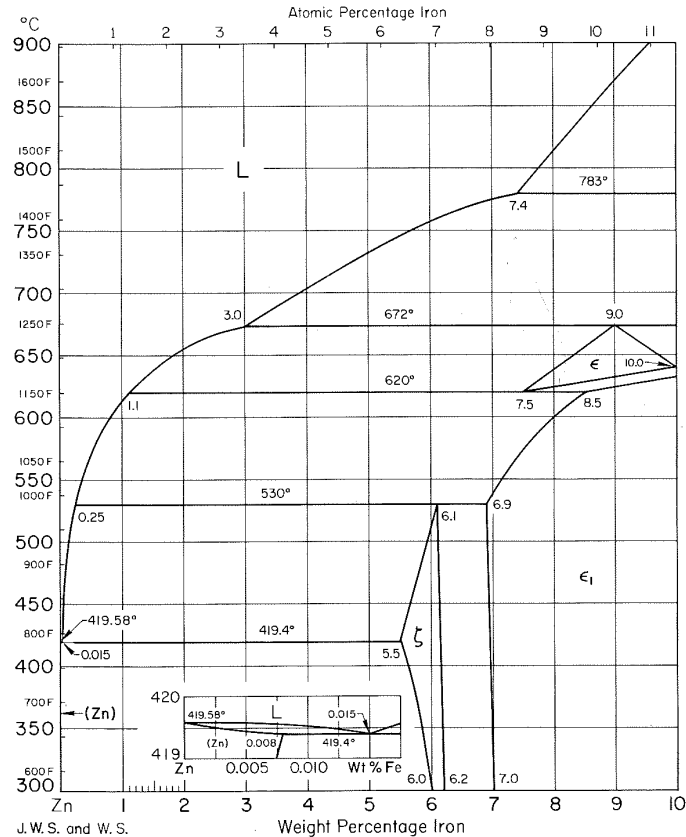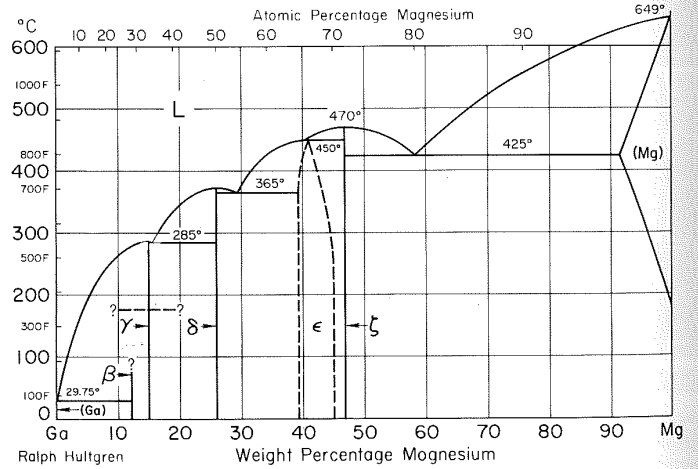
M. B. Panish and M. Ilegems   Weight Percentage Antimony
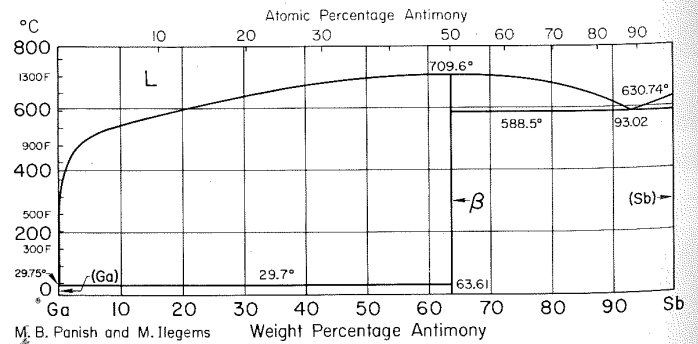
H-Pd   Hydrogen-Palladium
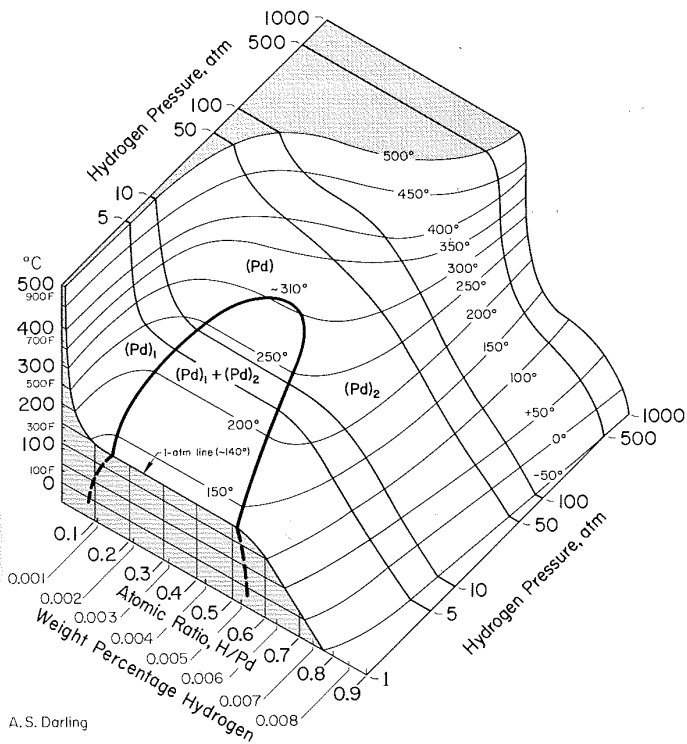
A.S. Darling
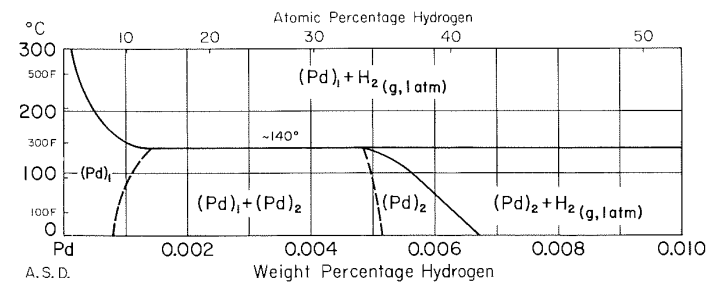
A.S.D.

Hf-Mo   Hafnium-Molybdenum

D.T.H.
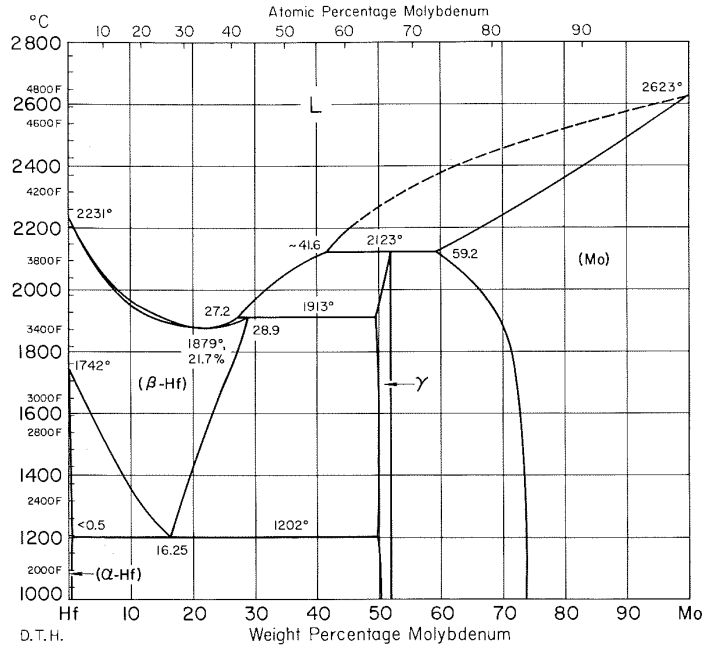
Hf-Ni   Hafnium-Nickel
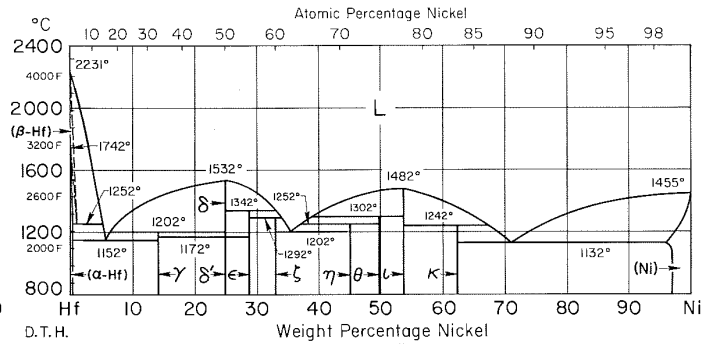
D.T.H.

Hf-Ir   Hafnium-Iridium
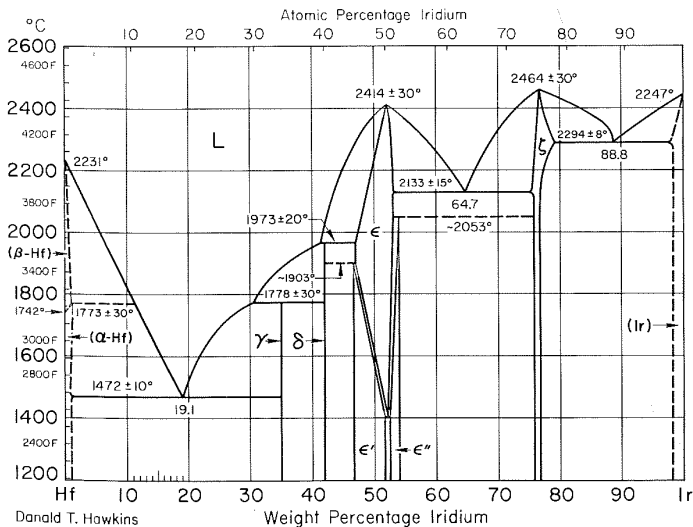
Donald T. Hawkins

Hf-Ta   Hafnium-Tantalum
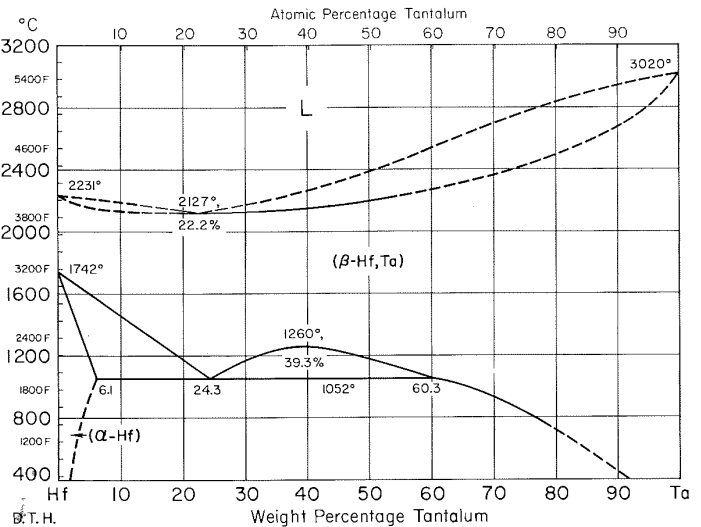
D.T.H.

Hf-Ti   Hafnium-Titanium

Donald T. Howkins
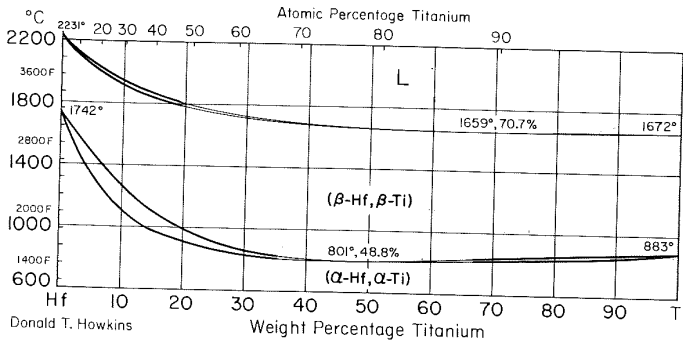
Hf-W   Hafnium-Tungsten

D.T.H.
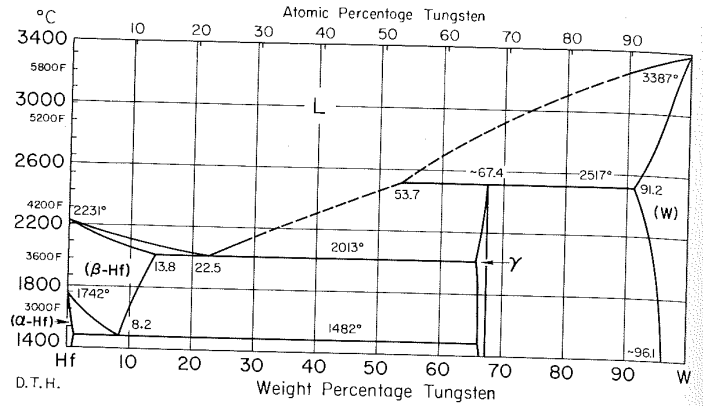
Hf-U   Hafnium-Uranium

D.T.H.
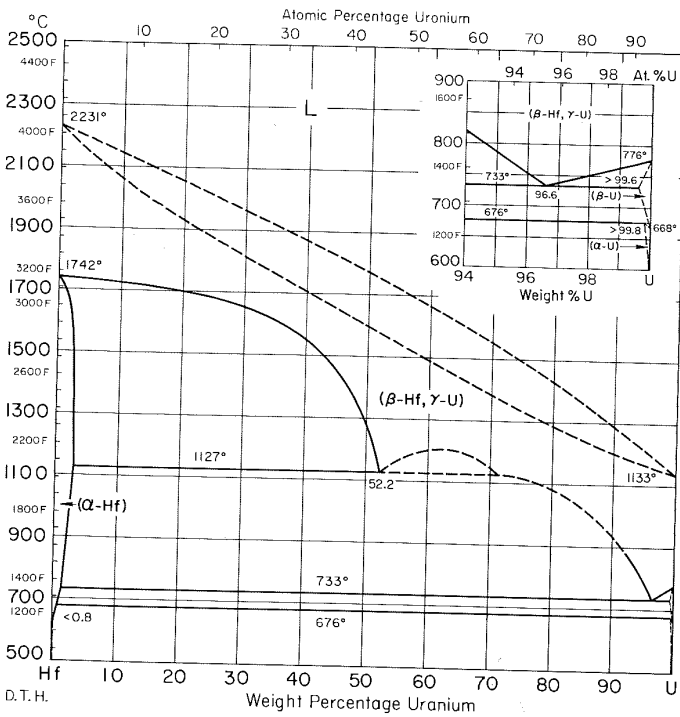
Hf-Zr   Hafnium-Zirconium

D.T.H.
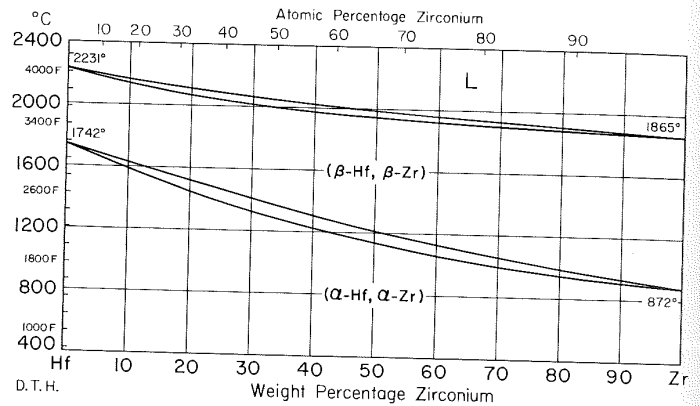
Hf-V   Hafnium-Vanadium

D.T.H.
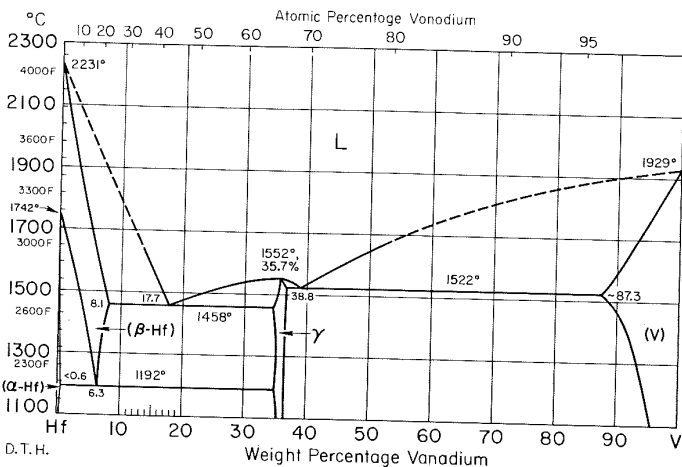
Hg-In   Mercury-Indium

D.T.H.
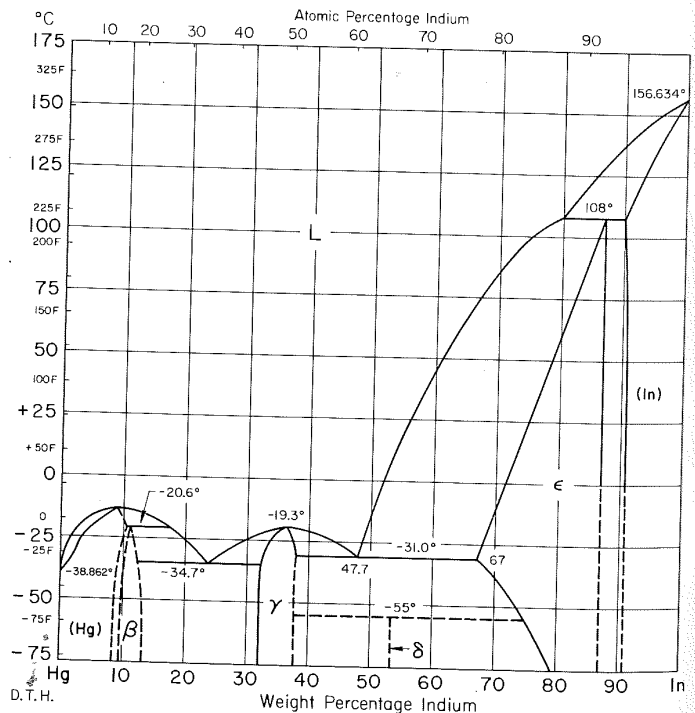
Hg-Pb   Mercury-Lead
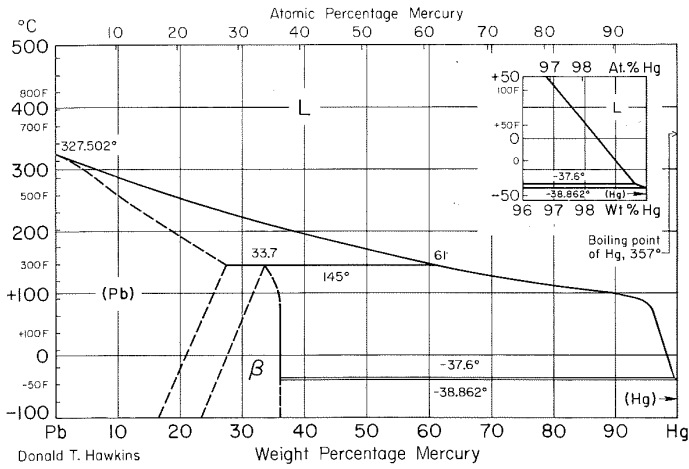
Donald T. Hawkins

In-Mg   Indium-Magnesium

Ralph Hultgren

Hg-Sn   Mercury-Tin

D.T.H.
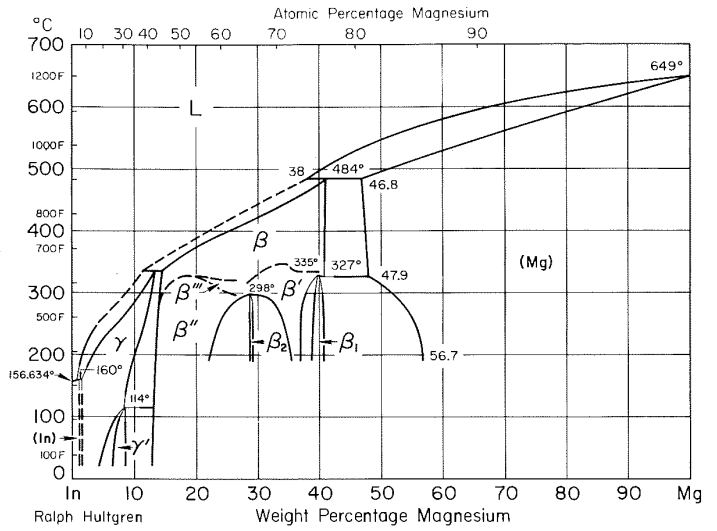
In-P   Indium-Phosphorus
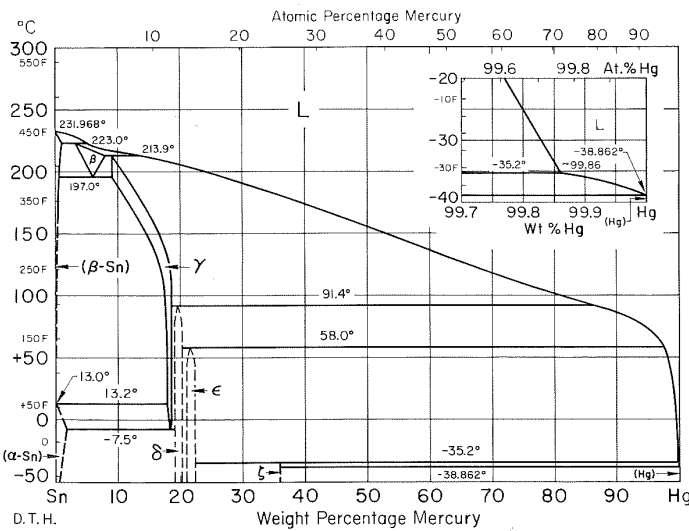
M. B. Panish and M. Ilegems

Hg-Zn   Mercury-Zinc

D.T.H.

In-Pb   Indium-Lead

C. DiMartini
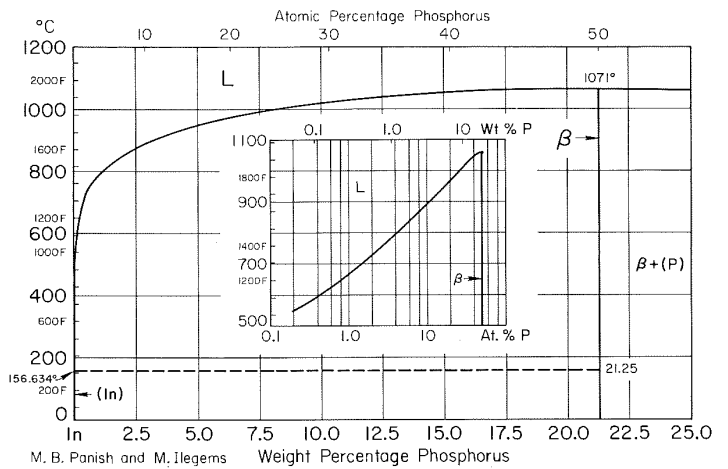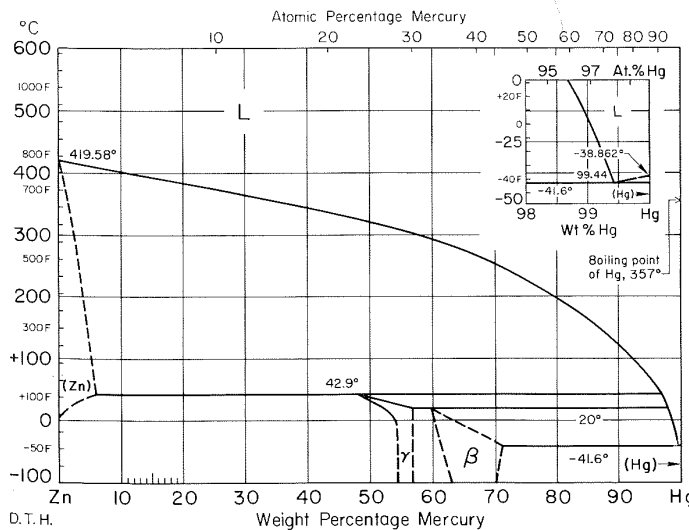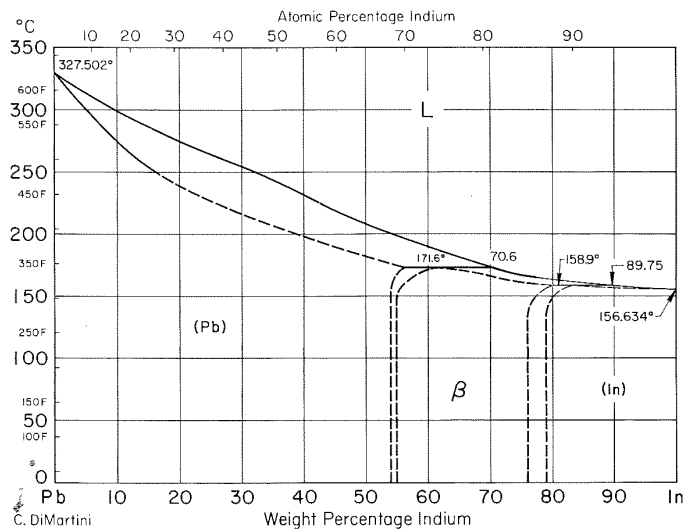
In-Sb   Indium-Antimony

M. B. Panish and M. Ilegems   Weight Percentage Antimony
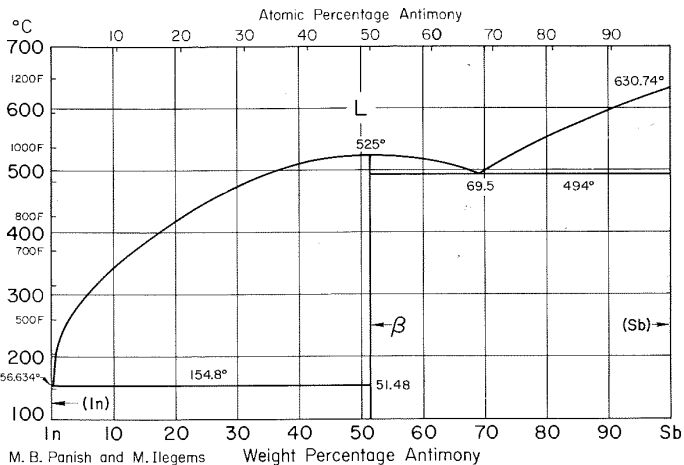
Ir-Mo   Iridium-Molybdenum

A. G. Knapton   Weight Percentage Molybdenum
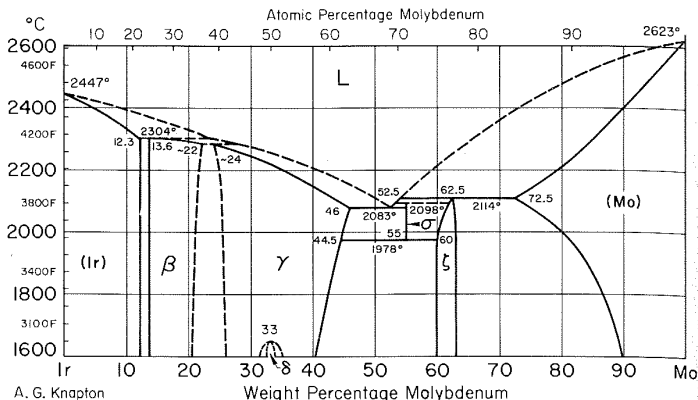
In-Sn   Indium-Tin

Donald T. Hawkins   Weight Percentage Tin
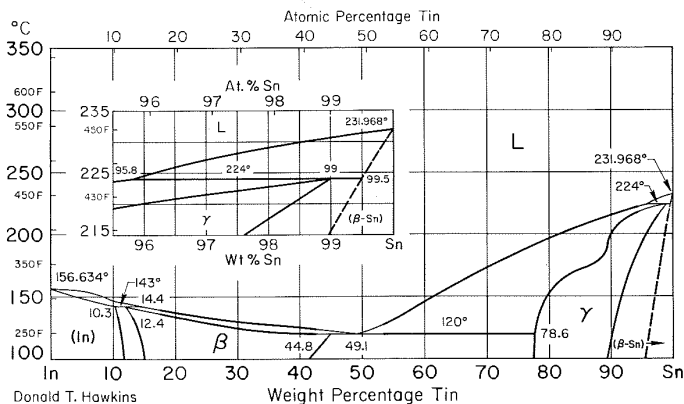
Ir-Os   Iridium-Osmium

J. C. Chaston   Weight Percentage Osmium
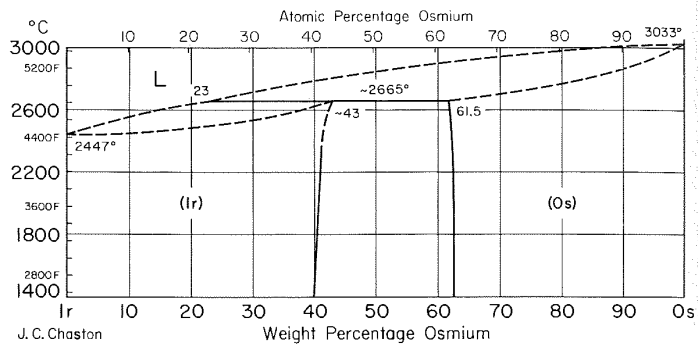
In-Tl   Indium-Thallium

Ralph Hultgren   Weight Percentage Thallium
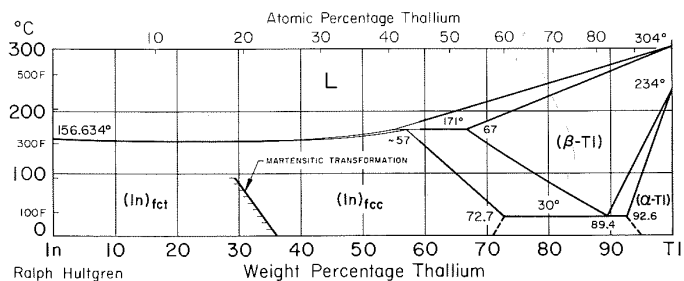
Ir-Pd   Iridium-Palladium

D.T.H.   Weight Percentage Iridium

In-Zn   Indium-Zinc

D.T.H.   Weight Percentage Zinc
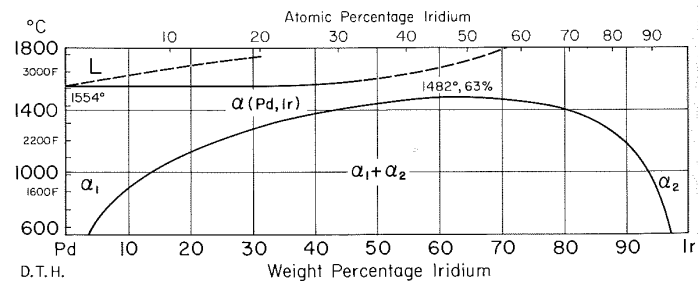
Ir-Pt   Iridium-Platinum

A. S. Darling   Weight Percentage Iridium

Ir-Re   Iridium-Rhenium

Atomic Percentage Rhenium

A. G. Knapton

Weight Percentage Rhenium

Ir-Rh   Iridium-Rhodium

Atomic Percentage Rhodium

A. S. Darling

Weight Percentage Rhodium

Ir-Ru   Iridium-Ruthenium

Atomic Percentage Ruthenium

Donald T. Hawkins

Weight Percentage Ruthenium

Ir-Ta   Iridium-Tantalum

Atomic Percentage Tantalum

D.T.H.

Weight Percentage Tantalum

Ir-Ti   Iridium-Titanium

Atomic Percentage Titanium

Richard M. Waterstrat

Weight Percentage Titanium

Ir-W   Iridium-Tungsten

Atomic Percentage Tungsten

A. G. K.

Weight Percentage Tungsten

K-Na   Potassium-Sodium

Atomic Percentage Sodium

°C / °F axis

L

63.2°

(K)

21.6   −12.63°

54.0   6.90°

97.8°

β

(Na)

K   Na

Weight Percentage Sodium

Donald T. Hawkins

K-Pb   Potassium-Lead

Atomic Percentage Potassium

570°, 15.9%

327.502°

372°

338°   11.2

292°   8.6

274°   4.5

1.8%

β → γ   δ → ε

L

52°

63.2

(Pb)

? (K)

Pb   K

Weight Percentage Potassium

C. DiMartini

K-Rb   Potassium-Rubidium

Atomic Percentage Rubidium

63.2°

L

34°   39.48°

(K, Rb)   ~83.6%

K   Rb

Weight Percentage Rubidium

Ralph Hultgren

Li-Mg   Lithium-Magnesium

Atomic Percentage Lithium

649°   589°, 7.5%

595°, 10.2%

5.5   8.5

L

(Mg)

(Li)

180.5°

Mg   Li

Weight Percentage Lithium

D. T. H.

Li-Pb   Lithium-Lead

Atomic Percentage Lithium

726°, 10.5%

642°   658°   650°

8.2   9.1   12.85

L

482°, 3.2%   464°

5.2

β   γ   δ   ε   ζ

327.502°

0.7   235°

0.1   214°   186°   177°   177°   180.5°

(Pb)   12.85

β'

77 (Li)

Pb   Li

Weight Percentage Lithium

C. DiM.

Mg-Mn   Magnesium-Manganese

Atomic Percentage Manganese

L

L + (β-Mn)   707°

649°   2.0   L + (α-Mn)   653°

(Mg)

(Mg) + (α-Mn)

Mg   Weight Percentage Manganese

D. T. H.
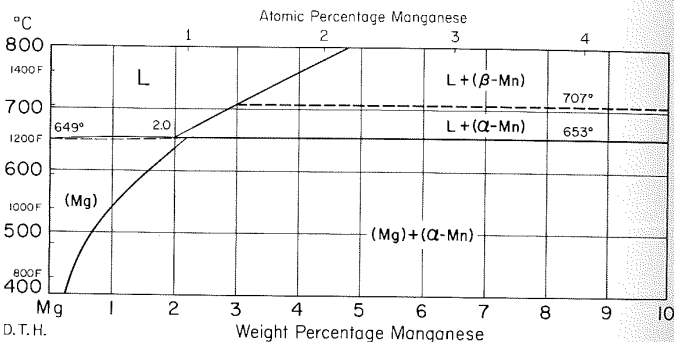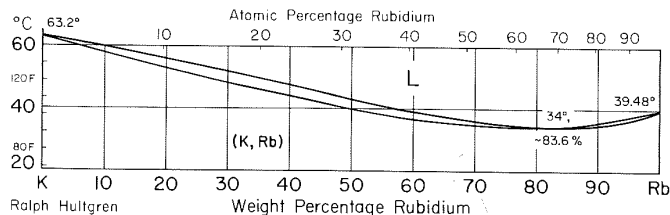
Mg-Nd   Magnesium-Neodymium

Atomic Percentage Neodymium

1017°

L   856°

649°   (β-Nd)

(Mg)   552°   37.0   560°   551°

3.6   33.0

γ   δ   ε   ζ   (α-Nd)

Mg   Nd

Weight Percentage Neodymium

R. H.

Mg-Ni   Magnesium-Nickel

Atomic Percentage Magnesium

1455°

1147°

1097°   17.8   11

761°   49.8   L

(Ni)   45.4   507°   649°

β   γ   76.5

358° (Curie Temperature)   (Mg)

Ni   Mg

Weight Percentage Magnesium

D. T. H.

Mg-Pb   Magnesium-Lead

Atomic Percentage Lead

°C

L

649°

538.2° 79% 549°, 82.1%

81.0

466.2°

(Mg)   41.8   67.4

β → β′

327.502°
96.6

291±5°, 81.3%
97.7

248.7°
99.3

(Pb)

Weight Percentage Lead

Donald T. Hawkins
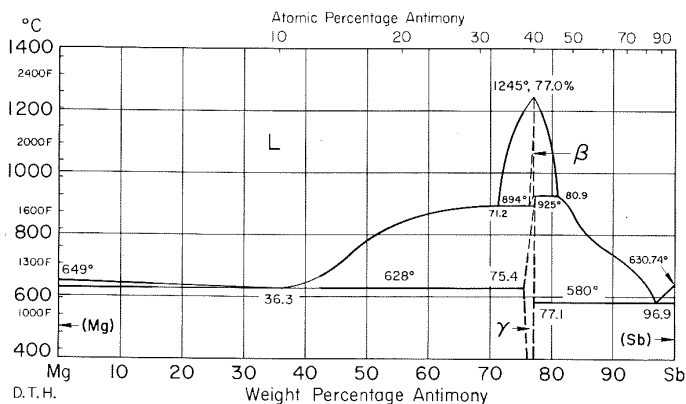
Mg-Pr   Magnesium-Praseodymium

Atomic Percentage Praseodymium

°C

932°

796°

L

799°   767°

752°

(β-Pr)

649°   630°   ε

(α-Pr)

573°

(Mg)   0.5   9.1

528°

γ   δ   ζ

Weight Percentage Praseodymium
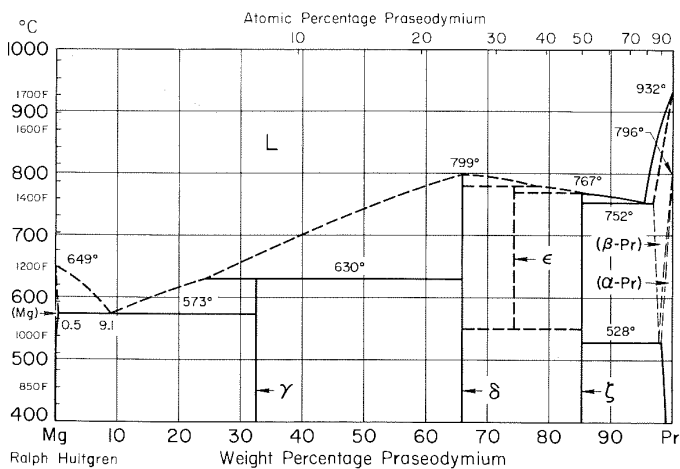
Ralph Hultgren
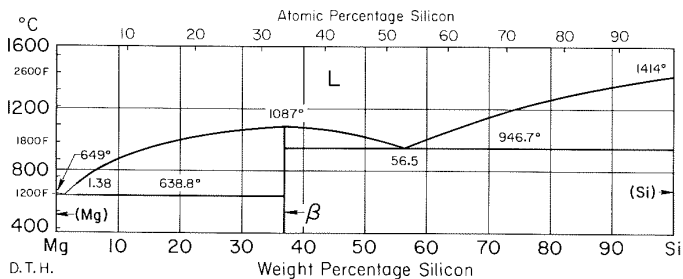
Mg-Pu   Magnesium-Plutonium

Atomic Percentage Plutonium

°C

L₁   L₂

649°   640°

(Mg)   ~63.4   (ε-Pu)

480°   (δ′-Pu)

457°   (δ-Pu)

315°   (γ-Pu)

ζ

207°   (β-Pu)

122°   (α-Pu)

η

Weight Percentage Plutonium

R. H.

Mg-Sb   Magnesium-Antimony

Atomic Percentage Antimony

°C

1245°, 77.0%

L   β

894°   925°   80.9

71.2

649°   628°   75.4   630.74°

(Mg)   36.3   580°

γ   77.1   96.9

(Sb)

Weight Percentage Antimony

D. T. H.

Mg-Si   Magnesium-Silicon

Atomic Percentage Silicon

°C

L   1414°

1087°

649°   946.7°

56.5

1.38   638.8°

(Mg)   β   (Si)

Weight Percentage Silicon

D. T. H.

Mg-Sn   Magnesium-Tin

Atomic Percentage Tin

°C

771.5°, 70.6%

L

649°

37.6   561.2°

(Mg)

14.85

4.4% at 400°   β

203.5°   231.968°
97.9

0.45% at 200°   (β-Sn)

Weight Percentage Tin

D. T. H.

Mg-Sr   Magnesium-Strontium

Atomic Percentage Strontium

°C

769°

L   680°

(β-Sr)

649°   606°   39.8   608°   557°

582°   592°

18.4

426°

89.5   95.5

(Mg)   γ   δ   ε   ζ   (α-Sr)

Weight Percentage Strontium

R. H.
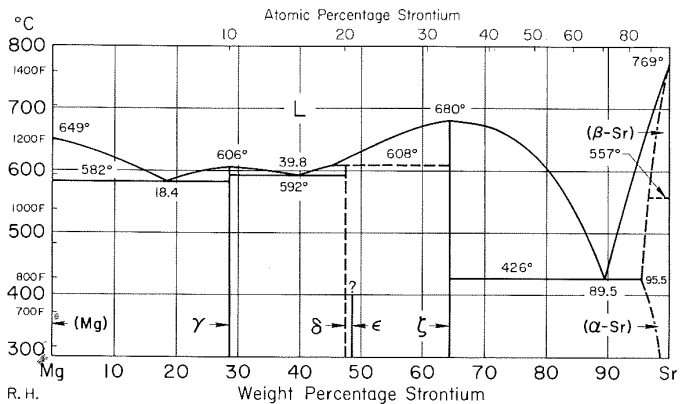
Mg-Th   Magnesium-Thorium

S. L. Couling
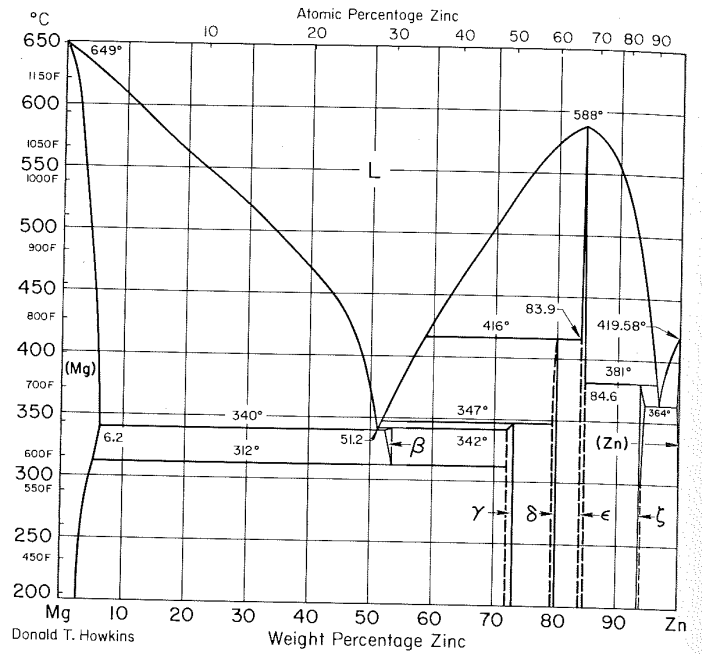
Mg-Tl   Magnesium-Thallium

Ralph Hultgren

Mg-Zn   Magnesium-Zinc

Donald T. Howkins

D. T. H.
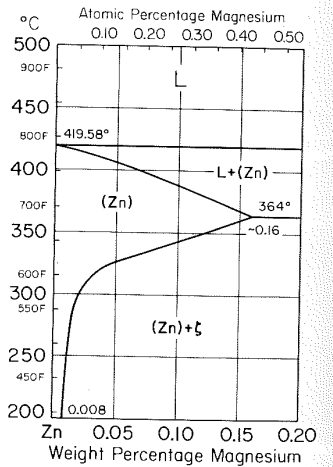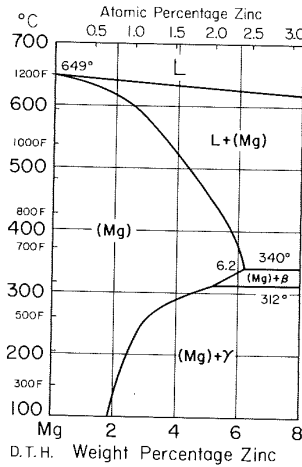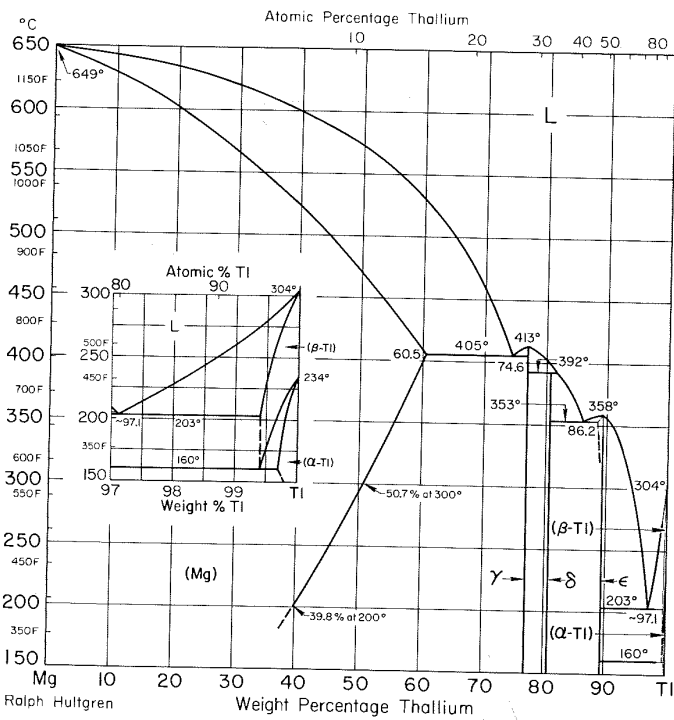
Mg-Y   Magnesium-Yttrium

R. H.
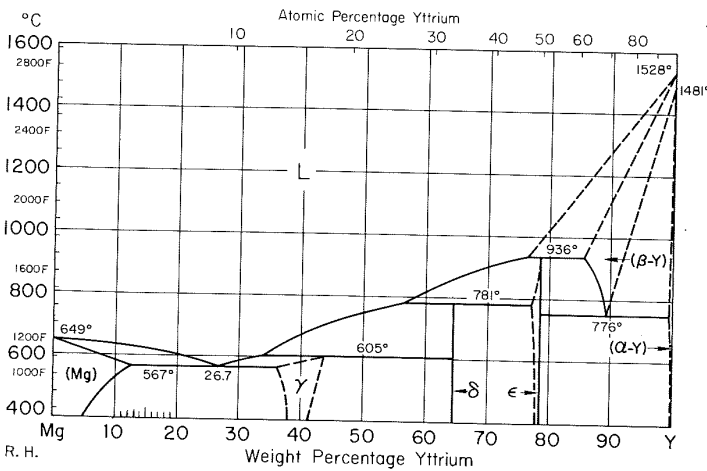
Mg-Zr   Magnesium-Zirconium

D. T. H.

Mn-Ni   Manganese-Nickel

Atomic Percentage Manganese

Donald T. Hawkins   Weight Percentage Manganese
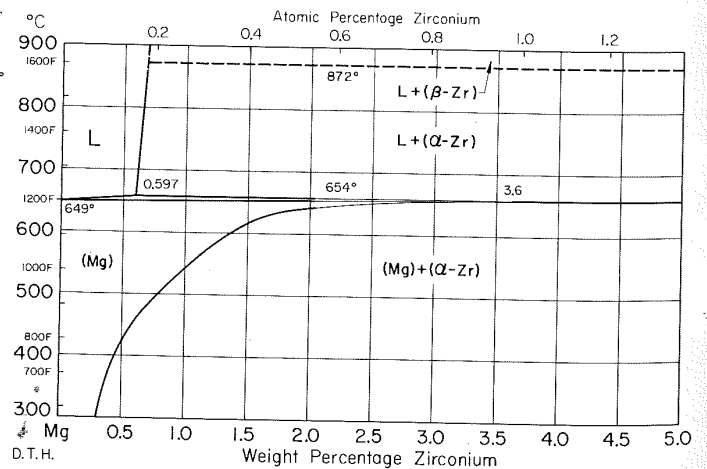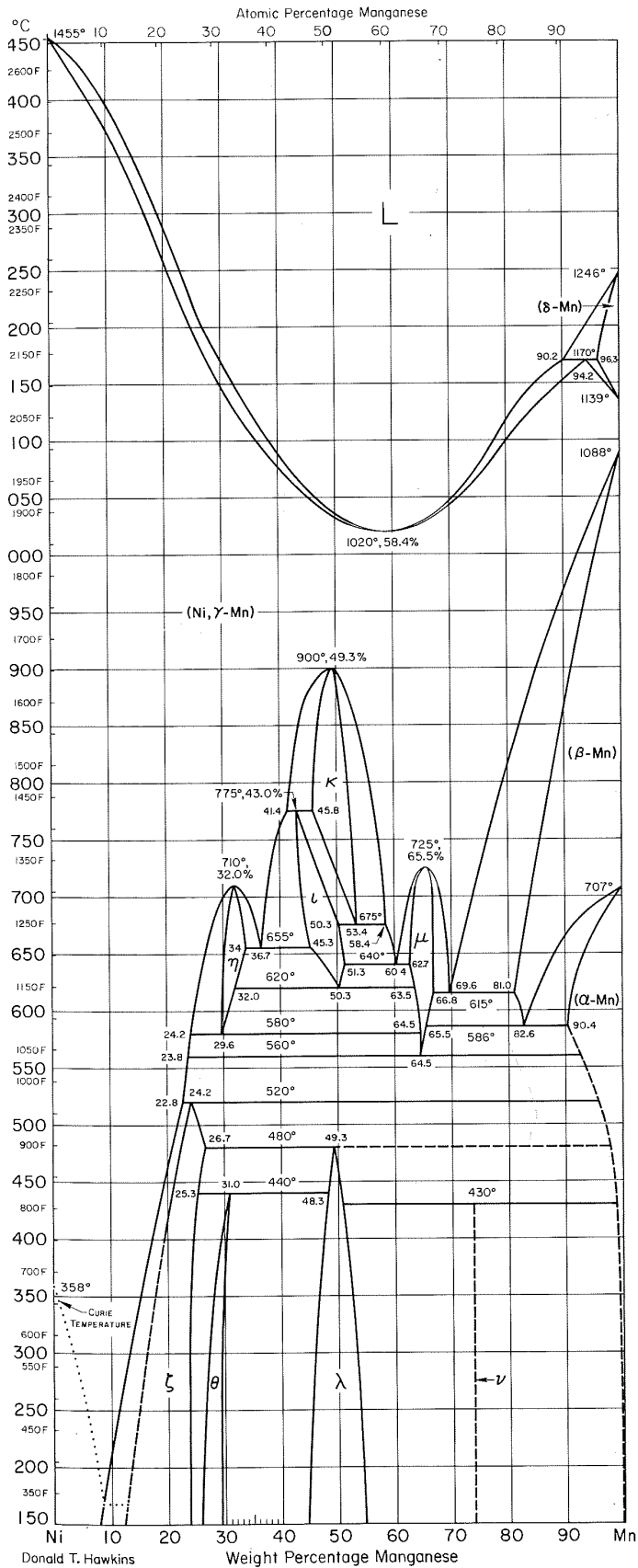
Mn-Pd   Manganese-Palladium

Atomic Percentage Manganese

D.T.H.   Weight Percentage Manganese
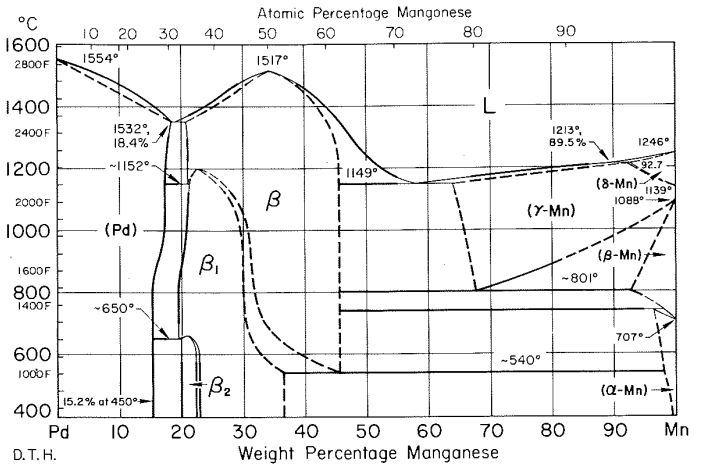
Mn-Pt   Manganese-Platinum

Atomic Percentage Manganese

D.T.H.   Weight Percentage Manganese
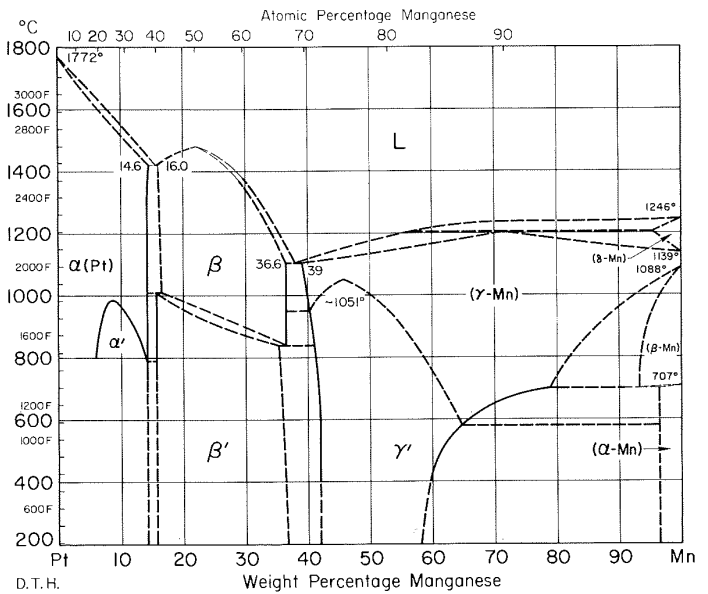
Mn-Pu   Manganese-Plutonium

Atomic Percentage Plutonium

Philip A. Tucker   Weight Percentage Plutonium
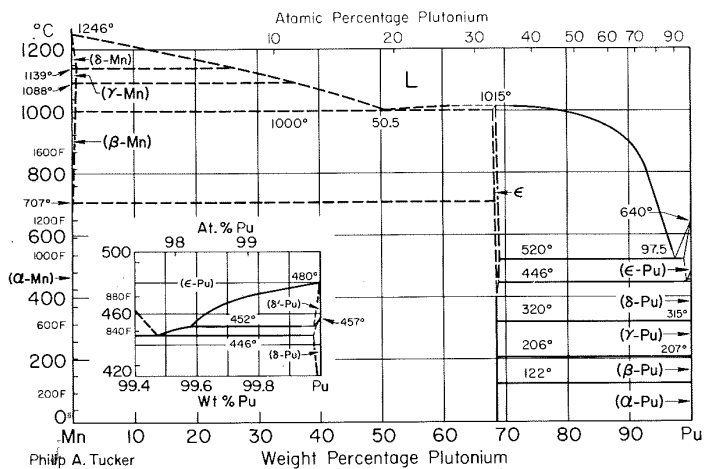
Mn-Si　Manganese-Silicon

Donald T. Hawkins
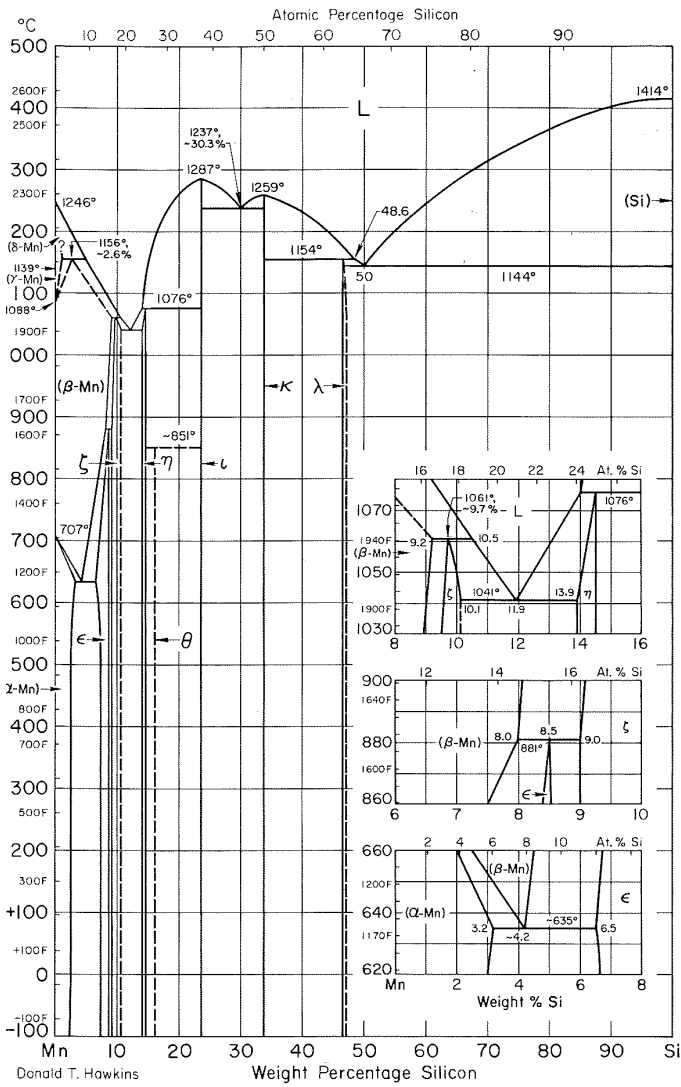
Mn-Ti　Manganese-Titanium

Doniel J. Maykuth
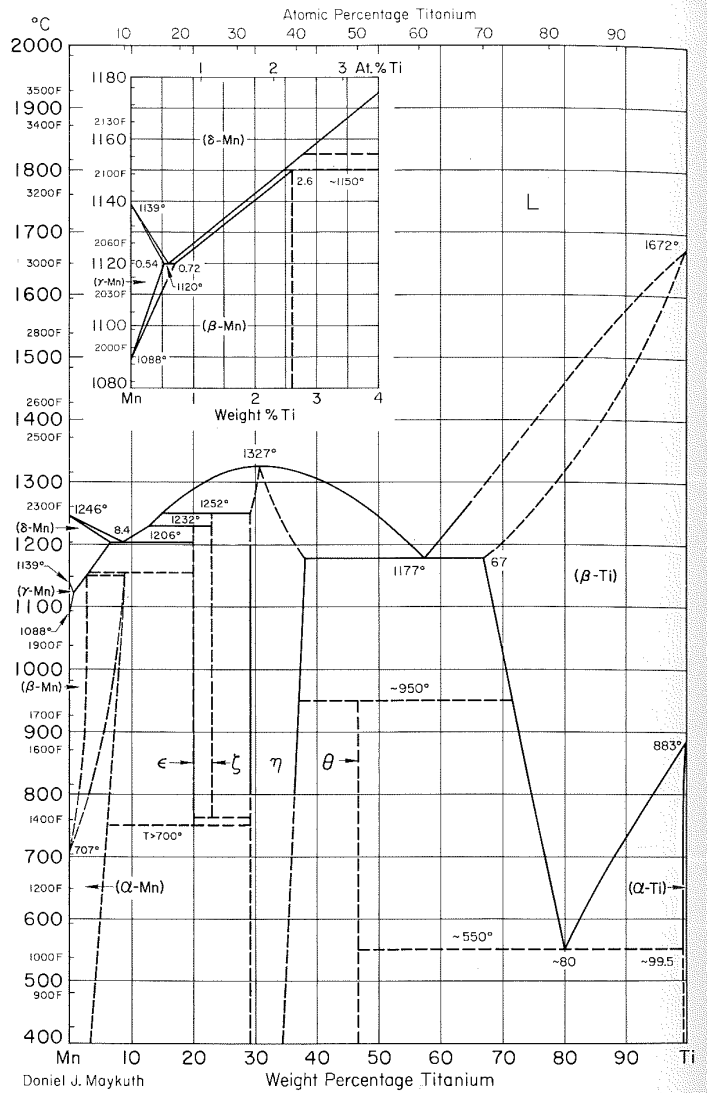
Mn-Sn　Manganese-Tin

D.T.H.
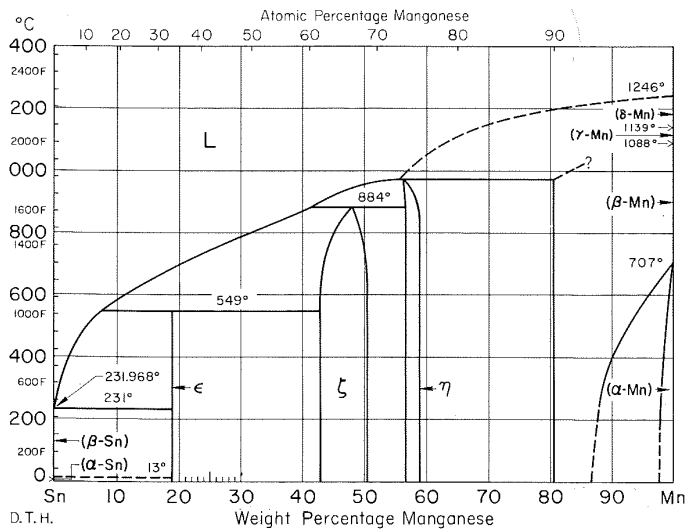
Mn-U　Manganese-Uranium

D.T.H.
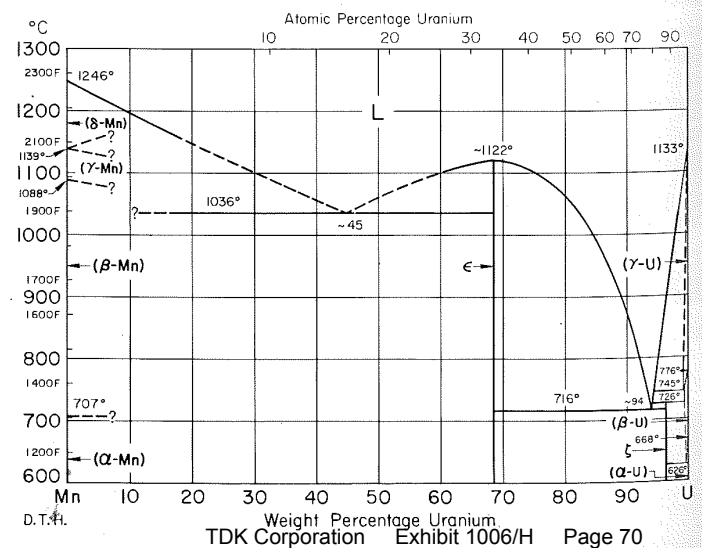
Mn-Zn   Manganese-Zinc
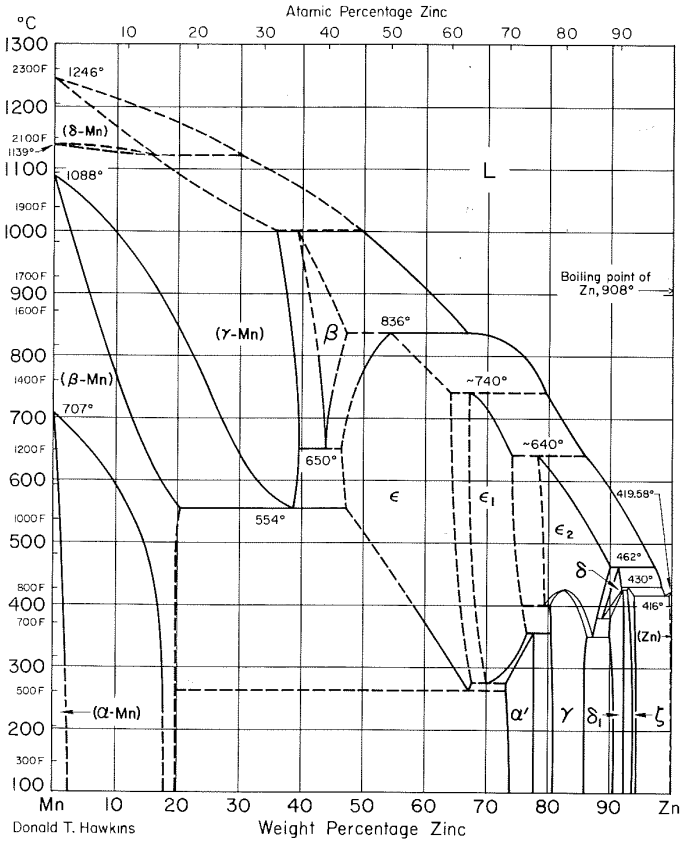
Donald T. Hawkins

Mn-Zr   Manganese-Zirconium

D. T. H.

D. T. H.
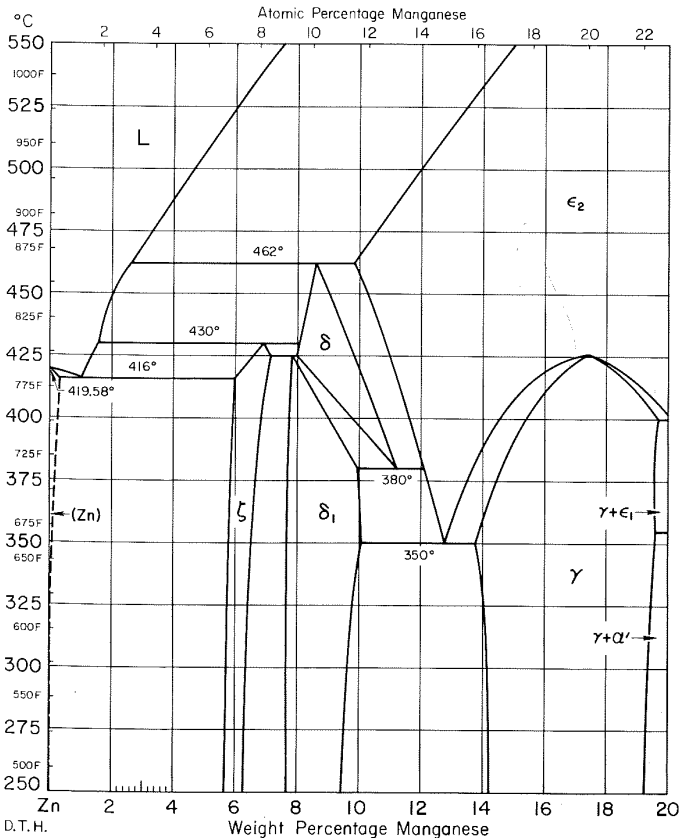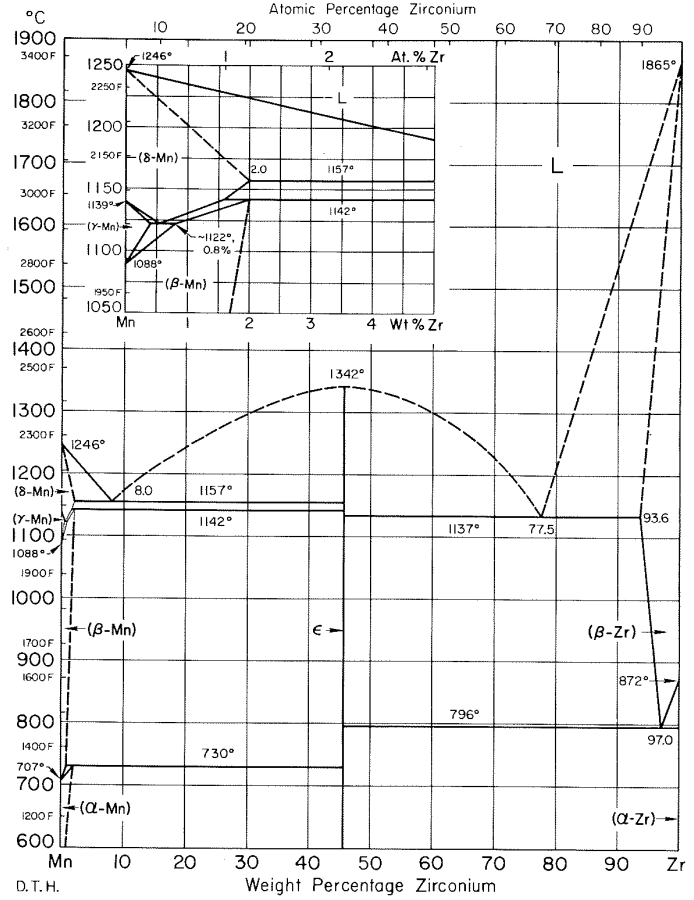
Mo-Ni   Molybdenum-Nickel

D. T. H.

Mo-Os   Molybdenum-Osmium

°C
Atomic Percentage Osmium
3000
2623°
2434±10° 54   65
~32.5 2384±10° ~45.5
~27.5 2214±10° 40
2600
2200
1800
1400
1000
L
(Mo)
β→ σ
(Os)
Mo 10 20 30 40 50 60 70 80 90 Os
A. G. Knopton   Weight Percentage Osmium

Mo-Pd   Molybdenum-Palladium

°C
Atomic Percentage Molybdenum
2600
L
2400
2200
2000
1800
1762°, 36.6% ~44.2
1742° 93.0
(Mo)
38.5
1600 1554° 1737°, 43.4% β
1400
1200
(Pd)
Pd 10 20 30 40 50 60 70 80 90 Mo
Donald T. Hawkins   Weight Percentage Molybdenum

Mo-Pt   Molybdenum-Platinum

°C
Atomic Percentage Molybdenum
2600
2400
2200
2000
1800
1600
1400
1200
1000
L
2178°, 35.3%
55.5
2023° 2083°
23
~1803°, ~21% δ
1772° 1803° (Mo)
28
~1662° 1602°
(Pt) ~1478° ε
β ~1302° 1302°
32.6 δ'
γ
Pt 10 20 30 40 50 60 70 80 90 Mo
G. L. Selman   Weight Percentage Molybdenum

Mo-Re   Molybdenum-Rhenium

°C
Atomic Percentage Rhenium
3200
3186°
3000
2800
2623°
2600
66 80 2525°
59.5 2444° 68 83.5 92
L
(Mo) σ (Re)
82.5 85.5
1853° 94
X
43 1152°
Mo 10 20 30 40 50 60 70 80 90 Re
A. G. K.   Weight Percentage Rhenium

Mo-Rh   Molybdenum-Rhodium

°C
Atomic Percentage Rhodium
2600 2623°
2400
2200
2000
1800
1600
L
2075°, 68.2%
(Mo) 21.1
1940° 2000° 92.5
40.7 45.5 82.1 85.9 1963°
β
(Rh)
Mo 10 20 30 40 50 60 70 80 90 Rh
Richard M. Waterstrat   Weight Percentage Rhodium

Mo-Ru   Molybdenum-Ruthenium

°C
Atomic Percentage Ruthenium
2600 2623°
2400
2200
2000
1800
L
2254°
(Mo) 1948° 42.9 (Ru)
~32 ~51
σ 1923°
Mo 10 20 30 40 50 60 70 80 90 Ru
A. G. K.   Weight Percentage Ruthenium
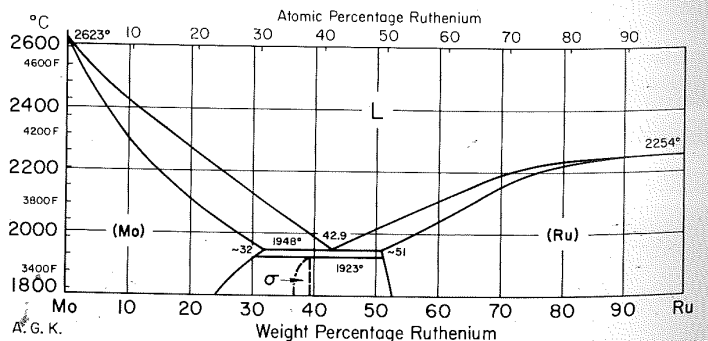
Mo-Si   Molybdenum-Silicon

Donald T. Hawkins
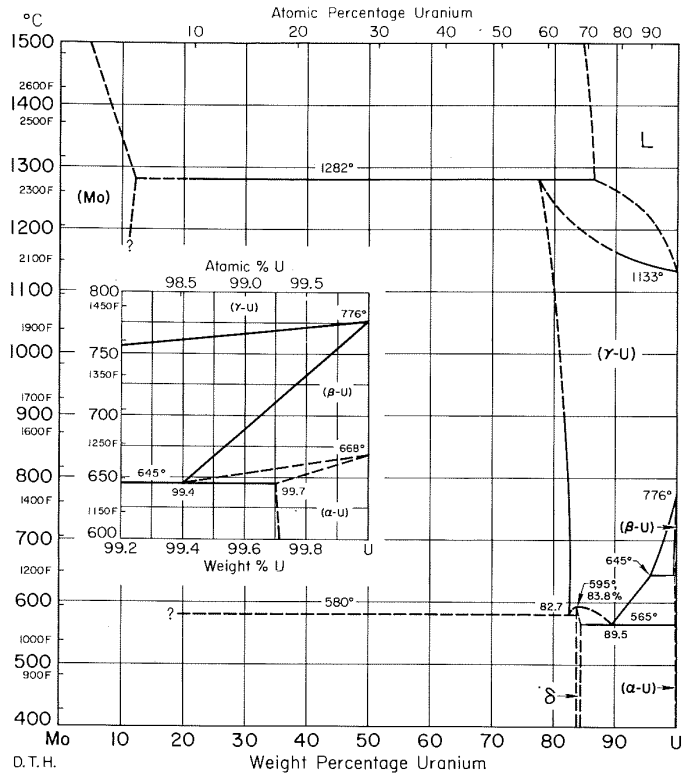
Mo-Ta   Molybdenum-Tantalum

D.T.H.

Mo-Ti   Molybdenum-Titanium

D.T.H.

Mo-U   Molybdenum-Uranium

D.T.H.
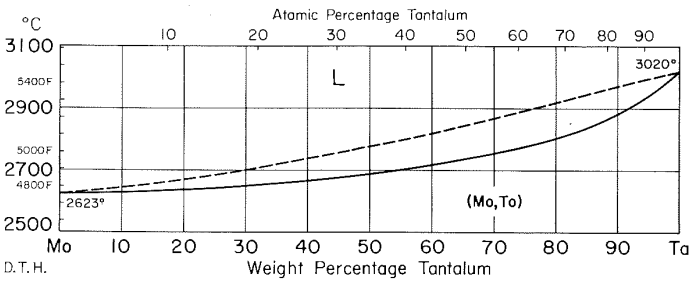
Mo-V   Molybdenum-Vanadium

D.T.H.
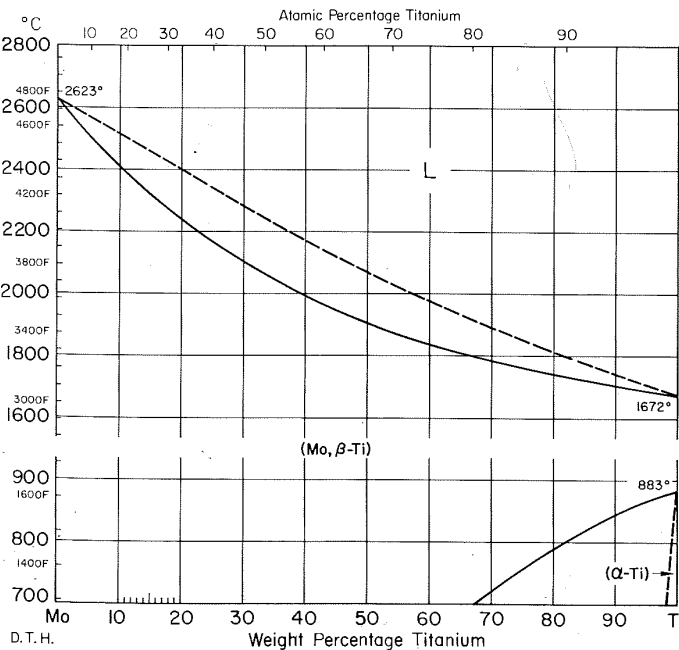
Mo-W   Molybdenum-Tungsten

D.T.H.
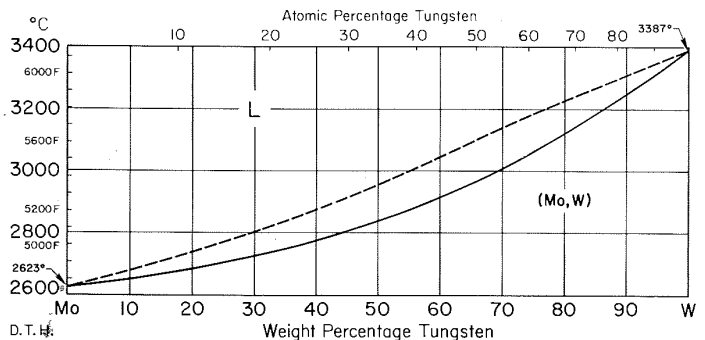
Mo-Zr   Molybdenum-Zirconium

Donald T. Hawkins
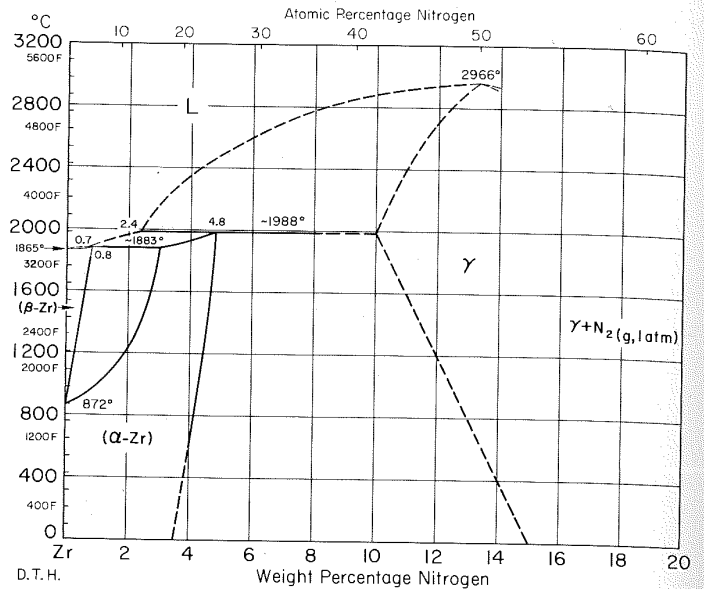
N-Ti   Nitrogen-Titanium

D.T.H.

N-U   Nitrogen-Uranium

D.T.H.

N-Zr   Nitrogen-Zirconium

D.T.H.

Na-Pb   Sodium-Lead

D.T.H.
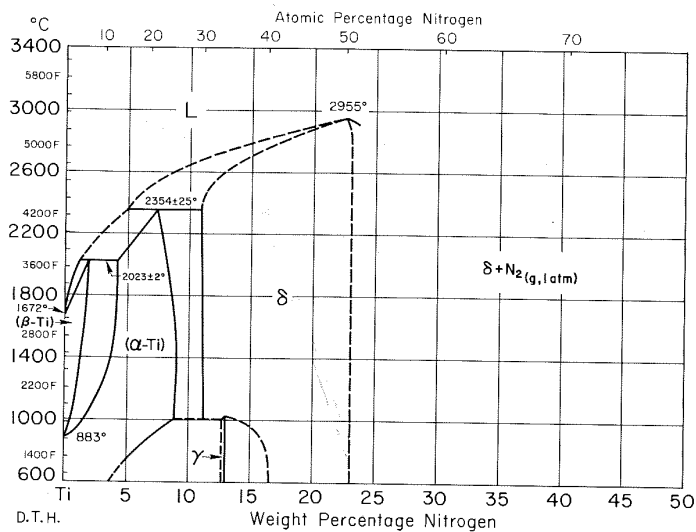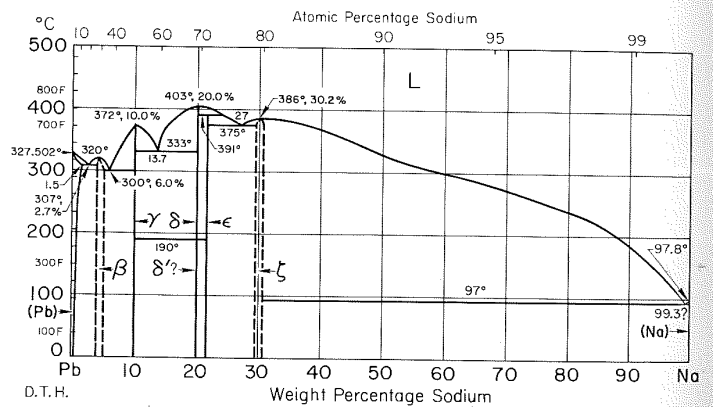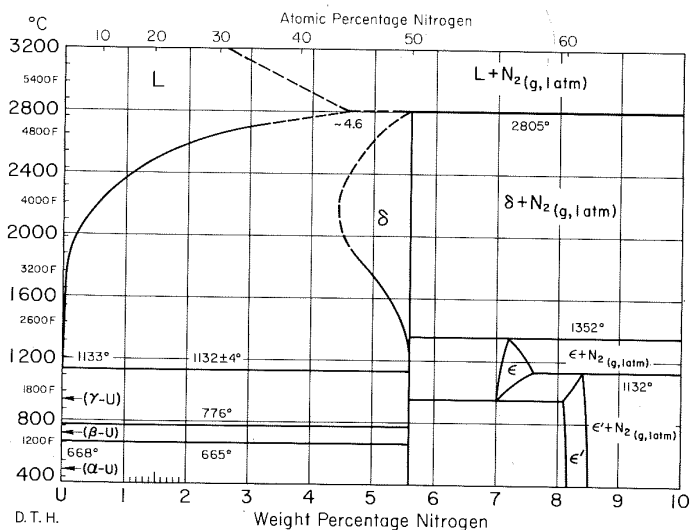
Na-Rb   Sodium-Rubidium

D.T.H.
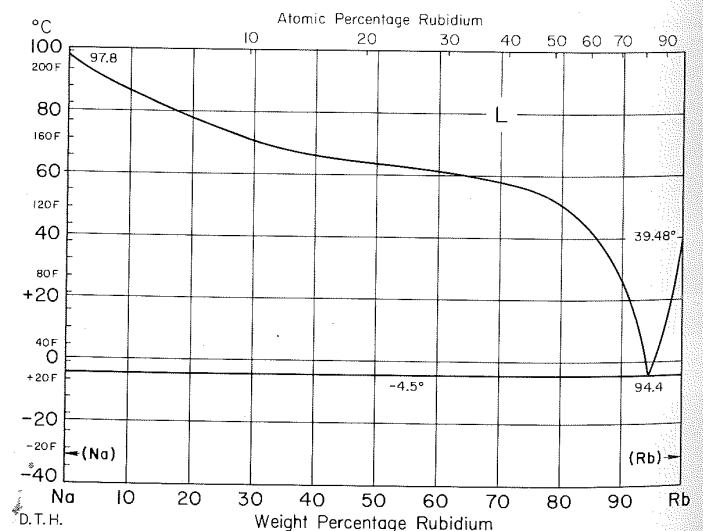
Na-Sb   Sodium-Antimony

Donald T. Hawkins
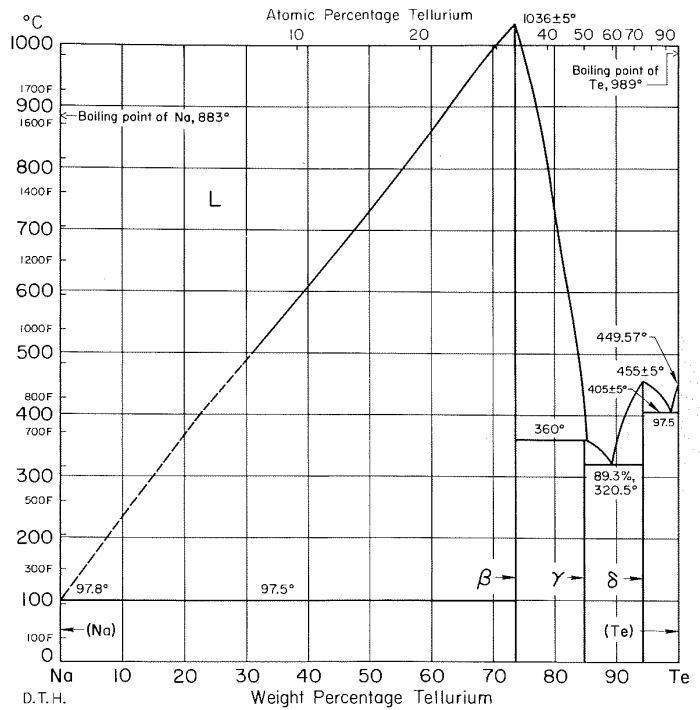
Na-Se   Sodium-Selenium

D. T. H.

Na-Sn   Sodium-Tin

D. T. H.

Na-Te   Sodium-Tellurium

D. T. H.
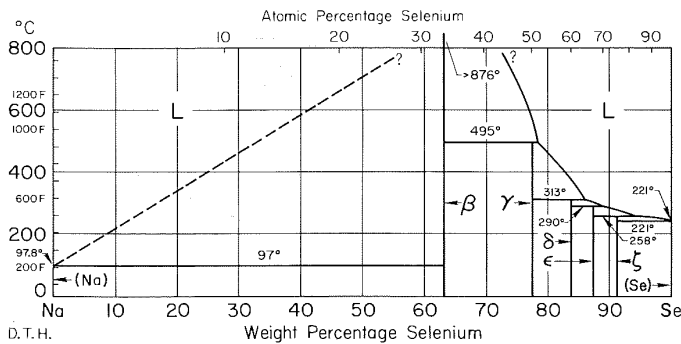
Na-Tl   Sodium-Thallium

D. T. H.

Na-Zn   Sodium-Zinc

D. T. H.
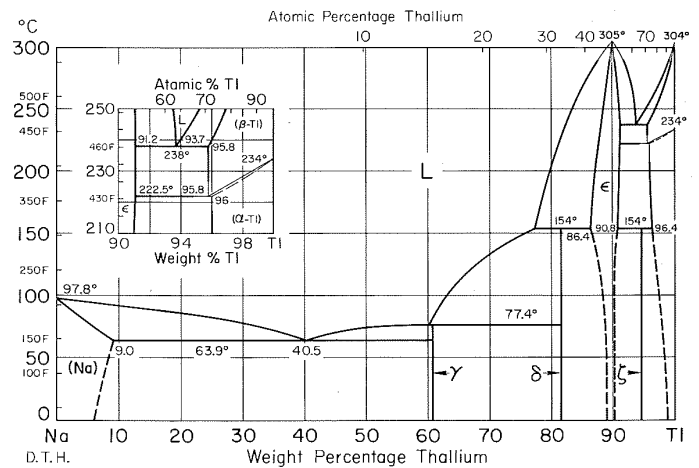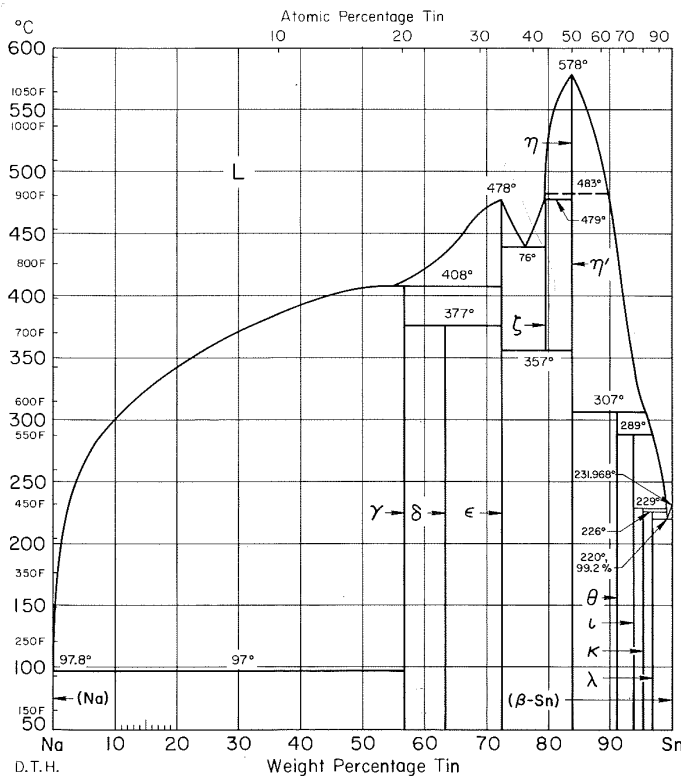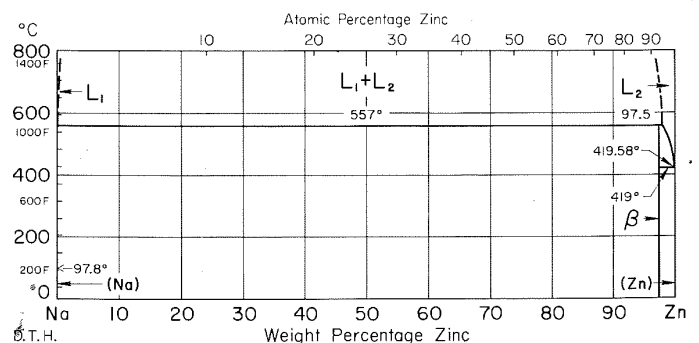
Nb systems

See Cb

Ni-O　Nickel-Oxygen

Donald T. Hawkins

Ni-Pb　Nickel-Lead

D.T.H.

Ni-Pd　Nickel-Palladium

D.T.H.

Ni-Pt　Nickel-Platinum

D.T.H.
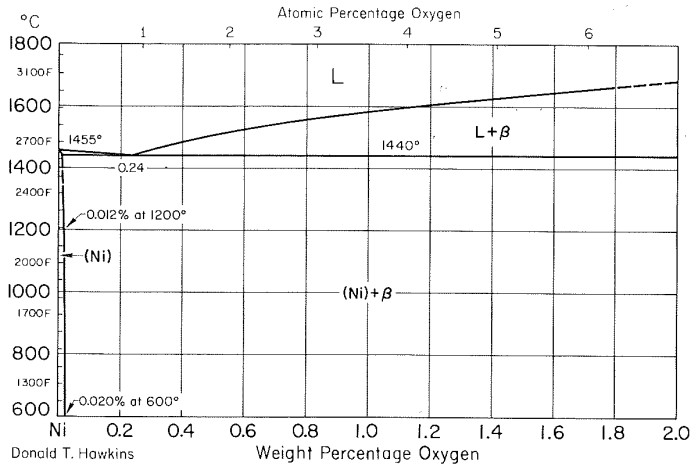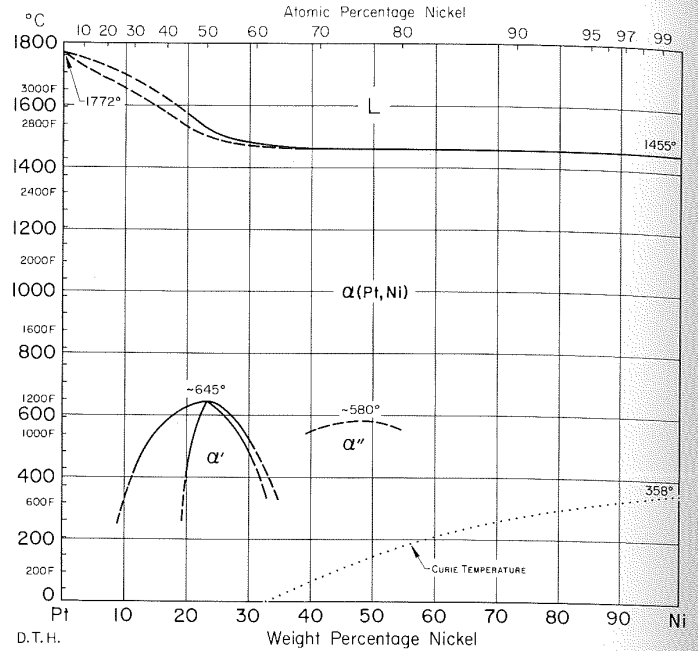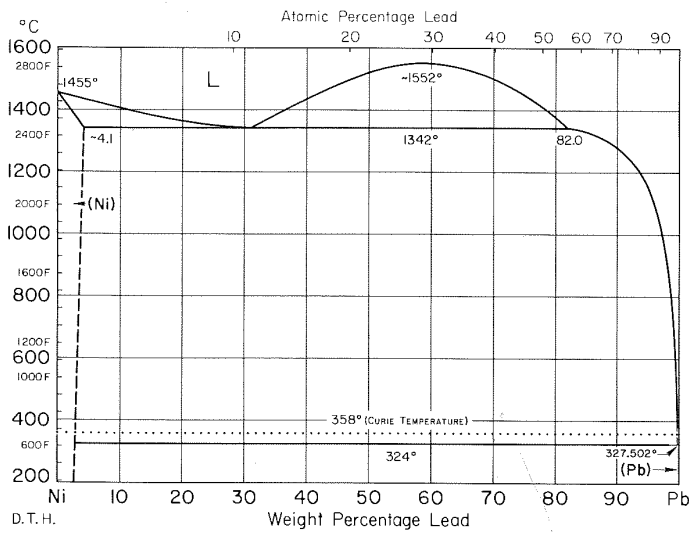
Ni-Re　Nickel-Rhenium

D.T.H.

Ni-Ru　Nickel-Ruthenium

D.T.H.

Ni-S   Nickel-Sulfur

Donald T. Hawkins

Ni-Si   Nickel-Silicon

D.T.H.

Ni-Sn   Nickel-Tin

D.T.H.

Ni-Sb   Nickel-Antimony

D.T.H.

Ni-Ta   Nickel-Tantalum

Atomic Percentage Tantalum

Donald T. Hawkins
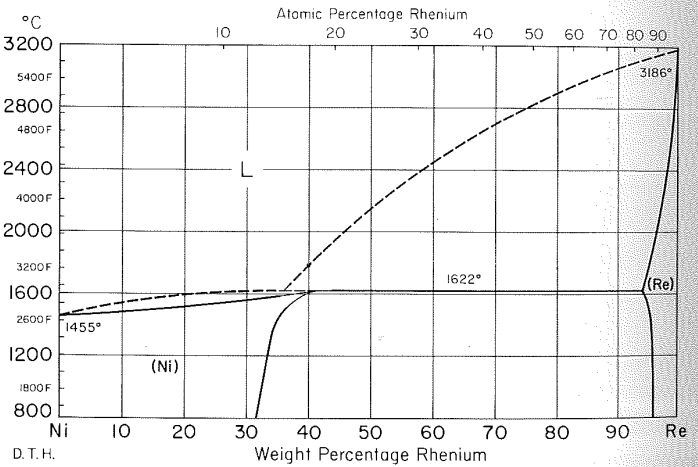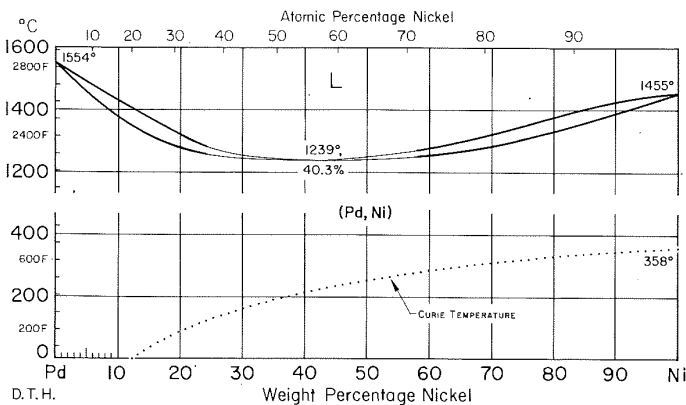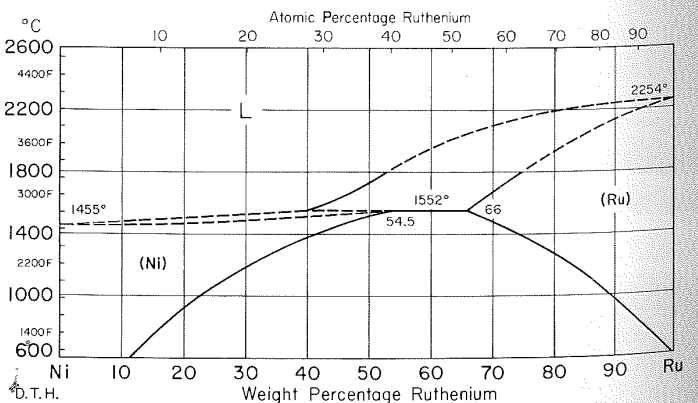
Weight Percentage Tantalum

Ni-V   Nickel-Vanadium

Atomic Percentage Vanadium

D.T.H.

Weight Percentage Vanadium

Ni-Ti   Nickel-Titanium

Atomic Percentage Titanium

D.T.H.   Weight Percentage Titanium

Ni-W   Nickel-Tungsten

Atomic Percentage Tungsten

D.T.H.

Weight Percentage Tungsten

Ni-Zn   Nickel-Zinc

Atomic Percentage Zinc
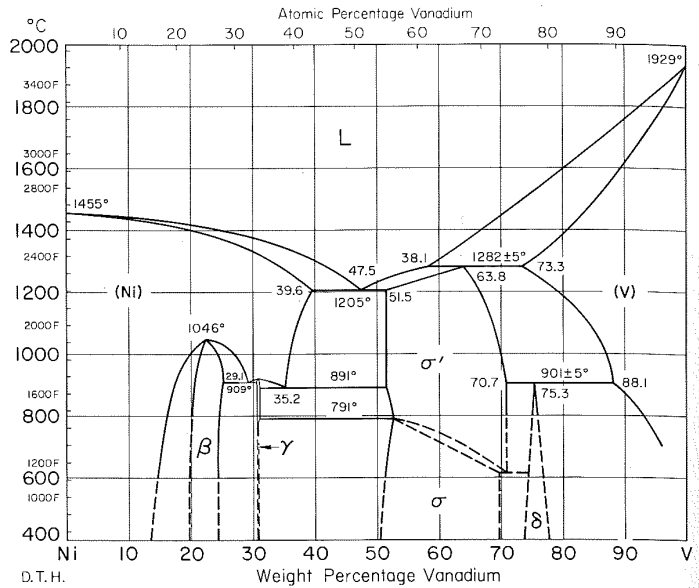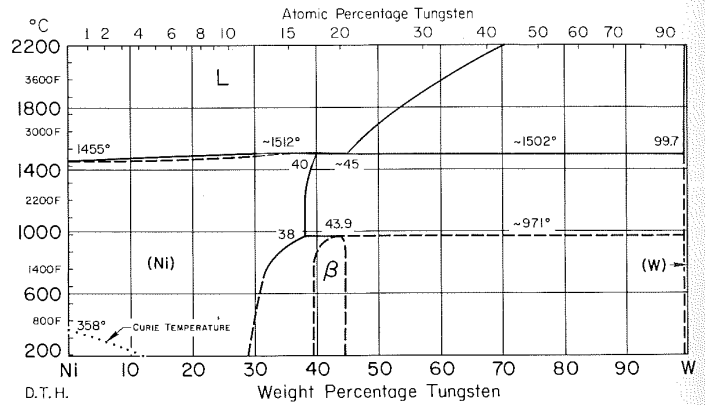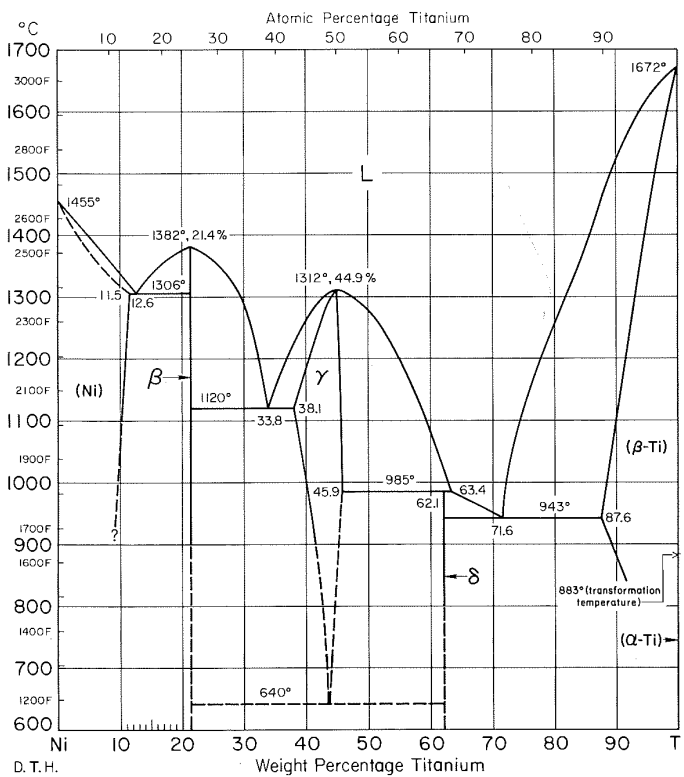
Y. A. Chang   Weight Percentage Zinc
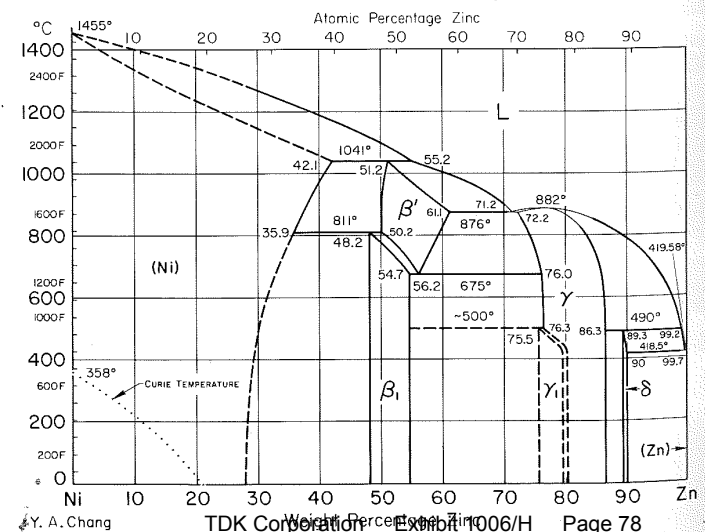
Ni-Zr   Nickel-Zirconium

Donald T. Hawkins
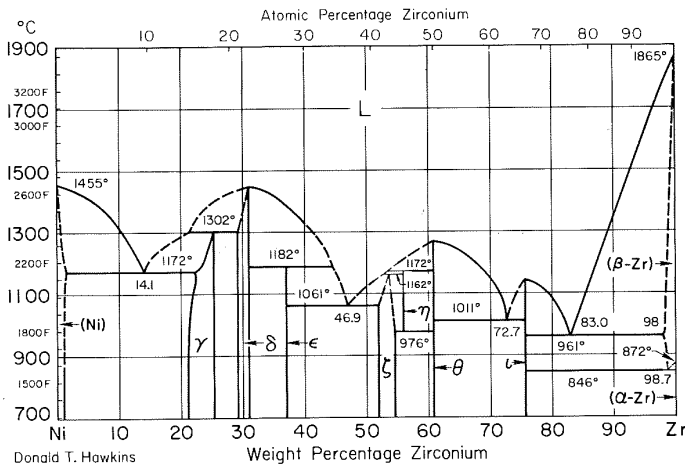
O-Ti   Oxygen-Titanium

D.T.H.
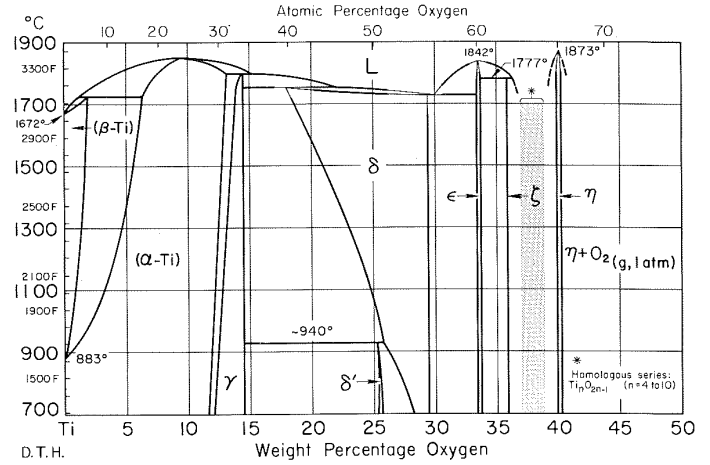
Np-U   Neptunium-Uranium

D.T.H.
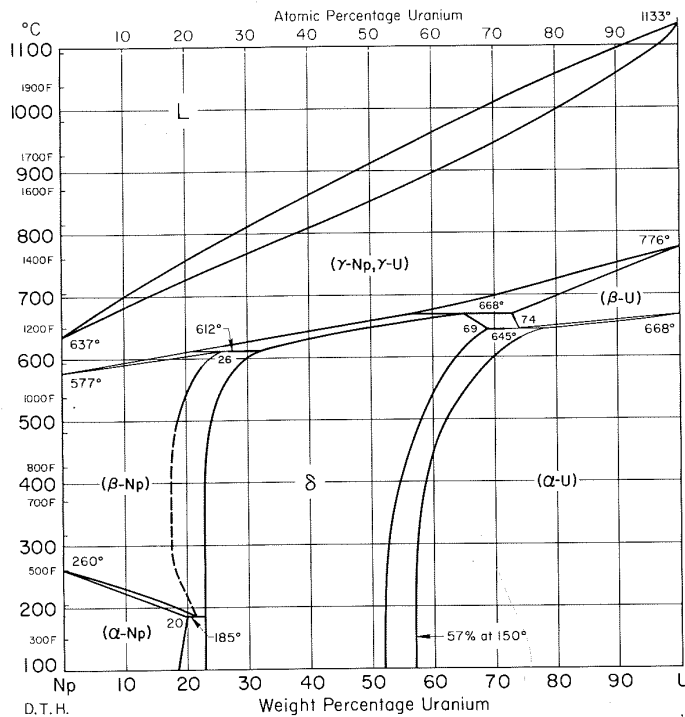
O-V   Oxygen-Vanadium

David G. Alexander

O-Pb   Oxygen-Lead

D.T.H.
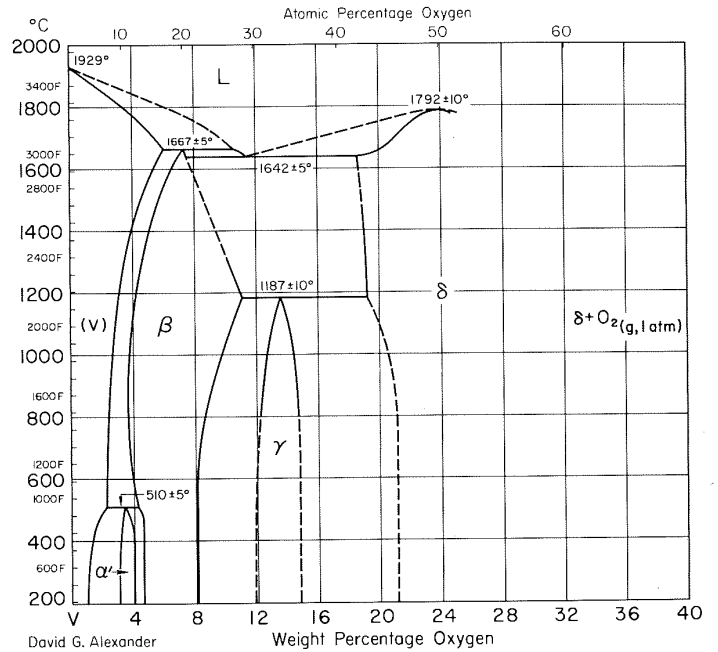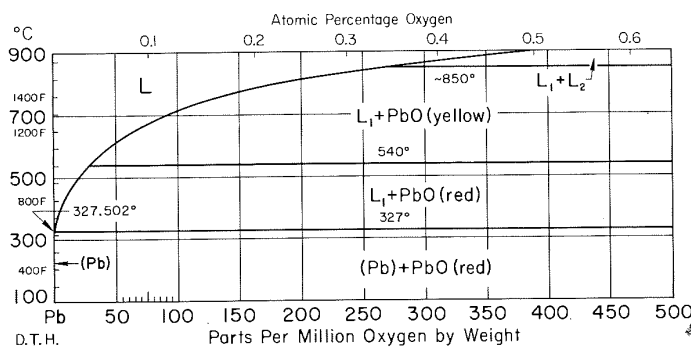
O-Zr   Oxygen-Zirconium

D.T.H.
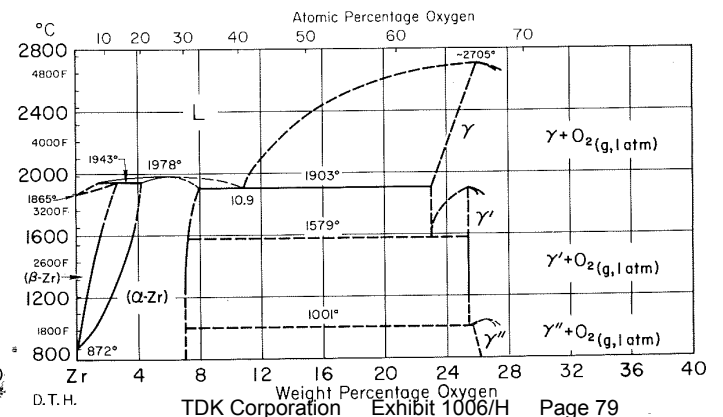
Os-Pd Osmium-Palladium
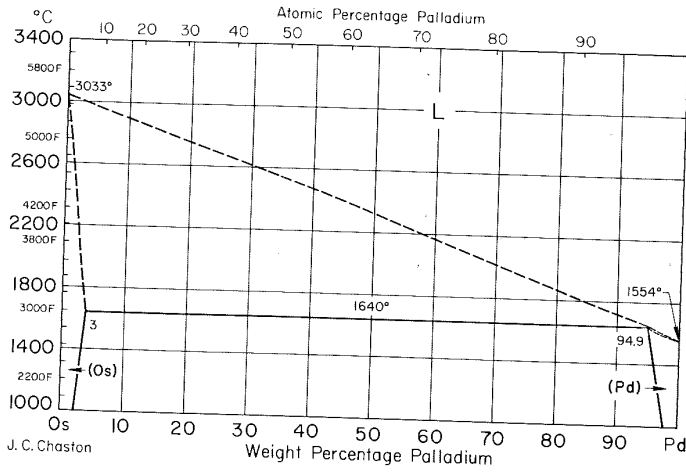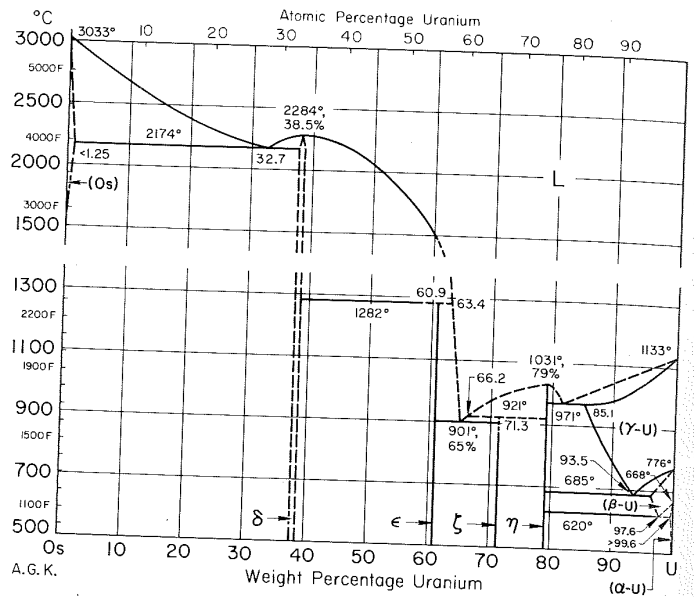
J. C. Chaston

Os-Re Osmium-Rhenium
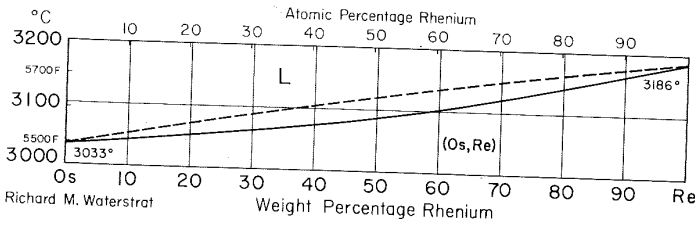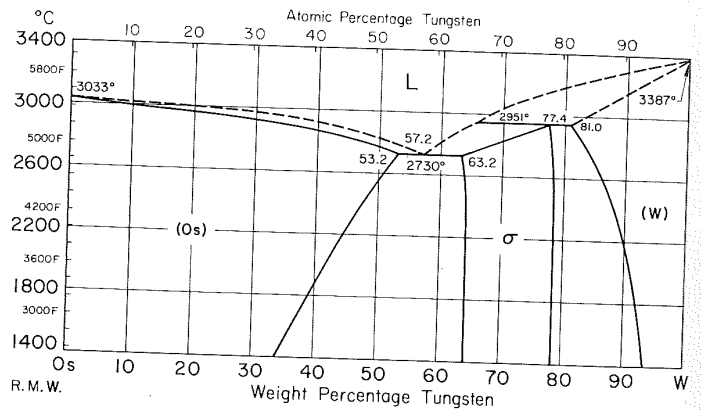
Richard M. Waterstrat

Os-Ru Osmium-Ruthenium
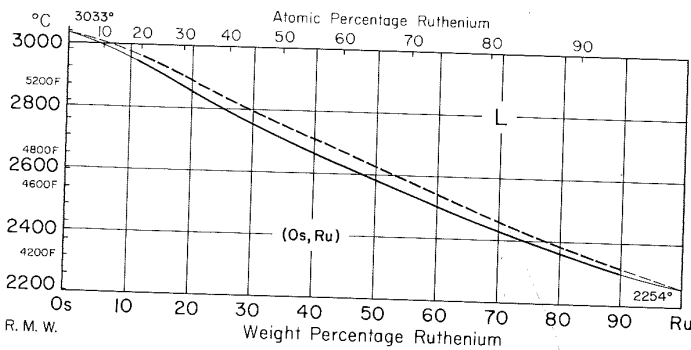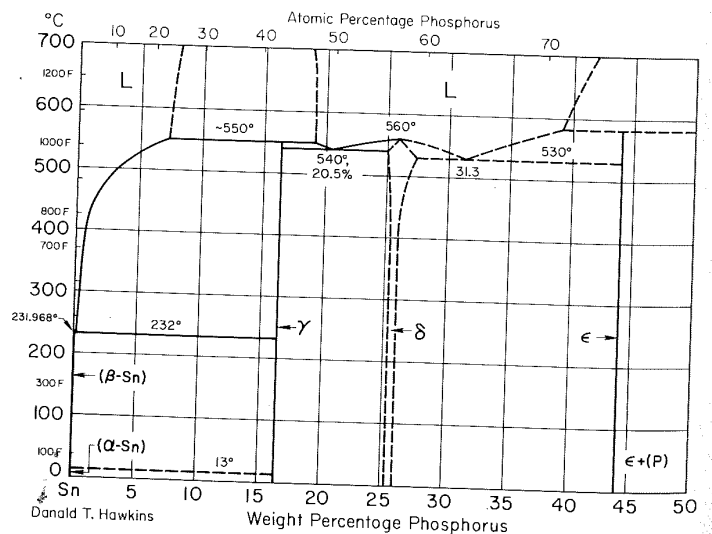
R. M. W.

Os-Ta Osmium-Tantalum

A. G. Knapton

Os-U Osmium-Uranium

A. G. K.

Os-W Osmium-Tungsten

R. M. W.

P-Sn Phosphorus-Tin

Donald T. Hawkins

Pb-Pd   Lead-Palladium

Atomic Percentage Lead

°C

C. DiMartini

Weight Percentage Lead

Pb-Sb   Lead-Antimony

Atomic Percentage Antimony

°C

C. DiM.

Weight Percentage Antimony

Pb-Pt   Lead-Platinum

Atomic Percentage Lead

°C

C. DiM.

Weight Percentage Lead

Pb-Se   Lead-Selenium

Atomic Percentage Selenium

°C

C. DiM.

Weight Percentage Selenium

Pb-S   Lead-Sulfur

Atomic Percentage Sulfur

°C

Donald T. Hawkins

Weight Percentage Sulfur

Pb-Si   Lead-Silicon

Atomic Percentage Silicon

°C

D.T.H.

Weight Percentage Silicon

Pb-Sn   Lead-Tin

°C
Atomic Percentage Tin
C. DiMartini
Weight Percentage Tin

327.502°
L
231.968°
(Pb)
19
183°
61.9
2.5
(β-Sn)
13°
(α-Sn)

Pb-Te   Lead-Tellurium

°C
Atomic Percentage Tellurium
Donald T. Hawkins
Weight Percentage Tellurium

925°, 38.1%
Boiling point of Te, 989°
L
β
326.5°
378°
72.4
449.57°
92
(Te)
(Pb)

Pb-Tl   Lead-Thallium

°C
Atomic Percentage Thallium
D.T.H.
Weight Percentage Thallium

L
380°, 62.2%
327.502°
86.0
312°
304°
94.0
92.7
(β-Tl)
234°
(Pb)
180°
(α-Tl)

Pb-Zn   Lead-Zinc

°C
Atomic Percentage Zinc
C. DiM.
Weight Percentage Zinc

L₁
798°, 45%
L₂
L₁+L₂
417.66°
419.58°
2
318.2°
99.1
.502°
0.5
(Pb)
(Zn)

Pd-Pt   Palladium-Platinum
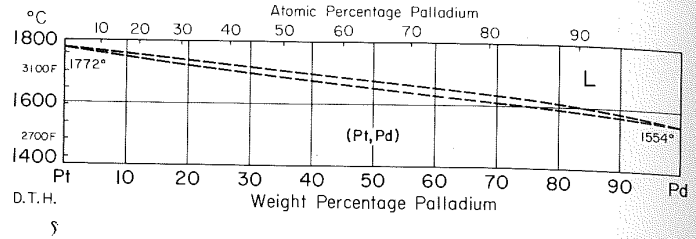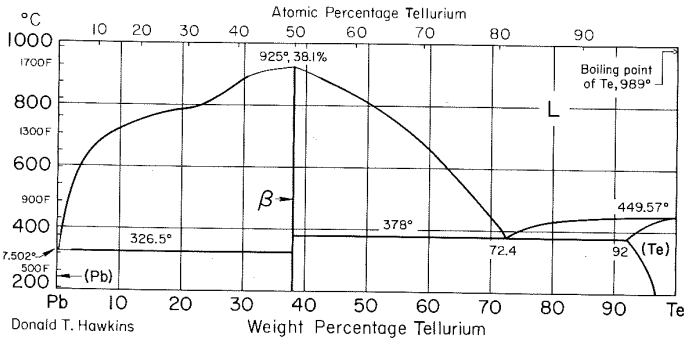
°C
Atomic Percentage Palladium
D.T.H.
Weight Percentage Palladium

1772°
L
(Pt,Pd)
1554°

Pd-Rh   Palladium-Rhodium

°C
Atomic Percentage Rhodium
A.S. Darling
Weight Percentage Rhodium

L
1963°
α(Pd,Rh)
1554°
846°
α₁
α₁+α₂
α₂

Pd-Ru   Palladium-Ruthenium

°C
Atomic Percentage Ruthenium
A.S.D.
Weight Percentage Ruthenium

L
2254°
1554°
16.5
1583°
82
(Ru)
(Pd)
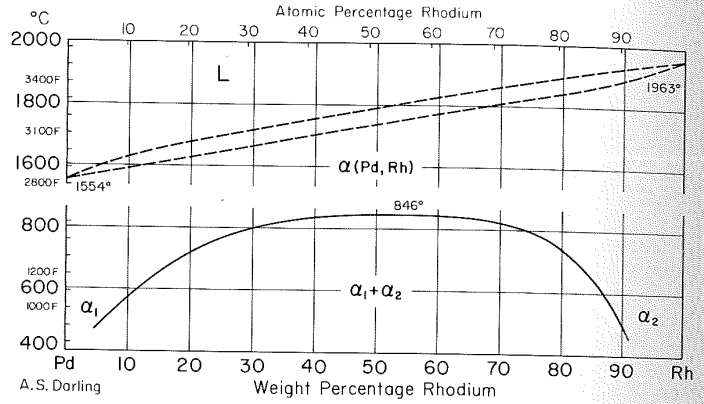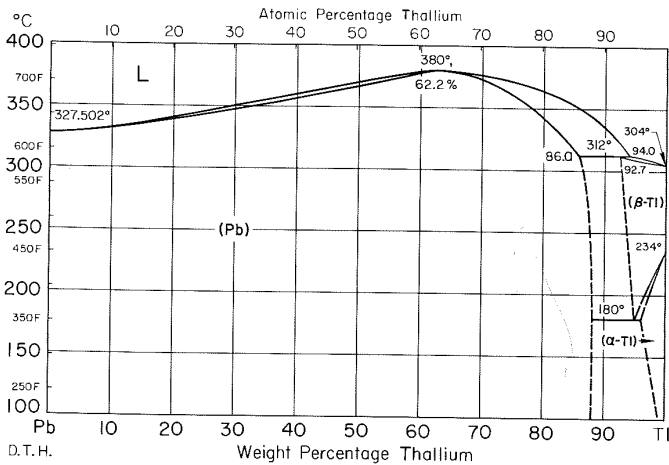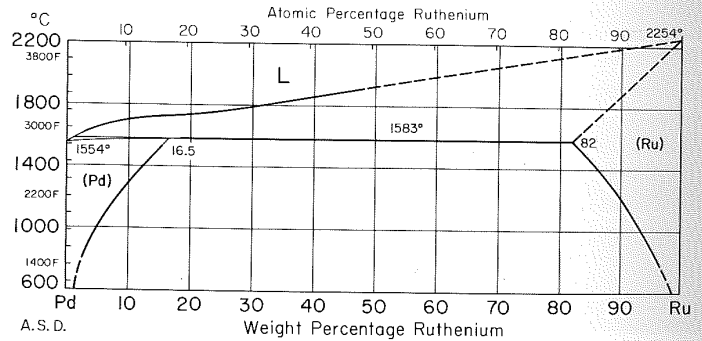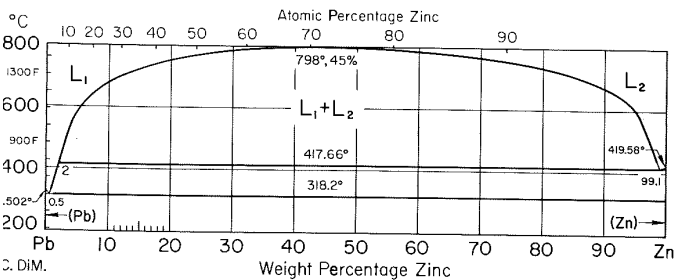
Pd-Ti   Palladium-Titanium

°C
Atomic Percentage Titanium
D.T.H.
Weight Percentage Titanium

1672°
1554°
~6.8
1452°
1392°
1312°
1352°
1282°
L
1142°
~50.1
(Pd)
ε
ζ
θ
(β-Ti)
951°
883°
γ
δ
η
796°
781°
ι
κ
578°
520°
510°
~97.7
η'
(α-Ti)

Pd-V   Palladium-Vanadium

°C

Atomic Percentage Vanadium

1929°

1800 (3100F)
1600 (2800F) 1554°
L
1400 (2400F) 1340° / 44.8 / 39.8 / 41.8
1200 (2000F) (Pd)   (V)
1000 (1600F) 905°, 19.0%
815°, 13.8%   35.0   840°   58.9   69.3
800 (1300F) 720°
600   β   L   γ   δ

Pd 10 20 30 40 50 60 70 80 90 V

Richard M. Waterstrat   Weight Percentage Vanadium

Pt-V   Platinum-Vanadium

°C

Atomic Percentage Vanadium

2000 (3500F)
1805°, 10.1%
1800 (3100F) 1772°   L   37.9   1929°
31.2 / 1720° / 34.6 / 54.0 / 1800° / 65.3
25.7
1600 (2700F) 1500°, 20.7% / 24.2
1400 (2400F) (Pt)   1410°   ε   (V)
1200 (2000F) 1105°, 11.5%
1015°, 8.0% / 14.3
1000 (1700F) ~980°
800 (1300F) β   γ   δ
600

Pt 10 20 30 40 50 60 70 80 90 V

R.M.W.   Weight Percentage Vanadium

Pd-W   Palladium-Tungsten

°C

Atomic Percentage Tungsten

2000 (3400F)
23.5 / 33 / 1815° / 97
1600 (2600F) 1554°   L   (Pd)   32   (W)
1200

Pd 10 20 30 40 50 60 70 80 90 W

J. C. Chaston   Weight Percentage Tungsten

Pt-W   Platinum-Tungsten

°C

Atomic Percentage Tungsten

3600 (6200F)
3387°
3200 (5400F) L
2800 (4800F)
2400 (4000F) ~2464°   (W)
2000 (3200F) (Pt)   ?   ?
1600 1772°

Pt 10 20 30 40 50 60 70 80 90 W

D.T.H.   Weight Percentage Tungsten

Pt-Rh   Platinum-Rhodium

°C

Atomic Percentage Rhodium

2000 (3500F)
1900 (3400F) L   1963°
1800 (3200F) (Pt,Rh)
1772°
1700

Pt 10 20 30 40 50 60 70 80 90 Rh

A. S. Darling   Weight Percentage Rhodium

Pt-Ti   Platinum-Titanium

°C

Atomic Percentage Titanium

2000 (3500F) 1953°
1833°
1800 (3000F) 1772° / 15 / 1783°   L   1672°
1600 (2700F) γ
1372°
1400 (2300F) 32 / 1322° / 57.1 / (β-Ti)
1200 (2100F) δ   ε
1000 (1700F) 883°
88.1
800   841°   (α-Ti)   98

Pt 10 20 30 40 50 60 70 80 90 Ti

Donald T. Hawkins   Weight Percentage Titanium

Pt-Zr   Platinum-Zirconium

°C

Atomic Percentage Zirconium

2200 (3900F) 2154°
2104°
2000 (3500F) 1963° / 2004°   L
1800 (3100F) 1772°   1727°   1865°
1600 (2700F)
1400 (2300F)
1200 (2100F) (Pt)   γ   δ   ε   ~64   (β-Zr)
1000 (1700F)
872°
800 (1300F)   827°   ~91.5   >99
600   (α-Zr)

Pt 10 20 30 40 50 60 70 80 90 Zr
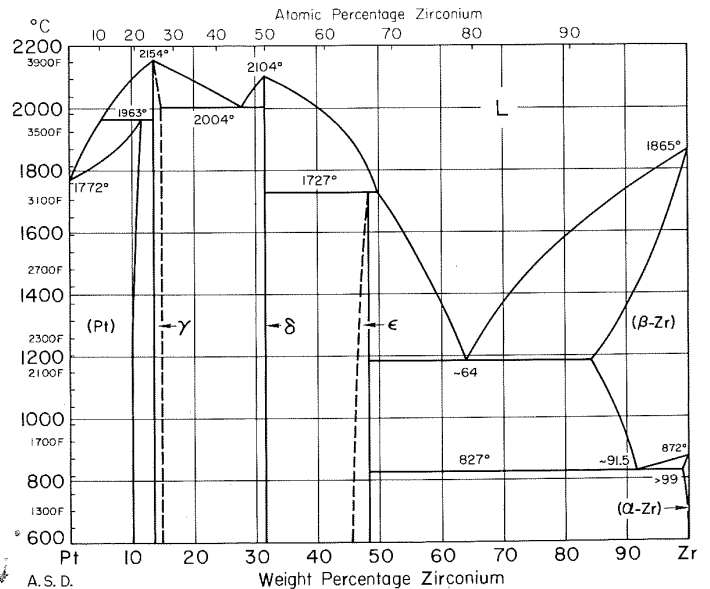
A.S.D.   Weight Percentage Zirconium

Pu-U   Plutonium-Uranium

Philip A. Tucker

P. A. T.
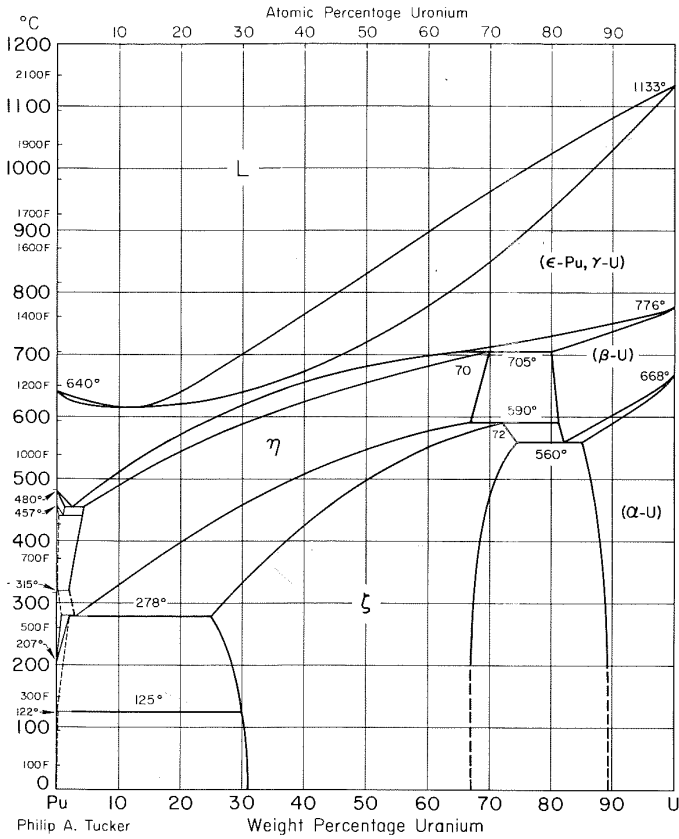
Re-Rh   Rhenium-Rhodium

A. G. Knapton
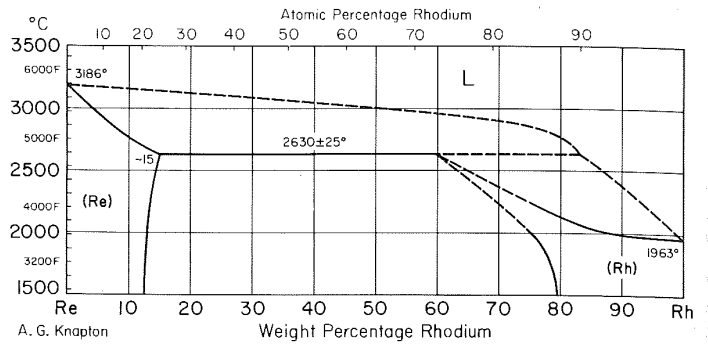
Re-Ru   Rhenium-Ruthenium

J. C. Chaston
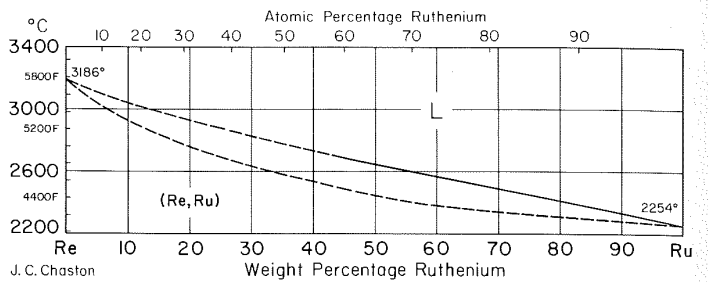
Re-Si   Rhenium-Silicon

A.G.K.
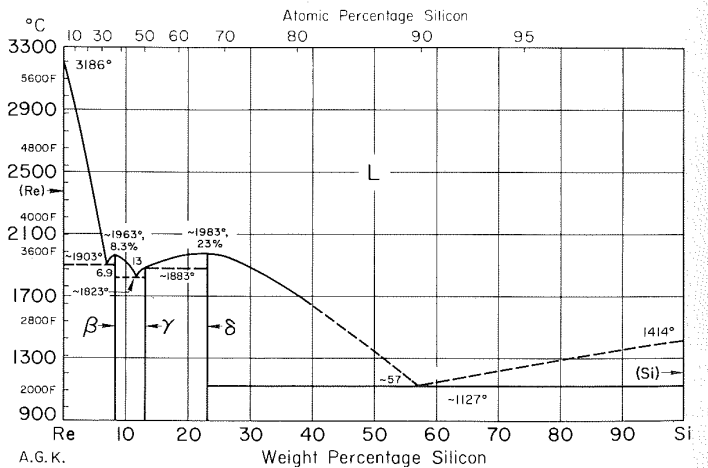
Re-Ta   Rhenium-Tantalum

A.G.K.
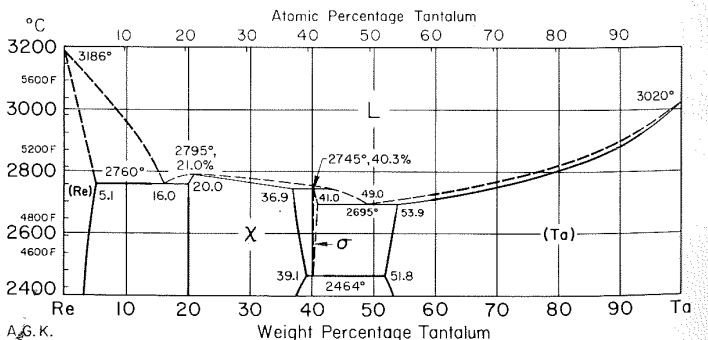
Re-W   Rhenium-Tungsten

A. G. Knapton
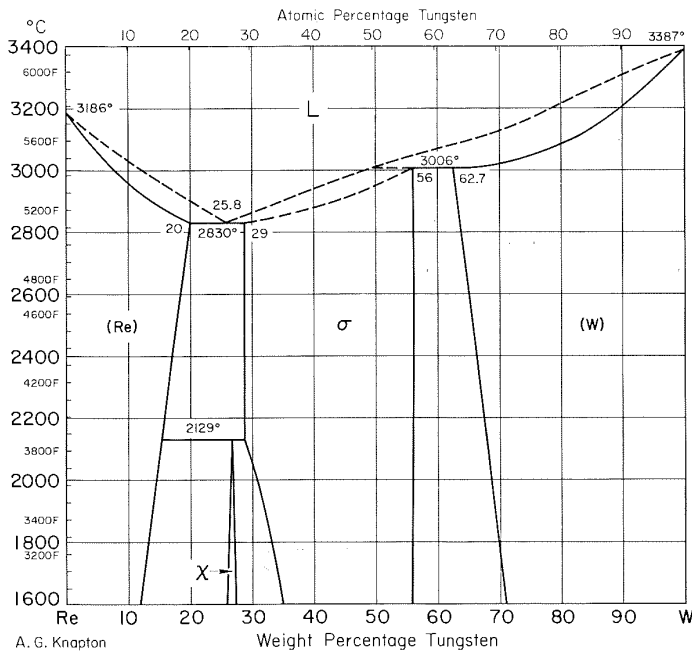
Ru-Ta   Ruthenium-Tantalum

A.G.K.
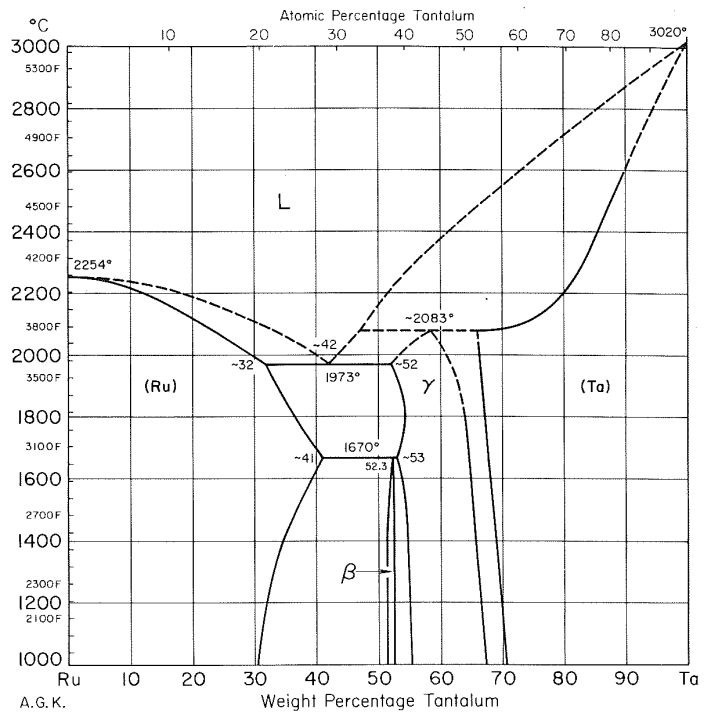
Rh-Ta   Rhodium-Tantalum

Donald T. Hawkins
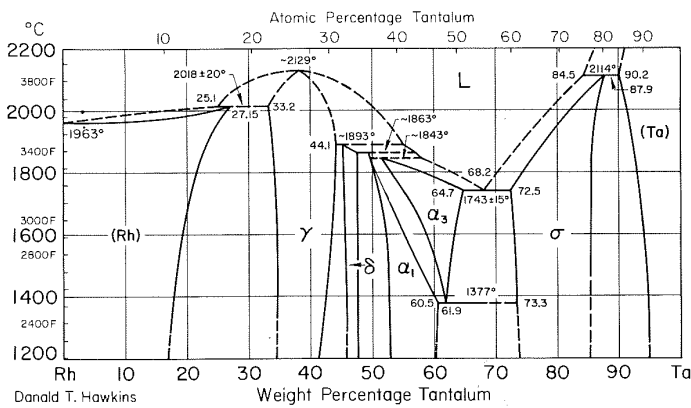
Ru-W   Ruthenium-Tungsten

Richard M. Waterstrat

Rh-W   Rhodium-Tungsten

D.T.H.

Sb-Sn   Antimony-Tin

D. T. H.

Sb-Zn   Antimony-Zinc

Donald T. Hawkins

Si-Sn   Silicon-Tin

D.T.H.
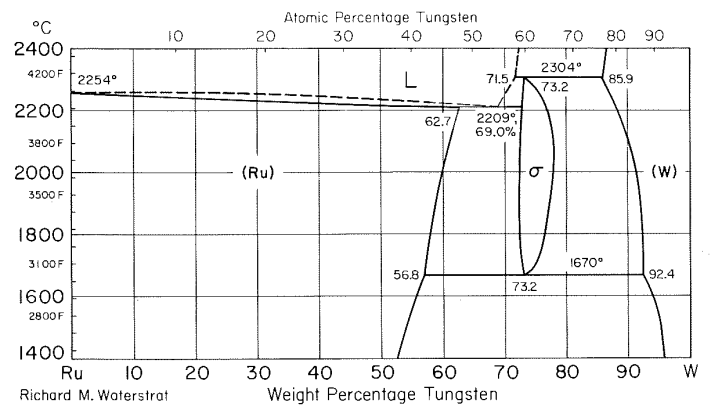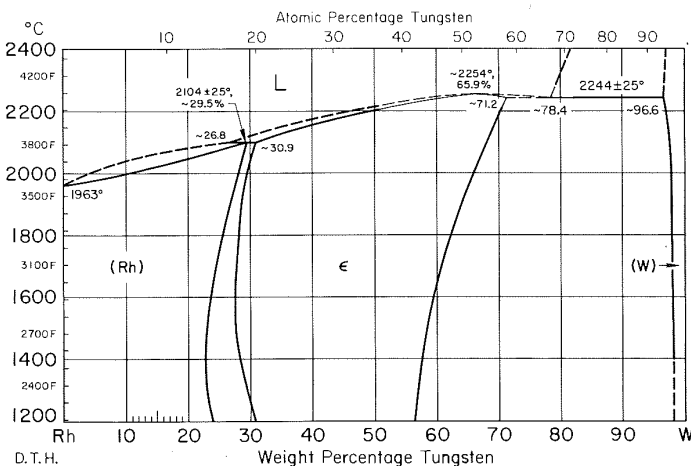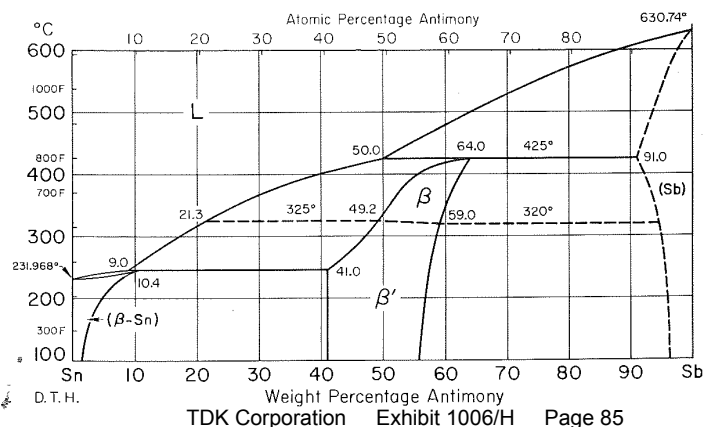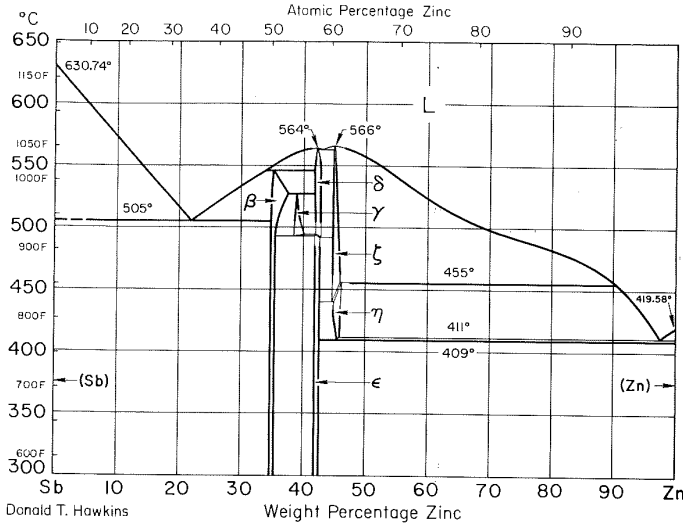
Si-Ta   Silicon-Tantalum

D.T.H.
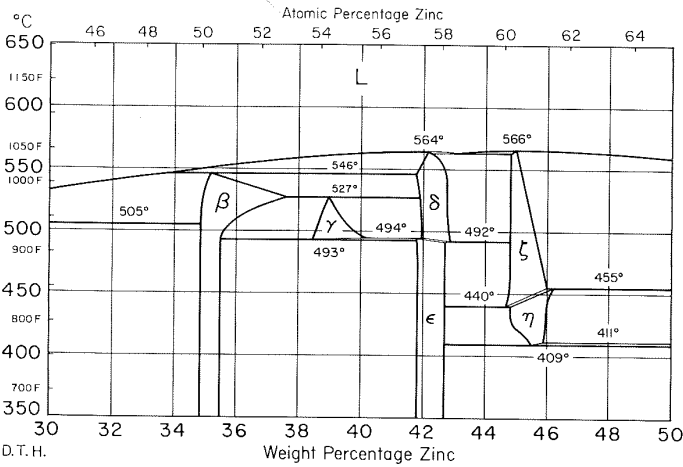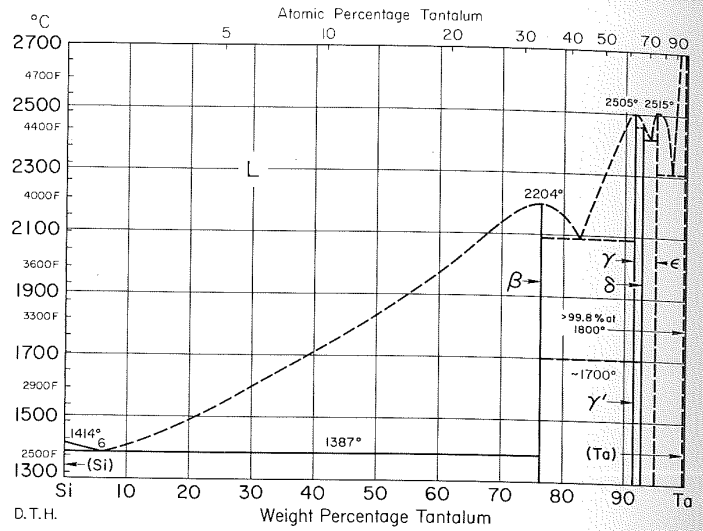
Si-Ti   Silicon-Titanium

D.T.H.
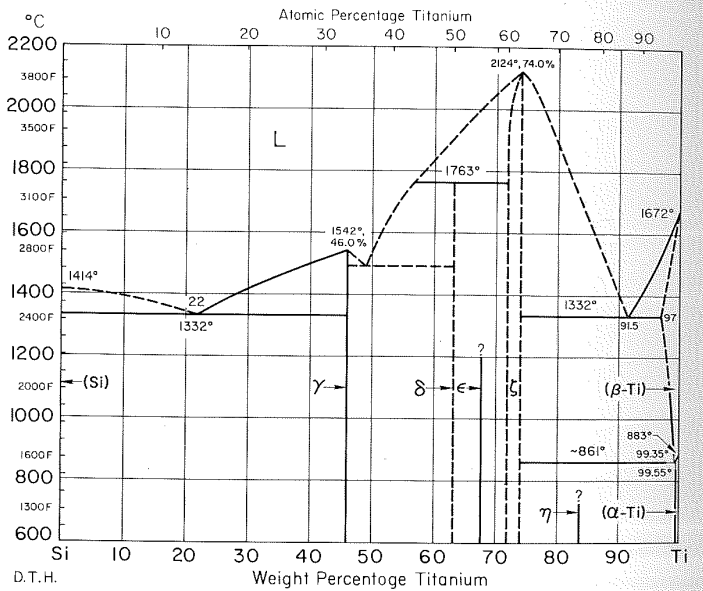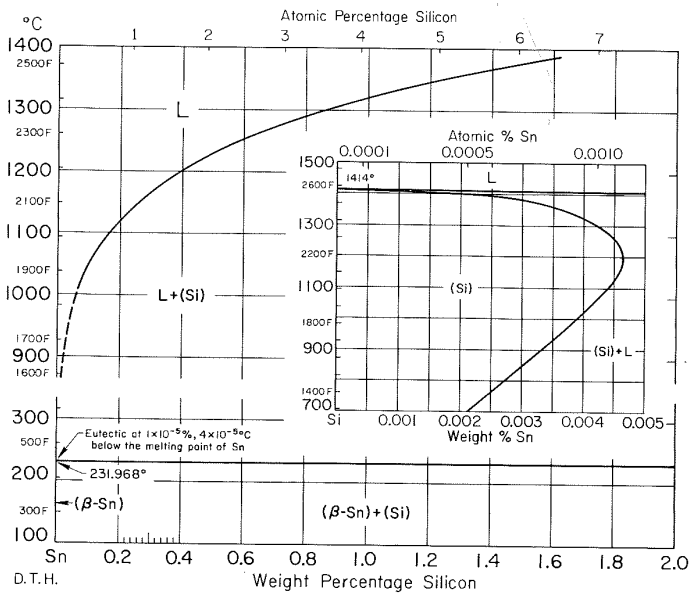
Si-V   Silicon-Vanadium

D.T.H.
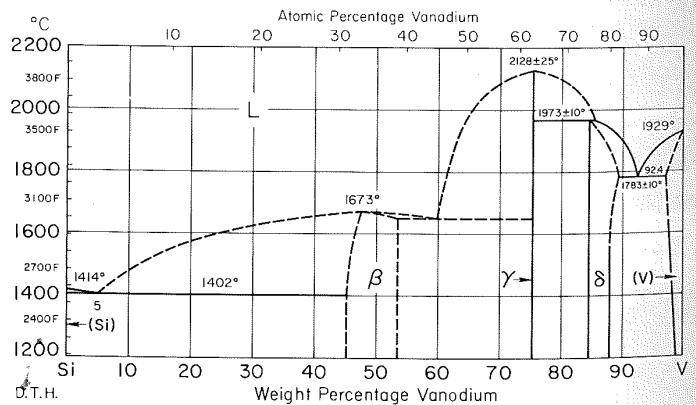
Si-W   Silicon-Tungsten

Donald T. Howkins
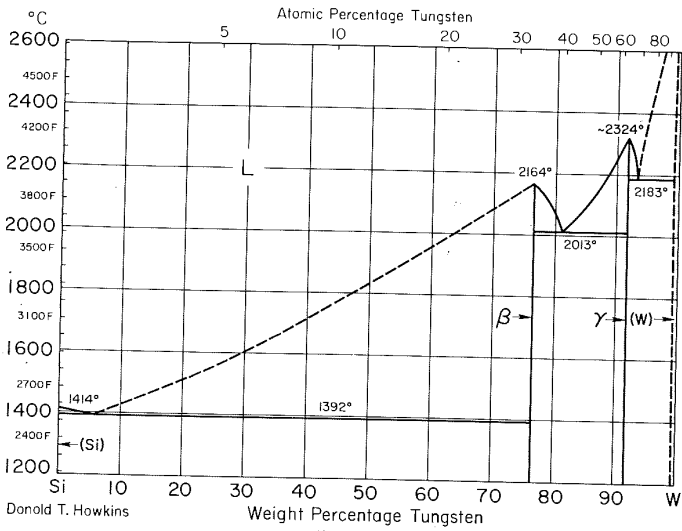
Sn-Te   Tin-Tellurium
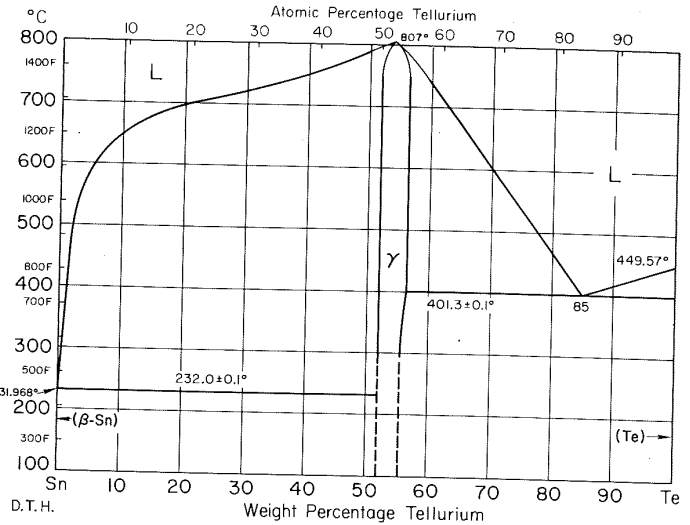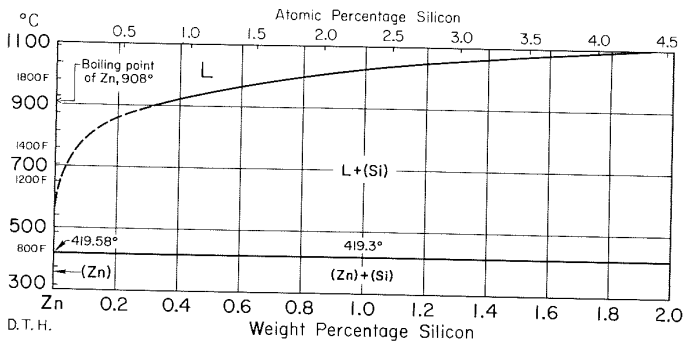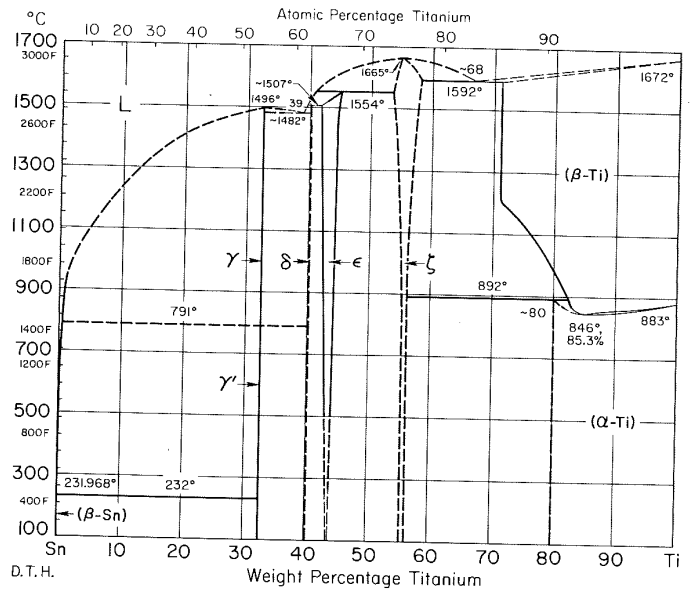
D.T.H.

Si-Zn   Silicon-Zinc

D.T.H.

Si-Zr   Silicon-Zirconium
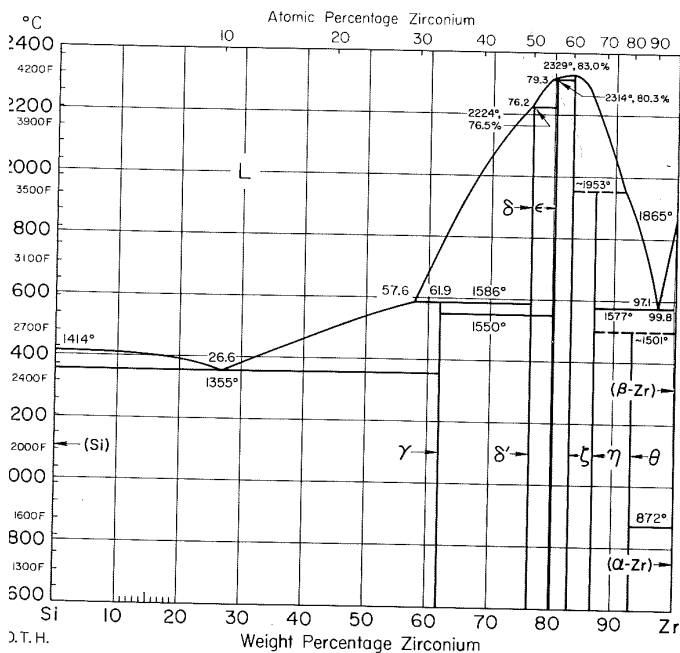
D.T.H.

Sn-Ti   Tin-Titanium

D.T.H.

Sn-Tl   Tin-Thallium

D.T.H.

Sn-Zn　Tin-Zinc

Atomic Percentage Zinc

°C

L

231.968°

~1.7 8.9

(β-Sn)

198°

~99.9

(Zn)

Weight Percentage Zinc

J. W. Simpson and W. Showak

Ta-W　Tantalum-Tungsten

Atomic Percentage Tungsten

°C

3600

L

3387°

3020°

(Ta, W)

Ta

Weight Percentage Tungsten

D. T. H.

Sn-Zr　Tin-Zirconium

Atomic Percentage Zirconium

°C

2000

L

1988°

1865°

1592° ~76.5

~79

(β-Zr)

1327°

1142°

~17

982°

872°

γ δ ε (α-Zr)

231.968°

(β-Sn) 13°

(α-Sn) Sn

Weight Percentage Zirconium

Ralph Hultgren
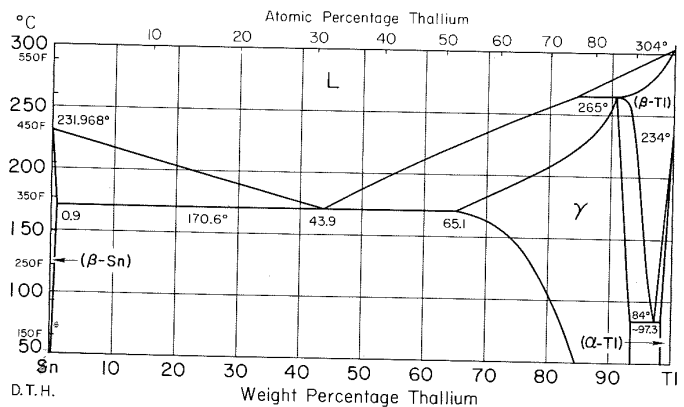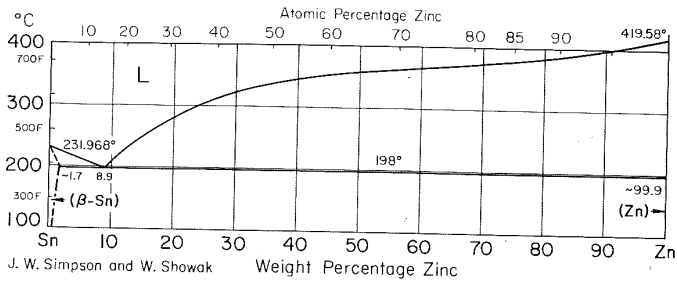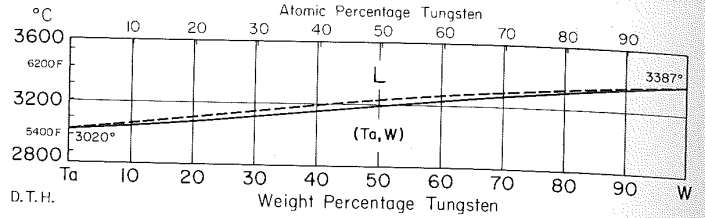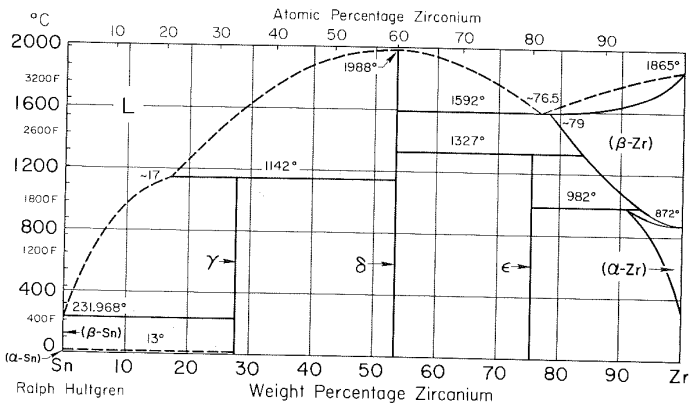
Ta-Zr　Tantalum-Zirconium

Atomic Percentage Zirconium

°C

3000

3020°

L

1782°, 1822°

19.9% 75.6%

1865°

(Ta, β-Zr)

~47 801°

(α-Zr)

872°

~88.8 ~96J

Ta

Weight Percentage Zirconium

D. T. H.

Ta-Ti　Tantalum-Titanium

Atomic Percentage Titanium

°C

3020°

2800

L

1672°

(Ta, β-Ti)

883°

(α-Ti)

Ta

Weight Percentage Titanium

Daniel J. Maykuth

Te-Zn　Tellurium-Zinc

Atomic Percentage Tellurium

°C

1400

L

1292±2°

Boiling point of Te, 989°

Boiling point of Zn, 908°

β

422±2° 447±2° 449.57°

419.58° >99.5

(Zn) (Te)

Zn

Weight Percentage Tellurium

D. T. H.

Ta-V　Tantalum-Vanadium

Atomic Percentage Vanadium

°C

3020°

3000

L

2500

(Ta, V) 1929°

~1322°

σ

Ta

Weight Percentage Vanadium

Donald T. Hawkins

Th-Ti　Thorium-Titanium

Atomic Percentage Titanium

°C

1800

1758°

(β-Th) L 1672°

1365°

~12.1 1192±10°

(β-Ti)

883° 883°

(α-Th) (α-Ti)

Th

Weight Percentage Titanium

D. T. H.

Th-U   Thorium-Uranium

Donald T. Hawkins

Ti-U   Titanium-Uranium

A. G. Knapton

Th-V   Thorium-Vanadium

D.T.H.

Th-Zn   Thorium-Zinc

D.T.H.
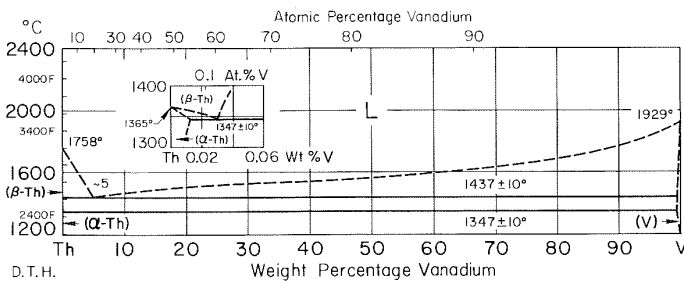
Ti-V   Titanium-Vanadium

D.T.H.

Th-Zr   Thorium-Zirconium

D.T.H.
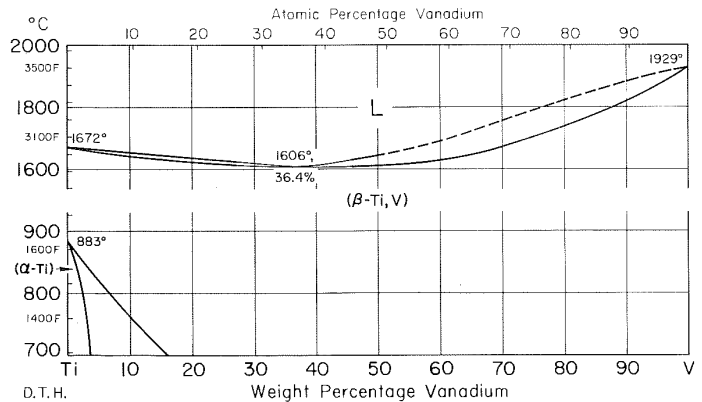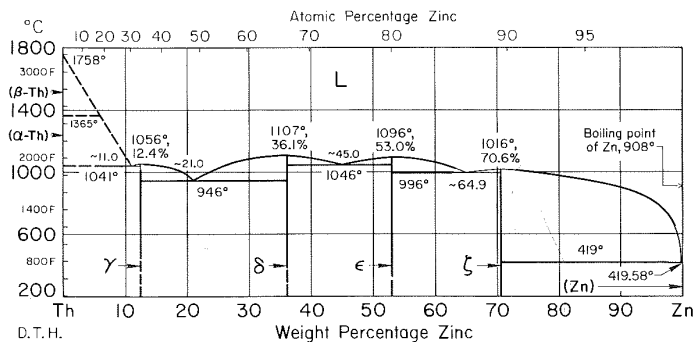
Ti-W   Titanium-Tungsten

Daniel J. Maykuth
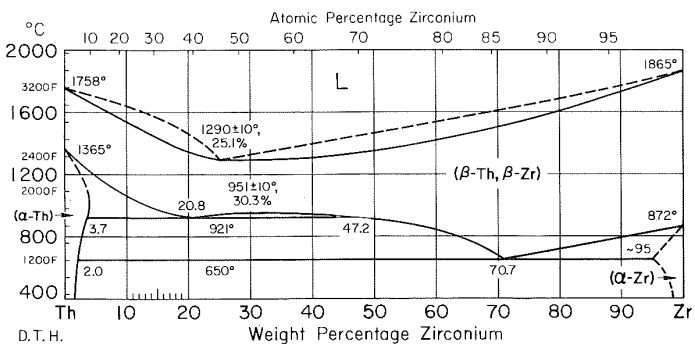
Ti-Zr   Titanium-Zirconium

U-Zr   Uranium-Zirconium

A. G. Knapton

V-W   Vanadium-Tungsten

D.T.H.
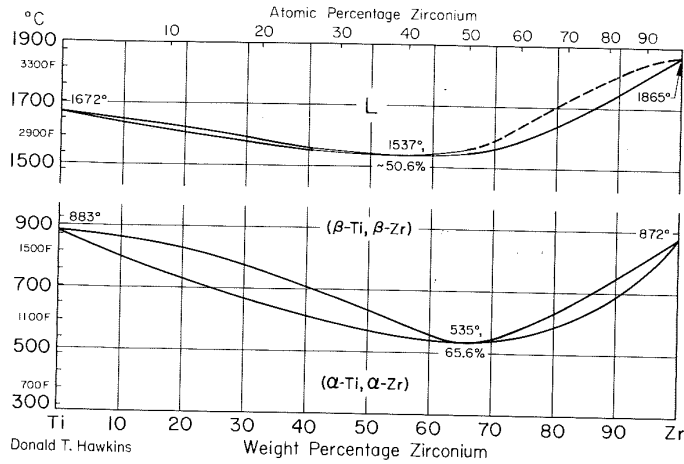
V-Zr   Vanadium-Zirconium
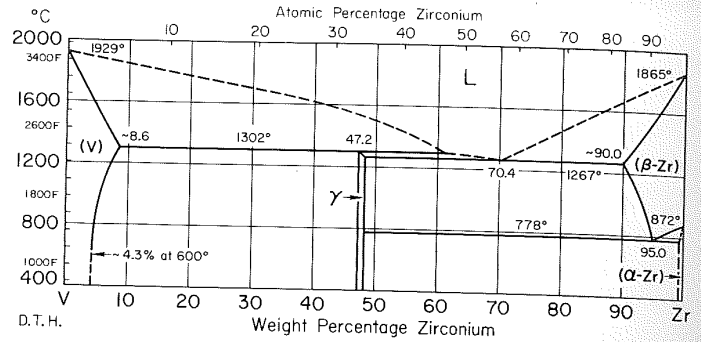
D.T.H.

W-Zr   Tungsten-Zirconium

D.T.H.

Zn-Zr   Zinc-Zirconium

D.T.H.
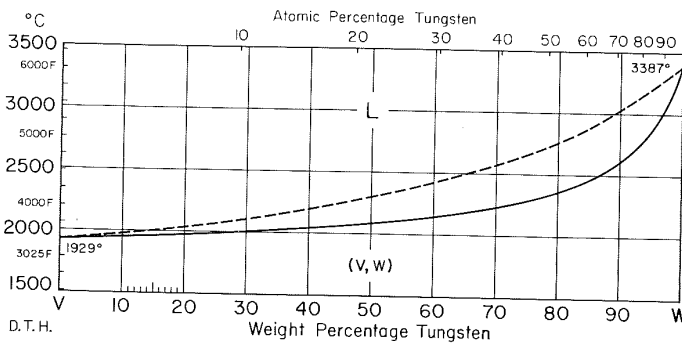
Donald T. Hawkins

The Fe-Ni (Iron-Nickel) System

By L.J. Swartzendruber
National Institute of Standards and Technology
V.P. Itkin
University of Toronto
and
C.B. Alcock
University of Notre Dame

Equilibrium Diagram

The equilibrium phases of the Fe-Ni system are: (1) the liquid, L; (2) the bcc, high-temperature (δFe) solid solution; (3) the fcc (γFe,Ni) solid solution; (4) the bcc, low-temperature (αFe) solid solution; and (5) the FeNi$_3$ intermetallic compound, which forms by a first-order order-disorder transformation below 517 °C and has an extended range of homogeneity.

Early systematic efforts to construct a phase diagram for Fe-Ni were made by [1899Osm], [05Gue], [10Heg], and [10Rue]. Evaluated phase diagrams for the Fe-Ni system were given previously by [38Mar], [Hansen], [Shunk], and [82Kub]. The present assessed Fe-Ni equilibrium diagram is shown in Fig. 1.

Liquidus and Solidus

The liquidus and solidus for Fe-rich alloys up to about 12 at.% Ni were measured by [57Hel] using thermal analysis. [23Han] measured the liquidus and solidus over the entire range of composition. Measurements were also made by [05Gue], [25Kas], [31Ben], [37Jen], [25Vog], [27Vog] and [28Vog]. The data are summarized in Table 1. According to [23Han], the minimum in the liquidus curve is located at 1438 °C (temperatures quoted throughout were converted to IPTS-68) and about 67 at.% Ni. According to [37Jen], the minimum is between 1422 and 1427 °C. Based on a least-squares fit taking into account both the measured boundaries and available thermodynamic data (see Thermodynamics), we find the most probable location for the minimum to be 1440 °C and 66.0 at.% Ni, in good agreement with [23Han].

[64Hum] calculated the Fe-rich liquidus/solidus based on an ideal-solution model. This procedure gives too large a separation between the liquidus and solidus when extended to Ni-rich alloys. The liquidus and solidus separations of Fig. 1 are based primarily on those predicted by the measured thermodynamic parameters in the liquid and fcc phases, with the assessed boundary location giving greatest weight to the measurements of the liquidus. These boundaries are close to the predictions of [85Tom], which were based on thermodynamic parameters measured using mass spectrometry. They are shown on an expanded scale in Fig. 2.

Phase Boundaries

Measurements of the (αFe/δFe) phase boundaries were made by [20Han], [23Han], [25Kas], and [57Hel]. Comparisons with thermodynamic measurements (see below) and with liquidus and solidus measurements indicate a narrow two-phase (αFe) + (δFe) region and a narrow peritectic reaction—L + (δFe) $\leftrightarrow$ (γFe,Ni) at

1514 ± 2 °C and 3.5, 4.9, and 4.2 ± 0.5 at.% Ni, respectively. Measured values are listed in Table 1 and compared with the equilibrium diagram in Fig. 3.

(αFe) / (γFe,Ni) Phase Boundaries

Due to the sluggishness of the (γFe,Ni) $\rightarrow$ (αFe) and (αFe) $\rightarrow$ (γFe,Ni) phase transformations below 800 °C, the (αFe)/(γFe,Ni) equilibrium boundaries are difficult to determine (see Metastable Phases). [36Jet], [39Owe], [41Owe], and [49Owe] used powder X-ray diffraction (XRD) techniques down to 300 °C. [65Gol] used electron microprobe techniques to measure concentration profiles on samples equilibrated at temperatures as low as 500 °C. [80Rom] used a scanning transmission electron microscope (STEM) on samples equilibrated between 670 and 300 °C. These results, along with those of [69Sta], demonstrated clearly the retrograde solubility of Ni in (αFe). The data of [49Owe], [49Jon], [65Gol], and [80Rom] agree fairly well at 500 °C and above. The boundaries shown in Fig. 1 were constructed using these data, giving greatest weight to the results of [80Rom]. Numerical values determined by the various investigators are given in Table 2. Figure 3 shows the assessed boundaries and compares them with the experimental data. Enthalpies of the (αFe) $\rightarrow$ (γFe,Ni) transformation were measured by [26Kaw], [36Sam], [37Koe], [40Zui], [59Sch], and [67Hil].

FeNi$_3$

Evidence for ordered FeNi$_3$ was obtained first by [32Dah], [33Dah], [36Dah], [39Kus], and [39Lee] using XRD. Because of the nearly equal X-ray scattering factors for Fe and Ni, the ordering is difficult to observe with X-rays (see [38Haw]). The results of [39Lee] were confirmed by [39Haw], also with X-rays. Variations in the magnetic properties, electrical resistance, and hardness with heat treatment of alloys showing FeNi$_3$ order were investigated by [32Dah], [33Dah], and [36Dah]. Based on X-ray and electron microscope observation of annealed thin films and on the results of [52Hun], [63Heu] concluded that the (γFe,Ni) phase decomposes eutectoidally to (αFe) and FeNi$_3$ at 345 °C and 52 at.% Ni, a conclusion that still appears valid. (The existence of a eutectoid near this same point based on the magnetic transition had been postulated earlier; see [21Mer].)

The critical behavior of the temperature derivative of the resistivity around the FeNi$_3$ composition was investigated by [82Ore]. No anomaly in the resistivity was found at the order-disorder temperature, but one was found at the Curie temperature. The phase diagram in the composition range 69 to 77 at.% Ni and in the temperature range around 510 °C was studied in considerable detail by [80Van] and [81Van] using Mössbauer spectroscopy. They ex-

plained a 15 °C hysteresis zone between ordus and disordus as a magnetic effect. [81Lef] investigated the local atomic arrangement in FeNi₃ using neutron diffuse scattering and a single crystal quenched from four different temperatures. [72Cal] found that the order-disorder transformation of FeNi₃ is not second order and observed a two-phase zone of 5 or 6 °C for alloys between 71 and 75 at.% Ni. On the basis of a calorimetric study, [52Iid] and

[54Iid] concluded that short-range order forms in FeNi₃ before long-range order is observable by other methods.

The ordering behavior of FeNi₃ was also investigated by [37Kal], [39Haw], [39Kay], [40Nix], [48Kal], [50Jos], [53Rhi], [53Gei], [57Lya], [57Vit], [58Kus], [62Kac], [63Dav], [63Tre], [65Gon], [72Cal], [73Cal], [75Bil], [75Leb], [77Hut], [79Des], and
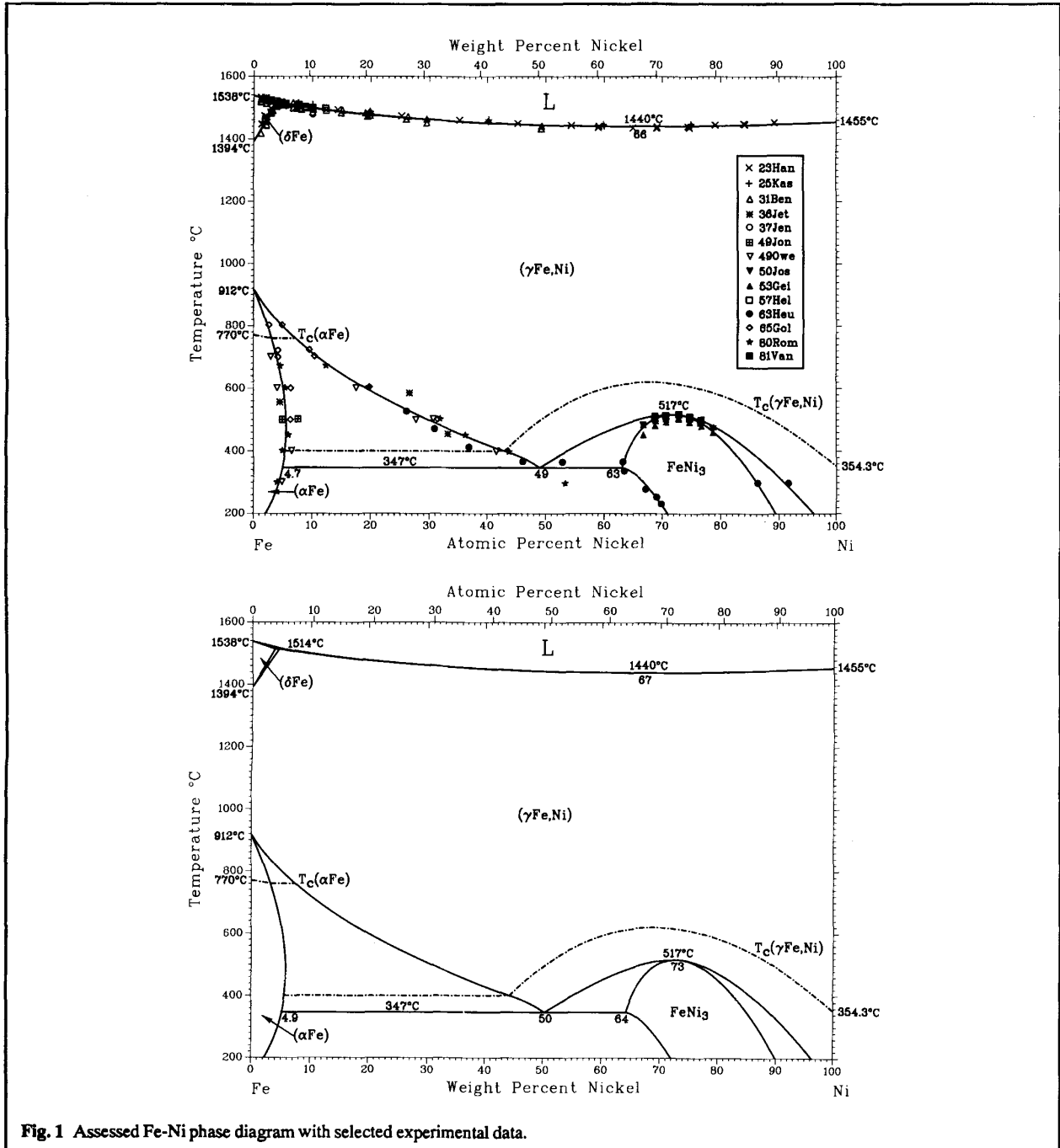
Fig. 1 Assessed Fe-Ni phase diagram with selected experimental data.

Table 1   High-Temperature Phase Boundary Data for Fe-Ni Alloys

Composition, at.% Ni	Liquidus	Solidus	Temperature, °C (δFe)/(δFe) + (γFe,Ni)	(δFe) + (γFe,Ni)/(γFe,Ni)
From [10Rue]				
0	1538	...	...	...
9.6	1515	...	...	...
19.2	1488	...	...	...
29.0	1472	...	...	...
38.8	1452	...	...	...
48.8	1448	...	...	...
58.8	1443	...	...	...
68.9	1441	...	...	...
79.2	1446	...	...	...
100	1455	...	...	...
From [23Han]				
1.1	1532	...	1447	...
2.0	1530	...	1471	...
2.9	1523	...	1497	...
3.7	1521	...	1504	...
5.1	1506	...	...	...
5.8	1506	...	...	...
8.0	1501	...	...	...
10.0	1496	...	...	...
14.6	1493	...	...	...
24.7	1474	...	...	...
34.8	1460	...	...	...
45.1	1449	...	...	...
54.6	1443	...	...	...
59.3	1442	1437	...	...
65.1	1439	1435	...	...
66.7	1439	...	...	...
69.3	1439	1434	...	...
74.5	1440	1436	...	...
79.2	1445	...	...	...
84.2	1447	...	...	...
89.1	1453	...	...	...
From [25Kas]				
1.3	1532	1526	1454	...
2.0	1530	1520	1470	...
5.0	1518	...	...	...
7.5	1516	1510	1512	...
10.0	1510	1504	...	...
20.0	1488	1488	1484	...
40.0	1463	1456	...	...
60.0	1447	1441	...	...
80.0	1448	1443	...	...
From [31Ben]				
1.1	1526	1519	1417	...
2.1	1526	1512	1443	...
3.0	1523	...	1490	...
3.9	1518	1507	...	...
6.6	1514	1499	...	...
7.1	1511	1497	...	...
7.8	1507	1497	...	...
8.0	1509	1493	...	...
10.0	1504	1485	...	...
14.9	1492	1483	...	...
19.5	1477	1472	...	...
19.9	1483	1475	...	...
25.7	1472	1462	...	...
29.3	1464	1451	...	...
49.2	1441	1432	...	...

(continued)

Note: All results corrected to IPTS-68 and to agree with 1538 °C as the melting temperature of pure Fe and 1455 °C as the melting temperature of pure Ni.

Table 1 High-Temperature Phase Boundary Data for Fe-Ni Alloys (continued)

Composition, at.% Ni	Temperature, °C Liquidus	Solidus	(δFe)/(δFe) + (γFe,Ni)	(δFe) + (γFe,Ni)/(γFe,Ni)
From [37Jen]				
10.0	...	1479	...	...
20.0	...	1458	...	...
30.0	...	1447	...	...
40.0	...	1441	...	...
50.0	...	1440	...	...
60.0	...	1439	...	...
70.0	...	1418	...	...
80.0	...	1423	...	...
90.0	...	1438	...	...
From [57Hel]				
1.84	1528	1526	1455	1462
2.79	1524	1520	1484	1483
3.76	1520	1514	1503	1506.5
4.62	1516	1511.5	1514	...
5.72	1513.5	1510	...	...
7.61	1508.5	1503.5	...	...
8.95	1502.5	1598.5	...	...
12.23	1497	1491	...	...

Note: All results corrected to IPTS-68 and to agree with 1538 °C as the melting temperature of pure Fe and 1455 °C as the melting temperature of pure Ni.

[84Lef]. Experimental values reported by various investigators are listed in Table 3 and compared in Fig. 4.

Metastable Phases

At low temperature (under about 800 °C), the (αFe) + (γFe,Ni) field is relatively broad, and attainment of equilibrium involves considerable diffusion. Diffusion rates at these lower temperatures are low; consequently, very long times are required to establish equilibrium, and normal conditions favor a diffusionless (or martensitic) transformation. This transformation exhibits considerable hysteresis. In early work, [20Han] used metallography to determine two sets of boundaries for the (αFe) + (γFe,Ni) two-phase region—one on heating, and one on cooling. The (γFe,Ni)/(αFe) + (γFe,Ni) boundary determined in this way agrees closely with that determined by thermal analysis (the (αFe)/(αFe) + (γFe,Ni) boundary is not detected by thermal analysis). [20Han] also concluded that the (αFe) → (γFe,Ni) transformation is accelerated by the presence of impurities.

From a practical standpoint, a diagram giving the details of this irreversible transformation is often of more importance than one giving the equilibrium boundaries in this region. Figure 5 exhibits experimental transformation measurements of [25Pes], [27Hon], [49Jon], and [56Kau] and compares them with the equilibrium boundaries. In this figure, the supersaturated bcc phase that results from the diffusionless transformation is denoted α_2. The solid lines are estimates of A_s, M_s, A_f, and M_f, where A_s and M_s are the so-called austenite and martensite start temperatures (10 vol.% of the alloy having transformed), and A_f and M_f are the so-called austenite and martensite finish temperatures (90 vol.% of the alloy having transformed). These lines are valid only over a range of cooling and heating temperatures between approximately 2 and 150 °C/min. The uncertainties in the estimated A_s, A_f, M_s, and

M_f temperatures are large, but decrease as the Ni concentration decreases.

In the α_2 or (γFe,Ni) field, the alloy will be all (γFe,Ni) if it is being cooled from the (γFe,Ni) field or all α_2 if it is being heated from the α_2 field. Because the transformation from (γFe,Ni) to α_2 is diffusionless, it can occur at very low temperatures for alloys with greater than 30 at.% Ni. [56Kau] reported the M_s temperature of (−223 °C) (50 K) for a 33 at.% Ni alloy. In addition, the M_s temperatures of various steels are known [54Mey, 48Fis, 74Ume, 63Yeo, 82Bro1] to change with the temperature at which they are austenized. That this change is due to the effect of austenizing temperature on grain size was shown by [51Mac] and [74Ume]. For an Fe-31 at.% Ni alloy, [74Ume] found that the M_s temperature varied between 200 and 230 °C as the grain size varied between 5 and 70 μm. Impurities and internal stresses also have an important effect on the transformation temperatures [e.g. 82Rod].

The diffusionless character of the α_2 → (γFe,Ni) transformation was shown clearly by [32Sch]. [34Deh] reported that the transformed alloy is bcc, and is not tetragonal as is Fe-C martensite, with the microstructural similarity of the two martensites being due to the similar way in which they transform from the γ phase. [35Sch] found that for greater than 10 at.% Ni, the (γFe,Ni) → (αFe) transformation temperature could not be lowered by long annealing times (up to 100 h). Some early diagrams, such as that of [36Mer], were drawn showing the irreversibility of the diffusionless transformation directly.

[62Gil] reported that the diffusionless transformation is massive type for Ni contents less than about 15 at.%. For very rapid cooling and/or for higher Ni concentration, [66Hum] and [62Gil] reported that the transformation is martensitic type.

According to [49Jon], the diffusionless α_2 → (γFe,Ni) transformations are independent of the cooling or heating rate for rates between 2 and 150 °C/min. [76Ino] and [82Ray] showed that the

Fig. 2 High-temperature region of the Fe-Ni phase diagram.

Fig. 3 (αFe)/(δFe) boundaries and the peritectic reaction in Fe-Ni.
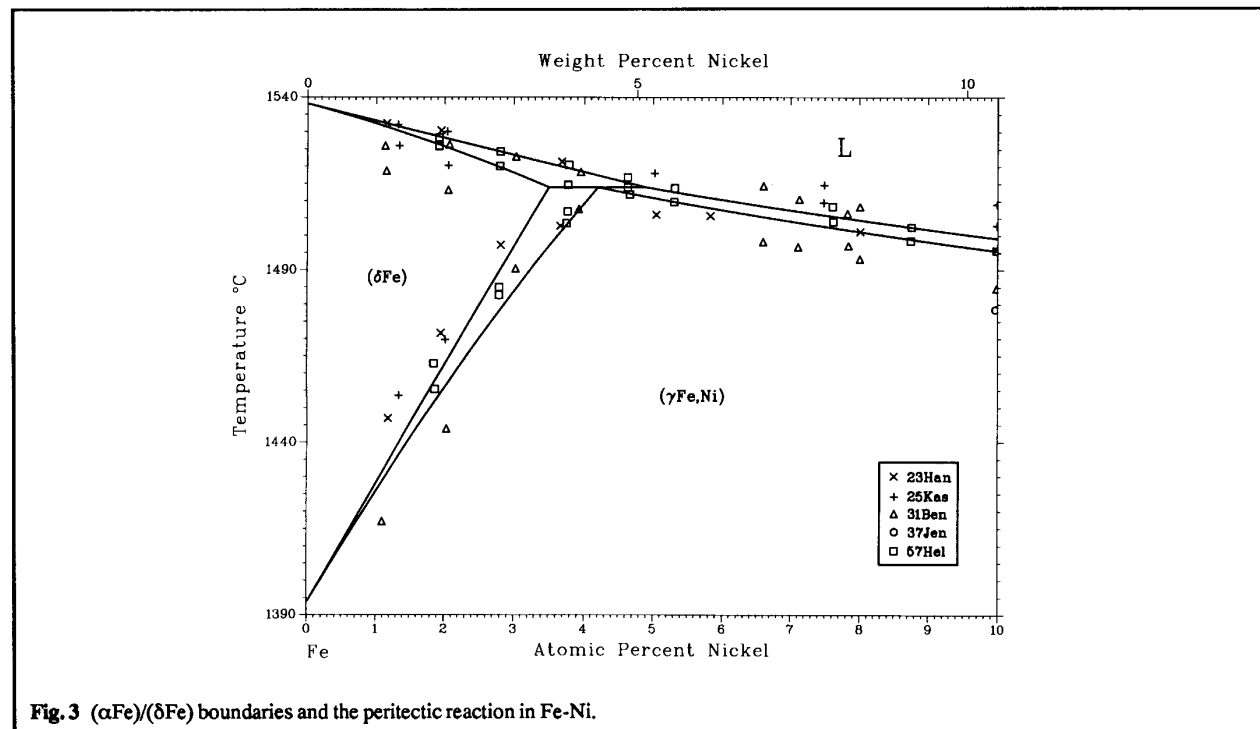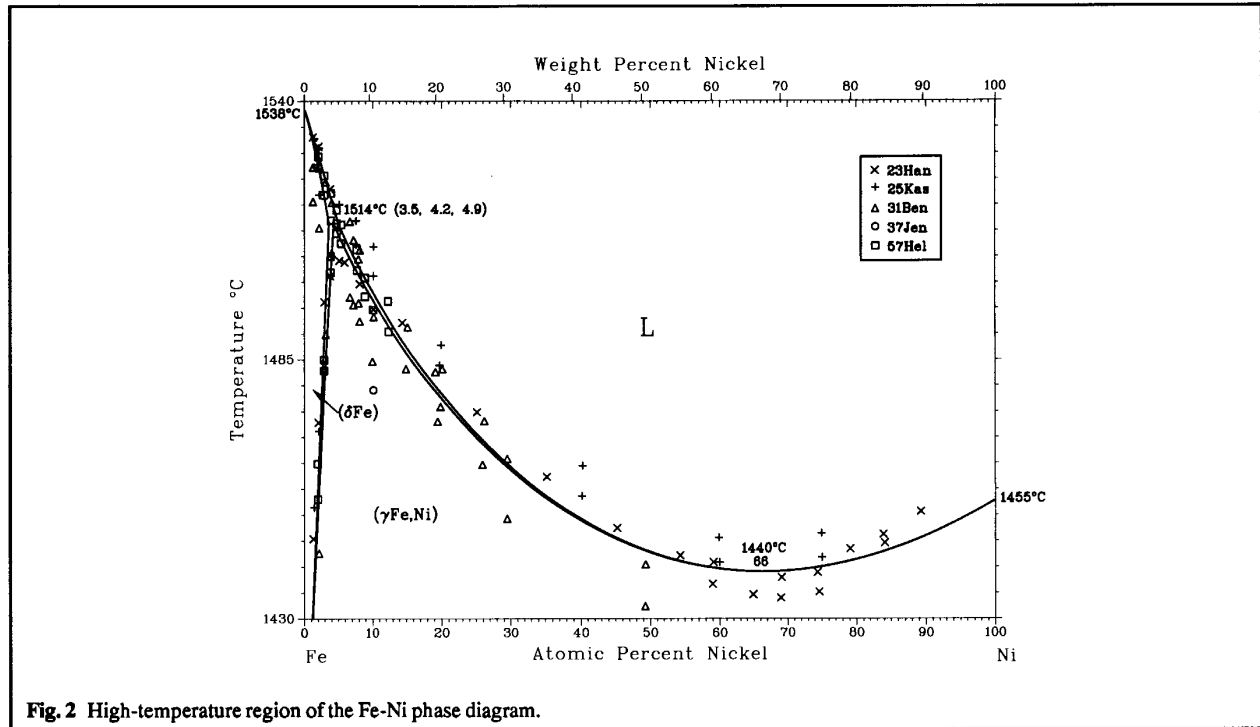
Table 2   (αFe)/(γFe,Ni) Equilibrium Phase Boundary Measurements

Temperature, °C	Composition, at.% Ni (αFe)/(αFe) + (γFe,Ni)	(αFe) + (γFe,Ni) + (γFe,Ni)	Anneal time, days	Technique	Reference
817	1.0	...	...	X-ray	[30Rob]
806	...	3	...	Magnetic	[40Pic]
800	1.0	4.5	...	X-ray	[39Owe]
	1.9 ± 0.15	3.5 ± 0.3	31	(a)	[65Gol]
744	...	6	...	Magnetic	[40Pic]
721	...	7.6	...	Magnetic	[40Pic]
720	3.8 ± 0.3	8.5 ± 0.3	7	(b)	[65Gol]
717	2.6	...	...	X-ray	[30Rob]
705	...	9	...	Magnetic	[40Pic]
700	2.5	9	...	X-ray	[39Owe]
	3.9 ± 0.2	9.4 ± 0.2	56	(b)	[65Gol]
672	3.94	...	0.7	X-ray	[36Jet]
670	4.3 ± 0.2	12.1 ± 0.4	74	(b)	[80Rom]
668	...	12	...	Magnetic	[40Pic]
672	2.7	...	...	X-ray	[39Owe]
657	4.1	...	...	X-ray	[30Rob]
625	...	16	...	Magnetic	[40Pic]
600	3.5	14	...	X-ray	[39Owe]
	5.3 ± 0.3	19.3 ± 0.5	180	(a)	[65Gol]
	5.2 ± 0.5	19.4 ± 1.4	127	(b)	[80Rom]
585	...	26.20	457	X-ray	[36Jet]
	...	20	...	Magnetic	[40Pic]
572	...	23	...	Magnetic	[40Pic]
557	4.0	...	...	X-ray	[39Owe]
550	...	18.5	...	X-ray	[39Owe]
540	...	25	...	Magnetic	[40Pic]
526	...	25.9 ± 4	...	(c)	[63Heu]
523	11.2	...	...	X-ray	[30Rob]
557	4.22	...	1	X-ray	[36Jet]
518	12.6	...	...	X-ray	[30Rob]
500	5.0	26.5	...	X-ray	[39Owe]
	6.0 ± 1.0	31.5 ± 0.5	608	(a)	[65Gol]
	5.5 ± 0.4	31.7 ± 2.3	270	(b)	[80Rom]
496	5.0	...	...	X-ray	[39Owe]
	6.07	...	734	X-ray	[36Jet]
467	...	31.1 ± 4	...	(c)	[63Heu]
456	5.5	...	...	X-ray	[39Owe]
	5.91	33.36	3150	X-ray	[36Jet]
450	5.8 ± 0.5	36.4 ± 2.8	120	(b)	[80Rom]
412	...	37.0 ± 4	...	(c)	[63Heu]
400	6.5	41.5	...	X-ray	[39Owe]
	4.9 ± 0.5	43.8 ± 3.1	270	(b)	[80Rom]
370	...	46.3 ± 4	...	(c)	[63Heu]
365	...	34	...	Magnetic	[43Has]
350	5.8	49	28	X-ray	[39Owe]
	...	49	...	X-ray	[52Hun]
300	...	56.5	28	X-ray	[39Owe]
	4.0 ± 0.5	53.4 ± 4.1	430	(b)	[80Rom]

(a) Diffusion couple, analyze with electron probe. (b) Quench as α_2, anneal, analyze with electron probe. (c) Carbonyl vapor pressure.

martensitic transformation in Fe-24 wt.% Ni can be suppressed to below room temperature by splat cooling. For alloys with less than about 30 at.% Ni, the transformation is isothermal, and the transformation temperature is strongly dependent on impurity contents. Above 30 at.% Ni, the transformation is athermal and less dependent on impurities [83Kam]. Further investigations of the nature of the $\alpha_2 \rightarrow$ (γFe,Ni) transformation were made for example by [29Gos], [30Rob], [48Fis], [47Oel], [51Smo], [62Bre], [62Yeo], [63Gol], [67Rob], [71Geo], [77Roi], [79Mat], [81Bor], [82Duf], [84Bor], [84Izm], and [84Rin].

Considerable supercooling of liquid Fe-Ni alloys is possible. [78Con] observed supercooling of up to 150 K in an alumina crucible for alloys between 6 and 90 at.% Ni. [83Abb] studied supercooling in levitation melted 25 at.% Ni samples, obtaining supercooling up to 270 °C, somewhat less than the 300 °C reported by [66Kat] for alloys surrounded by glass coatings. Transformation of (γFe,Ni) to (αFe) in thin films was investigated by [78Gal].

Alloys containing approximately 20 to 50 at.% Ni—the so-called Invar alloys—exhibit anomalous thermomechanical and thermochemical behavior, including a region of very low coefficient

Fig. 4 Low-temperature region of the Fe-Ni phase diagram.

of thermal expansion. [79Cha] showed that these Invar anomalies tend to disappear in alloys that have been electron irradiated to enhance diffusion and thereby accelerate the approach to true equilibrium. Thus it is probable that the Invar anomalies are a characteristic of metastable alloys. Literature on the Invar state is extensive, and we refer here to [60Kon], [64Ban], [72Wei], [78Kat], [78Cha], and [79Shi], where many additional references may be found. Recently, [85Chu2] proposed that the presence and disappearance of the Invar anomalies are related to a spinodal gap due to a tricritical point arising from the magnetic transition in fcc alloys (see Fig. 6).

An orthorhombic phase in thin films with a composition in the (αFe) + (γFe,Ni) region of the equilibrium diagram was indicated by [58Pin]. This phase was not retained above 650 °C. [56Cec] postulated that small particles of 30 at.% Ni that were rapidly cooled from the liquid state could pass directly to the (αFe) phase. A surface phase, either orthorhombic or tetragonal, which formed on 50 at.% Ni magnetic tapes after 18 months at room temperature was reported by [59Ana]. A reversible transformation from one fcc structure to two fcc structures below about 150 °C in 30 to 45 at.% Ni alloys was reported by [61Ana]. Rapidly solidified Fe-Ni alloys were also studied by [73Miz], [79Bos], [84Gor], and [84Miu].

Metastable FeNi and Fe₃Ni

The existence of ordered structures based on Fe₃Ni and FeNi have been proposed by a number of investigators. For the equiatomic composition, an order-disorder reaction below 321 ± 2 °C was reported by [60Pau], [62Pau1], and [62Pau2] for alloys that were heavily irradiated by neutrons. [56Tin] gave X-ray data supporting the existence of an ordered structure near the Fe₃Ni composi-

tion. The existence of Fe₃Ni and FeNi ordered structures was investigated further by [43Hos], [58Kus], [60Pau], [61Ban], [63Heu], [63Mar], [64Nee], [70Gro], [71Hau], [79Sco], and [84Cen]. Ordering in FeNi after either electron or neutron irradiation was observed by [78Cha] and [79Cha]. FeNi superstructure was observed in meteorites by [77Pet] and investigated further by [79Sco], [80Meh], and [82Gol]. In a study of meteorites, [82Jag] found that compositions of 30 to 40 at.% Ni consisted of ordered (γFe,Ni) + ordered FeNi, whereas [79Lin], in a STEM study of Fe-Ni meteorites, found decomposition into (αFe) + (γFe,Ni) with ~5 and 47 at.% Ni, respectively.

[82Gol] proposed a metastable phase diagram, with FeNi having AuCu superlattice structure to account for the "cloudy zone" structure found in meteorites [78Alb1, 78Alb2]. [84Ros1] and [84Ros2] recently proposed that ordered FeNi be included as an equilibrium phase in the Fe-Ni diagram. Figure 6 compares the cluster variation calculations of [84Yam] for the ordering reactions with the assessed diagram of Fig. 1. Also shown in Fig. 10 are the calculations by [85Chu2], [85Chu3], and [86Chu] of a possible tricritical point and spinodal arising from the magnetic interaction. [71Hau] identified Fe₃Ni order in Invar alloys using electron diffraction and pointed out its similarity to Fe₃Ni. Computer modeling of the order-disorder transformation in FeNi₃ was performed by [74Gol]. Recent work on Fe-Ni meteorites by [89Reu] also pointed to the existence of FeNi and Fe₃Ni in the equilibrium diagram.

The FeNi and Fe₃Ni ordered structures are not shown on the diagram of Fig. 1. Although still an open question, it is probable that these ordered phases are metastable or unstable structures

Table 3   FeNi$_3$ Equilibrium Boundary Measurements

Reference	Technique	Equilibrium	Temperature, °C	Composition, at.% Ni
[50Jos]	Dilatometry	(γFe,Ni)/FeNi$_3$	479	67
			491	69
			500	71
			504	73
			501	75
			492	77
			474	79
[53Gei]	Dilatometry	(γFe,Ni)/(γFe,Ni) + FeNi$_3$	482	67
			495	69
			504	71
			509	73
			503	75
			494	77
			477	79
	Dilatometry	(γFe,Ni) + FeNi$_3$/(γFe,Ni)	452	67
			481	69
			494	71
			503	73
			492	75
			480	77
			461	79
[63Heu]	Carbonyl vapor pressure	(γFe,Ni)/(γFeNi) + FeNi$_3$	365	53 ± 4
		(γFeNi) + FeNi$_3$	365	62 ± 4
		FeNi$_3$/FeNi$_3$ + (γFe,Ni)	300	87 ± 4
		FeNi$_3$ + (γFe,Ni)/(γFe,Ni)	300	92 ± 4
		(αFe) + FeNi$_3$/FeNi$_3$	333	63.3
			319	64.5
			277	67.4
			253	69.2
			232	70.2
[81Van]	Mössbauer spectroscopy	(γFe,Ni)/(γFe,Ni) + FeNi$_3$	510	69
			516	71
			516	73
			511	75
			501	77
		(γFe,Ni) + FeNi$_3$/(γFe,Ni)	505	69
			512	71
			515	73
			508	75
			494	77

reached in alloys in which the sluggish (γFe,Ni) → (αFe) + FeNi$_3$ eutectoid reaction has been suppressed.

Crystal Structures and Lattice Parameters

A summary of the crystal structures found in Fe-Ni alloys is given in Table 4, and lattice parameters are listed in Table 5. Measured values of the lattice parameters for the (αFe) and (γFe,Ni) phases vs composition are shown in Fig. 7 and 8. The solid lines in Fig. 7 and 8 represent a weighted least-squares fit to these values.

[37Owe1] found that the (γFe,Ni) phase lattice parameter at room temperature (20 °C) as a function of composition reaches a maximum value of 0.3597 nm at 39 at.% Ni and then diminishes at almost the same rate at which it increases. [37Bra] made lattice spacing measurements on alloys containing 27 to 100 at.% Ni that were quenched from 700, 800 and 900 °C. This quenching gave larger lattice spacings than annealed, ordered alloys. Values shown in Fig. 8 are for their annealed alloys, which are more rep-

resentative of equilibrium. [26Osa1] and [26Osa2] measured the lattice parameters and the densities for alloys annealed at 1150 °C and then slow cooled. [63Dav] investigated the variation in lattice parameter in FeNi$_3$ on annealing at 480 °C for up to 1000 h.

Lattice parameters were also measured by [21And], [22Kir], [23Bai], [23Mck], [27Jun], [31Phr], [37Owe1], [37Owe2], [37Owe3], [37Owe4], [37Owe5], [41Owe], [49Hah], [53Wak], [54Lih], [55Roy], [55Sut], [66Abr], [69Ree], [69Asa], and [83Sen]. The most extensive work is that of [41Owe]. Over most of the region of the Fe-Ni diagram, lattice parameters measured at room temperature will depend on the exact heat treatment given the alloy.

Thermodynamics

[Hultgren,B] assessed the thermodynamic work on Fe-Ni through about 1972. [73Kau] and [70Pre1] reviewed thermodynamic properties of the system for use in calculations of the phase diagram. Since then, phase diagram calculations were
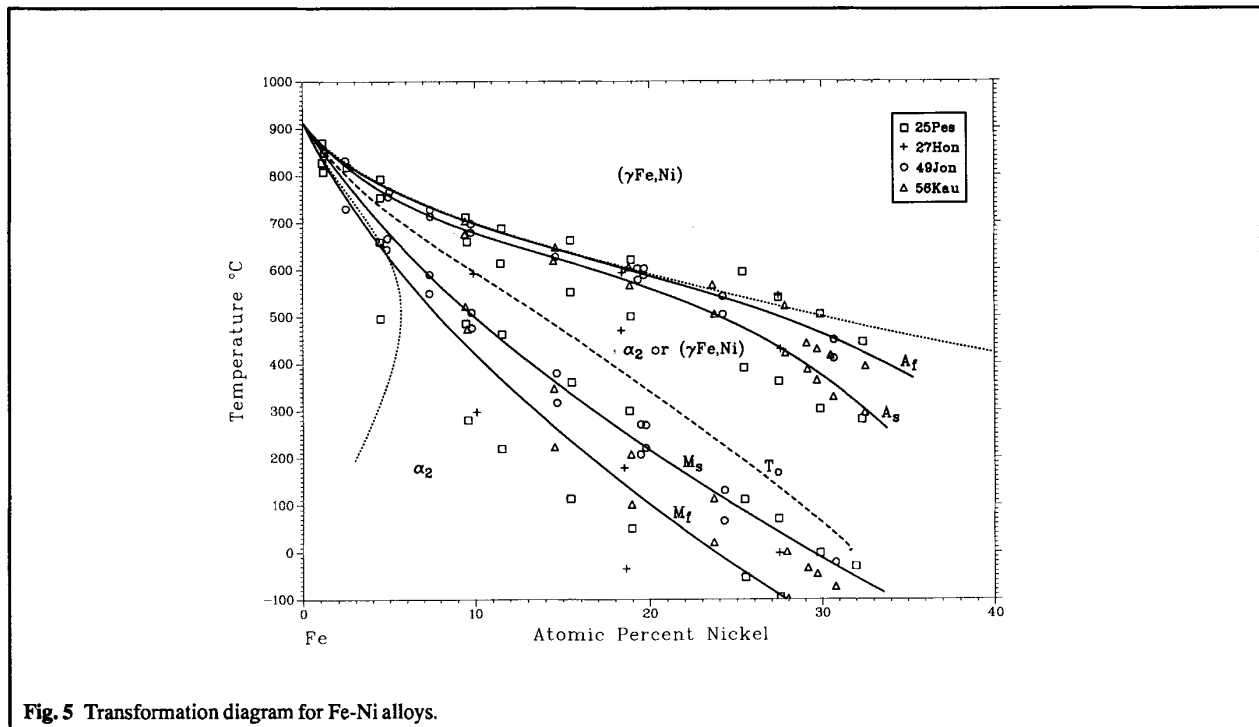
Fig. 5 Transformation diagram for Fe-Ni alloys.
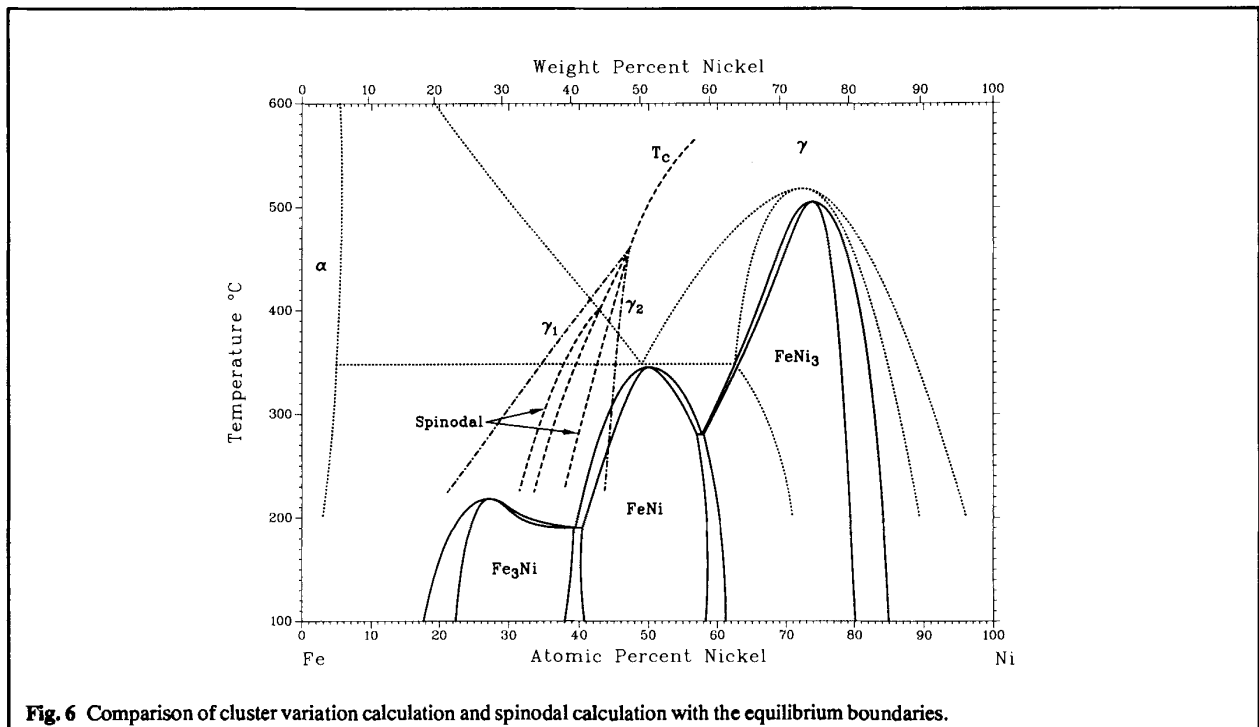
Fig. 6 Comparison of cluster variation calculation and spinodal calculation with the equilibrium boundaries.

Table 4   Fe-Ni Crystal Structure Data

Phase	Composition, at.% Ni	Pearson symbol	Space group	Strukturbericht designation	Prototype
(δFe)(a)	0 to 3.5	cI2	Im$\bar{3}$m	A2	W
(γFe,Ni)(b)	0 to 100	cF4	Fm$\bar{3}$m	A1	Cu
(αFe)(c)	0 to 5.5	cI2	Im$\bar{3}$m	A2	W
FeNi$_3$	63 to 85	cP4	Pm$\bar{3}$m	L1$_2$	AuCu$_3$
Metastable phases					
FeNi	...	tP2	P4/mmm	L1$_0$	AuCu
Fe$_3$Ni	...	cP4	Pm$\bar{3}$m	L1$_2$	AuCu$_3$

(a) From 1538 to 1394 °C at 0 at.% Ni. (b) From <1394 to 912 °C at 0 at.% Ni; at all temperatures at 100 at.% Ni. (c) Below <912 °C at 0 at.% Ni.

Table 5   Fe-Ni Lattice Parameter Data

Phase	Composition, at.% Ni	Lattice parameter, nm	Comment	Reference
(δFe)	0 to 3.5	0.29322	At 1394 °C, 0 at.% Ni	[65Pea]
(γFe,Ni)	0 to 100	0.36468	At 916 °C, 0 at.% Ni	[65Pea]
		0.35240	At 25 °C, 100 at.% Ni	[Massalski2]
(αFe)	0 to 5.5	0.28664	At 20 °C, 0 at.% Ni	[65Pea]
FeNi$_3$	63 to 85	0.35523	At 20 °C, 75 at.% Ni	[65Pea]
Metastable phases				
FeNi	...	...	...	...
Fe$_3$Ni	...	...	...	...

made by [74Bas], [74Rao], [77Has], [77Lar], [79Lar], [80Lar], [81Imr], [81Nis], [82Cha], [82Vel], [85Chu2], [86Chu1], and [86Chu2].

[74Rao] analyzed phase diagram data, together with thermochemical information, to deduce analytical equations for the thermodynamic functions in solutions. [77Kub] assessed partial and integral enthalpies and entropies of mixing for (γFe,Ni) alloys. [82Vel] derived analytical polynomial expressions for the integral enthalpies of mixing, excess entropies, and the Gibbs energies for the liquid and (γFe,Ni) alloys and used those expressions for the evaluation of the phase diagram.

Enthalpies of mixing of liquid alloys were measured in calorimeters by dropping one pure solid component into a bath with the other component molten. This method was used by [71Toz], [81Igu], [74Bat], and [66Elt]. [70Pre1] used differential thermal analysis for determination of the heat of mixing. The study of [66Elk] contradicts the other investigations, has considerable scatter of experimental values, and was dropped from further consideration. The study of [71Toz] gave unreasonably low values of heats of mixing; they were replaced with new values by the same authors in [81Igu]. The experimental results of [81Igu], [74Bat], and [70Pre1] agree satisfactorily (see Fig. 9).

Enthalpies of mixing for solid alloys were obtained by calorimetric measurement of the heat of reaction between powdered components at 1400 to 1600 K. This method was used by

[63Den], [67Kub], and [71Spe]. [61Ste] dissolved solid components and alloys in liquid tin inside the calorimeter at 1123 K. The results of [63Den], [67Kub], [71Spe], and [61Ste] agree satisfactorily and they are also shown in Fig. 9. When all the experimental results are plotted in one graph (see Fig. 9), it is obvious that the data for solid and liquid alloys are partially overlapping, i.e., the enthalpies of mixing for solid and liquid alloys are the same, within the experimental error.

The problem of differentiating the data for liquid and solid alloys was discussed by [77Kub] and [70Pre1]. [70Pre1] measured heats of melting of ten alloys. Their results deviate from the additive value by 400 to 700 J/mol, which can be compared with the errors in determination of the heat of melting of components given by [70Pre2]: ±750 J/mol. If the experimental data for both the solid and liquid heats of mixing are least-squares fitted to a four-term Redlich-Kister expression, the following equation is obtained for the excess enthalpy:

$$H^{ex} = X_{Fe} X_{Ni}[-16\ 226 - 14\ 982(X_{Fe} - X_{Ni}) + 200(X_{Fe} - X_{Ni})^2 + 11\ 382(X_{Fe} - X_{Ni})^3]$$

This curve is plotted as a solid line in Fig. 9. The uncertainty in the integral values of heat of mixing is on the order of ±600 J/mol. In Fig. 9, the dotted line represents the liquid excess enthalpies calculated from the thermodynamic model below, and the dashed line represents the solid excess enthalpies calculated from the same model.

bcc Phase Lattice Parameters

Fig. 7 Lattice parameters of (αFe) at 20 °C.

fcc Phase Lattice Parameters

Fig. 8 Lattice parameters of (γFe,Ni) at 20 °C.

Fig. 9 Heats of mixing for solid and liquid Fe-Ni alloys.

Fig. 10 Ni activity coefficients for liquid Fe-Ni alloys at 1873 K.

Fig. 11 Fe activity coefficients for liquid Fe-Ni alloys at 1873 K.

Fig. 12 Ni activity coefficients for (γFe,Ni) at 1473 K.

Fig. 13 Fe activity coefficients for (γFe,Ni) at 1473 K.

Fig. 14 Ni activity coefficients for (γFe,Ni) at 1273 K.

Fig. 15 Fe activity coefficients for (γFe,Ni) at 1273 K.

Table 6   Thermodynamic Parameters Used to Model the Fe-Ni Phase Diagram

Liquid phase

$G(Fe,L) = 0$
$G(Ni,L) = 0$
$G^{ex}(L) = X_{Fe} X_{Ni}[-16\,391 + 3.17\,T + (12\,075 - 2.6\,T)(X_{Fe} - X_{Ni}) + (-2000 + T)(X_{Fe} - X_{Ni})^2 + (-1500 - T)(X_{Fe} - X_{Ni})^3]$

bcc phase

$G(Fe,bcc) = 12\,736.4 - 17.216\,T + 23.18\,T \ln T - 0.0048155\,T^2$
$G(Ni,bcc) = -12\,500 + 9\,T$
$G^{ex}(bcc,T > 1667\,K) = X_{Fe} X_{Ni}[1950 - 3.05\,T + (-2000 + T)(X_{Fe} - X_{Ni})^2 + (-1500 - T)(X_{Fe} - X_{Ni})^3]$
$G^{ex}(bcc,T < 1185\,K) = X_{Fe} X_{Ni}[13\,274 - 13\,T + (-2000 + T)(X_{Fe} - X_{Ni})^2 + (-1500 - T)(X_{Fe} - X_{Ni})^3]$
$G^{ex}(bcc,500 < T < 1850\,K) = X_{Fe} X_{Ni}(9381 - 8.775\,T)$
$G(bcc,mag) = RT_C(bcc) \ln[\beta(bcc) + 1] f(t)$
$t = T/T_C(bcc)$
$f(t < 1) = -0.9053 + t - 0.153\,t^4 - 0.068\,t^{10} - 0.00153\,t^{16}$
$f(t > 1) = -0.06417\,t^{-4} - 0.002037\,t^{-14} - 0.0004278\,t^{-24}$
$T_C(bcc) = 1043 X_{Fe} + X_{Fe} X_{Ni}[-757.6 + 1946(X_{Fe} - X_{Ni}) + 2153(X_{Fe} - X_{Ni})^2 - 2779(X_{Fe} - X_{Ni})^3]$
$\beta(bcc) = 2.22 X_{Fe} + X_{Fe} X_{Ni}[1.176 + 1.445(X_{Fe} - X_{Ni}) + 2.275(X_{Fe} - X_{Ni})^2 - 2.042(X_{Fe} - X_{Ni})^3]$

fcc phase

$G(Fe,fcc) = 11\,274 - 16.3878\,T + 22.03\,T \ln T - 0.0041755\,T^2$
$G(Ni,fcc) = 3667.6 - 14.4177\,T + 20.113\,T \ln T - 0.004561\,T^2$
$G^{ex}(fcc) = X_{Fe} X_{Ni}[-15\,291 + 3.47\,T + (12\,061 - 2.5\,T)(X_{Fe} - X_{Ni}) + (-2000 + T)(X_{Fe} - X_{Ni})^2 + (-1500 - T)(X_{Fe} - X_{Ni})]$
$G(fcc,mag) = RT_C(fcc) \ln[\beta(fcc) + 1] f(t)$
$t = T/T_C(fcc)$
$f(t < 1) = -0.5597 - 0.6315\,t - 0.09178\,t^4 + 0.001872\,t^{10} - 0.007715\,t^{16}$
$f(t > 1) = -0.03184\,t^{-4} + 0.002468\,t^{-14} - 0.0019904\,t^{-24}$
$T_C(fcc) = -80 X_{Fe} + 627.4 X_{Ni} + X_{Fe} X_{Ni}[2040.5 - 1250(X_{Fe} - X_{Ni}) - 2627(X_{Fe} - X_{Ni})^2 - 1784(X_{Fe} - X_{Ni})^3]$
$\beta(fcc) = -1.59 X_{Fe} + 0.62 X_{Ni} + X_{Fe} X_{Ni}[8.644 + 7.691(X_{Fe} - X_{Ni}) + 4.435(X_{Fe} - X_{Ni})^2 + 0.585(X_{Fe} - X_{Ni})^3]$

FeNi₃ phase

$G(Fe \text{ in } FeNi_3) = 1127.4 - 16.388\,T + 22.03\,T \ln T + 0.0041755\,T^2$
$G(Ni \text{ in } FeNi_3) = 3667.6 - 14.418\,T + 20.11\,T \ln T - 0.0045610\,T^2$
$G^{ex}(FeNi_3) = X_{Fe} X_{Ni}[-24\,185 + 1.9\,T + 21\,475(X_{Fe} - X_{Ni}) + (-1700 + T)(X_{Fe} - X_{Ni})^2 + (-1500 - T)(X_{Fe} - X_{Ni})^3]$
$G(FeNi_3,mag) = RT_C(FeNi_3) \ln[\beta(FeNi_3) + 1] f(t)$
$t = T/T_C(FeNi_3)$
$f(t < 1) = -0.5597 - 0.6315\,t - 0.09718\,t^4 + 0.001872\,t^{10} - 0.007715\,t^{16}$
$f(t > 1) = -0.03184\,t^{-4} + 0.002468\,t^{-14} - 0.0019904\,t^{-24}$
$T_C(FeNi_3) = -80 X_{Fe} + 627.4 X_{Ni} + X_{Fe} X_{Ni}[2040.5 - 1250(X_{Fe} - X_{Ni}) - 2627(X_{Fe} - X_{Ni})^2 - 1784(X_{Fe} - X_{Ni})^3]$
$\beta(FeNi_3) = -1.59 X_{Fe} + 0.62 X_{Ni} + X_{Fe} X_{Ni}[8.644 + 7.691(X_{Fe} - X_{Ni}) + 4.435(X_{Fe} - X_{Ni})^2 + 0.585(X_{Fe} - X_{Ni})^3]$

Note: X_{Fe} and X_{Ni} are atomic fractions; Gibbs energy values are in J/mol; and T is in K.

Measurements of the activities in liquid alloys using the transportation method with a stream of inert gas were made by [59Zel] at 1830 to 1891 K, by [78Mar] at 1873 K, and by [66Oni] in dilute alloys at 1825 to 1930 K. The transpiration method based on analysis of condensate evaporated in vacuum was used by [59Spe] at 1783 to 1873 K, by [72Mil] at 2178 to 2558 K, and by [71Tse] at 1873 K. The Knudsen cell with a mass spectrometer was used by [77Kub] at 1773 to 1923 K, by [78Con] at 1500 to 1900 K, by [67Bel] at 1863 K, and by [81Ram] at 1373 to 1923 K. The results obtained by [71Tse] deviate considerably from other studies and were discarded. All other investigations appear to be in reasonable agreement, at least over most of the concentration range. Most of the results are plotted in Fig. 10 and 11. (In these figures, the dotted lines represent the values calculated from the thermodynamic model given below.) From the analysis of information given in the original papers, it is difficult to reject a study completely or to give preference to any particular group of investigations.

[72Dav], [78Con], and [81Ram] also made measurements of activities in the solid alloys. Solid alloy activity measurements using CO/CO₂ equilibrium over the Fe-Ni-O system were made by [77Gri] at 1573 K for alloys between 0 and 27 at.% Ni. [76Rob] reported on Ni activities in two alloys with 4.8 and 9.4 at.% Ni at 1400 to 1550 K measured by Knudsen cell with a mass spectrometer. These results agree satisfactorily and are plotted in Fig. 12 and 13. (In these figures, the dotted lines represent the values calculated from the thermodynamic model given below.) Early investigations of solid activities were made by [58Lyu], who measured vapor pressures of alloys using a mass spectrometer at 1463 to 1583 K and by [74Vre] using the transpiration method at 1509 K for alloys between 13 and 94 at.% Ni. The results of [58Lyu] are close to ideal values for both components—in considerable contradiction with the other results—and were dropped from further consideration. The results of [74Vre], plotted in Fig. 12 and 13, were given low weight because of their scatter and contradiction with the later investigations.

Table 7 Average Magnetic Moments Measured for Ferromagnetic Fe-Ni Alloys

Phase	Composition, at.% Ni	μ, Bohr magnetons	Reference
(αFe)	0	2.22	[63Cra]
	1.4	2.21	[25Pes]
	1.5	2.24	[63Cra]
	3.0	2.26	[63Cra]
	3.5	2.22	[25Pes]
	4.3	2.27	[63Cra]
	5.1	2.23	[25Pes]
	6.2	2.29	[63Cra]
	6.9	2.24	[25Pes]
	9.3	2.28	[63Cra]
	11.3	2.23	[25Pes]
	11.5	2.29	[63Cra]
	15.9	2.22	[25Pes]
	18.9	2.23	[63Cra]
	19.0	2.21	[25Pes]
	23.3	2.17	[63Cra]
	25.2	2.13	[25Pes]
	25.5	2.12	[25Pes]
	29.7	2.00	[25Pes]
	30.4	2.00	[63Cra]
	0	2.20	[25Pes]
(γFe,Ni)	32.5	1.93	[63Cra]
	30.8	1.25	[63Cra]
	32.1	1.61	[63Cra]
	34.3	1.77	[63Cra]
	35.3	1.82	[63Cra]
	40.8	1.80	[25Pes]
		1.84	[63Cra]
	42.0	1.79	[25Pes]
	43.5	1.77	[25Pes]
	49.6	1.67	[25Pes]
	49.8	1.69	[63Cra]
	51.0	1.65	[25Pes]
	57.7	1.52	[25Pes]
	60.0	1.50	[63Cra]
	67.0	1.36	[25Pes]
	79.7	1.07	[63Cra]
	80.2	1.06	[25Pes]
	87.7	0.88	[25Pes]
	100	0.61	[25Pes, 63Cra]

With decreasing temperature, the vapor pressure and the reliability of activity measurements drop rapidly. The difference in values of the Ni activity coefficients at 1473 K (Fig. 12) between two similar investigations [78Con, 67Bel] looks natural, considering the probable uncertainty of the methods used. For both solid and liquid alloys, the uncertainty in determination of the activity coefficient of either of the components is on the order of ±0.03 for a component in an alloy near the pure component, ±0.08 in alloys around the equiatomic composition, and ±0.15 for a component in alloy near infinite dilution.

Other reports of activities in solid alloys were provided by [49Kub], [53Ori], [69Kus], [64Roe], [70Gat], [72Dav], [75Tri], [76Dal], [77Ono], and [79Tan]. Most of these contradict each other, and it is worthwhile to plot only some of the latest studies. [75Tri] measured CO/CO_2 equilibrium over the Fe-Ni-O system at 1273 K. [76Dal] used the same technique at 1065 to 1380 K.

[77Ono] measured the Fe activities by the emf method at 1023 to 1423 K. Figures 14 and 15 show that at 1273 K, the results of three of these studies agree satisfactorily. (The dotted lines in the figures represent the values calculated from the thermodynamic model given below.)

Specific heat measurements in the Fe-Ni system at low temperatures were reported by [40Kee], [64Gup], [65Ehr], and [66Shi] and at higher temperatures by [39Lee], [73Kol], and [82Bro2].

An attempt was made to construct a thermodynamic model that represents the Fe-Ni diagram over the widest possible temperature range and agrees, within the above stated experimental errors, with the thermodynamic measurements. This model was used as an aid in the evaluation of the measured phase diagram boundaries, and greater weight was given to these boundaries than to the thermodynamic measurements. In the model, the Gibbs energy for a phase p is represented by:

$$G(p) = X_{Fe}G(p,\text{Fe}) + X_{Ni}G(p,\text{Ni}) + G(p,\text{mag})$$
$$+ RT(X_{Fe} \ln X_{Fe} + X_{Ni} \ln X_{Ni}) + G(p)^{ex}$$

where $G(p,\text{Fe})$ is the Gibbs energy of pure Fe, and $G(p)^{ex}$ is the nonmagnetic excess free energy. Following [74Ind], the magnetic contribution to the Gibbs energy is of the form:

$$G(p,\text{mag}) = RT_C(p) \ln (\beta(p) + 1)f(t)$$

where t is the reduced temperature T/T_C, T_C is the Curie temperature, and β is magnetic moment in Bohr magnetons. Both T_C and β are functions of composition. In the Fe-Ni system, all three phases in the equilibrium diagram are ferromagnetic, and the magnetic contribution is significant, especially at temperatures below 912 °C. Early estimates of the magnetic contributions to phase equilibrium in the Fe-Ni system were given by [73Sch].

The functions for T_C and β for the bcc and fcc phases were obtained by least-squares fitting the literature data. For the FeNi$_3$ phase, T_C and β values were taken to be approximately equal to those in the fcc phase. For the bcc phase, the function $f(t)$, as expanded in a power series by [78Hil], was used (the resultant contribution to the Gibbs energy agrees well with the alternate form used by [85Chu1]). For the fcc phase, the same power series for $f(t)$ was used, with the coefficients being obtained by least-squares fitting the evaluated specific heat data of [84Des] for Ni. For pure Fe, the thermodynamic functions given by [79Agr] were used. For pure Ni, the enthalpies of melting and specific heat values given in the evaluation of [84Des] were used to construct the nonmagnetic part of the thermodynamic functions. For bcc Ni, the lattice stability estimates of [73Kau] were used. In assessing the diagram, the thermodynamic modeling and optimization procedure of [81Sun] were used. For the liquidus and solidus, greatest weight was given to the liquidus measurements, especially those of [57Hel].

The parameters found by a combination of optimization and trial and error to best fit the diagram are given in Table 6, and the calculated Fe-Ni diagram is shown in Fig. 16. Above about 500 °C, the calculated and assessed diagrams are nearly identical (± 1 °C in temperature and ±0.5 at.% in composition). At lower temperatures, the assessed and calculated boundaries differ somewhat. Especially noticeable is the tricritical point predicted by the model and arising from the influence of the magnetic contribution

Table 8 Measured Curie Temperatures vs Composition for Fe-Ni Alloys

Phase	Composition, at.% Ni	Curie, Temperature, °C	Reference	Phase	Composition, at.% Ni	Curie, Temperature, °C	Reference
(αFe)	0	771	[25Pes]	(γFe,Ni)(cont.)	55.0	558	[53Wak]
		770	[29Gos]		57.7	590	[25Pes]
	1.4	766	[25Pes]		60.0	592	[53Wak]
	2.8	763	[29Gos]			591	[63Cra]
	3.5	758	[25Pes]		65.0	613	[53Wak]
	4.8	755	[29Gos]		67.0	612	[25Pes]
	5.1	752	[25Pes]		68.0	616	[53Wak]
	6.9	748	[25Pes]		70.0	614	[53Wak]
	15.9	740	[25Pes]		72.0	608	[53Wak]
	19.0	715	[25Pes]		74.0	600	[53Wak]
	23.0	565	[43Hos]		75.0	598	[53Wak]
	29.7	597	[25Pes]		76.0	589	[53Wak]
	31.3	535	[25Pes]		78.0	585	[53Wak]
	33.3	460	[25Pes]		79.7	570	[63Cra]
	33.8	435	[25Pes]		80.0	577	[53Wak]
(γFe,Ni)	29.7	120	[25Pes]		80.2	576	[25Pes]
	30.8	100	[63Cra]		81.0	571	[53Wak]
	31.3	160	[25Pes]		85.0	543	[53Wak]
	31.8	174	[25Pes]		87.7	511	[25Pes]
	32.1	156	[63Cra]		100.0	360	[25Pes]
	33.3	228	[25Pes]			361 ± 1	[63Cra]
	33.8	245	[25Pes]			354.3	[68Kou]
	35.3	261	[25Pes]	FeNi₃	45.0	494 ± 5	[53Wak]
		228	[63Cra]		50.0	543	[53Wak]
	36.1	250	[63Cra]		55.0	580	[53Wak]
	37.0	285	[25Pes]		60.0	616	[53Wak]
	38.5	300	[29Gos]		65.0	636	[53Wak]
	39.0	317	[25Pes]		68.0	668	[53Wak]
	40.8	321	[25Pes]		70.0	680	[53Wak]
		354	[63Cra]		72.0	696	[53Wak]
	42.0	346	[25Pes]		74.0	691	[53Wak]
	43.5	403	[25Pes]		75.0	681	[53Wak]
	45.0	468	[53Wak]		76.0	654	[53Wak]
	47.1	415	[29Gos]		78.0	624	[53Wak]
	49.3	506	[25Pes]		80.0	599	[53Wak]
	49.8	513	[63Cra]		81.0	584	[53Wak]
	50.0	520	[53Wak]		85.0	543	[53Wak]
	51.0	522	[25Pes]				

to the Gibbs energy. (The tricritical point was also calculated by [77Hut].) [85Chu2] gave convincing arguments for the existence of this tricritical point, but further experimental confirmation appears necessary. In fitting the (αFe)/(δFe) and (αFe)/(γFe,Ni) experimental boundaries, better fits are obtained if the expression for the excess energy of the bcc phase is divided into two temperature regions—one for the (αFe) and one for the (δFe) region. An expression for the bcc excess energy that covers the entire temperature range, which gives a good approximation to the observed boundaries and which is more sensible from a thermodynamic point of view, is also included in Table 6.

In Fig. 9, the heats of mixing obtained from the parameters of Table 6 are compared with the measured values (the dotted line is for the liquid, the dashed line for the solid). In Fig. 10 through 15, the theoretical values of the activities calculated from the model parameters (dotted lines) are compared with measured values. In all instances, agreement is within experimental error. However, the fits are in some respects unsatisfying, especially for the Ni-rich heats of mixing and Fe-rich Ni activities. The slight oscillation in the Ni activity coefficients on the Fe-rich side (Fig. 12 and 14) evidently is unjustified by the data. This may be in part due to

the poor accuracy of the measured values of the solidus and liquidus of the Ni rich alloys.

Pressure

The equilibrium diagram for 50, 100, and 150 kbar was calculated by [61Kau1]. [61Kau2] showed that pressure lowers the (γFe,Ni) → (αFe) transformation temperatures. [66Mcq] investigated the effect of pressure on the density of Fe-Ni alloys by the shock technique up to 2000 kbar. Using XRD, [68Tak] measured the effect of pressure on the crystal structure and molar volume.

Magnetism

The saturation magnetization, average magnetic moments, and Curie temperatures for single-phase fcc alloys from 30 to 100 at.% Ni were measured by [63Cra]. They also measured the average magnetic moment for single-phase bcc alloys in the range 0 to 30 at.% Ni. Magnetic moments on individual Fe and Ni atoms were measured by [62Col], [73Cab], [74Nis], and [55Shu] between 40 and 100 at.% Ni. The use of magnetic measurements for
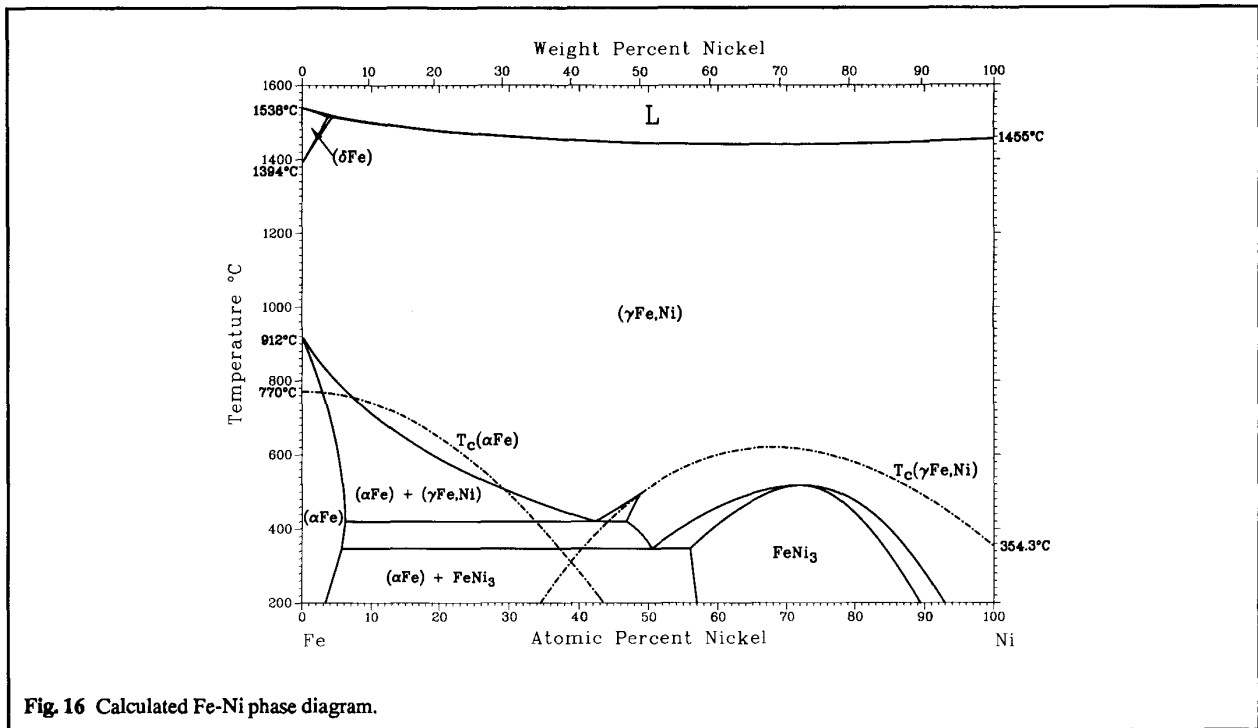
Fig. 16 Calculated Fe-Ni phase diagram.
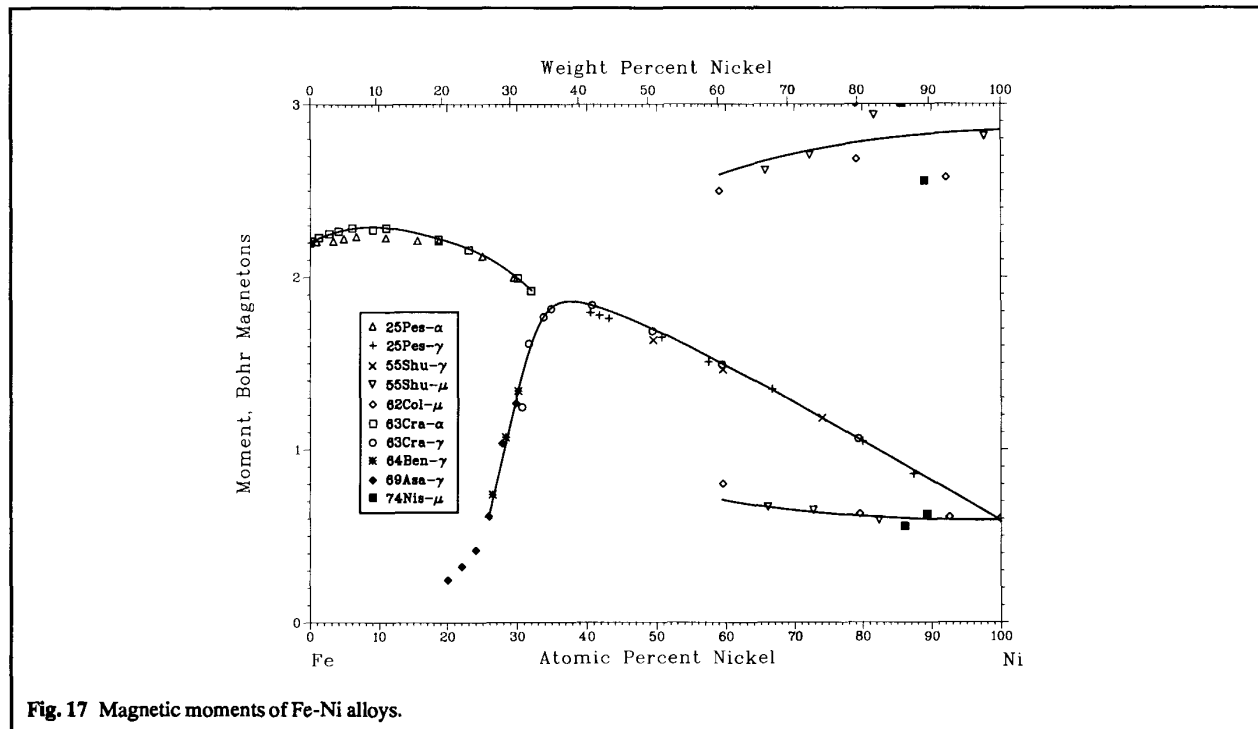
Fig. 17 Magnetic moments of Fe-Ni alloys.
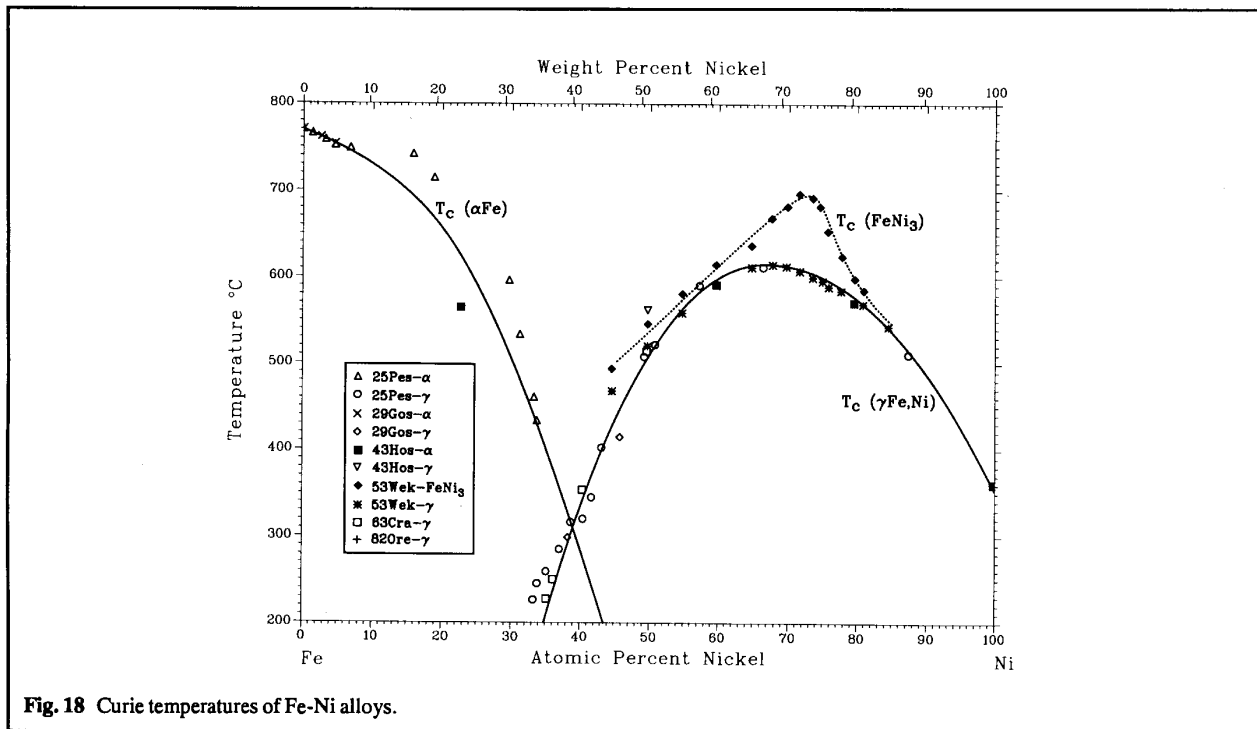
Fig. 18 Curie temperatures of Fe-Ni alloys.

studying two-phase Fe-Ni alloys was described by [39Suc] and [40Pic]. The effect of heat treatment on the magnetic properties of FeNi₃, including the maximum permeability, coercive force, remanent, and saturation magnetization was investigated by [53Wak]. By extrapolating the magnetization vs temperature curves, they estimated the Curie temperatures for ordered FeNi₃ and found a higher Curie temperature for the ordered alloys than for the disordered. A slightly higher saturation magnetization is also found for the ordered alloys ([40Gra], see Table 7). Figure 17 and Table 7 compare the various measured magnetic moments, and Fig. 18 and Table 8 compare the various measured Curie temperatures. The Curie temperature of pure Ni is taken as 627.4 K, in accordance with [68Kou] and [82Rhy].

Alloys of high maximum permeability, the so-called permalloys, can be formed by rapidly cooling alloys near the FeNi₃ composition [32Dah, 38Kay, 53Boz1, 53Boz2, 64Sch]. The magnetic properties of an equiatomic single crystal of FeNi that had been ordered metastably in the AuCu structure by neutron irradiation below 320 °C were studied by [64Nee]. Further anomalies in magnetic properties and phase separation have been observed by [51Suc], [59Dek] and [61Gor]. [75Ind] showed how the Curie temperature variation in (γFe,Ni) may be closely fitted to a Red-lich-Kister form with a single interaction term. [77Mio] showed how this interaction parameter is related to the two-moment model for γFe of [63Wei]. [73Miz] measured Curie temperatures and magnetic moments in rapidly quenched amorphous quasibinary alloys with 0 to 90 at.% Ni and boron and phosphorus additions.

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Section II: Phase Diagram Evaluations

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83Kam: D.S. Kamenetskaya, O.P. Maksimora, and V.I. Shiryayev, "Features of the Martensite Transformation in High Purity Iron-Nickel Alloys," *Fiz. Met. Metalloved.*, *55*(5), 967-972 (1983) in Russian; TR: *Phys. Met. Metallogr.*, *55*(5), 121-127 (1983). (Meta Phases; Experimental)

83Sen: A. Sen Gupta and B.K. Banarjee, "High Temperature X-ray Study of Some Iron-Nickel Alloys," *Indian J. Phys. A*, *57*, 196-199 (1983). (Crys Structure; Experimental)

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84Cen: P. Cenedese, F. Bley, and S. Lefebvre, "Atomic Short Range Order in a Fe-Ni Invar Alloy," *Phase Transformations in Solids*, Mater. Res. Symp. Proc., T. Tsakalakos, Ed., North-Holland, New York, 351-353 (1984). (Meta Phases; Experimental)

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84Ros2: P.L. Rossiter and P.J. Lawrence, "Phase Transformations in Fe-Ni Invar Alloys," *Philos. Mag. A*, *49*(4), 535-546 (1984). (Meta Phases; Experimental)

84Yam: H. Yamauchi and S. Radelaar, "Cu-Ni-Fe Coherent Phase Diagram," TMS-AIME, Warrendale, PA (1984). (Meta Phases; Theory)

85Chu1: Y.Y. Chuang, R. Schmid, and Y.A. Chang, "Magnetic Contributions to the Thermodynamic Functions of Pure Ni, Co, and Fe," *Metall. Trans. A*, *16*, 153-165 (1985). (Thermo; Theory)

85Chu2: Y.Y. Chuang, Y.A. Chang, and R. Schmid, "Magnetic Contribution to the Thermodynamic Functions of Alloys and the Phase Diagram of Fe-Ni System Below 1200 K," *Metall. Trans. A*, *16*, 153-165 (1985). (Meta Phases, Thermo; Theory)

85Tom: J. Tomiska and A. Neckel, "Thermodynamic Investigation of Fe-Ni Alloys: Mass Spectrometric Determination of Thermodynamic Mixing Effects and Calculation of the Melting Diagram," *Ber. Bunsenges. Phys. Chem.*, *89*, 1104-1109 (1985). (Equi Diagram; Thermo; Experimental)

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EDUCATION

B.A.	Materials Science	Cambridge University	1968
Ph. D., M.A.	Materials Science	Cambridge University	1972

CAREER

Permanent Positions

University of Newcastle-upon-Tyne, U.K.	Research Associate	1971 – 73
University of California, Berkeley	Research Engineer	1973 – 77
Stanford University		
Department of Materials Science and Engineering	Assistant Professor	1977 – 80
	Associate Professor (with tenure)	1980 – 84
	Professor	1984 – present
	Chair	2004 –2014
	Charles M. Pigott Professor in the School of Engineering	2009 – present
Stanford Nanocharacterization Laboratory	Director	2003 – 13
Bing Overseas Studies Program	Director	2010 – 12
Wallenberg Research Link	Associate Director	2013 – present

Visiting Positions

Centre d'Etudes Nucleaires, Grenoble	1981
HREM Laboratory, Cambridge University	1985
Matsushita Electric Industrial Company, Osaka	1987, 1989, 1991 – 94
Stanford Center for Japanese Studies, Kyoto	1997
Stanford Center in Oxford, U.K.	2001, 2010
Adjunct Advisor for International Center for Young Scientists, NIMS, Tsukuba	2004
Visiting Professor in the World Class University Project, Seoul National University, Korea	2008 – 2010

AWARDS

First Prize, Modern Metallography Micrograph Competition, 1972
First Prize Physical Science, Electron Microscopy Society of America Scientific Exhibit, 1975, 1976
Robert Lansing Hardy Gold Medal, The Metallurgical Society of AIME, 1976
Eli Franklin Burton Award, Electron Microscopy Society of America, 1977
Alfred P. Sloan Foundation Fellowship, 1979
Marcus E. Grossman Award, American Society for Metals, 1982
Excellence in Undergraduate Teaching, Stanford University Society for Black Scientists and Engineers, 1984, Stanford Society of Chicano/Latino Engineers and Scientists, 1993
Yamaha Prize for Best Poster, 1st International Conference on Metallic Multilayers, Kyoto, 1993
Fellow, (inaugural class) Microscopy Society of America, 2009
Distinguished Scientist, Physical Sciences, Microscopy Society of America, 2009
David Turnbull Lectureship Award, Materials Research Society, 2012
John M. Cowley Distinguished Lecture, Arizona State University, 2015

SELECTED PROFESSIONAL ACTIVITIES

Electron Microscopy Society of America: Program Committee, 1979, 1980, 1990, 1993; Bulletin Editorial Board, 1975-1981; Northern California Society President, 1980; Executive Committee, 1979-1982; Twelfth International Congress (ICEM) Program Committee, 1988-1990; Fourteenth ICEM Program Committee, 1997-1998; Fifteenth ICEM Program Committee, 2001-2002.

The Metallurgical Society of AIME: Alloy Phases Committee, 1977-1992; Northern California Section Chairman, 1979.

Materials Research Society: Symposium Organizer, 1987, 1990, 1994, 1995, 2010.

Organizer: Stanford Symposium on Applications of Contemporary Electron Microscopy, 1979-1994.

Organizer: US-France Asilomar Symposium on Amorphous Nickel-Titanium 1987.

A.S.U. National HREM Facility: Outside Proposal Review Committee, 1982-1990; Winter School Instructor, 1982-2006, 2011.

Electron Microscopy Short Courses: Harbin Institute of Technology, China, 1980; Linkoping University, Sweden, 1980, 1985; Korea Advanced Institute of Science and Technology, Seoul, 1988; Samsung Advanced Institute of Technology, Suwon, Korea, 2001, 2002.

Stanford University Short Course for Philips Technicians, 1989-1992, 1994.

Editorial Board: Journal of Applied Physics, 1994-1996; Journal of Electron Microscopy, 1996-present; and other journals.

Organizer: U.S.–Japan Workshop on "The Contributions of *In Situ* Electron Microscopy to the Understanding and Creation of Advanced Materials", Stanford Japan Center, Kyoto, Japan, 2000.

Co-Organizer: United Engineering Foundation Conference on Nanostructured Magnetic Materials, Irsee, Germany, 2002.

Co-Organizer: 70th Birthday Symposium in honor of Professor Gareth Thomas, ICEM XV, Durban, South Africa, 2002.

Organizer: In Situ Electron Microscopy Symposium, ICEM XV, Durban, South Africa, 2002.

Co-Organizer: Symposium on Semiconductor and Magnetic Materials, Microscopy and Microanalysis Conference, Quebec, Canada, 2003.

Chair: National Research Council Committee on Smaller Facilities, 2003-2006.

Organizer: ECI Conference: "Innovative Dynamic Studies of Materials at the Nanoscale", Gyeong-ju, Korea, 2008

Co-Organizer: "International Workshop on Remote Electron Microscopy for *In Situ* Studies": Stanford University, Stanford, California, 2008; Chalmers University of Technology, Gothenburg, Sweden, 2009; Carnegie Mellon University, Pittsburg, Pennsylvania, 2011.

Organizer: Symposium on Medical Applications of Nanotechnology, 11th International Congress on Advanced Materials, Rio de Janeiro, Brazil, 2009.

Co-Organizer: Symposium on Microscopy of Biological, Biomimetic and Medical Materials, 17th International Microscopy Congress, Rio de Janeiro, Brazil, 2010.

Co-Organizer: Symposium on Nanofunctional Materials, Nanostructures, and Nanodevices for Biomedical Applications II, Materials Research Society Fall 2010 Meeting, Boston, Massachusetts, 2010.

Co-Organizer: Stanford – Chalmers Workshop on Advancing Materials Innovatively, Stanford, California, 2012 Gothenburg, Sweden, 2013, Stanford 2014

Committee Member: National Science Foundation Materials 2022 Committee, 2012

Co-Organizer: Symposium on Nanoparticles: Applications and Bio-safety Issues, 18th International Microscopy Congress Prague, 2014

Co-Organizer: IAMNano 2014, International Workshop on Advanced and In-situ Microscopies of Functional Nanomaterials and Devices, Rio de Janeiro, 2014

COURSES TAUGHT (*present offerings)

Atomic Arrangements in Solids (G1); X-ray Diffraction Laboratory (UG1-4); Transmission Electron Microscopy (G2+)*; Nano-Characterization of Materials (G2+)*; Nanostructure and Characterization (UG1-4); Imperfections in Crystalline Solids (G1); Introduction to Materials Science: Nanotechnology Emphasis (UG1-4)*; Microscopic World of Technology (UG1-4); Japanese Companies and Japanese Society (UG2)*; Infrastructure of British Science and Technology (UG 3);Soccer and English Society (UG 3)

RESEARCH INTERESTS

Structure-property-processing correlations in materials, using high-resolution microscopy and diffraction techniques, application to development of integrated circuit and magnetic recording materials. Introduction of in situ high resolution electron microscopy.

PUBLICATIONS

1 NAS government report, 5 edited works, 6 book chapters, 238 archival journal articles, 204 conference articles, 2 patents. (List available on request).

PUBLICATIONS

A. EDITED WORKS AND BOOK CHAPTERS

    (a) Government Reports

        1. Committee on Smaller Facilities: R. Sinclair (chair), A. Aprahamian, A. I. Bienenstock, J. P. Bradley, D. R. Clarke, J. W. Davenport, F. J. DiSalvo, C. A. Evans, Jr., W. P. Lowe, F. M. Ross, D. J. Smith, J. M. Soures, L. Spicer, D. M. Tennant. National Research Council of the National Academy of Sciences. *Midsize Facilities: the Infrastructure for Materials Research*. Washington: National Academies Press, pp. 1-230 2006.

    (b) Edited Works

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