The effect of field cooling and field orientation on the martensitic phase transformation in a Ni$_2$MnGa single crystal

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The temperature and field dependence of the magnetization in a Ni$_2$MnGa single crystal was measured using a magnetometer with an applied field oriented in the [001] and [011] directions, respectively, of the parent cubic phase. It was found that the magnetic field magnitude and direction could be used to determine the magnetization of the sample during a thermal transformation from the austenitic phase to the martensite phase. This is explained in terms of a magnetic field induced growth of the twin variant having a favorable orientation to the external magnetic field. A model to interpret the magnetic response in terms of aligned twin variants in the shape memory material is discussed. © *2000 American Institute of Physics.* [S0021-8979(00)93208-0]

I. INTRODUCTION

A new mechanism for magnetically driven actuation has been suggested in Ni$_2$MnGa materials in terms of the choice of twin variants of a transformed martensitic phase. It has been previously reported that the twin variants of the martensite can be reoriented or aligned by an external magnetic field or stress.[1–4] The largest magnetostrictive strains in the tetragonal martensitic phase are predicted when a single twin variant exists with its c axis normal to the direction of the external magnetic field. However, typical experimental data shows only a small fraction of the lattice constant change ($\Delta c/c = -6.56\%$) due to the strain accommodation by different twin variant orientations.

It is well known that a martensitic phase transformation can be accompanied by the relaxation of strain associated with the formation of twin variants that choose configurations that minimize the strain energy. Each variant of the martensite has a unique value of its projected magnetization related to the angle between its c axis and the direction of the applied field. When an external magnetic field is applied, the total energy in the system can minimized by either nucleating favorable variants or increasing the volume fraction of the favorable variants present, through detwinning and/or twin boundary motion.

In comparison with the isotropic parent cubic phase, the tetragonal martensitic phase has a strong magnetocrystalline anisotropy.[5] This magnetic anisotropy energy density may play an important role in the nucleation of particular variants during a cooling procedure. In this work we explore this issue through the study of the field, field history, and temperature dependence of the magnetization near the martensitic phase transition temperature. When more than one variant exists in the sample determination of the anisotropy constants is more difficult, requiring more involved data analysis. We illustrate the use of the so-called ''singular point detection'' (SPD) technique to estimate the anisotropy con-

stants and the volume fraction of the twin variants with different orientations in Ni$_2$MnGa martensitic phase.

II. EXPERIMENTAL PROCEDURES

Crystals of Ni$_2$MnGa were grown by melting the pure elements in an evacuated flat-bottom quartz tube back-filled with a low partial pressure of Ar. The single crystal ($m = 23.4$ mg) employed here was cut and polished into a disk shape. Both circular faces were aligned parallel to the (100) plane of the parent cubic $L2_1$ room temperature structure. The ratio of diameter to thickness of the crystal was about 10. Clear evidence of the cubic to tetragonal martensitic phase transformation is seen in thermal hysteresis of the fixed field magnetization at a temperature $T_m \sim 190$ K as shown in Fig. 1.

A superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMSR2) was used to measure the dc magnetization of the sample in fields up to 5 T. The applied magnetic field, which was parallel to the both circular faces, was oriented along the [001] or [011] directions, respectively, of the sample at room temperature. We refer to these field orientations as the [001] orientation
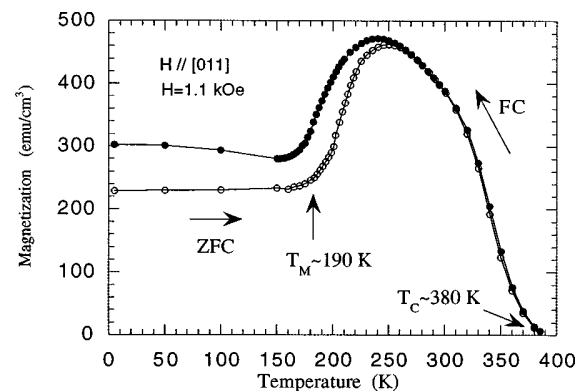

FIG. 1. Temperature hysteresis of the magnetization in a single crystal of Ni$_2$MnGa in a fixed external field of 1.1 kOe oriented along the [110] axis of the cubic lattice.

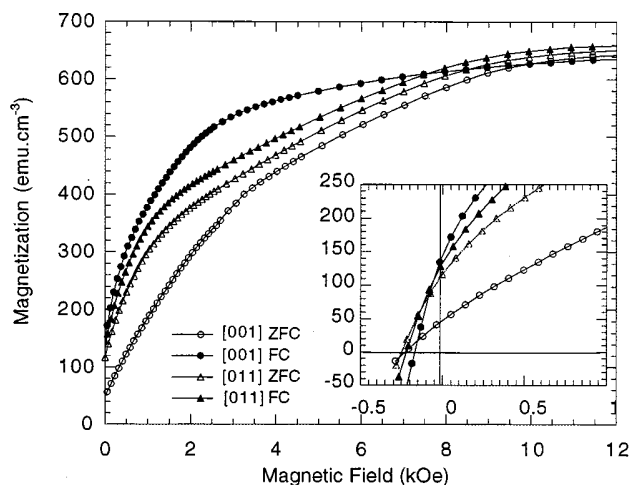[a)]Electronic mail: mm7g@andrew.cmu.edu

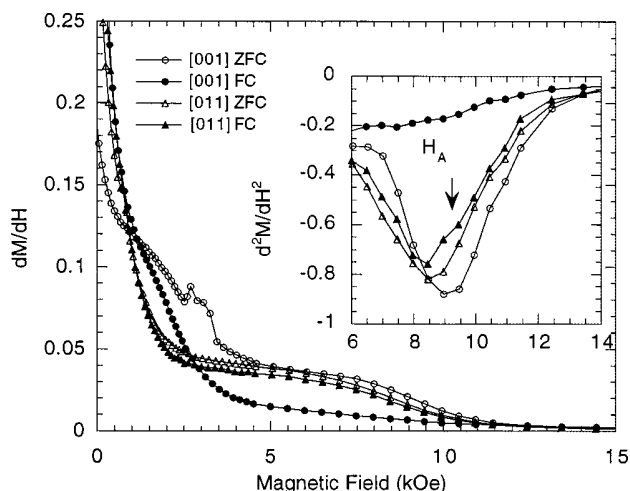FIG. 2. Magnetization curves, $M(H)$, of the single crystal Ni$_2$MnGa in the martensitic phase.

FIG. 3. Field dependence of the first and the second derivatives of the magnetization $M(H)$, with respect to H, dM/dH, and d^2M/dH^2.

and [011] orientation. At low temperature $T < T_m$, these arrangement would lead to different field orientations with the tetragonal crystal lattice for each individual twin variant in the sample. For our convention for labeling the different orientations we always let the [001] direction coincide with the short axis (i.e., $c \approx 5.44$ Å) and the [100] or [010] with either of the long axes (i.e., $a = b \approx 5.90$ Å).

To prepare the initial state of the transformed martensite and its twin variant distribution, two experimental processes were employed:

(a) for a so-called zero field cooling (ZFC) measurement, the sample was first cooled from its Curie temperature, $T_0 \sim 380$ K, to 170 K in zero field ($H < 1$ Oe). Subsequently, the sample was saturated in an applied field of 5 T. Its dc magnetic moment was then measured as a function of decreasing field;

(b) for a so-called field cooling (FC) process, after decreasing the temperature from 380 to 350 K in zero field, the sample was slowly cooled to 170 K in a field of 5 T. After cooling the moment was measured as the applied field was decreased.

III. RESULTS AND DISCUSSIONS

ZFC and FC magnetization curves for the [001] and [011] field orientations for the martensitic Ni$_2$MnGa are illustrated in Fig. 2. The amplitude of the field shown here is the internal magnetic field, which has been corrected for demagnetization effects based on the sample's geometry. The saturation magnetization of the sample, M_s, is 650 emu cm^{-3} for both, in fields of $H \sim 1$ T. However, the shapes of these magnetization curves are obviously different. Several observations can be made:

(1) It can be seen that the FC curves always lie above the ZFC curves regardless of the field arrangement.
(2) The difference between the FC and ZFC curve for the

The difference in the anisotropy energy density, required saturating the sample in different field orientations, cannot be interpreted in terms of an anisotropy change associated with the sample's shape. The largest field induced strain is -6.56%. Even if this strain was along one direction, the ellipticity of the sample caused by the strain would only change the demagnetization factor, D, by about 0.02%. Corresponding to this small change of the D factor, the energy density difference from that calculated using the original value of D is less than 0.5%. Our interpretation to the experimental result is that the crystal anisotropy energy of the martensite contributes to the field orientation dependence of the magnetization.

It has been indicated by a Ullakko *et al.*'s experiments that an external magnetic field can be used to align some of the twin variants in single crystal of Ni$_2$MnGa.[1,2] As compared with zero field cooling procedure, the field cooling induced a larger negative strain in the martensite phase with decreasing temperature. This implies that the favorable variants formed during the martensitic transformation are those for which the c axis is parallel to the direction of the applied magnetic field. The difference of the FC and the ZFC curves with [001] field orientation illustrated in the Fig. 2 supports the claim that the c axis of the tetragonal phase is the easy axis of magnetization.

It is well known that the magnetization curve, $M(H)$, for a single crystal with its field, H, oriented in a hard direction has a singularity at the saturation field, i.e., where the applied field, $H = H_A$, the anisotropy field. The singularity is a consequence of the intersection of the two different branches of the magnetization curve. For $H < H_A$, M depends on H, while as $H > H_A$, $M(= M_s)$ is a constant. The formula:

$$H_A = (2K_1 + 4K_2)/M_s \tag{1}$$

expresses the anisotropy field in terms of the first and second order anisotropy constants, K_1 and K_2, respectively, of the
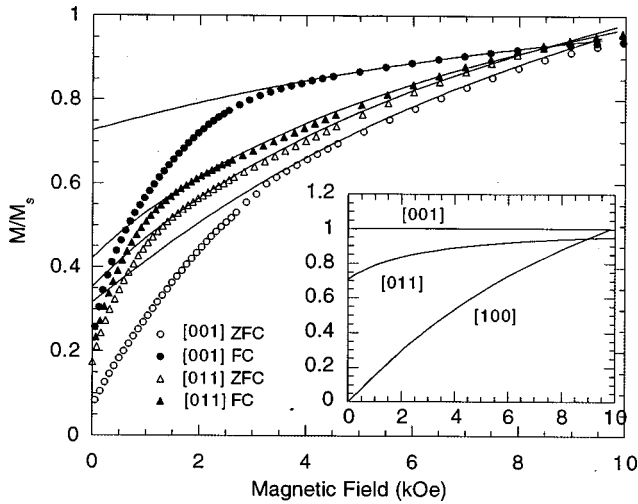
FIG. 4. Calculated magnetization curves (solid line) for fitting the experimental data to yield the crystal anisotropy constants and the volume fractions of the different twin variants in the sample. Inset shows the calculated magnetization curve for a single tetragonal variant.

FIG. 5. Schematic of the distribution of twin variants with different orientations in the martensitic Ni_2MnGa material.

smoother $M(H)$ behavior is observed. However, due to the contribution of the twinned regions oriented with their hard directions nearly parallel to H, the singularity in $M(H)$ can still be observed but at fields less than the saturating field. The sharpness of the change of $M(H)$ at H_A depends on the distribution of hard axes, and the ratio of the first to second order anisotropy constants.[6,7] Because of the static equilibrium achieved by contacting twinned regions along their edges, the most probable direction of the c axes of the variants is along one of the three primary orthogonal axes of the cubic lattice of the untransformed single crystal. The distribution of the three twin variants should reflect equal probability of the three orthogonal orientations in the absence of a field. Thus the volume fraction of each of the variants should equal one third for a single crystal that undergoes zero field cooling. However, application of a field will result in a distribution of the variants that minimizes the total energy, which now includes anisotropy and Zeeman energy terms.

We assume for our analysis that the transformed martensite has a small deformation (in comparison with the large strain in each of the individual variants) and that each variant has a unique projected magnetization. A singular point on the magnetization curve, $M(H)$, of our sample can be detected by observing successive derivatives of M with respect to the internal field, H. The first and the second derivatives, dM/dH and d^2M/dH^2, shown in Fig. 3 respectively, illustrate such a singular point detection. The peak position in dM^2/dH^2 as a function of H corresponds to the anisotropy field, H_A, of the martensite phase. A theoretical prediction is that the amplitude of the peak in the second derivative, d^2M/dH^2, as a function of H, should be proportional to the volume fraction of crystallites oriented with their easy axes perpendicular to H. Our results indicate that the field cooling process produces an increased volume fraction of variants
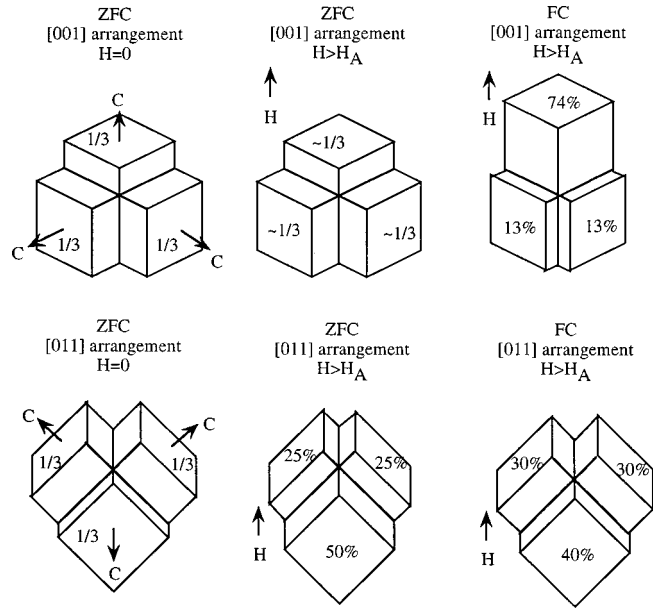
Considering Zeeman (field) and anisotropy energy densities, for a variant with it's c axis perpendicular to the field, the magnetization curve, $M(H)$ can be described by

$$HM_s = [(2K_1 + 4K_2(M/M_s)^2](M/M_s) \qquad (2)$$

for $H \leqslant H_A$. The best fits to the experimental $M(H)$ curve, using expression (2) are shown in Fig. 4, for which the first and second order anisotropy constants are $K_1 = 2.0 \times 10^6$ and $K_2 = 0.50 \times 10^6$ erg cm^{-3}, respectively. The derived value of $H_A = 9.5$ kOe is in good agreement with the observation of the SPD technique shown in Fig. 3. The volume fraction of each variant in the sample in initial state $(H \sim H_A)$ has been schematically illustrated in Fig. 5.

ACKNOWLEDGMENTS

Note added in proof: After submission of this paper it came to our attention that R. Tickle and R. D. James reported $K_n = 2.45 \times 10^6$ erg cm^{-3} for a single variant of Ni_2MnGa (Ref. 8).

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