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McCrone (1957, 1965) has also given detailed descriptions of the microscopic examinations and phenomena that can be used to distinguish polymorphism from other phenomena that sometimes have been mistakenly labelled as pseudopolymorphism: mesomorphism (i.e. liquid crystals), grain growth (boundary migration and recrystallization), and lattice strain.

### 1.2.3 *Conventions for naming polymorphs*

Part of the difficulty encountered in searching and interpreting the literature on polymorphic behaviour of materials is due to the inconsistent labelling of polymorphs. In many cases, the inconsistency arises from lack of an accepted standard notation. However, often, and perhaps more important, it is due to the lack of various authors' awareness of previous work or lack of attempts to reconcile their own work with earlier studies (see, for instance, Bar and Bernstein 1985). While many polymorphic minerals and inorganic compounds actually have different names (e.g. calcite, aragonite and vaterite for calcium carbonate or rutile, brookite, and anatase for titanium dioxide) this has not been the practice for molecular crystals, which have been labelled with Arabic (1, 2, 3, . . .) or Roman (I, II, III, . . .) numerals, lower or upper case Latin (a, b, c, . . . or A, B, C, . . .) or lower case Greek ( $\alpha$ ,  $\beta$ ,  $\gamma$ , . . .) letters, or by names descriptive of properties (red form, low-temperature polymorph, metastable modification, etc.).

As Threlfall (1995) and Whitaker (1995) have commented, arbitrary systems for naming polymorphs should be discouraged to avoid confusion surrounding the number and identity of polymorphs for any compound. Relative stability and/or order of melting point, as well as a specification of the monotropic or enantiotropic nature of the polymorphic form (see Section 2.2.4) have also been suggested as a basis for labelling (Herbstein 2001), but these do not allow for the discovery of forms with intermediate values, in addition to the fact that small differences in stability or melting point might lead to different order and different labelling by different workers. McCrone (1965) proposed using Roman numerals for the polymorphs in the order of their discovery, with the numeral I specifying the most stable form at room temperature. By Ostwald's Rule (Ostwald 1897) (Section 2.3) the order of discovery should in general follow the order of stability the least stable appearing first. McCrone also supported the suggestion by the Koflers (Kofler and Kofler, 1954) that the Roman numeral be followed by the melting point in parentheses. In fact, the successors of the Koflers at the Innsbruck school have very much followed this practice (Kuhnert-Brandstätter 1971), although in general it has not been adopted by others. The use of melting points is complicated by the fact that while this datum has a clear thermodynamic definition, a number of techniques are employed to determine the melting point (or melting point range, in many cases) so that real or apparent inconsistencies may arise from such a designation (see Sections 4.2 and 4.3).

In view of the body of literature already extant and the questions surrounding the definition of a polymorph it does not appear to be practical to define hard and fast rules for labelling polymorphs. The Kofler method has clear advantages, since the melting point designation may eliminate some questions of identity; hence its use should be



encouraged. For those studying (and naming) polymorphic systems it is important to be fully aware of previous work, to try to identify the correspondence between their own polymorphic discoveries and those of earlier workers, and to avoid flippancy in the use of nomenclature in the naming of truly new polymorphs.

### 1.3 Is this material polymorphic?

#### 1.3.1 Occurrence of polymorphism

Perhaps the most well-known statement about the occurrence of polymorphism is that of McCrone (1965): 'It is at least this author's opinion that every compound has different polymorphic forms and that, in general, the number of forms known for a given compound is proportional to the time and money spent in research on that compound.' As a corollary to this rather sweeping, even provocative, statement, McCrone noted that 'all the common compounds (and elements) show polymorphism', and he cited many common organic and inorganic examples.

These echo similar statements by Findlay (1951) p. 35, '[polymorphism] is now recognized as a very frequent occurrence indeed', Buerger and Bloom (1937), 'polymorphism is an inherent property of the solid state and that it fails to appear only under special conditions', and Sirota (1982), '[polymorphism] is now believed to be characteristic of all substances, its actual non-occurrence arising from the fact that a polymorphic transition lies above the melting point of the substance or in the area of yet unattainable values of external equilibrium factors or other conditions providing for the transition.'

Such statements tend to give the impression that polymorphism is the rule rather than the exception. The body of literature in fact indicates that caution should be exercised in making them. It appears to be true that instances of polymorphism are not uncommon in those industries where the preparation and characterization of solid materials are integral aspects of the development and manufacturing of products (i.e. those on which a great deal of time and money is spent): silica, iron, calcium silicate, sulphur, soap, pharmaceutical products, dyes, and explosives. Such materials, unlike the vast majority of compounds that are isolated, are prepared not just once, but repeatedly, under conditions that may vary slightly (even unintentionally) from time to time. Similarly, in the attempt to grow crystals of biomolecular compounds, much time and effort is invested in attempts to crystallize proteins under carefully controlled and slightly varying conditions, and polymorphism is frequently observed (Bernstein *et al.* 1977; McPherson 1982). Even with the growing awareness and economic importance of polymorphism, most documented cases have been discovered by serendipity rather than through systematic searches. Some very common materials, such as sucrose and naphthalene, which certainly have been crystallized innumerable times, have not been reported to be polymorphic. The *possibility* of polymorphism may exist for any particular compound, but the conditions required to prepare as yet unknown polymorphs are by no means obvious. There are as yet no comprehensive systematic methods for feasibly determining those conditions. Moreover, we are almost totally ignorant about the properties to be expected from any new polymorphs that might be obtained.

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