Ferroelasticity

V K WADHAWAN

Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Abstract. This paper surveys the present-day description of ferroelasticity in terms of the notion of symmetry descent. Based on the work of earlier authors, a symmetry classification of phase transitions is presented. A general classification of twinning in crystals is also attempted on the basis of this scheme. Most kinds of twinning fall into two broad categories: nonferroelastic and ferroelastic. The shape-memory effect associated with martensitic transitions is discussed briefly. The interesting possibilities of this effect in the case of ferroelectric ferroelastics, for which the electric field provides an additional control parameter, are also mentioned.

Keywords. Ferroelasticity; symmetry; phase transitions; twinning; ferroelectric ferroelastics.

1. Introduction

The elastic (or recoverable) response of a material to a small external stress can be nonlinear in general, although it is predominantly linear in a large number of crystalline substances, glass, and many cross-linked polymers. The elastic response is markedly nonlinear in cellular structures like wood and in “elastomers” like rubber, which consist of long, spaghetti-like, entwined molecules. The recoverable strain in materials of either the linear or the nonlinear type is usually a *single-valued* function of the small applied stress. There is, however, a technologically important class of materials for which the elastic response is neither linear nor single-valued. Ferroelastic materials belong to this class.

A good deal of our present understanding of ferroelastics has been obtained by considering them as the mechanical analogues of ferroelectric and ferromagnetic materials. In fact, the concept of ferroelasticity itself was introduced by direct analogy with ferroelectricity and ferromagnetism. In particular, one associates stress-strain hysteresis with a ferroelastic, which implies that the spontaneous strain is a double-valued function of stress, even for vanishingly small values of the stress (figure 1). The key to such mechanical behaviour lies in the domain structure of the ferroelastic. As we shall see, the most elegant and rational description of the domain structure of a crystal comes from considerations of broken symmetry at a real or hypothetical phase transition. A proper understanding of ferroelastic behaviour is hardly possible unless one pays attention to the ferroelastic phase transition.

The most significant factor contributing to this understanding has been the approach, initiated by Aizu (1970) and developed by a number of other workers, (Janovec *et al* 1975; Tolédano and Tolédano 1976, 1977, 1980, 1982), according to which ferroelastic phase transitions form part of the larger class of *ferroic phase transitions*: these are transitions which result in a change of the point-group symmetry of the crystal. A *ferroelastic* phase transition, by definition, entails not only a change of the

Figure 1. Stress-strain hysteresis curve for the ferroelastic β' - $\text{Au}_{26}\text{Cu}_{30}\text{Zn}_{44}$ martensite at 298 K (Nakanishi *et al* 1971).

point symmetry, but also a change of the crystal system (if we regard the hexagonal and trigonal crystal systems as a single system) (Tolédano and Tolédano 1980).

Ferroc behaviour of crystals encompasses not only ferroelasticity but also other, more subtle, types of mechanical properties like ferrobielasticity. Here I shall describe the salient features of the formalism of ferroicity, developed over the last decade and a half. It will be further argued that the notion of ferrocity also provides a very rational and fairly comprehensive description of the occurrence of twinning in crystals. Twinning, in its general sense, is a far more common feature of crystals than has been realized so far. Ferroelasticity itself is a type of mechanical twinning “with change in form” (Klassen-Neklyudova 1964).

2. Ferroelasticity

The term “ferroelasticity” has had a number of connotations, all similar, and yet not quite the same. It was first used in physical metallurgy by Frank in the early 1950’s to describe the “rubber-like” memory effect in the gold-cadmium alloy (see Lieberman *et al* 1975). A piece of $\text{Au}_{1.05}\text{Cd}_{0.95}$ or InTl , when deformed severely (with up to 10% strain) at room temperature, exhibits almost complete crystallographic and morphological recovery when the external stress is removed. As has been pointed out by Lieberman *et al* (1975), there is a tendency in the literature to use the term “ferroelasticity” somewhat indiscriminately in this context. It is important to distinguish clearly between two situations for describing this pseudoelastic behaviour, depending on whether the deforming stress is applied just above the phase transition temperature T_c , or at temperatures below T_c . Figure 2 depicts the two cases schematically. The first case represents “pseudoelasticity by transformation”, and the second “pseudoelasticity by reorientation” (Warlimont 1976). In the first case the crystal is initially in the parent phase and the application of a deforming stress causes a reversible stress-induced phase transition. When the stress is removed, all parts of the specimen revert to the parent phase. This behaviour is also described as *superelasticity* (Wasilewski 1975; Barrett and Massalski 1980), or *martensitic thermoelasticity* (Lieberman *et al* 1975). But it must not be called ferroelasticity. Ferroelastic response does not involve any phase transition. Pseudoelastic recovery by reorientation, depicted on the right in figure 2, does correspond to ferroelasticity (Lieberman *et al* 1975). The material is already in the lower-temperature, or ferroelastic phase. It is also capable of existing in more than one twin state or domain. The rubber-like pseudoelastic behaviour results from the reversible migration of the twin boundaries or

Figure 2. (a) Pseudoelasticity by transformation (or superelasticity), and (b) pseudoelasticity by reorientation (or ferroelasticity).

domain walls. This property is also referred to as *piezomorphic memory* by Lieberman *et al* (1975). As we shall see presently, shape recovery or memory is not regarded by physicists as an essential feature of ferroelasticity; the shape recovery at temperatures below T_c results from a volume-dependent restoring force, which may not always be present in a ferroelastic crystal.

The stress-assisted double phase transition in TiNi also leads to a mechanical response which resembles ferroelasticity (Wasilewski 1975). However, in keeping with the usage in the rest of physics, the term “ferroelastic” should not be used for those switching phenomena which involve a stress-assisted or any other kind of *phase transition*.

The term “ferroelasticity” was introduced in 1969 (Alefeld *et al* 1969; Aizu 1969) and was used in quite different contexts. Alefeld and coworkers (see Alefeld 1971) were dealing with the problem of hydrogen and other point defects in metals like Nb and Pd, whereas Aizu viewed ferroelastic behaviour as resulting from the occurrence of domain structure (or “orientation states”), taking no note of the presence of any defects in the crystal. We first consider the question of hydrogen or other interstitial impurities in crystals in brief, followed by an exposition of Aizu’s approach and its subsequent development by other workers.

Hydrogen occupies interstitial sites in metals and causes a displacement of the surrounding metal atoms, thus creating local strain fields, as well as a net macroscopic strain. Point defects like hydrogen which distort the host lattice are called *elastic dipoles* (see, *e.g.* Peisl 1978). In general the distortion may be anisotropic and one needs a second-rank polar tensor, (ϵ_{ij}^d), to describe the strain field around a defect. If a uniaxial stress is applied to such a system, a stress-induced diffusion of the interstitial defects to neighbouring sites occurs, resulting in a reorientation of the anisotropic elastic dipoles (figure 3). This time-dependent or anelastic relaxation is known as the *Snoek effect*. Obviously, a stress-strain hysteresis loop looking like the ferroelastic curve of figure 1, will result from such a process. If the defects are highly mobile, one observes the so-called *Gorsky relaxation*, in which the directed diffusion of the defects over many lattice distances occurs under a stress *gradient*. The strain field created by an elastic dipole is long-ranged and is felt by the other elastic dipoles in the metal. This “elastic interaction”

is believed to be largely responsible for the $\alpha \rightarrow \alpha'$ phase transition in the H-Nb and H-Pd systems (see Wagner 1978). The reason is that Landau's mean field theory works well for this phase transition and it is known that this theory is good for transitions driven by long-range interactions.

Clearly, ferroelastic behaviour resulting from the presence of point defects will disappear in the absence of these defects. This is where Aizu's concept of ferroelasticity differs from that of Alefeld *et al.* In the former, ferroelastic properties arise from the pseudosymmetry resulting from a (real or hypothetical) structural phase transition, and not from the presence of defects. The concept of a *prototype symmetry* plays a central role here. The prototype is the highest supergroup symmetry attainable by, or conceivable for, a given crystal without requiring a rupture or reconstructive rearrangement of chemical bonds. A ferroelastic phase (more generally, a ferroic phase) emerges from the prototype symmetry owing to a small, spontaneous, symmetry-breaking "distortion" when some control parameter such as the temperature is varied. Figure 4 provides an illustration of this, where an orthorhombic symmetry mmm (D_{2h}) is assumed for the prototype. A phase transition to monoclinic symmetry can lead to two possible *orientation states*, S_1 and S_2 , both of which are equally stable in the absence of an external force. Although the actual symmetry of the ferroelastic phase is monoclinic, it is also pseudo-orthorhombic because it differs only slightly from the prototype configuration. Since the two states S_1 and S_2 also differ only slightly from each other, it should be possible to switch S_1 to S_2 and *vice versa* by applying a small, suitably oriented, uniaxial stress, as shown in the lower part of figure 4. This possibility of the occurrence of more than one orientation state, (*i.e.*, the presence of domain structure), is what is responsible for ferroelastic behaviour, in particular the stress-strain hysteresis. Aizu (1969) defined a ferroelastic as a crystal which has two or more equally stable

Figure 3. Stress-induced diffusion of an interstitial impurity (Snoek effect).

Figure 4. Schematic of an orthorhombic-to-monoclinic ferroelastic phase transition, giving two equivalent orientation states S_1 and S_2 in the lower-symmetry phase.

Figure 5. Illustrating the distinction made in physical metallurgy between (a) ferroplastic behaviour and (b) ferroelastic behaviour. The curves shown are for the alloy $\text{Au}_{1.05}\text{Cd}_{0.95}$ (Lieberman *et al* 1975).

orientation states, and which can be switched from one such state to another by the application of a suitable uniaxial stress. Since all the orientation states are equally stable, the system may not bounce back to the initial state when the stress is removed. It is clear from the above definition that what is called ferroelasticity by Aizu would be described as *ferroplasticity* by physical metallurgists (see Lieberman *et al* 1975). The distinction between ferroelastic and ferroplastic behaviour is illustrated in figure 5 for a gold-cadmium alloy. Very often this distinction is not made in physics, because the term “ferroelastic” is used to imply “ferromechanical”, in the sense that the driving force conjugate to the ‘order parameter’ (strain) is mechanical or elastic in nature (and not electric or magnetic).

Aizu’s definition of ferroelasticity also supersedes the earlier usage of this word in physics for describing magnetostrictive and electrostrictive distortions in ferromagnetic and ferroelectric crystals. It is possible for a crystal to be ferroelastic without also being ferroelectric or ferromagnetic. The present concept of ferroelasticity has led to the development of an elegant, symmetry-based, classification of a very large class of phase transitions, and we turn now to an outline of this scheme.

3. A symmetry classification of phase transitions in crystals

Figure 6 presents a symmetry classification of phase transitions in crystals based on the work of various authors (Tolédano and Tolédano 1982 and references therein). We exclude from this scheme reconstructive phase transitions like the graphite-to-diamond transition. We also exclude those martensitic and other phase transitions where the lattice distortion is so drastic that it results in a change of coordination number. An example of this is the transition occurring in CsCl, where the structure changes from

Figure 6. A classification of phase transitions based on considerations of symmetry descent from a prototype symmetry.

simple cubic to fcc on heating through the phase transition at 733 K, resulting in a change of the coordination number from 8 to 6.

We use the term *distortive* for the phase transitions considered in figure 6, although even this term is not entirely adequate. It is intended to cover both displacive and order-disorder phase transitions (Muller 1981). The term "group-subgroup type phase transitions" would be perhaps more appropriate if we remember that a group permits the trivial possibility of being its own subgroup or supergroup. In this scheme, all phases of a crystal are regarded as derived from a certain supergroup symmetry called the *prototype* (Aizu 1981). The prototype is the highest conceivable crystallographic symmetry from which a given phase can result by a small distortion. Phase transitions in this classification are therefore not always between two consecutive phases, but between the prototype and the phase under consideration. All phase transitions in crystals can be divided into two categories: *isomorphous phase transitions* and *nonisomorphous phase transitions*. In the former, there is no change in the space-group symmetry of the crystal. A well-known example is the transition occurring in Ce at a pressure of 7.7 kbar (0.77 GPa), involving a volume collapse of about 14 %, but leaving the space-group symmetry unchanged as $Fm\bar{3}m$ (O_h^5). The change of space-group symmetry at a nonisomorphous phase transition can be of two types: *nonferroic* and *ferroic*. In a nonferroic phase transition there is a change in only the translational symmetry, but no change in the point-group symmetry (Tolédano and Tolédano 1982). Perhaps the best known example of this type is the order-disorder transition occurring in the alloy Cu_3Au at 667 K, where the symmetry changes from $Fm\bar{3}m$ (O_h^5) to $Pm\bar{3}m$ (O_h^1). The high pressure transition occurring in EuS at 215 kbar (21.5 GPa) is another example, involving the same symmetry change as Cu_3Au . Ferroic phase transitions involve a change of the point-group symmetry with or without a change of the translational symmetry. If there is a change of the point-group symmetry but no change of the crystal system (provided we do not regard the hexagonal and trigonal crystal systems as distinct for the purposes of this definition), the phase transition is defined as *nonferroelastic* (Tolédano and Tolédano 1976). Examples of nonferroelastic transitions include the ferroelectric transition in triglycine sulphate (symmetry changing from

$2/m(C_{2h})$ to $2(C_2)$), and the $\beta \rightarrow \alpha$ transition in quartz (symmetry changing from $622(D_6)$ to $32(D_3)$). With the above proviso about hexagonal and trigonal crystal systems, a change of crystal system becomes a necessary as well as a sufficient condition for a phase transition to be called *ferroelastic* (Tolédano and Tolédano 1980). A ferroelastic phase transition may be either purely ferroelastic, as in BiVO_4 , or it may be simultaneously ferroelectric as in BaTiO_3 , or simultaneously ferromagnetic as in Mn_3O_4 . The Ni-I boracite undergoes a phase transition which is simultaneously ferroelastic, ferroelectric and ferromagnetic.

I have recently come across a statement by Fleury and Lyons (1981) according to which a centre of symmetry is always preserved across a ferroelastic phase transition. The rationale behind this statement is not entirely clear; in the cubic-to-tetragonal phase transition in BaTiO_3 , for example, the centre of symmetry is not preserved even though the phase transition is ferroelastic; the fact that the order parameter of this transition does not have the symmetry of a strain component does not preclude the occurrence of ferroelasticity in the tetragonal and the other lower-symmetry phases of BaTiO_3 (see also Aizu 1972a).

4. Ferroic crystals

A ferroic crystal is one which can undergo a ferroic phase transition. The definition of a ferroic transition in terms of a change in the point-group symmetry has a deep significance. Among other things, it enables us to classify ferroic crystals in terms of their macroscopic physical properties like polarization, strain, etc. The reason for this is that these properties are described by the point group symmetry of the crystal, and a ferroic phase is derived, by definition, by deleting certain point-group operations of the prototype. The lowering of the point symmetry at a ferroic phase transition must necessarily be accompanied by the emergence of at least one new macroscopic tensor property component. If this component also has the symmetry of the order parameter, the corresponding response function becomes anomalously large in the vicinity of the transition. This is important in many of the device applications of ferroic crystals.

Let us imagine a crystal in a particular orientation state S_1 , under the influence of an external electric field (E_i), a magnetic field (H_i) and a stress (σ_{ij}). The free energy density for this orientation state can be written as

$$d\Phi = SdT - P_i dE_i - M_i dH_i - \varepsilon_{ij} d\sigma_{ij}, \quad (1)$$

where S denotes the entropy, P_i the polarization, M_i the magnetization, and ε_{ij} the strain. P_i , M_i and ε_{ij} consist of a spontaneous part (if any) and an induced part owing to the presence of the external fields. One can integrate (1) to obtain the free-energy density Φ_1 for state S_1 . Similarly, the free-energy density Φ_2 can be obtained for another orientation state S_2 . The difference $\Delta\Phi = \Phi_2 - \Phi_1$ determines whether the crystal makes a state shift from S_1 to S_2 , or vice versa under the action of the external forces. The final expression for $\Delta\Phi$ can be written as follows (see Wadhawan 1982 for details):

$$\begin{aligned} -\Delta\Phi = & \Delta P_i^0 E_i + \Delta M_i^0 H_i + \Delta \varepsilon_{ij}^0 \sigma_{ij} + \frac{1}{2} \Delta \kappa_{ij} E_i E_j + \frac{1}{2} \Delta \chi_{ij} H_i H_j \\ & + \frac{1}{2} \Delta s_{ijkl} \sigma_{ij} \sigma_{kl} + \Delta \alpha_{ij} E_i H_j + \Delta d_{ijk} E_i \sigma_{jk} + \Delta Q_{ijk} H_i \sigma_{jk} \\ & + \frac{1}{6} \Delta e_{ijk} E_i E_j E_k + \dots \end{aligned} \quad (2)$$

Here $\Delta P_i^0 = P_{2i}^0 - P_{1i}^0$ is the difference between the values of the i th component of the spontaneous polarization in the states S_2 and S_1 . The other difference terms are defined similarly. κ_{ij} , χ_{ij} and s_{ijkl} are, respectively, the elements of the electric susceptibility tensor, the magnetic susceptibility tensor, and the compliance tensor. α_{ij} , d_{ijk} and Q_{ijk} are elements of the magnetoelectric, piezoelectric and piezomagnetic tensors respectively, and e_{ijk} stands for the components of the third-order electric susceptibility tensor. Equation (2) serves to define the various types of ferroic crystals. A ferroelectric crystal is defined as one for which at least one pair of orientation states exists such that $\Delta P_i^0 \neq 0$ for one or more values of i . Similarly, a ferroelastic crystal is one for which $\Delta \epsilon_{ij}^0 \neq 0$ for at least one pair of orientation states. A ferromagnetic crystal is defined similarly. Ferroelectric, ferroelastic and ferromagnetic crystals are collectively called *primary ferroics*.

It is clear from (2) that other types of ferroicity are also possible. For example, if $\Delta s_{ijkl} \neq 0$ for one or more pairs of orientation states, the crystal is said to be a *ferrobielastic*. Quartz is a well-known example of a ferrobielastic crystal. The Dauphiné twins of α -quartz differ in the sign of the elastic compliance coefficient s_{1123} (as well as in the signs of other symmetry-related coefficients). Consequently, although the two twin states do not differ in spontaneous strain (and therefore quartz is not a ferroelastic), a difference in *induced* strain can be established between them under the action of a common uniaxial stress. A suitable stress can then act on this difference to cause switching from one twin state to the other. Lead germanate, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, is another crystal which can be expected to exhibit ferrobielastic and ferroelectric switching concomitantly. Hence, for applied stresses smaller than the elastic limit, crystals may exhibit elastic, ferroelastic and ferrobielastic (figure 7) mechanical response, or any combination of these.

Still other types of ferroic behaviour can be anticipated from (2). Differences in the piezoelectric tensor between two orientation states can result in *ferroelastoelectric* switching under the *combined* action of an electric field and a uniaxial stress. In an analogous manner, *ferromagnetoelastic* switching becomes possible through differences in the piezomagnetic tensor, and so on. Ferrobielasticity ($\Delta\Phi \sim \sigma^2$), ferrobielectricity ($\Delta\Phi \sim E^2$), ferrobimagnetism ($\Delta\Phi \sim H^2$), ferroelastoelectricity ($\Delta\Phi \sim \sigma E$), ferromagnetoelasticity ($\Delta\Phi \sim \sigma H$) and ferromagnetolectricity ($\Delta\Phi \sim HE$) are the six types of *secondary ferrocity* possible in crystals (Aizu 1972a, 1973). Aizu (1970) has derived 773 possible "species" of ferroic crystals (a species is characterized by the point symmetry of the prototype and the point symmetry of the ferroic phase in question) by assuming that: (a) every time-symmetric point group can become the prototypic point group in some species of ferroic crystal; (b) when a prototypic point group is specified, every one of its proper subgroups can become the ferroic point group in some species with this prototypic point group; and (c) when a

Figure 7. Typical curves illustrating the distinction between elastic, ferroelastic, and ferrobielastic response of crystals to external stress.

prototypic and a ferroic point group are specified, as many species are possible as the number of different ways in which the elements of the ferroic point group can be put in correspondence with the elements of the prototypic point group.

5. Domain structure

The mechanical behaviour of a ferroelastic is influenced in a crucial way by its domain structure. In fact, many of the applications of ferroelastics and other ferroic crystals depend on our ability to control the nucleation and mobility of their domain walls. The fracture-toughness achieved in zirconia by exploiting the ferroelastic phase transition is a case in point. A surprisingly large amount of information about the expected domain structure of a crystal can be obtained from symmetry considerations alone. Two or more domains or twin configurations become possible in a crystal because of the lowering of the prototype symmetry at a real or hypothetical phase transition. Regions of the crystal which were completely equivalent under the operations of the prototype symmetry group become nonequivalent either with respect to orientation, or with respect to mutual disposition, or both; this is what gives a crystal its domain structure.

In the spirit of the Landau theory, one holds the emergence of an order parameter responsible for the lowering of the prototype symmetry. The symmetry G of the daughter phase is determined by the symmetry G_0 of the prototype and the symmetry Γ of the order parameter. G can be obtained by the principle of superposition of symmetries, commonly known as the *Curie principle* (see Kopstik 1968). Shubnikov and Kopstik (1974) have stated a more updated version of it and called it the Neumann-Minnigerode-Curie principle, (NMC) principle. According to the Curie principle: "When several different natural phenomena are superimposed on one another, forming a single system, their *dissymmetries* add up. As a result, only those elements of symmetry common to all the phenomena remain". If, for example, G_1 and G_2 denote the symmetry groups corresponding to two physical properties of a crystal, the symmetry G of the crystal cannot be higher than the intersection of G_1 and G_2 . If we consider the symmetry groups G_i , $i = 1, 2, 3, \dots$, of all possible physical properties of the crystal, the symmetry G of the crystal is given by the intersection of all these groups:

$$G = G_1 \cap G_2 \cap G_3 \dots = \bigcap G_i \quad (3)$$

The more familiar Neumann's principle follows from the above as an inclusion relation:

$$G_i \supseteq G. \quad (4)$$

In other words, the symmetry element (G_i) of any physical property of a crystal include all the symmetry elements (G) of the crystal. G is contained in every G_i ; in fact, it is a subgroup of every G_i . Equations (3) and (4) can be combined (Shubnikov and Kopstik 1974) to read

$$G_i \supseteq G = \bigcap G_i \quad (5)$$

In the context of a phase transition accompanied by the emergence of an order parameter having the symmetry group Γ , it follows that the symmetry group G of the resultant phase is given by

$$G = G_0 \cap \Gamma, \quad (6)$$

where G_0 is the symmetry group of the disordered phase. G is that maximal subgroup of G_0 which leaves the order parameter invariant (Janovec 1972).

The Curie principle can be applied not only to determine the compatibility or incompatibility of G , G_0 and Γ , but also to understand inter-domain relationships. Suppose a crystal undergoes a phase transition from symmetry G_0 to G on cooling, (that is, under the influence of a scalar control parameter, T); it follows that, in the lower-temperature phase, the macroscopic symmetry of the sample crystal *as a whole* would be the intersection of G_0 and the symmetry group of a scalar. The intersection of these two is G_0 itself. Thus, macroscopically speaking, the crystal *as a whole* has an average symmetry G_0 even in the daughter phase. But the microscopic symmetry has actually been reduced from G_0 to G . The two statements, taken together, imply that the crystal must split into domains in the lower phase. It also follows that, since the symmetry group of each domain is G , transformation operations which can map one domain to another are those which are *lost* at the phase transitions (Janovec 1976). These are called Φ -operations (Aizu 1974). In particular, mirror planes of symmetry lost at a phase transition can become domain walls separating two contiguous domains of the lower phase (Mallard's law). To quote Shubnikov and Kopstik (1974): "The whole process of a phase transition obeys the astonishing law discovered by philosophers—the *symmetry compensation law*: If symmetry is reduced at one structural level, it arises and is preserved at another!"

Let G'_0 and G' denote the point groups of the space groups G_0 and G respectively. If n_p and n_f are the orders of the groups G'_0 and G' , the maximum possible number of orientation states or rotational domains possible in the ferroic phase is given by (Aizu 1970; Janovec 1972) $q' = n_p/n_f$. Any operation which is a symmetry operation of G'_0 , but not that of G' , is called an F -operation. An F -operation maps one orientation state to another. Choosing a common reference frame for all the orientation states, if G' is the point group for a particular orientation state S_1 and f is any F -operation from S_1 to another orientation state S'_1 , the set of all F -operations from S_1 to S'_1 is equal to fG' (Aizu 1970; Janovec 1972). The point group G'_0 can be split into a sum of q' left cosets of the subgroup G' :

$$G'_0 = f_1 G' + f_2 G' + \dots + f_{q'} G'. \quad (7)$$

Here a coset $f_i G'$ comprises all operations mapping the domain S_1 to the domain S_i . There is a one-to-one correspondence between domains and left cosets. Extending the above considerations from point groups to space groups, if G is a subgroup of G_0 of index q , G_0 can be written as a sum of left cosets as follows

$$G_0 = \phi_1 G + \phi_2 G + \dots + \phi_q G. \quad (8)$$

Once again, there is a one-to-one correspondence between a left coset and a possible structural configuration called a *situation* or a *terrain* (Aizu 1974). The ϕ 's are a representative set of Φ -operations from a particular situation to each of the q situations.

A single domain may consist of one or more terrains, but a uniterrain sample is necessarily unidomain also. The possible occurrence of more than one terrain in a domain is referred to as *domain degeneracy* (Janovec 1976). It can be determined with the help of *Hermann's theorem* (Hermann 1929), according to which, if G is a subgroup of a space group G_0 , then one can always find a space group Z which contains G as a klassengleiche or equipoint-group subgroup, and which is also a maximal equitranslational subgroup of G_0 ($G \subseteq Z \subseteq G_0$). The index of Z in G_0 is also equal to $q' (= n_p/n_f)$. The number of terrains (also called translational domains or antiphase

domains) possible in each (rotational) domain is given by the index m of G in Z . The domain degeneracy is m . It is also equal to the number of times by which the volume of the primitive unit cell of the daughter phase is nominally larger than that of the primitive cell of the prototype. The total number of situations, q , is related to the number of orientation states, q' , through m :

$$q = q'm. \quad (9)$$

The fact that q is a finite number is a consequence of the discrete nature of crystallographic space groups. If the prototype symmetry G_0 is described only by a continuous symmetry group, the symmetry group G of the ordered phase may have an infinite index q . In such a case the domain structure is replaced by its dynamical counterpart, namely the occurrence of *Goldstone modes*, which are gapless excitations that tend to restore the prototype symmetry (Janovec 1976).

6. An unsolved problem of ferroelasticity

The elegant and powerful group-theoretical formalism developed by physicists for describing ferroelastic and other forms of ferroic switching in crystals in a unified way is not without a flaw. This was first pointed out by Laves (1975) by citing the example of mechanical twinning in hcp metals like Mg. Such metals have a point-group symmetry $6/mmm$ (D_{6h}), and apparently undergo ferroelastic switching by shearing along the planes $\{1\ 0\ \bar{1}\ 2\}$ in the directions $\langle \bar{1}\ 0\ 1\ 1 \rangle$. This type of mechanical twinning results in a large reorientation (by 84°) of the slip plane (0001), and has a drastic influence on the plastic behaviour of these metals (Klassen–Neklyudova 1964). But this apparently ferroelastic twinning does not come within Aizu's formalism because it is not possible to conceive a *crystallographic* prototype symmetry, of which the symmetry $6/mmm$ of the ferroelastic phase is a subgroup.

Aizu (1970) gave a precise definition of prototype symmetry by demanding that the following two conditions be satisfied: (a) The point-group symmetry of the prototype should contain all the F -operations from each of the orientation states of the ferroic to all orientation states. (b) If any symmetry operation of the prototype point group is performed on any orientation state, the result must only be one of the possible orientation states, and none other.

The prototype group is also a proper supergroup of the ferroic point group. The example of Mg seems to indicate that ferroelasticity can also occur in materials with a symmetry such that only a subgroup of this symmetry is a subgroup of the prototype symmetry (Laves 1975). If a relaxing of the definition of a prototype is allowed so as to accommodate such a possibility, the prototype would not always contain *all* the symmetry elements of the point group of the ferroelastic phase. Such a modification of the theory does not look very appealing, particularly because it negates a good deal of the elegant description of domain structure of ferroelastic and other ferroic crystals (§ 5). It also goes against the spirit of the Landau theory of phase transitions. No really good solution of this problem is available at present.

7. Twinning

Before the development of x-ray crystallography, the classification of twinning in crystals was based mainly on morphological studies made by contact goniometry and

optical goniometry (Friedel 1926). X-ray diffraction patterns, particularly those obtained with Buerger's precession camera, give us directly a picture of the reciprocal lattice of a twinned crystal. This has led to what may be called the second stage in the classification of twinning (Donnay and Donnay 1974). All twinned crystals are divided into two categories, depending on whether the diffraction pattern reveals a single orientation of the reciprocal lattice for the twins ("obliquity" $\omega = 0$), or two or more orientations with a common origin ($\omega \neq 0$). In the first case one talks of *twinning by twin-lattice symmetry* (TLS), and in the second case *twinning by twin-lattice quasi-symmetry* (TLQS). A further subdivision of each of these main categories is made in terms of the *twin index* n , defined as the ratio of the volume per node in twin lattice to the volume per node in crystal lattice. The twin lattice is the lattice with the smallest cell that is common to both members of the pair. The twin lattice is perfectly continuous across the twin wall for $\omega = 0$, but has a small deviation at the wall when $\omega \neq 0$. Twinning by TLS and by TLQS is also called, respectively, "twinning without change of form" and "twinning with change of form" (Klassen-Neklyudova 1964).

This description of twinning concerns itself mainly with geometrical features like orientational relationships of the lattices. Although many crystallographers have indeed dealt with twinning at the structural level, the descriptive terminology available at present does not make evident certain features such as electrical twinning in a ferroelectric crystal, or more subtle effects like differences in the piezoelectric tensor in the twin structure of a crystal like NH_4Cl . I think a stage has now been reached where a more comprehensive and informative classification of twinning can be made in terms of the ideas of symmetry descent discussed in §§3 and 5. We shall use the word "twinning" in a very general sense here, covering all electric, magnetic, elastic or other forms of domain structure possible in a crystal.

Twinning in a crystal implies that the structure can exist in two or more configurations that are energetically equivalent, but differ in mutual orientation, or mutual disposition, or both. The enthalpy barrier for changing one configuration to the other across a twin wall may be either reasonably low (as in Dauphine twins in α -quartz), or it may be extremely high, even exceeding the breakdown field or the fracture strength (as in Brazil twins in quartz, and also many growth twins). In the former case, barring exceptions like magnesium (§6), an F - or Φ -operation derived from an appropriately assigned prototype symmetry should always be definable. In the latter case, there are two possibilities:

(a) The twins across the interface are lawfully related by an F - or Φ -operation, and the enthalpy barrier just happens to be high; (b) a proper F - or Φ -operation is not definable for mapping one twin into the other; this may happen when, for example, the crystal is in a prototypic phase, and not a ferroic phase (see Aizu 1981).

Thus all twinning can be divided into two types (I and II, say). Type I twins are related by an F - or Φ -operation, whereas type II twins are not. For type I twins a prototype symmetry is always conceivable. In many cases of this type, even if switching from one twin to the other is not possible at room temperature, it may become possible at temperatures sufficiently close to the transition temperature. In any case, demonstration of switching is neither a necessary nor a sufficient condition for assigning a twin to type I; It is necessary and sufficient that an F - or Φ -operation, derived from an appropriate prototype symmetry, is definable. In this scheme, twinning in magnesium will be classified as type II (§6). A better example of type II twinning is provided by Brazil twins in quartz. They are related by a mirror operation, which is not a part of the

symmetry 622 (D_6) of β -quartz. The symmetry 622 is prototypic for the symmetry 32 (D_3) of α -quartz, which can consequently exist in two orientation states related by an F -operation that is a two-fold rotation about the optic axis (Wadhawan 1982). These two orientation states are just the Dauphiné twins. Unless a prototypic symmetry higher than 622 can be conceived for this crystal (which is not possible because that would involve a drastic breaking and reassembling of the structure), Brazil twins do not constitute domains or terrains in the sense discussed in § 5. (The concept of the prototype has been discussed with great clarity by Aizu 1978, 1981.)

For type I twins, a nonisomorphous phase transition to the prototypic phase either actually exists, or can be imagined. In BaTiO_3 , for example, the cubic phase is prototypic to the tetragonal, trigonal and orthorhombic phases, whereas in $(\text{NH}_4)_2\text{SO}_4$ the hexagonal prototypic phase is hypothetical (Sawada *et al* 1976; also see Dvorak 1978). A nonisomorphous phase transition can be either nonferroic or ferroic (figure 6). If it is nonferroic, twinning comprises antiphase domains only. About 50 crystals undergoing nonferroic transitions have been listed by Tolédano and Tolédano (1982). This twinning is obviously of the TLS type, and the superlattice reflections resulting from it lead to a smaller primitive unit cell in the reciprocal lattice. For ferroic crystals, twinning can occur either by TLS or by TLQS, depending on whether the phase transition is nonferroelastic or ferroelastic (figure 6).

7.1 Nonferroelastic twinning

Although all nonferroelastic twinning will be dubbed as just twinning by TLS in the older scheme of classification, the advantage of the new scheme suggested here can be seen from the fact that many further subdivisions are possible: We can have ferroelectric twinning (as in TGS, SbSI and LiNbO_3), ferrobielastic twinning (as in α -quartz), ferroelectric-ferrobielastic twinning (as in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$), ferroelastoelectric twinning (as in NH_4Cl , CuCsCl_3 and α -quartz), ferromagnetoelastic twinning (as in CoF_2 , MnF_2 and FeCO_3), ferromagnetoelastic twinning (as in Cr_2O_3), and ferrotrilastic twinning (as in $\text{Cr}_5(\text{PO}_4)_3\text{Cl}$ and the mineral elapsolite (K_2NaAlF_6)). Inversion domains observed in $\text{Fe}_{36}\text{Cr}_{22-x}(\text{Ti}, \text{Mo})_x$, γ -brass, δ -NiMo, lithium ferrite and Al_4Mo (Amelinckx 1976) also constitute a subclass of nonferroelastic twinning.

Nonferroelastic twinning may indeed occur in ferroelastic crystals, in the so-called *partial* ferroelastics, in which some twins are ferroelastically related and some are nonferroelastically related. Examples of the latter are the antiparallel (180°) domains in TGS and BaTiO_3 . A partial ferroelastic is that for which $\Delta\epsilon_{ij}^0 = 0$ in (2) for at least one pair (but not all pairs) of orientation states.

An extremely useful tabulation of the “orders” of state shifts in ferroic crystals has been given by Aizu (1972a). The same tabulation can provide a very informative basis for defining the “order” of twinning in a ferroic crystal. For example, ferroelectric twinning can be described as “first-order electrical twinning”, and ferrobielastic twinning as “second-order mechanical twinning”.

TLS twinning or zero-obliquity twinning has two subclasses: (i) *twinning by merohedry*, for which the twin index $n = 1$, and (ii) *twinning by reticular merohedry*, for which $n > 1$. For the second case n is usually equal to 3, and very rarely equal to 5 (Donnay and Donnay 1974). For purposes of crystal structure determination, twinning by merohedry presents some special problems. Various procedures have been suggested to handle these (Catti and Ferraris 1976; Rees 1982; Jameson 1982). Both Dauphiné and

Brazil twinning in α -quartz is described as twinning by merohedry in the old scheme of classification (Donnay and Donnay 1974), whereas, in the present scheme, Brazil twins are type II twins, while Dauphiné twins are type I ferrobielastic-ferroelastoelectric twins.

7.2 Ferroelastic twinning

This corresponds to twinning by TLQS in the old scheme. Only one further subdivision is made in the old classification: The twinning is said to be by *pseudomerohedry* if $n = 1$, and by *reticular pseudomerohedry* if $n > 1$ (Cahn 1954; Donnay and Donnay 1974). In the new scheme, the twinning is characterized as purely ferroelastic in $\text{Pb}_3(\text{PO}_4)_2$ and BiVO_4 , ferroelectric-ferroelastic in BaTiO_3 , ferromagnetic-ferroelastic in Mn_3O_4 , and ferromagnetic-ferroelectric-ferroelastic in $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$. The presence of any antiphase domains can also be adequately rationalized in terms of reduction of the translational symmetry of the prototype.

8. Ferroelastic phase transitions

Ferroelastic phase transitions are characterized by a change of the crystal system, subject to the proviso that hexagonal and trigonal crystal systems are not regarded as distinct for the purpose of defining ferroelastic transitions (§ 3). The lattice distortion responsible for the change of crystal system is embodied in the spontaneous strain accompanying such transitions.

8.1 Proper ferroelastic transitions

A further subdivision of these is sometimes made between *true-proper* and *pseudo-proper* ferroelastic transitions. For the former, the strain itself is the primary order parameter. For the latter, though the strain ϵ has the same symmetry as the order parameter Q , the order parameter is some other primary instability. In $\text{LaP}_5\text{O}_{14}$, for example, the driving force of the transition is an instability with respect to a Raman-active optical mode (Errandonea 1980). The strain arises because of a bilinear coupling term of the form $K_1 Q \epsilon$. A typical Landau expansion of the free energy density in this case can be written as follows (Wadhawan 1982):

$$\Phi = \Phi_0 + \frac{a}{2} (T - T') Q^2 + \frac{b}{4} Q^4 + \frac{C_0}{2} \epsilon^2 + \frac{B}{4} \epsilon^4 + K_1 Q \epsilon. \quad (10)$$

The elastic stiffness coefficient goes to zero (that is, the response function corresponding to ϵ diverges) at the phase transition temperature T_c given by the equation

$$T_c - T' = K_1^2 / a C_0. \quad (11)$$

Here T' is the temperature at which the optical soft mode frequency *would* have gone to zero on cooling if the phase transition had not actually occurred at the higher temperature T_c . The distinction between true-proper and pseudoproper transitions disappears as $K_1 \rightarrow 0$. In any case most, if not all, proper ferroelastic transitions are of the pseudoproper type. Luthi and Rehwald (1981), who have listed a large number of them, make no distinction between the two types. Many other authors follow the same

practice. The temperature shift ($T_c - T'$) can be as large as 160 K in $\text{LaP}_5\text{O}_{14}$, and 230 K in BiVO_4 .

The Landau theory of phase transitions works well for systems for which the range of the interaction driving the phase transition is longer than the correlation length characterizing the critical fluctuations of the order parameter. The theory therefore provides a good description of proper ferroelastic transitions for which the critical fluctuations are the acoustic modes (Cowley 1976). (As already stated in §2, the theory holds exactly also for the “ferroelastic” phase transitions in hydrogen-metal systems (Alefeld and Volkl 1978; Wagner 1978), the elastic interaction mediated via the distortion fields around interstitial hydrogen atoms being a long-ranged attractive interaction.)

8.2 Improper ferroelastic transitions

In these transitions, the spontaneous strain arises only as a secondary effect, through a nonlinear coupling with the order parameter. The Landau expansion therefore contains a coupling term proportional to $\epsilon\eta^n$, where η is the order parameter modulus, and n is a finite integer called the *faintness index* (Aizu 1972b, c; Dvorak 1974). The spontaneous strain varies as the n th power of the order-parameter modulus, $\epsilon_0 \sim \eta^n$. The higher the value of n , the smaller is the spontaneous strain. Since strain is no longer the order parameter, the elastic response function does not show very large anomalies at the phase transition. Barring a few exceptions, the Landau theory does not, in general, provide a good description of this class of ferroelastic phase transitions (Wadhawan 1982).

8.3 Incommensurate phase transitions

This fundamentally new class of phase transitions (new, that is, for nonmagnetic systems) is currently attracting a good deal of attention (Pynn 1979; Bak 1982). In the usual “commensurate” phase transitions, the pattern of static displacements of atoms in the lower-symmetry phase can be described by a frozen-in wave of wavevector $\mathbf{k}$, which is a *rational* fraction of a prototype reciprocal-lattice vector $\mathbf{r}^*$ along the same direction:

$$\mathbf{k} = (n_1/n_2)\mathbf{r}^*, \quad (12)$$

where $n_1 = 0, \pm 1, \pm 2, \dots$ and $n_2 = \pm 1, \pm 2, \dots$. For example, for a “zone-centre” phase transition $n_1/n_2 = 0$, and for a “zone-boundary” phase transition it is equal to $1/2$. In an incommensurate transition, $\mathbf{k}$ is an *irrational* fraction of $\mathbf{r}^*$, so that no two atoms have the same static displacement. In other words, in the incommensurate phase no translational symmetry exists in the direction of $\mathbf{k}$. Therefore, the notion of antiphase domains or translational domains discussed in §5 does not apply any more for this direction. However, the incommensurate phase still has a well-defined point-group symmetry and the concepts of rotational domains or orientation states and of F -operations between them are still relevant.

In incommensurate transitions no finite-order coupling between the order parameter and any macroscopic property such as the strain or polarization is possible in the Landau expansion (Riste 1978). Consequently, no spontaneous strain or polarization can appear in the incommensurate phase. Such a polarization or strain gets averaged out to zero because of the zero-energy phase modulation of the displacement pattern.

However, as the temperature of the incommensurate phase is lowered, a point is reached where a "lock-in" transition occurs, at which the fraction connecting $\mathbf{k}$ to $\mathbf{r}^*$ becomes rational, and a finite-order nonlinear coupling between the order parameter and one or more macroscopic properties (each with a definite faintness index) can occur. The lock-in transition has been observed to be first-order in all the cases studied so far. The mechanical behaviour of a crystal near an incommensurate transition is influenced by the effect of the transition on its elastic constants. A number of studies of this have already been made, notably by ultrasonic techniques and include the following crystals listed by Luthi and Rehwald (1981): K_2SeO_4 , Rb_2ZnCl_4 , $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_4$, $(\text{NH}_4)_2\text{BeF}_4$ and $\text{K}_2\text{PbCu}(\text{NO}_2)_6$.

It is pertinent to mention here a relatively new experimental technique, namely, γ -ray diffractometry (Schneider 1981) which is particularly well suited for studying ferroelastic phase transitions, and especially the critical behaviour of the order parameter. Because of the small wavelength involved ($\lambda = 0.03 \text{ \AA}$ usually), γ -ray diffractometry is a forward-scattering experiment (with scattering angles seldom exceeding 2°). The change $\Delta\theta$ in the Bragg angle is related to the change Δd in the interplanar d -spacing by equation

$$\Delta\theta = -(\Delta d/d) \tan \theta. \quad (13)$$

As θ is very small, it follows that changes in the d -spacings have a vanishingly small effect on the Bragg peak position, θ . Therefore, any significant shifts of the peak position in the " ω -scan" normally employed for recording the diffraction pattern can be attributed almost entirely to a tilting (reorientation) of the concerned lattice planes, with a negligible contribution from changes in their d -spacing. This is in marked contrast to the situation in conventional x-ray or neutron crystallography where in the back-scattering region ($\theta \simeq 90^\circ$) normally preferred for lattice-parameter determination, $\Delta\theta$ is extremely sensitive to changes in the d -spacing. γ -ray diffractometry is therefore ideally suited for studying those phase transitions which entail spontaneous deformation of the crystal lattice, and the consequent tilting of the lattice planes. This is just what happens in ferroelastic phase transitions. The spectral width of the nuclear γ -rays used is extremely small ($\Delta\lambda/\lambda = 10^{-6}$ for the ^{198}Au source); this results in excellent angular resolution. A resolution of $1''$ of arc can be achieved. Further, since the γ -rays are extremely penetrative, the presence of massive high-pressure cells, or elaborate arrangements for achieving a high degree of sample temperature control, do not present any serious problems. The technique looks very promising. Its applications in this direction have begun only recently (see Bastie and Bornarel 1979; Alkire and Yelon 1981).

9. The shape-memory effect

The shape-memory effect (SME) in alloys is associated with martensitic phase transitions, which are first order, diffusionless, structural phase transitions involving a distortion of the crystal lattice. Their closeness to ferroelastic phase transitions is obvious. The SME pertains to the shape recovery of a material on heating to a certain temperature, after it has been subjected to a deforming strain of as much as 10% at a lower temperature. As in pseudoelastic recovery (§ 2), two situations are possible for the "one-way" SME: by transformation or by reorientation (Warlimont 1976). In the former

case, the deforming stress induces a phase transition to the martensitic phase, whereas in the latter case the material is already in the martensitic phase and the applied stress makes some domains grow at the cost of others. The shape recovery on heating in both cases involves a phase transition to the parent phase.

In a martensitic transition the parent and the martensitic phase coexist over a certain range of temperatures. For good shape recovery in the SME, it is necessary that the interface between the parent and the martensitic phases be created, annihilated or moved in a reversible manner. A number of conditions should be met for this (Nakanishi 1975; Wasilewski 1975). For example, plastic flow should not occur during deformation. Thus a high yield strength of the initial matrix is required. Also, the driving force required for the nucleation and/or growth of martensite plates should be low. The dominant term in the free energy barrier opposing the nucleation of martensite in the matrix can be written as $C\epsilon_m^2$, where C is the relevant shear elastic constant of the matrix and ϵ_m is the effective martensitic strain. A low value of C would be favourable for the stress-induced nucleation of martensite, but it would also imply a lower yield strength. The optimization of these two requirements indicates that one should apply the deforming stress at a temperature close to M_f , the martensite finish temperature (Wasilewski 1975).

In a proper ferroelastic phase transition, some stiffness constant, or a combination of stiffness constants, necessarily tends to zero (§8). The presence of such a transition should therefore indicate the possibility of SME in the material (Nakanishi 1975).

Over the last few years, the Landau theory has been increasingly applied to martensitic transitions. The Landau theory was initially formulated for dealing with second-order phase transitions. Further, a Landau expansion like that of (10) presupposes that the order parameter is a slowly varying quantity. Martensitic transitions are first-order phase transitions. One has therefore to employ Devonshire's (1954) generalization of the Landau theory to deal with them. Further, a first-order transition normally exhibits thermal hysteresis. In the temperature range of the thermal hysteresis, the two phases coexist. In addition to this, there also are domain walls associated with the domain structure of the daughter phase. At the domain walls and in the coexistence range of T , the order parameter changes rapidly. This makes the usual Landau expansion of the free energy inadequate, and one must include terms involving the derivatives of the order parameter, in the spirit of Ginzburg's (1955, 1960) extension of the Landau theory.

For understanding the SME, one has to deal not only with the effect of temperature on the martensitic transition, but also that of stress. In fact, many workers believe that the SME is merely one of the manifestations of the effect of stress on a martensitic phase transition, the martensitic transition for systems exhibiting the SME being taken as just a first-order proper ferroelastic transition (Wasilewski 1975; Falk 1980). In other words, some suitably defined spontaneous strain can be taken as the order parameter of the transition. A very simple but fairly universal model Landau expansion of the free energy has been proposed by Falk (1980), which explains a large number of features in a whole group of alloys exhibiting the SME. Falk's calculation is the mechanical counterpart of Devonshire's (1954) treatment of first-order proper ferroelectric phase transitions driven by the temperature and the electric field. The martensitic alloys CuZn, CuAlNi, AgCd, CuAuZn₂, NiTi and NiAl are treated together in this phenomenological theory, ignoring their superlattice structure and the differences in the stacking sequence of their close-packed layers. After a suitable rescaling, the

following ansatz is made for the free-energy:

$$f(e, t) = f_0(t) + (t + 1/4)e^2 - e^4 + e^6, \quad (14)$$

where f , e and t respectively denote the scaled values of the free-energy density, the shear strain (the order parameter), and the temperature. Equation (14) is a universal one for a large number of shape-memory alloys. The properties of specific materials enter through the scaling constants. All mechanical and thermodynamic properties are derived from (14). It is remarkable that this simplest of possible models leads to qualitative agreement with numerous experiments on shape-memory alloys; the stress-strain curves exhibiting elasticity, ferroelasticity and superelasticity in the appropriate temperature regions, the mode softening, the shape-memory effect, the occurrence of the stress-induced and temperature-induced phase transition, and the latent heat of the transition.

At the next level of complication, the electric field must also be brought in. From the point of view of theory, this is naturally a more difficult problem, but it also promises to present a richer variety of physical behaviour. One does not normally think of studying the effect of the electric field in alloys because of their high electrical conductivity. Especially interesting in this regard are materials such as PLZT and BaTiO₃ which are simultaneously ferroelastic and ferroelectric. The presence of ferroelectricity ensures that the spontaneous strain can be manipulated both by a mechanical stress and by an electric field. This is also important in applications of the SME because, by and large, electric fields are easier to apply in practice than mechanical stresses of appropriate magnitude and frequency. Experimental results on the effect of electric fields on the SME are just beginning to come in. Perhaps the first experiment of this type was that on PLZT ceramics (Wadhawan *et al* 1981). The composition of PLZT, that is (Pb, La) (Zr, Ti)O₃, is conveniently specified by the $x/y/z$ notation, where y/z indicates the Zr/Ti ratio, and x denotes the atomic percentage of La ions substituted for Pb. The composition $x/65/35$ has received a great deal of attention because of its closeness to the morphotropic phase boundary (Haertling and Land 1971; Haertling 1971). Its ferroelastic nature was first demonstrated by Meitzler and O'Bryan (1971). For $x > 4.5$, this material possesses a property known as *penferroelectricity* (Meitzler and O'Bryan 1973), or *quasiferroelectricity* (Carl and Geisen 1973). There is a very interesting phase transition, called the $\alpha \rightarrow \beta$ transition by Keve and Annis (1973), which is similar in many ways to a martensitic phase transition. Whereas above a temperature T_c the material behaves like a normal paraelectric, the dielectric behaviour immediately below T_c , *i.e.*, in the α -phase, is not that of a normal ferroelectric. The α -phase is "quasiferroelectric" in which there are polar distorted microregions shorter than the wavelength of light. Application of an electric field between T_c and a lower temperature T_p changes the microdomains to macrodomains, which, however, revert back to randomly distributed microdomains (giving a macroscopically nonferroelectric state) when the electric field is switched off. The experimentally observed "slim" hysteresis loops constitute evidence in favour of this model (Carl and Geisen 1973). When the electric field is applied at a temperature below T_p , stable macrodomains indicative of long-range order are induced and the material behaves like a normal ferroelectric (as well as a ferroelastic), exhibiting "fat" hysteresis loops. Materials showing this type of diffuse phase transition are called "relaxor" ferroelectrics (Smolensky 1970). In the temperature range between T_c and T_p , microdomains of polar short-range order coexist with the paraelectric matrix, just as martensite coexists with the parent matrix over a certain temperature range.

The SME in PLZT ceramic of composition $x/65/35$, with $4 \leq x \leq 8$, was investigated in some detail by Kimura *et al* (1981), and the effect of an electric field on the SME in 6.5/65/35 PLZT was studied by Wadhawan *et al* (1981) by performing very simple bending experiments on thin bars of the ceramic. The modification introduced by the electric field on the SME could be interpreted in terms of the above microdomain model. In the temperature region in which the microdomains exist, the system is "electrically soft", but not "mechanically soft", and the load does not produce a large bending. However, when the electric field is switched on, it changes the microdomains to macrodomains, the material also becomes mechanically soft, and the load produces an additional bending. This was only a preliminary experiment. Much more work is needed to understand the phenomena involved in detail. Since ferroelectricity and ferroelasticity are coupled properties in the case of PLZT, it should be possible to produce changes in strain, including shape-memory bending, purely by electrical means, without the need for any mechanically-produced deformation. Electrically-produced SME would present challenging possibilities for both theory and experiment, as well as for device applications.

10. Concluding remarks

The subject of ferroelasticity has gained maturity being viewed as a part of the much larger subject of ferroicity. Much has been learnt or predicted about ferroelasticity by analogy with ferroelectricity. It appears that we can improve, considerably, our understanding of the physical basis of mechanical behaviour by drawing analogies with electrical phenomena (Alefeld 1971).

Based on the symmetry classification of phase transitions, a more rational-looking classification of twinning in crystals has been attempted. Two broad categories of twinning emerge: nonferroelastic and ferroelastic. Although this appears to run parallel to the existing division into twinning by merohedry and twinning by pseudomerohedry, the advantage of the new scheme is that many finer features like piezoelectric twinning can also be distinguished.

As was brought out repeatedly, our present description of ferroelasticity is based on the concept of symmetry descent and the principle of superposition of symmetries (the Curie principle). In fact the Landau theory of phase transitions, which is so effective in explaining a large body of experimental facts, is itself based on the Curie principle. The Landau theory is being increasingly applied to martensitic phase transitions which have a substantial overlap with ferroelastic phase transitions. Although this is a promising development, a certain amount of caution is warranted because we are dealing with *first-order* phase transitions, many of them of so drastic a nature that a change of coordination number and "internal topology" is involved. In some of these transitions there is no group-subgroup relationship between the symmetries of the parent and the daughter phases. While the theoretical apparatus for dealing with second-order phase transitions is very well-developed, in first-order phase transitions only a beginning has been made in some respects (Aizu 1981).

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Discussion

G Venkataraman: It is observed that to understand the domain structure, one has to use not only the symmetry of the ferroelastic phase, but also that of the parent phase. This is similar to what Mermin does when he classifies defects using G , the symmetry of the disordered phase, and H , the symmetry of the ordered phase.

N Kumar: Is ferroelasticity a noncentrosymmetric phenomenon?

V K Wadhawan: The spontaneous-strain is a second-rank polar tensor. Thus the presence or absence of a centre of symmetry does not effect the occurrence of ferroelasticity in a crystal.

N Kumar: Since there was no prototype group for magnesium, can it be ferroic?

Wadhawan: The D_{6h} symmetry of magnesium does not admit of a crystallographic prototype group. Therefore we are not able to assign this crystal a place in the existing classification of ferroic crystals.

N Kumar: In order to have one-to-one correspondence is it necessary to have distortion connected with displacement vectors which are not some multiples of lattice spacing?

Wadhawan: We are talking here about the *one-way* SME and I think the question of one-to-one correspondence is more relevant for the two-way SME.