

## Symmetry-Determined Phenomena at Crystalline Phase Transitions

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We briefly survey the application of symmetry-related concepts to the structural phase transitions observed in crystals. The unifying concept of ferroicity which includes ferroelectricity, ferroelasticity, and similar phenomena is considered first. It is related to a modification in point symmetry. The frequent occurrence of ferroelastic transitions among observed phase transformations is pointed out. In particular, we underline the connection which exists between ferroelasticity and certain martensitic transformations in metallic alloys as well as with the cooperative Jahn-Teller transitions. The concepts of proper and improper ferroic transitions are then qualitatively introduced. They are related to the space-symmetry change and to the subsequent symmetry properties of the transitions's order parameter. The main differences between proper and improper ferroics are described.

Theories of phase transitions, concerned with the critical behavior of physical quantities, have popularized the fact that transitions and, in particular, crystalline transitions can be understood on the basis of the same principles which govern the onset of ferromagnetism at the Curie point. The quantity which is the substitute for the spontaneous magnetization is the order parameter of the transition considered. In the case of crystalline phase transitions the symmetry properties of this quantity have been precisely related by Landau (*I*) to the change in space symmetry which takes place at the transition. Physically, the order parameter can be associated with a certain collective motion of the atoms in the crystal (for displacive transitions) or with a probability distribution of certain kinds of atoms between different sites in the structure (for order-disorder transitions). Although it

contains all the information relative to the change in symmetry, the order parameter, unlike the magnetization, does not always have a clear meaning at macroscopic level. It does not show, in particular, which properties among the electric, elastic, or other macroscopical properties of the crystal will be mainly affected by the phase transition. Some physical quantity, with different symmetry properties, is sometimes more suitable for representing the main peculiarity of the phase transition one is studying. For instance, a ferroelectric transition is always conveniently characterized by the onset of a spontaneous polarization, although, as recent investigations have shown, this quantity does not necessarily constitute an order parameter of the corresponding transition.

In the first part of this brief review, we examine how the various categories of structural phase transitions encountered in crystals can be described, in a unified way, by macroscopic quantities, as in the case of ferromagnetics and ferroelectrics. The

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theoretical grounds for such a synthetic approach were established by Aizu (2) between 1969 and 1973. Some of the concepts it contains, such as that of ferroelasticity, have been very successfully applied in recent years. In the second part, we consider the relation between the above macroscopic quantities and the order parameter and describe the different situations which have been observed in actual phase transitions. We only consider transitions in which there is a group-subgroup relationship between the symmetries of the two phases.<sup>1</sup>

Among such structural phase transitions, many involve a change in the point symmetry of the crystal. This symmetry change gives rise, in the low-symmetry phase, to several possible states, equally stable, and possessing the same structure, but with different spatial orientations. These orientation states can coexist in the form of domains in a given crystal. Each one can be distinguished from the others by the values taken by the components of certain macroscopic quantities represented by polar tensors<sup>2</sup> (a common frame of reference must be chosen for all the states). As in the case of ferromagnetism and ferroelectricity these transitions are called ferroic. Since the high-symmetry phase is left invariant by the set of symmetry operations of all the differently oriented states, the former tensorial components vanish by symmetry in this phase. They can therefore be considered as "spontaneous" quantities. One can dis-

<sup>1</sup> In his work Aizu does not actually refer to a phase transition but to symmetry and energetic considerations relative to the different orientation states of the low-symmetry phase. The high-symmetry phase appears as a speculative "prototypic" phase which does not necessarily exist as a stable state of the crystal. Our view of analyzing observed phase transitions leads us to neglect this subtlety, which has nevertheless proved to be useful in a few cases.

<sup>2</sup> We restrict the discussion to nonmagnetic transitions and thus avoid considering axial tensors.

tinguish various types of ferroics on the basis of the lowest-rank polar tensor which acquires a spontaneous value. For instance, polar tensors of rank one (polarization), two (strain), three (piezoelectric modulus), and four (elastic modulus) define ferroelectric, ferroelastic, ferroelastoelectric, and ferrobielastic transitions, respectively. The rank and particular components of the relevant tensorial quantities are determined by the set of point groups of the two phases (the ferroic and high-symmetry phases). Thus the preceding classification of ferroics has both physical and crystallographical aspects, which are summarized in Table I. As shown by this table, nonferroic transitions only involve a change in the translations of the crystal. Superlattice structures in ordered metallic alloys (3) provide many examples of the latter type of transitions.

Ferroelectrics and ferroelastics differ from other ferroics because in these materials the switching energy between two orientation states is a linear function of the primary external forces, electric field, or mechanical stress, which can be applied to a crystal. Other categories of ferroics constitute secondary or higher-order ferroics in which the switching between equally stable states can only be obtained by a combination of the primary forces. For instance, in a ferroelastoelectric crystal one must apply simultaneously an electric field and a mechanical stress in order to favor a given domain orientation.

Few materials are known, at present, to possess secondary or higher-order transitions. On the basis of available structural data, Newnham and Cross (4) have indicated a number of chemical compounds which could possibly fall into those ferroic categories. These transitions are likely to be difficult to detect in polycrystalline samples by means of X rays, as the shape of the unit cell is not modified by the transition. Moreover the presence of ferroic domains in single crystals cannot be easily disclosed, as

TABLE I  
CRYSTALLOGRAPHICAL AND PHYSICAL CLASSIFICATION OF STRUCTURAL PHASE TRANSITIONS

|  |
|--|
| <b>NON-FERROIC TRANSITIONS</b>   |
| CHANGE IN THE TRANSLATIONAL<br>SYMMETRY ONLY   |
| No spontaneous macroscopic<br>quantities   |
| <u>Examples:</u> Cu <sub>3</sub> Au; CuZn ;<br>CsH <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> |

|   |
|---|
| <b>FERROIC TRANSITIONS</b>  |
| CHANGE IN THE POINT-SYMMETRY<br>(Possible change in translations) |
| Spontaneous components for polar<br>tensors of different ranks.   |

|   |   |
|---|---|
| <b>NON-FERROELASTIC</b>                             |   |
| CONSERVATION OF THE CRYSTAL SYSTEM                  |   |
| <u>PURE FERROELECTRIC</u>                           | <u>SECONDARY AND<br/>HIGHER ORDER FERROICIS</u>   |
| Spontaneous vector<br>(polarization)                | Tensors of rank r<br>higher than two  |
| <u>Examples</u> TGS ;<br>LiNbO <sub>3</sub><br>SbSI | <u>Ferroelastoelectric</u><br>(r=3)<br>(piezoelectric<br>electrooptic<br>SHG tensors)                       |
|   | <u>Ferrobiclastic</u><br>(r=4)<br>(elasticity)  |
|   | <u>Ferrotrelastic</u><br>(r=6)<br>(Third-order<br>elastic constants)  |
|   | <u>Examples:</u> NH <sub>4</sub> Cl; NbO <sub>2</sub><br>SiO <sub>2</sub> ; Na <sub>x</sub> WO <sub>3</sub> |

|  |  |
|--|--|
| <b>FERROELASTIC</b>  |  |
| CHANGE IN THE CRYSTAL SYSTEM   |  |
| <u>PURE<br/>FERROELASTIC</u>   | <u>SIMULTANEOUSLY<br/>FERROELECTRIC AND<br/>FERROELASTIC</u>             |
| Tensor of rank<br>two<br><br>(strain;<br>permittivity<br>birefringence)  | Tensors of rank<br>one and two<br><br>(polarization +<br>strain )        |
| <u>Examples:</u><br>LaP <sub>5</sub> O <sub>14</sub><br>Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub><br>BiVO <sub>4</sub><br>V <sub>3</sub> Si<br>C <sub>12</sub> H <sub>10</sub> | <u>Examples:</u><br>KDP; Tanane<br>BaTiO <sub>3</sub> ;<br>Rochelle salt |

these are not optically distinguishable in polarized light unless an external field or stress is applied. The scarcity of data concerning these transitions can be due to the fact that particular components of tensors with rank higher than two can be reached only through techniques such as second harmonic generation or electrooptic measurements, which generally need high-quality crystals. Substantial experimental data exist, however, for two secondary ferroics, namely, ammonium chloride and quartz. In these materials, ferroic domains have actually been observed (2, 5, 6), and the temperature dependence of the relevant piezoelectric or second harmonic generation tensorial components could be determined near the phase transition (7, 8). Recently, attention has also been given to the continuous ferroelastic transition in niobium dioxide (9).

Ferroelastic transitions, though only recently recognized as a group of transitions sharing common properties, already appear as the type of structural phase transitions most frequently encountered in crystals. This is probably related to the fact that the corresponding crystallographical requirements, allowing a modification of the crystal system, are not restrictive. The ferroelastic phase can be considered as the mechanical analog of a magnet since it is possible to generate in it a stress-strain hysteresis loop. Such a behavior denotes the occurrence of a multiplicity of strain-differing stable states. Other characteristic properties of ferroelastics are the optical distinguishability of domains with the help of polarized light; planar domain boundaries (10); and the occurrence of a pronounced anomaly, at the transitions, in certain elastic constants of the material. The latter property is the analog of the anomalous behavior of the dielectric susceptibility which is observed at ferroelectric transitions.

The preceding features are most clearly displayed by lanthanum pentaphosphate

$\text{LaP}_5\text{O}_{14}$ , which provides a textbook example of the ferroelastic behavior. This colorless insulating crystal, which can be grown in cubic-centimeter-sized samples of high quality (11), possesses, as shown by accurate  $\gamma$ -ray diffractometry (12), a perfectly continuous transition at 125°C (point symmetry change  $mmm \rightarrow 2/m$ ). The transition gives rise to two possible orientations of the low-symmetry structure corresponding to opposite shears of the high-symmetry orthorhombic cell. The spontaneous strain is  $4 \times 10^{-3}$  at room temperature, and its reversal requires only a small coercive stress of about 0.1 kg/cm<sup>2</sup> (13). The domain pattern of the crystal, consisting of parallel bands, is thus extremely easy to alter by application of a suitably oriented stress (14). On the other hand the  $C_{55}$  elastic constant, which is the inverse susceptibility associated to the ferroelastic shear, is observed to vanish at the transition. The transverse acoustic velocity controlled by this constant can be followed from a value of 3500 m/sec at room temperature down to less than 200 m/sec near the transition (15).

Many other ferroelastic transitions have been identified since 1969. We have listed in Table II some of the most recently investigated compounds. Other examples can be found in earlier reviews by Abrahams (16) and the present author (17) as well as in Ref. (10). An exhaustive investigation of existing ferroelastic transitions will be described elsewhere (18).

It can be noted, in Table II, that most of the ferroelastic transitions identified up to now occur in insulating materials. The question has been raised (19) whether the large number of phase transformations which are observed in metallic alloys could not also be associated with ferroelastic properties. This question is particularly meaningful in the case of the so-called martensitic transformations. These transformations, which differ from other metallic transitions by their specific kinetics (20), possess several com-

TABLE II  
EXAMPLES OF MATERIALS UNDERGOING A PURE  
FERROELASTIC TRANSITION

| Compounds   | Point symmetry change |            | $T_c$ | Proper or improper <sup>a</sup> |
|---|-----------------------|------------|-------|---------------------------------|
| <i>Mineral</i>                                    |                       |            |       |                                 |
| LiNH <sub>4</sub> SO <sub>4</sub>                 | <i>mm2</i>            | 2          | 10°C  | I                               |
| KH <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub>  | <i>mmm</i>            | <i>2/m</i> | 212°K | P                               |
| BiVO <sub>4</sub>                                 | <i>4/m</i>            | <i>2/m</i> | 255°C | P                               |
| Ba <sub>2</sub> NaNb <sub>5</sub> O <sub>15</sub> | <i>4mm</i>            | <i>mm2</i> | 300°C | I                               |
|   |                       |            | 105°K |                                 |
| Hg <sub>2</sub> Cl <sub>2</sub>                   | <i>4/mmm</i>          | <i>mmm</i> | 185°K | I                               |
| VO <sub>2</sub>                                   | <i>4/mmm</i>          | <i>2/m</i> | 70°C  | I                               |
| DyVO <sub>4</sub>                                 | <i>4/mmm</i>          | <i>mmm</i> | 14°K  | P                               |
| KCN   | <i>m3m</i>            | <i>mmm</i> | 160°K | P                               |
| Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>   | $\bar{3}m$            | <i>2/m</i> | 180°C | I                               |
| Sb <sub>5</sub> O <sub>7</sub> I                  | <i>6/m</i>            | <i>2/m</i> | 208°C | I                               |
| <i>Organic</i>                                    |                       |            |       |                                 |
| Biphenyl  | <i>2/m</i>            | $\bar{1}$  | 40°K  | I                               |
| P-Terphenyl                                       | <i>2/m</i>            | $\bar{1}$  | 108°K | I                               |
| Squaric acid                                      | <i>4/m</i>            | <i>2/m</i> | 100°C | I                               |

<sup>a</sup> "Proper" or "improper" qualifies the order-parameter symmetry of the transition (see text).

mon features (20) which make them resemble ferroelastic transitions: cooperative displacement of atoms in the structure; definite orientation relationship between the two phases; twinning of "plates" (single crystals) in the martensitic phase; and, mainly, a change of shape of the crystallographic unit cell. However, usual martensitic transformations (for instance in iron-carbon alloys) show significant differences with the

ferroelastic transitions which have been examined up to now. In particular, the two phases (the parent and martensitic phases) have a wide temperature range of coexistence associated with a large thermal hysteresis. Moreover, the deformation can amount to more than 10%, i.e., two orders of magnitude higher than in most ferroelastics. It can also happen that the group-subgroup relationship between phases is not fulfilled (for instance, in cubic-to-hexagonal martensites) (3).

Certain martensitic transformations escape the latter scheme. They involve very little thermal hysteresis and are sometimes nearly continuous. Some examples, indicated in Table III, possess a clear ferroelastic character which can be asserted on the basis of the observed symmetry change and also of their physical behavior. Thus, the specific softening of the ( $C_{11}-C_{12}$ ) combination of elastic constants has been established in In<sub>0.8</sub>Tl<sub>0.2</sub>, V<sub>3</sub>Si, and Nb<sub>3</sub>Sn. On the other hand the occurrence of ferroelastic properties in AuCuZn<sub>2</sub> has been claimed by Nakanishi *et al.* (21), who could generate a stress-strain hysteresis loop in the martensitic phase. These authors have also conjectured that, more generally, ferroelasticity could be responsible for the peculiar behavior of all the martensites which display the shape-memory effect. This effect, which has been found in a number of alloys (InTl, TiNi, AuCd, AgCd, AuCuZn, . . .), consists

TABLE III  
EXAMPLES OF MARTENSITIC TRANSFORMATIONS WHICH ARE ASSOCIATED  
WITH FERROELASTICITY

| Type of alloy   | Thermodynamic order | Symmetry change    | "Curie" point |
|---|---------------------|--------------------|---------------|
| Au <sub>x</sub> Cu <sub>1-x</sub> Zn ( $x = 0.5$ )      | First               | Cubic/orthorhombic | 290°K         |
| In <sub>0.8</sub> Tl <sub>0.2</sub>                     | Slightly first      | Cubic/tetragonal   | 45°C          |
| Ti <sub>0.45</sub> Ni <sub>0.5</sub> Fe <sub>0.05</sub> | Second              | Cubic/rhombohedral | 225°K         |
| Nb <sub>3</sub> Sn                                      | Slightly first      | Cubic/tetragonal   | 21°K          |
| V <sub>3</sub> Si                                       | Second              | Cubic/tetragonal   | 21°K          |

in the fact that a sample, plastically deformed in the martensitic phase, regains its original undeformed shape upon heating through the transformation (22). Its mechanism could proceed through the creation of ferroelastic domains in the martensitic phase and their removal by the onset of the high-symmetry phase (21). Conversely, it would be interesting to produce a shape-memory effect in insulating materials undergoing a ferroelastic transition. We can expect, however, that the recoverable plastic deformation will be one or two orders of magnitude lower than in alloys, in agreement with their smallest spontaneous strain.

Ferroelasticity also arises from another type of transitions which have been extensively studied in recent years. These are the transitions which are driven, at microscopic level, by the cooperative Jahn-Teller effect. Their mechanism involves the coupling of localized electronic orbitals, which are the degenerate ground state of a transition metal or rare earth ion, with the crystal lattice. Many examples of such transitions are known among compounds with the spinel or zircon structures (23). In all these compounds, the ferroelasticity has its origin in the fact that the motion of the crystal lattice which couples to the electronic states is a homogeneous strain. Accordingly, the usual manifestations of the ferroelastic behavior are also salient features of the cooperative Jahn-Teller transitions. Thus, a soft elastic constant has been observed in nickel chromite, uranium oxide, and dysprosium vanadate, while in the last material, stress-removable domains have also been detected in the distorted phase with the help of polarized light (23).

In all the preceding examples we have repeatedly associated the onset of ferroelasticity with the vanishing of some combination of the elastic constants. However, if the latter phenomenon always discloses a ferroelastic transition, the converse property is not general: Ferroelastic

transitions induce an elastic anomaly which is not always a vanishing of elastic constants. In a similar way, ferroelectric transitions do not always display the familiar peak in the dielectric constant. A clear experimental observation of such a situation was effected in 1968 in gadolinium molybdate  $Gd_2(MoO_4)_3$ , a crystal which possesses simultaneously ferroelectric and ferroelastic properties (24). In this material, the dielectric and elastic constants are nearly temperature independent in the high-symmetry phase, and they undergo only a moderate jump at the transition (160°C). A similar behavior has been found, since then, in a few other ferroelectrics and in many ferroelastics. These results have stimulated a great deal of work in recent years, aimed at interpreting such a behavior on the basis of the Landau phenomenological theory of continuous transitions (1). The two situations encountered in ferroelastics, i.e., either an anomalous vanishing of elastic constant or a moderate discontinuity of this quantity, are now well understood. The two corresponding types of transitions are called proper and improper, respectively. More generally one can speak in a similar way of proper and improper ferroic transitions. A rigorous distinction between those two types of ferroics would make use of group-theoretical arguments (25, 26). We have chosen, instead, to describe their main differences qualitatively by using a microscopic model of an improper ferroelectric transition.

As is well known, a usual (proper) ferroelectric transition corresponds to the onset of microscopic dipoles in each unit cell of the crystal. These dipoles have the same magnitude and direction in all the cells and thus determine the onset of a nonzero spontaneous polarization. In the simplest case, the dipole corresponds to the displacement of a single positive ion outside its initial location at the barycenter of the negative charges. This displacement will determine the new symmetry of the crystal which cor-

responds to a lower point symmetry. The uniform value of the dipoles in all the unit cells warrants that the primitive translations of the crystal are the same in both phases. In addition, as the ion responsible for the onset of a dipole moves spontaneously at the transition, its displacement can be induced very easily by an external field when the transition is approached, thus giving rise to a considerable increase of the dielectric constant.

The case of an improper ferroelectric is quite different. In the model, schematically described in Fig. 1, the high-symmetry phase corresponds to the  $P4_2/m$  space group. Only the positive ions, all identical, have been represented. During the transition toward the low-symmetric phase, two groups of ions, labeled  $\eta$  and  $\zeta$ , move independently. Each one is likely to undergo two opposite sets of displacements. It is clear from consideration of the high-symmetry phase that the four displacements represented in Fig. 1 are energetically equivalent and will lead to equally stable states. Their space groups are

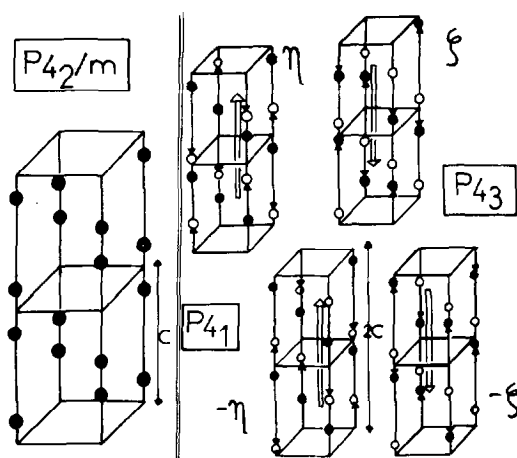


FIG. 1. Microscopic model of an improper ferroelectric transition. In the high-symmetry phase (left) two unit cells of the crystal have been represented. The right part reproduces the four equivalently stable states of the low-symmetry phase (see text). The black arrows indicate the ions which move at the transition, for each set of collective displacement. The large arrow inside the unit cell shows the direction of the spontaneous polarization.

easily identified as  $P4_1$  for  $\pm\eta$  and its enantiomorph  $P4_3$  for  $\pm\zeta$ . In all cases the primitive translation along the tetragonal axis is doubled, in comparison to its value in the high-symmetry phase. We can note that the change in point symmetry ( $4/m \rightarrow 4$ ) corresponds to a ferroelectric transition. However, though this symmetry change is directly induced by the represented ionic displacements, it is remarkable that these displacements do not generate any dipole in the unit cell. A dipole, whose existence is permitted by the symmetry, will eventually be determined by secondary displacements of the positive and negative ions in the structure occurring in compliance with the symmetry of the crystal. Our model shows that in an improper ferroelectric, the onset of a spontaneous polarization is a secondary effect of the transition. The absence of a strong dielectric anomaly is due to the fact that the ionic motions which become easier to induce near the transition are not directly related to the onset of a dipole. Let us now assume that the spontaneous polarization is directed upward for the  $+\eta$  state. It will have the same direction for  $-\eta$ , as this state is obviously transformed from  $+\eta$  by a uniform translation of the crystal of magnitude  $c$ , along the tetragonal axis. By contrast,  $\pm\zeta$  correspond to an opposite polarization because these states can be obtained from  $\pm\eta$  through an inversion center. Thus, the four stable states of the low-symmetry phase give rise to only two distinct orientation states which constitute the familiar ferroelectric domains. Whenever they coexist in a given crystal, the  $+\eta$  and  $-\eta$  states constitute the so-called antiphase domains which cannot be differentiated by any macroscopic quantity. These types of domains, which are frequently encountered in ordered metallic alloys (3), have, up to now, been observed in the ferroelectric-ferroelastic material, gadolinium molybdate (27), and indications of their presence have been obtained in ammonium bisulfate (28). Future investigations should

detect them in all the available examples of improper ferroelastic transitions (Table II).

The  $(\eta, \zeta)$  set of displacement is the order parameter of the considered transition. As shown by our model, it has three specific properties: (1) It vanishes in the high-symmetry phase; (2) it takes a nonzero spontaneous value in the low-symmetry phase; and (3) its onset determines the space group of the low-symmetry phase.

For an improper ferroelectric, the spontaneous polarization shares only the first two properties with the order parameter, while it complies with all of them for a proper ferroelectric transition. This is related to the fact that the onset of a macroscopic quantity will not modify the translation group of a crystal. More generally, one can distinguish improper from proper ferroic transitions by the onset of spontaneous macroscopic quantities which are not the suitable order-parameter of the corresponding transitions.

As suggested by the former model, the features of a proper or improper transition are directly related to the change in the space group of the crystal during the transition. It was established by Landau and Lifschitz (1) that, for continuous transitions, a space-group change will not necessarily occur. Definite symmetry criteria put severe restrictions on the transitions which can arise from a given high-symmetry space group. The total number of possible symmetry changes which originate at any of the 230 crystallographical space groups is limited to a few thousands. Therefore, on the basis of this theory, it should be possible to predict all the types of ferroic transitions one can encounter and infer from symmetry considerations their proper or improper character.

Such a systematic work was recently performed by Tolédano and the present author (29). The results mainly show that among ferroic transitions, pure ferroelastic transitions constitute the largest part of the transitions which are expected to be encountered in crystals. In addition, though a variety of

situations are found to be possible with respect to the symmetry of the order parameter, improper ferroelastic transitions will in most cases be associated with a doubling of the crystal's unit cell, as in the model described in Fig. 1. These predictions appear in good agreement with the experimental aspects emphasized in this paper. However, a more careful comparison, with respect to symmetry, of the former results with all the available experimental data on crystalline phase transitions is still in progress.

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