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Domains in Minerals

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Abstract

Mimetic twinning in minerals is reviewed in terms of the tensor properties of the orientation states, showing which forces are effective in moving domain walls. Following the Aizu method, various types of ferroic species are developed from the free energy function. Examples of ferroelectric, ferromagnetic, ferroelastic, ferrobielectric, ferrobimagnetic, ferrobielastic, ferroelastoelectric, ferromagnetoelastic, and ferromagnetoelectric minerals are described.

Introduction

Twinning is widely used in mineral identification and in elucidating the formation conditions of rocks. The distribution of transformation twins in rock-forming minerals enables one to establish the thermal processes that have occurred in the rock. Mechanical twinning is studied by petrologists in the analysis of flow effects. In rock magnetism, it is the arrangement of ferromagnetic domains which determines remanent magnetization. These are but a few examples of twin phenomena in minerals.

In the past twinned crystals have been classified according to twin-laws and morphology, or according to their mode of origin, or on a structural basis, but there is another classification scheme which has not been widely used by mineralogists, one which is based on the tensor properties of the twin domains. An advantage of such a classification is the straightforward relation between free energy and twin structure, from which it becomes apparent which forces and fields will be effective in moving twin walls. In a ferroelectric, for instance, electric fields are effective in moving domain walls, giving rise to hysteresis between electric polarization and electric field. Analogous magnetic hysteresis loops are caused by the reorientation of ferromagnetic domains under applied magnetic fields. The domain patterns in ferroelectric and ferromagnetic materials are strongly affected by external fields, but there are many other types of twinned crystals with hysteresis and movable twin walls. Aizu (1973) has classified such materials as ferroelastic, ferrobielastic, ferrobimagnetic, ferroelastoelectric, ferromagnetoelastic, and ferromagnetoelectric. As explained later, each type of domain reorientation arises from a particular term in the free energy function.

A *ferroic* crystal contains two or more possible orientation states or domains; under a suitably chosen driving force the domain walls move, switching the crystal from one orientation state to another. Switching may be accomplished by mechanical stress (σ), electric field ($\boldsymbol{E}$), magnetic field ($\boldsymbol{H}$), or some combination of the three. Ferroelectric, ferroelastic, and ferromagnetic materials are well known examples of primary ferroic crystals in which the orientation states differ respectively in spontaneous polarization $\boldsymbol{P}_{(s)}$, spontaneous strain $\epsilon_{(s)}$ and spontaneous magnetization $\boldsymbol{M}_{(s)}$. It is not necessary, however, that the orientation states differ in the primary quantities (strain, polarization, or magnetization) for the appropriate field to develop a driving force between orientations. If, for example, the twinning leads to different orientations of the elastic compliance tensor, a suitably oriented stress can produce different strains in the two domains. The stress may act upon the difference in induced strain to produce wall motion and domain reorientation. Aizu (1973) suggested the term *ferrobielastic* to distinguish this type of response from other ferroics and illustrated the effect with Dauphiné twinning in quartz. Other types of secondary ferroic crystals are listed in Table 1, along with the differences between domain states, and the driving fields required to switch from one state to another. The derivation of the various ferroic species from a free energy function is considered next.

TABLE 1. Primary and Secondary Ferroics

Ferroic Class	Orientation States Differ in	Switching Force	Example
Primary			
Ferroelectric	Spontaneous Polarization	Electric Field	$BaTiO_3$
Ferroelastic	Spontaneous Strain	Mechanical Stress	$CaAl_2Si_2O_8$
Ferromagnetic	Spontaneous Magnetization	Magnetic Field	Fe_3O_4
Secondary			
Ferrobielectric	Dielectric Susceptibility	Electric Field	$SrTiO_3$(?)
Ferrobimagnetic	Magnetic Susceptibility	Magnetic Field	NiO
Ferrobielastic	Elastic Compliance	Mechanical Stress	SiO_2
Ferroelastoelectric	Piezoelectric Coefficients	Electric Field & Mechanical Stress	NH_4Cl(?)
Ferromagnetoelastic	Piezomagnetic Coefficients	Magnetic Field & Mechanical Stress	$FeCO_3$
Ferromagnetoelectric	Magnetoelectric Coefficients	Magnetic Field & Electric Field	$LiMnPO_4$

Free Energy Formulation

The stability of an orientation state is governed by the free energy G. In differential form dG is comprised of thermal energy and various work terms:

$$dG = SdT - \epsilon_{ij}d\sigma_{ij} - P_i dE_i - M_i dH_i$$

S is entropy; T temperature; ϵ_{ij} strain; σ_{ij} stress; $\boldsymbol{P}_i$ electric polarization; $\boldsymbol{E}_i$ electric field; $\boldsymbol{M}_i$ magnetization; and $\boldsymbol{H}_i$ magnetic field. Rationalized MKS units are used to avoid awkward factors of 4π. The directional subscripts refer to cartesian coordinates; $i, j = 1, 2, 3$. A brief summary of the tensor properties of crystals is given in the Appendix. The entropy term is neglected in what follows since we assume the experiments are performed under isothermal conditions.

Strain ϵ is measured relative to the prototype structure and can be written as a spontaneous strain $\epsilon_{(s)}$ plus an induced strain. Induced strain may arise from applied mechanical stress (elasticity), from applied electric fields (piezoelectricity), or from applied magnetic fields (piezomagnetism).

$$\epsilon_{ij} = \epsilon_{(s)ij} + s_{ijkl}\sigma_{kl} + d_{kij}E_k + Q_{kij}H_k.$$

In this equation s_{ijkl} is a component of the fourth-rank elastic compliance tensor. The piezoelectric coefficients d_{kij} constitute a third rank tensor, as do the piezomagnetic coefficients Q_{kij}. Compliance and piezoelectricity are polar tensors whereas piezomagnetism is an axial tensor. Of the four terms in the expression for ϵ_{ij} given above, only the second term is always present. Piezoelectricity and piezomagnetism are null properties which disappear for certain symmetry groups, but all groups have non-zero elastic constants. Spontaneous strain is the change in shape measured relative to the prototype structure. Some twinned crystals possess spontaneous strain.

Electric polarization can be expanded in a manner similar to strain, with contributions from a spontaneous polarization $\boldsymbol{P}_{(s)}$ and several induced effects.

$$\boldsymbol{P}_i = \boldsymbol{P}_{(s)i} + \kappa_{ij}\boldsymbol{E}_j + d_{ijk}\sigma_{jk} + \alpha_{ij}\boldsymbol{H}_j$$

The second rank tensors κ_{ij} and α_{ij} represent the electric susceptibility and magnetoelectric coefficients, respectively. κ_{ij} is a polar tensor and α_{ij} is an axial tensor. Only the ten polar crystal classes possess spontaneous polarization $\boldsymbol{P}_{(s)}$. All materials have finite electric susceptibility coefficients, so that electrically-induced polarization is always present, but magnetoelectricity is found only in solids with certain types of magnetic symmetry.

Magnetization can be expanded in terms of the spontaneous magnetization, and induced effects arising from electric and magnetic fields, and mechanical stress.

$$\boldsymbol{M}_i = \boldsymbol{M}_{(s)i} + \chi_{ij}\boldsymbol{H}_j + Q_{ijk}\sigma_{jk} + \alpha_{ij}\boldsymbol{E}_j.$$

Only ferromagnetic and ferrimagnetic crystals have non-zero spontaneous magnetization. All materials possess non-zero magnetic susceptibility coefficients, (χ_{ij}), but the induced magnetization is often very small.

Substituting the expressions for ϵ_{ij}, $\boldsymbol{P}_i$, and $\boldsymbol{M}_i$ into the differential form for free energy, combining terms, and integrating gives the thermodynamic potential G, which applies to all orientation states. Let ^1G represent the free energy for the first orientation state and ^2G for the second, with the tensor terms referred to a common axial system. The driving potential for a state shift is the $\Delta G = {}^1G - {}^2G$. In the absence of external fields and forces, the energy of all orientation states is equal, so that $\Delta G = 0$. Under external forces the difference in free energy for the two orientation states is

$$\begin{aligned}\Delta G = {} & \Delta\epsilon_{(s)ij}\sigma_{ij} + \Delta \boldsymbol{P}_{(s)i}\boldsymbol{E}_i + \Delta \boldsymbol{M}_{(s)i}\boldsymbol{H}_i \\ & + \tfrac{1}{2}\Delta s_{ijkl}\sigma_{ij}\sigma_{kl} + \tfrac{1}{2}\Delta\kappa_{ij}\boldsymbol{E}_i\boldsymbol{E}_j + \tfrac{1}{2}\Delta\chi_{ij}\boldsymbol{H}_i\boldsymbol{H}_j \\ & + \Delta d_{ijk}\boldsymbol{E}_i\sigma_{jk} + \Delta Q_{ijk}\boldsymbol{H}_i\sigma_{jk} + \Delta\alpha_{ij}\boldsymbol{H}_i\boldsymbol{E}_j,\end{aligned}$$

where $\Delta\epsilon_{(s)ij}$ is ${}^2\epsilon_{(s)ij} - {}^1\epsilon_{(s)ij}$, the difference in a certain component of spontaneous strain for orientation states 1 and 2. $\Delta\boldsymbol{P}_{(s)i}$ and $\Delta\boldsymbol{M}_{(s)i}$ are the differences in the *i*th component of spontaneous polarization and spontaneous magnetization for the two domains. Differences in elastic compliance coefficients are represented by Δs_{ijkl}. The remaining four terms in ΔG arise from differences in electric and magnetic susceptibility, and from differences in piezomagnetic and magnetoelectric coefficients.

A wide variety of ferroic phenomena is possible, depending on which terms in ΔG are important. If $\Delta\boldsymbol{P}_{(s)}$ is non-zero, the material is ferroelectric, provided the coercive field does not exceed the electric breakdown limit. Materials with $\Delta\epsilon_{(s)} \neq 0$ are ferroelastic if the mechanical stress required to switch orientation states does not result in rupture. Ferromagnetic domains—the third type of primary ferroic—possess finite differences in spontaneous magnetization. Ferroic phenomena are not mutually exclusive. In barium titanate, for instance, 90° domains are both ferroelectric and ferroelastic.

The transition between domain states in a ferroelectric is said to be electrically first-order because ΔG is proportional to E. If $\Delta\boldsymbol{P}_{(s)} = 0$ and $\Delta\kappa \neq 0$, then $\Delta G \sim E^2$ and the material is potentially ferrobielectric. Other secondary ferroics are listed in Table 1. For a ferrobielastic $\Delta G \sim \sigma^2$, and for a ferrobimagnetic $\Delta G \sim H^2$. Cross-coupled ferroics include the ferroelastoelectric ($\Delta G \sim E\sigma$), ferromagnetoelastic ($\Delta G \sim H\sigma$) and ferromagnetoelectric ($\Delta G \sim EH$).

Almost all types of mimetic twins belong to one or more of the ferroic classes in Table 1. There are, however, a few cases in which the tensor properties of the orientation states are nearly identical. Consider a non-magnetic crystal belonging to crystal class 432 with pseudosymmetry *m*3*m*. The orientation states are mirror images of one another. Spontaneous polarization, spontaneous strain, and all piezoelectric coefficients are zero; therefore ferroelectricity, ferroelasticity, and ferroelastoelectricity are absent. Without magnetic order, the ferromagnetic, ferromagnetoelectric, and ferromagnetoelastic effects are also absent. Second and fourth-rank polar tensors are identical for the two orientation states, eliminating any differences in the susceptibility, permittivity, or elastic constant matrices. Domains of this type could not be switched by any of the primary or secondary ferroic mechanisms, and yet they could be seen optically. The sign of the optical-activity coefficient is different for the right- and left-handed domains.

An even more subtle type of twinning could occur in minerals such as elpasoite (Frondel, 1948). The structure ascribed to elpasoite (K_2NaAlF_6) is a slight distortion of the $(NH_4)_3FeF_6$ arrangement. Ammonium ferrifluoride consists of NH_4 ions packed together with octahedral $(FeF_6)^{3-}$ groups; the structure belongs to cubic space group *Fm*3*m*. Metal atoms occupy the same positions in elpasoite but the fluorines are distributed less symmetrically in space group *Pa*3 because of the K,Na ordering. Coordinates differ only slightly for the two structures, but the point symmetry is lowered from *m*3*m* to *m*3. With prototype symmetry *m*3*m*, the orientation states in *m*3 are identical for all tensor properties through rank four. All primary and secondary ferroic phenomena are therefore absent in elpasoite, making the domains immovable. Optical properties of the orientation states are also identical, making them invisible as well as immovable. In cases such as these, domains could be differentiated by X-ray diffraction or by etch-figure techniques.

In addition to the primary and secondary ferroics in Table 1, tertiary and even higher-order phenomena are possible, although not likely. Effects such as ferrotrielectricity ($\Delta G \sim E^3$) and ferroelastomagnetoelectricity ($\Delta G \sim E\sigma H$) will appear as higher-order terms in the free energy function. The coefficients for such terms are generally small, increasing the size of the coercive fields. Furthermore, tertiary effects will usually be obscured by primary and secondary ferroic behavior.

Mineralogical examples of ferroic phenomena are discussed in the following sections.

Ferroelectricity

A ferroelectric is a crystal possessing reversible polarization, as shown by a dielectric hysteresis loop. Domains in a ferroelectric differ in spontaneous polarization $\boldsymbol{P}_{(s)}$, and can be switched by an applied electric field.

A large number of ferroelectric compounds occur in the perovskite and pyrochlore families, although the minerals $CaTiO_3$ and $CaNaNb_2O_6F$ are not ferroelectric. Barium titanate and PZT (lead zirconate-titanate) are of considerable commercial importance because of their high permittivities and large piezoelectric coefficients. Other mineral-related ferroelectrics are found in the boracite family and among nitrates such as KNO_3-Phase III. However, the only ferroelectric investigated extensively using mineral specimens is colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$.

Ferroelectricity was discovered in the borate mineral colemanite by Goldsmith (1956). At room temperature colemanite is centric, point group $2/m$, but below approximately 0°C it transforms to a ferroelectric phase belonging to point group 2. Spontaneous polarization develops along the monoclinic *b* axis, accompanied by the formation of 180° domains. At -20°C the spontaneous polarization $\boldsymbol{P}_{(s)}$ is 0.45 μC/cm^2, and the coercive field required to switch domains is about 2000 volts/cm (Wieder, 1959). With increasing temperature $\boldsymbol{P}_{(s)}$ decreases continuously to zero, typical of a second order transition. The Curie point is strongly affected by space charge fields caused by impurities, but for most natural specimens it ranges from 0°C to -7°C.

Ferroelectric domains are sometimes visible in polarized light, but the 180° domains in colemanite cannot be distinguished in this way since the optical indicatrix is identical for both orientation states. There is a possibility that the difference in optical activity could be utilized, though this has yet to be demonstrated. The orientation states in colemanite are enantiomorphic, and potentially optically-active. Because of this, the 180° domains may be visible when viewed along an optic axis.

The structural basis of ferroelectricity in colemanite has been described by Hainsworth and Petch (1966). Above the transition, in the nonpolar phase, one of the hydrogen atoms of the water molecule and the hydrogen of an adjacent hydroxyl group are in a state of dynamic disorder. As the temperature is lowered, the rate of reorientation decreases until the hydrogens settle into ordered noncentric positions in the ferroelectric phase. The ordering of hydrogen atoms is accompanied by small displacements of other atoms from the positions they occupy in the centric phase.

Ferromagnetism

The orientation states of a ferromagnet differ in spontaneous magnetization, and can be switched by a magnetic field. This broad definition encompasses ferrimagnets (magnetite) and weak ferromagnets (hematite), as well as ordinary ferromagnets (iron). It does not include antiferromagnetic, paramagnetic, and diamagnetic substances which have no spontaneous magnetization. Such materials are not ferromagnetic but may be ferrobimagnetic.

Magnetite is the best example of a magnetic mineral. Below 585°C, Fe_3O_4 is ferrimagnetic with a magnetic moment of 4 Bohr magnetons per molecule corresponding to the four unpaired electron spins associated with Fe^{2+} (Smit and Wijn, 1959). Tetrahedral Fe^{3+} spins are directed antiparallel to octahedral Fe^{3+} and Fe^{2+} spins so that the Fe^{3+} moments cancel, leaving a spontaneous magnetization equivalent to one Fe^{2+} moment per molecule. The direction of easy magnetization is $\langle 111 \rangle$, giving rise to eight orientation states for $\boldsymbol{M}_{(s)}$. Magnetite belongs to magnetic point group $\bar{3}m'$, one of the 21 pyromagnetic classes (Birss, 1964), although the trigonal distortion is too small to be seen by X-ray diffraction. Magnetic domains are difficult to see because magnetite is opaque to visible light, even in thin section. The domains are probably similar to those in $MgFe_2O_4$ which has the same magnetic structure, but is transparent to red wavelengths. Sherwood, Remeika, and Williams (1959) observed snake-like domain patterns in a (111) thin-section of magnesium ferrite.

Domains in transparent ferromagnetic and ferrimagnetic crystals are visible in polarized light because of the Faraday effect, a nonreciprocal rotation of the plane of polarization. The angle of rotation ϕ is given by $\phi = \rho t \cos \theta$, where t is the specimen thickness, ρ the rotation per unit thickness, and θ the angle between the magnetization vector and the direction of propagation. Faraday rotation coefficients for ferrites are typically about 1000°/cm (Sherwood, Remeika, and Williams, 1959).

Hematite, α-Fe_2O_3, exhibits both antiferromagnetism and weak ferromagnetism. From 250K to 950K, the Fe^{3+} spins lie in the rhombohedral (111) plane and are nearly antiparallel, but with a small ferromagnetic component, also in (111). Mineralogists generally assign hematite to trigonal class $\bar{3}m$, but the magnetic point symmetry is $2/m$ at room temperature. Antiferromagnetic crystals often exhibit weak (parasitic) ferromagnetism when the ferromagnetic component does not violate the symmetry elements of the antiferromagnetic spin array (Birss, 1964). In hematite, weak spontaneous magnetization appears along the monoclinic two-fold axis, corresponding to one of the three diad axes in $\bar{3}m$. At 250K the spin direction changes to the rhombohedral axis [111], and the weak ferromagnetic effect disappears. Below the spin-flop transition, the magnetic point group is $\bar{3}m$.

Magnetic domains in hematite have been observed using the Faraday effect (Williams, Sherwood, and Remeika, 1958). The white, gray, and black regions in Figure 1 correspond to domains with three different magnetic axes; magnetic fields of only 10 oersteds produce significant differences in the domain pattern. When cooled through the spin-flop transition at −120°C, the domains disappear, and then reappear in a different pattern on heating.

Ferroelasticity

A crystal is ferroelastic if (1) it has two or more orientation states differing in spontaneous strain, and (2) can be transformed from one to another of these states by an external mechanical stress. Spontaneous strain is measured relative to the prototype structure. In the ferroelastic state the crystal symmetry is reduced to a subgroup of a higher symmetry class by a small distortion, typically on the order of parts per thousand, which is a measure of the spontaneous strain $\epsilon_{(s)}$. By analogy with the ferroelectric case, just as spontaneous polarization can be redirected by an electric field, so can the spontaneous strain of a ferroelastic be reoriented by mechanical stress.

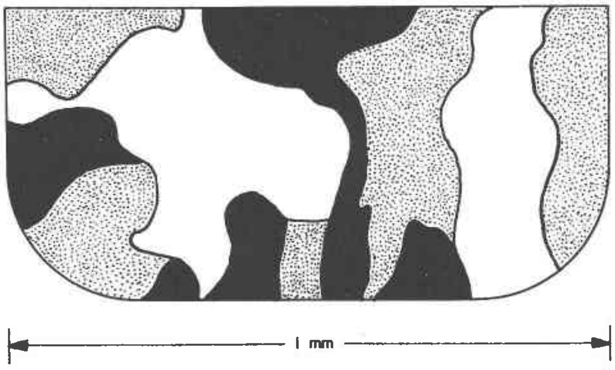

FIG. 1. Magnetic domain pattern in a hematite crystal observed by means of the Faraday effect. Three orientations of the parasitic ferromagnetism give rise to different light intensities. The specimen is a thin platelet (~0.03 mm thick) with major faces parallel to the rhombohedral (111) plane. To observe the domains it was necessary to tilt the platelet with respect to the light beam; otherwise the Faraday effect is absent because the magnetization vectors are perpendicular to the beam. (After Williams, Sherwood, and Remeika, 1958).

Ferroelasticity differs from ferroelectricity and ferromagnetism is one respect. Defining the zero reference for spontaneous strain is more subtle than that for spontaneous polarization or for spontaneous magnetization. If, in the absence of external forces, there is no electric or magnetic charge separation, then $\boldsymbol{P}_{(s)} = \boldsymbol{M}_{(s)} = 0$. To define $\epsilon_{(s)}$, a reference state of zero strain is required. The spontaneous strain of various orientation states may differ in sign or direction but must be equal in magnitude, otherwise equivalent free energies are not obtained for equivalent stresses. When measured relative to the prototype structure, the $\epsilon_{(s)}$ values of all orientation states are equal in magnitude. Therefore the prototype state containing all the pseudosymmetry elements is the zero reference for spontaneous strain.

Ferroelasticity is a type of mechanical twinning in which the lattice reorients rapidly in response to a mechanical stress. There is no diffusion or breaking of chemical bonds, only small rearrangements with atomic displacements of the order of 0.1 Å. Abrahams (1971) has discussed the structural basis of ferroelasticity, emphasizing the importance of pseudosymmetry and citing a number of examples. The symmetry classification of potential ferroelastic materials has been developed by Aizu (1970).

A summary of the earlier literature on mechanical twinning can be found in the book by Klassen-Neklyudova (1964). The book is divided into two parts: twinning with change in form, and twinning without change in form. Ferroelastic twinning is accompanied by a change in form associated with the reorientation of spontaneous strain. The triclinic feldspars show ferroelastic mechanical twinning. Twinning without change in form is exemplified by α-quartz. As discussed later, quartz is a ferrobielastic material with no spontaneous strain, but with orientation states that differ in elastic compliance.

Two views of the twin structure in triclinic feldspars are shown in Figure 2. Twinning is common in all the feldspars, and almost universal in microcline ($KAlSi_3O_8$) and the plagioclases ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$ series). The extinction angles in twinned crystals constitute one of the chief methods of identifying feldspars. The two most important types of

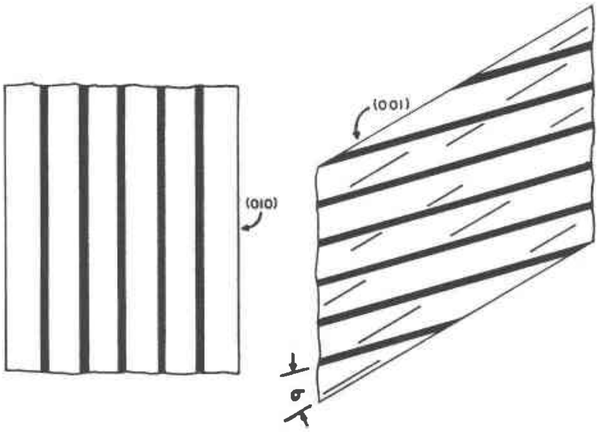

FIG. 2. Plagioclase feldspars exhibit perfect cleavage parallel to (001), and less perfect parallel to (010). Albite twin lamellae are usually present on (001) cleavage flakes (left). Albite lamellae are parallel to the straight edge formed by the intersecting (010) and (001) cleavage planes. Flakes parallel to (010) sometimes show pericline twins (right). Twin lamellae intersect the (001:010) edge at an angle σ, the so-called angle of the rhombic section. (After Rogers and Kerr, 1942).

twins in feldspars are polysynthetic albite and pericline twins. Albite twin lamellae are parallel to (010), and are related by reflection across (010). This is a symmetry element in the prototype point group $2/m$ found in sanidine, the high-temperature potash feldspar. Microcline, the low-temperature polymorph, belongs to the centric triclinic class $\bar{1}$, as do all the plagioclase feldspars. In pericline twins, the individuals are related by rotation of 180° about [010], the two-fold symmetry axis in the prototype point group. The triclinic symmetry in plagioclase feldspars is caused by crumpling of the aluminosilicate framework about the Na^+ and Ca^{2+} ions (Fig. 3).

Strain is a symmetric second-rank tensor with six components: three longitudinal strains ϵ_{11}, ϵ_{22}, ϵ_{33} and three shear components ϵ_{23}, ϵ_{13}, ϵ_{12}. The two orientation states in plagioclase feldspars are related by reflection across $b = X_2$. Reflection reverses the sign of X_2, leaving X_1 and X_3 unchanged. Tensor components with an odd number of 2 subscripts change sign under this operation. Thus the non-zero components of spontaneous strain are $\epsilon_{(s)23}$ and $\epsilon_{(s)12}$, shearing strains about X_1 and X_3, respectively.

The spontaneous strain associated with ferroelasticity in the plagioclase feldspars can be estimated from crystallographic data. For the varieties exhibiting mechanical twinning the cell angles are $\alpha = 93.5 \pm 0.5°$, $\beta = 116.0° \pm 0.5°$, $\gamma = 90.5 \pm 0.5°$, compared to $\alpha = 90°$, $\beta = 116.0 \pm 0.5°$, $\gamma = 90°$ for the monoclinic feldspars. Adopting an orthogonal axial system $X_1 = a^*$, $X_2 = b$, $X_3 = c$, and neglecting the small difference between the triclinic γ and 90°, the two components of spontaneous strain are $\epsilon_{(s)12} = 0$ and $\epsilon_{(s)23} = (\pi/360°)(\alpha° - 90°) = 0.03$. Compared to most ferroelastics, this is a rather large spontaneous strain. Based on this analysis, it appears that the difference in free energy for the two orientation states will take the form $\Delta G \cong 4\,\epsilon_{(s)23}\sigma_{23}$. The most effective stress in moving domain walls should be σ_{23}, a shearing stress about X_1 or a^*.

Mechanical twinning in anorthite was demonstrated by Mügge and Heide (1931). Albite and pericline twin lamellae spaced by about 0.03 mm were introduced under uniaxial stress. Coercive stresses were not measured, but are known to be considerably less than 25×10^4 N/cm². These observations were confirmed by Laves (1952). Untwinned cleavage flakes of disordered analbite ($Na_{0.8}K_{0.2}AlSi_3O_8$) were pressed lightly with the tip of a needle while viewed in a polarizing microscope. With changing pressure albite twin lamellae appear and disappear with changing widths.

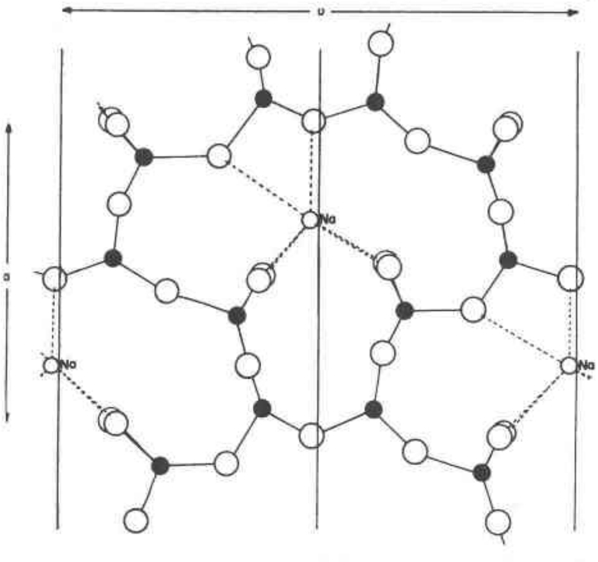

FIG. 3. Projection of the triclinic albite along the c axis. The tetrahedral (Al,Si) ions (solid circles) and oxygen (open circles) form an aluminosilicate framework with Na^+ ions in cavities. Sodium ions are not large enough to contact all corners of the cavity, so the framework is sheared and the symmetry is lowered from monoclinic to triclinic. Pseudo-mirror planes associated with the monoclinic prototype symmetry are shown as vertical dark lines (after Bragg, 1937).

Borg and Heard (1969) have studied mechanical twinning and slip in twelve types of plagioclase. Mechanical albite and pericline twins were induced by triaxial compression at 800°C and 8–10 kbar confining pressure. The critical resolved shear stress for albite and pericline twinning is approximately 1 kbar at strain rates of 10^{-4} to 10^{-5} sec^{-1}. Twinning was induced in seven specimens: disordered An_1 and An_{59}; slightly disordered An_{32}, An_{39}, and An_{53}; and An_{76} and An_{95} with transitional and primitive anorthite structure, respectively. No microscopic twinning was detected in comparable tests on ordered albite (An_1), ordered oligoclase (An_{20}), peristeritic feldspars (An_{11}, An_{14}), or in low-labradorite (An_{51}).

Pressure-twinning is easier in "high-temperature" varieties, indicating that Al-Si ordering tends to "freeze-in" the twin states, raising the coercive stress. Ordered albite will not twin in response to pressure because strong chemical bonds have to be broken during twinning. The Al-Si distribution in low albite has triclinic symmetry, so that Al-Si interchange is required in switching from one orientation state to the other. No interchange is required in ordered anorthite where Al and Si occupy alternate tetrahedra. Therefore glide twinning is easier in ordered Ca-rich plagioclases. The relation between structural state and ease of formation of pericline-albite twins by gliding has been discussed by Starkey (1967).

Ferrobielectricity

Ferrobielectricity is a secondary ferroic phenomenon arising from field-induced electric polarization, rather than spontaneous polarization as in a ferroelectric. Switching between orientation states occurs because of differences in the dielectric permittivity tensor. Permittivity is a second-rank tensor, like strain or magnetic susceptibility. Any orientation states that differ in spontaneous strain will also differ in both electric and magnetic susceptibility. Therefore all ferroelastics are potentially ferrobielectric and ferrobimagnetic.

Ferrobielectricity can be expected in non-polar crystals with mimetic twinning and substantial dielectric anisotropy. Antiferroelectric materials such as $NaNbO_3$ and $SrTiO_3$ are promising candidates because the dielectric permittivities are large enough to make a sizeable contribution to the induced polarization term in the free energy function. Below 110K, $SrTiO_3$ is ferroelastic and possibly ferrobielectric. The phase transition involves a symmetry change from cubic (class $m3m$) to tetragonal ($4/mmm$) at low temperatures. The TiO_6 octahedra of the ideal perovskite structure rotate about a fourfold axis. Alternate octahedra rotate clockwise and counterclockwise, causing the structure to crumple about the Sr^{2+} ions (Axe, 1971). On cooling through the transition, the tetragonal c axis may develop along any of the three cube edges, giving rise to 90° domains. The domains are ferroelastic and optically-distinct. For stress-free 90° domains in $SrTiO_3$, the difference in free energy will be proportional to $(\kappa_{33} - \kappa_{11}) E^2$. There is no apparent discontinuity in the dielectric constant or its slope at the cubic-tetragonal transition, but anisotropy in the permittivity develops at low temperatures. Dielectric constants as large as 25,000 have been reported (Saifi and Cross, 1970). Below 50K, electric double hysteresis loops are observed, along with changes in weak-field permittivity under DC bias. Such behavior may be associated with ferrobielectric domain wall movement.

Ferrobimagnetism

Anisotropic magnetic susceptibility may lead to ferrobimagnetism. Magnetic susceptibility is a polar second-rank tensor like strain and electric permittivity; therefore ferrobimagnetism has the same symmetry requirements as ferroelasticity and ferrobielectricity. In materials with spontaneous magnetization, ferrobimagnetism will be masked by the larger ferromagnetic effect. The effect is most likely to occur in antiferromagnetic crystals since χ_{ij} is relatively small and isotropic in paramagnetic and diamagnetic solids.

Nickel oxide (bunsenite) is both ferroelastic and ferrobimagnetic. At temperatures above the Néel point of 523 K, NiO is paramagnetic with the cubic rocksalt structure. Below T_N, antiferromagnetic ordering of the Ni^{2+} spins results in a small rhombohedral distortion. The unit cell contracts slightly along one of the $\langle 111 \rangle$ body diagonals with the angle between cube axes changing from 90° to 90°4′. Crystallographic twinning occurs because the contraction may take place along any of the four body diagonals. Each domain is optically uniaxial with the optical axis parallel to the contraction direction. The birefringence ($n_e - n_o = 0.003$ at 5900 Å) is large enough to make domains visible in polarized light (Roth, 1960).

In a well-annealed crystal, domain walls are easily displaced by a mechanical stress (ferroelasticity) or by a magnetic field (ferrobimagnetism). Elastic energy is lowest for domains with the contraction axis parallel to the applied stress. The walls can be moved distances of several mm and the movement observed with a polarizing microscope. Only small mechanical stresses (< 10 N/cm^2) are required to move domain walls. A multi-domain specimen can be converted to an untwinned state by pinching the crystal between thumb and index finger (Slack, 1960).

Untwinned NiO crystals possess an anisotropic magnetic susceptibility. For domains contracted along [111], the magnetic susceptibility parallel to [111] exceeds those measured in the perpendicular directions. At low fields the anisotropy in susceptibility is 3.3×10^{-6} emu/gram. In such a domain, spins lie in the (111) plane, perpendicular to the [111] contraction direction. As in most antiferromagnetic materials, the magnetic susceptibility is largest perpendicular to the spins.

Moderate magnetic fields of 5000 oersteds are sufficient to move domain walls in well-annealed crystals. Induced magnetic energy (and total free energy) is minimized when the maximum magnetic susceptibility is parallel to the applied magnetic field. Antiferromagnetic domains with contraction direction parallel to H are favored over other orientations. The response to an applied field is highly erratic because the walls are easily pinned by crystal imperfections. Domain wall movement in ferrobimagnetic NiO is illustrated in Figure 4.

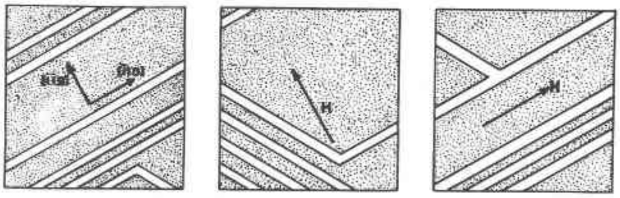

FIG. 4. Displacement of domain walls in antiferromagnetic NiO by a magnetic field. The crystal is a thin plate approximately 1 mm on edge with the major face parallel to (111). A magnetic field of 25000 oersteds was first applied along [$11\bar{2}$] and then along [$\bar{1}10$] to produce ferrobimagnetic switching. Domains are visible in polarized light because of the spontaneous strain associated with antiferromagnetic ordering. Viewed between crossed polarizer and analyzer, the major portion of the crystal is dark because the domains are contracted along [111]. Bright stripes sloping up to the left and up to the right correspond to domains contracted along [$\bar{1}11$] and [$11\bar{1}$], respectively (after Roth, 1960).

Ferrobielasticity

Ferrobielastic crystals are a class of secondary ferroics in which orientation states differ in elastic compliance, a fourth-rank polar tensor. Ferrobielastic switching in α-quartz has been reported by Aizu (1973). Under applied stress, the two twinned regions strain differently. This creates a difference in free energy favoring one domain over the other, causing domain walls to move. Ferrobielasticity is a second order effect in which the strain difference between orientation states is induced by applied stress. When the stress is removed, the induced strain and the difference in free energy disappear also. Domain changes under stress can be observed optically because of differences in the photoelastic tensor for the two twin segments. Photoelasticity—the change in refractive indices with stress—is a fourth-rank tensor like elasticity. Orientation states differing in elastic constants will also differ in photoelastic coefficients.

β-quartz is hexagonal, crystal class 622. On cooling through the phase transition at 573°C, the symmetry is lowered to 32. Transformation twins develop as β-quartz converts to α-quartz. The transformation twins, often called Dauphiné twins or electrical twins, consist of two orientation states related by 180° rotation about [$00\cdot1$], the trigonal axis. Dauphiné twins combine two right-handed (or two left-handed) individuals, often with irregular composition planes. Such twinning renders the crystals useless for piezoelectric applications because it reverses the direction of the X_1 axis and the signs of the piezoelectric coefficients. Because of the importance of piezoelectric quartz in communications applications, techniques for detwinning quartz were developed during World War II when quartz was scarce. The mechanical detwinning of quartz demonstrated by Thomas and Wooster (1951), and by others (see Klassen-Neklyudova, 1964), is an excellent example of ferrobielasticity.

When referred to the same axes, states of Dauphiné twin orientation differ in elastic constants. Class 32 has six independent compliance coefficients: s_{1111}, s_{1122}, s_{1133}, s_{1123}, s_{3333}, and s_{2323}. The twins are related by 180° rotation about X_3 which reverses the signs of X_1 and X_2. Polar tensor coefficients with an odd number of 1 and 2 subscripts change sign under such an operation. Therefore s_{1123} changes sign for the two orientation states, but the other coefficients do not. Under an appropriate stress σ, the difference in free energy between Dauphiné states is proportional to $s_{1123}\ \sigma^2$. As shown in Figure 5, a uniaxial stress at 45° to X_2 and X_3 is effective in switching the ferrobielastic domains.

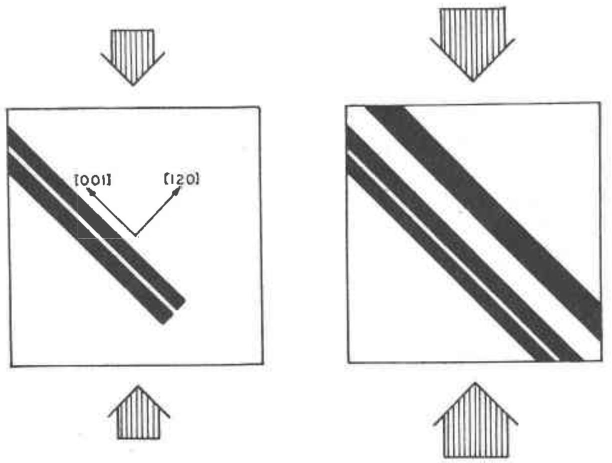

FIG. 5. Ferrobielastic switching of Dauphiné twins in quartz produced by uniaxial stress applied at 45° to X_2 and X_3. As the mechanical stress is increased slowly from 4.9 to 5.0 newtons/cm², the striped twin pattern changes abruptly. Specimen dimensions are 5 × 5 × 3 mm. Orthogonal property axes ($X_1X_2X_3$) correspond to the [10·0], [12·0], [00·1] crystallographic axes, respectively. The crystal is viewed along X_1 between crossed polarizer and analyzer. Domains are visible because of the photoelastic effect; the contrast in brightness disappears when the stress is removed (after Aizu, 1973).

Atomic movements in the Dauphiné twin operation are small and do not involve the breaking of Si-O bonds. In shifting from one orientation state to the other, silicon atoms are displaced by 0.3 Å, and oxygens by about twice that amount. Across the composition plane there is a slight difference in bond angles. Dauphiné twinning disappears at the α-β transformation.

Ferroelastoelectricity

Ferroelastoelectricity is a new cross-coupled ferroic phenomenon; at present there are no known examples. The domain states of a true ferroelastoelectric differ in the piezoelectric tensor, when referred to a common set of axes. The crystal can be switched from one state to another when an electric field and a mechanical stress are applied simultaneously. A ferroelastoelectric is not simply a ferroelectric which is also ferroelastic. Such materials can be switched by *either* an electric or mechanical force. *Both* forces are required to switch a true ferroelastoelectric, for it is neither ferroelectric nor ferroelastic.

Since all polar classes are potentially ferroelectric, a likely source of ferroelastoelectrics are the ten non-polar piezoelectric classes: 222, 32, $\bar{4}$, $\bar{4}2m$, 422, $\bar{6}$, $\bar{6}m2$, 622, 23, and $\bar{4}3m$. Quartz is potential ferroelastoelectric since Dauphiné twins differ in piezoelectric constants as well as elastic constants.

Sal ammoniac (NH_4Cl) is another possible ferroelastoelectric. Ammonium chloride undergoes a near second-order transition at −30°C accompanied by a λ-anomaly in the specific heat. The crystal structure is cubic, both above and below the transition, but the space group changes from $Pm3m$ at room temperature to $P\bar{4}3m$ at low temperatures. The NH_4Cl structure resembles CsCl with N at (0, 0, 0) and Cl at (1/2, 1/2, 1/2). Hydrogens lie along the body diagonals forming N–H—Cl hydrogen bonds. There are two possible orientations for the tetrahedral NH_4 group with hydrogens at x,x,x; $x,\bar{x},\bar{x}$; $\bar{x},x,\bar{x}$; $\bar{x},\bar{x},x$ ($x = 0.153$), or at $\bar{x},x,x$; $x,\bar{x},x$; $x,x,\bar{x}$; $\bar{x},\bar{x},\bar{x}$. Neutron diffraction data recorded at room temperature favor Frenkel's model in which there is random disorder between the two orientations (Levy and Peterson, 1952). Measurements below the transition at liquid air temperature have established an ordered model with only one set of positions occupied (Goldschmidt and Hurst, 1951).

In the absence of external forces the two orientation states are equal in energy, so that domains undoubtedly exist at low temperatures. Reflection across (100) brings the two states into coincidence. This is a very subtle type of twinning since the physical properties of the two orientation states are nearly identical. Only through third-rank tensor properties such as piezoelectricity and the electro-optic effect can the two states be distinguished.

Crystal class $\bar{4}3m$ has but one independent piezoelectric modulus d_{123} relating polarization along [100] to a shearing stress about [100]: $P_1 = d_{123}\sigma_{23}$. For the two orientation states, d_{123} is equal in magnitude but opposite in sign. Reflection across (100) takes X_1 to $-X_1$, and leaves X_2 and X_3 unchanged. Therefore d_{123} transforms to $-d_{123}$ for two domains related by a mirror parallel to (100).

Ammonium chloride is a potential ferroelastoelectric because its two orientation states differ in piezoelectric coefficients. Applying a uniaxial stress σ along [011] together with an electric field E along [100] leads to a difference in free energy $\Delta G = 2d_{123}\sigma E$. Domain switching will take place if the driving potential ΔG is large enough to overcome the resistance to domain wall motion.

Ferroelastoelectric switching has yet to be demonstrated for NH_4Cl, though domains should be distinguishable through the electro-optic effect. Indirect evidence comes from attempted measurements of the piezoelectric coefficient (Bahrs and Engl, 1937). Only a very small piezoelectric effect (20 times smaller than quartz) was observed in the low-temperature phase, and measurements on different samples were inconsistent, suggesting the possibility of domain effects.

Confirmation of domain formation comes from optical experiments in which laser light of frequency ν generates second-harmonic light of frequency 2ν. The symmetry requirements for second harmonic generation (SHG) are almost identical to those for piezoelectricity. Ammonium chloride crystals generate harmonic signals at low temperatures in keeping with the acentric point group $\bar{4}3m$. Small-angle optical-harmonic-scattering experiments provide evidence of domains in which the sense of the NH_4^+ ion orientation appears to alternate in a somewhat regular manner (Freund and Kopf, 1970).

A similar transition from $m3m$ to $\bar{4}3m$ symmetry may occur in spinel compounds (Grimes, 1973). Re-evaluation of diffraction data has suggested that the crystal structure is properly referred to acentric space group $F\bar{4}3m$ rather than the conventional $Fd3m$ symmetry. The discrepancy is associated with a small displacement ($\sim$ 0.03 Å) of the octahedral cation along [111] directions so that alternate tetrahedral groups expand and contract. This symmetry provides the possibility of antiferroelectric domains which may explain the high dielectric constants observed in Ni–Mn and Mg–Mn ferrites.

Ferromagnetoelastic Effect

The domains of a ferromagnetoelastic material differ in piezomagnetic coefficients. Siderite ($FeCO_3$) is antiferromagnetic below 30K. The magnetic structure (Fig. 6.) consists of antiparallel Fe^{2+} spins aligned along the hexagonal c axis (Pickart, 1960). Siderite belongs to crystal class $\bar{3}m$, and the magnetic point group is also $\bar{3}m$. Symmetry elements $\bar{3}'$ and m', in which the spatial operation is accompanied by time-reversal, are absent. Crystals with magnetic symmetry $\bar{3}m$ are potentially piezomagnetic (Birss, 1964). There are two independent piezomagnetic coefficients, Q_{222} and Q_{123}. Q_{222} relates a tensile stress along X_2 to a magnetization in the same direction; X_2 is the crystallographic [120] direction perpendicular to both the 2-fold (X_1) and 3-fold (X_3) symmetry axes. Piezomagnetic coefficient Q_{123} gives the magnetization component along X_1 resulting from a shearing stress about X_1.

Borovik–Ramanov, Aleksanjan, and Rudashevskij (1962) have studied the piezomagnetic effect in iron carbonate crystals at liquid hydrogen temperature using a magnetic torsion balance in which a press containing the specimen is suspended between the pole pieces of the magnet. Q_{123} was measured, but Q_{222} was below the limit of observation. The magnitude of Q_{123} is sensitive to bias during annealing. When cooled through the Néel point without stress bias, the effect was smaller, presumably because of antiferromagnetic domains. Domains in antiferromagnetic siderite are of the 180°-type in which all spins are reversed (Fig. 6.). The magnetic structures of neighboring domains are related by reflection across $(2\bar{1}0)$ accompanied by time reversal. m' converts Q_{123} to $-Q_{123}$ so that the piezomagnetic coefficient is of opposite sign for the two domains. Siderite is therefore a potential ferromagnetoelastic crystal in which domains can be switched by applying mechanical stress and magnetic field simultaneously. The field should be directed along X_1 together with a shearing stress about X_1.

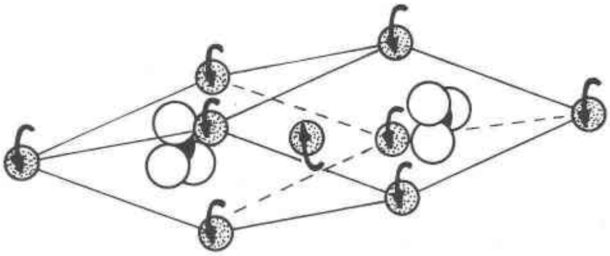

FIG. 6. Magnetic structure of siderite at low temperatures. Siderite has the calcite structure with Fe^{2+} ions at (0, 0, 0) and (½, ½, ½) in the unit cell. The magnetic moment of the Fe atom at the origin is parallel to [111] and antiparallel to the moment at the cell center. Both spin directions are reversed in the other antiferromagnetic domain.

Ferromagnetoelectricity

The coupling between the electric and magnetic variables of a material is called the magnetoelectric effect. More specifically, it is an induced magnetization linearly proportional to an applied electric field. In analytic form the electrically-induced magnetoelectric effect is $\boldsymbol{M}_i = \alpha_{ij}\boldsymbol{E}_j$, and the magnetically induced effect is $\boldsymbol{P}_i = \alpha_{ji}\boldsymbol{H}_j$. The subscripts refer to the three directions of a right-handed Cartesian coordinate system and the α_{ij} coefficients are the field-independent magnetoelectric coefficients.

Landau and Lifshitz (1958) employed symmetry arguments to predict the existence of the magnetoelectric effect and demonstrated that long-range magnetic order is a necessary, although not sufficient, requirement. Magnetoelectricity is permissible in 58 of the 90 magnetic point groups (Birss, 1964). Recent advances in experimental techniques and theoretical understanding have been reviewed by Bertaut and Mercier (1971). Magnetoelectric coefficients have been measured for about twenty materials, including Cr_2O_3 (eskolaite), $LiFePO_4$ (triphylite), and $LiMnPO_4$ (lithiophilite).

$LiFePO_4$ undergoes a paramagnetic-antiferromagnetic phase transition at 50 K. Magnetic susceptibility data collected in the paramagnetic region show typical Curie-Weiss behavior with an effective atomic moment of 5.45 μ_B and an extrapolated Curie constant of 88 K (Santoro and Newnham, 1967). Bozorth and Kramer (1959) obtained comparable results on a mineral specimen of composition $LiMn_{0.7}Fe_{0.3}PO_4$: $T_N = 42$ K, $p_{eff} = 6.1\ \mu_B$, $\Theta = 80$ K.

Triphylite is isostructural with olivine; lattice parameters for the orthorhombic unit cell are $a = 10.31$, $b = 6.00$, $c = 4.69$ Å. The space group is *Pnma* with four molecules per unit cell. Divalent iron atoms occupy mirror plane positions (equipoint 4*c*) with coordinates $\pm(0.28, 0.25, 0.98; 0.22, 0.75, 0.48)$. Low-temperature neutron diffraction studies gave a magnetic structure in which two of the Fe^{2+} spins are parallel to $+b$, the other two to $-b$. All four spins are reversed for the antiferromagnetic 180° domain.

The magnetic structure of triphylite conforms to magnetic point group mmm', one of the magnetoelectric groups. The symbol m' means that the mirror operation perpendicular to c includes a time reversal operator. Time reversal flips the spins by 180° since magnetic moments are associated with moving electric charge. The only non-zero magnetoelectric coefficients for mmm' are $\alpha_{12} = \alpha_{21}$. A value of 10^{-4} has been reported by Bertaut and Mercier (1971). In gaussian units, α is dimensionless.

Magnetoelectric measurements provide ample evidence for the existence of antiferromagnetic domains. The magnetoelectric coefficient α_{12} is identical in magnitude for the two domains but opposite in sign. If the sample is raised above the Néel temperature and cooled through the transition, the sign of α can be positive or negative. Rapid cooling produces both kinds of domains. Powder specimens exhibit no magnetoelectric effect unless annealed in bias fields to remove the degeneracy between the two domains (Shtrikman and Treves, 1963). The principle of the method is quite simple. In an electric field the induced magnetization for one domain is opposite to that of the other. If a magnetic field is then applied, the energies differ for the two time-reversed structures, making one more probable than the other. Domain wall motion is easiest just below the Néel point where coercive fields are smallest.

Summary

A unified approach to the study of domains in crystals can be derived from the free energy function by considering the various work terms. In the absence of applied forces, the free energies of the different orientation states are identical, but domains sometimes differ in energy under mechanical stress or under electric or magnetic fields. Under these circumstances, domain wall motion may occur, as low-energy twin domains grow at the expense of high-energy domains. If the domains differ in spontaneous magnetization, magnetic fields will usually alter the domain configuration giving rise to magnetic hysteresis, the characteristic feature of ferromagnetism, one of the three primary phenomena. Ferromagnetic, ferroelectric, and ferroelastic behavior have been reported in several minerals.

Secondary ferroic phenomena are less well known. These are induced effects caused by property tensor differences between orientation states. The best known example is the ferrobielastic effect in quartz where Dauphiné twin-walls can be shifted by mechanical stress. The study of ferroic phenomena is still in its infancy. Many new examples and applications will appear in the years ahead.

Acknowledgments

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Appendix

Summary of tensor properties (Nye, 1957; Birss, 1964). Many of the physical properties of crystals can be formulated in tensor notation. Tensors are defined in terms of transformations from one orthogonal axial system to another. Let x_1, x_2, x_3 be the old axes and x_1', x_2', x_3' be the new set. $a_{ij}(i, j = 1, 2, 3)$ is a set of nine numbers representing the cosines of the angles between the new axes x_i' and the old axes. The axes transform according to the equations $x_i' = a_{ij}x_j$ where summation is automatically understood for repeated subscripts.

A zero-rank tensor is unchanged by the transformation from old to new axes. Scalar properties such as density are zero-rank tensors. The transformation law for a first-rank tensor is the same as that for the coordinates. Force, electric field, and other vector quantities are first-rank tensors. The components of electric field for instance, transform as $\mathbf{E}_i' = a_{ij}\mathbf{E}_j$. The transformation law for a second-rank tensor is the same as that for the products of two coordinates. Electric susceptibility is a second rank tensor whose components transform as $\kappa_{ij}' = a_{ik}a_{jl}\kappa_{kl}$. A tensor of rank n has n subscripts and transforms as the products of n coordinates.

The tensors just described are polar tensors. The transformation law for a *polar tensor* is unaffected by handedness. It is the same regardless of whether the old and new axes are both of the same handedness or not. For an *axial tensor*, a change in handedness introduces a minus sign to the transformation law. Magnetic field is an axial first-rank tensor whose components transform as $\mathbf{H}_i' = \pm a_{ij}\mathbf{H}_j$. The positive sign applies if the old and new axial systems are both right-handed or both left-handed. If the transformation is from right to left, or from left to right, the negative sign is required.

The number of independent coefficients of a tensor property increases rapidly with rank. For a crystal belonging to triclinic point group 1, three coefficients are required to specify a first-rank tensor property; a symmetric second-rank tensor requires six, a third-rank tensor nine, and a symmetric fourth-rank tensor 21. Crystallographic symmetry reduces the number of independent coefficients in keeping with Neumann's Principle: The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal. The number of independent coefficients for each point group are tabulated by Nye (1957). Magnetic symmetry and magnetic properties require special consideration (Birss, 1964).

Defining relations for several important tensor properties appearing in the free energy function are listed below.

Extensive Quantities	Tensor	Intensive Quantities
Entropy S	Zero-rank polar	Temperature T
Electric polarization $\mathbf{P}_i$	First-rank polar	Electric field $\mathbf{E}_i$
Magnetization $\mathbf{M}_i$	First-rank axial	Magnetic field $\mathbf{H}_i$
Strain ϵ_{ij}	Second-rank polar	Stress σ_{ij}

Properties	Defining Relation	Tensor
Electric susceptibility κ_{ij}	$\mathbf{P}_i = \kappa_{ij}\mathbf{E}_j$	Second-rank polar
Magnetic susceptibility χ_{ij}	$\mathbf{M}_i = \chi_{ij}\mathbf{H}_j$	Second-rank polar
Magnetoelectric effect α_{ij}	$\mathbf{M}_i = \alpha_{ij}\mathbf{E}_j$	Second-rank axial
Magnetoelastic effect Q_{ijk}	$\mathbf{M}_i = Q_{ijk}\sigma_{jk}$	Third-rank axial
Piezoelectric effect d_{ijk}	$\mathbf{P}_i = d_{ijk}\sigma_{jk}$	Third-rank polar
Elastic compliance s_{ijkl}	$\epsilon_{ij} = s_{ijkl}\sigma_{kl}$	Fourth-rank polar

References

ABRAHAMS, S. C. (1971) Ferroelasticity. *Mat. Res. Bull.* **6**, 881–890.

AIZU, K. (1970) Possible species of ferromagnetic, ferroelectric, and ferroelastic crystals. *Phys. Rev.* **B2**, 754–772.

——— (1973) Second-order ferroic state shifts. *J. Phys. Soc. Japan*, **34**, 121–128.

AXE, J. D. (1971) Neutron studies of displacive structural phase transformations. *Trans. Am. Crystallogr. Assoc.* **7**, 89–109.

BAHRS, S., AND J. ENGL (1937) Zum piezoelektrischen Effekt an Ammoniumchloridkristallen beim Umwadlungspunkt —30.5°. *Z. Phys.* **105**, 470–477.

BERTAUT, E. F., AND M. MERCIER (1971) Magnetoelectricity in theory and experiment. *Mat. Res. Bull.* **6**, 907–922.

BIRSS, R. S. (1964) *Symmetry and Magnetism.* North-Holland Publishing Co., Amsterdam, 252 p.

BORG, I. Y., AND H. C. HEARD (1969) Mechanical twinning and slip in experimentally deformed plagioclases. *Contrib. Mineral Petrol.* **23**, 128–135.

BOROVIK-ROMANOV, A. S., G. G. ALEKSANJAN, AND E. G. RUDASHEVSKIJ (1962) Int. Conf. on Magnetism and Crystallography, Kyoto, Japan, Pap. **155**.

BOZORTH, R. M., AND V. KRAMER (1959) Some ferrimagnetic and antiferromagnetic materials at low temperatures. *J. Phys. Radium*, **20**, 393–401.

BRAGG, W. L. (1937) *Atomic Structure of Minerals.* Cornell University Press, Ithaca, New York, 292 p.

FREUND, I., AND L. KOPF (1970) Long range ordering in ammonium chloride. *Phys. Rev. Lett.* **24**, 1017–1021.

FRONDEL, C. (1948) New data on elpasoite and haggemanite. *Am. Mineral.* **32**, 84–87.

GOLDSCHMIDT, G. H., AND D. G. HURST (1951) The structure of ammonium chloride by neutron diffraction. *Phys. Rev.* **83**, 88–94.

GOLDSMITH, G. J. (1956) Ferroelectricity in colemanite. *Bull. Am. Phys. Soc.* **1**, 322.

GRIMES, N. V. (1973) Antiferroelectricity among compounds with spinel structure? *J. Phys. C: Solid State Phys.* **6**, L78–L79.

HAINSWORTH, F. N., AND H. E. PETCH (1966) The structural basis of ferroelectricity in colemanite. *Can. J. Phys.* **44**, 3083–3107.

KLASSEN–NEKLYUDOVA, M. V. (1964) *Mechanical Twinning of Crystals.* Consultants Bureau, New York, 213 p.

LANDAU, L. D., AND E. M. LIFSHITZ (1960) *Electrodynamics* *of Continuous Media.* Addison-Wesley Publishing Co., Reading, Massachusetts, p. 119.

Laves, F. (1952) Mechanische Zwillungsbildung in Feldspäten in Abhängigkeit von Ordnung/Unordung der Si/Al–Verteilung innerhalb des $(Si,Al)_4O_8$–Gerüstes. *Naturwissenshaften,* **39,** 546–547.

Levy, H. A., and S. W. Peterson (1952) Neutron diffraction study of the crystal structure of ammonium chloride. *Phys. Rev.* **86,** 766–770.

Morin, F. J. (1950) Magnetic susceptibility of αFe_2O_3 and αFe_2O_3 with added titanium. *Phys. Rev.* **78,** 819–820.

Mügge, O., and F. Heide (1931) Einfache Schiebungen am Anorthit. *Neues Jahrb. Mineral. Abt.* **A64,** 163–169.

Nye, J. F. (1957) *Physical Properties of Crystals.* Oxford University Press, London, 322 p.

Pickart, S. J. (1960) Antiferromagnetic ordering in $FeCO_3$. *Bull. Am. Phys. Soc.* **5,** 357.

Rogers, A. F., and P. K. Kerr (1952) *Optical Mineralogy.* McGraw-Hill Book Co., New York, 238 p.

Roth, W. L. (1960) Neutron and optical studies of domains in NiO. *J. Appl. Phys.* **31,** 2000–2011.

Saifi, M. A., and L. E. Cross (1970 Dielectric properties of strontium titanate at low temperatures. *Phys. Rev.* **B2,** 677–684.

Santoro, R. P., and R. E. Newnham (1967) Antiferromagnetism in $LiFePO_4$. *Acta Crystallogr.* **22,** 344–347.

Sherwood, R. C., J. P. Remeika, and H. J. Williams (1959) Domain behavior in some transparent magnetic oxides. *J. Appl. Phys.* **30,** 217–225.

Shtrikman, S., and D. Treves (1963) Observation of the magnetoelectric effect in Cr_2O_3 powders. *Phys. Rev.* **130,** 986–988.

Slack, G. A. (1960) Crystallography and domain walls in antiferromagnetic NiO crystals. *J. Appl. Phys.* **31,** 1571–1582.

Smit, J., and H. P. J. Wijn (1959) *Ferrites.* John Wiley and Sons, Inc., New York, 369 p.

Starkey, J. (1967) On the relationship of pericline and albite twinning to the composition and structural state of plagioclase feldspar. *Schweiz. Mineral. Petrogr. Mitt.* **47,** 257–268.

Thomas, L. A., and W. A. Wooster (1951) Piezocrescene: The growth of Dauphine twinning in quartz under stress. *Proc. Roy. Soc. (London),* **A208,** 43–62.

Wieder, H. H. (1959) Ferroelectric properties of colemanite. *J. Appl. Phys.* **30,** 1010–1018.

Williams, H. J., R. C. Sherwood, and J. P. Remeika (1958) Magnetic domains in αFe_2O_3. *J. Appl. Phys.* **29,** 1772–1773.

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