

Phase-transition-related crystal properties: the Neumann principle revisited

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 7499

(<http://iopscience.iop.org/0953-8984/4/36/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:32

Please note that [terms and conditions apply](#).

Phase-transition-related crystal properties: the Neumann principle revisited

Alfred K Agyei†

Department of Physics, University of Science and Technology, Kumasi, Ghana, West Africa

Received 24 September 1991, in final form 17 February 1992

Abstract. The primary properties acquirable by a crystal upon undergoing a displacive structural phase transition (DSPT) and/or magnetic and/or electric transition are defined with the aid of a Gibbs free-energy expansion, and a microscopic group-theoretical analysis of them is carried out. The properties are, apart from those which define the transitions, piezomagnetism, piezoelectricity, magnetoelectricity and piezomagnetoelectricity. It is shown that the macroscopic tensors characterizing them are sums of atomic property tensors, and, as a result, a crystal may exhibit spontaneous piezomagnetism and/or piezoelectricity below its DSPT point T_D and/or spontaneous magnetoelectricity below its ferroelectric transition point T_E . A crystal with a magnetic transition temperature $T_M < T_D$ or T_E (or one with $T_E < T_D$) may therefore be in a weak or secondary magnetic (or electric) state in the temperature region $T_M < T \leq T_D$ or T_E (or $T_E < T \leq T_D$). Thus it is found, in particular, that a crystal with $T_M < T_D$ or T_E may exhibit macroscopic properties characterized by axial c -tensors at temperatures $T \leq T_D$ or T_E , and not just at $T \leq T_M$. Among the crystals cited as being capable of going into the secondary magnetic and/or electric state are the transforming A-15 crystals. It is shown that they may exhibit not only the linear magnetoelectric effect, but also spontaneous piezomagnetism and piezoelectricity, and that their transition into the superconducting state and their high critical fields H_c may be connected with these properties. The analysis brings to the fore the limited scope of the Neumann principle.

1. Introduction

Crystals, as is well known, undergo four basic phase transitions that leave them in the crystalline state, namely structural (displacive and order–disorder), magnetic ((anti)ferromagnetic), electric ((anti)ferroelectric) and superconducting transitions. The result of one or more of the first three transitions in a crystal is the acquisition by the crystal of certain static tensor properties governed by the symmetry of the crystal's low-temperature phase (the daughter crystal).

These properties are usually described on the basis of the Neumann principle, which assumes the crystal point-group symmetry to be the governing symmetry. It states: *The static macroscopic properties of a crystal must be invariant under the crystal point-group operations.*

Thus the principle can be used to describe the macroscopic, but not, strictly speaking, the microscopic, aspects of the properties in question. In particular, it

† Mailing address: PO Box 736, Central Post Office, Accra, Ghana, West Africa.

cannot generally be used to determine the magnetic or electric structures of a crystal, and cannot say anything about phenomena whose effects average out to zero over the crystal unit cell, such as, for example, the phenomena of cell-preserving antiferromagnetism and antiferroelectricity, in which the magnetic and electric unit cells coincide with the crystallographic unit cells.

The limitations of the principle and of descriptions based on it have long been recognized (see e.g. Opechowski and Guccione 1965), and about a decade and a half ago Agyei and Birman (1977) constructed a microscopic group-theoretical theory of phase transitions in crystals, which allows easy determination of the magnetic and electric structures of crystals and describes the phenomena of cell-preserving antiferromagnetism and antiferroelectricity. In the present paper we define (section 2), and carry out on the basis of that theory, a microscopic analysis of a set of primary static tensor properties acquirable by a crystal upon undergoing magnetic and/or electric and/or displacive structural phase transitions. We shall show (sections 3 and 4) that the macroscopic or global tensors characterizing these properties possess a microscopic structure whose consideration reveals the possible existence of the phenomena of spontaneous piezoelectricity, piezomagnetism and magnetoelectricity, which give rise to weak (designated below as secondary) electric and magnetic states or crystals.

The secondary magnetic state is of particular interest because a crystal in such a state can, subject to the Neumann principle, also exhibit static properties characterized by axial c -tensors, i.e. axial tensors that change sign under time reversal. Thus, while the Neumann principle can be used to determine whether or not a known magnetic crystal can exhibit a static property characterized by an axial c -tensor, a crystal that is at present considered to be non-magnetic may require a microscopic analysis before a definitive conclusion as to whether or not it can exhibit such an effect can be drawn.

Such an analysis will require the use of the now generally recognized fact that magnetic and electric crystals are localized-moment (magnetic and electric-dipole) materials. We demonstrate in the present paper that a crystal below its displacive structural phase transition (DSPT) point can also be considered to be a localized-moment material, the moment here being an atomic displacement vector or a strain tensor. Thus all three types of phase transition give rise to localized-moment daughter crystals. The conclusion that a macroscopic property tensor must have a microscopic structure follows from this fact.

We also infer from this fact that these localized moments are the primary order parameters of the transitions, the bulk or sublattice magnetizations (polarizations) that are normally taken to be the order parameters of ferromagnetic or cell-doubling antiferromagnetic (ferroelectric or cell-doubling antiferroelectric) transitions being derived from these localized moments.

The atomic displacement or localized strain is now generally acknowledged to be the order parameter of a DSPT, but an inconsistency, due perhaps to adherence to the Neumann principle, can be perceived in the literature: whereas the microscopic (i.e. localized) entity is acknowledged to be the order parameter, the latter is nonetheless deemed to possess the point-group symmetry of the crystal (see e.g. Scott 1974). We shall show that a localized moment must possess the local or site symmetry, and that it is the set of localized moments in the crystal unit cell that must possess the crystal point-group symmetry. This principle applies equally to magnetic, electric and displacement or strain-tensor moments, and it reveals the similarity, from the group-theoretical standpoint, of magnetic, electric and displacive structural (MEDS) phase transitions. We shall demonstrate (section 5) that this similarity is manifested by the

DSPT and magnetic transition observed respectively in the cubic perovskites LaAlO_3 and Mn_3GaN .

These results are summarized in section 6.

The following are explanations of a few terms and symbols used in the paper. We shall designate as *prototypic* a non-magnetic, non-electric single crystal with no history of a DSPT, so that it is entirely free from internal stresses and strains. By the term *sublattice* we shall mean a crystal substructure possessing the full crystal symmetry, and formed by identical atoms (or ions) occupying equivalent sites in the crystal. The sublattices that actually undergo the magnetic or electric ordering or the distortion in a phase transition will be referred to as *t-sublattices*. Lastly, the spontaneous magnetizations, polarizations and strains that arise respectively in magnetic, electric and displacive structural transitions will be denoted by $M^{(0)}$, $P^{(0)}$ and $\epsilon^{(0)} = (\epsilon_1^{(0)}, \dots, \epsilon_6^{(0)})$ in matrix notation: $M^{(0)} = \chi^{(m)} \cdot H^{(i)}$, $P^{(0)} = \chi^{(e)} \cdot E^{(i)}$ and $\epsilon^{(0)} = s \cdot \sigma^{(i)}$, where $\chi^{(m)}$ ($\chi^{(e)}$) and s are the magnetic (electric) susceptibility and elastic compliance tensors and $H^{(i)}$, $E^{(i)}$ and $\sigma^{(i)} = (\sigma_1^{(i)}, \dots, \sigma_6^{(i)})$ are the corresponding magnetic, electric and stress-tensor field intensities.

Finally, below we assume that (i) the parent crystal is a single crystal, (ii) the daughter crystal is single-domain and (iii) one and the same t-sublattice undergoes all the transitions (magnetic and/or electric and/or displacive structural) observed in the crystal.

2. Primary static tensor properties associated with MEDS transitions

Consider a single-domain crystal with spontaneous magnetization $M^{(0)}$, polarization $P^{(0)}$ and strain $\epsilon^{(0)}$. Let the crystal be located in external magnetic $H^{(e)}$ and electric $E^{(e)}$ fields and let it be subjected to a symmetrized stress-tensor field $\sigma^{(e)}$. The Gibbs free energy Φ of the crystal will then be a function of the temperature T and the resultant fields $H = H^{(e)} + H^{(i)}$, $E = E^{(e)} + E^{(i)}$ and $\sigma = \sigma^{(e)} + \sigma^{(i)}$. Let these fields be sufficiently weak, so that Φ possesses a Taylor expansion in them. Then, if Φ_0 is the free energy in the absence of these fields, we can, using the Einstein summation convention, Greek letters for indices running from 1 to 6 and roman letters for those ranging from 1 to 3, write (see also Schmid 1975):

$$\begin{aligned} \Phi(H, E, \sigma, T) - \Phi_0(T) = & -\frac{1}{2}\chi_{ij}^{(m)} H_i H_j - \frac{1}{2}\chi_{ij}^{(e)} E_i E_j \\ & - \frac{1}{2}s_{\mu\nu} \sigma_\mu \sigma_\nu - \alpha_{ij} H_i E_j - \lambda_{i\nu} H_i \sigma_\nu - \gamma_{i\nu} E_i \sigma_\nu - \pi_{ij\nu} H_i E_j \sigma_\nu \\ & + \Phi^{(r)}(H, E, \sigma, T). \end{aligned} \quad (1)$$

Here, the first, second and third terms on the right-hand side describe, respectively, the first-order magnetization, polarization and deformation effects in the crystal, and the fourth, fifth, sixth and seventh terms describe the magnetoelectric, piezomagnetic, piezoelectric and piezomagnetoelectric effects, respectively, α , λ , γ and π being the magnetoelectric-susceptibility, piezomagnetic, piezoelectric and piezomagnetoelectric tensors.

For the three fields H , E and σ , these seven effects are the *primary* effects for crystals, in the sense that all the other possible effects, described by the terms in the expansion of the last term in (1), are higher orders (in weakness) of them. Indeed,

the expansion (1) with $\Phi^{(r)}$ ignored can be considered to be exact for zero external fields, when $H = H^{(i)}$, $E = E^{(i)}$ and $\sigma = \sigma^{(i)}$ (which is the case we shall mostly be concerned with below). To see this, we only have to note that, by making the requisite number of tensor contractions with the vectors $H^{(i)}$ and $E^{(i)}$ and the tensor $\sigma^{(i)}$ in any term of the $\Phi^{(r)}$ expansion, we can reduce that term to one identical in form with one of the seven terms. (Actually, the piezomagnetolectric term can be similarly reduced to one identical in form with the magnetolectric, piezomagnetic or piezoelectric term; we only include it here to make the number of primary effects combinatorially complete.) Therefore, we can, by appropriately renormalizing the tensors $\chi^{(m)}$, $\chi^{(e)}$, s , α , λ , γ and π , make the first seven terms on the right-hand side of (1) take account of $\Phi^{(r)}$. Thus there is no loss of generality when $\Phi^{(r)}$ is ignored in discussions of spontaneous fields or indeed of effects in external fields that are weak compared to the spontaneous fields. Consequently, below we shall ignore $\Phi^{(r)}$.

The effects described by the terms of the Gibbs free-energy expansion induce in the crystal a magnetization (M), an electric polarization (P) and a strain-tensor (ϵ) field. The fields produced by the primary effects are linear in H , E and σ , and can be obtained by differentiating the truncated or primary free energy $\Phi^{(p)} = \Phi - \Phi^{(r)}$ with respect to H , E and σ . Below we shall consider these fields in the limits when $H^{(e)} \rightarrow 0$ for M , $E^{(e)} \rightarrow 0$ for P , and $\sigma^{(e)} \rightarrow 0$ for ϵ . In this approximation we have

$$M = - \left(\frac{\partial \Phi^{(p)}}{\partial H} \right)_T \Big|_{H^{(e)}=0} = M^{(0)} + \alpha \cdot E + \lambda \cdot \sigma + E \cdot \pi \cdot \sigma \quad (2)$$

$$P = - \left(\frac{\partial \Phi^{(p)}}{\partial E} \right)_T \Big|_{E^{(e)}=0} = P^{(0)} + \alpha \cdot H + \gamma \cdot \sigma + H \cdot \pi \cdot \sigma \quad (3)$$

and

$$\epsilon = - \left(\frac{\partial \Phi^{(p)}}{\partial \sigma} \right)_T \Big|_{\sigma^{(e)}=0} = \epsilon^{(0)} + \lambda \cdot H + \gamma \cdot E + H \cdot \pi \cdot E. \quad (4)$$

Let us now consider the fields H , E and σ to be purely spontaneous fields, due (in the first approximation) to $M^{(0)}$, $P^{(0)}$ and $\epsilon^{(0)}$, respectively. Then M , P and ϵ must transform with the crystal under its symmetry operations. If they are considered to be macroscopic quantities, then they must be invariant under the crystal point-group operations. It then follows from the relations (2)–(4) that the property tensors α , λ , γ and π must, if the effects they characterize occur in the crystal in question, also be invariant under the point-group operations. This is the Neumann principle.

According to this principle, a static effect can occur in a crystal only if there exists a corresponding non-null property tensor that is invariant under the operations of the crystal point group. In particular, if the crystal is non-magnetic, then its property tensors must be i -tensors (i.e. tensors that are invariant under time reversal), and all c -tensors must identically vanish in such a crystal. Further, analysis shows (see e.g. Birss 1964) that polar i -tensors of odd rank and axial i -tensors of even rank should vanish identically in centrosymmetric crystals.

Thus the Neumann principle leads, in particular, to the following two 'selection' rules.

(i) Only magnetic crystals can exhibit static effects characterized by c -tensors.

(ii) Centrosymmetric crystals cannot exhibit static effects characterized by even-rank axial and odd-rank polar i -tensors.

These rules strictly apply only to the external-field-induced bulk effects. Centrosymmetric crystals clearly can exhibit spontaneous antiferroelectricity, and, as shown below, certain non-magnetic crystals may exhibit spontaneous magnetoelectricity (SME) and/or spontaneous piezomagnetism (SPM) and/or spontaneous piezoelectricity (SPE). A crystal exhibiting SME or SPM will be magnetic (albeit weakly so) and, hence, capable of exhibiting external-field-induced bulk effects characterized by axial c -tensors. Thus we shall find that the current definition of a magnetic crystal needs to be broadened to encompass such crystals.

These results are obtained in section 4. In the next section we show that the daughter crystals arising in strain-induced DSPT (referred to below as SIDSPT daughter crystals) can be considered to be localized strain-moment materials and, on the basis of this, argue that property tensors are, like magnetic and electric-dipole moments, entities belonging to the t -sublattice atoms, and that a global property tensor is the sum of the corresponding property tensors of the t -sublattice atoms. The results obtained in section 4 follow from these conclusions.

3. Localization of spontaneous strains and the microscopic structure of bulk property tensors

3.1. SIDSPT daughter crystals as localized-strain-moment materials

As Agyei and Birman (1977) have shown, the t -sublattice atom displacements that occur in a DSPT transform among themselves under the operations of the daughter t -sublattice transformation group, similarly to the magnetic and electric-dipole moments in magnetic and electric crystals. Consequently, we can, by analogy with the latter crystals, regard DSPT daughter crystals as localized-displacement-moment materials. Below we shall show that in strain-induced DSPT (SIDSPT) the atomic displacements are induced by localized strains, so that the resulting daughter crystals can be considered to be localized-strain-moment materials. We do this on the basis of Born's molecular theory of elasticity and Agyei and Birman's (1977) theory of phase transitions in crystals.

According to the Born theory (see Born and Huang 1968), any homogeneous crystal deformation, i.e. one that leaves the material in the crystalline state, can be built up by subjecting the crystal particles (molecules or atoms) to the following displacements:

$$\mathbf{u}(\mathbf{r}_m^q) = \mathbf{u}(m) + \boldsymbol{\epsilon} \cdot \mathbf{r}(m^q) \quad (5)$$

where $\mathbf{r}(m^q)$ is the initial position vector of the m th atom in the q th unit cell; $\mathbf{u}(m^q)$ and $\mathbf{u}(m)$ are respectively q -dependent and q -independent displacements of this atom; and $\boldsymbol{\epsilon}$ is a tensor composed of deformation parameters, i.e. a strain tensor.

The same mechanism can be assumed to underlie DSPT-induced homogeneous deformation of crystals, with the difference that the displacement $\mathbf{u}(m)$ and the tensor $\boldsymbol{\epsilon}$ arise spontaneously, and that not all the atoms in the crystal need undergo such displacements. Indeed, experiment shows that, normally, the atoms of only one

sublattice undergo displacements in a DSPT, and we shall assume this to be the case in the present paper.

Thus let a prototypic single crystal in zero external magnetic, electric and stress fields undergo a DSPT as a result of the spontaneous displacement of the atoms of one sublattice—the t-sublattice. In this case the continuum approach to the description of crystal deformation is inadmissible, and we must treat the set of vectors $r(\frac{q}{n})$ as a discrete set and the spontaneous tensor $\epsilon = \epsilon^{(0)}$, when it arises, as one localized at the site of the atom on which it acts. Further, since the atoms in a unit cell can be displaced in different directions, $\epsilon^{(0)}$ will generally vary from atom to atom within the t-sublattice unit cell. We shall take this fact into account by assigning to $\epsilon^{(0)}$ the label of the atom on which it acts. Also, because of the translational symmetry, we need to consider only the displacements of the t-sublattice atoms in a parent crystal cell corresponding to the daughter crystal unit cell. We shall designate this cell as the $q = 0$ or reference parent crystal cell (RPCC). Taking these points into account, and setting the translation vectors $u(\frac{0}{m}) = u_m^{(0)}$, $u(m) = u_m$ and $r(\frac{0}{m}) = w_{0m}$, we can write (5) in the form

$$u_m^{(0)} = u_m + \epsilon_m^{(0)} \cdot w_{0m} \quad m = 0, 1, \dots, n-1. \quad (6)$$

Here n is the number of t-sublattice atoms in the RPCC, and the $m = 0$ atom is the reference t-sublattice atom.

The vectors u_m and the strain tensors $\epsilon_m^{(0)}$ in (6) thus give the atomic displacements arising in the DSPT. Let us show that they virtually determine the transition (i.e. fix the order parameter and the daughter crystal point group) and elucidate the relation between them.

Let \mathcal{G}_0 and G_0 be the space and point groups of, and H_0 the t-sublattice site point group in, the parent crystal, and let \mathcal{G} , G and H be the corresponding groups for the daughter crystal. Finally, let \mathcal{T} be the translation group of the daughter crystal. Since DSPT-induced deformations are always slight, \mathcal{T} can be considered to be a subgroup of the parent crystal's translation group \mathcal{T}_0 , the two being identical when the transition is cell-preserving. The transformation group of the RPCC will be the factor group $F_0 = \mathcal{G}_0/\mathcal{T}$, i.e. the space group \mathcal{G}_0 modulo the translation group \mathcal{T} . By locating the coordinate origin at a t-sublattice site, we can write F_0 as a set of left cosets $\{R_m|V_{0m}\}H'_0$, where $m = 0, 1, \dots, n-1$; $R_m \in G_0 - H'_0$ for $m \neq 0$, and $R_0 = 1$, the identity element; the V_{0m} ($V_{00} = (0, 0, 0)$) are the t-sublattice atom position vectors relative to the new coordinate origin; H'_0 coincides with, or is a subgroup of, H_0 according to whether the transition is or is not cell-preserving; and n , the number of t-sublattice sites in the RPCC, is equal to the index of H'_0 in G_0 .

The coset decomposition of F_0 in the case of cell-preserving DSPT is trivial. Its feasibility in the case of cell-non-preserving transitions will be demonstrated elsewhere in an extension of the Agyei-Birman theory to cover such transitions. Here we shall only touch upon the general theory under the assumption that the coset decomposition can always be carried out. Further, we shall assume the DSPT in question to be a transition to a single-domain daughter crystal belonging to a given crystal class.

For such a transition the coset decomposition will be unique in the case of a cell-preserving DSPT, when $H'_0 = H_0$. For a cell-non-preserving DSPT more than one (l , say) transformation groups $F_{0j} = \mathcal{G}_0/\mathcal{T}_j$ comprising the cosets $\{R_m|V_{0m}\}H'_{0j}$ ($j = 1, 2, \dots, l$) will in general be admissible. It is, however, easy to see that the various H'_{0j} will be isomorphic subgroups of H_0 , and will yield the same daughter crystal

point group G . The corresponding daughter crystal space groups \mathcal{G}_j will generally not be the same since the translation groups T_j will generally not coincide, but being interested only in G here, we can ignore this subtlety and take any one of the admissible F_{0j} , with the index j dropped, as the RPCC transformation group.

In what follows then, by F_0 we shall mean an admissible set of cosets $\{R_m|V_{0m}\}H'_0$ in the case of cell-non-preserving DSPT and the set of cosets $\{R_m|V_{0m}\}H_0$ in the case of cell-preserving DSPT. This will constitute the transformation or symmetry group of the n t-sublattice atoms in the RPCC. Let us first suppose that the transition does not break up the t-sublattice into two or more daughter crystal sublattices. Then the daughter t-sublattice unit-cell transformation group $F = \mathcal{G}/T$ will contain the same number of cosets of the form $\{R_m|V_m\}H$, where the V_m are the new position vectors of the t-sublattice atoms: $m = 0, 1, \dots, n-1$. In consequence, the global transition $\mathcal{G}_0 \rightarrow \mathcal{G}$ will be governed by the site transition $H'_0 \rightarrow H$, whose order parameter must therefore be the order parameter of the global transition, i.e. of the DSPT.

Let us now suppose that the transition breaks up the parent t-sublattice into $s > 1$ daughter t-sublattices. It is easy to see that we can always split the coset decomposition $\{R_m|V_{0m}\}H'_0$ into s sets of cosets $\{R_{m_i}^{(i)}|V_{0m_i}^{(i)}\}H'_0$ ($i = 1, \dots, s$; $m_i = 0, 1, \dots, n_i - 1$; $\sum_{i=1}^s n_i = n$) that will go over into s transformation groups, with cosets $\{R_{m_i}^{(i)}|V_{m_i}^{(i)}\}H_i$, describing the s daughter t-sublattices. Thus in this case the global transition will be governed by the site transitions $H'_0 \rightarrow H_i$.

Let $H_1 \subset H'_0$ be the group of highest order in the set $\{H_i \neq H'_0 | 1 \leq i \leq s\}$. Then it can easily be shown that $H_i \subseteq H_1$. Further, if, following Landau (1937), we assume that the transition is induced by a single irreducible representation Γ of H'_0 (see below), then the site transitions must have the same order parameter, which must clearly be that component of the basis vector of Γ which is invariant under the operations of the H_i ($i = 1, 2, \dots, s$) or under the operations of H_1 since $H_1 \subseteq H_i$. This order parameter must be the order parameter of the DSPT.

Thus in either case the order parameter of the $H'_0 \rightarrow H_1$ ($= H$ in the $s = 1$ case) site transition is the order parameter of the DSPT in question. Let us show that this order parameter is the displacement u_0 or the tensor $\epsilon_0^{(0)}$ in relation (6) for the reference t-sublattice atom. In doing this we shall, for simplicity of exposition, consider only the $s = 1$ case, the generalization to the $s > 1$ case being trivial.

Evidently, the reduction in the t-sublattice site symmetry, i.e. the transition $H'_0 \rightarrow H$, is due to the t-sublattice atom displacements $u_m^{(0)}$, which must be such that $u_0^{(0)}$ is invariant under the operations of H and $u_m^{(0)} = \{R_m|V_m\}u_0^{(0)}$. Consequently, we need to consider only the $H'_0 \rightarrow H$ transition at the reference t-sublattice site.

On the basis of the Landau theory of phase transitions, this transition will be induced by an irreducible polar-vector or polar-tensor representation, Γ_p , of H'_0 . Let us consider the case when the transition takes the crystal into a given crystal system with the minimum degree of distortion.

The group H will, on the basis of the Goldrich-Birman chain subduction criterion (Goldrich and Birman 1968), then be that maximal subgroup of H'_0 whose polar-vector or polar-tensor unit representation Γ_1 is subduced once by Γ_p , and the order parameter of the transition will be Γ_1 's basis vector, which can be found from the character tables of the 32 crystallographic point groups. For a DSPT it, and hence the order parameter of the transition, may be (i) a displacement a_i in the direction \hat{e}_i , where $\hat{e}_i = (\hat{i}, \hat{j}$ or $\hat{k})$ is the unit vector along one of the coordinate axes, (ii) an

irreducible set η_i of strain-tensor components or, equivalently, the strain tensor ϵ_i with η_i as its sole non-trivial irreducible set of components (i.e. with η_i as the only irreducible set that is not invariant under the operations of H'_0), or (iii) either a_i or η_i (ϵ_i), which may or may not be coupled according as the vector $u_i = \epsilon_i \cdot \hat{e}_i$ is or is not different from zero. Expressed in the soft-mode language, this assertion states that a DSPT may be driven:

- (i) solely by a soft optic phonon;
- (ii) solely by a soft acoustic phonon, i.e. may be purely strain-induced;
- (iii) by coupled soft acoustic and optic phonons; or
- (iv) by a soft acoustic (or optic) phonon in the presence of a soft optic (or acoustic) phonon to which it is not coupled, at least in first order.

The order parameters a_i and ϵ_i arise spontaneously at the reference t-sublattice site, and can therefore be identified with the quantities u_0 and $\epsilon_0^{(0)}$ in relation (6) with $m = 0$. They are each invariant under the operations of the reference t-sublattice site point group, and determine the displacement $u_0^{(0)}$ at the site, the displacement $u_m^{(0)} = u_m + \epsilon_m^{(0)} \cdot w_{0m}$ at the m th site being given, as shown above, by $u_m^{(0)} = \{R_m | V_m\} u_0^{(0)}$ ($m \neq 0$). Hence the sets $\{u_m\}$ and $\{\epsilon_m^{(0)}\}$ defined by (6) each possesses the daughter crystal point-group symmetry (i.e. the elements of each set transform among themselves under the crystal point-group operations), while each element possesses the corresponding site point-group symmetry.

Thus the quantities u_m and $\epsilon_m^{(0)}$ behave under the crystal symmetry operations in precisely the same way as magnetic or electric-dipole moments do in magnetic or electric crystals. It is therefore not inappropriate to describe DSPT daughter crystals as displacement-moment or, in the case of SIDSPT daughter crystals, on which we shall henceforth focus our attention, strain-moment materials.

In SIDSPT daughter crystals, it is the strains $\epsilon_m^{(0)}$ that maintain the t-sublattice atoms in their new positions and determine the deformation or bulk strain of the crystal. Thus the first term on the right-hand side of (4), referred to the daughter crystal unit cell, is the sum $\epsilon^{(0)} = \sum_{m=1}^n \epsilon_m^{(0)}$, which may or may not be equal to zero. In other words, the crystal may be deformed even though its bulk strain is equal to zero, just as a crystal may be magnetic (electric) even though its bulk magnetization (polarization) is equal to zero.

3.2. The property tensors as sums of atomic property tensors

Let us now consider the low-temperature phase of a prototypic single crystal that undergoes in zero external H , E and σ fields a strain-induced DSPT and at or below the DSPT point a magnetic and/or electric transition, leading to the appearance of, besides the first term on the right-hand side of (4), one or more of the other terms. The effect of these terms is to distort the crystal further. Like the distortion due to the first term, the distortions induced by these terms must be due to t-sublattice atom displacements if the material is to remain truly crystalline. Hence these terms must also be the sums of localized strains: $(\lambda \cdot H)_m = \lambda_m \cdot H_m$, $(\gamma \cdot E)_m = \gamma_m \cdot E_m$, $(H \cdot \pi \cdot E)_m = H_m \cdot \pi_m \cdot E_m$, where H_m and E_m are the spontaneous magnetic and electric field intensities at the m th t-sublattice site and λ_m , γ_m and π_m can be described as the piezomagnetic, piezoelectric and piezomagnetoelectric tensors of the m th t-sublattice atom. As a result, ϵ from (4), referred to the crystal

unit cell, can be written as $\epsilon = \sum_{m=1}^n \epsilon_m$, where

$$\epsilon_m = \epsilon_m^{(0)} + \lambda_m \cdot H_m + \gamma_m \cdot E_m + H_m \cdot \pi_m \cdot E_m. \quad (7)$$

It follows from the foregoing that the macroscopic property tensors λ , γ and π are the sums of atomic property tensors, and we can conclude that the third and fourth terms on the right-hand sides of (2) and (3) must be sums of localized vectors. The magnetoelectric susceptibility tensor α has been shown by Agyei and Birman (1990) to be the sum of localized or atomic magnetoelectric susceptibility tensors α_m in localized magnetic and/or electric-dipole moment materials. In such materials, then, we have from (2) and (3), referred to the crystal unit cell, that

$$M = \sum_{m=1}^n M_m$$

and

$$P = \sum_{m=1}^n P_m$$

where

$$M_m = M_m^{(0)} + \alpha_m \cdot E_m + \lambda_m \cdot \sigma_m + E_m \cdot \pi_m \cdot \sigma_m \quad (8)$$

and

$$P_m = P_m^{(0)} + \alpha_m \cdot H_m + \gamma_m \cdot \sigma_m + H_m \cdot \pi_m \cdot \sigma_m. \quad (9)$$

Thus the global or macroscopic property tensors associated with MEDS transitions are sums of atomic property tensors. An atomic property tensor A_m ($= \alpha_m, \lambda_m, \gamma_m$ or π_m) must be invariant under the operations of the atom's site point group, and the set $\{A_m\}$ of such tensors in the crystal unit cell must have the crystal point-group symmetry.

If the macroscopic property tensor $A = \sum A_m$ is not a null tensor, then the macroscopic effect characterized by A may occur in the crystal. If, on the other hand, A is a null tensor, then the effect will be forbidden, but, as we shall show in the next section, the presence of the A_m may allow the occurrence of other effects in the crystal.

Finally, to conclude this section, we must note that DSPT driven solely by soft optic phonons are not covered by the expansion (1) since no spontaneous strains arise in such transitions. The crystal deformation in this case is brought about by a rigid displacement of the t-sublattice relative to some non-equivalent sublattice. This is, for example, the only mode of deformation possible in a cell-preserving DSPT in which the t-sublattice unit cell contains only one atom, such as, for example, in the cubic-to-tetragonal DSPT that occurs in the perovskites BaTiO_3 , PbTiO_3 and KNbO_3 . For such transitions the Gibbs free energy should be expanded in terms of the optic mode amplitude, with the frequency serving as the primary property tensor. The expansion will, in the absence of external stress, contain no stress terms and the crystal that it describes will not exhibit the spontaneous-stress-related properties discussed below.

4. Spontaneous piezoelectricity, piezomagnetism and magnetoelectricity (PPM) and their effects

4.1. Spontaneous PPM; secondary electric and magnetic states

It is well known from experiment that (i) most magnetic transitions are preceded by DSPT and (ii) a crystal that orders both electrically and magnetically usually goes into the electric phase first. Let us, on the basis of these facts, consider a prototypic crystal that undergoes in zero external H , E and σ fields an SIDSPT at a temperature T_D and/or an electric transition at T_E and a magnetic transition at T_M under the following assumptions:

- (i) $T_M < T_E < T_D$;
- (ii) one and the same sublattice is the t-sublattice for all the transitions that occur in the crystal;
- (iii) no DSPT occurs at T_E or in the temperature range from T_E to T_M .

Let us first consider the case when the crystal undergoes a DSPT and then an electric transition.

The transition into the electric state will be possible only if the site point group H of the t-sublattice below T_D admits of the existence of electric-dipole moments at the t-sublattice sites. Further, if the point group H also admits of a non-null piezoelectric tensor γ such that the piezoelectric moments $p_k = \gamma_k \cdot \sigma_k$ (where the σ_k are the spontaneous stress tensors arising as a result of the DSPT) coincide in direction with the electric-dipole moments $P_k^{(0)}$ that appear at T_E , then the moments p_k can be non-zero. A crystal in which the moments p_k are non-zero can be said to exhibit spontaneous piezoelectricity in the temperature range $T \leq T_D$.

Similarly, if the site point group of the daughter t-sublattice arising in the DSPT admits of a non-null piezomagnetic tensor λ and the existence at the t-sublattice sites of magnetic moments coinciding in direction with the piezomagnetic moments $m_k = \lambda_k \cdot \sigma_k$, then the latter can be non-zero and the crystal may exhibit spontaneous piezomagnetism below T_D .

Finally, if magnetic moments M_k can coexist with the electric-dipole moments $P_k^{(0)}$ at the t-sublattice sites in an electric crystal and the t-sublattice site point group admits of a non-null magnetoelectric tensor α such that the magnetoelectric moments $m_k = \alpha_k \cdot E_k$ (where E_k is the electric field due to $P_k^{(0)}$) coincide in direction with the admissible magnetic moments M_k , then the m_k can be non-zero and the crystal can be said to be capable of exhibiting spontaneous magnetoelectricity in the temperature range below T_E .

Thus a crystal can undergo spontaneous piezoelectric and/or piezomagnetic ordering at its DSPT point and/or spontaneous magnetoelectric ordering at its electric transition point. The ordering will be (anti)ferroelectric ((anti)ferromagnetic) according as $P = \sum_{k=1}^n p_k$ ($M = \sum_{k=1}^n m_k$) is or is not equal to zero. We can therefore speak of spontaneous (anti)ferropiezoelectricity, (anti)ferropiezomagnetism and (anti)ferromagnetoelectricity.

As electric and magnetic ordering effects, these phenomena are clearly second-order effects, and a crystal exhibiting spontaneous piezoelectricity can be described as being in the *secondary electric state* in the temperature region $T_E < T \leq T_D$, while a crystal exhibiting spontaneous piezomagnetism or magnetoelectricity can be described as being in the *secondary magnetic state* at temperatures $T_M < T \leq T_D$ or T_E . They are, however, of considerable interest, as we shall now proceed to demonstrate.

A crystal in the secondary magnetic state in the region $T_M < T \leq T_D$ or T_E will have as its symmetry group the same type-I or type-III Shubnikov space group that will be assigned to it in the temperature region below T_M . It will, in particular, not have time reversal as a symmetry operation and therefore can, subject to the Neumann principle, exhibit any macroscopic property characterized by an axial c -tensor. This generalizes and at the same time further elucidates the result, obtained by Agyei and Birman (1990), that certain non-magnetic electric crystals can exhibit the (external-field-induced) linear magnetoelectric (ME) effect, designated by them as the semi-spontaneous ME effect. Indeed all the crystals listed in table 2 in their paper may exhibit spontaneous magnetoelectricity and, as asserted there, the semi-spontaneous ME effect at $T \leq T_E$. All of them, except Ti_2O_3 , may also exhibit the external-field-induced piezomagnetic effect below T_E . The odd crystal Ti_2O_3 will be discussed below.

4.2. Secondary magnetic and electric crystals

In the foregoing discussion we have made no assumption about the value of T_M and there is no reason why it cannot be equal to absolute zero. In other words, the actual magnetic transition need not occur at all. The possibility of its occurrence, i.e. the admissibility of the existence of magnetic moments at the t-sublattice sites, is all that is required for the crystal to go into the secondary magnetic state at T_D or T_E . Such crystals, i.e. those that remain in the secondary state right down to absolute zero, can be designated as *secondary magnetic materials*.

Similarly, a crystal that orders piezoelectrically at the DSPT point can remain in the secondary electric state right down to absolute zero, and such a crystal can be called a *secondary electric material*.

Secondary magnetic (electric) crystals are legitimate magnetic (electric) crystals and the class of magnetic (electric) materials should, perhaps, be broadened to include them.

The crystal Ti_2O_3 does not undergo a magnetic phase transition, but, as conjectured by Agyei and Birman (1990) on the basis of its exhibition of the linear ME effect, it may be antiferroelectric. If this is indeed the case, then it should order antiferromagnetolectrically at its antiferroelectric transition point and should be an example of secondary magnetic crystals. Other probable secondary magnetic and electric crystals are the transforming A-15 crystals. Because of the importance of this group of crystals, we shall discuss them in a separate subsection.

4.3. Spontaneous piezomagnetism and piezoelectricity in the transforming A-15 crystals

Shirane and Axe (1971) have, on the basis of a neutron diffraction analysis, assigned the space group D_{4h}^9 ($P4_2/mmc$) to the low-temperature phase of Nb_3Sn . On the other hand, Agyei and Birman (1977) have shown that the (Fedorov) space group of the low-temperature phases of the transforming A-15 crystals, A_3B , exemplified by Nb_3Sn and V_3Si , should be C_{4v}^7 ($P4_2mc$). The A-atom displacements predicted by Agyei and Birman are in complete agreement with the displacements found by Shirane and Axe to occur in Nb_3Sn , and the question therefore is whether or not the tetragonal phase of these crystals contains a centre of inversion. It cannot be claimed that the experimental study has provided a definitive answer to the question because, according to Friedel's law, a neutron diffraction analysis cannot distinguish between a centrosymmetric and a non-centrosymmetric crystal.

The question could easily have been resolved by finding out whether or not the tetragonal phase is piezoelectric. But, perhaps, it has hitherto appeared not to be of such interest as to warrant such an investigation. Below we demonstrate that it is of considerable theoretical and, perhaps, practical interest. We shall show that, if the tetragonal phase has the space group C_{4v}^7 , then it may not only be piezoelectric, but may also exhibit spontaneous ferroelectricity and ferropiezoelectricity, as well as the semi-spontaneous ME effect.

As shown by Agyei and Birman (1977), the cubic-to-tetragonal DSPT of the A-15 crystals, A_3B , results in the break-up of the A-atom sublattice (the t-sublattice) into two daughter t-sublattices (DS). One of them, referred to below as DS I, has four atoms in the unit cell and site point group (SPG) $C_s (m)$, while the other, designated below as DS II, has two atoms per unit cell and SPG $C_{2v} (mm2)$. The DS I reference site (point group $C_s^y = 1, \sigma_y$) admits of the existence there of an electric-dipole moment and a magnetic moment

$$\begin{aligned} p'_0 &= (p_x, 0, p_z) \\ m'_0 &= (0, m_y, 0) \end{aligned} \quad (10)$$

with $H_I = m$ as its magnetic point group; while the DS II (reference site point group $C_{2v}^z = 1, C_{2z}, \sigma_x, \sigma_y$) can undergo an electric and a magnetic transition giving rise to the moments

$$\begin{aligned} p''_0 &= (p_x, 0, p_z) \\ m''_0 &= (0, 0, m_z) \end{aligned} \quad (11)$$

at the reference site and a sublattice site point group $H_{II} = m'm'2$ without any change in the sublattice's crystallographic symmetry group, i.e. the symmetry group with the time-reversal operator θ replaced by the identity operator 1.

Now, according to Agyei and Birman's (1977) theory, the order parameter of the DSPT is the irreducible component $\eta_1 = \epsilon_{xx} - \epsilon_{yy}$ of the strain tensor $\epsilon = (\epsilon_1, \epsilon_2, 0, 0, 0, 0)$. For the $H_I = m$ and $H_{II} = m'm'2$ groups, this tensor corresponds to the stress tensors $\sigma_I = (\sigma_1, \sigma_2, \sigma_3, 0, \sigma_5, 0)$ and $\sigma_{II} = (\sigma_1, \sigma_2, \sigma_3, 0, 0, 0)$, respectively. Further, the groups H_I and H_{II} admit of piezoelectric, γ_I , and γ_{II} , and piezomagnetic, λ_I and λ_{II} , tensors such that we have from equations (8) and (9) and the foregoing

$$\begin{aligned} p_I &= \gamma_I \cdot \sigma_I = (p_x, p_y, p_z) \\ m_I &= \lambda_I \cdot \sigma_I = (m_x, m_y, m_z) \end{aligned} \quad (12)$$

and

$$\begin{aligned} p_{II} &= \gamma_{II} \cdot \sigma_{II} = (0, 0, p_z) \\ m_{II} &= \lambda_{II} \cdot \sigma_{II} = (0, 0, m_z). \end{aligned} \quad (13)$$

Thus it follows from (10) and (12) that generally p_I and m_I will not be aligned along the directions p'_0 and m'_0 , respectively. Hence piezoelectric and piezomagnetic moments generally cannot arise at the DS I sites.

On the other hand, as can be seen from (11) and (13), p_{II} and m_{II} coincide in direction with p'_0 and m'_0 , all being aligned along the z direction. Such moments can therefore arise at the reference DS II site at the DSPT point. Further, from the transformation group of this sublattice it follows that the moments at the second site in the unit cell will also be aligned along the z direction. Hence the DS II may exhibit spontaneous ferropiezomagnetism and ferropiezoelectricity in the z direction. It will then have site point group (SPG) $m'm'2$, global point group (GPG) $4m'm'$ and space group (SG) $P4_2m'c'$, while the DS I will have SPG m , GPG $4mm$ and SG $P4_2mc$. The daughter B sublattice will have SPG $mm2$, GPG $4mm$ and SG $P4_2mc$ and the actual space group of the daughter crystal should then be $P4_2m'c'$.

The possibility of DS II exhibiting spontaneous ferropiezomagnetism and ferropiezoelectricity arouses interest in connection with the superconducting transition in these crystals.

The point is that the magnetic, H_p , and electric, E_p , fields that will be produced at the DS II sites by the spontaneous piezomagnetic and piezoelectric effects will be aligned along the z direction, and therefore will be parallel to each other. Further, the point groups $m'm'2$ and $4m'm'$ admit of non-null magnetoelectric susceptibility tensors, α_s and α_g , with only the diagonal elements different from zero (Birss 1964). Consequently, if indeed the DS II is ferropiezomagnetically and ferropiezoelectrically ordered, then it may also exhibit the linear ME effect (as indeed may the DS I and the B-atom sublattice). If it does, then the following interesting phenomenon should occur. The electric field E_{ME} due to the spontaneous magnetoelectric dipole moment $p_{ME} = \alpha_s \cdot H_p$ will be parallel to, and therefore will enhance, the field E_p . Similarly, the magnetic field H_{ME} due to the moment $m_{ME} = \alpha_g \cdot E_p$ will be parallel to, and therefore will enhance, the field H_p . This mutual enhancement of the piezomagnetic and piezoelectric fields H_p and E_p may intensify as the temperature is lowered below the DSPT point and may ultimately lead to the spontaneous ordering of the motion of the weakly bound electrons along the DS II chains and, thus, to the onset of superconductivity. The coexistence and parallel alignment of the H_p and E_p fields may also explain the high critical fields H_c of these superconductors.

But all this may hold only if the Fedorov space group of the crystals is $P4_2mc$ and not $P4_2/mmc$. The resolution of the question whether or not the crystals are centrosymmetric is therefore of considerable interest. The experimental observation of the ME effect in them will not only resolve this question, but will also confirm the prediction that their Shubnikov space group is $P4_2m'c'$ and, perhaps, open up a new avenue for research into the mechanism underlying the transition into the superconducting state.

5. Similarity of MEDS transitions

Underlying the foregoing treatment of the MEDS transition-related property tensors of crystals is the conclusion that MEDS transitions are, from the group-theoretical standpoint, entirely similar in the following sense. They all involve the ordering of localized moments in a manner entirely governed by the t-sublattice transformation group, so that the moment structure of a t-sublattice is determined solely by this group and is independent of the nature of the t-sublattice atom and of the type of transition if the difference between axial and polar vectors is taken into account. This is exemplified by the cubic-to-trigonal DSPT and magnetic transition observed

respectively in the isomorphous perovskites LaAlO_3 and Mn_3GaN , and it seems to us to be appropriate to conclude this paper with a brief discussion of them.

The t-sublattices in these crystals are respectively the O and Mn sublattices, which therefore have the same structure in the cubic phase. In the trigonal phase they have the point group D_{3d} and the displacements in LaAlO_3 and the magnetic moments in Mn_3GaN are disposed along the sides of equilateral triangles in the (111) planes. There is only one difference, viz. the transition in LaAlO_3 leads to a doubling of the crystal unit cell in the [111] direction, with the triangular dispositions of the displacement vectors in any two adjacent (111) planes having opposite senses. But this stems from the difference in behaviour of axial and polar vectors: while a magnetic moment can exist at a centre of inversion, a displacement vector cannot. As a result, the cubic-to-trigonal DSPT in a perovskite will be possible only if the inversion operator $\bar{1}$, which is a symmorphic symmetry operator for the parent crystal, becomes the point-group operator part of a non-symmorphic daughter crystal symmetry operator, which is possible only if the transition leads to a doubling of the crystal unit cell. In fact, to describe this transition, we only need to modify the coset decomposition that describes the magnetic transition in Mn_3GaN (Agyei 1981) to take account of this.

The modified coset decomposition can be reduced to the equivalent form

$$\begin{aligned}
 & \{1|0, 0, 0\}D_4 \\
 & \{C_{31}|\frac{1}{2}, 0, \frac{1}{2}\}D_4 \\
 & \{C_{31}^2|0, -\frac{1}{2}, \frac{1}{2}\}D_4 \\
 & \{\bar{1}|0, 0, 1\}D_4 \\
 & \{\bar{1}C_{31}|\frac{1}{2}, 0, \frac{1}{2}\}D_4 \\
 & \{\bar{1}C_{31}^2|0, \frac{1}{2}, \frac{1}{2}\}D_4
 \end{aligned} \tag{14}$$

where the coordinate origin has been shifted to the $(\frac{1}{2}, \frac{1}{2}, 0)$ site.

For this RPCC transformation group, the only site transition that takes the crystal into the trigonal phase with point group D_{3d} ($\bar{3}m$) is the transition $D_4 \rightarrow C_2^b = 1$, C_{2b} (where C_{2b} is rotation through 180° about the $[\bar{1}10]$ axis), induced by the Γ_4 (B_2) representation of D_4 . The displacement that occurs at the t-sublattice reference site (the $(\frac{1}{2}, \frac{1}{2}, 0)$ site in the original coordinate system) must therefore be in the $[\bar{1}10]$ direction, and can be denoted by the vector $u_0^{(0)} = (-\Delta, \Delta, 0)$. The displacements at the other sites can be obtained as the results of the action of the coset operators $\{R_k|V_k\}$ in (14) on $u_0^{(0)}$: $u_k^{(0)} = \{R_k|V_k\}u_0^{(0)}$, with $k = 1, \dots, 5$ in the order starting from $\{C_{31}|\frac{1}{2}, 0, \frac{1}{2}\}$. With the superscripts on the symbols $u_k^{(0)}$ dropped, these displacements are $u_1 = (0, -\Delta, \Delta)$, $u_2 = (\Delta, 0, -\Delta)$, $u_3 = (\Delta, -\Delta, 0)$, $u_4 = (0, \Delta, -\Delta)$, $u_5 = (-\Delta, 0, \Delta)$, in complete agreement with the experimentally observed O-atom displacement pattern (Cochran and Zia 1968).

The disposition of the magnetic moments in the Mn_3GaN unit cell is identical with that of the vectors u_0 , u_1 and u_2 , or, for that matter, with that of u_3 , u_4 and u_5 (Bertaut *et al* 1968, Agyei 1981).

Thus the magnetic moment structure in Mn_3GaN is the same as the displacement vector structure in LaAlO_3 , except for the change in sense of the triangular dispositions of the displacement vectors as we move from one (111) plane to the next.

Let us further note that, while the cubic-to-trigonal DSPT in the perovskites must necessarily be cell-doubling transitions for the reasons given above, the corresponding magnetic transitions need not always be cell-preserving. In other words, from the group-theoretical standpoint, a cubic perovskite can undergo a magnetic transition that gives rise to a magnetic structure identical with the displacement vector structure exhibited by LaAlO_3 . The point group of the daughter crystal will then be $\bar{3}'m'$.

6. Conclusions

In the present paper we have defined and carried out a microscopic group-theoretical analysis of the primary crystal properties associated with MEDS transitions. We have shown that:

(i) DSPT involve the ordering of atomic displacement vectors of microscopic strains, and are therefore similar to magnetic and electric transitions;

(ii) the macroscopic tensors characterizing MEDS-related bulk properties of crystals are sums of atomic property tensors; and

(iii) these atomic property tensors allow the appearance in a crystal of spontaneous piezomagnetism and/or piezoelectricity at its DSPT point T_D and/or spontaneous magnetoelectricity at its ferroelectric transition point T_E , so that the crystal can be in a weak (or secondary) magnetic state in the temperature region $T_M < T \leq T_D$ or T_E and/or weak (or secondary) electric state in the temperature region $T_E < T \leq T_D$.

As examples of crystals that may exhibit secondary magnetic and/or electric ordering, we cite, among others, the crystal Ti_2O_3 and the transforming A-15 crystals. The case of the transforming A-15 crystals is discussed in some detail; it is shown that these crystals may exhibit not only the semi-spontaneous ME effect, but also spontaneous piezomagnetism and piezoelectricity, and that their transition into the superconducting state and their high critical fields H_c may be connected with these effects.

Finally, the similarity of MEDS transitions is illustrated with the DSPT and magnetic transition observed respectively in the isomorphous perovskites LaAlO_3 and Mn_3GaN .

To the extent that the results obtained in the present paper encompass the results obtained by Agyei and Birman (1990), we can say that they have some experimental support. (Note also the illustration of the similarity of MEDS transitions.) However, they require more experimental corroboration. Of greatest interest is the verification of the predictions concerning the transforming A-15 crystals. Their experimental confirmation will undoubtedly lead to a better understanding of the mechanism underlying the transition into the superconducting state of these crystals.

In conclusion, let us note that these results could not have been obtained on the basis of the Neumann principle alone. Indeed, the analysis brings to the fore the limited scope of the principle.

References

- Agyei A K 1981 *J. Phys. C: Solid State Phys.* **14** 3433
Agyei A K and Birman J L 1977 *Phys. Status Solidi* **b** **82** 565
— 1990 *J. Phys.: Condens. Matter* **2** 3007
Bertaut E F, Fruchart D, Bouchand J P and Fruchart R 1968 *Solid State Commun.* **6** 25

- Birss R R 1964 *Symmetry and Magnetism* (Amsterdam: North-Holland)
- Born M and Huang K 1968 *Dynamical Theory of Crystal Lattices* (Oxford: Oxford University Press)
- Cochran W and Zia A 1968 *Phys. Status Solidi* **25** 273
- Goldrich F E and Birman J L 1968 *Phys. Rev.* **167** 528
- Landau L D 1937 *Phys. Z. Sowjetunion* **11** 26
- Opechowski W and Guccione R 1965 *Magnetism* ed G T Rado and H Suhl (New York: Academic) vol IIA
- Schmid H 1975 *Magnetoelectric Interaction Phenomena in Crystals* ed A J Freeman and H Schmid (London: Gordon and Breach) p 122
- Scott J F 1974 *Rev. Mod. Phys.* **46** 83-128
- Shirane G and Axe J D 1971 *Phys. Rev. B* **4** 2957