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On the linear magnetoelectric effect

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Abstract. A complete analysis of the linear magnetoelectric (ME) effect is carried out which exploits the PT symmetry of the ME susceptibility tensor α . The existing (or 'old') theory in effect considers only the time-reversal antisymmetry of α , with the result that it restricts the effect to magnetic crystals. It is shown that this presents only half the 'picture', and that consideration of the space-inversion antisymmetry of the tensor reveals, in accord with relativistic considerations, that the effect should also occur in certain paramagnetic electric (ferroelectric and antiferroelectric) crystals, which constitute the other half of the picture. A new classification of the eligible ME crystals is proposed. Among these crystals are BaCoF_4 and Ti_2O_3 , which, although prohibited by the old theory, have nonetheless been found to exhibit the effect. Other predicted candidates for the effect are presented.

1. Introduction

The linear magnetoelectric (ME) effect occurs in a crystal the expansion of whose Gibbs free energy $G(\mathbf{E}, \mathbf{H}, T)$ contains terms of the type $-\alpha_{ij}E_iH_j$, where \mathbf{E} and \mathbf{H} are an electric and a magnetic field, respectively, and α_{ij} is a second-rank tensor, called the ME susceptibility tensor. Because the product $\mathbf{E}\mathbf{H}$ is not invariant under time reversal, the effect was thought to be forbidden until Landau and Lifshitz (1960) pointed out that time reversal is not a symmetry operation for some magnetic crystals and, therefore, the effect could occur in such crystals. On the basis of this argument, Dzyaloshinskii (1959) predicted the effect should occur in the antiferromagnetic crystal Cr_2O_3 , and shortly afterwards the effect was indeed observed in this material (Astrov 1960, 1961).

Subsequently, 'from the example of Cr_2O_3 ', as Rado and Folen (1962) put it, the following condition for the occurrence of the effect in an arbitrary material was deduced. *For a crystal to exhibit the linear ME effect, it must be magnetic and must have a magnetic point group that allows the occurrence of E_iH_j -type terms in the Gibbs free-energy expansion.*

This is the condition (referred to below as the 'old condition') that has hitherto been used to identify crystals that should exhibit the effect (see, e.g., Cox 1975). It restricts the effect to the case in which the \mathbf{E} and \mathbf{H} fields can be treated on equal footing, and the symmetry of the ME susceptibility tensor α (which, being an axial c -tensor (Birss 1966), possesses PT symmetry) can be ignored. This is clearly admissible only when both fields are either internal or external fields. When one field is an internal, and the other an external, field, we should distinguish between them, since the former must conform

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strictly to the crystal symmetry, while the latter need not. On the basis of this assertion, the ME energy term $G_{\text{ME}} = -\alpha_{ij}E_iH_j$ (here and below summation over repeated letter indices is always implied) must admit of three different cases, namely, the cases when

- (i) one field (\mathbf{E} or \mathbf{H}) is an internal field and the other is an external field.
- (ii) both \mathbf{E} and \mathbf{H} are internal fields and
- (iii) both \mathbf{E} and \mathbf{H} are external fields.

Below we shall call the linear ME effects that occur under these conditions the semi-spontaneous, spontaneous and latent effects, respectively. Let us explain these terms further.

We use the term 'semi-spontaneous' to describe the case in which there exists in the crystal a spontaneous $\mathbf{E}(\mathbf{H})$ field (i.e. an internal $\mathbf{E}(\mathbf{H})$ field in the absence of external fields) to which an external \mathbf{H} (or \mathbf{E}) field can couple to produce a ME energy term in the Gibbs free-energy expansion.

In the 'spontaneous' case the crystal is both magnetic ((anti)ferromagnetic) and electric ((anti)ferroelectric), and the crystal symmetry allows the coupling of the internal \mathbf{E} and \mathbf{H} fields, so that the zero-field Gibbs free-energy expansion contains a ME energy term. As a result, in the case of a ferroelectromagnet with this property a single-domain sample will be 'magnetoelectrically' magnetised and polarised, although the corresponding second-order magnetisation and polarisation will be masked by the first-order spontaneous magnetisation and polarisation and cannot therefore be detected in zero fields.

Finally, the term 'latent' is used to describe the case in which the ME energy term occurs in the Gibbs free-energy expansion for the crystal in question only in the presence of external electric and magnetic fields oriented along the appropriate directions in the crystal. This case differs from the induced case first considered by O'Dell (1970) in that it is not necessary for the external fields to distort the crystal before the ME energy term appears. In fact, in all the cases considered below, the external fields are assumed to be so weak that their effect on the crystal symmetry can be ignored.

Thus, our classification of the linear ME effects is based on the nature of the fields entering into the expression for the ME energy term in the Gibbs free energy expansion. The effects have also been classified according to the modes of their detection. As can be discerned from the foregoing, an external field is always necessary for the detection of the ME effect and, for reasons that will become apparent below, the effect detected in an external electric (magnetic) field is called the electrically (magnetically) induced effect. Below we shall use these designations in conjunction with ours.

Thus, below we shall consider the electrically and magnetically induced semi-spontaneous (section 2), spontaneous (section 3) and latent (section 4) linear ME effects. We shall find the necessary and sufficient conditions for their occurrence under the assumption that the external fields are sufficiently weak, so that their effect on the crystal structure is negligible.

The internal $\mathbf{H}(\mathbf{E})$ field that enters into the ME energy term may be a first-order field, the result of the magnetic (electric) ordering of the crystal, or a second-order field, induced by the spontaneous electric (magnetic) field arising as a result of the electric (magnetic) ordering of the crystal. The primary difference between the present paper and all the others that have been published before on the linear ME effect lies in our discovery of the importance of these second-order (or secondary) fields for the effect. We shall show that the presence of these fields is a necessary condition for the occurrence of the semi-spontaneous effect in paraelectric magnetic crystals, and that it allows this

effect to occur in some paramagnetic electric crystals as well. Thus, the analysis will lead to the prediction of the existence of a new class of ME materials.

We shall examine and classify the majority of the crystals that have been found to exhibit the linear effect. We shall find that the overwhelming majority of these crystals exhibit the semi-spontaneous effect, thus indicating that this effect is natural (we shall therefore call the crystals that exhibit this effect the ‘natural magnetoelectric (NME)’ crystals). A few of them (all belonging to a family of isomorphous crystals) exhibit the latent effect. Two, BaCoF₄ and Ti₂O₃, which do not satisfy the old condition for the occurrence of the effect, and whose exhibition of the effect has hitherto not been explained, should, on the basis of our analysis, belong to the new class of ME materials. Other candidates for the effect are predicted.

We summarise the results of our investigation in section 5.

2. The semi-spontaneous linear ME effect

2.1. The electrically induced semi-spontaneous ME effect in magnetic crystals

Let a perfect single-domain paraelectric magnetic crystal with spontaneous sublattice magnetisation $\mathbf{M}_0^{(s)}$ magnetic and electric susceptibility tensors $\chi^{(m)}$ and $\chi^{(e)}$, and ME susceptibility tensor α be located in an external electric field \mathbf{E} . The expansion of the Gibbs free energy $G(\mathbf{E}, \mathbf{H}, T)$ for the sample in zero \mathbf{H} field has, up to second order in the fields, the form

$$G(\mathbf{E}, \mathbf{H}^{(s)}, T) = G_0 - \frac{1}{2}\chi_{ij}^{(e)} E_i E_j - \alpha_{ij} E_i H_j^{(s)}. \quad (1)$$

Here G_0 is the Gibbs free energy of the sample in zero electric field and $\mathbf{H}^{(s)}$ is the spontaneous internal magnetic field due to the magnetisation $\mathbf{M}_0^{(s)}$ ($\mathbf{H}^{(s)} = (\chi^{(m)})^{-1} \cdot \mathbf{M}_0^{(s)}$). (Here and below the superscript (s) denotes a spontaneous vector field, and the superscript (i) an induced field; an external field is designated by a letter with no superscript.)

It follows from (1) that there should, if the effect occurs in the crystal, exist in the sample a spontaneous polarisation field given in the same approximation by

$$\mathbf{P}^{(s)} = -(\partial G / \partial \mathbf{E})_{T|E=0} = \alpha \cdot \mathbf{H}^{(s)} \quad (2)$$

and that it is to this field that the external \mathbf{E} field couples to produce the ME energy term $G_{ME} = -\alpha_{ij} E_i H_j^{(s)}$ in the expansion (1).

Besides $\mathbf{P}^{(s)}$, there should also exist in the sample an induced magnetisation field

$$\mathbf{M}^{(i)} = -(\partial G / \partial \mathbf{H}^{(s)})_{T|H^{(s)}=0} = \alpha \cdot \mathbf{E} \quad (3)$$

which, being always (unlike $\mathbf{H}^{(s)}$, which may or may not be) unidirectional, can lead to the magnetisation of the sample (see section 2.3 below). It is this sample magnetisation that is observed in experiment, and it is from its origin (i.e. the fact that the $\mathbf{M}^{(i)}$ field can be said to be induced by the \mathbf{E} field) that this variant of the ME effect derives its designation as an ‘electrically induced’ effect.

2.2. The magnetically induced semi-spontaneous effect in magnetic crystals

Let the sample considered in section 2.1 now be located in an external magnetic field \mathbf{H} , with $\mathbf{E} = 0$. Let us show that there exists an induced polarisation $\mathbf{P}^{(i)} = \alpha \cdot \mathbf{H}$ in the crystal. To do this, let us, for the moment, assume that the sample is located in an \mathbf{E} field

as well. Then, to second order in the \mathbf{E} and \mathbf{H} fields and first order in the $\mathbf{H}^{(s)}$ field, the Gibbs free energy

$$G(\mathbf{E}, \mathbf{H}, \mathbf{H}^{(s)}, T) = G_0 - \frac{1}{2} \chi_{ij}^{(e)} E_i E_j - \chi_{ij}^{(m)} (H_i + H_i^{(s)}) H_j - \alpha_{ij} E_i (H_j + H_j^{(s)}) \quad (4)$$

from which we find the polarisation

$$\mathbf{P}^{(i)} + \mathbf{P}^{(s)} = -(\partial G / \partial \mathbf{E})_{T|E=0} = \boldsymbol{\alpha} \cdot \mathbf{H} + \boldsymbol{\alpha} \cdot \mathbf{H}^{(s)} \quad (5)$$

where $\mathbf{P}^{(s)} = \boldsymbol{\alpha} \cdot \mathbf{H}^{(s)}$ is the spontaneous polarisation due to the magnetic ordering of the crystal. Clearly, the field $\mathbf{P}^{(i+s)} = \mathbf{P}^{(i)} + \mathbf{P}^{(s)}$ is always unidirectional in the crystal, for $\mathbf{P}^{(s)}$ cancels out over the magnetic unit cell if the crystal is antiferromagnetic and is unidirectional in the case of a ferromagnet. Consequently, this field can lead to the polarisation of the whole sample (see section 2.3) and, because $\mathbf{P}^{(i)}$ is induced by an external \mathbf{H} field (for the significance of $\mathbf{P}^{(s)}$, see below), the resulting ME effect is said to be magnetically induced.

2.3. Condition for the occurrence of the semi-spontaneous ME effect in magnetic crystals

It follows from sections 2.1 and 2.2 that the existence of the spontaneous electric polarisation $\mathbf{P}^{(s)} = \boldsymbol{\alpha} \cdot \mathbf{H}^{(s)}$ (see (2) and (5)) in a magnetic crystal is necessary for the occurrence of the semi-spontaneous ME effect in the crystal. It guarantees the existence in the crystal of a non-null $\boldsymbol{\alpha}$ -tensor field and, hence, a magnetisation field $\mathbf{M}^{(i)}$, (3), in an external \mathbf{E} field, or a polarisation field $\mathbf{P}^{(i)}$, (5), in an external \mathbf{H} field, i.e. the electric (or magnetic) polarisation of the magnetic sublattice by an external magnetic (or electric) field (see also section 2.4 below).

Thus, we find that, for the semi-spontaneous ME effect to occur in a magnetically ordered crystal, *the crystal symmetry must be such that the spontaneous magnetisation $\mathbf{M}_0^{(s)}$ can coexist with the spontaneous polarisation $\mathbf{P}^{(s)}$, (2), in zero \mathbf{E} and \mathbf{H} fields.*

This condition, which in fact encompasses the old condition, is both necessary and sufficient in the case when the magnetic ions in question occupy crystal lattice sites whose magnetic point group (MPG) \mathcal{M}_s coincides with the full MPG \mathcal{M}_t of the crystal. It is, however, not sufficient when the magnetic-ion site point group (SPG) $\mathcal{M}_s \subset \mathcal{M}_t$. This case therefore needs to be considered further. Here we shall do this only for the case of paraelectric localised-moment magnetic crystals, i.e. the case when $\mathbf{M}_0^{(s)}$ and, hence, $\mathbf{P}^{(s)}$ are localised at the magnetic-ion sites.

The localisation of $\mathbf{M}_0^{(s)}$ and $\mathbf{P}^{(s)}$ on the magnetic ions implies, on the basis of the relation (2), the localisation of the tensor $\boldsymbol{\alpha}$ at the magnetic-ion sites[†]. The magnetisation or polarisation induced in the sample by an external \mathbf{E} or \mathbf{H} field is then equal to the sum of the $\mathbf{M}^{(i)}$, (3), or $\mathbf{P}^{(i+s)}$, (5), induced in a unit volume of the sample. Let the index of \mathcal{M}_s in \mathcal{M}_t be n . The magnetic unit cell will then contain n (or a multiple of it) magnetic-ion sites connected by point group operators $\hat{R}_\nu \in \mathcal{M}_t - \mathcal{M}_s$. Let us denote the ME susceptibility tensors at the sites (below we shall call these tensors the local ME susceptibility tensors) by $\boldsymbol{\alpha}_\nu$, $\nu = 1, 2, \dots, n$. These tensors will also be related to one another by the point group operators \hat{R}_ν : $\boldsymbol{\alpha}_{\nu+1} = \mathbf{R}_\nu \boldsymbol{\alpha}_\nu \mathbf{R}_\nu^{-1}$ (where $\boldsymbol{\alpha}_{n+1} = \boldsymbol{\alpha}_1$, the \mathbf{R}_ν are the matrix representatives of the operators \hat{R}_ν , and allowance must be made in the transformation for the fact that the tensors are axial c -tensors). Consequently, summation of (3) and (5) over the n sites leads to the result that the linear ME effect will occur if, and only if, the 'global' tensor

[†] By 'localisation' of the ME susceptibility tensor we mean that it is the intrinsic property of the atom or ion and is invariant under the SPG only. This is not the first time that the concept of localised ME susceptibility tensors has been introduced. Hou and Bloembergen (1965) use it in their treatment of the paramagnetolectric effect. The general question of the localisation of the properties of crystals will be dealt with elsewhere in a 'visit to the Neumann principle'.

$$\alpha = \sum_{\nu=0}^{n-1} \alpha_{\nu+1} = \sum_{\nu=1}^n \mathbf{R}\alpha_{\nu}\mathbf{R}_{\nu}^{-1} \quad \alpha_{n+1} = \alpha_1 \quad (6)$$

which, as is easy to see, has as its symmetry group the full MPG \mathcal{M}_t of the crystal, is not a null tensor.

This condition and the magnetic moment–electric moment coexistence requirement stated above constitute a necessary and sufficient condition for the occurrence of the semi-spontaneous ME Effect in a magnetic crystal. It can be formulated as follows: for a paraelectric localised-moment magnetic crystal to exhibit the semi-spontaneous effect, *the magnetic-ion SPG must allow the existence of spontaneous electric moments at the magnetic-ion sites, and the full MPG of the crystal must be such that the global ME susceptibility tensor α is not a null tensor.*

Let us consider the non-nullity condition for α , which can be found from Birss’s book once the full MPG \mathcal{M}_t is known. The tensor will be a null tensor if, in particular, \mathcal{M}_t contains the time-reversal or space-inversion operator $\hat{\theta}$ or \hat{I} as an independent operator or, since the magnetic moment–electric moment coexistence condition already excludes $\hat{\theta}$ and \hat{I} from \mathcal{M}_s , if the set $\mathcal{M}_t - \mathcal{M}_s$ contains $\hat{\theta}$ or \hat{I} as a separate operator. In other words, α will be a null tensor, and the linear ME effect will not occur if the space group of the magnetic-ion sublattice in question contains primed or barred translations, i.e. translations followed by time reversal or space inversion†.

The exclusion of primed and barred translations means that the linear ME effect can occur only in non-centrosymmetric ferromagnets and antiferromagnets described by type-I and type-III Shubnikov space groups and in centrosymmetric antiferromagnets described by type-III Shubnikov space groups. Hence we can expect antiferromagnetic NME crystals to be more common than ferromagnetic ones. Further, since centrosymmetric crystals can only order antiferroelectrically, a centrosymmetric NME crystal must not only be antiferromagnetic, it must also be antiferroelectric in its secondary electric-moment structure (SES). (It must be noted that here we are talking about the magnetic and electric ordering of a single magnetic-ion sublattice. We do not include structurally complex crystals containing both ferromagnetically and antiferromagnetically ordered sublattices. In other words, here, as everywhere below, we are, in effect, dealing with one-magnetic-sublattice crystals, but the theory can easily be generalised to crystals containing several magnetic sublattices‡. As will be seen below, these conclusions are confirmed by the experimental data at present available.

2.4. The semi-spontaneous ME effect in electric crystals; the general condition for the occurrence of the semi-spontaneous ME effect

The above-obtained necessary and sufficient condition for the occurrence of the semi-spontaneous ME effect in magnetic crystals immediately raises the question of the possibility of the effect’s occurring in paramagnetic electric crystals. Let us, restricting ourselves from now on to the consideration of only localised-moment crystals, note that the effect of the existence of the spontaneous electric moment $\mathbf{P}^{(s)}$, (2), in a paraelectric localised-moment magnetic NME crystal is not to make the crystal electric in the normal

† This is the proof of the assertion, made at the 1972 conference on magnetoelectric phenomena in crystals by Cox (1975), and questioned by Opechowski, that a magnetic crystal cannot exhibit the linear ME effect if its Bravais lattice contains an antittranslation, i.e. a primed translation.

‡ Here, as everywhere below, by the term sublattice we mean a crystal substructure formed by the minimal set of crystallographically identical atoms or ions (i.e. identical atoms or ions occupying equivalent sites in the crystal) that possess the full crystal symmetry.

sense, since it is only a secondary effect (its contribution, approximately $EP^{(s)}$, to the free energy of the crystal in an external \mathbf{E} field being only a second-order correction), but to exclude, in particular, the space-inversion operator from the magnetic-ion SPG. Similarly, a paramagnetic localised-moment electric crystal with spontaneous electric moments $\mathbf{P}_0^{(s)}$ and spontaneous secondary magnetic moments

$$\mathbf{M}_\nu^{(s)} = \boldsymbol{\alpha}_\nu \cdot \mathbf{E}_\nu^{(s)} \quad (7)$$

(where $\boldsymbol{\alpha}_\nu$ is a non-null tensor and $\mathbf{P}_0^{(s)} = \boldsymbol{\chi}_\nu^{(e)} \cdot \mathbf{E}_\nu^{(s)}$) localised on the electric ions cannot have time reversal as an electric-ion SPG symmetry operation. Such a crystal can, as is easy to show, acquire in an external \mathbf{H} (on \mathbf{E}) field a polarisation $\mathbf{P}_\nu^{(i)} = \boldsymbol{\alpha}_\nu \cdot \mathbf{H}$ (or magnetisation $\mathbf{M}_\nu^{(i)} = \boldsymbol{\alpha}_\nu \cdot \mathbf{E}$) at the electric-ion sites. As a result, if the global ME susceptibility tensor $\boldsymbol{\alpha} = \sum_{\nu=1}^n \boldsymbol{\alpha}_\nu$ (where n is the index of the electric-ion SPG in the full crystal point group) is not a null tensor then the electric crystal can exhibit the linear ME effect. Further, as found above, $\boldsymbol{\alpha}$ will not be a null tensor if the magnetic space group of the crystal does not, in particular, contain primed or barred translations. Hence we find that the linear ME effect should occur in those non-centrosymmetric ferroelectrics and antiferroelectrics described by type-I and type-III Shubnikov space groups and centrosymmetric antiferroelectrics described by type-III Shubnikov space groups for which the global ME susceptibility tensor $\boldsymbol{\alpha}$ is not a null tensor.

That the linear ME effect should indeed occur in some paramagnetic electric crystals is also apparent on the basis of relativistic considerations. To see this, consider a crystal that is paramagnetic and electric in its rest frame S . Let it have in this frame localised electric moments $\mathbf{P}^{(s)}$ aligned parallel or antiparallel to the x axis. Now consider the crystal in a reference frame S' moving in the direction parallel to the y axis of the S frame with velocity V relative to this frame. Then, as can easily be shown (Batygin and Toptygin 1978), to an observer in the S' frame the crystal will also be magnetic, with magnetic moments $\mathbf{M}^{(s)} = \pm(V/c) |\mathbf{P}^{(s)}| \mathbf{k}$, where \mathbf{k} is the unit vector along the z axis of the S frame. Thus, according to the old condition, the effect can occur in the S' frame, but not in the S frame, which contradicts the postulate that there are no preferred reference systems.

Hence, if indeed there are no preferred reference frames, then the semi-spontaneous ME effect should also occur in *any paramagnetic crystal with electric ions occupying sites where magnetic and electric moments can coexist, and the full MPG of the crystal is such that the global ME susceptibility tensor is not a null tensor.*

Combining this condition with the corresponding condition for magnetic crystals (see section 2.3), we obtain the following necessary and sufficient condition for the occurrence of the semi-spontaneous ME effect. For a crystal to exhibit the semi-spontaneous ME effect *it must be a paraelectric magnetic or a paramagnetic electric crystal with the magnetic or electric atoms or ions located at sites where magnetic and electric moments can coexist and a full MPG for which the global ME susceptibility tensor is not a null tensor.* We call such magnetic or electric atoms or ions ME atoms or ions and, as noted in section 1, a crystal that satisfies these conditions is a NME crystal. Let us further consider such crystals.

2.5. Twinning of NME crystals

Of particular interest are NME crystals with geometrically identical primary- and secondary-moment structures. Since the primary- and secondary-moment structures should not be transformable into each other by pure, primed and barred rotations, in perfect crystals these structures will be geometrically identical if, and only if, the primary

(secondary) magnetic and secondary (primary) electric moments are parallel to each other. It is easy to see that such structures can occur only in non-centrosymmetric NME crystals described by type-I Shubnikov space groups and in centrosymmetric NME crystals described by type-III Shubnikov space groups. Therefore, the analysis carried out below pertains to such crystals only.

If the magnetic and electric moments at the sites are parallel to each other, then the interchange $P \leftrightarrow M$ of the electric and magnetic moments leaves the crystal structure geometrically unchanged. This will clearly be the case if the interchange $\hat{\theta} \leftrightarrow \hat{I}$ leaves the magnetic space group of the structure unchanged. For NME crystals described by type-I Shubnikov space groups this condition is always satisfied. For those described by type-III Shubnikov space groups the condition will be satisfied if the space group can be written in the form $G = H + \hat{\theta}\hat{I}H$, where H is a type-I Shubnikov space group. This is clearly the case, since the operators $\hat{\theta}$ and \hat{I} commute with each other. We shall call the invariance under the interchange $\hat{\theta} \leftrightarrow \hat{I}$ 'twinning symmetry', and a NME crystal that possesses this symmetry a 'twin-symmetric' NME crystal.

The following conclusion follows immediately from the twinning symmetry. *If a given paraelectric magnetic NME crystal is twin symmetric, then there must exist, or can be synthesised, an isomorphous paramagnetic electric NME crystal that is also twin symmetric, with its magnetic and electric moments aligned along the same direction as the moments in the first crystal, and vice versa.* Evidently, any such pair of NME crystals are mirror images of each other in a plane perpendicular to the P - T plane of the space-time continuum. We call any such pair 'NME twins'. Below we show that the crystals Cr_2O_3 and Ti_2O_3 may be NME twins.

Naturally, there can be cases in which m isomorphous paraelectric magnetic NME crystals are twin symmetric. Then, as follows from the above-obtained result, there must exist m twin-symmetric paramagnetic electric NME crystals isomorphic to the first group, and having their magnetic and electric moments aligned along the same direction as those of the crystals of the first group, and vice versa. We call any such pair of groups of NME crystals 'twin groups'.

We find then that the occurrence of the semi-spontaneous ME effect in paramagnetic electric crystals and the existence of NME twins or twin groups are consequences of the PT symmetry of the ME susceptibility tensor and the non-existence of preferred reference frames. We shall give examples of paramagnetic electric crystals that we expect should exhibit the effect and, as noted above, a probable example of NME twins in section 2.7 below. But now let us, proceeding with the general analysis of the effect, address the question which magnetic- and electric-ion SPGs \mathcal{M}_s admit of the coexistence of magnetic and electric moments at the magnetic- and electric-ion lattice sites.

2.6. Magnetic point groups allowing the coexistence of magnetic and electric moments at lattice sites

Noting that the groups must be either type-I or type-III Shubnikov point groups, and using the ferroelectric and ferromagnetic transition schemes constructed by Agyei (1976), we find the required groups to be the following:

$$1, m, m', 2, 2', 3, m'm'2, m'm'2', 4, 6, 3m', 4m'm', 6m'm'. \quad (8)$$

That this list exhausts all the possibilities can be seen from the fact that they have, including themselves, precisely 58 magnetic point supergroups that admit of non-null global ME susceptibility tensors and thus admit of the linear ME effect. (Naturally, these

supergroups include the groups that admit of the spontaneous and latent effects.) Thus, as is well known, there are 58 ME point groups.

2.7. Examples of NME crystals

Except for the crystals DyPO_4 , GdVO_4 and HoPO_4 of the isomorphous family of compounds with the general formula RXO_4 , where R is a trivalent rare-earth ion and X is vanadium, arsenic or phosphorus, all the magnetic crystals that have been found to exhibit the linear ME effect, and whose magnetic-ion SPGs are known each has one of the groups in (8) as its magnetic-ion SPG and is generally a low-symmetry crystal, as is to be expected from the generally low orders of the groups in (8). These patently NME crystals are given in table 1. There is no ferromagnetic NME crystal among them. As far as we know (Cox 1975), only the ferromagnetic boracites $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$, $\text{Co}_3\text{B}_7\text{O}_{13}\text{Cl}$ and $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}$ and the ferromagnet FeGaO_3 have been found to exhibit the linear ME effect. However, these boracites are also ferroelectric, with ferroelectric transition temperatures T_E equal to (in the case of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}$) or higher than (in the case of the other two) the ferromagnetic transition temperatures T_C . Consequently, in the paramagnetic ferroelectric phase these crystals should be ferroelectric NME crystals, while in the ferromagnetic phase they properly belong to the spontaneous case (see section 3 below). As for FeGaO_3 , a non-centrosymmetric low-symmetry crystal, we do not know the Fe-ion SPG and so cannot work out its magnetic structure.

Finally, let us note that the magnetic sublattices of the centrosymmetric Cr_2O_3 , Fe_2TeO_6 and $\text{Nb}_2\text{Co}_4\text{O}_9$ -type and DyAlO_3 -type crystals listed in table 1 have four metal ions per unit cell, and, according to the results of our subgroup analysis (Agyei and Birman 1977), geometrically identical primary magnetic and secondary electric structures of the $\uparrow\downarrow\uparrow\downarrow$ or $\uparrow\downarrow\downarrow\uparrow$ type. Consequently, on the basis of the result obtained above, these NME crystals must have twins. Below we show that the compound Ti_2O_3 can be the twin of Cr_2O_3 . We do not at present know any compounds that could be the twins of the others. It is, of course, possible that some members of the various families of isomorphous compounds listed in the table are paramagnetic antiferroelectrics in temperature regions above their Néel points T_N . Such members of a family may be the twins of the remaining ones.

2.8. Probable paramagnetic electric NME crystals

As indicated above, the crystals listed in table 1 almost exhaust the list of crystals that have thus far been found to exhibit the linear ME effect. Since the old condition allows the effect to occur only in magnetic crystals, the experimental effort has naturally been directed at finding magnetic ME materials. There are, however, two crystals, BaCoF_4 and Ti_2O_3 , with experimentally observed ME behaviour that is at variance with the old condition, in the sense that they exhibit the effect in the paramagnetic state. In the present section we demonstrate that they could be electric NME crystals. We also give in table 2 other possible paramagnetic electric NME crystals.

2.8.1. The crystal BaCoF_4 . The orthorhombic crystal BaCoF_4 , which is ferroelectric and paramagnetic at room temperature (Keve *et al* 1970) and antiferromagnetic below $T_N = 69.6$ K (Eibschütz *et al* 1972), has been found (Al'shin *et al* 1970) to exhibit the linear ME effect in the temperature range $T \leq 200$ K. This behaviour contradicts the old condition, and Schmid (1975) explains it as being probably a second-order ME effect,

Table 1. Magnetic crystals that have been found to exhibit the linear ME effect and are, according to our classification, NME materials. They are all antiferromagnets. (The data were compiled from Freeman and Schmid (1975), where references to the original papers can be found.) Here, as in table 2, the spgs are Fedorov point groups.

Crystal	Crystal space group	T_N (K)	Assumed ME atom	ME-ion SPG	Spin ($M_0^{(s)}$) direction	Crystal MPG	Maximum $\alpha_{obs} \times 10^5$
Cr ₂ O ₃	R $\bar{3}c$	318	Cr	3	[111]	$\bar{3}'m'$	8
Fe ₂ TeO ₆	P4 ₂ /mnm	219	Fe	mm2	[001]	4/m'm'm'	3
Nb ₂ Co ₄ O ₉	P $\bar{3}c1$	27	Co	3	[001]	$\bar{3}'m'$	2
Nb ₂ Mn ₄ O ₉	P $\bar{3}c1$	110	Mn	3	[001]	$\bar{3}'m'$	0.2
Ta ₂ Co ₄ O ₉	P $\bar{3}c1$	21	Co	3	[001]	$\bar{3}'m'$	10
Ta ₂ Mn ₄ O ₉	P $\bar{3}c1$	104	Mn	3	[001]	$\bar{3}'m'$	1
LiCoPO ₄	Pnma	23	Co	m	[010]	mmm'	60
LiFePO ₄	Pnma	50	Fe	m	[010]	mmm'	10
LiNiPO ₄	Pnma	23	Ni	m	[010]	mmm'	4
LiMnPO ₄	Pnma	35	Mn	m	[001]	m'm'm'	2
DyAlO ₃	Pnma	3.5	Dy	m	[001]	m'm'm'	200
GdAlO ₃	Pnma	4.0	Gd	m	[001]	m'm'm'	10
TbAlO ₃	Pnma	4.0	Tb	m	[001]	m'm'm'	100
TbCoO ₃	Pnma	3.3	Co	m	[001]	m'm'm'	3
MnNb ₂ O ₆	Pbcn	4.4	Mn	2	[100]	m'mm	0.3
DyOOH	P2 ₁ /m	7.2	Dy	m	\perp [010]	2/m'	10
ErOOH	P2 ₁ /m	4.1	Er	m	[010]	2'/m	50
TbPO ₄	Imma	2.2	Tb	mm2	[110]	mmm'	1000

Table 2. Crystals expected to exhibit the semi-spontaneous ME effect in the paramagnetic electric phase: FE, ferroelectric; AFM, antiferromagnetic; AFE, antiferroelectric. The effect has already been observed in BaCoF₄ and Ti₂O₃. (Data were compiled from Freeman and Schmid (1975) and Smolenskii and Chupis (1982), where references to the original papers can be found.)

Crystal	Crystal space group	T_E (K)	T_C (K)	Assumed ME atom	ME-ion SPG	Electric order	Magnetic order	Direction of $P_0^{(s)}$	Crystal MFG
BaCoF ₄	Cmc2 ₁	1154	69.6	Co	m	FE	AFM	[001]	mm2
Ti ₂ O ₃	R3c	—	—	Ti	3	AFE	AFM	[111]	3'm'
							(conjectured)		
BaNiF ₄	Cmc2 ₁	1593	70	Ni	m	FE	AFM	[001]	mm2
YMnO ₃	P6 ₃ cm	913	80	Mn	m	FE	AFM	[001]	6mm or 6m'm'
HoMnO ₃	P6 ₃ cm	873	76	Mn	m	FE	AFM	[001]	6mm or 6m'm'
ErMnO ₃	P6 ₃ cm	833	79	Mn	m	FE	AFM	[001]	6mm or 6m'm'
YbMnO ₃	P6 ₃ cm	993	87.3	Mn	m	FE	AFM	[001]	6mm or 6m'm'
Cr ₃ B ₇ O ₁₃ Cl	Pca2 ₁	260	25	Cr	1	FE	AFM	[001]	mm2
Mn ₃ B ₇ O ₁₃ Cl	Pca2 ₁	680	6	Mn	1	FE	AFM	[001]	mm2
Mn ₃ B ₇ O ₁₃ Br	Pca2 ₁	566	6	Mn	1	FE	AFM	[001]	mm2

due to the *EHH* term in the Gibbs free-energy expansion. But this is doubtful, since the electrically induced effect was observed in zero-*H* field as well. Indeed, in the temperature range above 150 K the zero-*H* field effect has the same magnitude as the effect observed in fields with intensities of up to 500 Oe. Let us show that this crystal satisfies all the criteria for a NME material.

The space group of BaCoF₄ is Cmc2₁ (C_{2v}¹²), with all the ions, Ba²⁺, Co²⁺ and F⁻, occupying the 4(a) sites (Keve *et al* 1970), whose point group m (C_s) allows the coexistence of magnetic and electric moments (see (8)).

Now, according to Keve *et al* (1970), the crystal is essentially a localised-moment ferroelectric, with the Ba²⁺ ions as the electric ions and the dipole moments parallel to the [001] direction in the conventional unit-cell setting. Thus, the crystal meets all the criteria for a NME crystal and should, in accord with experiment, exhibit the linear ME effect. It is a ferroelectric NME crystal.

2.8.2. The crystals Cr₂O₃ and Ti₂O₃ as NME twins. The crystals Cr₂O₃ and Ti₂O₃ are crystallographically isomorphous crystals. Their space group is R $\bar{3}c$, with the metal ions (Cr³⁺ and Ti³⁺) located at the 4(c) sites, whose point group 3 (C₃) meets the magnetic moment–electric moment coexistence condition (see (8)).

Now, as noted in section 2.7, Cr₂O₃ is a localised-moment antiferromagnet, with the magnetic moments aligned along the [111] direction. The Cr³⁺-ion sublattice contains four ions per unit cell and has the $\uparrow \downarrow \uparrow \downarrow$ or $\uparrow \downarrow \downarrow \uparrow$ type of magnetic structure with MPG $\bar{3}'m'$. Now, from the subgroup analysis (Agyei and Birman 1977) we find that the (secondary) electric moments are parallel to the magnetic moments. The magnetic and electric structures are therefore geometrically identical, and the crystal should have a twin. We believe that the crystal Ti₂O₃ could be such a twin.

Al'shin and Astrov (1963) were led to investigate this crystal (Ti₂O₃) because of its isomorphism with Cr₂O₃ and the consequent expectation of a magnetic ordering in it. They found that the crystal exhibits the linear ME effect, but subsequent investigations (Moon *et al* 1969) revealed that it does not order magnetically. Consequently, the explanation for its observed ME behaviour must, as Cox (1975) puts it, be sought elsewhere.

Our theory provides the explanation under the assumption that the crystal is a localised-moment antiferroelectric. Indeed, assuming the Ti³⁺-ion sublattice is a localised-moment antiferroelectric, and carrying out a subgroup analysis (Agyei 1976), we find that the crystal possesses geometrically identical electric and magnetic structures of the types occurring in Cr₂O₃, the only difference being that now the electric structure is the primary, and the magnetic structure the secondary, structure. The crystal is then the NME twin of Cr₂O₃.

2.8.3. Other possible paramagnetic electric NME crystals. Evidently, a non-magnetic electric (non-electric magnetic) crystal that undergoes magnetic (electric) ordering without undergoing a structural change can be a NME material in the non-magnetic (non-electric) phase. This is because such an ordering indicates the presence in the non-magnetic (non-electric) phase of paramagnetic (paraelectric) atoms or ions located at sites whose MPG allows the coexistence of magnetic and electric moments at the sites. In table 2 we present (together with BaCoF₄ and Ti₂O₃) a list of electric crystals that pass this test, satisfy the criteria for NME crystals and go into magnetic phases (as experimentally observed) that are consistent with the results of our subgroup analysis. (We do not know of any magnetic crystals that go into the electric phase at a temperature lower than the magnetic transition temperature without a structural change.)

Notice that all the crystals in table 2 are ferroelectrics. This is probably because not many antiferroelectrics are known, there being at present no reliable and quick experimental method of identifying and determining the electric-moment structures of antiferroelectrics.

Finally, let us note that the non-zero components of the global ME susceptibility tensor can be found from table 9 in Birss's (1966) book once the crystal's full MPG is known. Consequently, in table 2 we give only the (predicted) MPGs of the crystals.

3. The spontaneous linear ME effect

The spontaneous ME effect occurs in a magnetically and electrically ordered crystal, i.e. in (anti)ferromagnetolectrics or (anti)ferroelectromagnets, whose symmetry allows the coupling of the internal magnetic ($\mathbf{H}^{(s)}$) and electric ($\mathbf{E}^{(s)}$) fields, so that its Gibbs free-energy expansion contains the ME energy term $G_{\text{ME}} = -\alpha_{ij} E_i^{(s)} H_j^{(s)}$ in zero external magnetic and electric fields. It is not difficult to see that, for this to be the case, and for the linear ME effect to occur, the point group symmetry of the magnetic- and electric- sites must allow the coexistence of magnetic and electric moments at the sites (this is clearly the case when the same sublattice is magnetic and electric), and the global ME susceptibility tensor must not be a null tensor.

Obvious examples of spontaneous ME materials are magnetic (electric) NME crystals that undergo electric (magnetic) transitions without changing their symmetry. The primary- and secondary-moment structures in the paraelectric magnetic (paramagnetic electric) phase will then be identical with the corresponding magnetic and electric structures in the magnetic–electric phase. Thus, all the crystals in table 1 that undergo electric (antiferroelectric, according to our analysis) transitions without changing their symmetry and all the crystals in table 2 will be spontaneous ME materials in their magnetic–electric phases.

Other examples of spontaneous ME materials can be found by examining the structures of other known magnetic–electric crystals. A list of such crystals has been compiled by Smolenskii and Chupis (1982). The difficulty in experimentally identifying antiferroelectric crystals is no doubt the reason why the list includes so few (two, in fact) positively identified antiferroelectromagnets and none of the crystals listed in table 1 in the present paper.

4. The latent linear ME effect

4.1. Necessary and sufficient condition for the occurrence of the latent linear ME effect

Let us consider a crystal in which none of the sublattices admits of the coexistence of magnetic and electric moments at its sites. In this case an external \mathbf{E} or \mathbf{H} field cannot couple to an internal field, and, therefore, for the ME energy term $G_{\text{ME}} = -\alpha_{ij} E_i H_j$ to occur in the Gibbs free-energy expansion, the sample must be located in external magnetic \mathbf{H} and electric \mathbf{E} fields. Here \mathbf{E} and \mathbf{H} are on equal footing, and so the old condition holds. In the language of our theory it can be formulated as follows. For the crystal to exhibit the linear ME effect, it must be magnetic and its MPG must be such that the global ME susceptibility tensor is not a null tensor.

If these conditions are fulfilled, then the local ME susceptibility tensors will not be null tensors and, by coupling to this tensor field, an external electric (magnetic) field

applied to the crystal can produce a measurable macroscopic magnetisation (polarisation) in the sample. Below we shall call such crystals latent ME (LME) crystals.

4.2. Examples of latent ME crystals

As noted in section 2.7, the isomorphous antiferromagnetic crystals DyPO_4 , GdVO_4 and HoPO_4 are not NME crystals. This is because the Dy, Ge and Ho ions occupy sites with magnetic SPG $\bar{4}2'm'$, which does not allow the coexistence of magnetic and electric moments at the sites. However, the group $\bar{4}2'm'$ admits of a non-null ME susceptibility tensor, as does the crystal's full MPG $4'/m'm'm$ (see table 9 in Birss's book). Hence these crystals are LME crystals. They are the only known LME crystals.

There is a simple explanation for the paucity of LME crystals.

Consider a magnetic sublattice in a crystal. According to the foregoing, such a sublattice will exhibit the latent effect if, and only if, the magnetic ions occupy sites where the magnetic moments cannot coexist with electric moments, but where the local ME susceptibility tensors are not null tensors. As can easily be verified, the only point groups that satisfy these conditions are $\bar{4}$ and $\bar{4}2'm'$. Hence, in terms of Fedorov (or ordinary) groups, only crystals with magnetic-ion SPGs $\bar{4}$ (S_4) and $\bar{4}2m$ (D_{2d}) and full MPGs $\bar{4}$ (S_4), $\bar{4}2m$ (D_{2d}), $4/m$ (C_{4h}) and $4/mmm$ (D_{4h}) can exhibit the latent ME effect. Furthermore, on the basis of the results obtained in section 2.3, ferromagnetic crystals with the last two groups, namely C_{4h} and D_{4h} , cannot exhibit the ME effect. Thus, only antiferromagnets with these site and full point groups and ferromagnets with magnetic-ion site and full point groups S_4 and D_{2d} can exhibit the latent ME effect. These are few indeed, compared with those that can exhibit the semi-spontaneous ME effect.

5. Conclusion

In the present paper we have carried out a detailed analysis of the linear ME effect. We have shown on the basis of symmetry and relativistic considerations that the effect should occur not only in some magnetic but also in some electric crystals. We have proposed a new classification of the eligible ME crystals, and have shown, in particular, that

- (i) the effect should occur predominantly in crystals in which magnetic and electric moments can coexist at the magnetic- or electric-ion sites,
- (ii) these NME crystals are predominantly antiferromagnetic in their primary or secondary magnetic structures and are mostly low-symmetry crystals,
- (iii) NME crystals with geometrically identical primary- and secondary-moment structures should occur in pairs (called 'twins' by us), one of them being primarily magnetic and the other electric, and their magnetoelectric structures being mirror images of each other in a plane perpendicular to the P-T plane in the space-time continuum and
- (iv) the crystals BaCoF_4 and Ti_2O_3 are respectively ferroelectric and antiferroelectric NME crystals, the latter being the twin of the prototypical ME crystal Cr_2O_3 .

The theory is in accord with the available experimental data, but more experiments need to be done, especially on electric crystals. The theory shows that a paramagnetic electric crystal with an electric-ion SPG and a full MPG that admit of non-null ME susceptibility tensors should be a NME crystal. Conversely, a paramagnetic crystal that exhibits the linear ME effect should be an electric crystal. Thus, the effect can be used to identify antiferroelectric paramagnetic crystals.

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