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Electric-field switchable magnetization via the Dzyaloshinskii–Moriya interaction: FeTiO_3 versus BiFeO_3

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Abstract

In this paper we review and discuss a mechanism for coupling between electric polarization and magnetization that can ultimately lead to electric-field switchable magnetization. The basic idea is that a ferroelectric distortion in an antiferromagnetic material can ‘switch on’ the Dzyaloshinskii–Moriya interaction which leads to a canting of the antiferromagnetic sublattice magnetizations, and thus to a net magnetization. This magnetization \vec{M} is coupled to the polarization \vec{P} via a trilinear free energy contribution of the form $\vec{P} \cdot (\vec{M} \times \vec{L})$, where \vec{L} is the antiferromagnetic order parameter. In particular, we discuss why such an invariant is present in $R3c$ FeTiO_3 but not in the isostructural multiferroic BiFeO_3 . Finally, we construct symmetry groups that in general allow for this kind of ferroelectrically-induced weak ferromagnetism.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the key challenges in the field of multiferroics is to design and/or discover materials that exhibit a strong coupling between magnetic and ferroelectric order parameters. Such materials are of fundamental interest as they provide a novel platform to study how microscopic degrees of freedom, such as spin and lattice, interact to produce macroscopic phenomena. These strongly coupled multiferroics are also anticipated to find application in future generations of novel devices in which magnetization can be controlled via an electric field and/or electric polarization can be controlled via a magnetic field.

Two different ways of controlling the state of a magneto-electric system are possible: *phase control* [1–3] or *domain control* [4, 5]. In the first case an external field is used to trigger a phase transition between two fundamentally different phases. By tuning to the vicinity of a phase transition where two such phases compete [6, 7], e.g., an antiferromagnetic–paraelectric phase and a ferromagnetic–ferroelectric phase, a large magneto-electric response can be produced [8] even in systems where the intrinsic coupling between magnetic and ferroelectric order parameters is not very strong [9]. In the case of domain control, the external field triggers a transition

between two equivalent, but macroscopically distinguishable domain states, i.e., different realizations of the same phase. Here, the magneto-electric coupling has to be large enough to overcome the energy barrier for domain switching, which in general depends on both the initial and the final domain. Once the field is removed, the system is stable in the new domain state.

Several materials have been identified that realize one of the two scenarios described above. In particular, much recent research has been focused on systems where magnetic order itself breaks spatial inversion symmetry and electric polarization therefore appears as a secondary order parameter [1, 2, 10]. Several different microscopic models have been proposed that lead to such ‘magnetically-induced ferroelectricity.’ In some cases this effect is caused by the presence of spin–orbit interaction [11, 12], whereas in other cases spin–orbit coupling is not required [13, 14]. See other contributions in this Focus Issue for a more detailed discussion of this interesting topic.

In the present paper we discuss a somewhat different, but in a certain sense complementary, possibility to realize coupling between magnetic and ferroelectric order parameters, which can then be used to achieve domain control of

the corresponding multiferroic system. The basic idea is that a ferroelectric distortion in an antiferromagnetically ordered material can cause a small magnetization due to the Dzyaloshinskii–Moriya interaction. In this case of ‘ferroelectrically-induced ferromagnetism’ [15] the polar distortion gives rise to both the electric polarization and the magnetization, hence the two quantities are inherently coupled. Here, in contrast to the case of magnetically-induced ferroelectricity mentioned above, the magnetization is the secondary order parameter that is coupled to the primary order parameter, the electric polarization.

The concepts and ideas reviewed and discussed in this paper are based mostly on a series of publications by the present authors, and recently have been used to identify a specific class of materials that are predicted to exhibit this effect [16–18]. The concept of ferroelectrically-induced ferromagnetism was first suggested by Fox and Scott [15] based on macroscopic symmetry properties for the magneto-electric fluoride BaMnF₄. Here we discuss a specific microscopic mechanism leading to such macroscopic behavior and analyze the corresponding symmetry requirements.

In the following we first review the basic idea behind the proposed mechanism, then summarize our previous work on this topic. We choose to illustrate the general concept by discussing one structure in detail, the ten-atom rhombohedrally distorted ABO₃ perovskite structure, paraelectric space group $R\bar{3}c$, and the corresponding ferroelectric subgroup $R3c$, although the established principles are easily generalizable. Specifically we show why the proposed effect is present in magnetic A-site $R3c$ perovskites such as FeTiO₃, but not in $R3c$ BiFeO₃, where the magnetic cations are situated on the perovskite B sites. Finally, we present a rather general discussion of the various symmetry aspects that have to be taken into account in order for a material to exhibit the desired behavior. Ultimately our goal is to highlight the unique and powerful approach of combining effective microscopic models with symmetry arguments to guide first principles calculations in the discovery of new phenomena and the design of their material realizations.

2. Weak ferromagnetism and electric polarization

It was realized by Dzyaloshinskii in 1957 that the appearance of ‘weak’ ferromagnetism in some antiferromagnetic materials such as e.g., Fe₂O₃, and its absence in the isostructural system Cr₂O₃ can be explained solely on grounds of symmetry [19]. The symmetry of a magnetically ordered material depends on the underlying crystallographic structure, the orientation of the magnetic moments relative to each other, and on the orientation of the individual magnetic moments with respect to the crystallographic axes [20, 21]. Dzyaloshinskii showed that an invariant in the free energy expansion of the form

$$E^{\text{DML}} = \vec{D} \cdot (\vec{M} \times \vec{L}), \quad (1)$$

where \vec{D} is a materials-specific vector coefficient, \vec{M} is the magnetization, and \vec{L} is an antiferromagnetic order parameter, results in the secondary order parameter \vec{M} appearing at the antiferromagnetic ordering temperature. In other words, if the

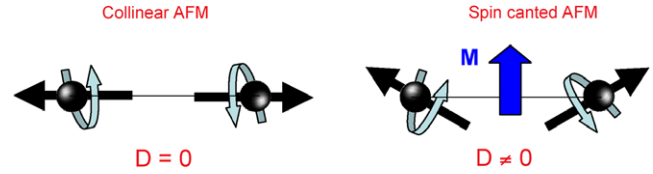


Figure 1. The presence of the Dzyaloshinskii–Moriya interaction ($\vec{D} \neq 0$) leads to a slight canting of the magnetic moments and a resulting net magnetization $\vec{M} \neq 0$ in an otherwise collinear antiferromagnet.

symmetry of the purely antiferromagnetic state is such that the appearance of a small magnetization does not lead to a further symmetry lowering, then any microscopic mechanism which favors a nonzero magnetization, even if it is rather weak, will lead to $\vec{M} \neq 0$.

It was later shown by Moriya that an invariant of the required form can result from an antisymmetric microscopic coupling between two localized magnetic moments \vec{S}_i and \vec{S}_j :

$$E_{ij}^{\text{DM}} = \vec{d}_{ij} \cdot (\vec{S}_i \times \vec{S}_j), \quad (2)$$

and that such an interaction arises from the interplay between superexchange and spin–orbit coupling [22]. Invariance of the interaction energy (2) with respect to exchanging \vec{S}_i and \vec{S}_j requires that $\vec{d}_{ij} = -\vec{d}_{ji}$. The energy (2) is minimized when the two magnetic moments form a 90° angle (or more accurately when \vec{d}_{ij} , \vec{S}_i , and \vec{S}_j form a left-handed system for $|\vec{d}_{ij}| > 0$), but due to the simultaneous presence of the generally much stronger Heisenberg-type interaction $E_{ij}^{\text{H}} = J_{ij} \vec{S}_i \cdot \vec{S}_j$, with $J_{ij} = J_{ji}$, which favors either 0° or 180° angles, the presence of the Dzyaloshinskii–Moriya (DM) interaction usually only leads to a small canting between the interacting moments, i.e. a small deviation from an overall collinear magnetic configuration as illustrated in figure 1.

Symmetry puts strict constraints on the DM vector \vec{d}_{ij} . In particular, \vec{d}_{ij} is identically zero if the midpoint between the magnetic moments is an inversion center. Turning this around, it means that in magnetic ferroelectrics, which do not exhibit any inversion centers, the DM interaction can be expected to be a rather common phenomenon (even though there can be other symmetry restrictions which prohibit the DM interaction even in the absence of any inversion centers). This raises the question of possible cross-correlations between electric polarization and DM interaction in ferroelectric magnets.

Many ferroelectric systems of interest today can be characterized by a small polar structural distortion away from a centrosymmetric reference structure. This reference structure is usually identical with the crystal structure of the paraelectric phase but need not be [23]. The distortion, which leads to an electric dipole moment, can be reversed by applying an appropriate electric-field (domain switching). This leads to the following scenario [16, 18]. If in the paraelectric reference structure the midpoint between two neighboring magnetic ions is an inversion center, which is destroyed by the ferroelectric distortion, then the ferroelectric distortion can ‘switch on’

the DM interaction between the two ions³. In this case the materials-specific parameter, \vec{D} , of Dzyaloshinskii's invariant, equation (1), can be identified with the electric polarization \vec{P} and the corresponding invariant in the free energy expansion is:

$$E^{\text{PML}} \sim \vec{P} \cdot (\vec{M} \times \vec{L}). \quad (3)$$

From equation (3) it can be seen that if it is possible to reverse the direction of \vec{P} (using an electric field) without changing the orientation of \vec{L} , then the magnetization will reverse too, in order to minimize the total free energy of the system. Reversal of \vec{L} can be prevented by sufficiently large magnetic anisotropy, and thus an invariant of type (3) opens up the possibility for electric field-induced magnetization switching.

In the preceding paragraph we have outlined the general scenario that can lead to electric-field switchable weak ferromagnetism. In order to find specific example materials that exhibit this effect it is important to point out that even for cases where the ferroelectric distortion destroys the inversion centers between adjacent magnetic sites, and thus provides a necessary requirement for nonzero DM interaction, there can be other symmetry operations that result in $\vec{d}_{ij} = 0$ or prevent the system from exhibiting a macroscopic magnetization⁴. In the following we briefly summarize our previous work along these lines and then discuss in detail why the desired coupling is present in $R3c$ FeTiO₃ but absent in BiFeO₃, even though these two systems have the same crystallographic space group symmetry.

3. First principles studies of BiFeO₃, BaNiF₄, and FeTiO₃

The possibility of an electric-field switchable DM interaction was first discussed in the context of BiFeO₃ [16]. BiFeO₃ is an antiferromagnetic ferroelectric with a Néel temperature of ~ 643 K and a ferroelectric Curie temperature of ~ 1103 K [24, 25]. It is thus a very rare example of a multiferroic with both magnetic and ferroelectric ordering temperatures above room temperature, and it is probably the most-studied multiferroic to date. The primary magnetic order in BiFeO₃ is 'G-type' antiferromagnetism [26], i.e., 'checkerboard'-like, but in addition it has been reported that bulk single crystals exhibit a superimposed cycloidal spiral magnetic ordering with a large period of ~ 620 Å [27]. This spiral ordering seems to be absent in thin film samples [28] where instead a small magnetization has been found [28–30]. Early reports of magnetizations up to $1 \mu_{\text{B}}/\text{Fe}$ [29] could not be confirmed in other samples [28, 30] and therefore seem to be caused by extrinsic effects.

In [16] it was shown by first principles calculations that spatially homogeneous BiFeO₃ (without the spiral spin structure) exhibits weak ferromagnetism as a result of the DM interaction, and that the resulting magnetization is about $0.1 \mu_{\text{B}}/\text{Fe}$. Furthermore, it has been shown in [31] that the magnetization is only weakly dependent on epitaxial strain, another indication that the very large magnetization of

about $1 \mu_{\text{B}}/\text{Fe}$ found in the original thin film samples [29] is most likely due to extrinsic effects. The calculated magnetization agrees well with more recent experimental thin film data [28, 30]. We point out that a meaningful comparison between measured and calculated magnetization requires that an antiferromagnetic mono-domain state has been achieved in the experiment.

It was also shown in [16] from explicit first principles calculations that the sign of the DM vector \vec{D} in BiFeO₃ is independent of the polar distortion, but that it is instead determined by a rotational (non-polar) distortion of the oxygen octahedra network present in BiFeO₃. As we review in section 4, this lack of coupling between the DM vector and the polarization in BiFeO₃ is a question of symmetry [16, 18] and not due to a 'weak coupling' as some authors have suggested [32, 33]. Despite this absence of coupling between \vec{P} and \vec{M} in BiFeO₃, it was nevertheless realized that the DM vector can indeed couple linearly to a structural distortion [16]. However, the relevant structural distortion in the case of BiFeO₃ (the octahedral rotations) is non-polar, and therefore it was concluded that electric-field switching of the weak magnetization in BiFeO₃ is unlikely as there is no obvious way to couple the electric field to the non-polar distortion. Still, it was suggested that if materials can be found where the polarization and the DM vector are due to the same structural distortion, then electric field-induced reversal of the weak ferromagnetic moment is possible, and that there are no general symmetry arguments that prevent such an effect. A specific material that realized the predicted effect, however, remained elusive until the work of [18].

A subsequent study of the antiferromagnetic ferroelectric BaNiF₄ revealed that the DM vector can indeed be proportional to a polar ferroelectric distortion [17]. However, the overall symmetry of BaNiF₄ does not allow a macroscopic magnetization, and it was shown that even though the DM interaction leads to a local canting of neighboring magnetic moments, all components cancel out when taking the sum over the whole unit cell such that $\vec{M} = 0$. BaNiF₄ can therefore be classified as a weak *antiferromagnet*. It was pointed out that it should be possible to switch the secondary antiferromagnetic order parameter in BaNiF₄ using an electric field [17].

Finally, it was recently shown in [18], that a series of $R3c$ titanates, ATiO₃ with magnetic cations $A = \text{Mn, Fe, Ni}$, do in fact combine all the symmetry properties necessary for ferroelectrically-induced weak ferromagnetism. These compounds can be synthesized at high pressure and remain metastable at ambient conditions [34, 35]. It was confirmed in [18] by explicit first principles calculations that a weak magnetization exists in these materials, and that it is reversed when the polar distortion is reversed while keeping all other order parameters (apart from the magnetization) fixed. It can therefore be expected, that in these materials the magnetization can be reversed using an electric field. This represents the first specific example for the general mechanism of magneto-electric coupling outlined in section 2.

In [18] two criteria for the rational design of ferroelectrically-induced weak ferromagnetism were formulated: a 'structural-chemical criterion' and a 'magnetic criterion'. As

³ This has been called the 'structural-chemical criterion' in [18].

⁴ This has been termed the 'magnetic criterion' in [18].

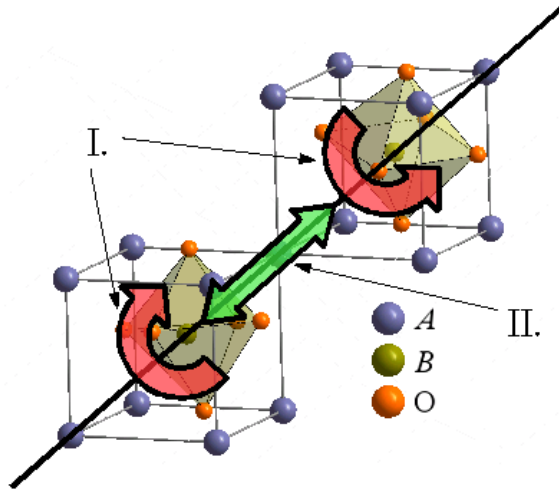


Figure 2. Schematic depiction of the structural distortions that lead from the perfect cubic perovskite structure to the $R3c$ structure of $\text{BiFeO}_3/\text{FeTiO}_3$: I counter-rotations of oxygen octahedra around $[111]$; II ionic displacements along $[111]$.

already briefly remarked via footnotes in section 2, the structural-chemical criterion implies that the midpoint between two magnetic sites is an inversion center in the paraelectric reference structure, whereas the magnetic criterion expresses the fact that there should be no other symmetry elements besides these inversion centers that prevent the system from exhibiting weak ferromagnetism. In the following we will present a detailed comparison between BiFeO_3 and FeTiO_3 (as representative for the titanate systems discussed in [18]), focusing on symmetry aspects, and discuss why in FeTiO_3 both criteria are fulfilled, i.e. the DM interaction is induced by the ferroelectric distortion, whereas in BiFeO_3 this is not the case. We will then develop guidelines to construct symmetry groups that generally allow ferroelectrically-induced weak ferromagnetism.

4. Magnetic A-site versus B-site $R3c$ distorted perovskites: symmetry aspects

The $R3c$ structure in which both BiFeO_3 and FeTiO_3 are found, can be regarded as a distorted version of the five-atom cubic perovskite structure. The deviation from the ideal perovskite structure can be decomposed into two components (see figure 2):

- (I) antiferrodistortive counter-rotations of the oxygen octahedra around the $[111]$ axis (leading to a unit cell doubling compared to the perovskite primitive unit cell), and
- (II) polar displacements of all the ionic sublattices relative to each other parallel to $[111]$.

In FeTiO_3 the rotations (I) are so large that $R3c$ FeTiO_3 is usually not considered to form a distorted perovskite structure but rather the ‘ferroelectric lithium niobate structure’⁵. Note that this LiNbO_3 polymorph of FeTiO_3 is structurally isomorphic to BiFeO_3 except that the positions of the Fe and

⁵ We point out that this distinction is not a question of symmetry but merely of structural connectivity.

Ti/Bi cations are exchanged, i.e.: $\text{FeTiO}_3 \rightarrow \text{BiFeO}_3$ implies $\text{Fe} \rightarrow \text{Bi}$ and $\text{Ti} \rightarrow \text{Fe}$.

Let us first consider BiFeO_3 and FeTiO_3 in the ideal perovskite structure, space group $Pm\bar{3}m$. Here we neglect both the octahedral rotations (component I) and the ferroelectric displacements (component II) while assuming that the spins order in a G-type antiferromagnetic pattern. For both BiFeO_3 and FeTiO_3 this paraelectric reference structure has inversion centers at all midpoints between magnetic sites. Furthermore, these inversion centers will be destroyed by any ferroelectric distortion, and thus the structural criterion described in [18] is fulfilled for both systems. However, since the cubic perovskite structure contains only a single magnetic cation per unit cell, an additional symmetry operation exists in the antiferromagnetically ordered state that requires $\vec{M} = 0$, i.e., the magnetic criterion is not fulfilled. The corresponding symmetry operation translates all ions by one unit cell and then inverts all magnetic moments through time inversion. In general, $\vec{M} = 0$ by symmetry, whenever the magnetic unit cell is a multiple of the chemical unit cell. Specifically for the case of $\text{BiFeO}_3/\text{FeTiO}_3$ this implies that the unit cell doubling caused by the octahedral rotations (component I) is essential for obtaining weak ferromagnetism and to fulfill the magnetic criterion. Therefore, the octahedral rotations cannot be ignored in a proper symmetry analysis of BiFeO_3 or FeTiO_3 , and we conclude that cubic perovskite is not a suitable paraelectric reference structure for obtaining ferroelectrically-induced weak ferromagnetism.

In contrast, if we only neglect the polar displacements (component II) while including the octahedral rotations (component I) in our paraelectric reference structure, we obtain the calcite or ‘paraelectric lithium niobate’ structure (space group $R\bar{3}c$). This is the closest centrosymmetric reference structure for both BiFeO_3 and FeTiO_3 and it is thus the proper starting point for a Landau free energy expansion describing the possible coupling between \vec{P} , \vec{L} , and \vec{M} in these systems (see section 5).

The crucial difference between BiFeO_3 and FeTiO_3 in the $R\bar{3}c$ structure is the different local site symmetry of the magnetic cations: in BiFeO_3 the magnetic cations (Fe^{3+}) are situated on Wyckoff positions 2b, corresponding to the B-site of the underlying perovskite structure, whereas in FeTiO_3 the magnetic cations (Fe^{2+}) occupy Wyckoff positions 2a, corresponding to the perovskite A sites (see figure 2). To see whether the structural criterion of [18] is fulfilled, we have to check whether the midpoints between the magnetic sites (i.e., the Fe sites) in each system are inversion centers or not. As illustrated in figure 3 this is the case for FeTiO_3 but not for BiFeO_3 , i.e., the structural criterion for ferroelectrically-induced ferromagnetism is fulfilled in FeTiO_3 but not in BiFeO_3 . Note that in the completely undistorted perovskite structure this criterion was fulfilled for both systems, i.e., inversion centers were located on the midpoints between the A sites as well as on the midpoints between the B sites. The latter are destroyed by the octahedral rotations (I). This is the reason why BiFeO_3 already exhibits weak ferromagnetism in the paraelectric $R\bar{3}c$ phase, i.e. weak ferromagnetism in BiFeO_3 is induced by the octahedral rotations and not by the polar distortion [16].

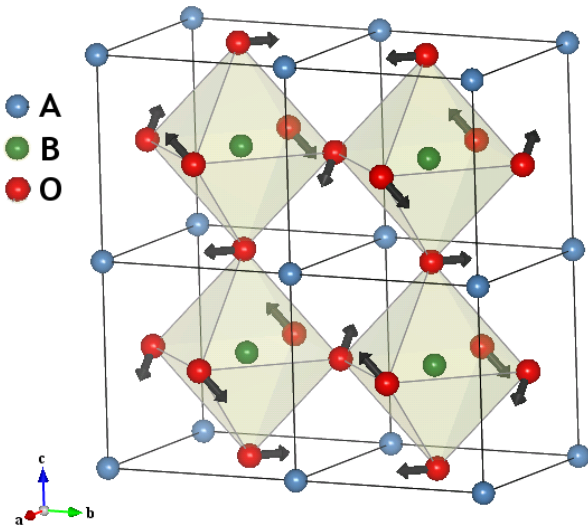


Figure 3. Displacement vectors of the oxygen anions corresponding to the octahedral rotations (I), relative to the ideal cubic perovskite structure. Due to the displacement of the oxygen anions located at the midpoints between adjacent B sites, the corresponding inversion centers are destroyed, whereas the inversion centers located at the midpoints between the A sites are conserved.

We point out that in some previous publications ‘ $R3\bar{c}$ ’ symmetry has been used as basis for a free energy expansion of BiFeO_3 (see e.g. [32, 36, 37]). ‘ $R3\bar{c}$ ’ is not standard space group notation⁶, and it is therefore not fully clear what the corresponding symmetry operations are, but apparently in this case it is assumed that inversion centers are located *between* the magnetic sites. As stated above this is not true for BiFeO_3 in the proper paraelectric reference structure. It follows that the symmetry analysis in [32, 36, 37] in fact applies to FeTiO_3 instead of BiFeO_3 .

It is now clear that only FeTiO_3 , but not BiFeO_3 , fulfills the structural-chemical criterion. What remains to be discussed is whether the inversion symmetry related to the midpoints between the magnetic cations in FeTiO_3 is the only symmetry operation that requires $\vec{M} = 0$, i.e., whether the magnetic criterion is satisfied. One candidate for such a symmetry operation was already mentioned earlier: the combination of a primitive translation of the paraelectric structure with time inversion. However, this can only be a symmetry operation if the magnetic unit cell is a multiple of the crystallographic unit cell. As discussed above, the presence of the octahedral rotations in $R\bar{3}c$ FeTiO_3 doubles the crystallographic unit cell compared to simple perovskite, and thus ensures that for the assumed G-type magnetic order the magnetic and crystallographic unit cells are identical.

Apart from such ‘magnetic Bravais lattice translations’ [21] the fulfillment of the magnetic criterion is mainly a question of how the individual magnetic moments are oriented relative to the crystal axes, which is determined by the magneto-crystalline anisotropy. As already shown by Dzyaloshinskii [19], an orientation of the magnetic moments

perpendicular to the rhombohedral axis is required for weak ferromagnetism to occur in crystallographic $R\bar{3}c$ symmetry. First principles calculations show that this orientation is indeed favored by the magneto-crystalline anisotropy in FeTiO_3 [18], and thus the magnetic criterion is fulfilled for this system.

In summary, we have shown that in FeTiO_3 both the structural-chemical and the magnetic criteria for ferroelectrically-induced weak ferromagnetism are fulfilled. Due to the different location of the magnetic cations in BiFeO_3 the structural criterion is not fulfilled in this system (and thus the magnetic criterion is not applicable). This shows that in FeTiO_3 the weak magnetization is linearly coupled to the electric polarization whereas this is not the case in BiFeO_3 , as was also verified by explicit first principles calculations in [16, 18]. It also becomes apparent that it is important to consider the full crystallographic symmetry to analyze possible coupling between \vec{P} and \vec{M} , including also non-polar structural distortions such as the octahedral rotations in $\text{BiFeO}_3/\text{FeTiO}_3$.

5. General symmetry considerations

In the preceding sections we described the general idea behind ferroelectrically-induced weak ferromagnetism, we reviewed results for some specific example materials, and presented a detailed comparison of the two $R3c$ structure materials BiFeO_3 and FeTiO_3 . In section 2 we mentioned that in order to achieve the desired coupling between the polarization and the magnetization, the free energy expansion of the high symmetry phase has to contain a term of the form (3). In this final section we discuss some general symmetry aspects and we list magnetic point groups that are compatible with the existence of such a coupling between \vec{P} and \vec{M} .

According to the Landau theory of phase transitions, which describes continuous transitions from a high symmetry configuration into a configuration with lower symmetry, the free energy of the system can be expanded in powers of the various order parameters [38, 39]. Each individual term in this expansion has to be invariant with respect to all the symmetry operations of the high symmetry phase. Here, we are concerned with a transition leading from a paramagnetic and non-polar phase (where $\vec{P} = \vec{M} = \vec{L} = 0$) into a lower symmetry phase where all three order parameters are nonzero. This transition also implicitly defines an intermediate non-polar antiferromagnetic phase where $\vec{L} \neq 0$ but $\vec{P} = \vec{M} = 0$.

In order to achieve the desired coupling between \vec{P} and \vec{M} , the term $\vec{P} \cdot (\vec{M} \times \vec{L})$ has to be allowed in the free energy expansion of the high symmetry phase. Since the transformation properties of the polar vector \vec{P} and the axial vector \vec{M} are well known, the question of whether such a trilinear coupling between \vec{P} , \vec{M} and \vec{L} is allowed, is basically a question about the symmetry properties of the antiferromagnetic order parameter \vec{L} . We point out that \vec{L} cannot generally be classified as either an axial or polar vector; its symmetry properties depend on the microscopic definition of \vec{L} in terms of ionic magnetic moments and the underlying crystallographic symmetry. Ultimately, the design criteria of [18] aim at designing an antiferromagnetic order parameter with the required macroscopic symmetry to couple \vec{P} and \vec{M} .

⁶ Note that here the ‘bar’ indicating space inversion is combined with the c -type glide plane and not with the threefold rotation as in $R\bar{3}c$.

A first symmetry requirement for \vec{L} has already been discussed in section 4: the magnetic unit cell has to be identical to the crystallographic unit cell. Otherwise, a symmetry element exists which consists of time reversal combined with a lattice translation of the paramagnetic phase. Such a transformation leaves \vec{L} and \vec{P} invariant, but changes the sign of \vec{M} and thus (3) is not an invariant of the corresponding high symmetry phase. This symmetry requirement for \vec{L} is implicitly expressed in [18] as part of the magnetic criterion.

The next symmetry operation to consider is space inversion. The presence of space inversion in the high symmetry group is not a necessary requirement, but it simplifies the following analysis considerably. We therefore restrict ourselves to cases where the high symmetry paramagnetic, non-polar reference structure is centrosymmetric. Notice, since \vec{P} is a polar vector that changes sign under space inversion and \vec{M} is an axial vector that is invariant under space inversion, that the antiferromagnetic vector has to be odd under space inversion to allow an invariant of the form $\vec{P} \cdot (\vec{M} \times \vec{L})$. It is apparent that such an antiferromagnetic order parameter arises for example if the inversion centers of the high symmetry structure are located between two antiferromagnetically coupled cations, but not if these inversion centers are located on the magnetic cation sites themselves. This symmetry requirement for \vec{L} is thus related to the structural criterion discussed previously.

We now construct symmetry groups that allow for an antiferromagnetic order parameter with the two symmetry requirements outlined in the two preceding paragraphs. To simplify the presentation we only discuss magnetic point groups, not the full magnetic space group symmetry. Note that the macroscopic point group corresponding to a particular microscopic space group is obtained by neglecting all translational parts of the corresponding space group operations [21]. Therefore, the symmetry properties of \vec{L} outlined above are equivalent to stating that the magnetic point group of the intermediate non-polar antiferromagnetic phase can contain neither space inversion nor time reversal symmetries individually (i.e., neither $\bar{1}$ nor $1'$), but only the combined operation of space inversion followed by time reversal (i.e., $\bar{1}'$). Note that these are also the symmetry requirements for the existence of a magnetic toroidal moment \vec{T} (see [40, 41]), which hints at a close connection between the presence of a magnetic toroidal moment and the presence of the magneto-electric coupling expressed in (3) (the exact nature of this connection will be the subject of future investigations).

In addition, we realize that a free energy invariant of the form (3) with an antiferromagnetic order parameter that can be classified as a toroidal moment gives rise to an antisymmetric linear magneto-electric effect (see e.g. [41]), and we can therefore now list all the magnetic space groups of the desired intermediate state (where $\vec{L} \neq 0$ but $\vec{P} = \vec{M} = 0$). They are those which display an antisymmetric linear magneto-electric effect and contain the combined symmetry operation of space inversion followed by time reversal:

$$\bar{1}', 2/m', 2'/m, m'mm, 4/m', \bar{3}', 6/m', 4/m'mm, \bar{3}'m, \text{ and } 6/m'mm. \quad (4)$$

These are all possible space groups of the targeted antiferromagnetic paraelectric phase, where a polar distortion

can induce a weak magnetization as a secondary order parameter. In order to construct the possible polar subgroups we simply add a polar distortion along one of the directions connecting antisymmetrical components of the linear magneto-electric tensor to all these groups, and calculate the resulting symmetries. This results in the following five point groups:

$$1, 2', m, m', \text{ and } 2'm'm. \quad (5)$$

We note that these are precisely those determined by Fox and Scott by considering all magneto-electric point groups which allow both a spontaneous polarization and a spontaneous magnetization and requiring $\vec{P} \perp \vec{M}$ [15].

We point out that even though within our analysis we have first proceeded from the paramagnetic-non-polar case to the non-polar antiferromagnetic case, and then subsequently to the polar-magnetic case, it is not required that in the real system the magnetic phase transition occurs at a higher temperature than the ferroelectric transition. The important point is that an antiferromagnetic paraelectric reference phase with the required symmetry can be constructed in principle. In fact displacive ferroelectric phase transitions often occur well above room temperature, and therefore the critical temperature for the effect described in this article is expected to be determined by the antiferromagnetic Néel temperature in most cases⁷. The Néel temperature of antiferromagnetic oxides with strong superexchange interaction is often above room temperature and thus the described effect is not limited to low temperatures.

6. Summary and outlook

In this paper we have illustrated the general principle behind ferroelectrically-induced ferromagnetism through the DM interaction, focusing on the corresponding symmetry requirements. We have discussed in detail why these requirements are fulfilled for $R3c$ FeTiO_3 , where the magnetic Fe^{2+} cations occupy the perovskite A sites, but not for isostructural BiFeO_3 , where the magnetic Fe^{3+} cations are located on the perovskite B sites. As discussed in section 4, the crucial difference is that in the $R\bar{3}c$ paraelectric reference structure inversion centers are located at the midpoints between the A sites (structural criterion) but not between the B sites. These inversion centers are destroyed by the ferroelectric displacements, and since they are the only symmetry operations prohibiting a DM interaction between the A sites (magnetic criterion), the ferroelectric distortion ‘switches on’ weak ferromagnetism in FeTiO_3 . As a result, polarization and magnetization in FeTiO_3 are coupled via the trilinear invariant, equation (3).

In section 5 we have reformulated the design criteria of [18] as symmetry requirements for the antiferromagnetic order parameter \vec{L} , and we then constructed magnetic point groups that are compatible with ferroelectrically-induced weak ferromagnetism. In the most common case, where space inversion is a symmetry element of the paraelectric reference

⁷ In this case, the magnetization will appear at T_N , rather than at the ferroelectric transition, but the effect is still ferroelectrically-induced.

structure, this requires \vec{L} to transform like a magnetic toroidal moment, i.e. \vec{L} has to be odd under both space and time inversion but invariant under the combined operation.

Of course symmetry analysis gives only qualitative information, i.e., it tells us whether or not a certain effect is in principle possible for a given symmetry. On the other hand, it is also desirable to subsequently quantify the corresponding effect. Here, first principles calculations using density functional theory represent an invaluable tool. Within certain constraints, these calculations can provide very reliable quantitative information about e.g., structural parameters, lattice instabilities, magnetic coupling, and magnetization. First principles calculations have been used in [16–18] to verify and quantify weak magnetic order and its relation to structural distortions, both polar and non-polar. Combined symmetry analysis and first principles calculations have identified FeTiO₃ (and the related Ni and Mn compounds) as prime candidate for the realization of electric-field switchable weak ferromagnetism close to room temperature [18]; this now awaits experimental verification.

Symmetry guided first principles design of novel promising materials is in line with the general strategy for a rational computational materials design outlined by Spaldin and Pickett [42]: after a candidate material with the right symmetry has been found on symmetry grounds, first principles calculations can be used to verify whether this material really shows the desired effect and to determine the relevant quantities.

Such a strategy is particularly useful for the design of novel complex oxide materials, where intrinsic properties can easily be hidden by extrinsic effects, such as oxygen deficiency, micro-crystallinity, or the presence of small amounts of competing phases, and can thus easily be missed in a purely experimental approach. We therefore believe that a rational materials design based on first principles calculations indeed represents a very powerful approach to search for novel materials with unexpected and technologically useful properties.

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