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On the symmetry and the signature of atomic mechanisms in multiferroics: the example of $Ba_2CoGe_2O_7$

J. Manuel Perez-Mato[a]* and Jose Luis Ribeiro[b]

[a]Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apdo 644, Bilbao 48080, Spain, and [b]Centro de Física da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal. Correspondence e-mail: jm.perez-mato@ehu.es

The systematic use of symmetry arguments, with inclusion of magnetic symmetry, is scarce in the investigation of magnetic materials. This is an unfortunate situation particularly when multiferroics are being studied. The lack of a consistent complete symmetry framework often prevents the distinction of what is the signature of a specific atomic mechanism and what is symmetry-forced and therefore common to any possible underlying microscopic model. Here the recently reported magnetoelectric properties of $Ba_2CoGe_2O_7$ [Murakawa *et al.* (2010). *Phys. Rev. Lett.* **105**, 137202] are discussed as an extreme example of this situation, and it is shown how three of the four magnetoelectric responses that have been reported for this compound can be predicted by symmetry considerations without appealing to any specific atomic mechanism.

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1. Introduction

Tensor properties of any crystal are constrained by the point-group symmetry of the crystal. The point group to be considered for magnetic properties is the magnetic point group (Shubnikov point group). When characterizing the physical properties of a non-magnetic crystal, the necessity of knowing its point group is taken for granted. In contrast, it is surprising how much research on multiferroics, and magnetoelectrics in general, is being carried out without caring about the actual magnetic point group of the system. Symmetry considerations, if existing, are marginal or are reduced to the symmetry of the atomic positional structure, which may often be inconsistent with the actual magnetic symmetry of the reported magnetic structure. This situation is caused by the usual practice when determining magnetic structures. The successful application of the so-called representation analysis (Bertaut, 1968) in the determination of magnetic structures has implied that magnetic symmetry is not essential for the characterization of most magnetic structures. Magnetic structures are usually described by a nuclear positional structure with symmetry given by a normal space group, plus a set of static waves of atomic magnetic moments with symmetries described by irreducible representations of this space group. This has the advantage that it can be used even in the cases that the waves are incommensurate, where conventional magnetic space-group symmetry cannot be defined. But it has the disadvantage that one ignores in general the underlying magnetic symmetry of the investigated phase, and as a consequence loses the perspective and control of what is symmetry-allowed in this phase, both concerning the possible configuration of the magnetic moments, the induced nuclear structural distortions and the macroscopic properties. As long as the coupling between lattice and magnetic moments is so small that it can be neglected, the lack of magnetic symmetry considerations is not much of a problem. But these latter become essential in materials like multiferroics, magnetoelectrics, magnetoelastics *etc.*, where precisely this coupling is a fundamental issue. In these cases a rigorous use of magnetic symmetry is a fundamental tool for achieving a consistent framework to describe and explain their properties (Schmid, 2008).

The lack of symmetry considerations often prevents a clear distinction between what can be the signature of a specific microscopic mechanism and a symmetry-forced property that must necessarily be fulfilled by any symmetry-consistent microscopic model. The recent study reported by Murakawa *et al.* (2010) is an extreme example of this problem. This article reports various peculiar magnetoelectric properties of the multiferroic $Ba_2CoGe_2O_7$ and the authors explained their observations using a so-called *spin-dependent hybridization model*. These successful explanations were then presented as a validation of the proposed microscopic model. We reconsider here these magnetoelectric properties as a representative case that demonstrates the benefits of an extensive and systematic use of magnetic symmetry considerations in the investigation of multiferroics. We will show that three of the four magnetoelectric features reported by Murakawa *et al.* (2010) can be

predicted by using simple arguments based on the symmetry of the material, and therefore these properties should not be claimed as the signature of any specific atomic mechanism.

2. Magnetoelectric response of $Ba_2CoGe_2O_7$ explained from its magnetic symmetry

2.1. Magnetic field in the plane *xy*

The space group of $Ba_2CoGe_2O_7$ in the paramagnetic phase is $P\bar{4}2_1m$, and the system becomes a collinear antiferromagnet (AFM) at low temperatures with the two Co atoms in its unit cell having opposite spins in the *xy* plane (Zheludev *et al.*, 2003). Murakawa *et al.* (2010) report, and present as proof of the microscopic model they propose, the variation of a spontaneous polarization along the *z* axis (P_z) for magnetic fields rotating in the *xy* plane. The magnitude of this polarization depends on the angle between the magnetic field and the *x* axis (Φ_H), according to the approximate law $P_z \propto \sin 2\Phi_H$ (see Fig. 1). In fact this magnetoelectric response can be predicted by using only the symmetry properties of the magnetic phase as follows. The AFM magnetic ordering in this material breaks the paramagnetic space group $P\bar{4}2_1m1'$ into different magnetic space groups depending on the orientation of the spins, being $P2_1'2_12'$ and $Cm'm2'$ for the AFM spin configurations along the directions [100] and [110], respectively. For the symmetry-related orientations [010] and [−110], the equivalent $P2_12_1'2'$ and $Cmm'2'$ are realized, while for a more general direction on the plane the symmetry reduces to $P112'$ (Litvin, 2008). The magnetic point groups associated with these symmetries ($2'22'$, $22'2'$, $m'm2'$, $mm'2'$ and $2'$, respectively) allow a weak secondary induced ferromagnetic (FM) component (M_x, M_y) in the *xy* plane (Aizu, 1970). If a magnitude is allowed by the

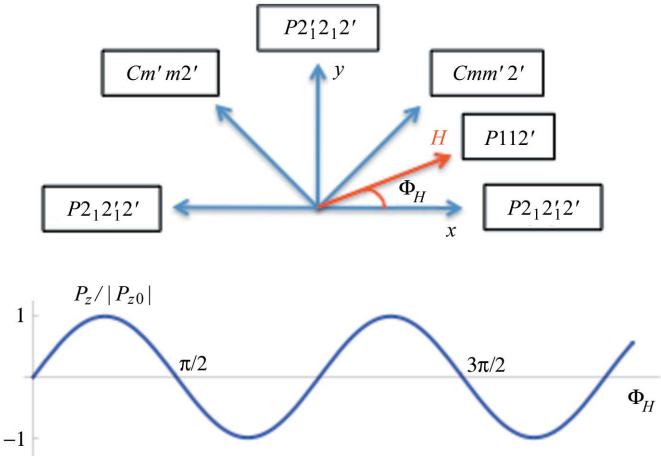

Figure 1
Scheme of the spontaneous polarization P_z in $Ba_2CoGe_2O_7$ as a function of the orientation of a magnetic field in the *xy* plane, with Φ_H being its angle with the *x* axis. The different magnetic symmetries realized depending on this orientation are indicated. The nodes of the sinusoidal response correspond to non-polar magnetic space groups. P_z has, in general, two contributions: a spontaneous component induced by the primary AFM ordering plus an induced component owing to the linear magnetoelectric response (see text).

symmetry of a thermodynamic phase, according to the Von Neumann principle, it will be present in whatever small quantity, and its presence can be explained as an induced effect through coupling with the symmetry-breaking order parameter. Indeed, if we denote by (L_x, L_y) the amplitudes of the AFM configuration, *i.e.* the order parameter, one can see that L_xM_y–L_yM_x is invariant for the operations of $P\bar{4}2_1m1'$ and is therefore the lowest-order symmetry-allowed coupling between these degrees of freedom. This is the consequence of the fact that (M_x, M_y) and (L_y, $-L_x$) have the same transformation properties for the operations of $P\bar{4}2_1m1'$, *i.e.* they transform according to the same irreducible representation of $P\bar{4}2_1m1'$ (Stokes *et al.*, 2007). The symmetry-allowed coupling term L_xM_y–L_yM_x in the energy implies that the energy minimization will introduce an FM component (M_x, M_y) proportional to (L_y, $-L_x$). In other words, the magnetic symmetry of the structure allows a spin canting through a weak induced FM component perpendicular to the direction of the primary AFM ordering. A magnetic field in the plane *xy* is then expected to align this weak spontaneous FM component along the field direction and, as a consequence, the dominant AFM component will be perpendicular to the field direction. Thus, the orientation of the AFM configuration will correlate with the magnetic field angle Φ_H in the form (with the sign of L_0 unknown)

$$(L_x, L_y) = L_0(\sin \Phi_H, -\cos \Phi_H). \quad (1)$$

The magnetic point-group symmetry of the system is therefore changing as a function of the field angle Φ_H among the different magnetic space groups mentioned above, as indicated in Fig. 1. Non-polar magnetic point groups $22'2'$ and $2'22'$ are realized for $\Phi_H = 0 \pmod{\pi}$ and $\Phi_H = \pi/2 \pmod{\pi}$, respectively. For these orientations, no spontaneous electrical polarization is expected, in agreement with the experiment, but for any other direction the magnetic point groups are polar along **z**. One can therefore predict that a spontaneous electrical polarization in this direction will occur as a secondary or induced effect of the magnetic ordering. Similarly to that carried out for the FM component, we can obtain the approximate behaviour of this spontaneous polarization P_z by considering the symmetry-allowed coupling term of lowest order between this magnitude and the order parameter [L_x, L_y]. This is the $P\bar{4}2_1m1'$-invariant term: $P_zL_xL_y$. This coupling term in the energy implies that the energy minimization requires a spontaneous polarization P_z proportional to L_xL_y. Considering the Φ_H dependence of the L_x and L_y amplitudes [equation (1)], P_z should then vary as $P_z = P_{z0}\sin 2\Phi_H$, as observed (see Fig. 1). It should be stressed that the dependence of P_z on the magnetic field direction is established because the field controls the orientation of the order parameter and P_z depends on this orientation. However, the magnitude of this polarization depends only on the amplitude of the spontaneous AFM order parameter and not on the intensity of the magnetic field. In fact, for zero magnetic field a non-zero P_z is expected, as the easy axis for the AFM ordering seems to be the [110] direction (Zheludev *et al.*, 2003). The system is therefore an improper ferroelectric with

spontaneous polarization along **z**. The switch of this polarization can be achieved through a rotation of the magnetic field by 90°. Reversely, a switch of the polarization along **z** by means of an electric field will produce a 90° rotation of both the AFM and the weak FM components in any of the two possible senses.

Apart from the spontaneous polarization P_z discussed above, one should expect an additional contribution to the polarization along **z**, *i.e.* P_z^H, proportional to the applied magnetic field and caused by the linear magnetoelectric effect, which is symmetry-allowed in the ordered AFM phase. Indeed, for a general orientation of the magnetic field in the plane xy, the actual magnetic symmetry of the system, as discussed above, is $P112'$ (magnetic point group $2'$, unique axis z). This implies a linear magnetoelectric tensor with non-zero coefficients α_{31}, α_{32} (and α_{13}, α_{23}) responsible for a polarization along **z** related to the magnetic field in the xy plane (Rivera, 2009). At the special direction $\Phi_H = 0 \pmod{\pi}$ the coefficient α_{31} must be zero, as it is forbidden for the higher point-group symmetry corresponding to this orientation. For similar reasons, α_{32} should vanish for $\Phi_H = \pi/2 \pmod{\pi}$. This implies that the additional contribution to the polarization along **z** that could originate in the linear magnetoelectric response is zero for these field orientations. Hence, the nodes of the function $P_z(\Phi_H)$ are maintained when the linear magnetoelectric effect is included. Furthermore, one can demonstrate that the functional dependence $P_z \propto \sin 2\Phi_H$ is robust when these effects are included in a first-order approximation. Indeed, from the transformation properties of the relevant magnitudes under the symmetry operations of the paramagnetic space group $P\bar{4}2_1m1'$, one can easily conclude that the lowest-degree coupling terms responsible for the linear magnetoelectric response are of the form $(M_yL_y–M_xL_x)P_z$ and $(P_yL_y–P_xL_x)M_z$. At the AFM phase these terms in the energy imply that

$$\begin{aligned} \alpha_{31} &= cL_x, \;\; \alpha_{32} = -cL_y, \\ \alpha_{13} &= c'L_x, \;\; \alpha_{23} = -c'L_y, \end{aligned} \tag{2}$$

where c and c' are unknown constants. Therefore, by inserting in (2) the angle dependence of the amplitudes of the AFM order parameter given by (1), one obtains

$$P_z^H = \alpha_{31}H_0\cos\Phi_H + \alpha_{32}H_0\sin\Phi_H \propto \sin 2\Phi_H. \tag{3}$$

That is, the characteristic π-periodic sinusoidal variation of the electrical polarization along **z** is maintained when linear magnetoelectric effects are included. The above prediction of this phenomenon is based only on symmetry considerations and symmetry-based phenomenology. This implies that this magnetoelectric property cannot be taken as the signature of any specific microscopic model. Note that the magnetic field orientation considered in this first set of experiments does not cause any additional symmetry break; we have worked only with possible symmetries of the spontaneous magnetic ordering which, being dependent on the orientation of the AFM order parameter, can be controlled by the magnetic field. This is no longer true for the geometry of the experimental result discussed next.

2.2. Magnetic field in the plane *yz*

A second type of magnetoelectric behaviour of $Ba_2CoGe_2O_7$ was reported by Murakawa *et al.* (2010) for a magnetic field rotating in the plane yz. A ferroelectric polarization along the x axis (P_x) was observed. Its magnitude depends on the field angle with respect to the z axis (θ_H) following a law that can be approximated as $P_x = P_{x0}\cos\theta_H$ if $-\pi < \theta_H < 0$ or $P_x = -P_{x0}\cos\theta_H$ if $0 < \theta_H < \pi$ (see Fig. 2). The polarization P_x has therefore a strong discontinuity as the field crosses the z axis. Again this behaviour was explained by Murakawa *et al.* (2010) making use of the proposed microscopic mechanism and this explanation was presented as additional support for the model. But, as in the previous case, the observed behaviour of P_x can be predicted from pure symmetry arguments, as shown in the following. The y component of the field drives the in-plane weak FM magnetization along [010] and the AFM component into the configuration $(L_0, 0)$ with magnetic space group $P2_1'2_12'$. The additional field-induced magnetization along **z**, *i.e.* M_z, further reduces the symmetry to $P2_1'11$, with a polar magnetic point group $2'$ (unique axis x) that allows a polarization along the x axis, P_x. This polarization should vary in the first approximation as $P_x \propto L_xM_z$ because the lowest symmetry-allowed coupling is $(P_yL_y–P_xL_x)M_z$. The modulus of L_x is expected to be essentially independent of the field direction in the plane yz but its sign must differ for field orientations with θ_H smaller or larger than 0, since at this threshold value the field component H_y switches sign, forcing the FM magnetization M_y and also the AFM amplitude L_x to switch their signs. Therefore, as long as the magnetization M_z responds linearly to the z component of the magnetic field component $H_z = H_0\cos\theta_H$, one should

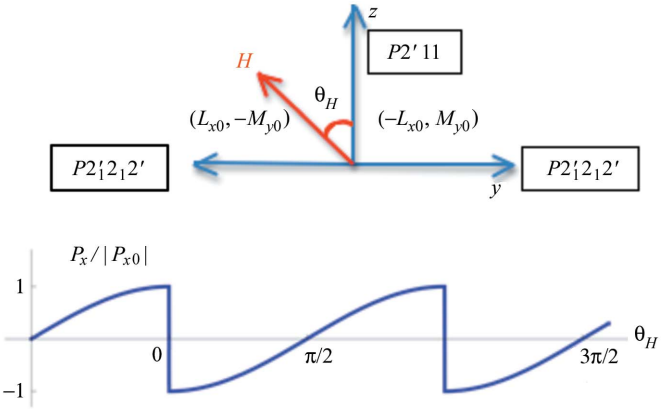

Figure 2
Scheme of the spontaneous polarization P_x in $Ba_2CoGe_2O_7$ as a function of the orientation of a magnetic field in the yz plane, with θ_H being its angle with the z axis. The nodes of the sinusoidal polarization at $\theta_H = \pi/2$ and $3\pi/2$ correspond to non-polar configurations. P_x is a linear magnetoelectric response to the z component of the magnetic field. The discontinuities at $\theta_H = 0$ and π reflect the change of sign of the corresponding magnetoelectric coefficient through the switch of the spontaneous magnetic ordering, $(L_0, 0)$, $(0, -M_0)$, by the change of sign of the magnetic field y component.

expect that $P_x = P_{x0}\cos\theta_H$, with the mentioned change of sign caused by the switch of the sign of L_x, as illustrated in Fig. 2 and observed experimentally.

This second type of magnetoelectric response can alternatively be explained considering the linear magnetoelectric effect discussed above. In fact, the peculiar dependence of P_x is just the signature of the fact that the phase point-group symmetry $2'22'$ only allows α_{13} (and α_{31}) as non-zero linear magnetoelectric coefficients. Therefore, the application of a magnetic field in the plane yz should induce a polarization along **x**, according to the law

$$P_x^H = \alpha_{13}H_z \propto L_x H_0 \cos\theta_H, \qquad (4)$$

where we have used equation (2). The magnetoelectric coefficient α_{13} is caused by the magnetic ordering and switches sign whenever the AFM order parameter is switched, causing the discontinuity at $\theta_H = 0$ and π.

It should be stressed that the sinusoidal response of the induced polarization observed in this case, in contrast with the previous one, is not intrinsic. It just reflects the sinusoidal variation of the magnetic field component that is magnetoelectrically active. We are simply observing a conventional linear magnetoelectric response to a sinusoidal magnetic field component H_z, as expected from the magnetic symmetry of the system, superposed with one additional effect: the relevant magnetoelectric tensor coefficient changes sign when the spin pattern is switched by the reversal of H_y, which is a component of the magnetic field not directly active in the linear magnetoelectric response. Notice also that the polarization P_x disappears if the magnetic field is set to zero; this is a quite different situation to the spontaneous polarization P_z discussed above, which has a spontaneous part induced by the magnetic ordering, and not by the magnetic field.

As the magnetoelectric coefficient α_{31} is also non-zero in a phase with point-group symmetry $2'22'$, it is interesting to consider its possible detection, as carried out in the previous experiment for α_{13}. In principle, a magnetic field along **x** should induce an electric polarization along **z**. However, we have seen in the first set of experiments that a magnetic field on the plane xy is bound to change the orientation of the order parameter so that the field direction is along the weak FM component. This implies that the geometry necessary to observe the α_{31} magnetoelectric response in the $P2_12_12'$ configuration, with the weak FM component perpendicular to the applied magnetic field, cannot be achieved in practice.

2.3. Magnetic-field-induced ferroelectricity

Murakawa *et al.* (2010) report a third type of experiment, showing a so-called 'electrical control' of the magnetization direction. Keeping a fixed magnetic field along the z axis, a hysteresis loop of the polarization P_x as a function of an electric field applied along **x** is observed, and the switch of the polarization P_x, through the reversal of the electric field, is seen to be accompanied by a switch of the weak ferromagnetic magnetization along [010], so that the total magnetization reverses its tilt in the yz plane with respect to the z direction. As with the previous experiments, this behaviour can be explained by considering the symmetry-forced linear magnetoelectric properties of the compound and its multistability. According to the considerations above [equation (4)], the polarization along **x** induced by a magnetic field along **z** is given by $P_x \propto L_x H_z$. Keeping H_z fixed, an electric field applied along **x** will therefore tend to orient the AFM spin configuration so that L_x is maximal, *i.e.* the order parameter will orient as $(L_0, 0)$, and the symmetry of the system becomes $P2_1'11$, as in the second type of experiments. We have seen above that in this case two degenerate equilibrium states with opposite values for the polarization P_x^H exist, depending on the sign of L_x. In other words, the fixed magnetic field, together with the multistability of the magnetic ordered configurations, produce a kind of magnetic-field-induced ferroelectric system. A sinusoidal electric field along **x** is bound to switch the polarization P_x^H between the two energy-equivalent states, producing a hysteresis loop with a remnant polarization proportional to the applied magnetic field H_z. Given the proportionality with $L_x H_z$ of this remnant polarization, it is obvious that its switch in the hysteresis loop must be accompanied by the switch of the order parameter L_x, and as a consequence of the associated weak FM component M_y, resulting in the magnetization tilt discussed by Murakawa *et al.* (2010).

3. Conclusions

The above considerations demonstrate that the results of three of the four types of magnetoelectric measurements reported by Murakawa *et al.* (2010) for $Ba_2CoGe_2O_7$ can be explained solely by the magnetic symmetry and the symmetry-forced multistability of this material. The remarkable and complex response of the material to magnetic and electric fields can be predicted by considering the possible ferroic species (Aizu, 1970; Schmid, 2008) of the magnetic ordered phase, *i.e.* the magnetic point-group symmetries of both the paramagnetic and the AFM phase. Therefore these magnetoelectric properties cannot be seen as signatures of specific atomic mechanisms. Of course, the magnitude (and sign) of the predicted behaviour cannot be given by symmetry arguments, and it is in this field where the quantitative predictions of different possible atomic mechanisms should be tested. But the geometrical atomic mechanism proposed by Murakawa *et al.* (2010) does not provide a quantitative prediction for the magnitudes of the magnetoelectric effects, as it includes adjustable parameters that are adapted to the observed magnitude of the effects. Consequently, the fit of the model predictions to the experimental results, in view of the above considerations, can only be considered a demonstration of the model being symmetry-consistent.

In the fourth type of experiments, Murakawa *et al.* (2010) reported the dependence of P_z on the magnitude of the magnetic field applied along [110] (see Fig. 3 of this reference). This dependence is strongly non-linear with a change of sign occurring at high fields. This behaviour can be accounted for

by the proposed model, while it is beyond a direct prediction from symmetry arguments. Hence, it is only this fourth type of behaviour that can indeed be considered a support for the proposed geometric microscopic model. Therefore, in this article, we are not refuting the possible validity of the specific atomic model proposed by Murakawa *et al.* (2010) (against which we have no fundamental objection), but we are calling attention to the fact that, when looking for specific atomic mechanisms in a given compound, one should take care to clearly distinguish what is symmetry-forced (and therefore model-independent) and what is a signature of a specific microscopic mechanism. The paper by Murakawa *et al.* (2010) is just one example of a common type of problem in the field of multiferroics, where the predictive power of symmetry arguments is very often disregarded. Using it as a representative case, we have underlined how a proper and systematic use of symmetry arguments may permit the main features of the magnetoelectric behaviour of a given system to be predicted and understood, without appealing to any particular atomic mechanism. This provides new arguments and examples to a general discussion on this matter that underlies the present research on multiferroics (see, for instance, Kenzelmann & Harris, 2008).

The system discussed here has a commensurate magnetic structure and its possible magnetic symmetries are therefore described by Shubnikov magnetic space groups. As many multiferroics have incommensurate magnetic ordering, their lack of lattice periodicity precludes the use of these groups. However, the symmetry of incommensurate magnetic phases can be described by means of generalized symmetry groups, which can be defined applying the same superspace formalism as in non-magnetic incommensurate structures (Janner & Janssen, 1980; Petříček *et al.*, 2010). The rotational operations of these magnetic superspace groups constitute the point groups defining the macroscopic symmetry of these systems. As a consequence, fully consistent systematic analyses of the crystal tensor properties of incommensurate multiferroics can also be carried out using this generalized symmetry.

After completion of this work, we have become acquainted with a preprint of Toledano *et al.* (2010), where a symmetry analysis of this magnetic phase is presented. This article is, however, focused on spontaneous toroidic effects and considers them a major agent in the magnetoelectric behaviour of the system. We think, however, that at least the three magnetoelectric properties discussed here can be simply explained, as shown above, without introducing the concept of a spontaneous toroidal moment.

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