The magnetoelectric effect due to local noncentrosymmetry

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Abstract

Magnetoelectrics often possess ions located in noncentrosymmetric surroundings. Based on this fact we suggest a microscopic model of magnetoelectric interaction and show that the spin–orbit coupling leads to spin-dependent electric dipole moments of the electron orbitals of these ions, which results in non-vanishing polarization for certain spin configurations. The approach accounts for the macroscopic symmetry of the unit cell and is valid for both commensurate and complex incommensurate magnetic structures. The model is illustrated by the examples of MnWO$_4$, MnPS$_3$ and LiNiPO$_4$. Application to other magnetoelectrics is discussed.

1. Introduction

Curie [1] was the first to predict the interplay between magnetism and ferroelectricity. The macroscopic symmetry consideration of the magnetoelectric (ME) effect was given by Dzyaloshinskii only in 1959 [2], whereas experimentally it was discovered by Astrov in Cr$_2$O$_3$ in 1960 [3]. In the last decade whole new classes of magnetoelectric materials have been discovered and experimentally studied (for a recent review see, for example, [4]).

From the point of view of crystallographic classes, magnetoelectricity has been studied in a number of works (see, for example, [5] for a recent review), where all magnetoelectric interactions compatible with the macroscopic symmetry have been found. Another approach is based on the crystal symmetry in the paraelectric and paramagnetic state. It was noted recently [6–8] that in the majority of magnetoelectrics the experimentally observed magnetoelectric phases are described by a combination of magnetic order parameters transforming according to different irreducible representations (IR) of the symmetry group of the paraphase, which induce electric polarization acting together. Indeed, in the case where the space group of the initial paraphase possesses spatial inversion $I$ and the resulting magnetic cell of the magnetically ordered phase coincides with the initial chemical cell (i.e. when $k = 0$) a single magnetic order parameter cannot induce polarization [9]. This is explained by the following. The symmetry of the disordered phase is $G \otimes R$, where $G$ is the space group and $R$ is time inversion. When $k = 0$, for any of the IRs of $G \otimes R$ a unit matrix corresponds to either $I$ or $IR$. Therefore, upon a phase transition according to this IR one of these symmetry elements is preserved in the ordered phase, but none of them allow nonzero electric polarization. However, this is generally not the case for $k \neq 0$, for which a single magnetic order parameter may induce electric polarization [10]. Furthermore, it has been shown that in many magnetoelectrics the observed magnetically ordered phases are induced by a single IR either of the space group of the paraphase [11] or of the symmetry group of the exchange Hamiltonian [12].

Despite the long history of the ME effect its microscopic origin is still a subject of debate. The fact that ferroelectricity commonly occurs in incommensurately modulated magnetically ordered phases predominates the assumption and consideration of various complex types of magnetic order such as screw, cycloidal, helix, and others in most of the microscopic models of magnetoelectricity [4, 13]. From the macroscopic crystal symmetry point of view the close connection between the appearance of modulated and ferroelectric phases in magnetoelectrics was recently pointed out [10]. Whereas electric polarization indeed often occurs concurrently with complex modulated spin structures it can also be induced by commensurate magnetic order (such as the case, for example, in some rare-earth manganites RMn$_2$O$_5$ [14]).
Currently two models of ME coupling are widely accepted in the literature. In the model by Sergienko et al. [15] the electric polarization $\mathbf{P} \sim [\mathbf{S}_i \times \mathbf{S}_{i+1}]$ is induced by the Dzyaloshinskii–Moriya (DM) interaction between two magnetic ions $i$ and $i+1$ with superexchange. In the spin current model by Katsura et al. [16] the electric polarization is due to the spin supercurrent, $\mathbf{P} \sim \mathbf{\tilde{e}}_{ij} \times [\mathbf{S}_i \times \mathbf{S}_j]$, with $\mathbf{\tilde{e}}_{ij}$ being the unit vector connecting the sites $i$ and $j$. Interpretation of the experimentally observed polarization using these models meets difficulties though and has been a subject of critique [17, 18]. It was argued [18] that the DM coupling [15] is 2 orders of magnitude weaker than the induced polarization [18]. Several other mechanisms of the current model [16] the authors also overestimated by up to 2 orders of magnitude the value of the magnetically induced polarization [18]. Several other mechanisms of the ME effect have been proposed [18, 19] but as argued by the authors themselves they are insufficient to explain the magnetoelectricity in some Cu$^{2+}$ magnetoelectrics.

From our point of view, most of the microscopic models proposed so far do not take into account the macroscopic crystal symmetry, mainly focusing on three-site clusters (two metal ions and oxygen) and considering various spiral magnetic structures. The authors of the DM model of the ME effect [15], for example, applied it to the case of rare-earth manganites RMnO$_3$, whereas it can be shown that the macroscopic polarization vanishes when one considers orthorhombic symmetry of the unit cell. Indeed, the authors took TbMnO$_3$ as an example using the spiral magnetic structure available from neutron diffraction data. They considered the polarization induced in the $x$ and $y$ chains of Mn–O–Mn, but erroneously took into account only the $z = 0$ plane. Indeed, when one considers also the $z = 1/2$ plane (obtained from the first one by $\sigma_x(00\frac{1}{2})$) the macroscopic polarization cancels out.

The aim of any ME model is to find the mechanism of inversion symmetry breaking by magnetic order. At the same time, some authors explicitly start with a centrosymmetric cluster such as, for example, in the spin current [16, 20] or MeO$_4$ cluster models [18]. This dismisses the fact that in many magnetoelectrics some types of ions are located in noncentrosymmetric surroundings already in the paramagnetic phase. In this work, using MnWO$_4$ as an example, we suggest a microscopic magnetoelectric coupling model taking into account the macroscopic symmetry of the unit cell and the noncentrosymmetric surrounding of the Mn$^{2+}$ ions. We then apply our microscopic model to estimate the linear magnetoelectric coefficients in MnPS$_3$ and LiNiPO$_4$ and discuss its application to other magnetoelectrics.

## 2. The microscopic model

Wolframite, MnWO$_4$, possesses a monoclinic structure at room temperature (figure 1(a)) described by the space group $P2_1/c$ ($C_{2h}^2$). On lowering the temperature it undergoes a sequence of magnetic phase transitions at 13.5 K ($T_N$), 12.7 K ($T_2$) and 7.6 K ($T_1$), leading to the appearance of the magnetically ordered states AF$_3$, AF$_2$ and AF$_1$ [21], respectively. The low temperature phase AF$_1$ is characterized by the wave vector $\mathbf{k} = (1/4, 1/2, 1/2)$, whereas the incommensurate phases AF$_2$ and AF$_3$ are characterized by $(-0.214, 1/2, 0.457)$. Electric polarization in MnWO$_4$ appears in the AF$_2$ phase along the crystal $b$ axis [22]. The phenomenological model of phase transitions in wolframite was suggested earlier based on the assumption that the magnetic order is driven by the instability in the (1/4; 1/2; 1/2) point of the Brillouin zone [23]. However, for our purpose of building a microscopic model of the ME effect we first start with a hypothetical magnetic order with $k = 0$ in MnWO$_4$ (i.e. without multiplication of the unit cell) and then consider the real magnetic structure.

MnWO$_4$ contains two magnetic Mn$^{2+}$ ions, Mn$_1$ and Mn$_2$, in the unit cell located at positions (0.5; 0.6853; 0.25) and (0.5; 0.3147; 0.75), respectively. In the following we define the orthogonal $x$, $y$ and $z$ axes parallel to the $a$, $b$ and $c$ axes of the monoclinic cell, respectively. For the description of the magnetic order with $k = 0$ we can introduce ferromagnetic and antiferromagnetic order parameters $\mathbf{F} = \mathbf{S}_1 + \mathbf{S}_2$ and $\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2$, respectively, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the magnetic moments of Mn$_1$ and Mn$_2$. Table 1 summarizes the IRs possessed by the $P2_1/c$ space group in the center of the Brillouin zone and shows how the components of $\mathbf{F}$, $\mathbf{A}$ and the electric polarization $\mathbf{P}$ transform according to the symmetry operations of the group. As is evident from the table, the following magnetoelastic interactions are allowed by the macroscopic symmetry:

$$P_{\mu\alpha} A_{F\alpha}, \quad P_{\mu\alpha} A_{F\alpha}, \quad P_{\mu\alpha} A_{F\alpha}, \quad P_{\mu\alpha} A_{F\alpha},$$

where $\mu = x, y, z$ and $\alpha = x, y, z$. Thus any combination of ferromagnetic and antiferromagnetic ordering produces electric polarization. Polarization also arises in the case where only one of the Mn$^{2+}$ moments orders (e.g. when $\mathbf{S}_1 \neq 0$ and $\mathbf{S}_2 = 0$, which corresponds to $\mathbf{F} = \mathbf{A}$). Such collinear commensurate magnetic ordering gives no polarization according to any of the microscopic models proposed so far, since they are usually concentrated on noncollinear modulated
Table 1. IRs of the $P2_1/c$ space group corresponding to $\tilde{k} = 0$. The last column lists the components of $\tilde{F}$, $\tilde{A}$ and $\tilde{P}$ according to the IRs upon which they transform. Note that $\tilde{F}$ and $\tilde{A}$ are odd under time inversion.

| IR        | $C_2v(00\frac{1}{2})$ | $I(000)$ | Order parameters |
|-----------|------------------------|----------|------------------|
| GM$^{1+}$ | 1                      | 1        | $F_x$            |
| GM$^{1-}$ | 1                      | $-1$     | $P_y, A_y$       |
| GM$^{2+}$ | $-1$                   | 1        | $F_x, F_z$       |
| GM$^{2-}$ | $-1$                   | $-1$     | $P_x, P_z, A_x, A_z$ |

magnetic structures. Nevertheless, from the crystal symmetry point of view, such magnetic order breaks the crystallographic equivalency of the Mn$_1$ and Mn$_2$ atoms, which are connected by inversion (i.e. breaks the inversion symmetry), and electric polarization arises.

In order to build a valid microscopic model of ME interaction we proceed with the following consideration. First we note that the Mn$_1^{2+}$ ions in MnWO$_4$ are located in noncentrosymmetric positions. This can be seen from the fact that $I(000)$ interchanges Mn$_1$ and Mn$_2$ or by direct examination of the oxygen positions around the Mn$_2^{2+}$ ions [21]. Since $C_{2v}(00\frac{1}{2})$ transforms each Mn$_2^{2+}$ ion into itself their local crystal symmetry is $C_2$ as depicted in figure 1(b). Thus the manganese ions are located in polar surroundings and all their electrons’ orbitals have electric dipole moment along the $y$ axis. Every monoclinic cell has two Mn$_2^{2+}$ ions with opposite dipole moments, thus preserving zero dipole moment of the unit cell as schematically shown in figure 2(a).

Figure 2(b) shows an ion in a polar crystal environment (local symmetry $C_2$). All electron orbitals possess, therefore, an electric dipole moment. If one takes the spin degree of freedom into account then the spin–orbit coupling alters the electric dipole moment. When the spin is directed away from the two-fold rotational axis it breaks the rotational symmetry resulting in modification of the dipole moment as schematically shown in figure 2(c). We now proceed from this simple physics consideration to a semiquantitative quantum mechanical treatment.

The manganese ions in MnWO$_4$ are located in distorted oxygen octahedra as shown in figure 1(b). Therefore we start with a Mn$_2^{2+}$ ion in an octahedral crystal field and for simplicity consider only the $e_g$ orbitals. Inclusion of $t_{2g}$ levels is straightforward. Thus as a zeroth order perturbation we have

$$H_0|d_{\gamma}\rangle = E_{\gamma}|d_{\gamma}\rangle,$$

where $\gamma = z^2$ or $x^2 - y^2$. $H_0$ is the Hamiltonian including the octahedral splitting field and $E_{\gamma}$ is the $e_g$ energy level. Next, we include as perturbation the monoclinic crystal field of $C_2$ symmetry assuming the polar axis along the $z$ axis

$$V_{CF} = c_z z + c_{xy} x y + c'_{xy}(\lambda^2 - y^2) + c'_z z^2$$

and spin–orbit coupling

$$V_{SO} = -\lambda(\vec{L} \cdot \vec{S}).$$

Here $c_z, c_{xy}, c'_{xy}$ and $c'_z$ are coefficients, $\vec{L}$ is the angular momentum operator, $\vec{S}$ is the spin and $\lambda$ is the spin–orbit coupling constant. Thus, the perturbed Hamiltonian has the form $H = H_0 + V$, with $V = V_{CF} + V_{SO}$.

The perturbation $V$ mixes the unperturbed $3d$ $e_g$ states with other states and for simplicity it is sufficient to consider only the 4$p$ states $H_0|p_{\alpha}\rangle = E_{\alpha}|p_{\alpha}\rangle$ with the energy $E_{\alpha}, \alpha = x, y, z$. The two-fold degeneracy is removed in the first order and one can write for one of the perturbed eigenvectors

$$|\psi\rangle = |0\rangle + \sum_{\alpha} A_{\alpha}|p_{\alpha}\rangle,$$

where $A_{\alpha}$ are coefficients and $|0\rangle$ is an eigenvector from the subspace spanned by $|d_{\gamma}\rangle$. The electric dipole moment is given then by

$$\vec{d} = \langle \psi|\vec{e}\vec{r}|\psi\rangle = \sum_{\alpha} A_{\alpha}\langle 0|\vec{e}\vec{r}|p_{\alpha}\rangle + c.c.$$

Assuming $|0\rangle = q_1|d_{z^2}\rangle + q_2|d_{x^2-y^2}\rangle$ we obtain in the first order of perturbation the $z$-component of the electric dipole moment induced by the local crystal field

$$d_{0z} = \frac{2q_1^2 c_z e}\Delta.$$
where $\Delta = E_d - E_p$ and $t_{a,b,c} = \langle \psi_a | d_{oc} \rangle$. Due to the local C2 crystal field symmetry $d_{0x} = d_{0y} = 0$. Performing the perturbation up to the third order we get the spin-independent first order contribution and the spin-dependent part of the dipole moment as

$$
d_x = -Q_x \left( \frac{\lambda}{\Delta} \right)^2 S_x S_z, \\
d_y = -Q_y \left( \frac{\lambda}{\Delta} \right)^2 S_y S_z, \\
d_z = d_{0z} + Q_z \left( \frac{\lambda}{\Delta} \right)^2 (S_x^2 + S_y^2),
$$

(5)

where

$$
Q_{\alpha} = \frac{2q_1 e^2 r_{\alpha}^2 (q_1 I_{a,2}^z + q_2 I_{a,2}^{z-z})}{\Delta}.
$$

Thus, in addition to the crystal field induced electric dipole moment the spin–orbit coupling gives rise to a spin-dependent contribution.

We now apply the results obtained in the above case of magnetic ordering to MnWO4 with $k = 0$. Each unit cell has two Mn$^{2+}$ ions in opposite polar surroundings with polar axes along y. Therefore, using (5) for both of them and performing the proper cyclic permutation of indices $x, y, z$ we get the electric polarization

$$
P_x = -Q_x \frac{1}{2v} \left( \frac{\lambda}{\Delta} \right)^2 (A_x F_y + A_y F_x), \\
P_y = d_{0y} - Q_y \frac{1}{2v} \left( \frac{\lambda}{\Delta} \right)^2 (A_y F_x + A_x F_y), \\
P_z = -Q_z \frac{1}{2v} \left( \frac{\lambda}{\Delta} \right)^2 (A_x F_y + A_y F_x),
$$

(6)

where $v$ is the unit cell volume. Therefore, we obtain the same polarization as the one implied by the ME interactions (1). Figure 2(d) schematically illustrates relations (6) showing same polarization as the one implied by the ME interactions is given by $\vec{P} \sim \vec{F}$. The implications of the suggested microscopic model

The spin-dependent dipole moments (5) we assumed the polar spin–orbit coupling gives rise to a spin-dependent first order contribution and the spin-dependent part of the electric polarization

(6)

omitted. We find $\vec{P} \sim y(A_y F_x - A_x F_y, 0, A_y F_x - A_x F_y)$, where we used the unit vectors $\hat{e}_1 = (x, y, z)$ and $\hat{e}_2 = (-x, y, -z)$ for the two pairs discussed above ($\hat{e}_1$ is the unit vector connecting Mn1 and Mn2 inside the unit cell). Thus, in contrast to (6), both models fail to reproduce the magnetoelectric interactions of the form $P_x A_y F_x$, since these models require noncollinear spins (e.g. both of them give zero polarization for the hypothetical case of $\vec{F} = \vec{A}$ discussed above). Furthermore, the spin current model gives no electric polarization along the $b$ axis. Similarly to (6) both models do not give all of the magnetoelectric interactions present in (1), which may appear, though, upon quantum perturbations to higher orders in the respective models. From our point of view the relevant ME model may be case specific and further research in favor of one model over the other is required.

### 3. Magnetic ordering in MnWO4 with $\vec{k} = (1/4; 1/2; 1/2)$

Equations (6) give the electric polarization for magnetic structures with $k = 0$. In MnWO4 the magnetic phase transitions can be described by the order parameters with $k = (1/4; 1/2; 1/2)$ [23]. In this point of the Brillouin zone the space group $P2_1/c$ possesses two two-dimensional IRs, $G_1$ and $G_2$. Using the magnetic representation analysis conducted earlier [23], for every direction $\alpha = x, y, z$ we introduce two order parameters $(\eta_{1a}, \xi_{1a})$ and $(\eta_{2a}, \xi_{2a})$ transforming according to $G_1$ and $G_2$, respectively. The spin components along $x$ induced by these order parameters are given in table 2.

| $k$ | 0 · $\hat{a}_i$ | 1 · $\hat{a}_j$ |
|-----|-----------------|-----------------|
|     | $\hat{S}_{1a}$ | $\hat{S}_{2a}$ |
|     | $\eta_{1a} + \xi_{1a}$ | $\eta_{1a} + \xi_{1a}$ |
|     | $\eta_{2a} - \xi_{2a}$ | $\eta_{2a} - \xi_{2a}$ |
|     | $\eta_{1a} + \eta_{2a} + \xi_{1a} + \xi_{2a}$ | $\eta_{1a} + \eta_{2a} + \xi_{1a} + \xi_{2a}$ |
|     | $\eta_{1a} - \xi_{1a} + \eta_{2a} - \xi_{2a}$ | $\eta_{1a} - \xi_{1a} + \eta_{2a} - \xi_{2a}$ |

Table 2. Components along $x$ of Mn1 and Mn2 spins induced by $(\eta_{1a}, \xi_{1a})$ and $(\eta_{2a}, \xi_{2a})$ in the reference unit cell, $(0 · \hat{a}_i)$, and in the unit cell displaced by one period of translation along $a$, $(1 · \hat{a}_j)$. The last two lines show the spin structures in each cell rewritten in terms of $\vec{F}$ and $A$.

For every unit cell one can rewrite the spin components in table 2.

| $k$ | 0 · $\hat{a}_i$ | 1 · $\hat{a}_j$ |
|-----|-----------------|-----------------|
|     | $\hat{S}_{1a}$ | $\hat{S}_{2a}$ |
|     | $\eta_{1a} + \xi_{1a}$ | $\eta_{1a} + \xi_{1a}$ |
|     | $\eta_{2a} - \xi_{2a}$ | $\eta_{2a} - \xi_{2a}$ |
|     | $\eta_{1a} + \eta_{2a} + \xi_{1a} + \xi_{2a}$ | $\eta_{1a} + \eta_{2a} + \xi_{1a} + \xi_{2a}$ |
|     | $\eta_{1a} - \xi_{1a} + \eta_{2a} - \xi_{2a}$ | $\eta_{1a} - \xi_{1a} + \eta_{2a} - \xi_{2a}$ |

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Equations (6) give the electric polarization for magnetic structures with $k = 0$. In MnWO4 the magnetic phase transitions can be described by the order parameters with $k = (1/4; 1/2; 1/2)$ [23]. In this point of the Brillouin zone the space group $P2_1/c$ possesses two two-dimensional IRs, $G_1$ and $G_2$. Using the magnetic representation analysis conducted earlier [23], for every direction $\alpha = x, y, z$ we introduce two order parameters $(\eta_{1a}, \xi_{1a})$ and $(\eta_{2a}, \xi_{2a})$ transforming according to $G_1$ and $G_2$, respectively. The spin components along $x$ induced by these order parameters are given in table 2.

For every unit cell one can rewrite the spin components in terms of $\vec{F}$ and $A$ as shown in the table. Analogous analysis can be conducted for the $y$ and $z$ spin components.

The magnetic unit cell in MnWO4 is 16 times the crystallographic one. We now sum up $A_x F_x$ over the magnetic cell $\frac{1}{16} \sum A_x F_x = 2(\eta_{1a} \eta_{2a} + \xi_{1a} \xi_{2a})$ to obtain the electric polarization using (6):

$$
P_y = d_{0y} - \frac{2}{v} \left( \frac{\lambda}{\Delta} \right)^2 (\eta_{1a} \eta_{2a} + \xi_{1a} \xi_{2a}).
$$

(7)

Equation (7) gives $P_y$ in accordance with the polarization that can be derived from the ME interaction $P_x (\eta_{1a} \eta_{2a} + \xi_{1a} \xi_{2a})$ obtained from the macroscopic symmetry analysis [23]. In agreement with the experiment [22] and phenomenological model [23] $P_y$ arises in the AF2 phase when both $G_1$ and $G_2$ condense. Long-wavelength modulation does not lead to cancelation of (7) as shown earlier [23]. Similarly to (7)
other contributions to polarization can be obtained using the remaining ME interactions (1).

The numerical value of \( P_z \) from (7) for MnWO\(_4\) can be estimated as follows. We use the real crystal data and oxygen positions from [21] to perform the crystal field expansion (2) and obtain \( c_z \approx 4.9 \times 10^{-9} \) N and \( \nu \approx 138 \) Å\(^3\). For the matrix elements \( t_{a,y} \) we use the hydrogen-like orbitals and obtain \( t_{a,y} \approx 0.67 \alpha_0 / Z \), where \( \alpha_0 \) is the Bohr radius and \( Z \) is the charge of the nucleus and core electrons in units of \( e \).

Using \( Z \approx 5, \lambda \approx 0.05 \) eV, \( \Delta \approx 1 \) eV and \( q_1 \approx 1, \mu_1 \mu_2 \approx \xi_1 \xi_2 \) we obtain \( P_z \approx 17 \mu \text{C m}^{-2} \) in good agreement with the experimental value of the order of 50 \( \mu \text{C m}^{-2} \) [22, 24]. In this numerical estimate, however, we considered only one \( e_g \) level whereas other 3d electrons give comparable contributions to \( P_z \).

### 4. Discussion

Thus, we have built a microscopic model of ME interactions in magnetoelectrics using MnWO\(_4\) as an example. Starting with the hypothetical magnetic order with \( k = 0 \) we determined the ME interactions (1). Noting that the Mn\(^{2+}\) ions in wolframite are located in noncentrosymmetric polar surroundings we suggested a microscopic model of magnetoelectricity. The orbitals of the 3d electrons of Mn\(^{2+}\) ions possess electric dipole moments due to the crystal field influence, which gives rise to additional contributions (such as the considered 4p states) to their wave functions (4). The spin–orbit coupling (3) induces spin-dependent electric dipole moments (5) since the angular momentum operator \( \hat{L} \) mixes different \( |p_\alpha \rangle \) states. In this part our approach combining phenomenological and microscopic models resembles that suggested for the description of weak ferromagnetism by Dzyaloshinskii [25] and Moriya [26]. Our approach differs from those of Sergienko et al [15] and Katsura et al [16], who obtain the electric polarization as either \( \vec{P} \sim |S_i \times S_{i+1}| \) or \( \vec{P} \sim \vec{e}_y \times (|S_i \times S_j|) \), which is essentially the result of interacting spins located at two different ions. In contrast, in our model due to local noncentrosymmetry each magnetic ion has a spin-dependent electric dipole moment. We show that for certain spin configurations the sum over all magnetic ions of these spin-dependent electric dipole moments gives rise to macroscopic polarization.

We then apply this approach to describe real magnetic structures in MnWO\(_4\) with \( k = 1/4; 1/2; 1/2 \) by summing up local contributions to the polarization in every unit cell of the magnetic cell. Our approach naturally accounts for the macroscopic symmetry of the unit cell and is valid in cases of both collinear (hypothetical) magnetic ordering with \( k = 0 \) and the complex long-wavelength modulated magnetic structure observed in MnWO\(_4\).

We have chosen MnWO\(_4\) as an example since it has Mn\(^{2+}\) ions in polar surroundings and is directly applicable to our approach. At the same time magnetoelectrics with magnetic ions in a noncentrosymmetric environment are numerous and a brief review of the recently discovered multiferroics gives the following examples. Similarly to MnWO\(_4\) the local C\(_2\) symmetry is found for Fe\(^{3+}\) ions in NaFeSi\(_2\)O\(_6\) [27] and for Ni\(^{3+}\) ‘spine’ spins in Ni\(_3\)V\(_2\)O\(_8\) [28]. Local C\(_3\) symmetry is found for Cu\(^{2+}\) ions in LiCu\(_2\)O\(_2\) [29] and for one of the C\(_2\)\(^3+\) positions in \( \alpha\)-CaCr\(_2\)O\(_4\) [30]. All of the nonequivalent Fe\(^{3+}\) ions in FeVO\(_3\) [31] and FeTe\(_2\)O\(_3\)Br [32] have local C\(_1\) symmetry. For all these magnetic ions the linear in \( \Gamma \) part of the crystal field expansion can be written as \( V_{C\Gamma}(\vec{r}) = V_0 + \vec{c} \cdot \vec{r} \) with \( |\vec{c}| \) taking values from \( 9 \times 10^{-10} \) N for Ni\(_3\)V\(_2\)O\(_8\) to \( 6 \times 10^{-9} \) N for LiCu\(_2\)O\(_2\).

The magnetoelectric effect was recently found in manganese phosphorus trisulfide, MnPS\(_3\) [33]. MnPS\(_3\) possesses a monoclinic crystal structure \( C2/m \) and shows an antiferromagnetic collinear order with \( k = 0 \) below \( T_N = 78 \) K. Similarly to MnWO\(_4\) it has two Mn\(^{2+}\) ions in the unit cell with the local C\(_2\) symmetry, and our analysis performed above for \( k = 0 \) magnetic structures in wolframite is directly applicable to MnPS\(_3\). According to the neutron diffraction data the magnetic structure is characterized by \( A_1 \) and \( A_2 \neq 0 \) below \( T_N \). Thus, following equations (1) one can expect a linear magnetoelectric effect below \( T_N \) with magnetoelectric interactions \( P_\mu A_1 F_\nu, F_\mu A_2 F_\nu, F_\mu A_2 F_\nu, F_\nu A_2 F_\mu, F_\nu A_2 F_\mu, F_\mu A_2 F_\nu \), where \( \mu, \nu = x, z \). According to equations (6) the magnetoelectric coefficient \( \alpha_{yz} = dP_z/dH_\mu \), for example, can be estimated as \( \alpha_{yz} \approx \frac{1}{2} \eta_0 (1/\nu)(\Delta^2 A_z \cdot dF_\mu/dH_\nu, dF_\mu/dH_\nu \approx 2 \times 10^{-6} \mu \text{C m}^{-2} \) [34] and \( A_1 \sim 1 \). The polar local distortion of the Mn\(^{2+}\) environment in MnPS\(_3\) is much smaller than in wolframite, giving \( c_z \approx 1.4 \times 10^{-11} \) N. Using \( v \approx 207 \) Å\(^3\) we obtain \( \alpha_{yz} \approx 3.4 \times 10^{-8} \mu \text{C m}^{-2} \mu \text{eV}^{-1} \), which is rather small.

LiNiPO\(_4\) possesses an orthorhombic symmetry with space group \( Pnma \) and shows a linear magnetoelectric effect in the low temperature C-type commensurate antiferromagnetic phase with \( k = 0 \) below 20.8 K [35, 36]. The spins are predominantly directed along the \( c \) axis and the magnetic structure is described by the order parameter \( C_z \) transforming according to the IR \( GM^{4-} \). The phenomenological magnetoelectric interactions \( C_z P_x, C_z P_y \) and \( C_z P_x P_z \) were suggested earlier [35] and here we can estimate the magnetoelectric coefficient according to our microscopic model. Our microscopic approach differs from that suggested for LiNiPO\(_4\) earlier [37], which was based on lowering the superexchange interaction energy due to the uniform displacement of oxygen tetrahedra. The local symmetry of the Ni\(^{2+}\) ion surroundings is \( C_z \), with \( |\vec{c}| \approx 4.3 \times 10^{-9} \) N. Similarly to the above case of MnPS\(_3\) using \( dM_z/dH_\mu \approx 2 \times 10^{-12} \mu \text{B T}^{-1} \) per Ni-atom [36], we obtain an estimation of the value of the magnetoelectric coefficient, \( \alpha_{xz} \approx 0.31 \mu \text{C m}^{-2} \text{T}^{-1} \), in good agreement with the experimental value of 0.2 \( \mu \text{C m}^{-2} \text{T}^{-1} \) [35] and about three orders of magnitude higher than that in MnPS\(_3\).

At the same time in many other magnetoelectrics magnetic ions are located in centrosymmetric positions. Such is the case, for example, in the rare-earth manganites RRMnO\(_3\) [38] and CuO [39] where the local symmetry around Mn\(^{3+}\) and Cu\(^{2+}\) is \( C_z \). Nevertheless, our approach is valid also in these cases. The application of our model becomes more complicated and will be published elsewhere [40], but briefly can be described as follows. The local symmetry around the rare-earth ions in RRMnO\(_3\) is \( C_z \). The importance
of rare-earth ions in the formation of electric polarization in RMnO$_3$ was recently pointed out [41, 42]. Indeed, the magnetic order of the Mn$^{3+}$ ions induces magnetic ordering of the rare-earths through various exchange mechanisms, which makes our approach applicable. In the case of CuO the oxygens have local symmetry $C_2$. The role of the oxygen in the superexchange is still a subject of debate [18, 43]. As it is the intermediate ion conducting superexchange, O$^{2-}$ should possess an induced magnetic moment when the copper spins order, which again allows application of our model. The antiferromagnetic spin polarization at the oxygen sites was measured, for example, in the multiferroic TbMn$_2$O$_5$ [44].

The microscopic mechanism of the suggested ME model implies that the specific features of materials with large magnetically induced electric polarization are large local distortions breaking the inversion symmetry at magnetic sites and the presence of magnetic ions with large spin–orbit coupling. The suggested ME model is also directly applicable to magnetoelectrics, which crystallize in noncentrosymmetric positions. The model is illustrated by the examples of MnWO$_4$ and LiNiPO$_4$, for which we obtained good correspondence between the theoretical and experimental values of the electric polarization and magnetoelectric coefficient, respectively. We also give an estimate of the magnetoelectric coefficient in MnPS$_3$.

5. Conclusions

We have suggested a microscopic model of magnetoelectric interactions, which directly exploits the fact that in many magnetoelectrics the magnetic ions are located in noncentrosymmetric positions. The model is illustrated by the examples of MnWO$_4$ and LiNiPO$_4$, for which we obtained good correspondence between the theoretical and experimental values of the electric polarization and magnetoelectric coefficient, respectively. We also give an estimate of the magnetoelectric coefficient in MnPS$_3$.

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