Antiferromagnetic spin cantings as a driving force of ferroelectricity in multiferroic Cu$_2$OSeO$_3$

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Abstract
Ferroelectric properties of cubic chiral magnet Cu$_2$OSeO$_3$ can emerge due to the spin noncollinearity induced by antiferromagnetic cantings. The cantings are the result of the Dzyaloshinskii–Moriya interaction and in many ways similar to the ferromagnetic cantings in weak ferromagnets. An expression for the local electric polarization is derived, including terms with gradients of magnetization $\mathbf{M}(\mathbf{r})$. When averaged over the crystal the electric polarization has a non-vanishing part associated with the anisotropy of the crystal point group 23. In the framework of the microscopic theory, it is shown that both scalar and vector products of spins, $(s_1 \cdot s_2)$ and $[s_1 \times s_2]$, can give contributions of the same order of magnitude into the electric polarization.

Keywords: multiferroics, chiral magnets, magnetoelectric coupling, antiferromagnetic cantings

(Some figures may appear in colour only in the online journal)
then $H_{\text{ss}}$, required for full unwinding of the magnetic structure [18]. As will be shown in the paper, the noncollinearity induced by the cantings can lead to observable effects similar to those predicted by the single-spin model. In addition, new terms are predicted in the expression for the electric polarization, containing magnetization gradients.

Section 2 shows how the spin noncollinearity may give rise to a ferroelectricity in the type-II multiferroics. Section 3 provides a brief description of the magnetic properties of the chiral cubic magnets in two complementary models: the continuous phenomenological approximation and the discrete microscopic approach. In section 4 an expression is derived for the local electric polarization induced by a magnetization field. Section 5 discusses the polarization averaged over the crystal for different magnetic structures, including the A-phase. In section 6 a phenomenological theory is suggested, which describes adequately the magnetoelectric properties of the Cu$_2$OSeO$_3$ crystal. Section 7 briefly discusses the methods developed by other authors, and draws a comparison with the results obtained in the article.

2. Electric polarization in the type-II multiferroics

Unlike the type-I multiferroics, where the ferroelectric properties are determined by a crystal structure symmetry, in the type-II multiferroics the electric polarization appears simultaneously with a magnetic ordering, i.e. at a phase transition from the high-symmetry paramagnetic state to a low-symmetry ferromagnetic one. An additional condition of ferroelectricity is a noncollinear magnetic structure, which is often associated with gradients of the magnetization [19, 20]. Nevertheless, the noncollinearity due to cantings can cause a polarization even in the homogeneous state, where spirals are untwisted by an external magnetic field.

Within the framework of the microscopic description, a local electric polarization can be associated with pairs of neighboring magnetic atoms, and different models define it either through the scalar product of two spins $(s_1 \cdot s_2)$ [21–23], or through their vector product $[s_1 \times s_2]$ [21–26]. We will keep both of these products, because further arguments show that the contributions of these terms can be approximately of the same order of magnitude. Indeed, the energy associated with the interaction of spins $s_1$ and $s_2$ is

$$E_{\text{ss}} = -J_{12}(s_1 \cdot s_2) + D_{12} \cdot [s_1 \times s_2],$$

(1)

where parameters $J_{12}$ and $D_{12}$ correspond to the isotropic exchange and the Dzyaloshinskii–Moriya interaction, respectively. Let $q$ be a charge participating in the exchange interaction of the spins. It could be a charge of one of the interacting magnetic ions, 1 or 2, or a non-magnetic ion charge, through which superexchange interaction is performed. A displacement of the charge $q$ from its equilibrium position at a distance of $u$ should change the values of the interaction parameters resulting in a change in energy (1). This gives rise to a local electric dipole moment $p = qu$.

The total polarization of the bond is calculated as the sum over all charges involved in the magnetic interaction of two spins. A correction of spins $s_1$ and $s_2$ due to the change of the exchange parameters can also affect the energy. In order to avoid the difficulties of direct calculations and to take into account the symmetry of the crystal structure, it is convenient to introduce a phenomenological expression for the electric polarization of the bond,

$$p_{12,\alpha} = v_{\alpha}(s_1 \cdot s_2) + T_{\alpha \beta} [s_1 \times s_2]_{\beta}.$$ 

(2)

Here, vector $v$ possesses the point symmetry of bond 12, and pseudotensor $T$ is transformed as follows: it is symmetric with respect to all the symmetry transformations, which do not permute spins $s_1$ and $s_2$, and antisymmetric if the symmetry operation rearranges the spins (such a pseudotensor can be of form $T_{\alpha \beta} = T_{\alpha \beta} r_{12,\gamma}$, with $r_{12}$ being the distance between atoms 1 and 2).

In this model, the total electric moment density is the sum of the electric polarizations of all the bonds in the unit cell. Obviously, this takes into account the symmetry of the crystal. Assuming that $J_{12}(u)$ and $D_{12}(u)$ change significantly on the same length scale, the components of pseudotensor $T$ are less than the components of vector $v$ by a factor of order of $DIJ \ll 1$. Moreover, if we consider weak, also of order of $DIJ$, noncollinearity of spins, the first term in equation (2) is greater than the second one by approximately two orders of magnitude. However, upon averaging over all the bonds within the unit cell, e.g. in the case of cubic symmetry, $\langle v \rangle = 0$ and the contributions of the first and second terms in equation (2) can be of the same order.

3. Two approaches to the description of cubic helimagnets

3.1. Continuous approximation

The global magnetic structure of a cubic helimagnet can be described using the phenomenological Landau—Lifshitz theory, which in the simplest case is given by the energy [27]

$$E = J \frac{\partial M_0}{\partial r_j} \frac{\partial M_0}{\partial r_j} + D M \cdot [\nabla \times M] - H \cdot M,$$

(3)
where $J$ is an isotropic exchange parameter, $D$ is a constant of the Dzyaloshinskii–Moriya interaction, $H$ is an external magnetic field, and magnetization $M$ has a constant absolute value $M_0$. Minimization of (3) in the absence of a field ($H = 0$) gives the solution in the form of magnetic helix with the wavenumber $k = D/2J$, and the magnetization vector $M$ rotating in the plane perpendicular to the helix axis $n$. The direction $n$ is not fixed by the energy (3), but it can be easily found by taking into account the cubic crystal anisotropy [27]. Thus, there are two possible orientations of the spiral axis, either $(1 \ 0 \ 0)$ or $(1 \ 1 \ 1)$ (figure 2).

Upon application of a small magnetic field the helix axis becomes separated from the crystallographic direction and aligned along the field. A constant average magnetization along the field also appears. This kind of spiral structure is linearly with the field, and at $H = H_{c2} = D^2M_0/2J$ the cone collapses and the helix goes into a homogeneous state. Note that the wave number of the conical spiral does not depend on the magnetic field.

### 3.2. Microscopic details

The phenomenological theory describes magnetic structure as a continuous field of magnetization, $M(r)$. However, the magnetic moment is not smoothly distributed in a crystal-line space, but concentrated mostly near atoms discretely arranged in a lattice. Figure 3 shows a typical distribution of the magnetic moment density inside the unit cell, calculated with the open-source computer codes for electronic and magnetic structure calculations ‘Quantum ESPRESSO’ [28] (the details of the calculations will be published elsewhere). Thus, the actual magnetic structure has features, which are not described by the continuous model, but can be found in a microscopic approach, such as, for example, the Heisenberg model of chiral ferromagnet with energy [29–31]

$$E = \sum_{\langle ij \rangle} (-J_{ij} (s_i \cdot s_j) + D_{ij} \cdot (s_i \times s_j)) - \mathbf{H} \cdot \sum_i g_i \mu_B s_i \cdot$$

(4)

Here the first sum is taken over bonds $(ij)$ between magnetic atoms, the second one is over the atoms $(i)$. $g_i \mu_B s_i$ is the magnetic moment of the $i$th atom, $s_i$ is its classical spin $(|s_i| = 1)$, $J_{ij}$ and $D_{ij}$ are parameters characterizing the isotropic exchange and the Dzyaloshinskii–Moriya interaction.

It has been shown in [17, 18, 32, 33], that there is a transition from equation (4) to equation (3), and phenomenological constants $J$ and $D$ can be calculated as functions of $J_{ij}$ and $D_{ij}$ at least for smoothly varying magnetic structures. Some features of the spin structure are revealed beyond the continuous model. In particular, it is found that, if the unit cell of a crystal contains several magnetic atoms, then each individual spin is tilted from the average direction of magnetization (figure 4(a)). These tilts, called cantings, in the first approximation, have the form $[\rho_i \times \mu]$, where $\mu = M/M_0$ is the magnetization direction near the atom, and the “canting angle” $\rho_i$ has the following properties: (1) $\rho_i$ possesses the symmetry of the atomic position; for example, for the $B20$ structure, where the atoms lie on the 3-fold axes of the crystal, the vectors $\rho_i$ are also directed along the local 3-fold axes; (2) canting angles of equivalent atoms in the unit cell are connected to each other by the symmetry transformations of the crystal point group [17]. The spin tilts can reach up to ten degrees for Cu2OSeO3 [17], and they are weakly dependent on the magnetic field strength. Indeed, the dependence is determined by multiplier $(aJ + b\mu_0H)^4$, with $J$ being a characteristic isotropic exchange value [18]. Giving the fact that a nonhomogeneous magnetization can exist at $H < H_c2 \ll J\mu_0$, we can neglect the influence of the magnetic field on cantings.

Another kind of cantings is associated with spatial gradients of $M(r)$. When the magnetization varies smoothly along the crystal, such as forming a magnetic helix, it is

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**Figure 2.** In the absence of an external magnetic field, due to the cubic anisotropy there are two possible orientations of the magnetic helix, either $(1 \ 0 \ 0)$ (blue) or $(1 \ 1 \ 1)$ (red) depending on cubic anisotropy [27]. In a magnetic field the helix becomes conical and aligned along the field (green).

**Figure 3.** The calculated distribution of $m_z$ component of the magnetic moment density in the unit cell of Cu2OSeO3. The magnetic field $H$ is directed along the $z$ axis. The picture shows the plane $z = 0.875$, near which four copper atoms are placed: three Cu-II and one Cu-I (in the top right corner). The insets show distribution of small $m_x$ and $m_y$ components of the local magnetization, corresponding to spin tilts from the $z$ axis.
necessary to consider several spin spirals (according to the number of magnetic atoms in the unit cell) with phase shifts between them determined from minimization of equation (4) (figure 4(b)). This problem can be solved by assuming that the atoms are placed in some fictitious positions (shown in gray) makes all the helices co-phased. Shown are the manganese atoms in the MnSi crystal. The directions of cantings and shifts are chosen as in the B20 structure; their absolute values, as well as the helix wavenumber are enlarged for visibility.

Figure 4. Two kinds of cantings. (a) Because of the Dzyaloshinskii–Moriya interaction all the spins are tilted from the magnetization \( \mathbf{M} \). (b) Every magnetic position in the unit cell is connected with an individual spin helix; the ‘shift’ of the atoms to fictitious positions (shown in gray) makes all the helices co-phased. Shown are the manganese atoms in the MnSi crystal. The directions of cantings and shifts are chosen as in the B20 structure; their absolute values, as well as the helix wavenumber are enlarged for visibility.

As a result, in the first approximation, the cantings are small (of the order of \( D/J \)) corrections to the spins, almost perpendicular to the magnetization direction \( \mu \). In addition, the sum of the cantings of all spins in the unit cell, \( \sum \rho_i \times \mu \), is equal to zero by virtue of the cubic symmetry of the crystal. This allows us to consider the cantings as a demonstration of a weak antiferromagnetism on the background of a strong ferromagnetic state. Thus, this case is symmetric to the case of a weak ferromagnet, where weak cantings against the background of an antiferromagnetic spins give rise to a small net magnetization [35, 36].

Both kinds of cantings discussed above are important for macroscopic properties of the crystal. For example, they are needed for the correct calculation of the phenomenological constants \( J \) and \( D \) of the model (4) [17]. As will be shown later, the cantings can also give rise to an electric polarization of multiferroics. Recently [37], some microscopic details of the spin structure of the helimagnet MnSi were experimentally observed, that could be interpreted as the cantings of the second kind, associated with gradients of the magnetization (figure 4(b)).

Along with the spin cantings, caused by the Dzyaloshinskii–Moriya interaction and the twist of the magnetic structure, there are spin tilts arising from the interaction with a local crystal field. These tilts are of the form \( \pm \alpha_i \cdot \mu || (\alpha_i \times \mu) \times \mu \), where vectors \( \alpha_i \) have the same symmetry properties as \( \rho_i \). Note that for the B20 structure, where the atoms lie on the axes 3, the vectors \( \rho_i \) and \( \alpha_i \) are collinear to the axes and, therefore, the cantings owing to the Dzyaloshinskii–Moriya interaction and the local anisotropy should be perpendicular to each other. Below, we will not consider the cantings due to the local crystal field, neglecting their possible participation in the formation of the electric polarization.

### 4. Electric polarization in cubic chiral magnets

Let us consider the cubic crystals of the space group \( P2_13 \), exemplified by the B20 structure magnets (MnSi, MnGe, etc) and Cu2OSeO3. It is known that due to the chirality of the crystals a magnetic helix can arise, simple or conical (the latter in an external magnetic field), with a helical pitch much greater than the period of the crystal lattice. For instance, in the Cu2OSeO3 crystal the helix pitch is about 70 lattice periods. The bonds between the magnetic atoms in the structures do not have symmetry elements, and therefore all \( \mathbf{v} \) and \( \mathbf{T} \) are vectors and pseudotensors of general form.

Because the electric polarization is an additive vector, we can consider only one of the equivalent bonds within the unit cell. In order to calculate the spin directions, we will replace the discrete magnetic moments by continuous spin fields [17, 33]. So, the polarization will also be a continuous function of the spatial coordinates.

Suppose that the macroscopic magnetization in atomic position 1 is directed along a unit vector \( \mu \). Then the spins of the magnetic atoms in two close positions 1 and 2 can be defined as
are invariants of the symmetry operations of \( R \). This rotation enhances the symmetry to \( cT \), where the sum is taken over the perpendicular to \( \mu \) spin change of the first order in \( D/J \), and the last term in the parentheses represents the reduction of the spin along \( \mu \), being of the second order in \( D/J \).

The canting of spin 1 is associated with the Dzyaloshinskii–Moriya interaction only,

\[
w_{\perp 1} = [\rho_1 \times \mu],
\]

whilst spin 2 has an additional tilt due to the global twist of the magnetic structure,

\[
w_{\perp 2} = [\rho_2 \times \mu] + k(\mathbf{n} \cdot \mathbf{r}_{12})(\mathbf{n} \times \mu).
\]

Here, \( k \) and \( \mathbf{n} \) are the helix wavevector and direction, respectively, and \( \rho_1 \) are the canting angles corresponding to the atomic positions within the unit cell.

Note that vector \( \mathbf{r}_{12} \) contains the exchange coordinates of the atoms, which are functions of the isotropic exchange parameters \( J_{ab} \). The product \( (\mathbf{n} \cdot \mu) \) is equal to zero for the simple helices and has a non-zero constant value for each of the conical spirals.

In order to calculate the contribution of the bond to the polarization, it is necessary to average equation (2) over the operations of the point symmetry group 23. Note that these operations act on vectors \( \mathbf{v}, \rho_1, \rho_2, \mathbf{r}_{12} \) and pseudotensor \( T \), whereas \( \mathbf{n} \) and \( \mu \) assumed to be invariant for the given point. We can also use the weakness of the Dzyaloshinskii–Moriya interaction (D), as compared with the isotropic exchange (J):

\[
\rho \sim k \sim T/v \sim D/J \ll 1.
\]

Upon averaging, the terms of the zero and first orders in \( D/J \) disappear. We confine ourselves to second-order terms. Then averaging of equation (2) gives

\[
\langle \mathbf{p} \rangle = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 + \mathbf{p}_4,
\]

\[
\mathbf{p}_1 = a(\mu_{1z}, \mu_{1z}, \mu_{1z}),
\]

\[
\mathbf{p}_2 = bk\{(n_{1z}, n_{1z}, n_{1z}, n_{1z}) - (n \cdot \mu)(n_{1z}, n_{1z}, n_{1z}, n_{1z})\},
\]

\[
\mathbf{p}_3 = ck\{(n_{1z}, n_{1z}, n_{1z}, n_{1z}) - (n \cdot \mu)(n_{1z}, n_{1z}, n_{1z}, n_{1z})\},
\]

\[
\mathbf{p}_4 = dl^2\{(1 - (n \cdot \mu)^2)(n_{1z}, n_{1z}, n_{1z}, n_{1z})\}.
\]

The coefficients \( a, b, c, \) and \( d \) are calculated by the formulas

\[
a = c\varepsilon_{12}\{(R + L)(v \otimes \Delta \rho \otimes \Delta \rho) - 6 - [R + L](T \otimes \Delta \rho)\}/3,
\]

\[
b = c\varepsilon_{12}\{-[(R \otimes \mathbf{r}_{12} \otimes \Delta \rho) + L(T \otimes \mathbf{r}_{12})]/3\},
\]

\[
c = c\varepsilon_{12}\{-[(R \otimes \mathbf{r}_{12} \otimes \Delta \rho) - R(T \otimes \mathbf{r}_{12})]/3\},
\]

\[
d = c\varepsilon_{12}\{(R + R)(v \otimes \mathbf{r}_{12})\}/6.
\]

The smallness of coefficients \( a, b, c, d \) depends, therefore, on how close the symmetry of the crystal is to the point group 432. It has been shown in [17] that the cubic crystal \( \text{Cu}_2\text{OSeO}_3 \), first described in [38], can be seen as deformed structure of a crystal with the space group \( \text{P}4_132 \). Because this group contains right-handed axes \( 4_1 \), it is natural to call the crystal described in [38] a right one, and its mirror-image enantiomer a left one. The left crystal \( \text{Cu}_2\text{OSeO}_3 \) also possesses the spatial symmetry \( \text{P}2_13 \), but its structure is approximated by the high-symmetry group \( \text{P}4_132 \) with left-handed axes \( 4_3 \). We can assume that for \( \text{Cu}_2\text{OSeO}_3 \) coefficients \( a, b, c, d \) of the anisotropic terms can be small. Nevertheless, it is possible that there are crystals of the group \( \text{P}2_13 \), whose structures are not approximated by high-symmetry groups, and these coefficients are large.

It is useful to explore the symmetry properties of equations (9) and (10) under inversion, changing the chirality of the crystal. The quantities determining the coefficients (10) possess the following properties: \( \mathbf{v} \) and \( \mathbf{r}_{12} \) are vectors, \( T \) is a pseudotensor, the canting angles \( \rho_i \) are axial vectors (pseudovectors). It is easy to find that \( b \) and \( c \) are scalars, whereas \( a \) and \( d \) are pseudoscalars. The pseudovector \( \mu \) and the helix direction \( \mathbf{n} \), whose symmetry is similar to that of a liquid crystal director, are presented in quadratic combinations only; whereas the magnetic chirality of the crystal is fully determined by a pseudoscalar wavenumber \( k \). So, the invariance of coefficients \( b \) and \( c \) is compensated by the change of the sign of \( k \) and, as expected, the electric polarization changes the sign under inversion. All the above can be summarized as follows:

\[
I:
\]

\[
\mathbf{v} \to -\mathbf{v}, \mathbf{r}_{12} \to -\mathbf{r}_{12}, T \to -T, \rho_i \to \rho_i,
\]

\[
a \to -a, b \to b, c \to c, d \to -d,
\]

\[
\mu \to \mu, \mathbf{n} \to \pm \mathbf{n}, k \to -k, \mathbf{p} \to -\mathbf{p}.
\]
5. Electric polarization averaged over crystal

The part of the electric polarization described by equation (11) vanishes both for the cases of a simple helix \((\mathbf{n} \perp \mathbf{\mu})\) and a homogeneous magnetization \((\mathbf{n} || \mathbf{\mu})\), and has a maximum value in the external magnetic field with magnitude of \(H_c\), when the angle between vectors \(\mathbf{n}\) and \(\mathbf{\mu}\) is equal to \(\pi/4\). In addition, when moving along the helix, the polarization vector described by equation (11) rotates in the plane perpendicular to \(\mathbf{n}\), therefore its average value is zero. However, in the case of the space group \(P2_13\), there exists an electric polarization associated with the crystal anisotropy, and its average value over the crystal can differ from zero.

Indeed, averaging of equation (9) over the crystal gives

\[
\langle \mathbf{P} \rangle = \left[ (Dk^2 + Bk + Ck - A/2) - (Dk^2 + Bk + Ck - 3A/2)(\mathbf{n} \cdot \mathbf{\mu})^2 \right] \mathbf{n} \cdot (n, n_x, n_y, n_z),
\]

(13)

where constants \(A, B, C, D\) arise from \(a, b, c, d\) after summing over all the bonds in the unit cell. Recall that equation (9), and hence equation (13), is derived for a conical spiral in an external magnetic field, particular cases of which are the simple helix at \(H = 0\) and the homogeneous state at \(H > H_c\). The product \((\mathbf{n} \cdot \mathbf{\mu})\) changes linearly from 0 to 1 with increase of \(H\) from 0 to \(H_c\), and thus, the electric polarization magnitude \(\langle \mathbf{P} \rangle\) is a quadratic function of the field. Measurements of \(\langle \mathbf{P} \rangle\) for different magnetic field values allow us to distinguish \(A\) and \(Dk^2 + Bk + Ck\). In principle, the separation of coefficient \(D\) and \(B + C\) is also possible, measuring the electric polarization for spirals with different wavenumbers. The difficulty here is that the equilibrium value of \(k\) is determined by the ratio of the parameters of the isotropic exchange and the Dzyaloshinskii–Moriya interaction. The spirals with different \(k\) can be obtained, for example, by fixing the magnetization direction at the boundaries of a thin crystalline sample. Finally, equation (13) does not imply a possibility of separation of coefficients \(B\) and \(C\); this will require a more subtle experiment to measure the local electric polarization \(\mathbf{P}\).

5.1. Average electric polarization of the A-phase

The A-phase possesses a hexagonal symmetry and more complex structure compared to the helices [39-41]. There is an energy gain in the A-phase due to the double twist of the magnetization direction \(\mathbf{\mu}\). Whilst the spatial orientation of a helix is defined only by vector \(\mathbf{n}\), in order to describe the A-phase, two perpendicular vectors are needed: \(\mathbf{\pi}\), directed along an applied magnetic field and perpendicular to the plane of vortices, and \(\mathbf{e}_\phi\), specifying an azimuthal rotation angle of the triangular lattice of vortices (figure 5(a)). As in the case of a conical spiral, the average magnetic moment is different from zero and directed along \(\mathbf{\pi}\). The diffraction pattern contains six symmetrically spaced peaks with a wavenumber close to that of the helical structure (figure 5(b)). We can assume that, in the simplest approximation, the A-phase is a superposition of a homogeneous magnetization field with \(\mathbf{\mu} || \mathbf{\pi}\) and three perpendicular to \(\mathbf{\pi}\) helices with the angles of \(2\pi/3\) between them. Assuming the additivity of the electric polarization, it is easy to find that the average polarization does not depend on the azimuthal angle and is determined only by \(\mathbf{\pi}\)-vector, so that \(\langle \mathbf{P} \rangle \sim (n, n_x, n_y, n_z).

5.2. The angular dependence of the electric polarization

Summarizing the results of this section, the average electric polarization for different magnetic structures observed in the cubic multiferroics with the space group \(P2_13\) can be written in general form as

\[
\langle \mathbf{P} \rangle \sim (e_x e_z, e_y e_z, e_y e_z),
\]

(14)

where unit vector \(\mathbf{e}\) can take the values \(\mathbf{\mu}, \mathbf{n}, \mathbf{\pi}\), and \(\mathbf{\pi}\), respectively, for a homogeneous magnetization field, a single spiral, and the A-phase. The components of \(\mathbf{e}\) are defined in the Cartesian system associated with the cubic crystal lattice. It can be seen that the angular dependence of the average polarization on the direction of \(\mathbf{e}\) is strongly anisotropic. Thus, the polarization magnitude

\[
|\langle \mathbf{P} \rangle| \sim \sqrt{1 - e_x^2 - e_y^2 - e_z^2}
\]

(15)

varies from zero for \(\mathbf{e} \sim (100)\) to its maximum value for \(\mathbf{e} \sim (111)\) (figure 6). In principle, the average electric polarization \(\langle \mathbf{P} \rangle\) can be at an arbitrary angle to \(\mathbf{e}\). For example, the polarization is parallel to \(\mathbf{e}\) for directions (111), and perpendicular to it for directions (110).

In the case of a homogeneous magnetization field \(\mathbf{\mu}\), equation (14) has been derived in [9] using a single-spin model and confirmed experimentally for Cu2OSeO3 crystal [2, 6].
Figure 6. The dependence of the average electric polarization and its absolute value (in the corner) on the orientation of the magnetic structure with respect to the crystallographic axes in a chiral cubic multiferroic with the space group $P2_13$. The polarization is maximal for the crystallographic directions $(111)$ and zero for $(100)$.

6. The phenomenological expression for electric polarization

The equation (9) for the electric polarization is derived for the case of a spiral magnetic structure and contains the wave-number $k$ and the helix axis direction $\mathbf{n}$. The helical twist, however, is not the only possible type of spin ordering, and, in particular, the A-phase in MnSi and Cu$_2$OSeO$_3$ crystals possesses a complex magnetic structure with a double twist of the magnetization [39-41]. In general, an arbitrary field $\mathbf{M}(\mathbf{r})$ should be considered with a possible restriction concerning the constancy of its magnitude, $\mathbf{M}(\mathbf{r}) = M_0 \mathbf{\mu}(\mathbf{r})$. In this case it is necessary to replace equation (9) by expressions for the electric polarization, depending only on $\mathbf{\mu}$ and its spatial derivatives. These expressions can serve as a basis for a continual phenomenological theory, which describes the appearance of ferroelectricity as a result of a magnetic ordering in the crystal.

In the case of a conical spiral, the derivatives of the magnetization direction $\mathbf{\mu}$ are of the form

$$\frac{\partial \mathbf{\mu}}{\partial r_i} = k n_\alpha (\mathbf{n} \times \mathbf{\mu}), \alpha = x, y, z.$$  \hspace{1cm} (16)

Using equation (16), it is easy to find a generalization of equation (9) for an arbitrary field $\mathbf{\mu}(\mathbf{r})$:

$$\mathbf{P} = \mathbf{P}_{iso} + \mathbf{P}_A + \mathbf{P}_{BC} + \mathbf{P}_D,$$

$$\mathbf{P}_{iso} = \frac{B - C}{2} (\mathbf{\mu}(\nabla \cdot \mathbf{\mu}) - (\mathbf{\mu} \cdot \nabla) \mathbf{\mu}),$$

$$\mathbf{P}_A = A (\mu_x \mu_z - \mu_z \mu_x + \mu_y \mu_y),$$

$$\mathbf{P}_{BC} = \frac{B + C}{2} \left( \begin{array}{c} \frac{\partial \mu_x}{\partial y} - \frac{\partial \mu_y}{\partial x} - \frac{\partial \mu_z}{\partial x} + \frac{\partial \mu_x}{\partial z} \\ \frac{\partial \mu_y}{\partial z} - \frac{\partial \mu_z}{\partial y} - \frac{\partial \mu_x}{\partial y} + \frac{\partial \mu_y}{\partial x} \\ \frac{\partial \mu_z}{\partial x} - \frac{\partial \mu_x}{\partial z} - \frac{\partial \mu_y}{\partial x} + \frac{\partial \mu_z}{\partial y} \end{array} \right),$$

$$\mathbf{P}_D = D \left( \begin{array}{c} \frac{\partial \mu_x}{\partial y} \frac{\partial \mu_y}{\partial z} \frac{\partial \mu_z}{\partial x} \frac{\partial \mu_x}{\partial z} \frac{\partial \mu_y}{\partial x} \frac{\partial \mu_z}{\partial y} \end{array} \right).$$  \hspace{1cm} (17)

Here $\mathbf{P}_{iso}$ is corresponding to equation (11) ‘isotropic’ contribution, which does not depend on the orientation of the magnetic structure with respect to the crystallographic axes. On the other hand, terms $\mathbf{P}_A$, $\mathbf{P}_{BC}$, and $\mathbf{P}_D$ are associated with the cubic anisotropy of the considered crystals (vector $\mathbf{P}_{BC}$ written in a column for convenience). All contributions are of the same order in $D/J$, however, as has been discussed above, the anisotropic terms may have an additional degree of smallness for symmetry reasons. Thus, $\mathbf{P}_A$, $\mathbf{P}_{BC}$, and $\mathbf{P}_D$ are nonzero for the crystals of the point group 23, but disappear when the symmetry is enhanced to 432.

In order to obtain equation (17) within the framework of the phenomenological theory, the free energy expression should contain the term of the form

$$F_p \sim P^2/2 - \mathbf{P}_s \cdot (\mathbf{P}_{iso} + \mathbf{P}_A + \mathbf{P}_{BC} + \mathbf{P}_D).$$  \hspace{1cm} (18)

7. Discussion

In [19, 20] an expression for the electric polarization is found, which coincides with term $\mathbf{P}_{iso}$ in equation (17). It was shown above that $\mathbf{P}_{iso}$ is the main contribution to the local polarization, but, under the condition $\nabla \cdot \mathbf{M} = 0$, valid in some important cases, such as simple and conical helical magnetic structures, $\mathbf{P}_{iso}$ reduces to a surface term and its impact to the average electric polarization becomes negligible. Here we show that, along with the polarization $\mathbf{P}_{iso}$ for an isotropic magnetic medium, there exist terms associated with the crystal anisotropy, cubic in our case. These terms ($\mathbf{P}_A$, $\mathbf{P}_{BC}$, $\mathbf{P}_D$) cause a nonzero electric polarization when averaged over the crystal, which allows to control the magnetic structure of multiferroic Cu$_2$OSeO$_3$ by the electric field.

An alternative microscopic approach, which takes into account the anisotropy of cubic crystal, is developed in [9]. In particular, the expression (14) is found, connecting the electric polarization with the magnetization at a given point. However, in order to derive equation (14) without taking into account the spin cantings, a single-spin model has been used, with the local polarization being calculated by summing the terms of form $r_s(s_i r_j)^2$, where $s_i$ is the spin of the $i$th ion Cu$_{2}^{2+}$ and $r_s$ is the distance from the copper atom to the neighboring $j$th ion O$^{2-}$ [6, 9, 16]. A more general single-spin model has been used in [42]. As a result, the local polarization has no the gradient part, including the largest contribution $\mathbf{P}_{iso}$. In the present paper, we use a model that takes into account the spin noncollinearity due to the cantings in order to derive terms $\mathbf{P}_{iso}$, $\mathbf{P}_{BC}$, $\mathbf{P}_D$ containing spatial derivatives of the magnetization. The choice between the single-spin and two-spin models can be made experimentally. This requires measuring the average electric polarization of the conical magnetic helix occurring in a bulk sample in an external magnetic field with intensity varying from zero to $H_{z}$. To compare with theory, equation (13) can be used, with the single-spin model corresponding to the additional condition $B = C = D = 0$. The experiment will separate the values of $A$ and $Dk^2 + Bk + Ck$, etc.
and, if the latter is not zero, the two-spin model of the electric polarization is needed.

The appearance of ferroelectricity in the chiral type-II multiferroics can be also considered within the framework of a phenomenological approach [43–48]. The method is especially effective for description of the phase transition from the paramagnetic phase to a low-temperature multiferroic state. In this case, the expression for the free energy contains terms permitted by the crystal point symmetry, which connect the electric polarization \( \mathbf{P} \) with the magnetization \( \mathbf{M} \) and its spatial derivatives. Besides, as a rule, restrictions are imposed on the power and the number of derivatives, reflecting the characteristic smallness of spatial gradients. For the chiral magnets discussed in the paper it is determined by the smallness of the Dzyaloshinskii–Moriya interaction as compared with the isotropic exchange, \( \mathcal{D}J \ll I \). The result obtained from our microscopic consideration shows that terms with different numbers of derivatives may be of the same order in \( \mathcal{D}J \). Thus, equation (17) contains the terms \( P_{x}, P_{yc}, \) and \( P_{y} \) of comparable magnitude with 0, 1 and 2 derivatives, respectively. These terms should be taken into account in the phenomenological description, e.g. by including the term (18) into the free energy.

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References

[1] Pyatakov A P and Zvezdin A K 2012 Magnetoelastic and multiferroic media Phys. Usp. 55 557–81
[2] Seki S, Yu X Z, Ishiwata S and Tokura Y 2012 Observation of skyrmions in a multiferroic material Science 336 198–201
[3] Adams T, Chacon A, Wagner M, Bauer A, Brandl G, Pedersen B, Berger H, Lemmens P and Pfleiderer C 2012 Long-wavelength helimagnetic order and skyrmion lattice phase in Cu₂OSeO₃ Phys. Rev. Lett. 108 237204
[4] Seki S, Kim J-H, Inosov D S, Georgii R, Keimer B, Ishiwata S and Tokura Y 2012 Formation and rotation of skyrmion crystal in the chiral-lattice insulator Cu₂OSeO₃ Phys. Rev. B 85 220406
[5] Onose Y, Okamura Y, Seki S, Ishiwata S and Tokura Y 2012 Observation of magnetic excitations of skyrmion crystal in a helimagnetic insulator Cu₂OSeO₃ Phys. Rev. Lett. 109 037603
[6] Seki S, Ishiwata S and Tokura Y 2012 Magnetoelastic nature of skyrmions in a chiral magnetic insulator Cu₂OSeO₃ Phys. Rev. B 86 060403
[7] Belesly M, Rouschakizaki I, Abid M, Röllle U K, Berger H and Ansermet J-P 2012 Magnetoelastic effects in single crystals of the cubic ferrimagnetic helimagnet Cu₂OSeO₃ Phys. Rev. B 85 224413
[8] Jansoon O, Rouschakizaki I, Tsirilin A A, Belesly M, Leonov A A, Röllle U K, van den Brink J and Rosner H 2014 The quantum nature of skyrmions and half-skyrmions in Cu₂OSeO₃ Nat. Commun. 5 5376
[9] Mochizuki M and Seki S 2015 Dynamical magnetoelectric phenomena of multiferroic skyrmions J. Phys.: Condens. Matter. 27 503001
[10] Ovchinnikov S G and Rudenko V V 2014 Anisotropic interactions in magnetic crystals with S-state ions. Nanostructures Phys.—Usp. 57 1180–98
[11] Grigoriev V S, Maleyev S V, Okorokov A I, Chetverikov Yu O, Boni P, Georgii R, Lamago D, Eckerlebe H and Pranzas K 2006 Magnetic structure of MnSi under an applied field probed by polarized small-angle neutron scattering Phys. Rev. B 74 214414
[12] Mühlbauer S, Binz B, Jonietz F, Pfleiderer C, Rosch A, Neubauer A, Georgii R and Böni P 2009 Skyrmion lattice in a chiral magnet Science 323 915–9
[13] Münzer W et al 2010 Skyrmion lattice in the doped semiconductors Fe₃₋ₓCoₓSi Phys. Rev. B 81 041203
[14] Adams T et al 2011 Long-range crystalline nature of the skyrmion lattice in MnSi Phys. Rev. Lett. 107 217206
[15] White J S et al 2012 Electric field control of the skyrmion lattice in Cu₂OSeO₃ J. Phys.: Condens. Matter. 24 432201
[16] Ruff E, Lunkenheimer P, Loidl A, Berger H and Krohns S 2015 Magnetoelastic effects in the skyrmion host material Cu₂OSeO₃ Sci. Rep. 5 15025
[17] Chizhikov V A and Dmitrienko V E 2015 Microscopic description of twisted magnet Cu₂OSeO₃ J. Magn. Magn. Mater. 382 142–51
[18] Dmitrienko V E and Chizhikov V A 2012 Weak antiferromagnetic ordering induced by Dzyaloshinskii–Moriya interaction and pure magnetic reflections in MnSi-type crystals Phys. Rev. Lett. 108 187203
[19] Mostovoy M 2006 Ferroelectricity in spiral magnets Phys. Rev. Lett. 96 067601
[20] Pyatakov A P, Sergeev A S, Nikolaeva E P, Kosykh T B, Nikolaev A V, Zvezdin K A and Zvezdin A K 2015 Micromagnetism and topological defects in magnetoelectric media Phys. Usp. 58 981–92
[21] Chapon L C, Radaelli P G, Blake G R, Park S and Cheong S-W 2006 Ferroelectricity induced by acentric spin-density waves in YMn₂O₅ Phys. Rev. Lett. 96 097601
[22] Jia C, Onda S, Nagaosa N and Han J H 2007 Macroscopic theory of spin-polarization coupling in multiferroic transition metal oxides Phys. Rev. B 76 144424
[23] Zobkalo I A, Gayrivol S V, Sav Nyi N Z, Barilo S N and Shiryaev S V 2014 Magnetic ordering in NdMn₂O₅ studied by the neutron diffraction J. Magn. Magn. Mater. 354 85–9
[24] Katsura H, Nagaosa N and Balatsky A V 2005 Spin current and magnetoelectric effect in noncollinear magnets Phys. Rev. Lett. 95 057205
[25] Arima T-H 2007 Ferroelectricity induced by proper-screw type magnetic order J. Phys. Soc. Japan 76 073702
[26] Radaelli P G and Chapon L C 2008 A neutron diffraction study of RMn₂O₅ multiferroics J. Phys.: Condens. Matter. 20 434213
[27] Bak P and Jensen M H 1980 Theory of helical magnetic structures and phase transitions in MnSi and FeGe J. Phys. C: Solid State Phys. 13 L881–5
[28] http://quantum-espresso.org/
[29] Hopkinson J M and Kee H Y 2009 Origin and consequences of unpinned helical order: application to MnSi under pressure Phys. Rev. B 79 014421
[30] Shekhtman L, Entin-Wohlman O and Aharony A 1992 Moriya’s anisotropic superexchange interaction, frustration and Dzyaloshinsky’s weak ferromagnetism Phys. Rev. Lett. 69 836–9
[31] Yildirim T, Harris A B, Aharony A and Entin-Wohlman O 1995 Anisotropic spin Hamiltonians due to spin-orbit and Coulomb exchange interactions Phys. Rev. B 52 10239–67
[32] Chizhikov V A and Dmitrienko V E 2012 Frustrated magnetic helices in MnSi-type crystals Phys. Rev. B 85 014421
[33] Chizhikov V A and Dmitrienko V E 2013 Multishell contribution to the Dzyaloshinskii–Moriya spiraling in MnSi-type crystals Phys. Rev. B 88 214402
[34] Bos J-W G, Colin C V and Palstra T T M 2008 Magnetoelectric coupling in the cubic ferrimagnet Cu$_2$OSeO$_3$ Phys. Rev. B 78 094416
[35] Dzyaloshinsky I 1958 A thermodynamic theory of 'weak' ferromagnetism of antiferromagnetics J. Phys. Chem. Solids 4 241–55
[36] Moriya T 1960 Anisotropic superexchange interaction and weak ferromagnetism Phys. Rev. 120 91–8
[37] Dalmas de Rétio P, Maisuradze A, Yaouanc A, Roessli B, Amato A, Andreica D and Lapertot G 2016 Determination of the zero-field magnetic structure of the helimagnet MnSi at low temperature Phys. Rev. B 93 144419
[38] Effenberger H and Pertlik F 1986 Die kristalstrukturen der kupfer(II)-oxo-selenite Cu$_2$O(SeO$_3$) (kubisch und monoklin) und Cu$_4$O(SeO$_3$)$_3$ (monoklin und triklin) Monatsh. Chem. 117 887–96
[39] Bogdanov A N and Yablonskii D A 1989 Thermodynamically stable ‘vortices’ in magnetically ordered crystals. The mixed state of magnets Sov. Phys.—JETP 68 101–3
[40] Rößler U K, Bogdanov A N and Pfleiderer C 2006 Spontaneous skyrmion ground states in magnetic metals Nature 442 797–801
[41] Ambrose M C and Stamps R L 2013 Melting of hexagonal skyrmion states in chiral magnets New J. Phys. 15 053003
[42] Yang J H, Li Z L, Lu X Z, Whangbo M-H, Wei S-H, Gong X G and Xiang H J 2012 Strong Dzyaloshinskii–Moriya interaction and origin of ferroelectricity in Cu$_2$OSeO$_3$ Phys. Rev. Lett. 109 107203
[43] Marchenko V I 2014 On antiferromagnetic transition in CuCrO$_2$ J. Exp. Theor. Phys. 119 1084–7
[44] Pikin S A and Lyubutin I S 2012 Increase in the electric polarization in a multiferroic induced by the flexoelectric effect JETP Lett. 96 240–4
[45] Pikin S A and Lyubutin I S 2012 Phenomenological model of multiferroic properties in langasite-type crystals with a triangular magnetic lattice Phys. Rev. B 86 064414
[46] Pikin S A and Lyubutin I S 2013 First order phase transition from an antiferromagnetic ferroelectric to a cycloidal multiferroic with weak ferromagnetism during the joint action of applied magnetic and electric fields J. Exp. Theor. Phys. 117 392–8
[47] Lyubutin I S and Pikin S A 2013 Coexistence of spiral magnetic state and weak ferromagnetism in a multiferroic, cross-controlled by external magnetic and electric fields J. Phys.: Condens. Matter. 25 236001
[48] Pikin S A 2014 On the ferroelectric polarization of multiferroicsemiconductor CuCrO$_2$ at various external pressures JETP Lett. 99 391–5