

Spin-orbital driven ferroelectricity

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 J. Phys.: Condens. Matter 26 395901

(<http://iopscience.iop.org/0953-8984/26/39/395901>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 210.32.147.165

This content was downloaded on 08/09/2014 at 09:10

Please note that [terms and conditions apply](#).

Spin-orbital driven ferroelectricity

Shan Zhu and You-Quan Li

Zhejiang Institute of Modern Physics and Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: shanzhu010@gmail.com

Received 16 January 2014, revised 23 July 2014

Accepted for publication 31 July 2014

Published 5 September 2014

Abstract

We study the effect of octahedron rotation on the electric polarization with spin-orbit coupling. Employing local coordinates to represent the tilting of the ligands' octahedra, we evaluate the electric polarization in a chain of transition metal ions with non-polar octahedron rotation. We find the orbital ordering produced by the ligands' rotation and the spin order, together, determine the polarization features, manifesting that non-vanishing polarization appears in collinear spin order and the direction of polarization is no more restricted in the plane of spin rotation in cycloidal ordering.

Keywords: multiferroics, unpolar octahedron rotation, magnetoelectric

(Some figures may appear in colour only in the online journal)

1. Introduction

Multiferroics refer to materials in which the spontaneous ferroelectricity and magnetism coexist, which makes it possible to control magnetization through an electric field or vice versa [1–6]. Since the discovery of spin-driven multiferroics TbMnO_3 [7] and TbMn_2O_5 [8], multiferroics have attracted more and more attention. A number of multiferroics with different kinds of magnetic order, such as cycloidal order [7, 9–12], proper-screw order [13–16], skyrmion crystal order [17, 18] and collinear order [19] have been found. In cycloidal magnetic order, a spin-current mechanism [20], which is also referred to as 'inverse Dzyaloshinskii–Moriya (DM) interaction' [21, 22], has successfully explained the relationship between the electric polarization and cycloidal magnetic order. The inverse DM mechanism predicts that the electric polarization \mathbf{P} is perpendicular to the unit vector $\mathbf{e}_{i,j}$ connecting site i, j and in the cycloidal spin rotation plane. Furthermore, in proper-screw magnetic order, the p - d hybridization [23, 24] due to spin-orbit coupling has been proposed to induce an electric polarization. This hybridization has been elucidated to host \mathbf{P} both parallel and normal to the magnetic modulation vector in some specific proper-screw magnetic order in triangular lattice [13, 16, 23, 24]. This mechanism also has important application in $\text{Ba}_2\text{CoGe}_2\text{O}_7$ [25, 26] and skyrmion lattice phase of Cu_2OSeO_3 [17, 18, 27]. Moreover, in collinear spin order systems the ferroelectricity is induced by the inverse Goodenough–Kanamori mechanism where the exchange interaction is responsible for the presence of ferroelectricity in Ising chain magnets [19] and E -type spin order [28–30]. Besides,

the general theory of ferroelectricity induced by spin-spiral order [31] and the polarization in a triangle originated from spin correlation [32, 33] are proposed.

In the recently found ferroaxials [34, 35], both the spin order and special crystal structure are responsible for the inversion symmetry breaking. In ferroaxials $\text{Cu}_3\text{Nb}_2\text{O}_8$ with cycloidal magnetic order, the electric polarization is not restricted to the spin rotation plane [34]. In $\text{CaMn}_7\text{O}_{12}$, the electric polarization is even found to be perpendicular to the spin rotation plane [35]. In ferroaxials, the direction of electric polarization cannot be explained by all these known mechanisms. In $\text{CaMn}_7\text{O}_{12}$ a 'propeller-like' structure for which the tilted ligands' octahedra take shape, the axial vector due to the relative rotation between nearby octahedra (we simply call octahedron rotation hereafter) is essential in the inversion symmetry breaking [36]. There has been a phenomenological explanation [35, 36] for the relationships between the electric polarization and the axial vector as well as spin orders, but there is not yet a microscopic mechanism to clarify the role that an octahedron rotation plays in conventional spin-driven multiferroics. On the other hand, recently a first-principle research has demonstrated that the octahedron rotation can be controlled by an electric displacement field [37]. It is therefore obligatory, from a microscopic point of view, to elucidate the effect of octahedron rotation on spin induced ferroelectricity. Thus in this paper we investigate how the occurrence of the non-polar octahedron rotation affects the electric polarization in spin-driven multiferroics with spin-orbit coupling based on the work by Katsura *et al* [20]. In next the section, we propose

a microscopic model such that the effect of octahedron rotation can be characterized by introducing local coordinates. In section 3, we solve the ground states by second-order perturbation and evaluate the induced electric polarization. We obtain an explicit expression to exhibit the relation between electric polarization and spin orders as well as octahedron rotation. In section 4, we apply the obtained expression to various spin orders. In the last section, we summarize and discuss our main results.

2. The model in the presence of octahedral rotation

We consider a system consisting of transition metal ions placed in a one-dimensional lattice space L_M . Their bonds are bridged through an oxygen atom in between the ions. Let L_O denote the lattice space where oxygen atoms are placed. The present model is actually defined on a bundle [38], a mathematical concept that we describe in the following. In a bipartite lattice $L = L_M \cup L_O$, each lattice point of L_M is attached with a fibre \mathcal{F}_d and that of L_O is attached with a fibre \mathcal{F}_p where \mathcal{F}_d and \mathcal{F}_p stand for the Hilbert space of d electrons and p electrons respectively. The structure group \mathcal{G} that connects the nearby fibres is the rotation group. Then the Hamiltonian reads

$$H = \sum_{i,\sigma} H_\sigma^{(i)} - U \sum_i e_i \cdot S_i, \quad (1)$$

with

$$H_\sigma^{(i)} = V (p_{y,\sigma}^{(i)\dagger} d_{xy,\sigma}^{(i)} + p_{z,\sigma}^{(i)\dagger} d_{xz,\sigma}^{(i)} - \tilde{p}_{y,\sigma}^{(i)\dagger} d_{xy,\sigma}^{(i)} - \tilde{p}_{z,\sigma}^{(i)\dagger} d_{xz,\sigma}^{(i)}) + V_0 (p_{x,\sigma}^{(i)\dagger} - \tilde{p}_{x,\sigma}^{(i)\dagger}) (d_{3z^2-r^2,\sigma}^{(i)} - \sqrt{3}d_{x^2-y^2,\sigma}^{(i)}) + \text{H.c.},$$

where $\sigma = \uparrow, \downarrow$, $i \in L_M$, $V = t_{pd\pi}$ and $V_0 = -\frac{1}{2}t_{pd\sigma}$. The summation in equation (1) is taken over the lattice sites in which the transition metal ions are placed. The first term in equation (1) describes the hopping between the transition metal ion and its nearby ligand, and the second one refers to the Hund's coupling. According to octahedral symmetry, the d orbitals of every metal ion are expressed in the local octahedral basis. Thus we introduce local coordinates for every transition metal ion. In other words, the above $H_\sigma^{(i)}$ is defined on the i -th neighborhood $\mathcal{U}^{(i)}$, in which $d_{v,\sigma}^{(i)}$ ($v = xy, xz, yz$, etc) annihilates a d electron at site M_i in figure 1, $\tilde{p}_{k,\sigma}^{(i)\dagger}$ ($k = x, y, z$) creates a p electron in the left side of M_i , whereas $p_{k,\sigma}^{(i)}$ creates one in the right side. Here we use the superscript ' i ' to emphasize that the corresponding wave functions are expressed in terms of local coordinates in the neighborhood $\mathcal{U}^{(i)}$. We emphasize that the quantization axis of spin is taken to be the z -axis of the local frame rather than the global frame. The coordinate frame for wave function is locally defined on each neighborhood $\mathcal{U}^{(i)}$, which changes from neighborhood to neighborhood.

In order to visualize the relation between electric polarization and spin order, we need a final expression in terms of a global coordinate frame, saying (x, y, z) . Hereafter, polarization means electric polarization for simplicity. Suppose the local coordinate in the neighborhood $\mathcal{U}^{(i)}$ is related to the global coordinate through a rotation matrix $(x', y', z')^T = R(\alpha_i) (x, y, z)^T$ (the superscript ' T ' means

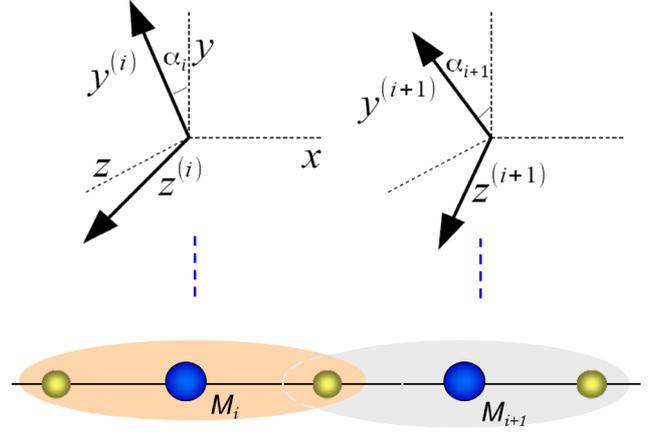


Figure 1. Schematic illustration of local coordinate frames for the model. The neighborhood $\mathcal{U}^{(i)}$ shaded in the same color covers a transition metal ion M_i (large ball) and its neighboring oxygen atoms (small balls, i.e. a left one and a right one, they are denoted, respectively, by \tilde{p} and p in the Hamiltonian of this paper for notation convenience). One can see that the right oxygen atom in $\mathcal{U}^{(i)}$ is simultaneously the left one in the next neighborhood $\mathcal{U}^{(i+1)}$. This overlapping in description naturally defines a metric. The rotation angle α specifies the relation between the global coordinate frame (x, y, z) and a local frame (specified with a superscript i and $i + 1$) that is the same for both d and p states in the same neighborhood. One needs a non-trivial bundle description in mathematical modeling in the presence of octahedron rotation in the material.

transpose of matrix, and $R(\alpha)$ is the fundamental representation of the rotation group), the spin states expressed in local frame and global frame are connected through the spinor representation of the rotation group, which we denote by $R_s(\alpha)$. As illustrated in figure 1, the p -states in the oxygen site between M_i and M_{i+1} can be expressed in terms of either the local frame of the neighborhood $\mathcal{U}^{(i)}$ or that of the neighborhood $\mathcal{U}^{(i+1)}$. These two expressions give us a metric

$$\langle p_{k,\sigma}^{(i)} | \tilde{p}_{k',\sigma'}^{(i+1)} \rangle = G_{k\sigma,k'\sigma'}. \quad (2)$$

which will appear in the formula of second-order perturbation theory. This metric matrix is given by $(R(\alpha_i) \otimes R_s(\alpha_i))^\dagger (R(\alpha_{i+1}) \otimes R_s(\alpha_{i+1}))$ generally. We are interested in the case that the rotation occurs along the chain as illustrated in figure 1. For simplicity, the direction $e_{i,i+1}$ that represents the chain direction of the transition metal ions is chosen as the x -axis. Then the local coordinate in the neighborhood $\mathcal{U}^{(i)}$ is related to the global coordinate through a rotation of α_i around the x -axis, then we have $R(\alpha) = e^{\alpha \hat{\ell}_x}$ where the generator $\hat{\ell}_x$ is a 3 by 3 matrix,

$$\hat{\ell}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

and $R_s(\alpha) = e^{-i\frac{\alpha}{2}\hat{\sigma}_x}$ with $\hat{\sigma}_x$ denoting the Pauli matrix as the spin is quantized along the local z' -axis. The metric $G_{k\sigma,k'\sigma'}(\alpha_{i,i+1})$ is characterized by the relative rotation angle $\alpha_{i,i+1} = \alpha_{i+1} - \alpha_i$ between the nearest-neighbors. For the octahedral symmetry in F_d , the rotation with a special angle like $\pi/2$ or its multiplier is equivalent to the case without rotation. So the twisting that causes non-trivial rotation is parameterized by $-\pi/4 < \alpha_{i,i+1} < \pi/4$.

3. Electric polarization

To obtain the electric polarization we need to know the orbital components of the ground state. The second part of equation (1) describes the d electron of spin S'_i coupling with the local magnetic moment along the direction $e'_i = (\sin \theta'_i \cos \phi'_i, \sin \theta'_i \sin \phi'_i, \cos \theta'_i)$. Here we use prime to emphasize that the coordinate parameters are defined with respect to the local coordinate frame. Like in [20], we consider the case that the strength of spin-orbit coupling is the largest energy scale of the system. Then the first part of equation (1) can be applied as a perturbation in the Hilbert subspace for the ground states of the second one. Diagonalizing the $-U e'_i \cdot S'_i$ term, one obtains

$$\begin{aligned} |P_i\rangle &= \sin \frac{\theta'_i}{2} |a^{(i)}\rangle + e^{i\phi'_i} \cos \frac{\theta'_i}{2} |b^{(i)}\rangle, \\ |\tilde{P}_i\rangle &= \cos \frac{\theta'_i}{2} |a^{(i)}\rangle - e^{i\phi'_i} \sin \frac{\theta'_i}{2} |b^{(i)}\rangle, \end{aligned} \quad (3)$$

where $|a^{(i)}\rangle = \frac{1}{3}(|d_{xy,\uparrow}^{(i)}\rangle + |d_{yz,\downarrow}^{(i)}\rangle + i|d_{zx,\downarrow}^{(i)}\rangle)$ and $|b^{(i)}\rangle = \frac{1}{3}(|d_{xy,\downarrow}^{(i)}\rangle - |d_{yz,\uparrow}^{(i)}\rangle + i|d_{zx,\uparrow}^{(i)}\rangle)$ are the Γ_7 doublet defined in the local coordinate of the neighborhood $\mathcal{U}^{(i)}$. Since $\langle P_i | \sigma | P_i \rangle = e'_i$ and $\langle \tilde{P}_i | \sigma | \tilde{P}_i \rangle = -e'_i$ where σ is the vector of the Pauli matrix, $|P_i\rangle$ and $|\tilde{P}_i\rangle$ are called parallel and anti-parallel states respectively. The eigenenergy of $|\tilde{P}_i\rangle$ and $|P_i\rangle$ are $U/3$ and $-U/3$ respectively. For convenience in calculation, one can abbreviate the aforementioned parallel state as

$$|P_i\rangle = \sum_{v\sigma} B_{v\sigma}^{(i)} |d_{v,\sigma}^{(i)}\rangle$$

with the corresponding coefficients: $B_{yz\downarrow}^{(i)} = B_{zx\downarrow}^{(i)} = B_{xy\uparrow}^{(i)} = \sin \frac{\theta'_i}{2} / \sqrt{3}$, and $-B_{yz\uparrow}^{(i)} = -iB_{zx\uparrow}^{(i)} = B_{xy\downarrow}^{(i)} = e^{i\phi'_i} \cos \frac{\theta'_i}{2} / \sqrt{3}$.

In the second-order perturbation for the degenerate ground states $|P_i\rangle$ and $|P_{i+1}\rangle$, only the terms $H_\sigma^{(i)}$ and $H_\sigma^{(i+1)}$ are of relevance because they describe hopping to or from the oxygen atom in between M_i and M_{i+1} . From the secular equation

$$\sum_{j'} (K_{j,j'} - \mathcal{E} \delta_{j,j'}) C_{j'} = 0, \quad (j, j' = i, i+1), \quad (4)$$

for the 2 by 2 matrix

$$K_{j,j'} = \sum_{k,\sigma,k'\sigma'} \frac{\langle P_j | H_\sigma^{(i)} | p_{k\sigma}^{(i)} \rangle G_{k\sigma,k'\sigma'} \langle \tilde{p}_{k'\sigma'}^{(i+1)} | H_\sigma^{(j')} | P_{j'} \rangle}{-\Delta},$$

where Δ is the energy difference between the p and d orbitals, we obtain two roots (eigenenergies) $\mathcal{E}^I = -\frac{2V^2}{3\Delta}(1 + |b|)$ and $\mathcal{E}^{II} = -\frac{2V^2}{3\Delta}(1 - |b|)$ and the corresponding eigenvectors $(C_i^I, C_{i+1}^I) = \frac{1}{\sqrt{2}}(-\frac{b}{|b|}, 1)$; $(C_i^{II}, C_{i+1}^{II}) = \frac{1}{\sqrt{2}}(\frac{b}{|b|}, 1)$ where $b = \mu_{i+1}^\dagger R_s(3\alpha_{i,i+1})\mu_i$, with $\mu_i^\dagger = (\cos \frac{\theta'_i}{2} e^{i\phi_i}, \sin \frac{\theta'_i}{2})$. Then we have two eigenkets

$$\begin{aligned} |\Psi_i^a\rangle &= C_i^a |P_i\rangle + C_{i+1}^a |P_{i+1}\rangle \\ &+ \frac{V}{\Delta} \sum_{k,\sigma} (-D_{k\sigma,i}^a |p_{k\sigma}^{(i)}\rangle + \tilde{D}_{k\sigma,i+1}^a |\tilde{p}_{k\sigma}^{(i+1)}\rangle), \end{aligned} \quad (5)$$

where $a = I, II$ label the two lowest energy states. Those coefficients in equation (5) are $D_{x\sigma,i}^a = \tilde{D}_{x\sigma,i+1}^a = 0$, $D_{y\sigma,i}^a = C_i^a B_{xy\sigma}^{(i)}$,

$D_{z\sigma,i}^a = C_i^a B_{xz\sigma}^{(i)}$, $\tilde{D}_{y\sigma,i}^a = C_i^a B_{xy\sigma}^{(i+1)}$, $\tilde{D}_{z\sigma,i}^a = C_i^a B_{xz\sigma}^{(i+1)}$. Note that the $|P_i\rangle$, $|p_{k\sigma}^{(i)}\rangle$, $|P_{i+1}\rangle$ and $|\tilde{p}_{k\sigma}^{(i+1)}\rangle$ in equation (5) are expressed in terms of local coordinates. In the presence of octahedron rotation, the orbital state implied in $|P_i\rangle$ differs in different site i , which is illustrated in figure 3. Thus the orbitals at each site of transition metal are no more uniformly ordered along the chain. Such an orbital ordering is characterized by the twisting angle $\alpha_{i,i+1}$ along the x -axis. Only for either parallel or anti-parallel spin orders meanwhile $\alpha_{i,i+1} = 0$, the state in equation (5) becomes an eigenstate of the operator of inversion transformation. If $\alpha_{i,i+1} \neq 0$, however, the inversion symmetry is still broken even for collinear spin orders, and hence non-vanishing polarization is expected to appear then.

Now we are in the position to evaluate the induced polarization. The overlapping integrals of d and p orbitals contributed in the calculation of the expectation value for er are [20],

$$\int d_{yz,\sigma}^{(i)} y^{(i)} \tilde{p}_{k,\sigma'}^{(i+1)} d^3 r = G_{z\sigma,k\sigma'}(\alpha_{i,i+1}) A, \quad (6)$$

where $A = \int d_{yz,\sigma}^{(i)}(r) y^{(i)} p_{z,\sigma}^{(i)}(r) d^3 r$. The same is true for $y \rightarrow z, z \rightarrow y$ in the above. Let us discuss the polarization for the cases of one hole as well as two holes in the one-electron picture. In the one hole case, we have the hole in the lowest energy state, $|\Psi_i^I\rangle$. The polarization is given by $P_i = e \langle \Psi_i^I | r | \Psi_i^I \rangle / \langle \Psi_i^I | \Psi_i^I \rangle$. If there are two holes that will occupy the two lowest states respectively, the polarization is defined as $P_i = e \langle \Psi_i^I | r | \Psi_i^I \rangle / \langle \Psi_i^I | \Psi_i^I \rangle + e \langle \Psi_i^{II} | r | \Psi_i^{II} \rangle / \langle \Psi_i^{II} | \Psi_i^{II} \rangle$. Consequently, we have

$$P_i = \lambda e_{i,i+1} \times (e^{-2\alpha_{i,i+1}\hat{\ell}_x} e_i \times e^{2\alpha_{i,i+1}\hat{\ell}_x} e_{i+1}), \quad (7)$$

where $\lambda = \lambda_0 \cos(4\alpha_{i,i+1})$. Here $\lambda_0 = \frac{1}{3} eAV / (\Delta|b|)$ and $\lambda_0 = -\frac{4}{9} eA(V/\Delta)^3$ for one hole and two holes, respectively. In the above formula (7) the rotation matrix acts on the left so the vector e_i and e_{i+1} are written in column form. We can see from equation (7) that the expression of polarization is dependent on both the spin order and the relative tilting angle $\alpha_{i,i+1}$. Thus it is no longer the spin chirality itself but the spin order together with the orbital ordering that determine the polarization. For the special case $\alpha_{i,i+1} = 0$, our result (7) recovers the one obtained by Katsura *et al* [20]. As the tilting angle modulates the magnitude of polarization via $\cos(4\alpha_{i,i+1})$, the order of magnitude of ferroelectricity stays unchanged compared with [20].

It is worthwhile to discuss the spin current emerging in the lowest energy state (5). The spin current at i -site flowing along the chain (x -axis) is the expectation value $J_{i \rightarrow i+1} = \langle \Psi_i^I | \hat{J}_{i,i+1} | \Psi_i^I \rangle$ with $\hat{J}_{i,j} = \frac{i}{\hbar} (t_{ji} d_{j\alpha}^\dagger(\sigma)_{\alpha\beta} d_{i\beta} - t_{ij} d_{i\alpha}^\dagger(\sigma)_{\alpha\beta} d_{j\beta})$. Expressing both $|P_i\rangle$ and $|P_{i+1}\rangle$ in terms of global coordinates, we obtain

$$J_{i \rightarrow i+1} \propto (e^{-2\alpha_{i,i+1}\hat{\ell}_x} e_i \times e^{2\alpha_{i,i+1}\hat{\ell}_x} e_{i+1}) + J_0 e_{i,i+1}, \quad (8)$$

where J_0 depends on the orientations of spin at sites i and $i+1$ as well as the twisting angle $\alpha_{i,i+1}$. Note that the first term of the above spin current happens to be the spin current of a tilt Heisenberg superexchange model [39] with $U_{j,j'}^J = e^{-2i\alpha_{j,j'}\hat{\sigma}_x}$, for which the covariant form [40] of the continuity-like

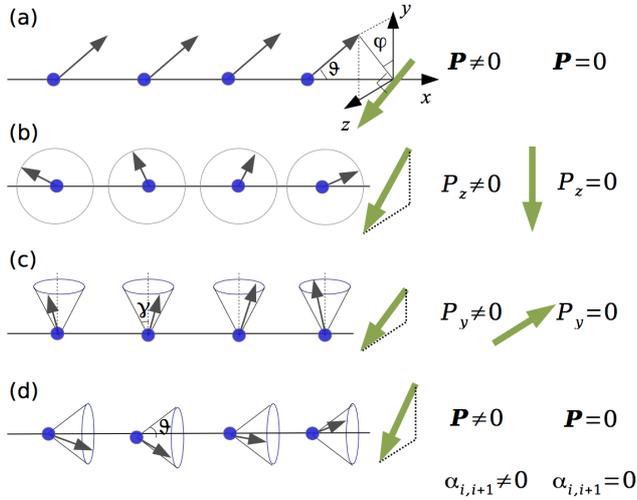


Figure 2. Illustration of the relations between total polarization P and various magnetic orders, such as collinear (a), cycloidal (b), transverse conical (c) and longitudinal conical (d) orders. Here the black arrows denote the spin direction at every site and the green one represents the induced polarization. As a comparison, the induced polarization for the special case without twisting $\alpha_{i,i+1} = 0$ are also plotted at the right accordingly. It is worthwhile to emphasize that, for (a) and (d), the polarization vanished in the uniform case $\alpha_{i,i+1} = 0$ but returns to appear in the non-uniform case $\alpha_{i,i+1} \neq 0$.

equation of the spin current needs to be considered. Clearly, the relation between spin current and the vector spin chirality is modified in the presence of octahedron rotation. Thus the relation between the electric polarization and spin current can still be written as $P \propto e_{i,i+1} \times J_{i \rightarrow i+1}$ which implies that the spin current mechanism remains intact [20]. In the following sections, we apply the formula (7) to various spin orders and make discussions thereof.

4. Applications to various spin orders

4.1. Non-vanishing polarization appearing in collinear magnetic order

Let us consider a ferromagnetic order, i.e. parallel spin aligning along the direction $(\cos \vartheta, \sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi)$ where ϑ denotes the zenith angle from the positive x -axis and φ denotes the azimuthal angle in the y - z plane from the y -axis as shown in figure 2(a), equation (7) gives rise to

$$P_i = \lambda \sin 2\alpha_{i,i+1} \sin 2\vartheta (0, -\sin \varphi, \cos \varphi), \quad (9)$$

that implies the appearance of non-vanishing polarization P_i for the parallel spin order. For the case of anti-parallel neighboring spins, the polarization P_i in equation (7) will have an opposite sign. Actually, as we can see from the above equation the P_i is perpendicular to the spin direction as well as $e_{i,i+1}$ which is also demonstrated in figure 2(a). Our formula also manifests that the induced polarization P_i in the collinear case is in the same order of magnitude as that for the spiral insulators [20]. Thus the combination of collinear spin order and non-uniform orbital ordering due to octahedron rotation (see figure 3) will break the inversion symmetry. We notice that in

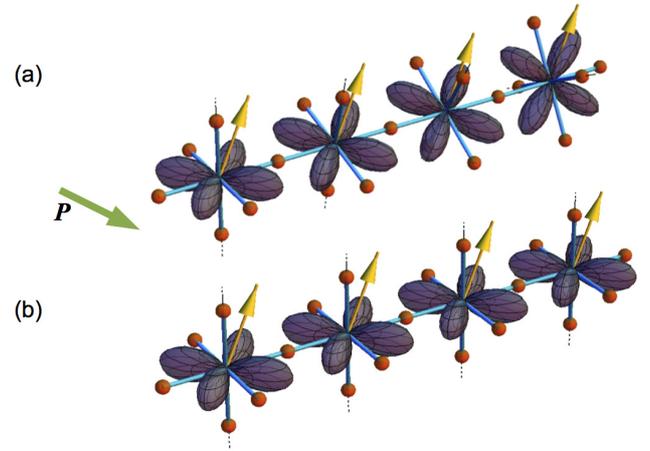


Figure 3. Depiction of the spin order (yellow arrows), orbital ordering (d_{xz}) in the presence of octahedron rotation along the x -axis and the resulting total polarization (green arrow). For collinear spin order, the total polarization P returns to appear in the presence of octahedron rotation (a) though it is known [20] to vanish in the absence of octahedron rotation (b). Here the non-uniform orbital ordering produced by octahedron rotation (a) plays an important role.

o -RMnO₃ with E -type spin order the P_i is also perpendicular to the spin direction [28–30, 41, 42].

4.2. Out-of-plane tilting of the polarization existing in cycloidal magnetic order

We consider the cycloidal magnetic order shown in figure 2(b), namely, $e_i = (\cos \vartheta_i, \sin \vartheta_i, 0)$. Here the spin lies in the x - y plane and ϑ_i denotes the angle between the x -axis and the spin on the i th site. Equation (7) becomes

$$\begin{cases} (P_i)_x = 0, \\ (P_i)_y = \lambda \cos(2\alpha_{i,i+1}) \sin(\vartheta_i - \vartheta_{i+1}), \\ (P_i)_z = -\lambda \sin(2\alpha_{i,i+1}) \sin(\vartheta_{i+1} + \vartheta_i). \end{cases} \quad (10)$$

If there is no octahedron rotation, i.e. $\alpha_{i,i+1} = 0$, the above polarization formula reduces to the one of [20], which means the polarization is just along the y -axis. Whereas, in the presence of octahedron rotation $\alpha_{i,i+1} \neq 0$, equation (10) tells us that there will be a non-zero z -component in the induced polarization, which is shown in figure 2(b).

Actually, it is worthwhile to discuss a general spin spiral order. Let β denote the angle of inclination between the normal vector n_s of the spin rotation plane and the bond $e_{i,i+1}$. If we define the direction of the bond as the x -axis, the normal vector reads $n_s = (\cos \beta, \sin \beta, 0)$ and the general spiral magnetic order is expressed as $e_i = (-\sin \beta \cos \theta_i, \cos \beta \cos \theta_i, \sin \theta_i)$. Consequently, one can write out the electric polarization according to formula (7) for a general spiral order. The special case of proper-screw order corresponds to $\beta = 0$ and the cycloidal order corresponds to $\beta = \pi/2$. The conventional inverse DM mechanism predicts that electric polarization lies in the spin rotation plane in the absence of octahedron rotation, i.e. $P \perp (e_i \times e_{i+1})$. In the presence of octahedron rotation ($\alpha \neq 0$), electric polarization will not be restricted to the spin

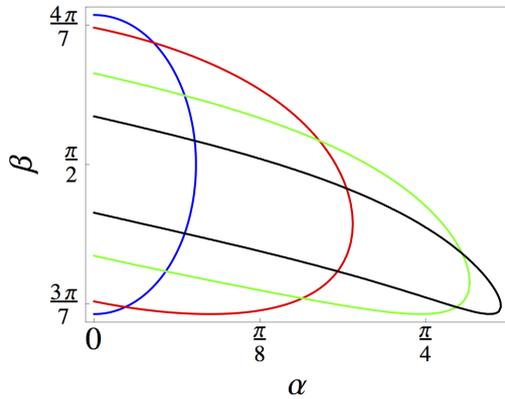


Figure 4. Illustration of the range of $2\alpha_{i,i+1}$ (x -axis) and β (y -axis) with $\theta_i - \theta_{i+1} = \pi/10$ which is comparable to that of $\text{Cu}_3\text{Nb}_2\text{O}_8$ when $\theta_i + \theta_{i+1} = 1.1\pi$ (blue curve), 1.3π (red curve), 1.6π (green curve), 1.8π (black curve).

rotation plane. Let's take $\text{Cu}_3\text{Nb}_2\text{O}_8$ [34] as an example. In $\text{Cu}_3\text{Nb}_2\text{O}_8$ [34], Cu^{2+} sites are located in a sawtooth chain along the a -axis with a unit cell $-\text{Cu}1-\text{Cu}2-\text{Cu}2-$. The ligand field of $\text{Cu}1$ is different from $\text{Cu}2$ as the former is CuO_4 squares while the latter is CuO_4 pyramid. The experiment finds the angle between electric polarization and n_s is about 14 degrees in $\text{Cu}_3\text{Nb}_2\text{O}_8$ [34]. This angle can be recovered from our expression (7) for certain parameters β and $\alpha_{i,i+1}$. We give the range of β and $\alpha_{i,i+1}$ in figure 4 where for a certain magnitude of $\alpha_{i,i+1}$ there will be two values of β with various $\theta_i + \theta_{i+1}$.

4.3. Variations in conical magnetic order

4.3.1. Transverse conical order. For transverse conical order that is expressed as $e_i^T = (\sin \gamma \cos \psi_i, \cos \gamma, \sin \gamma \sin \psi_i)$ where ψ_i denotes the azimuthal angle and γ the polar angle with respect to the generatrix paralleling to the y -axis, the polarization we obtained is given by

$$\begin{cases} (P_i)_x = 0, \\ (P_i)_y = w_1 \sin 2\gamma \sin \frac{\psi_i + \psi_{i+1}}{2} - 2w_2 \sin^2 \gamma \sin \frac{\psi_i + \psi_{i+1}}{2}, \\ (P_i)_z = 2w_1 \sin^2 \gamma \cos \frac{\psi_i - \psi_{i+1}}{2} + w_2 \sin 2\gamma \cos \frac{\psi_i - \psi_{i+1}}{2}, \end{cases} \quad (11)$$

where $w_1 = \lambda \cos 2\alpha_{i,i+1} \sin \frac{\psi_i - \psi_{i+1}}{2}$ and $w_2 = \lambda \sin 2\alpha_{i,i+1} \cos \frac{\psi_i + \psi_{i+1}}{2}$. Here we need to figure out that the total polarization P has a y -component, which is shown in figure 2(c).

4.3.2. Longitudinal conical order. For the longitudinal conical order which is expressed as $e_i^L = (\cos \vartheta, \sin \vartheta \sin \varphi_i, \sin \vartheta \cos \varphi_i)$ where φ_i denotes the azimuthal angle and ϑ the polar angle with respect to the x -axis as the conical generatrix, the polarization is given by

$$P_i^L = w(0, -\cos \frac{\phi_1 + \phi_2}{2}, \sin \frac{\phi_1 + \phi_2}{2}) \quad (12)$$

where $w = \lambda \sin 2\vartheta \sin \frac{4\alpha_{i,i+1} + \phi_2 - \phi_1}{2}$. The total polarization P is not zero unless one considers the uniform case [20] of $\alpha_{i,i+1} = 0$, which is shown in figure 2(d). Clearly, when $\vartheta = \pi/2$ the longitudinal conical order turns to be the screw order, $e_i = (0, \cos \varphi_i, \sin \varphi_i)$ and the polarization vanishes then. We predict that the polarization will be in the y - z plane for both longitudinal and transverse conical spin orders as long as there is an octahedron rotation along the magnetic propagation x -axis.

5. Summary and discussion

In order to study the effect of octahedron rotation, we proposed a microscopic formulism in terms of local coordinates to evaluate the electric polarization for a class of multiferroics in which the neighboring ligands' octahedra twist. We find that the spin order together with the orbital ordering produced by the octahedron rotation determine the appearance of polarization. This is because the spin order and the orbital ordering, together, break the inversion symmetry. The spin current that emerged in the perturbed ground state confirms that the electric polarization can still be expressed as a cross product of the spin polarization vector of the spin current and the direction vector that the spin current flows. However, the conventional relation between the spin current and the vector spin chirality is modified in the presence of octahedron rotation (or non-uniform orbital ordering in other words). Thus the ferroelectricity in this class of multiferroics can be called the spin-orbital driven ferroelectricity.

As the obtained explicit expression of the polarization is related to both the spin order and the relative rotation of the nearby octahedron of ligands, we found several distinct features for various cases. In collinear spin order, a non-vanishing polarization appears, which implies that the ligands' rotation can significantly enhance the bulk magnetization while keeping the polarization in the same order of magnitude as in spiral multiferroics. In the case of cycloidal spin order, the electric polarization is no more restricted to the plane of spin rotation, or in other words, the electric polarization will have the component perpendicular to the spin rotation plane.

Acknowledgments

We thank N Nagaosa, F C Zhang and R B Tao for helpful discussions. The work is supported by NSFCs (grant no. 11074216 & no. 11274272) and the Fundamental Research Funds for the Central Universities of China.

References

- [1] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123
- [2] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442** 759
- [3] Cheong S W and Mostovoy M 2007 *Nat. Mater.* **6** 13
- [4] Fiebig M and Spaldin N A 2009 *Eur. Phys. J. B* **71** 293
- [5] Wang K, Liu J and Ren Z 2009 *Adv. Phys.* **58** 321
- [6] Khomskii D 2009 *Physics* **2** 20
- [7] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 *Nature* **426** 55

- [8] Hur N, Park S, Sharma P A, Ahn J S, Guha S and Cheong S W 2004 *Nature* **429** 392
- [9] Goto T, Kimura T, Lawes G, Ramirez A P and Tokura Y 2004 *Phys. Rev. Lett.* **92** 257201
- [10] Arima T, Tokunaga A, Goto T, Kimura H, Noda Y and Tokura Y 2006 *Phys. Rev. Lett.* **96** 097202
- [11] Prokhnenko O, Feyerherm R, Dudzik E, Landsgesell S, Aliouane N, Chapon L C and Argyriou D N 2007 *Phys. Rev. Lett.* **98** 057206
- [12] Kagawa F, Mochizuki M, Onose Y, Murakawa H, Kaneko Y, Furukawa N and Tokura Y 2009 *Phys. Rev. Lett.* **102** 057604
- [13] Soda M, Kimura K, Kimura T, Matsuura M and Hirota K 2009 *J. Phys. Soc. Japan* **78** 124703
- [14] Kurumaji T, Seki S, Ishiwata S, Murakawa H, Kaneko Y and Tokura Y 2013 *Phys. Rev. B* **87** 014429
- [15] Seki S, Murakawa H, Onose Y and Tokura Y 2009 *Phys. Rev. Lett.* **103** 237601
- [16] Kurumaji T, Seki S, Ishiwata S, Murakawa H, Tokunaga Y, Kaneko Y and Tokura Y 2011 *Phys. Rev. Lett.* **106** 167206
- [17] Seki S, Yu X Z, Ishiwata S and Tokura Y 2012 *Science* **336** 198
- [18] Seki S, Ishiwata S and Tokura Y 2012 *Phys. Rev. B* **86** 060403
- [19] Choi Y J, Yi H T, Lee S, Huang Q, Kiryukhin V and Cheong S W 2008 *Phys. Rev. Lett.* **100** 047601
- [20] Katsura H, Nagaosa N and Balatsky A V 2005 *Phys. Rev. Lett.* **95** 057205
- [21] Sergienko I A and Dagotto E 2006 *Phys. Rev. B* **73** 094434
- [22] Mostovoy M 2006 *Phys. Rev. Lett.* **96** 067601
- [23] Arima T 2007 *J. Phys. Soc. Japan* **76** 073702
- [24] Jia C, Onoda S, Nagaosa N and Han J H 2007 *Phys. Rev. B* **76** 144424
- [25] Murakawa H, Onose Y, Miyahara S, Furukawa N and Tokura Y 2010 *Phys. Rev. Lett.* **105** 137202
- [26] Yamauchi K, Barone P and Picozzi S 2011 *Phys. Rev. B* **84** 165137
- [27] Liu Y H, Li Y Q and Han J H 2013 *Phys. Rev. B* **87** 100402
- [28] Sergienko I A, Sen C and Dagotto E 2006 *Phys. Rev. Lett.* **97** 227204
- [29] Picozzi S, Yamauchi K, Sanyal B, Sergienko I A and Dagotto E 2007 *Phys. Rev. Lett.* **99** 227201
- [30] Yamauchi K, Freimuth F, Blügel S and Picozzi S 2008 *Phys. Rev. B* **78** 014403
- [31] Xiang H J, Kan E J, Zhang Y, Whangbo M H and Gong X G 2011 *Phys. Rev. Lett.* **107** 157202
- [32] Bulaevskii L N, Batista C D, Mostovoy M V and Khomskii D I 2008 *Phys. Rev. B* **78** 024402
- [33] Khomskii D I 2010 *J. Phys.: Condens. Matter* **22** 164209
- [34] Johnson R D, Nair S, Chapon L C, Bombardi A, Vecchini C, Prabhakaran D, Boothroyd A T and Radaelli P G 2011 *Phys. Rev. Lett.* **107** 137205
- [35] Johnson R D, Chapon L C, Khalyavin D D, Manuel P, Radaelli P G and Martin C 2012 *Phys. Rev. Lett.* **108** 067201
- [36] Mostovoy M 2012 *Physics* **5** 16
- [37] Hong J and Vanderbilt D 2013 *Phys. Rev. B* **87** 064104
- [38] Schutz B F 1980 *Geometrical Methods of Mathematical Physics* (Cambridge: Cambridge University Press)
- [39] Li Y Q, Liu Y H and Zhou Y 2011 *Phys. Rev. B* **84** 205123
- [40] Jin P Q, Li Y Q and Zhang F C 2006 *J. Phys. A: Math. Gen.* **39** 7115
- [41] Lorenz B, Wang Y Q and Chu C W 2007 *Phys. Rev. B* **76** 104405
- [42] Chai Y S, Oh Y S, Wang L J, Manivannan N, Feng S M, Yang Y S, Yan L Q, Jin C Q and Kim K H 2012 *Phys. Rev. B* **85** 184406