

# Microscopic Origin of Electric and Magnetic Ordering in BiFeO<sub>3</sub>

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**Abstract** The microscopic origin of electric and magnetic ordering in multiferroic materials is described. Multiferroic materials are systems with strong spin–orbit coupling. There is an electric mechanism for which ferroelectricity is generated by dynamic magnetism though vanishing of the electric current; this result is demonstrated in this paper. The multiferroic material BiFeO<sub>3</sub> is shown to be a Mott’s insulator. An expression describing the connection between the polarization, magnetization, and the spin–orbit coupling parameter is derived.

**Keywords** Magnetization · Magnetoelectric coupling · Multiferroics · Polarization · Spiral magnetic ordering

## 1 Introduction

Multiferroics are materials in which two or three ferroic orders, ferroelectrics, ferromagnetics, and ferroelastics occur in the same phase. Ferroelectricity and magnetization not only coexist in the same material but can be coupled so strongly that magnetic ordering can be manipulated by an electric field and the electric ordering can be manipulated by a magnetic field [1,2]. This class of materials is very interesting because of its potential application in memory devices. Multiferroic materials, by virtue of their properties, can be used in magnetoelectric or spintronic devices. Wide-ranging and accurate investigations of multiferroic materials can be used to understand the fundamental physics that gives rise to the specific properties.

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Typical multiferroics belong to the group of perovskite transition metal oxides. One of the basic multiferroic materials is bismuth ferrite,  $\text{BiFeO}_3$ . Many theoretical and experimental studies have been performed recently in order to characterize the properties of  $\text{BiFeO}_3$  [3–7]. Bismuth ferrite ( $\text{BiFeO}_3$ ) is a compound with magnetic and electric ordering with a high antiferromagnetic Néel temperature ( $T_N = 643 \text{ K}$ ) and with a high ferroelectric Curie temperature ( $T_C = 1103 \text{ K}$ ) [8].  $\text{BiFeO}_3$  shows a magnetoelectric effect, with applied magnetic fields inducing weak ferromagnetism and a large increase in polarization [9]. We know that the  $\text{Fe}^{3+}$  ion in  $\text{BiFeO}_3$  has the  $d^5$  electron configuration, and therefore is not a  $d^0$  ion; thus, the ferroelectricity is almost certainly driven by the stereochemical activity of the  $\text{Bi}^{3+}$  lone pairs. The average crystal lattice of  $\text{BiFeO}_3$  is a rhombohedral distorted perovskite structure, which belongs to the space group  $R3c$ . Literature data show that the space group  $R3c$  allows the existence of both antiferromagnetic and ferroelectric orders with very high transition temperatures. The  $R3c$  symmetry permits the development of spontaneous polarization along [111], and Bi, Fe, and O are displaced relative to one another along this three-fold axis. The largest relative displacements are those of Bi relative to O, consistent with stereochemically active Bi lone pairs [3]. The hexagonal unit-cell parameters are  $a_{\text{hex}} = 0.5571(5) \text{ nm}$ ,  $b_{\text{hex}} = 0.5571(5) \text{ nm}$ , and  $c_{\text{hex}} = 1.3858(5) \text{ nm}$  [10]. Microscopically, the antiferromagnetic spin order is not homogenous for  $\text{BiFeO}_3$ . There is a space modulated magnetic structure of a spiral type with a long wavelength  $\lambda = 62 \text{ nm}$  for  $\text{BiFeO}_3$  single crystals [10, 11].

$\text{BiFeO}_3$  is one of the most promising lead-free piezoelectric materials, by exhibiting multiferroic properties at room temperature. The goal of this work is to answer the question: what is the microscopic mechanism that causes the strong coupling between magnetic and electric ordering in  $\text{BiFeO}_3$ .

## 2 Magnetoelectric Coupling

Dynamic electricity such as an electric current can generate magnetization, and there is also an inverse process. Namely, magnetization can generate an electric current. This means that dynamic magnetism and dynamic electricity are coupled with each other.

We derive a quantum–mechanical expression for the electric current density when a charged particle moves in both a magnetic field and an electric field. We start from the well known classical electrodynamics expression [12]

$$\delta\mathbf{H} = -\frac{1}{c} \int \mathbf{j}\delta\mathbf{A}dV, \quad (1)$$

where  $\delta\mathbf{H}$  is a variation of Hamilton's function,  $\mathbf{j}$  is the electric current density,  $\mathbf{A}$  is a vector potential of the electromagnetic field,  $V$  stands for the total volume, and  $c$  is the velocity of light.

This expression determines the change of the Hamilton's function of charges distributed in space when the vector potential is varied. The electron is described by

Hamilton's function, which has the following form [12]:

$$\mathbf{H}_e = \frac{\left(\hat{\mathbf{p}} - e\frac{\mathbf{A}}{c}\right)^2}{2m^*} + \alpha \left(\hat{\mathbf{p}} - e\frac{\mathbf{A}}{c}\right) \cdot [\hat{\sigma} \times \nabla V(\mathbf{r})] - \mu (\nabla \times \mathbf{A}) \cdot \hat{\sigma}, \quad (2)$$

where  $\hat{\mathbf{p}} = -i\hbar\nabla$  is the momentum operator ( $i$  is the imaginary unit),  $e$  is the charge of an electron,  $m^*$  is the effective mass of an electron,  $\alpha$  is the spin-orbit coupling parameter,  $\hat{\sigma}$  is the spin of the electron operator which is described by Pauli matrices,  $\nabla$  is the Nabla operator,  $V(\mathbf{r})$  is a scalar potential of the field, the  $\mu$  parameter is expressed as

$$\mu = \frac{ge}{2m^*c}, \quad (3)$$

and  $g$  is the Landé factor.

We applied Eq. 1 to the mean value of the Hamiltonian of the charged particle. The mean value of the Hamiltonian is expressed as follows:

$$\bar{\mathbf{H}}_e = \int \Psi^* \left\{ \frac{\left(\hat{\mathbf{p}} - e\frac{\mathbf{A}}{c}\right)^2}{2m^*} + \alpha \left(\hat{\mathbf{p}} - e\frac{\mathbf{A}}{c}\right) \cdot [\sigma \times \nabla V(\mathbf{r})] - \mu (\nabla \times \mathbf{A}) \cdot \sigma \right\} \Psi dV, \quad (4)$$

where  $\psi$  and  $\psi^*$  are a wave function of the system and its complex conjugate, respectively. Applying the variation and keeping in mind that  $\delta\mathbf{H} = \nabla \times \delta\mathbf{A}$ , we find the variation of the Hamiltonian (Eq. 4) which is expressed as

$$\delta\bar{\mathbf{H}}_e = -\frac{ie\hbar}{2m^*c} \int \delta\mathbf{A} [(\nabla\Psi^*)\Psi - \Psi^*(\nabla\Psi)]dV - \mu c \int \delta\mathbf{A} [\nabla \times (\Psi^*\sigma\Psi)]dV - \alpha ec \int \delta\mathbf{A} [(\Psi^*\sigma\Psi) \times \nabla V(\mathbf{r})]dV. \quad (5)$$

After comparing Eq. 1 with Eq. 5, we find the expression for the electric current density in the following form:

$$\mathbf{j} = \mathbf{j}_0 + \mu c \nabla \times (\Psi^*\sigma\Psi) + \alpha e (\Psi^*\sigma\Psi) \times \nabla V(\mathbf{r}), \quad (6)$$

where

$$\mathbf{j}_0 = -\frac{ie\hbar}{2m^*c} [(\nabla\Psi^*)\Psi - \Psi^*(\nabla\Psi)]. \quad (7)$$

This definition of an electric current density (Eq. 6) includes three terms. These terms are generated from three different physics phenomena, as illustrated in a quantum textbook [12]. The first term is connected with the standard momentum, which is connected with the linear velocity of charged particles. The second one is connected with

the spin contribution, and the third one is connected with the contribution of spin–orbit coupling.

The first term usually dominates over the other two terms in transport phenomena; therefore, the last two terms are usually ignored in theoretical investigations. We assumed that in multiferroic materials, which are insulators, all three terms (Eq. 6) are important in transport phenomena.

In BiFeO<sub>3</sub>, non-collinear spiral magnetic ordering has been observed [10, 13]. This spiral magnetic ordering is formed by the localized spins of Fe atoms. The electrons in the band couple to the localized spins of the Fe atoms through spin exchange coupling. This exchange coupling causes the magnetic ordering of the localized spins to generate the same magnetic ordering for the electrons in the band. The magnetization of the electrons in the band is a simple spiral magnetic ordering; therefore, we attempt to describe it by

$$\mathbf{M}_0 = M_0 (\cos(qa), \sin(qa), 0), \quad (8)$$

where  $q = \pi/31 \text{ nm}^{-1}$  is the magnon wave vector [14]. The propagation vector  $\mathbf{q}$  is along the [110] direction [10] and  $a$  is a unit-cell parameter. The electric current resulting from the magnetization is given by the following expression:

$$\mathbf{j}_M = \mu c \nabla \times \mathbf{M}_0 = \frac{\mu c q}{a} M_0 (0, 0, \cos(qa)). \quad (9)$$

Equation 9 shows that the magnetization current is a current along the  $z$  direction. In fact, this is the total current along the  $z$  direction.

Kohn [15] proved that in an insulator the total electric current must be zero. The electric current contributed from  $\mathbf{j}_0$  vanishes as a result of the lattice mirror symmetry in the  $x - y$  plane in BaFeO<sub>3</sub>. The electric current described by the second and third terms (Eq. 6) should also vanish. That is, the electric current from the magnetic ordering (the second term of Eq. 6) must be balanced by the electric current induced from the spin–orbit coupling (the third term in Eq. 6):

$$\mu c \nabla \times \mathbf{M}_0 + \alpha e \mathbf{M}_0 \times \nabla V(\mathbf{r}) = 0, \quad (10)$$

where

$$\nabla V(\mathbf{r}) = -e\mathbf{E}(\mathbf{r}), \quad (11)$$

and  $\mathbf{E}(\mathbf{r})$  means a vector of the electric field.

For any magnetic ordering of the localized spins of Fe atoms, the electrons in a fully filled band do not have a magnetization response independent of the strength of the spin exchange coupling between them. That is, the magnetization is equal to zero for any magnetic ordering of the localized spins of Fe atoms and Eq. 10 is not correct. Thus, BiFeO<sub>3</sub> cannot be a conventional insulator just like ferroelectric materials. There is no contribution to the ferroelectricity from the completely filled bands. The contribution comes from the band that is partially filled. This is a fundamental difference from the

physics in conventional ferroelectric materials where the ferroelectricity is generated by the lattice dynamics, and the electron bands are either fully occupied or empty. Therefore, we can treat multiferroic BiFeO<sub>3</sub> as a Mott's insulator.

There are two interactions that can be responsible for BiFeO<sub>3</sub> being a Mott's insulator, that is, an insulator with a partially filled band. The first is the strong electron–electron interaction, and the second is the strong spin exchange coupling between the electrons in the band and the localized spin moments. Both mechanisms can split a band into two sub-bands. If a gap exists for the new sub-band, and if the lower energy gap is completely filled and the upper energy band is empty, then we have a Mott's insulator.

By algebraic manipulation and averaging over the total space, we obtain the following expression:

$$\frac{\alpha e^2}{\mu c} \langle \mathbf{E} \rangle = \left\langle \frac{(\mathbf{M}_0 \cdot \mathbf{E}) \mathbf{M}_0}{M_0^2} \right\rangle + \left\langle \frac{\mathbf{M}_0 \times (\nabla \times \mathbf{M}_0)}{M_0^2} \right\rangle, \quad (12)$$

The first term on the right-hand side of Eq. 12 vanishes if we take the space average, and the total ferroelectricity is given by

$$\mathbf{P} = \frac{\varepsilon_0 \mu c}{\alpha e^2} \left\langle \frac{\mathbf{M}_0 \times (\nabla \times \mathbf{M}_0)}{M_0^2} \right\rangle. \quad (13)$$

Equation 13 provides information about spin–orbit coupling. Namely, the total polarization is inversely proportional to the spin–orbit coupling, and the value of the polarization does not depend on the amplitude of the magnetization. This equation is consistent with the work of Mostovoy [16], in which the relationship between the ferroelectric order  $\mathbf{P}$  and magnetic order  $\mathbf{M}$  in spiral magnets was presented.

### 3 Quantitative Discussion of the Ferroelectricity for BiFeO<sub>3</sub>

Now we can quantitatively discuss the ferroelectricity predicted by Eq. 13 for the multiferroic material BiFeO<sub>3</sub>. The spin–orbit coupling parameter  $\alpha$  can be rewritten as  $\alpha = (2m^* \Delta_e)^{-1}$  where  $\Delta_e$  represents the effective spin–orbit gap. This effective spin–orbit gap can be viewed as analogous to the spin–orbit gap in a semiconductor. By simple algebraic modifications, Eq. 13 can be rewritten as

$$P = \frac{\varepsilon_0 g}{ea} q \Delta_e \left\langle \cos^2 \frac{q}{a} x \right\rangle. \quad (14)$$

Taking into account experimental data for BiFeO<sub>3</sub> such as the value of the polarization  $P = 1.4 \mu\text{C} \cdot \text{cm}^{-2}$  [17], the value of the wavelength  $\lambda = 62 \text{ nm}$  [11], and the lattice parameter  $a_{\text{hex}} = 0.557 \text{ nm}$  [10], we can calculate the value of the energy spin–orbit gap in the multiferroic material BiFeO<sub>3</sub>.

The connection of the value of the polarization with the value of the energy spin–orbit gap results from Eq. 14. Namely,  $P = 0.2 \Delta_e \mu\text{C} \cdot \text{cm}^{-2} \cdot \text{eV}^{-1}$  and now we

can calculate the value of the spin–orbit gap that is equal to 0.7 eV for BiFeO<sub>3</sub>. Equation 14 suggests that the value of ferroelectricity is limited by the energy spin–orbit gap, because the polarization is directly proportional to the energy gap  $\Delta_e$ . The method discussed above allows us to calculate not only the energy spin–orbit gap, but also the value of the polarization. With a knowledge of the value of the energy spin–orbit gap, we can predict the ferroelectricity for multiferroic materials.

### 3.1 Results

Multiferroic materials have simultaneous ferromagnetic, ferroelectric, or ferroelectric ordering. Coupling between the magnetic and ferroelectric order parameters can lead to magnetoelectric effects, in which the magnetization can be tuned by an applied electric field and vice versa.

The starting point of our considerations was the expression describing the electric current density. This expression contains three terms generated from three different physics phenomena that have contributions to the total electric current.

Taking into account these three terms in the electric current density, we tried to describe the magnetoelectric coupling in the multiferroic material BiFeO<sub>3</sub>. The proposed mechanism showed that the ferroelectricity can be generated by the partially filled electron bands and therefore BiFeO<sub>3</sub> cannot be a conventional ferroelectric with completely filled electron bands. In order to generate the magnetoelectric coupling, multiferroic BiFeO<sub>3</sub> should be a Mott's insulator. The mechanism of magnetoelectric coupling explains why the value of the total ferroelectricity in BiFeO<sub>3</sub> is several orders smaller than in conventional ferroelectric materials. This mechanism enables calculations of the value of the energy spin–orbit gap.

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