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Microscopic mechanism of spin-order induced improper ferroelectric polarization

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ABSTRACT

Type-II multiferroic is an important area in the big family of multiferroics, in which its polarization originates from the spin order, resulting in a strong magnetoelectric coupling. Here we briefly review the previous mechanisms of the spin-order induced polarization, including the Katsura–Nagaosa–Balatsky (KNB) model, inverse Dzyaloshinskii-Moria (DM) interaction model, exchange striction model, and the bond polarization model. Then our unified polarization model is discussed in detail, which contains pure electronic, ion displacement and lattice deformation contributions. And a feasible approach for constructing the unified model based on the first-principles calculations is presented. With this model, we unravel the microscopic mechanisms of the ferroelectricity in several typical multiferroics. New type-II multiferroics with strong magnetoelectric coupling and giant polarization are expected to be discovered and/or designed through the use of this model.

1. Introduction

Multiferroics [1–7], in which magnetism, ferroelectricity and ferroelasticity can coexist, have attracted great interest in the last decades, not only for their fascinating physics but also for their potential applications in memory devices, spintronics and magnetoelectric sensors, etc. Multiferroicity occurs in both single phase and composite materials. In composite multiferroics [8–12], the magnetoelectric effect is usually generated as a product property of a magnetostrictive and a piezoelectric substance. Hereafter we only discuss the single phase multiferroics. Multiferroics are found from 3d to 4f transition metal compounds and have perovskite structures, spinel structures or pyrochlore structures, etc. The magnetism in multiferroics almost has the same origin: The partially filled d or f shells of transition metal or rare earth ions. The mechanism of the origin of the ferroelectric polarization is more complicated. Khomskii [13] defines two types of multiferroics. Type-I multiferroics are the materials in which ferroelectricity and magnetism have different sources and appear largely independent of one another. The coupling between the magnetism and ferroelectricity in type-I multiferroics is usually weak. The representative type-I multiferroics are Zn_2FeTaO_6 and Zn_2FeOsO_6 [14], $PbVO_3$ [15], $BiFeO_3$ [16], $BiMnO_3$ [17], and $YMnO_3$ [18], etc. While in type-II multiferroics, the ferroelectricity originates from special spin orders: cycloid, proper screw, etc. The magnetic order breaks the inversion symmetry in type-II multiferroics. Thus one would expect strong magnetoelectric coupling in type-II multiferroics, which provides a promising route for electrical writing and nondestructive magnetic readout memory devices. This new type of memory devices has the advantages of high storage density, high read-write speed and low energy consumption. The representative type-II multiferroics are $TbMnO_3$ [19], $DyMnO_3$ [20], $TbMn_2O_5$ [21] and $CaMn_7O_{12}$ [22,23], etc.

The magnetoelectric coupling in type-II multiferroics is much stronger than that in type-I multiferroics. However, the polarization in most known type-II multiferroics is much smaller than the traditional type-I multiferroics. This limits the realistic applications of type-II multiferroics. Therefore, discovering and/or designing new type-II multiferroics with large polarization is an active and important research area. To gain insight into the mechanism of spin-order induced polarization in type-II multiferroics and guide the search for new materials for room-temperature applications, several theories have been built up. In 2005, Katsura, Nagaosa and Balatsky [24] proposed a microscopic pure electronic model (i.e., KNB model) combined with spin orbit coupling (SOC) and on site Coulomb repulsion to explain the polarization induced by the spiral spin structure. Then in 2006, Sergienko and Dagotto [25] attributed the polarization in $RMnO_3$ (R = Gd, Tb, Dy) to the

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inverse DM interaction. Both models require the same conditions, namely, the SOC effect and noncollinear spin order. In the same year, Sergienko, Sen and Dagotto [26] showed that the E-type collinear magnetic order can also evoke ferroelectric polarization even without SOC. Later, Jia et al. [27] proposed a bond polarization model to explain the longitudinal polarization in the spin spiral system. Some phenomenological theories based on symmetry analysis have also been built to describe the coupling between spin order and ferroelectric polarization [28]. More recently, we [29–34] established a unified model for the microscopic mechanism of spin-order induced ferroelectricity in multiferroics, which includes the pure electronic, ion displacement and lattice deformation contributions. It should be noted that in type-I multiferroics, there may also exist spin-order induced polarization and the model is also applicable.

In this review, we first briefly introduce the previous models. Then our unified model will be discussed in detail.

2. Previous models for the spin-order induced ferroelectric polarization

In this part, we briefly review the previous models of the spin-order (both noncollinear and collinear) induced ferroelectric polarization.

2.1. Noncollinear spin structure induced electric polarization

There are various types of noncollinear magnetic structures, among which the two famous configurations are known as cycloidal spiral and proper screw spin structures (see Fig. 1b and c). In both cases the inversion symmetry is broken, where cycloidal spiral spin configuration often induces polarization and proper screw rarely produces polarization. In the following, we will introduce various models of noncollinear spin structures induced ferroelectric polarization.

2.1.1. KNB model

In 2005, Katsura, Nagaosa and Balatsky [24] proposed a microscopic model to explain the origin of electric polarization induced by noncollinear magnetic order. In their model, they first consider a three atoms cluster (i.e. two magnetic ions and the ligand oxygen ion) with inversion symmetry (Fig. 1(a)), and thus no DM interaction appears. The low-energy Hilbert space here is two dimensional with the basis generated from t_{2g} orbitals plus the on-site SOC effect. The Hamiltonian contains the on-site Coulomb repulsion of the magnetic ions and the hopping processes between the magnetic site and the oxygen site, and the hopping term is treated as perturbation. After a series of derivation, they obtain a concise result that the polarization direction is perpendicular to both the spin current direction and the vector connecting the magnetic ions. In both the double-exchange interaction and superexchange interaction cases, the polarization has the same form that $\vec{P} \cong A\vec{e}_{12} \times (\vec{e}_1 \times \vec{e}_2)$ (see Fig. 1(a)) where A is coefficient, $\vec{e}_{12}$ is the unit vector from site M1 to site M2 and $\vec{e}_1$ and $\vec{e}_2$ are the noncollinear spin directions. The spin current between M1 and M2 is described as $\vec{j}_s \propto \vec{e}_1 \times \vec{e}_2$.

With KNB model, one can easily find that the cycloidal spin structure (see Fig. 1(b)) induces a net polarization, while the proper screw spin structure (see Fig. 1(c)) gives no polarization. In 2003, Kimura et al. [19] found spontaneous polarization and strong magnetoelectric coupling in single crystal $TbMnO_3$ below 27 K. And in 2005, Kenzelmann et al. [35] established the magnetic structure of $TbMnO_3$ using neutron diffraction. They confirmed that the paraelectric, magnetically incommensurate phase (28–41 K) holds a sinusoidally modulated collinear magnetic order. In the ferroelectric phase (below 28 K), a noncollinear cycloidal spiral spin structure lies in the bc plane. Applying the KNB model to $TbMnO_3$, one can deduce a reasonable result that no polarization occurs in sinusoidally modulated collinear magnetic order and the direction of polarization induced by cycloidal spiral spin structure is along c axis which consists with experiment. Note that the cations and anions are fixed in the KNB model, and it is a pure electronic model. In Kimura and his coworkers' [19] experiment they found atomic displacements, which indicate KNB model cannot explain experiment completely. Moreover, polarization induced by proper screw spin configuration has also been observed in MnI_2 [36], $CuFeO_2$ [37,38] and $ACrO_2$ (A = Cu, Ag) [39], while KNB model predicts a zero polarization in these systems.

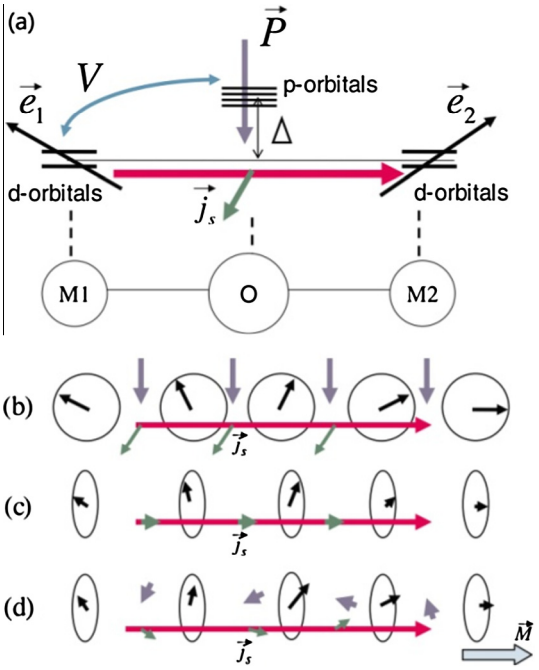

Fig. 1. (a) The cluster model with two transition metal ions M1, M2 with the oxygen atom O between them. The spin current $\vec{j}_s \propto \vec{e}_1 \times \vec{e}_2$ arises from the noncollinear spin direction $\vec{e}_1$ and $\vec{e}_2$. The direction of the electric polarization $\vec{P}$ is given by $\vec{P} \propto \vec{e}_{12} \times \vec{j}_S$ where $\vec{e}_{12}$ is the unit vector connecting M1 and M2. (b–d) Some of the specific configurations ((b): cycloidal spiral, (c): proper screw, (d): conical proper screw) where the geometrical relation among spins (black arrows), spin current (gray arrows), and electric polarization are shown [24]. © 2005, American Physical Society.

2.1.2. Inverse Dzyaloshinskii–Moryia (DM) interaction model

In order to explain the experiment that cycloidal spiral spin structure is accompanied by structural modulation in $TbMnO_3$, Sergienko and Dagotto [25] claimed that the noncollinear spin structure originates from DM interaction and its inverse interaction induces ferroelectric lattice displacement. DM interaction has the form: $\vec{D}_{ij} \cdot [\vec{S}_i \times \vec{S}_j]$, which was firstly proposed by Dzialoshinski [40] in 1958 to phenomenologically explain the weak ferromagnetism in α-Fe_2O_3. Then in 1960, Moriya [41] presented a microscopic picture by extending the theory of superexchange interaction to include the effect of SOC. In ferroelectric phase of $TbMnO_3$, it distorts from the cubic perovskite structure with the $GdFeO_3$-type cooperative rotation of the MnO_6 octahedra [42], where the bond angle of Mn–O–Mn deviates from 180° to about 145°. Adapting the symmetry analysis proposed by Moriya [41], the DM vector is nonzero with the direction perpendicular to the Mn–O–Mn bond plane. Sergienko and Dagotto [25] showed that the DM interaction linearly depends on the displacements of the O ions surrounding transition-metal ions. By minimizing the Hamiltonian containing the anisotropic exchange interaction and