

Studies on multiferroic materials in high magnetic fields

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In this article, studies on the magnetoelectric effects of multiferroic materials in high magnetic fields, particularly pulsed magnetic fields, are discussed and results for some representative materials are presented. In the discussions on representative materials, the relationship between the crystallographic symmetry and the linear magnetoelectric effect in Cr_2O_3 is introduced. Then drastic changes in polarization caused by magnetic transitions are discussed through a case study of manganites with a perovskite-type structure. In addition, high field studies on the magnetoelectric effects in BiFeO_3 , which is an exceptional multiferroic material, are presented and discussed in the framework of the Landau–Ginzburg theory.

Keywords high magnetic field, multiferroic materials, magnetoelectric effect

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1 Introduction

Recently, the studies that are classified with the keyword *multiferroics* have attracted much attention in the field of solid state physics [1–3]. According to Schmid, who coined the term in 1994 [4], a multiferroic state is defined as a state in which “two or all three of the properties of ‘ferroelectricity’, ‘ferromagnetism’, and ‘ferroelasticity’ occur simultaneously in the same phase”. Among the various kinds of multiferroic materials, the materials that exhibit both ferroelectricity and (anti)ferromagnetism are of particular interest to many scientists. Among such ferroelectric (FE) materials, materials whose ferroelectricity is accompanied by a magnetic order have been studied as ferroelectric magnets since the 1960s [5]. The

recent revival of research in this field is not merely a renewal of terminology. Technical progress in microscopic experimentation and crystal / thin-film growth in the past several decades has enabled us to understand the phenomena of multiferroicity in a more fundamental manner and uncovered a new multidisciplinary research field spanning the fields of magnetism and ferroelectrics.

If we search for research papers with the keyword *multiferroic*, we can see how quickly this research field has developed, as shown by solid circles in Fig. 1 [6]. In particular, the number of publications dramatically increased in 2003, a year in which two epoch making papers were published. The first one was on the magnetic field control of electric polarization in TbMnO_3 [7]. Manganites with perovskite-type structures have been extensively studied after the discovery of colossal magnetoresistance (CMR) effects [8, 9]. The interaction among coupled spin, charge, and orbital degrees of freedom in such manganites results in a variety of unusual phenomena. The discovery of gigantic magnetoelectric (ME) effects in these well-known manganites naturally attracted the attentions of many scientists in this research field. The second paper reported the discovery of the coexistence of large electric polarization and weak ferromagnetism in BiFeO_3 thin films reported by Wang *et al.* [10]. The magnitude of electric polarization observed in this study was larger than that exhibited by standard ferroelectrics. When the coexistence of switchable spontaneous polar-

ization and magnetization at room temperature was discovered, it was suggested that this phenomenon can be possibly applied to the development of memory devices with two degrees of freedom. This possibility stimulated a large numbers of studies proposing other practical applications of the phenomenon.

Although the coexistence of magnetism and ferroelectricity is an unusual state in solid, the scientific interests and applicability of this phenomenon are restricted only by the emergence of the multiferroic state. The key ingredient is the cross-coupling between two order parameters, i.e., the ME effect, which suggests the possible existence of phenomena such as magnetic (electric) control of the static order in electric polarization (magnetic moments) and/or magnon excitation by the electric field components of terahertz light [11]. Here, it is important to note that multiferroic materials do not necessarily exhibit ME effects, and vice versa [12].

Research on ME effects in solids has preceded the discovery of ferroelectric magnets (open circles in Fig. 1). Pierre Curie is considered to be to propose the possibility of ME effects, in 1894 [13]. It took more than 60 years for this effect to be observed in real materials. Soon after Dzyaloshinskii [14] theoretically predicted that Cr_2O_3 would exhibit ME effects, his prediction was experimentally proven by two individual groups [15, 16]. For phenomenological understanding, a free energy argument based on the Landau–Ginzburg theory has been quite effective.

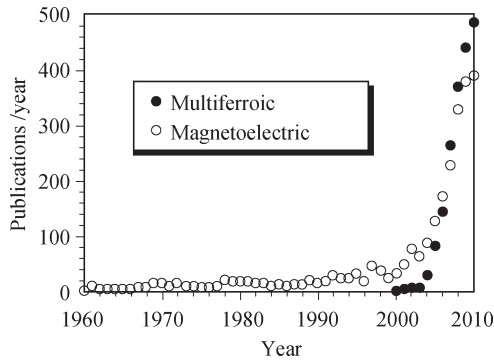


Fig. 1 Increase in the number of publications per year retrieved by the keywords *magnetoelectric* and *multiferroic* from Web of Science [6], Copyright © 2011 Thomson Reuters.

In an infinite homogeneous medium without spontaneous magnetization and polarization, the series expansion of free energy is given in terms of the i th component of the magnetic field ($\mathbf{H}_i$) and the electric field ($\mathbf{E}_i$) under the Einstein summation convention as follows [12, 17]:

$$-F = -F^0 + \frac{1}{2}\mu_0\mu_{ij}\mathbf{H}_i\mathbf{H}_j + \frac{1}{2}\epsilon_0\epsilon_{ij}\mathbf{E}_i\mathbf{E}_j + \alpha_{ij}\mathbf{E}_i\mathbf{H}_j + \frac{\beta_{ijk}}{2}\mathbf{E}_i\mathbf{H}_j\mathbf{H}_k + \frac{\gamma_{ijk}}{2}\mathbf{H}_i\mathbf{E}_j\mathbf{E}_k$$

$$+ \frac{\delta_{ijkl}}{2}\mathbf{E}_i\mathbf{E}_j\mathbf{H}_k\mathbf{H}_l + \dots \quad (1)$$

Here, F^0 is the free energy independent of $\mathbf{E}$ and $\mathbf{H}$. The second and third terms on the right hand side denote the permeability and permittivity terms, as is usual in magnets and dielectrics. The fourth term represents the linear ME effect, which becomes finite only in crystals that are odd under the symmetry operations of space inversion and time reversal. The fifth and sixth terms correspond to second-order ME effects. Because the application of $\mathbf{H}$ breaks the time reversal symmetry, the second order ME effect of $\beta_{ijk}\mathbf{E}_i\mathbf{H}_j\mathbf{H}_k$ can exist even in crystals that are even under the time reversal operation. The situation is similar for the γ_{ijk} term. The biquadratic term can be finite in any crystal.

Usually, higher order terms are small, and hence, the ME effects are dominated by the first order term if it exists. According to Brown [18], the upper bound of α_{ij} is given by

$$\alpha_{ij}^2 \leq \epsilon_0\mu_0\epsilon_{ii}\mu_{ii} \quad (2)$$

According to this limitation, α_{ij} is generally small. Therefore, high magnetic fields are needed to determine α_{ij} through the magnetic field dependence of the electric polarization ($\mathbf{P}$).

Symmetry arguments based on the group theory determine the forms of the ME tensors α_{ij} , β_{ijk} , and γ_{ijk} , as will be seen in Section 4.1. Conversely, by investigating the form of the ME tensor in various configurations of $\mathbf{P}$ and $\mathbf{H}$, we can identify the possible magnetic symmetry in an unknown magnetically ordered state. An example of the argument on the unknown phase in high magnetic fields is introduced in Section 4.2.

In multiferroic materials, in which spontaneous magnetic moment and electric polarization coexist, Eq. (1) can be expressed as a series expansion of magnetization $\mathbf{M}$ (or the antiferromagnetic vector $\mathbf{L}$, which is defined as the difference in the sublattice magnetization) and $\mathbf{P}$ [5, 19]. In this case, the spatial derivative in the order parameter, which becomes finite in a spatially modulated spin structure, plays a crucial role in breaking the spatial inversion in the magnetic lattice. The argument for this approach will be given in Section 4.3.

The purpose of this article is to examine the role of the efficiency of high magnetic fields in studies on multiferroics. In short, we focus on three representative compounds, Cr_2O_3 , RMnO_3 (R denotes a rare-earth ion), and BiFeO_3 , and present their ME effects, which were mainly studied in pulsed magnetic fields. On the other hand, many multiferroic materials have been studied in high magnetic fields. Readers interested in particular materials can see reviews or original articles for delafossite [20–27], cuprates [28–30], molybdates [31], RMn_2O_5 [32], boracite [33], and an organic spin-Peierls material [34].

2 Classification of multiferroic materials

Because there are a variety of multiferroic materials, it is hard to treat them in the same framework. Here, we classify them into the three groups.

The first group includes materials in which ferroelectricity is derived from the magnetic order. Since the discovery of gigantic magnetoelectric effect in TbMnO_3 [7], these spin-driven multiferroics have been the most extensively studied. With the formulation of theoretical prescriptions that explain the generation of ferroelectricity in spatially modulated spin system [35–37], research on this class of materials was revived and many materials belonging to this class were newly discovered, e.g., RMnO_3 [7, 38], RMn_2O_5 [39], $\text{Ni}_3\text{V}_2\text{O}_8$ [40], CoCr_2O_4 [41], CuFeO_2 [21], MnWO_4 [42], LiCu_2O_2 [43]. The general form of the spin-driven polarization can be expressed as follows [44, 45]:

$$\mathbf{P} = \sum_{\langle i,j \rangle} \{ P^{\text{ms}}(\mathbf{S}_i \cdot \mathbf{S}_j) \mathbf{e}_{ij} + P^{\text{sp}} \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j) + P^{\text{orb}}[(\mathbf{e}_{ij} \cdot \mathbf{S}_i) \mathbf{S}_i - (\mathbf{e}_{ij} \cdot \mathbf{S}_j) \mathbf{S}_j] \} \quad (3)$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ denote the spins at the adjacent sites i and j , and $\mathbf{e}_{ij}$ is the unit vector connecting these sites. P^{ms} , P^{sp} , and P^{orb} are the coefficients. The first term on the right hand side of Eq. (3) originates from exchange striction as an inverse effect of the symmetric superexchange interaction. This contribution becomes finite for the long wavelength spin order that is commensurate with the lattice. In some crystals with special symmetry, lattice modulation caused by the exchange striction breaks the inversion symmetry, and hence, makes the crystal polar. The second term is explained as an inverse effect of the Dzyaloshinskii–Moriya (DM) interaction [37] or spin–current mechanism [35]. This antisymmetric term becomes finite in spatially modulated noncollinear spin system. According to this scenario, electric polarization caused by spin order is ubiquitously observed in cycloidal magnets. The third term is the so-called d – p hybridization mechanism [44–46]. The mixing ratio in the metal–ligand bond depends on the spin–orbit interaction, which in turn depends on the direction of the spin.

In spin-driven multiferroic materials, direct coupling between the spin and electric polarization guarantees strong ME effects; on the other hand, the observed values of electric polarization in such materials are marginal, about two or three orders of magnitude smaller than those in typical ferroelectrics. Because of the smallness of the polarization, the thermodynamics of phase transitions is mostly dominated by the magnetic term. In addition, because most of the spatially modulated spin states are attributable to geometric frustration, the ordering

temperatures are inherently low. These two characteristics of spin-driven multiferroic materials make them unsuitable for use in practical applications.

The second group becomes ferroelectric because of the charge ordering. LuFe_2O_4 [47] and $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$ [48] belong to this group. When a certain type of charge order superimposes onto a centrosymmetric lattice, the inversion symmetry is removed by the charge disproportionation. The resultant electric polarization in LuFe_2O_4 amounts to $17 \mu\text{C}/\text{cm}^2$ even at room temperature [47]. In addition, a significant change in P at the Néel temperature of $T_N = 250 \text{ K}$ suggests the presence of coupling between the spin system and the dielectric system. Although there is theoretical suggestion of ME effects in these materials [49], their poor insulation, which is inevitable in this group of materials, makes the experimental determination of the ME effect difficult. It is expected that future experiments in high magnetic fields will clarify the potential magnetoelectric effects in these materials.

Here, we classify the remaining multiferroic materials as belonging to the third group. Typical examples are magnets that contain stereochemically active ions such as Bi^{3+} and Pb^{2+} . The representative material BiFeO_3 is the most promising candidate for application because it exhibits the coexistence of magnetic order [50–52] and a huge reversible polarization larger than $100 \mu\text{C}/\text{cm}^2$ in the form of both thin films and bulk crystals at room temperature [10, 53, 54]. Because there is a significant difference between the ordering temperatures (ferroelectric Curie temperature $T_{\text{FE}} \sim 1100 \text{ K}$ and magnetic $T_N = 600\text{--}643 \text{ K}$ [50, 51]), whether significant coupling between magnetism and ferroelectricity exists is a nontrivial issue. High field studies of the ME effects in BiFeO_3 will be described in detail in Section 4.3.

3 Experimental

As mentioned in the previous section, spin-driven ferroelectricity is frequently realized in geometrically frustrated magnets. Application of pulsed high magnetic fields is known to induce various magnetic transitions in these systems, which have been studied mainly through the measurement of magnetization and electron spin resonance (ESR). In addition, recent progress in the fabrications of light sources enabled us to perform X-ray or neutron diffraction measurements in high magnetic fields even if these fields are pulsed fields, whose very nature provides a limited duration for conducting such experiments [23, 55–58]. Although these experiments are also quite effective for studying multiferroics, here, we describe only the technical aspects of the measurement of ME effects, which are only applicable for multiferroic materials.

There are two ways of measuring the magnetic field dependence of electric polarization: the first involves the measurement of the electric potential at the sample surface as a function of applied magnetic fields, and the second involves the detection of the polarization/depolarization current (I_d) that corresponds to the time derivative of the polarization (dP/dt) in changing magnetic fields. The latter method is well compatible with measurements in pulsed fields. A schematic of the experimental system is illustrated in Fig. 2(a). At IMGSL-ISSP, we can generate magnetic fields of up to 70 T utilizing non-destructive magnets driven by a capacitor bank, whose profiles are shown in Fig. 2(b) [59]. Because the field-sweep ratio in pulsed fields are approximately five orders of magnitude faster than those in the fields of superconducting magnets, the enhanced dP/dt ($= dP/dH \times dH/dt$) enables us to accurately determine the ME effects. The I_d is captured by a fast analog-digital converter through a voltage drop in the shunt resistor connected in series with the measurement circuit [see Fig. 2(a)] and is numerically integrated to calculate the P . By mounting the sample on a rotational probe, we can apply magnetic fields to the sample from arbitrary directions.

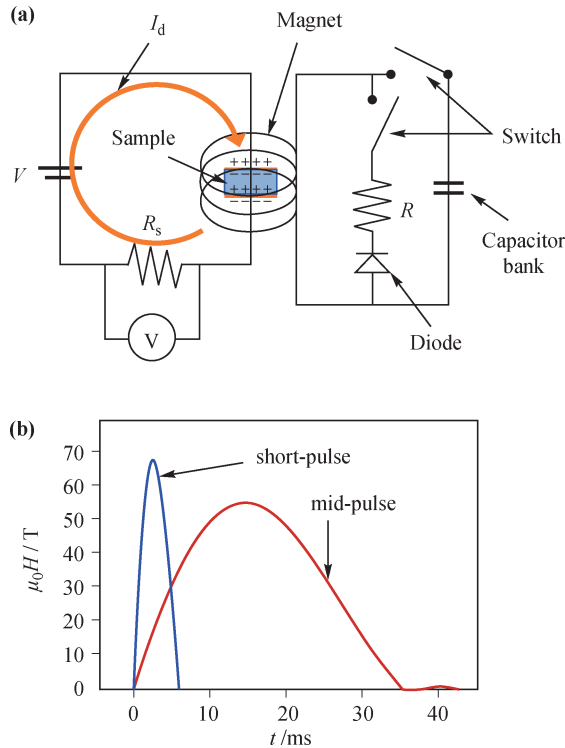


Fig. 2 (a) Schematic illustration of the measurement system for magnetoelectric effects in pulsed fields. (b) Typical profiles of pulsed magnetic fields for short- and mid-pulse magnets installed at IMGSL-ISSP.

However, the following points must be noted before conducting measurements in pulsed fields. First, to measure the ME effects, we usually have to cool the sample down in the presence of external magnetic and electric fields in order to polarize the ferroelectric domains be-

fore the measurements are taken. Because this procedure cannot be used for conducting measurements in pulsed fields, we have to be careful about the presence of possible domains. Second, in experiments involving pulsed fields, we can only detect the change in P from the initial value. Appropriate determination of the offset is required for some experiments. Third, performing fast field sweeps cause the induced voltage in finite loops in the electric wiring, which should be removed through the appropriate comparative experiments. Fourth, for some materials that have large spin angular momenta, fast field sweeps in pulsed fields result in heating of the sample due to the magnetocaloric effect in the quasi-adiabatic magnetization process. If we pay sufficient attention to these points, our ME effect measurements [60–62] are expected to be highly accurate and in reasonable agreement with those obtained in steady fields [21, 63–65] over a wide range of magnetic field.

4 Examples of the ME effects

4.1 Cr_2O_3

We now present the argument of ME effects in actual materials, starting with that of Cr_2O_3 . As mentioned previously, Cr_2O_3 is the material in which ME effects were observed for the first time [15, 16]. This material has the corundum structure, which belongs to the space group of $R\bar{3}c$ in the paramagnetic phase as shown in Fig. 3. The unit cell contains four Cr ions that form honeycomb layers in the ab -plane. Each chromium is sandwiched by oxygen triangles of different sizes. The magnitude relation between the upper and lower triangles is reverse for the adjacent chromium ion along the c -axis; hence, the chromium sites are classified into two different oxygen

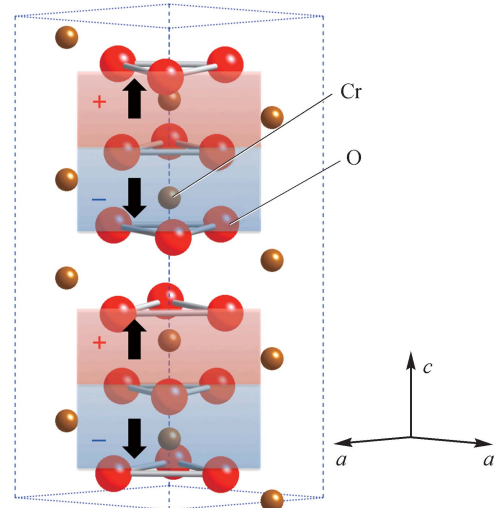


Fig. 3 Crystal structure of Cr_2O_3 . The dotted line represents the unit cell. The thick arrows denote the chromium spins in the antiferromagnetic state.

environments, as marked by + and – in Fig. 3. When the crystal is cooled to below 307 K, the chromium spins order antiferromagnetically as shown by thick arrows in Fig. 3, or toward their opposite direction in each site. The Cr ions in each magnetic sublattice experience the same ligand field. In this antiferromagnetic state, the simultaneous inversion of space and time (IR) becomes the symmetry element, so that first-order ME effect can be finite.

From the symmetry point of view, an individual symmetry operation can be described as a three-fold rotation axis around the c -axis (C_3), a two-fold rotation axis orthogonal to the C_3 (U_2), and the spatiotemporal inversion (IR). Because the equation $\mathbf{M} = \tilde{\alpha}\mathbf{E}$ has to be invariant for these symmetry operations,

$$\tilde{C}_3^{-1}\tilde{\alpha}\tilde{C}_3 = \tilde{\alpha} \quad \text{and} \quad \tilde{U}_2^{-1}\tilde{\alpha}\tilde{U}_2 = \tilde{\alpha} \quad (4)$$

and thus,

$$\tilde{\alpha} = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \quad (5)$$

Therefore, to determine the ME tensor of Cr_2O_3 , it is sufficient to measure the two elements of the matrix $\tilde{\alpha}$. A similar argument is applicable for general magnets. The forms of the ME tensor for each magnetic point group are tabulated in Ref. [66] and Ref. [67].

In the case of Cr_2O_3 , the ME effect expressed by Eq. (5) can be intuitively interpreted as follows. If we apply an electric field along the c -axis, the field will shift all the cations up or down. Thus the ligand field becomes inequivalent for each magnetic sublattice. The magnetic moments of these two sublattices need not to be canceled, and hence, magnetization emerges along the c -axis in the presence of a parallel electric field. When we apply the electric field normal to the c -axis, the principal axes of crystalline field are tilted, which makes the up and down spins noncollinear. As a result, in-plane magnetization is induced by E .

Although the ligand arrangement around the chromium ions can be modified by E , the microscopic origin of the axial ME effect in this material has been a controversial topic. Rado and Folen first ascribed the origin of this ME effect to the electric field dependence of the anisotropy constant [68, 69], whereas Date *et al.* insisted that this ME effect originates from the change in the intrasublattice exchange interaction [70]. In addition, Alexander and Shtrikman mentioned that an applied electric field can change the g -factor [71]. Although several experiments on ESR were performed to determine which factor is responsible for the axial ME effect in Cr_2O_3 [70, 72, 73], the issue remains unsettled. In addition, recent theoretical studies proposed novel approaches to this issue [74, 75], which should be tested

in future experiments. For example, multifrequency ESR in high magnetic fields is expected to be resolving this issue.

The application of high magnetic fields is known to induce a spin-flop transitions [76, 77]. Foner studied the ME effects in magnetic fields up to 10.5 T generated by a Bitter magnet and observed steep changes in the electric polarization at this transition field [78]. This ME effect can be seen more clearly in the P – H curves as shown in Fig. 4(b) [79]. Above the transition field of ~ 7 T, the P_a linearly changes as a function of the H applied nearly parallel to the c -axis, which indicates the change in the non-zero matrix elements in the ME tensor.

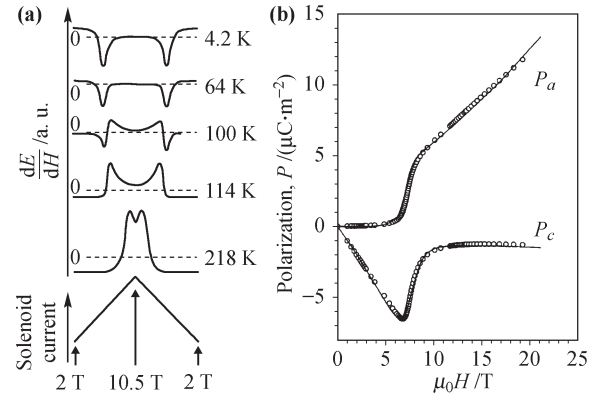


Fig. 4 (a) Axial ME effects in Cr_2O_3 studied in dc magnetic fields [78], Copyright © 1963 The American Institute for Physics. (b) Magnetic field dependence of electric polarization in pulsed magnetic fields at 150 K [79], Copyright © 1999 International Academic Publishing Company (IAPC) “Nauka/Interperiodica”.

In the spin-flopped phase, there are two possible spin configurations, which have different spin orientation within the ab -plane: spins lying in the mirror plane or parallel to the twofold axis [29]. Because these two phases belong to different magnetic point groups ($2/m'$ and $2'/m$, respectively), we can determine the actual symmetry from the form of the ME effects in the high field phase. Although there are several studies on the ME effects in a high magnetic field, the results appear to be inconclusive [29, 78, 80, 81]. In the high field state, a small misalignment of the magnetic field may make a finite contribution to the electric polarization. Therefore, systematic studies on ME effects in precisely rotatable magnetic fields are expected to provide conclusive data. Although, here, we are not going in more detail for this transition, a phenomenological argument can be seen in a literature [79].

4.2 (Eu,Y) MnO_3

Although Cr_2O_3 exhibits significant linear ME effects, it does not exhibit spontaneous electric polarization in zero field, i.e., it is not multiferroic. When magnetic order coexists with spontaneous electric polarization, the

cross-correlation between magnetism and dielectrics exhibits dramatic non-trivial changes in the physical properties. In this section, we will introduce the ME effects in orthorhombic $RMnO_3$ as an example of such multiferroic materials (R denotes a rare-earth ion). As mentioned in the introduction, many recent studies on multiferroic materials were sparked by the discovery of the gigantic ME effects in $TbMnO_3$ [7].

Manganites with a perovskite-type structure have been extensively studied owing to their extraordinary response to external perturbation, e.g., CMR effects [8, 9]. In contrast to the CMR materials, which are all mixed-valence compounds, $RMnO_3$ is a single-valence compound; all Mn spins in $RMnO_3$ are trivalent. The absence of mobile electrons that mediate ferromagnetic double-exchange interaction makes the system an insulating antiferromagnetic system.

The perovskite lattice of $RMnO_3$ is orthorhombically distorted as illustrated in Fig. 5, and belongs to the $Pbnm$ space group. This orthorhombic distortion becomes more significant with a smaller-sized R ion. Because of the Jahn–Teller effect, the MnO_6 octahedra are deformed and arranged alternately in the ab -plane; this results in the ordering of the e_g orbitals of Mn $3d$ electrons. Corresponding to the orbital order, the antiferromagnetic second neighbor interaction (J_2) plays a substantial role with respect to the ferromagnetic nearest neighbor interaction (J_1) (Fig. 5). A change in the ionic radius of the R ions modifies the balance between J_1 and J_2 , and in turn, alters the magnetic ground states [82].

Below $T_N \sim 42$ K, the Mn spins in $TbMnO_3$ form a sinusoidally modulated collinear spin structure with the modulation vector directed along the b -axis. Further cooling changes the spin state to the cycloidal one at around 27 K, at which temperature ferroelectricity sets in. Because the Tb spins order at significantly lower temperature (~ 7 K), the occurrence of ferroelectricity can be ascribed to the Mn-spin system.

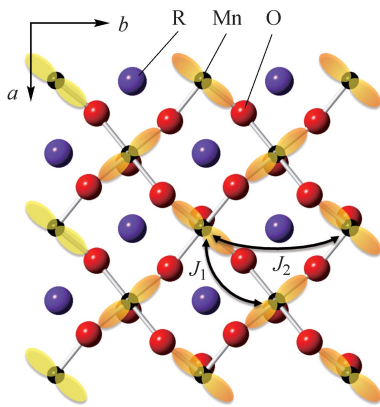


Fig. 5 Crystal structure of $RMnO_3$ in the ab -plane of the $Pbnm$ notation. Lobes denote the orbital order.

As is usual in frustrated magnets, the application of a

magnetic field is effective in altering the nearly degenerated spin states. In the case of $TbMnO_3$, the application of H along the b -axis induces a magnetic transition accompanied with the flop of P from the c - to the a -axis, as shown in Fig. 6(a) [7]. The appearance of the polarization flop is significantly modified by the change in the R ion even at temperatures higher than the ordering temperatures of the spins in the R ions [83]. Therefore, the presence of highly anisotropic spin moments in the R ions complicates the system, which makes the fundamental understanding of the origin of this phenomenon difficult.

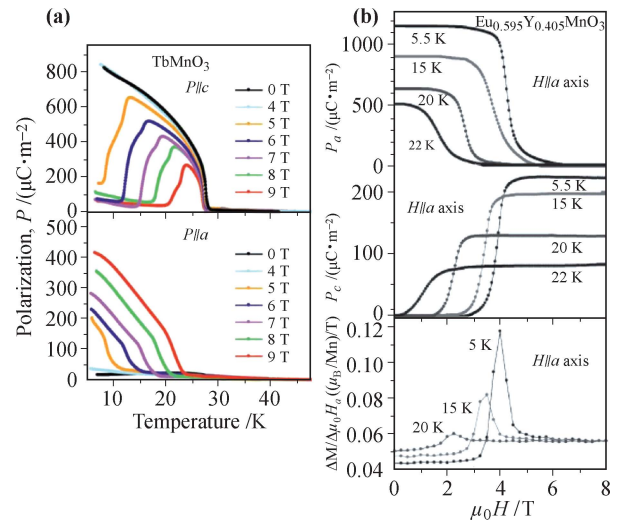


Fig. 6 (a) Temperature dependence of electric polarization parallel to the c - (upper) and a -axis (lower) in various magnetic fields [7], Copyright © 2003 Nature Publishing Group. (b) Magnetic field dependence of $P//a$ (upper) and $P//c$ (middle) in $Eu_{0.595}Y_{0.405}MnO_3$ at several temperatures. The lower panel shows differential susceptibility for $H//a$ -axis [64], Copyright © 2006 The American Institute for Physics.

Therefore, $Eu_{1-x}Y_xMnO_3$ is the appropriate system for studying this phenomenon because both Eu^{3+} and Y^{3+} ions are nonmagnetic [64, 65, 84, 85]. The average ionic radius of the R site becomes almost the same as that of Tb for $x \sim 0.4$, whereas the observed flop in P takes place from the a - to the c -axis in the magnetic field along the a -axis [Fig. 6(b)], contrary to the flop from $P//c$ to $P//a$ by $H//b$ in $TbMnO_3$. Recent magnetic and structural studies on $Eu_{0.6}Y_{0.4}MnO_3$ revealed that H -induced flop in P is caused by a flop of the rotational axis in the cycloidal spin structure from the c - to the a -axis, which agrees with the intuitive interpretation of a reduction in the Zeeman energy [65]. According to the inverse-DM model [35, 37], this spin flop scenario is compatible with the change in the spin-driven polarization from $P//a$ to $P//c$.

On the other hand, the application of a high magnetic field reveals a different aspect of this system, which contrasts with these intuitively imaginable ME effects. On-cooled in zero field, $EuMnO_3$ shows a successive mag-

netic transition from the sinusoidal to the canted antiferromagnetic (CAFM) structure. Although both the phases are paraelectric, the application of a magnetic field $H//b$ of about 20 T causes a magnetic transition to the high-field phase in which electric polarization emerges along the a -axis as shown in Figs. 8(a) and (b) [62, 86]. In addition, the application of further field induces additional transition to a non-polar phase [62]. The latter transition is slightly unclear in the magnetization measurements, whereas it is well defined in the polarization measurements, as seen in Figs. 7(a) and (b). In the field-induced ferroelectric phase, the nonlinear profile of the P - H curve cannot be expressed by a linear ME effect as a function of H , showing remarkable contrast with that in the spin-flop phase of Cr_2O_3 .

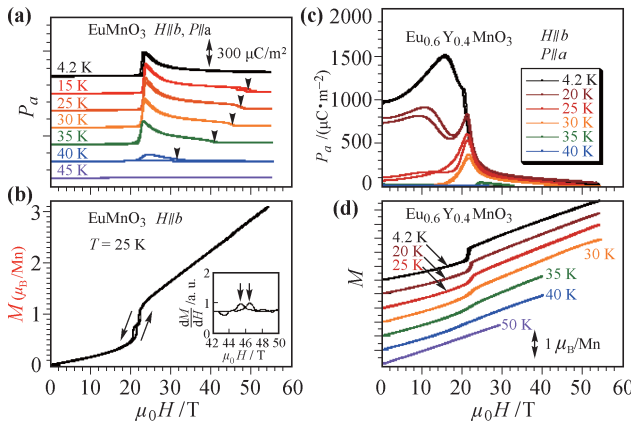


Fig. 7 Magnetic field dependence of (a) $P//a$ and (b) magnetization in EuMnO_3 . (c) and (d) are the P_a - H_b and M_b - H_b curves for $\text{Eu}_{0.6}\text{Y}_{0.4}\text{MnO}_3$. Data in (a) and (d) were vertically offset for clarity [62], Copyright © 2009 The American Physical Society.

This transition reminds us of the field-induced transition from paraelectric CAFM phase to a cycloidal $P//a$ phase in GdMnO_3 [83, 87]. This cycloidal $P//a$ phase can be induced in zero field by substituting Tb for Gd [83]. Similarly, in EuMnO_3 , the cycloidal $P//a$ phase is realized in zero field by partially substituting Y for Eu. Therefore, the question naturally arises as to whether the field-induced $P//a$ phase observed in EuMnO_3 is continuously connectable to the cycloidal $P//a$ phase of $\text{Eu}_{0.6}\text{Y}_{0.4}\text{MnO}_3$ in zero field. Figures 7(c) and (d) show the P - H and magnetization curves of $\text{Eu}_{0.6}\text{Y}_{0.4}\text{MnO}_3$ up to 55 T [62]. The results show the presence of a phase transition from the low-field $P//a$ (P_a -I) phase to the high-field $P//a$ (P_a -II) phase. The similarity between the profiles of the P - H and the M - H curves implies that the high-field $P//a$ phases in EuMnO_3 and $\text{Eu}_{0.6}\text{Y}_{0.4}\text{MnO}_3$ share the same origin.

The transition from the P_a -I phase to the P_a -II phase cannot be accounted for by the same scenario as that for $H//a$ at low field. In $H//a$, the spin-rotational axis flops from the c - to the a -axis so as to gain Zeeman energy, which results in a change in polarization from $P//a$ to

$P//c$ [65]. An analogous argument suggests the change in the spin-rotational axis to the b -axis. The resultant proper screw spin structure, however, cannot be responsible for the emergence of the electric polarization within the framework of the inverse-DM model.

In the field range of the P_a -II phase, it is very difficult to determine the spin structure microscopically using the currently available experimental techniques. In this situation, model calculations are expected to predict the most plausible spin arrangement. As for the system of RMnO_3 , Mochizuki *et al.* developed a model, which can reasonably reproduce the magnetoelectric phase diagram in the temperature and composition plane in zero-field [88, 89]. The Hamiltonian is given as

$$\mathcal{H} = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{sia}} + \mathcal{H}_{\text{DM}} + \mathcal{H}_{\text{Zeeman}} \quad (6)$$

where

$$\mathcal{H}_{\text{ex}} = J_1 \sum_{\langle i,j \rangle}^{x,y} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle i,j \rangle}^b \mathbf{S}_i \cdot \mathbf{S}_j + J_c \sum_{\langle i,j \rangle}^c \mathbf{S}_i \cdot \mathbf{S}_j \quad (7)$$

$$\mathcal{H}_{\text{sia}} = D \sum_i \mathbf{S}_{\xi i}^2 + E \sum_i (-1)^{i_x+i_y} (\mathbf{S}_{\xi i}^2 - \mathbf{S}_{\eta i}^2) \quad (8)$$

$$\mathcal{H}_{\text{DM}} = \sum_{\langle i,j \rangle} d_{ij}^\alpha \cdot (\mathbf{S}_i \times \mathbf{S}_j) \quad (9)$$

$$\mathcal{H}_{\text{Zeeman}} = \mu_B \sum_i \mathbf{S}_i \cdot \mathbf{H} \quad (10)$$

Here, the first term represents the superexchange interactions: the ferromagnetic nearest neighbor interaction in the ab -plane ($J_1 < 0$), the antiferromagnetic second-neighbor interaction along the b -direction ($J_2 > 0$), and the antiferromagnetic interaction along the c -axis J_c (Fig. 5). The second term denotes the single-ion anisotropy, where ξ_i , η_i , and ζ_i are the directional vectors of the local axes of the i -th MnO_6 octahedron. The third term corresponds to the DM interaction in which the DM vectors d_{ij} are defined on the $\text{Mn}(i)$ -O-Mn(j) bonds. The fourth term denotes the Zeeman coupling. This model can reproduce the phase diagram as shown in Fig. 8 with an appropriate set of parameters [62].

First, with the adopted set of parameters, the theoretical result in Fig. 8(b) reproduces the transition from the sinusoidal to the cycloidal state upon cooling in zero field. In this theoretical result, application of $H//b$ to the cycloidal $P//a$ phase (I_b) induces successive transitions to the other $P//a$ phase (II_b) and to the paraelectric phase (III_b); these transitions are similar to the experimentally observed transitions from the P_a -I phase to the P_a -II phase and the paraelectric phase, as exhibited in Fig. 8(a). According to the calculated result, the P_a -I phase shows a cycloidal (or conical in the presence of H_b) spin structure with the spin rotational axis parallel to the

c -axis, which is consistent with the emergence of $P//a$ by the inverse-DM effect. The spin structure in the II_b phase becomes a fan-type one with sinusoidally modulated spin a components as shown in Fig. 8(d). The point here is that the spin modulation vector becomes commensurate ($q_b = 0.25$) with the lattice period in phase II_b . As was pointed out by Arima *et al.* [87], the occurrence of a commensurate modulation that breaks the b' -glide symmetry operation in $Pbnm$ crystal makes the crystal polar with $P//a$.

Let us look more closely into the magnetoelectric state of phase II_b . The arrangement of the spin a components (S_a) in phase II_b at $T = 0$ is shown in Fig. 8(f). The S_a shows eight-times periodicity along the x and y bonds in the figure with the sign of $(++++-- --)$. Such a long period spin order is compatible with the emergence of the net electric polarization caused by the symmetric exchange-striction mechanism. In the present case, the ferromagnetic (antiferromagnetic) arrangement between two neighboring Mn spins in the ab -plane favors the larger (smaller) Mn–O–Mn bond angle to gain the exchange energy. Consequently, this magnetic order will modify the oxygen location from the solid to the dotted circles in Fig. 8(f). In the zigzag Mn–O–Mn–O– chain along the x -axis, the oxygen ions between positive and negative spin a components always shift in the $-y$ direction. On the other hand, in the chain along the y -axis, net displacement of the oxygen ions takes place in the $+x$ direction. These two contributions eventually give rise to

the net polarization $P//a$, as observed for phase II_b . The c components of the local polarizations, if any, are necessarily canceled out because of the presence of a mirror plane between the two MnO_2 planes.

On further increasing H_b , the system enters into phase III_b , and a CAFM emerges; this CAFM does not coincide with the ferroelectricity in both the inverse-DM or the symmetric exchange mechanism [see Fig. 8(e)].

As seen above, the magnetic control of the electric polarization in orthorhombic RMnO_3 is dominated by the magnetic energy, which is expressed in Eq. (6). Magnetic field-induced transitions result in changes in magnetic symmetry; these changes appear as changes in the parasitic polarization, which are caused by several microscopic mechanisms as described in Eq. (3). This situation is commonly seen in most spin-driven multiferroic materials. The change in P is the effective indicator for specifying the symmetry of the unknown magnetic phases in these frustrated magnets observed in high magnetic fields. Recently developed techniques for diffraction measurements in high magnetic fields are expected to play a crucial role in clarifying the exact spin arrangement in the future [23, 55–58].

4.3 BiFeO_3

As mentioned in a previous section, the thermodynamics of the spin-driven multiferroic materials is dominated by the magnetic terms in the free energy expression. The overwhelming dominance of magnetic energy is a consequence of the smallness of the electric polarization in most multiferroic materials. If multiferroic materials were to have a sizable electric polarization comparable with those in standard ferroelectrics, we would have been able to see the other aspects of the multiferroics. In this context, BiFeO_3 is a unique multiferroic material that exhibits significant switchable polarization.

BiFeO_3 has a highly distorted perovskite-type structure, as illustrated in Fig. 9. The Fe ions are octahedrally coordinated by six O ions. The neighboring FeO_6 octahedra rotate in opposite directions around the $[111]$ axis

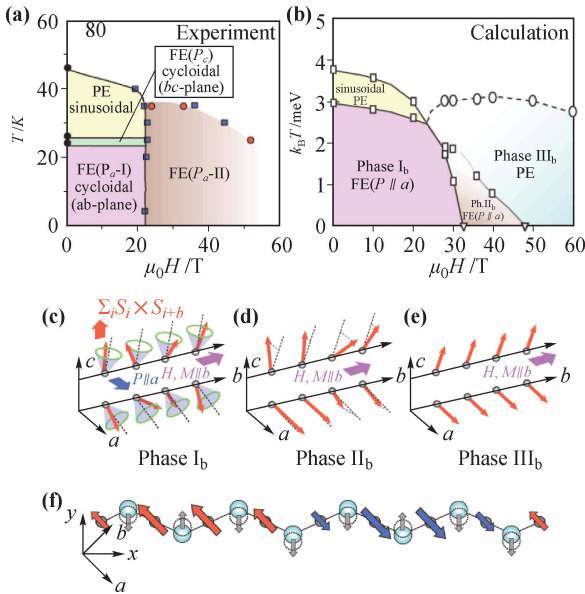


Fig. 8 (a) Experimental and (b) theoretical T - H phase diagram of $\text{Eu}_{0.4}\text{Y}_{0.6}\text{MnO}_3$ for $H//b$. (c)–(e) Spin configurations of phases I_b – III_b . Both I_b and II_b are ferroelectric with $P//a$, but their origin is different. Other phases are paraelectric (PE). (f) Blue (red) arrows represent positive (negative) spin a components. Displacements of the oxygen ions due to the spin alignment are also shown by gray arrows. Reproduced from Ref. [62], Copyright © 2009 The American Physical Society.

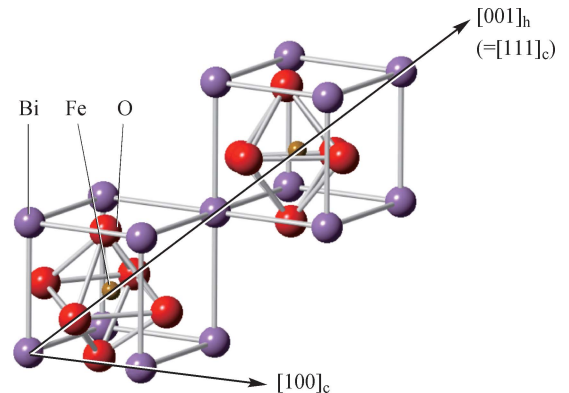


Fig. 9 Crystal structure of BiFeO_3 .

of the pseudocubic cell ($[111]_c$). In addition, the relative displacement of Bi, Fe, and O makes the crystal a non-centrosymmetric $R3c$ crystal in which the electric polarization emerges along the $[111]_c$ axis, i.e., the c -direction of the hexagonal cell ($[001]_h$), approximately below 1100 K. In particular, the largest relative displacement between Bi and O is caused by the stereochemically active 6s electrons in Bi ions and results in the significant electric polarization.

On the other hand, the $S = 5/2$ spins in Fe^{3+} ions order antiferromagnetically at $T_N = 600\text{--}643$ K [50, 51]. The ordering pattern is close to that in a G-type antiferromagnet in which all the adjacent spins become antiparallel. A detailed investigation of the spin structure revealed that the spins form a cycloidal structure with a periodicity of 62 nm [90].

Because there is an eight-fold degeneracy along the $[111]$ direction in the cubic crystal (including the sign), it is not easy to obtain single FE domain crystals. This fact makes the accurate estimation of P difficult. Teague *et al.* reported that the spontaneous polarization is larger than $6.1 \mu\text{C}/\text{cm}^2$ at room temperature from the unsaturated P - E hysteresis loop [91].

Recently, it was observed that BiFeO_3 thin films exhibit a huge switchable polarization; this discovery has suggested new possible practical applications for this material [10]. Apart from multiferroicity, the existence of large switchable polarization in a lead-free compound is an attractive property by itself. Moreover, this film simultaneously exhibits spontaneous magnetization at room temperature; this behavior contrasts with that of bulk crystals, which exhibit the cycloidal antiferromagnetic state. The difference in the magnetic ground state may originate from the stress from the substrate, whereas the existence of huge switchable polarization is a common feature for bulk crystals and thin films. Crystals consisting of single ferroelectric and ferroelastic domains can be grown from the $\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3/\text{Fe}_2\text{O}_3$ flux [92]. Recent experiments in these monodomain crystals have revealed that the existence of switchable polarization exceeding $100 \mu\text{C}/\text{cm}^2$ is part of the intrinsic nature of bulk crystals [53, 54].

Although large polarization and magnetic order coexist in BiFeO_3 at room temperature, whether they have a strong cross-correlation is a non-trivial issue, which should be examined experimentally. Studies conducted in high magnetic fields have played an important role in obtaining the answer to this question. The first high-field study of the ME effects in BiFeO_3 was reported by Popov *et al.* in 1993 [93]. As shown in Fig. 10(a), they observed moderate variation in longitudinal electric polarization, together with a steep change at approximately 20 T applied along the $[100]_c$ direction. The change in polarization is about $20 \mu\text{C}/\text{m}^2$ along the cubic axis, which is less than $1/1000$ of the spontaneous polarization in zero

field. The steep change in P is accompanied with a small jump in M , as shown in Fig. 10(b) [94], indicating the presence of magnetic transition at this field. The linear extrapolation of the high-field M - H curve (the dotted line) indicates the presence of a finite ferromagnetic component in the high-field phase. On the basis of the results of the experiments on multifrequency ESR for fields up to 25 T, the high-field state is reasonably explained as a CAFM state [Fig. 10(c)] [95].

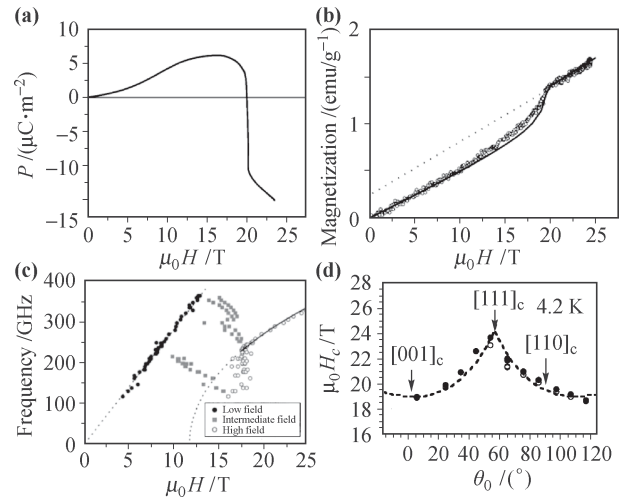


Fig. 10 (a) Longitudinal magnetoelectric effect of a BiFeO_3 crystal along the $[100]_c$ direction at 10 K [93], Copyright © 1993 International Academic Publishing Company (IAPC) “Nauka/Interperiodica”. (b) Magnetization curve at 10 K [94], Copyright © 2004 Kluwer Academic. White circles represent experimental data. (c) Electron spin resonance frequency as a function of magnetic field at 4.2 K [95], Copyright © 2004 The American Physical Society. (d) Angular dependence of transition field. The circles and the dashed line represent the experimental data and the results calculated using Eq. (13) [99], Copyright © 2010 The Physical Society of Japan.

Phenomenological explanation for this transition is given in the framework of the Landau–Ginzburg theory [95–97]. The free-energy density in this system can be expressed as

$$f = -\gamma P_z (l_x \nabla_x l_z + l_y \nabla_y l_z - l_z \nabla_x l_x - l_z \nabla_y l_y) + A \sum_{x,y,z} (\nabla l_i)^2 - K_u l_z^2 - \frac{1}{2} \chi_{\perp} H_{\perp}^2 \quad (11)$$

where $\mathbf{l} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is a unit antiferromagnetic vector, and γ , A , and K_u are constants representing the magnetoelectric coupling, exchange stiffness, and single-ion anisotropy, respectively. The terms $\chi_{\perp}$ and $H_{\perp}$ denote, respectively, the susceptibility and effective field perpendicular to $\mathbf{l}$; $H_{\perp}$ includes the effective field produced by the Dzyaloshinskii–Moriya interaction. If we neglect the third and the fourth terms, this equation gives the following two stable solutions:

$$\begin{aligned} \phi &= \arctan(q_y/q_x), \quad \theta = q_x x + q_y y \\ \phi &= \pi/2, \quad \theta = \pi/2 \end{aligned} \quad (12)$$

The first solution represents the cycloidal state with propagation vector $\mathbf{q} = (q_x, q_y)$ and $|\mathbf{q}| = (\gamma P_z)/(2A)$, whereas the second one corresponds to the homogeneous antiferromagnetic state. When the other terms are introduced perturbatively, the two minimum energy solutions change to the deformed cycloidal state and the CAFM spin state. When the anisotropy is less dominant, the cycloidal state in a zero field is stabilized because of the presence of a large P .

The application of a high magnetic field stabilizes the CAFM state. The field-induced transition takes place at [95, 98]

$$H_c(\theta_H) = \frac{-2m_s \sin \theta_H}{\chi_{\perp} \cos^2 \theta_H} + \frac{2\sqrt{m_s^2 \sin^2 \theta_H + \chi_{\perp} a \cos^2 \theta_H}}{\chi_{\perp} \cos^2 \theta_H} \quad (13)$$

$$a = \frac{(\gamma P_z)^2}{4A} + \frac{K_u}{2} \quad (14)$$

where θ_H is the angle of the applied magnetic field with respect to the $[001]_h$ axis, and m_s denotes the ferromagnetic moment in the CAFM state.

The angular dependence of the transition field was recently determined by magnetic torque measurements in a monodomain crystal of BiFeO_3 [99]. The results shown in Fig. 10(d) are reasonably reproduced using $m_s = 0.3$ emu/g, $a = 6.8 \times 10^5$ erg/cm³, and $\chi_{\perp} = 4.7 \times 10^{-5}$ [100], as shown by the dashed line in Fig. 10(d). The qualitative and quantitative agreement in the profile of $H_c(\theta)$ indicates the relevance of this phenomenological model to express the field-induced transition.

On the basis of this phenomenological model, the change in the magnetic and dielectric order in BiFeO_3 can be explained through the schematic illustration shown in Fig. 11. Starting from the high-temperature limit (a), net electric polarization caused by the ionic displacement (P_d) emerges at $T_{\text{FE}} \sim 1100$ K (b). On

further cooling, spins in the Fe ions order at $T_N \sim 600$ –643 K. Here, the G-type antiferromagnetic state (c) is not realized because of the ME coupling between the large P_d and the spin system. In the realized state (d), the reported cycloidal spin structure [90] will generate finite electric polarization parallel or antiparallel to the $[001]_h$ direction through the inverse-DM effect; the polarization can be expressed as

$$\mathbf{P}_m = \sum_{\langle i,j \rangle} P^{\text{sp}} \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j) \quad (15)$$

The application of H causes a transition to the CAFM state (e), in which the spin system does not induce any $\mathbf{P}_m$ [given by Eq. (15)]. From the $\mathbf{P}_m$ measurements, we can evaluate the magnitude of P^{sp} , which characterizes the strength of ME coupling in this material.

Figure 12 shows the magnetic field dependence of P in a monodomain crystal of BiFeO_3 at various temperatures [99]. In this experiment, the electrodes were formed on the as-grown surfaces of the dendritic crystals, which are normal to the principal axes of the cubic lattice $[001]_c$. Therefore, the measured P is the projection on the cubic principal axis, which corresponds to $1/\sqrt{3}$ of the magnitude of $P//[001]_h$. To remove the possible contribution of the ME effects in the CAFM state, we define P_m as the difference in P at zero field as shown by the arrow in Fig. 12. The P_m observed in the monodomain crystal is one order of magnitude larger than those reported earlier [93, 96], and is comparable to that in other multiferroic materials. In addition, the evaluated value of P^{sp} in BiFeO_3 is comparable to that in TbMnO_3 [99]. Therefore, the ME effect in BiFeO_3 cannot be regarded as being insignificant.

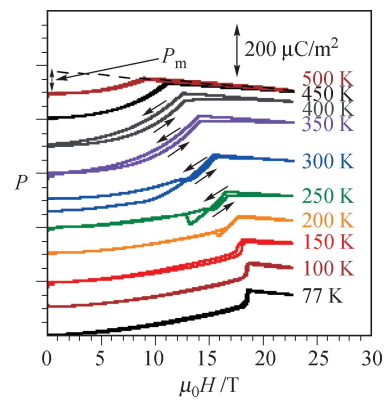


Fig. 12 Magnetic field dependence of electric polarization in a monodomain crystal of BiFeO_3 [99], Copyright © 2010 The Physical Society of Japan.

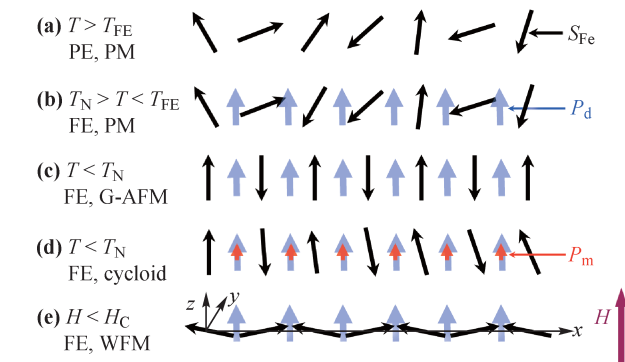


Fig. 11 Schematic drawings for each magnetic and dielectric phase. Thick and thin arrows represent electric polarization and magnetic moment, respectively. (a) paraelectric (PE) and paramagnetic (PM) state, (b) ferroelectric (FE) PM state, (c) FE and G-type antiferromagnetic state, (d) FE and cycloidal spin state, and (e) field-induced canted antiferromagnetic state [99], Copyright © 2010 The Physical Society of Japan.

As seen above, the presence of a magnetic phase transition at around 20 T is explained phenomenologically as the change from the cycloidal to the CAFM state, which is accompanied with the change in parasitic polarization $\mathbf{P}_m$. However, there are several unresolved problems that should be studied.

First, ME effects in the low-field phase show different profiles with changing temperature; the profile changes from being almost linear at 77 K to quadratic above 350 K and shows an additional fine structure in the intermediate temperature range of 200–300 K (Fig. 12). These changes in the P – H curves below H_c may be related to the deformation of the cycloidal spin structure [101, 102]; however, this issue remains a subject of controversy [103] and is expected to be clarified through systematic study of the ME effects together with microscopic measurements, such as neutron diffraction, in high magnetic fields.

Second, the ME effects in the CAFM phase remain unclear. Although several experimental reports have demonstrated finite ME effects in the high-field CAFM phase, their profiles are not consistent with each other [93, 96, 99]. Further careful and systematic study of the ME effects in monodomain crystals is expected to provide conclusive data for the ME effects in the CAFM state; these data will be crucial in the practical application of thin films. In addition, Lisenkov *et al.* predicted the occurrence of another phase transition from the CAFM phase in a magnetic field of 70 T on the basis of first principles calculation [104]. Although the predicted transition field is not easy to generate, it is currently achievable in some of the high-field facilities in the world [59, 105, 106].

5 Summary

The magnetoelectric effect is the phenomenon that directly reflects the symmetry of the underlying magnetic order. Because this effect is usually weak, a high magnetic field is needed to extract it in a discernible form. The application of high magnetic fields sometimes induces phase transitions. In most multiferroic materials, the thermodynamics of these phase transitions is dominated by magnetic energy because of the smallness of the electric polarization. In this case, multiferroicity plays a crucial role in determining the magnetic symmetry of the induced phase, which is done through the measurement of magnetoelectric effects. On the other hand, when a large polarization exists, as is in the case of BiFeO_3 , the spin order is modified through the magnetoelectric effect. The overall relationship between two order parameters in a magnetic phase diagram remains unclear. The topic of multiferroic materials encompasses a wide range of issues in condensed matter physics. Further studies using high magnetic fields are expected to yield significant breakthroughs in this research field.

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