Electric-Field Switching of Magnetization using Multiferroics

Ameneh Najafi

Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

Supervised by: Prof. dr. B. Noheda

Abstract

This review paper describes new techniques of electrically controlling magnetism by means of novel materials so-called multiferroics. Multiferroics are of interest for important practical applications like multifunctional spintronic devices, as they display simultaneous ferroelectric and magnetic ordering together with coupling between their dual order parameters. The first technique introduced by this review is based on electromagnetic coupling which revealed in compounds with layers of ferromagnet and multiferroic in contacting with each other. Here, exchange interaction at the interface between a ferromagnet ($Ni_{0.78}Fe_{0.22}$) and the antiferromagnetic domains in $BiFeO_3$ is the dominating mechanism. The other approach is that by applying consequent different lattice distortions in perovskites materials one can provide ferromagnetism, ferroelectricity and electromagnetic coupling as well, for instance study on layered perovskite $Ca_3Mn_2O_7$, with this point of view, is described. The presented experimental and theoretical studies on multiferroics promote new methods of controlling ferromagnetism via an electric field.

Contents

1. Introduction

Multiferroics, owners of simultanius ferroelectric and magnetic ordering property, have become a hot topic of research in recent years [1,2]. A subclass of them are magnetoelectrics in which an external magnetic field is able to impose an electric polarization. They have been proposed to be used in a new generation of devices which overcome critical limitations in technology [3-5]. Discovering of this utilization in new devices promotes concerted interesting among scientists to search for suitable promising materials. Realizing this promise in new systems, promotes concerted interesting among experimentalists and theoreticians alike in the search for candidate materials. The idea is to identify mechanisms that provide the situation in that both spatial inversion symmetry and time reversal symmetry are broken simultaneously, while the coupling of these two different types of order is the most important goal. This property was first discovered in Boracites [6], and soon after that other natural or artificial multiferroics were figure out [7]. For example, Ramesh's group achievements, in 2003, revealed thin films of a very famous multiferroic, $BiFeO_3$ [8], and at the same time, Tokura and Kimura discovered a coexistence of magnetism and ferroelectricity in $TbMnO_3$ in which magnetism causes ferroelectricity [9]. Indeed, such materials have great potential for new practical applications more than other materials with magnetic or electrical ordering due to the opportunity of accessing two different types of order at the same time and also the beneficial of coupling property between magnetic and electrical ordering, which leads to an additional degree of freedom in device design. Applications include electrically addressing a magnetic memory (without currents), storing data both in the electric and the magnetic polarizations in multiple state memory elements, or writing a ferroelectric data bit and reading that magnetically in a novel memory media.

Recent developments in magnetoelectronics and spintronics excited a great interest among scientists due to the possibility to control the magnetization of materials externally [10,11]. In this pursuit, multiferroics are promising materials for electric field control of magnetization [3,12 and13]. Till now $BiFeO_3$ (BFO) is the only known multifferoic that operates at room temperature. In order to reach the ability of modifying and controlling magnetization electrically, exchange coupling is a much desired mechanism. In this approach, most experimental results reveal a shift, or bias of the magnetization hysteresis loops or show enhancement of ferromegnetic (FM) coercivity. A lot of works have proposed a design in which a ferromegnetic layer is deposited on top of a multiferroic substrate to produce exchange coupling in a ferromagnet–multiferroic structure [14-16]. This exchange coupling is originated from either the coupling between ferromagnetism of ferromegnetic layer and antiferromagnetism of multiferroic substarte at the interference of them, or the coupling between ferroelectricity and antiferromagnetism within the multiferroic layer. In this paper, we present the observations of such electric-field control of local magnetism that has been done by

Lebeugle et al. [14]. It has been shown that easy and hard magnetic directions can be induced in the FM layer, and exchange coupling existing at the interface of BFO/ $Ni_{0.78}Fe_{0.22}$ bilayers provides the ability of controlling ferromagnetism by an electric field with using the utility of $BiFeO_3$ as the multiferroic layer. Parallel studies have been done by Ramesh's group on $Co_{0.9}Fe_{0.1}$ layers attached to thin films of $BiFeO_3$ [15]. In Ref. [16] researchers have considered thin films of $YMnO_3$, a multiferroic which possess antiferromagnetic and ferroelectric trait, and with a very similar experiments they have shown that it is possible to modify and control the magnetic exchange property of ferromagnetic layer attached to multiferroic substrate, by exerting appropriate electric field.

Other efforts propose a new mechanism by which ferroelectricity and ferromagnetism are imposed by the lattice instabilities accompanied by electromagnetic coupling between them [9]. The utility of this method is that it can be applicable to a large class of materials, for example, the ABO_3 perovskites. In this field, Benedek and Fennie have exhibited interesting results of their calculations in Ref. [17], where, octahedron rotations provided the preconditions for electrically controlling the magnetization induced in $Ca_3Mn_2O_7$ multiferroic. The details of the mechanism that they used are introduced in this paper.

These discovered mechanisms may create revolution in generation of magnetic devices, so that is why we are interested in having an overview on recent achievements in this field. To savvy the primary conceptions in the sense of multiferroics, first, we briefly review the basics of ferroelectricity, ferromagnetism and multiferroism in sections 2, 3 and 4, respectively. Section 5 is devoted to the classification of multiferroics. In section 6, we introduce different mechanisms, underlying multiferroic behavior, for electric-field controlling magnetism. Finally, we end the paper with a brief conclusion.

2. Ferroelectricity

Ferroelectricity, the discovered electric trait of Rochelle salt in 1921 [18], is the property attributed to the materials with spontaneous electric polarization that is switchable under the applied electric field. Scientifically speaking, a ferroelectric material is an ordinary dielectric in high temperatures that means it shows electric polarization provided that an electric field is appled and by decreasing the temperature it exhibits intrinsic electric ordering whose direction can be switched by an external electric field. This phase transition phenomenon in ferroelectric materials occurs below certain temperature which is called the Curie temperature, T_c.

Interesting features of ferroelectrics make them useful materials for specific device applications, for example the nonlinear nature (the electric permittivity of ferroelectrics has a nonlinear behavior as a function of the external electric field) of ferroelectric materials can be used to make capacitors with tunable capacitance. Besides, since the electric permittivity of ferroelectric capacitors is very high in value the size of this kind of capacitors are smaller than the size of dielectric capacitors with the same capacitance.
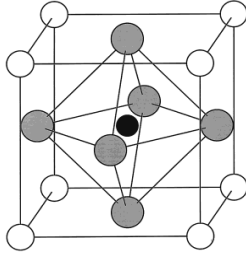
Fig. 1. Schematic of cubic perovskite structure. A small cation, B (in black) states in the center of cubic, oxygen anions (in gray) surround the Bcation in octahedran shape and the large A cations (in white) positioned at the corners of the unit cell [1].

Also, ferroelectric materials have domains and show hysteresis effect, so they can be used as a memory function such as ferroelectric random access memory in computers.

Study of ferroelectric materials was originally on Rochelle salt, $KNa(C_4H_4O_6)$. Due to the complexity of such structures having a unique and complete theory for all ferroelectrics based on the results of experiments of Rochelle salt was inaccessible. The pursuit of the studies has been continued on perovskite-structure oxides, ABO_3 (They are schematically depicted in Fig. 1). In fact, ferroelctricity is a result of displacement of cations or anions from the equilibrium position which leads to polarization. To describe this, there are two successful theory models: order-disorder model and soft-mode model. In the order-disorder model, the B cations in ferroelectric perovskite oxides should always displace along one of the cubic diagonals to lower their energy, which depends on temperature; at high temperature, all possible <111> directions are allowed, and at low temperature, all displacements occur with

the same orientation which leads to rhombohedral symmetry, or with two or three preferred <111> directions that gives rise to tetragonal or orthorhombic symmetry. Due to the unobserved large change in configurational entropy at the phase transition, this model may be applicable in higher temperature regimes away from the phase transition temperature. The "double-well" potential energy characteristic as a function of the position of the B cation between the oxygen anions {R} in perovskite ferroelectrics can be observed at high temperatures by this model, the feature which is not seen in the soft-mode model [Fig. 2]. In the soft-mode model, displacements of cations are stable below the Curie temperature. Above this temperature there is a restoring force that pushes the B cations back to the center if they are displaced.
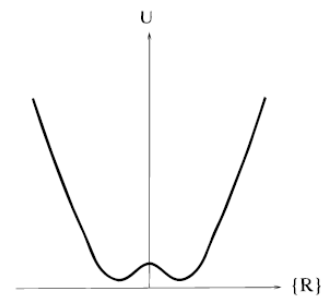

Fig. 2. The "double- well" potential energy characteristic of perovskite ferroelectrics based on order-disorder model [1].

The identity of the B cations also plays important role, it can affects ferroelectric property of materials. The two famous perovskite-structure compounds are $PbTiO_3$ and $BaTiO_3$ in that Ti^{4+} has empty d states, d^0, resulting hybridization effects between them and the filled oxygen p states.

3. Ferromagnetism

A general definition for a ferromagnetic material is that, it could exhibit spontaneous magnetization without application of an external magnetic field, though, the more precise identification categorizes it into ferromagnetic and ferrimagnetic material. At high temperature, a ferromagnet consists of randomly aligned magnetic dipole moments of atoms while at low temperature they reorient to be in the same direction, as depicted in Fig. 3, below a certain critical temperature so-called Curie temperature. This phase transition is the basic property of ferromagnets and has been explained successfully by two main theories: the Curie-Weiss localized-moment theory [19] and the Stoner band theory of ferromagnetism [20].
Based on Curie-Weiss localized-moment theory there is an internal magnetic field which is responsible for parallel alignment of magnetic moments. In competition between the thermal energy, kT, and the energy of molecular field corresponding to the alignment, at high temperatures, thermal energy overcomes, so magnetic moments orient randomly ,known as paramagnetism, while below the Curie temperature magnetic field dominates, resulting in ferromagnetism. This explanation is consistent with the experimentally observed behavior of the magnetic susceptibility, χ, of many magnetic materials, which is introduced by Eq. 1.
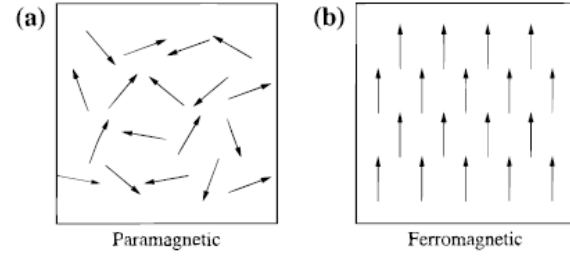
$$\chi = \frac{c}{T - T_c} \qquad (1)$$

Fig. 3. Orientation of magnetic momemts at. temperatures (a) higher than Curie temperature and (b) below the Curie temperature, in magnetic materials [1].

Although, the susceptibility of many magnets like ferromagnets, ferrimagnets and antiferromagnets are introduced well by the Curie-Weiss localized-moment theory, there are still some discrepancies. Experimentally, the magnetic moment per atom in the ferromagnetic phase differs from that of paramagnetic phase which is in contrast with the results of the Weiss localized-moment theory. In addition, according to localized-moment theory the magnetic dipole moment on each atom or ion should correspond to an integer number of electrons which is not the case in experiments. To overcome these contradictions, Stoner improved the above mentioned theory. In Stoner theory, like in Weiss localized-moment theory, exchange energy is the main justification for ferromagnetism, but here, opposing the sign of alignment of spins consumes a lot of energy to transfer electrons from lowest band states (involving pair electrons with up and down spins) to higher energy band states. This band energy is the reason of why simple metals do not show ferromagnetisity, the phenomenon which had not been understood by Weiss localized-moment theory. Besides, Stoner theory demonstrates that magnetic moments of the
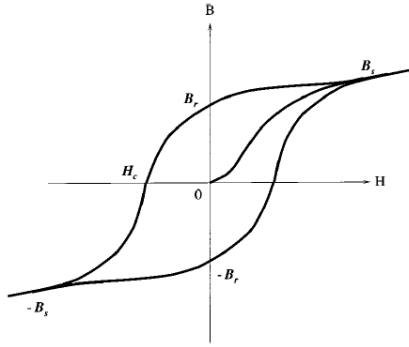
Fig. 4. Typical hysteresis loop for a ferromagnet or ferrimagnet [1].

transition metals do not correspond to integer numbers of electrons by considering 3d and 4s densities of states in transition metals and the position of Fermi levels in them.

The most important property of ferromegnets is their hysteresis loop in the plot of magnetization and flux density, B, versus applied magnetic field, H, which is illustrated in Fig. 4. External magnetic field, H, would result in the alignment and reorientation of domains in a macroscopic magnet. A saturated, B_s, and residual, B_r, induction magnetization appears in this figure. The shape of the hysteresis loop implies different applications for ferromagnets, for instance, hysteresis loops with the property of being square in shape and involving two stable states in magnetization, are proper for storing data, and on the other hand, a small hysteresis is appropriate for a transformer core with a rapidly switching field direction as it is easily cycled.

4. Multiferroism

Multiferroism is attributed to materials which posses two or three of the traits spontaneous ferroelectricity,ferromagnetism,
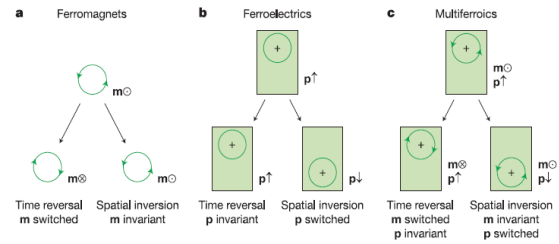

Fig. 5. (a) Symmetry operations for ferromagnets show magnetic moment, which defined by rotating electron, is not changed under spatial inversion but it is switched under time reversal. (b) Spatial inversion switches dipole moment, P, which is an asymmetric point charge in a unit cell, while time reversal does not affect it. (c) Both symmetries will be broken in multiferroics, as they posse electric and magnetic orderings simultaneously [21].

and ferroeleasticity at the same time. Commonly, a multiferroic includes a combination of both properties of ferromagnetic and ferroelectric. Since, being ferroelectric means that the material is asymmetric under spatial inversion and being ferromagnetic means the sign of it's magnetic moment, m, and magnetic field, H, are changed under time inversion, a multiferroic has breaking of both symmetries at the same time, in order to exhibit both properties of ferroelectricity and ferromagnetism [21]. Figure 5 shows time-reversal and spatial-inversion symmetry in ferroics. Nowadays, multiferroic materials are extended to be classified including any kind of magnetic or electric ordering as well. For example, magnetoelectric coupling may occur in paramagnetic ferroelectrics or a very famous multiferroic, $BiFeO_3$ [8], has been known as an antiferromagnetic-ferroelectric material. A complete definition of multiferroics can be illustrated by Fig. 6.
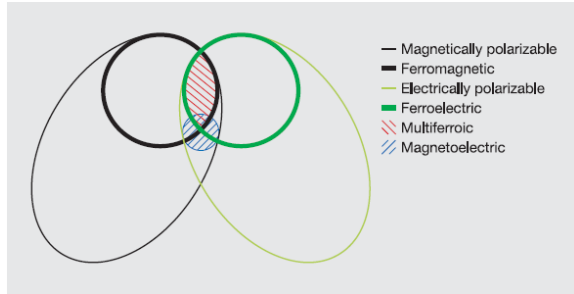
Fig. 6. Schematic comparison of multiferroics and magnetoelectrics [21].

As the driving mechanisms of ferroelectrics and ferromagnets are not only different from each other but also they actually seem to exclude each other, it is difficult to find intrinsic multiferroics. Mostly, transition materials with empty d-shell in the crystal exhibit ferroelectricity while transition materials with a partially filled d-shell show ferromagnetic characteristics. Therefore, synthesise of materials handling both two different properties at the same time is a challenge for scientists [1,3]. There are a lot of attempts to produce such ferroic materials for instance, Smolenskii et al. [22] proposed doping of paramagnetic cations into known non-magnetic ferroelectric compounds. By considering pervoskites [Fig. 1], B sites cations may contain a cation with empty and filled d-shell to produce ferroelectricity and magnetization simultaneously. The first material produced by this approach is $(1-x)Pb(Fe_{2/3}\ W_{1/3})O_3-xPb(Mg_{1/2}\ W_{1/2})O_3$, in that Mg and W ions are diamagnetic and cause the ferroelectricity, and Fe^{3+} ion with d^5 shell is the reason of magnetic ordering [1,23]. Another possible solution for this incompatible mechanisms problem is to use lone-pairs of ions like Bi^{3+} and Pb^{2+} to combine ferroelctricity and magnetism [1].

Therefore, to understand more clearly the concept and origin of multiferroism in known multiferroic materials, it is useful to have a quick review on classification of multifferoics based on the mechanism that defines their characteristics. This review is mostly inspired of Ref. [3].

5. Different types of multiferroics

After theoretical studies, experimental improvements characterized two different classes of multiferroics [8,9 and 24]. The first group is the ferroics which have different and incompatible sources regarding to their ferroelectrical and magnetic properties that appear independently of one another. In this class, ferroelectricity appears in higher temperatures together with large polarization in comparison with magnetism. This class is called Type-I multiferroics. The second group, in which magnetism causes ferroelectricity, can be called type-II multiferroics [9,24]. In this group a strong electromagnetic coupling is implied, though the polarization is not much considerable.

5.1. Type-I multiferroics

Type-I multiferroics are often good ferroelectrics and based on the primary mechanism of their ferroelectricity they will be categorized in different subclass of type-I. The opportunity of them is that the critical transition temperatures of ferroelecticity as well as magnetism are above the room temperature. On the other hand, weak coupling between their dual orderings is the negative aspect of them. Below, we will point to four of the major subclasses.

5.1.1. Multiferroic perovskites

There are a lot of ferroelectric and magnet materials with perovskites structures but the combination of them are rare. The reason of that is so-called "d^0 vs d^n" problem, which has been mentioned in the previous section. It is related to the d-shell of transition materials which are responsible for ferroelectric and magnetic properties of the material. A reasonable solution about this problem is to create mixed prevoskites with d^0 and d^n ions, although, the electromagnetic coupling in mixed perovskites is still not strong enough [See Fig. 7(a)].
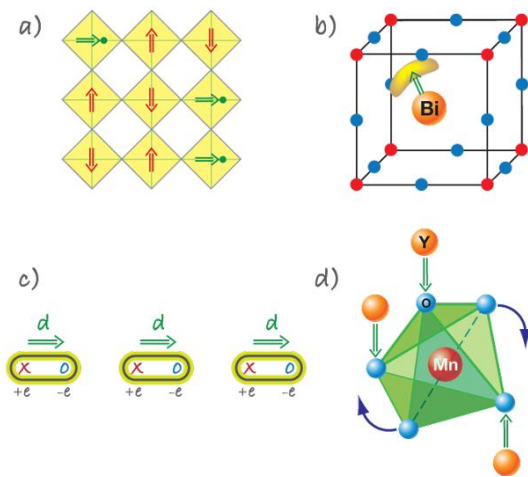

Fig. 7. Different subclasses of type-I multiferroics. (a) Illustration of a mixed perovskite. Green circles are d^0 ions that by shifting from the centers of O_6 octahedra provide ferroelectricity, red arrows indicate magnetic orders related to d^n ions. (b) Orientation of lone pairs (yellow lobes) in ions like Bi^{3+} leads to electric polarization (green arrow). (c) Charge ordered systems give rise to ferroelectricity due to coexistence of inequivalent sites with different charge and inequivalent bonds. (d) Schematic of tilting distortion in $YMnO_3$ multiferroic which results ferroelectricity [3].

5.1.2. Ferroelectrics with lone pairs

In some multiferroics such as $BiFeO_3$ and $PbVO_3$ [25], lone pairs of Bi^{3+} and Pb^{2+} play important role to show ferroelectric property. Actually these lone pairs are nonbonding electron pairs of outer orbital shell 6s. It is believed that the ordering in one direction of these lone pairs is the origin of ferrolectricity in these compounds [It is shown in Fig. 7(b)].

5.1.3. Ferroelectricity due to charge ordering

Charge ordering is another mechanism results in ferroelctricity in type-I multiferroics. This mechanism essentially appears in multifferoics consisting of transition metal ions with different valence. In these systems ferroelectricity can be observed provided that inequivalent sites, including different charges, as well as inequivalent bonds coexist [Fig. 7(c)]. $Pr_{1/2}Ca_{1/2}MnO_3$ or nickelates $RNiO_3$ are examples of such charge ordering systems [26,27]. Also, there are some multiferroics in which one of the conditions, inequivalent sites or inequivalent bonds, would result in ferroelectricity. For instance, Ca_3CoMnO_6 is a newly discovered multiferroic which involves ions with unequal charge [28] while $LuFe_2O_4$ presents the case with inequivalent bonds [29].

5.1.4. "Geometric" ferroelectricity

In this case structural instability causes ferroelectricity. This phenomenon functions by size effects or by other geometrical assumptions. As shown in Fig. 7(d), tilting of the MnO_5 unit in $YMnO_3$ leads to ferroelectricity; since by this tilting The

oxygen and Y ions are closer to each other and produce dipole moments which are more in one particular direction than the other directions, so ferroelectricity appears [30].

5.2. Type-II multiferroics: Magnetic multiferroics

Type-II multiferroics are related to novel multiferroics in which a specific magnetism would result in ferroelectricity. Several reports indicate that ferroelectricity in such magnetically ordered multiferroics is strongly affected by magnetic field [9,24]. Based on the mechanism of multiferroic behavior, we focus on the two main groups of them. The first group; spiral type, and the other; collinear type.
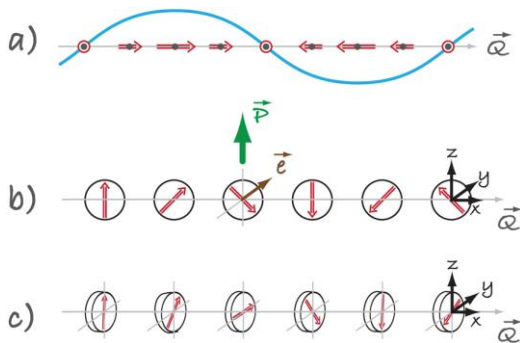

Fig. 8. Schematics of several spiral magnetic structures in type-II multiferroics. (a) Magnetic moments are aligned in one direction with different magnitude in each half period of sinusoidal spin density wave. Due to centrosymmetry there is no ferroelectricity. (b) Spins rotate cycloidal in a plane of wave vector $Q = Q_x$, here polarization P is implied. (c) Cycloidal spiral in which magnetic moments rotate in a plane perpendicular to the wave vector, in most of the cases there is no polarization with this magnetic structure [3].

5.2.1. Spiral type-II multiferroics

In this large subgroup of type-II multiferroics, ferroelectricity is induced by a spiraling magnetic phase. $TbMnO_3$ is the famous one which has been studied with this approach [9]. In this case, magnetic ordering appears at $T_{N1}=41K$, but as shown in Fig. 8(a), this ordering is sinusoidal and as a result there is neither net magnet moment (i. e. antiferromagnetic) nor ferroelectricity. At lower temperatures, below $T_{N2}=28K$, the magnetic structure changes together with the onset of ferroelectricity [Fig. 8(b)]. Mn spins move cycloidal, in Fig. 8(b) the dipoles rotate in a plane including wave vector. This situation has been investigated by Mostovoy [31], he demonstrated that here a polarization, P, is also created. If the rotation occurs around the axis parallel to the wave vector no polarization is expected [Fig. 8(c)], although, Arima [32] have shown this result can not be generalized to other symmetries and the polarization may be developed in some cases with special cycloidal movements.

We note that spin-orbit interaction is the microscopic mechanism of polarization in a cycloidal spiral multiferroic. In spiral multiferroics, magnetic fields can strongly affect the electric polarization.

5.2.2. Collinear type-II multiferroics

This group points to the multiferroics in which ferroelectricity is derived in structures with collinear magnetic moments. Collinear magnets are structures with aligned magnetic moments parallel to a special axis. In this case, spin-orbit interaction is not necessary to produce ferroelectricity, whereas, exchange striction causes

polarization. A very good example is Ca_3CoMnO_6 [28] where exchange striction originates from transition metal ions with characteristic of unequal valences (here, Co^{2+} and Mn^{4+} are positioned alternatively in a chain). Also, this effect may be expected in compounds with identical magnetic ions because the exchange in transition metal oxides usually occurs via intermediate oxygens.

6. Mechanisms for controllable polarization-magnetization coupling

In order to increase the performance of microelectronic devices, scientists try to propose a promising route to control devices via electric fields. By this way, the resulted heating from the device is remarkably less than that produced by the conventional magnetic devices. For this technology, materials like magnetoelectrics (ME) are desirable, because they prepare the possibility of controlling the magnetism by electric field or vice versa. There are several mechanisms to achieve an electrically controllable magnetic device. One of them which is promoted a lot among scientists is to deposit a ferromagnetic layer on top of multiferroic and try to control the magnetization of FM layer with electric fields using magnetoelectric effect [14-16]. Magnetoelectric coupling between the antiferromagnetic (here, mostly an antiferromagnet-ferroelectric multiferroic is used) and the ferromagnetic order, first, within the multiferroic layer and second at the interface between the multiferroic and ferromagnetic layers of structure where exchange interactions are dominating mechanism, are the commonly two

successive coupling mechanisms that are exploited in this approach.

The other mechanism is a desirable mechanism where specific lattice instability whould result in both induced ferromagnetism and ferrolectrisity. Recently, Nicole A. Benedek and Craig J. Fennie [17] proposed that using two special lattice rotations subsequently, provides ferroelectricity and ferromagnetism together with the coupling of them (magnetoelectric coupling), and what is interesting is that none of these rotations, individually, develops the ferroelectricity. magnetoelectric coupling, weak ferromagnetism, and ferroelectricity can be developed from the combination of two lattice rotations, neither of which produces ferroelectric order individually. Hopefully, one can control the magnetization by applying external electric field using this point of view to produce magnetoelectric coupling.

In the current chapter we explain more precisely the above mentioned mechanisms based on experimental efforts presented in Refs. [14,17,33 and 34].

6.1. Electric-field control of magnetism in a ferroelectric-multiferroic structure

D. Lebeugle et al. [14] demonstrated that a Permalloy ($Ni_{0.78}Fe_{0.22}$) layer attached to a multiferroic $BiFeO_3$ (BFO) single crystal acquires an easy magnetic axis which can be toggled by electric field-induced change of electric polarization through the magnetoelectric effect. They use $BiFeO_3$ as a multiferroic substrate because BFO is still the only multiferroic which operates at room temperature. It is known with T_C=1103 K
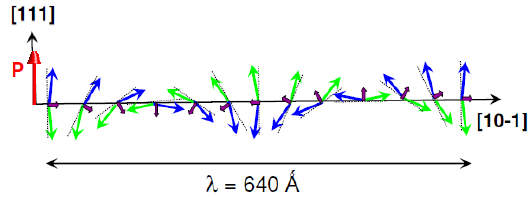
Fig. 9. Schematic of the magnetic configuration of antiferromagnetic vectors in the 64nm periodic circular cycloid [35].

(Curie temperature) and $T_N=643$ K (antiferromagnetic Néel temperature). This compound has a rhombohedral symmetry. A local spin canting of the Fe^{3+} moments are induced magnetoelectrically and their G-type antiferromagnetic moments describe a cycloid. The period measured, reported in Ref. [35], is 64 nm [Fig. 9]. It can be seen from this figure that the magnetic moment rotates in a plane determined by the polarization vector (along the [111] direction) and the cycloidal propagation vector. In a polarization domain along [111], the cycloid has three directions that they are equivalent because of the rhombohedral symmetry. Here, BFO single crystals have been synthesized using a flux technique. Under the magnetic field of 200 Oe in different directions, a thin layer of Permalloy ($Ni_{0.78}Fe_{0.22}$, Py) was deposited on the BFO substrate, which is majority ferroelectrically single domain, and at the end it was covered by a thin layer of Au (about 3 nm).

The magnetic hysteresis loops of Py layers along the easy axis and hard axis are plotted in Fig. 10. The tow nonequivalent in-plain magnetic directions oriented 90° from each other. Zero retentivity and almost 100% retentivity which are the characteristics of hard axis and easy axes,
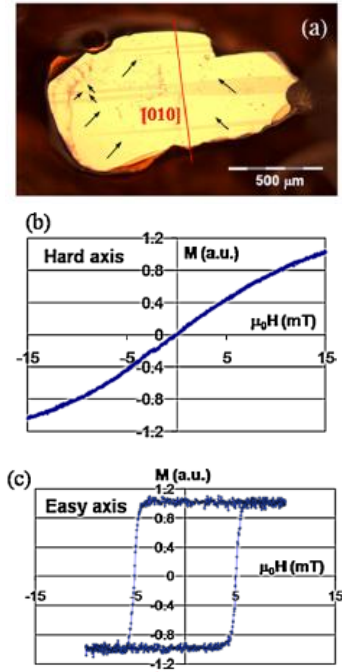

Fig. 10. (a) Polarized light image of BFO. (b) Hysteresis loop of a thin layer of Py (deposited on top of the BFO) along hard axis [100] and (c) along easy axis [010] [14].

respectively, are clearly demonstrated in the figure.

The authors have mentioned that the easy axis of deposited Py is connected to the crystallographic axes of multiferroic layer during the whole various situations of deposition processes. Interestingly enough, only the propagation vector, which is cycloid, has the right projection. They attributed this behavior to the exchange coupling of ferromagnetic moments of Py layer with the antiferromagnetic moments of BFO substrate which have cycloid manner. To be more clear, consider Fig. 11, this figure shows how ferromagnetic moments of Py layer behave under the influence of underlying cycloid pattern. This treatment is induced by exchange coupling. Moreover,
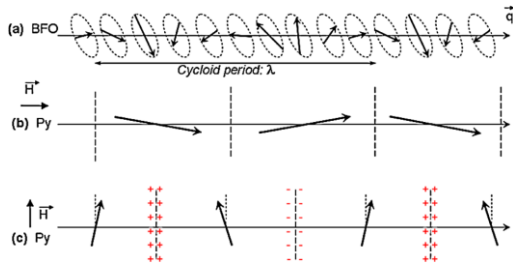
Fig. 11. (a) Projection of cycloidal arrangement of magnetic moments in BFO, $\vec{q}$ is the propagation vector. (b) and (c) the rearrangement of magnetic moments in Py layer under the influence of exchange coupling with BFO layer [14].

this kind of rearrangement of ferromagnetic moments of Py layer gives rise to have easy axis of magnetism along the cycloid propagation direction. The reason is that exchange coupling is not affected by the local direction of magnetization, and also the demagnetization energy is minimum when $M \parallel \vec{q}$ while it is maximum when $M \perp \vec{q}$ (because, as depicted in Figs. 11(b) and 11(c), an enhancement of virtual magnetic charges are built up at the domain walls whenever the magnetization is perpendicular to the propagation direction).

The goal is to use this phenomenon to control the magnetism in ferromagnetic layer by means of electric field. It is implied from previous arguments that the exchange induced easy axis should be changed by using electric field; because, as it has been mentioned, the magnetic moments of Fe have to rotate in a plane made by propagation and polarization vectors, so whenever $\vec{P}$ changes the antiferromagnetic vector of BFO switches in a way to provide this precondition and the easy axes also follows that. D. Lebeugle and his coworkers applied an electric field with the value of
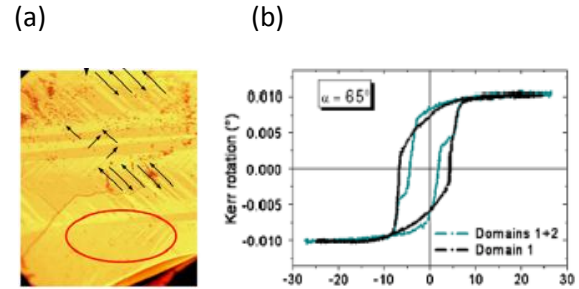

Fig. 12. (a) Image of the ferroelectric domains of BFO, the projections of polarizations in the plane are noted by arrows. (b) Hysteresis loop for Py layer impressed by an electric field [14].

25 kV/cm on the same sample of Fig. 10. Their MOKE hysteresis loops measurements reveal two contributions with two different sets of coercivities when the angle between applied field H and the [100] direction of BFO is 65°. This feature of typical hysteresis cycle indicates the generation of another magnetic coupling domain in Py as a result of change in polarization. In addition, the easy axis and hard axis of this new domain are at 90° from those belong to the domain before applying the electric field. These results are presented in Fig. 12.

Furthermore, in this study, the magnetization of Py along easy axes could be modified corresponding to the scheme of underlying ferroelectric domains. This observation emerges as a result of magnetoelectric coupling existing in the multiferroic layer; an effect which enables the polarization to impress the direction of the antiferromagnetic vector belongs to multiferroic layer. We note that by these experimental results, D. Lebeugle et al. empirically showed addressing of the magnetization of deposited ferroelectric layer by means of electric field, could be possible.

Parallel results have been manifested by Ramesh's group [15], where, a $Co_{0.9}Fe_{0.1}$ layer attached to the same canonical multiferroic BFO was used as a MF layer. One can follow similar efforts in Ref. [16] in which, researchers have exhibited results of compounds involving epitaxial thin films of $YMnO_3$, a multiferroic which shows antiferromagnetic and ferroelectric characterizations. Using the above mentioned method, they have shown that changes in the direction of polarization of $YMnO_3$ layer through electric field can significantly modify the magnetization of ferromagnetic layer.

6.2. Electric field control of the magnetization by hybrid improper ferroelectricity in multiferroics

Recently, in [17], a fresh approach to introduce magnetoelectric coupling in multiferroics have resulted in a new perspective in multiferroics world. Nicole Benedek and Craig Fennie [17], by refashion the arrangement of oxygen, using rotation and tilt distortions in perovskite structures, have proposed that ferroelectricity and modification of the magnetic order can be induced in layered perovskite $Ca_3Mn_2O_7$ and have promoted a magnetoelectric coupling. Based on group theoretical methods, ferroelectric phase of this structure ($A2_1am$) can be relataed to the paraelectric phase ($I4/mmm$) through three separate atomic distortions. They are a polar zone-center mode transforming (Γ_5^-) and two zone-boundary modes (a rotation (X_2^+) and a tilt (X_3^-) modes related to oxygen). It has been indicated that combination of the two last ones is sufficient to establish a
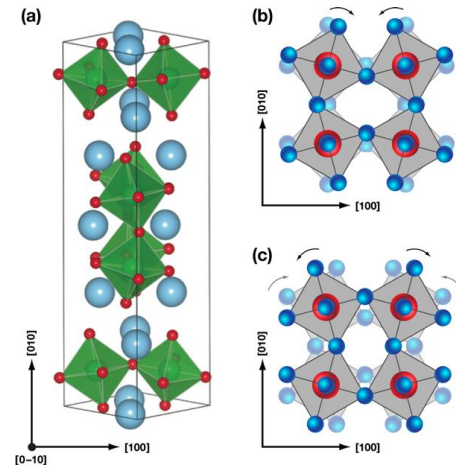

Fig. 13. (a) Ferroelectric phase structure of $Ca_3Mn_2O_7$. Ca, Mn and O ions are respectively represented by blue, green and red sphers. (b) Schematic of rotation distortion (X_2^+). Here Mn ions are red and O ions are blue. (c) Schematic of tilt distortion (X_3^-) [17, 34].

transition in polarization; from the paraelectric to the ferroelectric. The crystal structure of $Ca_3Mn_2O_7$, under the influence of such instabilities can be illustrated by Fig. 13(a). As shown in this figure, in the polar structure (ferroelectric phase), the oxygen octahedra are changed significantly in orientation in comparison with the paraelectric structure. Figures 13(b) and 13(c) schamitally show the rotation and tilt distortions, respectively.

Nicole Benedek and Craig Fennie state that the instabilities can create either isothermally or in different temperatures but what is crucial to note is that the combination $X_2^+ \oplus X_3^-$ can break spatial inversion leading to ferroelectric polarization. They calculated the $T = 0$ energy surface around the paraelectric phase structure from first principles; calculations of the total energy versus the amplitude of distortions , initially for each distortion
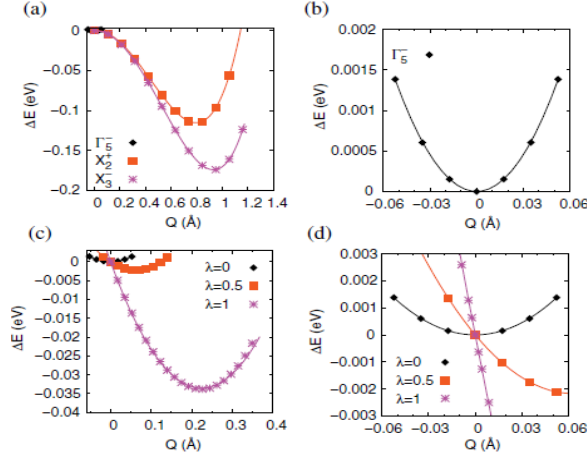
Fig. 14. Energy surface around undistorted structure of $Ca_3Mn_2O_7$ versus the amplitude of (a) the rotation (X_2^+) and tilt (X_3^-) instabilities, (b) the polar distortion (Γ_5^-). (c) and (d) ferroelectric polarization as a result of hybrid order parameter, $Q_{X_{23}} = \lambda X_3^- X_2^+$ [17].

separately [Fig. 14(a) and 14(b)], then by considering impression of both distortions together $Q_{X_{23}} = \lambda X_2^+ X_3^-$ [Fig. 14(c) and 14(d)]. Their findings show large energy gains in a double-well potential characteristic for each distortion [Fig. 14(a)] but not for the polar contribution [Fig. 14(b)]. Also, the fact that the polarization originates from a combination of two instabilities, $Q_{X_{23}} = \lambda X_2^+ X_3^-$, is manifested in Figs. 14(c) and 14(d). These investigations indicate that the fundamental operator terminated to a ferroelectric phase is the combination of rotation and tilt modes which in Ref [17] is called the hybrid improper mode and known as a single distortion mode $Q_{X_{23}}$. By knowing this fact, the first idea that comes to mind is the direction of ferroelectric polarization will be changed if only one of the X_2^+ or X_3^- is reversed. Consequently, in the presence of an electromagnetic coupling, using electric

field may be a useful manner to address the magnetization in this kind of multiferroics, though first of all one must be sure about the existence of magnetic domains and electromagnetic coupling. In the following we will introduce how Benedek and Fennie justify the induction of magnetization and also a linear coupling between magnetization and ferroelectric polarization ,which is essential for controlling the magnetization by electric field.

Investigations of Benedek and Fennie show that similar distortions which provide ferroelectricity would result in a small net magnetic ordering too. This magnetization arises from the oxygen tilt mode denoted by X_3^-. The sign of the induced magnetization is changed only by reversing the octahedral tilt X_3^- and not by varying the octahedral rotation X_2^+. However, this feature implies a mechanism for addressing the direction of polarization as well as magnetization by altering X_2^+ or X_3^-, the authors sought to search a method to provide magnetoelectric coupling which is the last requirement for developing useful multiferroics. They found that by applying rotation mode, X_2^+, on a high-temperature crystal, a magnetic state would be produced which has a symmetry appropriate for magnetoelectric coupling. Therefore, the magnetoelectric coupling is exhibited also by rotation and tilt distortions. Up to here, this case study on $Ca_3Mn_2O_7$ has demonstrated a magnetic ordering (emanating from X_3^-), a ferroelectric polarization (due to the product $X_2^+ \oplus X_3^-$) and a coupling of them (emerging from X_2^+) can be provided through rotations and tilts. The final step, controlling the net magnetization using an applied electric field,
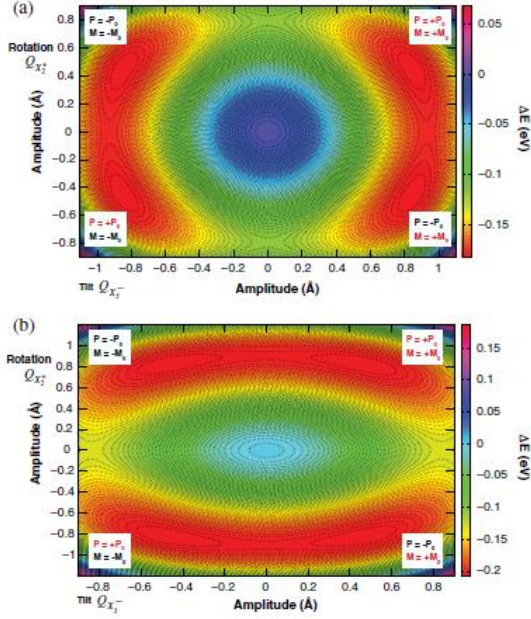
Fig. 15. Patterns of different domains resulted with the following conditions; (a) $P_0 \rightarrow -P_0$ and $M_0 \rightarrow M_0$ by varying X_2^+ rotations and starting with fixed X_3^- in an unstrained sample, and (b) $P_0 \rightarrow -P_0$ and $M_0 \rightarrow -M_0$ by modifying X_3^- tilts and starting with fixed X_2^+ in a biaxial strained structure [17].

still remains; because, in this bulk structure (unstrained), when an applied electric field is reversed, the ferroelectric polarization flips direction by varying the rotation X_2^+, while this distortion does not impress the magnetization. In order to reach the ability of modifying the magnetism by an external electric field, Benedek and Fennie explored the influence of strain on this structure. They achieved this goal when they considered an additional of a 1.5% compressive biaxial strain to the system. These calculations are presented in Fig. 15. Figure 15(a) shows that X_2^+ switching path is the lowest energy pathway to flip the polarization which does not reverse the sign of the magnetization, whereas Fig. 15(b) illustrates that a 1.5%

compressive strain shifts the lowest energy pathway along the octahedral tilt switching path, X_3^-, which as mentioned previously, switches the direction of the spin canted moment. Therefore, Benedek et. al. have demonstrated that biasing the polarization of strained $Ca_3Mn_2O_7$ thin films by an external electric field, should switch the direction of the equilibrium magnetic moments by 180°.

7. Conclusions

In summary, we have studied a new class of materials, called multiferroics, and have investigated two known strategies of switching magnetism with electric fields using multiferroics. Different kinds of multiferroics, emerging from different origin or mechanisms which lead to multiferroism, have been introduced after explanation of the basic physical concepts, i. e. ferroelectricity, ferromagnetism and multiferroism. In our discussion, we have pointed especially to the large group of multiferroics which are perovskite oxides and have mentioned the "d^0 vs d^n" problem in them. However, although creating "mixed" perovskites with d^0 and d^n ions has been proposed as a favorite solution to provide the potential for simultaneous magnetic and ferroelectric ordering, one also can study other types of ferroelectrics like non-oxide-based ones to hopefully find multiferroic behavior in them. For example, in ferroelectric $NaCaF_3$, Coulomb interactions play a key role in ferroelectricity. Dealing with these kinds of materials may allow overlooking the d^0 requirement. Discovering new materials as a multiferroic is still an exciting subject for scientists. Obviously, each new one is a new

challenge and opens a wide world in multiferroics. Basic physics introduces a third set of moments in addition to electric and magnetic moments, which is called toroidal moments relevant to the electromagnetic field, so this could be an idea to be explored [36]

In addition, coupling between ferromagnetic layers, such as Permalloy ($Ni_{0.78}Fe_{0.22}$, Py) layers, and multiferroic materials, like $BiFeO_3$ crystals, have been investigated as an applicable mechanism to control the magnetization by electric field. Measurements compiled in Ref. [14] have shown that the existence of exchange coupling between two layers (ferromagnetic layer and multiferroic layer) gives rise to a linking between patterns of the magnetism of two layers. An electric field was applied to reorient the polarization resulting in a modified easy magnetic axis in the Py via exchange coupling at the interface of ferromagnetic layer and $BiFeO_3$ crystal. This switching might be possible in nanostructures in which there is a complete control on biasing the direction of polarization with electric field. This is the case in $BiFeO_3$ because the cycloids in them play the most important role in coupling, and resulted exchange coupling is not strong enough to be able to rearrange a macroscopic magnetization in ferromagnetic layer, individually. In this approach, there is also another coupling mechanism which is within the multiferroic material.

The other mechanism [17], providing new revenue to achieve a control of magnetization with electric field, has been introduced. It has been confirmed that magnetoelectric coupling arises from specific combinations of lattice distortions can be controlled via electric field to direct the magnetic order. Reasonable candidates for this lattice instability are octahedron rotations (which mostly appear in perovskites), because of their strong coupling to magnetic properties. The ferroelectricity that induced by more than one octahedron rotation mode has been introduced as hybrid improper ferroelectricity, for instance, the one which is seen in $Ca_3Mn_2O_7$. It has been shown that in the case of $Ca_3Mn_2O_7$ octahedron rotations simultaneously induce magnetic order and ferroelectricity, and develop a magnetoelectric coupling such a way that this coupling could be modified by electric field and as a result, control of magnetization might be achieved. As oxygen rotation distortion may lead to an enhanced magnetoelectric effect, and these oxygen rotations in perovskites are known to respond strongly to pressure and epitaxial strain, compressive biaxial strain $Ca_3Mn_2O_7$ has been considered. This mechanism is suitable for large number of materials, as there is no restriction on the temperature range. The temperature over which the hybrid improper ferroelectric mechanism proceeds is commonly above room temperature, although Neel temperature, T_N=115 K, is the ''limiting'' temperature in the case of $Ca_3Mn_2O_7$.

The field of designing new room temperature multiferroics and magnetoelectrics in order to incorporate them in ferromagnetic resonance devices, with the ability of electric-field-controlling, is actually in progress either in fundamental physics or in applications.

Acknowledgments

I would like to thank my supervisor Prof. B. Noheda for her productive discussions and critical comments.

References

[1] N.A. Hill, J. Phys. Chem. B **104**, 6694 (2000).

[2] M. Gajek, M. Bibes, A. Barthélémy, K. Bouzehouane, S. Fusil, M. Varela, J. Fontcuberta, and A. Fert, Phys. Rev. B **72**, 020406(R) (2005).

[3] D. Khomskii, Physics **2**, 20 (2009).

[4] Ch. Binek and B. Doudin, J. Phys.: Conds. Matter **17**, L39 (2005).

[5] M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).

[6] E. Asher, H. Rieder, H. Schmid, and H. Stossel, J. Appl. Phys. **37**, 1404 (1966).

[7] G. A. Smolenskii and I. E. Chupis, Sov. Phys. Usp. **25**, 475 (1982).

[8] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig and R. Ramesh, Science **299**, 1719 (2003).

[9] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature **426**, 55 (2003).

[10] Prinz, G. A. Magnetoelectronics. Science **282**, 1660 (1998).

[11] de Boeck, J. & Borghs, G. Magnetoelectronics. Phys. World **12**, 27 (1999).

[12] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T.-h. Arima, and Y. Tokura, Nature Mater. **8**, 558 (2009).

[13] M. Bibes and A. Barthelemy, Nature Mater. **7**, 425 (2008).

[14] D. Lebeugle, A. Mougin, M. Viret, D. Colson, and L. Ranno, Phys. Rev. Lett. **103**, 257601 (2009).

[15] Y.H. Chu, L. W. Martin, M. B. Holcomb, M. Gajek, S.-J. Han, Q. He, N. Balke, C.-H. Yang, D. Lee, W. Hu, Q. Zhan, P.-L. Yang, A. Fraile-Rodriguez, A. Scholl, S. X. Wang, and R. Ramesh, Nature Mater. **7**, 478 (2008).

[16] V. Laukhin, V. Skumryev, X. Martí, D. Hrabovsky, F. Sánchez, M. V. García-Cuenca, C. Ferrater, M. Varela, U. Lüders, J. F. Bobo, and J. Fontcuberta, Phys. Rev. Lett. **97**, 227201 (2006).

[17] Nicole A. Benedek and Craig J. Fennie, Phys. Rev. Lett. **106**, 107204 (2011).

[18] J. Valasek, Physical Review **17**, 475 (1921).

[19] Weiss, P. J. Phys. **6**, 661 (1907).

[20] Stoner, E. C. Philos. Mag. **15**, 1080 (1933).

[21] W. Eerenstein, N. D. Mathur and J. F. Scott, Nature **442**, 756 (2006).

[22] G. A. Smolenskii, A. I. Agranovskaia, S. N. Popov, V. A. Isopov. Sov. phys. Tech, **3** (1981-1982).

[23] G. A. Smolensky, V. A. Isupov, N. N. Krainik, Agranovskaya, A. I. *IsVest. Akad. Nauk SSSR, Ser. Fiz. 25*, 1333 (1961).

[24] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha and S-W. Cheong, Nature **429**, 392 (2004).

[25] R. V. Shpanchenko, V. V. Chernaya, A. A. Tsirlin, P. S. Chizhov, D. E. Sklovsky, E. V. Antipov, E. P. Khlybov, V. Pomjakushin, A. M. Balagurov, J. E. Medvedeva, E. E. Kaul and C. Geibel, Chem. Mater. **16**, 3267 (2004).

[26] J. van den Brink and D. I. Khomskii, J. Phys.: Condens. Matter **20**, 434217 (2008).

[27] C. J. Howard and M. A. Carpenter. Acta Cryst. B**66**, 40 (2010).

[28] Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S.-W. Cheong, Phys. Rev. Lett. **100**, 047601 (2008).

[29] N. Ikeda, K. Kohn, N. Myouga, E. Takahashi, H. Kitôh and S. Takekawa, J. Phys. Soc. Japan. **69**, 1526 (2000).

[30] B. B. Van Aken, Th. T.M. Palstra, A. Filippetti and N. A. Spaldin, Nature Materials **3**, 164 (2004).

[31] M. V. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).

[32] T. Arima, J. Phys. Soc. Jpn. **76**, 073702 (2007).

[33] Wolfgang Kleemann, Physics **2**, 105 (2009).

[34] Gavin Lawes, Physics **4**, 18 (2011).

[35] D. Lebeugle, D. Colson, A. Forget, M. Viret, A. M. Bataille, and A. Gukasov, Phys. Rev. Lett. **100**, 227602 (2008).

[36] H. Schmid, *J. Phys.: Condens. Matter* **20,** 434201 (2008).