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Phil. Trans. R. Soc. A 2011 **369**, doi: 10.1098/rsta.2010.0344, published 4 July 2011

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REVIEW

Multi-ferroic and magnetoelectric materials and interfaces

BY J. P. VELEV,^{1,2} S. S. JASWAL¹ AND E. Y. TSYMBAL^{1*}

¹*Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588-0299, USA*

²*Department of Physics, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931-3343, USA*

The existence of multiple ferroic orders in the same material and the coupling between them have been known for decades. However, these phenomena have mostly remained the theoretical domain owing to the fact that in single-phase materials such couplings are rare and weak. This situation has changed dramatically recently for at least two reasons: first, advances in materials fabrication have made it possible to manufacture these materials in structures of lower dimensionality, such as thin films or wires, or in compound structures such as laminates and epitaxial-layered heterostructures. In these designed materials, new degrees of freedom are accessible in which the coupling between ferroic orders can be greatly enhanced. Second, the miniaturization trend in conventional electronics is approaching the limits beyond which the reduction of the electronic element is becoming more and more difficult. One way to continue the current trends in computer power and storage increase, without further size reduction, is to use multi-functional materials that would enable new device capabilities. Here, we review the field of multi-ferroic (MF) and magnetoelectric (ME) materials, putting the emphasis on electronic effects at ME interfaces and MF tunnel junctions.

Keywords: ferroelectric; multi-ferroic; magnetoelectric; multi-functional; interface; tunnel junction

1. Introduction

The field of spintronics has been successful in producing magnetoresistive devices for magnetic memory and sensor applications [1]. These employ giant magnetoresistance (GMR) [2,3] or tunnelling magnetoresistance (TMR) [4–6] phenomena that provide a sizeable change of resistance in response to altering magnetic alignment of two ferromagnetic electrodes in spin valves or magnetic tunnel junctions (MTJs; for reviews of GMR and TMR, see [7,8] respectively). The evolution beyond passive magnetoelectronic components is envisioned in the next generation of spintronics devices, which combine memory and logic functions and promise to set new standards in future information technology

*Author for correspondence (tsymbal@unl.edu).

One contribution of 12 to a Theme Issue ‘New directions in spintronics’.

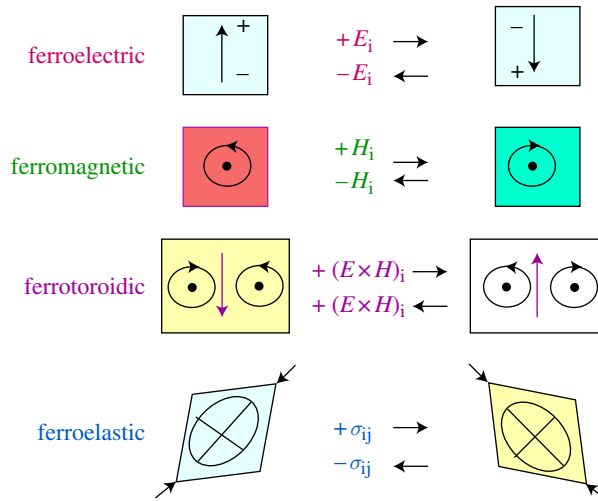


Figure 1. Schematic of the ferroic orders, conjugated fields and corresponding symmetry operations. Adapted from Schmid [24]. (Online version in colour.)

and nanoelectronics [9]. These perspectives have broadened into a search for a new class of multi-functional spintronic materials and structures whose properties can be manipulated by several independent stimuli by affecting physical degrees of freedom set by the order parameters. This field of multi-ferroic (MF) and magnetoelectric (ME) materials has recently received a great deal of attention [10–23].

MF materials exhibit two or more ferroic orders, such as magnetic: ferromagnetic (FM), antiferromagnetic (AFM) or ferrimagnetic; ferroelectric (FE); ferroelastic; or ferrotoroidic (figure 1) [24]. ME materials, on the other hand, exhibit coupling between the electric and magnetic degrees of freedom so that, in these materials, an electric (magnetic) polarization can be induced by a magnetic (electric) field. Although there are MF materials that are not ME and vice versa, for fundamental reasons, the ME coupling in single-phase materials is largest in MF materials. For this reason, the development of these classes of materials is intimately related. ME/MFs allow the possibility of switching the magnetization with electric field [25]. This offers a wealth of opportunity for information storage applications. In particular, it could remove the main hindrance in the miniaturization of magnetic random access memory (MRAM), where the write operation requires magnetic fields or large currents [26]. Another possibility is the development of memory bits with multiple stable states [27,28] or mixed memory and logic functions [29,30].

The development of MF and ME materials started in Russia in the late 1950s and continued intensively in the 1960s (see [10] for a review). However, interest waned since very few such compounds were found that were MF only at low temperatures and the ME effect was generally very weak. Despite these early discouraging results, interest in these materials has been renewed recently. There are two main forces driving the revitalization of the field. First, scientific: a dramatic improvement in materials fabrication techniques, especially thin film deposition, enabled engineering of materials combinations which could overcome

the impasse reached in single-phase compounds [18]. Second, economic: the urgent necessity to overcome the projected failure of Moore's Law in the near future requires the development of new functional materials and new computational paradigms [31]. This brief review outlines the field of ME and MF materials. A special emphasis is placed on electronically driven effects at ME interfaces and FE and MF tunnel junctions, which are the hallmarks of our expertise. In this respect, this paper complements the existing excellent reviews [10–23].

2. Single-phase multi-ferroic materials

(a) Order parameters and coupling

FE and FM materials are characterized by their spontaneous polarization (electric or magnetic respectively). However, most materials do not exhibit a spontaneous order, but they do interact with applied fields. An electric field (E) produces an electric dipole moment and hence electric polarization (P) in the material. Conversely, a magnetic field (H) produces magnetization (M). Stress (σ) produces strain (ϵ). The electro-magnetic source vector (S) produces toroidal moment (τ). The relationship between the order parameters and the respective fields is illustrated in figure 1. For small fields, the relationship is linear, but nonlinear effects become important for larger fields.

Certain materials exhibit non-zero-order parameters in zero field that can be switched between two or more stable configurations. Ferromagnetism arises from the spontaneous alignment of atomic magnetic moments, which produces a net magnetization [32]. Similarly, ferroelectricity is a spontaneous alignment of atomic dipole moments that can produce a net polarization [33]. Other ferroic orders exist, such as ferroelastic—a spontaneous alignment of microscopic deformations [34]—and ferrotoroidic—spontaneous toroidal moment [35]. MFs are materials that exhibit two or more ferroic orders at the same time [11]. Here, we will concentrate on a subclass of MFs that are simultaneously magnetic and FE. The subset of ME and MF materials is shown diagrammatically in figure 2.

The ferroic order parameters are cross-coupled [36]. The linear coupling is responsible for the piezoelectric, piezomagnetic and ME effects. The piezoelectric effect is the ability of a material to induce an electric polarization in response to applied mechanical stress. (The inverse piezoelectric effect is inducing strain by applied electric field.) Similarly, the piezomagnetic effect is the ability to induce a magnetic polarization in response to applied stress. (The inverse piezomagnetic effect is inducing strain by applied magnetic field.) The ME effect is the production of electric polarization with the application of magnetic field or conversely magnetization with electric field. Higher order coupling between electric (magnetic) polarization and strain is electrostriction (magnetostriction). Macroscopically, the interaction of the electric (E) and magnetic (H) fields and the stress tensor (σ) with the material can be described within the Landau theory of phase transitions [37]. The expansion of the free energy (F) up to second order in the fields in the SI system of units can be written as

$$F = F_0 - P_S E - \mu_0 M_S H - \epsilon_S \sigma - \frac{1}{2} \epsilon_0 \chi_E E^2 - \frac{1}{2} \mu_0 \chi_M H^2 - \frac{1}{2} s \sigma^2 - \alpha E H - d E \sigma - q H \sigma - \dots, \quad (2.1)$$

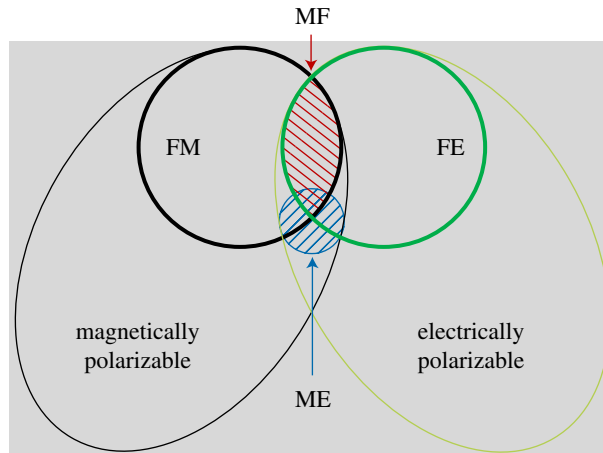


Figure 2. Schematic of the relationship between ferromagnetic (FM), ferroelectric (FE), multi-ferroic (MF) and magnetoelastic (ME) materials. Adapted from Eerenstein *et al.* [14]. (Online version in colour.)

where an implicit summation over the vector and tensor indices is understood. The first term is the free energy at zero fields (F_0). The next three first-order terms represent the dipole energies related to the spontaneous electric polarization (P_S), magnetization (M_S) and elastic deformation (ε_S) interacting with the conjugated fields. The next three second-order terms reflect the electrostatic, magnetostatic and elastic energy in materials with electric susceptibility (χ_E), magnetic susceptibility (χ_M) and elastic tensor (s), respectively. The remaining second-order terms represent the linear ME (α), piezoelectric (d) and piezomagnetic (q) effects. Higher order terms involving electrostriction (σE^2 , $E\sigma^2$), magnetostriction (σH^2 , $H\sigma^2$) and nonlinear magnetoelectricity (HE^2 , EH^2) are not included in equation (2.1) for simplicity. Taking derivatives of the free energy with respect to the fields, we can obtain the macroscopic order parameters

$$\left. \begin{aligned} P &= -\frac{\partial F}{\partial E} = P_S + \varepsilon_0 \chi_E E + \alpha H + d\sigma + \dots \\ \mu_0 M &= -\frac{\partial F}{\partial H} = \mu_0 M_S + \mu_0 \chi_M H + \alpha E + q\sigma + \dots \\ \varepsilon &= -\frac{\partial F}{\partial \sigma} = \varepsilon_S + s\sigma + dE + qH + \dots \end{aligned} \right\} \quad (2.2)$$

and

As follows from equation (2.2), the material can be polarized with electric (magnetic) polarization by an applied magnetic (electric) field through the ME effect. The respective bulk ME coefficient (susceptibility) is defined by

$$\alpha = \mu_0 \frac{\partial M}{\partial E} = \frac{\partial P}{\partial H}. \quad (2.3)$$

In SI units, α is measured in $\text{Tm V}^{-1} = \text{s m}^{-1}$ (for details on the phenomenology and unit conventions, see [38]).

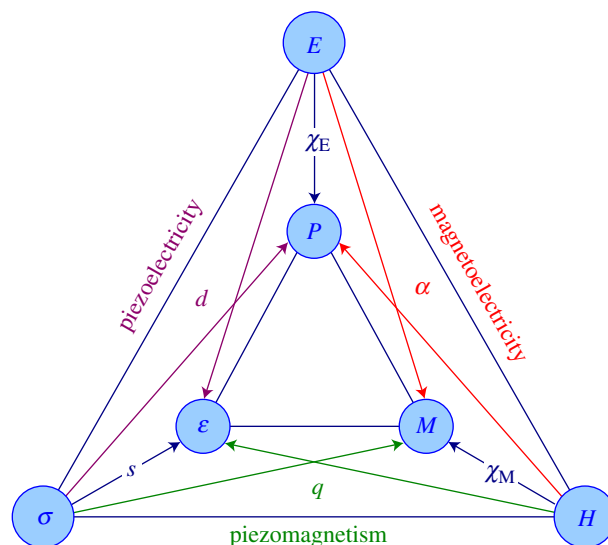


Figure 3. Schematic of the different types of coupling corresponding to terms in equation (2.1). Order parameters can be induced directly by the field or through a third-order parameter. Adapted from Martin *et al.* [18]. (Online version in colour.)

In addition to the intrinsic cross-coupling terms defined by coefficients α , d and q , *product couplings* can be engineered through a third-order parameter [39]. For example, a common way to engineer ME coupling is through strain. In laminates consisting of piezomagnetic and piezoelectric materials, application of magnetic field causes elastic deformations in a magnetic material, which in turn causes polarization changes in a piezoelectric and vice versa. The resulting ME coefficient of the composite is given by [40]

$$\alpha = \frac{\partial P}{\partial H} = kdq, \quad (2.4)$$

where k is a coefficient ($0 \leq |k| \leq 1$) accounting for how well the strain is transferred from one material to the other. The possible couplings between different order parameters are illustrated in figure 3.

(b) Origin and scarcity

The standard tables of magnetic [41] and FE compounds [42] indicate very little overlap between the two classes of materials. The scarcity of MF materials could be understood from symmetry arguments [24]. The free-energy expansion (2.1) has to be invariant under the symmetry of the system. Thus, some terms are prohibited by the crystal symmetry and spontaneous order cannot develop. For example, the electric field (E) is a polar vector that changes sign under space inversion. Thus, in crystals with space inversion symmetry, odd orders of E cannot appear in the expansion (2.1) and therefore spontaneous polarization cannot develop. Similarly, the magnetic field H is an axial vector that changes sign under time inversion. In systems with time-reversal symmetry, magnetization

cannot develop. Therefore, materials that can support both magnetic and FE order and/or ME coupling must have symmetry, where both time and space inversion are broken. These include only 13 point groups: 1, 2, 2', m , m' , 3, 3 m' , 4, 4 $m'm'$, $m'm2'$, $m'm'2'$, 6 and 6 $m'm'$. Thus, the number of such materials is very limited because the allowed structures represent a very restricted set of all the possible structures. An excellent review of the symmetry aspects of MF materials is given by Schmid [24].

In addition to symmetry considerations, electronic structure arguments indicate contradicting requirements for ferroelectricity and ferromagnetism to exist in the same material [43]. Two significant conflicting requirements are as follows. (i) *Electrical properties*: FEs must be insulators because polarization introduces bound charges. If there are free carriers, the charges will be screened and the polarization will vanish. In other words, ferroelectricity requires filled bands. On the other hand, magnetic materials tend to be metals because ferromagnetism requires partially filled d-bands. (ii) *Bonding properties*: At least in the conceptually simple perovskite FEs, such as BaTiO₃, polarization is caused by displacement of the centre ion (Ti) with respect to the middle of the oxygen cage. This distortion is the result of a balance between an increase in Coulomb repulsion from the neighbouring ions if the ion is moved off-centre and the gain in covalent bonding energy when the ion comes closer to one of its neighbours. It seems that the energetics is only favourable when the central ion is in a formally d⁰ state. Magnetism produces a partially occupied d^{*n*} band, which reduces the bonding contribution [44,45].

(c) Bulk multi-ferroic and magnetoelectric materials

The existence of the ME phenomenon was predicted for Cr₂O₃ [46] and then experimentally observed [47,48]. The ME coefficient was found to be 4×10^{-12} Tm V⁻¹, which implies that an applied electric field as large as 1 V nm⁻¹ can induce a magnetic moment of only $m \approx 4 \times 10^{-3} \mu_B$ per Cr atom. Such a small value of α can be understood by the fact that, in single-phase materials, the ME effect is limited by the geometrical mean of the electric and magnetic susceptibilities (e.g. [12])

$$\alpha^2 < \epsilon_0 \mu_0 \chi_E \chi_M. \quad (2.5)$$

This implies that the largest ME effect can be expected in MF materials in which both susceptibilities are large. The first MF materials were grown by substituting magnetic ions in FE perovskite lattices (see [10] for review). A large number of MF compounds have been found since the study by Wang *et al.* [22]. Some of the important families of MF materials are outlined below [12,18,20].

(i) Split-order multi-ferroics (type I)

Common MF materials are those in which the FE and magnetic order are produced by different sublattices or parts of the lattice. In these MFs, the FE order breaks the spatial inversion symmetry, whereas the magnetic order breaks the time-reversal symmetry. Owing to this separation, the ME coupling is weak in type I MFs [49]. The main effort is concentrated on improving the ME coupling in these MF materials.

Perovskites (displacement type). Materials of the type $A(B',B'')O_3$ are made by FM ion substitution in an FE lattice. In these materials, the B' sublattice is responsible for the polarization and the B'' sublattice for the magnetization. $PbFe_{1/2}Nb_{1/2}O_3$ and $PbFe_{1/2}Ta_{1/2}O_3$ compounds are examples of this kind [10].

Perovskites (lone pair type). These materials are of the type ABO_3 , where B is a magnetic ion and A has an electron pair occupying the outlying s-orbital that is not used in bonding (lone pair). These electrons are highly polarizable. Thus, the polarization is produced by the lone pair s-electrons and the magnetization by the magnetic site partially filled d-orbitals. Examples are the Bi- and Pb-based perovskites, including the only room temperature MF material $BiFeO_3$ [50,51].

Hexagonal rare earth manganites (geometric type). This group of materials includes hexagonal manganites of the type $RMnO_3$, where R is a rare earth element [52]. A particular example is $YMnO_3$ [53]. Magnetism in this compound is due to the Mn ion. Ferroelectricity, on the other hand, is caused by rather complex geometrical distortion of the O cage that favours a closer packing of the structure. ME coupling of magnetic and electric domains has been observed in $YMnO_3$ [54]. The FM ordering in hexagonal $HoMnO_3$ was shown to be reversibly switched on and off by applied electric field via ME interactions at low temperatures [55].

More complex structures. Other materials exist in which ferromagnetism is caused by a magnetic ion, while ferroelectricity is caused by a whole ionic complex. Examples include the boracite compounds with the general formula $M_3B_7O_{13}X$, where M is a transition metal and $X = Cl, Br, I$ [56,57]. They are one of the few MF compounds that occur naturally, but they have been artificially synthesized as well. Boracites are FE antiferromagnets, where the magnetism arises from the magnetic M ions and the polarization from the X–O octahedron. Fluorites of the type $BaMF_4$, where M is a transition metal, also display simultaneous ferroelectricity and antiferromagnetism [58,59].

(ii) Joint-order multi-ferroics (type II)

A relatively new class of materials was recently discovered in which the magnetic order breaks both the spatial and temporal inversion symmetry. In these MFs, the resulting ferroelectricity is magnetically induced, and hence the ME coupling is typically larger than in type I materials [60]. A common feature of this class of MFs is a small value of polarization, typically 10^{-4} – 10^{-5} C m⁻² when compared with 0.1–1 C m⁻² in many established FEs.

Spiral type. In some materials, such as $TbMnO_3$ [61] or $TbMn_2O_5$ [62], the magnetic ground state is a long-range spiral. In this case, FE polarization develops in conjunction with the magnetic phase owing to the spin–orbit interaction $\mathbf{P} \sim \mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$, where \mathbf{r}_{ij} is the vector connecting the neighbouring spins \mathbf{S}_i and \mathbf{S}_j [63,64]. This mechanism allows the polarization of $TbMnO_3$ to rotate by 90° when a critical magnetic field is applied along a certain direction [61]. In $TbMn_2O_5$, the polarization changes sign with the field [62].

Collinear type. Polarization may appear in collinear magnets as long as the magnetic order involves different magnetic atoms between which the exchange coupling varies. This is the case, for example, for Ca_3CoMnO_6 , which consists of one-dimensional chains of Co and Mn [65]. The magnetic order distorts the bonds, thus breaking the space inversion symmetry and allowing for polarization to develop.

There are other MF materials and ME coupling mechanisms that have been discovered. The main and some more exotic types have been summarized in a recent review [22]. Despite this rich phenomenology, bulk single-phase MF materials consistently show: (i) weak ME coupling, not enough for cross-order parameter control, (ii) low Curie and/or Néel temperatures, and (iii) little room for improvement.

(d) Thin films

Further development in the field of MF materials was caused by advancements in thin-film growth techniques. The advantages of single-phase MF materials in thin-film form are twofold: (i) on a suitable substrate new and non-equilibrium phases can be stabilized and (ii) strain introduced by the substrate can be used as an additional parameter to tune materials properties.

One of the earliest materials to be grown in thin film form is YMnO_3 [66]. The bulk YMnO_3 is FE with the Curie temperature $T_{\text{CE}} = 570\text{--}990\text{ K}$ and AFM with the Néel temperature $T_{\text{N}} = 70\text{--}130\text{ K}$ [67]. It was shown that the strained hexagonal YMnO_3 can be stabilized in orthorhombic perovskite phase, which is an excellent example for strain engineering [68]. Strain has been found to be crucial in stabilizing other RMnO_3 in the FE hexagonal form [18]. However, these compounds display MF properties only at low temperature.

The greatest success in that respect is the growth of only the room temperature MF material BiFeO_3 in thin-film form [69,70]. The bulk BiFeO_3 is AFM with $T_{\text{N}} = 643\text{ K}$ [71] and FE with $T_{\text{CE}} = 1103\text{ K}$ [72]. A different monoclinic structure that was stabilized in thin-film geometry led to the enhanced room temperature polarization and ME response [69]. Electrical control of the AFM domains in BiFeO_3 (001) films was demonstrated at room temperature [73]. High-resolution images of AFM and FE domain structures revealed a clear domain correlation, indicating a strong ME coupling. Figure 4 shows the observed AFM domain switching induced by FE polarization switching, as measured by piezo force microscopy (PFM) and X-ray photoemission electron microscopy (PEEM).

Similar work has been done on BiMnO_3 , which can only be grown in bulk under high pressure [74,75]. The perovskite BiMnO_3 in the bulk is FM with the Curie temperature $T_{\text{CM}} = 105\text{ K}$ [76,77] and FE with $T_{\text{CE}} = 450\text{--}490\text{ K}$ [78,79]. It can be stabilized in thin-film form in a distorted perovskite structure [80].

For further details of work on MF thin films, we refer the reader to Martin *et al.* [18].

(e) First-principles studies

An important contribution to the development of MF materials has come from first-principles calculations based on density functional theory (DFT) [81–84]. Recent advances in computational power and algorithm development make it possible to rationalize experimental observations, investigate possible mechanisms for ME coupling, and even to design new MF materials [85–87].

Stimulated by experimental efforts, a number of theoretical studies were focused on BiFeO_3 [88–90]. It was found that ionic sublattices of BiFeO_3 in the rhombohedrally distorted perovskite structure are displaced relative to each other along the polar [111] direction, and the oxygen octahedra are rotated around the same [111] axis, alternately clockwise and counter-clockwise (figure 5).

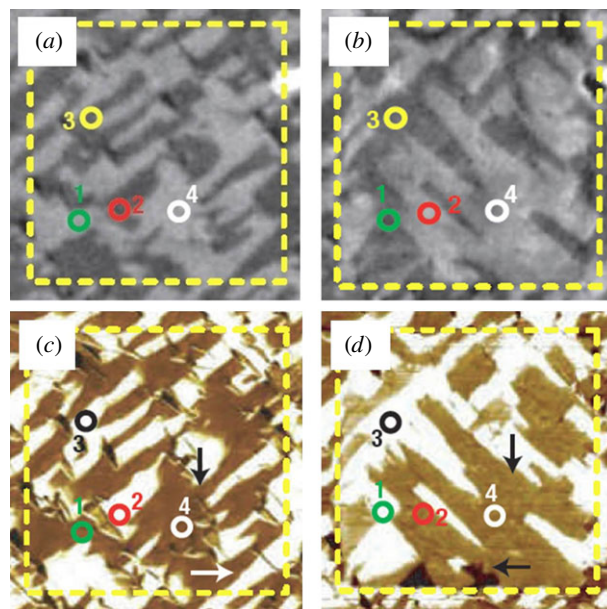


Figure 4. (a) PEEM and (b) PFM images of a BiFeO_3 film before (a,c) and after (b,d) electrical poling. The arrows show the direction of the in-plane FE polarization. The circles indicate the regions where FE polarization switched. Adapted from Zhao *et al.* [73]. (Online version in colour.)

A large spontaneous polarization of 0.95 C m^{-2} induced by polar displacements was predicted, which is consistent with experimental studies on high-quality single crystals [91].

Bulk BiFeO_3 exhibits G-type AFM order, where the magnetic moment of each Fe cation is antiparallel to that of its nearest neighbours. The calculated magnetocrystalline anisotropy (MCA) predicts that a preferred orientation of the Fe magnetic moments is perpendicular to the polar [111] direction (figure 5) [89]. A small canting of the Fe magnetic moments leads to a net magnetic moment of about $0.05 \mu_{\text{B}}$ per Fe atom. This weak ferromagnetism raises a question of whether the small magnetization is coupled with the electric polarization, so that it can be manipulated by applied electric fields.

First-principles methods have been successfully used to study a number of ME and MF materials, such as the manganites BiMnO_3 [92] and YMnO_3 [53,93], as well as BiCrO_3 [94], BaMnO_3 [45] and CaMnO_3 [95]. More details about first-principles studies of MF materials, including type II MFs, can be found in the dedicated recent reviews [83,84].

3. Composite multi-ferroic materials

Thin-film geometry naturally leads to the idea of composite MF materials, such as layered heterostructures of FE and FM materials. The advantage of composites is that fundamental limitations on the strength of the ME coupling equation (2.5) no longer apply. However, the problem changes to how to couple the ferroic orders in the different phases. In general, two types of ME coupling can

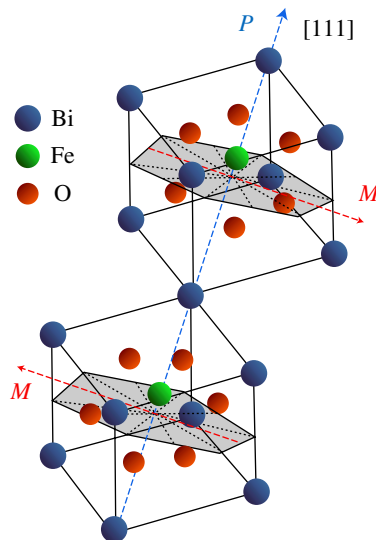


Figure 5. Atomic and magnetic structure of BiFeO_3 . The polarization is pointing along the $[111]$ direction. The magnetic plane is perpendicular to the polarization direction. Adapted from Ederer & Spaldin [89]. (Online version in colour.)

be expected: (i) direct, owing to electronic effects at the interface (limited to the interface), and (ii) indirect, mediated by strain (bulk effect). The indirect effect is a product property in the sense of equation (2.4). Almost all practical structures to date use the elastic properties of the material to mediate ME coupling [96].

Typical measurements of the ME response in MF composites are performed by inducing an electric polarization by a weak AC magnetic field oscillating in the presence of a DC bias field. An induced AC voltage (electric field) produced by the oscillating polarization is measured. The experimentally measured ME *voltage* coefficient α_E is related to the ME coefficient α defined by equation (2.3) through the relationship $P = \epsilon_0 \chi_E E$,

$$\alpha_E = \frac{\partial E}{\mu_0 \partial H} = \frac{c^2}{\chi_E} \alpha. \quad (3.1)$$

In SI units, α_E is measured in $\text{V} (\text{m} \cdot \text{T})^{-1}$. Note that the ME response depends on AC frequency and DC bias field. In particular, resonant behaviour of the ME response is expected when the modulation frequency coincides with eigenmodes of the system.

To describe the properties of composite MFs, it is conventional to use the concept of phase connectivity [97]. This concept employs the notation $d_1 - d_2$, where each number represents the dimensionality of the respective component. For example, 0–3 denotes granular compounds, i.e. FM particles embedded in an FE matrix [98,99]; 1–3 structures with columns of FM material in an FE matrix [100,101]; and 2–2 planar structures with alternating layers of FE and FM materials [102].

(a) Planar 2–2 structures

Planar 2–2 structures are interesting because of additional parameters, such as lattice strain, interlayer interaction, film thickness, etc., that can be tuned to obtain desired properties. There are two approaches: (i) laminates in which strain is transferred via a binder and (ii) epitaxial heterostructures in which the interface chemical bonding is used to transfer the strain.

(i) Laminates

Laminates are MF composites (typically a piezoelectric layer sandwiched between two magnetostrictive layers) in which the two phases are connected through and chemically isolated by a binder. The binder is designed to efficiently transmit the strain. The best laminates today exploit strong piezoelectric materials such as $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ and magnetostrictive materials such as ferrites, e.g. NiFe_2O_4 [103], or alloys, e.g. TbDyFe_2 (Terfenol-D) [104,105]. Significantly enhanced ME effects are reported when compared with single-phase MF materials. For example, a giant ME voltage coefficient (3.1) is measured for Metglas (high-magnetic-susceptibility magnetostrictive alloy)/polyvinylidene-fluoride (piezoelectric polymer) laminates, reaching $3 \times 10^8 \text{ V (m} \cdot \text{T)}^{-1}$ [106], albeit only at microwave frequencies and resonant conditions. A comprehensive review of this field of research can be found in Nan *et al.* [40].

(ii) Epitaxial structures

In epitaxial 2–2 structures both electronic and strain effects can play a role. Of particular interest are heterostructures made of the rich family of transition-metal oxides that exhibit an astounding variety of properties.

Strain coupling at a single epitaxial interface in a $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BaTiO}_3$ heterostructure was reported [107]. A large magnetic response of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ was found to be associated with changes in the BaTiO_3 FE domain structure in an electric field. Similar studies demonstrated reversible changes in the magnetic properties of an Fe thin film deposited on a BaTiO_3 single crystal [108]. Strain-mediated large magnetization changes emerged in response to FE switching and structural transitions of BaTiO_3 controlled by applied electric fields and temperature. We note, however, that the strain-mediated effects in these studies are largely limited to the unsaturated FM state and almost disappear when the FM film is magnetically saturated.

(b) Columnar 1–3 structures

When the ME coupling is exclusively caused by elastic interactions, the effect in a planar 2–2 structure is reduced owing to clamping to the substrate [109]. On the other hand, in vertically aligned nanostructures, there is no such constraint and the ME effect is expected to be stronger. Such a behaviour was demonstrated for ferrimagnetic CoFe_2O_4 nanopillars embedded in an FE BaTiO_3 matrix [100]. Temperature-dependent magnetic measurements demonstrated the coupling between the two-order parameters, which was manifested as a change in magnetization at the FE Curie temperature. Electric field-induced

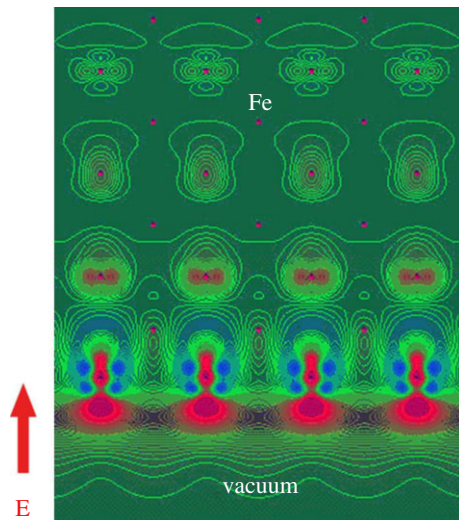


Figure 6. Induced spin density on the Fe (001) surface owing to an applied electric field. Adapted from Duan *et al.* [112]. (Online version in colour.)

local magnetization reversal was reported in epitaxial FE BiFeO₃/ferrimagnetic CoFe₂O₄ columnar nanostructures [110]. A large static ME susceptibility, $\alpha \sim 10^{-9} \text{ T m V}^{-1}$, was found in this system.

4. Magnetoelectric interfaces

Here, we focus on interface ME effects caused by pure electronic mechanisms. In addition to changing the interface (surface) magnetization by applied electric field, we address effects on surface MCA and exchange bias.

(a) Interface magnetization

By symmetry, all FM interfaces (surfaces) are ME because the time-reversal symmetry is broken by the ferromagnetism and the space-reversal symmetry by the interface (surface). There are two mechanisms that produce the interface ME effect: (i) spin-dependent screening and (ii) interface bonding.

When a metal film is exposed to an electric field, the induced surface charge $\sigma = \epsilon_0 E$ screens the electric field over the screening length of the metal. If the metal is FM, the screening charge is spin dependent owing to the exchange splitting of the spin bands, which induces a *surface* magnetization M_{surf} [111], as demonstrated in figure 6. A linear contribution to M_{surf} is determined by the surface ME susceptibility α_S as follows [112]:

$$\mu_0 M_{\text{surf}} = \alpha_S E. \quad (4.1)$$

In SI units, α_S is measured in $\text{T m}^2 \text{ V}^{-1} = \text{s}$. In a simple approximation, the screening contribution to α_S is

$$\alpha_S = \frac{\mu_B}{ec^2} \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}}, \quad (4.2)$$

where $n_{\uparrow,\downarrow}$ are the surface spin-dependent density of states at the Fermi energy. The ME susceptibilities have been calculated from first principles for elemental FM metals Fe, Co and Ni [112]. It was found that the effect is small, $\alpha_S \sim 10^{-22} \text{ Tm}^2 \text{ V}^{-1}$, which is about the same order as for Cr_2O_3 but limited to the surface (i.e. $\alpha_S \sim \alpha/a_0$, where $a_0 \sim 1 \text{ \AA}$). Interestingly, as follows from equation (4.2), for half metals the surface ME coefficient is a universal constant $\alpha_S = \mu_B/ec^2$ [113].

The ME effect can be substantially enhanced at the interface between a ferromagnet and a dielectric, because the induced surface charge scales with the dielectric constant $\sigma = \epsilon_0 \kappa E$. For high- κ dielectrics, the dielectric constant can be as large as $\kappa = \epsilon/\epsilon_0 \sim 100$ and even higher, which increases the ME effect by two or more orders of magnitude. First-principles calculations have predicted the enhanced ME susceptibility at the $\text{SrRuO}_3/\text{SrTiO}_3$ interface [114], i.e. $\alpha_S \sim 2 \times 10^{-20} \text{ Tm}^2 \text{ V}^{-1}$, which is larger by two orders in magnitude than that for the FM metal surfaces [112] owing to a large dielectric constant of SrTiO_3 .

These electronically driven ME effects can be further enhanced by employing an FE material to produce a field effect. In this case, the spin-dependent screening in an FM material occurs in response to the polarization charge at the FE/FM interface. The latter can be changed by switching the FE polarization orientation by applied electric field. Such an ME effect was predicted for the $\text{SrRuO}_3/\text{BaTiO}_3$ interface, where a magnetic moment change of $0.31 \mu_B$ on the interface Ru atom results from BaTiO_3 polarization switching [115]. In this case, the ME effect is *nonlinear* owing to nonlinear variation of the FE polarization with applied electric field. However, as a figure of merit, the interface ME coefficient can be estimated by assuming a typical coercive field of BaTiO_3 , i.e. $E_c = 10 \text{ MV m}^{-1}$, which leads to $\alpha_S \sim 2 \times 10^{-18} \text{ Tm}^2 \text{ V}^{-1}$.

In addition to the spin-dependent screening, the interface bonding mechanism may play an important role in the ME effect at the FM/FE interfaces [116]. Change in atomic displacements at the interface driven by polarization reversal alters orbital hybridizations, altering the interface magnetic moments. First-principles calculations for the Fe/BaTiO_3 interface have shown a large change in the interface magnetic moment, $0.25 \mu_B$, when the direction of the electric polarization is switched by electric field [116,117]. The estimated surface ME coefficient, $\alpha_S \sim 2 \times 10^{-18} \text{ Tm}^2 \text{ V}^{-1}$, is four orders of magnitude higher than that for the Fe/vacuum interface [112]. Similar effects were predicted for $\text{Fe}_3\text{O}_4/\text{BaTiO}_3$ [118] and $\text{Co}_2\text{MnSi}/\text{BaTiO}_3$ [119] interfaces.

Experimental manifestation of the predicted ME effects driven by the purely electronic mechanisms is limited. Recently, however, a large change in magnetization was reported for the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO)/ $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) bilayers in response to polarization reversal [120]. The observed effect is equivalent to chemical doping except that it is dynamically reversible with polarization switching. Variation in the LSMO magnetization exhibits a hysteresis loop reflecting PZT polarization switching, as is seen from the magneto-optical Kerr response (figure 7). The *bulk* ME coefficient found in this work is $\alpha \approx 0.8 \times 10^{-9} \text{ Tm V}^{-1}$ at 100 K. Given the LSMO film thickness of 4 nm this corresponds to $\alpha_S \approx 3.2 \times 10^{-18} \text{ Tm}^2 \text{ V}^{-1}$, which is comparable to the values found by Niranjana *et al.* [115] and Duan *et al.* [116].

An interesting prediction was made recently for the $\text{La}_{1-x}\text{A}_x\text{MnO}_3/\text{BaTiO}_3$ (001) interface, where A is a divalent cation [121]. First-principles calculations

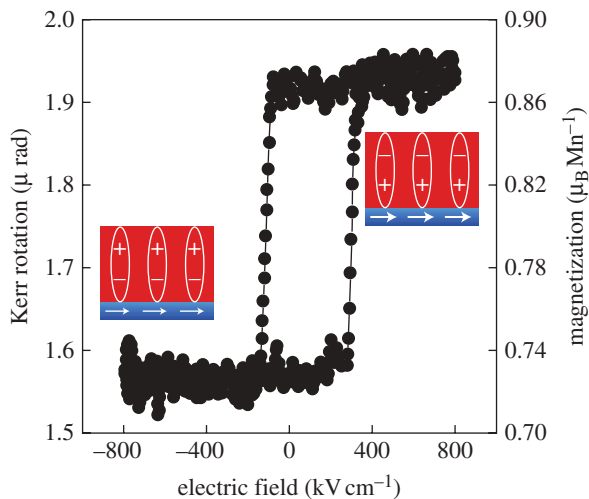


Figure 7. ME hysteresis curve at 100 K showing the magnetic response of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ as a function of the applied electric field. Adapted from Molegraaf *et al.* [120]. (Online version in colour.)

showed a possibility to switch a magnetic order at the interface from FM to AFM by reversing the polarization of BaTiO_3 . Some indications of the predicted behaviour have recently been found experimentally [122].

An electronically driven ME response may be more pronounced in dilute magnetic semiconductors where the screening length is larger than in metals. Modulation of the Curie temperature of a GaMnAs semiconductor was reported to be driven by polarization reversal of the gate by an applied voltage pulse [123]. The ME effects in dilute magnetic semiconductors are, however, limited by their low Curie temperature. A theoretical study of the effect of surface charge on the Curie temperature of ultrathin *metallic* films has been reported recently [124]. It was also predicted that it may be possible to induce a paramagnetic to FM phase transition at a metal surface (interface) by an applied electric field [125,126]. Very recently, it was demonstrated experimentally that by applying an electric field of approximately 10 MV cm^{-1} to a scanning tunnelling microscope (STM) tip above the Fe (001) surface 10 nm Fe islands can be switched from an AFM fcc to an FM bcc structure [127].

(b) Surface magnetocrystalline anisotropy

Especially interesting is the possibility of controlling the MCA of a magnetic material by an applied electric field. Since the MCA determines stable orientations of magnetization, tailoring the anisotropy of an FM film by electric fields may yield entirely new device concepts, such as electric field-assisted magnetic data storage.

For metallic ferromagnets, the applied electric field affects only the surface (interface) MCA owing to electrostatic screening being confined to the surface (interface). The electric field changes the relative population of the d-orbitals, as is schematically demonstrated in figure 8a and as is seen from the calculation

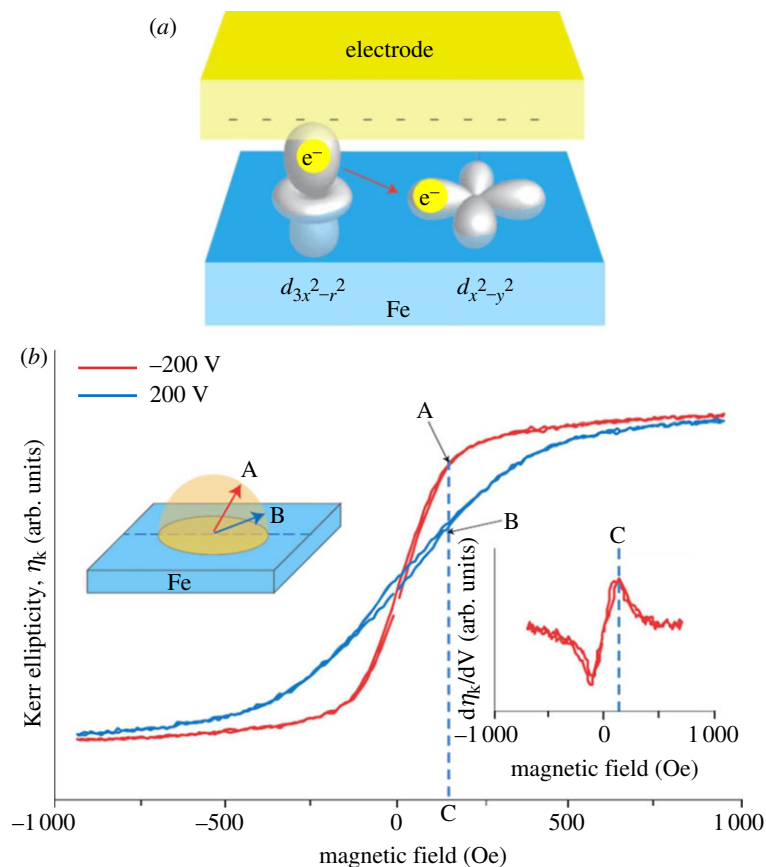


Figure 8. Effect of electric field on Fe/MgO magnetocrystalline anisotropy (MCA). (a) Schematic of the electric field effect on electron filling of the 3d orbitals. (b) Magneto-optical Kerr ellipticity η_k for different applied voltages as a function of the magnetic field. Adapted from Maruyama *et al.* [130]. (Online version in colour.)

(figure 6). This affects the surface MCA owing to the different contribution of these orbitals to the MCA energy [112]. Recent first-principles calculations have demonstrated the importance of these effects [128,129].

Recently, a strong effect of applied electric field on the interface MCA was demonstrated for the Fe/MgO (001) interfaces [130]. It was found that application of a relatively small field 0.1 V nm^{-1} leads to a large change of about 40 per cent in the MCA of the Fe films. Figure 8b demonstrates the effect of an electric field on the MCA that is evident from the change in magneto-optical Kerr ellipticity with applied voltage. These results are corroborated by the recent first-principles calculations [131] and are very promising in view of using magnetic Fe/MgO-based tunnel junctions for spintronic applications [4,5,132].

The change in the interface MCA energy can be used for switching the magnetization by applied electric field [112]. The total MCA energy of a magnetic film involves the magnetostatic shape anisotropy energy, which favours the in-plane alignment of magnetization, whereas positive MCA energy favours

out-of-plane alignment. The volume contribution of the latter is inversely proportional to film thickness, whereas the former is thickness independent. Thus, with the electric-field control of the interface MCA energy, it is possible to design FM films that are switchable between in-plane and out-of-plane orientations. Recently, this prediction was confirmed experimentally for a MgO/FeCo interface exhibiting perpendicular MCA [133]. Using an FeCo film thickness to be at the point where the MCA and shape anisotropy energies are equal, voltage-assisted magnetization switching was achieved.

Experimentally, a change in the surface MCA of a few per cent was demonstrated in FePt(Pd)/electrolyte films [134]. In this case, the strong field effect was achieved because of charged ions of the electrolyte accumulated at the FePd surface and controlled by applied voltage. Magnetic easy axis manipulation by electric field was also achieved in the dilute magnetic semiconductor (Ga,Mn)As [135]. In this case, the easy axis orientation was tailored by the whole concentration being dependent on the electric field. A change in the MCA of a few per cent was also observed in Fe/GaAs Schottky junctions [136].

Even more efficiently, the MCA can be controlled at the FE/FM interface. First-principles calculations of the Fe/BaTiO₃ bilayer have shown that a reversal of the electric polarization of BaTiO₃ produces a sizeable change in the surface MCA energy of the Fe film [137].

(c) *Exchange bias*

Another possibility for switching magnetization by electric field is via control of the exchange bias. Exchange bias is due to exchange coupling at the interface between FM and AFM layers, which allows ‘pinning’ of the FM moment (see [138] for a review on exchange bias). The capability to dynamically control the exchange bias by an electric field would open new perspectives for applications of this phenomenon. The major challenge is to realize the reversible and laterally uniform electric tuning of the exchange bias field at room temperature.

First attempts to electrically control the exchange bias exploited the linear ME susceptibility of the AFM Cr₂O₃ [139]. An ME active pinning layer permits electrical tuning of the AFM interface magnetization and thus leads to a change in the exchange coupling at the FM/AFM interface. ME tuning of the exchange bias was demonstrated for a Cr₂O₃(111)/(Co/Pt) system by applying an electric field during cooling below the Néel temperature of the ME Cr₂O₃ [139].

Further attempts to electrically control the exchange bias exploited a larger ME susceptibility of MF materials. The most promising single-phase MF materials to use as an AFM pinning layer are YMnO₃ and BiFeO₃. ME control of the exchange bias has been demonstrated at YMnO₃/NiFe interfaces [140]. However, this effect is irreversible and exists only at low temperatures. A local magnetization reversal was demonstrated in BiFeO₃/CoFe heterostructures on a lateral length scale of up to 2 μm [141]. However, global magnetization reversal, which could be revealed in macroscopic magnetic hysteresis, has not been achieved. This is due to the fact that only domain walls in BiFeO₃ are responsible for the local control of pinning effects. In similar experiments, it was shown that, in BiFeO₃/NiFe, the MCA of the permalloy can be toggled by the electric field owing to the exchange coupling with the BiFeO₃ [142]. Unfortunately, the coupling is not strong enough to reorient the macroscopic magnetization.

Very recently, a reversible switching between two distinct exchange-bias states of FM $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ was demonstrated by switching the FE polarization of BiFeO_3 [143]. A reversible, isothermal and global electric control of exchange bias at room temperature has been reported using Cr_2O_3 as a pinning layer [144]. This was evidenced by reproducible electrically induced discrete shifts of the global magnetic hysteresis loops along the magnetic field axis. These experimental results are very promising for controlling magnetization by electric fields.

(d) *Interlayer exchange coupling*

Another possibility to control the magnetization by electric fields is to affect interlayer exchange coupling across an FE barrier. Interlayer exchange coupling occurs in magnetic multi-layers in which FM layers are separated by a non-magnetic spacer (for a review, see [145]). Interlayer exchange coupling was first observed for metallic spacers [146], where it was found to oscillate as a function of spacer thickness [147]. If the barrier is insulating the interlayer exchange, coupling is non-oscillatory and decays exponentially as a function of barrier thickness reflecting the evanescent nature of exchange-mediating states. For example, strong AFM coupling was reported in epitaxial Fe/MgO–Fe junctions [148,149]. Using an FE barrier allows the magnitude of the interlayer exchange coupling to be affected by FE polarization orientation [150]. Although the predicted effect is relatively small, it presents an alternative to explore experimentally.

5. Ferroelectric and multi-ferroic tunnel junctions

Multi-ferroic tunnel junctions (MFTJs) involve a new concept for a multi-functional device and have recently attracted significant interest [151]. MFTJs exploit the capability to control electron and spin tunnelling via FM and FE polarizations of the MFTJ constituents. In this section, we will first discuss ferroelectric tunnel junctions (FTJs) as a prerequisite for MFTJs and then address MFTJs themselves.

(a) *Ferroelectric tunnel junctions*

The concept of a polar switch involving an FE was proposed by Esaki *et al.* [152]. However, at the time, there were no experimental techniques and capabilities to fabricate thin-film FEs to serve as a tunnelling barrier. Moreover, it was believed that the critical thickness for ferroelectricity in thin films is much larger than the thickness necessary for tunnelling to take place. The discovery of ferroelectricity in ultrathin films [153–156] opened the exciting prospect for FTJs, in which an FE thin film is used as a barrier (figure 9b) [151].

The key property of an FTJ is tunnelling electroresistance (TER), which is the change in resistance of an FTJ with reversal of FE polarization. The origin of the TER effect is illustrated in figure 10. Polarization affects the interface transmission function by changing (i) the electrostatic potential at the interface, (ii) interface bonding strength, and/or (iii) strain associated with the piezoelectric response [151].

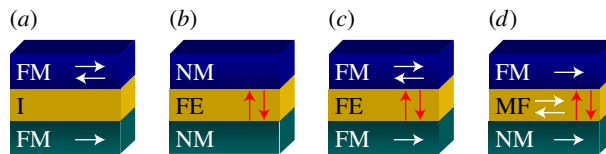


Figure 9. Schematic of the different types of tunnel junctions: (a) magnetic tunnel junction (MTJ), (b) ferroelectric tunnel junction (FTJ) and (c, d) multi-ferroic tunnel junction (MFTJ) with (c) a FE barrier in the MTJ and (d) a MF barrier. The ferromagnetic (FM), FE, normal metal (NM), insulating (I) and MF layers are indicated where appropriate. (Online version in colour.)

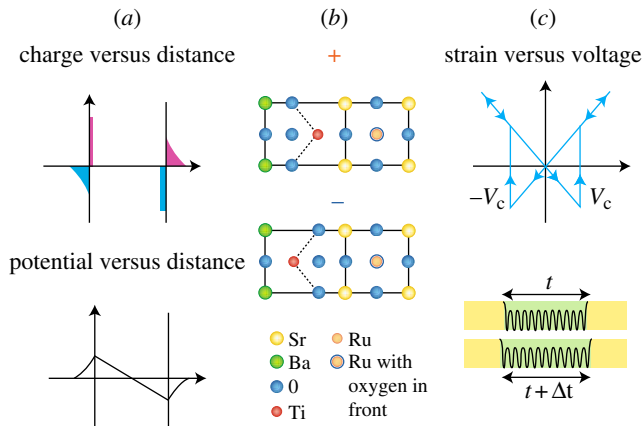


Figure 10. Mechanisms affecting tunnelling in FTJs: (a) electrostatic potential at the interface, (b) interface bonding and (c) strain effect. Adapted from Tsymbal & Kohlstedt [151]. (Online version in colour.)

The electrostatic effect results from incomplete screening of the polarization charges at the interface of FTJs [157]. This creates finite-size charge depletion regions at the interfaces and hence an asymmetric potential profile in FTJs with different electrodes. The predicted TER effect becomes especially strong if an additional thin dielectric layer is placed at the FTJ interface [158].

The interface bonding effect on TER becomes apparent in atomistic calculations [159]. In displacive FEs, such as perovskite oxides, the electric dipole is produced by shifting of atoms within the unit cell from their high-symmetry positions. The presence of interfaces imposes restrictions on the atomic displacements since the atoms at the boundary of the FE are bonded to the electrodes. This effect was demonstrated in KNbO_3 FE films placed between SrRuO_3 or Pt electrodes [160], as well as BaTiO_3 with SrRuO_3 [161,162], Fe [116] and Pt [163] electrodes. First-principles transport calculations for Pt/ BaTiO_3 /Pt FTJs show that the interface transmission function [164] of the Pt/ BaTiO_3 interface differs by a factor of three depending on the polarization direction [159].

The piezoelectric effect is important because most FEs are piezoelectric; both effects originate from lattice distortions. Tetragonal distortions along the axis of the junction, caused by applied bias, change the barrier thickness and hence affect the tunnelling conductance [165]. In addition, atomic displacements influence the decay rate in the barrier and consequently the transmission through it [159].

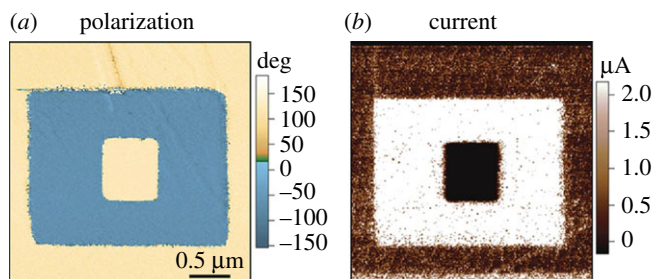


Figure 11. Tunnelling electroresistance in a $\text{BaTiO}_3/\text{SrRuO}_3$ FTJ: (a) polarization pattern produced by PFM and (b) the corresponding tunnelling current map measured by C-AFM. Adapted from Gruverman *et al.* [169]. (Online version in colour.)

Experimentally, a prototype junction was demonstrated in which the resistance exhibits a hysteretic behaviour; however, the origin of the effect was not clear [166]. Since many oxides exhibit resistive switching behaviour [167], the key problem is to reveal the correlation between the FE polarization and tunnelling conductance. This has been achieved very recently when three experimental groups reported independently experimental observations of the TER effect associated with the switching of FE polarization of BaTiO_3 or $\text{Pb}_{1-x}\text{Zr}_x\text{TiO}_3$ FE films [168–170]. The correlation between polarization orientation and conductance is evident from figure 11, which shows results of local probe measurements using piezoelectric force microscopy (PFM) (figure 11a) in conjunction with conductive–atomic force microscopy (C-AFM; figure 11b). As predicted [157,158], the observed effects are really giant, showing the resistance change by two to three orders in magnitude. These experimental results prove the concept of FTJs and show the capability of thin-film FEs to serve as a nanoscale material that can act as a switch to store binary information.

(b) Multi-ferroic tunnel junctions

An MFTJ is an FTJ with FM electrodes or equivalently an MTJ with an FE barrier (figure 9c) [151]. Electron tunnelling from an FM metal electrode through a thin insulating barrier layer is spin polarized [171]. As a consequence, in an MTJ, the tunnelling current depends on the relative magnetization orientation of the two FM electrodes, a phenomenon known as TMR [8]. In MFTJs, the TER and TMR effects coexist, as was first predicted by Zhuravlev *et al.* [172]. Therefore, MFTJs represent a four-state resistance device where resistance can be switched by both electric and magnetic fields [28,173,174].

First-principles transport calculations of $\text{Fe}/\text{BaTiO}_3/\text{Fe}$ MFTJs show that FE displacements affect differently the interface transmission for parallel and antiparallel magnetization orientation of the electrodes [175]. The importance of interfaces in controlling the tunnelling spin polarization is known from studies of MTJs (e.g. [176–181]). In MFTJs with asymmetric interfaces (electrodes), this could lead to electric-field control of TMR. Indeed, four resistance states have been predicted from transport calculations of $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ MFTJs [28]. Here, the TMR effect has the same origin as in ordinary MTJs [8,181]. The asymmetric interface termination (RuO_2/BaO versus TiO_2/SrO) creates a

different polarization profile when the FE polarization is switched, producing the TER effect. The same principles should apply to any MFTJ with asymmetric interfaces.

Experimentally, there have been so far only a very few attempts to study MFTJs. Garcia *et al.* [182] have fabricated $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BaTiO}_3/\text{Fe}$ MFTJs in which a 1 nm BaTiO_3 barrier film was shown to be FE at room temperature. In these junctions, the amplitude of the TMR was found to vary reversibly with poling voltage pulses used to orient the FE polarization in the BaTiO_3 barrier towards or away from the Fe electrode [182]. These exciting results indicate the possibility of controlling the transport spin polarization by FE polarization of the barrier in MFTJs.

Another type of MFTJ is feasible in which a single-phase MF is used as a barrier. Note that MFs cannot be used as electrodes because they are not conducting. Gajek *et al.* [27] demonstrated a $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BiMnO}_3/\text{Au}$ MFTJ in which resistance is controlled by both electric and magnetic fields. In this MFTJ, the TMR effect is due to the spin-filtering properties of the MF barrier [183], while the TER effect is due to the change in the barrier potential profile when the polarization is switched [157]. The main problem with this type of MFTJ is that BiMnO_3 is one of the very few known FM/FEs. Most MFs have AFM or more complex magnetic ordering. Besides, FM properties of BiMnO_3 appear only at low temperature [80].

Very much remains to be done in the exciting novel field of MFTJs. In particular, issues related to FE stability at the nanoscale [184] and defects known to be important in MTJs (e.g. [185–187]) need to be resolved. Nevertheless, the above theoretical and experimental results are very promising to propose alternative solutions for the local manipulation of spin-dependent transport properties.

6. Perspectives for applications

Although the mechanisms governing multiple ferroic orders in the same material and the coupling between them is of fundamental interest, the overwhelming interest in MF and ME materials is due to the promise they hold for applications.

MTJs serve as a basis of non-volatile memories (MRAM) in which the information is stored in the mutual orientation of the magnetization in the electrodes. Using ME coupling to switch the magnetic moment via electric field can lead to devices entirely controlled by voltage and not by current. This can dramatically reduce power dissipation and relieve problems with miniaturization in both solid-state memory (MRAM) and magnetic storage (hard drives). The most promising developments seem to be ME control of the magnetic anisotropy and the exchange bias.

Using the interplay of FM and FE orders at interfaces can have other interesting applications. The large change of resistance in FTJs depending on the polarization orientation can make the read operation non-destructive in non-volatile FE random access memories and can make this technology competitive. In addition, conceptually new multi-level memories or combined logic and memory devices are possible in MFTJs.

Although a lot of issues remain to be resolved and many breakthroughs will be necessary to produce commercially viable devices, the possible impact of these technologies is tremendous. The field has been developing at a blistering pace with new exciting developments appearing all the time. In addition, the marriage of state-of-the-art experiment with predictive modelling has contributed significantly to this effort.

The authors acknowledge support from the National Science Foundation (NSF) through the Materials Research Science and Engineering Center (MRSEC) at the University of Nebraska-Lincoln (NSF grant no. 0213808), the Institute for Functional Nanomaterials of the University of Puerto Rico (NSF grant no. 0701525) and the Experimental Programme to Stimulate Competitive Research (NSF grant nos. 1010674 and 1010094). The authors are grateful to Verona Skomski for helping to prepare the manuscript for submission.

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