

Electric-Field Control of Magnetism in Complex Oxide Thin Films

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Abstract

In this article, we review current research efforts to control the magnetic behavior of complex oxide thin films using electric fields. After providing fundamental definitions of magnetoelectric response, we survey materials, architectures, and mechanisms that exhibit promise for such electric-field control of magnetism. Finally, we mention ideas for future research and discuss prospects for the field.

Introduction

The search for a general means to control the coupling between electricity and magnetism has intrigued scientists since Ørsted's discovery of electromagnetism in the early 19th century. Traditionally, however, the study of magnetoelectric materials has been confined to academic interest, likely because of fundamental limitations on the magnitude of the magnetoelectric response. The past few years, however, have seen a tremendous revival of activity in the field of magnetoelectrics,¹ motivated in large part by the entirely new device paradigms that would be enabled by electric-field control of magnetism.^{2,3} First, the replacement of magnetic fields—which are generated by comparatively hot, heavy, and bulky electric currents—by electric fields in existing magnetic device applications would reduce power consumption and allow for enhanced miniaturization. In addition, entirely new device paradigms could be envisaged, such as magnetoelectric storage elements, electrically tunable filter devices, and electric field manipulation of spintronics.

In this article, we review recent research on the magnetoelectric effect as it pertains to oxide electronics: the electric-field control of magnetism in complex oxide thin films and heterostructures. After briefly introducing some essential definitions, we describe four mechanisms by which the

magnitude or orientation of magnetization can be modified using an electric field in thin films. Finally, we offer some perspectives and challenges for future work.

Definitions and Formalism

We begin this section with a brief summary of the linear magnetoelectric effect, which describes the relation between magnetic and electric fields in matter; for a detailed review, see Reference 1. The term “magnetoelectric” was first introduced in 1957 by Landau and Lifshitz, who pointed out in their classic work, *Electrodynamics of Continuous Media*,⁴ that applied electric fields should, in principle, induce magnetization in certain magnetically ordered crystals. The first practical proposal came two years later from Dzyaloshinskii,⁵ who used symmetry arguments and thermodynamics to show that the effect should occur in Cr₂O₃; in the same year, it was realized experimentally in this material by Astrov.⁶ The linear magnetoelectric effect is defined to be the first-order magnetic response, M , of a system to an applied electric field, E , or, equivalently, the electrical polarization, P , induced by an applied magnetic field, H ,^{1,7}

$$P_i = \alpha_{ij} H_j \quad (1)$$

$$M_i = \alpha_{ji} E_j \quad (2)$$

where α is the magnetoelectric tensor (in Gaussian units).

On a microscopic level, the details of the mechanism leading to a linear magnetoelectric response remain to be clarified and are likely highly material-dependent. Broadly, an electric field both shifts the positions of the magnetic cations relative to the anions and modifies the electronic wave functions; both effects result in a change in the magnetic interactions, mediated primarily by the spin-orbit coupling. Three important restrictions on α are relevant in the design of new magnetoelectric materials or systems: (1) specific symmetry requirements must be met for α to be nonzero; (2) in cases where α is symmetry-allowed, there are well-defined bounds on the magnitude of its components; and (3) the material must, of course, be electrically insulating so that it is able to sustain an electric polarization.

In terms of symmetry requirements, the elements of α can be nonzero only in materials that are neither time-reversal-symmetric (i.e., they are not symmetric with respect to reversal of the directions of the magnetic moments) nor space-inversion-symmetric (i.e., they are not centrosymmetric). The linear magnetoelectric effect is described by a term in the thermodynamic potential that is linear in both the magnetic and electric fields:

$$\Phi = -\alpha_{ij} E_i H_j \quad (3)$$

Therefore, because E is a polar vector and H is an axial vector, α must be odd under both space inversion and time reversal and symmetric under the product of the two operations for the free energy to be invariant. In practice, this means that, in order to have a nonzero linear magnetoelectric response, a material must both be magnetically ordered (to lift the time-reversal symmetry) and lack an inversion center (to lift the space-inversion symmetry). These requirements can be met in magnetic polar materials or in cases where a noncentrosymmetric magnetic ordering lifts the inversion center.

Regarding magnitude restrictions, the magnitudes of all elements of the magnetoelectric tensor are bounded by the product of the geometric means of the corresponding elements of the magnetic permeability and dielectric permittivity tensors μ and ϵ .⁸ That is

$$\alpha_{ij} \leq \sqrt{\mu_{ii} \epsilon_{jj}} \quad (4)$$

or more rigorously

$$\alpha_{ij} \leq \sqrt{\chi_{ii}^m \chi_{jj}^e} \quad (5)$$

where χ^m and χ^e are the magnetic and electric susceptibilities, respectively. This

represents a rather severe limitation on the magnitude of the linear magnetoelectric response in single-phase materials. As is now well-established through the study of multiferroics (materials that display simultaneous ferromagnetism and ferroelectricity), magnetic ions, with moments caused by spin-polarized localized electrons, are not highly polarizable. Hence, the occurrence of simultaneously large permeability and large permittivity is *chemically* contraindicated,⁹ and the possibilities for achieving an enhanced linear magnetoelectric response through optimization of α in single-phase materials are rather limited.

In the next section, we review recent novel approaches that seek to circumvent this limitation, by either exploiting nonlinear responses or using multiphase materials (or both). We restrict our discussion to phenomena that have been observed in thin-film architectures, which are commonly found in electronic devices. Of these, one of the most promising material classes is that of the oxide heterostructures, which provide a platform in which the charge, spin, orbital, and lattice degrees of freedom can be manipulated through judicious selection of the individual layers.

New Materials and Mechanisms: Recent Observations and Proposals Field Effects

In field-effect devices, an electric field is used to modulate the carrier concentration in a material through its contact with a metallic electrode; the effect is widely used in the microelectronics industry where semiconductor field-effect transistors are ubiquitous. In complex oxides, where many phases with distinctly different properties (metallic/insulating, ferromagnetic/nonmagnetic, etc.) are close in energy, a change in carrier concentration through such electrostatic doping can be exploited to induce dramatic changes in behavior.¹⁰ Relevant for this article are recent demonstrations of electric-field-induced changes in magnetic ordering temperatures or even transitions from magnetic to nonmagnetic behavior. In this case, the physics is conceptually quite simple: Ferromagnetic alignment of the magnetic moments in many complex oxides is mediated by carriers and so is associated with electrical conductivity. Enhancement (reduction) of the conductivity by injection (depletion) of carriers can therefore enhance (reduce) the magnetism. Note that the magnetoelectric response is highly nonlinear.

Most explorations in oxides have been on colossal magnetoresistive manganites, for example, the successful electric-field modulation of the transition temperature between the paramagnetic insulating and ferromagnetic metallic phases in $\text{La}_{0.9}\text{Ba}_{0.1}\text{SrMnO}_3$ on Nb-doped SrTiO_3 .¹¹ Particularly large effects can be obtained if a ferroelectric oxide is inserted between the electrode and the magnetic material.^{12,13} Similar behavior has also been reported with oxide-based diluted magnetic semiconductors such as Co-doped TiO_2 .¹⁴ Many studies now indicate that an efficient oxide-based field-effect device, which could open the possibility for non-volatile, nondestructive data-storage elements, will require all oxide-based heterostructures, with oxide electrodes as well as active layers. Many issues still remain unresolved; in particular, ON/OFF ratios and carrier mobilities comparable to those in standard semiconductor devices have not yet been achieved.

Strain-Mediated Magnetoelectricity in Composites

In composites of magnetostrictive or piezomagnetic materials combined with electrostrictives or piezoelectrics, an extrinsic magnetoelectric coupling is mediated by strain at the interface.^{15–17} Here, an electric field causes strain in the electrical component that is mechanically transferred to the magnetic component, where it changes the magnetization (and vice versa). Such strain-based coupling has been used in two geometries: In horizontally layered systems, macroscopic bilayers or multilayers can be bonded by a compliant glue material.¹⁵ Tuning of the ferromagnetic resonance frequencies with an electric field has already been demonstrated by this approach.^{16,18,19} Alternatively, in nanoscale horizontal structures, heteroepitaxy at the interfaces can be exploited to control magnetoelectric coupling on an atomic level. Vertical heteroepitaxial nanostructures are particularly appealing because the magnetoelectric response should be enhanced by both the larger interfacial area and the diminished influence of clamping from the substrate.

Figure 1 shows an example of a film containing vertical nanopillars of a ferromagnetic spinel, formed by self-assembly within a ferroelectric medium.¹⁷ A particularly exciting recent development in this area is the experimental observation of switching of the magnetism in such nanopillars using an electric field (Figure 2).²⁰ The shape anisotropy causes the net magnetization to lie along the long axis of the pillars, with up and down directions degenerate and independent of the orien-

tation of the ferroelectric polarization. Electric-field switching of the ferroelectric causes a structural distortion of the pillar and perturbs the magnetization so that, after ferroelectric switching, the magnetization can point along its original direction or the opposite direction with equal probability. A small external magnetic field, far smaller than the coercive field required to switch the magnetization independently, is required to lift the time-reversal symmetry and set the new magnetization direction.

Elastic Coupling and Domain Reorientation

Multiferroics are materials that are both ferroelectric and magnetically ordered in the same phase, and so, by definition, they break both time-reversal and space-inversion symmetries. One possible route to achieving magnetoelectric coupling in a multiferroic is to combine the elastic coupling between the ferroelectric polarization and the strain with the magnetic anisotropy to give an effective coupling between polarization direction and magnetization orientation. A schematic of the physical principle is shown in Figure 3: The ferroelectric polarization is coupled to a structural distortion in the system (tetragonal in the figure), which sets the easy axis of magnetization (perpendicular to the polar direction in the figure) through the magnetic anisotropy. Electric-field reorientation of the polarization then reorients the magnetic easy axis through the elastic coupling. Note that 180° switching of the polarization has no effect on the symmetry and, hence, does not cause a change in the magnetic easy axis in this case.

Such a mechanism is now well-established in “spin-spiral” multiferroics, such as TbMnO_3 , in which ferroelectricity is induced by the formation of a symmetry-lowering magnetic ground state that lacks inversion symmetry.²¹ (For a review,

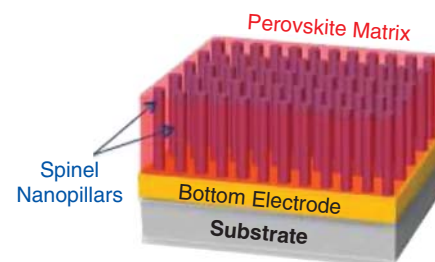


Figure 1. Cartoon of vertical nanopillars of a ferromagnetic spinel formed by self-assembly within an epitaxial perovskite ferroelectric matrix. An electric field can switch the orientation of the magnetization in the pillars.¹⁷

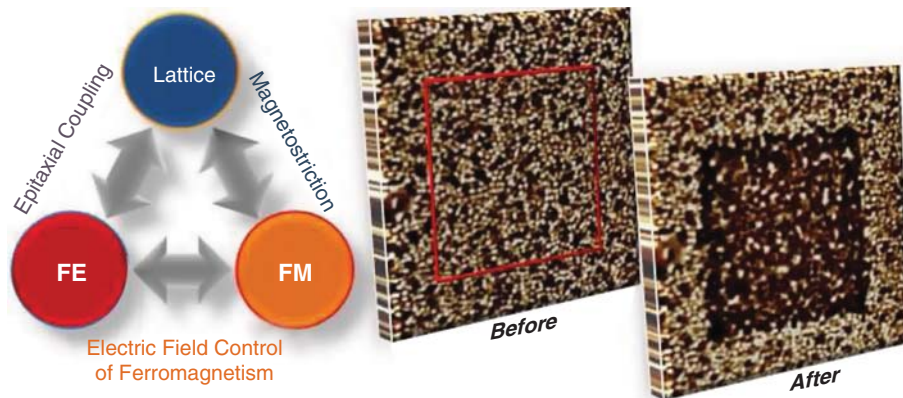


Figure 2. Both the ferroelectric polarization (FE) and the ferrimagnetic magnetization (FM) are coupled elastically to the lattice structure. As a result, switching of the ferroelectric with an electric field can cause switching of the orientation of the magnetization.

see Reference 22.) The resulting polarization is small, but because it is caused directly by the magnetic ordering, its direction is determined by the orientation of the magnetic ordering. As a result, the polarization can be reoriented using a magnetic field. Although initially observed only at low temperature (a few Kelvin), it has recently been reported in copper oxide at 230 K,²³ which is much closer to room temperature than had previously been achieved.

The reciprocal behavior has been demonstrated at room temperature in thin films of the antiferromagnetic ferroelectric BiFeO₃.²⁴ BiFeO₃ is a perovskite-structure ferroelectric, with the ferroelectric polarization oriented along the [111] direction; this reduces the symmetry to rhombohedral and introduces an elastic strain. The magnetic ordering is G-type antiferromagnetic, with a long-wavelength spiral of the antiferromagnetic vector in the bulk; this is believed to be suppressed in thin films.²⁵ First-principles calculations of the magnetocrystalline anisotropy energy show that, in the absence of the spiral, the antiferromagnetic spins lie in an easy plane that is perpendicular to the ferroelectric polarization.²⁶ As a result, one expects that polarization switching by either 71° or 109° should change the orientation of the easy magnetization plane. Indeed, this has been demonstrated in both epitaxial films²⁴ and single crystals using neutron scattering.²⁷

Perhaps the most important recent breakthrough from a technological standpoint has been the experimental demonstration of electric-field switching of ferromagnetic Co, through its exchange-bias coupling to BiFeO₃, whose switching we just described.²⁸ At the interface between a ferromagnet and an antiferromagnet, the orientation of the magnetization in the ferromagnet is influenced by

the spin structure of the antiferromagnet, leading to shifts and broadening of the magnetic hysteresis loops.^{29,30} This exchange-bias coupling causes a “pinning” of the ferromagnetic orientation to the antiferromagnetic axis.

This phenomenon was first exploited by the magnetoelectrics community to achieve electric-field control of exchange-bias fields through coupling of a ferromagnet to antiferromagnetic magnetoelectric Cr₂O₃.³ When the antiferromagnet is also a ferroelectric, as in BiFeO₃, the electric-field control of the antiferromagnetism²⁴ suggests a route to controlling ferromagnetism with an electric field through the exchange-bias coupling. Exchange coupling between a conventional ferromagnet (Co) and multiferroic BiFeO₃ is now well-established, although not yet well-understood.^{31,32} Furthermore, on-going work²⁸ suggests that the orientation of the magnetization in the exchange-coupled Co can be controlled and switched through application of an electric field to the BiFeO₃. Research in this field is still in its infancy, however, and extensive further study is required to explore the intricacies of coupling in such heterostructures.

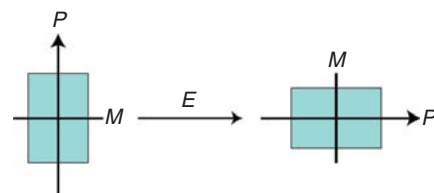


Figure 3. Elastic strain associated with the ferroelectric polarization, *P*, sets the easy axis of magnetization, *M*, through the magnetoelastic anisotropy. Reorientation of the polarization with an applied electric field reorients the magnetic easy axis. Note that 180° switching of *P* has no effect on the orientation of the easy axis.

Change in Symmetry at Interfaces

Recently, it was pointed out that thin-film growth of heterostructures can be exploited to create structures that break inversion symmetry, even when the parent bulk materials are centrosymmetric.³³ Indeed, at the interface between any two unlike materials, space-inversion symmetry is intrinsically broken. Therefore, any interface between materials that are magnetically ordered must break both time-reversal and space-inversion symmetries. One effect of this requirement is a nonlinear magneto-optical response, which has been demonstrated for SrTiO₃/LaAlO₃/La_{0.6}Sr_{0.4}MnO₃ superlattices.³³ Another is a nonreciprocal directional dichroism seen in LaMnO₃/SrMnO₃/LaAlO₃ superlattices.³⁴ Importantly for this work, such interfaces should yield a linear magnetoelectric effect, provided, of course, that the system is insulating and remains so in the presence of reasonable electric fields.

Recent first-principles density functional computations demonstrated such a linear magnetoelectric response, and also established its mechanism, at the interfaces in SrRuO₃/SrTiO₃ heterostructures.³⁵ As shown in Figure 4, when the dielectric

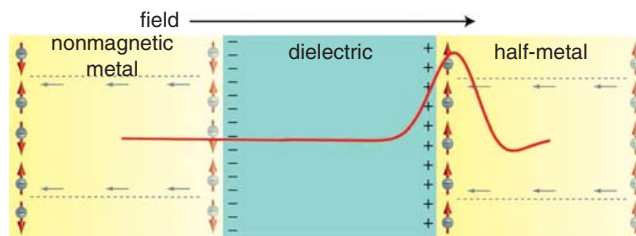


Figure 4. Schematic of the mechanism causing an induced magnetization at the interface between a ferromagnetic metal and a nonpolar dielectric. The accumulation of spin-up electrons adjacent to the positive face of the dielectric, and their depletion from the negative face, leads to the net change in magnetization (red line).

SrTiO₃ is polarized by an applied electric field, electrons in the metal flow to the positively charged face of the dielectric (and away from the negatively charged face) in order to screen the surface charge. In the case when the states at the Fermi energy are spin-polarized, the net accumulation of charge is also spin-polarized, leading to a change in interfacial magnetization that is linear in the applied electric field. Note that the effect occurs only in the region of the interface where the space-inversion symmetry is broken and is zero in the case of a nonmagnetic metal that does not break time-reversal symmetry.³⁵ A recent observation of electric-field-tunable magnetization at the surface of a ferromagnetic electrode in an electrochemical cell³⁶ is likely a manifestation of this spin-capacitor effect.

Prospects

Many of the breakthroughs described in this article would not have been possible without the evolution of thin-film deposition processes for oxides such as molecular beam epitaxy (MBE), coupled with the ability to monitor the heterostructure growth through sophisticated *in situ* surface analytical tools such as reflection high-energy electron diffraction (RHEED). In addition, the emergence of a host of electron-, x-ray-, and neutron-based characterization tools promises to dramatically improve the ability to probe the properties of complex oxide films with unprecedented structural, chemical, electronic, and functional resolution. Examples include sub-angstrom-resolution direct atomic imaging and spectroscopy, time-resolved photoemission spectromicroscopy, scanning probes, and high-flux neutron sources such as the spallation neutron source. Imaging and locating small concentrations (around 1 ppm) of impurities such as oxygen vacancies continues to be a challenge. On the theoretical side, advances in computational first-principles techniques promise more widespread *ab initio* design of new thin-film magnetoelectric materials or

mechanisms. Indeed, a recent editorial in *Nature Nanotechnology* pointed out the increasingly important role of theoretical approaches in generating new ideas for nanoscience and nanotechnology.³⁷ Particularly important for thin-film magnetoelectrics are a newly developed method for applying finite electric fields to metal-insulator heterostructures³⁸ and an approach for efficient calculation of the lattice contribution to the linear magnetoelectric response,³⁹ both within the density functional formalism.

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