# Multiferroics: Past, present, and future

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**Working in concert, theorists and experimentalists have found promising new ways to get two traditional foes—ferroelectricity and magnetism—to coexist.**

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**The interplay** between electricity and magnetism has fascinated scientists and engineers for centuries, ever since Hans Christian Oersted noticed in 1820, quite by accident, that a magnetic compass needle deflected when he switched the current in a nearby battery on or off. Over the 40 years or so following Oersted's observation, the classical theory of electromagnetism was worked out, with seminal contributions from the likes of André Marie Ampère and Michael Faraday; that work culminated in the 1860s with James Maxwell's unified theory. The implications of those discoveries for society need no elaboration. This article focuses on how electricity and magnetism interplay in a class of real materials—the multiferroics—in which spontaneous magnetic and dielectric ordering occur.

Over the past few years, the field has evolved rapidly; many of the materials science and solid-state chemistry issues that once plagued sample quality have been resolved, and genuine physical effects can be studied. It is now particularly timely for physicists to tackle the fundamental questions underlying multiferroicity. Our goal in this article is to outline what, in our opinion, are the most exciting open problems in the field and to place them in historical context. Our hope is that the combined creativity of the broader physics community will further accelerate progress and inspire a new generation of practical, paradigm-shifting electromagnetic devices.
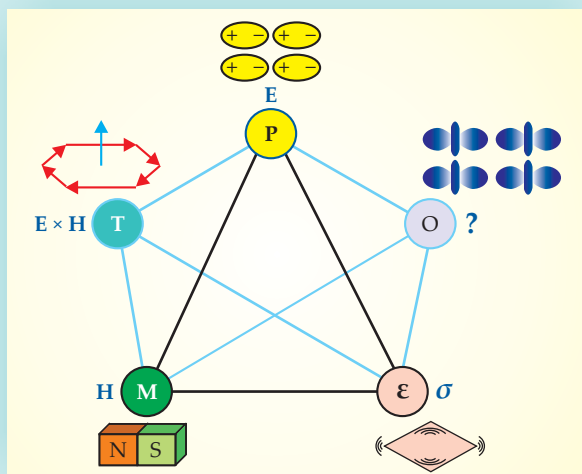
## Why multiferroics?

A ferroic is a material that adopts a spontaneous, switchable internal alignment: In ferromagnetics, the alignment of electron spins can be switched by a magnetic field; in ferroelectrics, electric dipole-moment alignment can be switched by an electric field; and in ferroelastics, strain alignment can be switched by a stress field. Individually, the ferroics are already of great interest both for their basic physics and for their technological applications. For example, electrical polarization in ferroelectrics and magnetization in ferromagnets are exploited in data storage, with opposite orientations of the polarization or magnetization representing "1" and "0" data bits (see the article by Orlando Auciello, James Scott, and Ramamoorthy Ramesh, Physics Today, July 1998, page 22).

A multiferroic combines any two or more of the primary ferroic orderings in the same phase,[1] such as the ferroelectric ferroelastics that form the basis of piezoelectric transducers (see figure 1). Current convention, however, applies the term "multiferroic" primarily to materials that combine ferroelec-

tricity with ferromagnetism or, more loosely, with any kind of magnetism. The terminology is often extended to include composites, such as heterostructures of ferroelectrics interlayered with magnetic materials.

One of the most appealing aspects of multiferroics is their so-called magnetoelectric coupling. Whereas a ferroic property is usually modified using its conjugate field (magnetic fields modify magnetization, electric fields modify polarization, and so on), in a multiferroic a magnetic field can tune the electric polarization and an electric field can tune the



**Figure 1. Interactions in multiferroics.** The well-established primary ferroic orderings, ferroelectricity (**P**), ferromagnetism (**M**), and ferroelasticity (**ε**), can be switched by their conjugate electric (**E**), magnetic (**H**), and stress (**σ**) fields, respectively. Cross coupling allows those ferroic orderings to also be tuned by fields other than their conjugates; in magnetoelectric multiferroics, for example, an electric field can modify magnetism. Physicists are also exploring the possibility of ferrotoroidics, a promising new ferroic ordering of toroidal moments (**T**), which should be switchable by crossed electric and magnetic fields. The "O" represents other possibilities—such as spontaneous switchable orbital orderings, vortices, and chiralities—that will likely enrich future research. (Adapted from ref. 14.)

magnetization. That is intriguing from a basic physics point of view: Since magnetization, represented by an axial vector, and polarization, represented by a polar vector, have different symmetry properties, it is not immediately obvious that one should be addressable by the other's conjugate field. In terms of applications, the prospect of electric-field control of magnetism is particularly exciting, as it could lead to smaller, more energy-efficient devices for magnetic technologies. Indeed, the development of multiferroics during the 1970s and 1980s—spearheaded by the group of Hans Schmid in Geneva and funded, curiously enough, by the Swiss Post Office—was intimately linked to the development of the magnetoelectric effect. (For a comprehensive review, see reference 2.) Several physics and materials challenges remain to be addressed, however, to achieve practical devices based on the magnetoelectric effect; we discuss those later.

## Contraindication

Among the first topics to occupy physicists during the late 1990s renaissance period of multiferroics was the question of why so few exist.[3] The first obvious restriction is that ferroelectrics, to sustain a polarization, must be robust insulators. Most magnetic materials, however, are conducting metals. In fact, even among materials that are formally insulating, any

leakage—due, say, to impurities or inexact ratios of atoms—is highly detrimental to ferroelectricity.

That restriction aside, there is a second, more vexing conundrum. In conventional ferroelectric materials, the polarization arises when nonmagnetic cations shift away from the center of their surrounding anions. The uneven displace-

ment, or noncentrosymmetricity, between positive and negative charges is what gives rise to the electric dipole moment. But in magnetic materials, the magnetic cations tend to sit exactly at the center of the surrounding anions, in centrosymmetric positions, such that no dipole moment forms. The difference in behavior between magnetic and nonmagnetic cations is now understood to be a consequence of the competition between energy-lowering covalent bond formation (larger for $d^0$ cations with their empty $d$ shells) and energy-raising electronic Coulomb repulsion (larger for cations with $d$ electrons). That balance favors off-centering of $d^0$ ions such as the $Ti^{4+}$ ions in barium titanate, the prototypical ferroelectric. In contrast, magnetism occurs in materials that have unpaired localized electrons, such as those in the partially filled $d$ orbital of a transition metal. We therefore describe magnetism and conventional ferroelectricity as being chemically contraindicated.[4] (For more on the chemical makeup of multiferroics, see box 1.)

## Theory and experiment intertwine

Circumvention of multiferroics' fundamental contraindication has required close interplay between theory and experiment, as demonstrated even in the early history of the magnetoelectric effect. The first experiment that can really be considered to have directly measured a magnetoelectric response occurred in 1888, when Wilhelm Röntgen showed that the dielectric displacement **D** and magnetic induction **B** in a moving body depend on both the electric **E** and magnetic **H** fields. The next development was theoretical: In 1894 Pierre Curie presented symmetry arguments that an **E** field should induce a magnetization and an **H** field an electric polarization in certain classes of materials. That idea, it seems, was neglected until the 1950s, when a brief discussion of magnetoelectric terminology appeared in Lev Landau and Evgeny Lifshitz's classic *Electrodynamics of Continuous Media*. Then, Igor Dzyaloshinskii ushered in a 1960s "golden age" with his prediction, based on phenomenological theory, that the magnetoelectric effect should occur in chromium oxide,[5] a prediction confirmed later that year in experiments by D. N. Astrov.[6]

Today's renaissance of magnetoelectrics and multiferroics was enabled by a combination of theoretical and experimental factors: First, improved fundamental understanding of the contraindication between magnetism and ferroelectricity led to the identification of new routes to combine them (see box 2); then the availability of modern synthesis techniques—particularly thin-film and single-crystal growth methods—allowed precise control over crystalline perfection and chemical stoichiometry in samples large enough to allow for accurate characterization (see figure 2).

The story of bismuth ferrite is a useful illustration of how the back-and-forth between theoretical and experimental efforts has both advanced the field of multiferroics and prompted developments in theoretical methodology and experimental techniques. We tell that story next. (Many other multiferroic materials and mechanisms are also of scientific interest, and we do not mean to suggest that $BiFeO_3$ will necessarily prove to be the most significant in the long term.)
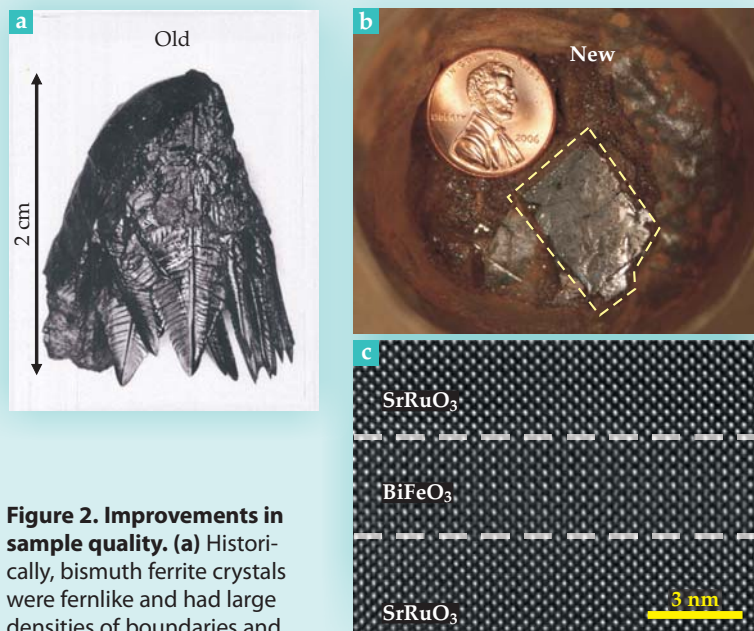


**Figure 2. Improvements in sample quality. (a)** Historically, bismuth ferrite crystals were fernlike and had large densities of boundaries and defects. (Image courtesy of Hans Schmid and Cristobal Tabares-Muñoz.) Modern samples, such as this rectangular-shaped crystal **(b)** and the $BiFeO_3$ thin film shown sandwiched between strontium ruthenate layers in this transmission electron micrograph image **(c)**, have fewer defects. Thus, intrinsic properties, such as the large electric polarization (around 90 µC/cm²), can be accurately determined.

## A case study: Bismuth ferrite

Long known to be both antiferromagnetic—its magnetic moments align in opposing directions, so that the net magnetization is zero—and ferroelectric, bismuth ferrite is multiferroic in the popular use of the term. Since it is readily synthesized in bulk and thin-film forms and both its antiferromagnetic Néel temperature and ferroelectric Curie temperature are well above room temperature (approximately 643 K and 1100 K, respectively) it is undoubtedly the most-studied multiferroic today.

When we first became interested in $BiFeO_3$ in the late 1990s, the only published ferroelectric measurement—performed on a bulk polycrystalline sample—reported a rather small value for the ferroelectric polarization, around 6 µC/cm². That value struck us as somewhat curious, since the stereochemically active lone pair of electrons on the $Bi^{3+}$ ions should lead to large local dipole moments (see box 2). Indeed, in the early 2000s, the first density functional theory (DFT) calculations of the ground-state structure indicated large relative Bi–O displacements, of similar magnitude to those of Pb–O in lead titanate, a strongly polar ferroelectric. The theoretical situation, however, was complicated by the fact that the standard DFT approximations in use at the time failed to produce an insulating ground state for the high-symmetry reference structure and thus could not calculate the evolution of the polarization from the nonpolar state.

Clarification followed many late-night, heated discussions among ourselves and our coworkers at conferences and required developments on both experimental and theoretical fronts. First, the growth of high-quality thin films yielded much larger ferroelectric polarizations,[7] in fact, even larger than that of $PbTiO_3$. Second, the combination of contempo-
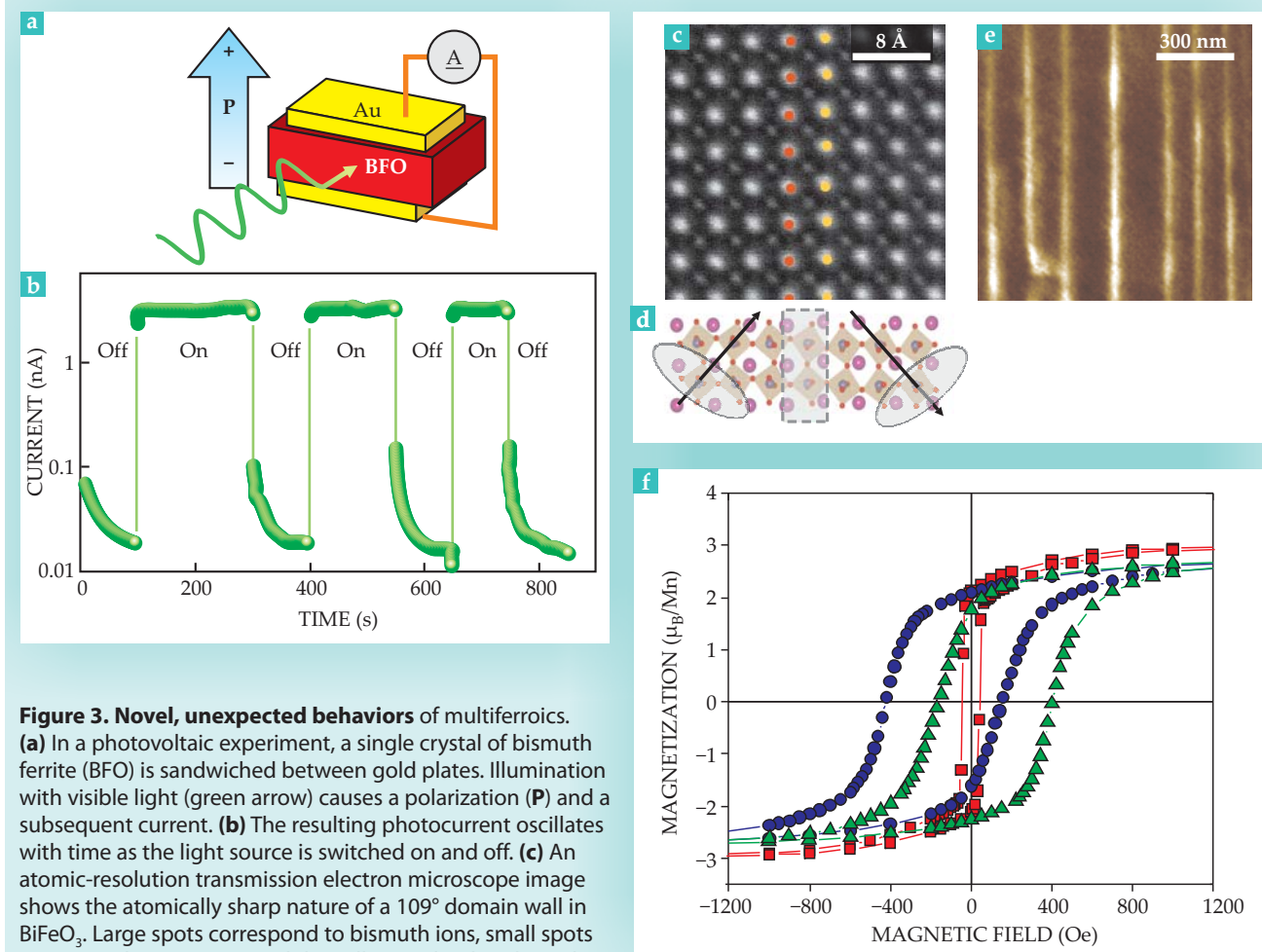
**Figure 3. Novel, unexpected behaviors** of multiferroics. **(a)** In a photovoltaic experiment, a single crystal of bismuth ferrite (BFO) is sandwiched between gold plates. Illumination with visible light (green arrow) causes a polarization (**P**) and a subsequent current. **(b)** The resulting photocurrent oscillates with time as the light source is switched on and off. **(c)** An atomic-resolution transmission electron microscope image shows the atomically sharp nature of a 109° domain wall in $BiFeO_3$. Large spots correspond to bismuth ions, small spots correspond to iron ions, and the yellow and red circles indicate the domain wall. **(d)** The structure near the domain wall, calculated using density functional theory, shows the 109° shift in polarization direction (black arrows) and in magnetic easy-plane orientation (gray ovals). **(e)** A conducting atomic force microscope image shows measurable conduction along the domain walls. **(f)** As-yet-unexplained physics at the interface of $BiFeO_3$ and lanthanum strontium manganite ($La_{1-x}Sr_xMnO_3$) leads to a strong dependence of the magnetic hysteresis on the magnetic history of the sample. Blue and green curves show the behavior after cooling in fields of 10 000 oersted (1 tesla), applied in opposite orientations; the red curve shows the behavior of lanthanum strontium manganite without $BiFeO_3$.

rary DFT techniques with modern methods for calculating ferroelectric polarization yielded polarization values consistent with experiment—the first application of the modern theory of polarization to a magnetic system. And third, production of high-quality bulk single crystals allowed for accurate structural and magnetic characterization, and for determination of the optical bandgap, which is important for the exciting photovoltaic (PV) applications described next.

**Diodes and photovoltaics.** Leakage currents in ferroelectrics are usually considered a serious problem. However, they may be an advantage for diode-like applications, since the direction of the ferroelectric polarization can influence the magnitude of electrical conduction. Single $BiFeO_3$ crystals exhibit significant conduction due to their small optical bandgap and, possibly, to the presence of oxygen vacancies, and consist of a single ferroelectric domain without grain or domain boundaries. The result is a strong correlation between polarization direction and electronic conduction, which can produce diode-like unidirectional current flow.[8]

Intriguingly, illumination of $BiFeO_3$ with visible light induces a significant current flow without external voltages, indicative of a PV effect (see figures 3a and 3b). Such ferroelectric PV phenomena have been well known for the past four decades, but $BiFeO_3$ is unique in its combination of large PV currents (around 10 $\mu A/cm^2$) and drastically enhanced photovoltages at domain walls.

The origin of diode and PV behavior in $BiFeO_3$ needs further study but is likely closely related to the structure of the $d$ electrons and, in turn, to magnetism and multiferroicity. The nature of the interface with the electrode may also be important; we discuss the physics of such interfaces later. Meanwhile, the PV effects are being explored for technological applications such as solar cells, optical sensors, and nondestructive readout.

**Magnetoelectric coupling.** The next step in the $BiFeO_3$ story was to understand on a microscopic level the nature of polarization and magnetism and the interactions between them. Theory provided the answer: DFT calculations, with
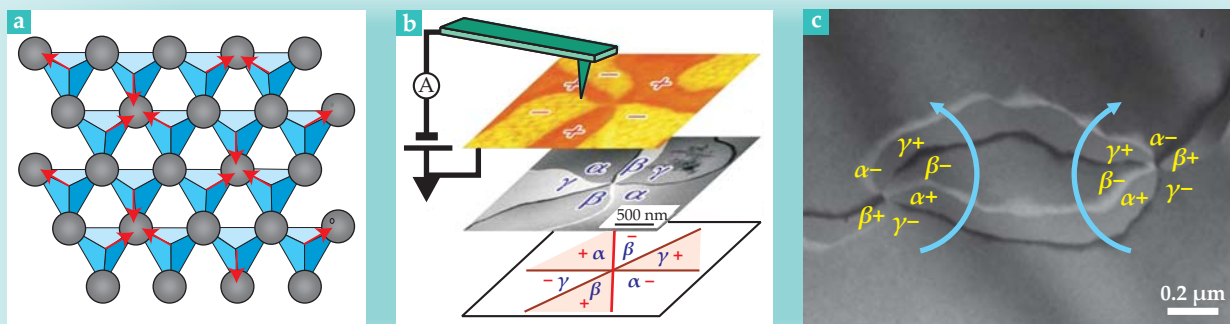
**Figure 4. Multiferroic vortices. (a)** At temperatures below 100 K, the polyhedral structure of yttrium manganite ($YMnO_3$) distorts, with trimers of oxygen atoms (at the vertices of the polyhedra) displacing toward Y sites (gray spheres), as indicated by the red arrows. The displacements generate three possible domains of trimerization (α, β, and γ), each of which can sustain two directions of ferroelectric polarization (+ and −). **(b)** Those polarization domains can form a cloverleaf-shaped topological defect known as a multiferroic vortex, shown here in a conductive atomic force microscope image (top layer), a dark-field transmission electron microscope image (middle layer), and a schematic illustration (bottom layer). **(c)** A dark-field transmission electron microscope image shows a vortex–antivortex pair, characterized by a reversal in the vorticity—defined here as the α-β-γ direction—of the domain configuration.

spin–orbit coupling explicitly included, determined the easy plane of magnetization (the plane perpendicular to the polarization), showed that it corresponds to a symmetry that permits weak ferromagnetism, and quantified the magnitude of the resulting magnetization. Symmetry analysis showed, however, that switching the ferroelectric polarization leaves the weak ferromagnetism unchanged, which would seem to preclude direct electric-field control of the magnetization.

Instead, we pursued an extremely simple idea that exploits the fact that the structural distortion associated with the ferroelectric polarization is responsible for setting the orientation of the magnetic easy axis through the magnetocrystalline anisotropy: Though reversal of the ferroelectric polarization will not result in a new magnetic easy plane, rotation of the polarization to one of the other symmetry-equivalent axes will. As a first step, we demonstrated that idea with electric-field control of the antiferromagnetic vector in $BiFeO_3$ films (Ramesh, Spaldin, and coworkers) and in single crystals (Cheong, Valery Kiryukhin of Rutgers University, and coworkers). Then, by exploiting the fact that interfacial coupling causes the ferromagnetic orientation of cobalt to align with the antiferromagnetic orientation of $BiFeO_3$, we were able to achieve our ultimate goal—electric-field control of ferromagnetism.[9]

The mechanism underlying the interfacial magnetic coupling between ferromagnets and antiferromagnets is far from well understood; electric-field control of magnetism provides an additional parameter for studying the basic physics of the phenomenon. A group led by Agnès Barthélémy at Université Paris–Sud in Orsay, France, is doing particularly important work in that direction and, in the process, revealing a multitude of open research questions: How does the interfacial coupling depend on the nature of the ferromagnetism? What are the critical parameters that control the strength and stability of the coupling? And does orbital physics play a role? Details aside, the importance of interfaces in mediating magnetoelectric coupling and enabling the production of multiferroics-based devices is clear.

## The future lies at the interfaces

By far the most exciting recent developments in the field, and the areas in which we see the most promise for future discoveries, are in interfacial phenomena. Interfaces can be categorized into two broad classes: those that emerge spontaneously, such as domain walls in ferroics, and those that are artificially engineered, for example, by growing multilayers of different materials in coherent heterostructures, a technique known as heteroepitaxy.

**Domain-wall phenomena.** One consequence of the large structural anisotropy inherent in ferroelectrics is that their domain walls are narrow, typically just a few nanometers wide or less (see figures 3c–e). (For comparison, domain walls in conventional ferromagnets are typically around 100 nm wide.) Largely by chance, we found that certain orientations—109° and 180°—of domain walls in $BiFeO_3$ are electrically conducting.[10] Such walls could potentially act as highly miniaturized information channels. While our first-principles calculations are consistent with the observed behavior, a full explanation is still lacking and many questions remain: What happens to the magnetic order and electronic structure at such an interface? Is the conductivity a consequence of the multiferroic or correlated electron behavior, and should it be a universal feature of multiferroics? Perhaps most importantly, can we control the electronic behavior so as to tune between insulating and metallic behavior at the domain wall?

Similarly fortuitous was the discovery of a new topological defect we call a multiferroic vortex—a cloverleaf-shaped swirl of ferroelectric domains, each opposed by its structural antiphase (see figure 4).[11] Vortex–antivortex pairs, which are topologically protected and cannot annihilate, lead to intriguing patterns (see Back Scatter, page 96), and are likely to form a focus of much future research.

**Heteroepitaxy-generated phenomena.** A mismatch in the lattice constants of a thin-film material and its substrate can induce large strains and novel multiferroic phenomena. Our first-principles calculations indicate that when subjected to a biaxial (100) compressive strain of around 4.5%, $BiFeO_3$ transitions to a phase with a strikingly different structure and larger polarization than the unstrained material. That phase is indeed observed in coherent epitaxial films grown on yttrium aluminate, which has a suitably small lattice constant compared with $BiFeO_3$. Intriguingly, in samples grown on a $LaAlO_3$ substrate, which has an exactly 4.5% lattice-constant

mismatch with $BiFeO_3$, the two structural phases coexist, separated by a smooth, dislocation-free boundary.[12] That continuity at the interface is remarkable, since the two phases have drastically different structures and polarization orientations, although the same symmetry. As a result, the position of the boundary can be controlled with an electric field. Though our studies of the magnetic behavior of the interface are ongoing, early indications suggest a possible net magnetization, which could provide an alternative route to electric-field control of magnetism.

Another route to magnetoelectric coupling involves the use of two or more different materials to create interfaces that have different properties from the parent phases. Adopting that approach, a team led by Yoshinori Tokura of the University of Tokyo exploited the reduction in symmetry associated with an interface to permit polarization and magnetoelectric response where it would otherwise be symmetry-prohibited.

In the past several years, many studies have produced evidence of electronic reconstructions at oxide–oxide interfaces (see PHYSICS TODAY, June 2007, page 23), which can be particularly intriguing if one of the layers is highly polar or polarizable. For example, one recent study found electric-field-controllable ferromagnetism at the interface between $BiFeO_3$ and lanthanum strontium manganite ($La_{1-x}Sr_xMnO_3$), as well as a shift in hysteresis behavior (see figure 3f). For a more comprehensive review of thin-film heteroepitaxy and multiferroics, see reference 13. Of particular interest for future research is the exciting possibility of tuning not only the spin and charge ordering at the interface but also the orbital degree of freedom. Stay tuned for more exciting developments in that direction.

## Toward applications

The past decade has witnessed dramatic progress in the fundamental physics of multiferroics and magnetoelectrics. The initial driver from a technology perspective was the potential to control and manipulate ferromagnetism with electric fields. That remains an important focus and could have tremendous impact in areas as diverse as information storage, sensing and actuation, and spintronics, where electric-field control of magnetic spins would consume significantly less power than magnetic-field control, which requires electric currents to generate the magnetic fields (see the article by Jagadeesh Moodera, Guo-Xing Miao, and Tiffany Santos, PHYSICS TODAY, April 2010, page 46). The challenge—and opportunity—for solid-state physicists is to identify mechanisms that provide large, robust, and coupled magnetization and polarization, combined with large susceptibilities at low electric or magnetic fields, all at room temperature. Though there are occasional reports of single-phase room-temperature multiferroics in the literature and on the conference circuit, reproducibility still seems as elusive as for the reports of room-temperature superconductors.

Still, multiferroics continue to reveal novel, unanticipated physics, and the potential applications now stretch far beyond electrical control of ferromagnetism. The recent discoveries of domain-wall-associated functionalities—such as electrical conduction, magnetotransport, and vortex formation—suggest the possibility of electrically controllable nanoscale storage or logic elements. The electrical control of resonances in multiferroic heterostructures has already led to prototypes of electrically controlled microwave devices; the antiferromagnetic resonance frequencies in the orthoferrites (the parent compounds of $BiFeO_3$) are in the hundreds of gigahertz range, suggesting the possibility of electric-field control at up to terahertz frequencies, an area that is essentially unexplored. Extending the range of addressable order

parameters to include orbital ordering, chirality, and toroidal or higher-order multipolar orderings, and identifying their associated conjugate fields, will further increase the palette of parameters for tuning, coupling, and controlling functionalities. We hope that the recent progress on the basic materials physics aspects will stimulate the physics community to dream up entirely new device paradigms that exploit the novel and unique functionalities of multiferroics.

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