Electric Field Control of Magnetism Using Multiferroic Bismuth Ferrite

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Abstract
This article presents a review of some salient aspects of a broad class of functional materials, namely complex oxides. These materials, exemplified by the rare earth manganites, superconducting cuprates and more recently multiferroics such as bismuth ferrite, are characterized by a complex crystal chemistry, that is central to competing/cooperating spin, charge, orbital and lattice degrees of freedom. In addition to this, a fundamental defining feature of such materials is the complex nanoscale phase coexistence that appears to be central to the appearance of large responses. The emergence of pulsed laser deposition as a tool to create artificially engineered heterostructures has provided researchers with a powerful approach to create new states of matter at such heterointerfaces. This combined with modern x-ray, electron, neutron and proximal probes (such as conducting AFM, piezoresponse SPM, etc) and ab initio theoretical studies has provided us with deep insight into the various physical phenomena that manifest themselves in such materials.

Key Words: Multiferroics, Complex oxides, Electric field control of magnetism

I. INTRODUCTION
During the past couple of decades, complex oxides have attracted intense research interest especially from the condensed matter physics and materials science communities. They present a broad range of interesting functionalities, such as high temperature superconductivity, colossal magnetoresistance, (anti-) ferromagnetic, (anti-) ferroelectric, piezoelectric and more recently multiferroic properties. The rich spectrum of materials physics involved has triggered extensive studies to understand the fundamental nature of existing systems, so as to control/design novel materials for applications. These materials are characterized by a strong interplay between the fundamental degrees of freedom, namely the electronic spin, charge, orbital and their interplay with the lattice, Fig.1. New states of matter have emerged as a consequence of competition/cooperation between these degrees of freedom. Second, nanoscale complexity, driven by chemical/ionic/electronic inhomogeneities is a key feature that underpins large physical responses (for example, piezoelectric/dielectric responses in relaxors, colossal magnetoresistance in doped manganites, high temperature superconductivity in cuprates).

Finally, the use of state-of-the-art thin film deposition tools (such as RHEED assisted pulsed laser deposition (also known as laser MBE), conventional MBE and chemical vapor deposition) has driven the synthesis of atomically sharp, artificial heterostructures that have exhibited novel physical phenomena, especially at the heterointerfaces.

The interplay between the dielectric and magnetic responses in materials is a fascinating and rich playground in condensed matter. By itself these responses are not unusual; indeed, even a spontaneous order parameter (broken time reversal symmetry leading to a spontaneous magnetization in a

Fig. 1 (a) A schematic of the ABO$_3$ perovskite crystal structure, with the electronic structure of the 3d transition metal ion shown on the right side; (b) the left side is a schematic illustration of a prototypical epitaxial oxide interface, wherein the fundamental degrees of freedom interact leading to new states of matter.
ferromagnet, broken spatial inversion symmetry leading to a spontaneous dielectric polarization in a piezoelectric/ferroelectric) is quite common in many materials. However, a rather limited set of materials exhibit multiple order parameters, or multiferroicity (for example, ferromagnetism and ferroelectricity, or antipolar derivatives thereof), Fig. 2(a). A key reason for this limited set is of course the fact that these two order parameters are “contra-indicating”, i.e., they have exactly the opposite requirements in terms of the electronic structure. Typically, ferromagnetism (especially in metallic systems) arises as a consequence of exchange interactions and requires the kinetic energy of the electron to be dominant; on the other hand, stabilization of a spontaneous dielectric polarization requires a perfectly insulating state. Thus, it should be no surprise that there are not too many such examples. Indeed, it is much easier to find materials that are ferromagnetic and also have a spontaneous strain order parameter (for example, shape memory alloys). Consequently, many multiferroics typically exhibit ferroelectricity in conjunction with antiferromagnetism, as exemplified by several model systems. Finally, if there is coupling between the magnetic and dielectric degrees of freedom, then such materials are termed magnetoelectrics.

BiFeO$_3$ (BFO) is the only room temperature multiferroic (antiferromagnetic and ferroelectric) so far, which has attracted great interest and extensive investigation in the past decade, Fig.2(b,c). It has a rhombohedral unit cell, built with two distorted perovskite cells connected along a pseudocubic [111] direction [1,2]. It is also a G-type antiferromagnet with a Neél temperature of $\sim$ 673 K [100] and a symmetry-allowed, small canted moment due to the Dzyaloshinskii-Moriya interaction [2,3]. The hybridization between the two 6s electrons in Bi [4] with surrounding oxygen ions leads to a large displacement of the Bi cations relative to the oxygen octahedra along the [111] direction with a Curie temperature of 1103 K and a spontaneous ferroelectric polarization of about 90 $\mu$C/cm$^2$ [5].

II. ELECTRIC FIELD CONTROL OF MAGNETISM

By far, the most exciting aspect of work on multiferroics is the potential to control magnetism (AFM or FM) with an electric field. While this is of fundamental importance (i.e., how does one couple an axial vector to a polar vector with high efficiency?) the potential technological implications are equally tantalizing. Specifically, if one is able to switch ferromagnetism with an electric field in a robust and repeatable fashion, the potential to create information storage and communication devices that consume much less energy compared to devices driven by electric currents. Thus, the first step is to ask the question: is there coupling between ferroelectricity and antiferromagnetism? The simplest of possibilities would be the one in which the ferroelectric polarization is switched by 180$^\circ$ and this leads to a corresponding
rotation of the antiferromagnetic vector, L. However, this does not appear to be the case, at least from a theoretical perspective [6]. On the other hand, ferroelastic rotations of the polarization vector, for example through a 71° or 109° switching process does indeed change the AFM vector direction in thin films [7]. This has also been confirmed by neutron scattering studies in single crystals [8]. It is interesting to note that recent work has demonstrated the electric field manipulation of antiferromagnetic electromagnons in this system [9]. Thus, although electric field control of the AFM state is now well established, the inability of the AFM state to be sensed by the external world, unlike ferromagnetism, is an impediment. Therefore, a significant focus in recent years has been on exchange coupled FM-AFM heterostructures.

Two types of ferromagnets can be envisioned. The first is a conventional ferromagnet, such as CoFe (or other such metallic ferromagnets). A significant amount of exchange coupling studies between such ferromagnets and multiferroics have already been carried out in previous work. Magnetic coupling, manifested as a combination of a directional, exchange bias as well as an enhancement of the coercive field has now been well established. An interesting aspect of the interfacial coupling is the role of domain walls in influencing the coupling mechanism; for example, samples with a high density of 109° domain walls invariably show a strong exchange bias, suggesting that the uncompensated moments at the domain walls are likely to be possible sources for exchange bias. More recent work using a combination of element specific xray spectromicroscopy, magnetotransport and scanning electron microscopy polarization analysis has demonstrated the direct coupling between the canted moment in a domain and the moment in the CoFe ferromagnet [10,11].

Angle-dependent magnetic measurements clearly show that the externally applied magnetic field is not the most important parameter; instead, the internal coupling between the canted moment in the BFO and the ferromagnetic moment in the CoFe appears to be more important, Fig.3(a). This coupling is also evident from direct PEEM imaging of the CoFe layer, Fig.3(b). There is a direct, one-to-one correlation of the ferroelectric domains (shown on top) and the magnetic “domains” in the ferromagnet (shown at the bottom). Such a correlation is useful in establishing the notion that the ferromagnetic moment in the CoFe layer is coupling to the canted moment in the BFO layer (which, incidentally projects normal to the domain long axis). Having established the coupling, many critical questions remain to be answered. For example, how robust is this interfacial coupling, particularly with respect to repeated switching of the ferroelectric?

Fig. 3 (a) Angle dependent ferromagnetic hysteresis loops for a 2.4nm CoFe layer deposited on an epitaxial BFO thin film; the easy axis of the CoFe layer is along the in-plane projection of the canted moment of the BFO; (b) the top panel is the piezoforce microscopy (PFM) image of the BFO layer showing the set of 2 domains in which the polarization vector is rotated by 71°; the corresponding XMCD-PEEM image is in the bottom panel and shows that the magnetic domain structure of the CoFe layer is directly aligned with that of the BFO layer.

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In the case of heterostructures involving oxide ferromagnets such as La-Sr-Mn-O, we observe several fascinating interfacial phenomena that are driven by spin, charge and orbital reconstructions at the interface. At such epitaxial interfaces, all the degrees of freedom, namely the spin, charge, orbital and lattice degrees are likely to be active, especially in materials such as BFO, as illustrated in Fig.1&4. Since recent reviews have already dealt with the possible origins of the magnetic coupling and the electric field control of this magnetic coupling [12], the reader is requested to refer to them to explore these topics. Most interestingly, an enhanced magnetic moment in the BFO layer is observed right at the interface, and is one of the key indicators that the charge, spin and orbital structure at such interfaces can be quite different from the bulk. Similar enhancements of the magnetic moment in BFO have also been observed in BFO/LSMO superlattices [13]. Of interest as well is the recent proposal of a suppression in the oxygen octahedral tilt at the BFO/LSMO interface [14]. These results, coupled with the observation of magnetism and magnetotransport at domain walls, strongly indicate that interfaces do indeed have significantly different magnetic behavior.

III. FUTURE DIRECTIONS

Where are we going? On the basic science of oxide interfaces, a lot remains to be understood. The ability to heteroepitaxially engineer interfaces with almost atomic perfection is the key to opening up new directions in exploring electronic structure, phase equilibrium and the interplay between the fundamental degrees of freedom, as illustrated in Fig.1. In the current reincarnation, we have seen almost ten years of basic science on multiferroics and magnetoelectrics and have learnt a huge amount about the intricacies of such coupled phenomena, especially in complex systems such as BFO. It is also clear that these fundamental discoveries need to be translated into meaningful technologies. Thus, it is critical that applied programs be initiated and funded to make progress towards useful technologies. Within the US,
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Motors in which multiferroics and magnetoelectrics will play a key role. Stay tuned for progress reports from TANMS. DARPA has also initiated programs on multiferroics and magnetoelectrics, albeit on a smaller scale. Other agencies, such as the Semiconductor Research Corporation (SRC) have also initiated R&D activities leading to devices based on multiferroics, primarily focused on electric field control of magnetism. So, the next few years should be quite promising in terms of possible device manifestations of multiferroics and magnetoelectrics.

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