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Electric Field Control of Magnetism

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Summary: Electric field control of magnetism is an extremely exciting area of research, from both a fundamental science and an applications perspective and has the potential to revolutionize the world of computing. To realize this will require numerous further innovations, both in the fundamental science arena as well as translating these scientific discoveries into real applications. Thus, this article will attempt to bridge the gap between condensed-matter physics and the actual manifestations of the physical concepts into applications. We have attempted to paint a broad-stroke picture of the field, from the macroscale all the way down to the fundamentals of spin-orbit coupling that is a key enabler of the physics discussed. We hope it will help spur more translational research within the broad materials physics community. Needless to say, this article is written on behalf of a large number of colleagues, collaborators, and researchers in the field of complex oxides as well as current and former students and postdocs who continue to pursue cutting-edge research in this field.

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I.Introduction: The macro-systems perspective for this article is based on the field of information technologies, writ large. Microelectronics components and systems form an ever-increasing backbone of our society, pervading many parts of our daily life, for example through a host of consumer electronics systems, providing sensing, actuation, communication, and processing and storage of information. All of these are built upon an approximately $470B/year global market that is growing at a pace of 10-15% annually[1,2]. Many of them likely started as materials physics research ideas, often first discussed within the confines of physics and materials conferences worldwide. A few emerging global phenomena will likely completely change this microelectronics landscape. The first among them is the "Internet of Things" (IoT), which is the network of physical devices, transportation systems, appliances, and other items embedded with electronics for sensing/actuating, computing, storage and communications functions.[3], illustrated in **Fig. 1**. As an example, a modern automobile has a large number of sensing, communicating and computing components embedded and this is only going to increase; for example, the emergence of autonomous vehicles will require orders of magnitude higher levels of computing and energy efficiency of computing.

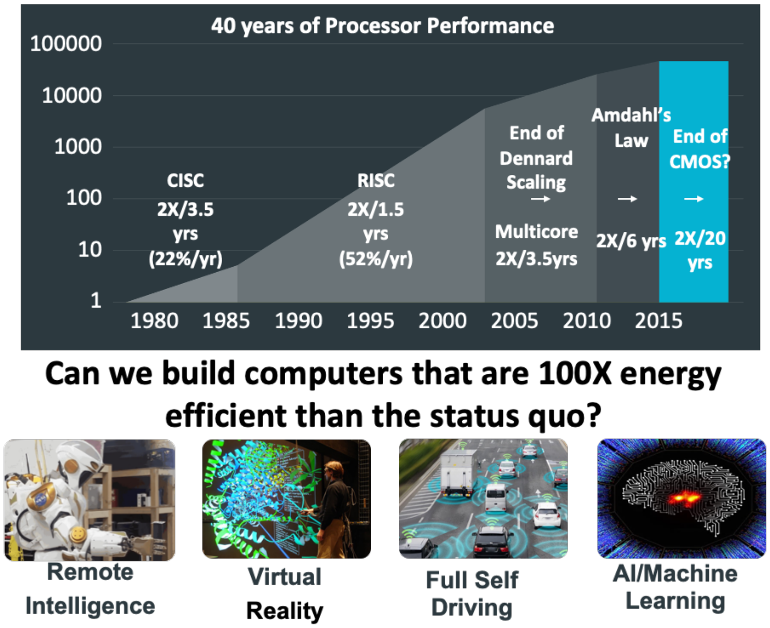
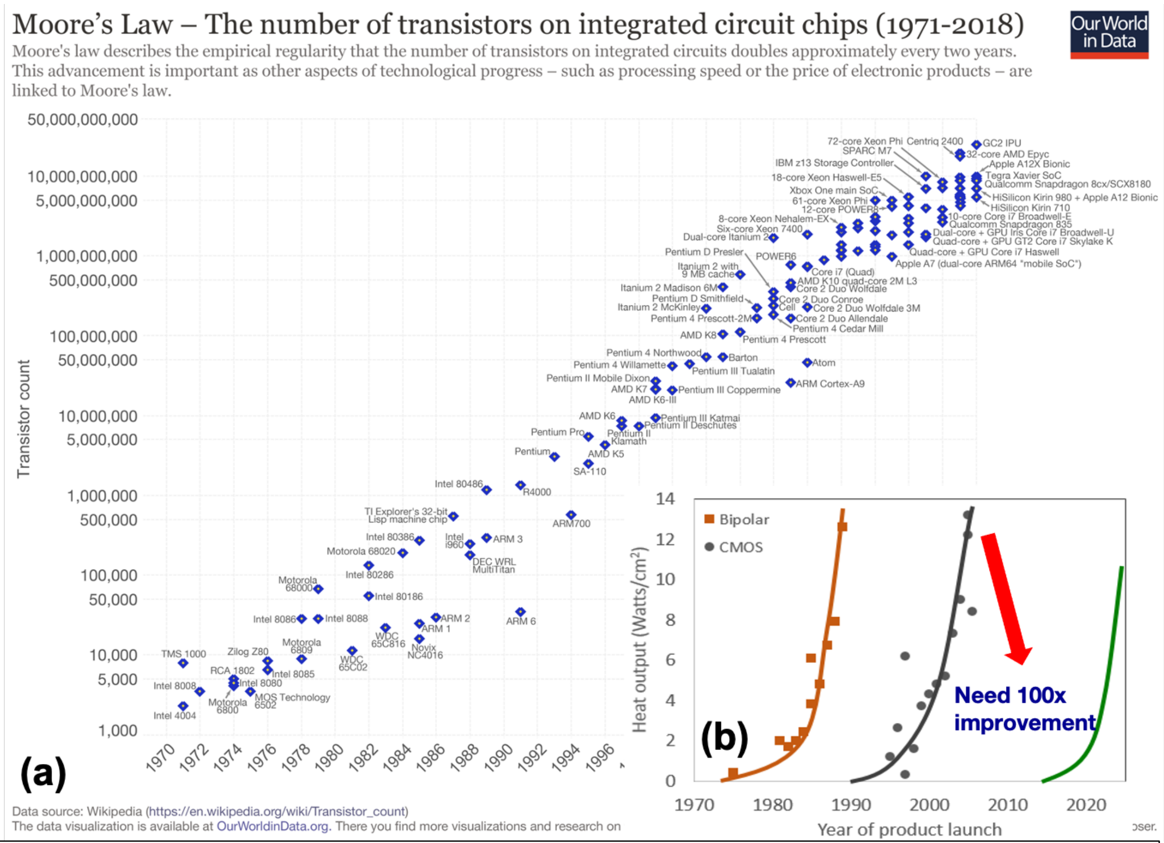


Fig.1:A schematic illustrating the emergence of the "Internet of Things" and Machine Learning/ Artificial Intelligence as macroscale drivers for the Beyond Moore's Law R&D. Describes the leveling off the various scaling laws as a function of time, leading to the end of Moore's Law.

The second major phenomenon is the emergence of machine learning (ML) / artificial intelligence (AI), that is taking the technology world by storm. It uses a large amount of computing and data analytics which, in turn, provides the system the ability to "learn" and do things better. Of relevance to us is the fact that microelectronic components are critical underpinnings for this field.

We can now ask the question: how do these macroscale phenomena relate to microelectronics and, more importantly, to new materials and physics underpinning them? Stated differently, what can *materials physics* do to enable this coming paradigm shift? To put this into perspective, we now need to look at the fundamental techno-economic framework that has been driving the microelectronic field for more than five decades. This is the well-known "Moore's Law" [4], the techno-economic principle that has so far underpinned the field of microelectronics through the scaling of CMOS-based transistors (**Fig. 2**). Broadly, it states that the critical dimensions of



Data source: Wikipedia (https://en.wikipedia.org/wiki/Transistor_count)
The data visualization is available at OurWorldinData.org. There you find more visualizations and research on

Figure 2: (a)captures the evolution of semiconductor electronics, illustrating Moore's Law, which is the doubling of the number of transistors in a chip every ~18-24 months, vs. year of implementation (source: Wikipedia); (b) is a plot of heat output from microprocessors as a function of time for two generations of electronics, Bipolar and CMOS. Every ~20 years, this has led to a new paradigm of computing requiring an ~100X improvement in computing efficiency. The GREEN plot is a projection of the heat output vs. time for a future computing paradigm, which is at least 100X more energy efficient compared to CMOS.

the CMOS transistor shrink by 50% every 18-24 months. At their inception, CMOS transistors were "macroscopic" with the critical dimension well over 1 μm and Dennard scaling provided a path to shrinking such transistors, while keeping the power density constant[5,67]. Today, this power scaling is not as easy while the critical dimensions of modern transistors are rapidly approaching sub-10 nm scales, the point at which both the fundamental science (*i.e.*, classical electron dynamics) is no longer sufficient to adequately describe the physics of the transistor and ever more complex manufacturing issues have to be addressed. Therefore, in the past 5-8 years, there has been an ever-increasing sense that something has to be done about this issue[8,9,10,11,12].

One can approach pathways to address this impending crisis in many ways. In some sense, this is a matter of perspective: circuit design engineers may prefer to go to specialized architectures[13] or go away from the conventional Boolean or von Neumann architecture into a Neuromorphic architecture[1]. Another pathway could be to go away from highly deterministic computing (which tolerates errors at the scale of 1e-10 to 1e-12[1] to more of a stochastic computing[14]. The third way is the one which we will be espousing, which overtly involves "Quantum Materials", materials in which the quantum mechanical effects such as exchange interactions, spin-orbit coupling that directly lead to exotic physical phenomena (to start with magnetism,

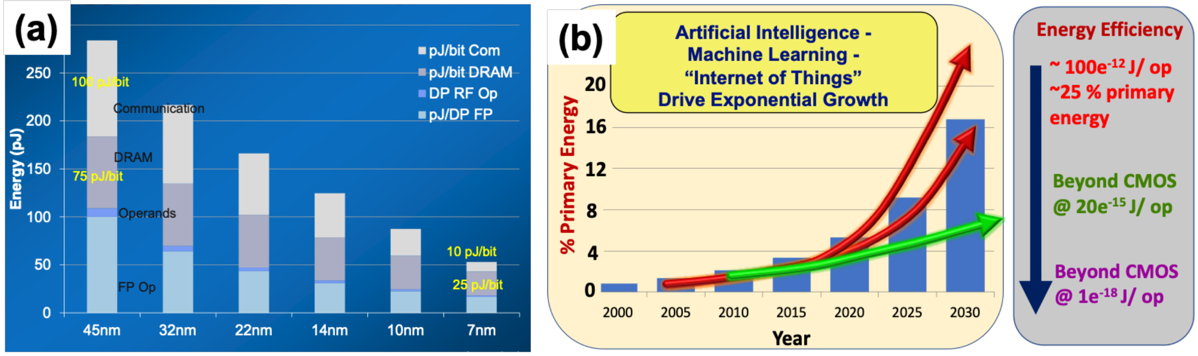


Fig.3: (a) Energy consumed per logic operation as a function of integration node as well as various components of the computing system (source Shekar Borkar & Intel); (b) Estimation of the total energy consumed in all of Microelectronics by 2030, if nothing is done to reduce the energy consumption/operation from the ~100pJ/operation level, while the number of microelectronic components is growing exponentially due to the emergence of the "Internet of Things" and Artificial Intelligence/Machine Learning (RED curves). A New Moore's Law at 20 femtoJoule/operation (GREEN curve) will enable us to keep the energy consumption at the ~8% level. Fundamental science is required to get to an attoJoule/operation energy scale.

ferroelectricity, multiferroic behavior, and more recently topological behavior arising from band topology). We get to this after a short description of another looming challenge, namely energy.

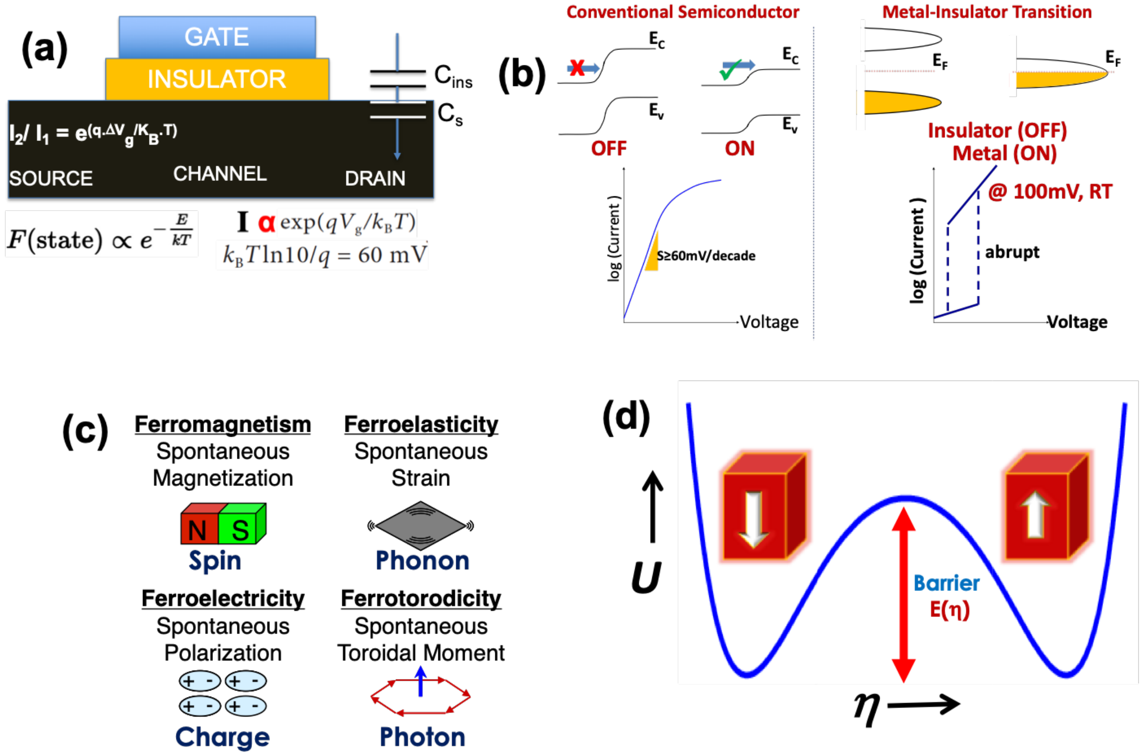


Figure 4: (a) schematically describes the Boltzmann distribution function for electrons in the CMOS channel, leading to the 60mV/decade of current as the limit, which is known as the "Boltzmann Tyranny", shown in (b) which also shows a possible manifestation of metal-insulator transition as the base for the next generation of logic; (c) describes the various fundamental order parameters in condensed matter systems and the external carrier of the order parameter; (d) schematically describes the ratio of the energy required to switch a ferroelectric element compared to the barrier height.

We can now introduce perhaps the single most important aspect into consideration, namely, **energy consumption** (**Fig. 3**). Of the many issues to address, energy consumption (or conversely energy efficiency of computing) has the potential to be the most impactful. The energy consumed per logic operation in today's CMOS transistor is of the order of 50-100 pJ/logic operation. If we assume that there is no change to this number in the near future, and at the same time the demand for microelectronic components in IoT and AI/ML is growing exponentially, the total energy consumption in all of microelectronics could grow to ~20-25% of primary energy by 2030[15]. At this scale, microelectronics would become a significant part of the worldwide energy consumption and thus deserves to be addressed from the energy efficiency perspective as well. Thus, these three global phenomena, form the backdrop for our discussion as we ask: **what can we do with the new materials physics**?

II. An Opportunity: We begin the exploration of new materials physics by going back to the fundamentals of CMOS devices, i.e., the behavior of an electron within the CMOS transistor which is governed by the Boltzmann distribution (**Fig. 4(a)**). A quick analysis shows that the current changes exponentially with voltage, with an ideal slope of 60 mV/decade of current[16], **Fig.4(b)**. This result is termed as the "Boltzmann Tyranny"[1,11] since the Boltzmann physics is imposed as a fundamental limit on the functioning of the device; in real transistors, this voltage slope can be larger[15]. This fundamental behavior is central to the performance of the transistor, both in terms of the minimum voltage that is required and the energy consumed in the process of operating the transistor. In recent years, there has been the realization that this Boltzmann Tyranny needs to be addressed – setting the stage for new materials and new phenomena. One proposed pathway is to use materials exhibiting a metal-to-insulator transition, such as in correlated-electron systems, Fig.4(b)[17,18]. Under ideal conditions, such a metal-to- insulator transition can be very abrupt. Another key realization[1] identifies the broad class of quantum materials as possible candidates to overcome this tyranny, mainly through the insertion of an additional, internal interaction energy into the Boltzmann distribution. A core guiding principle that a significant opportunity exists to enable highly energy efficient computing by exploiting correlated phenomena in materials and consequently lowering the operating voltage. Conventional CMOS has been built around non-interacting materials where the energy dissipation in such a transition is $Nk_BT\ln(2)$, where N is the number of constituent particles (*e.g.,* spin or charge). By contrast, correlated materials (ferromagnets, ferroelectrics, multiferroics, correlated-electron systems) provide a pathway to bring down this dissipation to only $k_BT\ln(2)$. For example, this could be the exchange interaction in a ferromagnet or the dipolar interaction in ferroelectrics. In its simplest form, such an interaction can be represented by an additional term in the Hamiltonian that represents the exchange interaction energy for a magnet given by: $E_{ex} = -J \cdot S_1 \cdot S_2$, where J is the exchange integral and S_1 and S_2 are the two neighboring spins (or the corresponding dipolar energy in the case of a ferroelectric). Depending on the sign of J, S_1 and S_2 are either parallel (ferromagnet) or antiparallel (antiferromagnet)[19]. This term then becomes the key component within the Boltzmann distribution and it modifies the energy landscape. That is, the exchange energy (or the dipolar energy in a ferroelectric) makes the spins (or the dipoles) align collectively *without the need* for an external source of energy (such as an applied field). Therefore, orders of magnitude improvement in energy efficiency are possible by exploiting correlations (electronic charge/spin and dipolar). Thus, if one could use a spontaneous magnetic/ dipole moment as the primary order parameter rather than electronic charge in a CMOS device, one could take advantage of such internal collective order to reduce the energy consumption. Indeed, this is the premise behind two recent research articles[1,11], where the rudiments of a possible magneto-electric spin orbit (MESO) coupled memory-logic device are discussed. While many parts of this device require further research innovation, one aspect that we will focus on, pertains to electric-field control of magnetism.

III. Electric-field Control of Magnetism – The Key Role of Energy Consumption:

We can begin this discussion with a question: why would one use an electric field to control magnetism, when it would rather be straightforward to use a magnetic field instead? The answer is energy. In fact, one can potentially reduce the energy consumption by a few orders of magnitude through the use of electric fields as opposed to magnetic fields. To illustrate this, we explore two possible scenarios. The first describes how a moving electron can create a spin torque, of interest in spin transfer torque (STT) based memory devices[20]. The key is that each electron carries a moment of 1 μ_B and therefore generating a large enough spin torque to switch the magnetization requires a large number of electrons (*i.e.*, a large current), which, in turn, requires an appropriate current source (*e.g.,* a battery). For a nominal device lateral dimension (*e.g.*, 10 x 10 nm) one can estimate the energy consumed (E_{STT} =

$I_{STT}.V_d.t_{STT}$) in this process, and it is of the order of a few fJ (10^{-15} J, **Fig. 5a**). Recent developments in using spin-orbit torques may very well supersede these, but that would require efficiencies orders higher than what is currently possible; thus requiring more fundamental physics innovations[1,11]. One can contrast this to a capacitive device, with an electric field modulating the charge, where for a similar 10 x 10 nm device with a dielectric constant of ~100 (which is reasonable for ferroelectrics), one can generate relatively large fields of the order of 10 kV/cm consuming just about an aJ of energy (10^{-18} J, (**Fig. 5b**), for a voltage of 100mV ($E = 1/2CV^2$). One could ask the converse question, namely, why not use a ferroelectric and thus use a spontaneous dipole as the order parameter? Indeed, this could be possible and attempts are underway to explore the possibility of using a ferroelectric as the medium for both logic and memory. The advantage with using the spin as the primary order parameter is that one can use the huge knowledge-base of spintronics and indeed carry out logic operations with spins [11].

In order to calibrate these observations, lets now look at the energy scales in magnetic and electric fields. As an extreme exemplar, we look at the manganites, which exhibit both colossal magnetoresistance as well as colossal electroresistance[17, 21], as

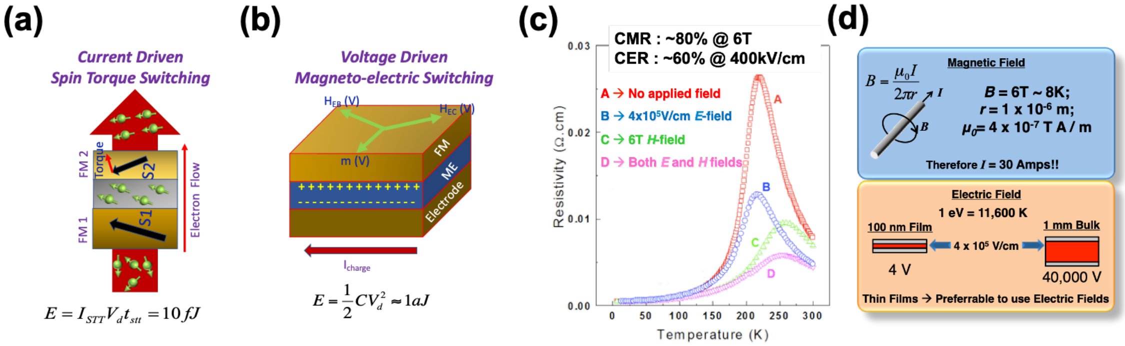


Figure 5: A set of schematics illustrating the energy consumption for nominal devices. (a) On the left is a current driven spin torque switching device and (b) is a voltage driven magnetoelectric switch in which FM is the ferromagnet, ME is the magnetoelectric, H_{EB}(V) is the voltage manipulated exchange bias, H_{EC}(V) is the voltage manipulated exchange coupling and m(V) is the voltage manipulated magnetic state in the ferromagnet; (c) presents the original data for the colossal magnetoresistance effect of ~80% at 6T and a ~60% colossal electro-resistance effect at an electric field of 400kV/cm; (d) presents a simple calculation of the current required to create a magnetic field of 6T at a distance of 1 micrometer from the center of the current-carrying wire while the bottom shows the calculation of the voltage required to create the 400kV/cm electric field. This voltage scales with the dimensions of the object, while the magnetic field does not scale with the dimensions of the object.

illustrated in **Fig.5(c)**. The colossal magnetoresistance is obtained with a magnetic field of 6T, while the corresponding colossal electroresistance is achieved with an electric field of 400kV/cm. We can now ask the question : what is required to create both these fields. Focusing first on the magnetic field, **Fig.5(d)**-top panel, shows that if a magnetic field of 6T is to be created at a distance of 1 micrometer from a wire carrying an electrical current (the classical way to create a magnetic field using Ampere's Law), that current would be of the order of ~30Amps. While this is a relatively small energy scale from a physics perspective, from an engineering or energy perspective, this current is significant. It is also noteworthy, that this magnetic field is the same (i.e., 6T) whether the sample is a mm-sized crystal or a 100nm thick film. In contrast, if we look at the electric field driven colossal electro-resistance at a field of 400kV/cm: this corresponds to an applied voltage of 4V across a 100nm thick film; if it becomes a 1mm size crystal, the voltage required is 40,000V. A second, key learning from this is that if one is dealing with thin films and nanostructures, where the physical length scales are small, electric fields (and thus voltages) are more useful from a technological perspective. Thus, this figure is perhaps one of the key learnings (at least from our perspective): namely, voltage (*i.e.,* electric field) is a much more energy efficient pathway to manipulate states, if the physics of that state allows one to do so. For the same reason, one has to be aware of the fundamental differences between the various symmetries in solids (in terms of whether they break time reversal or spatial inversion symmetry). Finally, and perhaps more importantly, regarding this article and the work on electric field control of magnetism, it is important to ensure that physical phenomena exist that will enable us to manipulate the magnetic state with an electric field. The existence of magnetoelectricity and coupled multiferroic order does provide us with such a pathway.

With this as background, let us now explore the physics of electric-field control of magnetism with a focus on multiferroic and magnetoelectric materials. Needless to say, the pace and breadth of the work in this field means that it will be impossible to cover all the developments. Furthermore, this article is also somewhat of a personal perspective of the field; therefore, the reader is requested to look at a number of excellent recent reviews[22,23] on this subject for in-depth information on other aspects of such approaches. Particularly, ref.22 outlines several possible pathways for manipulation of magnetism (carrier modulation, strain effect, exchange coupling, orbital reconstruction, and electrochemical effects), all of which play some complementary role in some of the discussion on magnetoelectric coupling in La-substituted $BiFeO_3$ that follows. Therefore, instead of reproducing that in our review, here we review progress in the fundamental understanding and design of new multiferroic materials, advances in characterization and modeling tools to describe them, and explore devices and applications. We identify the key open questions in the field where targeted research activities could have maximum impact in transitioning scientific discoveries into real applications.

IV. Multiferroics and Magnetoelectrics: Multiferroics exhibit more than one primary ferroic ordering (*i.e.*, ferromagnetism, ferroelectricity, ferroelasticity, or ferrotoroidicity) in the same phase[24]. The terminology is usually extended to include other types of order such as antiferromagnetism as well as composites of individual ferroics and is most often used to refer specifically to magnetoelectric[25] materials combining ferroelectric and magnetic behavior in a single material. The co-existence of ferroic orders can lead to coupling between them, so that one ferroic property can be manipulated with the conjugate field of the other[26,27]. A good example of a multiferroic is the case of ferromagnetic shape memory alloys (FSMA), which exhibit ferromagnetism along with a spontaneous strain[28]. Similarly, piezoelectrics combine a spontaneous strain along with a spontaneous polarization. There are numerous examples of both FSMA and piezoelectrics. In contrast, the coexistence of spin and charge order (particularly ferromagnetism and ferroelectricity) is challenging, since ferroelectricity requires an insulator while typical ferromagnets require electronic exchange interactions[29]. Many insulating magnets are either antiferromagnets or ferrimagnets (driven by super-exchange interaction). This requires understanding the electronic structure at the most fundamental level, new materials chemistries to implement them, the development of new tools to compute and characterize the novel properties associated with the coupled behaviors in parallel with new approaches to synthesize such materials with atomic-scale precision. When this is successful, it presents possible routes to entirely new device architectures, as exemplified by the MESO[10] device. The field of multiferroics is now vast, we would direct the reader to other recent reviews with different emphases.[30,31,32,33,34]

V. Pathways to Design Multiferroic and Magnetoelectric Materials. There are now many established routes to circumvent the "contra-indication" between ferroelectricity (typically associated with ionic species with empty *d*-orbitals) and magnetism (typically associated with partially filled *d* orbitals)[26]. Such a "bottom-up" design can be described by a "multiferroic-tree" in **Fig. 6**[23]. Although there are several known multiferroics, there is still a dearth of technologically viable multiferroics, *i.e.*, those that can be manipulated at room temperature and exhibit strong coupling between the spin and charge degrees of freedom. Thus, there should be no doubt that a more diverse palette of new materials with robust room-temperature coupling of magnetism and ferroelectricity is still urgently needed and indeed should be the focus of interdisciplinary research. **Table 1** provides a summary of the top five physical principles that have led to the discovery of several multiferroics. Of these, the two

Pathway	Fundamental Mechanism	Example Systems
A-site driven	Stereochemical activity of lone pairs on A-site leads to ferroelectricity; magnetism from B-site	$BiFeO_3$; $BiMnO_3$
Geometrically Driven	Long range dipole-dipole interactions and oxygen rotations breaks inversion symmetry	$YMnO_3$; $BaNiF_4$, $LuFeO_3$
Charge ordering	Non-centrosymmetric charge ordering leads to ferroelectricity in magnetic materials (e.g., Vervey transition)	$LuFe_2O_4$
Magnetic Ordering	Ferroelectricity induced by a lower symmetry ground state that breaks inversion symmetry	$TbMnO_3$; $DyMnO_3$
Atomically Designed Superlattices	Still under investigation; likely lattice mediated	$LuFeO_3$ – $LuFe_2O_4$
Vertical Epitaxial Nanocomposites	Coupling mediated by 3-D interfacial epitaxy, e.g., Spinel-Perovskite	$CoFe_2O_4$-$BiFeO_3$ $NiFe_2O_4$-$BiFeO_3$ $CoFe_2O_4$-$BaTiO_3$

Table I: This table complements Figure 7. It summarizes the various identified mechanisms for creating multiferroics and magnetoelectrics.

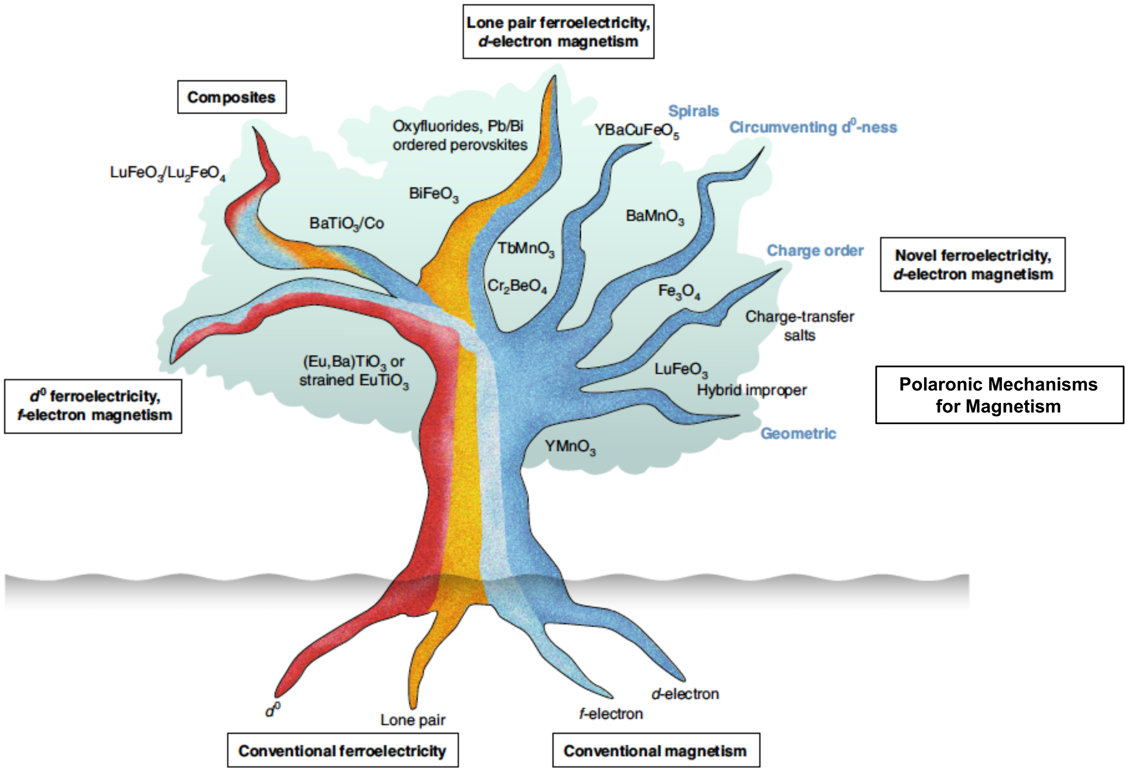


Figure 6: The "Multiferroic Tree" that depicts how one can design multiferroics from the basic elements of bringing together magnetic species (for example, ions with f/d-electrons) and polar species (i.e., chemical species that lead to the emergence of a spontaneous polarization). Each branch depicts exemplar multiferroic systems; the boxes on the outside identify the dominant mechanism responsible for the formation of multiferroics.[23]

most studied are multiferroics in which the polar order comes from one of the crystal sites and the magnetic order is built into the other chemical site, as is the case, for example, in $BiFeO_3$ and $BiMnO_3$. The second type, which has received considerable interest from the physics community, is based on a polar order emerging as a consequence of a magnetic transition as, for example, in the manganites[35]. An emerging third pathway is *via* the power of heteroepitaxy and superlattice design[36]. In this regard, although there were numerous attempts in the past to synthesize complex crystal symmetries to induce multiferroic behavior, this has not been extensively revisited in recent years. There appears to be a significant opportunity to "design" multiferroic behavior by selecting magnetic materials with low symmetry and then induce inversion symmetry breaking through heteroepitaxy. We will use these as examples to explore both the fundamental materials physics of coupling as well as the potential for future applications. We will revisit this issue of new materials discovery in the last segment of this article.

Of the known multiferroics, bismuth ferrite, $BiFeO_3$(BFO) remains arguably the most important, and certainly the most widely studied, with more than 6000 papers published over the last decade. The establishment of its large (~90 μC/cm^2) ferroelectric polarization, combined with magnetic ordering persisting well above room temperature[37] has spawned an intense research effort that continues to unveil fascinating new physics and potential new applications[38].

$BiFeO_3$ formally belongs to the perovskite family of oxides, albeit highly rhombohedrally distorted from the cubic prototypical structure in which the spontaneous polarization points along the eight equivalent <111> directions(**Fig. 7**). While there was considerable debate in the early days regarding the magnitude of the spontaneous polarization (which was experimentally measured in epitaxial thin films to be ~90 μC/cm^2 and confirmed theoretically[39]), it is now well established. In parallel with the scientific debate on the ferroelectric properties, there was an equal degree of debate as to the state of magnetism, particularly since it is complicated not only by the fundamental spin-orbit coupling physics but also from domain walls, that exhibit enhanced magnetic moments. Although the ground state is a robust G-type antiferromagnetic structure (which can be described by spins in {111} that are ferromagnetically coupled in-plane but antiferromagnetically coupled out of plane along the [111]), the magnetic structure is quite a bit more sophisticated. As a

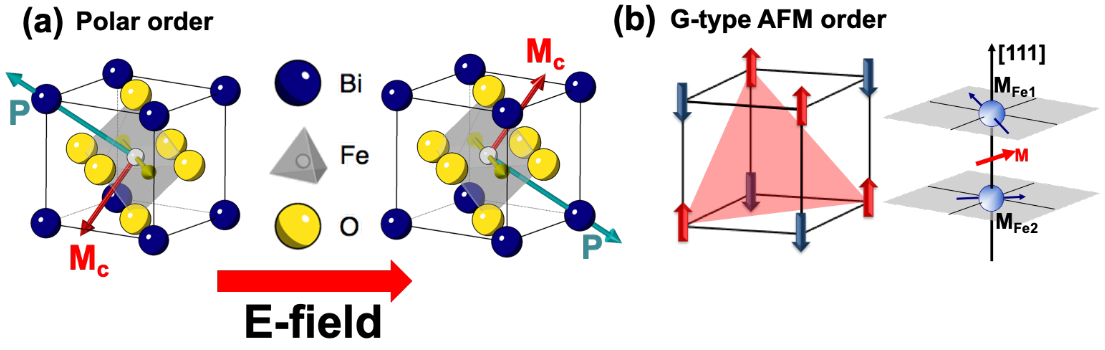


Figure 7: (a) A schematic illustration of the rhombohedral crystal structure of $BiFeO_3$ as well as the 180° switching of the polar axis and the associated changes in the canted moment direction ; (b) the G-type antiferromagnetic order and the canted moment arising as a consequence of the Dzyalozhinski-Moriya coupling.

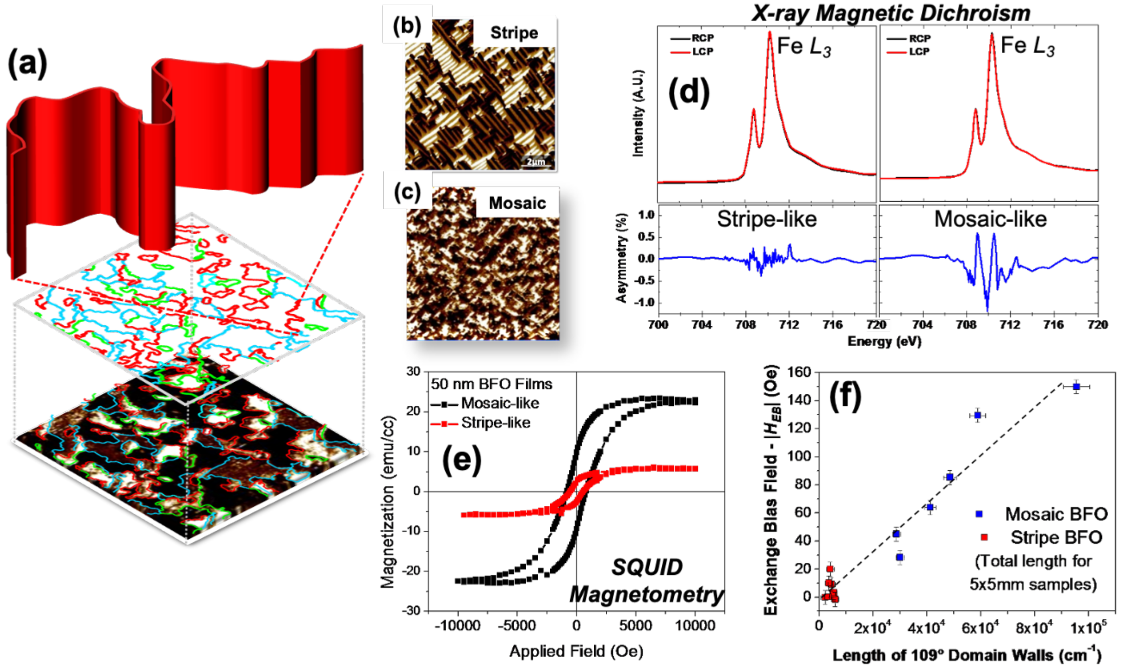


Figure 8: (a) shows an in-plane piezoforce microscopy image (bottom) of a $BiFeO_3$ (BFO) thin film with a large density of 109° and 180° domain walls as illustrated by the detailed analysis (middle); a magnified schematic of the tortuous nature of the 109° wall is shown on top; (b) an in-plane piezoforce microscopy image of a BFO layer grown at a low deposition rate on a $SrTiO_3$ substrate showing two orthogonal sets of 71° domains; (c) when the same film is deposited at a faster rate, the domain structure progressively takes on a mosaic-like structure, as also shown in (a); (d) shows xray absorption spectra (XAS) and magnetic circular dichroism (XMCD) for the stripe like and mosaic-like domain patterns which show measurably different XMCD, indicating the role of 109° domain walls in enhancing the magnetic response of the film, as also revealed by magnetic measurements shown in (e); (f) plots the exchange bias field, H_{EB} of the BFO layer with a CoFe layer deposited on top, showing the systematic increase in the H_{EB} with the density of 109° domain walls. These results point to the existence of pinned uncompensated spins at the 109° domain walls.

consequence of the antisymmetric Dzyalozhinski-Moriya coupling (which is symmetry allowed for the *R*3*c* crystal symmetry), a small canted moment arises, which lies in the {111} (*i.e.*, perpendicular to the spontaneous polarization direction). In single crystals, this canted moment spirals about the [1-10] so that it does not exhibit a macroscopically measurable magnetic moment until this spin spiral is broken, either by elastic strain (for example through epitaxial thin-film growth) or through the application of a magnetic field of ~16-18 T[40]. Ferroelectric domain walls can play a key role in the emergence of a magnetic moment, which typically manifests in the form of a spin glass[41] described in Figure 8. The underlying ferroelectric domain structure can be manipulated through the deposition rate to form well-ordered stripe domains (at low deposition rates) and a more mosaic-like domain structure at high deposition rates, Fig.8(a-c). The mosaic-like domain structure incorporates a high density of 109° domain walls, which exhibit spin frustration and an enhanced magnetic moment. As a consequence of this, BFO films with such a domain structure also couple strongly to a ferromagnet, leading to an enhanced exchange bias arising from the pinned uncompensated spins at the domain walls, Figure 9(d-f). Subsequent to this original work, some systematic studies to create ordered arrays of 71° and 109° walls[42] led to a better resolution of the role of pinned uncompensated spins at such domain walls leading to an exchange bias coupling to a ferromagnet. This is illustrated in Figure 9.

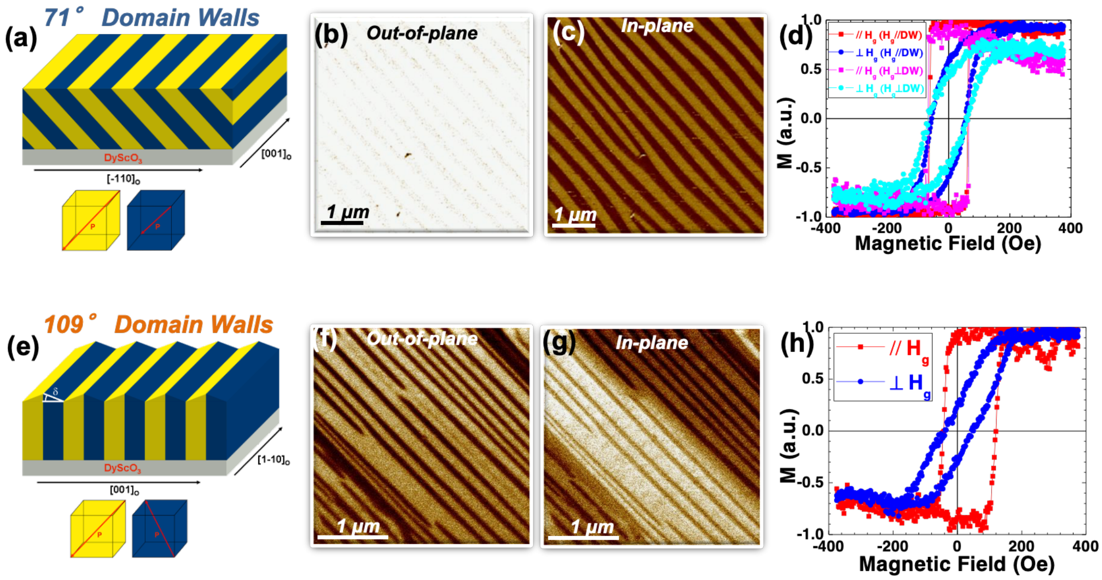


Figure 9: (a) a schematic of ordered arrays of 71° domain walls in the $BiFeO_3$ layer, which can be created through epitaxial growth on a $DyScO_3$ substrate with a thin (~5-10nm) of $SrRuO_3$ as the bottom electrode, as shown by the piezoforce microscopy (PFM) images in (b,c); (d) shows magnetization(M)-magnetic field(H) loops for a 2nm CoFe layer deposited on such a 71° domain wall array, both parallel and perpendicular to the direction in which the magnetic field (200Oe) was applied during growth; (e) is a schematic of an array of 109° domain walls in the BFO layer which is grown without the bottom SRO layer, as illustrated in the PFM images in (f,g); (h) is the M-H loops for the CoFe layer deposited on such a 109° domain wall array, showing a clear indication of exchange bias (RED loop) due to the existence of pinned uncompensated spins at the 109° domain walls.

The role of isovalent and aliovalent chemical substitutions at both the bismuth and iron sites has been extensively studied[38,39]. Outside of the fundamental understanding of the polar and magnetic order, these studies have also focused on the possibility of creating phase boundaries (much like the morphotropic phase boundary in the $PbZr_{1-}$

$_xTi_xO_3$ family of ferroelectrics) that can lead to large piezoelectric responses and allow for tuning of the ferroelectric switching behavior[43,44,45]. Chemical substitutions at the Fe^{3+} site (e.g., Mn^{3+} or Co^{3+}) have mainly attempted to manipulate the antiferromagnetic nature[46]. While these studies have indicated a certain degree of success, detailed studies of the magnetoelectric coupling in such alloyed $BiFeO_3$ materials are still lacking. Indeed, a grand challenge would be to discover pathways to enhance the magnetic moment to ~50 emu/cc (the canted moment in pure $BiFeO_3$ is only ~6 emu/cc) while at the same time demonstrating magnetoelectric coupling. In this regard, Co-doping at the Fe-site has been shown to enhance the saturation moment to ~80 emu/cc[47,48]. Verification of these observations with theoretical studies as well as by other synthesis routes would be valuable. Similarly, a robust ferroelectric state as well as strong magnetoelectric coupling in such systems is still lacking and should be an active topic of research.

Thin-film synthesis of $BiFeO_3$ (and other multiferroics) has been a very fruitful pathway to study the materials physics of magnetoelectric coupling as well as pointing the way to possible applications. The perovskite symmetry and lattice parameters (pseudocubic lattice parameter of 3.96 Å) close to a large number of oxide-based substrates means that epitaxial synthesis is possible and has indeed been demonstrated. Films with thicknesses down to just a few unit cells and as large as a few microns have been synthesized by physical-vapor deposition (*e.g.*, pulsed laser deposition, sputtering, molecular beam epitaxy), chemical-vapor deposition[49], and chemical-solution deposition. Many studies have used conducting perovskite electrodes (such as $SrRuO_3$, $La_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xCoO_3$) as bottom electrodes to both template the perovskite phase as well as provide a bottom contact for electrical measurements. These synthesis studies have led the way to enable a wide range of materials physics studies including thickness-size effects down to just a few unit cells [50]. Consistent with other perovskite ferroelectrics, a suppression of the magnitude of the polar order is observed, although both theory and experiments indicate that a polar state is stable down to even a couple of unit cells.

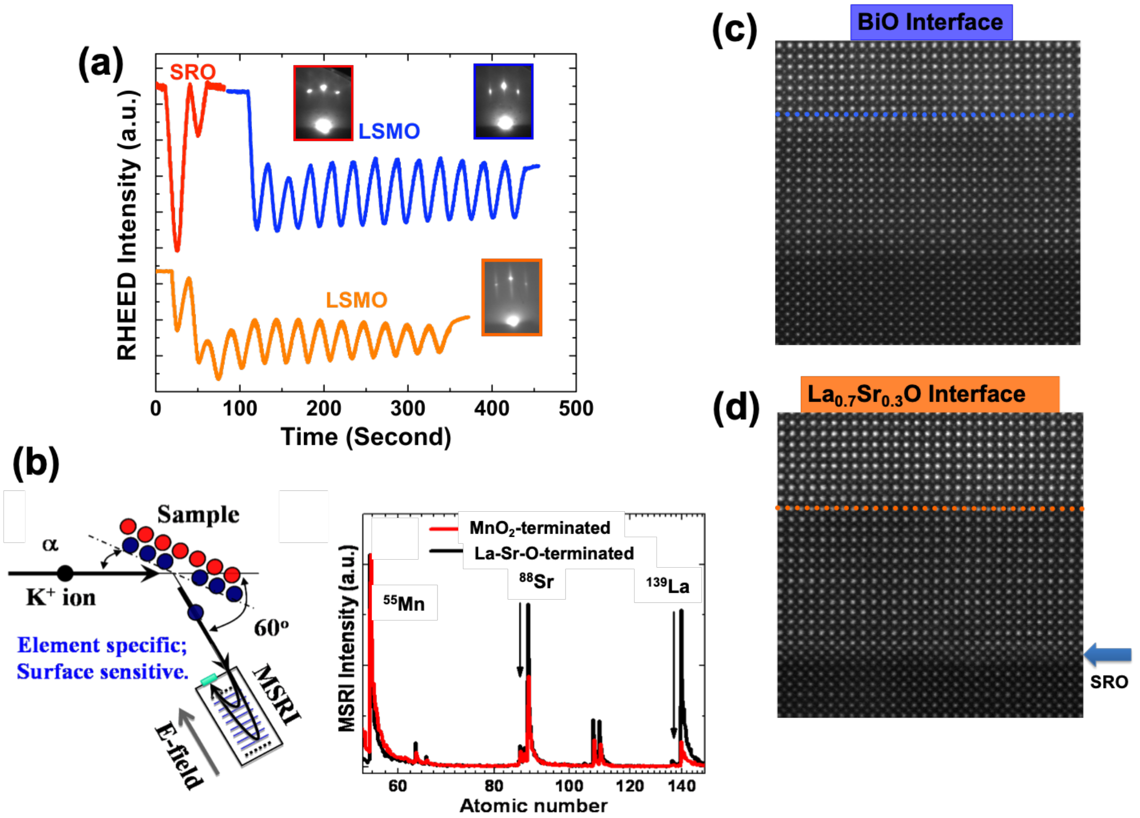


Figure 10: Synthesis of Model Systems. This figure illustrates epitaxial synthesis as a pathway to create model systems at the scale of a single unit cell. (a) is a RHEED pattern of the growth of the LSMO bottom electrode on a TiO_2 terminated $SrTiO_3$ substrate; insertion of 2 unit cells of $SrRuO_3$ leads to a conversion of the termination from B-site to A-site; (b) Time of flight- ion scattering and recoil spectroscopy (TOF-ISARS) of the two types of substrate surfaces. The spectra are normalized to the Mn peak and it is clear that the La content for one of them (BLACK) is much higher than that of the other (RED); (c,d) are atomic resolution STEM images of the two types of interfaces showing that atomically sharp interfaces can be obtained.

Using epitaxy as a building block, one can start to explore magnetic and magnetoelectric coupling between an oxide ferromagnet (such as La-Sr-Mn-O (LSMO)) and $BiFeO_3$. The ability to grow such atomically perfect heteroepitaxial using techniques such as molecular beam epitaxy and RHEED-assisted pulsed laser deposition have been instrumental in enabling the study of magnetism across such interfaces, as illustrated in Fig.10. In situ probes, such as time of flight- ion scattering and recoil spectroscopy (TOF-ISARS) indeed show that the interface termination can be manipulated at the scale of the individual perovskite building blocks, namely the A-O plane or the B-O_2 plane as shown by the atomic resolution images in Fig.10(c,d). This is accomplished by inserting a of a 1.5-2.5 unit cell thick layer of $SrRuO_3$ (SRO) on the TiO_2-terminated $SrTiO_3$ substrate surface. Deposition of 2-3 unit cells of SRO on the substrate followed by a short wait (3-5 mins) enables the desorption of the topmost Ru-layer, thus converting the RuO_2 terminated surface to a Sr-O terminated surface; this Sr-O terminated surface then seeds epitaxial growth of the LSMO layer and converts the MnO_2 termination to a La(Sr)-O termination, as shown by the TOF-ISARS spectra in Fig.10(b). We get back to the issue of magnetoelectric coupling in such model interfaces after a short summary of theoretical approaches.

From a theoretical perspective, while first-principles density functional theory (DFT) calculations remain central for understanding and predicting the properties of multiferroics, second-principles calculations with embedded model Hamiltonians are proving increasingly valuable in the study of larger systems, for example heterostructures, domain walls and defects, as well as longer time-scales in molecular dynamics. They have been applied to describe structural phase transitions of prototypical ferroelectrics[51,52,] and recent extensions to include additional lattice degrees of freedom[53], as well as magnetic interactions[54], have extended their applicability to multiferroics. For example, an effective Hamiltonian consisting of a lattice part incorporating ferroelectric distortions, octahedral rotations and strain, a contribution from the interaction of the magnetic moments with each other, and coupling between the magnetic moments and the lattice, has been shown to accurately reproduce the crystal and magnetic structures of bulk BFO. On a larger length scale, a Landau-Ginzburg thermodynamic potential that includes both polar and antipolar distortions and their coupling to magnetism has been successful in reproducing the bulk behavior of BFO and offers great promise for predicting properties in thin film heterostructures and nanostructures.[55] Multi-scale approaches that allow treatment of the electronic and lattice degrees of freedom on the same footing[56] could lead to vastly enhanced system size and accuracy when combined with improved tools for generating effective potentials using input from first principles[57]. Modeling of the dynamics of ferroelectric switching[58] and its effect on magnetic order[59], both of which are on time- and length-scales that are far outside the ranges accessible using density functional methods, has now become feasible. Such models in combination with molecular dynamics start to allow calculation of dynamical magnetoelectric responses in the THz region[60], which is particularly timely as it coincides with advances in experimental methods for generating THz radiation[61]. Finally, the possibility of magnetoelectric multipole as an order parameter for phase transitions that break both space-inversion and time-reversal[62] [63] seems intriguing, although not fully explored experimentally.

With this basic understanding of the order parameters and symmetry in systems such as BFO, we can now ask the most important question: how does magnetism couple to an electric field and how can the state and direction of magnetism can be manipulated

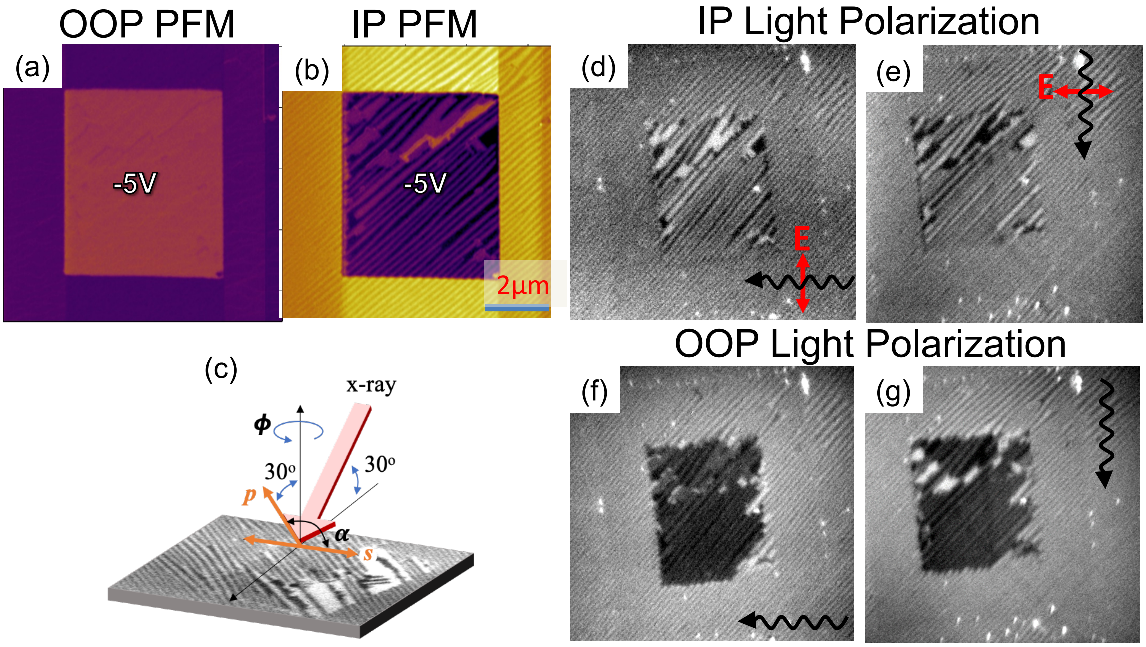


Figure 11: Electric field control of antiferromagnetism probed using XLD-PEEM. On the left (a,b) is piezoforce microscopy showing the ferreoelectric domain structure before and after switching; (c) is a schematic that illustrates the XMLD-PEEM imaging process; (d,e) are XMLD-PEEM images of a switched region with light polarization in-plane (IP) with two orthogonal azimuthal angles; (e,f) are similar images obtained with the light polarization out of plane (OOP).

through the application of an electric field? In nature this coupling between electricity and magnetism occurs through electromagnetism. However, in order to be able to dramatically change the state of magnetism with an electric field, it is desirable for the magnetoelectric coupling to be significantly stronger than what is available in nature.

Understanding electric-field control of antiferromagnetism (AFM) in BFO requires probing AFM using X-rays or neutrons. Such studies of $BiFeO_3$ have shown that when the polarization state switches with the application of an electric field, there is a corresponding rotation of the magnetic order[64,65]. Such a change can also be spatially probed using a combination of piezoresponse force microscopy (to image the ferroelectric order) and X-ray magnetic linear dichroism (XLD) photoemission electron microscopy (PEEM) (to image the antiferromagnetic order) (**Fig. 11**). It is interesting to note that there has been little detailed work on a full understanding of the dynamics of the manipulation of the AFM state by an electric field – with most studies assuming the magnetic order merely follows that of the polar order, but not clarifying that pathway. This is an opportunity for future ultrafast dynamics research, since the antiferromagnetic resonance frequencies are in the several hundred GHz range and $BiFeO_3$ has ferroelectromagnons in the 700 GHz to 1 THz range. Given the current surge in interest in antiferromagnetic spintronics, such insulating multiferroics would also garner more interest.

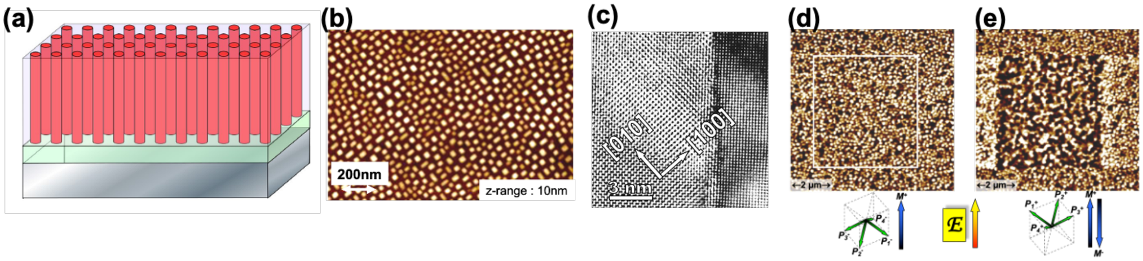


Figure 12: (a) a schematic of the 3-D vertically epitaxial magnetoelectric nanocomposite; (b) AFM image of the ferrimagnetic $CoFe_2O_4$ nanopillars (in bright contrast embedded in a ferroelectric $BiFeO_3$ matrix (in dark contrast); (c) A high resolution STEM image of the interface between the spinel ferrimagnet and the perovskite ferroelectric ; (d) is a magnetic force microscopy (MFM) image after magnetization at 2T, in which the ferrimagnetic nanopillars appear in bright contrast; (e) is the corresponding MFM image after the matrix was switched with a -16V applied with an AFM tip. The schematics below describe the magnetic state before and after the electric field switching.

VI.1 Electric field control of mixed magnetic states and nanocomposites.

Early on in the evolution of the modern version of multiferroics and magnetoelectrics[66], it was realized that nanocomposites comprised of ferrimagnets embedded (in many cases epitaxially) in a ferroelectric/piezoelectric matrix could lead to efficient magnetoelectric coupling controlled by interfacial epitaxy. Such nanocomposites, exemplified by single crystalline nanopillars (**Fig. 12**a) of ferrimagnetic spinels (*e.g.*, $CoFe_2O_4$) embedded epitaxially in a ferroelectric perovskite matrix (*e.g.*, $BiFeO_3$), are illustrated in the AFM images (**Fig. 12**b). The epitaxial nature of the lateral interfaces is shown in corresponding planar section TEM images (**Fig. 12**c). Electric field driven switching studies reveals perhaps the most interesting aspects of such nanocomposites of relevance to deterministic switching of the magnetic state with an electric field. While the initially magnetized state (**Fig. 12**d), can be switched with an electric field, only ~50% of the magnetic nanopillars switch their state (for example from magnetization pointing up to down; **Figs. 12**d,e). Detailed analysis of this data[67] shows that this is indeed true and is a direct consequence of the fact that the electric field assists in manipulating the magnetic anisotropy of the ferrimagnetic nanopillar through the epitaxial interface between the perovskite ferroelectric and spinel ferrimagnet. However, the magnetic anisotropy of the nanopillar is the same whether it is magnetized up or down (along the long axis of the nanopillars), t hus leading to a ~50/50 mixture of up/down states after the electric field is applied. This study also throws light on the most important

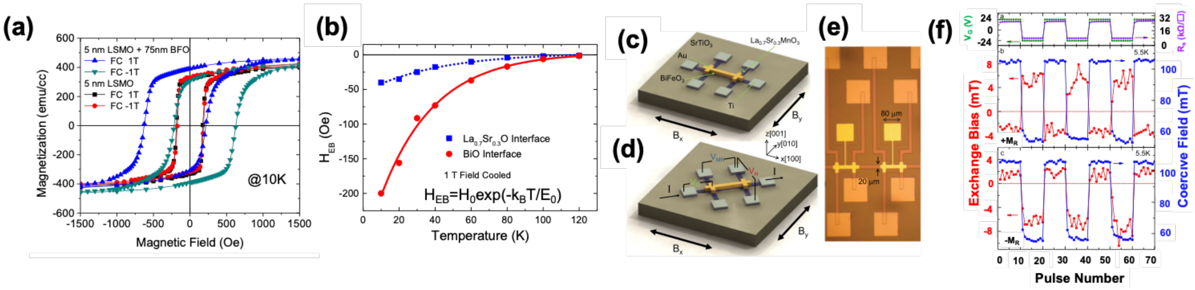


Figure 13: Electric field manipulation of interfacial magnetic coupling in epitaxial heterostructures. (a) 1 Tesla, field cooled magnetic hysteresis loops at 10K showing a strong exchange bias of 200Oe for a 5nm LSMO-75nm BFO heterostructure; (b) the magnitude of the exchange bias field as a function of temperature and interface termination (La/Sr-O vs. Bi-O interfaces; (c,d) are device layouts for magnetoelectric measurements, with the corresponding SEM image shown in (e) ; (f) shows the bipolar voltage profile and the corresponding exchange bias and coercivity showing full electric field switching of the exchange bias.[71]

physics of such coupling phenomena, namely that switching the magnetization direction in a deterministic fashion, i.e., by 180°, requires that there be a field that breaks time-reversal symmetry. However, the electric field and corresponding piezolectric stress that is generated does not break time-reversal symmetry and thus cannot deterministically switch the magnetization, but can indeed alter, during the switching process, the magnetic anisotropy. This is further supported by the observation that the application of a small magnetic field to the nanopillar arrays during the electric field induced switching event leads to a complete switching of their magnetic state[62]. These results also point to the need to have a coupling mechanism that is magnetic in nature, for example, interfacial exchange bias coupling, which we focus on next.

VI.2 Electric-field control of magnetization direction through interfacial exchange coupling. There are a few possible manifestations of electric field control of magnetism; the review by Song and coworkers[22] provides a complete summary of these pathways. The first pathway would be to manipulate the direction of magnetization, while the magnitude remains essentially unchanged; another approach would be to manipulate the magnitude of the net, macroscopic magnetization, for example through a ferromagnetic to an antiferromagnetic phase change[74-78]. A third pathway would manipulate the magnetic anisotropy, for example using strain, as already illustrated by the nanocomposite example in Fig.12. From a practical perspective, especially in terms of carrying out logic-in-memory operations with spins[1,11] it is most useful if the direction of magnetization can be robustly switched. Perhaps the most significant breakthrough in the past few years is the demonstration that the magnetization direction in conventional ferromagnets (*e.g.*, $Co_{1-x}Fe_x$) can be rotated by 180° with an electric field[68,69] when it is exchange coupled to $BiFeO_3$. The extension to all-oxide $La_{0.7}Sr_{0.3}MnO_3/BiFeO_3$ interfaces (**Fig. 13**), with chemically abrupt *A*-site termination[70], allowed for electric-field control of exchange bias coupling at temperatures below 100 K[71].

Earlier work on the same system has shown the ability to reversibly switch between two exchange-biased states with the same polarity (unipolar modulation) without the need for additional magnetic or electric fields in a multiferroic field effect device, but eventually the ability to reversibly switch between these two states with opposite polarity (bipolar modulation) was demonstrated as well (**Fig. 13**). The key was modifying the direction of the magnetization in the $La_{0.7}Sr_{0.3}MnO_3$ with respect to the current in the device channel. A reversible shift of the polarity of exchange bias through the zero applied magnetic field axis was thus achieved with no magnetic or electric-field cooling and no additional electric or magnetic bias fields – in essence, full direct electric field control of exchange bias. This also helped clarify the mechanism underlying the change in exchange bias coupling.

An important open problem is the development of oxide ferro- or ferri-magnets with high T_c, a significant remanent moment and strong exchange coupling and Ohmic contacts with $BiFeO_3$ or other multiferroics; spinels or double perovskites are promising candidates in this regard[72,73]. In a complementary direction, the antiferromagnetic domain orientation in magnetoelectric Cr_2O_3, which can be controlled by an electric field, has been shown to affect the exchange-bias coupling to a ferromagnetic overlayer[74] opening a pathway to electric-field switchable exchange-bias devices.

Manipulating magnetic state (or magnitude of the magnetization) with an electric field: In parallel to these efforts to control the direction of magnetization with an electric field, there have been successes in electric-field manipulation of the magnetic state (or the magnitude of the net macroscopic magnetization), for example, by switching between ferromagnetism and antiferromagnetism using composites[75]. One example is electric-field modification of the magnetic exchange interactions in magnetic $Fe_{1-x}Rh_x$ heterostructured with piezoelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-PT). Motivated by the volume change at the ferromagnetic to antiferromagnetic transition in $Fe_{1-x}Rh_x$[76,77], an electric field was used to drive the reciprocal effect, a ferromagnet-to-antiferromagnet transition induced by a structural deformation[78,79]. Since the resistivities of the two magnetic phases differ, the magnetic transition is accompanied by a ~25% change in film resistivity. Open challenges include reducing the optimal working temperature from around 100°C to room temperature, tuning the chemical composition to optimize the strengths of the exchange interactions, achieving complete conversion between the ferromagnetic and antiferromagnetic phases and reducing the required applied voltages. Other promising systems are the Mn-Pt intermetallics and half-doped perovskite manganites such as $La_{0.5}Sr_{0.5}MnO_3$, in which an electric-field-driven charge-ordered antiferromagnetic insulator to ferromagnetic metal transition could be possible[80].

VII. Ultra-low Power Logic-Memory Devices based on Multiferroics:

A large number of pathways are currently being explored to create low power nonvolatile memories within the context of next-generation computing (for example, refs. 1,2, 12). A full description of these various pathways is a dedicated review in itself and is not the prime focus of this review. Instead, we will attempt to capture the state of the art of various approaches as a summary after a brief summary of the magnetoelectric and multiferroic approaches.

The push for ultra-low power logic-memory devices builds from seminal observations of the potential of magnetoelectric control using multiferroics– the key being the ability to control magnetism with electric field at room temperature[81] using a spin-valve device (**Fig. 14(a)**) to demonstrate the coupling. Efforts in this direction are currently being undertaken. For example, magnetoelectric switching of a magnetoresistive element was recently shown to operate at or below 200 mV, with a pathway to get down to 100 mV[82]. The fact that the voltage (which is relevant from the device perspective) and the electric field (which drives the switching physics) means that reducing the thickness is an obvious pathway to get to such low voltages. A combination of structural manipulation via lanthanum substitution and thickness scaling in multiferroic $BiFeO_3$ has helped to scale the switching energy density to ≈10 μJ cm^{-2} and provides a template to achieve attojoule-class nonvolatile memories. Lanthanum substitution is known to both lower the polarization and the ordering temperature (and therefore the energy of switching) of the ferroelectric and to take advantage of innate thickness scaling effects (thinner films require smaller voltages for switching)[40]. Using this approach, it was possible to show that the switching voltage of the giant magnetoresistance (GMR) response can be progressively reduced from ≈1 V to 500 mV by a reduction of the film thickness down to 20 nm (**Figure 14**). Robust electric-field control of the magnetization direction in the bottom $Co_{0.9}Fe_{0.1}$ layer was shown in measurements both in a magnetic field of 100 Oe as well as in the remanent state (*i.e.*, zero magnetic field) (**Figure 14b,c**). The low-voltage magnetoelectric switching in multiferroic $Bi_{0.85}La_{0.15}FeO_3$ was further probed by XMCD-PEEM imaging at the Co L_3 edge via studies (inset, **Figure 14d,e**) where application of +/- 500 mV revealed contrast changes consistent with reversal of the in-plane magnetization[81].

Building from such observations, a promising recently developed logic-memory architecture [83] brings together the inverse Rashba–Edelstein (spin-Hall) effect

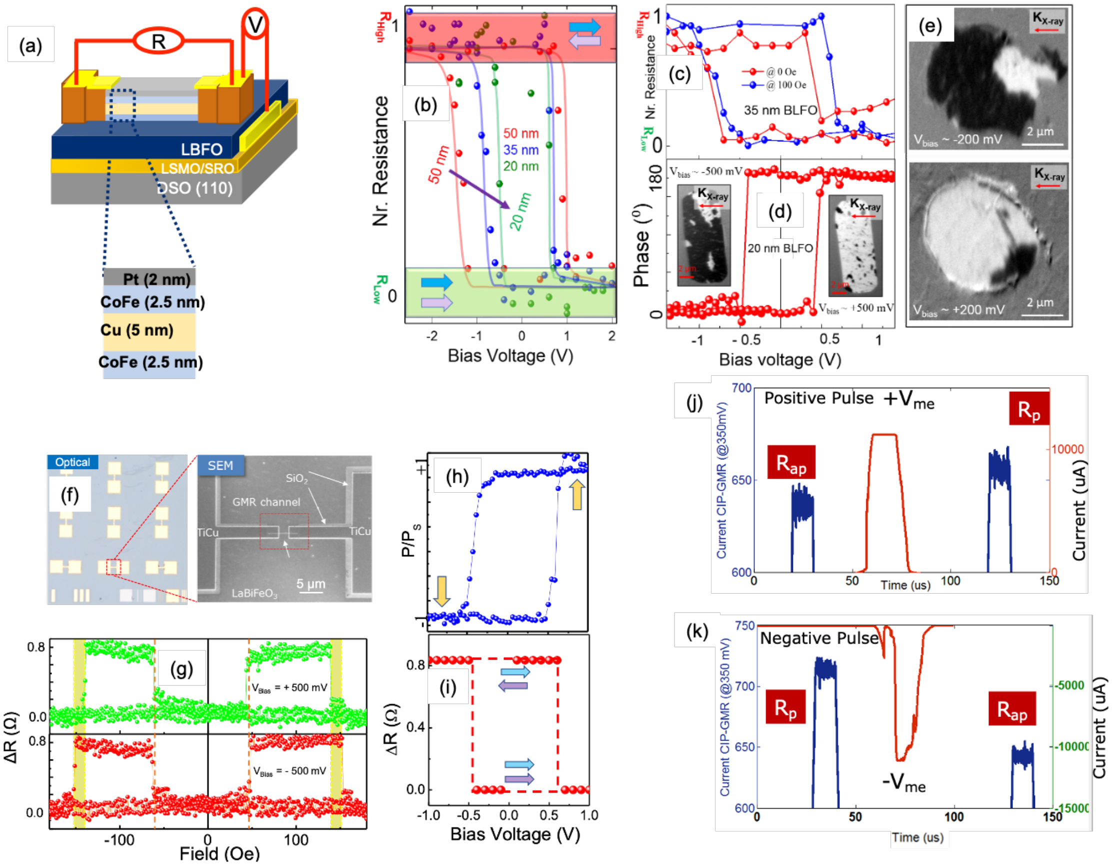


Figure 14: (a) a Schematic of the magnetoelectric test structure comprised of a CoFe-Cu-CoFe spin valve in contact with the La-BFO surface; (c) shows voltage dependent GMR hysteresis as a function of La-BFO thickness from 50nm down to 20nm; (b) shows the normalized resistance of the GMR stack as a function of applied voltage at zero field (RED) and at 100Oe (BLUE); (d) is the corresponding piezoelectric phase data showing switching of the polar state at ~500mV for the 20nm LBFO layer; also shown are the corresponding XMCD-PEEM (at the Co-edge) for a CoFe dot that has been switched (from BLACK to WHITE) with a bias of 500mV; (e) is the corresponding XMCD-PEEM data for a CoFe dot on a 10nm LBFO layer showing switching at ~200mV (adapted from ref.81); (f) is a composite of optical and SEM images of ~100nm GMR spin valve channels fabricated using e-beam lithography; (g) is the corresponding resistance change vs. magnetic field for both +500mV and -500mV applied electric field; (h) is the normalized ferroelectric loop for the La-BFO and (i) the corresponding normalized GMR resistance as a function of applied voltage; (j,k) are the GMR resistance for the parallel (R_p) and antiparallel (R_{ap}) states measured with 20 microsecond electric field pulses.

(IREE) [84,85,86,108] and electric-field control of magnetism using a multiferroic. The resulting magnetoelectric, spin-orbit coupled logic device (MESO) [11], Figure 16, uses the IREE effect to convert spin to charge (or voltage) and the multiferroic to perform

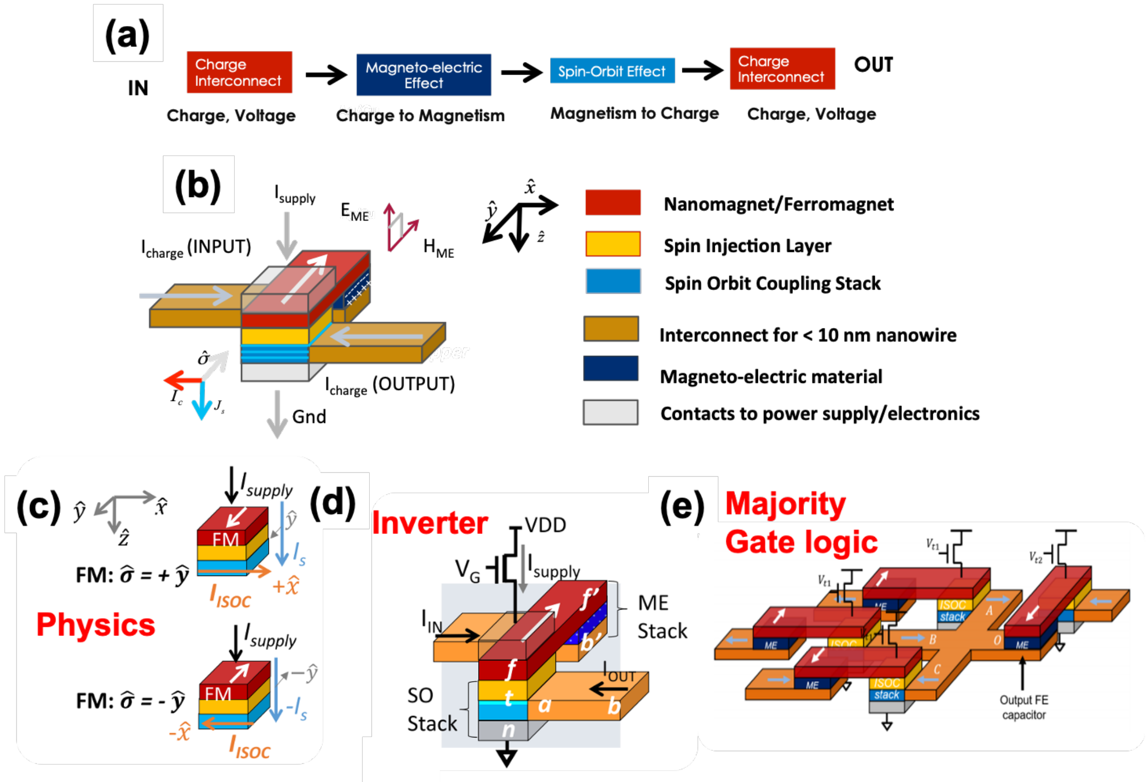


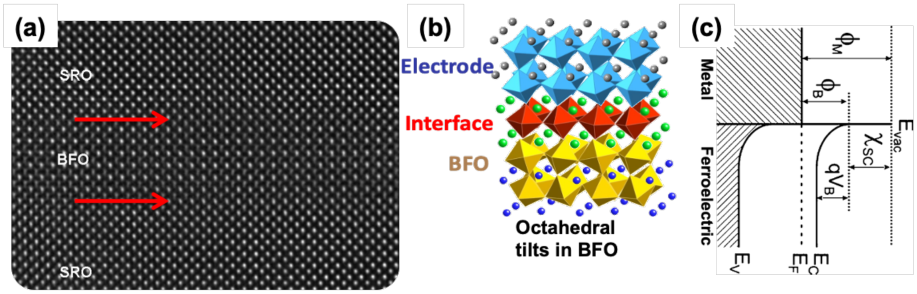
Figure 15: (a) a schematic that illustrates how the magnetoelectric, spin-orbit (MESO) device works; the input voltage signal is converted into a spin signal by the magnetoelectric layer; the logic operation is then carried out and the spin-orbit layer converts this back to a voltage signal, which is easier to read out compared to a spin signal; (b) is a schematic of an individual MESO element comprised of the various layers shown to the right; (c) depicts the fundamental physics behind the MESO device in which the direction of the ferromagnetic layer (in RED) sets the direction of the direction of the spin-orbit coupled current; (d) is a schematic of how the basic MESO building block is used to make an Inverter (which is a fundamental unit for logic operations) and (e) depicts how a majority gate logic is constructed from the MESO device (figure adapted from ref 11).

the opposite conversion of charge to spin. Success of the device rests on an increase in the IREE voltage output from current values of hundreds of µV to hundreds of mV as well as a reduction in voltage requirement for the magnetoelectric component from the current value down to ~100 mV. Such breakthroughs could lead to a transformative 1 aJ (10^{-18} J) per memory bit or logic element, illustrated schematically in **Figure 15**[11].

Despite all of the prior work, switching a ferroelectric state (as well as a multiferroic state) with a voltage as small as 100 mV remains a challenge and a research opportunity. Since the electric field scales with the dimensions of the ferroelectric, progression towards switching voltages of 100 mV automatically require that either the switching field is very low or that the switching behavior scales well with thickness. Therefore, it is critical to understand ferroelectric switching behavior in the ultrathin limit (< 20 nm). Quantitative studies of the switching dynamics at such a thickness are still lacking and should be a fruitful area of research especially on the experimental side. What are the limits to the switching speed of ferroelectrics / multiferroics? There have been speculations that one limit could be acoustic phonon mode (i.e., the velocity of sound in the material) since the switching of the polar state clearly involves the time-dependent deformation of the lattice. For nominal values of the velocity of sound in such oxides (~3000m/sec), this would suggest switching time of the order of a few ten's of picoseconds. Thus, the role of lattice dynamics during the dipolar switching event needs considerable further work. Measuring at such time scales requires very fast electronics (for example, pulse generators with rise times smaller than a few ten's of psec and oscilloscopes that can capture the switching transients as commensurate speeds); thus it is not surprising that there have been only a few measurements of the polarization switching dynamics approaching such time scales[87]. This is true for both ferroelectrics and multiferroics[88] and as we go forward into this exciting field of electric field controlled magnetic devices, such studies are critically needed.

An equally important aspect is the stability of the polar state as the thickness is scaled down. Such size effects have been extensively studied in classical ferroelectrics[89] and is characterized by a suppression of the order parameter as the thickness is scaled down. Similar studies have been undertaken in the case of the $BiFeO_3$ system, albeit in an incomplete sense. Several studies have shown that the polar order parameter is suppressed, but still maintained; The antiferromagnetic order has also been shown to exist at room temperature in films that are as thin as 4nm (10 unit cells). What has not been shown is the coupling between the two order parameters at such length scales, and more importantly, electric field manipulation of this coupling. Thus, a deeper, quantitative understanding of the stability of the individual order parameters, the coupling between them as well as E-field manipulation of this coupling at a thickness less than ~10nm would be of significant interest. This is captured in Fig.16.

While challenges at these voltage/energy, length, and time scales exist for all ferroelectric materials, special attention is now being given to such responses in multiferroics such as BFO. The ferroelectric switching process in BFO is believed to be limited by nucleation and growth of reverse domains[90] broadly captured by the Kay-Dunn model[91], in which the coercive field scales as film thickness $d^{-2/3}$. Consequently, progressively larger reductions in film thickness are needed to reduce the coercive voltage as it is pushed to smaller values. In BFO, lanthanum substitution has been shown[92] to reduce the switching energy by reducing the polarization[93], although to an insufficient extent to date. Pushing $BiFeO_3$ close to a phase boundary between ferroelectric and antiferroelectric states or identifying materials without the octahedral rotations of BFO could be an alternative pathway to smaller coercive fields. The challenges facing the spintronics community in enhancing the output of the inverse Rashba-Edelstein effect component by two to three orders of magnitude[94] are equally exciting.



(d)

Materials Physics Challenges & Opportunities

How to make chemically perfect <10nm LBFO?
Stability of order parameter & magnitude below 10nm
Thickness scaling of magnetoelectric coupling
Various contributions to the switching voltage
How to measure switchability without artifacts?
Lattice dynamics vs. dipolar dynamics

Roto-mechanics : role of octahedral tilts
Limits of ME-FM coupling dynamics
Lateral scaling of ME coupling
Role of granularity and orientation distribution
Interface electronic structure & Schottky barriers
Contact electrode conductivity and defect chemistry

Figure 16(a) is an atomic resolution image of a 6 unit cell thick $BiFeO_3$(BF) layer sandwiched between epitaxial $SrRuO_3$(SRO) top and bottom electrodes as a representative of sub-10nm thick multiferroics as model systems; (b) is the corresponding crystal model showing the octahedral tilts (in both the SRO and BFO layers) as well as the possibility for the formation of interface Schottky barriers, shown in (c);(d) summarizes several key unanswered materials physics questions for such sub-10nm multiferroics

Several important considerations towards carrying out such quantitative measurements need mentioning. First, dielectric leakage becomes an ever-increasing component at such thickness; an extreme case would be a "shorting" of the test element. Thus, measurements at such thicknesses automatically mean that the test structures will have to be laterally quite confined (likely in the 50-100nm range), thus requiring sophisticated lithography and definition. Second, interfaces will play an increasingly important role in determining both the stability of the polar state as well as transport across such small thicknesses. For example, interfacial Schottky barriers can significantly alter the potential drops across the sample and thus the voltages required to switch the polar state. Incomplete screening of the spontaneous polarization at the interface[95] can lead to its suppression. The role of point defects (both ionic and electronic) will become all the more important since we are now dealing with films of ~10 unit cell thickness.

Finally, **Fig.17** summarizes, the state of the art of the various memory technologies (both mature technologies such as the NOR-FLASH, DRAM and SRAM) as well as emerging technologies and puts the magnetoelectric approach described in this review into perspective. As a broad conclusion, voltage-driven devices do offer the potential for a significant reduction in energy consumption compared to current-driven devices. Having said that, the recent developments in spin-orbit torque (SOT) based switching of the magnetic state offers significant promise for lowering the energy consumption, if the efficiency of spin-to-charge conversion is significantly enhanced.

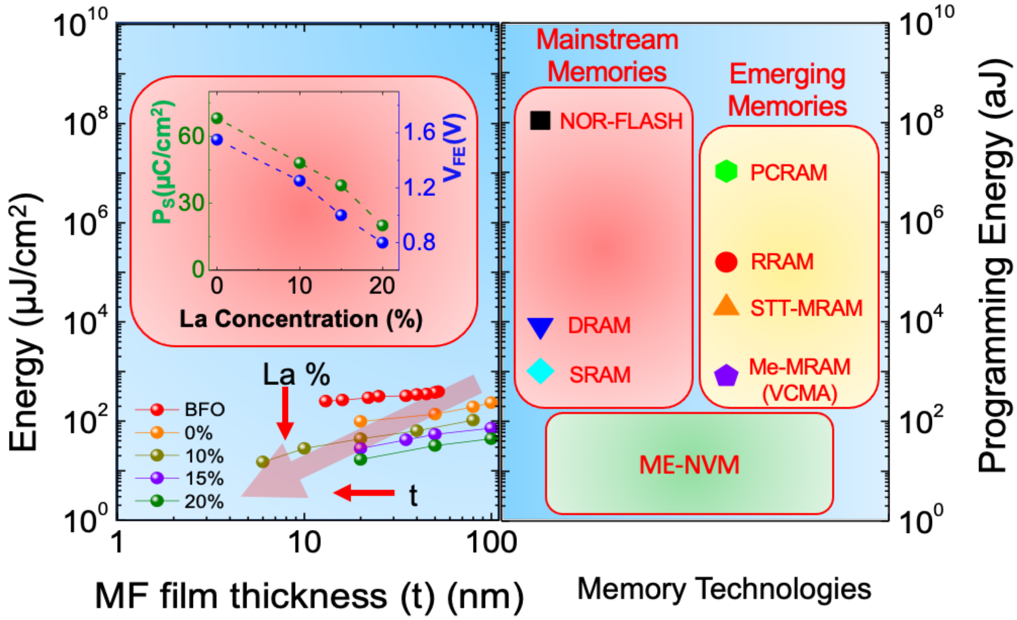


Fig.17: This figure captures the state of the art in tuning the switching voltage and spontaneous polarization of $BiFeO_3$ through La-substitution and film thickness at the Bi-site, which therefore leads to a reduction in the energy consumed (the left panel); the right side of the panel compares Mainstream memories (NOR-FLASH, DRAM and SRAM) to Emerging memories (PCRAM, RRAM, STT-RAM and ME-MRAM) as well as the magnetoelectric nonvolatile memory-based logic (ME-NVM).

VIII. Challenges and Opportunities

It seems inappropriate to write a concluding section when, in reality, the exciting journey has just begun. Electric-field control of the magnetization direction at room temperature is now clear with the voltage required to accomplish this dropping down to just 0.5 V. To get to an aJ switch, it is critical to reduce these switching voltages down even further (to at least 100m V) in conjunction with a switching charge density of ~10 μC/cm². The key materials physics issues are captured in Fig.16; at the broader level, Table 2 summarizes some of the key basic science and translational issues to be addressed. How robust can this be, especially with respect to repeated cycling of the electric and magnetic states? In this regard, like in the field of ferroelectric thin films for memory applications, it appears that we need to increase the focus on the nature of the ferromagnet and its interface to the multiferroic. Prior experience with

Materials Physics	Translational
•Discovery of new, room temperature multiferroics with robust coupling between magnetism and ferroelectricity, strong coupling, and magnetic moment larger than 50 emu/cc	•Achieving thermal stability of ferroelectric and magnetic order parameters, as well as robust coupling between them, in 10nm length-scales at room temperature. Thus, careful measurements of magnetoelectric and multiferroic phenomena at such length scales is critical
•Developing new mechanisms for magnetoelectric coupling and understanding and approaching the limits of the strength of such phenomena	•Reducing the voltage required for ferroelectric / magnetoelectric switching to ~100mV.
•Atomic-scale design and layer-by-layer growth as an attractive pathway to discover and synthesize new room temperature multiferroics	• A second key requirement for ultralow power electronics (e.g., an AttoJoule switch) would be designing proper ferroelectric multiferroics with small but stable spontaneous polarization of ~1-5 $\mu C/cm^2$
•Understanding the scaling limits, controlling and exploiting dynamics: Magnetoelectric coupling at <20nm length scale; <1nsec time scale; <100kT energy scale	•Integration and scale-up of synthetic approaches to enable manufacturing would be valuable.
• From a longer timescale perspective, reaching the theoretical Landauer limit for switching (kT(ln2) would be desirable and will require significant effort	•Convergence of memory and logic

Table 2: A summary of challenges and opportunities both at the fundamental materials physics level as well as translation into technologies.

ferroelectric capacitors has shown that a conducting oxide contact yields a very robust capacitor; in a similar vein, we expect an oxide ferromagnet to form a more robust contact to the oxide multiferroic. Thus, there is an urgent need to discover and interface an oxide ferromagnet that couples magnetically to the multiferroic at room temperature. A template for this is already available from the work on $La_{0.7}Sr_{0.3}MnO_3/BiFeO_3$ interfaces, which display robust electric-field control of the magnetization direction, albeit at 100 K. Can the double perovskites, such as $Sr_2(Cr,Re)O_6$[70] with a high magnetic Curie temperature be possible alternatives to the LSMO system? In the same vein, there is an urgent need to discover more room-temperature multiferroics so that one can explore multiple pathways to use these novel functionalities. Finally, searching for new room temperature multiferroics would be a very worthwhile pursuit for the materials community, especially when armed with the computational discovery platforms such as the Materials Genomics approach driven by Machine Learning pathways [96]. The confluence of crystal chemistry, computational discovery and atomically precise synthesis is a potent combination that has already shown to lead to unexpected phenomena[97].

As mentioned in Table I, there is a lot of potential in designing magnetoelectrics at the atomic scale using epitaxial superlattices. The original work of Mundy et al[36] on $LuFeO_3$-$LuFe_2O_4$ superlattices showed that the epitaxial pathway to magnetoelectric coupling is indeed possible. The work of Fan and co-workers [98] revealed the microscopic details of the coupling across the ferroelectric ($LuFeO_3$) ferrimagnet ($LuFe_2O_4$) interface. A key issue with $LuFe_2O_4$ is the fact that the Curie temperature is lower than room temperature (~240K in the bulk; ~280K in epitaxial superlattices [36]). Thus, it would be desirable to replace this with other structurally and chemically compatible ferrites. Research in this regard is underway, using $CoFe_2O_4$ as the replacement for $LuFe_2O_4$ and publications outlining the coupling in such systems will be forthcoming.

In this sense, tremendous progress has been made in understanding chemistry-structure-property relationships, and in engineering specific atomic architectures, so that an era of "multiferroic materials by design" is already underway. In particular, targeted functionalities, such as large magnetization and polarization and even exotic polarization topologies, are now within reach. Electric-field control of magnetism, while demonstrated in multiple implementations, must be optimized so that it can be achieved with smaller voltages, ideally below 100 mV. For multiferroic devices to be technologically competitive will therefore require precise growth of ultra-thin films guided by theoretical studies to exactly define the chemical compositions needed to optimize the polarization and coercive field. This will require a greater fundamental understanding, which will be facilitated by improved first- and second-principles methods. Even with such a low-field-switching breakthrough, scale-up and integration, in particular compatibility with existing silicon processing methods, and integration with the appropriate peripheral electronics are key challenges. An oxide-based ferromagnet or ferrimagnet that couples strongly to $BiFeO_3$ and has a Curie temperature well above room temperature would be desirable.

The recent discovery of polar vortices and skyrmions in ferroelectric superlattices presents a tantalizing opportunity to create analogous, coupled spin-charge textures out of multiferroics such as BFO[99,100,101,102]. This could present a unique pathway to overcome the antiferromagnetic ground state through such curling patterns spin/dipolar patterns. A first set of studies have been carried out to explore the possibility of forming polar textures in the BFO system[95]. Imposing electrostatic boundary conditions by interfacing to a lattice matched, non-polar La-BFO however, leads to the formation of an array of 109° domains as well as stabilizing an anti-polar structure in the BFO layer[98]. These results seem to suggest that while the idea of imposing electrostatic boundary conditions, does work in a general sense, the consequences are governed more by the structural details, particularly the octahedral tilts, that are such a key component of the crystal structure of BFO. The rather surprising outcome of the formation of the anti-polar structure can be rationalized through the fact that the electrostatic energy is more than sufficient to raise the free energy of the polar phase above that of the antipolar phase[98]. Indeed, this seems to be a hallmark of the BFO system, where a number of phases are within a close proximity in energy scale to the ground state[103].

It is noteworthy that, although the focus of this article is on the materials physics aspects, crystal chemistry plays a dominant role in establishing the ground state of the material as well as the long-term degradation. A good example of this is the role of oxygen vacancies in inducing polarization fatigue in ferroelectrics. Such charged defects can play an equally important role in defining the degradation behavior of multiferroics. The role of defects (point defects, dislocations and interfaces) is only going to become even more important as we get into the sub-10nm thickness regime. At this scale, we need to be able to account for each atom in the film as well as the cationic perfection of the structure. Indeed, this could be said for the field of complex oxides. Unlike Si based electronics, where, until recently, the materials have been relatively simple, in the case of oxides complexity is an inherent feature.

Another aspect that would benefit from a detailed crystal chemistry based phase equilibrium study is the formation of metastable phases; for example, one could be looking for polytypoids (phases that have the same crystal structure but different chemical/stacking sequence, for example Y-Si-Al-O-N's)[104] of the $BiFeO_3$ composition or chemically distinct derivatives thereof. Two examples of this could be: (i) based on the hexagonal BaM type layered ferrites[105], (ii) the Ruddelsen-Popper type perovskites or the Aurivillius type phases[106]. Of these multiferroic behavior has been demonstrated in the hexagonal ferrites[107]. Further, chemically substituted Aurivillius phases have been known to exhibit magnetoelectric behavior, although the magnetic state is not a robust ground state (more like a spin glass)[108]. On this note, it seems worthwhile to start with ferrimagnets (such as the layered hexaferrites) and attempt to induce a robust ferroelectric state into them, through chemical substitution or epitaxy[109]. Charge ordering transitions, such as the Vervey transition in Fe_3O_4, were thought to lead to breaking inversion symmetry[110]; demonstrating a robust magnetoelectric effect in such systems as well as the others described in this section should be a focus for research in the coming years.

In terms of the magnetoelectric nanocomposites[65, 111], perhaps several opportunities for future research are available. One would be to explore pathways by which the interface between the ferrimagnetic nanopillar is exchange coupled to the matrix phase (for example bismuth ferrite). Work so far seems to demonstrate that there is strong enhancement in the magnetic anisotropy of the magnetic phase (mediated through a 3-dimensional heteroepitaxy at the nanopillar-matrix interface), creating such an exchange bias will require the existence of pinned uncompensated spins at that interface. If this can be accomplished, perhaps through improving the structural and chemical perfection of this interface then the possibility of using just an electric field to manipulate this interfacial coupling to reverse the magnetization direction (without the application of any magnetic field) in the ferrimagnetic nanopillar exists. This would be a growth challenge since the spinel and perovskite phases are typically lattice mismatched by ~5%. From the synthesis perspective, it is noteworthy that the crystal chemistry aspects of such nanocomposites and the long-range order amongst the nanopillars is still an open question. So also, what are the limits of the lateral dimensions of the nanopillars? Another pathway to achieve magnetoelectric coupling that is yet to be explored is to use a spinel-perovskite magnetic nanocomposite (such as LSMO-$NiFe_2O_4$) that is magnetically coupled to a multiferroic such as BFO across the lateral interface (like that described in Fig.12). This could be a pathway to enhance the exchange coupling temperature to room temperature (compared to the 100K for the LSMO/BFO interface, Fig.13). Such a 3-level nanocomposite has recently been demonstrated with strong electric field manipulation of the exchange coupling at room temperature. This appears to be a very fruitful direction to pursue.[112]

A topic that would of significant interest is multiferroic and magnetoelectric behavior in non-oxide materials. This has not been explored extensively, as yet, although some of the early multiferroics were fluorides[113]. There are examples of magnetic nitrides (*e.g.,* Fe_4N)[114] and nitride based piezoelectrics and ferroelectrics are emerging[115,116,117118]. There are fewer experimental studies of the ferroelectric polarization and its switchability, which would be a key requirement for applications. Doping or alloying the ferroelectric nitrides to induce magnetic order could be one pathway. An easier pathway may be to use heterostructuring to induce coupling. Of course, if this coupling is primarily strain based, then manipulating the magnetization direction with an electric field will be difficult; instead, one may have to use this to manipulate the anisotropy of the magnet.

What are the limits on the length scales of the spin-charge coupling? For example, can we manipulate the spin state of a single ion using an electric field? Recent work in this direction is poised to impact not only the fundamental physics of spin-orbit coupling and its coherent manipulation with an electric field, but also has the potential to impact the field of quantum computing in which all of the coherent operations are carried out using an electric field[119]. Although impurities in ferroelectrics is a well-studied subject, including probing them with electron paramagnetic resonance[120], there has been very little focus on coherent manipulation of the electron spins in such systems. Recent work has shown that this is indeed possible. Ab initio calculations show that the spins in tetragonal lead titanate are aligned in a plane perpendicular to the spontaneous polarization direction, as a direct consequence of the magnetocrystalline anisotropy from spin-orbit coupling. When the spontaneous polarization is rotated by the application of an electric field, the spin easy plane also rotates by the same angle. Furthermore, electric field-controlled Hahn spin echo studies have shown that the EPR spin echo can be manipulated by an electric field, thus presenting the possibility of an all-electric field manipulation of spins.

We expect dynamical effects in multiferroics to increase in importance over the next years, driven by new experimental capabilities such as ultrafast X-ray sources[121,122], and that the fundamental limits on the dynamics of spin-charge-lattice coupling phenomena will be experimentally established. Theoretical proposals of dynamical multiferroic phenomena, in which a time-dependent polarization induces a magnetization in the reciprocal manner from that in which spin spirals induce polarization[123] should be validated by careful experiments. At the same time, more work on antiferromagnetic resonance in multiferroics is required; while many studies were carried out in the 1960s [124] and 1970s on conventional antiferromagnets, such measurements with modern multiferroics, which typically have higher resonance frequencies (~700 GHz in $BiFeO_3$[125], compared with ~350 GHz in perovskite orthoferrites [126]), has been scarce. The recent surge in antiferromagnetic spintronics should be a welcome boost to such studies[127]. On top of the materials physics/chemistry issues outlined above, there is significant potential for translational research in this field. As discussed by Manipatruni et al., applications such as the MESO, logic-in-memory device will require integration with Si peripheral circuitry. While this was perceived to be a challenge twenty years ago, the process integration issues have all been well addressed in the process of integrating other oxide ferroelectrics (such as lead zirconate titanate and more recently, the hafnium zirconate tantalate ferroelectrics). But, it is also clear to us that one should get into the process integration after the key fundamental issues are sorted out.

It is clear that the field of multiferroics and magnetoelectrics is poised to make further significant breakthroughs and we hope that this article motivates additional research on this fascinating class of materials and their applications. While scientific interest in the field is beyond question, the need to identify market niches and enable pathways to products, so that multiferroics go beyond being an "area to watch" and address contemporary technological challenges. To achieve this, a shift of focus from fundamental materials discoveries to translational research and development will be needed, similar to that which occurred in the field of GaN-based light-emitting diodes two decades ago. The complexity of oxide-based material systems raises particular additional challenges, as we have seen for example in the colossal magnetoresistive manganites, making the active engagement of applied physicists and device engineers early in the research and development process even more essential. In this vein, the recent engagement of large microelectronic companies in the field of multiferroics[104,105] is particularly encouraging. While basic research in multiferroics is vibrant, the field would benefit from an injection of focused programs that address the transition to devices, in particular scale-up and integration issues.

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X. References

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[1] Manipatruni, S., D. E. Nikonov, and I. A. Young. "Beyond CMOS computing with spin and polarization." *Nature Physics* 14, no. 4 (2018): 338.

[2] H. N. Khan, D. A. Hounshell and E. R. H. Fuchs, "Science and research policy at the end of Moore's law", *Nature Electronics*, Vol. 1, 14–21(2018).

[3] Wikipedia

[4] Moore, Gordon E. "Cramming more components onto integrated circuits," *Proceedings of the IEEE* 86, no. 1 (1998): 82-85.

[5] Moore, Gordon E. "Cramming more components onto integrated circuits," *Proceedings of the IEEE* 86, no. 1 (1998): 82-85.

[6] Dennard, Robert H., V. L. Rideout, E. Bassous, and A. R. Leblanc. "Design of ion-implanted MOSFET's with very small physical dimensions." *IEEE Journal of Solid-State Circuits*, 9, no. 5 (1974): 256-268.

[7] Shannon, C. E. A Universal Turing machine with two internal states. *J. Symb. Log.* **36,** 532 (1971).

[8] Kuhn, Kelin J. "Considerations for ultimate CMOS scaling." *IEEE Trans. Electron Devices* 59, no. 7 (2012): 1813-1828.

[9] Ferain, Isabelle, Cynthia A. Colinge, and Jean-Pierre Colinge. "Multigate transistors as the future of classical metal-oxide-semiconductor field-effect transistors." *Nature* 479.7373 (2011): 310-316.

[10] Theis, Thomas N., and Paul M. Solomon. "It's time to reinvent the transistor!" *Science* 327, no. 5973 (2010): 1600-1601.

[11] Manipatruni, S., Nikonov, D. E. Lin, C.-C., Gosavi, T., Bhagwati, P., Huang, Y., Li, H., Ramesh, R. and Young, I. A., Magnetoelectric Spin Orbit Logic: A Scalable Charge Mediated Nonvolatile Logic, *Nature*, 5 6 5(2019), 35.

[12] S.Salahuddin and S.Datta, "The era of hyperscaling in electronics", *Nature Electronics*, VOL 442, 442–450(2018).

[13] David A Patterson and John L. Hennessy, Computer Architecture: A Quantitative Approach, Sixth Edition, Morgan Kaufman Publishers.

[14] William A. Borders, Ahmed Z. Pervaiz, Shunsuke Fukami, Kerem Y. Camsari, Hideo Ohno & Supriyo Datta, Integer factorization using stochastic magnetic tunnel junctions, *Nature*, Vol. 5 7 3 , p390 (2019).

[15] Adapted from, Gadgets and Gigawatts, Policies for Energy Efficient Electronics, International Energy Agency, 2009.

[16] S. Salahuddin, K. Ni and S. Datta, *Nature Electronics*, 1, (2018), 442-450.

[17] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen. Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O films. *Science* 264, 413-415 (1994).

[18] M. Imada, A. Fujimori and Y. Tokura, Metal-insulator transitions, *Reviews of Modern Physics*, Vol. 70, No. 4, p1039-1262, October 1998.

[19] S. Chikazumi, Physics of Magnetism, Wiley Publishers, 1964.

[20] B. Dieny et al., Opportunities and challenges for spintronics in the microelectronics industry, *Nature Electronics*, Vol. 446 (2020), p446–459.

[21] T. Wu, S.B. Ogale, J.E. Garrison, B. Nagaraj, A. Biswas, Z. Chen, R.L. Greene, R. Ramesh, and T. Venkatesan. Electroresistance and electronic phase separation in mixed-valent manganites. *Phys. Rev. Lett.* 86, 5998-6001 (2001).

[22] Song, C., Cui, B., Li, F., Zhou, X. and Pan, F., Recent progress in voltage control of magnetism: Materials, mechanisms, and performance, *Progress in Materials Science* **87**, 33-82 (2017).

---

[23] N.A. Spaldin and R.Ramesh, Advances in Magnetoelectric Multiferroics, *Nature Materials*, VOL 18(2019), 203–212.

[24] Schmid, H., Multiferroic magnetoelectrics, *Ferroelectrics* **162**, 317 (1994).

[25] Fiebig, M. Revival of the magnetoelectric effect, *J. Phys. D* **38**, R123 (2005).

[26] Ramesh, R. and Spaldin, N. A., Multiferroics: Progress and prospects in thin films, *Nature Mater.* **6**, 21 (2007).

[27] Areas to watch, *Science* **318**, 1858 (2007).

[28] Ullakko, K. "Magnetically controlled shape memory alloys: A new class of actuator materials". *Journal of Materials Engineering and Performance*. 5(1996), p 405–409. doi:10.1007/BF02649344. ISSN 1059-9495.

[29] Hill, N. A., Why are there so few magnetic ferroelectrics?, *J. Phys. Chem. B* **104**, 6694 (2000).

[30] Wang, Y., Hu, J., Lin, Y. and Nan, C.-W., Multiferroic magnetoelectric composite nanostructures, *NPG Asia Mater.* **2**, 61 (2010).

[31] Pyatakov, A. P. and Zvezdin, A. K., Magnetoelectric and multiferroic media, *Physics – Uspekhi* **55**, 557 (2012).

[32] Tokura, Y., Seki, S. and Nagaosa, N., Multiferroics of spin origin, *Rep. Prog. Phys.* **77**, 076501 (2014).

[33] Dong, S., Liu, J.-M., Cheong, S. W. and Ren, Z., Multiferroic materials and magnetoelectric physics: symmetry, entanglement, excitation, and topology, *Adv. Phys.* **64**, 519 (2015).

[34] Fiebig, M., Lottermoser, T., Meier D. and Trassin, M., The evolution of multiferroics, *Nature Rev. Mater.* **1**, 16046 (2016).

[35] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T, Tokura Y. 2003. *Nature* 426:55–58.

[36] Mundy, J. et al. Atomically engineered ferroic layers yield a room temperature magnetoelectric multiferroic. *Nature* 537, 523–527 (2016).

[37] Wang, J., Neaton, J. B., Zheng, H., Nagarajan, V., Ogale, S. B., Liu, B., Viehland, D., Vaithyanathan, V., Schlom, D. G., Waghmare, U. V., Spaldin, N. A., Rabe, K. M., Wuttig, M. and Ramesh, R., Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, *Science* **299**, 1719 (2003).

[38] Catalan, G. and Scott, J. F. Physics and applications of bismuth ferrite, *Adv. Mater.* **21**, 1 (2009).

[39] J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Physical Review* B 71, 014113 (2005).

[40] A.K. Zvezdin, A.M. Kadomtseva, S.S. Krotov, A.P. Pyatakov, Yu.F. Popov, G.P. Vorob'ev, Magnetoelectric interaction and magnetic field control of electric polarization in multiferroics, *Journal of Magnetism and Magnetic Materials* 300 (2006) 224–228.

[41] L. W. Martin, Y.H. Chu, M. B. Holcomb, M.Huijben, S.J. Han, D. Lee, S. X. Wang, and R. Ramesh, "Nanoscale control of exchange bias with $BiFeO_3$ thin films" *Nanoletters*. 8, 2050(2008).

[42] He, Q.; Yeh, C-H.; Yang, J-C.; Singh-Bhalla, G.; Liang, C-W.; Chiu, P-W.; Catalan, G.; Martin, L. W.; Chu, Y-H.; Scott, J. F.; Ramesh, R., Magnetotransport at Domain Walls in $BiFeO_3$, *Physical Review Letters*, 108.067203(2012).

[43] Yang, C. H., Kan, D., Takeuchi, I., Nagarajan, V. & Seidel, J. Doping $BiFeO_3$: approaches and enhanced functionality. *Phys. Chem. Chem. Phys.* 14, 15953–15962 (2012).

[44] Kan, D. et al. Universal behavior and electric-field-induced structural transition in rare-earth-substituted $BiFeO_3$. *Adv. Funct. Mater.* 20, 1108–1115(2010).

[45] Y. Huang et al., Manipulating magnetoelectric energy landscape in multiferroics, *Nature Communications* (2020), https://doi.org/10.1038/s41467-020-16727-2.

[46] Hiroshi Naganuma, Shintaro Yasui, Ken Nishida, Takashi Iijima, Hiroshi Funakubo, and Soichiro Okamura, *Journal of Applied Physics* 109, 07D917 (2011).

---

[47] Shintaro Yasui, Ken Nishida, Hiroshi Naganuma, Soichiro Okamura, Takashi Iijima, and Hiroshi Funakubo, Crystal Structure Analysis of Epitaxial $BiFeO_3$–$BiCoO_3$ Solid Solution Films Grown by Metalorganic Chemical Vapor Deposition, *Japanese Journal of Applied Physics*, Vol. 46, No. 10B, 2007, pp. 6948–6951.

[48] Shintaro Yasui, Osami Sakata, Mitsumasa Nakajima, Satoru Utsugi, Keisuke Yazawa, Tomoaki Yamada, and Hiroshi Funakubo, Piezoelectric Properties of {100}-Oriented Epitaxial $BiCoO_3$–$BiFeO_3$ Films Measured Using Synchrotron X-ray Diffraction, *Japanese Journal of Applied Physics* 48 (2009) 09KD06.

[49] Manish K. Singha, Yi Yanga, Christos G. Takoudis, *Coordination Chemistry Reviews* 253 (2009) 2920–2934.

[50] Maksymovych P, et al. (2012) Ultrathin limit and dead-layer effects in local polarization switching of $BiFeO_3$. *Phys Rev B* 85:014119.

[51] Zhong, W., Vanderbilt, D. and Rabe K. M., Phase transitions in $BaTiO_3$ from first principles, *Phys. Rev. Lett.* **73**, 1861 (1994).

[52] Rabe, K. M. and Waghmare, U. V., Localized basis for effective lattice Hamiltonians: Lattice Wannier functions, *Phys. Rev. B* **52**, 13236 (1995).

[53] Liu, S. and Grinberg, I. and Rappe, A. M. Development of a bond-valence based interatomic potential for $BiFeO_3$ for accurate molecular dynamics simulations, *J. Phys. Condens. Matter* **25**, 102202 (2013).

[54] Rahmedov, D., Wang, D., Íñiguez, J. and Bellaiche, L., Magnetic cycloid of $BiFeO_3$ from atomistic simulations, *Phys. Rev. Lett.* **109**, 037207 (2012).

[55] Karpinsky, D. V. et al., Thermodynamic potential and phase diagram for multiferroic bismuth ferrite ($BiFeO_3$), *NPJ Comp. Mater.* 3, 20 (2017).

[56] Garcia-Fernandez, P., Wojdel, J. C., Iniguez, J. and Junquera, J., Second-principles method for materials simulations including electron and lattice degrees of freedom, *Phys. Rev. B* **93**, 195137 (2016).

[57] Wojdel, J. C., Hermet, P., Ljungberg, M. P., Ghosez, P. and Iniguez, J., First-principles model potentials for lattice-dynamical studies: general methodology and example of application to ferroic perovskite oxides, *J. Phys.: Condens. Matter* **25** 305401 (2013).

[58] Liu, S. Grinberg I. and A. Rappe, A., *Nature* **534**, 360 (2016).

[59] Bhattacharjee, S., Rahmedov, D., Wang, D., Íñiguez, J. and Bellaiche, L., Ultrafast switching of the electric polarization and magnetic chirality in $BiFeO_3$ by an electric field, *Phys. Rev. Lett.* 112, 147601 (2014).

[60] Wang, D., Weerasinghe, J., Albarakati, A. and Bellaiche, L., Terahertz dielectric response and coupled dynamics of ferroelectrics and multiferroics from effective Hamiltonian simulations, *Int. J. Mod. Phys. B* **27**, 1330016 (2013).

[61] D.S. Rana, I. Kawayama, K. Mavani, K. Takahashi, H. Murakami, and M.Tonouchi, Understanding the Nature of Ultrafast Polarization Dynamics of Ferroelectric Memory in the Multiferroic $BiFeO_3$, *Adv. Mater.* 2009, 21, 2881–2885.

[62] Spaldin, N. A., Fiebig, M. and Mostovoy, M., The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect, *J. Phys.: Condens. Matter* **20**, 434203 (2008).

[63] Tolédano, P., Ackermann, M., Bohaty, L., Becker, P., Lorenz, T., Leo, N. and Fiebig, M., Primary ferrotoroidicity in antiferromagnets, *Phys. Rev. B* **92**, 094431 (2015).

[64] Zhao, T. *et al.* Electrical control of antiferromagnetic domains in multiferroic $BiFeO_3$ films at room temperature. *Nat. Mater.* **5,** 823–9 (2006).

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

---

[66] H. Zheng, J. Wang, S.E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S.R. Shinde, S.B. Ogale, F. Bai, D. Viehland, Y. Jia, D.G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, "Multiferroic $BaTiO_3$-$CoFe_2O_4$ Nanostructures," *Science* 303, 661 (2004).

[67] F. Zavaliche, H. Zheng, L.M. Ardabili, S.Y. Yang, Q. Zhan, P. Shafer, E. Reilly, R. Chopdekar, Y. Jia, P. Wright, D.G. Schlom, Y. Suzuki, and R. Ramesh. Electric field-induced magnetization switching in epitaxial columnar nanostructures. *Nano Lett.* 5, 1793-1796 (2005).

[68] Allibe, S. Fusil, K. Bouzehouane, C. Daumont, D. Sando, E. Jacquet, C. Deranlot, M. Bibes, and A. Barthélémy, *Nano Lett.* **12**, 1141 (2012).

[69] Heron, J. T., Bosse, J. L., He, Q., Gao, Y., Trassin, M., Ye, L., Clarkson, J. D. et al., Deterministic switching of ferromagnetism at room temperature using an electric field, *Nature* **516**, 370 (2014).

[70] Yu, P.; Luo, W.; Yi, D.; Zhang, J. X.; Rossell, M. D.; Yang, C. -H.; You, L.; Singh-Bhalla, G.; Yang, S. Y.; He, Q.; Ramasse, Q. M.; Erni, R.; Martin, L. W.; Chu, Y. H.; Pantelides, S. T.; Pennycook, S. J.; Ramesh, R., Interface control of bulk ferroelectric polarization, *Proc. Nat. Acad. Sci.*, 109, 9710 (2012).

[71] Wu, S. M. et al. Reversible electric control of exchange bias in a multiferroic field effect device. *Nature Mater.* **9**, 756 (2010).

[72] Y. Suzuki, Epitaxial Spinel Ferrite Thin Films, *Annu. Rev. Mater. Res.* 2001. 31:265–89.

[73] D Serrate, J M De Teresa and M R Ibarra, Double perovskites with ferromagnetism above room temperature, *J. Phys.: Condens. Matter* 19 (2007) 023201.

[74] He, X. et al., Robust isothermal electric control of exchange bias at room temperature, *Nature Mater*. 9, 579 (2010)].

[75] Cherifi, R. O. et al. Electric-field control of magnetic order above room temperature, *Nature Mater.* **13**, 345 (2014).

[76] Gruner, M., Hoffmann, E. & Entel, P. Instability of the rhodium magnetic moment as the origin of the metamagnetic phase transition in α-FeRh, *Phys. Rev. B* **67**, 064415 (2003).

[77] Moruzzi, V. L. & Marcus, P. M. Antiferromagnetic-ferromagnetic transition in FeRh, *Phys. Rev. B* **46**, 2864 (1992).

[78] Lee, Y. et al. Large resistivity modulation in mixed-phase metallic systems. *Nature Commun*. **6**, 5959 (2015).

[79] Liu, Z. Q. et al., Full electroresistance modulation in a mixed-phase metallic alloy. *Phys. Rev. Lett.* **116**, 097203 (2016).

[80] Di Yi, Jian Liu, Satoshi Okamoto, Suresha Jagannatha, Yi-Chun Chen, Pu Yu, Ying-Hao Chu, Elke Arenholz, and R. Ramesh, Tuning the Competition between Ferromagnetism and Antiferromagnetism in a Half-Doped Manganite through Magnetoelectric Coupling, *Physical Review Letters* 111, 127601 (2013).

[81] Heron, JT, Schlom, D.G , Ramesh, Electric field control of magnetism using $BiFeO_3$-based heterostructures, *Applied Physics Reviews* Volume: 1 Issue: 2 Article Number: 021303 DOI: 10.1063/1.4870957 Published: JUN 2014.

[82] Bhagwati Prasad, Yen-Lin Huang, Rajesh V. Chopdekar, Zuhuang Chen, James Steffes, Sujit Das, Qian Li, Mengmeng Yang, Chia-Ching Lin, Tanay Gosavi, Dmitri E. Nikonov,Zi Qiang Qiu, Lane W. Martin, Bryan D Huey, Ian Young, Jorge Íñiguez, Sasikanth Manipatruni, and Ramamoorthy Ramesh, Ultralow Voltage Manipulation of Ferromagnetism, *Adv. Mater.* 2020, 2001943.

[83] Manipatruni, S., Nikonov, D. E. and Young, I. A., Beyond CMOS computing with spin and polarization, *Nature Physics*, **14**, 338 (2018).

[84] Zutic, I., Fabian, J. and Das Sarma, S. Spintronics: Fundamentals and applications, *Rev. Modern Phys.*,**76**, 323 (2004).

---

[85] Nakayama, H., Kanno, Y., An, H., Tashiro, T., Haku, S., Nomura, A. and Ando, K., Rashba-Edelstein magnetoresistance in metallic heterostructures, *Phys. Rev. Lett.* **117**, 116602 (2016).

[86] Hoffmann, A. and Bader, S. D., Opportunities at the frontiers of spintronics, *Phys. Rev. Appl*. **4**, 047001 (2015).

[87] J. Li, B. Nagaraj, H. Liang, W. Cao, C. H. Lee, and R. Ramesh, *Appl. Phys. Lett.* 84, 1174 (2004).

[88] E. Parsonnet, Y.-L. Huang, T. Gosavi, A. Qualls, D. Nikonov, C.-C. Lin, I. Young, J. Bokor, L. W. Martin, R. Ramesh, *Phys. Rev. Lett.* 2020, 125, 067601.

[89] Rabe, Karin M., Ahn, Charles H., Triscone, Jean-Marc, Physics of Ferroelectrics, A Modern Perspective, *Springer Topics in Applied Physics* (2007).

[90] James J. Steffes, Roger A. Ristau, Ramamoorthy Ramesh, and Bryan D. Huey, Thickness scaling of ferroelectricity in $BiFeO_3$ by tomographic atomic force microscopy, *Proc. of the National Academy of Sciences*, pnas.org/cgi/doi/10.1073/pnas.1806074116 (2018).

[91] Chandra, P., Dawber, M., Littlewood, P. B. and Scott, J. F., Scaling of the Coercive Field with Thickness in Thin-Film Ferroelectrics, *Ferroelectrics* **313**, 7 (2004).

[92] Chu, Y. H., Zhan, Q., Yang, C.-H., Cruz, M. P., Martin, L. W., Zhao, T., Yu, P., Ramesh, R., Joseph, P. T., Lin, I. N., Tian, W. and Schlom, D. G., *Appl. Phys. Lett.* **92**, 102909 (2008).

[93] Maksymovych, P., Huijben, M., Pan, M., Jesse, S., Balke, N., Chu, Y.-H., Chang, H. J., Borisevich, A. Y., Baddorf, A. P., Rijnders, G., Blank, D. H. A., Ramesh, R. and Kalinin, S. V., *Phys. Rev. B* **85**, 014119 (2012).

[94] Lesne, E. Fu, Y., Oyarzun, S., Rojas-Sánchez, J. C., Vaz, D. C., Naganuma, H., Sicoli, G., Attané, J.-P., Jamet, M., Jacquet, E., George, J.-M., Barthélémy, A., Jarès, H., Fert, A., Bibes, M. and Vila, L., Highly efficient and tunable spin-to-charge conversion through Rashba coupling at oxide interfaces, *Nature Mater*. **15**, 1261 (2016)

[95] I. P. Batra, P. Wurfel, and B. D. Silverman, Phase Transition, Stability, and Depolarization Field in Ferroelectric Thin Films, *Physical Review B*, 8(1973) 3257.

[96] Anubhav Jain, Joseph Montoya, Shyam Dwaraknath, Nils, E. R. Zimmermann, John Dagdelen, Matthew Horton, Patrick Huck, Donny Winston, Shreyas Cholia, Shyue Ping Ong, and Kristin Persson, The Materials Project: *Accelerating Materials Design Through Theory-Driven Data and Tools*, W. Andreoni, S. Yip (eds.), Handbook of Materials Modeling, https://doi.org/10.1007/978-3-319-42913-7_60-1.

[97] R. Ramesh and Darrell G. Schlom, *Nature Review Materials*, 4 258 (2019).

[98] Site-specific spectroscopic measurement of spin and charge in $(LuFeO3)_m/(LuFe2O4)_1$ multiferroic superlattices, *Nature Communications* | (2020) 11:5582 | https://doi.org/10.1038/s41467-020-19285-9 .

[99] Yadav, A. K. et al. Observation of polar vortices in oxide superlattices. *Nature* 530, 198–201 (2016).

[100] Das, S. et al. Observation of room temperature polar skyrmions. *Nature* 568, 368-372 (2019).

[101] S. Das et al., Local negative permittivity and topological phase transition in polar skyrmions, *Nature Materials* (2020), https://doi.org/10.1038/s41563-020-00818-y.

[102] J. Mundy, et al., Liberating a hidden antiferroelectric phase with interfacial electrostatic engineering, *Science Advances*, submitted, (2021).

[103] O. Diéguez, O. E. González-Vázquez, J. C. Wojdeł, J. Íñiguez, First-principles predictions of low-energy phases of multiferroic $BiFeO_3$. *Phys. Rev. B*. **83**, 094105 (2011).

[104] Thompson D.P., Korgul P., Hendry A. (1983) The Structural Characterisation of Si-Al-O-N Polytypoids. In: Riley F.L. (eds) *Progress in Nitrogen Ceramics*. NATO ASI Series (Series E:

Applied Sciences), vol 65. Springer, Dordrecht. https://doi.org/10.1007/978-94-009-6851-6_4.

[105] T. Kimura, Magnetoelectric Hexaferrites, *Annu. Rev. Condens. Matter Phys*. 2012. 3:93–110.

[106] D. Lee and H.N. Lee, Controlling Oxygen Mobility in Ruddlesden–Popper Oxides, *Materials* 2017, 10(4), 368; https://doi.org/10.3390/ma10040368.

[107] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T, Tokura Y. 2003. *Nature* 426:55–58

[108] G. A. Smolenskii and I. E. Chupis, Ferroelectromagnets, *Usp. Fiz. Nauk* 137, 415-448 (1982).

[109] T. Chen et al., A new room temperature multiferroic bismuth hexaferrite, *Nature*, under revision (2021).

[110] Ikeda, N. et al. Ferroelectricity from iron valence ordering in the charge- frustrated system LuFe$_2$O$_4$. *Nature* 436, 1136–1138 (2005).

[111] W. Zhang, A. Chen, Z. Bi, Q. Jia , J. L. MacManus-Driscoll, H. Wang, "Interfacial coupling in heteroepitaxial vertically aligned nanocomposite thin films: From lateral to vertical control", *Current Opinion in Solid State and Materials Science*, 18 (2014) 6–18.

[112] Wu, R., et al., Self-biased magnetoelectric switching at room temperature in three phase ferroelectric-antiferroelectric-ferrimagnetic nanocomposites, Nature Electronics, 4, 333(2021).

[113] Scott, J. F. & Blinc, R. Multiferroic magnetoelectric fluorides:why are there so many magnetic ferroelectrics? *J. Phys.: Condens. Matter*. 23, 113202 (2011).

[114] Coey, J.M.D. and Smith, P.A.I., Magnetic nitrides, *Journal of Magnetism and Magnetic Materials* 200 (1999) 405}424.

[115] Jena, D. et al., The new nitrides: layered, ferroelectric, magnetic, metallic and superconducting nitrides to boost the GaN photonics and electronics eco-system, *Japanese Journal of Applied Physics* 58, SC0801 (2019).

[116] Talley, et al., K. R., Synthesis of ferroelectric LaWN3 - the first nitride perovskite, arXiv:2001.00633**.**

[117] Sarmiento-Pérez, R. et al., Prediction of Stable Nitride Perovskites, *Chem. Mater*. 2015, 27, 5957–5963.

[118] Zhang, S., et al., Tunable optoelectronic and ferroelectric properties in Sc-based III-nitrides, *J. Appl. Phys*. 114, 133510 (2013).

[119] J.Liu et al., Coherent Electric Field Manipulation of Fe^{+3}-spins in PbTiO$_3$, *Science Advances*, 7 : eabf8103 3 (2021).

[120] K. A. Müller, Paramagnetic point and pair defects in oxide perovskites, *J. Physique* 42 (1981) 551-557.

[121] For example, Linac Coherent Light Source (LCLS) at Stanford Linear Accelerator Center, Stanford University.

[122] Dhillon, S. S. et al., The 2017 terahertz science and technology road map, *J. Phys D: Appl. Phys.* **50**, 043001 (2017).

[123] Juraschek, D., Fechner, M., Balatsky, A.V. and Spaldin, N. A., Dynamical multiferroicity, *Phys. Rev. Mater.* **1**, 104401 (2017).

[124] Abraha, K. and Tilley, D. R., Theory of far infrared properties of magnetic surfaces, films and superlattices, *Surface Science Reports* **24**, 129 (1996).

[125] Talbayev, D., Trugman, S. A., Lee, S., Yi, H. T., Cheong, S.-W. and Taylor, A. J., Long-wavelength magnetic and magnetoelectric excitations in the ferroelectric antiferromagnet BiFeO$_3$, *Phys. Rev. B* **83**, 094403 (2011).

[126] Abraha, K. and Tilley, D. R., Theory of far infrared properties of magnetic surfaces, films and superlattices, *Surface Science Reports* **24**, 129 (1996).

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[127] T. Jungwirth, X. Marti, P. Wadley and J. Wunderlich, *Nature Nanotechnology* Vol. 11, 231(2016).