THE "HOLY GRAIL" OF MULTIFERROIC PHYSICS

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THE CROSS-CORRELATION PROBLEM: IS MAGNETISM CONTROLLABLE BY ELECTRIC FIELDS?

What happens if a compass' needle is held fixed in the presence of an external $\boldsymbol{B}$ field? If the $\boldsymbol{B}$ field is strong enough, the microscopic magnetic dipoles forming the magnet (Fig. 1) will reorient themselves within the material so that they get aligned parallel to $\boldsymbol{B}$ (with the needle's orientation remaining the same). It is this functionality that allows ferromagnetic materials to work as memory bits in a computer hard drive. A ferromagnet with $\boldsymbol{M}$ pointing up can represent bit "1", while $\boldsymbol{M}$ pointing down can represent bit "0". Writing "0" or "1" to a magnetic memory requires the application of a $\boldsymbol{B}$ field that is stronger than the magnetic anisotropy of the material. In today's computers this is achieved by running a large electric current to the hard drive write head [1] [See "Spin-based memory devices", by Arora *et al.* in this issue].

We can also build an "electric compass" that responds to an external electric field $\boldsymbol{E}$ in a similar way that the magnetic compass responds to $\boldsymbol{B}$. In this case we need to build the compass' needle out of a ferroelectric material, the electric analog of a ferromagnet. Such a material consists of a collection of microscopic electric dipoles (formed by equal numbers of positively and negatively charged atoms), all aligned with each other, giving rise to non-zero electric polarization density $\boldsymbol{P}$. Similarly to the magnetic case, if the material is held fixed, a strong $\boldsymbol{E}$ larger than the material's electric anisotropy would be able to force a reorientation of $\boldsymbol{P}$ inside the material. Ferroelectrics can also function as memories; in contrast to magnetic memories, the write operation can be achieved with an $\boldsymbol{E}$ field as opposed to a $\boldsymbol{B}$ field. This difference makes ferroelectric memories potentially faster, perhaps as fast as our current RAM, which use charged and discharged capacitors to represent each bit [2,3].

SUMMARY

Electric-field control of magnetism may bring bismuth ferrite ($BiFeO_3$) closer to the "holy grail" ferromagnet-ferroelectric at room temperature.

If we make a *composite* compass needle with ferromagnetic and ferroelectric materials attached to each other, the compass would certainly respond to both $\boldsymbol{E}$ and $\boldsymbol{B}$ simultaneously. But what would happen if the needle is held fixed in the presence of a strong $\boldsymbol{B}$ field? The answer is that for the overall majority of composite materials, the ferromagnet would reorient its $\boldsymbol{M}$ to point along $\boldsymbol{B}$, but the ferroelectric wouldn't care; its $\boldsymbol{P}$ would remain along the original direction. Similarly, if we were to apply a strong $\boldsymbol{E}$ instead of $\boldsymbol{B}$, the $\boldsymbol{P}$ would reorient, but the $\boldsymbol{M}$ wouldn't change. The reason for the absence of cross-correlation between electric and magnetic states is because the interactions coupling them are very small; they arise either from relativistic effects (such as spin-orbit coupling) or from the dependence of magnetic interactions on the distance between magnetic ions (the exchange striction effect ["Spin mechanics" by Losby and Freeman in this issue]).

MULTIFERROIC MATERIALS

One way around this problem is to obtain a material that displays both ferromagnetic and ferroelectric order within the same crystal structure and at the same temperature. In this case, a reorientation of one of the order parameters (either $\boldsymbol{M}$ or $\boldsymbol{P}$) would affect the material internally, perhaps forcing the other order parameter to change along. Then magnetism would be coupled to electricity, enabling a variety of applications. For example, we can imagine an ideal magnetic memory whose state could be written electrically (without the need for generating a $\boldsymbol{B}$ field from a current pulse) and read magnetically. Such a memory would minimize Joule heating allowing the integration of the hard drive with the processor in personal computers [4].

It turns out that a single crystal material with coexisting ferromagnetic and ferroelectric orders at room temperature has never been found and was never synthesized artificially in the laboratory. Its search is the subject of prolific research in the field of multiferroic materials – where the ferromagnet-ferroelectric at room temperature is often denoted the "holy grail" or "dream" material.

Multiferroic materials are defined as materials that possess at least two of the three ferroic or antiferroic orders at the same temperature: (Anti)ferromagnetism, (anti) ferroelectricity, and (anti)ferroelasticity [5] (See Fig. 1).

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Most multiferroic materials available to date combine antiferroic orders with ferroic ones. This includes one of the few materials who shows multiferroicity at room temperature, bismuth ferrite ($BiFeO_3$ or BFO for short), a strong antiferromagnet-ferroelectric in bulk and thin-film forms. The overall majority of multiferroics are low temperature. For example, strained films of $EuTiO_3$ become a strong ferromagnet-ferroelectric at $T < 4$ K [6], and the family of rare earth manganites $RMnO_3$ (R a rare earth atom such as Gd, Tb, Dy, . . .) display coexisting antiferromagnetism with ferroelectricity at $T < 30$ K. The reason why multiferroicity is such a rare property is because magnetism and ferroelectricity tend to be mutually exclusive [7]. The usual mechanism for ferroelectricity is a Jahn-Teller crystal distortion associated with *empty* d orbitals (consider, e.g., the textbook ferroelectric $BaTiO_3$ in which Ti^{4+} has no electrons in its d shell). In contrast, magnetism usually occurs in materials with *filled* d orbitals, such as in the transition metals Cr, Mn, Fe, Co, etc. For this reason, magnetoelectric multiferroics are rare.

Multiferroic materials can be classified in two types [8]. Type I multiferroics are the ones whose coexisting orders originate from independent mechanisms. For example, BFO becomes ferroelectric at $T < 1093$ K, where it is well into the paramagnetic phase; it becomes antiferromagnetic only at much lower temperatures (below 643 K). This indicates that the mechanism driving ferroelectricity is completely independent of the mechanism driving magnetism.

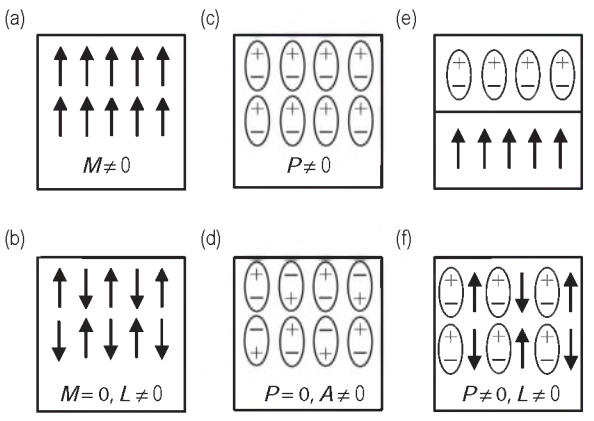

Fig. 1 (a) A ferromagnet described by order parameter $\boldsymbol{M}$, the magnetization. At $T < T_c$ $\boldsymbol{M}$ becomes non-zero spontaneously (with external $B = 0$). (b) An antiferromagnet with $\boldsymbol{M} = 0$ and staggered order parameter $\boldsymbol{L} = \boldsymbol{M}_1 - \boldsymbol{M}_2$ non-zero (here 1 and 2 refer to nearest-neighbor sublattices). (c) A ferroelectric described by order parameter $\boldsymbol{P}$, the electric polarization. At $T < T_c$, P becomes non-zero spontaneously (with external $E = 0$). (d) An antiferroelectric with $\boldsymbol{P} = 0$ and staggered polarization $\boldsymbol{A}$ non-zero. (e) A compound material made of a ferroelectric attached to a ferromagnet. (f) A multiferroic material showing coexistence of ferroelectricity and antiferromagnetism in the same crystal phase.

In contrast, type II multiferroics have one of its orders induced by the other one. For example, terbium manganite ($TbMnO_3$) is a frustrated magnet that becomes a collinear-sinusoidal antiferromagnet at temperatures $T < 41$ K; at $T < T_{\text{lock}} = 28$ K its magnetic phase changes to a non-collinear spiral (a cycloid, see below). As it turns out, at exactly at $T < T_{\text{lock}}$ the material also becomes ferroelectric [9]. This is not a coincidence; $TbMnO_3$ is an example of a material with magnetically induced ferroelectricity. The origin of its ferroelectricity is a special kind of magnetic interaction called spin-current interaction [10]:

$$\mathcal{H}_{\text{SC}} = \sum_{\langle i,j \rangle} J_{\text{SC}} \boldsymbol{P} \cdot [\boldsymbol{R}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)], \qquad (1)$$

where the sum runs over all nearest neighbors $\langle i, j \rangle$, with $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ representing the spins of ions located at $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$, respectively, with $\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$ denoting their separation vector. When the spins are aligned parallel or antiparallel to each other (collinear phase) the vector product in Eq. (1) is always zero, and the spin-current interaction has no effect. However, in a non-collinear spiral phase each non-zero $\boldsymbol{E}_{\langle i,j \rangle} = -J_{\text{SC}} \boldsymbol{R}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$ acts as an internal electric field that transforms the originally paraelectric material into a ferroelectric (Note how Eq. (1) can be written as $\mathcal{H}_{\text{SC}} = -\boldsymbol{P} \cdot \sum_{\langle i,j \rangle} \boldsymbol{E}_{\langle i,j \rangle}$, with $\boldsymbol{E}_{\langle i,j \rangle}$ of magnetic origin). This generates a spontaneous $\boldsymbol{P}$ that is controllable by a external magnetic field: applying a B field perpendicular to the spin spiral plane forces the spins to form a spiral in a different plane, rotating $\boldsymbol{P}$ by 90° [9].

While type II multiferroics can be viewed as the ideal material to search for strong coupling between magnetism and ferroelectricity, their multiferroicity usually occurs at low temperatures, and their secondary order parameter ($\boldsymbol{P}$ for magnetically induced ferroelectricity) is quite weak. This does not make type II multiferroics attractive for applications. For example, in $TbMnO_3$ the largest P is less than 0.1 μC/cm^2. In contrast, the type I multiferroic BFO has room temperature multiferroicity with $P = 100$ μC/cm^2 (among the largest P of all ferroelectrics).

ELECTRIC-FIELD CONTROL OF MAGNETISM IN BFO

Can we control magnetism with an external E field in type I multiferroics? The answer is a definite yes as shown by many experiments in bulk and thin-film BFO. The key mechanism is once again the spin-current interaction Eq. (1). When BFO becomes antiferromagnetic at $T < 643$ K, its $\boldsymbol{P}$ is already quite close to the maximum value of 100 μC/cm^2, pointing along one of the eight cube diagonals of the perovskite unit cell (Fig. 2a). Antiferromagnetism sets in in the presence of a very strong $\boldsymbol{P}$,

and the spin-current interaction drives an instability towards a spiral magnetic state. In other words, in BFO the spin-current interaction has the inverse effect that it has in $TbMnO_3$: Here it causes spin frustration instead of ferroelectricity. This leads to an inhomogeneous magnetic state, with order parameters depending on position [11–13]:

$$\boldsymbol{L}(\boldsymbol{r}) = L_0\left[\sin(\boldsymbol{q}\cdot\boldsymbol{r}+\phi_0)\,\hat{\boldsymbol{q}} + \cos(\boldsymbol{q}\cdot\boldsymbol{r}+\phi_0)\,\hat{\boldsymbol{P}}\right], \qquad (2a)$$

$$\boldsymbol{M}(\boldsymbol{r}) = M_0(\hat{\boldsymbol{\omega}}_{\mathrm{AFD}}\times\boldsymbol{q})\sin(\boldsymbol{q}\cdot\boldsymbol{r}), \qquad (2b)$$

with amplitudes $L_0 = 4.1\mu_B$/Fe and $M_0 = 0.09\mu_B$/Fe [14]. Thus the antiferromagnetic order parameter $\boldsymbol{L}$ forms a spiral of the cycloid type (wavevector $\boldsymbol{q}$ in the same plane as the spins), with $\boldsymbol{M}$ displaying sinusoidal order along a single direction perpendicular to the cycloid plane (the antiferrodistortion vector $\hat{\boldsymbol{\omega}}_{\mathrm{AFD}}$ describes a staggered rotation of oxygen octahedra in the perovskite cells; $\hat{\boldsymbol{\omega}}_{\mathrm{AFD}}$ can point parallel or antiparallel to $\boldsymbol{P}$). Both order parameters average out to zero at macroscopic length scales larger than the cycloid wavelength $2\pi/q = 620$ Å.

A key feature is that the cycloid's wavevector $\boldsymbol{q}$ is "tied" to $\boldsymbol{P}$ so that the spin-current energy Eq. (1) is minimized. As a result, $\boldsymbol{q}$ is always perpendicular to $\boldsymbol{P}$. This dependence of $\boldsymbol{q}$ on $\boldsymbol{P}$ is central to all experimental demonstrations of electric control of magnetism in BFO. Applying external $E > 3.5 \times 10^4$ V/cm switches $\boldsymbol{P}$ from one cube diagonal to the other, forcing the cycloid plane to change accordingly (Fig. 2b). This effect was demonstrated in pure bulk BFO using neutron diffraction measurements [15]. In addition, it enabled E-field control of ferromagnetism in a junction formed by CoFe (a room temperature ferromagnet) and BFO. Switching BFO's $\boldsymbol{P}$ domains by 180° was shown to switch the CoFe's $\boldsymbol{M}$ domains by 180°, a remarkable effect whose origin is not yet completely understood [16,17]. A similar control of exchange bias (a shift of magnetic hysteresis used in hard drive write heads) was demonstrated in junctions formed by $LaMnO_3$ and BFO [18]. Based on these remarkable experiments, one may be inclined to believe that the only way to control magnetism in a type I multiferroic such as BFO is to switch $\boldsymbol{P}$ from one equilibrium direction to the other (Fig. 2b). Actually, our research has found that this is not the whole story. A key development was our realization that BFO's cycloid state makes it much more "visible" with optics [19]. When we shine light on BFO, the optical electric field produces vibrations of $\boldsymbol{P}$. Since the spins are confined to the plane of $\boldsymbol{P}$ and $\boldsymbol{q}$, these vibrations generate magnetic excitations, the so called spin waves or magnons [See "Instability processes for manganese in ferromagnetic nanostructures" by Cottam and Haghshenasfard in this issue]. As shown in Fig. 3, there are two kinds of magnons: The ones that are within the cycloid plane (tangential to the cycloid), and the ones that are perpendicular to the cycloid plane. We call these cyclons (denoted by ϕ) and extra-cyclons (ψ), respectively.

The cycloid breaks translation symmetry along the $\boldsymbol{q}$ direction, so that the spin waves are not simple plane waves like $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$; they are in fact Bloch states, i.e., linear combinations of plane waves with higher harmonics. As a result, an optical excitation with wave vector $\boldsymbol{k}$ is capable of exciting cyclon and extra-cyclon modes at $\boldsymbol{k} + n\boldsymbol{q}$ where n is an integer. In other words,

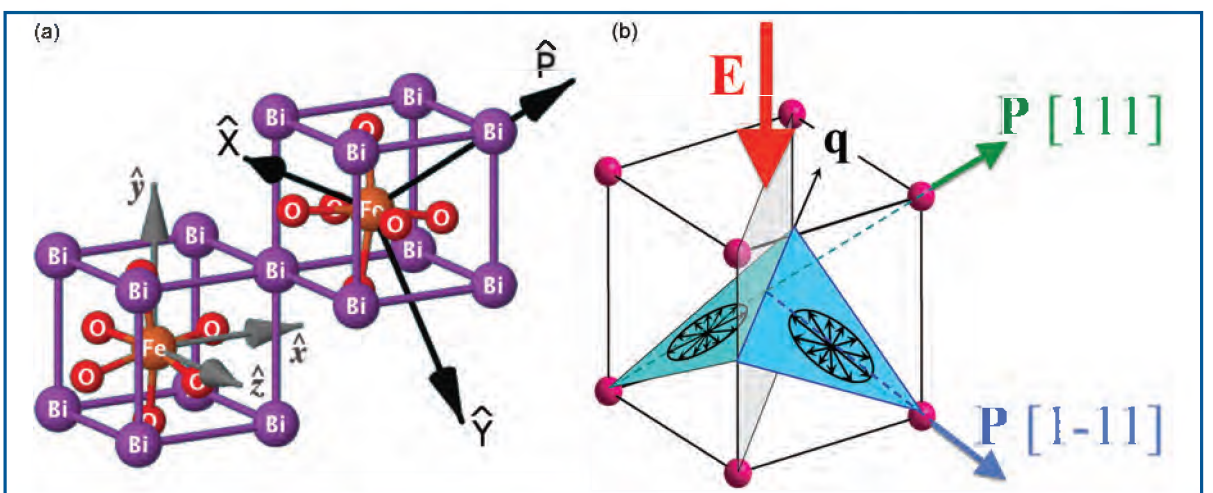

Fig. 2 (a) Crystal lattice of room temperature multiferroic $BiFeO_3$ (BFO). The ferroelectric moment P arises from the ionic displacement of cations (Fe, Bi) relative to anions (O). Due to electric anisotropy, $\boldsymbol{P}$ points along one of the eight cube diagonals of the perovskite unit cell. (b) E-field control of magnetism by switching $\boldsymbol{P}$. In BFO the Fe spins are ordered antiferromagnetically with a weak ferromagnetic moment ($L \gg M > 0$). $\boldsymbol{L}$ forms a cycloidal spiral with wavelength $2\pi/q = 620$ Å. The plane of the cycloid is tied to $\boldsymbol{P}$. Therefore, when $\boldsymbol{P}$ is switched with an external E field, the cycloid plane is forced to change.

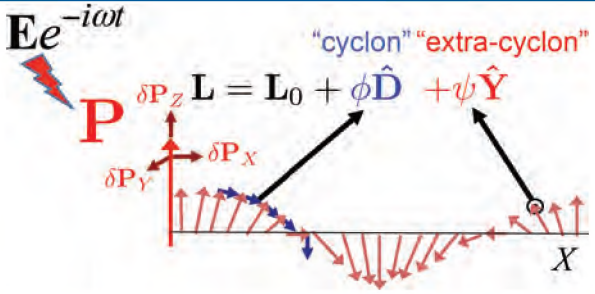

Fig. 3 Magnetic excitations of the spin cycloid. An oscillatory electric field (e.g., light) vibrates $\boldsymbol{P}$, producing in plane spin fluctuations (cyclons ϕ) and out of plane fluctuations (extra cyclons ψ).

light scattering is able to emit and absorb magnons with wave vectors $\boldsymbol{k}' = \boldsymbol{k} + n\boldsymbol{q}$, giving rise to a series of optical resonances that "map out" the magnon dispersion relations. Indeed, Raman scattering experiments in bulk BFO reveal the presence of two distinct series of optical resonances: The cyclons at frequency $\omega_\phi(nq) \propto |n|$ and the extra-cyclons with frequency $\omega_\psi(nq) \propto \sqrt{1+n^2}$, with n integer [20]. Later it was shown that the modes split in the presence of magnetic anisotropy [21] and external B field [22]. These optical experiments are much more sensitive than neutron scattering measurements; while neutron scattering requires large bulk samples, optical scattering can be done in much smaller samples, including gated devices and thin films.

A NEW TYPE OF MAGNETIC CONTROL IN MULTIFERROICS: *E*-FIELD CONTROL WITHOUT SWITCHING *P*

This led us to try an experiment. Using Raman scattering, we tracked the frequency of the cyclonic magnons as a function of an external E field. The result was quite surprising [23]: The magnon frequencies displayed a hysteresis loop as a function of E that was quite different from the P vs. E ferroelectric loop. Remarkably, some of the magnon frequencies shifted by as much as 5 cm^{-1} *without switching* $\boldsymbol{P}$. Such a shift is considered gigantic, in view of the fact that it is 10^5 times larger than previous measurements of E-field magnon shifts [24].

Our interpretation of this result was that BFO possessed an additional interaction energy coupling E fields to spins. Using microscopic theory, we were able to show [25] that BFO's magnetic anisotropy energy is quite sensitive to an applied E-field, leading to the following energy density,

$$\mathcal{H}_E = -\frac{\xi'}{4}\boldsymbol{E}_\perp \cdot \left[\left(L_Y^2 - L_X^2\right)\hat{\boldsymbol{X}} + 2L_XL_Y\hat{\boldsymbol{Y}} + 2\sqrt{2}L_Z\boldsymbol{L}\right], \quad (3)$$

where $\boldsymbol{E}_\perp$ is the component of the E field perpendicular to $\boldsymbol{P}$, and $\boldsymbol{L}$ is the antiferromagnetic order parameter in cgs units. The coupling energy ξ' was measured to be $\xi' = 1/(2 \times 10^4$ V/cm), a value anomalously large for a magnetoelectric effect. In addition, ξ' was shown to scale with material properties as [25].

$$\xi' \propto \frac{\Delta_{SO}^2 P}{\Delta_{gap}^2}, \quad (4)$$

where Δ_{SO} is the spin orbit splitting of the 6p orbitals of bismuth, and Δ_{gap} is BFO's band gap energy. Hence, the large ξ' stems from the large values of Δ_{SO} and P. Both are among the largest in nature: Bi has the largest spin-orbit splitting of all non-radioactive atoms of the periodic table; and BFO has one of the largest values of P of all ferroelectrics. Therefore, the coexistence of two phases (ferroelectricity and antiferromagnetism) acts to amplify a particular property (magnetic anisotropy as a function of E field).

Under the application of an external E field, the interaction (3) will compete against the usual ($E = 0$) magnetic anisotropy energy, giving rise to the E-field phase diagram shown in Fig. 4. It leads to the prediction that an external E field along particular directions in the plane perpendicular to P can convert the cycloid into a homogeneous antiferromagnet ($\boldsymbol{L}$ independent of $\boldsymbol{r}$) with the direction of $\boldsymbol{M}$ and $\boldsymbol{L}$ controllable by the particular direction that $\boldsymbol{E}_\perp$ is applied. We predict that a minimum $E = 9 \times 10^4$ V/cm is required to unwind the cycloid[1].

Our prediction of E-field control of magnetism without switching $\boldsymbol{P}$ is yet to be realized experimentally. Such a demonstration would open up a pathway for E-field control of magnetism that avoids charge displacement and energy dissipation associated to the relaxation of $\boldsymbol{P}$ into another direction (switching $\boldsymbol{P}$ dissipates 5 J/m^2) [26]. In BFO, the weak magnetization $\boldsymbol{M} \propto \hat{\boldsymbol{Z}} \times \boldsymbol{L}$ is tied to $\boldsymbol{L}$. Thus our predicted mechanism allows the electrical switching of $\boldsymbol{M}$ from a sinusoidal state with zero spatial average to a homogeneous state with non-zero $\langle \boldsymbol{M} \rangle$. This effect converts an E-field pulse into a magnetic pulse. By combining BFO with another magnetic material (as done in [16,17]), we can envision the writing of data in a magnetic memory element using an E-field pulse in an insulator instead of the usual current pulse in a metal.

1. An important point is that $\boldsymbol{P}$ can be switched by the external E-field, changing the effective direction of $\boldsymbol{E}_\perp$ in Fig. 4 (note that Fig. 4 assumes $\boldsymbol{P} \,//\, [111]$ at all magnitudes of $\boldsymbol{E}_\perp$). To avoid switching, one can apply the E-field with the largest component along the [111] direction. For example, using $\boldsymbol{E} = E[\cos(30°)\hat{\boldsymbol{Z}} - \sin(30°)\hat{\boldsymbol{X}}]$ allows control of magnetism without changing $\boldsymbol{P}$, at the expense of having $\boldsymbol{E}_\perp = E/2$. Using $\xi' = 1/(2 \times 10^4$ V/cm) we get that a minimum $E = 0.9 \times 10^5$ V/cm is required to induce the homogeneous state, a value that falls in the practical range.

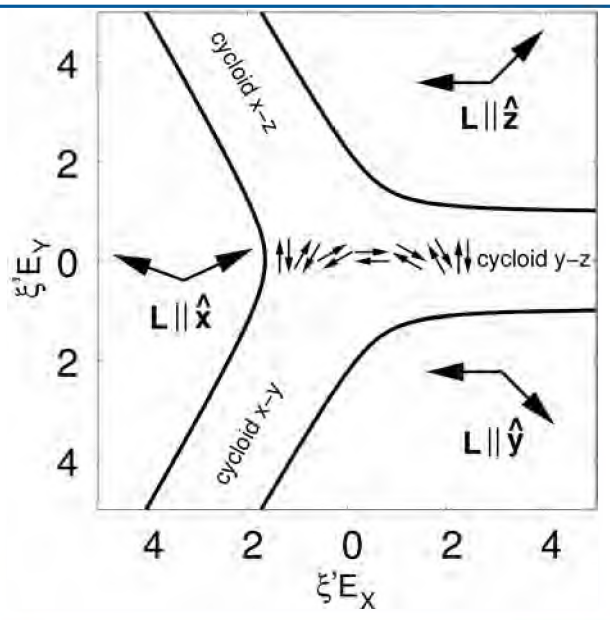

Fig. 4 Predicted phase diagram for BFO as a function of an external electric field [25]. E fields of the order of $1/\xi' = 2 \times 10^4$ V/cm applied along certain directions in the plane perpendicular to $\boldsymbol{P}(\hat{\boldsymbol{X}}, \hat{\boldsymbol{Y}}$ plane in Fig. 2a) are capable of unwinding the spin cycloid, converting BFO into a homogeneous antiferromagnet with canted ferromagnetic moment that does not average out over macroscopic length scales. The directions of $\boldsymbol{L}$ and $\boldsymbol{M}$ are controllable by the direction of $\boldsymbol{E}$.

CHALLENGE FOR FUTURE RESEARCH: CAN WE MAKE KNOWN MULTIFERROICS CLOSER TO THE "HOLY GRAIL" FERROELECTRIC-FERROMAGNET?

Despite all these amazing effects, BFO still falls short of being the holy grail of multiferroic physics. Its ferromagnetic moment is sinusoidal in bulk samples, with a quite small amplitude ($M_0 = 0.09\mu_B$/Fe). The challenge for future research is to figure out a way to increase M_0 in BFO and related structures.

One possibility is to apply strain, or to combine strain with applied E fields. Recent experiments in thin-film samples of BFO show that the cycloid is unwound in the presence of large epitaxial strain [27]. The origin of this effect is thought to be due to additional magnetic anisotropy, but no microscopic theory has been carried out to confirm this scenario. Indeed, strain was shown to tranform $EuTiO_3$ into a strong ferromagnet-ferroelectric at low temperatures [6]. Who knows whether there exists a magical region in BFO's strain- E field phase diagram where M_0 is amplified. Perhaps this is wishful thinking, but BFO has given us so many surprises that we feel enticed to speculate.

Another promising direction is the exploration of the proximity effect. When BFO is interfaced with a strong ferromagnet such as CoFe [16,17] its magnetic order is subject to a strong local magnetic field that can unwind the cycloid [22] and increase M_0 for BFO's Fe spins close to the interface. The length scale for such a proximity effect has never been measured or calculated. Such a length scale would characterize an interface "holy grail" with strong $\boldsymbol{P}$ and $\boldsymbol{M}$.

Finally, there exists an exciting effort to synthesize new materials closely related to BFO. Thin films of Bi_2FeCrO_6 (BFCO) were shown to be a strong ferroelectric and perhaps ferrimagnetic at room temperature [28].

The search for the "holy grail" ferromagnet-ferroelectric at room temperature is at full steam, either by synthesizing new materials or by modifying existing ones. While we may never find it, we have already discovered one thing: that searching for it brings out remarkable phenomena in material science and condensed matter physics.

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