Multiferroics: a magnetic twist for ferroelectricity

Magnetism and ferroelectricity are essential to many forms of current technology, and the quest for multiferroic materials, where these two phenomena are intimately coupled, is of great technological and fundamental importance. Ferroelectricity and magnetism tend to be mutually exclusive and interact weakly with each other when they coexist. The exciting new development is the discovery that even a weak magnetoelectric interaction can lead to spectacular cross-coupling effects when it induces electric polarization in a magnetically ordered state. Such magnetic ferroelectricity, showing an unprecedented sensitivity to applied magnetic fields, occurs in ‘frustrated magnets’ with competing interactions between spins and complex magnetic orders. We summarize key experimental findings and the current theoretical understanding of these phenomena, which have great potential for tuneable multifunctional devices.

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In 1865, James Clerk Maxwell proposed four equations governing the dynamics of electric fields, magnetic fields and electric charges, which are now known as Maxwell’s equations1. They show that magnetic interactions and motion of electric charges, which were initially thought to be two independent phenomena, are intrinsically coupled to each other. In the covariant relativistic form, they reduce to just two equations for the electromagnetic field tensor, succinctly reflecting the unified nature of magnetism and electricity2. A number of interesting parallels exist between electric and magnetic phenomena, such as the quantum scattering of charge off magnetic flux (Aharonov–Bohm effect3) and the scattering of magnetic dipoles off a charged wire (Aharonov–Casher effect4). The formal equivalence of the equations of electrostatics and magnetostatics in polarizable media explains numerous similarities in the thermodynamics of ferroelectrics and ferromagnets, for example their behaviour in external fields, anomalies at a critical temperature, and domain structures. These similarities are particularly striking in view of the seemingly different origins of ferroelectricity and magnetism in solids: whereas magnetism is related to ordering of spins of electrons in incomplete ionic shells, ferroelectricity results from relative shifts of negative and positive ions that induce surface charges.

Magnetism and ferroelectricity coexist in materials called multiferroics. The search for these materials is driven by the prospect of controlling charges by applied magnetic fields and spins by applied voltages, and using this to construct new forms of multifunctional devices. Much of the early work on multiferroics was directed towards bringing ferroelectricity and magnetism together in one material5. This proved to be a difficult problem, as these two contrasting order parameters turned out to be mutually exclusive6–10. Furthermore, it was found that the simultaneous presence of electric and magnetic dipoles does not guarantee strong coupling between the two, as microscopic mechanisms of ferroelectricity and magnetism are quite different and do not strongly interfere with each other11,12.

The long-sought control of electric properties by magnetic fields was recently achieved in a rather unexpected class of materials known as ‘frustrated magnets’, for example the perovskites RMnO3, RMnO2 (R: rare earths), Ni3V2O8, delafossite CuFeO2, spinel CoCrO4, MnWO4, and hexagonal ferrite (Ba,Sr)ZnFe12O22 (refs 13–20). Curiously, it is not the strength of the magnetoelectric coupling or high magnitude of electric polarization that makes these materials unique; in fact, the coupling is weak, as usual, and electric polarization is two to three orders of magnitude smaller than in typical ferroelectrics. The reason for the high sensitivity of the dielectric properties to an applied magnetic field lies in the magnetic origin of their ferroelectricity, which is induced by complex spin structures, characteristic of frustrated magnets13,21–27. Recent reviews of this rapidly developing field can be found in refs 28–30. Here, we mainly focus on the relationship between magnetic frustration and ferroelectricity, discuss different types of multiferroic materials and mechanisms inducing electric polarization in magnetic states, and outline the directions of the future research in this field.

PROPER AND IMPROPER FERROELECTRICS

Why is it difficult to find materials that are both ferroelectric and magnetic10,11? Most ferroelectrics are transition metal oxides, in which transition ions have empty d shells. These positively charged ions like to form ‘molecules’ with one (or several) of the neighbouring negative oxygen ions. This collective shift of cations and anions inside a periodic crystal induces bulk electric polarization. The mechanism of the covalent bonding (electronic pairing) in such molecules is the virtual hopping of electrons from the filled oxygen shell to the...
Table 1 Classification of ferroelectrics

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<thead>
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<th>Mechanism of inversion symmetry breaking</th>
<th>Materials</th>
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<tr>
<td>Proper</td>
<td>Covalent bonding between 3d electronic transition metal (Ti) and oxygen</td>
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<td>Polarization of 6s$^1$ lone pair of Bi or Pb</td>
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<td>Improper</td>
<td>Structural transition</td>
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<td>‘Electronic ferroelectrics’</td>
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empty $d$ shell of a transition metal ion. Magnetism, on the contrary, requires transition metal ions with partially filled $d$ shells, as the spins of electrons occupying completely filled shells add to zero and do not participate in magnetic ordering. The exchange interaction between uncompensated spins of different ions, giving rise to long-range magnetic ordering, also results from the virtual hopping of electrons between the ions. In this respect the two mechanisms are not so dissimilar, but the difference in filling of the $d$ shells required for ferroelectricity and magnetism makes these two ordered states mutually exclusive.

Still, some compounds, such as BiMnO$_3$ or BiFeO$_3$ with magnetic Mn$^{3+}$ and Fe$^{3+}$ ions, are ferroelectric. Here, however, it is the Bi ion with two electrons on the 6s orbital (lone pair) that moves away from the centrosymmetric position in its oxygen surrounding.$^{32}$ Because the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak. For example, BiMnO$_3$ shows a ferroelectric transition at $T_{FE} \approx 800$ K and a ferromagnetic transition at $T_{FM} \approx 110$ K, below which the two orders coexist.$^{32}$ BiMnO$_3$ is a unique material, in which both magnetization and electric polarization are reasonably large.$^{21,23,33,34}$ This, however, does not make it a useful multiferroic. Its dielectric constant $\varepsilon$ shows only a minute anomaly at $T_{FE}$ and is fairly insensitive to magnetic fields: even very close to $T_{FE}$, the change in $\varepsilon$ produced by a 9-T field does not exceed 0.6%.

In the ‘proper’ ferroelectrics discussed so far, structural instability towards the polar state, associated with the electronic pairing, is the main driving force of the transition. If, on the other hand, polarization is only a part of a more complex lattice distortion or if it appears as an accidental by-product of some other ordering, the ferroelectricity is called ‘improper’$^{11}$ (see Table 1). For example, the hexagonal manganites RMnO$_3$ (R = Ho–Lu, Y) show a lattice transition which enlarges their unit cell. An electric dipole moment, appearing below this transition, is induced by a nonlinear coupling to nonpolar lattice distortions, such as the buckling of R–O planes and tilts of manganese–oxygen bipyramids (geometric ferroelectricity)$^{31,33,36}$.

Another group of improper ferroelectrics, discussed recently, are charge-ordered insulators. In many narrowband metals with strong electronic correlations, charge carriers become localized at low temperatures and form periodic superstructures. The celebrated example is the magnetite Fe$_3$O$_4$, which undergoes a metal–insulator transition at $T_{CO}$, with two electrons on the 6s orbital (lone pair) that moves away from the centrosymmetric position in its oxygen surrounding.$^{32}$ Because the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak. For example, BiMnO$_3$ shows a ferroelectric transition at $T_{FE} \approx 800$ K and a ferromagnetic transition at $T_{FM} \approx 110$ K, below which the two orders coexist.$^{32}$ BiMnO$_3$ is a unique material, in which both magnetization and electric polarization are reasonably large.$^{21,23,33,34}$ This, however, does not make it a useful multiferroic. Its dielectric constant $\varepsilon$ shows only a minute anomaly at $T_{FE}$ and is fairly insensitive to magnetic fields: even very close to $T_{FE}$, the change in $\varepsilon$ produced by a 9-T field does not exceed 0.6%.

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transition at ~125 K (the Verwey transition) with a rather complex pattern of ordered charges of iron ions\(^7\). When charges order in a non-symmetric fashion, they induce electric polarization. It has been suggested that the coexistence of bond-centred and site-centred charge orders in Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) leads to a non-centrosymmetric charge distribution and a net electric polarization\(^8\) (see Fig. 1a). A polar lattice distortion induced by charge ordering has been reported in the bilayer manganite Pr(Sr\(_x\)Ca\(_{1-x}\))\(_2\)MnO\(_3\), which also shows an interesting reorientation transition of orbital stripes\(^9\). Charge ordering in LuFe\(_2\)O\(_4\), crystallizing in a bilayer structure, also appears to induce electric polarization. The average valence of Fe ions in LuFe\(_2\)O\(_4\) is 2.5+, and in each layer these ions form a triangular lattice. As suggested in ref. 40, the charge ordering below ~350 K creates alternating layers with Fe\(^{2+}\):Fe\(^{3+}\) ratios of 2:1 and 1:2, inducing net polarization (see Fig. 1c).

FERROELECTRICITY IN FRUSTRATED MAGNETS

Naturally, improper ferroelectricity puts lower constraints on the coexistence with magnetism. In fact, materials with electric dipoles induced by magnetic ordering are the best candidates for useful multiferroics, because such dipoles are highly tuneable by applied magnetic fields. The current revolution in the field of multiferroics began with the discovery of the high magnetic tuneability of electric polarization and dielectric constant in the orthorhombic rare-earth manganites Tb(Dy)MnO\(_3\) and Tb(Dy)MnO\(_5\) (refs 13,14,41,42). The onset of ferroelectricity in TbMnO\(_5\) clearly correlates with the appearance of spiral magnetic ordering at ~28 K (ref. 43). In applied magnetic fields, Tb(Dy)MnO\(_3\) shows a spin-flop transition, at which the polarization vector rotates by 90° (see Fig. 2a) and the dielectric constant \(\varepsilon\) (in DyMnO\(_3\)) increases.

**Figure 2** High magnetic tunability of magnetic ferroelectrics. **a**, Electric polarization in perovskite TbMnO\(_3\) versus magnetic field along the \(c\) axis\(^{11}\). The magnetic field of ~5 T flips the direction of electric polarization from the \(c\) axis to the \(a\) axis. Numbers show the sequence of magnetic field variation. **b**, Dielectric constant \(\varepsilon\) along the \(a\) axis versus magnetic field along the \(c\) axis at various temperatures in perovskite DyMnO\(_3\). The sharp peak in \(\varepsilon\) accompanies the flipping of electric polarization from the \(c\) axis to \(a\) axis. **c**, The highly reversible 180° flipping of electric polarization along the \(b\) axis in TbMnO\(_3\) can be activated by applying magnetic fields along the \(a\) axis\(^{14}\). **d**, The temperature dependence of \(\varepsilon\) along the \(b\) axis in DyMnO\(_3\) in various magnetic fields. The magnitude of the step-like increase of \(\varepsilon\) below ~25 K is strongly field-dependent. Parts **b** and **d** are reprinted with permission from refs 42 and 41, respectively. Copyright (2004) APS.
by ~500% in a narrow field range. This colossal magneto-dielectric effect is shown in Fig. 2b.

Many of the rare-earth manganites RMnO₃, where R denotes rare earths from Pr to Lu, Bi and Y, show four sequential magnetic transitions: incommensurate sinusoidal ordering of Mn spins at \( T_2 = 42–45 \) K, commensurate antiferromagnetic ordering at \( T_3 = 38–41 \) K, re-entrance transition into the incommensurate sinusoidal state at \( T_4 = 20–25 \) K, and finally, an ordering of rare-earth spins below \( T_N \leq 10 \) K (ref. 44–49). Ferroelectricity sets in at \( T_2 \) and gives rise to a peak in \( \varepsilon \) at this magnetic transition (see Fig. 3d).

Furthermore, \( \varepsilon \) in DyMnO₃ shows a remarkably strong dependence on magnetic fields below \( T_4 \) (see Fig. 2d)⁴⁰. The magnetic field rotates the electric polarization of TbMn₂O₅ by 180° in a highly reversible way, as shown in Fig. 2c.

Complex magnetic structures and phase diagrams are observed in all multiferroics showing strong interplay between magnetic and dielectric phenomena⁴¹–⁴⁸. All these materials are ‘frustrated’ magnets, in which competing interactions between spins preclude simple magnetic orders. The disordered paramagnetic phase in frustrated magnets extends to unusually low temperatures. For example, the Curie–Weiss temperature, \( T_{\text{CW}} \), of YMnO₃, obtained by fitting its magnetic susceptibility \( \chi \) with the high-temperature asymptotic, \( \chi \approx (C/(T+T_{\text{CW}})) \), is ~250 K (see Fig. 3b). The temperature \( T_{\text{CW}} \) reflects the strength of interaction between spins, and in usual magnets it gives a good estimate of the spin ordering temperature. The fact that the long-range magnetic order sets in at \( T_N \approx 45 \) K, which is about five times smaller than \( T_{\text{CW}} \), is clear indication for the presence of significant magnetic frustration in YMnO₃.

**HOW MAGNETIC SPIRALS INDUCE FERROELECTRICITY**

The key questions are how it is possible that magnetic ordering can induce ferroelectricity and what role of frustration is. The coupling between electric polarization and magnetization is governed by the symmetries of these two order parameters, which are very different. The electric polarization \( \mathbf{P} \) and electric field \( \mathbf{E} \) change sign on the inversion of all coordinates, \( r \rightarrow -r \), but remain invariant on time reversal, \( t \rightarrow -t \). The magnetization \( \mathbf{M} \) and magnetic field \( \mathbf{H} \) transform in precisely the opposite way: spatial inversion leaves them unchanged, whereas the time reversal changes sign. Because of this difference in transformation properties, the linear coupling between \( \mathbf{P} \) and \( \mathbf{E} \) and \( \mathbf{M} \) and \( \mathbf{H} \) described by Maxwell’s equations is only possible when these vectors vary both in space and in time: for example, spatial derivatives of \( \mathbf{E} \) are proportional to the time derivative of \( \mathbf{H} \) and vice versa.

The coupling between static \( \mathbf{P} \) and \( \mathbf{M} \) can only be nonlinear. Nonlinear coupling results from the interplay of charge, spin, orbital and lattice degrees of freedom. It is always present in solids, although it is usually weak. Whether it can induce polarization in a magnetically ordered state crucially depends on its form. A small energy gain proportional to \( -\mathbf{P}\cdot\mathbf{A}\mathbf{F} \) does not induce ferroelectricity, because it is overcompensated by the energy cost of a polar lattice distortion proportional to \( +\mathbf{P}^2 \). This fourth-order term accounts for small changes in dielectric constant below magnetic transition, observed for example in YMnO₃ and BiMnO₃ (refs 11,12). If magnetic ordering is inhomogeneous (that is, \( \mathbf{M} \) varies over the crystal), symmetries also allow for the third-order coupling of \( \mathbf{P}\mathbf{M}\mathbf{M} \). Being linear in \( \mathbf{P} \), arbitrarily weak interaction of this type gives rise to electric polarization, as soon as magnetic ordering of a proper kind sets in. For cubic crystals, the allowed form of the magnetically induced electric polarization is

\[
P \propto \left[ (\mathbf{M} \cdot \partial)\mathbf{M} - \mathbf{M} (\partial \cdot \mathbf{M}) \right].
\]

This is where frustration comes into play. Its role is to induce spatial variations of magnetization. The period of magnetic states in frustrated systems depends on strengths of competing interactions and is often incommensurate with the period of crystal lattice. For example, a spin chain with a ferromagnetic interaction \( J < 0 \) between neighbouring spins has a uniform ground state with all parallel spins. An antiferromagnetic next-nearest-neighbour interaction \( J' > 0 \) frustrates this simple ordering, and when sufficiently strong, stabilizes a spiral magnetic state (see Fig. 4a):

\[
S_n = S [\mathbf{e}_1 \cos Q x_n + \mathbf{e}_2 \sin Q x_n],
\]

where \( \mathbf{e}_1 \) and \( \mathbf{e}_2 \) are two orthogonal unit vectors and the wavevector \( Q \) is given by

\[
\cos(Q/2) = -J'/(4J).
\]

Like any other magnetic ordering, the magnetic spiral spontaneously breaks time-reversal symmetry. In addition it breaks inversion symmetry, because the change of the sign of all coordinates inverts the direction of the rotation of spins in the spiral. Thus, the symmetry of the spiral state allows for a simultaneous...
presence of electric polarization, the sign of which is coupled to the direction of spin rotation. In contrast, a sinusoidal spin-density-wave ordering, $S_n = S \cos Q x_n$, cannot induce ferroelectricity, as it is invariant in inversion, $S_{-n} = S_n$. Because magnetic anisotropies are inevitably present in realistic materials, the sinusoidal ordering usually appears at a higher temperature than the spiral one, which is why in frustrated magnets the temperature of ferroelectricity is typically somewhat lower than the temperature of the first magnetic transition.

Spiral states are characterized by two vectors: the wavevector $Q$ and the axis $e_\zeta$ around which spins rotate. In the example considered above, $Q$ is parallel to the chain direction, and the spin-rotation axis $e_\zeta = e_x \times e_z$. Using equation (1), we find that the induced electric dipole moment is orthogonal both to $Q$ and $e_\zeta$:

$$P \parallel e_\zeta \times Q \quad (3)$$

A plausible microscopic mechanism inducing ferroelectricity in magnetic spirals was discussed in refs 24 and 27. It involves the antisymmetric Dzyaloshinskii–Moriya (DM) interaction, $D_{\alpha \beta} = D_{\alpha \beta} \mathbf{S}_n \times \mathbf{S}_{n+\alpha}$, where $D_{\alpha \beta}$ is the Dzyaloshinskii vector. This interaction is a relativistic correction to the usual superexchange and its strength is proportional to the spin–orbit coupling constant. The DM interaction favours non-collinear spin ordering. For example, it gives rise to weak ferromagnetism in antiferromagnetic layers of La$_2$CuO$_4$, the parent compound of high-temperature superconductors (see Fig. 5). It also transforms the collinear Neél state in ferroelectric BiFeO$_3$ into a magnetic spiral. Ferroelectricity induced by spiral magnetic ordering is the inverse effect, resulting from exchange striction: that is, lattice relaxation in a magnetically ordered state. The exchange between spins of transition metal ions is usually mediated by ligands, for example oxygen ions, forming bonds between pairs of transition metals. The Dzyaloshinskii vector $D_{\alpha \beta}$ is proportional to $x \times r_{\alpha \beta}$, where $r_{\alpha \beta}$ is a unit vector along the line connecting the magnetic ions $n$ and $n+\beta$, and $x$ is the shift of the oxygen ion from this line (see Fig. 5). Thus, the energy of the DM interaction increases with $x$, describing the degree of inversion symmetry breaking at the oxygen site. Because in the spiral state the vector product $S_n \times S_{n+\beta}$ has the same sign for all pairs of neighboring spins, the DM interaction pushes negative oxygen ions in one direction perpendicular to the spin chain formed by positive magnetic ions, thus inducing electric polarization perpendicular to the chain (see Fig. 5). This mechanism can also be expressed in terms of the spin current, $j_{\parallel} = S_x \times S_y$, describing the precession of the spin state the vector product $S_{\alpha \beta}$ is proportional to spin–orbit coupling, and depends on the position of the oxygen ion (open circle) between two magnetic transition metal ions (filled circles), $D_{\alpha \beta} \propto \lambda x \times e_\zeta$. Weak ferromagnetism in antiferromagnets (for example, La$_2$CuO$_4$ layers) results from the alternating Dzyaloshinskii vector, whereas (weak) ferroelectricity can be induced by the exchange striction in a magnetic spiral state, which pushes negative oxygen ions in one direction transverse to the spin chain formed by positive transition metal ions.

Although equation (3) works for many multiferroics (see discussion below), the general expression for magnetically induced polarization is more complicated. In particular, when the spin rotation axis $e_\zeta$ is not oriented along a crystal axis, the orientation of $P$ depends on strengths of magnetoelastic couplings along different crystallographic directions (such a situation occurs in MnWO$_4$; refs 18,19). Furthermore, when the crystal unit cell contains more than one magnetic ion, the spin-density-wave state, strictly speaking, cannot be described by a single magnetization vector, as was assumed in equation (1). With additional magnetic vectors, one can construct other third-order terms that can induce electric polarization. In this case, one can classify all possible spin-density-wave configurations according to their symmetry properties with respect to transformations that leave the spin-density-wavevector intact. According to the Landau theory of second-order phase transitions, close to transition temperatures the amplitudes of all spin configurations with the same symmetry should be proportional to a single order parameter. The sinusoidal phase is then described by one order parameter, whereas the ferroelectric state with additional broken symmetries is described by two order parameters, which are generalizations of the two orthogonal components of the simple spiral state.

**SPIRAL MAGNETIC ORDER AND FERROELECTRICITY IN PEROVSKITE RMNO$_3$**

These considerations explain the interplay between magnetic and electric phenomena observed in TbDyMnO$_4$. Because of the orbital ordering of Mn$^{3+}$ ions in orthorhombic RMnO$_3$, the exchange between...
neighbouring spins is ferromagnetic (FM) in the $a$–$b$ planes and antiferromagnetic (AFM) along the $c$ axis. Consistently, spins in each $a$–$b$ plane of LaMnO$_3$ order ferromagnetically and the magnetization direction alternates along the $c$ axis. The replacement of La by smaller ions such as Tb or Dy increases structural distortion, inducing next-nearest-neighbour AFM exchange in the $a$–$b$ planes comparable to the nearest-neighbour FM exchange. This frustrates the FM ordering of spins in the $a$–$b$ planes, and below $\sim 42$ K Tb(Dy)MnO$_3$ shows an incommensurate magnetic ordering with a collinear sinusoidal modulation along the $b$ axis, which is paraelectric. However, as temperature is lowered and magnetization grows in magnitude, a spiral state with rotating spins becomes energetically more favourable, sets in at $\sim 28$ K, and induces ferroelectricity. The wavevector $\mathbf{Q}$ is parallel to the $b$ axis, and spins rotate around the $a$ axis, which according to equation (3) induces $\mathbf{P}$ parallel to the $c$ axis, in agreement with experimental results. A similar transition from the paraelectric sinusoidal spin-density-wave state to the ferroelectric spiral state is observed in Ni$_3$V$_2$O$_8$.

The orientation of the polarization vector $\mathbf{P}$ can be changed by applied magnetic fields. In zero or weak fields, spins rotate in the easy plane and thus the spin rotation axis $\mathbf{e}_3$ is parallel to the hard axis of a magnet. In strong fields, spins prefer to rotate around $\mathbf{H}$, which can force the spin-rotation axis to flop and induce a concomitant reorientation of $\mathbf{P}$. Such a 90° polarization flop was indeed observed in Tb(Dy)MnO$_3$ at $\sim 5$ T. The low-temperature magnetic behaviour of these materials is, however, obscured by the fact that the rare-earth ions, Tb$^{3+}$ and Dy$^{3+}$, which are also magnetic with a strong anisotropy, undergo their own spin-flop transitions in magnetic fields.

It is much easier to interpret the field-induced transitions in orthorhombic manganites with non-magnetic rare earth ions, such as Eu$_{1-y}$Y$_{0.25}$MnO$_3$. As was already mentioned, the size of the rare earths in RMnO$_3$ is essential for the magnetic frustration, ferroelectricity as well as the stability of orthorhombic perovskite structure. Thus, orthorhombic RMnO$_3$ with $R = \text{La–Gd}$ does not show ferroelectricity, whereas for rare earths smaller than Dy, RMnO$_3$ crystallizes in the hexagonal YMnO$_3$ structure in ambient conditions. Desired physical properties can be obtained by mimicking the size of Tb(Dy) with an appropriate mixture of non-magnetic Eu and Y ions. For example, Eu$_{1-y}$Y$_{0.25}$MnO$_3$ has the orthorhombic perovskite structure and undergoes magnetic and ferroelectric transitions similar to those in Tb(Dy)MnO$_3$. The temperature dependence of magnetic susceptibility $\chi$ of Eu$_{1-y}$Y$_{0.25}$MnO$_3$, shown in Fig. 6c, is consistent with an easy-[$b$ axis sinuousoidal state below $\sim 50$ K, and a magnetic spiral with the easy $a$–$b$ plane below $\sim 30$ K. The magnetic spiral is ferroelectric with polarization along the $a$ axis (the temperature dependence of $\chi$ is shown in Fig. 3c), presumably because $\mathbf{Q}$ is parallel to $b$ and $\mathbf{e}_3$ is parallel to $c$. For $|H| > 3$ T applied in the $c$ direction, induces a spin-flop transition, which forces spins to form a spiral state and induces electric polarization in the $a$–$b$ plane.

**EXCHANGE STRICITION WITHOUT MAGNETIC SPIRALS**

Spiral spin ordering is not the only possible source of magnetically induced ferroelectricity. Electric polarization can also be induced by collinear spin orders in frustrated magnets with several species of magnetic ions, such as orthorhombic RMnO$_3$, with Mn$^{2+}$ ions ($S = 2$) in oxygen pyramids and Mn$^{4+}$ ions ($S = 3/2$) in oxygen octahedra. A view along the $c$ axis (Fig. 6c) reveals that Mn spins are arranged in loops of five spins: Mn$^{2+}$–Mn$^{4+}$–Mn$^{2+}$–Mn$^{4+}$–Mn$^{2+}$. The nearest-neighbour magnetic coupling in the loop is AFM, favouring antiparallel alignment of neighbouring spins. However, because of the odd number of spins in the loop, ordered spins cannot be antiparallel to each other on all bonds, which gives rise to frustration and favours more complex magnetic structures. Figure 6c shows the Mn spin configuration in the commensurate phase of RMnO$_3$, which appears below $T_c$ and consists of AFM zigzag chains along the $a$ axis (dashed green lines).

To understand how ferroelectricity can be induced by this (nearly) collinear magnetic state, we note that half of the Mn$^{3+}$–Mn$^{4+}$ pairs across neighbouring zigzags have approximately antiparallel spins, whereas the other half have more-or-less parallel spins. The exchange striction shifts ions (mostly Mn$^{4+}$ ions inside pyramids) in a way that optimizes the spin-exchange energy: ions with antiparallel spins are pulled to each other, whereas ions having parallel spins, despite the AFM exchange interaction, move away from each other. This leads to the distortion pattern shown with open black arrows in Fig. 6c, which breaks inversion symmetry (in particular, on oxygen sites connecting two Mn$^{4+}$ pyramids) and induces net polarization along the $b$ axis.

In the commensurate magnetic phase below $T_c = 20–25$ K, the magnetization of the Mn ions in each zigzag chain is modulated along the $a$ axis and spins in every other chain are rotated slightly toward the $b$ axis. This behaviour is reflected in the temperature dependence of $\chi$, showing a sudden increase and drop of $\chi$ along the $a$ and $b$ axes, respectively, at $T_c$ on cooling. This results in the reduction as well as the...
180° rotation of the net ferroelectric distortion. To make things even more complicated, there also seems to be a net ferroelectric moment associated with the ordering of rare-earth spins, which is opposite to that induced by the incommensurate ordering of Mn ions (thus, in the same direction as that in the commensurate state). In TbMnO₃, at low temperatures, the net distortion associated with Tb spins is larger than that due to Mn spins, but disappears when Tb spins align along H//a. This explains the 180° rotation of net polarization induced by magnetic fields at low temperatures.

A conceptually simpler example of how a collinear spin ordering can induce ferroelectricity is the frustrated spin chain with competing FM and AFM interactions, where spins can orient only up or down, as in the so-called ANNNI model⁶⁸. A strongly frustrated Ising spin chain with nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic coupling has the up–up–down–down (↑↑↓↓) ground state (see Fig. 4b). If the charges of magnetic ions or tilts of oxygen octahedra³⁵,⁶⁰ alterate along the chain, this magnetic ordering breaks inversion symmetry on magnetic sites and induces electric polarization (see Fig. 1b). As in the case of magnetic spirals, ions are displaced by exchange striction, which shortens bonds between parallel spins and stretches those connecting antiparallel spins in the ↑↑↓↓ state. In the Landau description, the coupling term inducing the polarization has the form of \( P(L_i - L_j) \), typical for improper ferroelectrics⁶⁹,⁷⁰, where \( L_i = S_i + S_j - S_j - S_i \) and \( L_j = S_j - S_j - S_j + S_i \) represent two possible types of the (↑↑↓↓) order. Similarly, the electric polarization in the R MnO₃ compounds is induced by the (↑↑↓↓) or (↓↓↑↑) spin ordering along the b axis, which has the same period as the alternation of the Mn charges (Mn⁺⁺–Mn⁺⁺–Mn⁺⁺) along this axis. Because the lattice distortion in this mechanism is driven by the Heisenberg (rather than the weak DM) exchange, the induced polarization can be large. It would be interesting to explore multiferroics in which ferroelectricity appears as a combined effect of charge and magnetic ordering that together break inversion symmetry. Note that site-centred charge ordering coexisting with the spin ordering of the up–up–down–down type has been observed in perovskites RNiO₃, (see Fig. 1d)³⁴–⁴⁴.

WHERE TO GO FROM HERE?

Magnetic frustration is a powerful source of ‘unconventional’ magnetic orders, which can induce ferroelectricity. Particularly suited for magnetic control of polarization are conical magnets, such as the spinel CoCr₂O₄ (ref. 17), in which magnetization has both rotating and uniform ferromagnetic parts:

\[
\mathbf{S}_n = \mathbf{S} \left[ \mathbf{e}_x \cos Q x \pm \mathbf{e}_z \sin Q x \right] + \mathbf{S}_c \mathbf{e}_y,
\]

While the rotating part of the magnetization gives rise to ferroelectricity, the net ferromagnetic moment of the spiral provides a ‘handle’, with which the orientation of the spin rotation axis, and hence the polarization vector, can be tuned by applied magnetic fields. Magnetic fields required to reverse the orientation of electric polarization in CoCr₂O₄ are substantially lower than those in rare earth manganites. The simultaneous presence of electric polarization and net magnetization in the conical ferroelectric CoCr₂O₄ gives rise to an average toroidal moment (\( \mathbf{T} \times \mathbf{P} \times \mathbf{M} \)), which is parallel to the spiral wave vector and remains unchanged when \( \mathbf{P} \) and \( \mathbf{M} \) are rotated by low magnetic fields²³–²⁵.

Unfortunately, the strong effects of magnetic fields on electric polarization and dielectric constant do not imply strong dependence of magnetic properties on applied electric fields, as magnetoelectric coupling in frustrated magnets is rather weak. Furthermore, as spontaneous electric polarization does not break time-reversal symmetry, it cannot induce magnetic ordering in the same way as a magnetic order with broken inversion symmetry induces ferroelectricity. To achieve control of magnetism by electric fields, one has to find other mechanisms, such as mutual clamping of ferroelectric and antiferromagnetic domains, which appears to be relevant to a linear magnetoelectric effect in hexagonal HoMnO₃ (refs 65–67).

From a technological point of view, a challenge in this field is to find room-temperature multiferroics. As was mentioned above, magnetic frustration usually delays magnetic transitions down to low temperatures, so that finding high-temperature insulating spiral magnets is not straightforward (but not impossible — in the multiferroic hexaferrite Ba₆Sr₂ZnFe₁₂O₃₂, spins order above room temperature²⁸). An alternative route is to artificially fabricate composite ferroelectric and magnetic materials with high transition temperatures. There have been considerable efforts to optimize the cross-coupling effects in composite multiferroics with magnetostrictive ferromagnets and piezoelectric materials²⁸–²⁹ (see also the accompanying review by Ramesh and Spaldin on page 21 of this issue²⁹).

Equation (1) states that the polarization density is proportional to the gradient of the angle \( \phi \), describing the orientation of spins in the spiral: \( \mathbf{P} = \partial \mathbf{P} / \partial \phi \). This has two immediate consequences: first, the total electric polarization is proportional to the total number of revolutions of spins in the spiral and is insensitive to the presence of higher harmonics, and second, Néel domain walls carry net electric polarization and magnetic vortices have electric charge²,²⁹. The 180° Néel wall separating spin-up and spin-down domains induces polarization, because it has electric properties of a half period of a magnetic spiral with \( \mathbf{e} \perp \mathbf{Q} \). On the other hand, the Bloch wall, where spins rotate around the normal to the wall, induces no net polarization, similar with the spiral with \( \mathbf{e} \parallel \mathbf{Q} \). The electric polarization induced by domain walls may be of practical importance, as domain walls can form in thin films of conventional ferromagnetic materials above room temperature and show very strong sensitivity to applied magnetic fields.

The coupling between electric and magnetic dipoles in multiferroics also gives rise to unusual dynamic effects, which can be observed in optical experiments²₁–²₃,²₄. The salient feature of many proper ferroelectrics is the softening of optical phonons at the critical temperature, resulting in divergent \( \epsilon \) (refs 6,9,75). The freezing of this soft mode below the transition temperature leads to a bulk ferroelectric distortion. In magnetic ferroelectrics, the soft mode seems to be absent despite the divergence of \( \epsilon \) at the magnetic phase transition that induces electric polarization. The peak in \( \epsilon \) in this case results from the linear coupling between the polar phonon mode and the soft magnetic mode. The mixing of magnetic excitations (magnons) with optical phonons and, eventually, with light makes it possible to ‘see’ magnons in optical absorption experiments. The photoexcitation of magnons also occurs in ordinary magnets, but there the single magnon excitation occurs only through magnetic dipole coupling of the light (known as magnetic resonance) and is much weaker than electric dipole excitations such as the optical phonons. On the other hand, in multiferroics the coupling can result from the third-order term \( P \cdot M \). The linear coupling is obtained by replacing one vector \( \mathbf{M} \) by the static magnetization with the wavevector \( \mathbf{Q} \) of the magnetic structure, while another vector \( \mathbf{M} \) is replaced by the dynamic magnetization with the wavevector \( \mathbf{Q} \). This coupling induces significant ‘magnetic’ peaks in the optical absorption spectrum. The theory of the coupled spin-phonon excitations (‘electro-magnons’) was discussed in the 1970s and more recently in ref. 76. Since then, a few reports have appeared on the absorption peaks at frequencies typical for magnetic excitations, most recently²⁷–²₉ in the spiral magnets Tb(Gd)MnO₃. Still, dynamic phenomena in multiferroics remain largely unexplored and require future work.

In summary, magnetic frustration naturally gives rise to multiferroic behaviour. Competing magnetic interactions in frustrated magnets often result in eccentric magnetic structures that lack the inversion symmetry of a high-temperature crystal lattice. The ionic relaxation in such magnetic states, driven by lowering of the magnetic energy.

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of the Heisenberg and Dzyaloshinskii–Moriya exchange interactions, induces polar lattice distortions. These magnetic ferroelectrics can produce unprecedented cross-coupling effects, such as the high tunability of the magnetically induced electric polarization and dielectric constant by applied magnetic fields, which has given a new impulsion to the search for other multiferroic materials and raised hopes for their practical applications.

References


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