

Multiferroic and magnetoelectric materials

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A ferroelectric crystal exhibits a stable and switchable electrical polarization that is manifested in the form of cooperative atomic displacements. A ferromagnetic crystal exhibits a stable and switchable magnetization that arises through the quantum mechanical phenomenon of exchange. There are very few ‘multiferroic’ materials that exhibit both of these properties, but the ‘magnetoelectric’ coupling of magnetic and electrical properties is a more general and widespread phenomenon. Although work in this area can be traced back to pioneering research in the 1950s and 1960s, there has been a recent resurgence of interest driven by long-term technological aspirations.

Since its discovery less than one century ago, the phenomenon of ferroelectricity¹, like superconductivity, has been considered in relation to the ancient phenomenon of magnetism. Just as recent work has shown that magnetic order can create superconductivity², it has also been shown that magnetic order can create (weak) ferroelectricity³ and vice versa^{4,5}. Single-phase materials in which ferromagnetism and ferroelectricity arise independently also exist, but are rare⁶. As this new century unfolds, the study of materials possessing coupled magnetic and electrical order parameters has been revitalized. In this Review we set recent developments in the context of the pioneering works of the 1950s–1960s.

The field of research that we are describing has a tortuous taxonomy and typically involves terms such as ‘multiferroic’ and ‘magnetoelectric’, whose overlap is incomplete (Fig. 1). By the original definition, a single-phase multiferroic⁷ material is one that possesses two—or all three—of the so-called ‘ferroic’ properties: ferroelectricity, ferromagnetism and ferroelasticity (Fig. 2 and Table 1; see Box 1 for a glossary of terms). However, the current trend is to exclude the requirement for ferroelasticity in practice, but to include the possibility of ferrotoroidic order (Box 1) in principle. Moreover, the classification of a multiferroic has been broadened to include antiferroic order (Box 1). Magnetoelectric coupling (Box 1), on the other hand, may exist whatever the nature of magnetic and electrical order parameters, and can for example occur in para-

magnetic ferroelectrics⁸ (Fig. 1). Magnetoelectric coupling may arise directly between the two order parameters, or indirectly via strain. We also consider here strain-mediated indirect magnetoelectric coupling in materials where the magnetic and electrical order parameters arise in separate but intimately connected phases (Fig. 3).

A confluence of three factors explains the current high level of interest in magnetoelectrics and multiferroics. First, in 2000, Hill (now Spaldin) discussed the conditions required for ferroelectricity and ferromagnetism to be compatible in oxides, and declared them to be rarely met⁶. Her paper in effect issued a grand materials development challenge that was taken up because empirically there are indeed few multiferroic materials, whatever the microscopic reasons. Second, the experimental machinery for the synthesis and study of various contenders was already in place when this happened. Third, the relentless drive towards ever better technology is aided by the study of novel materials. Aspirations here include transducers and magnetic field sensors, but tend to centre on the information storage industry.

It was initially suggested that both magnetization and polarization could independently encode information in a single multiferroic bit. Four-state memory has recently been demonstrated⁹, but in practice it is likely that the two order parameters are coupled^{10,11}. Coupling could in principle permit data to be written electrically and read magnetically. This is attractive, given that it would exploit the best

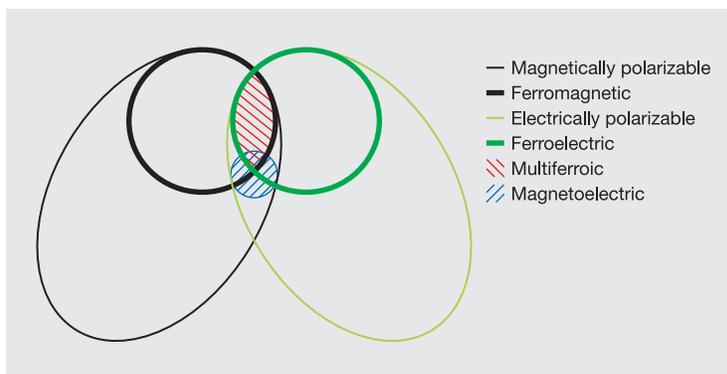


Figure 1 | The relationship between multiferroic and magnetoelectric materials. Ferromagnets (ferroelectrics) form a subset of magnetically (electrically) polarizable materials such as paramagnets and antiferromagnets (paraelectrics and antiferroelectrics). The intersection (red hatching) represents materials that are multiferroic. Magnetoelectric

coupling (blue hatching) is an independent phenomenon that can, but need not, arise in any of the materials that are both magnetically and electrically polarizable. In practice, it is likely to arise in all such materials, either directly or via strain.

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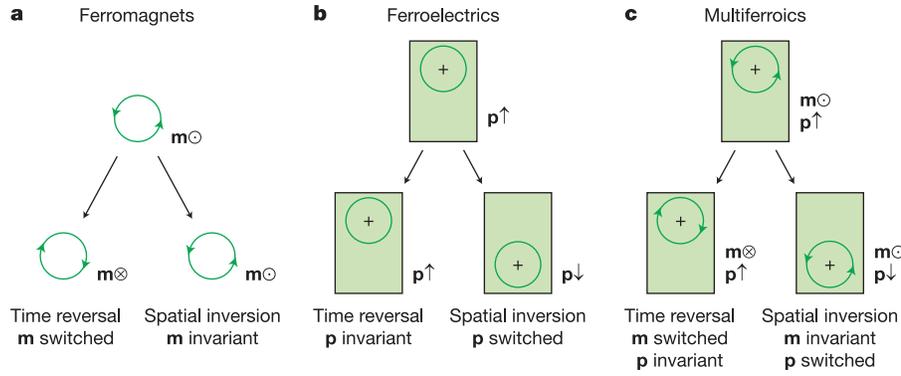


Figure 2 | Time-reversal and spatial-inversion symmetry in ferroics.
a, Ferromagnets. The local magnetic moment **m** may be represented classically by a charge that dynamically traces an orbit, as indicated by the arrowheads. A spatial inversion produces no change, but time reversal switches the orbit and thus **m**. **b, Ferroelectrics.** The local dipole moment **p**

may be represented by a positive point charge that lies asymmetrically within a crystallographic unit cell that has no net charge. There is no net time dependence, but spatial inversion reverses **p**. **c, Multiferroics** that are both ferromagnetic and ferroelectric possess neither symmetry.

aspects of ferroelectric random access memory (FeRAM) and magnetic data storage, while avoiding the problems associated with reading FeRAM and generating the large local magnetic fields needed to write. Unfortunately, significant materials developments will be required to generate magnetoelectric materials that could make a real contribution to the data storage industry. But given the paucity of serious competitors to contemporary memory technologies, the study of novel materials remains important if disruptive technologies are ultimately to emerge. In the shorter term, niche applications are more likely to emerge in strain coupled two-phase systems of the type that we describe later.

The purpose of this Review is to assess the current state of the field, to remind readers of the relevant work performed in the latter half of the twentieth century, and to discuss matters of scientific ‘hygiene’ pertaining to accurate measurements and analyses. For further details we refer the reader to three reviews written at different stages of this re-emerging field^{12–14}.

Magnetolectric coupling

The magnetolectric effect in a single-phase crystal is traditionally described^{13,15} in Landau theory by writing the free energy *F* of the system in terms of an applied magnetic field **H** whose *i*th component is denoted *H_i*, and an applied electric field **E** whose *i*th component is denoted *E_i*. Note that this convention is unambiguous in free space, but that *E_i* within a material encodes the resultant field that a test particle would experience. Let us consider a non-ferroic material, where both the temperature-dependent electrical polarization *P_i(T)* (μC cm⁻²) and the magnetization *M_i(T)* (μ_B per formula unit, where μ_B is the Bohr magneton) are zero in the absence of applied fields and there is no hysteresis. It may be represented as an infinite, homogeneous and stress-free medium by writing *F* under the Einstein summation convention in S.I. units as:

$$-F(E, H) = \frac{1}{2} \epsilon_{0ij} E_i E_j + \frac{1}{2} \mu_{0ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \dots \tag{1}$$

The first term on the right hand side describes the contribution resulting from the electrical response to an electric field, where the permittivity of free space is denoted ε₀, and the relative permittivity ε_{ij}(*T*) is a second-rank tensor that is typically independent of *E_i* in non-ferroic materials. The second term is the magnetic equivalent of the first term, where μ_{ij}(*T*) is the relative permeability and μ₀ is the permeability of free space. The third term describes linear magneto-lectric coupling via α_{ij}(*T*); the third-rank tensors β_{ijk}(*T*) and γ_{ijk}(*T*) represent higher-order (quadratic) magnetolectric coefficients.

In the present scheme, all magnetolectric coefficients incorporate the field independent material response functions ε_{ij}(*T*) and μ_{ij}(*T*). The magnetolectric effects can then easily be established in the form *P_i(H_j)* or *M_i(E_j)*. The former is obtained by differentiating *F* with respect to *E_i*, and then setting *E_i* = 0. A complementary operation involving *H_i* establishes the latter. One obtains:

$$P_i = \alpha_{ij} H_j + \frac{\beta_{ijk}}{2} H_j H_k + \dots \tag{2}$$

and

$$\mu_0 M_i = \alpha_{ji} E_j + \frac{\gamma_{ijk}}{2} E_j E_k + \dots \tag{3}$$

In ferroic materials, the above analysis is less rigorous because ε_{ij}(*T*) and μ_{ij}(*T*) display field hysteresis. Moreover, ferroics are better parameterized in terms of resultant rather than applied fields¹⁶. This is because it is then possible to account for the potentially significant depolarizing/demagnetizing factors in finite media, and also because the coupling constants would then be functions of temperature alone, as in standard Landau theory. In practice, resultant electric and magnetic fields may sometimes be approximated¹⁷ by the polarization and magnetization respectively.

A multiferroic that is ferromagnetic and ferroelectric is liable to display large linear magnetolectric effects. This follows because ferroelectric and ferromagnetic materials often (but not always) possess a large permittivity and permeability respectively, and α_{ij} is bounded by the geometric mean of the diagonalized tensors ε_{ii} and μ_{jj} such that¹⁸:

$$\alpha_{ij}^2 \leq \epsilon_{0ii} \mu_{jj} \tag{4}$$

Equation (4) is obtained from equation (1) by forcing the sum of the first three terms to be greater than zero, that is, ignoring higher-order coupling terms. It represents a stability condition on ε_{ij} and μ_{ij}, but if the coupling becomes so strong that it drives a phase transition to a more stable state, then α_{ij}, ε_{ij} and μ_{ij} take on new values in the new phase. Note that a large ε_{ij} is not a prerequisite for a material to be ferroelectric (or vice versa); and similarly ferromagnets do not necessarily possess large μ_{ij}. For example, the ferroelectric KNO₃ possesses a small ε = 25 near its Curie temperature of 120 °C (ref. 19),

Characteristic symmetry	Spatial-inversion symmetry?	Time-reversal symmetry?
Ferroelastic	Yes	Yes
Ferroelectric	No	Yes
Ferromagnetic	Yes	No
Multiferroic*	No	No

* A multiferroic that is both ferromagnetic and ferroelectric possesses neither symmetry.

Box 1 | Glossary of terms**Ferroids**

Ferroelectric materials possess a spontaneous polarization that is stable and can be switched hysteretically by an applied electric field; **antiferroelectric** materials possess ordered dipole moments that cancel each other completely within each crystallographic unit cell. **Ferromagnetic** materials possess a spontaneous magnetization that is stable and can be switched hysteretically by an applied magnetic field; **antiferromagnetic** materials possess ordered magnetic moments that cancel each other completely within each magnetic unit cell.

Ferroelastic materials display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress.

Ferrotoroidic materials possess a stable and spontaneous order parameter that is taken to be the curl of a magnetization or polarization. By analogy with the above examples, it is anticipated that this order parameter may be switchable. Ferrotoroidic materials have evaded unambiguous observation.

Ferrimagnetic materials differ from antiferromagnets because the magnetic moment cancellation is incomplete in such a way that there is a net magnetization that can be switched by an applied magnetic field.

Order parameter coupling

Magnetolectric coupling describes the influence of a magnetic (electric) field on the polarization (magnetization) of a material.

Piezoelectricity describes a change in strain as a linear function of applied electric field, or a change in polarization as a linear function of applied stress.

Piezomagnetism describes a change in strain as a linear function of applied magnetic field, or a change in magnetization as a linear function of applied stress.

Electrostriction describes a change in strain as a quadratic function of applied electric field.

Magnetostriction describes a change in strain as a quadratic function of applied magnetic field.

whereas paraelectric SrTiO₃ exhibits $\epsilon > 50,000$ at low temperatures²⁰. Therefore large magnetolectric couplings need not arise in, or be restricted to, multiferroic materials.

Nonlinear coupling. Most materials have small values of either ϵ_{ij} or μ_{ij} or both, so the linear magnetolectric effect will also be small, given that permittivity and permeability appear as a product in equation (4). However, no such restriction applies to higher-order couplings, such as those described by β_{ijk} and γ_{ijk} . For example, in some materials terms such as $\beta_{ijk}H_jH_k$ can dominate the linear term $\alpha_{ij}H_j$ in equation (2), as first shown experimentally at low temperatures in the piezoelectric paramagnet NiSO₄·6H₂O (ref. 21). In order to achieve large magnetolectric effects at room temperature through higher-order terms, we suggest investigating magnetic materials with reduced dimensionality. Indeed, two-dimensional spin order associated with $\beta(T)$ can persist to a temperature T_{2D} that exceeds the temperature T_{3D} at which three-dimensional spin order associated with $\alpha(T)$ is destroyed. This scenario arises²² at low temperature in BaMnF₄.

Indirect coupling. So far, our discussion of linear and higher-order magnetolectric coupling has ignored the effects of strain. Such effects could be significant or even dominant. For example, the inclusion of piezomagnetism (magnetostriction) would generate cross terms in equation (1) that are proportional to strain and vary linearly (quadratically) with H_i . Analogous expressions would arise from piezoelectricity or electrostriction (see Box 1). Furthermore, mixed terms involving products of strain, H_i and E_j have been predicted²³. In two-phase materials, magnetic and electrical properties are strain-coupled by design in the quest for large magnetolectric effects. The strength of this indirect coupling is not restricted by equation (4), and enhancements over single-phase systems of several orders of magnitude have been achieved²⁴.

Determination of coupling constants

The magnetolectric behaviour of a material can only be fully understood if its magnetic point group symmetry is known. This is because the magnetolectric coefficients α_{ij} , β_{ijk} and γ_{ijk} possess the symmetry of the material^{12,13,15}. For example, α_{ij} can only be non-zero for materials that do not have a centre of symmetry and are time-asymmetric¹². Conversely, information regarding the magnetolectric coefficients based on electrical²⁵ or optical²⁶ experiments can aid the determination of magnetic point group symmetries.

Below we discuss experimental issues relating to magnetolectric measurements. The major challenge is to make samples sufficiently insulating to prevent leakage currents contributing to the measured signal—a widespread problem undermining the measurement of ferroelectric polarization loops, as described in refs 16 and 27. Another complication arises if ferroic domains are present, and care should be taken to prepare single-domain states¹¹.

Magnetolectric coupling can be measured indirectly by simply recording changes in either the magnetization near, say, a ferroelectric transition temperature or the dielectric constant near a magnetic transition temperature. The resulting effects are described using various terms such as ‘magnetocapacitance’ or ‘magnetodielectric response’. Catalan has recently shown²⁸ that the frequently reported effects could misleadingly arise owing to magnetoresistance effects alone, and that the signature of true magnetocapacitance effects is persistence to high frequencies and low loss. However, even true magnetocapacitance measurements do not provide mechanistic insight nor yield coupling constants.

Direct measurements are more challenging. They record either a magnetic response to an applied electric field or an electrical response to an applied magnetic field. The former scenario typically requires electrically addressing the sample in a magnetometer. In the latter scenario, the electrical response can be measured in terms of either current or voltage. The time-integrated current per unit area directly represents the magnetically induced change of polarization in equation (2), that is, $\alpha = \partial P/\partial H$, ignoring higher-order terms. Measurements of voltage, however, yield empirical coupling coefficients commonly also denoted α , which assuming linearity take the form $\partial E/\partial H$.

Single-phase studies

Research into magnetolectrics and multiferroics took off during the latter half of the twentieth century. In 1957, the linear magnetolectric coupling coefficient α was predicted to occur in Cr₂O₃ (ref. 29). Then, in the 1960s, α was experimentally observed^{30,31} to be non-zero below the antiferromagnetic Néel temperature of 307 K, near which it peaked to a value of $\alpha = \partial P/\partial H \approx 4.1 \text{ ps m}^{-1}$. This work on Cr₂O₃ and other antiferromagnetic crystals, such as Gd₂CuO₄, Sm₂CuO₄, KNiPO₄, LiCoPO₄ and BiFeO₃, is well summarized in refs 13 and 32.

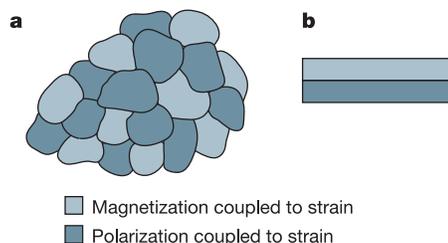


Figure 3 | Strain-mediated magnetolectric coupling in two-phase systems. Magnetic materials in which the magnetic order parameter couples to strain may be electrically addressed via an intimately connected material that develops a strain in response to an electrical stimulus. Equally, a magnetic stimulus may produce an electrical response. Suitable structures include mixtures of grains (a) and thin-film heterostructures (b). Note that in a but not b the magnetic material must be electrically insulating in order to avoid the possibility of short-circuits.

Magnetoelectric switching. The application potential for multiferroic materials in data storage lies in the possibility of reversing the magnetization by applying an electric field (or vice versa). Magnetoelectric switching was first demonstrated¹¹ 40 years ago in the boracite $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$. The weak magnetic and electrical order set in simultaneously¹¹ below 60 K, and a magnetic-field-induced reversal of the magnetization was found to flip the polarization ($0.076 \mu\text{C cm}^{-2}$). This hysteretic response is shown in Fig. 4a. Alternatively, in the paramagnetic ferroelectric $\text{Tb}_2(\text{MoO}_4)_3$, a magnetically induced persistent polarization can arise in large applied magnetic fields⁸ (Fig. 4b). Recently, magnetoelectric switching has been observed in orthorhombic manganites, REMnO_3 or REMn_2O_5 , where RE is a rare earth element. These are antiferromagnets that display improper (weak) ferroelectricity. A small polarization appears at the magnetic Néel temperature (~ 30 K) because the magnetic transition gives rise to crystalline distortions. The polarization of $0.04 \mu\text{C cm}^{-2}$ in TbMn_2O_5 has been magnetically reversed³³, and the polarization of $0.08 \mu\text{C cm}^{-2}$ in TbMnO_3 has been magnetically rotated³ by 90° . Similarly, in the hexaferrite³⁴ $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, a polarization of $0.015 \mu\text{C cm}^{-2}$ may be magnetically induced and subsequently rotated 360° about the c axis. Unfortunately, these changes in polarization are not persistent, and arise at low temperatures only.

Role of magnetic and crystallographic structure. As magnetoelectric coupling is determined by the structure and magnetic symmetry of a crystal, small modifications might alter, eliminate or allow magnetoelectric effects. Here we discuss key examples.

Spontaneous magnetoelectric coupling in BaMnF_4 permits the ferroelectric order to cant the spins of the two anti-aligned magnetic sub-lattices along the a axis of the crystal, giving a small net ferromagnetic magnetization⁵. The periodicity of this magnetization

is commensurate with the crystal lattice, but the periodicity of the ferroelectricity is incommensurate, and therefore the spatial average of the magnetoelectric coupling is nearly zero and difficult to measure directly. Instead, evidence for coupling comes from changes in the dielectric constant²² observed at magnetic transition temperatures. The magnetization of BaMnF_4 orders two dimensionally below T_{2D} , where a change in the b -axis dielectric constant is observed (Fig. 5). This has been quantified in terms of the magnetic correlation energy^{22,35}. A 1% replacement of Mn with Co destroys the spin canting, and strongly influences the changes in the dielectric constant near the magnetic phase transition, clearly highlighting the key role of magnetic symmetry³⁶.

BiFeO_3 is a commensurate ferroelectric³⁷ and an incommensurate antiferromagnet at room temperature³⁸. The spins are not collinear, but instead take the form of a long-wavelength (62 nm) spiral³⁸. Consequently, the linear magnetoelectric effect also averages to zero here, and indeed only the quadratic effect has been observed³⁹. However, the linear effect may be recovered if the spiral is 'unwound' by applying⁴⁰ large magnetic fields of 20 T, by chemical substitutions⁴¹, or by attempting to introduce thin-film epitaxial constraints⁴². Note that the concept of unwinding has been successfully employed in the case of smectic liquid crystals by confinement within treated glass plates. This surface-stabilized ferroelectric liquid crystal technology (SSFLC) has become the basis for the flat-screen television industry and display screens in cameras.

The linear magnetoelectric effect is also symmetry-forbidden in hexagonal manganites⁴³ of the form REMnO_3 . These materials are ferroelectric, and possess antiferromagnetically aligned Mn^{3+} ions (Néel temperature 70–130 K). RE-site magnetic ordering is seen below ~ 5 K, but large moments may only be achieved in large magnetic fields⁴⁴. Large Néel temperature dielectric anomalies of 42% and 60% are observed in YMnO_3 and HoMnO_3 (ref. 45), respectively. In a landmark experiment, ferroelectric and antiferromagnetic domain walls were seen⁴³ to be coincident in YMnO_3 . Coupling via such walls could then arise because the local magnetization in an antiferromagnetic domain wall either possesses reduced magnetic symmetry⁴⁶, or else interacts with the strain from the coincident ferroelectric wall⁴³. In HoMnO_3 , an electrically driven magnetic phase transition is observed¹⁷. This is a dramatic form of switching that suggests a new approach for magnetoelectric switching.

Circular or toroidal ordering of domains in magnetic or magnetoelectric materials can arise from two unrelated effects. Non-ferroelectric magnetic nanodots typically show vortex (circular) domains⁴⁷ that may be treated as topological defects⁴⁸. In the bulk, ordered magnetic or ferroelectric moments are usually collinear, but toroidal magnetoelectric phenomena have been proposed in ferroelectric ferromagnetic systems^{49,50}. Experimental searches for toroidal ordering⁵¹ became unpopular following irreproducible reports⁵² in

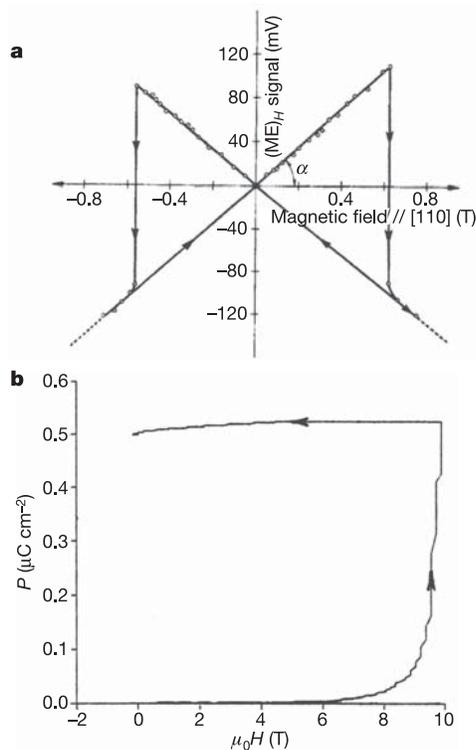


Figure 4 | Examples of magnetoelectric coupling. **a**, $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ at 46 K (after ref. 11, with permission). The magnetoelectric $(\text{ME})_H$ voltage signal, and therefore the polarization via equation (2), may be reversed in magnetic fields ($-0.6 \text{ T} < \mu_0 H < 0.6 \text{ T}$) that are much lower than the switching fields of recently studied materials^{5,55}. **b**, $\text{Tb}_2(\text{MoO}_4)_3$ at 78 K (after ref. 9, with permission). A persistent polarization (P) of $\sim 0.5 \mu\text{C cm}^{-2}$ develops after exposure to magnetic fields in excess of 8 T.

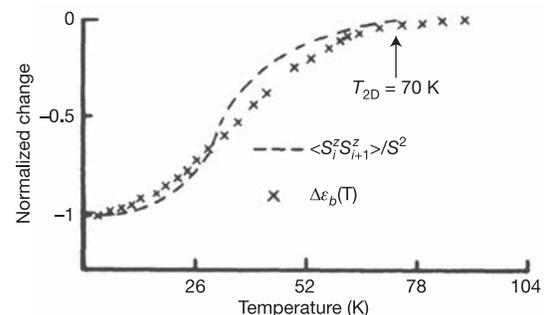


Figure 5 | Link between the magnetic and electrical properties of BaMnF_4 . The temperature dependence of the (7%) change in b -axis dielectric anomaly $\Delta\epsilon_b$ at $T_{2D} = 70$ K closely follows the temperature dependence of the normalized magnetic correlation function $\langle S_i^z S_{i+1}^z \rangle / S^2$. Here S_i^z is the z component of spin S at site i . (After ref. 22, with permission.)

Table 2 | Magnetolectric coupling constants in two-phase systems

Morphology	Materials	Coupling constant ($\text{mV cm}^{-1} \text{Oe}^{-1}$)	Ref.
Composite	BaTiO ₃ and CoFe ₂ O ₄	50	69
Composite	Terfenol-D and PZT in polymer matrix	42	70
Laminated composites	Terfenol-D in polymer matrix/PZT in polymer matrix	3,000	71
Laminate	Terfenol-D/PZT	4,800	24
Laminate	La _{0.7} Sr _{0.3} MnO ₃ /PZT	60	72
Laminate	NiFe ₂ O ₄ /PZT	1,400	72

PZT (Pb(Zr,Ti)O₃) and BaTiO₃ are piezoelectric, and terfenol-D (Tb_xDy_{1-x}Fe₂), the manganite and the ferrites are magnetostrictive.

1974, but there is now fresh hope that its existence will be experimentally established^{53,54}. The symmetry requirements for toroidal ordering and their relationship with magnetolectric coupling are reviewed in refs 13 and 14. The area is not well explored, and the possibility of large magnetolectric coupling exists; however, other possible phenomena, such as ferromagnetism inside antiferromagnetic domain walls, complicate measurements.

Ferromagnetic ferroelectric multiferroics. In 1958, Smolensky's group studied weakly ferromagnetic mixed perovskites, such as $(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3-x\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (ref. 55). These were doped to increase resistivity, but the boracite discussed above was the first highly insulating ferromagnetic ferroelectric to be studied¹¹.

The perovskite BiMnO₃ is a promising low-temperature multiferroic that has been considered for quite some time^{56,57}. Ferromagnetic ordering below 105 K is attributed to orbital ordering of the Mn³⁺ ions ($3d^4$) and a large magnetization of $3.6 \mu_B$ per formula unit has been measured for polycrystalline samples⁵⁷. These samples tend to be electrically conducting, restricting evidence of ferroelectricity to low temperatures and precluding definitive measurements of polarization. Multiferroic behaviour was seen⁵⁸ at ~ 80 K ($\sim 1 \mu_B$ per Mn, $< 0.15 \mu\text{C cm}^{-2}$), and a peak change of -0.6% in the dielectric constant in 8 T was recorded at T_C (ref. 59). This inspires investigations into less-conducting samples. We have recently shown⁶⁰ that epitaxial films can be highly insulating, even at room temperature ($10^7 \Omega \text{ cm}$).

The spinel CdCr₂S₄ is reported to be a low-temperature multiferroic. In 1965 it was known⁶¹ to be ferromagnetic ($6 \mu_B$ per formula unit) and insulating below 97 K, but only recently was it reported to display⁶² relaxor ferroelectricity ($0.5 \mu\text{C cm}^{-2}$) below 135 K. A colossal magnetocapacitance of 450% in 5 T was also reported, but magnetoresistance effects²⁸ could be responsible.

Reports of room temperature multiferroic materials have centred on BiFeO₃ and its derivatives. Promising multiferroic behaviour ($1 \mu_B$ per formula unit, $\sim 50\text{--}60 \mu\text{C cm}^{-2}$) was reported in thin epitaxial films⁶³, triggering widespread activity. However, subsequent works^{64–66} did not reproduce these findings. The large magnetization only arises in deoxygenated films that are too electrically conducting for valid ferroelectric measurements to be made⁶⁴. Moreover, the presence of impurity phases could play a role^{65,66}. Preliminary reports of multiferroicity in chemically doped BiFeO₃ (ref. 67) and PbTiO₃ (ref. 68) remain unconfirmed.

Two-phase systems

An alternative strategy for engineering enhanced magnetolectric effects is to introduce indirect coupling, via strain⁶⁹, between two materials such as a ferromagnet and a ferroelectric. Each phase may then be independently optimized for room temperature performance, and the coupling limit of equation (4) is lifted. Strain coupling requires intimate contact (Fig. 3) between a piezomagnetic (or magnetostrictive) material and a piezoelectric (or electrostrictive) material. This can be achieved in the form of composites^{69,70}, laminates^{24,71,72} or epitaxial multilayers⁷³ (Table 2). The coupling constant depends on the frequency of the a.c. applied magnetic field⁷⁴, and such multiferroic structures could thus find applications in, for example, microwave frequency transducers.

Epitaxial thin-film heterostructures could permit precise magne-

toelectric studies, because crystallographic orientation, layer thickness and interfacial roughness may be controlled accurately, but direct measurements of α in epitaxial systems have not been forthcoming. However, ferroelectric layers can generate strains of the order of 1% in magnetic epilayers owing to structural phase transitions. For example, the tetragonal to monoclinic structural phase transition in a BaTiO₃ substrate at 278 K produces⁷³ a 70% change in the magnetization of an epitaxial film of the ferromagnetic manganite La_{0.67}Sr_{0.33}MnO₃ (Fig. 6). Alternatively, one may attempt to alter the magnetic structure of a film by applying a voltage to the underlying piezoelectric material^{75,76,77}. Promising results⁷⁸ were found for a thin film heterostructure of CoPd and Pb(Zr,Ti)O₃ (PZT), where the application of an electric field to the PZT layer rotated the magnetization of the CoPd film by 90°.

The ferromagnetic and ferroelectric phases may be distributed laterally in a film while preserving an epitaxial relationship with one another and the substrate. This has been achieved for nanopillars of CoFe₂O₄ in a BaTiO₃ matrix, grown on a SrRuO₃ electrode with a SrTiO₃ substrate. However, the observed change in magnetization of the CoFe₂O₄ pillars at the ferroelectric Curie temperature was⁷⁹ just 5%, possibly due to either clamping from the underlying epitaxial structure which is not piezoelectric, or electric field effects associated with the ferroelectric. Nevertheless, when the matrix was changed to BiFeO₃, an electrically induced magnetization reversal in the CoFe₂O₄ nanopillars was reported⁸⁰.

Devices. Ferroelectrics may be used to address magnetic materials in devices for two reasons that in practice are not easy to separate^{81–83}. First, their superlative piezoelectric properties permit them to strain intimately connected layers as discussed above. Second, the large

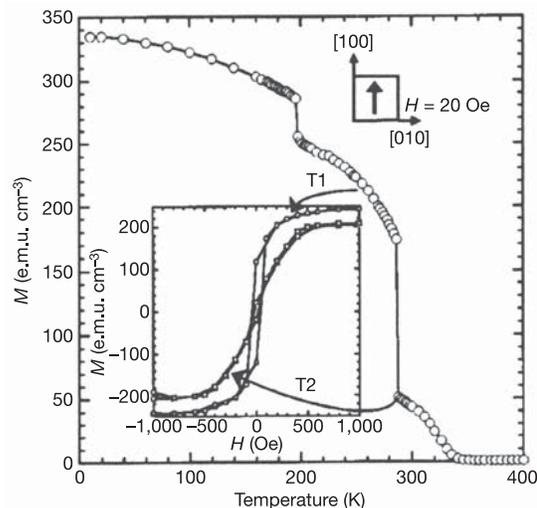


Figure 6 | Magnetolectric coupling in two-phase systems. Main figure, the magnetization M of an epitaxial La_{0.67}Sr_{0.33}MnO₃ film measured in a small applied field H (top inset) shows sharp changes due to structural phase transitions in the underlying BaTiO₃ substrate. Lower inset, the hard and easy axes are reversed between temperatures T1 and T2. (After ref. 73, with permission.)

polarization can be used in a field-effect transistor geometry to influence the charge density in a magnetic channel.

Various other two-phase magnetoelectric devices that have been explored include a heterostructure comprising PZT and a magnetic garnet between crossed polarizers, where it is possible to electrically influence the Faraday rotation in the garnet and thus control the optical transmission of the device⁸⁴. Exchange bias in $\text{Cr}_2\text{O}_3/(\text{Co}/\text{Pt})_3$ may be electrically reversed but requires thermal cycling⁸⁵, whereas exchange bias in $\text{YMnO}_3/\text{permalloy}$ heterostructures can be electrically tuned directly⁸⁶. Also, tunable microwave devices with superconductor/ferroelectric/ferromagnetic multilayers have been proposed⁸⁷. In other devices, strain-coupled magnetostrictive and piezoelectric layers can lead to voltage gain⁸⁸, and the detection of magnetic fields⁸⁹. The sensor devices seem particularly promising compared to existing superconducting quantum interference device (SQUID) technology because not only would they be cheaper and simpler, but also they can operate at room temperature.

Outlook

The flurry of activity during the past six years has not yet produced a great leap forward for multiferroics and magnetoelectrics, for two reasons. First, although new materials such as the manganite TbMnO_3 have come to light³, they do not necessarily compare favourably with the boracite¹¹ $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$, which was studied almost three decades before Schmid coined the term⁷ 'multiferroic'. The boracite possesses smaller switching fields and higher ordering temperatures than the manganite. Second, most of the modern systems under study remain to be formally analysed in terms of magnetic point group symmetries, which are vital for the analysis and prediction of magnetoelectric effects.

There are nevertheless plenty of reasons to be optimistic about the health of the field in both the short and the long term. A unified quantum mechanical theoretical approach may be possible in the future because magnetism is necessarily a quantum mechanical phenomenon, and modern theories of ferroelectricity calculate the polarization as a quantum mechanical observable⁹⁰ rather than using the semi-classical ball-and-stick model that has hitherto been so successful. Therefore *ab initio* modelling could in future show the way forward. In fact, there is plenty of scope for development, given that the ferroelectric moment cannot necessarily be determined by the rigid displacement of an ion. This is the case whenever electronic orbitals are not tied rigidly to ions^{91–93}.

Several strategies for achieving properties of interest also give rise to optimism. For example, ferrimagnetic materials are more likely to be electrically insulating than ferromagnets, and indeed the classic lodestone material Fe_3O_4 shows a magnetically addressable⁹⁴ polarization⁹⁵ of $5 \mu\text{C cm}^{-2}$ below the Verwey transition at 120 K. Alternatively, non-centrosymmetric structures may be achieved in thin films by exploiting epitaxial strain, defects or composition gradients, for example, in garnets⁹⁶. Epitaxial multilayers offer particularly close control of the strain coupling discussed earlier⁹⁷.

Magnetic switching by a voltage has the chance to compete with magnetic switching driven by light⁹⁸ or spin-polarized currents⁹⁹. Devices that would benefit from single-phase magnetoelectric materials (that are ferromagnetic) include, for instance, spin filters¹⁰⁰ for data storage and spatial light modulators⁸⁴ for optical switching.

We close by highlighting several issues that focus upon the scientific and technological promise of multiferroic and magnetoelectric materials. First, it remains to be seen whether there exists a ferromagnetic ferroelectric multiferroic in which the two order parameters are both either strong at any temperature, or non-zero at room temperature. Second, reports of electrically induced magnetic reversal remain rare. Third, a deeper understanding of single-phase magnetoelectric materials would be enhanced by establishing whether couplings are direct or strain-mediated. Fourth, the symmetry of magnetoelectric systems under study can yield valuable information. Fifth, we stress that ferroelectricity arises in a wide range of materials systems

including fluorides, and the search should not be limited to oxides. Sixth, the acquisition of ferroelectric data differs from magnetic measurements in that it involves a complete system with contacts and leads; the results are prone to misinterpretation^{16,27} if sample resistivities stray far below $10^7 \Omega \text{cm}$. Seventh, we reiterate that the nomenclature of the field is confused. Consequently 'the field' is an imperfectly defined entity, as reflected in the composite title of this Review. Finally, we suggest that the complex materials discussed here are in their infancy. Therefore the current scientific interest may one day lead to developments that contribute to technology.

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Acknowledgements We thank P. B. Littlewood, M. Fiebig and A. D. Kent for discussions and S. Celotto for assistance with reproducing figures. This work was supported by an EU Marie Curie Fellowship (W.E.), The Royal Society (N.D.M.) and the UK EPSRC.

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