

* Jens Kreisel¹ and Michel Kenzelmann²,

* ¹ Laboratoire Matériaux et Génie Physique CNRS, Minatec, Grenoble Institute of Technology, 3 parvis Louis Néel, 38016 Grenoble, France, jens.kreisel@grenoble-inp.fr

* ² Laboratory for Developments & Methods Paul Scherrer Institute 5232 Villigen, Switzerland michel.kenzelmann@psi.ch

* DOI: 10.1051/ePN/2009702

MULTIFERROICS

THE CHALLENGE OF COUPLING MAGNETISM AND FERROELECTRICITY

The origin and understanding of coupling phenomena between different physical properties within one material is a central subject of solid state science. It has fascinated physicists for decades. Multiferroics possess several so-called ferroic properties: ferromagnetism, ferroelectricity, and/or ferroelasticity. Their cross-coupling reflects interesting electron-phonon interactions, and they have great potential for new spintronic devices.

A material is generally considered functional if it possesses a physical property that is usable in applications. A considerable amount of research currently concentrates on multifunctional materials in which several physical properties could potentially be used simultaneously [1-5]. One of the key questions for the future development and understanding of multifunctional materials concerns the mutual coupling between the properties, its underlying mechanism and whether it can be used in applications. Multiferroics are multifunctional materials *par excellence*, because they simultaneously possess several so-called ferroic orders such as ferromagnetism, ferroelectricity and/or ferroelasticity. The class of ferroics is also commonly extended to anti-ferroics: antiferromagnetism and antiferroelectricity. Note that the prefix *ferro* refers historically to iron (*ferrum* in Latin), which shows a spontaneous magnetization M that can be controlled (and namely reversed) by the application of a magnetic field. In analogy, the electrical polarization P of a ferroelectric material can be controlled by the application of an electric field, and the ferroelastic deformation e by a mechanical strain (Figure 1). Ferroelectric-ferroelastic materials have been extensively studied and are at the origin of numerous applications. The showcase example - and industrial standard - is PZT, in which the coupling between deformation and electric polarization leads to a remarkable piezoelectric response, much larger than in quartz.

Ferroelectric and magnetic?!

Although ferroelectric-ferroelastic materials also belong to the class of multiferroics, the community uses the term “multiferroic” currently for magnetoelectric (ME) multiferroics which are both ferroelectric and magnetic, but not necessarily ferromagnetic. In the past ferroelectric-magnets have been much less studied due to their scarcity and indeed they seem to exclude each other, at least at first sight. First, it has been argued that the presence of electrons in the d -orbitals of transition metals (favorable for magnetism) inhibits hybridization with the p -orbitals of the surrounding oxygen-anions and thus a cation displacement (necessary for ferroelectricity) [6]. Second, a ferroelectric has to be a good insulator so that mobile charges do not neutralize ferroelectric polarization, but most ferromagnets are rather conducting. In fact, even though ferroelectric-magnets are rare, those which present a direct coupling (magnetoelectric multiferroics) are even rarer. As a consequence, the research for both new materials systems and new coupling mechanisms are the *sine qua non* conditions for a better understanding of magnetoelectric coupling mechanisms and the development of future applications in the field of spintronics.

Different materials – different coupling

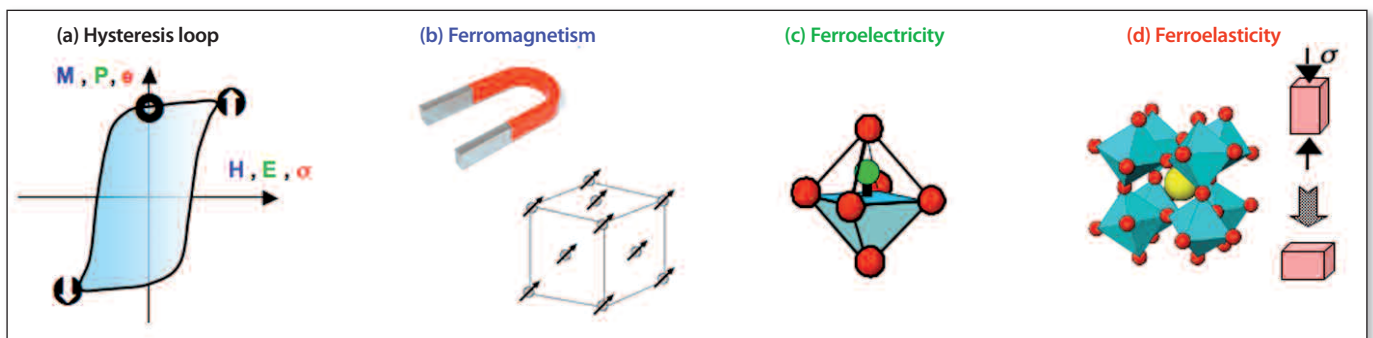
The known multiferroic materials can be classified into three different classes depending on the microscopic mechanism of ferroelectricity. Ferroelectricity arises because

▲ Piezo-Force Microscopy (PFM) image of the domain structure in the model multiferroic BiFeO₃. © F. Zavaliche *et al.*, Multiferroic BiFeO₃ Films: Domain Structure and Polarization Dynamics, *Phase Transitions* 79, 991 (2006)

■ of either (i) hybridization effects, (ii) geometric constraints and/or (iii) electronic degrees of freedom (spin, charge or orbital). All three classes attract an intense research interest: (i) In this class of multiferroic, the magnetic and ferroelectric ordering are associated with two chemically different cations [6], which can lead to both strong magnetic and ferroelectric properties, but their coupling is unfortunately not necessarily strong. The best example of this class of multiferroic is probably BiFeO₃ (BFO). This is perhaps the only material that is both magnetic and a strong ferroelectric at room temperature, making it the preferred model system for fundamental and theoretical studies of multiferroics. Its impact on the field of multiferroics is comparable to that of yttrium barium copper oxide (YBCO) on superconductors [7]. In BFO the magnetism is associated with the 3*d* electrons of the Fe³⁺ cations. The ferroelectricity arises from the hybridization between the oxygen 2*p* orbitals and the empty Bi 6*p* orbitals, which are low lying in the conduction band and spatially extended due to the presence of the so-called lone-pair 6*s*² electrons. A recently observed electric-field-induced spin flop in BFO single crystals demonstrates that the antiferromagnetic and ferroelectric order parameters in BFO are coupled [8]. It has been argued that the magneto-electric coupling in BFO is intimately related to the presence of a magnetic cycloid structure that allows a coupling of *M* and *P* on an atomic level even in antiferromagnetic structures where on average the linear ME-effect is forbidden.

(ii) In geometric multiferroics, the ferroelectric instability has its origin in the topology of the chemical structure, and the ferroelectric distortions are driven by ionic size effects. In contrast to covalent-bond driven ferroelectrics, geometric ferroelectrics feature no significant hybridization effects or significant charge transfer between cations and anions. The first material identified as a geometric ferroelectric was the hexagonal manganite YMnO₃ [9], illustrated in Figure 2. Ferroelectricity in YMnO₃ arises from the rotation of MnO₅ bipyramids which separate two-dimensional triangular planes of Y ions. Because of the topology of differently charged ions in the chemical lattice, this rotation leads to ferroelectric polarization even in the absence of charge transfer from one ion or bond to another.

(iii) In correlation-induced ferroelectrics, the ferroelectric polarization results from long-range order of an electronic degree of freedom such as orbital, charge or spin. In this class of multiferroics, magnetically-induced ferroelectrics such as TbMnO₃ and Ni₃V₂O₈ are probably the best understood [10]. Ferroelectricity in these two materials arises from a magnetic spiral structure that breaks inversion symmetry and creates a polar axis (Figure 3). Magnetic order and ferroelectricity are thus directly coupled because there is not ferroelectric polarization without magnetic order. Changing the symmetry of the magnetic order can switch or suppress ferroelectricity. Competing magnetic interactions seem to play a key role in the emergence of magnetically-induced ferroelectricity, as they do not clearly favour a fully ordered magnetic state at low temperatures. Ferroelectricity in



▲ FIG. 1: Ferroic materials

- (a) The term **ferroic** unifies common characteristics of ferromagnetic, ferroelectric and ferroelastic materials. A shared key property of these three ferroics is the hysteresis loop (cf. Figure) which describes the control of the macroscopic physical property (magnetization, polarization, deformation) by an external field (magnetic, electric, mechanic), leading to two important characteristics: 1) The macroscopic property remains different from zero - remanent or spontaneous - under zero field (●) and 2) reversing the field allows the inversion of the physical property (◐◑).
- (b) **Ferromagnetism** was in ancient times the first identified ferroic property, used for example in a compass by Chinese 100BC. A ferromagnet presents a spontaneous magnetization *M* that can be driven by a magnetic field *H*. The electrons' orbital angular momentum is responsible for so called orbital-magnetism, while the spin of an electron is responsible for spin-magnetism, which is often preponderant for the magnetic structure.
- (c) Although studied since the 17th century, the term **ferroelectricity** has been introduced by Erwin Schrödinger only in 1912. Initially considered as a rare phenomenon, a vast number of ferroelectrics is known today, namely in form of the ABO₃ perovskite. A ferroelectric material is characterized by an electric polarization *P* of which the direction can be reversed by an electric field. In a schematic picture the macroscopic polarization is on the microscopic level related to a displacement of positively charged cations (in green) with respect to the centre of gravity of negatively charges anions (in red).
- (d) The **ferroelastic** deformation has long been considered as a property linked to ferromagnetism (leading to magnetostriction) or to ferroelectricity (electrostriction). It is only in the 70'ties that the ferroelastic deformation *e* has been recognized as an independent property of which the direction can be controlled by a mechanical stress *σ*. The Figure illustrates the microscopic mechanism of a spontaneous ferroelastic deformation, even in absence of stress, for the example of the perovskite SrTiO₃ (Sr in yellow, oxygen in red and Ti in the centre of the octahedra). A mechanical stress can modify the angle of the octahedra tilting (left) and thus the state of macroscopic deformation (right). Just as for the other ferroic properties a hysteresis loop can be obtained by applying a uniaxial stress.

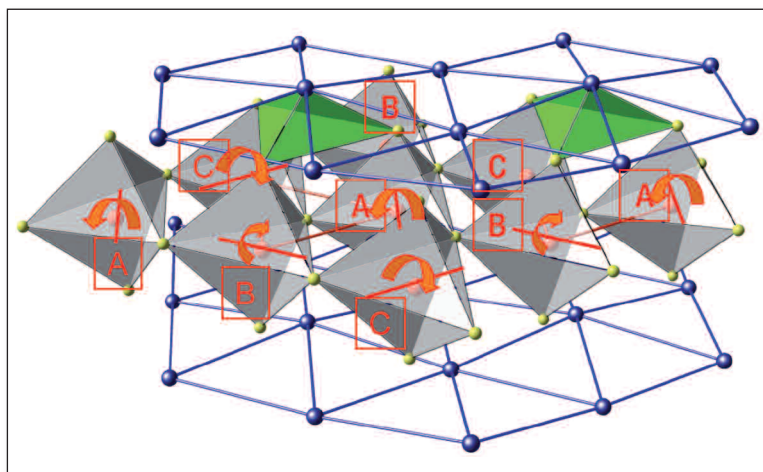
these systems is driven by a lattice distortion that allows Dzyaloshinskii-Moryia interactions which stabilize a magnetic spiral, thereby reducing the magnetic entropy. Some of the electric polarization may also arise from the so-called spin-current effect where the exchange of electrons from a non-collinear structure leads to electric polarization from a distortion of electronic orbitals without ion displacements. The maximum ferroelectric polarization that has been observed in spin-spiral ferroelectrics is rather small and of the order of $0.2 \mu\text{C}/\text{cm}^2$, probably due to the small size of the magneto-electric coupling that is mediated by spin-orbit interactions.

Ferroelectric polarization on the order of $2\text{--}6 \mu\text{C}/\text{cm}^2$ has been predicted for another class of magnetically-induced ferroelectrics which feature commensurate collinear magnetic order [11]. Ferroelectricity in collinear spin ferroelectrics is mediated by symmetric exchange strain which does not depend on the presence of spin-orbit in interactions and can be of the order of the dominant exchange interactions in a material. Examples of this class include orthorhombic HoMnO_3 , TmMnO_3 but also rare-earth-nickelates ReNiO_3 in their charge ordered state. These materials are difficult to produce as single crystals, but powder measurements provide evidence for ferroelectric polarization that is larger than any previously observed ferroelectric polarization in a magnetically-induced ferroelectric.

Probably the most promising class of correlations-induced ferroelectrics are charge-order induced ferroelectrics. These are materials with competing charge interactions or charge frustration that leads to a charge instability that carries ferroelectric polarization. An example of this class of ferroelectrics is LuFe_2O_4 [12] where competing charge interactions arise from an intermediate valence iron ion which is arranged in bi-layers of triangular lattices. The lowest energy state of this strongly-correlated charge lattice appears to be a charge-ordered state which carries ferroelectric polarization. Because the charge order is driven directly by charge-charge interactions, the ordering temperature and ferroelectric polarization can be high. Magnetic order is established at low temperature due to the magnetic degrees of freedom associated with the charge ordered iron ions, and increases the ferroelectric polarization.

Composite multiferroics

So far we have discussed intrinsic multiferroics, where the different ferroic properties are united within *one* material (single-phase multiferroics). To overcome the shortage of single-phase multiferroics and to provide new magnetoelectric coupling mechanisms, recent work also concentrates on the class of *artificial* multiferroics in the form of composite-type materials or thin film nano-/hetero-structures [5,13]. It was shown that composite-type multiferroics, which incorporate both ferroelectric and magnetic phases, can yield a giant



magnetolectric (ME) coupling response even above room temperature. In such systems neither the ferroelectric (thus piezoelectric) nor the magnetic phase shows the ME effect, but composites of these two phases have a remarkable ME effect. Thus the ME effect is a result of the product of the magnetostrictive effect (magnetic/mechanical effect) in the magnetic phase and the piezoelectric effect (mechanical/electrical effect) in the piezoelectric one [13], *i.e.* the coupling between both components is mediated by strain: for instance the magnetic phase changes its shape magnetostrictively when a magnetic field is applied and, in turn, the strain is passed along to the piezoelectric phase giving rise to an electric polarization. Thus, the ME effect in composites is extrinsic. This field remains full of scientific challenges and certainly deserves a particular attention in view of future applications of multiferroics.

Applications

Most of the research in multiferroics has been curiosity-driven basic research, but there are a number of ideas for device applications based on multiferroic materials. One of the more popular ideas is that multiferroic bits may be used to store information in the magnetization M and the polarization P . The feasibility of such a 4 stage memory (two magnetic $M_{\uparrow\downarrow}$ and two ferroelectric $P_{\uparrow\downarrow}$) has been demonstrated recently [14]. Such a memory does not require the coupling between ferroelectricity and magnetism; a cross coupling would be even disastrous. If magneto-electric coupling is present, device applications could be realized where information is written magnetically, but stored in the electric polarization, leading to non-volatile memory. Multiferroics bits could also be used to increase the magnetic anisotropy to increase the decay time for magnetic storage. Other applications include magnetically field-tuned capacitors with which the frequency dependence of electronic circuits could be tuned with magnetic fields, or multiferroic sensors which measure magnetic fields through a zero-field current measurements.

▲ **FIG. 2:** Ferroelectricity in YMnO_3 arises because of the cooperative rotation of the bipyramids indicated by the axes and by the arrows. All oxygen (in yellow) of the green YO_3 pyramid move closer together, leading to a uniform shift of ions perpendicular to the triangular planes. Because of the symmetry of the chemical lattice, this thus leads to a overall shift of positively and negatively charged ions in the opposite direction [9]. The Y ions are shown in blue, the Mn ions in red and the O ions in yellow.

Outlook

The rapid development in the field of multiferroics in the last few years has been exciting and revealed fascinating physics in condensed matter. There are several important conclusions that we can draw regarding future directions of research. A first important question is what multiferroic mechanisms can lead to high ferroelectric polarization. Many of the investigated materials like the spin-spiral ferroelectrics are far away from charge instabilities, and magnetoelectric interactions are mediated by spin-orbit interactions. This combination naturally limits the ferroelectric polarization to relatively small values. Theory gives us a good guide in what type of materials we can expect larger polarizations and larger coupling effects. These are materials where magneto-electric effects are mediated by symmetric exchange or materials with intrinsic charge instabilities. However, experimental work has been limited due to a lack of novel materials.

A second important issue will be to develop further techniques allowing to provide experimental evidence for magnetoelectric coupling and to estimate its strength. One promising way may be the investigation of magnetic spin waves which couple to optical phonons (lattice vibrations). Such novel excitations - called electromagnons - are directly related to electromagnetic coupling and reflect the intimate relationship between magnetic and ferroelectric magnetic orders in multiferroic materials. The study of electromagnons may thus shed light on the strength of magnetoelectric coupling interactions. Electromagnons probably belong to the most challenging open questions in the field and are currently under intense investigation.

Another key question is in what kinds of other materials we can also expect multiferroic behavior. With a few exceptions, the multiferroics materials that have been investigated are transition metal oxides. It will be interesting to see how different types of magnetic and electric interactions found in rare-earth insulators without transition metal oxides, in organo-metallic materials, in

magnetic chalcogenide-based phase-change material or in polymer-based magnets affect the magnetic and ferroelectric properties, and the magneto-electric coupling. Finally, it remains a challenge to recreate some of the fascinating multiferroic properties in artificially engineered thin films and heterostructures. Without doubt, the study of such materials will be an important pillar of multiferroic research towards applications and for basic research, particularly for key model materials that cannot be grown as clean single-crystals. ■

About the authors

Jens Kreisel is working on phase transitions in functional materials. After a PhD from the Grenoble Institute of Technology (F) and a post-doc at Oxford University (UK), he is currently a CNRS Director of Research in Grenoble and Editor-in-Chief of the international journal *Phase Transitions*.

Michel Kenzelmann is working on materials with strong magnetic fluctuations such as low-dimensional antiferromagnets, multiferroics and heavy-fermion superconductors and holds a D.Phil. from Oxford University (UK). After a post-doc shared between the Johns Hopkins University and NIST (USA) and an assistant professorship at ETH Zürich, he now heads the Laboratory for Developments and Methods at the Paul Scherrer Institute, Switzerland.

References

- [1] M. Fiebig, T. Lottermoser, D. Fröhlich, A.V. Goltsev, and R.V. Pisarev, *Nature* (London) **419**, 818 (2002).
- [2] W. Eerenstein, N.D. Mathur and J.F. Scott, *Nature* (London) **442**, 759 (2006).
- [3] S.W. Cheong and M. Mostovoy, *Nature Materials* **6**, 13 (2007).
- [4] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and T. Tokura, *Nature* (London) **426**, 55 (2003).
- [5] R. Ramesh and N.A. Spaldin, *Nature Materials* **6**, 21 (2007).
- [6] N.A. Hill, *J. Phys. Chem. B* **104**, 317 (2000).
- [7] G. Catalan and J.F. Scott, *Advanced Materials* **21**, 1 (2009).
- [8] D. Lebeugle, D. Colson, A. Forget, M. Viret, A.M. Bataille and A. Gukasov, *Phys. Rev. Lett.* **100**, 227602 (2008).
- [9] B.B. Van Aken, T.T.M. Palstra, A. Filippetti and N.A. Spaldin, *Nature Materials* **3**, 164 (2004).
- [10] M. Kenzelmann, A.B. Harris, S. Jonas, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.W. Cheong, O.P. Vajk and J.W. Lynn, *Phys. Rev. Lett.* **95** (2005)
- [11] S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko and E. Dagotto, *Phys. Rev. Lett.* **99**, 227201 (2007).
- [12] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe and H. Kito, *Nature* (London) **436**, 1136 (2005).
- [13] C.W. Nan, M.I. Bichurin, S.X. Dong, D. Viehland and G. Srinivasan, *J. Appl. Phys.* **103**, 35 (2008).
- [14] M. Gajek, M. Bibes, S. Fusil, K. Bouzehouane, J. Fontcuberta, A. Barthélémy and A. Fert, *Nature Materials* **6**, 296 (2007).

► **FIG. 3:** A generic example of a magnetic structure that breaks the inversion symmetry of the lattice: The magnetic structure is even under a two-fold rotation around the vertical direction and odd under a two-fold rotation around the horizontal axis, allowing ferroelectricity along the vertical direction [10].

