Multiferroics

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A Magnetoelectric Effect in $YMnO_3$ and $HoMnO_3$

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The term multiferroism was originally coined for crystals in which at least two of the properties ferroelectricity, ferromagnetism, and ferroelasticity are operative.[1,2] Multiferroics exhibit at least two types of order: polarization, magnetization, or deformation.[3]

In a multiferroic crystal with both electric and magnetic order, an interdependence between the two orders may exist: An applied electric field induces a linear change of magnetization and an applied magnetic field induces a linear change of polarization. This kind of coupling is called a magnetoelectric (ME) effect and was predicted 1894 and observed first in 1960.[4]

The microscopic origins of the ME effect are twofold: 1) The magnetic ordering is driven by (super)exchange interactions whose strength depends sensitively on the overlap of magnetic orbitals, that is, on bond lengths and bond angles. 2) These structural parameters may be changed in an applied electric field, because the metal cations and the ligand anions move in opposite directions. Moreover, the electric field induces local distortions which change the ligand field, which in turn changes the orbital contribution to the magnetic dipole moment of the metal ions.[5]

This ME effect makes so-called magnetoelectric multiferroics interesting materials for future information-technology devices in which data can be written to magnetic memory elements by applied electric fields. Apart from this technological motivation, multiferroics are of immense interest in fundamental research because the magnetic order can be controlled through the ferroelectric order (and vice versa) at a microscopic level. However, the design of magnetoelectrics has to overcome a principal obstacle: Ferroelectricity and magnetic ordering tend to be mutually exclusive and usually interact only weakly with each other when they coexist.[2c] An example illustrates the dilemma. The prototype of a so-called "proper" ferroelectric is $BaTiO_3$, where the Ti^{4+} ion has an empty d subshell. Below approximately 400 K the cubic perovskite structure transforms into a non-centrosymmetric one, caused by the transition-metal ions leaving the octahedral center of symmetry in a coordinated movement. Corresponding magnetic systems, need d^N configurations with unpaired electrons. Yet, if in a ferroelectric system AMO_3, the M ion with d^0 configuration is replaced by a d^N one, the phase will usually no longer be ferroelectric, unless the cation A carries a sterically demanding lone pair (Bi^{3+}, Pb^{2+}) or the d^N material gains its polarization by a more complex lattice distortion ("improper" ferroelectricity).[6]

The improper ferroelectricity situation is encountered in the hexagonal $LnMnO_3$ phases[7] $YMnO_3$ (ferroelectric below $T_{FE} = 920$ K where T_{FE} is the Curie temperature), and $HoMnO_3$ ($T_{FE} = 875$ K) whose magnetically active ions are high-spin Mn^{3+} [$3d^4$] ($S = 2$) and Ho^{3+} [$4f^{10}$] (ground-state multiplet $^5I_8$). Research activities, related to these phases, enormously intensified at the beginning of the new millennium triggered by the finding that with the hexagonal $LnMnO_3$ phases the long-sought-after control of magnetic properties by electric fields and of electric properties by magnetic fields could be accomplished. Temperature-dependent measurements of physical properties of these phases (through X-ray and synchroton structure investigations, high-resolution neutron scattering, nonlinear optical measurements, and magneto-optical techniques, specific heat measurements, SQUID magnetometry) using high-grade single crystals, and application of first-principles density-functional calculations[6b] produced a deeper understanding of the driving effects and the microscopic mechanisms during phase transitions. Herein the outstanding magnetoelectric properties of the multiferroics $YMnO_3$ and $HoMnO_3$ are illustrated.

The hexagonal structure of both phases (non-centrosymmetric space group $P6_3cm$) consists of layers of corner-sharing distorted and tilted MnO_5 trigonal bipyramids. Adjacent layers are interlinked by corrugated layers of Y^{3+} (Ho^{3+}) ions (see Figure 1).[6a] The structure is derived from the aristotype (base structure) with space group $P6_3/mmc$ in a two-step phase transition.[8] The Mn^{3+} ions (position 6*c*, site symmetry *m* (C_s)) form layers of nearly ideal triangular nets stacked in the AB sequence along the *c* axis, widely separated from each other by intervening O^{2-} and Y^{3+} (Ho^{3+}) ions. The ligand field of pseudosymmetry $\bar{6}m2$ (D_{3h}), acting on Mn^{3+}, produces two low-lying doublets E″ (d_{xz}, d_{yz}) and E′ (d_{xy}, $d_{x^2-y^2}$), occupied by the four valence electrons, and a singlet A_1' (d_{z^2}), so that the Mn^{3+} ion in this coordination sphere is not Jahn–Teller active. However, as a result of the distorted and tilted MnO_5 units, as well as of the displacement of the Y^{3+} (Ho^{3+}) ions, there is a net polarization collinear to the *c* axis.

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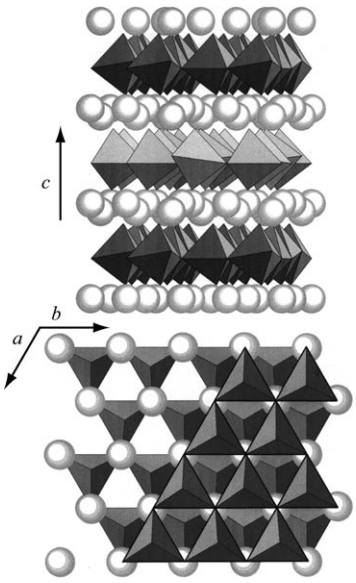

Figure 1. The crystal structure of $YMnO_3$ in the paraelectric and ferroelectric phases. The trigonal bipyramids depict MnO_5 polyhedra and the spheres represent Y ions; top: A view of the ferroelectric phase from perpendicular to the *c* axis, showing the layered nature of $YMnO_3$; bottom: The stacking of two consecutive MnO_5 layers and the Y layers sandwiched in between, looking down the *c* axis in the paraelectric phase. (Adapted from ref. [6a]).

The two phases $YMnO_3$ and $HoMnO_3$ differ in their low-temperature properties. In $YMnO_3$, magnetic ordering within the manganese partial structure is switched on below the Néel temperature $T_N = 75$ K, and coexists with the ferroelectric ordering. The magnetic ordering is dominated by antiferromagnetic intralayer Mn-O-Mn superexchange interactions. Weaker interlayer interactions Mn-O-O-Mn guarantee long-range magnetic order. On account of the anisotropy, the magnetic dipoles are oriented parallel to the *ab* plane with a so-called 120° structure. This structure is typical for a frustrated magnetic system of classical spins and is a consequence of the triangular network.[9] The orientation of the Mn spins with respect to the crystal axes *a* and *b* occurs according to the pattern α shown in Figure 2 (left) where $\varphi = 0°$.[10] In this projection neighboring spins on line of layer A (●, $z = 0$) and layer B (○, $z = {}^1/_2$) are parallel and coplanar. The alternative model β (Figure 2, right) is not observed. On the basis of these results (electric dipole moment parallel to the *c* axis and magnetic dipoles perpendicular to the *c* axis) a direct coupling of the two orderings, that is, the ME effect, is symmetry-forbidden.[1b]

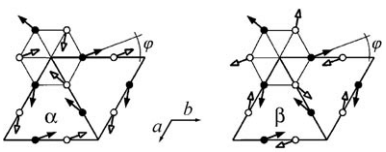

Figure 2. Planar triangular magnetic structures of hexagonal $LnMnO_3$. A projection of the Mn spins at $z = 0$ (closed arrows) and $z = {}^1/_2$ (open arrows) on the *ab* plane of the magnetic unit cell shows parallel (α model) or antiparallel orientation (β model) of neighboring spins on a line. (Adapted from ref. [10a]).

However, anomalies in the dielectric constant of $YMnO_3$ have been observed near its Néel temperature,[11] indicative of a coupling between the ferroelectric and antiferromagnetic orderings. To trace the cause of the ME effect in $YMnO_3$, the structures of the ferroelectric and antiferromagnetic domains have been analyzed.[10,12] Since the direct coupling of the orderings in this case is symmetry-forbidden, coupling between only the electric and magnetic domain walls must be the leading cause. Several innovative nonlinear optical measurements elucidated that ferroelectric and antiferromagnetic domain walls coincide in $YMnO_3$. Coupling through such walls can then arise because the local magnetization in an antiferromagnetic domain wall has either reduced magnetic symmetry or interacts with the elastic strain from the coincident ferroelectric wall.[13] Consequently, the "clamping" of the ferroelectric and the antiferromagnetic domain walls enforces reversal of the magnetic moments whenever the electric dipoles are reversed, and an ME effect emerges. In this way a form of ME control is established although the ME effect is macroscopically forbidden.

The low-temperature behavior of $HoMnO_3$ distinctly differs from its yttrium analogue: The presence of magnetically active holmium instead of diamagnetic yttrium ions leads—in addition to the antiferromagnetic Mn^{3+}–Mn^{3+} interactions—to Ho^{3+}–Mn^{3+} and, importantly, Ho^{3+}–Ho^{3+} exchange interactions.[14] Concerning the magnetic ordering of Mn^{3+}, the frustrated spin structure below the Néel temperature $T_N = 75$ K evolves into model α with $\varphi = 90°$ (Figure 2) and then changes (as a result of a collective rotation of all spin vectors) at ≤ 37 K into a structure with $\varphi = 0°$, similar to the structure observed for $YMnO_3$. Antiferromagnetic Ho^{3+} ordering occurs below 4.6 K. An exceptional feature of $HoMnO_3$ below $T_N = 75$ K is the effect of a static electric field applied along the *c* axis. If the field is strong enough to acquire a ferroelectric single-domain state, that is, full alignment of all electrical dipole moments, an antiferromagnetic reordering of the Mn^{3+} spins occurs with intermittent spin angles ($0° < \varphi < 90°$); concomitantly the Ho^{3+} sublattice orders ferromagnetically with the rather large atomic dipole moment $\mu_a \approx 3\mu_B$. In other words, the electric field triggers a giant ME effect and converts the $HoMnO_3$ phase from para-/antiferromagnetism (in the absence of an electric field) into a ferromagnet.

What drives the magnetoelectrical coupling in the hexagonal $LnMnO_3$ phases on a microscopic level? Quite recently a decisive indication has come from high-resolution neutron diffraction data taken on $YMnO_3$ between 300 and 10 K.[15] While the temperature dependence of the atomic position parameters is almost negligible from 300 K to T_N, a striking structural anomaly emerges just below the Néel temperature: 1) Both the unit cell parameters *a* and the volume suddenly shrink whereas the *c* axis expands. 2) While maintaining the space group ($P6_3cm$) all atoms exhibit atomic displacements that are two orders of magnitude larger than those found in any other magnetic compound. For example, the manganese ion occupies a nearly ideal site in the paramagnetic phase, leading to an almost regular triangular

arrangement. As soon as the Mn spins start to order magnetically below T_N the manganese ions shift considerably away from the ideal position by an amount comparable to the atomic displacement of Ti in $BaTiO_3$. Strong variations occur in the Mn–O separations within the basal plane thereby producing a further coupling to electric dipole moments. Clearly, the following scenario is realized in $YMnO_3$: On account of the structural alterations at the antiferromagnetic transition a giant magnetoelastic coupling is evident. This coupling then induces a change in the electric dipole moments.

In summary, the phases $YMnO_3$ and $HoMnO_3$ define an attractive class of ferroelectromagnets characterized by magnetic frustration and ferroelectricity. Driven by lowering of the magnetic energy of the exchange interactions, polar lattice distortions are induced. This situation also applies to systems with non-collinear spiral magnetic structure. A multiferroic of this type is $TbMnO_3$ which adopts the orthorhombically distorted perovskite structure (space group *Pbnm*). Although the unit cell has an inversion center, ferroelectric order evolves which is triggered by the transition into a spiral magnetically ordered phase.[16]

Multiferroics of this category have great potential as tunable multifunctional devices. The coupling of magnetic and electric order, together with additional magnetoelastic effects, form the foundation for subsequent rational design of magnetoelectric materials that promise to replace the slow magnetic writing process by a fast magnetization reversal through electric fields.

Recently multiferroic behavior has also been predicted for molecular magnets.[17] Single-ion and exchange anisotropy effects have been studied for tetranuclear single-molecule species with varying symmetry and have shown that geometrically frustrated systems with S_4, D_{2d}, and C_{2v} symmetry are likely candidate materials for multiferroic states.

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[3] a) There is a trend to include an ordered arrangement of magnetic vortices (termed ferrotoroidicity) in the group of ferroic properties (B. B. Van Aken, J.-P. Rivera, H. Schmid, M. Fiebig, *Nature* **2007**, *449*, 702); b) Besides the herein described magnetoelectric single-phase systems, the term multiferroics includes composite materials that consist of ferroelectric (and piezoelectric) and ferromagnetic (and piezomagnetic) components.[2a,b]

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[7] a) Ln = Ho, Er, Tm, Yb, Lu, Y; b) In the physical literature the denomination rare-earth manganites is often used for these lanthanide manganese trioxides.

[8] The nonpolar high-temperature space group of the hexagonal $LnMnO_3$ series is $P6_3/mmc$. All ions are constrained to planes perpendicular to the unique hexagonal axis *c*. With decreasing temperature a two-step transition to the non-centrosymmetric ferroelectric phase occurs: $P6_3/mmc \rightarrow P6_3cm$ at the temperature T_{npt} of the nonpolar transition and, without change of symmetry, $P6_3cm \rightarrow P6_3cm$ at T_{FE}, where $T_{npt} \approx 1430$ K and $T_{FE} \approx 1050$ K determined for Ln = Tm. The first step is a paraelectric to triangular-antiferroelectric phase transition where the pseudo threefold main axis O-Mn-O of the MnO_5 bipyramid tilts and the Ln layer corrugates. The subsequent triangular-antiferroelectric to ferroelectric transition is generated by a displacement of the O^{2-} and Mn^{3+} ions within the MnO_5 unit. (Ref.: T. Lonkai, D. G. Tomuta, U. Amann, J. Ihringer, R. W. A. Hendrikx, D. M. Többens, J. A. Mydosh, *Phys. Rev. B* **2004**, *69*, 134108).

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[12] Domains are small regions in ferroelectric and ferromagnetic materials, within which all the electric (magnetic) dipole moments are aligned parallel to each other. The domains are separated by domain walls, most often by a 180° twist boundary where the orientation of the moments changes gradually. Domains are also detected in antiferromagnets.[10]

[13] The mechanism that interlocks the ferroelectric and antiferromagnetic domain walls can be explained as follows:[10c] 1) The distortion at the ferroelectric domain wall as a result of to the reversal of the electric dipoles produces an elastic strain; 2) the gradual rotations of the magnetic moments across an antiferromagnetic wall result in a non-zero local magnetic moment. So, the electric and magnetic perturbations can interact through the piezomagnetic effect. (Piezomagnetism describes a change in strain as a linear function of an applied magnetic field, or a change in magnetization as a linear function of applied stress.)

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