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Magnetic ferroelectric materials

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Abstract. In the form of a succinct overview the structure and symmetry requirements of magnetic ferroelectrics are discussed. Boracites are the best-studied examples and have phases being simultaneously ferroelectric, ferromagnetic and ferroelastic. One of the salient features of such materials is the obligatory occurrence of the linear and bilinear magnetoelectric effects. They represent an invaluable auxiliary information for magnetic symmetry determination by neutron diffraction. Owing to the complexity of property combinations, work with single crystals and polarized light microscopy is obligatory. Key references of the field are given.

Keywords. Ferromagnetic ferroelectrics; antiferromagnetic ferroelectrics; ferroelasticity; magnetoelectric effects.

1. Introduction

In 1994 we celebrate the centennial of Pierre Curie's idea of a material which can be electrically polarized by means of a magnetic field and magnetized by means of an electric field (Curie 1894). There were many unsuccessful attempts of different scientists at finding such an effect (well chronicled by O' Dell 1970). Finally Landau and Lifshitz remarked that time reversal symmetry has to be taken into account and that the magnetoelectric and piezomagnetic effect should be possible in magnetic structures (Landau and Lifshitz 1960). On that basis Dzyaloshinskii predicted the linear magnetoelectric effect to exist in the antiferromagnetic phase (with Shubnikov point symmetry $\bar{3}'m'$) of chromium oxide Cr_2O_3 (Dzyaloshinskii 1959). Shortly thereafter Astrov confirmed the prediction by measuring the electric field-induced magnetization in Cr_2O_3 (Astrov 1960), and the detection of the magnetic field-induced polarization followed step (Folen *et al* 1961; Rado and Folen 1961). These two manifestations of the magnetoelectric effect—measurable in insulators only—can be considered as the two facets of Curie's prediction.

If we take a compensated antiferromagnet like Cr_2O_3, permitting the linear magnetoelectric effect, we can alternatively say that owing to the magnetoelectric interaction the material becomes a *very weak ferromagnet* under the influence of an electric field and a *very weak ferroelectric* under the influence of a magnetic field. Such a magnetic field-induced ferroelectric is unusual in the sense that its antiferromagnetic domains, which become simultaneously the ferroelectric domains, can be switched by means of an electric field (Martin 1965; Martin and Anderson 1966). We might also speak of an *induced electronic ferroelectric* because in contrast to common ferroelectrics the nuclear structure remains in first approximation immobile and essentially only the spins of the magnetically active unpaired electrons are reversing during the domain switching process.

Independently of the rigorous symmetry approach by Dzyaloshinskii, Smolensky and Ioffe were trying to synthesize ferroelectric ferromagnets by replacing partially diamagnetic ions by paramagnetic ones on the B-site of oxyoctahedral ferroelectric perovskites. By this approach initially the antiferromagnetic ferroelectric perovskite $Pb(Fe_{1/2}Nb_{1/2})O_3$ was synthesized in ceramic form (Smolensky and Ioffe 1958). Later, by studying single crystals, the compound was recognized to have a weak spontaneous magnetic moment in the ferroelectric phase below 9K (Astrov *et al* 1968). Because of the solid solution approach, implying dilution by diamagnetic ions, the magnetic coupling is, however, substantially reduced.

The simultaneous occurrence of ferroelectricity and (weak) ferromagnetism was first discovered in nickel iodine boracite $Ni_3B_7O_{13}I$ (below 61 K) (Ascher *et al* 1966). This compound is a member of a large crystal structure family with the general formula $M_3B_7O_{13}X$, where M stands for a bivalent cation of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, etc and X for a monovalent anion like OH^-, F^-, Cl^-, Br^-, I^-, or NO_3^-. Nearly all the boracite compositions with paramagnetic metal ions undergo phase transitions from a cubic high-temperature phase to fully ferroelectric/fully ferroelastic phases (for nomenclature see Aizu 1970), most of which undergo at low temperatures a transition to a (weakly) ferromagnetic phase with orthorhombic, monoclinic or triclinic symmetry (Tolédano *et al* 1985; Rivera *et al* 1985).

2. Conditions for ferromagnetic and antiferromagnetic ferroelectrics

The conditions for the occurrence of ferroelectricity and magnetic order in the same phase—often accompanied by ferroelasticity (for a definition see Aizu 1970)—comprise (i) the presence of adequate structural building blocks, e.g. with double or multiple potential wells permitting ferroelectric-type ionic movements, (ii) magnetic-interaction pathways, usually of the superexchange type, and (iii) the fulfilment of symmetry conditions (Schmid 1973; Ascher 1973; Freeman and Schmid 1975).

Among the 122 Shubnikov–Heesch point groups there are 31 allowing a spontaneous magnetization and 31 allowing a spontaneous polarization. However, the occurrence of both ferro(i)magnetism and ferroelectricity in the same phase is permitted in 13 point groups only (Ascher 1973; Schmid 1973). The presence of both ferroelectricity and antiferromagnetism is allowed in 8 point groups (Schmid 1973); however, this number increases drastically when the possible symmetries of incommensurate phases are included.

For symmetry reasons all ferro(i)electric ferromagnets allow *a fortiori* the linear and both bilinear (in the electric field and the magnetic field) type magnetoelectric effects (Ascher 1968; Schmid 1973; Freeman and Schmid 1975). In the boracite family the linear and bilinear (in the magnetic field) magnetoelectric effect has been measured for a variety of compositions (for a bibliography see: Burzo 1994).

For those ferromagnetic ferroelectrics which are simultaneously ferroelastic, a coupling between the spontaneous polarization, spontaneous magnetization and spontaneous deformation is possible. Such a coupling has for the first time been demonstrated for $Ni_3B_7O_{13}I$ (Ascher *et al* 1966), in which *an electric field-induced 180° reversal of the spontaneous polarization* causes a symmetry-conditioned *90° reorientation of the spontaneous magnetization,* and *a magnetic field-induced 90° reorientation of the spontaneous magnetization causes a 180° reversal of the spontaneous polarization.* Such coupling between the spontaneous polarization and the spontaneous magnetization requires ferroelasticity to be allowed and leads to nonlinear effects with hysteresis cycles and memory behaviour, whereas the linear and bilinear (special case: quadratic) magnetoelectric effects are in principle non-lossy, thermodynamically reversible effects, if domain switching and possible relaxation phenomena are disregarded.

3. Examples of ferromagnetic and antiferromagnetic ferroelectrics

The simultaneous occurrence of ferroelectricity and ferromagnetism has reliably been proved in the boracite family (Tolédano *et al* 1985) and recently in the phosphate $KNiPO_4$ (Lujan *et al* 1994). The new family of perovskite–orthoferrite solid solutions, $Bi_{1-x}RE_xFeO_3$ (RE = La, Dy, Gd), with pyroelectric, ferrimagnetic, magnetoelectric phases and Curie temperatures above room temperature, are very promising (Gabbasova *et al* 1991).

Ferroelectric antiferromagnets like $BiFeO_3$, $BaMnF_4$, $REMnO_3$ (RE = rare earth), etc are more frequent (Schmid 1973; Freeman and Schmid 1975). It is noteworthy that in $BiFeO_3$ and $BaMnF_4$ the linear magnetoelectric effect cancels because of incommensurate structures (Tabares-Munoz *et al* 1984; Sciau *et al* 1990). As a consequence the magnetoelectric behaviour was found to be only that of a non-centrosymmetric paramagnet, as manifested by the bilinear (in the magnetic field) magnetoelectric effect (Tabares-Munoz 1984; Sciau *et al* 1990). In the large perovskite family many compositions are potential magnetic ferroelectrics (Venevtsev and Gagulin 1994). However, these materials, often known in ceramic form only, are hardly investigated. There is a reason for that: in perovskites and other compounds with a cubic high-temperature prototypic point symmetry $m\bar{3}m1'$ the number of domain states may climb up to 96 for a triclinic ferroelectric ferromagnetic or antiferromagnetic phase. Therefore, when studying such complex ferroelectric magnetics, reliable physical measurements necessitate the availability of single crystals and the preparation of single-domain specimens in conjunction with the indispensable visual control of the domain state by low-temperature and high-temperature polarized light microscopy, both in transmitted and reflected light (Schmid 1993). There is great paucity of such investigations on single crystals of perovskites and other materials up to now.

4. Applications of the magnetoelectric effect

One of the important applications of the linear and higher-order magnetoelectric effects, occurring in magnetic ferroelectrics, resides in the fact that they give us precious auxiliary information for determining the magnetic point group, and herewith the magnetic space group, because the Schönflies–Federov space group is usually known from X-ray diffraction work. This means that they provide a precious complementary tool for neutron diffraction, which seldom allows us to determine the magnetic point and space group unequivocally.

Other important scientific applications of the magnetoelectric effect are the accurate determination of magnetic phase-transition temperatures and critical exponents; the study, switching and 'poling' of antiferromagnetic domains by means of simultaneous application of magnetic and electric fields; the study of defects in magnetic phases; magnetic and electric field-induced phase transitions (e.g. spin-flop and metamagnetic transitions); etc (Freeman and Schmid 1975; Schmid *et al* 1994).

5. Conclusions

In the Proceedings of the 2nd International Conference on Magnetoelectric Interaction Phenomena in Crystals (Schmid *et al* 1994), the reader will find more information on magnetic ferroelectrics, related materials, their properties, and in particular on theory and experiment of the magnetoelectric effect. This effect represents one of the most salient features of magnetic ferroelectrics.

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