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Abstract

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MULTI-FERROIC MAGNETOELECTRICS

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Domain aspects of multi-ferroics are reviewed, i.e. of materials, in which two or all three of the properties 'ferroelectricity,' 'ferromagnetism' and 'ferroelasticity' occur simultaneously in the same phase, and in which the magnetic point group has been reliably established by magnetoelectric, optical, dielectric, magnetic and related studies on single crystals and single domains. Nearly only members of the boracite crystal family are concerned, whereas for the perovskite family and other classes of material there is great paucity of data on single crystals. Polarized light microscopy is shown to be an indispensable tool for the study of multi-ferroics, in particular when ferroelasticity is involved. Potential multi-ferroic magnetoelectrics, so far only known in ceramic form, are excluded from the survey.

Keywords: Ferroelectricity, ferromagnetism, ferroelasticity, magnetoelectric effect, polarized light microscopy, symmetry, domains, boracites, perovskites.

1. INTRODUCTION

The search for ferromagnetic ferroelectrics started in the late nineteen fifties in Russia by trying to replace partially diamagnetic ions by paramagnetic ones on the B-site of oxyoctahedral perovskites.^{1,2} At that time it was thought that the presence of diamagnetic ions with rare gas configuration like Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , etc., would be indispensable for ferroelectric properties to occur in oxyoctahedral lattices.³⁻⁵ This approach implies, however, weakening of the magnetic coupling due to dilution with diamagnetic ions. The first compounds synthesized in ceramic form according to that principle, were $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Fe_{1/2}Ta_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})O_3$, with disorder of the unequal metal ions on the perovskite B-site. The two former compositions were found to be ferroelectric and antiferromagnetic.^{1,2} The latter compound was initially thought to be ferroelectric, too, but recently single crystal studies showed that ferroelectricity can only be induced by means of an electric field.⁶ Many more magnetically ordered perovskite compositions have later been synthesized in ceramic form, but unfortunately there is great paucity of single crystal data up to now.⁷

Nickel iodine boracite $Ni_3B_7O_{13}I$ was the first compound for which simultaneous onset of ferroelectricity and ferromagnetism (of the weak type) was observed to occur (below about 61 K).⁸ Later, many more boracite compositions were also found to be both ferroelectric and ferromagnetic (see Table I).

In those pioneering days, the useful concepts of "ferroelasticity" and "ferroics," introduced by Aizu in 1969⁹ and 1970,¹⁰ respectively, did not yet influence the thinking of researchers in the field. By ferroelasticity we understand the onset of a spontaneous deformation ϵ_S , described by a second rank symmetric tensor, at a

TABLE I
Different types of observed phase sequence in boracites.

CUBIC	TETRA- GONAL	ORTHO- RHOMBIC	MONO- CLINIC	RHOMBO- HEDRAL	ORTHORHOMBIC	MONOCLINIC	TRICLI- NIC	BORACITE COMPOUNDS	
PROTO- TYPE	FULL FERRO- ELASTIC	FULL FERROELECTRIC / FULL FERROELASTIC						M3B7O13X (M - X)	
PARA- OR DIAMAGNETIC				ANTI FERRO- MAGNE- TIC	FERROMAGNETIC			M = BIVALENT IONS OF Mg, Cd OR 3d- METAL	
					PARTIAL	FULL	PARTIAL	FULL	X = F, OH, Cl, Br, I, NO3
$\bar{4}3m1'$	NO PHASE TRANSITION OBSERVED DOWN TO 4 K								Cr-Br, Cr-I, Cu-I (?)
$\bar{4}3m1'$	←—————→ m'								Ni-I
$\bar{4}3m1'$	←————→ $mm21'$								Mg-Cl, Mg-Br, Mg-I (?); Zn-Br, Zn-I; Zn-NO3, [$\bar{4}3m1'$]; Cd-Cl, Cd-Br, Cd-I; Cd-NO3, [$\bar{4}3m1'$]
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $m'm2'$								Ni-Cl; Ni-NO3 (?), [$\bar{4}3m1'$]; Co-Br, Co-I; Co-NO3 (?), [$\bar{4}3m1'$]
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $m'm2'$ ←————→ 1								Ni-Br
$\bar{4}3m1'$	←————→ $\bar{4}2m1'$ → $mm21'$ ←————→ $mm2$ → $m'm'2$								Cr-Cl
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $m'm'2$								Cu-Cl, Cu-Br (?); Cu-NO3 (?), [$\bar{4}3m1'$]
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $m1'$ ←————→ $3m1'$								Zn-Cl
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $m1'$ ←————→ $3m1'$ ←————→ m								Co-Cl; Fe-Cl (?), Fe-I
$\bar{4}3m1'$	←————→ $mm21'$ ←————→ $3m1'$ ←————→ m								Fe-Br (?)
$\bar{4}3m1'$	←————→ $3m1'$ ←————→ m								Co-F (OH) (?), [$\bar{4}3m1'$]
$\bar{4}3m1'$	←————→ $3m1'$								Mg-OH, Mg-F; Zn-F

Phases given in Shubnikov-Heesch point group symbols; double arrows indicate transitions between phases, their length has no physical meaning; transition temperatures are omitted for clarity (for values see Reference 74 and 102); all transitions to or between magnetic phases are of 2nd order, those between para- or diamagnetic phases are of 1st order; "(?)" after composition M-X means "magnetic point group probable, but not yet verified," exceptions: "(?)" after Cu-I means "no phase transition probable down to very low temperature"; "(?)" after Mg-I means "transition to $mm21'$ probable, but not tested"; "[$\bar{4}3m1'$]" stands for "prototype $\bar{4}3m1'$ hypothetical," i.e. decomposition before transforming to $\bar{4}3m1'$.

phase transition and its reorientability to other equivalent orientation states (domains) under the influence of mechanical stress. The accent lies on *reorientability*, and on *the analogy of hysteresis properties and domains*, also found in ferromagnetic and ferroelectric materials.

The term "ferroic" has been suggested by Aizu to describe all types of mimetically twinned crystals in which one or more twin component may be switched to other equivalent states by the application of suitable external driving "forces." These "forces" are magnetic field, electric field and mechanical stress for the domains which differ with respect to a given coordinate system in orientation of spontaneous magnetization \mathbf{M}_S , spontaneous polarization \mathbf{P}_S and spontaneous deformation ϵ_S , respectively.

In a thermodynamic *classification of ferroics*,^{11,12} the Ferroelectrics, Ferromagnetics and Ferroelastics are considered as *primary ferroics*, whereas six kinds of *secondary ferroics* have been defined, namely Ferrobielectrics, Ferrobimagnetics, Ferrobielastics, Ferroelastoelectrics, Ferromagnetoelastics and Ferromagnetoelastics, the domain states of which differ in electric susceptibility, magnetic susceptibility, elastic compliance, piezoelectric coefficients, piezomagnetic coefficients and magnetoelectric coefficients, respectively.

In the present short overview we will concentrate on primary ferroics and consider as "multi-ferroic" those, having two or more primary ferroic properties in the same phase. Except for the linear magnetoelectric (ME) effect, secondary ferroic phenomena will not enter into the discussion.

2. REQUIREMENTS FOR FERROELECTRICITY, FERROMAGNETISM AND FERROELASTICITY TO OCCUR SIMULTANEOUSLY IN A CRYSTAL

2.1 Structural Requirements

The presence of adequate structural building blocks, for example with double or multiple electrostatic potential wells permitting ferroelectric-like ionic movements, is mandatory. In order to avoid magnetic dilution, paramagnetic ions being responsible both for ionic shifts and magnetic coupling, are very desirable. For example Ni in ferroelectric/ferromagnetic/ferroelastic nickel boracites (see Part 4) or Fe in antiferromagnetic ferroelectric/ferroelastic BiFeO_3 (see Part 6) have such functions, although these ions are not exclusively responsible for the ferroelectricity in these specific cases.

The structure must provide magnetic interaction pathways between the magnetic ions, with direct exchange, or as found more frequently in oxides and other non-metals, with superexchange interaction.^{13,14} So-called "long range superexchange" (see Part 4.4) also gives rise to magnetic order, but at lower temperatures than for classical superexchange.

2.2 Symmetry Requirements

Among the 122 Shubnikov-Heesch point groups 31 groups allow a spontaneous polarization \mathbf{P}_S (ferroelectricity or pyroelectricity only), 31 groups a spontaneous

magnetization M_S (ferro(i)magnetism or weak ferromagnetism) and 13 intersecting groups both properties simultaneously in the same phase. These latter groups¹⁵⁻¹⁸ are the following:

$$1, 2, 2', m, m', 3, 3m', 4, 4m'm', m'm2', m'm'2, 6, 6m'm'.$$

They are unique in the sense that they allow, beside ferroelectricity and ferromagnetism, the linear and bilinear ME effects, piezoelectricity, piezomagnetism, the linear electro-optic and linear magneto-optic effect, etc. (cf. Tables I and II of Reference 18).

The onset of spontaneous polarization and/or spontaneous magnetization at a phase transition is usually coupled with the onset of a spontaneous deformation ϵ_S . Depending on the particular high temperature point group/low temperature point group relationship, ϵ_S may be reorientable by mechanical stress or not. If it is, we speak of ferroelasticity, if it is not, we are in presence of a "non-ferroelastic" phase (N.B.: phase transitions with large non-orientable spontaneous deformation have been named "co-elastic,"¹⁹ but the necessity of introducing this term is considered questionable^{19a}).

At variance with the possible occurrence of spontaneous polarization and spontaneous magnetization, ferroelastics can not be characterized by a single point group. We have to indicate the pair of groups comprising the "prototype" high temperature point group and the low temperature phase point group. This pair of groups, called "species" and described by the two group symbols separated by the letter F in the nomenclature of Aizu,¹⁰ characterizes the possible domain patterns and switching properties of the ferroelastic domains and it tells us, whether the ferroic phase can be ferroelastic or not. In an analogous way, the symmetry permission of ferroelectricity, i.e. 180 degree switching or reorientability of P_S at other angles, also depends on the species and not on a single point group alone.

Ferroelastic domains can be seen in polarized light by means of birefringence contrast, and *vice versa*, the observation of domains by birefringence contrast indicates ferroelasticity,²⁰ provided we disregard possible confusion between optically anisotropic growth sectors²¹⁻²³ and true ferroelastic domains.

* All 13 Shubnikov groups permitting M_S and P_S vectors, may occur in 'non-ferroelastic' phases. However, if we look for ferroelectric ferromagnets being simultaneously ferroelastic, this additional requirement reduces the number of possible groups. Quite generally speaking, ferroelasticity is not possible if the prototype of the ferroic phase is of the same crystal system, as well as if a rhombohedral phase has a hexagonal prototype. For our particular case of the 13 groups allowing both ferroelectricity and ferromagnetism, this means that the two hexagonal groups, 6 and $6m'm'$, do not allow ferroelasticity to occur, whereas the remaining 11 groups do so.

3. DIFFERENT TYPES OF COMPLEXITY OF DOMAIN STRUCTURES

When working with multiferroics, the degree of complexity of the domain patterns, and herewith the degree of experimental difficulties, e.g. for producing single domains and measuring the components of the ME tensor quantitatively, is rising with the number of possible domain states. This number rises for example with increasing

TABLE II

The nine Shubnikov-Heesch point groups (column 1) permitting simultaneously ferroelasticity, ferroelectricity and ferromagnetism in case of prototype $\bar{4}3m1'$ (e.g. boracites)

Species $\bar{4}3m1'$ F (1)	P_s, M_s orientation (2)	σ_s (3)	P_s (4)	M_s (5)	Ferro- elast. (6)	Ferro- electr. (7)	Ferro- magn. (8)	Opt. active (9)	Remarks
1	arbitrary	24	= 24	48	full	full	full	+	observed
2	$P_s \parallel M_s \parallel [100]_c$	12	= 12	24	full	P	P	+	
2'	$P_s \parallel [100]_c$	12	= 12	24	full	P	full	+	
	$M_s \perp [100]_c$								
m	P_s in $(110)_c$	12	= 12	24	full	full	P	+	observed
	$M_s \perp (110)_c$								
m'	P_s in $(110)_c$	12	= 12	24	full	full	full	+	observed
	M_s in $(110)_c$								
3m'	$P_s \parallel M_s \parallel [111]_c$	4	= 4	8	full	full	full	-	
3	$P_s \parallel M_s \parallel [111]_c$	4	= 8	16	P	P	P	d./l.	
m'm'2	$P_s \parallel M_s \parallel [100]_c$	6	= 6	12	full	full	P	+	observed
m'm'2'	$P_s \parallel [001]_c$	6	= 6	12	full	full	full	+	observed
	$M_s \parallel [110]_c$								

Column 2: explicit orientation of P_s and M_s relative to the cubic reference system. Columns 3-5: number of ferroelastic (" σ_s "), ferroelectric (" P_s ") and ferromagnetic (" M_s ") domains; note the equality between the ferroelastic and ferroelectric domains, except for group 3. Columns 6-8: "full" and "P" stand for full and partial coupling of mechanical stress, electric field and magnetic field with the ferroelastic, ferroelectric and ferromagnetic domains, respectively. Column 9: "d./l." stands for "ferroelectric domains are allowed with dextro- and levo-rotation."

symmetry of the prototype and decreasing symmetry of the ferroic phase. For illustrating this statement, the number of possible domain states for all ferroelastic/ferroelectric/ferromagnetic phases allowed by prototypes $\bar{4}3m1'$ (boracites) and $m\bar{3}m1'$ (perovskites, spinels) have been assembled in Tables II and III, respectively.

In the same sense as the number of possible domains rises, that of the walls is rising, too. This fact is often felt as a nuisance because usually accompanied by a decrease of the individual domain size in the single crystals. But the study of the presence, number and orientation of the domain walls^{23a} is also of utmost importance with a view to deriving the correct point group of the ferroic phase.

The pair of groups ("species"¹⁰) determines the maximally possible number of single domain states. This number is group theoretically given^{10,10a} by the index $N = (|G|:|F|) \cdot (Z_F:Z_G)$, where $|G|$, $|F|$ stand for the order (i.e. the number of symmetry elements¹⁹) of the prototype and ferroic phase point group, respectively, and Z_G , Z_F for the number of formula units in the primitive unit cells. The possible change of this number of formula units leads to antiphase domains, which are disconsidered in Tables II and III because optically not distinguishable. Whereas this rule for N holds well for non-ferroelastic ferroic phases, experience has shown that the number of possible orientations of ferroelastic domains in a real crystal may exceed the number of orientational states given by the index (concept of "superorientational states"²⁵).²⁶ These latter phenomena evidently increase even further the complexity and may lead to erroneous symmetry deductions. They come into play and become well observable by X-rays when the spontaneous deformation is important, as is e.g. the case in the orthorhombic, ferroelastic phase of $YBa_2Cu_3O_{7-x}$.²⁴

Before starting to make physical measurements on materials with phase transitions, like multi-ferroics, it is therefore of greatest importance to begin by studying in polarized light the phase transitions, domain structures and crystal optical prop-

TABLE III

The eleven Shubnikov-Heesch point groups (column 1) permitting simultaneously ferroelasticity, ferroelectricity and ferromagnetism in case of prototype $m\bar{3}m1'$ (e.g.: perovskites, spinels)

Species $m\bar{3}m1'$ F (1)	Aizu symbol (2)	P_s, M_s orientation (3)	σ_s (4)	P_s (5)	M_s (6)	Ferro- elast. (7)	Ferro- electr. (8)	Ferro- magn. (9)	Opt. active (10)
1	-	arbitrary	24	48#	96	P	full	P	+
2	(p)	$P_s \parallel M_s \parallel [100]_c$	12	24*	48	P	P	P	+
2	(s)	$P_s \parallel M_s \parallel [110]_c$	12	24*	48	P	P	P	+
2'	(p)	$P_s \parallel [100]_c$ $M_s \perp [100]_c$	12	24*	48	P	P	P	+
2'	(s)	$P_s \parallel [110]_c$ $M_s \perp [110]_c$	12	24*	48	P	P	P	+
m	(p)	P_s in $(100)_c$ $M_s \perp (100)_c$	12	24*	48	P	full	P	+
m	(s)	P_s in $(110)_c$ $M_s \perp (110)_c$	12	24*	48	P	full	P	+
m'	(p)	P_s in $(100)_c$ M_s in $(100)_c$	12	24*	48	P	full	P	+
m'	(s)	P_s in $(110)_c$ M_s in $(110)_c$	12	24*	48	P	full	P	+
m'm'2	(pp)	$P_s \parallel M_s \parallel [001]_c$ $a_o \parallel [100]_c$	6	12*	24	P	P	P	+
m'm'2	(ps)	$P_s \parallel M_s \parallel [001]_c$ $a_o \parallel [110]_c$	6	12*	24	P	P	P	+
m'm'2	(ss)	$P_s \parallel M_s \parallel [110]_c$	6	12*	24	P	full	P	+
m'm'2'	(pp)	$P_s \parallel [001]_c$ $b_o \parallel M_s \parallel [010]_c$	6	12*	24	P	P	P	+
m'm'2'	(ps)	$P_s \parallel [001]_c$ $b_o \parallel M_s \parallel [110]_c$	6	12*	24	P	P	P	+
m'm'2'	(ss)	$P_s \parallel [110]_c$ $b_o \parallel M_s \parallel [110]_c$	6	12*	24	P	full	P	+
m'm'2'	(sp)	$P_s \parallel [110]_c$ $b_o \parallel M_s \parallel [001]_c$	6	12*	24	P	full	P	+
4m'm'	-	$P_s \parallel M_s \parallel [100]_c$	3	6	12	P	full	P	-
4	-	$P_s \parallel M_s \parallel [100]_c$	3	12	24	P	P	P	d./l.
3m'	-	$P_s \parallel M_s \parallel [111]_c$	4	8	16	P	full	P	-
3	-	$P_s \parallel M_s \parallel [111]_c$	4	16	32	P	P	P	d./l.

Column 3: explicit orientation of P_s and M_s relative to the cubic reference system, with correspondence to the Aizu symbol¹⁰ (column 2); a_o, b_o stand for orthorhombic cell parameters. Columns 3–5: number of possible ferroelastic (" σ_s "), ferroelectric (" P_s ") and ferromagnetic (" M_s ") domain states. The symbols "#" and "*" stand for electro-ambidextrous^{20,32a-c} and electro-pseudo-ambidextrous,^{20,32a-c} respectively. Columns 7–9: "full" and "P" stand for full and partial coupling of stress, electric field and magnetic field to the ferroelastic, ferroelectric and ferromagnetic domains, respectively. Column 10: "d./l." stands for "all dipole directions of the ferroelectric domains are allowed to occur with dextro- and levo-rotation."

erties (optical indicatrix) of the individual non-magnetic and magnetic domains. In the following we want to discuss some major cases which may be encountered.

3.1 Ferromagnetic* Ferroelectrics

Because in ferromagnetic ferroelectrics we have the superposition of the reciprocal optical properties of the structural, ferroelectric (and ferroelastic) domains (linear

*We use here the term "ferromagnetic" as synonymous with the presence of a spontaneous magnetization M_s , irrespective of its origin (ferromagnetic, ferrimagnetic or weakly ferromagnetic).

birefringence, optical rotatory power) with the non-reciprocal ones of the ferromagnetic domains (spontaneous Faraday rotation), it is worthwhile to study first the crystal optics and domain structures of the non-magnetic domains in the paramagnetic state. For facilitating such a study and to understand the different possibilities of contrast formation between the domains under the (polarized) light microscope, a systematic classification of the 212 non-magnetic Aizu species has been proposed.²⁰ By splitting them up into a matrix of nine kinds of species, generated by the properties *fully ferroelectric*, *partially ferroelectric* and *non-ferroelectric*, on the one hand, and *fully ferroelastic*, *partially ferroelastic* and *non-ferroelastic*, on the other hand (see Table I of Reference 20), some better insight is achieved.

In Aizu's nomenclature¹⁰ *fully ferroelectric* means that the electric field has full command over all possible domain states, *partially ferroelectric* means that the electric field is able to realize switching between some, but not all possible domain states. The same holds true for *full and partial coupling of ferroelastic* domains with respect to stress, and for *full and partial coupling of ferromagnetic* domains with respect to an applied magnetic field, respectively.

3.1.1 Non-Ferroelastic Ferroelectric Ferromagnets

For this case the least complex situation is encountered with a total of four domain states, when the ferroelectric is non-ferroelastic with colinear \mathbf{P}_S and \mathbf{M}_S , for example for the species $mmm1'Fm'm'2$ or $6/mmm1'F6m'm'$, where the electric field has full command over the two antiparallel ferroelectric states. Every ferroelectric domain may house two ferromagnetic domains, but the magnetic field has no command over the ferroelectric polarization vector. It will only be able to switch the ferromagnetic domains inside the ferroelectric domains, whence we have a partially ferromagnetic/fully ferroelectric species with a total of four domain states. No material with these kinds of species is known.

The situation is somewhat more complex if we take a non-ferroelastic which is partially ferroelectric and partially ferromagnetic. This is for example the case for species $6/m1'F3$ with a total of 8 domain states. This number is due to the fact that $6/m1'$ splits up into polar dextro- and levo-domains of opposite polarity in the rhombohedral phase 3. The electric field has no command over interchange of *d*- and *l*-domains and the magnetic field can neither control the polar states nor the chiral domains.

In the case of the aforementioned rhombohedral ferroelectric and ferromagnetic phase we have to take into account the complication that the spontaneous, non-reciprocal Faraday rotation parallel to \mathbf{M}_S ($\parallel \mathbf{P}_S$) is superimposed on reciprocal rotatory power, whereas in the mentioned orthorhombic phase $m'm'2$, the spontaneous Faraday rotation parallel to \mathbf{M}_S ($\parallel \mathbf{P}_S$) is superimposed on reciprocal linear birefringence and possibly linear dichroism. No real example of such a crystal is known.

3.1.2 Ferroelastic Ferroelectric Ferromagnets

A further factor of complexity is introduced, when the ferroelectric phase is also ferroelastic. This means that the ferroelectric spontaneous polarization vector \mathbf{P}_S

and/or the spontaneous magnetization vector \mathbf{M}_s is coupled to reorientable spontaneous deformation states (ferroelastic domains). If this is the case, we can distinguish four kinds of ferroelectric species²⁰:

i) *Fully ferroelectric/fully ferroelastic phases.* If the polarization vector is *fully coupled* to the deformation state, i.e. to the ferroelastic domain, we speak of *fully ferroelectric/fully ferroelastic*. Here we have—at least in principle—the chance of being able to create a ferroelectric (simultaneously ferroelastic) single domain by stress alone, or *vice versa* a ferroelastic (simultaneously ferroelectric) single domain by an electric field alone. If the prototype symmetry is for example tetragonal $\bar{4}2m1'$, as is the case for the rare earth molybdates,²⁷ the situation is particularly simple, because there are only two possible ferroelectric/ferroelastic domains¹⁰ in the para- or diamagnetic phase and in case of ferromagnetic or antiferromagnetic order the total number of magnetic domains becomes four²⁰ (neglecting states not described by the index).

If we choose a cubic, non-centrosymmetric prototype point group, as is the case for boracites with $\bar{4}3m1'$ (Table II), the number of fully coupled ferroelectric/ferroelastic domains climbs up to 24 if the ferroic, ferroelectric phase is paramagnetic triclinic and this number doubles to 48 states in case of ferromagnetic or antiferromagnetic order. A real example is nickel bromine boracite $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$, which is fully ferroelectric/fully ferroelastic/fully ferromagnetic both in the orthorhombic phase between 30 and 21 K (12 states, species $\bar{4}3m1'\text{Fm}'m2'$)²⁸ and in the triclinic one below 21 K (48 states, species $\bar{4}3m1'\text{F1}$).²⁸⁻³⁰ Since both phases are fully ferromagnetic and fully coupled to the ferroelectric and ferroelastic states, it should in principle be possible to produce a single domain state of one of the 12 or 48 domain states, respectively, by means of a magnetic field alone, an electric field alone or mechanical stress alone. In practice this is unfortunately seldom the case, because the angular differences in orientation of \mathbf{P}_s , \mathbf{M}_s and ϵ_s in the different ferroic domains may be too small for easily lifting the degeneracy. For example for the triclinic phase of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$ the maximum reduction achieved was from 48 to 8 possible states by initial mechanical isolation of one of the 6 ferroelectric/ferroelastic orthorhombic domains, which transforms only to 1/6 of the totally possible triclinic states at zero magnetic field. By superposition of a magnetic bias field, a further reduction is possible, in principle even to one single domain, but during the magnetoelectric measurements^{28,31} probably more domains than one were present.

Magnetic field-induced poling of fully coupled ferroelectric/ferroelastic/ferromagnetic domains has not been studied systematically in boracites, but evidence for that possibility has been demonstrated for Ni-I boracite close below the Curie temperature.⁸

The complexity is somewhat further increased, when a fully ferroelectric/fully ferroelastic phase is only *partially ferromagnetic*. This case applies to the monoclinic phase of Fe-Cl-, Fe-Br-, Fe-I- and Co-Cl- boracites with species $\bar{4}3m1'\text{Fm}$ [24 states] and species $\bar{4}3m1'\text{Fm}'m'2$ [12 states] of Cu-Cl and Cr-Cl boracite. (cf. Tables I, II and Part 4).

One remarkable property of fully ferroelectric/fully ferroelastic phases is the fact that after correlation of the dipole direction of the ferroelectric domain (identical with the ferroelastic one) with the absolute structure and the optical indicatrix, the

direction of the dipole can be determined in a domain pattern from the orientation of the refractive index ellipsoid by purely optical means!²¹

ii) *Fully ferroelectric/partially ferroelastic.* For example the species $m\bar{3}m1'F4m'm'$, which might occur in a perovskite or spinel, is fully ferroelectric, partially ferromagnetic and partially ferroelastic, with a total of 12 domain states. The ferroelectric 180° -domains inside the ferroelastic ones are non-ferroelastic relative to one ferroelastic domain and can unfortunately not be distinguished by birefringence contrast, but in principle by electro-pseudo-dexterity^{20,32a-c} (cf. Table III). But the spontaneous Faraday rotation, if perceptible, will be maximal along the 4-fold axis because of the isotropic indicatrix cross section.

The antiferromagnetic perovskite BiFeO_3 is fully ferroelectric/partially ferroelastic and behaves magnetoelectrically in the antiferromagnetic phase like species $m\bar{3}m1'F3m1'$ due to an incommensurate magnetic phase.³²

In this category of species we also find the most complex possible situation, with 48 ferroelectric, 24 ferroelastic and 96 ferromagnetic or antiferromagnetic domains, if the cubic prototype has point group $m\bar{3}m1'$ and the ferroic, ferroelectric phase the triclinic ferromagnetic or antiferromagnetic point group 1 or $1'$, respectively. This is shown in Table III and applies e.g. to perovskites. This table also shows the situation for all allowed ferroic symmetries higher than the triclinic one. The reader will remark that for prototype $m\bar{3}m1'$ most ferroelectric phases are electro-pseudo-ambidextrous, and that for point group 1 electro-ambidextrous.^{20,32a-c} This means that 180° ferroelectric domains can in principle be distinguished optically when observing with uncrossed nicols along one of the optical axes of the optically biaxial domains. However, this possibility would require both very high specific rotatory power and domain walls lying parallel to the plane of the optical axes, i.e. conditions, difficult to satisfy.

Magnetite has been reported to be a triclinic, ferroelectric and ferrimagnetic magnetoelectric below the Verwey transition, but so far all studies have been made without visual control of the domain states (cf. Part 4).

A triclinic magnetic phase has also been reported for a certain concentration range of the bismuth perovskite/RE-orthoferrite solid solution system $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$, where RE stands for rare earth.⁶⁸

iii) *Partially ferroelectric/fully ferroelastic.* This case is for example given for species $\bar{4}2m1'F21'$ with four states, doubling to 8 states if a ferromagnetic moment would develop along the 2-fold axis, leading to $\bar{4}2m1'F2$. In this case the superposition of Faraday rotation and birefringence may cause some experimental complication. No ferromagnetic with this type of combinations is known.

iv) *Partially ferroelectric/partially ferroelastic.* The domain situation becomes rather complex, when the coupling between ferroelectric polarization and ferroelastic domain state is mutually partial. No ferromagnetic ferroelectric of this type is known.

All "species" with non-magnetic ("grey") and magnetic groups corresponding to the property combinations i) to iv) can be found in Aizu's Tables,¹⁰ whereas the optical contrast possibilities between domains of the corresponding non-magnetic species have been treated in Reference 20.

4. REAL MATERIALS WITH SHUBNIKOV-HEESCH POINT GROUPS ALLOWING BOTH SPONTANEOUS POLARIZATION AND SPONTANEOUS MAGNETIZATION

We dispose now upon some well-established examples of compounds allowing both ferroelectricity and ferromagnetism. They have the point groups: 1, m , m' , $m'm2'$ and $m'm'2$, hence so far not all the thirteen possible groups are represented.

4.1 Point Group 1 ($\mathbf{P}_S, \mathbf{M}_S$ in Arbitrary Directions)

For the triclinic group 1, the lowest possible symmetry for uniting both a spontaneous electric and a spontaneous magnetic moment, exists a well established example: Ni-Br boracite, $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Br}$, at $T < 21$ K. The triclinic symmetry has been deduced from magnetic domain studies inside an originally orthorhombic ferroelectric/ferroelastic single domain of the paramagnetic phase $mm21'$ (cf. Table I), using the spontaneous Faraday effect^{28,29} and SQUID-magnetometer measurements of the components of the spontaneous magnetization vector,³⁰ which lies in a general crystallographic direction. The α_{23} coefficient of the linear ME effect of the orthorhombic $m'm2'$ phase, stable between 21 and 30 K, showed, however, no anomaly versus temperature upon the passage to the triclinic phase, whereas the α_{32} coefficient did show an anomaly at about 21 K. Nonetheless the ME effect did not permit to state that an orthorhombic-to-triclinic symmetry change took place. This is plausible because of the presence of several possible triclinic domains, which have not been tried to be disentangled.

The ferroelectric and weakly ferromagnetic character of the phosphate KNiPO_4 below 23 K has been clearly established,³³ but there still remains an apparent inconsistency between the antiferromagnetic symmetry $mm2$ "seen" by neutron diffraction as well as by the linear magnetoelectric effect (only the coefficients α_{12} and α_{21} are measurable), whereas magnetization measurements both on powders and ferroelectric single domains indicate a weak ferromagnetic moment.³³ However, the two measurable ME coefficients and the existence and orientation of the spontaneous magnetization are only compatible with triclinic point group 1. The seven other ME coefficients, allowed for triclinic symmetry, have all been tested, but proved to be too weak to be measurable. This shows clearly that utmost caution is recommended when trying to deduce magnetic symmetry from the ME effect alone or from neutron diffraction alone. The most sensitive method of symmetry detection will always have the last word.

For magnetite, Fe_3O_4 , the triclinic symmetry has been reported by several authors³⁴⁻³⁸ for temperatures below the Verwey transition temperature, together with a claim for ferroelectricity on the basis of very asymmetric hysteresis cycles^{39,40} and magnetoelectric measurements.³⁸ However, none of these assertions are sustained by direct optical domain observations. Therefore in the writer's opinion the symmetry and magnetoelectric properties of the very complex material magnetite⁴¹⁻⁴³ are far from being clarified. Because very strong absorption of magnetite in the visible impedes transmission polarized light microscopy to be practiced, low temperature Kerr effect microscopy, IR-visible conversion polarized light microscopy

copy or microscopy with a LEED-detector for spin polarization analysis^{43a} would be necessary to gain further insight.

4.2 Point Groups 2 ($\mathbf{P}_S // \mathbf{M}_S // 2$) and 2' ($\mathbf{M}_S \perp \mathbf{P}_S // 2'$): No Examples Known

4.3 Point Group m ($m \perp \mathbf{M}_S \perp \mathbf{P}_S$)

This monoclinic point group is well established for the ferroelectric/ferromagnetic/ferroelastic phases of the boracites $\text{Co}_3\text{B}_7\text{O}_{13}\text{Cl}$ ^{18,44,45} and $\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$.⁴⁶ The boracites $\text{Fe}_3\text{B}_7\text{O}_{13}\text{Cl}$, $\text{Fe}_3\text{B}_7\text{O}_{13}\text{Br}$ and $\text{Co}_3\text{B}_7\text{O}_{13}\text{F}(\text{OH})$ are expected to have also a magnetic phase with point group m (cf. Table I). The ferromagnetic properties of the Fe-Cl, Fe-Br, and Fe-I boracites are known from measurements on powders,⁴⁷ whereas for Co-F(OH) boracite no data on magnetic ordering are known. All aforementioned compositions have a paramagnetic fully ferroelectric/fully ferroelastic $3m1'$ phase in common (see Table I), which undergoes magnetic ordering. For Co-Cl boracite the m -symmetry has been established on the basis of magnetic domain studies using the Faraday effect and the linear ME effect on ferroelectric/ferroelastic single domains, obtained by poling in fields up to 800 kV/cm!⁴⁴ Due to the high ferroelectric poling fields very thin samples had to be used, their geometry permitting the measurement of the α_{32} ME coefficient only.

On ferroelectric/ferromagnetic/ferroelastic polydomain samples of Fe-Cl, Fe-Br and Co-Cl boracite the linear ME effect has been measured vs temperature without visual inspection,⁴⁸ thus the contributions from different coefficients and domains have not been disentangled.⁴⁸

For the boracite $\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$, the monoclinicity of the magnetic phase has been established by means of domain studies (birefringence contrast) and high resolution birefringence measurements versus temperature,⁴⁶ the spontaneous Faraday rotation in the visible being too small in iron boracites for monitoring the ferromagnetic domains by visual inspection in polarized light.

4.4 Point Group m' (\mathbf{M}_S and \mathbf{P}_S with Arbitrary Directions in the m' Plane)

For the monoclinic point group m' the spontaneous magnetization and polarization vectors lie in the m' -plane and are allowed to have dispersion of their orientation as a function of temperature, and the optical indicatrix may rotate with temperature and wavelength.

For ferroelectric/ferromagnetic/ferroelastic nickel iodine boracite $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ m' symmetry has been established⁴⁹ and reconfirmed,⁵⁰ following the initial erroneous attribution of orthorhombic point group $m'2'$ at the occasion of the discovery of simultaneous ferroelectricity and ferromagnetism.^{8,21}

On single crystals of the antiferromagnetic ($T_N = 161 \text{ K}$ ⁵¹) fully ferroelectric partially ferroelastic $\text{Pb}_2(\text{FeNb})\text{O}_6$ a weak ferromagnetic moment had been measured below 9 K⁵² and was recently reconfirmed.⁵³ On the basis of dynamic ME measurements on single crystals point group m' has recently been attributed to this perovskite for temperatures below 9 K. The crystals had been poled in electric fields, however, without visual inspection of the degree of poling.⁵³ Therefore, in

the writer's opinion rhombohedral point group $3m'$ —having only diagonal tensor components of the linear ME effect—cannot be entirely ruled out, because a ferroelectric polydomain sample with point group $3m'$ and species $m\bar{3}m'1'F3m'$ may well simulate off-diagonal coefficients and herewith symmetry m' ! This point group may also be due to tetragonal growth sectors which behave as prototype, as recently found in the isotopic $Pb_2(FeTa)O_6$,⁵⁴ which also has a magnetic transition at 9 K.⁵⁵ Since $3m1'$ and $3m'$ are not subgroups of a tetragonal prototype, intrinsic m' symmetry is possible, but an optically controlled experiment on single growth sectors will have to decide, which interpretation applies.

Independently of this symmetry problem, it is noteworthy that the reported signal of the linear ME-effect below the Curie point of 9 K is extremely weak.⁵³ This may indicate that the observed ME effect is due to a tiny volume percentage of B-site clusters with elpasolite-like order—Fe—O—Nb—O—Fe—O—Nb—, giving rise to weak “long-range superexchange” interactions which lead in perovskite type structures to rather low Néel temperatures of the order of 9 to 20 K.⁵⁶

A recent example of perovskite with 100% elpasolite type order is $Pb_2(CoW)O_6$ with a ferromagnetic ordering temperature of only 9 K,⁵⁵ typically due to long-range superexchange. If the assumption of long-range superexchange clusters for $Pb_2(FeNb)O_6$ is correct, the linear magnetoelectric effect would act as a more sensitive detector of partial ordering than X-rays, which only “see” complete B-site disorder for Nb and Fe. In spite of that Fe/Nb disorder it is remarkable that the bulk of $Pb_2(FeNb)O_6$ undergoes an antiferromagnetic type ordering at 161 K as demonstrated by neutron diffraction.⁵¹ This strong coupling of the bulk may be due to clusters with dominating ordinary 180° and 90° superexchange.

4.5 Point Group $m'm2'$ ($M_S \perp m \perp P_S // 2'$)

The first ferrimagnetic compound with this type of group for which the linear and quadratic (in the magnetic field) ME effect was studied is $Ga_{2-x}Fe_xO_3$ ($2'm'm$).⁵⁷ It is pyroelectric, non-ferroelectric (i.e. P_S is not reversible by 180°) and non-ferroelastic. Because of these facts there are only two ferrimagnetic domain states, which can easily be switched.

The boracites $Ni_3B_7O_{13}Cl$,⁵⁸⁻⁶⁰ $Ni_3B_7O_{13}Br$,^{28-31,60,61} $Co_3B_7O_{13}Br$,⁶²⁻⁶⁴ $Co_3B_7O_{13}I$ ⁶⁵⁻⁶⁷ have a $m'm2'$ phase in common, being ferroelectric, ferromagnetic and ferroelastic with species $43m1Fm'm2'$ and twelve domain states (i.e. 6 ferroelectric/ferroelastic domains, each of which housing up to 2 magnetic domains). Hence the domain structures are rather complex, but these compositions have the advantage that the spontaneous Faraday rotation in the visible, due to Ni^{++} and Co^{++} is strong, allowing to identify conveniently the ferromagnetic domains under the polarizing microscope and herewith, in conjunction with magnetic domain wall studies, the orientation of M_S , in particular along directions close to the optic axes.^{28,60}

A perovskite/orthoferrite solid solution crystal, $Bi_{1-x}Dy_xFeO_3$, has been reported to be polar ($Pna2_1$), ferromagnetic and magnetoelectric.^{68,69} Therefore $m'm2'$ or $m'm'2$ point group may be expected (cf. Table III). Although being pyroelectric, the ferroelectric nature has, however, so far not been demonstrated.

4.6 Point Group $m'm'2$ ($M_S//P_S//2$)

Among boracites we find the following examples with point group $m'm'2$: boracite $Cu_3B_7O_{13}Cl$,^{70,71} probably also $Cu_3B_7O_{13}Br$ boracite and recently $Cr_3B_7O_{13}Cl$ boracite.^{72,73} In these cases the coupling is partially ferromagnetic/fully ferroelectric/fully ferroelastic (cf. Table I).

4.7 Point Groups 4, $4m'm'$ ($M_S//P_S//4$) and 3 ($M_S//P_S//3$): No Examples Known

4.8 Point Group $3m'$ ($M_S//P_S//3$)

As pointed out above (see 4.4), on the basis of ME measurements the monoclinic group m' has been claimed to hold true for the B-site (Fe, Nb) disordered perovskite $Pb_2(FeNb)O_6$ below 9 K.⁵¹ However, a final decision, whether m' or $3m'$ applies, will only be possible after experiments with optical domain control.

4.9 Point Groups 6 and $6m'm'$ ($M_S//P_S//6$): Ferroelasticity Not Possible; No Examples Known

The majority of ferroelectric ferromagnets, for which the magnetic point group has so far been determined, is found in the boracite structural family. All of these ferroic boracite phases are fully ferroelectric/fully ferroelastic and most of them fully ferromagnetic. Some compositions have a monoclinic m phase and Cu-Cl and Cr-Cl boracite have an orthorhombic $m'm'2$ phase. Both of these phases are partially ferromagnetic (cf. Table I). The "full coupling" represents a considerable advantage over partial coupling of ferroic phases with a centrosymmetric cubic prototype $m\bar{3}m1'$ (as is e.g. the case for perovskites and magnetite), leading to fully (or partially) ferroelectric/partially ferroelastic species and to a doubling of the maximally attainable number of domain states (Table III), compared with the species derived from $\bar{4}3m1'$ prototype (Table II). It follows that the detwinning procedures with a view to magnetoelectric and other measurements become much more cumbersome in the latter case, compared e.g. with the non-ferroelastic antiferromagnetic Cr_2O_3 or ferrimagnetic pyroelectric $Ga_{2-x}Fe_xO_3$ with only two well controllable magnetic domain states!

For the case of boracites we have represented in Table I different types of observed phase sequence of non-magnetic and magnetically ordered phases. The symmetry of the magnetic phases has been determined by combined optical, magnetoelectric and domain switching studies. We see on Table I that many 3d-transition metal boracites have question marks. This means that the magnetic symmetry has not yet been confirmed by single domain work. This holds also true for the sulfur, selenium and tellurium boracites, which have not been incorporated into the table, because only known in polycrystalline form.⁷⁴

5. SOME PARTLY SOLVED CASES

As concerns the vast family of perovskites, a great number of magnetically ordered ferroelectric compositions⁷ awaits investigations on single crystals. Even many per-

ovskite phases, already listed about 20 years ago,¹⁸ have not yet been elucidated in single crystalline form, so as to study seriously the magnetoelectric effects. For example the idea of forming perovskite/rare earth orthoferrite solid solutions, similar to the above-mentioned BiFeO₃-DyFeO₃ system, was already explored long ago by ceramic techniques in the system BiFeO₃-PrFeO₃,⁷⁵ and ferroelectricity and compensated antiferromagnetism in the rhombohedral phase, and ferroelectricity and weak ferromagnetism in the tetragonal phase of the system had been postulated.⁷⁵ However, to the best of our knowledge no verification of these properties on single crystals seems to have been realized up to now.

So far only for a single perovskite composition, Pb₂(CoW)O₆, with elpasolite type B-site order of Co and W, ferromagnetic domains have been observed under the polarizing light microscope below $T_c = 9\text{ K}$ ⁷⁶ by means of the spontaneous Faraday rotation in transmission and in an electrically unpoled state of the orthorhombic phase. In an electrically poled, metastable state the crystals show the linear ME effect below 9 K, probably due to a metastable electric field induced $m'm'2$ or $m'm'2'$ type symmetry.⁵⁵ A complete study of the crystal optics and the symmetry of the paramagnetic and ferromagnetic phases has so far been impeded due to unsuccessful untwinning of the imbricated ferroelastic domain structure of the low temperature orthorhombic phase.⁷⁷⁻⁷⁹

The A-site substituted perovskite (Ba_{1/2}Eu_{1/2})TiO₃⁸⁰ was reported to be ferroelectric below 170 K and to develop a strong induced magnetic moment at 1.8 K, when placed into a magnetic field. It is not known whether a magnetic ordering occurs, but the material would at least be an interesting candidate for studying the magnetoelectric effect due to the $\beta_{ijk} E_i H_j H_k$ term of the density of stored free enthalpy, either on ceramic or single crystalline samples.

6. ANTIFERROMAGNETIC (FERROELASTIC) FERROELECTRICS

Antiferromagnetic ferroelectrics and ferroelastics seem to be more numerous than ferromagnetic ones,^{18,81,82} but only very few ones are studied in single crystalline form. A critical analysis of these materials is out of the present scope, but let us just cite two examples:

The bilinear $\beta_{ijk} E_i H_j H_k$ -type ME effect of the fully ferroelectric/partially ferroelastic antiferromagnetic incommensurate perovskite BiFeO₃ has been studied on ferroelectric single domain areas, an important condition, because in an unpoled single crystal or in an unpoled ferroelectric ceramic the effect will cancel out, in the same way as the piezoelectric effect cancels in an unpoled ferroelectric ceramic.³²

Another example of a ferroelectric/ferroelastic antiferromagnet with an incommensurate phase is BaMnF₄⁸³⁻⁸⁵ and in a quite recent magnetoelectric study of the magnetoelectric effect in Cr₃B₇O₁₃Cl, an antiferromagnetic ferroelectric/ferroelastic phase with species $\bar{4}3m1'$ Fmm2 has been postulated.^{72,73}

7. EXPERIMENTAL PROBLEMS AND RESEARCH STRATEGY WHEN STUDYING COMPLEX MULTI-FERROICS

Heading for the Magnetic Point Group

In the case of boracites frequently large ferroelectric coercive fields^{44,86} are encountered. Thus, as a rule only very thin single domain plates are obtainable by poling with easily accessible voltages. Such small wafers with a surface of about 1–3 mm² allow measurements of magnetoelectric effect, spontaneous polarization, permittivity, piezoelectric effect, spontaneous magnetic and crystallographic birefringence, Faraday rotation and X-ray single domain structure determinations, etc. However, they usually do not permit to determine all allowed tensor components of the linear ME effect and they represent far too small a volume for performing single domain neutron diffraction work for elucidating the magnetic structure and providing herewith the key to the understanding on the microscopic mechanisms of the ME effect.

To the most salient features of ferroelectric ferromagnets belong the linear and higher order ME effects ($\beta_{ijk}E_iH_jH_k$ and $\gamma_{ijk}H_iE_jE_k$ terms) (see "Introduction" and Rivera, "Definitions . . ."), which are *a fortiori* allowed by symmetry in these materials. For an explanation of the ME effects on a microscopic level, a good knowledge of the magnetic structure is mandatory. However, as a consequence of the complex domain structure, experience and literature show that magnetic structure determinations of perovskites and boracites, using neutron diffraction on powders without auxiliary information, always lead to partial or equivocal results and one does not end up with the desirable magnetic space group. The situation is not better by using large polydomain single crystals for neutron diffraction, which usually have a non-equi-weight distribution of the domains, leading to the simulation of a wrong symmetry and structure. Therefore, in the case of boracites, the determination of the magnetic point group was considered as the first objective. This goal can be reached by combining measurements of the ME effect and spontaneous magnetization (with a SQUID) with polarized light microscopy of the ferroelectric/ferroelastic domains (birefringence contrast²⁰) and that of the ferromagnetic domains (Faraday rotation dispersion contrast).^{87–89} In order to assure ferroelastic/ferroelectric/ferromagnetic single domain samples for performing measurements of the tensor components of the linear and bilinear magnetoelectric effect, of permittivity, spontaneous polarization, birefringence, etc., as a first step an in-depth-study of the optical indicatrix of the ferroelectric/ferroelastic domains has to be undertaken.²⁰

Crystallo-Optical Complexity

Magnetically ordered (ferroelastic) ferroelectrics based on 3d-metal ions and rare earth ions are often characterized by important absorption regions in the visible due to crystal field spectra. Even in the paramagnetic phases this leads for example to linear dichroism and 'anomalous' dispersion of the birefringence, rendering the determination of the optical indicatrix difficult. For example for determining the correct order of the path difference, the application of Beugnie's method^{90,91} may

be necessary and the measurement of birefringence in presence of linear dichroism requires special techniques,⁹² not described in common text-books of crystal optics.

When entering the ferromagnetic (ferroelastic) ferroelectric phase, the non-reciprocal spontaneous Faraday rotation is often superposed on linear birefringence. Space does not allow to treat the phenomenology in this context, but the interested reader may consult some references treating the superposition of birefringence with relatively strong Faraday rotation⁸⁷⁻⁸⁹ (well visible under the polarizing microscope). This latter case was found in nickel and cobalt boracites, cf. Part 4), whereas for superposition of birefringence with weak reciprocal and/or non-reciprocal rotation (only measurable but not visible), the HAUP-method^{93,94} and Sagnac interferometer⁹⁵ may be adequate techniques, respectively.

The change of birefringence due to the onset of magnetic ordering is usually too weak to be observable with the bare eye under the microscope. In that case dynamic high resolution techniques using a photoelastic modulator,⁹⁶ are extremely helpful to detect very weak 2nd order transitions and magnetic anomalies (see e.g. References 28 and 97).

Limitations Due to High or Inaccessibly High Electric Poling Fields

When ferroelectric/ferroelastic single domains can only be obtained by poling in high electric fields,⁴⁴ we have the restriction that the obtainable sample, e.g. a thin plate with \mathbf{P}_s perpendicular to the plane, will be inadequate for determining *all* of the allowed components of the magnetoelectric tensor. This holds true *a fortiori* when the ferroelectric(/ferroelastic) Curie temperature lies below room temperature (Ni-I, Co-I, Cr-Cl, Cu-Br boracites), i.e. when the poling, obligatorily preceding the magnetoelectric measurements, has to be done in the cryostat.

The situation is somewhat more comfortable when the ferroelectric/ferroelastic Curie point lies above room temperature, so that ferroelectric/ferroelastic single domain samples can be prepared at room temperature, i) by cutting them out of as-grown/as-cooled poly-domain crystals (see e.g.: Ni-Cl boracite,^{58,59} Co-Br boracite⁶⁴; inaccessible coercive fields!), ii) by practicing mechanical detwinning (see e.g. Ni-Br boracite,³⁰ cf. also $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ⁹⁸) or iii) by poling in electric fields (e.g. case of Cr-Cl boracite⁷³). If very high electric fields are required for poling, the use of liquid electrodes at room temperature (e.g. practiced for the trigonal phase of Co-Cl boracite⁴⁴) may be advantageous for visual domain control and for avoiding electronic charge injection. Alternatively, transparent gold electrodes may be used. They are also useful for visual domain control, for poling in a (paraffine) oil bath, which may be heated with a view to decreasing the threshold switching field strength, and for avoiding herewith electric breakdown. Thin transparent gold electrodes have the additional advantage of avoiding mechanical clamping at first order phase transitions due to hardening of silverpaste electrodes at low temperatures.⁹⁹ Such clamping may lead to the simulation of a second order phase transition, as well as to clamping of ferroelastic domain switching.⁹⁹

By combining the magnetic point group, determined in the abovementioned way using optical input, with the crystallographic space group determined usually previously by X-rays, only a single magnetic space group or very few ones are at choice.¹⁵ By using this information and X-ray data as input for powder neutron

diffraction, which has the advantage of equi-weight distribution of the domains, the number of possible magnetic structure models becomes greatly reduced.⁶¹

8. HOW DO WE RISK TO OBTAIN ERRONEOUS MAGNETIC SYMMETRIES?

Non-verification of the single domain state or non-characterization of the poly-domain state of a single crystal by polarized light microscopy can easily lead to the deduction of a wrong symmetry, be it on the basis of X-ray diffraction, neutron diffraction, magnetoelectric effect or other criteria.

In a single crystal with a non-equi-weight distribution of domains, their superposition may simulate a symmetry lower than that of the single domain, but an equi-weight distribution of part or of all the possible domain states may also lead to simulating a symmetry higher than the true one.

Let us illustrate these statements by examples of artefact encountered during the course of studies of the properties of ferroelectric/ferromagnetic/ferroelastic nickel iodine boracite. This compound provides us with historical examples of both types of artefact stated above:

i) The determination of the magnetic structure of nickel-iodine boracite below 61 K by neutron diffraction, using a single crystal, led to the determination of triclinic symmetry with Shubnikov point group 1,⁹⁸ the lowest possible symmetry for a ferroelectric ferromagnet. In spite of efforts of the investigator with a view to poling the single crystal both electrically and magnetically, but without optical control of the domain state by direct inspection in order to preserve a sufficient crystal size for neutron diffraction, apparently only partial poling was achieved, with subsistence of a non-equi-weight distribution of domains. The superposition of such domains was most probably at the origin of the simulation of triclinic symmetry.

ii) Following the discovery of simultaneous onset of ferroelectricity and ferromagnetism of Ni-I boracite at about 61 K, too high a magnetic symmetry was deduced when interpreting the initial results of the magnetoelectric measurements.^{8,21} During those studies the orthorhombic group $m'm2'$ was rather perfectly simulated by a magnetoelectric butterfly loop, jumping upside down and turning by 90° upon reversal of spontaneous polarization, as expected for species $\bar{4}3m1'Fm'm2'$.^{8,21}

iii) In later magnetoelectric measurements, performed on Ni-I boracite *without optical control*, evidence was obtained that its magnetic symmetry must be lower than orthorhombic. However, the authors were unable to differentiate between monoclinic and triclinic.¹⁰¹

iv) The correct symmetry was finally found by means of different physical measurements, performed *with simultaneous observation of the domain state(s) along all three pseudo-orthorhombic principal axes*: monoclinic point group m' .⁴⁹ Preceding and triggering these more rigorous studies, the first hint for a symmetry different from orthorhombic was obtained by J.-P. Rivera by means of an improvised microscope, allowing the observation of ferromagnetic domains on an electrically poled cubic (100) cut, hence indicating a component of spontaneous mag-

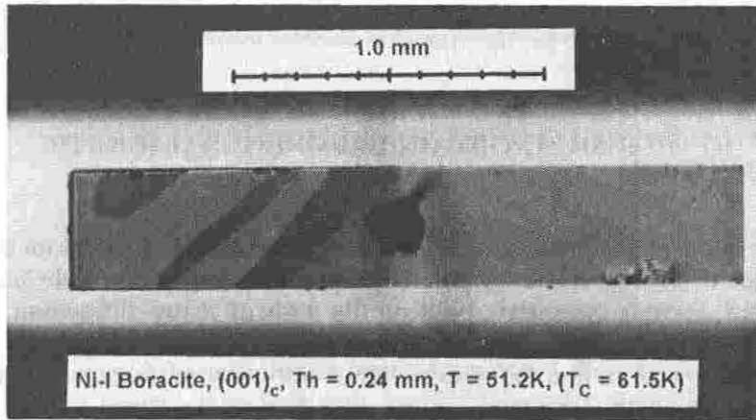


FIGURE 1 Ferromagnetic domain pattern of a Ni-I boracite plate, in the form of a piezoelectric oscillator, poled electrically perpendicular to a cubic (100) face; transparent gold electrodes; spontaneous Faraday rotation contrast with polarizer and analyzer uncrossed by 4 degrees, objective $4\times$, ocular $10\times$. Photograph: J.-P. Rivera (according to Reference 49). See Color Plate XI.

netization parallel to the spontaneous polarization direction (Figure 1). Similar observations were first made at Würenlingen around 1972 by von Wartburg and the writer, but that study was not brought to a positive end.

The artefact ii), having led to a too high symmetry, was due to the presence of lamellar monoclinic domains, having had their composition plane perpendicular to the pseudo-orthorhombic polar c -axis (cf. Figure 1 of Reference 102). The degeneracy of these domains could not be lifted by the electric switching field applied perpendicular to the composition plane. These piles of lamellae, in which the c -axis component of the Faraday rotation was cancelled due to a small magnetic bias field perpendicular to the c -axis, and in which the monoclinic optical indicatrix rotation, seen later,⁴⁹ escaped observation because of too poor resolution of the improvised microscope, simulated admirably well Aizu species $\bar{4}3m1'$ Fm' $m2'$. The decisive criteria for finding the true symmetry were i) the observation of the confinement of the magnetization vector into the monoclinic principal plane⁴⁹ and ii) the observation and measurement of the rotation with temperature of the optical indicatrix principal section in the plane containing the magnetization vector, i.e. in the monoclinic principal plane m' .⁴⁹ Hence the errors made were entirely due to non-observation or incomplete observation by means of our eyes.

As explained above, we may also obtain an erroneous magnetic symmetry by putting too much confidence in information from measured magnetoelectric tensor components and from neutron diffraction. The case of KNiPO_4 (Part 4) reminds us to be very critical.

9. CONCLUSIONS

The survey allows to make a few statements:

i) It is striking that reliable data on magnetic point symmetry and phase sequences of magnetoelectric multi-ferroics are nearly exclusively restricted to the boracite

crystal family, whereas for the large perovskite family, which was traditionally the major hunting ground for magnetic ferroelectrics, there is great paucity of data on single crystals.

ii) One of the reasons which may be advanced for explaining statement i), may reside in the degree of complexity of the systems considered. This complexity is roughly proportional to the maximally possible number of domain states of the crystal. It rises with increasing number of spontaneous ferroic quantities (P_s , M_s and ϵ_s) on the one hand and with increasing prototype symmetry and decreasing ferroic phase symmetry on the other hand.

iii) It follows from item ii) that for example perovskites and spinels (magnetite) with the highest possible prototype symmetry, $m\bar{3}m1'$, belong to the most complex systems, in particular when the ferroic phase is of monoclinic or triclinic symmetry (Table III). For boracites with the non-centrosymmetric prototype $\bar{4}3m1'$, the situation is somewhat more comfortable (Table II), because of the full coupling between spontaneous deformation, polarization and magnetization, leading to only half the number of domains which are allowed with the centrosymmetric prototype $m\bar{3}m1$, and facilitating herewith to some extent the interpretation of domain patterns and the preparation of single domains.

iv) One of the main reasons why most information is available on boracites, resides certainly in the fact that the principle has rigorously been practiced, to work with single crystals and single domains, and to perform physical measurements whenever possible under simultaneous polarized light microscopical control.

v) The magnetoelectric effect does in fact play an important rôle in determining the magnetic symmetry of complex magnetoelectric ferroics and is herewith an important complementary tool for neutron diffraction. However, as shown with the example of KNiPO_4 (see Part 4), it is not infallible and has obligatorily to be used in conjunction with as many complementary techniques as possible, for example optical domain control, switching experiments and SQUID-magnetometer measurements on properly isolated single domains (vibrating-sample magnetometers have insufficient sensitivity). As a consequence, it will also become plausible that work exclusively performed on ceramic samples of multi-ferroics will only provide a rough exploratory scanning, risking to miss the essential points.

vi) After having seen the great obstacles and the risks of artefact we may encounter in research on complex multi-ferroics due to domains, we may ask the heretic question: does it make sense to invest so much effort for studying these complex materials? In fact, for learning to understand the basic mechanisms of the linear and higher order magnetoelectric effects, it may be more rewarding to work in a first stage on simpler, i.e. preferentially non-ferroelastic phases, such as found in Cr_2O_3 , LiCoPO_4 or non-ferroelastic ferroelectrics, thus avoiding loss of time with the "technology" of detwinning and the demanding "micro-technology" of sample preparation. However, in our opinion these complex materials are endowed with great beauty of symmetry and domain properties. They are of particular importance in the teaching and training fields, because we can learn from them in a unique way how nature is capable of combining elegantly in a single phase, but within the strict framework of symmetry rules, a whole palette of properties. Thus the scientist has a chance to familiarize himself with a great variety of interwoven fields, such as solid state chemistry and physics, crystallography, symmetry, ther-

modynamics, crystal optics, magnetism, dielectrics, transducer effects of various type and so forth.

vii) As concerns future work, a host of compounds is awaiting more detailed investigations. Even in the boracite crystal family, several 3d-metal compositions and in particular the sulfur, selenium and tellurium boracites⁷⁴ have hardly been touched. In the great perovskite family all has still to be done, because present knowledge on magnetic multi-ferroics is nearly exclusively based on data from polycrystalline materials, and often not reliable. Also many more structure families should be explored, for example the fascinating new molecular-based magnets.¹⁰³⁻¹⁰⁶

viii) The key message that we wish to convey to researchers working or envisaging to work experimentally in the field of magnetoelectric multi-ferroics: without making use of single crystals and low and high temperature polarized light microscopy techniques, published results and data risk to grow rapidly obsolete, to misguide theoreticians and to waste space in data banks and on the shelves of our libraries. This categorical demand applies in particular to ferroelastic multi-ferroics, which can be made transparent in the form of very thin plates. In case of strongly absorbing materials, e.g. mixed valency compounds like magnetite, we have to accept working in reflected (polarized) light, which provides much less significant information than transmission microscopy, but here the development of low temperature Kerr effect microscopy or microscopy with spin polarization analysis would be beneficial for studying the magnetic domains of such types of material.

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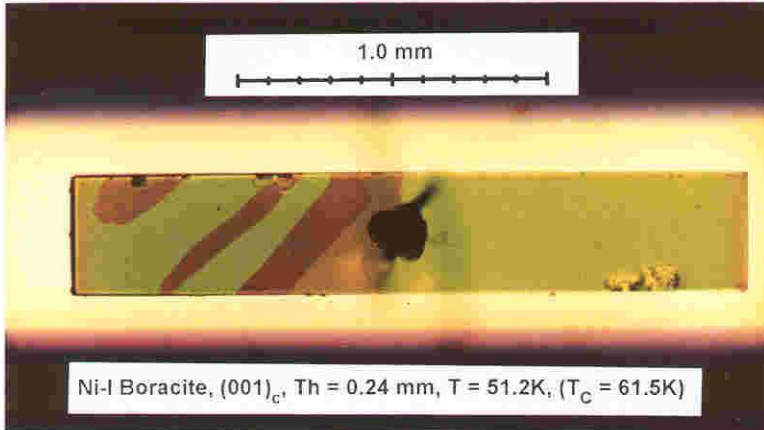
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COLOR PLATE XI. See H. Schmid, Figure 1.
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