Some symmetry aspects of ferroics and single phase multiferroics*

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Abstract

The symmetry conditions for the occurrence in a same phase of one or more of the four primary ferroic properties, i.e., ferroelectricity, ferromagnetism, ferrotoroidicity and ferroelasticity, are discussed. Analogous conditions are outlined for the admission of so-called secondary and tertiary ferroic effects, such as magnetoelectric, piezoelectric, piezomagnetic, piezotoroidic, etc. Formerly postulated 'magnetotoroidic' and 'electrotoroidic' effects are found to be describable as tertiary ferroic magnetoelectric effects. For understanding ferroic and multiferroic domains and their possibilities of switching, knowledge of the pairs of prototype point group/ferroic phase point group (so-called 'Aizu species') is decisive. A classification into ensembles of species with common properties, recently extended to ferrotoroidic crystals, allows distinguishing between full, partial or no coupling between order parameters and understanding domain patterns and poling procedures. The switching by reorientation with angles other than 180° of ferromagnetic, antiferromagnetic and ferroelectric domains by magnetic fields, electric fields or by stress requires the ferroic phase to be ferroelastic. For ferromagnetic/ferrotoroidic and antiferromagnetic/ferrotoroidic phases, the ferrotoroidic domains are found to be identical with the ferromagnetic and antiferromagnetic ones, respectively. As a consequence and depending on symmetry, ferrotoroidic domains can be switched by crossed electric *and* magnetic fields, by collinear electric *and* magnetic fields or by a magnetic field alone. Examples of ferrotoroidic domains are discussed for $Fe_{2-x}Ga_xO_3$, $Co_3B_7O_{13}Br$ and $LiCoPO_4$. Recent new results on symmetry and domains of the antiferromagnetic incommensurate phase of $BiFeO_3$ are also discussed.

*Dedicated to the memory of Edgar Ascher (1921–2006)

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1. Introduction

Astonishingly, in the recent prolific literature on multiferroics with an accent on magnetoelectric interactions (Fiebig 2005a), symmetry aspects are seldom evoked. The object of this paper is therefore to recall some of these aspects and to discuss recent developments concerning ferrotoroidic properties.

The term 'multiferroic' was originally understood as the simultaneous presence of two or all three primary ferroic properties *in the same phase*, i.e., ferromagnetism, ferroelectricity and ferroelasticity (Schmid 1994). Since the presence and not the magnitude of a spontaneous magnetization is determinative for the magnetic point group, the term 'ferromagnetic' used in this paper may also stand for 'ferrimagnetic' or 'weakly ferromagnetic' if not otherwise specified. Currently a fourth type of primary ferroic, i.e., ferrotoroidicity, is advocated (Van Aken *et al* 2007, Ederer and Spaldin 2007, Sannikov 2007, Janovec 2008). The emphasis of the definition of multiferroics lies on '*in the same phase*', as distinct from hetero-phase composite systems (ceramics or multilayers). By 'phase' we mean a solid, homogeneous and crystallized composition in the sense of Gibbs' phase rule, but extended also to the external constraints *electric field* and *magnetic field,* in addition to the usual ones, i.e*., pressure, temperature and concentration.* The scope of this paper is limited to simple ferroics and single phase multiferroics with physical properties describable on the level of point groups only. The common, analogous feature of the four types of primary ferroics is the formation of domains upon a phase transition from a high temperature *prototype* phase to a low temperature *ferroic* phase with a group → subgroup relation. Switching of these domains is associated with a hysteresis loop since it can be assimilated to an isothermal/isostructural first order phase transition (figure 1).

How is it possible that these four different ferroic properties can live peacefully together in one and the same phase of a crystal? In fact they can, if the right symmetry of the ferroic phase and the appropriate pair of prototype phase point group/ferroic phase point group, the so-called 'Aizu species' (Aizu 1969, 1970), are given. Among the four primary ferroics, ferroelasticity in a way plays the rôle of an outsider. Whereas spontaneous polarization, magnetization and toroidization are characterized by a vector and a single Heesch–Shubnikov point group, spontaneous strain (=spontaneous deformation) is described by a symmetric 2nd rank tensor.

It will be shown that ferroelasticity plays a major rôle in the intrinsic symmetry-given coupling or partial coupling of the different order parameters upon domain switching, similar to the way that piezoelectric, electrostrictive, piezomagnetic and magnetostrictive properties act as an 'extrinsic mechanical clutch' in hetero-phase magnetoelectric systems. However, we shall see later on that in this coupling function ferroelasticity may sometimes also play the rôle of 'devil's advocate'.

The common prefix '*ferro*' for all ferroics goes back to *ferro*magnetism, for which the existence of tiny uniformly magnetized regions was imagined by Weiss (1907) and later
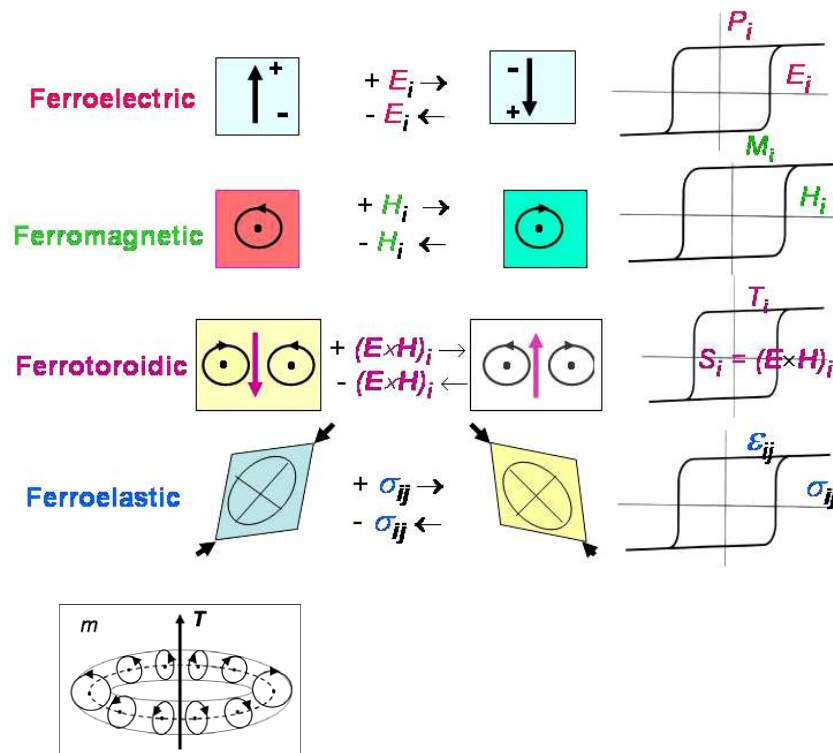
Figure 1. Schematic domain switching and hysteresis cycles of the four primary ferroics. The symmetry symbol used for the toroidal moment corresponds to the co-axial mirror plane cross-section of a toroid with an even number of windings (see inset). Note that for certain symmetries, a toroidal moment cannot only be switched by $(E \times H)_i$, but also by collinear electric and magnetic fields or by a magnetic field alone (cf section 3.2.2).

Table 1. Different physical quantities classified according to the behaviour with respect to space inversion $\bar{1}$, time reversal $1'$ and the product of both $\bar{1}'$, i.e., to the different representations of the 'parity group'. Note: legend: ρ = charge density, P = polarization, M = magnetization, j = current density, A = vector potential, v = velocity, p = (linear) momentum, T = toroidization, ε = strain (symmetric 2nd rank tensor), G = an axial vector, e.g., director n of nematic crystals or the electric toroidal moment G (Prosandeev *et al* 2008).

Ascher (1966a)					Ascher (1974)	Dubovik *et al* (1987, 1990)		Van Aken *et al* (2007)	
1	$\bar{1}$	$1'$	$\bar{1}'$			Limiting group			
1	1	1	1	ρ	$\partial M/\partial t$, grad P	G	$\infty/m1'$	ε	Ferroelastic
1	−1	1	−1	P	P, $\partial v/\partial t$	P	$\infty/mm1'$	P	Ferroelectric
1	1	−1	−1	M	M, grad v	M	$\infty/mm'm'$	M	Ferromagnetic
1	−1	−1	1	j	$j, v, p, A, \partial P/\partial t$, grad M	T	$\infty/m'mm$	T	Ferrotoroidic

named *domains* (Weiss and Foëx 1926). They were in fact soon seen in a silicon–iron alloy (Bitter 1931, 1932, Hámos and Thiessen 1931). After the discovery of ferroelectricity (Valasek 1922) the observation of analogous ferroelectric domains and hysteresis loops followed shortly. The concept of ferroelasticity and ferroelastic domains was developed by Aizu (1967, 1969, 1970), although such types of domain were well known before and sometimes called *mechanical twins* (Klassen-Neklyudova 1964, 1960).

For the occurrence of two or more ferroic properties in the same phase, strict symmetry conditions are required. The Heesch–Shubnikov point groups permitting both a spontaneous polarization (polar vector) and a spontaneous magnetization (axial vector) in a crystal had first been determined by Shuvalov and Belov (1962a, 1962b), who showed that among the 31 groups permitting a spontaneous polarization (invariant under time reversal) and the 31 groups permitting a spontaneous magnetization (invariant under space inversion), 13 are intersecting and allow both properties in the same phase. The synthesis of magnetically ordered ferroelectrics was initiated in Russia (Smolenskii and Chupis 1982). Nickel iodine boracite, $Ni_3B_7O_{13}I$, was the first material, in which (weak) ferromagnetism and ferroelectricity were shown to occur in the same phase (Ascher *et al* 1966, Schmid 1967, 1969, Rivera and Schmid 1981). We know today that the compound and many of its homologues are also ferroelastic and ferrotoroidic. In 1966 Ascher determined a further 31 Heesch–Shubnikov point groups describing crystals allowing 'spontaneous currents', hoping to explain superconductivity. However, this hope did not materialize with the framework of the BCS-theory. The current density is characterized by an 'axio-polar', i.e., a 'time-odd polar' vector, invariant under the product of space *and* time reversal (cf table 1). In the same year Koptsik (1966) also pointed out this vector and indicated its correct limiting group, $\infty/m'mm$. He called it very appropriately 'magnetoelectric vector', but did not go further. Beside current density, the vector transforms like velocity, linear momentum, vector potential, etc (Ascher 1966a, 1974; table 1). It turned out that only 9 intersecting point groups allow all three types of vector (Schmid 1973, Ascher 1974; table 2 and figure 2). We had to wait until 1984, when Ginzburg *et al* (1984) remarked that those 31 groups determined by Ascher, also describe crystals with a spontaneous toroidal moment and that they are necessarily associated with the linear magnetoelectric effect. Independently of Ascher, the time-odd polar vector was also

mentioned by Zel'dovich (1957, 1958), when he predicted the existence of nuclear 'anapole' moments with a toroidal dipole symmetry of their spin part. Only a few years ago the existence of 'anapole' moments was confirmed by the measurement of parity nonconservation in the 6S → 7S transition of the caesium ^{133}Cs nucleus (Wood *et al* 1997). Beside the great importance of anapoles in nuclear and particle physics, they also seem to make inroads into chemistry with the discussion of a quantum mechanical formalism for molecular anapole moments (Ceulemans *et al* 1998).

To allow ferroelasticity to occur simultaneously in addition to the three vectorial primary ferroics, a change of crystal class has to take place at the prototype → ferroic phase transition. Then ferroelastic domains with differing orientation of spontaneous strain and therefore of optical indicatrix (Schmid 1993) are formed and are reorientable by stress, electric and magnetic fields in principle (Schmid 1999). In the case of equi-class and hexagonal → rhombohedral phase transitions the spontaneous strain is finite but not reorientable. In such a case we speak of 'co-elastic' (Salje 1990) phase transitions.

2. Relation between stored free enthalpy and crystallo-physical effects

To obtain an overview of the possible symmetry-controlled physical effects and the associated possibilities of switching domains in ferroics and multiferroics, it is practical to develop a stored free enthalpy function as a limited series and to test, thereafter, for all Heesch–Shubnikov point groups which of the terms and which of their tensor coefficients remain invariant under the symmetry operations of the group. It is a function dependent on the constraints of the system: electric field E, magnetic field H, source vector S, with components $S_i = (E \times H)_i$, of the toroidal moment (Gorbatsevich *et al* 1983a, 1983b), mechanical stress tensor σ (with indices running from 1 to 3), and temperature T, which we keep constant:

$$g = g(E, H, S, \sigma; T). \tag{1}$$

For simplifying the approach, the 'strict' relation $S = (E \times H)_i$, will be used in the present work, however, it has to be stressed that in addition to the expression $(E \times H)_i$, other vector fields violating space- and time-inversion symmetry can function as a 'toroidal field'. For example in table 1 (column Ascher 1974) it can be seen that a magnetic field gradient, with

Table 2. Classification of the 122 Heesch–Shubnikov point groups ('the 122 reduced superfamilies of magnetic groups', Opechowski 1986) according to 'magnetoelectric types' (adapted from Schmid (1973); for a derived version see table 1.5.8.3 in Borovik-Romanov and Grimmer (2003)). (Legend: 'weak ferromagnetism' permitted (Dzyaloshinsky 1957a,1957b), determined by Tavger (1958a, 1958b) for nearly uniaxial antiferromagnets (dotted rectangles: 'weak ferroelectricity', not confirmed). Types of order: M = pyro-, ferro or ferrimagnetic; P = pyro-, ferro, or ferrielectric; $\bar{M}$ = antiferromagnetic; $\bar{P}$ = antiferroelectric or orthoelectric, D = diamagnetic, or paramagnetic, or antiferromagnetic; O = orthoelectric, or paraelectric, or antiferroelectric, V_s = invariant velocity vector (Ascher 1974); 'V_s' stands also for 'T = toroidization', H: spontaneous magnetization permitted; E: spontaneous polarization permitted; EH: linear magnetoelectric effect permitted; EHH: bilinear magnetoelectric effect (I) (= 'paramagnetoelectric effect'), Pockels effect (= linear electro-optic effect), etc permitted; HEE: bilinear magnetoelectric effect (II), piezomagnetism, 'Mockels' effect (= linear magneto-optic effect Kharchenko 1994), etc, permitted. The groups allowing the piezomagnetoelectric effect (Grimmer 1992, Rivera and Schmid 1994) are exactly those which in the column 'type of ordering' have no 'D' in the sub-column 'magnetic' and no 'O' in the sub-column 'electric').

Magneto-electric type	Type of ordering		Permitted terms of stored free enthalpy	Shubnikov point groups		Number of Shubnikov groups
	Magnetic	Electric		V_s not permitted	V_s permitted	
FE IV	D	P	E ... EHH	1̄, 2̄1̄, m1̄, mm21̄ , 41', 4mm1', 31', 3m1', 61', 6mm1'		10 ⎫ 31
FE III	$\bar{M}$	P	E ... HEE EHH	6', 6'mm'		2
FE II	$\bar{M}$	P	E EH HEE EHH	4', 4'mm'	m̄m̄2, 4mm, 3m, 6mm	6
FE I/FM I	M	P	E H EH HEE EHH	m'm'2 , 3m', 4m'm', 6m'm'	1̄, 2̄, 3, 4, 6, m̄, 2̄, m̄', mm'2'	13 ⎫ 49
FM II	M	$\bar{P}$	H EH HEE EHH	4̄, 4̄2'm'	2'2'2, 4̄2'm, 32', 62'2'	6
FM III	M	$\bar{P}$	H ... HEE EHH	6̄, 6̄m'2'		2 ⎫ 31
FM IV	M	O	H ... HEE	1̄, 2/m, 2'/m', m'm'm, 4/m, 4/mm'm', 3̄, 3̄m', 6/m, 6/mm'm'		10
AA I	$\bar{M}$	$\bar{P}$	EH HEE EHH	222, 422, 4̄2m, 4'22', 4̄'2m', 32, 622, 6̄'m'2, 4̄'3m'	4̄', 4̄'2'm, 6̄', 6̄'m2'	14 ⎫ 122
AA II	$\bar{M}$	$\bar{P}$	HEE EHH	6̄m2, 6'2'2		2
AA III	$\bar{M}$	$\bar{P}$	EH	m'm'm, 4'/m', 4'/m'm'm, 4/m'm'm', 3'm', 6/m'm'm', 432, m'3, m'3m'	1̄', 2/m', 2'/m, mmm', 4/m', 4/m'mm, 3̄', 3̄'m, 6/m', 6/m'mm	19
AA IV	$\bar{M}$	O	HEE	mmm, 4'/m, 4̄mmm, 4'/mmm', 6/mmm, 3̄m, 6'/m', 6'/m'm'm, m3, m3m'		10
	$\bar{M}$	$\bar{P}$		4'32'		1
AA V	$\bar{M}$	$\bar{P}$	EHH	4̄3m		1
	D	$\bar{P}$		2221', 4̄1', 4221', 4̄2m1', 6221', 321', 6̄1', 6̄m21', 231', 4̄3m1'		10 ⎫ 73
AA VI	$\bar{M}$	O		m3m		1
	D	P		4321'		1
	$\bar{M}$	$\bar{P}$		6'/m, 6'/mm'm, m'3m		3
	D	O		1̄1', 2/m1', mmm1', 4/m1', 4/mmm1', 3̄1', 3̄m1', 6/m1', 6/mmm1', m31', m3m1'		11

the same transformation properties as the toroidal moment, can also act as a toroidal field. Moreover, whereas all toroidal moments lead to an anti-symmetric magnetoelectric contribution the reverse is not the case.

The function g is the free enthalpy g_0, from which the contributions of the electric and magnetic fields in the vacuum have been subtracted (Schmid 1973):

$$g = g_0 - (\varepsilon_0/2)E^2 - (\mu_0/2)H^2. \quad (2)$$

Here ε_0 and μ_0 are the electric permittivity and magnetic permeability of free space, respectively.

In equation (3) g is developed as a limited series and as a function of E_i, H_i, S_i and σ_{ij}:

$$\begin{aligned}
-g = \cdots &P_{(s)i}E_i + M_{(s)i}H_i + T_{(s)i}S_i + \varepsilon_{(s)ij}\sigma_{ij} \\
&+ \tfrac{1}{2}\chi_{(e)ij}E_iE_j + \tfrac{1}{2}\chi_{(m)ij}H_iH_j + \tfrac{1}{2}\tau_{ij}S_iS_j + s_{ijkl}\sigma_{ij}\sigma_{kl} \\
&+ \alpha_{ij}E_iH_j + \theta_{ij}E_iS_j + \zeta_{ij}H_iS_j \\
&+ d_{ijk}E_i\sigma_{jk} + q_{ijk}H_i\sigma_{jk} + g_{ijk}S_i\sigma_{jk} \\
&+ \tfrac{1}{2}\gamma_{ijk}H_iE_jE_k + \tfrac{1}{2}\beta_{ijk}E_iH_jH_k + \cdots .
\end{aligned} \quad (3)$$

The first line of (3) represents the first order invariants with $P_{(s)i}$, $M_{(s)i}$, $T_{(s)i}$ and $\varepsilon_{(s)ij}$ standing for spontaneous polarization, spontaneous magnetization, spontaneous toroidization and spontaneous strain, respectively. They describe the *Primary ferroics*. The 2nd order terms of the second line of (3) represent the susceptibility terms allowed in every point group, with $\chi_{(e)ij}$, $\chi_{(m)ij}$, τ_{ij} and s_{ijkl} standing for electric, magnetic, toroidic susceptibility and elastic compliance, respectively. In the third line we have from left to right the 2nd order invariants of the linear magnetoelectric, linear 'electrotoroidic', linear 'magnetotoroidic', piezoelectric, piezomagnetic and 'piezo-toroidic' effects. The 2nd order terms of line two and three of (3) are named *secondary ferroics* and the magnetoelectric invariants of 3rd order in line four of (3) belong to the *tertiary ferroics*. In table 5 a more complete list of the invariants of equation (3) and the corresponding nomenclature is given.

In an attempt to classify the terms of the free enthalpy and their corresponding physical effects, a nomenclature has been introduced (Newnham 1974, Newnham and Cross 1974a, 1974b), distinguishing between *primary, secondary*
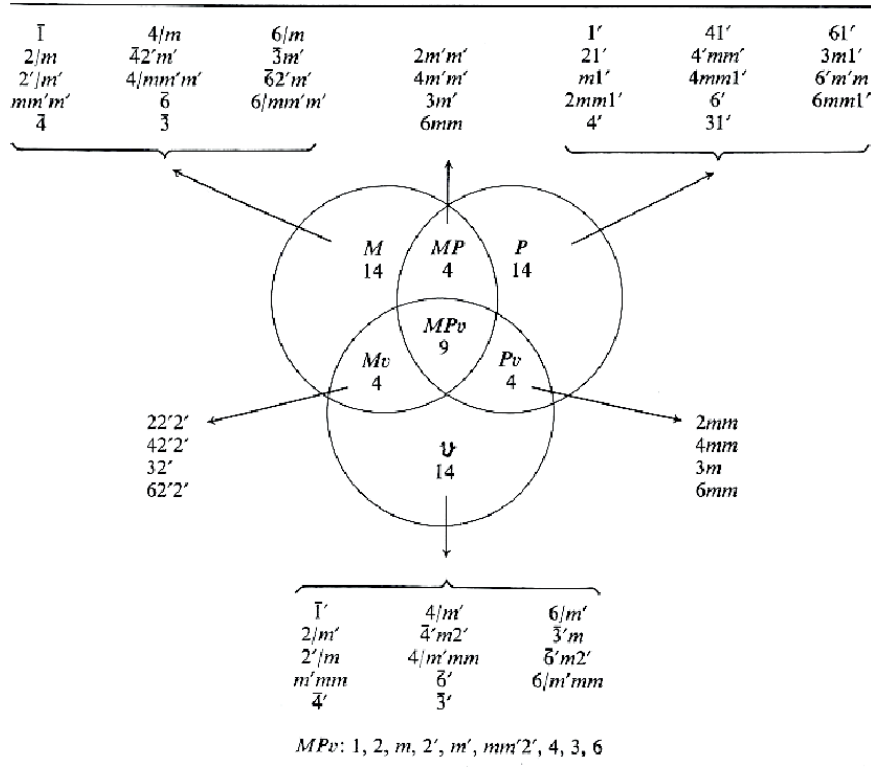
(a)
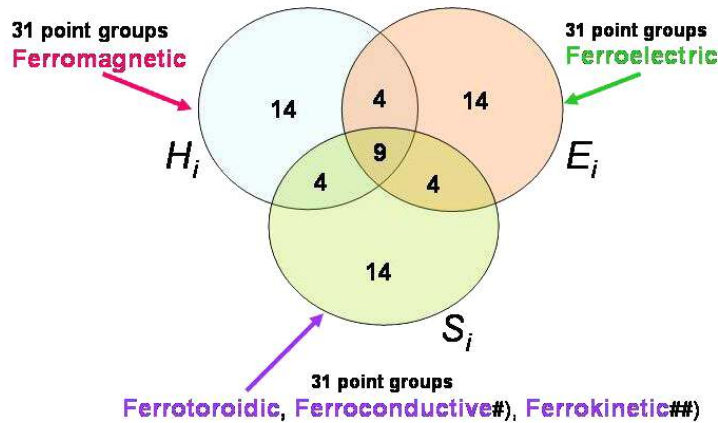
(b)

Figure 2. The 'magic trinity' of groups I. (a) Seven ensembles of point groups with common sets of allowed terms in the free enthalpy function (cf table 2), produced by the intersection of the ensembles of the 31 ferroelectric, 31 ferromagnetic and 31 ferrotoroidic (ferrokinetic, ferroconductive) point groups. The letters P, M, v stand for spontaneous polarization, magnetization and velocity, respectively. Velocity v can be replaced by linear momentum p or spontaneous toroidization T_s with equal transformation properties. (b) Simplified explicative representation of (a). (Adapted and corrected from Ascher 1966a, 1974 ##.)

and, corresponding to the first, second and third order terms of the potential, respectively (table 5). However, the use of the names of the secondary and tertiary ferroics, for which the prefix 'Ferro' has also been introduced, does not seem to have made extended inroads in the literature, so far.

In table 2 ensembles of Heesch–Shubnikov point groups are represented, permitting one, more or none of the invariants E, H, EH, EHH and HEE (abbreviated form) of equation (3). The 122 'black and white' point groups, originally determined by Heinrich Heesch in 1930 and called 'the 122 reduced

superfamilies of magnetic groups' by Opechowski (1986), are now called *Heesch-Shubnikov point groups* (Küppers and Molzow 2006, Küppers 1996). In that table, which proved to be useful for the experimentalist, also the 31 'ferrokinetic' point groups, allowing the velocity vector V_S (Ascher 1974), are given. In a related presentation the intersection of the ensemble of the 31 'ferrokinetic' groups with those of the 31 ferroelectric and 31 ferromagnetic groups is shown in figure 2.

There exists a contribution to the free enthalpy, $\propto T_i(\boldsymbol{E} \times \boldsymbol{H})_i$, in which the physical meaning of the order parameter

'toroidal moment T' has been identified (up to a constant) as the anti-symmetric component of the magnetoelectric tensor (Gorbatsevich *et al* 1983a, 1983b). In the general case the three components of the vector T are proportional to the three components of the anti-symmetric component of the magnetoelectric tensor, while the source for the vector T is the vector S with components $S_i \propto (E \times H)_i$, in the same way as electric and magnetic field are source vectors for polarization and magnetization, respectively. This latter vector S transforms like the spontaneous toroidal moment T_s and necessitates off-diagonal components of the magnetoelectric tensor. It is consistent that the 31 Heesch–Shubnikov point groups permitting a spontaneous toroidal moment, do have off-diagonal magnetoelectric coefficients, a few of them in addition diagonal ones (cf appendix A and table 7). Then it should be permitted to add in (1) the source vector S as further variable and the invariant $T_{(S)i} S_i$ in equation (3), and to add the 'driving force' $\sim \Delta T_{(S)i} S_i$ for domain switching in the list of 'driving forces' of primary, secondary and tertiary ferroics in table 5). Thus we can also replace in table 2 'V_S permitted' by 'T_S permitted'.

2.1. The 'magic trinity' of groups I (ferroelectric, ferromagnetic, ferrotoroidic)

In figures 2(a) and (b) are represented the 31 ferroelectric, the 31 ferromagnetic and the 31 ferrotoroidic Heesch–Shubnikov point groups and the intersection of their ensembles. The ferrotoroidic groups correspond to the symbol 'v' (velocity) of the 'ferroconductive' (Ascher 1966a) and the 'ferrokinetic' (Ascher 1974) vector. Only 9 groups admit all three kinds of vector, 13 admit two kinds of primary ferroics and 14 of each ferroic ensemble admit no other kind of ferroic vector. In table 3 the mutual orientation of the three vectors in a crystal and the potential occurrence of weak ferromagnetism are given for the 13 point groups admitting both ferromagnetism and ferroelectricity. Group $mm'2'$ is unique with all three vectors being mutually perpendicular. In contrast to that the three vectors have independent arbitrary directions in the triclinic group 1. For point groups 2, 3, 4 and 6 the spontaneous polarization, spontaneous magnetization and spontaneous toroidization are allowed to be parallel.

Because the spontaneous toroidization T_s is proportional to the anti-symmetric component of the linear magnetoelectric effect tensor (Gorbatsevich *et al* 1983a, 1983b), the tensor form of the linear magnetoelectric effect of the 31 ferrotoroidic groups has been assembled in table 7. Those tensor forms give us information about the different possibilities of switching of ferrotoroidic domains (cf section 3.2).

2.2. The 'magic trinity' of groups II (magnetoelectric, 'electrotoroidic', 'magnetotoroidic')

As pointed out in section 2, the invariant $\alpha_{ik} E_i H_k$ (abbreviated *EH*) in the free enthalpy function (equation (3)), corresponds to the linear magnetoelectric effect (cf table 2). It has been known since the theoretical prediction by Dzyaloshinskii (1959) for antiferromagnetic Cr_2O_3 and its measurement by Astrov (1960,

Table 3. Mutual orientation of spontaneous polarization P_s, spontaneous magnetization M_s and spontaneous toroidization T_s among 13 Heesch–Shubnikov point groups (adapted from Ascher 1970). (Legend: P_s, M_s T_s, v_s invariant vectors of spontaneous polarization, magnetization, toroidization, and velocity, respectively. The symbol (z) means perpendicular to z and $*$ means any direction. Point groups permitting 'weak ferromagnetism' (Dzyaloshinsky 1957a, 1957b), determined by Tavger (1958a, 1958b).)

P_s	M_s	$T_s(v_s)$	Weak ferromagnetism[a]	
$*$	$*$	$*$	1	
z	z	z	2	4, 3, 6
z	z	0	$m'm'2$	$m'm'4, 3m', m'm'6$
(z)	(z)	z	m'	
z	(z)	(z)	$2'$	
(z)	z	(z)	m	
z	x	y	$mm'2'$	

[a] For nearly uniaxial antiferromagnets.

1961) via the electric-field-induced magnetization (symbol 'ME_E'),

$$M_i = \alpha_{ki} E_k \tag{4}$$

and by Folen *et al* (1961) via the magnetic-field-induced polarization (symbol 'ME_H')

$$P_k = \alpha_{ki} H_i. \tag{5}$$

According to the classification by Newnham and Cross (1974a, 1974b) and Newnham (1974) of the terms of the free enthalpy function and the associated physical effects, the linear *EH*-effect, termed 'ferromagnetoelectric', belongs to the *secondary ferroics*. An extended list of terms of primary, secondary and tertiary ferroics, all of which belong to equation (3), is presented in table 5.

The magnitude of the coefficients α_{ij} of some materials are given in table 1.6.8.3 of Borovik-Romanov and Grimmer (2003) and reproduced in Schmid (2003). In appendix A the components of the tensor of the *EH*-effect are given in Nye notation (Nye 1990) for the 58 magnetic point groups permitting the effect. All permutations are represented for the monoclinic and orthorhombic groups for the attention of the experimentalist. For example at magnetic → magnetic phase transitions to a lower symmetry phase, the magnetic structural change may be so subtle that the expected increase of tensor components of the ME-effect may not be observed. Then it is important to find easily the adequate permutation to deduce the compatible point group of the lower symmetry phase. An example of the procedure is described in detail for $LiCoPO_4$ by Vaknin *et al* (2002). For accurate magnetoelectric measurement techniques see Rivera (1994a) and Hehl *et al* (2008).

In figure 3 the intersection of the ensembles of the 58 point groups of the linear magnetoelectric effect (invariant *EH*), with those of the 58 groups of the linear 'magnetotoroidic' effect (invariant *SH*) and of the 58 groups of the linear 'electro-toroidic' effect (invariant *SE*) are shown. The point groups permitting these latter two invariants have been determined by Ascher (1974) and attributed to the so-called kinetomagnetic and kinetoelectric effects (cf appendix B) and the tensor form
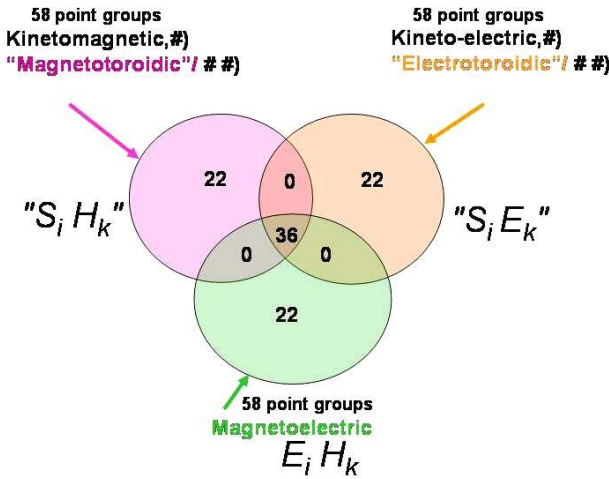
Figure 3. The 'magic trinity' of groups II. Intersection of the ensembles of 58 point groups of the linear magnetoelectric effect, with those of the 58 'magnetotoroidic'## (kinetomagnetic#) and the 58 'electrotoroidic'## (kinetoelectric#) groups (# Ascher 1974; ## Schmid 2001); For the tensor form of the magnetoelectric groups see appendix A and table 7. For the point groups of all three types of 58 groups see appendix B and for the tensor form of all three types of 58 groups see Litvin (2008).

Figure 4. The 'magic trinity of groups' III. The intersections of the ensembles of 66 piezoelectric, 66 piezomagnetic and 66 piezotoroidic (Schmid 1999) (piezoconductive, # Ascher 1966a; piezokinetic, ## Ascher 1974) point groups. The tensor form of the piezoelectric, piezomagnetic and piezotoroidic coefficients is given by Grimmer (1994) in transposed matrix form and by Litvin (2008).

of their corresponding coefficients has only recently been determined by Litvin (2008).

The 'ferrokinetic', 'kinetoelectric' and 'kinetomagnetic' terms of the density of free enthalpy g were defined by Ascher (1974) respectively as

$$-g(\boldsymbol{E}, \boldsymbol{B}, \boldsymbol{v}) = \cdots + {}^o p_i v_i + \eta_{ik} v_i E_k + \xi_{ik} v_i c B_k, \quad (6)$$

where ${}^o\boldsymbol{p}$ = spontaneous linear momentum without electric ($\boldsymbol{E}$) and magnetic ($\boldsymbol{B}$) fields, $\boldsymbol{v}$ = the 'field' velocity and c = light velocity. To the best of our knowledge, the physical reality of the 'ferrokinetic', 'kinetoelectric' and 'kinetomagnetic' effects, as well as of the 'ferroconductive' effect (Ascher 1966a), have so far not been examined. Theoretical and experimental work in these fields would be welcome.

One can say, e.g., that a crystal, allowing the vector ${}^o\boldsymbol{p}$ and propagating at high velocity in the direction of allowed ${}^o\boldsymbol{p}$, will not change its symmetry, whereas when propagating along other crystalline directions, a velocity-induced phase transition, i.e., a change of symmetry, will be induced. This can be considered analogous to a ferromagnet, which preserves its symmetry when superposing a magnetic field along the direction of spontaneous magnetization, but it will change it when applied along other directions, i.e., a magnetic-field-induced phase transition will then occur. Since ${}^o\boldsymbol{p}$ and $\boldsymbol{v}$ transform like the vectors $\boldsymbol{T}$ and $\boldsymbol{S}$, we can anticipate on mere symmetry grounds the existence of analogous 'ferrotoroidic', 'electrotoroidic' and 'magnetotoroidic' terms $T_i S_i$, $S_i E_k$ and $S_i H_k$, respectively. From the explicit forms $(\boldsymbol{E} \times \boldsymbol{H})_i E_k$ and $(\boldsymbol{E} \times \boldsymbol{H})_i H_k$ we can identify these effects simply as special cases of the bilinear magnetoelectric effects with the terms $\gamma_{ijk} H_i E_j E_k$ and $\alpha_{ijk} E_i H_j H_k$, respectively, but restricted to tensor components, allowing crossed electric and magnetic
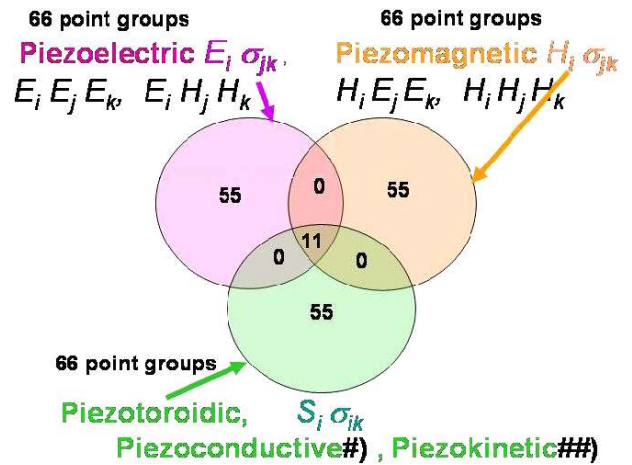
fields only. In a similar way $T_i S_i$ was identified as a special case of the linear magnetoelectric effect.

Since $\boldsymbol{S}$ transforms like the current density, the set of secondary ferroic effects may also be enlarged by a 'piezotoroidic' effect term $S_i \sigma_{jk}$, where σ_{jk} is the stress tensor, in analogy with the 'piezoconductive' term (Ascher 1966a) (see (3) and section 2.3).

2.2.1. Influence of incommensurability on the linear magnetoelectric effect. It has been shown for BiFeO$_3$ (Tabares-Muñoz *et al* 1985), BaMnF$_4$ (Sciau *et al* 1990, Scott and Tilley 1994) and LiNiPO$_4$ (Vaknin *et al* 2004a, 2004b) that due to incommensurability of the magnetic phase, any linear magnetoelectric effect is annihilated. In the case of BiFeO$_3$ and BaMnF$_4$ the average nuclear structure of the IC-phases being non-centrosymmetric, the crystals behave like non-centrosymmetric paramagnets in the antiferromagnetic IC-phases and allow the bilinear magnetoelectric effect with *EHH*-invariants. In this context a new kind of ferroelectric is worth mentioning, in which the spontaneous polarization is induced by an incommensurate magnetic order. This occurs in Ni$_3$V$_2$O$_8$ (Lawes *et al* 2005) and TbMnO$_3$ (Kenzelmann *et al* 2005) and has been reviewed by Harris (2006) and Harris and Lawes (2006). In analogy with the above-mentioned 'classical' ferroelectrics with magnetically incommensurate structure, the linear magnetoelectric effect in these new kinds of ferroelectric is also expected to be absent, whereas the bilinear *EHH*-effect should be allowed. Since this type of ferroelectricity seems to be of an 'electronic type', the related coefficient β_{ijk} is possibly very small, but may be detectable by a very sensitive, dynamic measurement technique developed by Rivera (1994a).

2.3. The 'magic trinity' of groups III (piezoelectric, piezomagnetic, piezotoroidic)

In table 2 the Heesch–Shubnikov point groups are indicated allowing the bilinear magnetoelectric terms *EHH* and *HEE*.

Table 4. Some corresponding tensor notations.

Coefficient	Litvin (2008) Jahn notation	Grimmer (1994)	Birss (1964)
			Rank odd Axial i-tensor
Piezomagnetic	aeV [V^2]	i-tensor s-tensor	Axial c-tensor
Piezoelectric	V [V^2]	t-tensor	Axial i-tensor
Piezotoroidic	aV [V^2]	u-tensor	Polar c-tensor

Table 5. Ferroic driving potential Δg of domain switching and reorientation between two domain states of primary, secondary and tertiary ferroics (adapted from Newnham and Cross 1974a, 1974b, Newnham 1974, Schmid 2001, Litvin 2008).

Type of ferroic	Driving potential $\Delta g \propto$ Difference in free enthalpy	Name of coefficient	
Primary Ferroics			
Ferromagnetic	$\Delta M_{(s)i} H_i$	Spontaneous magnetization	$M_{(s)i}$
Ferroelectric	$\Delta P_{(s)i} E_i$	Spontaneous polarization	$P_{(s)i}$
Ferrotoroidic	$\Delta T_{(s)i} S_i$	Spontaneous toroidization	$T_{(s)i}$
Ferroelastic	$\Delta \varepsilon_{(s)ij} \sigma_{ij}$	Spontaneous strain (deformation)	$\varepsilon_{(s)ij}$
Secondary ferroics			
Ferro**bi**electric	$1/2 \Delta \chi_{(e)ij} E_i E_j$	Electric susceptibility	χ_{ij}
Ferro**bi**magnetic	$1/2 \Delta \chi_{(m)ij} H_i H_j$	Magnetic susceptibility	κ_{ij}
Ferro**bi**toroidic	$1/2 \Delta \tau_{ij} S_i S_j$	Toroidic susceptibility	τ_{ij}
Ferro**bi**elastic	$1/2 \Delta s_{ijkl} \sigma_{ij} \sigma_{kl}$	Elastic compliance	s_{ijkl}
Ferromagnetoelectric[c]	$\Delta \alpha_{ij} E_i H_j$	Magnetoelectric[a] coefficient	α_{ij}
'Ferroelectrotoroidic'	$\Delta \theta_{ij} E_i S_j$	'Electrotoroidic' coefficient	θ_{ij}
'Ferromagnetotoroidic'	$\Delta \zeta_{ij} H_i S_j$	'Magnetotoroidic' coefficient	ζ_{ij}
'Ferroelastotoroidic'	$\Delta d_{ijk} E_i \sigma_{jk}$	'Piezotoroidic' coefficient	d_{ijk}
Ferromagnetoelastic	$\Delta q_{ijk} H_i \sigma_{jk}$	Piezomagnetic coefficient	q_{ijk}
Ferroelastotoroidic	$\Delta g_{ijk} S_i \sigma_{jk}$	Piezotoroidic coefficient	g_{ijk}
Tertiary ferroics			
Ferro**tri**electric	$\Delta \kappa_{ijk} E_i E_j E_k$	Nonlinear electric susceptibility	κ_{ijk}
Ferro**tri**magnetic	$\Delta \chi_{ijk} H_i H_j H_k$	Nonlinear magnetic susceptibility	χ_{ijk}
Ferroelasto**bi**electric	$\Delta \alpha_{ijkl} \sigma_{ij} E_k E_l$	Electrostriction coefficient	α_{ijkl}
Ferroelasto**bi**magnetic	$\Delta \beta_{ijkl} \sigma_{ij} H_k H_l$	Magnetostriction coefficient	β_{ijkl}
Ferromagneto**bi**electric	$\Delta \gamma_{ijk} H_i E_j E_k$	Magneto**bi**electric[b] coefficient	γ_{ijk}
Ferroelectro**bi**magnetic	$\Delta \beta_{ijk} E_i H_j H_k$	electro**bi**magnetic[b] coefficient	β_{ijk}
Ferromagnetoelectroelastic	$\Delta \pi_{ijkl} H_i E_j \sigma_{kl}$	Piezomagnetoelectric coefficient	π_{ijkl}
Ferromagneto**bi**elastic	$\Delta \psi_{iklmn} H_i \sigma_{kl} \sigma_{mn}$	Magneto**bi**elastic coefficient	ψ_{iklmn}

[a] Linear magnetoelectric effect.

[b] Bilinear magnetoelectric effects.

[c] The term 'Ferromagnetoelectric' in the nomenclature of Newnham, used in this table, is somewhat unfortunate because it is also sometimes used in literature for a ferroelectric being simultaneously ferro(i)magnetic in the same phase.

Since $H_j H_k$ transforms like $E_j E_k$ and the stress tensor σ_{jk}, the symbol *EHH* in table 2 stands also for the piezoelectric term $E_i \sigma_{jk}$ and the 'Pockels-effect'-term $E_i E_j E_k$. Analogously the symbol *HEE* stands also for the piezomagnetic term $H_i \sigma_{jk}$ and the 'Mockels-effect'-term $H_i H_j H_k$ (see footnote of table 2). Whereas the *EHH* and associated terms are allowed in paramagnets, diamagnets and in spin-ordered phases, the *HEE* term and associated effects are allowed in magnetically ordered structures only. In figure 4 the intersection of the ensembles of the 66 piezoelectric, 66 piezomagnetic and 66 piezotoroidic point groups is shown. The three kinds of term of the free enthalpy function are simultaneously allowed by the following 11 antiferromagnetic point groups only:

1, 2, 3, 4, 6, 222, 422, 32, 622, 23, (432).

However, for the cubic group 432 the 3rd rank tensor is zero, so that only 10 groups allow the three types of effect in the same phase. The tensors of all point groups of the three types of effect are given by Litvin (2008) and in matrix form by Grimmer (1994). For the use of Grimmer's and Litvin's tables the correlations given in table 4 may be helpful.

3. Domains and domain switching

Phase transitions from a high temperature *prototype phase* to a low temperature *ferroic phase*, related by a group/subgroup relationship, are always accompanied by a decrease of symmetry and as consequence the splitting up into domains of the ferroic phase. They are related one to another by the lost symmetry elements of the prototype phase. For understanding

the formation of domains and the switching from one domain state to another by external constraints (stress, electric and magnetic fields or simultaneous electric and magnetic fields) the knowledge of the Aizu species, i.e., the point group of both phases, is crucial.

The driving potential of domain switching is the difference Δg in free enthalpy of two domain states which to second order (also up to third order in table 5) in external fields is

$$
\begin{aligned}
\Delta g = {} & \Delta P_{(s)i} E_i + \Delta M_{(s)i} H_i + \Delta T_{(s)i} S_i + \Delta \varepsilon_{(s)ij} \sigma_{ij} \\
& + \tfrac{1}{2} \Delta \kappa_{ij} E_i E_j + \tfrac{1}{2} \Delta \chi_{ij} H_i H_j \\
& + \tfrac{1}{2} \Delta \tau_{ij} S_i S_j + \tfrac{1}{2} \Delta s_{ijkl} \sigma_{ij} \sigma_{kl} \\
& + \Delta \alpha_{ij} E_i H_j + \Delta \theta_{ij} E_i S_j + \Delta \zeta_{ij} H_i S_j \\
& + \Delta d_{ijk} E_i \sigma_{jk} + \Delta q_{ijk} H_i \sigma_{jk} + \Delta g_{ijk} S_i \sigma_{jk} + \cdots . \quad (7)
\end{aligned}
$$

Here $\Delta \varepsilon_{(s)ij}$, $\Delta M_{(s)i}$, $\Delta P_{(s)i}$, $\Delta T_{(s)i}$ are the difference of, respectively, the spontaneous strain, magnetization, polarization and toroidal moment in a pair of domain states and σ_{ij}, H_i, E_i, and S_i are, respectively, external stress, magnetic field, electric field, and crossed electric and magnetic fields $S_i = (\boldsymbol{E} \times \boldsymbol{H})_i$ (cf also Litvin 2008).

Whereas there is a prolific literature on domain switching of primary ferroics, this is less the case for secondary and tertiary ferroics. However, a list of material examples with different types of ensemble of species, can be found in Schmid (1999). In this context the reported higher order ferroic switching, induced by scanning force microscopy, is worth mentioning (Abplanalp *et al* 2001).

It is noteworthy that the crystal physical properties enumerated in table 5 and based on the terms of the free enthalpy, represent only a tiny part of what exists and of what can be imagined. The field is greatly enlarged by introducing frequency as a variable into the invariants of the potential, leading for example to optical harmonics and nonlinear phenomena (cf, e.g., Franken and Ward (1963), Fiebig (2005b, cf) and table 1 in Schmid (1973)).

3.1. The notion of species and the number of domain states

Aizu (1969, 1970) has classified all possible ferroic phase transitions into *species* with the symbol **G1'**F**H**, where **G1'** denotes the para or diamagnetic prototype point group, **H** the ferroic phase point group below the phase transition and 'F' denotes 'ferroic'. Then the index $n = |\mathbf{G1'}|/|\mathbf{H}|$ gives the number of domain states $\mathbf{S}_i$, $i = 1, 2, \ldots, n$, where $|\mathbf{G1'}|$ and $|\mathbf{H}|$ denote the number of symmetry elements ('order' of the group) in **G1'** and H, respectively (Litvin 2008). While using only prototype point groups with time inversion 1' and magnetic *and* non-magnetic ferroic phase point groups, Aizu (1970) obtains 773 species. Why are magnetic prototypes excluded? This may be justified since all magnetic materials do not have Curie or Néel points up to the melting or decomposition temperature. But species with magnetic prototype groups may be of interest in case of materials with a sequence of magnetic transitions.

It is worth noting that the determination of the number of ferroelastic domain states, using the relation $n = |\mathbf{G1'}|/|\mathbf{H}|$, represents an *approximation*, because at ferroelastic transitions shear deformations (table 6) do occur. Due to the tendency of

Table 6. Some ferroelastic shear angles, $\alpha = |90° - 2\,\mathrm{tg}^{-1}(a/b)|$, normalized for different symmetries (Schmid and Schwarzmüller 1976, Schmid *et al* 1988).

	'Ferroelastic'	Shear angle α (min)
$YBa_2Cu_3O_{7-\delta}$	$4/mmm1'Fmmm1'$	≈ 60
$Ni_3B_7O_{13}Cl$	$\bar{4}3m1'Fmm21'$	30
$BiFeO_3$	$m\bar{3}m1'F3m1'$	≈ 30
$BaTiO_3$	$m\bar{3}m1'F4mm1'$	17
$Gd_2(MoO_4)_3$	$\bar{4}2m1'mm21'$	10
$Fe_3B_7O_{13}I$	$\bar{4}3m1'Fmm21'$	2.5
$Bi_4Ti_3O_{12}$	$4/mmm1'Fm(s)1'$	1.5
'Spontaneous magnetostriction' $\equiv$ 'ferroelastic'		
$CoFe_2O_4$	$m\bar{3}m1'F4/mmm$	0.38
Ni	$m\bar{3}m1'F\bar{3}m'$	0.13
α-Fe	$m\bar{3}m1'F4/mm'm'$	0.017

the crystal to maintain spatial coherence along *allowed domain walls* (Fousek and Janovec 1969, Sapriel 1975), this leads to a doubling of the number of states. At high shear angles ($\alpha \approx 60$ min) this phenomenon can become readily observable, both in polarized light and by x-ray techniques. A classical example thereof is the ferroelastic orthorhombic phase of $YBa_2Cu_3O_{7-d}$ with specie $4/mmm1'Fmmm1'$ (Schmid *et al* 1988). This problem is discussed in great detail by Janovec and Prívratská (2003). However, in the majority of cases—with shear angles of a few minutes of arc—Aizu's concept is a good approximation.

Under quasi-static conditions ferroelastic or ferroelectric/ferroelastic phases often minimize elastic energy by forming very fine lamellar domains. Under dynamic conditions the crystal often has no time to minimize elastic energy and fatigue phenomena may become a major handicap. For example crossing of mutually perpendicular ferroelectric/ferroelastic domain walls (e.g., with $\bar{4}2m1'mm21'$ and $\bar{4}3m1'Fmm21'$) may lead to dislocations or cracks, elastic back-switching at zero electric field or 'mechanical cross-talk' (induction of undesirable domain orientations), even at shear angles as small as $\alpha \approx 2.5$ mn (Pétermann and Schmid 1976). The recently reported rapid degradation of ferroelectric hysteresis cycles of initially perfect single crystals of $BiFeO_3$ (Lebeugle 2007 and Lebeugle *et al* 2007) was certainly caused by such mechanical interaction due to a too high ferroelastic shear angle (cf table 6). In the early nineteen seventies–before holographic memories were discarded because allowing only insufficient information density and before the breakthrough of liquid crystals—many millions of research money were wasted worldwide with the attempt at using the ferroelectric perovskite lead zirconate titanate ('PLZT') for building so-called page composers (X–Y-matrix with electrical input and optical readout) in the framework of the 'all-optical computer' idea of Rajchman (1970), Rajchman (1972). This was because the importance of ferroelasticity-generated fatigue was realized too late (Schmid and Schwarzmüller 1976). Therefore when ferroelectric switching is envisaged, non-ferroelastic ferroelectric species are preferable or clamped ferroelastic single domains, in the interior of which the spontaneous polarization can be

Table 7. Tensor form of the linear magnetoelectric effect of the 31 ferrotoroidic point groups (for the complete set of permutations of the monoclinic and orthorhombic groups see appendix A).

Ferrotoroidic/ferromagnetic/ferroelectric					
1	2, m'	$2'$, m	$m'm2'$	4, 3, 6	- - - - -
Ferrotoroidic/antiferromagnetic/ferroelectric					
- - - - -	- - - - -	- - - - -	- - - - -	- - - - -	$2mm$, $4mm$, $3m$, $6mm$
Ferrotoroidic/ferromagnetic					
- - - - -	- - - - -	- - - - -	- - - - -	- - - - -	$22'2'$, $42'2'$, $32'$, $62'2'$
Ferrotoroidic/antiferromagnetic					
$\bar{1}'$	$2/m'$	$2'/m$	mmm'	$\bar{4}'$, $4/m'$, $\bar{3}'$, $\bar{6}'$, $6/m'$	$\bar{4}'2'm$, $4/m'mm$, $\bar{6}'m2'$, $6/m'mm$, $\bar{3}'m$

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix} \quad \begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{pmatrix} \quad \begin{pmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{pmatrix} \quad \begin{pmatrix} \alpha_{11} & \alpha_{12} & 0 \\ -\alpha_{12} & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \quad \begin{pmatrix} 0 & \alpha_{12} & 0 \\ -\alpha_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

switched by 180° in a non-ferroelastic way (e.g., in fully ferro-electric, partially ferroelastic perovskite phases). This situation seems to prevail in thin ferroelectric films. It has, however, to be recalled that a 180° switching of P_s is invariant under time reversal. This implies that no coupling between P_s and M_s and/or T_s is possible. If nonetheless reorientation-switching of a magnetic order parameter would be desirable for a de-vice, the use, e.g., of pseudo-cubic or pseudo-tetragonal lattice parameters would imitate non-ferroelastic switching and avoid mechanical fatigue. Examples are boracite $Fe_3B_7O_{13}I$ (species $\bar{4}3m1'Fmm21'$), which becomes pseudo-tetragonal when the orthorhombic a-and b- parameters become identical close to the transition to the rhombohedral ($3m1'$) phase (Kobayashi *et al* 1970), and specific solid solutions between rhombohedral zinc and iron boracites, for which the spontaneous strain along P_s is of opposite sign, leading to a pseudo-cubic rhombohedral phase ($3m1'$) at a specific Fe/Zn concentration (Schmid and Tippmann 1978).

When both the prototype and the ferroic phase are dia or paramagnetic, the total number of possible species is 212 (Aizu 1969, Schmid 1993; cf figure 5). When magnetic point groups are also taken into account for the ferroic phase, this number increases to 773 *species* (Aizu 1970; cf appendix D). Recently this latter classification has been extended by Litvin (2008) to ferrotoroidic crystals within the framework of the 773 species.

From the point of view of research and technical applications, the system of species is important

(i) concerning the distinguishability of domain states (Litvin 2008), for example by means of polarized light (Schmid 1993), but also

(ii) for understanding the full, partial or absence of coupling between the spontaneous ferroic quantities in different types of species.

With a view to a better understanding of the large number of species for research and applications, their totality has been broken up into *ensembles* with common distinguishability type of the domains and common coupling properties of the different order parameters. This was first done for para and diamagnetic species (Schmid 1993), later including ferro and antiferromagnetic ferroic phases (Schmid 1999) and most

recently by the extension to ferrotoroidic phases (Litvin 2008). These aspects will be discussed in the following.

3.1.1. Ensembles of 'non-magnetic' (paramagnetic or diamagnetic) species. In figure 5(a) the intersecting and non-intersecting 9 ensembles of para or diamagnetic species is shown with the number of species, forming an ensemble. In figure 5(b) examples of optical indicatrix cross-sections of domain patterns are given for the same 9 types of species. The form and orientation of the indicatrix cross-section of the domains determines their distinguishability in polarized light and helps in understanding the concepts of full, partial or no coupling between spontaneous polarization and spontaneous strain.

The spontaneous strain tensor being rigidly coupled with the optical indicatrix, the observation of birefringent (dichroic or bireflective) domains normally indicates the presence of a ferroelastic phase. However, these domains, separated by sharp domain walls, must not be confused with birefringent or dichroic pyramidal growth sectors (Schmid 1967, 1969), which have usually more or less blurred boundaries. Although the phenomenon had already been discovered by Sir David Brewster in 1815 (Kahr and McBride 1992), it is widely ignored by present day chemists, physicists and crystallographers because difficult to detect by x-rays. However, these defects usually decrease the symmetry of the ideal prototype phase and can cause a variety of artifacts: asymmetric ferroelectric hysteresis loops due to 'internal bias fields', huge differences in phase transition temperature between sectors with differing (*hkl*) of the growth facets (Rossignol *et al* 1985), clamping of domains, etc.

It has been pointed out (Schmid 1994,1999) that the maximum of coupling is achieved for species with a non-centrosymmetric prototype point group in conjunction with all ferroic properties being labelled 'full', in the present case, 'fully ferroelectric/fully ferroelastic'. Then for example for species $\bar{4}3m1'Fmm21'$ (boracites) or $\bar{4}2m1'Fmm21'$ ($Gd_2(MoO_4)_3$) the ferroelectric and ferroelastic domains are identical. Therefore a 180° reversal or other reorientations of the spontaneous polarization vector are coupled to a reorientation of the spontaneous strain (figure 5(b), box I).
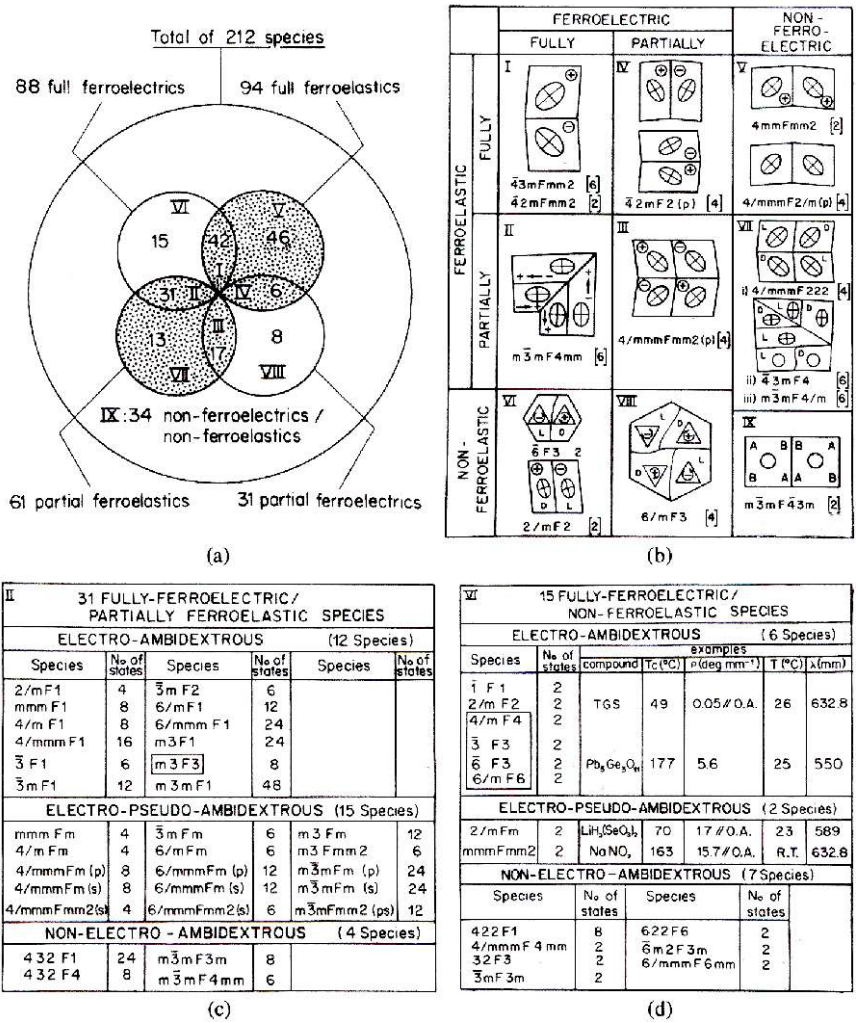
Figure 5. Splitting of the 212 non-magnetic Aizu species into 9 ensembles: (a) ensembles of intersecting and non-intersecting types, (b) examples of domain patterns of the 9 ensembles, characterized by optical indicatrix cross-sections, (c) subdivision of the 31 fully ferroelectric/fully ferroelastic species and (d) the 15 fully ferroelectric/non-ferroelastic species into electro-ambidextrous, electro-pseudo-ambidextrous and non-electro-ambidextrous types (reprinted with permission from Schmid 1993. Copyright 1993 Birkhäuser Verlag).

Special species of this kind are those, in which the spontaneous polarization is only divertible, but not reversible by 180°. They have been determined by Aizu (1967) and rhombohedral boracites were found to be the first typical example (Schmid 1970, Ye *et al* 1997). For the case of partially ferroelectric/fully ferroelastic (figure 5(b), box IV) this means that stress is able to transform one ferroelastic domain into all other possible ones, whereas the electric field applied along the pseudo-tetragonal axis, is unable to distinguish between two ferroelectric domains with same polarity but different ferroelastic orientation of strain. In perovskite with the centrosymmetric cubic prototype we have full ferroelectric phases, i.e., the electric field has full command over all possible ferroelectric domain states, whereas stress is labelled 'partial', because it cannot differentiate between ferroelastic domains with the opposite sign of spontaneous polarization (figure 5(b), box II).

In figures 5(c) and (d) ensembles of *electro-ambidextrous* and *electro-pseudo-ambidextrous* species are shown. Electro-ambidextrous means that the optical rotatory power of the ferroelectric domain switches from dextrogyre to laevogyre upon 180° reversal of the spontaneous polarization. Here 'dextrogyre' and 'laevogyre' stand, respectively, for right hand and left hand rotation of linearly polarized light propagating along an optical axis. A well known example is the non-ferroelastic/ferroelectric $Pb_5Ge_3O_{11}$ with specie $\bar{6}1'F31'$, which played for some time in the 1970s, i.e., before the breakthrough of liquid crystals, the rôle as a candidate for ferroelectric page composers with electric read-in and optical read-out. Electro-pseudo-ambidextrous means, when observing along one of the two directions of optical axis in optically bi-axial crystals, the dextro-laevo interchange occurs upon 180° switching of the spontaneous polarization (Newnham and Cross 1974c, Schmid 1993). An example is sodium nitrate $NaNO_2$ with species $mmm1'Fmm21'$, where the phenomenon is easily understood by the loss of mirror m_z of the prototype in the ferroic phase.

3.1.2. Ensembles extended to ferro and antiferromagnetic ferroic phases. By extending the 212 'non-magnetic',

i.e., para or diamagnetic species (Aizu 1969) to ferro- and antiferromagnetic species, Aizu obtained 773 species, which are described by distinction triplets: ferroelectric, ferromagnetic, ferroelastic with the sub-characteristics 'full', 'partial' or 'non-existing' for each of the three types of ferroic. Species with antiferromagnetic phases have not been explicitly named in table 1 of Aizu (1970), but can be recognized by the multiplier '×2' in the column 'Number of states' and three dots, '···', in the column 'Ferromagnetic'. For a better understanding of the great number of species in research and their potential application for switching elements, they have been split up into 36 ensembles (Schmid 1999), some of which remain empty, as shown in appendix C. A great number of material examples of species with different property combinations, including switching phenomena using secondary and tertiary ferroic invariants, are given in Schmid (1999). All species of the ensembles of appendix C are now incorporated in the listing of Litvin (2008), extended to ferrotoroidics. There the 36 ensembles are maintained, but divided in sub-ensembles taking account of ferrotoroidicity. The species of ensemble No. 1 in appendix C, being fully ferroelectric/fully ferroelastic and fully ferromagnetic, are found to be particularly interesting, because spontaneous polarization, spontaneous magnetization, spontaneous toroidization (as far as allowed) and spontaneous strain are rigidly coupled. This means that an electric field is able to reorient the orientation of spontaneous strain, the direction and sign of spontaneous polarization, the directions of magnetization and toroidization, but not their sign. How is this possible? If a ferroelastic single domain is, e.g., also ferromagnetic, ferrotoroidic, ferroelectric and permitting a 180° reversal of spontaneous polarization *inside* that ferroelastic domain (example: the perovskite species $m\bar{3}m1'Fm'm2'(pp)$), there will be no coupling between the magnetic structure (here ferromagnetic/ferrotoroidic). However, in that species the polarization can also be rotated by 90°. In that case, because the spontaneous strain is rigidly coupled with the direction of spontaneous polarization, magnetization and toroidization, a coupling of the direction of spontaneous polarization (not of its sign) with the magnetic structure is given. Thus in this species 180° reversal of P_S is *not* accompanied and 90° reorientation of P_S is accompanied by coupling with the orientation of the magnetic structure. We call this a partial coupling.

This important 'coupling function' of ferroelasticity holds equally well for non-ferrotoroidic, antiferromagnetic ferroelectrics. This has recently been exemplified on a BiFeO$_3$ single crystal by a 71° ferroelastically coupled switching of the spontaneous polarization from pseudo-cubic [111] with $(-12-1)$ as plane of spin rotation of the incommensurate cycloid to $[1\bar{1}1]$ with (121) as spin rotation plane (Lebeugle 2007). This experiment, monitored by neutron scattering, also revealed for the first time that the average point group of the incommensurate phase is not $3m1'$, as hitherto admitted (Tabares-Muñoz *et al* 1985), but monoclinic (Lebeugle *et al* 2008). However, the term 'electric-field-induced spin-flop', used in the latter reference, is misleading because 'spin-flop' is usually used for a field-induced change of symmetry and

structure of a magnetic phase. Here occurs simply a coupled reorientation of spontaneous polarization, spontaneous strain and plane of cycloid into an equivalent domain state. The neutron data show that the $\vec{k}$-vector of the cycloid lies along a pseudo-cubic [110] direction. This implies that the principal axis of the IC monoclinic average structure coincides with the direction of the $\vec{k}$-vector, leading to point group $m1'$ and herewith to Aizu species No 660 $m\bar{3}m1'Fm1'(s)$ with 24 possible ferroelectric/ferroelastic domain states. Since the phase is antiferromagnetic, a total of 48 domain states is allowed. However, BiFeO$_3$ forms also nuclear anti-phase domains (Wan *et al* 2007, cf Palai *et al* 2008), doubling the possible number of domain states once more.

The mirror $m1'$ lies parallel to a pseudo-cubic (110)-plane, containing the spontaneous polarization along a pseudo-cubic [111]-direction. Because the IC-phase cancels the linear magnetoelectric effect, these antiferromagnetic domains cannot be switched by that effect. However, by cycling the crystal via a magnetic field-induced ferromagnetic phase, such a switching may be feasible. For understanding the expected ferroelastic domain pattern of BiFeO$_3$ in the 'average monoclinic' phase, a related, but not identical, rhombohedral $\rightarrow$ monoclinic transition in Fe$_3$B$_7$O$_{13}$I (Ye *et al* 1997) is highly instructive.

In contrast to the perovskite structure with a centrosymmetric prototype, the boracite species $\bar{4}3m1'Fm'm2'$ with the same magnetic point group as in the perovskite case, but with a non-centrosymmetric prototype, allows full coupling between all four primary ferroic quantities. This is due to the fact that in this case a ferroelectric domain is identical with a ferroelastic domain. Thus a 180° switching of P_S results in a reorientation of the ferroelastic tensor and herewith of the directions (not the sign!) of magnetization and toroidization, which are rigidly coupled with that tensor. The first experimental evidence of such kind of species was found in nickel iodine boracite, Ni$_3$B$_7$O$_{13}$I, (Ascher *et al* 1966) in which the reorientation of the spontaneous magnetization was realized by a 180° switching of the polarization and monitored by the spontaneous Faraday effect (figure 6). This experiment was originally interpreted by Aizu species $\bar{4}3m1'Fm'm2'$, but later recognized as species $\bar{4}3m1'Fm'$ (Rivera and Schmid 1981) because of an initially not observed component of magnetization (allowed by the monoclinic group m') parallel to the spontaneous polarization. Silver paste electrodes hindered its observation! This lesson teaches us that transparent gold electrodes should be used whenever possible. Today we can add that the electric field also reoriented spontaneous strain and the direction, but not the sign of spontaneous toroidization, except if a magnetic bias field is applied, which controls also the sign of toroidization (for details of the switching and coupling see section 3.2.3.1).

Herewith we wanted to stress the important 'special' rôle of ferroelasticity in the coupling between magnetic and ferroelectric properties. In addition, we want to stress that not the magnitude of the spontaneous ferroelastic strain matters—in the limiting case it might even be zero at the prototype/ferroic phase transition—but the symmetry of prototype *and* ferroic phase matters.

Species $\bar{4}3m1'Fm'm2$, originally assumed for Ni$_3$B$_7$O$_{13}$I, exists in Ni–Cl-, Ni–Br-, Co–Br- and Co–I-boracite (Schmid
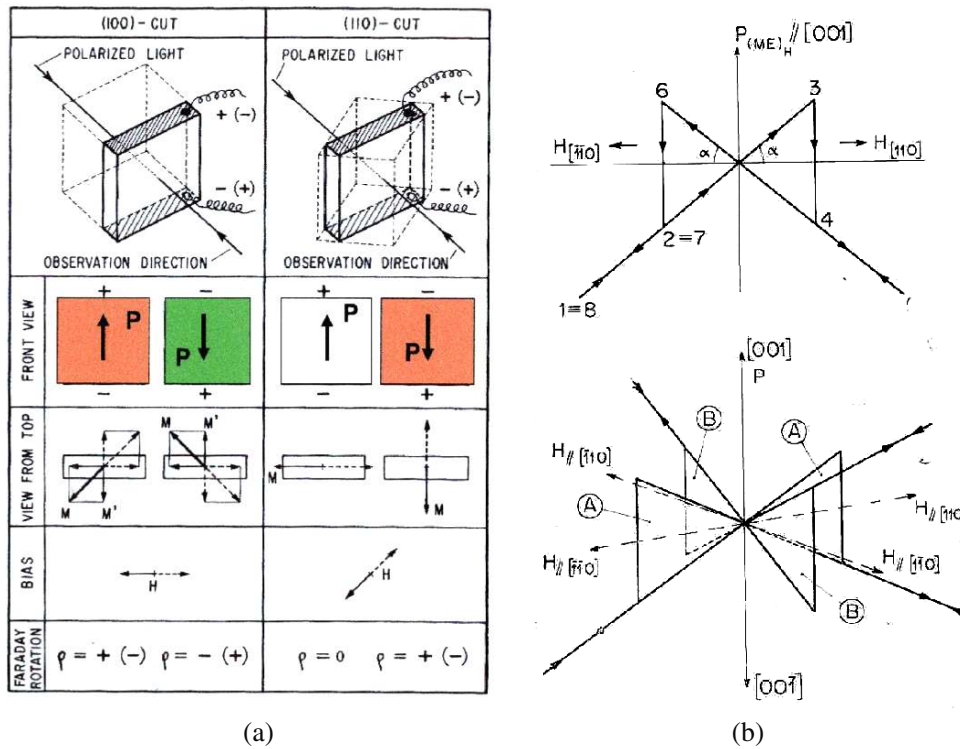
Figure 6. (a) Switching of the spontaneous polarization P_S of boracite $Ni_3B_7O_{13}I$ by 180° causes a 90°-rotation of the direction of the spontaneous magnetization M_S component, i.e., from pseudo-cubic [110] to [$\bar{1}$10], monitored by colour contrast due to spontaneous Faraday rotation and its dispersion. A magnetic bias field controls the sign of M_S. (b) The ferroelectric domain switching described in (a) is accompanied by a 90° rotation and an inversion of the 'butterfly' loop of the linear magnetoelectric effect. The magnetic coercive fields of the two 'butterfly' loops are identical with the ferromagnetic coercive fields at constant plus and minus P_S. The behaviour in (a) and (b) is due to the lost $\bar{4}$-axis of the cubic phase (adapted from Schmid 1967, 1969).

1994), which could be used in principle for switching experiments as explained in figure 6. However, the ferroelectric coercive fields being too high in the magnetically ordered phases at low temperature, the experiments remain hypothetic only. Possibly in the form of very thin layers (Schmid and Tippmann 1979) with perfect stress–strain-free lattice-matching, electric switching may become possible at low temperatures.

3.1.3. Ensembles extended to ferrotoroidic crystals. The 773 species, comprising 'non-magnetic', ferromagnetic and anti-ferromagnetic ferroic point groups, are described by distinction triplets 'ferroelectric', 'ferromagnetic', 'ferroelastic' with the distinguishability characteristics 'full', 'partial' and 'non-existing' (Aizu 1970). By extending this latter system to ferrotoroidic crystals, Litvin (2008) introduces a distinction quadruplet notation for characterizing the species with respect to their ability to distinguish between the single domain states of spontaneous toroidal moment 'T', spontaneous magnetization 'M', spontaneous polarization 'P' and spontaneous strain 'E'. This leads to a 12×12 matrix of property combinations, a certain number of which remain, however, empty. Each species is characterized by four letters with the following meaning:

'F' 'Full' distinguishes all n domain states.

'P' 'Partial' distinguishes m, $1 < m < n$, domain states, i.e., some but not all domain states.

'N' 'Null' does not distinguish any domain state and is non-zero.

'Z' 'Zero' does not distinguish any domain state, i.e., the ferroic order is absent.

N.B.:

(1) T and M can be F, P or Z, but never N, because one admits that T and M can always get time-reversed with the ability of forming domains.

(2) E can be F, P or N, but never Z, because we admit that a spontaneous strain takes always place at a phase transition. If E becomes N, this means that the spontaneous strain is finite, but cannot get reoriented as is typical of ferroelastics. In such a case the transition is *co-elastic* (Salje 1990). This occurs in equi-class and co-axial hexagonal → rhombohedral phase transitions. A multiferroic is not necessarily ferroelastic. Also non-ferroelastics (co-elastics) may be multiferroic, if we define 'multiferroic' for a phase having two, three or four primary ferroic properties. In appendix C one can easily see that the non-ferroelastic ensembles Nos 7, 8, 16 and 17 are multiferroic..The non-ferroelastic antiferromagnetic ensembles Nos 25 and 26 are splitting up into ferrotoroidic and non-ferrotoroidic antiferromagnetics as can be seen in table 3 of Litvin (2008). Those non-ferroelastic ferrotoroidic ensembles of species are also multiferroic.

(3) P can be F, P, Z or N, and if N, this means that the polarization has a finite value, but cannot be reversed. An example is Si/Ge-fresnoite (Schmid *et al* 1978) with species $4mm1'Fmm21'$, i.e., with a polar $\rightarrow$ polar phase transition. The Litvin notation is then 2 (domain states) and Z Z N F for T M P E, respectively. A 180° reversal of P would mean an electric-field-induced transition to a different phase, separated by an energy barrier. In case of a surmountable barrier this may lead to an asymmetric ferroelectric hysteresis loop and/or to back-switching into the field-free state.

(4) Such a small energy barrier is, e.g., artificially created in triglycine sulfate (TGS) by doping the ferroelectric phase with polar L-alanine molecules, the polar orientation of which is retained in the originally centrosymmetric prototype phase, i.e. the Aizu species is changed from non-polar $\rightarrow$ polar to polar $\rightarrow$ polar. This creates an asymmetric internal 'bias field' which leads to ferroelectric single domains on cool-down through the phase transition. By applying an electric field opposite to the stable direction of the weak polarization of the new prototype phase, a new, metastable phase will be formed, which will switch back to the stable polar phase at zero electric field. This behaviour reminds one of the hetero-phase exchange bias phenomenology (Meiklejohn and Bean 1957), currently much studied.

Summarizing, we can say that by Litvin's introduction of the quadruplet notation and the additional characteristic 'null', we can now settle upon a concise characterization system of primary ferroic, antiferromagnetic and dia or paramagnetic species, the properties of which are immediately catching the eye. However, the Aizu system has some shortcomings: species with incommensurate prototype and/or ferroic phases are not covered. This would require the use of 4-, 5- and 6-dimensional point and space groups.

3.2. Ferrotoroidic domains

Ferrotoroidic domains were proposed as existing for quite a while (Schmid 2001, Sannikov 2003a, 2003b) and are currently of renewed interest (Van Aken *et al* 2007, Ederer and Spaldin 2007, Sannikov 2007). Therefore some recent progress in their understanding will be summarized.

3.2.1. What is the nature of ferrotoroidic domains? One can ask the question: does a ferromagnetic domain, with a symmetry allowing also a ferrotoroidic vector, split up into ferromagnetic/ferrotoroidic sub-domains, somehow like ferroelastic and ferroelectric domains split up into ferro and antiferromagnetic sub-domains below the magnetic phase transition? The answer is 'no'. The recent study by Litvin (2008), extending Aizu's classification of the 773 species of phase transitions by magnetization, polarization and strain to ferroic phases allowing a spontaneous toroidization, has shown that the number of distinguishable domain states remains the same as that determined by Aizu, without taking ferrotoroidicity into account. The reason is simple: since both magnetization and toroidal moment change sign under

time reversal, all the spins of the magnetic structure will change sign coherently, e.g., by acting with a magnetic field on the ferromagnetic moment of a ferrotoroidic/ferromagnetic domain, provided that all interactions between the spins are sufficiently strong. *Thus a ferrotoroidic single domain will always be identical with the corresponding ferromagnetic or antiferromagnetic domain.*

3.2.2. How can ferrotoroidic domains be switched? In table 7 the tensor form of the linear magnetoelectric effect of the 31 ferrotoroidic point groups is given. In the first four columns the tensor is not symmetric. The anti-symmetric coefficient, proportional to the spontaneous toroidal moment, can be found here by decomposing the tensor into its symmetric and anti-symmetric part (Popov *et al* 1998a, 1998b). In the last two columns the tensor is anti-symmetric; there the toroidal moment is directly proportional to $\alpha_{12} = -\alpha_{21}$. The simplest case is represented by the 11 'purely ferrotoroidic' groups in the 6th column, which allow $\alpha_{12} = -\alpha_{21}$ only. In this case the totally anti-symmetric coefficients correspond clearly to the ferrotoroidic domains, by definition antiferromagnetic. No additional non-toroidic antiferromagnetic domains can be expected to co-exist with the ferrotoroidic ones, i.e., here the antiferromagnetic domains are identical with the ferrotoroidic ones, as conjectured earlier (Schmid 2001). In the first, second and fifth column the tensor has also diagonal components. This shows us that in crystals of the category 'Ferrotoroidic/antiferromagnetic', having magnetoelectric tensor forms of the first, second or fifth column (table 7), the sign of the ferrotoroidic moment and its rigidly coupled antiferromagnetic domain can not only be switched by crossed magnetic and electric fields, but also by collinear magnetic and electric fields, provided the respective coercive product, $(\boldsymbol{E} \times \boldsymbol{H})_c$ or $(E_i H_i)_c$, has been reached. So if, e.g., α_{12} and α_{33} are both allowed, switching of the latter by z-oriented H and E fields will also switch the former. The question may be asked: why should this be the case? The signs of the tensor components are always rigidly linked to the absolute structure of a single domain, be it antiferromagnetic or ferromagnetic. They do not change sign relative to the time-reversed absolute structure, i.e., when the coordinate system is assumed to switch, too. Consequently however, in an experimental setup with a fixed coordinate system, an apparent change of sign of the tensor components takes place. Since time reversal affects the entire magnetic structure, all coefficients should be affected by the change of sign.

Collinear switching of antiferromagnetic domains has been studied in detail on Cr_2O_3 (Martin 1965, Martin and Anderson 1966), using magnetic fields well below the spin-flop field of 5.8 T. That phase of Cr_2O_3 with point group $\bar{3}'m'$ is not ferrotoroidic and has diagonal magnetoelectric coefficients only. Isothermal switching of ferrotoroidic/antiferromagnetic domains with crossed electric and magnetic fields does not seem to have been studied in detail so far.
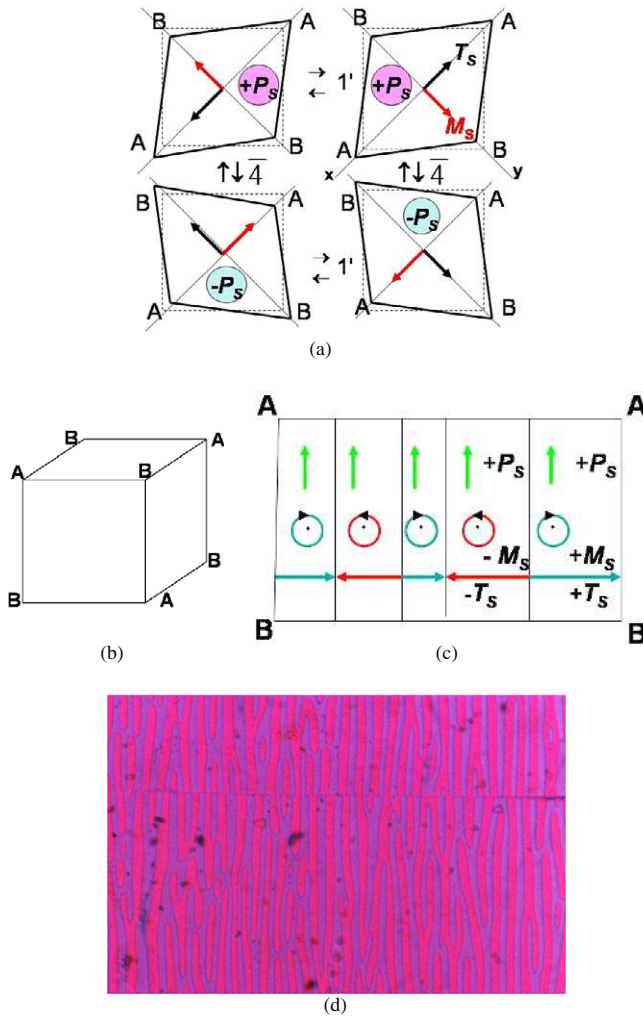
(a)

(b)   (c)

(d)

Figure 7. Four among the 6×2 possible orthorhombic domain states of species $\bar{4}3m1'Fm'm2'$. (a) The effect of time reversal $1'$ and of the $\bar{4}$-twinning operation. (b) Reference cube of $\bar{4}3m1'$ prototype with polar $\langle 111 \rangle$ directions. (c) Pseudo-cubic (110) cross-section of ferroelectric/ferroelastic single domain, split up into antiparallel ferromagnetic domains, corresponding to head–head/tail–tail ferrotoroidic domains. (d) ferromagnetic/ferrotoroidic lamellar domains of a ferroelectric/ferroelastic single domain of Co–Br boracite $Co_3B_7O_{13}Br$ with the orientation and explanations given in (c); slightly uncrossed polarizers parallel to crystal edges; lateral extension ≈ 2 mm; thickness ≈ 50 μm; $T \approx 10$ K, $T_c = 16$ K; cooled in zero magnetic field; sharp horizontal line probably a growth discontinuity (photo Schmid 1986; cf Mendoza Alvarez *et al* 1984).

Figure 8. Transparent pseudo-cubic $(100)_c$ cross-section of $Ni_3B_7O_{13}Cl$ in polarized light, species $\bar{4}3m1'Fmm21'$ above $T_C = 9$ K and species $\bar{4}3m1'Fm'm2'$ below 9 K. The large red and green ferroelectric/ferroelastic domains are related by the lost $\bar{4}$-axis of the cubic phase perpendicular to plate, corresponding to the domain states related by $\uparrow\downarrow\bar{4}$ in figure 7(a). Refractive indices n_γ and n_α always parallel to $\pm M_s$ and $\pm T_s$, respectively. Photo at room temperature with inscriptions of M_s and T_s for below T_C. Lateral extension: ≈ 2 mm. Possible antiparallel ferromagnetic domains (cf figure 7(c)) are ignored for clarity. For details of the ferroelectric/ferroelastic domain structure of $Ni_3B_7O_{13}Cl$ and $Ni_3B_7O_{13}Br$ see Schmid (1967, 1969).

For the nine ferrotoroidic/ferromagnetic/ferroelectric groups of table 7 it is evident that in this case the ferrotoroidic vector can be switched by means of a magnetic field. Because of the identity of the ferromagnetic and ferrotoroidic domain in this case, we can say retrospectively, e.g., 'The ferrotoroidic domains of many boracites with species $\bar{4}3m1'Fm'_xm_y2'_z$ (Schmid 1994) have been revealed by means of spontaneous Faraday rotation (Schmid 1967, 1969; cf figures 6 and 7) thanks to their ferromagnetic property', or 'The ferrotoroidic domains of $LiCoPO_4$ have been switched by means of magnetic-field-induced time reversal thanks to their (weakly)
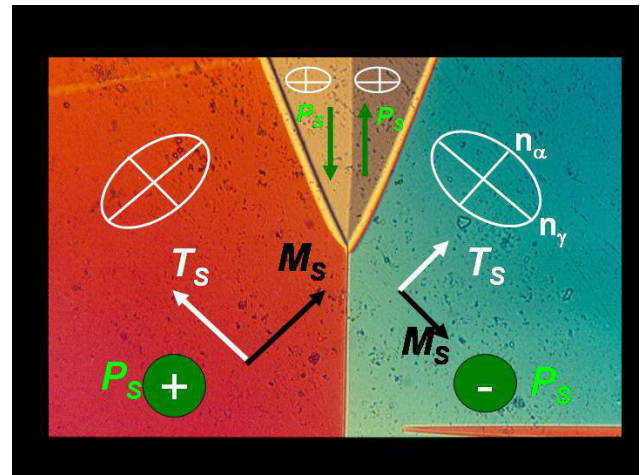
ferromagnetic property, as testified by the measurement of magnetoelectric 'butterfly loops' (Rivera 1994b, Wiegelmann 1994, Kornev *et al* 2000) and of a very weak spontaneous magnetization (Kharchenko *et al* 2004, Kharchenko 1994).

'Switching the (anti-)ferromagnetic order parameter will always switch an allowed toroidal moment. However, when switching the spontaneous polarization of (anti-)ferromagnetic ferrotoroidics, different cases may arise, depending on the particular species. For example, in case of fully ferrotoroidic, ferromagnetic. ferroelectric, ferroelastic species (Litvin notation: FFFF) switching of the polarization will reorient the ferromagnetic/ferrotoroidic order parameter and the spontaneous strain, but will have no influence on the sign of the reoriented ferromagnetic/ferrotoroidic domains because polarization and electric field are invariant under time reversal. For the same latter reason, in the case of non-ferroelastic (anti-)ferromagnetic (ferrotoroidic) ferroelectrics the reversal of polarization causes neither a reorientation nor a switching of the magnetic order parameters in principle, however, crystal defects may sometimes cause local switching or reorientations. If a controlled sign of reoriented magnetic domains is aimed at, a magnetic or magnetoelectric bias field has to be applied (cf figure 6(a))'.

Thus depending on the particular point group, we can summarize by saying that the toroidal moment may not only be switched by means of crossed electric and magnetic fields, but also via collinear magnetic and electric fields or by a magnetic field alone.

It is noteworthy that Prosandeev *et al* (2008) have shown by an *ab initio* study that the direction of a macroscopic electric toroidal moment can be controlled by means of an inhomogeneous static electric field. This raises the question, whether the analogy holds for switching a macroscopic magnetic toroidal moment by means of a magnetic inhomogeneous static field. Possibly this is related to the fact that the gradients of polarization (electric field) and magnetization (magnetic field) transform like the electric and magnetic toroidal moment, respectively (table 1). Thus switching terms of the type

$$T_{S(\text{electr.})}\,\text{grad}\,P \qquad \text{and} \qquad T_{S(\text{magn.})}\,\text{grad}\,H$$

become imaginable.

3.2.3. Examples of multiferroics with ferrotoroidic domains. To understand better the effect and behaviour of a toroidal moment in a crystal, let us discuss three examples: boracites, $Fe_{2-x}Ga_xO_3$ and $LiCoPO_4$.

3.2.3.1 Example I: Boracites with species $\bar{4}3m1'Fm'm2'$. This species occurs in many boracite compositions (Schmid 1994). For the Litvin notation we find:

No 634 $\bar{4}3m1'Fm'm2'$

$\quad 4-(z)3(xyz)m(xy)1'Fm(xy)'m(x-y)2(z)'$

$\quad 6\times 2\quad\begin{matrix} \text{T} & \text{M} & \text{P} & \text{E} \\ \text{F} & \text{F} & \text{F} & \text{F} \end{matrix}.$

In Litvin's terminology (Litvin 2008) this means the following: 'In this phase transition there arise $6\times 2 = 12$ domains. The first two F's mean that the magnetization and toroidal moment in each of these 12 domains is *distinct*, in a different orientation. The third F means that there are 6 *distinct* orientations for the polarizations, each orientation appearing twice among the 12 domains. The final F means the same thing for the strain, i.e. there are 6 distinct strains, each distinct strain appearing twice among the 12 domains.'

In other words, we can interpret '6×2' by saying that we have 6 ferroelectric and 6 ferroelastic domains in the paramagnetic phase. However, due to the *non-centrosymmetric* cubic prototype phase, these two kinds of domain are identical ('merged'), i.e. we have in fact only 6 spatially differently oriented ferroelectric/ferroelastic domains. Below the magnetic Curie temperature two time-reversed ferrotoroidic/ferromagnetic i.e., domains may form in the interior of the former ones, i.e., a total of 12 domain states is possible, the same number as given in Aizu's notation, which was ignoring ferrotoroidicity. The coset representatives of the coset decomposition of **G1**′ with respect to **H** (Litvin 2008) yields the result shown in figures 7(a)–(d) in a schematic way and figure 7(d) a real ferroelectric/ferroelastic single domain containing time-reversed ferrotoroidic/ferromagnetic domains. Figure 8 shows four of the allowed six ferroelectric/ferroelastic domains of Ni–Cl boracite at room temperature in the paramagnetic state. The large domains with P_S+ and P_S- polarity are related by the lost $\bar{4}$-axis of the cubic prototype, as explained by the relations

'$\uparrow\downarrow\bar{4}$' in figure 7(a). Possible orientations of spontaneous magnetization and toroidization at low temperature have been inscribed. Ferromagnetic/ferrotoroidic domains of this compound have been observed earlier by spontaneous Faraday rotation (Brunskill and Schmid 1981). The presence of a toroidal moment in Co–Br, Co–I and Ni–Cl boracites was deduced theoretically on the basis of a measured singularity of the magnetoelectric coefficients α_{32} (Sannikov 1998).

The important result is the coupled change of sign both of magnetization and toroidization upon time reversal, but consistent since both vectors transform under this operation. A change of sign of M_s alone would mean that part of the spins of the magnetic unit cell would follow and some others not, forming magnetic-field-induced new phases, unlikely at moderate field strengths. The behaviour can also be understood geometrically by a combined symmetry/energy consideration. When superposing the current loop symbol of magnetization (first used by Pierre Curie!) and the mirror plane cross-section of a toroid with a even number of windings (figure 9, cf figure 1), one can see that the superposition figure becomes asymmetric, i.e., it assumes a polar direction p along the axis containing the spontaneous polarization P_s (a kind of spontaneous magnetoelectric effect) and which changes sign when reversing the magnetization. However, since P_s does not change sign, this would create two different energy states. By changing also the sign of toroidization, the sign of the induced polarization p is kept invariant. Thus initial and final energy states remain identical when both magnetization and toroidization change sign in a coupled way. As a consequence of this behaviour we can make the statement: *For ferromagnetic and antiferromagnetic phases with point groups allowing a toroidal moment, the ferromagnetic and antiferromagnetic domains are identical in volume and structure with the toroidal domains, i.e., we have two ways of describing the same physical reality.* An equivalent statement was made earlier as a conjecture (see 'conclusions' in: Schmid 2001) and has now received confirmation by group theory (Litvin 2008) in conjunction with energy considerations.

3.2.3.2 Example II: $Fe_{2-x}Ga_xO_3$ 'with specie $m2m1'Fm'2'm$. For this compound the existence of a spontaneous toroidal moment has been deduced from magnetoelectric measurements and the separation of the anti-symmetric part of the off-diagonal coefficients, $\alpha_{32} = -\alpha_{23}$ (Popov *et al* 1998a, 1998b). The Litvin (2008) notation for $Fe_{2-x}Ga_xO_3$ is the following:

No 45 $m2m1'Fm'2'm\quad m'(x)2(y)'m(z)1'Fm(x)'2(y)'m(z)$

$\quad 1\times 2\quad\begin{matrix} \text{T} & \text{M} & \text{P} & \text{E} \\ \text{F} & \text{F} & \text{N} & \text{N} \end{matrix}.$

Here F F means that the crystal is fully ferrotoroidic and fully ferromagnetic and N N means that the crystal is polar, but not ferroelectric and that it is not ferroelastic, but co-elastic. There exist 1×2 ferrotoroidic and two ferromagnetic domains, but as explained in sections 3.2.1 and 3.2.2, they are identical. On (001)-cuts with a thickness of about 10–20 μm these domains may possibly be made visible in transmission using spontaneous Faraday rotation. A reliable alternative method for visualization would be magnetic SHG imaging
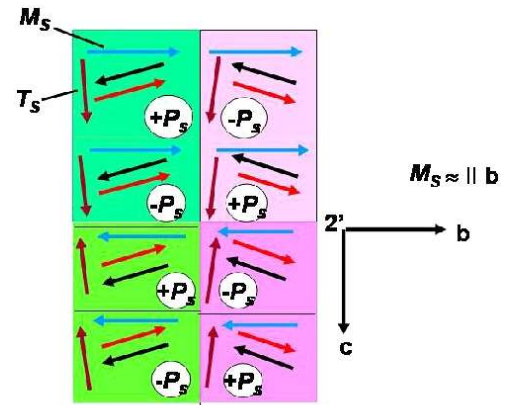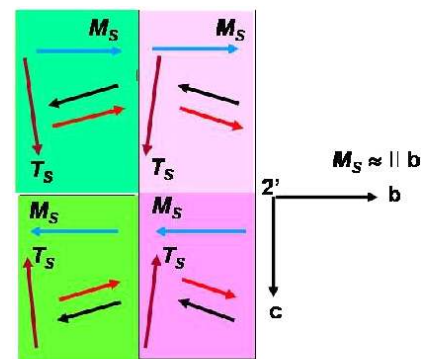
(a)

(b)
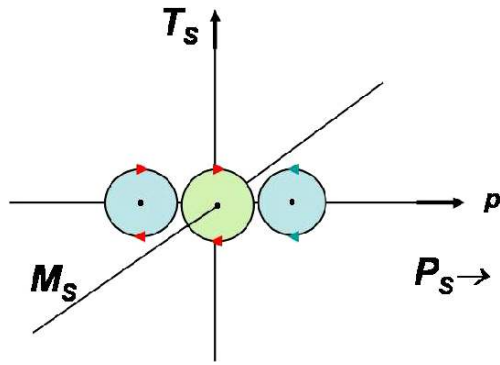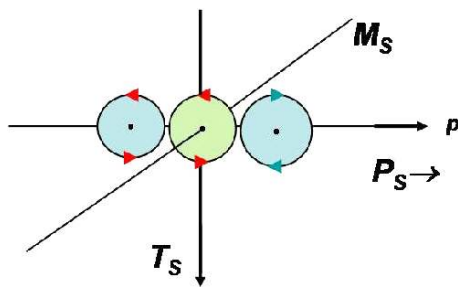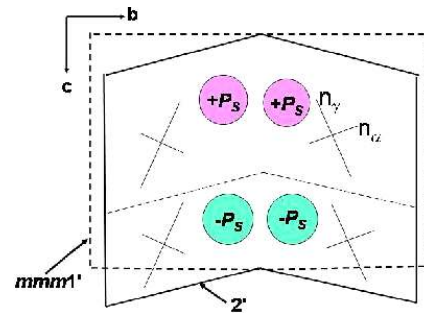
Figure 9. (a) Superposition of toroid mirror plane cross-section (cf figure 1 with inset) with magnetization vector, (b) time-reversed configuration. Magnetoelectric generation of polarization p.

(Fiebig 2005b). One polar/ferromagnetic/ferrotoroidic single domain of $Fe_{2-x}Ga_xO_3$ has the same symmetry as one of the 12 ferroelectric/ferroelastic/ferrotoroidic/ferromagnetic single domains of the boracite in figure 7.

3.2.3.3 Example II: LiCoPO$_4$ with species $mmm1'F2'$. For this compound the observation of ferrotoroidic domains has been claimed (Van Aken *et al* 2007). Therefore a more detailed analysis is desirable. The Litvin notation for LiCoPO$_4$ is the following:

No 53 $mmm1'F2'$ $m(x)m(y)m(z)1'F2(x)'$

4×2 $\begin{matrix} T & M & P & E \\ P & P & P & P \end{matrix}$.

This means that 4 ferroelectric/ferroelastic domains are possible (figure 10(a)), each of which has two possible time-reversed magnetic domain states (omitted in figure 10(a) for clarity), hence a total of 8. states follows (figure 10(b)). All four primary ferroic properties, T M P E, are allowed and all four are characterized by 'P', i.e., by partial distinguishability. This can be seen for spontaneous polarization and strain in figure 10(a). An electric field cannot distinguish between different ferroelastic domains having same direction of P_s,

(a)

(b)

(c)

Figure 10. Model for ferrotoroidic/weakly ferromagnetic domains in LiCoPO$_4$ with species $mmm1'F2'$. Note that the arrows of the spin and magnetization directions are only a guide for the eyes since they do not characterize their axial symmetry. (a) Sketch of the 4 monoclinic allowed ferroelectric/ferroelastic domains, observable in principle, e.g., by spontaneous birefringence $n_\gamma - n_\alpha$ (magnetic domains are omitted for clarity). (b) Sketch of the allowed 4×2 domain states, assuming ferroelectricity, but with experimentally ascertained zero ferroelastic deformation; the antiparallel pairs of red/black arrows represent the antiferromagnetic spin direction, rotated by 4.6°. off the pseudo-orthorhombic b-axis, ferrotoroidic vector rotated by an estimated similar amount off the c-axis (rotation angles exaggerated) and ferromagnetic vector approximately along b-axis. (c) The experimentally ascertained absence of spontaneous polarization requires 4 pairs of domains with equal spin states (in (b) with equal background colour) to merge, ending up with 4 magnetic domain states only, consistent with experiment (Van Aken *et al* 2007).

and stress can not distinguish same ferroelastic states having opposite direction of P_s. The same partial distinguishability 'P' holds true for M_s and T_s, too (cf figures 10(b), (c)).

Although species $mmm1'F2'$, deduced from neutron diffraction (Vaknin *et al* 2002), magnetoelectric 'butterfly loops' (Rivera 1994b, Wiegelmann 1994) and spontaneous magnetization measurements (Kharchenko *et al* 2001, 2004), allows ferroelectricity and ferroelasticity, neither ferroelasticity nor a spontaneous polarization were detectable (Van Aken *et al* 2007). The only evidence for monoclinic symmetry is therefore the $\pm 4.6°$-tilting of the spins around the orthorhombic a-axis, deduced from neutron scattering. The rotation of the T_S-vector around the a-axis is estimated to be of the same order of magnitude. Although in the mentioned magnetization measurements the M_S-vector was found to lie along the pseudo-orthorhombic b-axis, as shown in figures 10(b), (c), in monoclinic symmetry it has also—alike T_S—a degree of liberty to rotate around the a-axis (cf table 3). This angle may be very small or zero. In figures 10(b) and (c) the straight domain walls serve for clarity only, whereas in reality they were found to have amoeba-like forms (Van Aken *et al* 2007). Thus we end up with four equivalent domain states in the present model, which have in fact been observed experimentally. In the initial interpretation (Van Aken *et al* 2007) the domain pairs designated as 'antiferromagnetic' correspond to the left hand or right hand top/bottom domain pairs of figure 10(c), i.e., with differing S_y-component, and those designated as 'ferrotoroidic' correspond to the angle diagonal pairs of figure 10(c), i.e, with differing T_y component (Fiebig 2008). All of them are both ferrotoroidic and weakly ferromagnetic. The preceding description must be considered as a model for the observation of the four weakly ferromagnetic/ferrotoroidic domains.

3.3. Anti-phase domains and equi-translation phase transitions

In addition to the discussed ferroic domains, which can be described by the system of species involving point groups, anti-phase domains (translation domains) may also occur in ferroics and multiferroics in principle when a change of translation between the prototype phase space group and the ferroic phase space group takes place (Wondratschek and Jeitschko 1976). This will lead to doubling of the possible number of domain states relative to the number given by the Aizu species. Examples are: (i) $BiFeO_3$, species $m\bar{3}m1'F3m1'$ (Palai *et al* 2008), (ii) $GdDy(MoO_4)_3$, species $\bar{4}2m1'Fmm21'$ (Capelle and Malgrange 1984), (iii) $Ni_3B_7O_{13}Cl$, $Ni_3B_7O_{13}Cl$, species $\bar{4}3m1'Fmm21'$ (Castellanos-Guzman *et al* 1999). On the other hand, in the case of an equi-translation relationship between prototype and ferroic phase, Ascher's maximal polar subgroup rule (Ascher 1966b) applies. For example in $BaTiO_3$, the space groups of $R3m/C_{3v}^5$, $Amm2/C_{2v}^{14}$ and $P4mm/C_{4v}^1$ of the ferroelectric phases are maximal polar subgroups of the cubic prototype space group $Pm\bar{3}m/O_h^1$ (Ascher 1966b). Thus no anti-phase domains are allowed in this case.

4. Conclusions

The point groups permitting the primary ferroic effects ferroelectricity, ferromagnetism and ferrotoroidicity and their ensembles of intersecting groups have been outlined. An analogous presentation has been given for the secondary ferroic effects linear magnetoelectric, linear 'electrotoroidic' and linear 'magnetotoroidic', on the one hand and piezoelectric, piezomagnetic and piezotoroidic, on the other hand.

(1) For understanding domain patterns and domain switching of simple ferroics and multiferroics, the easy handling of the so-called 773 species, by which Aizu (1970) classified all group → subgroup phase transitions, is important. The splitting of the species into 36 ensembles with different domain-state distinguishability by, spontaneous magnetization, polarization and strain (Schmid 1999) has now been enlarged by the creation of sub-ensembles, permitting the inclusion of the domain-state distinguishability of a spontaneous toroidal moment (Litvin 2008). This allows a succinct and straightforward characterization of all commensurate species.

(2) The distinguishability types also give us information whether the external constraints electric field, magnetic field, toroidal vector and/or stress are capable of creating a corresponding single domain of the entire crystal, a partial orientation or remain without influence. Herewith they also inform us about the mutual full, partial or non-coupling of the primary ferroic invariants during switching of the domains.

(3) The full or partial coupling during domain switching between spontaneous polarization on the one hand and spontaneous magnetization, toroidization or any antiferromagnetic order parameter on the other hand, is possible in presence of ferroelasticity only. Because the polarization is invariant under time reversal, this coupling is limited to reorientation-switching of the direction of the magnetic order parameter (ferromagnetic, ferrotoroidic or antiferromagnetic), but has no control of the sign of the reoriented, time-reversible domains. This shortcoming can sometimes be compensated by using a magnetic (or magnetoelectric) bias field (cf, e.g., figure 6).Vice versa, the reorientation of the spontaneous polarization, in special species also by 180°, can be realized by reorienting a magnetic field or stress. Thus the special rôle of *ferroelastic spontaneous strain* consists in the coupling of the spontaneous strain-linked ferroic quantities in a same phase during 'reorientation-switching'. This is akin to the intermediate rôle of *induced strain*, using piezoelectric, piezomagnetic, magnetostrictive or electrostrictive effects in the case of multiferroic hetero-phase coupling in ceramics or layers.

(4) The toroidal moment, a 'two-faced individual'.

    (i) The spontaneous toroidal moment can be considered as a fourth kind of ferroic when putting stress on its particular kind of vector property, the 'axio-polar' or 'time-odd polar' vector, together with the possibility of it switching and forming domains, a common feature of primary ferroics. This description satisfies a search for simplicity and related aesthetics, as appearing in the trinity of intersecting ensembles of point groups (figures 2–4). The compact description of the symmetry properties of the four primary ferroics by the dihedral group of order four, the 'parity group' (table 1) is also aesthetically satisfying.

    (ii) A second, alternate way of description is simply that in the framework of the secondary ferroic classification, i.e., as the anti-symmetric part of a coefficient of the linear magnetoelectric effect, proportional to the toroidal moment, since the physical meaning of the order parameter 'toroidal moment T' has been identified (up to a constant) as the anti-symmetric component of the magnetoelectric tensor (Gorbatsevich *et al* 1983a, 1983a). It is a theoretical challenge to elucidate that constant, in order to correlate a toroidal moment calculated from the magnetic structure with the measured magnetoelectric coefficient.

    (iii) So far the only possible clear-cut experimental characterization of the toroidal moment is the well measurable magnetoelectric coefficient. Calculation of the toroidal moment from the magnetic structure is still difficult (Popov *et al* 1998a, 1998b, Ederer and Spaldin 2007). Depending on the particular point group, ferrotoroidic domains are found to be either identical with ferromagnetic domains or identical with antiferromagnetic domains. According to the point group and the corresponding particular tensor form of the linear magnetoelectric effect, ferrotoroidic domains can be switched by a magnetic field alone, by crossed electric and magnetic fields or either by crossed *or* collinear magnetic and electric fields. Other kinds of 'toroidal field' are imaginable, e.g., magnetic field gradients.

    (iv) The two-faced nature of the toroidal moment is also revealed by the 'electrotoroidic' and 'magneto-toroidic' effects, describable as second rank tensor analogues to the linear magnetoelectric effect, on the one hand, or as third rank magnetoelectric effects of the *HEE* and *EHH* type, respectively, but with tensor components requiring an $E \times H$ cross-product.

    (v) Considering the aforesaid, a great challenge will be to find a property, hopefully with applications, based on the genuine characteristics of the toroidal moment.

(5) The complexity of single phase multiferroics increases with increasing number of allowed primary ferroics and with the number of domain states, which is highest for a cubic prototype with the lowest, i.e., triclinic, ferroic phase symmetry. The number of domains can even be doubled when anti-phase (= translation) domains are allowed. It must also be remembered that in the case of the simultaneous presence of the four primary ferroics, all the physical effects of table 5, and even many more, are allowed. Therefore, with a view to applications and to the study of specific effects, species with a minimum of complexity will be preferable.

5. Complexity and beauty of single phase multiferroics

Heisenberg (1971) pointed out that in antiquity there existed two definitions of beauty, which are to some extent antagonistic to each other. One is describing beauty as the right agreement of the parts among themselves and with the whole. The other one, going back to Plotin, without reference to the parts, describes beauty as the shine of eternal splendour of the 'One' via the physical appearance.

    No doubt, the first definition is magnificently realized in a multiferroic single crystal as the 'whole' with its multiple coexisting, interwoven and well organized symmetry-governed domains as 'parts'. And whenever somebody has the chance of glimpsing into a polarized light microscope, revealing, ferromagnetic/ferrotoroidic/ferroelectric/ferroelastic domains, or of realizing the omnipresence of the time-odd polar vector in nuclear and particle physics as 'anapole', he may experience a feeling of that eternal splendour of 'the 'One', reaching out to the frontiers of the universe. Such a feeling is not new: in the introduction to his monumental work 'Lehrbuch der Kristallphysik', Voigt (1966)—fascinated by symmetry and the aesthetics of crystal physics—compares a crystal with an excellently directed orchestra, in which all molecules play perfectly together, and he concludes: '⋯ To my mind the music of physical laws sounds in no other field in such full and rich chords as in crystal physics'.

Acknowledgments

Appendix A

The tensor form in Nye notation (Nye 1990) of the 58 point groups permitting the linear magnetoelectric effect. (Reprinted with permission from Schmid 2004. Copyright 2004 SPIE Press.) For the 31 groups thereof, permitting a spontaneous toroidal moment, see figure 2(a) and tables 2 and 7.

Left column

	Group symbols	Setting
2	1　$\bar{1}'$	
0	(2)　(m')　(2/m')	1st setting
3	2　m'　2/m'	2nd setting
0	(2)　(m')　(2/m')	3rd setting
0	(2')　(m)　(2'/m)	1st setting
3	2'　m　2'/m	2nd setting
0	(2')　(m)　(2'/m)	3rd setting
3	222　(2m'm')　(m'2m')　m'm'2　m'm'm'	
3	2'2'2　mm2　(2'mm')　(m2'm')　mmm'	
1	(2'22')　(m2m)　mm'2'　(2'm'm)　(mm'm)	
0	(22'2')　(2mm)　(m'2'm)　(m'm2')　(m'mm)	

15

Right column

	Group symbols
8	4　$\bar{4}'$　4/m'　3　$\bar{3}'$　6　$\bar{6}'$　6/m'
3	4'　$\bar{4}$　4'/m'
11	422　4m'm'　[4'2m'　4'm'2]　4/m'm'm'　　32　3m'　$\bar{3}'m'$
	622　6m'm'　[6'm'2　6'2m']　6/m'm'm'
5	[4'22'　4'm'm　$\bar{4}$2m　$\bar{4}$m'2　4'/m'm'm]
	[4'2'2　4'mm'　$\bar{4}$m2　$\bar{4}$2m'　4'/m'm'm]
11	42'2'　4mm　[4'2'm　4'm2']　4/m'mm　　32'　3m　$\bar{3}$m
	62'2'　6mm　[6'm2'　6'2'm]　6/m'mm
5	23　$m'\bar{3}$　432　$\bar{4}'3m'$　$m'\bar{3}m'$

43 + 15 = 58

Key to notation:
- • zero component
- ● non-zero component
- ●—● equal components
- ●—○ components with equal modulus but opposite sign

Bold numerals: number of magnetic point groups.
Group symbols in round brackets have not to be counted.
Group symbols in square brackets belong to the same group.

Appendix B

Point groups of the linear magnetoelectric, linear kinetoelectric (toroidoelectric) and linear kinetomagnetic (toroidomagnetic) effect. (Adapted and corrected from Ascher 1974). The 22 groups which permit no other of the three considered effects, are underlined (cf figure 3).

	EH	*SE*	*SH*
1	1, $\bar{1}'$	1, $\bar{1}$	1, $\underline{1'}$
2	2, m', $\underline{2/m'}$	2, m', $\underline{2/m}$	2, m', $\underline{21'}$
3	m, $2'$, $\underline{2'/m}$	m, $2'$, $\underline{2'/m'}$	m, $2'$, $\underline{m1'}$
4	222, $2\underline{m'm'}$, $\underline{m'm'm'}$	222, $2\underline{m'm'}$, $\underline{mmm}$	222, $2m'm'$, $\underline{2221'}$
5	$2mm$, $22'2'$, $2'mm'$, $\underline{m'mm}$	$2mm$, $22'2'$, $2'mm'$, $\underline{mm'm'}$	$2mm$, $22'2'$, $2'mm'$, $\underline{mm21'}$
6	4, $\bar{4}'$, $\underline{4/m'}$	4, $\bar{4}'$, $\underline{4/m}$	4, $\bar{4}'$, $\underline{41'}$
	3, 6, $\underline{\bar{6}'}$, $\underline{\bar{3}'}$, $\underline{6/m'}$	3, 6, $\underline{\bar{6}}$, $\underline{\bar{3}}$, $\underline{6/m}$	3, 6, $\underline{6'}$, $\underline{31'}$, $\underline{61'}$
7	$\bar{4}$, $4'$, $\underline{4'/m'}$	$\bar{4}$, $4'$, $\underline{4'/m}$	$\bar{4}$, $4'$, $\underline{\bar{4}1'}$
8	422, $\bar{4}'2m'$, $4m'm'$ $\underline{4/mm'm'}$,	422, $\bar{4}'2m'$, $4m'm'$	422, $\bar{4}'2m'$, $4m'm'$
	32, $3m'$, 622 $\underline{\bar{3}'m'}$, $\underline{\bar{6}'m'2}$,	$4/mmm$, 32, $3m'$, 622 $\underline{\bar{3}m}$,	$\underline{4221'}$, 32, $3m'$, 622
	$6m'm'$, $\underline{6/m'm'm'}$	$\underline{\bar{6}m2}$, $6m'm'$, $\underline{6/mmm}$	$\underline{321'}$, $\underline{6'2'2}$, $6m'm'$, $\underline{6221'}$
9	$\bar{4}2m$, $4'22'$, $\bar{4}2'm'$,	$\bar{4}2m$, $4'22'$, $\bar{4}2'm'$,	$\bar{4}2m$, $4'22'$, $\bar{4}2'm'$,
	$4'm'm$ $\underline{4'/m'm'm}$	$4'm'm$ $\underline{4'/mmm'}$	$4'm'm$ $\underline{\bar{4}2m1'}$
10	4mm, $42'2'$, $\bar{4}m2'$,	4mm, $42'2'$, $\bar{4}m2'$,	4mm, $42'2'$, $\bar{4}m2'$,
	$\underline{4/m'mm}$, $3m$, $32'$, $\underline{\bar{3}'m}$	$\underline{4/mm'm}$, $3m$, $32'$, $\underline{\bar{3}m'}$	$\underline{4mm1'}$, $3m$, $32'$, $\underline{3m1'}$
	6mm, $62'2'$, $\underline{\bar{6}'m2'}$, $6/m'mm$	6mm, $62'2'$, $\underline{\bar{6}m'2'}$, $6/mm'm'$	6mm, $62'2'$, $\underline{6'mm'}$, $\underline{6mm1'}$
11	23, $\underline{m'3}$, 432, $\underline{\bar{4}'3m'}$, $\underline{m'\bar{3}m'}$	23, $\underline{m3}$, 432, $\underline{\bar{4}3m}$, $\underline{m\bar{3}m}$	23, $\underline{231'}$, 432, $\underline{4'32'}$, $\underline{4321'}$

Appendix C

Subdivision of the 773 species (Aizu 1970) into 36 ensembles with different ferroic property combinations (adapted from Schmid 1999).

		Fully ferroelectric		Partially ferroelectric		Non-ferroelectric		*Number of species*
		Ensemble No.	*Number of species*	*Ensemble No.*	*Number of species*	*Ensemble No.*	*Number of species*	
Fully ferromagnetic	Fully ferroelastic	**1**	*45*	**2**	*6*	**3**	*44*	*95*
	Partially ferroelastic	**4**	*None*	**5**	*None*	**6**	*None*	*0*
	Non-ferroelastic	**7**	*None*	**8**	*None*	**9**	*31*	*31*
Partially ferromagnetic	Fully ferroelastic	**10**	*18*	**11**	*6*	**12**	*27*	*51*
	Partially ferroelastic	**13**	*50*	**14**	*31*	**15**	*16*	*97*
	Non-ferroelastic	**16**	*18*	**17**	*8*	**18**	*27*	*53*
Antiferro-magnetic	Fully ferroelastic	**19**	*4*	**20**	*None*	**21**	*76*	*80*
	Partially ferroelastic	**22**	*9*	**23**	*5*	**24**	*21*	*35*
	Non-ferroelastic	**25**	*11*	**26**	*3*	**27**	*105*	*119*
Para- or dia-magnetic	Fully ferroelastic	**28(I)** [a]	*42*	**29 (IV)**	*6*	**30 (V)**	*46*	*94*
	Partially ferroelastic	**31 (II)**	*31*	**32 (III)**	*17*	**33 (VII)**	*13*	*61*
	Non-ferroelastic	**34 (VI)**	*15*	**35 (VIII)**	*8*	**36 (IX)**	*34*	*57*
Number of species			*243*		*90*		*440*	*773*

[a] Roman numbers refer to the corresponding numbers of ensembles in table I (a), (b), (c), (d) of Schmid (1993); grey cases are empty ensembles.

Appendix D

Relations of the invariants *E, H, EE, HH, EH, EHH* and *HEE* in SI-units for magnetoelectric measurements (Rivera 1994a, Hehl *et al* 2008).

This function, $g(E, H: T)$ (V A s m^{-3} = J m^{-3}), at constant temperature T and with the variables electric field E (V m^{-1}) and magnetic field H (A m^{-1}) (with indices running from 1 to 3) can be developed as follows:

$$g(E, H; T) = \cdots + P_{(s)i} E_i + M_{(s)i} H_i + \tfrac{1}{2}\varepsilon_0 \varepsilon_{ik} E_i E_k$$
$$+ \tfrac{1}{2}\mu_0 \mu_{ik} H_i H_k + \alpha_{ik} E_i H_k$$
$$+ \tfrac{1}{2}\beta_{ijk} E_i H_j H_k + \tfrac{1}{2}\gamma_{ijk} H_i E_j E_k + \cdots, \quad (D.1)$$

where $\varepsilon_0 = (1/(c^2\mu_0))$ (A s V^{-1} m^{-1}) = free space permittivity, ε_{ik} = relative permittivity, μ_0 (= $4\pi \times 10^{-7}$) (V s A^{-1} m^{-1}) = free space permeability, μ_{ik} = relative permeability, c = free space light velocity ($\approx 3 \times 10^8$ (m s^{-1})), P_s (A s m^{-2}) = spontaneous polarization, M_s (V s m^{-2}) = spontaneous magnetization, α (s m^{-1}) = tensor of linear ME-effect, '*EH*'-effect, α_{ik} non-symmetric in ik, β (s A^{-1}) = tensor of bilinear magnetoelectric '*EHH*'-effect, β_{ijk} symmetric in jk, γ (s V^{-1}) = tensor of bilinear magnetoelectric '*HEE*'-effect, γ_{ijk} symmetric in jk.

By differentiating $-g$ (equation (D.1)) with respect to E_k we obtain the components of the total polarization P_k (A s m^{-2}):

$$P_k(E, H; T) = -\partial g/\partial E_k$$
$$= \cdots + {}^S P_k + \varepsilon_0 \varepsilon_{ik} E_{i+} \alpha_{ki} H_i$$
$$+ \tfrac{1}{2}\beta_{kij} H_i H_j + \gamma_{ijk} H_i E_j. \quad (D.2)$$

From this result we obtain the basic equation in SI units (wherein $P = D$) for the magnetic-field-induced polarization of the ME$_H$ effect at $E = 0$:

$$Q/S_k = D_k = P_k = \alpha_{ki} H_i + \tfrac{1}{2}\beta_{kij} H_i H_j, \quad (D.3)$$

where Q ((C) = (As)) are the magnetic-field-induced bound charges and S_k (m^2) the surface of one of the crystal's electrodes.

By differentiating $-g$ with respect to H_k, we obtain the components of the total magnetization M_k (V s m^{-2}):

$$M_k(E, H; T) = -\partial g/\partial H_k = \cdots + M_{(s)k} + \mu_0 \mu_{ik} H_i$$
$$+ \alpha_{ik} E_{i+} \beta_{ijk} E_i H_j + \tfrac{1}{2}\gamma_{kij} E_i E_j. \quad (D.4)$$

For $H = 0$ the *total electric-field-induced magnetization* becomes

$$M_k = +\alpha_{ik} E_i + \tfrac{1}{2}\gamma_{kij} E_i E_j, \quad (D.5)$$

the basic equations for the ME_E measuring methods using SI units (Rivera 1994a). Very detailed magnetoelectric measurement techniques are also described in Hehl *et al* (2008).

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