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On the Possibility of Ferromagnetic, Antiferromagnetic, Ferroelectric, and Ferroelastic Domain Reorientations in Magnetic and Electric Fields

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By combining the thermodynamic classification of Primary, Secondary and Tertiary Ferroics and the corresponding symmetry-allowed or symmetry-forbidden driving forces for domain switching and reorientation, with a classification of Aizu's 773 *species* (prototype/ferroic phase point group pairs) into 30 *ensembles* of property combinations, permitting to evaluate presence or absence of coupling between the different primary ferroic spontaneous quantities, symmetry conditioned possibilities of ferroic domain switching and reorientation have been evaluated. Main accent is put on "cross"-effects, such as magnetic field induced reorientation of antiferromagnetic, para- or diamagnetic ferroelectric and/or ferroelastic domains, and the equivalent electric field induced effects. – Possibilities of "poling" antiferromagnetic domains have been evaluated. Examples referring to different types of *ensembles* are given.

Keywords: Ferroic domain reorientation; ferroelectrics; ferroelastics; ferromagnetics; antiferromagnetics

INTRODUCTION

The primary ferroic switching of spontaneous magnetization ${}^{s}M_i$, spontaneous polarization ${}^{s}P_i$ and spontaneous deformation ${}^{s}\varepsilon_{ij}$ by means of the driving forces magnetic field H_i, electric field E_i and mechanical stress σ_{ij}, respectively, is rather well documented in literature[1,2]. The following "cross-effects", however, seem to have received less attention:
i) reorientation of the *spontaneous magnetization* ${}^{s}M_i$ by means of an electric field E_i or mechanical stress σ_{ij}, ii) reorientation of the *spontaneous polarization* ${}^{s}P_i$ by means of a magnetic field H_i or mechanical stress σ_{ij} and iii) reorientation of the *spontaneous deformation* ${}^{s}\varepsilon_{ij}$ by means of a magnetic or an electric field. With a view to exploring all potential cases, we are using two tools, *first*, the thermodynamic classification into primary, secondary and tertiary ferroics giving us the different potential symmetry allowed terms of the free energy and the corresponding driving forces for domain switching and reorientation[1,2,3,4], and *second*, Aizu's classification[5] of the *prototype/ ferroic*

phase point group pairs ("*species*"), giving information on full, partial or no coupling between the different types of domain during switching. In an attempt at classifying the possibilities of contrast formation in polarized light between ferroelectric and ferroelastic domains, the 212 gray *species*, covering the para- and diamagnets, have been split into 9 *ensembles*[6], defined by the matrix *Fully ferroelectric, Partially ferroelectric, Non-ferroelectric* on the one hand and *Fully ferroelastic, Partially ferroelastic, Non-ferroelastic* (*co-elastic*[7]) on the other hand. By extending these 9 ensembles to *antiferromagnetic, fully* and *partially ferromagnetic* ones, i.e. to 773 species[5], 36 ensembles of species are obtained. For symmetry reasons ensembles 4, 5, 6, 7, 8 and 20 are empty, leading to a total of 30 possible ensembles (Tables I, II).

POSSIBILITIES OF REORIENTATION AND SWITCHING

1. *Reorientation of ferromagnetic, antiferromagnetic and ferroelectric domains by magnetic or electric fields* is possible in ferroelastic phases only.

2. For *ferroelastic domain reorientation the driving potential for wall motion is* $\Delta G \propto \Delta^s\varepsilon_{ij}\,\sigma_{ij}$, but ferrobimagnetic ($\Delta G \propto \Delta\chi_{ij}\, H_iH_j$) or ferrobielectric ($\Delta G \propto \Delta\kappa_{ij}\, E_iE_j$) reorientation is possible also in case of sufficient anisotropy of magnetic and electric susceptibility, $\Delta\chi_{ij}$ and $\Delta\kappa_{ij}$, respectively. Partial ferroelastics, however, can not be made single domain. In full ferroelectrics/full ferroelastics the ferroelastic, ferrobielectric and ferrobimagnetic driving forces allow control both of direction *and* sense of ^sP_i. If being i) fully ferromagnetic, the direction, but not the sense of ^sM_i, and if ii) partially ferromagnetic, the direction of ^sM_i, but not the domain state can be controlled.

3. The *driving potential for ferromagnetic* wall motion, $\Delta G \propto \Delta^sM_i\, H_i$, allows 180° reversal of ^sM_i in ferromagnetic non-ferroelastics (co-elastics) and inside ferroelectric and ferroelastic domains. In ferromagnetic fully and partially ferroelastic phases it permits also *reorientation of* the ferromagnetic /ferroelastic domains due to coupling of the orientation of ^sM_i with that of $^s\varepsilon_{ij}$. Ferrobimagnetic reorientation ($\Delta G \propto \Delta\chi_{ij}\, H_iH_j$) and a magnetostrictively induced effect ($\Delta G \propto \Delta^s\varepsilon_{ij}(\lambda_{ijkl}/s_{ijkl})\, H_iH_j$; without summation; see item 6), may contribute, too. In *full ferromagnetics/full ferroelectrics/full ferroelastics* the magnetic field controls all ferromagnetic and ferroelectric/ferroelastic states.

4. *The driving potential* for reversing ^sP_i by 180° in co-elastic ferroelectrics and inside ferroelastic domains, and for *reorientation of* ^sP_i (direction and sense) and of $^s\varepsilon_{ij}$ in fully ferroelastic/fully ferroelectrics is $\Delta G \propto \Delta^sP_i\, E_i$. Reorientation by ferrobielectric ($\Delta G \propto \Delta\kappa_{ij}\, E_iE_j$) and/or electrostrictive interaction ($\Delta G \propto \Delta^s\varepsilon_{ij}(\gamma_{ijkl}/s_{ijkl})E_iE_j$; without summation; γ_{ijkl} = electrostriction coeff., s_{ijkl} = elastic compliance) is also possible. For a crystal of *Ensemble* 1 (Tab.I,II) an electric field can command *all* fully coupled $^sP_i/^s\varepsilon_{ij}$ states, but ^sM_i being invariant under space inversion, it can control only the direction of ^sM_i and not its sense.

Probably nickel iodine boracite $Ni_3B_7O_{13}I$ is so far the only material, on which an electric field induced reorientation (rotation of 90°) of ^sM_i and $^s\varepsilon_{ij}$ and a electric field induced reorientation of ^sP_i (by ~180°) was realized (below 61K)[8,9]. In first experiments species $\bar{4}$3m1'Fm'm2' was mimicked [8,9] due to layered monoclinic domains. Later the true species was determined as $\bar{4}$3m1'Fm'[10,11]. Table II/*Ensemble* 1 gives other potential boracite candidates.

5. *Potential reorientation and spin reversal of antiferromagnetic domains.*

5.1 *Reorientation of antiferromagnetic domains* by magnetic field, electric field, or mechanical stress, and herewith *reorientation of their spin directions, is obligatorily linked with ferroelasticity* and may in principle operate via ferrobielectric, ferrobimagnetic, ferroelastic, magneto- or electrostrictively induced or ferroelectric domain reorientation, in the latter case in fully or partially coupled ferroelectric/ferroelastic phases. The ferrobimagnetic driving potential $\Delta G \propto \Delta\chi_{ij}\ H_iH_j$ may reorient antiferromagnetic/ferroelastic domains and herewith their spin directions. For NiO (m$\bar{3}$m1'F $\bar{3}$m [4×2]: at $T<T_N=525K$[1,2]), $DyVO_4$ (4/mmm1'Fmmm'(p) [2×2] (?): $T<T_N=3.04K$[12], $^sT \perp$ m') and $TbPO_4$ [13] 4/mmm1'F2/m'(s) [4×2] (?) (*Ensemble* 21) such magnetic field induced reorientations have been achieved. However, so far it is not clear, to what proportions ferrobimagnetic and/or magnetostrictive (see item 6) interactions were responsible.

5.2 *Antiferromagnetic domain "poling"* (180°-spin reversal) in non-ferroelastic (co-elastic) phases or inside antiferromagnetic/ferroelastic domains is possible in 39 antiferromagnetic Shubnikov point groups, (among a total of 59, see e.g. Table II/ref. [15]), permitting the magnetoelectric $\alpha_{ij}\ E_iH_j$ term and the driving potential $\Delta G \propto \Delta\alpha_{ij}\ E_iH_j$ ("(ferro)magnetoelectric"[1,2] switching). For four (6', 6'mm', $\bar{6}$m2, 6'2'2) of the remaining 20 groups, switching is in principle possible with the magnetobielectric $(\gamma_{ijk}H_iE_jE_k)$[16], magnetobimagnetic $(\beta_{ijk}E_iH_jH_k)$[16], piezoelectric $(d_{ijk}E_i\sigma_{jk})$ or piezomagnetic $(q_{ijk}H_i\sigma_{jk})$ term, for 11 ones by means of $\gamma_{ijk}H_iE_jE_k$ or $q_{ijk}H_i\sigma_{jk}$ only and one group ($\bar{4}$3m) with $\beta_{ijk}E_iH_jH_k$ only. Four groups (m$\bar{3}$m, 6'/m, 6'/mm'm and m'$\bar{3}$m) are left, not permitting the driving forces E_iH_j, $E_iH_jH_k$ or $H_iE_jE_k$, however, the three latter groups allow the piezomagnetoelectric term $\pi_{ijkl}E_iH_j\sigma_{kl}$ [17,18] (see foot-note on p. 270 of ref.[17]), which can in principle be used because it permits making the material magnetoelectric under stress σ_{kl}. Only for m$\bar{3}$m no useful term exists! Whereas the piezomagnetic term $H_i\sigma_{jk}$ has successfully been used to reverse the spins in an antiferromagnetic phase (CoF_2[19])(see *Ensemble* 27), the $H_iE_jE_k$ term (tensor form of piezomagnetic effect) does not seem to have been used so far to reverse antiferromagnetically ordered spins. The same holds true for the $E_iH_jH_k$ term (tensor form of piezoelectric effect). When in a paramagnetic non-centrosymmetric crystal a polarization $P \propto H^2$ is induced via the latter term, its sign is linked to the absolute structure (analogy with the piezoelectric effect).

In a spin ordered phase allowing $E_iH_jH_k$, the contribution of the spin system would be expected to be opposite in sign for spin reversed domains, but smaller or larger than the non-reversible lattice contribution.

6. *Potential reorientation of para- or diamagnetic, ferroelectric and ferroelastic domains*. i) A magnetic field alone can in principle act only via the ferrobimagnetic driving potential $\Delta G \propto \chi_{ij}H_iH_j$ for reorienting the fully or partially ferroelastic domains of full and partial ferroelectrics and non-ferroelectrics. The most interesting species are found in the fully ferroelectric/fully ferroelastic *Ensemble* 28, where the ferroelectric domains are identical with the ferroelastic ones, thus the magnetic field has in principle full control both over the orientation of all ferroelastic domains and due to the full coupling, even over the sense of ${}^sP_i$. The only materials on which such an experiment has been realized, seem to be the phosphates $Tb_2(MoO_4)_3$[14] and $TbGd(MoO_4)_3$[14] (species $\bar{4}$2m1'Fmm21'[2]). On the former one the application of a magnetic field of 10 Tesla (at 78K in the paramagnetic phase) along the orthorhomic b-axis leads to alignment of the a-axis along the field and 180°-reversal of ${}^sP_i$ along the c-axis. The hysteresis cycle had been repeated by interchanging the direction of the magnetic field by 90°. The phenomenon was attributed to a difference in magnetostriction along the a- and b-axes. The tertiary ferroic magnetostriction driving potential is $\Delta G \propto \Delta\lambda_{iljk}\sigma_{jk}H_iH_l$, requiring application of both magnetic field and stress. However, since a magnetic field alone reorienting the domains, the secondary ferroic driving potential involving magnetostriction, $\Delta G \propto \Delta^s\varepsilon_{ij}(\lambda_{ijkl}/s_{ijkl})\ H_iH_j$ (λ_{ijkl} = magnetostriction coefficient, s_{ijkl} = elastic compliance), must have been responsible in the case of $Tb_2(MoO_4)_3$.

CONCLUSION

The symmetry possibilities have been evaluated for magnetic field induced reorientation of ferroelelctric and ferroelastic domains, and for electric field induced reorientation of magnetic domains. Fully controlled reorientation and switching of domains is possible in the ensembles of species *Fully ferroelectric / Fully ferroelastic* on the one hand and *Fully ferromagnetic*, *Antiferromagnetic* or *Para-/or diamagnetic* on the other hand. For such species a magnetic field alone can in principle control all possible states of ${}^sM_i$, ${}^sP_i$ and ${}^s\varepsilon_{ij}$, but not the sense of the spins of antiferromagnetic domains, and an electric field can control the orientation of all ferroelectric/ferroelastic states and the orientation, but not the sign of the spins in the ferro- or antiferromagnetic domains. In certain species (e.g. *Ensemble* 1 / $\bar{4}$3m1'Fm'm2' [6×2]) the reorientation of H by 90° can reverse ${}^sP$ by 180°. An electric field, however, can never reverse ${}^sM_i$ by 180°. So far there is great paucity of experiments on H-induced reorientation of ${}^sP_i$ and ${}^s\varepsilon_{ij}$, and on E-induced reorientation of ${}^sM_i$.

Table I Ensembles of species with particular ferroic property combinations

		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)#)**	*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*

#) Roman numbers refer to the corresponding numbers in Table I a),b),c),d) of H. Schmid, in: N. Setter and E.L. Colla, Eds, *Ferroelectric Ceramics*, Monte Veritá, Birkhäuser Veralag, Basel, 1993, pp. 107-126/112

Table II Examples of materials in Ensembles of Species

Ensemble No.	*Examples*
1	***Fully ferromagnetic/Fully ferroelectric/Fully ferroelastic*** $\bar{4}3m1'Fm'm2'$ [6×2]: $Ni_3B_7O_{13}Cl$[111], $Ni_3B_7O_{13}Br$ (at 29K>T>21K) [111], $Co_3B_7O_{13}Br$[111], $Co_3B_7O_{13}I$[111], $Co_3B_7O_{13}NO_3$(?)[111], $Mn_3B_7O_{13}Cl$[20], $Mn_3B_7O_{13}Br$[20], $Mn_3B_7O_{13}I$[20,21], Ferrotoroidal, ^sT || a-axis, i.e. ⊥ m' $\bar{4}3m1'Fm'$ [12×2]: $Ni_3B_7O_{13}I$[10], Ferrotoroidal, ^sT || b-axis, i.e. ⊥ m' $\bar{4}3m1'F1$ [24×2]: $Ni_3B_7O_{13}Br$ at T<21K[111], Ferrotoroidal, ^sT: arbitrary
2	***No examples known***
3	***Fully ferromagnetic/Non-ferroelectric/Fully ferroelastic*** $m\bar{3}m\,1'F4/mm'm'$[3×2]: α-Fe (α-iron) at $T<T_c$=1042K $m\bar{3}m1'F\,\bar{3}m'$ [4×2]: magnetite Fe_3O_4, T_c=858K>T>T_{Verwey}=119K) [111] $\bar{3}m1'F2/m$ [3×2]: hematite α-Fe_2O_3 (T_c=950K>T>250K)[19]
4, 5, 6, 7, 8	***Not allowed***
9	***Fully ferromagnetic/Non-Ferroelectric/Non-ferroelastic*** $4/mmm1'F4/mm'm'$ [2]: CrO_2, $6/mmm1'F6/mm'm'$ [2]: $BaO.6Fe_2O_3$ $m2m1'Fm'2'm$ [2]: $Ga_{2-x}Fe_xO_3$ pyroelectric, ferrotoroidal[22], ^sT ⊥ m'
10	***Partially ferromagnetic/Fully ferroelectric/Fully ferroelastic*** $\bar{4}3m1'Fm'm'2$ [6×2]:$Cr_3B_7O_{13}Cl$[11,24],$Cu_3B_7O_{13}Cl$[111], $Cu_3B_7O_{13}Br$(?)[111] $Cu_3B_7O_{13}NO_3$(?)[111]; $\bar{4}3m1'Fm$ [12×2]: $Fe_3B_7O_{13}Cl$[111], $Fe_3B_7O_{13}Br$[111], $Fe_3B_7O_{13}I$[111], $Co_3B_7O_{13}Cl$[11,23],Ferrotoroidal, ^sT ⊥ b-axis (=in m-plane)
11, 12	***No examples known***
13	***Partially ferromagnetic/Fully ferroelectric/Partially Ferroelastic*** $m\bar{3}m1'F1$[48×2]: Magnetite Fe_3O_4 at $T<T_{Verwey}$ = 119K[111], Ferrotoroidal, ^{s}**T**: arbitrary direction
14, 15, 16, 17, 18	***No examples known***
19	***Antiferromagnetic/Fully ferroelectric/Fully ferroelastic*** $3m1'Fmm2$ [6×2]:$Cr_3B_7O_{13}Cl$ 13.5K>T>9.7K[11,24]; Ferrotoroidal,^{s}**T** || c
20	***Not allowed***
21	***Antiferromagnetic/Non- ferroelectric/Fully ferroelastic*** $m\bar{3}m1'F\,\bar{3}m$ [4×2]: NiO at $T<T_N$=525K[1,2] $4/mmm1'Fmmm'(p)$ [2×2] (?): $DyVO_4$ ($T<T_N$=3.04K)[12], ^{s}**T** ⊥ m' $4/mmm1'F2/m'(s)$ [4×2] (?): $TbPO_4$ [13]] (T_{N1}=2.28K<T<T_{N2}=2.13K)
22	***Antiferromagnetic/Fully ferroelectric/Partially ferroelastic*** $m\bar{3}m1'F''3m1'''$: $BiFeO_3$, antiferromagnetic/INC.[25,26], see *ens.* **31**
23	***Antiferromagnetic/Partially ferroelectric/Partially ferroelastic*** *No example known*
24	***Antiferromagnetic/Non-ferroelectric/Partially ferroelastic*** $m\bar{3}m1'F4'/m$ [6×2]: Garnet $Ca_2Mn_2Ge_2O_{12}$ [27]

25 ***Antiferromagnetic/Fully ferroelectric/Non-ferroelastic***
6/mmm1'F6'mm'[2×2]: $YMnO_3$ and $REMnO_3$ (RE = rare earth) [15]

26 ***Antiferromagnetic/Partially ferroelectric/Non-ferroelastic***
No example known

27 ***Antiferromagnetic/Non-ferroelectric/Non-ferroelastic***
$\bar{3}$m1'F$\bar{3}$'m' [2]: Cr_2O_3 at $T<T_N$=318K;
$\bar{3}$m1'F$\bar{3}$m [2]: hematite α-Fe_2O_3 at $T<T_N$=250K[1,2,19]
4/mmm1'F4'/mm'm [2]: CoF_2[19] (α-Fe_2O_3 and CoF_2 are piezomagnetic)
mmm1'Fmmm' [2]: $LiCoPO_4$ at $T<T_N$=21.9K[28], Ferrotoroidal: $^{s}T \perp m'$

28 ("1") ***Para- or diamagnetic/Fully ferroelectric/Fully ferroelastic***
$\bar{4}$2m1'Fmm21'[2]: GMO($Gd_2(MoO_4)_3$)-type[29], $Tb_2(MoO_4)_3$[14];
KDP-type[29]; TANANE[30], $RbLiMoO_4$[31];
$\bar{4}$3m1'F3m1' [4]: $Fe_3B_7O_{13}Cl$[6], $Fe_3B_7O_{13}Br$[6], $Fe_3B_7O_{13}I$[6],
$Co_3B_7O_{13}Cl$[6]; $CsLiMoO_4$[6,31], $CsLiWO_4$[6,31], $RbLiMoO_4$[6,31]
$\bar{4}$3m1'Fm 1'[12]: $Fe_3B_7O_{13}X$ (X=Cl,I)[6], $M_3B_7O_{13}Cl$ (M=Co,Zn)[6]

29("IV") ***Para- or diamagnetic/Partially ferroelectric/Fully ferroelastic***
No example known

30("V") ***Para- or diamagnetic/Non-ferroelectric/Fully ferroelastic***
4mm1'Fmm21' [2]: Ge-fresnoite $Ba_2TiGe_2O_8$ [6] polar only
4/mmm1'F2/m(s) [4]: VO_2 [6]; 4/mmm1'F2/m(p) [4] : $K_3Fe_5F_{15}$ [32]
4/mmm1'Fmmm1' [2]: $YBa_2Cu_3O_{7-\delta}$[33]

31("II") ***Para- or diamagnetic/Fully ferroelectric/Partially ferroelastic***
m$\bar{3}$m 1'F"3m1'" [8×2]: Perovskite $BiFeO_3$ (pseudo-3m1'-behavior, due to incommensurate antiferromagnetic structure at $T<T_N$=653±3K [25,26]
m$\bar{3}$m1'F4mm1' [6] and m$\bar{3}$m1'F3m1'[8]: $BaTiO_3$[34];
m$\bar{3}$m1'Fmm21' (s) [12]; $BaTiO_3$[34], Al-Sodalite $Sr_8[Al_{12}O_{24}](CrO_4)_2$[35]

32("III") ***Para- or diamagnetic/Partially ferroelectric/Partially ferroelastic***
m$\bar{3}$m1'F41' [12] and m$\bar{3}$m1'F31': Pyrochlore $Cd_2Nb_2O_7$[36]

33("VII") ***Para- or diamagnetic/Non-ferroelectric/Partially ferroelastic***
No example known

34("VI") ***Para- or diamagnetic/Fully ferroelectric/Non-ferroelastic***
61'F31'[2]: $Pb_5Ge_3O_{11}$ electro-ambidextrous[37]
2/m1'Fm1' [2]: $LiH_3(SeO_3)_2$ [38], pseudo-electro-ambidextrous[38]
mmm1'Fmm21': $NaNO_2$ [38], pseudo-electro-ambidextrous[38]

35("VIII") ***Para- or diamagnetic/Partially ferroelectric/Non-ferroelastic***
No example known

36("IX") ***Para- or diamagnetic/Non-ferroelectric/Non-ferroelastic***
6221'F321' [2]: α-quartz, ferrobielastic[1];
m$\bar{3}$m1'F$\bar{4}$3m1' [2]: NH_4Cl, ferroelastoelectric[1]

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