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The Interactions between Magnetization and Polarization: Phenomenological Symmetry Considerations on Boracites

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§ 1. Introduction

Let the state of the crystal be described by a single-valued function, ϕ, of the electric, of the magnetic, of the stress field, etc., which is invariant under continuous translation in space and in time. This means that one views the crystal as an infinite, continuous homogeneous, anisotropic medium in a steady state. While the theory of such a medium can be treated as an exact theory on its own right, it may also be considered as the continuum approximation of a more detailed atomistic theory. From the latter point of view one may say that the continuum approximation is valid for phenomena that imply only wave length much greater than a lattice constant.

The anisotropy of the continuous medium is characterized by the crystallographic point group of the medium. The various properties of the crystal manifest themselves in the appearance of various tensors as coefficients in the Taylor expansion of the function ϕ in terms of the components of the electric field, of the magnetic field, of the stress field, etc.

$$-\phi=\kappa_i E^i+\chi_i H^i+\tfrac{1}{2}\varepsilon_0\kappa_{ik}E^iE^k+\tfrac{1}{2}\mu_0\chi_{ik}H^iH^k+\alpha_0\alpha_{ik}E^iH^k+\cdots, \quad (1)$$

$$-\frac{\partial\phi}{\partial E^i}=P_i=\kappa_i+\varepsilon_0\kappa_{ik}E^k+\alpha_0\alpha_{ik}H^k, \quad \kappa_i=P_i^s, \quad (2)$$

$$-\frac{\partial\phi}{\partial H^i}=M_i=\chi_i+\alpha_0\alpha_{ki}E^k+\mu_0\chi_{ik}H^k, \quad \chi_i=M_i^s. \quad (3)$$

Each term of such an expansion is manifestly an invariant under the orthogonal group. A term is however different from zero only if the product of the components of the fields that appear in the term is invariant. Thus writing down such a development for a given symmetry group consists in writing down the invariants that may be constructed from the components of the fields. This is most easily done, once the way in which the components of the three types of vector (electric field, magnetic field, velocity) transform.[1-3] A product of field components is invariant if and only if it transforms with the identity transformation.

Here we shall limit our discussion to ferromagneto-electric media. Ferromagneto-electrics are those crystals which contain terms linearly proportional to the electric field and to the magnetic field, respectively. Only 13 out of the 122 Shubnikov point groups admit the existence of a spontaneous electric polarization and of a spontaneous magnetization (see Table I).

Table I. Ferromagneto-electric Shubnikov groups.

P^s	M^s	weak		v_s
*	*	1		*
z	z	2	4, 3, 6	z
z	z	$m'm'2$	$m'm'4$, $3m'$, $m'm'6$	0
(z)	(z)	m'		z
z	(z)	$2'$		(z)
(z)	z	m		(z)
z	x	$mm'2'$		y

The notation (z) means perpendicular to z. The heading "weak" refers to Dzialoshinski's weak ferromagnetism.[4] The Shubnikov point groups compatible with such a phenomenon in a (almost) uniaxial antiferromagnets have been determined by Tavger.[5] The heading v_s refers to an invariant velocity vector.[6] When there is no such vector, there is no relativistic crystal symmetry.

§ 2. Switching Behaviour

The impetus for the search for ferromagneto-electric compounds has been given by Smolensky and Joffe's paper read at the Grenoble Conference in 1958.[7] Nevertheless, so far only two classes of compound have been found which have a spontaneous magnetic moment together with ferroelectric behaviour. First of all there are some solid solutions having crystal structures of the perovskite-type. They have been investigated by

Smolensky and collaborators.[8] Then there are the ferromagneto-electric boracites investigated at Battelle in Geneva.[9–11] Good single crystals were prepared. The strong coupling between magnetization and polarization manifests itself in the following unusual switching behaviour (in orthorhombic Ni-I-boracite): when the spontaneous electric polarization P^s changes by 180°, from say [100] to −[100], then the spontaneous magnetization M^s changes by 90°, for instance from [011] to [01$\bar{1}$]; it can be explained by symmetry considerations. This explanation is based on three things:

(i) On the application of Curie's principle to transitions into ferromagneto-electric phases. Curie says: "The characteristic symmetry of a phenomenon is the maximum symmetry compatible with the existence of the phenomenon. A phenomenon may exist in a medium which possesses its characteristic symmetry or that of one of the subgroups of the characteristic symmetry."[12] Zheludev and Shuvalov[13,14] applied this principle to determine the symmetries that may arise in ferroelectric or ferromagnetic phase transitions. Ascher applied this kind of reasoning later[1,2,6] in a slightly different form and to some new problems. When correctly interpreted, the new version is a, perhaps convenient, rewording of the older one.

(ii) On the theory of polysynthetic twins. Again Zheludev and Shuvalov have shown how this theory applies to the domain configuration of ferroelectrics and ferromagnetics.[13,14] It can however be also shown that there are relations to Weiss' theory of ferromagnetism and to the modern theory of broken symmetries.[15]

(iii) On the hypothesis that the switching of a crystal is nothing but the change from one possible domain to another, *i.e.* that the applied electric or magnetic field does not induce a transition to a phase with a new symmetry, which would be a typical situation where Curie's principle would not apply.[16]

The possible magneto-electric phases of boracites (which are cubic in the high-temperature phase) are shown in Fig. 1.[3,17] Ferroelectric transitions are represented by plain lines, the ferromagnetic ones by broken lines. Each number at the left is the index ι and refers to all the subgroups placed on the same horizontal line. The number between parentheses preceding the symbol of a group gives its multiplicity ν (*i.e.* the number of its conjugates in $\bar{4}3m'$). The letters below the symbol of a group stand for the directions of P^s, M^s, v^s corresponding to a given subgroup. The directions are noted according to the convention shown in Table II. There are two magneto-electric phases, $3m'$ and $mm'2'$, that can arise as the result of a single, ferromagnetic, phase transition.

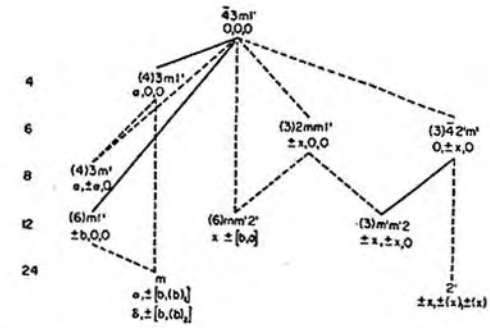


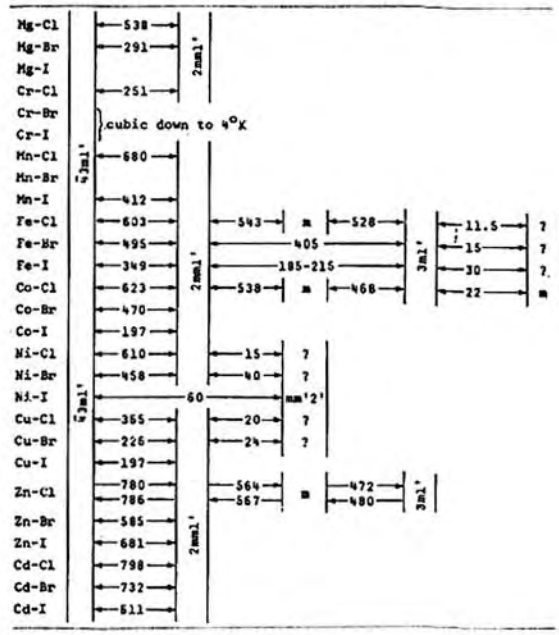
Fig. 1. Possible magneto-electric phases of boracites.

Table II. Notation for crystallographic directions.

x	y	z	α	β	γ	δ	a	b	c	d	e	f
001	010	001	1$\bar{1}$1	$\bar{1}$11	$\bar{1}\bar{1}$1	111	011	0$\bar{1}$1	101	10$\bar{1}$	110	$\bar{1}$10

For a given phase, there are ι equivalent configuration of P^s, M^s, v^s, thus to each subgroup there correspond ι/ν such configurations. This enables one to obtain a list of the equivalent P^s, M^s, v^s-configurations. This list can be established more explicitly by observing that all possible domains are obtained by applying the symmetry operations lost in the phase transition to any of

Table III. Phases of boracites.



them. These lost symmetries are the operations contained in the high-temperature group, but not contained in any of the ν conjugate subgroups describing the possible domains of the new phase.

The phase-transitions in boracites metals known so far are shown in Table III.[18] The succession of transitions undergone by a compound does of course not lie necessarily on a path indicated in Fig. 1 (*e.g.* $mm21' \rightarrow 3m1'$). If however the symmetry of a phase does not prescribe a definite direction for a spontaneous vector, this direction will be determined by the neighbouring phase. Thus in boracite with the symmetry m, at temperatures close to the temperature of transition from $3m1'$, the direction of the spontaneous polarization will be a [111]-direction lying in the mirror plane.

For boracites with the symmetry $mm'2'$, the triplets of spontaneous vectors corresponding to a spontaneous polarization, *e.g.* in the x-direction, are (x, a, b), $(x, -a, -b)$, $(-x, b, a)$, $(-x, -b, -a)$. If now, as was supposed, polarization reversal is a change of domain, one sees immediately that in order to change the electric polarization from, say, the $(+x)$-direction to the $(-x)$-direction, it is necessary to turn the magnetization by 90° for $\pm a$ to $\pm b$.

A similar analysis performed for perovskites with the high-temperature symmetry $m3m1'$ shows that $mm'2'$ is a possible ferromagneto-electric phase in this case too (Fig. 2). Only here such a

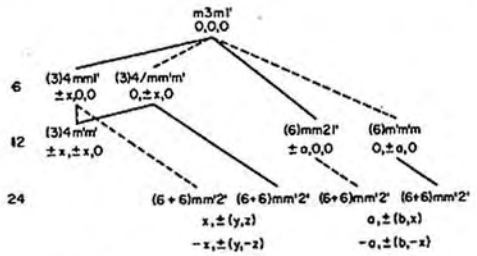


Fig. 2. The phase $mm'2'$ in perovskites.

phase cannot be the result of a single-phase transition. There are four essentially different ways to arrive at this symmetry, and consequently there are four distinguishable types of domain configuration. To each one there correspond two families of (six) conjugate subgroups. Table IV shows the directions of P^s and M^s that go together in these four cases.

The same reasoning when applied for example to purely ferroelectric phases of point symmetry 2 gives the results concerning polarization reversal shown in Table V.

Table IV. Directions of P^s and M^s for phases $mm'2'$ in perovskites.

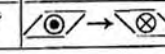
P	M
x	$yz\,ab$
y	$zx\,cd$
z	$xy\,ef$

P	M
$yz\,ab$	x
$zx\,cd$	y
$xy\,ef$	z

P	M
a	$x\,b$
b	$x\,a$
c	$y\,d$
d	$y\,c$
e	$z\,f$
f	$z\,e$

P	M
$x\,b$	a
$x\,a$	b
$y\,d$	c
$y\,c$	d
$z\,f$	e
$z\,e$	f

Table V. Polarization reversal in some ferroelectric phases with point group symmetry 2.

space group	compound	
C_2^2 C_2^3	TGS colemanite NH_4ClCH_2COO $K_4Fe(CN)_6 \cdot 3H_2O$	RS MASD KDP
lost element	1 or m	2
polarization reversal	inversion or mirror	rotation
		

§ 3. Sublattice Formation

In this part we take into account the periodic structure of the crystal. Consequently our medium shall not be invariant under continuous translations in space but only under a group T of discrete translations. The symmetry of the medium is then characterized by a space group G. The group T of translations is a normal subgroup of G. The quotient group K with respect to these translations is a point group representing the crystal class of the space group.

There are three types of subgroup of a space group; the nature of the phase transition depends on the type of subgroup that arises in a transition. (i) If the subgroup is equi-translation, *i.e.* contains the same subgroup of translations as the original group, the crystal is split into domains. (ii) If the subgroup is equi-class, *i.e.* belongs to the same crystal class as the original group, a splitting into sublattices occurs. (iii) If the subgroup is neither equi-translation nor equi-class, both domains and sublattices appear (see Fig. 3).

Both in the attempts of Smolensky and coworkers and in that of the Geneva group the idea of sublattice formation played an essential rôle in the search for ferromagneto-electric compounds.

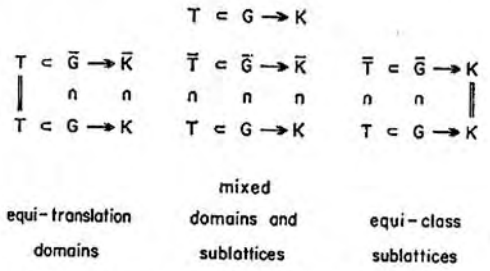


Fig. 3. The three types of subgroup of a space group.

In Leningrad several kinds of ion were introduced into the octahedral sites of a perovskite, and a splitting into sublattices was achieved by an ordering of these ions.

In Geneva a single 3d-metal was placed in an environment that favoured an ordering process. This environment is the mixed, elongated, O_4Cl_2-octahedron of the boracite structure.[19] It provides two energy minima along the fourfold Cl-Cl axis*. Other crystal structures containing anion configurations exist however that provide several energy minima for a cation. In the high-temperature phase the metal ion oscillates between these two minima, in the low temperature it is trapped in one of the minima, thus giving rise to an electric moment. This view has received confirmation by Troster's Mössbauer investigations.[20] A similar ordering may occur also for the halogen ions. The result is that the metal ions, which occupy 24 equivalent positions of the cubic unit cell, are distributed in the orthorhombic phase among three families of equivalent site.

The spontaneous magnetization is in both cases the outcome of an uncompensated antiferromagnetism. In the perovskite it is ferromagnetism, in the boracites it is weak ferromagnetism. Thus in the perovskites as well as in the boracites the transition to a ferromagneto-electric phase cannot be described by a symmetry change from a space group to an equi-translation subgroup. The application of the usual form of Curie's principle to space group can yield however only equi-translation space groups. Ito *et al.* have determined the space group of orthorhombic Mg-Cl-boracite to be C_{2v}^5 ($Pca2$).[19] Now C_{2v}^5 cannot be an equi-class subgroup of the high-temperature symmetry group T_d^5 ($F\bar{4}3c$). Therefore Sonin and Zheludev[21,22] have come to the conclusion that Mg-Cl-boracite cannot be ferroelectric. The merit of their work nontheless is that it shows that the transition in boracites must be accompanied by sublattice formation.

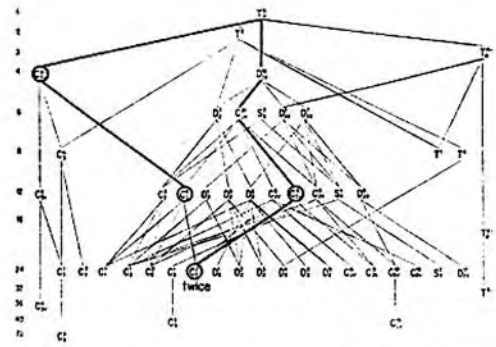


Fig. 4. Lattice of subgroups of T_d^5 ($F\bar{4}3c$).

Figure 4 shows the lattice of subgroups of T_d^5 ($F\bar{4}3c$), the high-temperature space group of boracite. (For the equi-translation subgroup, see;[23] for the equi-class subgroup, this is based on a private communication from H. Wondratschek.) The groups appear only with their maximal index. But furthermore, of two groups having the same symbol, one may be a subgroup of the other. Such subgroups are not presented in the lattice, but should nevertheless not be forgotten.

The Shubnikov space group of the trigonal phase found in the Fe-boracites and in Co-Cl-boracite is $R3c1'$. That of the monoclinic ferromagneto-electric phase is probably C_s^4 (Bb). This may be an equi-translation subgroup, but it need not be so. Indeed C_s^4 may appear also as subgroup of C_{3v}^3 or of C_{3v}^4. It then has index 36 or 108 respectively (in T_d^5), and of course is not equi-translation. The Shubnikov space group of the orthorhombic ferromagneto-electric phase is C_{2v}^5/C_s^4, that is, a Shubnikov space group which is isomorphic to the space group C_{2v}^5 and contains the ordinary space group C_s^4 as subgroup of order two. Two orientations of this space group may occur, and they are noted differently in the international crystallographic notation, namely as $Pca'2'$ or $Pc'a2'$.

§ 4. Relativistic Symmetries**

Relativistic symmetries may help to understand the interactions between the spontaneous electric polarization and the spontaneous magnetization. It may indeed be shown that such symmetries may imply relations between the spontaneous polarization and magnetization and the magneto-electric susceptibility.

Curie has said that the characteristic symmetry, that is, the symmetry group of a phenomenon, is the maximum symmetry compatible with the ex-

istence of the phenomenon. In Curie's definition it is not said from among which symmetry operations one has to choose the maximal symmetry. Curie took it for granted that candidates for membership in the maximal symmetry group were only orthogonal transformations. Time reversal should however be added if one is to understand magnetic phenomena.[24] Consequently, the candidates for symmetry operations are taken from the direct product of the infinite orthogonal group $O(3)$ and the two-element time-reversal group $1'$, which is a subgroup of the Lorentz-group, so that it is a natural next step to admit candidates from the whole Lorentz group. One may go even further and include, for instance, affine transformations or conformal mappings.[25]

Let us now consider the symmetry group of constant and uniform electric and magnetic fields (Table VI).

Curie[12] himself has determined the orthogonal

Table VI. Generators of the symmetry groups K of magneto-electric polarization.

magneto-electric polarization	candidate chosen from		
	$O(3)$	$O(3)\times 1'$	$O(1,3)$
P_z	$\{R_z,\ m_x\}$	$\{R_z,\ m_x,\ 1'\}$	$\{A_z,\ R_z,\ m_x,\ 1'\}$
M_z	$\{R_z,\ m_z\}$	$\{R_z,\ m_z,\ 2_x'\}$	$\{A_z,\ R_z,\ m_z,\ 2_x'\}$
$P_z,\ M_z$	$\{R_z\}$	$\{R_z,\ m_y'\}$	$\{A_z,\ R_z,\ m_y'\}$
$P_z,\ M_x$	m_x	$\{m_x,\ m_y'\}$	$\{L_z(a),\ L_x(a),\ m_x,\ m_y'\}$

transformations, *i.e.* the elements of $O(3)$, that are compatible with these fields. R_z denotes the rotations around the z-axis. The largest subgroups of $O(3)\times 1'$ are also known.[26] However, we shall need also the Lorentz transformations leaving these vectors invariant. They have been determined by Janner and Ascher,[27] and are shown in the last column. A_z denotes the accelerations in the z-direction, *i.e.* transformations to inertial systems moving with any uniform velocity in the z-direction.

If now we consider not only a single field but simultaneously an electric field P and a magnetic field M, we may perhaps expect to obtain the intersection, that is, the common part, of the group of the electric field and the group of magnetic field. But this is not so in the relativistic case, except when the two fields are parallel. The group for the case of perpendicular fields, for instance, is much larger than the intersection of the groups of the separate fields, which simply would be m_x. Indeed $L_z(a)$ and $L_x(a)$ are generators of Lorentz transformations depending on one real parameter a. The parameter a is fixed by the electro-magnetic field and is essentially the ratio of the polarization to the magnetization:

$$a=\left(\frac{\mu_0}{\varepsilon_0}\right)^{1/2}\frac{|P|}{|M|}=c\frac{|P|}{|J|},\quad M=\mu_0 J.$$

So far we have found the relativistic symmetry group of the tensor $P^{\alpha\beta}$ of spontaneous polarization. This group is larger than the symmetry group of the crystal. Accordingly we must determine a subgroup of the symmetry group of $P^{\alpha\beta}$ that leaves the crystal invariant. But what does the notion "to leave the crystal invariant" mean in the frame of our macroscopic theory? Remember that we ignore the translational symmetry of the crystal and that, to characterize a crystal, we retain only the point groups. Now we assume that the crystal is completely described by its Shubnikov point group. All implications of this hypothesis have not yet been worked out. Those which are derived here, however, follow logically without any further assumption from the above hypothesis. "Leaving a crystal invariant" now necessarily must signify leaving its point group invariant. That is to say, nothing more and nothing less than that the point group should be an invariant subgroup of the new symmetry group; in other words, a normal subgroup. We shall therefore look for a subgroup of the symmetry group of the electromagnetic field such that the old point group is contained in it as normal subgroup. The groups that leave invariant both the point group of the crystal and the uniform constant polarization of the crystal are the relativistic symmetry groups of a crystal in the theory of an anisotropic continuum that we are considering here.

These relativistic symmetry groups will be derived elsewhere.[28] Let us however mention that a crystal may have a relativistic symmetry only if there exists a velocity-vector that is left invariant

by the Shubnikov group of the crystal.

Here we shall be concerned with the relativistic symmetry groups related to the Shubnikov group $mm'2'$ (or orthorhombic boracites).

These groups are listed in Table VII together with the new conditions that they impose on the susceptibility tensor. These conditions are found by requiring that the relativistic permittivity tensor $\varepsilon^{\alpha\beta\sigma\tau}$ be invariant under the relativistic symmetry group. The tensor $\varepsilon^{\alpha\beta\sigma\tau}$ relates the two electromagnetic fields $G^{\alpha\beta}$ and $F_{\alpha\beta}$:

$$G^{\alpha\beta}=\begin{pmatrix} 0 & -E_1 & -E_2 & -E_3 \\ E_1 & 0 & cB_3 & -cB_2 \\ E_2 & -cB_3 & 0 & cB_1 \\ E_3 & -cB_2 & -cB_1 & 0 \end{pmatrix},$$

$$F_{\alpha\beta}=\begin{pmatrix} 0 & cD_1 & cD_2 & cD_3 \\ -cD_1 & 0 & H_3 & -H_2 \\ -cD_2 & -H_3 & 0 & H_1 \\ -cD_3 & H_2 & -H_1 & 0 \end{pmatrix},$$

$$G^{\alpha\beta}=\tfrac{1}{2}\varepsilon^{\alpha\beta\sigma\tau}F_{\alpha\beta}.$$

It has the following form [29,30]

$$\left(\frac{\mu_0}{\varepsilon_0}\right)^{1/2}\varepsilon^{\alpha\beta\sigma\tau}=\left(\begin{array}{c|c} -\varepsilon^B & \alpha\phi \\ \hline \phi\tilde{\alpha} & \phi \end{array}\right),$$

$$\varepsilon^B=\varepsilon-\alpha\phi\tilde{\alpha}, \qquad \phi=\frac{1}{\mu}.$$

The three-by-three sub-tensor ε^B is the electric permittivity at constant magnetic induction and $\tilde{\alpha}$ means the transpose of the inverse magnetic permeability ϕ.

In the case of the symmetry $mm'2'$, the permittivity is given by:

$$\left(\frac{\mu_0}{\varepsilon_0}\right)^{1/2}\varepsilon^{\alpha\beta\sigma\tau}=$$

$$\left(\begin{array}{ccc|ccc} -\varepsilon_{11}+\dfrac{\alpha_{13}^2}{\mu_{33}} & 0 & 0 & 0 & 0 & \dfrac{\alpha_{13}}{\mu_{33}} \\ 0 & -\varepsilon_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\varepsilon_{33}+\dfrac{\alpha_{31}^2}{\mu_{11}} & \dfrac{\alpha_{31}}{\mu_{11}} & 0 & 0 \\ \hline 0 & 0 & \dfrac{\alpha_{31}}{\mu_{11}} & \dfrac{1}{\mu_{11}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \dfrac{1}{\mu_{22}} & 0 \\ \dfrac{\alpha_{13}}{\mu_{33}} & 0 & 0 & 0 & 0 & \dfrac{1}{\mu_{33}} \end{array}\right).$$

The various relativistic symmetry groups impose various relations among the components of this tensor. In the case where there is only a spontaneous electric polarization or only a spontaneous magnetization, or where both exist and are perpendicular and equal ($a=1$), the Shubnikov group is already the relativistic symmetry group. Consequently there are no new conditions imposed on the components of the permittivity tensor. Such new conditions do exist, however, when the crystal is spontaneously polarized and magnetized, and provided the ratio a is different from 1. In this case there are relativistic transformations that leave the crystal and its polarization tensor in-

Table VII. Relativistic point groups $\overline{G}$ related to the Shubnikov group $mm'2'$.

magneto-electric polarization	generators of $\overline{G}$	new relations imposed on the electric (ε), magnetic (μ) and magneto-electric (α) permeabilities
P_z	m_x, m_y'	
M_x	m_x, m_y'	
P_z, M_x $a=1$	m_x, m_y'	
P_z, M_x $a>1$	$1'A_y(a)$, m_x, m_y'	$\varepsilon_{11}\mu_{33}=(\alpha_{13}-(1/a))(\alpha_{13}-a)$
P_z, M_x $a<1$	$\bar{1}A_y(a)$, m_x, m_y'	$\varepsilon_{33}\mu_{11}=(\alpha_{31}+(1/a))(\alpha_{31}+a)$
0	$1'A_y(a)$, m_x, m_y' $\bar{1}A_y(a)$, m_x, m_y'	$\mu_{11}\alpha_{13}\varepsilon_{33}+\mu_{33}\alpha_{31}\varepsilon_{11}$ $=(\alpha_{13}+\alpha_{31})(\alpha_{13}\alpha_{31}+1)$
	A_y, m_x, m_y' $1'A_y$, m_x, m_y' $1'A_y(b)$, $A_y(c)$, m_x, m_y' $\bar{1}A_y(b)$, $A_y(c)$, m_x, m_y' etc.	$\alpha_{13}=\alpha_{31}=0$ $\varepsilon_{11}\mu_{33}=\varepsilon_{33}\mu_{11}=1$ $\mu_{11}<1$, $\mu_{33}<1$

variant. Consequently there are new conditions imposed on the components of the permittivity tensor. The generators $1'A_y(a)$ and $\bar{1}A_y(a)$ are Lorentz transformation of order 2. One obtains the same relations for the components of the susceptibility tensor, whenever the only relativistic transformation contained in the relativistic symmetry group is of order 2. This case may arise also in the absence of any spontaneous polarization in the crystal. Of course a now cannot mean the ratio of the spontaneous polarization to the spontaneous magnetization; it is any given real number (the same letter has been chosen only to be able to use the same formula). Besides, the parameter a can be eliminated, and one obtains a single formula relating the six quantities ε_{11}, ε_{33}, μ_{11}, μ_{33}, α_{13}, and α_{31}. Now, however, in the absence of any spontaneous polarization, symmetry groups leading to a different result are also possible. The relativistic symmetry group may indeed contain a continuous subgroup: either the group of accelerations in a given direction or these accelerations combined with the total inversion $\bar{1}'$. Or else it may contain a Lorentz transformation of order 2, for example $1'A_y(b)$, together with at least one other Lorentz transformation, $A_y(c)$, b and c being two incommensurable real parameters. In the case of such relativistic symmetry groups, the consequences are that there is no magnetoelectric effect and that the crystal is diamagnetic.

It is now a question of experiment to determine whether in some cases the consequences of relativistic crystal symmetries are realized, whether—in other words—a crystal does effectively have one of its possible relativistic symmetries.

Acknowledgements

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References

1) E. Ascher: Phys Letters **20** (1966) 352.
2) E. Ascher: Helv. phys. Acta **39** (1966) 465.
3) E. Ascher and A. Janner: Properties of Shubnikov Point Groups, BI-technical report.
4) I. F. Dzialoshinski: Soviet Physics-JETP **5** (1957) 1259.
5) B. A. Tavger: Kristallografiya **3** (1959) 339.
6) E. Ascher: Helv. phys. Acta **39** (1966) 40.
7) G. A. Smolensky and V. A. Joffe: *Communications du Colloque International de Magnétisme, Grenoble, 1958*, Communication No. 71.
8) G. A. Smolensky, V. A. Isupov, N. N. Krainik and I. Agranovskaya: Izv. Akad. Nauk SSSR Ser. fiz. **25** (1961) 1333.
9) E. Ascher, H. Rieder, H. Schmid and H. Stössel: J. appl. Phys. **37** (1966) 1404.
10) H. Schmid: Prost. Kristallov. **7** (1967) 32; Abstract in Acta cryst. Suppl. **21** (1967) A263.
11) H. Schmid and E. Ascher: to be appeared.
12) P. Curie: J. Phys., Ser. 3. **3** (1894) 393.
13) I. S. Zheludev and L. A. Shuvalov: Izv. Akad. Nauk SSSR, Ser. fiz. **21** (1957) 266.
14) L. A. Shuvalov: Kristallografiya **4** (1959) 399.
15) E. Ascher and A. Janner: to be appeared.
16) E. Ascher: Phil. Mag. **17** (1968) 149.
17) E. Ascher and A. Janner: Acta cryst. **18** (1965) 325.
18) H. Schmid, G. Kliegl and J. Kobayashi: to be appeared in Helv. phys. Acta.
19) T. Ito, N. Morimoto and R. Sadanaga: Acta cryst. **4** (1951) 310.
20) J. M. Troster: Phys. Status solidi **32** (1969) 179.
21) A. S. Sonin and I. S. Zheludev: Kristallografiya **4** (1959) 487.
22) A. S. Sonin and I. S. Zheludev: Kristallografiya **8** (1963) 283.
23) E. Ascher: Lattices of Equi-translation Subgroups of the Space Groups, BI-technical report.
24) L. L. Landau and E. M. Lifshitz: *Statistical Physics* (Pergamon, London, 1959)
25) E. Ascher and A. Janner: to be appeared.
26) B. A. Tavger and V. M. Zaitsev: Soviet Physics-JETP **30** (1956) 64.
27) A. Janner and E. Ascher: to be appeared.
28) E. Ascher and A. Janner: to be appeared.
29) E. J. Post: *Formal Structure of Electromagnetism* (North-Holland, Amsterdam, 1962)
30) T. H. O'Dell: Phil. Mag. **7** (1963) 1653.

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* The idea of mixed octahedra was developed by Janner and Ascher. A list of crystal structures containing such octahedra was established that comprised, among a few others, the boracites. At that moment the arrival of B. Elschner, who had done EPR-experiments on boracites, decided the preference given to these crystals.

** A systematic investigation of relativistic symmetries is being conducted together with A. Janner. The considerations presented here are part of that investigation.

DISCUSSION

G. A. SMOLENSKY: I find that the report by Dr. Ascher is very interesting. Today, we have three groups of compounds in which simultaneous electric polarization and magnetization take place: 1) perovskites, 2) hexagonal manganise, 3) boracites. The first group was discovered in the USSR, but these compounds have diffuse phase transitions and sometimes high conductivity. The second group was discovered in France. But this group has very big difference between electrical and magnetical Curie points. The third group was discovered by Ascher and Schmid it prooved to be most successful these authors have discovered interaction between magnetism and electrical polarization. The existence of electrical-magnetical effect may be understood from the following. It is well known that $\kappa_{mn}=-\partial^2\phi/\partial H^2$ and $\kappa_{ee}=-\partial^2\phi/\partial E^2$. Hence electrical-magnetical susceptibility is determined $\kappa_{me}=\kappa_{em}=-\partial^2\phi/\partial E\partial H$. While writing the thermodynamic pontential we must consider the magnetical structure of compounds. Unfortunately we have now only ferroelectrics-antiferromagnetics. It is very interesting to obtain ferroelectric-ferromagnetics.

E. ASCHER: I would be very interesting to find ordinary ferromagnetics with ferroelectric properties. It may be however that the interaction between the two spontaneous polarizations would be weaker than in the case of weak ferromagnetism. It seems indeed that the canting of the sublattice magnetizations is due precisely to the electric polarization in the case of Ni-I-boracite.

A. R. von HIPPEL: How far can the group-theoretical approach predict ferroelectric and anti-ferroelectric phenomena. It seems to me you can correct us experimental scientists as far as observations on structure and magnitude of constants is concerned, but a real molecular engineering starting with the periodic system is not yet possible. Which experimental parameters do you need as a starting point?

E. ASCHER: Indeed, it is impossible to predict by group-theory or otherwise, whether a compound with a given chemical formula will be ferroelectric or not. First one should predict whether the compound exist, then its crystal structure, and only after all that one could start thinking about the possible properties given however a known crystal it is possible, by considering some group theory with a detailed knowledge of the crystal structure to make me useful guesses. This however is perhaps not science but craft.

L. A. SHUVALOV: I should like to note that two points of view are possible when one consider usual crystal symmetry of the crystals having ferroelectric and ferromagnetic properties simultaneously. One can change operations of magnetic symmetry by operations of crystal symmetry; on the other hand one can reject these operations. Both approaches have no contradictions in terms. The first one is used in physics;[1,2] the second one is natural for crystalphysics.[3] Let us consider the example. The phase, in which Ni-I-boracite posseses ferroelectric and ferromagnetic properties simultaneously, has magnetic symmetry $mm'2'$. Consequently from the first point of view its usual crystal symmetry equals $mm2$, from the second one $-m$. Therefore crystalphysic approach shows that really Ni-I-boracite has in this phase monoclinic crystal symmetry and must have typical properties of monoclinic crystals. Particularly the index ellipsoid of the crystal must be rotated with change of the temperature around the normal to the mirror plane m. This effect can be found experimentally. At the same time first approach leads us to the conclusion that this phase of the Ni-I-boracite has orthorhombic crystal symmetry. Thus some morphic effects can fall out our consideration when first approach is used.

1) L. D. Landau and E. M. Lifshiz: *Elektrodinamika Sploshnykh Sred.* (Gostekhizdat, Moskva, 1957).
2) B. A. Tavger and V. M. Zaicev: Zh. eksper. teor. Fiz. 30 (1956) 564.
3) L. A. Shuvalov: Kristallografiya 4 (1959) 399.

E. ASCHER: This is a very interesting remarks and I completely agree. It seems to me that the mass distribution is described by $mm2$ the electromagnetic properties however by m.