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Magnetic Symmetry of Crystals

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The symmetry of crystals with a magnetic moment is considered. Besides coordinate transformations, transformations involving time reversal are investigated. The corresponding point groups are derived. It is shown that the structure of crystals which possess a magnetic moment is not invariant under time reversal.

1. INTRODUCTION

IN the determination of crystal symmetry, one regards the crystalline matter as a definite continuum. Such a description is statistical. In fact, the atoms and molecules of a crystal are all the time in motion. The crystalline continuum is to be understood as a time average over the state of the crystal. Below we shall be concerned with this average state.

A transformation which transforms this continuum into itself is called a symmetry transformation. The possible symmetry transformations depend on the properties of the continuum. One usually attributes to the crystalline continuum the following properties: (1) it is of infinite extent, (2) it is "rigid", i.e., under any symmetry transformation the distance between any two points of the continuum does not change; (3) it possesses a three-dimensional space lattice.

Condition (2) restricts the symmetry transformations of the continuum so as to reduce them to translations, rotations and reflections.[1] Condition (3) limits the possible symmetry transformations still further.[2] The existence of a space lattice rules out, for example, the occurrence of a rotation by $2\pi/5$.

The picture of a crystal as a continuum with the above properties is not rigorous. In a crystal some parts may move relative to the others. This motion may be described by a time averaged current density $\mathrm{j}(x,y,z)$. If charge is moving, then $\mathrm{j}(x,y,z)$ represents the time average of the electric current. In the equilibrium state of a crystal the average current density $\mathrm{j}(x,y,z)$ satisfies two conditions: (a) there must not be any sinks or sources for the current i.e., $\mathrm{div}\,\mathrm{j}=0$; (b) there must be no macroscopic current, i.e., the integral $\int \mathrm{j}\, dS$, taken over the surface of a unit cell, must vanish, since otherwise the state of the crystal would be energetically unfavorable.

For the vast majority of substances[3] $\mathrm{j}\equiv 0$; this applies to nonmagnetic, as well as paramagnetic and diamagnetic substances. On the other hand, ferromagnetic, antiferromagnetic and pyromagnetic substances must have $\mathrm{j}\neq 0$.

Crystals with $\mathrm{j}\neq 0$ should not be visualized as "rigid" structures, but rather as the stationary flow of a liquid, in which the flow velocity $\mathrm{v}(x,y,z)$ represents the current density $\mathrm{j}(x,y,z)$ and satisfies the conditions (a) and (b). In this manner we arrive at a picture of a crystalline continuum which differs from the usual one. This continuum may, in general, possess symmetry transformations which are not rotations, reflections, or translations. Any symmetry transformation of the continuum which we have defined can be made up of a transformation which treats it as a "rigid" structure, i.e., which satisfies condition (2), and a transformation of the current density $\mathrm{j}(x,y,z)$ which does not change the space coordinates.

The distribution of the mean current density j allows a transformation which is peculiar to vector quantities, viz., a reversal of its direction. This transformation is equivalent to a time reversal.[3] Following Landau and Lifshitz,[3] we denote this transformation by R. Then our continuum allows the transformations

$$M = RB, \qquad (1)$$

where B is a transformation which satisfies condition (2), i.e., consists of translations, rotations and reflections.

2. SOME PROPERTIES OF THE TRANSFORMATIONS INTRODUCED ABOVE. STATEMENT OF THE PROBLEM

Not every M can be a symmetry transformation.

[1] B. N. Delone, N. N. Padurov and A. D. Aleksandrov, *Mathematical Foundations of Structure Analysis*, Moscow-Leningrad, 1934.

[2] N. V. Belov, *Structural Crystallography*, Acad. Sci. USSR Press, 1951.

[3] L. L. Landau and E. M. Lifshitz, *Statistical Physics*, GITTL (State Tech. Lit. Press), 1951, p. 129.

If, in the expression (1) for M, which represents a symmetry transformation, we replace the time reversal by the identity operation E, M must go over into a symmetry transformation of the usual type, A.* Therefore, if M is a symmetry transformation,

$$M = RA. \tag{2}$$

In other words, a crystal with $\mathrm{j} \neq 0$ may possess symmetry transformations of the normal type A and those of the type $M = RA$.

However, not all transformations of the type (2) may occur as symmetry transformations for a crystal with $\mathrm{j} \neq 0$. For instance, in such a case R itself is not a symmetry transformation.[3] Indeed, if we apply R, we obtain $\mathrm{j} \equiv -\mathrm{j}$, which is possible only if $\mathrm{j} \equiv 0$. Equally excluded are those $M = RA$ for which A is of odd order ν. (The order of a symmetry transformation is the smallest positive exponent ν for which A^{ν} equals the identity operation E.[4]) To prove this, we first note the obvious properties of R: (a) R commutes with the symmetry transformations of the usual type A, i.e., $RA = AR$, since R acts only on j; (b) $RR = R^2 = E$.

Let $M = RA$, where A is of odd order ν. Then $M^{\nu} = R^{\nu} A^{\nu} = RA^{\nu} = R$. If we assume that M is a symmetry transformation, then M^{ν} must also be a symmetry transformation, and we arrive at a contradiction.

It follows from this, in particular, that the transformations R, and RL_3, where L_3 is a rotation through 120°, are ruled out.

We note the following properties for later use:

$$M^n = \begin{cases} M' & \text{for odd } n \\ A'' & \text{for even } n \end{cases} \tag{3}$$

$$M'M'' = A, \quad AM = M', \quad MA = M''$$

The set of symmetry transformations of a given crystal forms a group in the mathematical sense of the word. The elements of the group are the symmetry transformations, and the products of elements represent their successive application. The set of symmetry transformations for a crystal with $\mathrm{j} \neq 0$ also must form a group. There arises the question as to the possible groups of symmetry transformations of crystals with $\mathrm{j} \neq 0$. We shall in the following be concerned only with point transformations. The determination of these possible groups of point transformations is the main object of the present paper.

3. ALGORITHM FOR CONSTRUCTING THE POINT GROUPS

As a preliminary, we prove the following properties of the groups under consideration.

1. If the point transformations M_k and A_i form a group, it is impossible to choose i and k in such a way that $M_k = RA_i$. Assume the contrary: $M_k = RA_i$. Multiply both sides of this equality by $A^{\nu-1}$, where ν is the order of A: $M_k A_i^{\nu-1} = RA_i^{\nu} = R$. Since M_k and $A_i^{\nu-1}$ form a group of point transformations, $M_k A_i^{\nu-1}$ must also be a symmetry point transformation for the crystal with $\mathrm{j} \neq 0$. But R is not such a symmetry transformation. Hence we have arrived at a contradiction.

On the basis of this property we may adopt the following convention for the labels k and i. If M_k and A_i form a group, we shall always assume $i \neq k$, choosing $k = 1, 2, \ldots, m$; $i = m+1, m+2, \ldots, n$.

2. Assume that $M_k = RA_k$ and A_i form a group of point symmetry transformations. If we replace R by the identity E, i.e., M_k by A_k, then the resulting elements A_k and A_i form a group,[3] which must belong to one of the 32 symmetry classes, since after replacing R by E we no longer consider j, and thus arrive at the usual picture of the crystal as a rigid structure.

3. If $M_k = RA_k$ and A_i form a group of point symmetry transformations, the elements A_i form a subgroup. Indeed, $A_{i'} A_{i''}$ is a transformation of the normal type A, and hence not equal to M_k. Consequently $A_{i'} A_{i''} = A_{i'''}$, since the A_i and M_k form a group. The subgroup of the elements A_i must belong to one of the 32 crystal classes.

The properties listed above lead to an algorithm, as yet incomplete, for finding the groups of point symmetry transformations. Take a symmetry class. Let its elements form the group G. We find a subgroup H amongst the elements of G. The sub-

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*B differs from A in that B is an arbitrary combination of rotations, reflections and translations, whereas A includes only those compatible with a space lattice, which may belong to a crystal.

[4]A. G. Kurosh, *Theory of Groups*, GITTL (State Tech. Lit. Press), 1953.

Groups of point symmetry transformations for crystals with nonvanishing current density.

System	Symbol of symmetry class: Shubnikov	Symbol of symmetry class: Shoenfliess	Elements of symmetry class	Number of elements in the class (order)
Triclinic	1	C_1	E	1
	$\bar{2}$	C_i	$E,\ C$	2
Monoclinic	2	C_2	$E,\ L_{2z_0}$	2
	m	C_{1h}	$E,\ P$	2
	$2:m$	C_{2h}	$E,\ L_{2z} P_z,\ C$	4
Rhombic	$2:2$	D_2	$E,\ L_{2x},\ L_{2y},\ L_{2z}$	4
	$2\cdot m$	C_{2v}	$E,\ L_{2z},\ P_x,\ P_y$	4
	$m\cdot 2:m$	D_{2h}	$E,\ L_{2x},\ L_{2y},\ L_{2z},\ P_x,\ P_y,\ P_z,\ C$	8
	4	C_4	$E,\ L_{4z},\ L_{2z},\ L_{4z}^{-1}$	4
	$4:2$	D_4	$E,\ L_{4z},\ L_{2z},\ L_{4z}^{-1},\ L_{2x},\ L_{2y},\ L_{2xy},\ L_{2-xy}$	8
	$4:m$	C_{4h}	$E,\ L_{4z},\ L_{2z},\ L_{4z}^{-1},\ P_z,\ S_{4z},\ S_{4z}^{-1},\ C$	8
	$4\cdot m$	C_{4v}	$E,\ L_{4z},\ L_{2z},\ L_{4z}^{-1},\ P_x,\ P_y,\ P_{xy},\ R_{-xy}$	8
	$m\cdot 4:m$	D_{4h}	$E,\ L_{4z},\ L_{2z},\ L_{4z}^{-1},\ L_{2x},\ L_{2y},\ L_{2xy},\ L_{2-xy}$ $P_x,\ P_y,\ P_{xy},\ P_{-xy},\ P_z,\ S_{4z},\ C,\ S_{4z}^{-1}$	16
	$\bar{4}$	S_4	$E,\ S_{4z},\ L_{2z},\ S_{4z}^{-1}$	4
	$\bar{4}\cdot m$	D_{2d}	$E,\ S_{4z},\ L_{2z},\ S_{4z}^{-1},\ P_x,\ P_y,\ L_{2xy},\ L_{2-xy}$	8
Hexagonal	3	C_3	$E,\ L_{3z},\ L_{3z}^{-1}$	3
	$3:2$	D_3	$E,\ L_{3z},\ L_{3z}^{-1},\ 3L_{2\perp}$	6
	$3\cdot m$	C_{3v}	$E,\ L_{3z},\ L_{3z}^{-1},\ 3P_{\parallel}$	6
	$\bar{6}$	S_6	$E,\ S_{6z},\ L_{3z},\ C,\ L_{3z}^{-1},\ S_{6z}^{-1}$	6
	$\bar{6}\cdot m$	D_{3d}	$E,\ S_{6z},\ L_{3z},\ C,\ L_{3z}^{-1},\ S_{6z}^{-1},\ 3P_{\parallel},\ 3L_{2\perp}$	12
	$3:m$	C_{3h}	$E,\ L_{3z},\ L_{3z}^{-1},\ P_z,\ S_{3z},\ S_{3z}^{-1}$	6
	$m\cdot 3:m$	D_{3h}	$E,\ L_{3z},\ L_{3z}^{-1},\ 3P_{\parallel},\ P_z,\ S_{3z},\ S_{3z}^{-1},\ 3L_{2\perp}$	12

Groups of point symmetry transformations for crystals with nonvanishing current density.

Groups of point symmetry transformations for crystals with nonvanishing current density
1) E 1) E, C; 2) E, RC
1) E, L_{2z}; 2) E, RL_{2z} 1) E, P; 2) E, RP 1) $2:m$; 2) 2, RP_z, RC; 3) m, RL_{2z}, RC; $\overline{4}$) 2, RL_{2z}, RP_z
1) $2:2$; 2) 2, RL_{2x}, RL_{2y} 1) $2\cdot m$; 2) 2, RP_x, RP_y; 3) m, RL_{2z}, RP_y 1) $m\cdot 2:m$; 2) $2:2$, RP_x, RP_y, RP_z, RC 3) $2\cdot m$, RL_{2x}, RL_{2y}, RP_z, PC; 4) $2:m$, RL_{2x}, RL_{2y}, RP_x, RP_y
1) 4; 2) 2, RL_{4z}, RL_{4z}^{-1} 1) $4:2$; 2) 4, RL_{2x}, RL_{2y}, RL_{2xy}, RL_{2-xy}; 3) $2:2$, RL_{4z}, RL_{4z}^{-1}, RL_{2xy}, RL_{2-xy} 1) $4:m$; 2) 4, RP_z, PS_{4z}, RS_{4z}^{-1}, RC 3) $2:m$; RL_{4z}, RL_{4z}^{-1}, RS_{4z}, RS_{4z}^{-1}; 4) $\overline{4}$, RL_{4z}, RL_{4z}^{-1}, RP_z, RC 1) $4\cdot m$; 2) 4, RP_x, RP_y, RP_{xy}, RP_{xy}; 3) $2\cdot m$, RL_{4z}, RL_{4z}^{-1}, RP_{xy}, RP_{-xy} 1) $m\cdot 4:m$; 2) $4:2$, RP_x, RP_y, RP_{xy}, RP_{-xy}, RP_z, RS_{4z}, RS_{4z}^{-1}, RC 3) $4:m$, RL_{2x}, RL_{2y}, RL_{2xy}, RL_{2-xy}, RP_x, RP_y, RP_{xy}, RP_{-xy}; 4) $4\cdot m$, $RL_{2x}RL_{2y}RL_{2xy}$, RL_{2-xy} RP_z, RS_{4z}, RC, RS_{4z}^{-1}; 5) $m\cdot 2:m$, RL_{4z}, RL_{4z}^{-1}, RS_{4z}, RS_{4z}^{-1}, RL_{2x}, RL_{2y}, RP_{xy}, RP_{-xy} 6) $\overline{4}\cdot m$, RL_{4z}, RL_{4z}^{-1}, RP_{xy}, RP_{-xy}, RL_{2x}, RL_{2y}, RC, RP_z 1) $\overline{4}$; 2) 2, RS_{4z}^{-1}, RS_{4z} 1) $\overline{4}\cdot m$; 2) $\overline{4}$, RP_x, RP_y, RL_{2xy}, RL_{2-xy} 3) $2:2$, RS_{4z}, RS_{4z}^{-1}, RP_x, RP_y; 4) $2\cdot m$, RS_{4z}^{-1}, RS_{4z}, $RL_{2xy}RL_{2-xy}$
1) 3 1) $3:2$; 2) 3, $3RL_{2\perp}$ 1) $3\cdot m$; 2) 3, $3P_{\perp}P_{\parallel}$ 1) $\overline{6}$; 2) 3, RS_{6z}, RC, RS_{6z}^{-1} 1) $\overline{6}\cdot m$; 2) $3:2$, RS_{6z}, RC, RS_{6z}^{-1}, $3RP_{\parallel}$ 3) $3\cdot m$, RS_{6z}, RC, RS_{6z}^{-1}, $3RL_{2\perp}$; 4) $\overline{6}$, $3RP_{\parallel}$, $3RL_{2\perp}$ 1) $3:m$; 2) 3, RP_z, RS_{3z}, RS_{3z}^{-1} 1) $m\cdot 3:m$; 2) $3\cdot m$, $3RP_{\parallel}$, $3RL_{2\perp}$; 3) $3\cdot m$, RP_z, RS_{3z}, RS_{3z}^{-1}, $3RL_{2\perp}$ 4) $3:2$, RP_z, RS_{3z}, RS_{3z}^{-1}, $3RP_{\parallel}$

Hexagonal	6	C_6	$E, L_{6z}, L_{3z}, L_{6z}^{-1}, L_{3z}^{-1}, L_{2z}$	6
	6 : 2	D_6	$E, L_{6z}, L_{3z}, L_{6z}^{-1}, L_{3z}^{-1}, L_{2z}, 6L_{2\perp}$	12
	6 : *m*	C_{6h}	$E, L_{6z}, L_{3z}, L_{2z}, L_{3z}^{-1}, L_{6z}^{-1}, P_z, S_{6z}$ $S_{3z}, S_{3z}^{-1}, S_{6z}^{-1}, C$	12
	6·*m*	C_{6v}	$E, L_{6z}, L_{3z}, L_{2z}, L_{3z}^{-1}, L_{6z}^{-1}, 6P_{\parallel}$	12
	m·6 : *m*	D_{6h}	$E, L_{6z}, L_{3z}, L_{2z}, L_{3z}^{-1}, L_{6z}^{-1}, 6P_{\parallel}$ $6L_{2\perp}, P_z, S_{6z}, S_{3z}, C, S_{3z}^{-1}, S_{6z}^{-1}$	24
Cubic	3/2	T	$E, 3L_2, 4L_3, 4L_3^{-1}$	12
	$\overline{6}/2$	T_h	$E, 3L_2, 4L_3, 4L_3^{-1}, 4S_6, C, 4S_6^{-1}, 3P$	24
	$3/\overline{4}$	T_d	$E, 3L_2, 4L_3, 4L_3^{-1}, 6P, 3S_4, 3S_4^{-1}$	24
	3/4	O	$E, 3L_2, 4L_3, 4L_3^{-1}, 3L_4, 3L_4^{-1}, 6L_2$	24
	$\overline{6}/4$	O_h	$E, 3L_2, 4L_3, 4L_3^{-1}, 3L_4, 3L_4^{-1}, 6L_2$ $6P, 3P, C, 3S_4, 3S_4^{-1}, 4S_6, 4S_6^{-1}$	48

Hexagonal	1) 6; 2) 3, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}$
	1) 6 : 2; 2) 6, $6RL_{2\perp}$; 3) 3 : 2, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, 3RL_{2\perp}$
	1) 6 : *m*; 2) 3 : *m*, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, RS_{6z}, RS_{6z}^{-1}, RC$; 3) 6, $RP_z, RS_{6z}, RS_{3z}, RC, RS_{3z}^{-1}, RS_{6z}^{-1}$; 4) $\overline{6}$, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, RP_z, RS_{3z}, RS_{3z}^{-1}$
	1) 6·*m*; 2) 6, $6RP_{\parallel}$; 3) 3·*m*, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, 3RP_{\parallel}$
	1) *m*·6 : *m*; 2) *m*·3 : *m*, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, 3RP_{\parallel}, 3RL_{2z}, RS_{6z}, RC, RS_{6z}^{-1}$; 3) 6 : *m*, $6RP_{\parallel}, 6RL_{2\perp}$; 4) $\overline{6}$·*m*, $RL_{6z}, RL_{2z}, RL_{6z}^{-1}, 3RP_{\parallel}, 3RL_{2\perp}, RP_z, RS_{3z}, RS_{3z}^{-1}$; 5) 6 : 2, $6RP_{\parallel}, RP_z, RS_{6z}, RS_{3z}, RC, RS_{3z}^{-1}, RS_{6z}^{-1}$; 6) 6·*m*, $6RL_{2\perp}, RP_z, RS_{6z}, RS_{3z}, RC, RS_{3z}^{-1}, RS_{6z}^{-1}$
Cubic	1) 3/2
	1) $\overline{6}/2$; 2) 3/2, $4RS_6, 4RS_6^{-1}, RC, 3RP$
	1) $3/\overline{4}$; 2) 3/2, $6RP, 3RS_4, 3RS_4^{-1}$
	1) 3/4; 2) 3/2, $3RL_4, 3RL_4^{-1}, 6RL_2$
	1) $\overline{6}/4$; 2) 3/4, $6RP, 3RP, RC, 3RS_4, 3RS_4^{-1}, 4RS_6, 4RS_6^{-1}$; 3) $3/\overline{4}$; $3RL_4, 3RL_4^{-1}, 6RL_2, 3RP, RC, 4RS_6, 4RS_6^{-1}$; 4) $\overline{6}/2$; $3RL_4, 3RL_4^{-1}, 6RL_2, 6RP, 3RS_4, 3RS_4^{-1}$

group H must also belong to one of the 32 symmetry classes. Multiply by R all elements of G-H, i.e., all those belonging to G, but not to H. These give $RA_k = M_k$. If the set of elements M_k and A_i forms a group, then this is of the required type. This algorithm would allow us to derive all the required groups. However, the construction of all the required groups by means of this proposed algorithm is extremely laborious, since it involves checking the group property for many sets of elements.

In order to perfect an algorithm to derive the groups of point symmetry transformations we prove the following theorem, which makes it easy to pick out from the symmetry classes such subgroups, for which the set A_i and M_k automatically form a group.

Theorem. Let the set A_k ($k = 1, 2, \ldots, m$) and A_i ($i = m+1, m+2, \ldots, n$) form a group G, and let the set A_i ($i = m+1, m+2, \ldots, n$) be a subgroup H of G. Then a necessary and sufficient condition for the set $M_k = RA_k$ ($k = 1, 2, \ldots, m$) and A_i ($i = m+1, m+2, \ldots, n$) to form a group is that the index* of H be 2.

We note that $A_k A_i$ and $A_i A_k$ do not belong to H. Consequently

$$A_k A_i = A_{k'} \in G - H, \tag{4}$$

$$A_i A_k = A_{k''} \in G - H.$$

We first prove our condition to be necessary.

$M_k M_{k'} = A_k A_{k'} R^2 = A_k A_{k'}$, which by (3) equals A_i:

$$A_k A_{k'} = A_i. \tag{5}$$

Take one A_k and multiply it successively by all the A_k. The products will according to (5) be A_i elements, which must all be different. Hence the number of elements A_k does not exceed the number of the elements A_i, i.e., the index of the subgroup must be 2.

Now we prove the condition to be sufficient.

Since the number of elements is finite, it is not necessary for establishing the group property of the set to show the existence of a unit element or of an inverse. The associative property is obvious. It remains only to prove that the set is closed. There exist the following types of products of elements: $A_i A_i$, $A_i M_k$, $M_k A_{i'}$, $M_k M_{k'}$.

$A_i A_{i'} = A_{i''}$ since the set of the A_i forms a subgroup; $A_i M_k = A_i A_k R$ is by (4) equal to $A_{k'} R = M_{k'}$; $M_k A_i$ is similarly equal to $M_{k''}$; $M_k M_{k'} = A_k A_{k'} R^2 = A_k A_{k'}$. Since the index of the subgroup is 2, any $A_k = \alpha A_i$, where α is one of the A_k. Hence $M_k M_{k'} = \alpha A_i A_{k'}$ and by (4) this is equal to $\alpha A_{k''} = \alpha^2 A_{i'}$. In other words, $M_k M_{k'} = \alpha A_{i'}$. It is easy to see that $\alpha^2 = A_{i''} \in H$. Therefore $M_k M_{k'} = A_{i'''}$.

This completes the proof.

Now we can formulate the final algorithm for finding all point symmetry groups. The groups of point transformations of the symmetry of crystals with $j \neq 0$ will contain, in the first place the 32 symmetry classes. To find all the others, we take a symmetry class, select from it a sub-class (the subgroup H) which has index 2. The elements of the class A_k which do not belong to the subclass are replaced by $M_k = RA_k$. The elements A_i of the suclass and the elements $M_k = RA_k$ form the required group. In order to find all possible such groups we have to investigate all 32 symmetry classes.

We must only remember that in a crystal with $j \neq 0$ the transformations R and RL_3 cannot occur as symmetry transformations. This point will prove important in the hexagonal and cubic systems.

4. LIST OF GROUPS OF POINT TRANSFORMATIONS FOR THE SYMMETRY OF CRYSTALS WITH A MEAN CURRENT DENSITY.

We list below the groups of point transformations obtained by the method proposed above. In the table we use the following notation:

L_2, L_3, L_3^{-1}, L_4, L_4^{-1}, L_6, L_6^{-1} are rotations by 180, 120, -120, 90, -90, 60 and -60 degrees, respectively. S_3, S_3^{-1}, S_4, S_4^{-1}, S_6, S_6^{-1} are, respectively rotations by 120, -120, 90, -90, 60, -60 degrees together with reflection in the plane at right angles to the axis of rotation. C is the inversion, P the

*By the index of a subgroup we denote the number of classes in the expansion of the group with respect to the subgroup. The index of a subgroup equals the ratio of the number of elements of the group (its order) to the number of elements of the subgroup.[4]

reflection in a plane.

The subscripts x, y, z, xy, $-xy$ on L_i and S_i indicate the direction of the axis of rotation; the same subscripts on P indicate the direction of the normal to the plane of reflection.

The suscript $\perp$ or $||$ indicates that the axis of rotation through 180° or the normal to the reflection plane is perpendicular or parallel to the main crystal axis of threefold or higher symmetry. The table also shows the symmetry class to which each group of point symmetry transformation belongs, i.e., the class obtained from it by substituting E for R.

In the last column of the table the symbol of a symmetry class stands for the set of transformations belonging to that class.

The allocation of the groups of point symmetry transformations to symmetry classes has a definite meaning. The point is that goniometric and X-ray analysis discloses only the symmetry of the charge distribution $\rho(x,y,z)$ and does not notice the current $j(x,y,z)$. The symmetry which is found by goniometric and X-ray methods is therefore just that of the symmetry class which is obtained if we replace R by E in the group of point symmetry transformations, since for the charge density $\rho(x,y,z)$ the transformation R has the same effect as the identity operation. Altogether there are 90 groups of point symmetry transformations for crystals with $j \neq 0$; of these 32 coincide with the 32 symmetry classes, and 58 are new.

The groups obtained in this way are isomorphous with the groups of transformations of finite figures, with oriented grains, which were derived by Shubnikov[5] by a different method. There the part of time reversal is played by an "anti-identity" transformation. The 58 new groups are isomorphous with the groups of mixed polarity.*

5. POSSIBLE APPLICATIONS OF THE GROUPS OF POINT SYMMETRY TRANSFORMATIONS OF CRYSTALS

Above we have discussed the symmetry of crystals with $j \neq 0$. It is well known that a magnetic moment is equivalent to a current, and therefore the groups we have derived for crystals with $j \neq 0$ are also the symmetry groups for crystals with a magnetic moment. It has to be remembered that the magnetic moment is an axial vector. A symmetry transformation which does not contain a reflection acts on the magnetic moment as on an ordinary vector, but a reflection changes the direction of the axial vector in the opposite sense to that of an ordinary vector. The symmetry of the magnetic moment vector includes the symmetry transformations of the class $\infty : m$. In addition, the magnetic moment vector is symmetrical under the transformation $RP_{||}$, where $P_{||}$ is a reflection in a plane passing through the magnetic moment vector, and the transformation $RL_{2\perp}$ where $L_{2\perp}$ is a rotation through 180° about an axis at right angles to the magnetic moment vector.

As an example, let us find the possible symmetry of a pyromagnetic substance. We use the symmetry principle in a similar manner to the one used for pyromagnetic crystals in reference 6. Remembering what was said above about the symmetry of the magnetic moment vector, it turns out that pyromagnetic crystals cannot belong to the cubic system. This conclusion differs from that drawn in Ref. 6.

Recently the opinion has been expressed[7] that pyromagnetism, piezomagnetism, etc., are impossible. This paper starts from the assumption that the crystal structure must be symmetric under time reversal. But this does not hold for crystals which possess a magnetic moment. We therefore consider that the conclusions drawn in Ref. 7 as to the impossibility of pyromagnetism and piezomagnetism, is unfounded.

*Shubnikov has 57 groups of mixed polarity. Actually there are 58.

[5]A. N. Shubnikov, *Symmetry and Antisymmetry of Finite Figures*, Acad. Sci. USSR Press, 1951.

[6]A. N. Shubnikov, E. E. Flint and T. B. Bokii. *Foundations of Crystallography*, Acad, Sci. USSR Press, 1940.

[7]W. Zochera and H. Török, Proc. Nat. Acad. Sci. 39, 681 (1953).

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