

# THE CHANGE OF COMPLETE SYMMETRY OF THE CRYSTALS DURING THE PHASE TRANSITIONS IN FERROELECTRICS AND FERROMAGNETICS

BY I. S. ZHELUDEV\*

(Department of Physics, Indian Institute of Science, Bangalore-12)

Received September 23, 1963

(Communicated by Dr. R. S. Krishnan, F.A.Sc.)

## 1. INTRODUCTION

COMPLEMENTARY and complete symmetries of scalars, vectors and tensors of the second rank and the derivation of complete symmetry groups for these values were given in the paper [Zheludev, 1960 (a)]. By definition, the elements of complementary symmetry are antirotation axes (antiaxes) and antireflection-rotation axes (antimirror axes). These are denoted by  $\underline{1}, \underline{2}, \underline{3}, \underline{4}, \underline{5}, \underline{6} \dots \underline{\infty}$  and  $\overline{1}, \overline{2}, \overline{3}, \overline{4}, \overline{5}, \overline{6} \dots \overline{\infty}$  respectively (the antireflection axis  $\overline{1}$ , being an antiplane, is denoted by  $\underline{m}$ ) and satisfy the following conditions:

(a) a tensor has, as a complementary symmetry element, an antiaxis of any order, if a simple rotation of the system through an angle corresponding to the order of this axis, causes all components of the tensor to change the signs without changing their absolute value;

(b) a tensor has, as a complementary symmetry element, an antimirror axis of any order, if all components of the tensor change in sign without change in value, when the co-ordinate system is transformed in accordance with the corresponding operation of the mirror axis.

The groups of complete symmetry of the tensors are the groups which include both the ordinary symmetry operations (rotations and mirror rotations) and the operations of complementary symmetry (antirotations and antimirror rotations). The comparison of antisymmetry (Shubnikov, 1951), magnetic symmetry (Tavger and Zaitsev, 1956) and complete symmetry is given in the paper [Zheludev (1960 c)].

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\* Visiting Professor from the Institute of Crystallography, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

As was shown in the paper referred to earlier [Zheludev, 1960 (a)] there are only ten groups of complete symmetry of a polar tensor of the second rank (determining, in particular, a scalar and an axial vector) namely,  $\infty/m.\infty:m$  (scalar group),  $\underline{m}.\infty:m$  (axial vector group),  $m.\infty:m$ ,  $\infty:m$ ,  $m.2:m$ ,  $\underline{m}.4:m$ ,  $2:m$ ,  $\underline{m}.2:m$ ,  $2:\underline{m}$ ,  $\bar{2}$ .

In a similar manner, it can be shown that ten groups of complete symmetry for an axial tensor of the second rank (which, in particular case, determines pseudoscalar and polar vector) are:  $\infty/\underline{m}.\infty:\underline{m}$  (pseudoscalar group);  $m.\infty:\underline{m}$  (polar vector group),  $\underline{m}.\infty:\underline{m}$ ,  $\infty:\underline{m}$ ,  $\underline{m}.2:\underline{m}$ ,  $\underline{m}.4:\underline{m}$ ,  $2:\underline{m}$ ,  $\underline{m}.2:m$ ,  $2:m$ ,  $\bar{2}$ .

## 2. PRINCIPLE OF SYMMETRY SUPERPOSITION IN COMPLETE SYMMETRY. ULTIMATE AND CRYSTALLOGRAPHICAL GROUPS OF COMPLETE SYMMETRY

The interpretation of complete symmetry can be referred not only to tensors but also to the finite figures. This can be easily done by considering the superposition of elements of complete symmetry of the figures presenting the tensor symmetry. For this purpose, first of all, it is necessary to generalize the superposition principle (Curie principle) for the case of complete symmetry. The simplest formulation of the principle of symmetry superposition (Curie principle) is as follows: *the symmetry elements of the composed figure are identical coinciding elements of its components*. The symmetry group of the composed figure will be the highest common subgroup of the symmetry groups of the components, corresponding to the mutual orientation considered of the symmetry elements of the parts.\*

The natural extension of the principle of the symmetry superposition for the case of complete symmetry is a generalization, stating that *the elements of complete symmetry of the composed figure are identical coinciding elements of complete symmetry of its parts*. This means, for instance, that if the antiplanes  $\underline{m}$  of the two parts do coincide, then composed figure will have the antiplane  $\underline{m}$ ; if the plane  $m$  and the antiplane  $\underline{m}$  of the components coincide, then there will be no similarly oriented plane and antiplane in the composed figure. The same is also true for the rotation axes, mirror rotation axes, anti-axes and antimirror axes. For instance, two mirror rotation axes coinciding in direction can form mirror rotation axis in a composed figure.

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\* The cases of superposition resulting in enhancing the symmetry are not considered here.

However, a coincidence in direction of a mirror axis and an antimirror axis of the components will not give any axis for the composed figure, etc. Another statement that can be made in case of complete symmetry is as follows: *the groups of complete symmetry of composed figure is the highest common subgroup of the groups of complete symmetry of the parts, corresponding to the mutual orientation considered of the elements of the symmetry of the parts.* Ultimate and crystallographical groups of complete symmetry will be obtained below by considering the superpositions of complete symmetries of scalars, vectors and tensors.

It was shown in the paper [Zheludev, 1960 (b)] that there are 14 ultimate groups of complete symmetries of scalars, vectors and tensors of the second rank. Eight of them are the groups of complete symmetry (mentioned in the introduction) of polar and axial tensors of the second rank having axes of symmetry of the infinite order ( $\infty$ ). Six new groups  $\infty/\infty$ ,  $\infty.m$ ,  $\infty.\underline{m}$ ,  $\infty:2$ ,  $\infty:\underline{2}$ , and  $\infty$  are obtained as a result of various superpositions of the elements of complete symmetry of the figures which represent the above said eight groups. It is to be noted, however, that new ultimate groups can be obtained only in the superpositions in which the symmetry axes ( $\infty$ ) coincide with each other.

All the above-mentioned 14 ultimate groups of complete symmetry include all the seven ultimate groups of usual symmetry introduced by P. Curie, namely,  $\infty/m$ ,  $\infty:m$ ,  $\infty/\infty$ ,  $m.\infty:m$ ,  $\infty:2$ ,  $\infty:m$ ,  $\infty.m$ ,  $\infty$ .

There are twelve crystallographical groups among the groups of complete symmetry of the polar and axial tensors of the second rank. Various combinations of the figures having the symmetry of these groups result in 21 new crystallographical groups, namely:  $\underline{4}:m$ ;  $\underline{4}:\underline{m}$ ;  $\bar{4}$ ;  $\bar{4}$ ;  $\bar{4}.\underline{m}$ ;  $\bar{4}.m$ ;  $\bar{4}.\underline{m}$ ;  $\bar{4}.m$ ;  $\underline{4}:2$ ;  $\underline{4}:2.m$ ;  $\underline{2}.m$ ;  $\underline{2}.\underline{m}$ ;  $\underline{2}:2$ ;  $\underline{2}:2$ ;  $m$ ;  $\underline{m}$ ;  $2$ ;  $\underline{2}$ ;  $1$ .

From the total number of 33 (12 + 21) crystallographical groups of complete symmetry, 20 groups represent all the symmetry groups of low systems (triclinic, monoclinic, rhombic) and 13 groups represent a part of the tetragonal system groups.

These above-considered 33 crystallographical groups and 14 ultimate groups can be arranged in 11 rows, their type being as follows:

$$m.1:m (2.m); m.2:m \dots m.\infty:m$$

$$\underline{m}.1:\underline{m} (2.\underline{m}); \underline{m}.2:\underline{m} \dots \underline{m}.\infty:\underline{m}.$$

It is obvious that 33 new crystallographical groups  $m.3:m$ ;  $m.4:m$ ;  $\underline{m}.6:m$ , etc., can be obtained by changing the axis  $\infty$  for the crystallographical axis of the order 3, 4 and 6 (medium systems) in each row.

Having arranged some groups out of 33 in 11 rows, another 13 rows can be formed. They are as follows:

$$\underline{2}: \underline{m}; \underline{4}: \underline{m} \dots$$

$$\underline{2}.m; \underline{4}.m \dots$$

and are not completed by the ultimate groups but they can produce additional 13 crystallographical groups possessing the axes  $\underline{6}$ ,  $\bar{6}$ ;  $\bar{6}$ . Thus, the total number of groups of low and medium systems found appears to be equal to 79 (33 + 33 + 13). The number of crystallographical groups of the cubic system is equal to 11. They can be obtained by considering the symmetry of the cube distorted by scalar, vector and tensor influences, as well as by combination of these influences, *i.e.*, influences exerted by polar, scalar and axial tensors together.

Thus, the total number of crystallographical groups of complete symmetry is equal to 90. They include the 32 groups of usual symmetry. In complete symmetry, these groups are considered as the groups which do not include the polar vector components (these are polar, one-colour groups in the anti-symmetry). Table I shows complete symmetry for all the crystal classes by enumerating all elements of symmetry belonging to the given class. The rotations are designated by the letter L, the order of the axis being given in the indices. For simple rotations, they are given above, for antirotations, mirror-rotations and antimirror-rotations—below. The symmetry plane (operation  $\bar{1}$ ) is designated by P, an antiplane (operation  $\bar{1}$ ) by  $\underline{P}$ . The centre of symmetry (operation  $\bar{2}$ ) is designated by C, the anticentre (operation  $\bar{2}$ ) by  $\underline{C}$ . The symbols of the complete symmetry classes according to the international convention (international symbols) and the subclasses of usual symmetry for all classes of complete symmetry are also given in Table I. Geometrical interpretation for some groups of complete symmetry is given in Fig. 1.

### 3. FERROELECTRIC PHASE TRANSITIONS

By ferroelectric phase transitions are meant such transitions in which there appears an electrical polarization  $\vec{P}_s$  in the initially non-polar para-electric

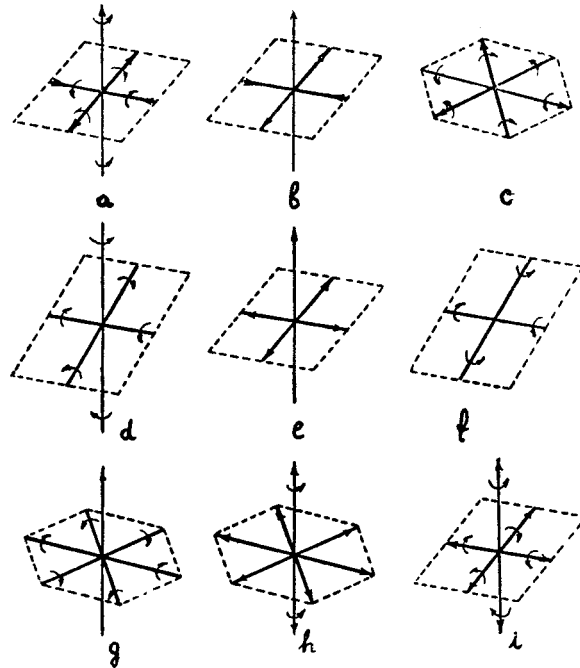


FIG. 1. Some of the groups of complete symmetry in vector and tensor interpretation: *a*,  $\underline{2}:2$ ; *b*,  $\underline{4}.m$ ; *c*,  $\underline{6}:2$ ; *d*,  $\underline{m}.2:m$ ; *e*,  $\underline{4}.m$ ; *f*,  $\underline{2}.m$ ; *g*,  $\underline{m}.3:m$ ; *h*,  $\underline{6}:m$ ; *i*,  $\underline{4}:2$ .

unit cells of the crystals. The directions of polarization in adjacent cells of the ferroelectric crystals are parallel and in the antiferroelectric crystals they are antiparallel. As a result of the polarization, the cells become *polar* and acquire the complete symmetry of one of the polar crystal classes. Complete symmetry of the polar crystals is described by one of the groups of complete symmetry, these being the subgroups of complete symmetry of a polar vector  $m.\infty:\underline{m}$ . There are 31 subgroups of the polar groups of complete symmetry of the crystals (see Table I):  $1$ ;  $\underline{2}$ ;  $\underline{2}$ ;  $\underline{2}$ ;  $\underline{m}$ ;  $\underline{m}$ ;  $\underline{2}:\underline{m}$ ;  $\underline{2}:\underline{m}$ ;  $\underline{2}:\underline{2}$ ;  $\underline{2}.m$ ;  $\underline{2}.m$ ;  $\underline{m}.\underline{2}:\underline{m}$ ;  $\underline{4}:\underline{4}:\underline{2}$ ;  $\underline{4}:\underline{m}$ ;  $\underline{4}.m$ ;  $\underline{m}.\underline{4}:\underline{m}$ ;  $\underline{4}$ ;  $\underline{4}.m$ ;  $\underline{3}$ ;  $\underline{3}:\underline{2}$ ;  $\underline{3}.m$ ;  $\underline{6}$ ;  $\underline{6}.m$ ;  $\underline{3}:\underline{m}$ ;  $\underline{m}.\underline{3}:\underline{m}$ ;  $\underline{6}$ ;  $\underline{6}:\underline{2}$ ;  $\underline{6}:\underline{m}$ ;  $\underline{6}.m$ ;  $\underline{m}.\underline{6}:\underline{m}$ . The same groups can be named the groups of complete symmetry of the *pyroelectric crystals*. In ferroelectric crystals, one of these groups of complete symmetry has the domain—a region of spontaneous polarization with the same direction of  $\vec{P}_s$ . In the antiferroelectric crystals, these groups of complete symmetry have the subcells, *i.e.*, the former unit cells of the para-electric modification.

TABLE I  
Classes of complete symmetry of the crystals

Systems		Notation of the class by Shubnikov	“International” symbols	The formula of complete symmetry	Subclass of usual symmetry
1	2	3	4	5	6
1	Triclinic	.. 1	1	$L^1$	1
2	„	.. $\underline{2}$	$\bar{1}'$	$L^1_{\underline{2}} = \underline{C}$	1
3	„	.. $\bar{2}$	$\bar{1}$	$L^1_{\bar{2}} = \underline{C}$	$\bar{2}$
4	Monoclinic	.. $\underline{2}$	$2'$	$L^1_{\underline{2}}$	1
5	„	.. 2	2	$L^2$	2
6	„	.. $\underline{m}$	$m'$	$L^1_{\underline{1}} = \underline{P}$	1
7	„	.. m	m	$L^1_{\underline{1}} = \underline{P}$	m
8	„	.. $\underline{2} : \underline{m}$	$2'/m'$	$L^2_{\underline{2}} \underline{PC}$	$\bar{2}$
9	„	.. $\underline{2} : \underline{m}$	$2/m'$	$L^2_{\underline{2}} \underline{PC}$	2
10	„	.. $\underline{2} : m$	$2'/m$	$L^2_{\underline{2}} \underline{PC}$	m
11	„	.. $\underline{2} : m$	$2/m$	$L^2_{\underline{2}} \underline{PC}$	$2 : m$
12	Rhombic	.. $\underline{2} : 2$	$2'2'2$	$L^2_{\underline{2}} L_{\underline{2}}$	2
13	„	.. $\underline{2} : 2$	222	$3L^2$	$2 : 2$
14	„	.. $\underline{2} : \underline{m}$	$m'm'2$	$L^2_{\underline{2}} \underline{P}$	2
15	„	.. $\underline{2} : m$	$m'm'2'$	$L^1_{\underline{2}} \underline{PP}$	m
16	„	.. $\underline{2} : m$	mm2	$L^2_{\underline{2}} \underline{P}$	$2 : m$
17	„	.. $\underline{m} : 2 : m$	$m'm'm$	$L^2_{\underline{2}} 2L_{\underline{2}} \underline{P} 2 \underline{PC}$	$2 : m$
18	„	.. $\underline{m} : 2 : \underline{m}$	$m'm'm'$	$3L^2_{\underline{2}} 3 \underline{PC}$	$2 : 2$
19	„	.. $\underline{m} : \underline{2} : m$	$m'mm$	$L^2_{\underline{2}} 2L_{\underline{2}} \underline{P} 2 \underline{PPC}$	$2 : m$
20	„	.. $\underline{m} : 2 : m$	mmm	$3L^2_{\underline{2}} 3 \underline{PC}$	$\underline{m} : 2 : m$
21	Tetragonal	.. $\underline{4}$	$4'$	$L^2_{\underline{4}}$	2
22	„	.. 4	4	$L^4$	4
23	„	.. $\underline{4} : 2$	$4'22'$	$L^2_{\underline{4}} 2L^2_{\underline{2}} L_{\underline{2}}$	$2 : 2$
24	„	.. $\underline{4} : \underline{2}$	$42'2'$	$L^4 L_{\underline{2}}$	4
25	„	.. $\underline{4} : 2$	422	$L^4 L^2$	$4 : 2$
26	„	.. $\underline{4} : m$	$4'/m$	$L^2_{\underline{4}} \underline{PC}$	$2 : m$
27	„	.. $\underline{4} : \underline{m}$	$4/m'$	$L^2_{\underline{4}} \underline{PC}$	4

TABLE I (Contd.)

Systems	Notation of the class by Shubnikov	"International" symbols	The formula of complete symmetry	Subclass of usual symmetry	
1	2	3	4	5	6
28	Tetragonal ..	$\underline{4:m}$	$4'/m'$	$L^2_{\frac{1}{2}\frac{1}{2}}PC$	$\bar{4}$
29	„ ..	$4:m$	$4/m$	$L^4_4PC$	$4:m$
30	„ ..	$\underline{4.m}$	$4'm'm$	$L^2_{\frac{1}{2}}2P2P$	$2.m$
31	„ ..	$\underline{4.m}$	$4m'm'$	$L^4_4P$	$4$
32	„ ..	$4.m$	$4mm$	$L^4_4P$	$4.m$
33	„ ..	$\underline{m.4:m}$	$4'/mmm'$	$L^2_{\frac{1}{2}\frac{1}{2}}2L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}3P2PC$	$m.2:m$
34	„ ..	$\underline{m.4:m}$	$4/m'm'm'$	$L^4_4L^2_{\frac{1}{2}}5PC$	$4:2$
35	„ ..	$\underline{m.4:m}$	$4/mm'm'$	$L^4_4L^2_{\frac{1}{2}}P4PC$	$4:m$
36	„ ..	$\underline{m.4:m}$	$4/m'mm$	$L^4_4L^2_{\frac{1}{2}}4PPC$	$4.m$
37	„ ..	$\underline{m.4:m}$	$4'/m'mm'$	$L^2_{\frac{1}{2}\frac{1}{2}}2L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}2P3PC$	$\bar{4}.m$
38	„ ..	$\underline{m.4:m}$	$4/mmm$	$L^4_4L^2_{\frac{1}{2}}5PC$	$m.4:m$
39	„ ..	$\bar{4}$	$\bar{4}'$	$L^2_{\frac{1}{2}}$	$2$
40	„ ..	$\bar{4}$	$\bar{4}$	$L^2_{\frac{1}{2}}$	$\bar{4}$
41	„ ..	$\underline{\bar{4}.m}$	$\bar{4}'2'm'$	$L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}2P$	$2$
42	„ ..	$\underline{\bar{4}.m}$	$\bar{4}'2'm$	$L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}2P$	$2.m$
43	„ ..	$\underline{\bar{4}.m}$	$\bar{4}'2m'$	$L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}2P$	$2:2$
44	„ ..	$\underline{\bar{4}.m}$	$\bar{4}2m$	$L^2_{\frac{1}{2}}2L^2_{\frac{1}{2}}2P$	$\bar{4}.m$
45	Rhombohedral..	$3$	$3$	$L^3$	$3$
46	„ ..	$3:\underline{2}$	$3/2'$	$L^3_3L^2_{\frac{1}{2}}$	$3$
47	„ ..	$3:2$	$3/2$	$L^3_3L^3$	$3:2$
48	„ ..	$3:\underline{m}$	$3m'$	$L^3_3P$	$3$
49	„ ..	$3.m$	$3m$	$L^3_3P$	$3.m$
50	„ ..	$\bar{6}$	$\bar{3}'$	$L^3_{\frac{1}{2}}3C$	$3$
51	„ ..	$\bar{6}$	$\bar{3}$	$L^3_{\frac{1}{2}}C$	$\bar{6}$
52	„ ..	$\underline{\bar{6}.m}$	$\bar{3}'/m'$	$L^3_{\frac{1}{2}}3L^2_{\frac{1}{2}}3PC$	$3:2$
53	„ ..	$\underline{\bar{6}.m}$	$\bar{3}'/m$	$L^3_{\frac{1}{2}}3L^2_{\frac{1}{2}}3L^2_{\frac{1}{2}}3PC$	$3.m$
54	„ ..	$\underline{\bar{6}.m}$	$\bar{3}/m'$	$L^3_{\frac{1}{2}}3L^2_{\frac{1}{2}}3L^2_{\frac{1}{2}}3PC$	$\bar{6}$
55	„ ..	$\underline{\bar{6}.m}$	$\bar{3}/m$	$L^3_{\frac{1}{2}}3L^2_{\frac{1}{2}}3PC$	$\bar{6}4m$

TABLE I (Contd.)

Systems		Notation of the class by Shubnikov	“International symbols	The formula complete of symmetry	Subclass usual of symmetry
1	2	3	4	5	6
56	Hexagonal ..	3: <u>m</u>	$\bar{6}'$	$L^3_3P$	3
57	„ ..	3: <u>m</u>	$\bar{6}$	$L^3_3P$	3: m
58	„ ..	<u>m</u> .3: <u>m</u>	$\bar{6}'m'2$	$L^3_33L^2_24P$	3: 2
59	„ ..	<u>m</u> .3: <u>m</u>	$\bar{6}'m'2'$	$L^3_33L^2_23PP$	3. m
60	„ ..	<u>m</u> .3: <u>m</u>	$\bar{6}m'2'$	$L^3_33L^2_2P3P$	3: m
61	„ ..	<u>m</u> .3: <u>m</u>	$\bar{6}m2$	$L^3_33L^2_24P$	<u>m</u> .3: <u>m</u>
62	„ ..	<u>6</u>	$6'$	$L^3_6$	3
63	„ ..	<u>6</u>	6	$L^6$	6
64	„ ..	<u>6</u> : 2	$6'2'2$	$L^3_63L^2_23L^2_2$	3: 2
65	„ ..	<u>6</u> : 2	$6'2'2'$	$L^6_6L^2_2$	6
66	„ ..	<u>6</u> : 2	622	$L^6_6L^2_2$	<u>6</u> : 2
67	„ ..	<u>6</u> : <u>m</u>	$6'/m'$	$L^3_{\bar{6}6}PC$	$\bar{6}$
68	„ ..	<u>6</u> : <u>m</u>	$6'/m$	$L^3_{\bar{6}6}PC$	3: m
69	„ ..	<u>6</u> : <u>m</u>	$6/m'$	$L^6_{\bar{6}}PC$	6
70	„ ..	<u>6</u> : <u>m</u>	$6/m$	$L^6_{\bar{6}}PC$	<u>6</u> : <u>m</u>
71	„ ..	<u>6</u> . <u>m</u>	$6'm'm$	$L^3_{\bar{6}}3P3P$	3. m
72	„ ..	<u>6</u> . <u>m</u>	$6m'm'$	$L^6_6P$	6
73	„ ..	<u>6</u> . <u>m</u>	6mm	$L^6_6P$	<u>6</u> . <u>m</u>
74	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6'/m'mm'$	$L^3_{\bar{6}6}3L^2_23L^2_23P4PC$	$\bar{6}$ . <u>m</u>
75	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6'/mmm'$	$L^3_{\bar{6}6}3L^2_23L^2_24P3PC$	<u>m</u> .3: <u>m</u>
76	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6/m'm'm'$	$L^6_{\bar{6}}6L^2_27PC$	<u>6</u> : 2
77	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6/mm'm'$	$L^6_{\bar{6}}6L^2_26PPC$	<u>6</u> : <u>m</u>
78	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6/m'mm$	$L^6_{\bar{6}}6L^2_26PPC$	<u>6</u> . <u>m</u>
79	„ ..	<u>m</u> . <u>6</u> : <u>m</u>	$6/mmm$	$L^6_{\bar{6}}6L^2_27PC$	<u>m</u> . <u>6</u> : <u>m</u>
80	Cubic ..	3/2	23	$3L^2_24L^3$	
81	„ ..	<u>3/4</u>	$\bar{4}'3m'$	$3L^2_24L^3_6P$	
82	„ ..	<u>3/4</u>	$\bar{4}3m$	$3L^2_24L^3_6P$	
83	„ ..	<u>6/2</u>	$m'3$	$3L^2_24L^3_63PC$	



TABLE I (Contd.)

Systems		Notation of the class by Shubnikov	" Inter-national symbols	The formula of complete symmetry	Subclass usual of symmetry
1	2	3	4	5	6
84	„	.. $\bar{6}/2$	m3	$3L^2_2 4L^3_6 3PC$	
85	„	.. $3/4$	4'32'	$3L^2_4 4L^3_6 L_2$	
86	„	.. $3/4$	432	$3L^4 4L^3 6L^2$	
87	„	.. $\bar{6}/4$	m'3m	$3L^2_{4\bar{4}\bar{2}} 4L^3_{\bar{6}} 6L_{2\bar{2}} 6P3\underline{PC}$	
88	„	.. $\bar{6}/4$	m3m'	$3L^2_{4\bar{4}\bar{2}} 4L^3_{\bar{6}} 6L_{2\bar{2}} 3P6\underline{PC}$	
89	„	.. $\bar{6}/4$	m'3m'	$3L^4_{\bar{4}} 4L^3_{\bar{6}} 6L^2_{\bar{2}} 9\underline{PC}$	
90	„	.. $\bar{6}/4$	m3m	$3L^4_{\bar{4}} 4L^3_{\bar{6}} 6L^2_{\bar{2}} 9PC$	

Under ferroelectric phase transitions, spontaneous polarization can appear in the crystal along different directions. A new crystal symmetry (more exactly, its domain or only a unit cell) will correspond to these different directions. In complete symmetry, the change of the symmetry during a ferroelectric phase transition can be found by the analogy, as it was made in case of usual symmetry (Zheludev and Shuvalov, 1956, 1957). Using the generalization of the Curie principle of symmetry for the case of complete symmetry, one can get the crystal symmetry (a new symmetry) after the ferroelectric phase transition by considering the superpositions of complete symmetry of the crystal in the para-electric (non-polar) phase and the vector of spontaneous polarization  $\vec{P}_s$ . For instance, it is not difficult to see from Table I that a superposition of the complete symmetry of a crystal belonging to the class  $\bar{6}/4$  and the complete symmetry of the vector  $\vec{P}_s$  ( $m. \infty : m$ ) results in a group  $m. \underline{2} ; m$  (in the case of a coincidence of  $\vec{P}_s$  with the axis  $\bar{4}$ ). When  $\vec{P}_s$  coincides with the axis  $\bar{6}$ , it results in the group  $\bar{6}. m$ . In case of a coincidence of the vector  $\vec{P}_s$  with the axis  $\underline{2}$ , it results in the group  $\underline{2}$ , etc.

The results of the change of complete symmetry of the crystal for cubic, rhombic, monoclinic and triclinic classes are given in Tables II, III\*. The

\* The tables of the changes of complete symmetry under the ferroelectric transitions in the crystal classes of other systems are not given here, since they are too extensive.

number of crystallographical directions equal to the given direction in the class considered is given in brackets after the polar groups. This number is equal to the number of the unit cells (they have already a polar symmetry) required for obtaining the crystal symmetry in the high-temperature phase. This means that when the crystal is broken up into domains having equal number of cells oriented along the crystallographical equal directions, it acquires complete symmetry of the para-electric phase.

Tables II and III show the possible polar classes of complete symmetry of the crystal after ferroelectric phase transitions. But they do not indicate as to whether a crystal of the given class can undergo any transition, ferroelectric or otherwise. They do not give also any idea about the sequence of these ferroelectric transitions. It is assumed in the Table that electric polarization appears in the crystal having a para-electric modification, the complete symmetry of which is shown in the upper line. This means, in particular, that if the crystal undergoes some ferroelectric transitions from one polar class into another one, then, every time, the transitions are through "returning" to the para-electric modification. It is impossible to say *a priori*, if the crystals undergo the change of the direction of spontaneous polarization existing before the transition without "returning" to the para-electric modification. These transitions will not be considered here. At present, the practical significance of Tables II and III is not clear. But in spite of it, one can draw some useful conclusions. Thus, in most well-known cases, low-temperature modifications of the crystals are the characteristic ferroelectric modifications. These modifications are of lower symmetry than the para-electric ones. In some cases, however, in the crystals after the ferroelectric region, on further cooling, there appears again a para-electric modification, its symmetry being higher. Typical example is Rochelle salt crystals. Above  $24^\circ$ , these crystals have a para-electric modification, the symmetry being  $2:2$ . In the temperature range  $+24^\circ \div -18^\circ$ , they have a ferroelectric modification, the symmetry of which is  $2$ . Below  $-18^\circ$  they have again a para-electric modification, the symmetry being  $2:2$ . It can be seen that the cooling results in an increase of the crystal symmetry. For complete symmetry, this transition can however be written in the form:  $\underline{m}.2:\underline{m}$  ( $2:2$ )—above  $24^\circ\text{C.}$ ;  $2.\underline{m}$  ( $2$ ) for  $+24 \div -18^\circ\text{C.}$ ,  $2:2$  ( $2:2$ ) below  $-18^\circ\text{C.}$  (The subgroups of common symmetry of the groups of complete symmetry are given in brackets). In this case, the transition to the low-temperature para-electric modification goes without increasing the symmetry, since three groups have the order 8, 4, 4 respectively.



TABLE III  
 The change of complete symmetry as a result of the appearance of electrical polarization  $\vec{P}_s$  in the non-polar crystals of the rhombic, Monoclinic and triclinic classes

The whole set of directions $\vec{P}_e$	Initial classes					
	$m \cdot 2 : m$	$\bar{m} \cdot 2 : \bar{m}$	$\bar{m} \cdot 2 : m$	$2 : 2$	$2 : m$	$2 : \bar{m}$
$\left. \begin{array}{l} \langle 001 \rangle \\ \langle 010 \rangle \\ \langle 100 \rangle \end{array} \right\}$	$2 \cdot m (2)$	$2 : m (2)$	$2 \cdot m (2)$	$2 (2)$	$m (2)$	$2 (2)$
$\left. \begin{array}{l} \langle hko \rangle \\ \langle hoi \rangle \end{array} \right\}$	$m (4)$	$\bar{2} (4)$	$\bar{m} (4)$	$1 (4)$	$1 (4)$	$1 (4)$
$\left. \begin{array}{l} \langle okl \rangle \\ \langle hkl \rangle \end{array} \right\}$	$1 (8)$		$1 (8)$		$1 (4)$	$1 (2)$
	Possible polar classes					
	$2 \cdot m (2)$		$2 \cdot m (2)$	$2 (2)$	$m (2)$	$2 (2)$
	$2 : 2 (2)$		$2 : \bar{2} (2)$		$2 (2)$	$\bar{m} (2)$
	$2 \cdot m (2)$		$\bar{m} (4)$		$m (2)$	$2 (2)$
	$\bar{m} (4)$		$m (4)$		$1 (4)$	$1 (4)$
	$m (4)$		$\bar{m} (4)$			
	$1 (8)$		$1 (8)$			

## 4. FERROMAGNETIC PHASE TRANSITIONS

Ferromagnetic phase transitions here are such, under which there appears magnetic moment  $\vec{M}_s$  in the non-magnetic cells of the crystals.\* The directions of  $\vec{M}_s$  in the neighbouring unit cells in the ferromagnetic crystals are parallel. In the antiferromagnetic crystals, these directions are antiparallel. As a result of the appearance of magnetic moment, the cells acquire complete symmetry of one of the axial classes, *i.e.*, such classes, the symmetry of which is one of the subgroups of the axial vector group (magnetic moment)  $\vec{M}_s$ —the group  $\underline{m}.\infty:m$ . The total number of such axial groups of complete crystal symmetry is 31 (*see* Table I):  $1, \bar{2}, \underline{2}, 2, \underline{m}, m, \underline{2}:m, 2:\underline{2}, \underline{2}.m, 2.\underline{m}, \underline{m}.2:m, 4, 4:\underline{2}, 4:m, 4.\underline{m}; \underline{m}.4:m, \bar{4}, \bar{4}.\underline{m}, 3, 3:\underline{2}, 3.\underline{m}, \bar{6}, \bar{6}.\underline{m}, 3:m, \underline{m}.3:m, 6, 6:\underline{2}, 6:m, 6.\underline{m}, \underline{m}.6:m$ .

These groups can be named the groups of complete symmetry of the *pyromagnetic crystals*. In the ferromagnetic crystals, the domain has a complete symmetry of one of these groups. In the antiferromagnetic crystals, a former unit cell of non-magnetic modification has a complete symmetry of one of these groups.

The modifications of the complete symmetry, when magnetic moments  $\vec{M}_s$  appear in them along different directions, can be found in the same way as was done under the ferroelectric phase transitions.† The superpositions of complete symmetries of the crystals in non-magnetic modifications and the symmetries of the vector of the magnetic moment  $\vec{M}_s$  should be considered for this purpose. For instance, it is not difficult to see from Table I that superposition of complete symmetries of the crystal, belonging to the class  $\bar{6}/4$  and that of the vector  $\vec{M}_s$  ( $\underline{m}.\infty:m$ ) results in the group  $\underline{m}.2:m$  (when  $\vec{M}_s$  coincides with the axis  $\underline{4}$ ). When  $\vec{M}_s$  coincides with the axis  $\bar{6}$ , it results in the group  $\bar{6}.\underline{m}$ . A coincidence of  $\vec{M}_s$  with the axis  $\underline{2}$  results in the group  $\underline{2}:\underline{m}$ , etc.

The results of considering the modifications of complete symmetry of the crystals under the phase transitions caused by the appearance of magnetic

\* *i.e.*, those which have no spontaneous magnetic moment.

† The modification of the *magnetic* symmetry of the crystal during the ferromagnetic-phase transitions was performed for the first time by Shuvalov, 1959,





moment  $\vec{M}_s$  are given in Tables IV and V. In these tables, along with new groups of complete symmetry, is indicated the number of crystallographical directions in the crystal that are equal to the direction in which the magnetic moment appears. If after the phase transition, ferromagnetic has this number of the domains (in the antiferromagnetics—the number of unit cells), which are equally oriented along the equal directions considered, then the whole set of domains (cells) will have the symmetry of the crystal which it had before the phase transition.

The remarks similar to those which were made for Tables II and III are true for Tables IV and V. It is assumed here that all transitions arise from the non-magnetic modification. The transitions between two magnetic modifications are performed by “returning” to the nonmagnetic modification, etc.

The tables similar to Tables IV and V can be used directly for investigating the physical properties and the structure of magnetic crystals.

The author of this paper expresses his gratitude to Prof. R. S. Krishnan and Dr. P. S. Narayanan for their help and attention.

## 5. SUMMARY

The extension of the superposition principle of the symmetries (P. Curie principle of symmetry) for the case of complete symmetry is given. The enumeration of all crystallographical groups of complete symmetry is presented, the number of elements having complete symmetry for each class of the crystals being indicated. The change of complete symmetry of the crystals under the phase transitions is obtained by superimposing the elements of complete symmetry of polar or axial vectors on the one hand, and the elements of complete symmetry of the crystals on the other.

The tables of complete symmetry changes for the cubic, rhombic, monoclinic and triclinic crystals during the ferroelectric and ferromagnetic phase transitions are given.

## REFERENCES

- Tavger, B. A. and Zaitsev, V. M. *JETP*, 1956, 30, 564. (*Eng. Trans.* 1956, 3, 430.)  
Shubnikov, A. V. .. “Symmetry and antisymmetry of the finite figures,” *Izd. Akad. Nauk, SSSR*, Moscow, 1951.  
Shuvalov, L. A. .. *Kristallografiya*, 1959, 4, 399.



- Zheludev, I. S. .. *Krystallografiya*, 1960 (a), 5, 346, English Translation; *Soviet Physics—Crystallography*, 1960, 5, 328.
- 
- .. *Ibid.*, 1960 (b), 5, 508; English Translation; *Soviet Physics—Crystallography*, 1961, 5, 489.
- 
- .. *Izvest. Akad. Nauk SSSR*, Ser. Fiz., 1960 (c), 24, 1436.
- Zheludev, I. S. and Shuvalov, L. A. .. *Krystallografiya*, 1956, 1, 681.
- 
- .. *Izvest. Akad. Nauk SSSR*, Ser. Fiz., 1957, 21, 264.