therefore we cannot explain the disagreement in this way. We have seen that the ratio B/a^2 at the Cl^- ion seems to be a linear function of the electron number of the cation at 300 °K. Buyers & Smith (1968) have very recently calculated the Debye–Waller coefficients of Na^+ and Cl^- in NaCl from the next-nearest-neighbour model (NNN) of Hardy & Karo (1966). These calculations show that the ratio of the sodium to the chlorine Debye–Waller coefficient at 300 °K is increased and this improves the agreement between the calculated and measured coefficients. The effect between the nearest neighbours could also explain the dependence indicated in Fig. 4. From these considerations we conclude that the discrepancy between the measured and calculated Debye–Waller coefficients (*cf.* Table 4) at 300 °K is a result of the repulsive forces between the next-nearest neighbours not included in the theory (DD model of Karo & Hardy, 1963).

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Non-crystallographic Shubnikov Groups

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It is argued that magnetic structures are likely to be found which will most fruitfully be explained with the aid of non-crystallographic magnetic point groups. The point groups are classified into families of 'halving subgroups' and it is shown diagrammatically, with the aid of representation theory, how non-crystallographic Shubnikov groups can be constructed.

Introduction

Crystallographers who think in terms of just 32 point groups immediately limit the mathematical equipment available for interpreting the physical properties of crystals. The fact that only 32 point symmetries are admissible as units for repetition in Bravais lattices does not mean that other symmetries must be de-

stroyed completely in the crystalline state, but merely that they suffer at least a small distortion so that strictly speaking they belong to one of the allowed symmetries. It would be futile to attempt to classify the normal modes of vibration of molecules of ferrocene, $Fe(C_5H_5)_2$, in the solid by starting off from the true site symmetry C_2; rather, we should consider them as spanning irreducible representations of the non-crystallographic point group D_{5d} and then consider how these representations decompose on descent in symmetry to C_2. We can say that since the distortion is small, the splitting of the degenerate modes will also be small, and we can also see which modes will mix in the lower symmetry. It is then easier to visualize the observed modes, assuming that the symmetry is higher.

We should also consider the possibility that non-crystallographic Shubnikov groups will likewise be useful. The existence of Friauf polyhedra and icosahedra in complex intermetallic compounds [for an excellent review see Samson (1968)], will surely lead to the study of intermetallic compounds in which there are observable magnetic interactions in these clusters of non-crystallographic symmetry within the unit cell. Hitherto only crystallographic Shubnikov groups have been discussed, and it is the purpose of this paper to investigate* the possibilities of inventing Shubnikov groups other than the 58 found by Tavger & Zaitsev (1956) and Zamorzaev (1953).

Theory

It will be convenient to distinguish at the outset between two types of magnetic point group, the 'grey' (or type II) point group and the 'black and white' (or type III) point group. To every ordinary (or type I) point group, G, there corresponds a 'grey' point group M, given by

$$M = G + RG\,, \qquad (2\cdot1)$$

where R is the operation of time-inversion and the summation is to be understood in the Galois sense, *i.e.* as a juxtaposition of elements. 'Black and white' point groups are defined by

$$M = H + R(G - H)\,, \qquad (2\cdot2)$$

where H is a halving subgroup of G, and $G - H$ means the set of elements of G that do not belong to H. A halving subgroup is defined as a subgroup of index 2 (*i.e.* it has half as many elements as G) and is, therefore, an invariant subgroup. We should notice from equations (2·1) and (2·2) that for a given group G, the grey group will be of *twice* the order of G, whilst the black and white group will be of the *same* order as G. The interest lies in the systematic construction (for Shubnikov originally only found 57) of the black and white groups which will henceforth be referred to as Shubnikov groups.

The freshest approach is in terms of representation theory since, as Bertaut (1968) has shown, one can not only place the 58 Shubnikov groups in 1:1 correspondence with the 58 *distinct* non-totally symmetrical real one-dimensional representations of the ordinary point groups, but one can also explain non-Shubnikov magnetic structures (*e.g.* helical orientations of spins) in terms of the other representations. One-dimensional representations are not considered *distinct* if they differ only in the orientation of the defining frame of axes from one another. In Table 1 are listed the fifty-eight crystallographic Shubnikov groups with their standard number, Hermann–Mauguin label, G, H and the representation D of G, which on descent in symmetry from G to H becomes the totally symmetric (*i.e.* unit or identity) representation of H. G and H are given in Schönflies notation as this specifies immediately their generators and is more readily extendible to non-crystallographic groups.

Table 1. *The 58 crystallographic Shubnikov point groups*

Number	Label	G	D	H
1	$\bar{1}'$	S_2	A_u	C_1
2	$2'$	C_2	B	C_1
3	m'	C_{1h}	A''	C_1
4	$2/m'$	C_{2h}	A_u	C_2
5	$2'/m$	C_{2h}	B_u	C_{1h}
6	$2'/m'$	C_{2h}	B_g	S_2
7	$22'2'$	D_2	B_1, B_2, B_3	C_2
8	$2m'm'$	C_{2v}	A_2	C_2
9	$2'm'm$	C_{2v}	B_1, B_2	C_{1h}
10	$m'm'm'$	D_{2h}	A_u	D_2
11	mmm'	D_{2h}	B_{1u}, B_{2u}, B_{3u}	C_{2v}
12	$m'm'm$	D_{2h}	B_{1g}, B_{2g}, B_{3g}	C_{2h}
13	$4'$	C_4	B	C_2
14	$\bar{4}'$	S_4	B	C_2
15	$42'2'$	D_4	A_2	C_4
16	$4'22'$	D_4	B_1, B_2	D_2
17	$4/m'$	C_{4h}	A_u	C_4
18	$4'/m'$	C_{4h}	B_u	S_4
19	$4'/m$	C_{4h}	B_g	C_{2h}
20	$4m'm'$	C_{4v}	A_2	C_4
21	$4'mm'$	C_{4v}	B_1, B_2	C_{2v}
22	$\bar{4}2'm'$	D_{2d}	A_2	S_4
23	$\bar{4}'2m'$	D_{2d}	B_1	D_2
24	$\bar{4}'2'm$	D_{2d}	B_2	C_{2v}
25	$4/m'm'm'$	D_{4h}	A_{1u}	D_4
26	$4/m'mm$	D_{4h}	A_{2u}	C_{4v}
27	$4'/mmm$	D_{4h}	B_{1g}, B_{2g}	D_{2h}
28	$4'/m'm'm$	D_{4h}	B_{1u}, B_{2u}	D_{2d}
29	$4/mm'm'$	D_{4h}	A_{2g}	C_{4h}
30	$32'$	D_3	A_2	C_3
31	$3m'$	C_{3v}	A_2	C_3
32	$\bar{6}'$	C_{3h}	A''	C_3

* The referee has kindly pointed out that the non-crystallographic Shubnikov groups have already been independently deduced as subgroups of the grey group $K_h + RK_h$ by Koptsik (1966). This approach is different from that through representation theory presented here, and Koptsik's diagram (Fig. 2, p. 28) showing relationships between the limiting groups is an ordinary subgroup diagram not to be confused with the 'halving subgroup diagrams' presented in this paper. In Koptsik's diagram, ordinary, grey and 'black and white' point groups appear together and no special significance is ascribed to the tie-lines. In the halving subgroup diagrams, only ordinary point groups appear and each tie-line is associated with a 'black and white' point group.

Table 1 (*cont.*)

Number	Label	G	D	H
33	$\bar{6}m'2'$	D_{3h}	A_2'	C_{3h}
34	$\bar{6}'m2'$	D_{3h}	A_2''	C_{3v}
35	$\bar{6}'m'2$	D_{3h}	A_1''	D_3
36	$6'$	C_6	B	C_3
37	$\bar{3}'$	S_6	A_u	C_3
38	$\bar{3}m'$	D_{3d}	A_{2g}	S_6
39	$\bar{3}'m$	D_{3d}	A_{2u}	C_{3v}
40	$\bar{3}'m'$	D_{3d}	A_{1u}	D_3
41	$62'2'$	D_6	A_2	C_6
42	$6'22'$	D_6	B_1, B_2	D_3
43	$6/m'$	C_{6h}	A_u	C_6
44	$6'/m'$	C_{6h}	B_g	S_6
45	$6'/m$	C_{6h}	B_u	C_{3h}
46	$6m'm'$	C_{6v}	A_2	C_6
47	$6'mm'$	C_{6v}	B_1, B_2	C_{3v}
48	$6'/mm'm$	D_{6h}	B_{1u}, B_{2u}	D_{3h}
49	$6'/m'm'm$	D_{6h}	B_{1g}, B_{2g}	D_{3d}
50	$6/m'm'm'$	D_{6h}	A_{1u}	D_6
51	$6/m'mm$	D_{6h}	A_{2u}	C_{6v}
52	$6/mm'm'$	D_{6h}	A_{2g}	C_{6h}
53	$m'3$	T_h	A_u	T
54	$\bar{4}'3'm$	T_d	A_2	T
55	$4'32'$	O	A_2	T
56	$m'3m'$	O_h	A_{1u}	O
57	$m'3m$	O_h	A_{2u}	T_d
58	$m3m'$	O_h	A_{2g}	T_h

In D_2 and D_{2h}, the choices $\{B_1, B_2, B_3\}$, $\{B_{1g}, B_{2g}, B_{3g}\}$ and $\{B_{1u}, B_{2u}, B_{3u}\}$ correspond to choosing the $\{z, y, x\}$ axes as the principal axes in the halving subgroups C_2, C_{2h} and C_{2v} respectively. In D_4 and D_6 the choice $\{B_1, B_2\}$ and in D_{4h} and D_{6h} the choices $\{B_{1g}, B_{2g}\}$ and $\{B_{1u}, B_{2u}\}$ determine whether the $\{C_2', C_2''\}$ axes are retained on descent to the halving subgroups $D_2, D_3, D_{2h}, D_{2d}, D_{3d}, D_{3h}$. In C_{4v} and C_{6v} the choice $\{B_1, B_2\}$ determines whether the $\{\sigma_v, \sigma_d\}$ planes are retained on descent to C_{2v} and C_{3v} respectively. The choice $\{B_1, B_2\}$ in C_{2v} determines whether the reflexion plane is $\{\sigma^{xz}, \sigma^{yz}\}$ in C_{1h}.

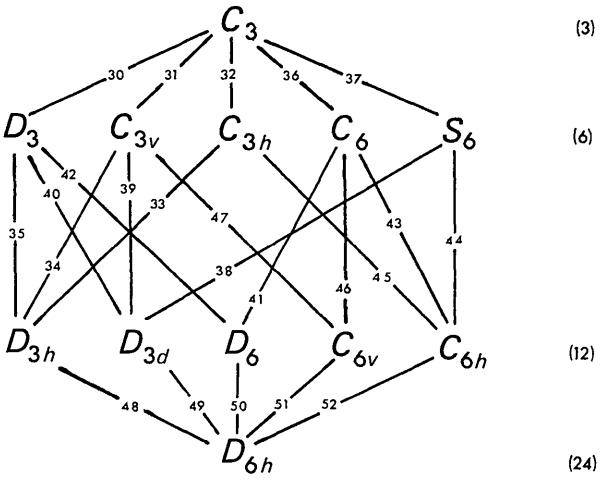

Fig. 2. The C_3 family of crystallographic point groups.

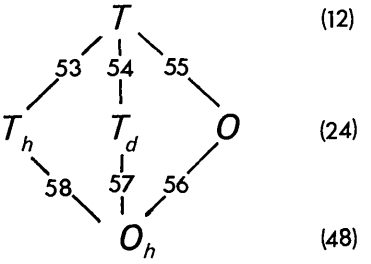

Fig. 3. The T (or cubic) family of crystallographic point groups.

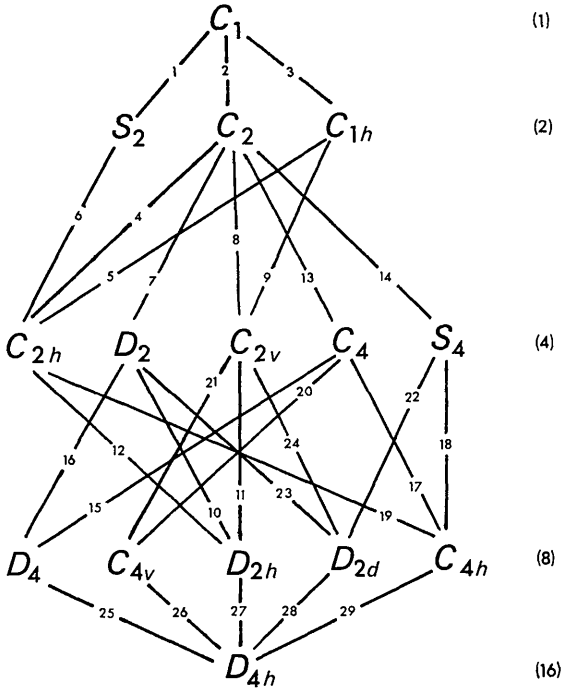

Fig. 1. The C_1 family of crystallographic point groups.

Considering then a Shubnikov group in terms of two groups G and H we find that the 32 crystallographic point groups can be divided into three families, as shown in Figs. 1–3. The horizontal rows contain groups of the same order (given in parentheses on the right) and adjacent rows differ in order by a factor of two. The tie-lines relate a group G to its halving subgroups H above, and the groups of which it is a halving subgroup below. Each tie line defines a Shubnikov group and there are exactly 58 tie lines. It is of interest, but probably of no significance, that precisely half of these are found in the C_1 family (Fig. 1).

The key to each family is the group at the top of each Figure. Since it is at the top, it has no halving subgroups. Construction of new families will, therefore, require us to find new groups without halving subgroups, and then the groups which they halve. We shall also be able to find new Shubnikov groups by extending the 'family trees' downwards. This is possible indefinitely in Figs. 1 and 2, though Fig. 3 is complete.

New families of point groups

The problem of finding new point groups without halving subgroups can be reduced to that of finding

finite subgroups of the infinite three-dimensional rotation group K. As explained by Murnaghan (1938) this is tantamount to finding the solutions of the Diophantine equation

$$\sum_{i=1}^{p} \frac{1}{k_i} = p - 2 + \frac{2}{n}, \qquad (2\cdot3)$$

where n is the order of the group. Examination of all the possible solutions of equation (2·3) shows that we can look for

(i) a family based on the icosahedral rotation group, I;
(ii) an infinite number of new families based on the axial rotation groups of odd order, C_{2x+1}.

The icosahedral family shown in Fig. 4 contains only one new Shubnikov group (which I have numbered 59) since one cannot have any finite pure rotation groups of even order greater than 60. I is, therefore, a halving subgroup only of I_h and this has no finite supergroups.

The first new family based on an axial rotation group of odd order is the C_5 family shown in Fig. 5. This family contains the point groups D_{5d} and D_{5h} relevant to ferrocene and ruthenocene respectively. The 'trees' of all such families will be isomorphic with that of the C_3 family, and it can be seen that the number assigned to a given C_5 Shubnikov group is 30 greater than the number of the analogous C_3 Shubnikov group.

Extension of the crystallographic families

Whilst Fig. 1 contains all point groups of orders 1, 2 and 4, the improper rotation group S_8 has been omitted from the point groups of order 8. The B representation of this group is reduced to the unit representation of C_4 on descent in symmetry, and hence a new Shubnikov group (No. 83) may be associated with this representation of S_8, or equivalently the tie-line between S_8 and its halving subgroup C_4. Amongst the point groups of order 16 omitted is D_{4d}, the group of the square antiprism, found in the puckered rings of S_8 and Se_8 and the octafluoride anion $[TaF_8]^{3-}$. Its one-dimensional representations A_2, B_1 and B_2 lead to the halving subgroups S_8, D_4 and C_{4v} respectively, and the Shubnikov groups Nos. 84–6 have been associated with these pairs.

The C_{2x+1} families are similarly capable of infinite extension, but it is doubtful whether these would in-

Table 2. *Some non-crystallographic Shubnikov point groups*

Number	Label	G	D	H
59	$m'53$	I_h	A_u	I
60	$52'$	D_5	A_2	C_5
61	$5m'$	C_{5v}	A_2	C_5
62	$\bar{1}0'$	C_{5h}	A''	C_5
63	$\bar{1}0m'2'$	D_{5h}	A_2'	C_{5h}

Table 2 (*cont.*)

Number	Label	G	D	H
64	$\bar{1}0'm2'$	D_{5h}	A_2''	C_{5v}
65	$\bar{1}0'm'2$	D_{5h}	A_1''	D_5
66	$10'$	C_{10}	B	C_5
67	$\bar{5}'$	S_{10}	A_u	C_5
68	$\bar{5}m'$	D_{5d}	A_{2g}	S_{10}
69	$\bar{5}'m$	D_{5d}	A_{2u}	C_{5v}
70	$\bar{5}'m'$	D_{5d}	A_{1u}	D_5
71	$102'2'$	D_{10}	A_2	C_{10}
72	$10'22'$	D_{10}	B_1, B_2	D_5
73	$10/m'$	C_{10h}	A_u	C_{10}
74	$10'/m'$	C_{10h}	B_g	S_{10}
75	$10'/m$	C_{10h}	B_u	C_{5h}
76	$10m'm'$	C_{10v}	A_2	C_{10}
77	$10'mm'$	C_{10v}	B_1, B_2	C_{5v}
78	$10'/mm'm$	D_{10h}	B_{1u}, B_{2u}	D_{5h}
79	$10'/m'm'm$	D_{10h}	B_{1g}, B_{2g}	D_{5d}
80	$10/m'm'm'$	D_{10h}	A_{1u}	D_{10}
81	$10/m'mm$	D_{10h}	A_{2u}	C_{10v}
82	$10/mm'm'$	D_{10h}	A_{2g}	C_{10h}
83	$\bar{8}'$	S_8	B	C_4
84	$\bar{8}'m'$	D_{4d}	A_2	S_8
85	$\bar{8}'2m'$	D_{4d}	B_1	D_4
86	$\bar{8}'2'm$	D_{4d}	B_2	C_{4v}

In D_{10} and D_{10h} the choices $\{B_1, B_2\}$, $\{B_{1g}, B_{2g}\}$ and $\{B_{1u}, B_{2u}\}$ determine whether the $\{C_2', C_2''\}$ axes are retained on descent to the halving subgroups D_5, D_{5d}, D_{5h}. In C_{10v} the choice $\{B_1, B_2\}$ determines whether the $\{\sigma_v, \sigma_d\}$ planes are retained on descent to C_{5v}.

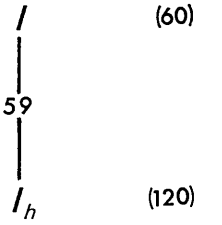

Fig. 4. The I (or icosahedral) family of non-crystallographic point groups.

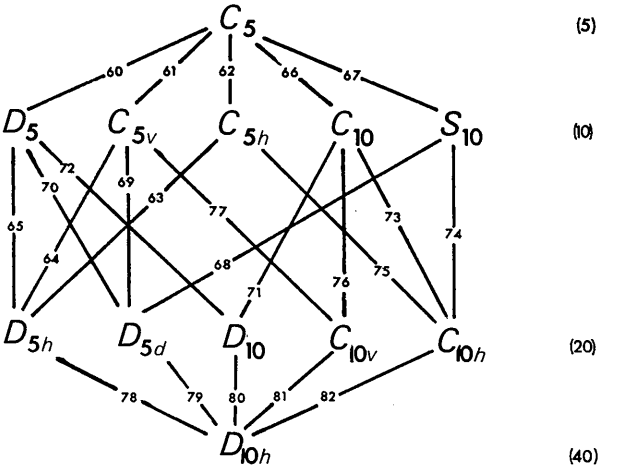

Fig. 5. The C_5 family of non-crystallographic point groups.

clude any physically relevant Shubnikov groups. The 28 non-crystallographic Shubnikov groups discussed above are listed in Table 2.

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High-Resolution Monochromatization of Neutrons by Multiple Bragg Reflection in Hexagonal Close-Packed Crystals*

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The conditions which give high-resolution monochromatization of neutrons by multiple Bragg reflection in hexagonal close-packed crystals have been studied theoretically. The role of reflections forbidden by special atomic positions has been clarified, and, contrary to a previous conclusion, it is found that these 'forbidden' reflections may be useful for high-resolution purposes. Detailed calculations of the necessary crystal orientations have been carried out for beryllium, magnesium and zinc. On the basis of somewhat arbitrary criteria the calculations show that these crystals can reflect a total of approximately 200 wavelengths in the range 0·7 to 4·9 Å (neutron energy 0·003 to 0·17 eV). Several orientations have been found at which *mosaic* crystals (with a sacrifice of angular resolution) should produce beams that are both intense and highly monochromatic.

Introduction

In a previous paper (hereinafter referred to as part I) it was pointed out that under suitable conditions in certain types of perfect crystals the phenomenon of multiple Bragg reflection (MBR) can provide highly monochromatic and highly collimated (semiparallel) beams of neutrons and X-rays at fixed wavelengths (Kottwitz, 1968*a*). The effect depends on the simulation of a forbidden (primary) reflection by the cooperative action of two allowed reflections (secondary and tertiary); this is the 'Umweganregung' phenomenon (Renninger, 1937). For each such simulation the reflected wavelength has a second-order extremum at a definite orientation (referred to in part I as the 'operating point') of the incident beam relative to the crystal. At such operating points even quite coarse external collimation can produce extremely high wavelength and angular resolution *provided* there is no 'interference', that is, provided no other simulation is close enough to make an impure contribution. Exploratory intensity measurements have been reported (Kottwitz, 1968*b*).

The main purpose of this paper is to present and discuss calculations of interference-free operating points for three hexagonal close-packed crystals: beryllium, magnesium and zinc. In contrast with the cubic diamond structure, for which the operating points are independent of lattice parameters, the h.c.p. structure permits various c/a ratios and thus requires separate calculations for each crystal. These particular crystals were chosen because they are suitable monochromators for neutrons (Bacon, 1962).

The general equations, nomenclature and conventions that provide the basis for this paper are identical with those in part I, and will be at most briefly described here. Attention will be concentrated on characteristics particularly relevant to the h.c.p. case.

Forbidden reflections in h.c.p. crystals

The h.c.p. structure (space group $P6_3/mmc$) has some reflections that are strictly forbidden by space-group symmetry; they are given by $hh\bar{2}hl$ with l odd. Calculations of operating points have been done for 0001, 0003, 0005, $11\bar{2}1$, $11\bar{2}3$ and $22\bar{4}1$. These are the preeminent candidates for use in high-resolution monochromatization by MBR.

The h.c.p. structure also has reflections that are only approximately 'forbidden' by special atomic positions; these are given by $hkil$ with l odd and $h-k=3n\neq 0$. They are represented in our calculations by $30\bar{3}1$, $30\bar{3}3$

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