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Extensions of Space-Group Theory

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Recent papers re-examining the effect of including an operation of antisymmetry among the permitted elements of symmetry and making further generalizations of the space groups are reviewed. Suggestions are made, and developed for the two dimensional case, for further elaboration arising from the superposition of symmetrical and antisymmetrical groups. The description of the physical properties of crystals is a possible field of applicability.

INTRODUCTORY: REPORT ON RECENT WORK

Nomenclature

Antisymmetry is the correspondence of faces, points or other crystallographic objects having some property denoted by a positive sign, to other faces, points or objects symmetrically related in position, but having the same property with the opposite sign.

Operations of antisymmetry transfer the object to a symmetrically related position and change its sign. The operations are denoted by the usual symbols with added primes. An additional operation t', which represents a translation of half a repeat distance followed by a reversal of sign, has to be introduced (Cochran, 1952).

In diagrams the relationship of antisymmetry is best represented by colouring corresponding objects black and white, and symmetry groups containing elements of antisymmetry are conveniently called *black and white groups*. The 1651 black and white space groups (infinite groups in three dimensions) have been named *Shubnikov groups* (Zamorzaev, 1953). Groups in which equal and opposite black and white objects are exactly superposed are designated as *grey*.

Symmetry elements relate identical objects; operations of antisymmetry transform objects which have two possible values of a given property from one value to the other; and, extending this concept (Belov & Tarkhova, 1956), related objects which have n possible values of a property and are transformed cyclically from one to another by *n-colour symmetry operations* can be systematised in *n-coloured symmetry groups*.

Discussion will be limited to infinitely repeating groups, and non-crystallographic point groups will be excluded.

The 46 black and white plane groups

If the 5 plane Bravais lattices are centred by points of a different colour, so that each contains equal numbers of black and white lattice points, then 5 new plane lattices are obtained. 'Two successive colour translations t' in the same direction are equivalent to one non-coloured translation in that direction. Thus, the length of the shortest coloured translation in any given direction is equal to half the length of the shortest non-coloured translation in the same direction' (Belov, Neronova & Smirnova, 1955). The 10 plane

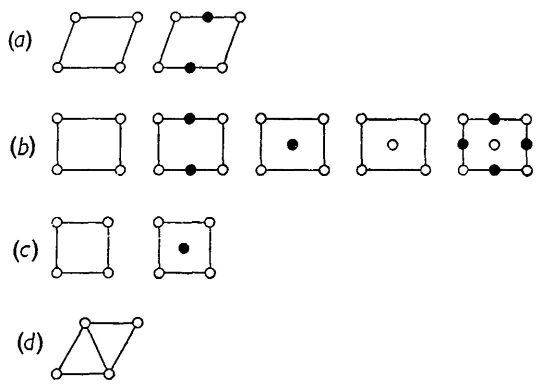

Fig. 1. The black and white plane lattices. (*a*) Oblique; (*b*) rectangular; (*c*) square; (*d*) hexagonal.

Bravais lattices (Fig. 1) are as follows (primed symbols denote black and white lattices, suffix b denotes centring on the b edge and suffix C denotes face centring):

Oblique

p, p'_b

Rectangular

p, p'_b, p'_C, c, c'

Square

p, p'_C

Hexagonal

p

In two dimensions lattices are p or c and the symmetry elements are 2, 3, 4, 6, m, g. For the black and white groups the lattices are as above, and the symmetry elements are increased by $2'$, $4'$, $6'$, m', g'. (The element $3'$ gives a grey group.) When the full symbols for the 17 plane groups are written down and their elements (lattices, axes and planes) are given primes in turn to give all possible combinations, the 46 black and white plane groups are generated.

If the 17 ordinary plane groups and 17 further plane groups, in which black and white objects are everywhere exactly superposed (grey groups), are added to the above, a total of 80 plane groups results. These were first described by Alexander & Herrmann (1928, 1929) and by Weber (1929) and were tabulated by Shubnikov (1940, 1946).

Cochran (1952) derives the plane groups without introducing the concept of black and white lattices and his notation differs slightly from that of Belov & Tarkhova: for example, Cochran uses $pm+t'$ for $p_b'm$ and $pm, m+m'$ for $p_b'mm$.

Lonsdale (in a note to Cochran, 1952) points out that the plane groups can be derived by collapsing the 230 space groups. For example, pm' is equivalent to $P2$ where $x = 0$ or $z = 0$, and $pm'g'$ to $P222_1$ where $x = 0$ or $y = 0$.

Belov & Tarkhova (1956) tabulate these generating groups but give an alternative derivation from those space groups which dispose equivalent points on two and only two levels, that is, from groups containing centred lattices, glide planes or screw axes 2_1, 4_2 or 6_3. If equivalent points lie only on levels z and $z+\frac{1}{2}$, then, if the former are coloured black and the latter white and the figure is projected on to the x–y plane, the plane groups will result. This approach proves capable of extension to colour groups (see below).

The 1651 black and white space groups (Shubnikov groups)

The full extension of the above concepts to three dimensions has been made by Zamorzaev (1953) by a mathematical method, and independently by Belov *et al.* (1955) by the Bravais-lattice method described above.

In three dimensions there are 36 black and white Bravais lattices (including the 14 uncoloured lattices but excluding a further 14 grey lattices). The usual lattice symbols, P, A, B, C, I, F, R, are used and the suffix denotes the mode of centring by coloured points. The suffix s (*sceles*—edge) denotes edge centring (Fig. 2).

The 1651 Shubnikov groups (which include the 230 space groups and the 230 corresponding grey groups, the latter denoted by adding the symbol 1′ to the space-group symbol) can be derived by writing down the full international symbol for each space group and making each element coloured in turn. All combina-

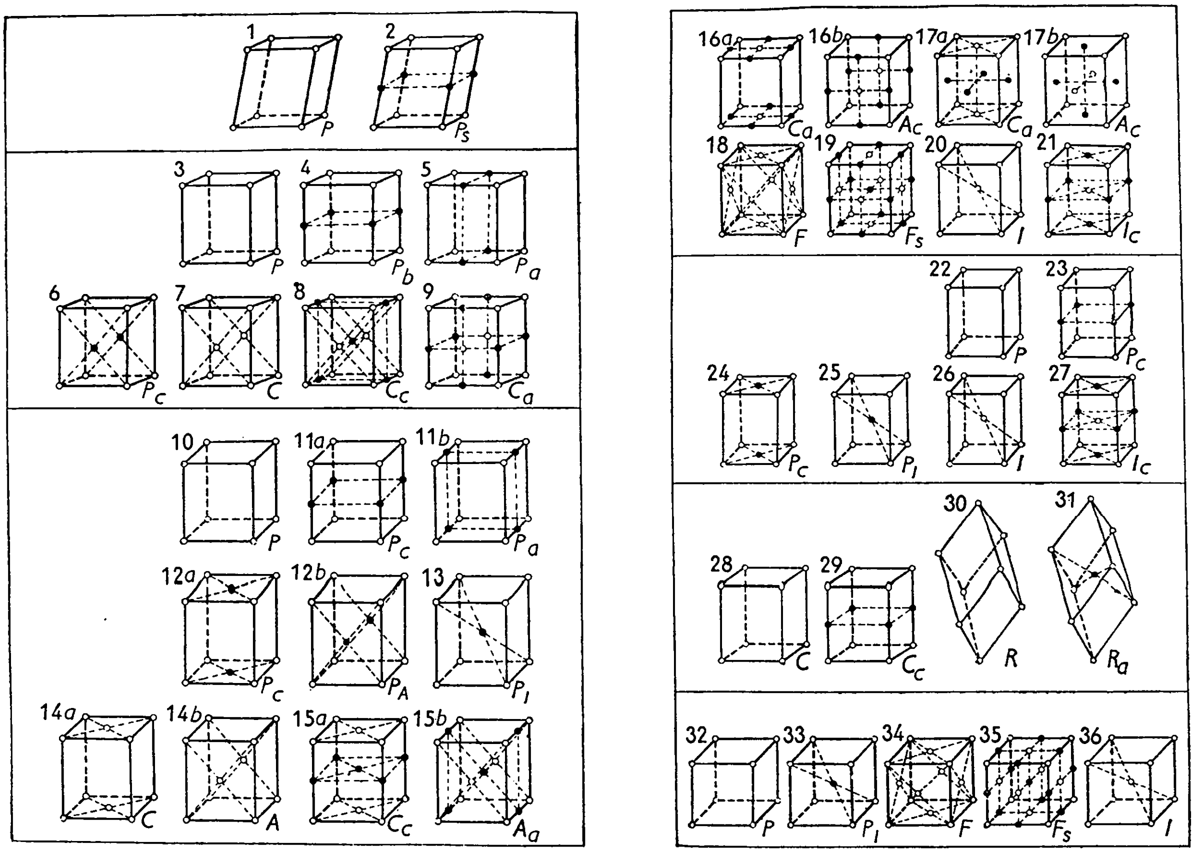

Fig. 2. The three-dimensional black and white lattices. 1–2: triclinic; 3–9: monoclinic; 10–21: orthorhombic; 22–27: tetragonal; 28–31: hexagonal; 32–36: cubic.

tions of coloured elements have to be examined and various identities recognized. Ten theorems concerned with this process are developed by Belov *et al.* Besides the lattices, the coloured symmetry elements are: $1'$, $2'$, $4'$, $6'$, $2_1'$, $\bar{3}'$, $\bar{4}'$, $4_1'$, $4_2'$, $4_3'$, $\bar{6}'$, $6_1'$, $6_2'$, $6_3'$, $6_4'$, $6_5'$, m', n', d', a', b', c'.

Except for the actual working out and listing of all of the black and white groups in three dimensions, most of the above is explicit or implicit in Heesch's examination (1930) of the four-dimensional groups of three-dimensional space. Some of the possible applications are also foreshadowed.

Coloured symmetry groups

Groups relating objects of more than two colours have been discussed (for the two-dimensional case) by Belov & Tarkhova (1956). The most easily visualized derivation is from the 230 space groups, as an extension of the procedure outlined above.

In the x–y projection of a space group certain symmetry elements (lattices, screw axes and glide planes) may relate objects with z coordinates z and $z+\frac{1}{2}$. When projected, objects so related can be coloured black and white and it has been shown that the 46 plane black and white groups result. If space groups containing the elements 3_1, 3_2, 6_2, 6_4, or R are similarly projected, triplets of symmetry-related objects lying at levels z, $z+\frac{1}{3}$, and $z+\frac{2}{3}$ can be similarly represented in projection by 3 colours, say red, green and yellow respectively.

The same procedure can be applied for 4 and 6 colours. The only low-symmetry space group giving rise to a multicoloured group is $Fdd2$.

As there are only 15 coloured crystallographic plane groups (including 4 enantiomorphous pairs) they have simply been named after the space groups from which they are derived (by projection along the principal polar axis). They are as follows:

3-colour plane groups
$P3_1$, $P3_2$, $P6_2$, $P6_4$, $R3$, $R3m$

4-coloured plane groups
$P4_1$, $P4_3$, $I4_1$, $I4_1md = F4_1dm$, $I4_1cd = F4_1dc$, $Fdd2$

6-colour plane groups
$P6_1$, $P6_5$, $R3c$

Ewald (1956) proposes the combination of the space groups S with the cyclic group

$$[1, \exp 2\pi i/p, \exp 4\pi i/p, \ldots \exp 2\pi i(p-1)/p]\,.$$

When $p = 2$ this would generate the black and white groups, and when $p = 3, 4, 6$ the coloured groups. Other values of p are not compatible with the crystallographic groups.

Belov (1956) further shows how three-dimensional coloured mosaics can be constructed.

Plane coloured groups with non-crystallographic symmetry elements

It is pointed out by Belov & Tarkhova that further types of plane symmetry groups can be constructed using 5, 7 or more colours. These can really be referred to the existing plane groups where the motive of pattern consists of a succession of an arbitrary number of coloured elements and itself has a certain regularity of arrangement. An example of such a group would be the plane group cm with a yellow object at $(x, y) = (0, 0)$, green at $(0, \frac{1}{7})$, white at $(0, \frac{2}{7})$ black at $(0, \frac{3}{7})$, red at $(0, \frac{4}{7})$, blue at $(0, \frac{5}{7})$ and brown at $(0, \frac{6}{7})$.

Practical crystallographic applications

The utility of the 46 black and white plane groups seems now established.

Cochran & Dyer (1952) and Vajnshtejn & Tischchenko (1955) show that generalized projections, where the functions plotted may have equal and opposite excursions of values, have the symmetries of these groups.

The earliest discussion of the subject by Alexander & Herrmann deals with the symmetries possible for quasi-two-dimensional layers of molecules (in liquid crystals). This topic is pursued more exhaustively by Kitaigorodskii (1955) as part of a systematic study of the packing of organic molecules of various symmetries.

It might be pointed out that the 46 black and white groups and the 15 coloured groups derive from those space groups from which Patterson–Harker syntheses are possible and may be useful in the interpretation of such sections.

The symmetries of antiferromagnetic crystals can be most concisely described in terms of Shubnikov groups, and work on this aspect is in progress. Other questions of crystal physics seem likely to call for the use of some such extension of symmetry theory.

COMPOUND GROUPS

Introduction

The 230 space groups describe the possible symmetries of a periodic scalar field (such as electron density) having one parameter per point. The extension of the concept of identity symmetry to that of antisymmetry at once suggests further extensions for this reason: if a vector field (3 components to be specified at every point) were restricted to identity symmetry no more than the 230 groups would occur; if, however, antisymmetry relationships were allowed, permutations of the signs of the various components could occur, thus giving further distinct groups.

For example, consider a vector field (having 3 components V_1, V_2, V_3) in which there is a plane M of generalized symmetry. The plane has the property that the V_1 components are reflected symmetrically and the V_2 and V_3 components are reflected anti-symmetrically. What then is the number of different space groups which the vector field **V** can have when such additional symmetry elements are introduced?

The question is not merely of mathematical but also of practical interest since, for example, the anisotropic temperature factor (different for every atom in the unit cell of a crystal) obviously represents a vector field.

In general, suppose that there exists in a crystal a field of a quantity F having n components. If $n = 1$, F may be a scalar or pseudo-scalar; if $n = 2$, F may be a complex number (such as the scattering factor near an absorption edge); if $n = 3$, F may be a polar or axial vector (such as **E** or **H**); if $n = 6$, F may be a symmetrical second-order tensor (such as susceptibility) etc. In fact, indefinitely complicated fields can be imagined, and the problem can be formulated thus: Considering the elements of symmetry and antisymmetry, how many space groups are there in N dimensions when n quantities have to be specified at each point in space and each of these quantities follows a symmetry arrangement independently of the others?

There appear to be two possible approaches:

(1) To introduce a number of compound symmetry elements with relatively complex properties describing the complete transformation of all n components. For example, a plane M_{+--} can be defined as one which reflects the V_1 component symmetrically and the V_2 and V_3 components anti-symmetrically.

As n increases this notation becomes almost unmanageably complicated.

(2) To consider the total symmetry group as made up of n superimposed symmetry and antisymmetry groups, each describing the behaviour of one component. This seemed more tractable and was developed further. It is, perhaps, analogous to the superposition of wave functions.

The two-dimensional case will be examined first.

It is obvious that not all pairs of symmetry groups are compatible. Let S denote symmetrical lattices (or groups) and let A denote antisymmetrical lattices (or groups). There are therefore three types of superposed lattices $(S{:}S)$, $(S{:}A)$, $(A{:}A)$. The conditions for superposition are (*a*) that the systems of the two lattices must be the same, and (*b*) that each lattice must include every point of the other.

The two-dimensional compound lattices

These are:

Oblique

$(2p{:}p_b')$ ($2p$ means that 2 unit cells of the p lattice are superimposed on one cell of the p_b' lattice.)

Rectangular

$(2p{:}p_b')$, $(4p{:}c')$, $(c{:}p_C')$, $(2p_b'{:}c')$

Square

$(4p{:}2p_C')$

There are 5 S lattices and 5 A lattices. By definition, there are no $(S{:}S)$ lattices. Each A lattice can be combined with an S lattice in one way giving 5 $(A{:}S)$ lattices. As in the rectangular system there are more A than S lattices, the same S lattice may be compatible with two different A lattices (A and A'). It follows that A and A' are compatible with each other. The rectangular $(2p_b'{:}c')$ is such a lattice.

The compound plane groups

The treatment can now be extended to the plane groups. In what ways can the 17 S groups be superimposed on the 46 antisymmetry (A) groups? If K antisymmetrical groups are all compatible with the same S group then there will be $\frac{1}{2}K(K-1)$ complex $(A{:}A')$ groups (neglecting which component is to be represented by which group) in addition to the K groups where A and A' are the same.

The plane groups are: 17 $(S{:}S)$ groups plus 46 $(A{:}A)$ groups plus:

Oblique

$(2pl{:}p_b'l)$, $(p2{:}p2')$, $(2p2{:}p_b'2)$ 3 $(S{:}A)$ groups
$(2p2'{:}p_b'2)$ $(A{:}A')$ group

Rectangular

$(pm{:}pm')$, $(pg{:}pg')$, $(cm{:}cm')$, $(2pm{:}p_b'm)$, $(2pm{:}p_b'g)$, $(2pm{:}p_b'lm)$, $(2pg{:}p_b'lg)$, $(cm{:}p_C'm)$, $(cm{:}p_C'g)$, $(4pm{:}c'm)$, $(pmm{:}pmm')$, $(pmm{:}pm'm')$, $(pmg{:}pm'g)$, $(pmg{:}pmg')$, $(pgg{:}pgg')$, $(pgg{:}pg'g')$, $(pmg{:}pm'g')$, $(cmm{:}cmm')$, $(cmm{:}cm'm')$, $(2pmm{:}p_b'mm)$, $(2pmg{:}p_b'mg)$, $(2pmm{:}p_b'gm)$, $(2pmg{:}p_b'gg)$, $(cmm{:}p_C'mm)$, $(cmm{:}p_C'mg)$, $(cmm{:}p_C'gg)$, $(4pm{:}c'mm)$
27 $(S{:}A)$ groups

The S group pm occurs six times, so there are 15 additional $(A{:}A')$ groups from it. Similarly pg occurs twice giving 1 group:

cm	$3\times$	giving	3
pmm	$4\times$	giving	6
pmg	$5\times$	giving	10
pgg	$2\times$	giving	1
cmm	$5\times$	giving	10

thus making a total of 46 $(A{:}A')$ groups in the rectangular system.

Hexagonal

$(p3ml{:}p3m')$, $(p3lm{:}p3lm')$, $(p6{:}p6')$
$(p6m{:}p6'm'm)$, $(p6m{:}p6'mm')$, $(p6m{:}p6m'm')$

That is, there are 6 $(S{:}A)$ groups plus 3 $(A{:}A')$ groups.

Square

$(p4{:}p4')$, $(4p4{:}p_C'4)$, $(p4m{:}p4'mm)$, $(p4m{:}p4'm'm)$, $(p4m{:}p4m'm)$, $(p4g{:}p4'gm')$, $(p4g{:}p4'g'm)$, $(p4g{:}p4g'm')$, $(4p4m{:}p_C'4mm)$, $(4p4m{:}p_C'4gm)$.

$p4$ occurs twice, $p4g$ three times and $p4m$ five times, so that there are 14 $(A{:}A')$ groups in this system.

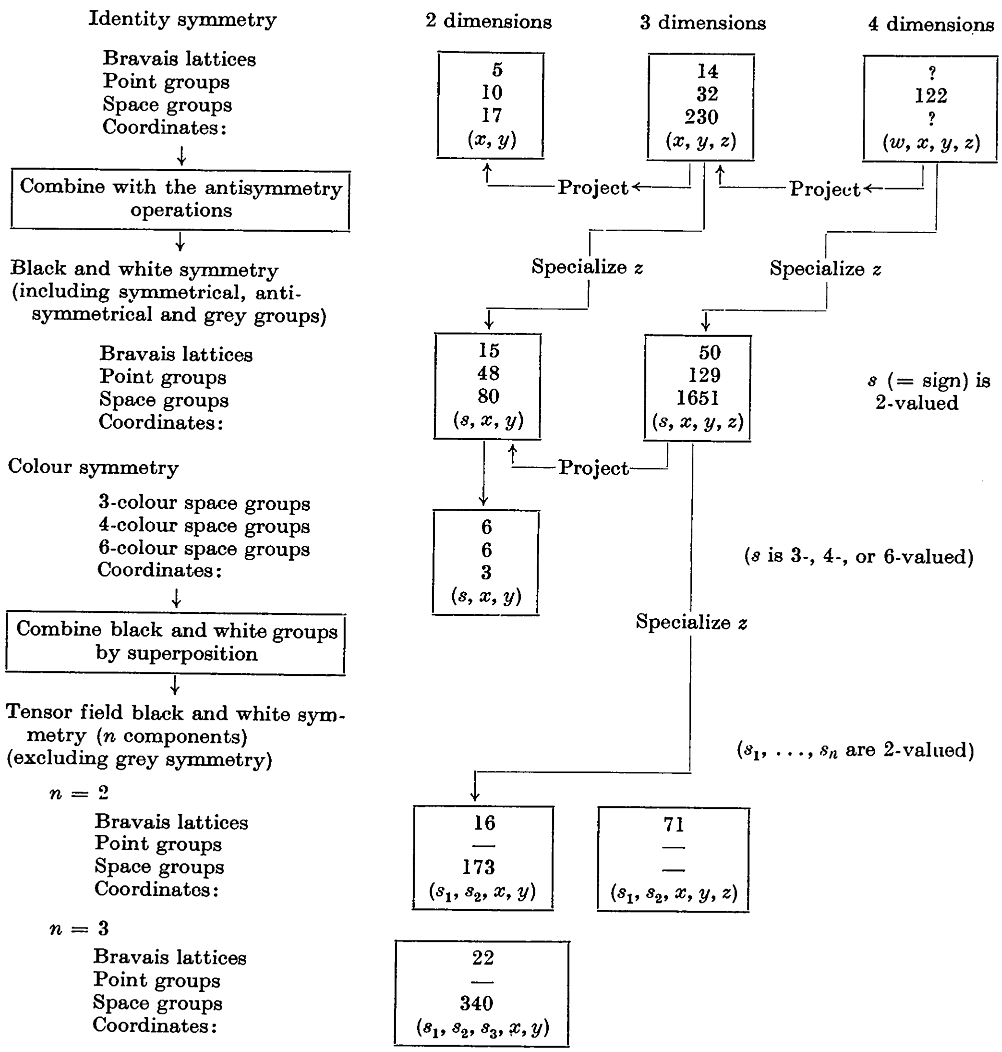

Fig. 3. The inter-relationship of the crystallographic symmetry classifications. The numbers of different types of groups.

Thus, a two-dimensional periodic field in which there are two signs attached to each point can have the following symmetries:

$$(S{:}S)\ 17 \text{ groups},\ (S{:}A)\ 46 \text{ groups},\ (A{:}A)\ 46 \text{ groups},\ (A{:}A')\ 64 \text{ groups}\,,$$

giving a total of 173 complex plane groups.

The extension of this treatment in which 3 or more signs are to be attached to each point is obvious but tedious. It can be seen that there will be the following types of groups if $n = 3$:

$$(S{:}S{:}S),\ (S{:}S{:}A),\ (S{:}A{:}A),\ (S{:}A{:}A'),\ (A{:}A{:}A),\ (A{:}A{:}A'),\ (A{:}A'{:}A'')\,.$$

The respective numbers of the groups of these types will be 17, 46, 46, 64, 46, 64, 57. The last figure, the number of ways in which three different antisymmetrical plane groups can be superposed, is obtained by taking the sum of the values of $\frac{1}{6}K(K-1)(K-2)$ for each of the 17 S groups, where K is the number of A groups compatible with each S group and hence mutually compatible. This gives a total of 340 groups.

Three dimensions

In three dimensions there are the following compound lattices:

Triclinic

$(2P{:}P_s)$

Monoclinic

$(2P{:}P_b)$, $(2P{:}P_a)$, $(C{:}P_C)$, $(2C{:}C_c)$, $(4P{:}C_a)$

Orthorhombic

$(2P{:}P_c)$, $(C{:}P_C)$, $(I{:}P_I)$, $(2C{:}C_c)$, $(4P{:}C_a)$, $(F{:}C_a)$, $(8P{:}F_s)$, $(2C{:}I_c)$

Tetragonal

$(2P{:}P_c)$, $(4P{:}2P_C)$, $(I{:}P_I)$, $(8P{:}2I_c)$

Hexagonal
$(2C{:}C_c)$

Rhombohedral
$(2R{:}R_I)$

Cubic
$(I{:}P_I)$, $(8P{:}F_s)$

(The cubic F lattice cannot be combined with any cubic A lattice.)

These lattices fall into classes, as follows:

	$(S:S)$	$(A:A)$	$(S:A)$	$(A:A')$
Triclinic	1	1	1	0
Monoclinic	2	5	5	$1+3=4$
Orthorhombic	4	8	8	$3+3=6$
Tetragonal	2	4	4	3
Hexagonal	1	1	1	0
Rhombohedral	1	1	1	0
Cubic	3	2	2	0
	14	22	22	13

making 71 in all.

In three dimensions the same principles can be applied to the space groups. There are 230 S groups and 1191 A groups so that the number of possible combinations rapidly becomes enormous. If two signs are attached to each point then each S group will correspond to an average of $1191/230 \approx 4$ A groups. Hence the number of $(A{:}A')$ groups will be very large as there will be a number of S groups which must have more than 10 compatible A groups.

The inter-relationship of the crystallographic symmetry groups

The numbers and inter-relationships of the various groups are summarized in Fig. 3.

The author is indebted to Prof. Ewald for a stimulating discussion of the possible generalization of the space groups.

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