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The Use of Directed Graphs in the Enumeration of Orthogonal Space Groups

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Theorems on directed graphs are used to obtain results on the enumeration of orthogonal space groups in arbitrary dimensions. In dimension 3 the graphs themselves provide a convenient notation for the orthorhombic space groups.

Recent work on space groups in arbitrary dimensions by various authors (Bülow, Neubüser & Wondratschek, 1971; Maxwell, 1975) has suggested algorithms for enumerating the space groups of certain crystal classes. In this paper we show how certain results (Schwarzenberger, 1974) can be interpreted to yield an enumeration of orthogonal space groups by directed graphs. This is of interest for two reasons. Firstly, the orthogonal space groups appear to be a particularly numerous family; thus one may hope that the work done on the enumeration of directed graphs [for references see Harary (1969)] might yield approximate estimates of the total number of space groups for a given dimension. Secondly, the enumeration for dimension 3 suggests for orthorhombic space groups a convenient diagram from which their Herman–Mauguin symbol may be readily found in any setting; it might therefore form the basis of a convenient classroom method for the derivation of the groups.

1. Orthogonal groups in arbitrary dimensions

Let $\mathscr{G}$ be a group of isometries in n-dimensional space. Elements of $\mathscr{G}$ may conveniently be represented in the form $(\mathbf{v},\theta)$ where $\mathbf{v}$ is a translation vector and θ is an orthogonal transformation. The action of $(\mathbf{v},\theta)$ is then to send $\mathbf{x}$ to $(\mathbf{v},\theta)(\mathbf{x})=\mathbf{v}+\theta\mathbf{x}$. The *lattice* of $\mathscr{G}$ is by definition the set T of all translation vectors $\mathbf{t}$ such that $(\mathbf{t},\iota)\in\mathscr{G}$. Here, and in what follows, ι denotes the identity transformation, so that the action of $(\mathbf{t},\iota)$ is to send $\mathbf{x}$ to $\mathbf{t}+\mathbf{x}$. The *point group* of $\mathscr{G}$ is the set $\mathscr{H}$ of all orthogonal transformations θ such that $(\mathbf{v},\theta)\in\mathscr{G}$ for some translation vector $\mathbf{v}$ (*not* necessarily a vector in T). The equation

$$(\mathbf{v},\theta)\,(\mathbf{t},\iota)\,(\mathbf{v},\theta)^{-1}=(\theta\mathbf{t},\iota)$$

shows that $\theta\mathbf{t}\in T$ for all $\mathbf{t}\in T$, $\theta\in\mathscr{H}$. Thus $\mathscr{H}$ is a subgroup of the *symmetry group* of T (by definition the set of all orthogonal transformations φ such that $\varphi\mathbf{t}\in T$ for all $\mathbf{t}\in T$). The group $\mathscr{G}$ belongs to the *orthogonal* crystal system if the symmetry group of T is generated by n reflexions $\mu_1,\ldots,\mu_n$ in mutually orthogonal hyperplanes. We denote this group by the symbol $m\ldots m$ (n factors). In the case $n=3$ orthogonal groups are usually called *orthorhombic*. The group $\mathscr{H}$ determines the *geometric* crystal class of $\mathscr{G}$; this is to be distinguished from the *arithmetic* crystal class which depends on the pair $T,\mathscr{H}$ [for terminology see Bülow, Neubüser & Wondratschek (1971) and Burckhardt (1966)].

Let $\mathbf{e}_i\in T$ be a shortest vector perpendicular to the mirror hyperplane of μ_i. Then T consists of all integral combinations of $\mathbf{e}_1,\ldots,\mathbf{e}_n$ with the addition, for centred lattices, of points which differ from an integral combination by a vector of the form

$$\mathbf{t}=\tfrac{1}{2}\sum_i b_i\mathbf{e}_i$$

where b_i is 0 or 1. It is convenient to denote such a centring vector $\mathbf{t}$ by the vector $(b_1\ldots b_n)$. If there are no centrings then T is said to be *primitive* and denoted P. If the only centring is $(1\ldots1)$ then T is said to be *centrally centred* and denoted Z, or I when $n=3$; if all possible centrings $(b_1\ldots b_n)$ with $\sum_i b_i=0 \bmod 2$ occur then T is said to be *everywhere face centred* and denoted U, or F when $n=3$ [for these and other notations see Bülow, Neubüser & Wondratschek (1971)]. Other centrings may occur when $n>3$. It was shown in a previous paper [see § 3 of Schwarzenberger (1974)] how a choice of centring corresponds to a choice of vector space over the field with two elements 0 and 1, and how the vector space determines the lattice T. The number of distinct lattices obtained in low dimensions is given by:

Theorem 1. The number O_n of distinct orthogonal lattices in n-dimensional space for $n=2,3,4$ is 2,4,8. Higher values are $O_5=16$, $O_6=36$, $O_7=80$.

2. Enumeration of primitive orthogonal groups

Let $\mathscr{G}$ be an orthogonal group with primitive lattice T. Then $\mu_i\in\mathscr{H}$ implies $(\mathbf{v}_i,\mu_i)\in\mathscr{G}$ for some translation vector $\mathbf{v}_i$. The equation

$$(\mathbf{v}_i,\mu_i)^2=(\mathbf{v}_i+\mu_i\mathbf{v}_i,\iota)$$

holds since each μ_i has order 2. It implies that $\mathbf{w}_i=\mathbf{v}_i+\mu_i\mathbf{v}_i\in T$ and that $\mathbf{v}_i$ can then be chosen so that

$$\mathbf{w}_i=\sum_{j\neq i}a_{ij}\mathbf{e}_j \quad\text{and}\quad \mathbf{v}_i=\sum_{j\neq i}\tfrac{1}{2}a_{ij}\mathbf{e}_j$$

where a_{ij} is 0 or 1. If $\mathbf{w}_i$ is non-zero then $(\mathbf{v}_i,\mu_i)$ is a glide with translation component given by the non-zero values of a_{ij}. These values may be represented on a directed graph with n vertices in which a directed edge runs from the ith vertex to the jth vertex if and only if $a_{ij}=1$. We obtain:

Theorem 2.1. The groups of arithmetic crystal class $Pm \dots m$ (n factors) are in one–one correspondence with the directed graphs with n vertices.

Corollary: The number d_n of such groups for $n=2,3,4$ is 3, 16, 218 [for complete tables of the various directed graphs see Appendix 2 of Harary (1969)]. Higher values are $d_5=9\,608$, $d_6=1\,540\,944$, $d_7=882\,033\,440$. In general d_n is bounded below by $2^{n(n-1)}/n!$.

It is easy to modify this representation to deal with groups of arithmetic crystal class $Pm \dots m$ ($n-1$ factors) where the point group $\mathscr{H}$ is generated by only $n-1$ reflections $\mu_1,\dots,\mu_{n-1}$. These determine $n-1$ mutually orthogonal vectors $\mathbf{e}_1,\dots,\mathbf{e}_{n-1}\in T$ as before; since T is primitive it consists of all integral combinations of these vectors and of the shortest vector $\mathbf{e}_n\in T$ orthogonal to all these. Constructing a directed graph in the same manner as before we find that there are no directed edges leaving the nth vertex which is distinguished from the remaining $n-1$ vertices. We obtain:

Theorem 2.2. The groups of arithmetic crystal class $Pm \dots m$ ($n-1$ factors) in n-dimensional space are in one–one correspondence with the directed graphs with n vertices, one of which is distinguished and from which no directed edges leave.

Corollary: The number c_n of such groups for $n=2,3,4$ is 2, 10, 104. Higher values are $c_5=3\,044$, $c_6=291\,968$, $c_7=96\,928\,992$. In general c_n is bounded below by $2^{(n-1)}/(n-1)!$ and above by $2^{n-1}d_{n-1}$.

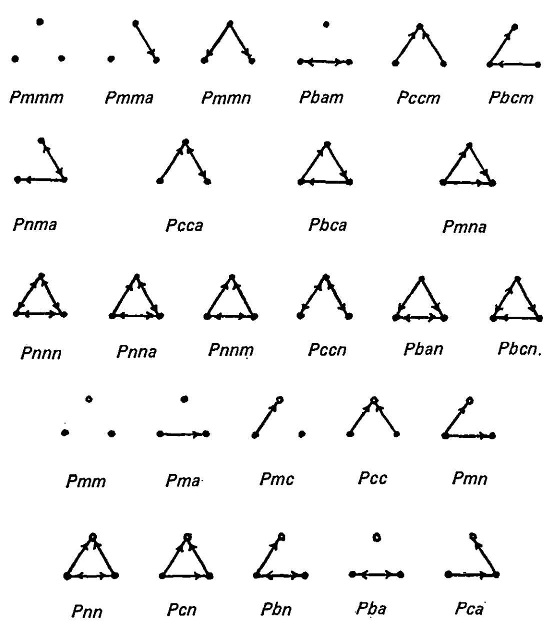

Fig. 1. Directed graphs for primitive orthorhombic space groups.

When $n=3$ these theorems do not, of course, give any new information but they do suggest for orthorhombic space groups convenient diagrams from which the Hermann–Mauguin symbol may be readily found in any setting. As the basis of a classroom method it is simpler than that of Belov (1951) or Belov & Klevtsova (1959). The corresponding directed graphs are displayed in Fig. 1; the great advantage of these diagrams is that they do not depend on a choice of setting. The Hermann–Mauguin symbol given in Fig. 1 is that which results from the setting in which coordinates x,y,z correspond to the vertices

$$\begin{array}{ccc} & z & \\ y & & x \end{array}$$

and to positions in the symbol $Pxyz$: in each position we write m if no directed edges leave the corresponding vertex; we write a, b, or c if a single edge leaves the vertex and runs to x, y, or z respectively; we write n if two edges leave the corresponding vertex (compare the diagrams for $Pmmm$, $Pmma$ and $Pmmn$ in Fig. 1).

The groups of arithmetic crystal class $Pm \dots m$ (k factors) in n-dimensional space for $k<n-1$ can be dealt with similarly. The k reflexions $\mu_1,\dots,\mu_k$ determine mutually orthogonal vectors $\mathbf{e}_1,\dots,\mathbf{e}_k$ and the glide vectors $\mathbf{v}_1,\dots,\mathbf{v}_k$ must therefore have the form:

$$\mathbf{v}_i=\tfrac{1}{2}\sum_{j\neq i} a_{ij}\mathbf{e}_j+\tfrac{1}{2}a_i\mathbf{t}_i$$

where $1\le j\le k$ and $\mathbf{t}_i\in T$ lies in the $(n-k)$-dimensional space orthogonal to $\mathbf{e}_1,\dots,\mathbf{e}_k$. However, there is no canonical choice of basis for the latter space: it follows that there is no longer a natural representation in terms of directed graphs and, equally, that the groups no longer belong to the orthogonal crystal system. Each group can be represented by a directed graph with n vertices, $n-k$ of which are distinguished and from which no directed edges leave; however it is now possible for distinct directed graphs to determine the same group. The reader will easily verify from this description that, if $c_{k,n}$ is the number of such groups then

$$c_{k+1}=c_{k,k+1}<c_{k,k+2}<\dots<c_{k,2k}=c_{k,n}$$

for all $n>2k$. Hence $c_{1,n}=2$ for $n>1$, $c_{2,n}=13$ for $n>3$, and $c_{3,n}=208$ for $n>5$.

3. Centrally centred orthogonal groups

Other lattices yield enumeration methods which are an adaptation of those for primitive lattices; we illustrate this by considering in detail the centrally centred lattice Z with centring $(1 \dots 1)$. The centring causes an equivalence relation between directed graphs, since the vectors

$$\mathbf{v}_i=\tfrac{1}{2}\sum_{j\neq i} a_{ij}\mathbf{e}_j \quad \text{and} \quad \mathbf{v}_i'=\tfrac{1}{2}\sum_{j\neq i}(1-a_{ij})\mathbf{e}_j$$

are related by $(\mathbf{v}_i',\mu_i)=(\mathbf{z},\iota)\,(\mathbf{v}_i,\mu_i)^{-1}$ and therefore these glides determine the same group $\mathscr{G}$. In terms of directed graphs this means that the r directed edges leaving the

ith vertex may be replaced by the complementary set of $n-1-r$ edges. Such replacements may occur at any number of vertices, and the resulting directed graphs all determine the same group $\mathcal{G}$. If n is even then such replacements alter the parity of the number of edges leaving a vertex. We therefore obtain:

Theorem 3.1. If n is even then the groups of arithmetic crystal class $Zm \ldots m$ (n factors) are in one–one correspondence with the directed graphs with n vertices such that each vertex v has an even number (possibly zero) of edges leaving v.

The case of groups of arithmetic crystal class $Zm \ldots m$ (n factors) for n odd is slightly more complicated: now each vertex has a parity which is unaltered by replacement and is an invariant of the group $\mathcal{G}$. In case $n=3$ this labelling of the 3 vertices (+ for even parity, − for odd parity) is sufficient to determine $\mathcal{G}$, as shown in Fig. 2 (the choice of Hermann–Mauguin symbol is now more arbitrary: the same group can, for example, be denoted *Imma* or *Immb* as is indicated by the label − of the z vertex). For higher values of n, whether even or odd, it is more convenient to use the replacements to make the number of directed edges leaving each vertex less than $n/2$.

Corollary: The number of groups of arithmetic crystal class $Zm \ldots m$ (n factors) is bounded below by $2^{n(n-2)}/n!$ and for $n=2,3,4,5,6$ is 1,4,19,342,25 112.

In the case of arithmetic crystal class $Zm \ldots m$ ($n-1$ factors) the replacements can be used to ensure that $a_{in}=0$ for $i=1,\ldots,n-1$. Thus the enumeration for $Zm \ldots m$ ($n-1$ factors) in n-dimensional space becomes identical to the enumeration for $Pm \ldots m$ ($n-1$ factors) in ($n-1$)-dimensional space, and we obtain:

Theorem 3.2. The groups of arithmetic crystal class $Zm \ldots m$ ($n-1$ factors) in n-dimensional space are in one–one correspondence with the directed graphs with $n-1$ vertices.

Corollary: The number of such groups is bounded below by $2^{(n-1)(n-2)}/(n-1)!$ and for $n=2,3,4,5,6$ is 1,3,16,218,9 608.

The directed graphs which arise in the case $n=3$ are illustrated in Fig. 2, together with those which arise from the centred lattices: A with centring (011), C with centring (110). In all cases replacements arising from the existence of centring vectors have been used to arrive at a directed graph with as few edges as possible; positions for edges which have been banned by such choices are indicated by dotted lines. This method can be applied in all cases where the possible glide vectors necessarily have integral multiples of $\frac{1}{2}$ as coefficients; it must be modified in cases, such as the everywhere face-centred lattice below, in which multiples of $\frac{1}{4}$ can occur.

4. Everywhere face-centred orthogonal groups

The everywhere face-centred lattice U stands at the opposite extreme from the primitive and centrally centred lattices in having the largest number of centring points. For any orthogonal lattice T, the groups of arithmetic crystal class $Tm \ldots m$ (n factors) and $Tm \ldots m$ ($n-1$ factors) are in one–one correspondence with equivalence classes of directed graphs with n vertices. The precise form of the equivalence relation depends on the lattice and in general will be complicated, but when $T=U$ it simplifies to give:

Theorem 4.1. The groups of arithmetic crystal class $Um \ldots m$ (n factors) are in one–one correspondence with the (non-directed) graphs with n vertices such that each vertex v has an even number (possibly zero) of edges with v as vertex.

Proof: The glide vectors $\mathbf{v}_i,\mathbf{v}_j$ determine a vector $\mathbf{t}_{ij}\in U$ by the equation

$$(\mathbf{v}_i,\mu_i)\,(\mathbf{v}_j,\mu_j)\,(\mathbf{v}_i,\mu_i)^{-1}\,(\mathbf{v}_j,\mu_j)^{-1}=(\mathbf{t}_{ij},\iota)\,.$$

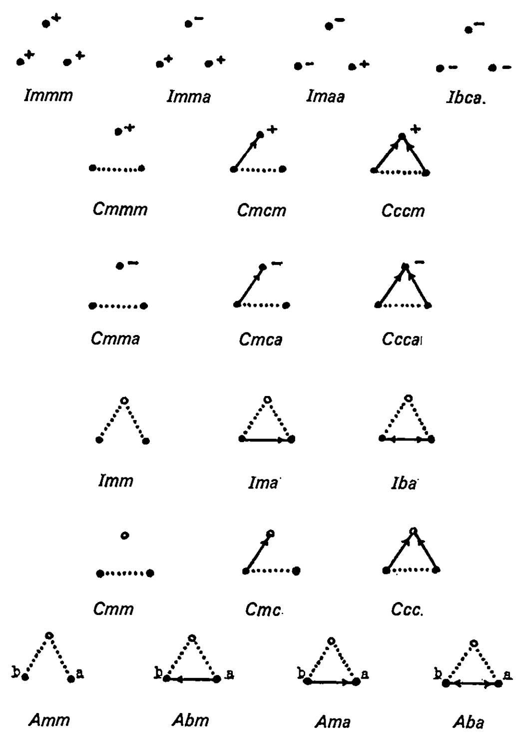

Fig. 2. Directed graphs for body-centred and centred orthorhombic space groups.

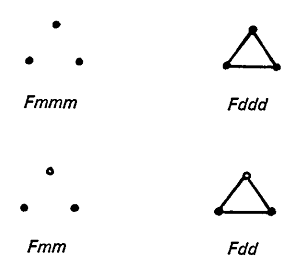

Fig. 3. Graphs for face-centred orthorhombic space groups.

On the other hand, they can be chosen to have the form

$$\mathbf{v}_i = \frac{1}{4} \sum_{j \neq i} a_{ij} \mathbf{e}_j \quad \text{where} \quad \sum_{j \neq i} a_{ij} = 0 \bmod 2 .$$

A calculation shows that

$$\mathbf{t}_{ij} = \tfrac{1}{2} a_{ij} \mathbf{e}_j - \tfrac{1}{2} a_{ji} \mathbf{e}_i$$

and therefore $a_{ij} = a_{ji}$ mod 2. The graph representing $\mathscr{G}$ (Fig. 3) is obtained by joining the ith vertex to the jth vertex by an edge if and only if a_{ij} is an odd integer.

Corollary: The number of such groups is bounded below by $2^{(n-1)(n-2)/2}/n!$ and for $n=2,3,4,5,6$ is 1,2,3,7,16 [for diagrams of the various graphs see Appendix 1 of Harary (1969)].

Theorem 4.2. The groups of arithmetic crystal class $Um \ldots m$ ($n-1$ factors) are in one–one correspondence with the (non-directed) graphs with $n-1$ vertices.

Proof: The above description shows that each group determines a graph with n vertices, one of which is distinguished. An even number of edges end at each vertex. Removing all edges which end at the distinguished vertex we obtain the required graph with $n-1$ vertices.

Corollary: The number of such groups is bounded below by $2^{(n-1)(n-2)/2}/(n-1)!$ and for $n=2,3,4,5,6$ is 1,2,4,11,34.

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About Quartets — Relation with the Invariant Phases of Triplets

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On the basis that quartet invariants are the difference between triplet invariants, we have determined a theoretical distribution of the quartet invariant phases. New formulae to estimate triplet invariant cosines are described and the results they give for a known test structure are compared .

Recently, Hauptman (1974) gave an estimate of the invariant cosine of the sum of phases of four linear dependent reflexions l,m,n,p such that the sum over each set of three indices is zero ($l+m+n+p=0$). Schenk (1973) had already spoken of such invariants as quartets of the second kind, and showed that they are obtained by constructing the difference of the phases of two invariant triplets relative to the same reflexion H, *e.g.*

$$\varphi_{\bar{H}} + \varphi_K + \varphi_{H-K} = \alpha_{H,K} ,$$

and

$$\varphi_{\bar{H}} + \varphi_L + \varphi_{H-L} = \alpha_{H,L} .$$

from which is derived the quartet $\varphi_K + \varphi_{H-K} + \varphi_{\bar{L}} + \varphi_{L-H}$ (the sum of indices of the four reflexions $K, H-K, \bar{L}, L-H$ is actually equal to zero) with a phase equal to $(\alpha_{H,K} - \alpha_{H,L})$.

The value of the invariant cosine cos $(\varphi_K + \varphi_{H-K} + \varphi_{\bar{L}} + \varphi_{L-H})$ may be estimated from the moduli of seven structure factors $E_K, E_{H-K}, E_L, E_{L-H}$ and also E_H, E_{K-L} and E_{K+L-H}. Such an estimation is more accurate than the estimation of the phases $\alpha_{H,K}$ or $\alpha_{H,L}$ of the generating triplets each of which is computed from only three structure factors E_H, E_K and E_{H-K} or E_H, E_L and E_{H-L}.

Furthermore, different algebraic formulae have been described to compute the invariant cosine of the phase of a triplet from the moduli of the structure factors of the whole reciprocal space: (1) triple product formula (Hauptman, Fisher, Hancock & Norton, 1969) and (2) MDKS formula (Fisher, Hancock & Hauptman, 1970).

We intend, here, to compare results provided respectively by the estimation of quartet phases and by al-