

if such crystals were used in precision spectroscopy. The Darwin-Prins theory, however, may be used to correct for this asymmetry in the instrumental window. The magnitude of the calculated correction (at $\lambda = 0.86 \text{ \AA}^*$) is such that the wavelength of monochromatic radiation as measured by a pair of Ge (111) crystals would be less than the true value by 17 ppm. The correction is approximately the same whether the peak or the average of the two half-intensity points is chosen as the wavelength criterion. In ordinary X-ray spectroscopy, the width of a spectral line is considerably greater than the width of the instrumental window, and in this case the appropriate corrections may be obtained from the Darwin-Prins theory by a method developed by Sauder (1966).

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Symmetry in the Generation of Trial Structures

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In the generation of trial structures by the systematic variation of the position and orientation of a molecule of known dimensions, the ranges to be scanned by the positional and orientational parameters depend on the symmetry of the molecule and on the space group. The set of transformations of the crystal axes that leave invariant the coordinates of equivalent positions for a given space group defines a corresponding derivative symmetry, conforming to one of thirty distinct 'Cheshire' groups. The direct product of this group with the molecular point group specifies the symmetry of the six-dimensional space of the trial-structure parameters. The asymmetric unit in this space is the region to be scanned by the several parameters.

Trial-structure parameters defined

A recurring problem is the determination of the structure of a crystal whose asymmetric unit comprises a chemical entity, e.g. a molecule, of known or reasonably conjectured internal dimensions. The initial task,

estimating the position and orientation of the molecule in the unit cell, may often be amenable to some kind of trial-and-error approach. Whatever the criterion chosen for judging the acceptability of a trial structure, some systematic procedure is needed for generating alternative models compatible with the available structural information. We suppose here that this information comprises the cell dimensions, the space group, and the postulated molecular dimensions. Our formu-

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lation follows that outlined in a preliminary examination of the problem (Hirshfeld & Rabinovich, 1966).

Let us define the molecule by assigning to each atom a chemical label and three coordinates l, m, n with respect to orthogonal molecular axes L, M, N . If we specify a second set of orthogonal axes A, B, C fixed in the crystal, we can define any molecular orientation by means of a matrix $[R]$ that relates the two sets of atomic coordinates, *i.e.*

$$(XYZ) = (lmn) [R],$$

where X, Y, Z are coordinates with respect to A, B, C . The matrix $[R]$, expressing the relative orientations of the two sets of axes, may be written as a function of a set of Eulerian angles φ, ψ, θ defined in Fig. 1. An auxiliary two-valued parameter e is needed to specify the chirality of the molecular axes; it takes the value $+1$ if the crystal and molecular axes are related by a proper rotation, -1 if by an improper rotation. (For given values of φ, ψ, θ , changing the sign of e corresponds to a reversal of the M axis, L and N remaining fixed.) The explicit form of $[R(e, \varphi, \psi, \theta)]$ is

$$[R] = \begin{bmatrix} \cos \varphi \cos \psi - \sin \varphi \sin \psi \cos \theta & \sin \varphi \cos \psi & \sin \psi \cos \theta \\ -e(\cos \varphi \sin \psi + \sin \varphi \cos \psi \cos \theta) & e \cos \varphi \sin \psi & e \sin \psi \cos \theta \\ \sin \varphi \sin \psi & -\cos \varphi \sin \psi & \cos \theta \end{bmatrix}.$$

Measuring φ, ψ, θ in revolutions, we find that the possible values of these angles lie in the ranges

$$0 \leq \varphi < 1, 0 \leq \psi < 1, 0 \leq \theta \leq \frac{1}{2}.$$

To obtain fractional atomic coordinates x, y, z with respect to the unit-cell edges a, b, c , we require a further transformation, defined by a second matrix $[A]$ that relates the orthogonal axes A, B, C to the crystal axes a, b, c . The complete expression is

$$(xyz) = (lmn) [R] [A] + (uvw), \quad (1)$$

where u, v, w are the fractional coordinates of the molecular origin in the unit cell. The form of $[A]$ depends on the cell dimensions and on the way the axes A, B, C are chosen. It is defined by the equation

$$A_k = A_{ki} a_i,$$

with implied summation over i , where we have used the notation a_i ($i=1, 2, 3$) for a, b, c , A_k ($k=1, 2, 3$) for A, B, C .

For given cell dimensions and space group and given molecular dimensions, any possible structure may be defined by specification of the seven parameters $e, \varphi, \psi, \theta, u, v, w$. We now ask: what ranges must these parameters scan so as to generate all possible structures? We can emphasize the analogy between this problem and the more familiar one of the demarcation of the limits of the asymmetric unit for a given space group by rephrasing our query in the form: what is the symmetry of the space defined by these seven parameters?

The answer evidently depends both on the symmetry of the molecule and on that of the crystal. We shall now consider these in turn.

Molecular symmetry

Consider, first, the effect of (non-crystallographic) molecular symmetry. Let $[S]$ be a matrix that relates the coordinates, with respect to the axes L, M, N , of symmetry-related pairs of atoms in the molecule so that every atom, with coordinates l, m, n , is matched by an identical atom with coordinates l_s, m_s, n_s , where

$$(l_s m_s n_s) = (lmn) [S].$$

Application of this matrix to the coordinates of all the atoms in the molecule leaves the list of coordinates unchanged but for a permutation of the atomic sequence. If we subsequently apply any transformation matrix $[R(e, \varphi, \psi, \theta)]$ to the permuted coordinates we shall obtain the same set of coordinates X, Y, Z , in permuted sequence, as if we had applied $[R]$ to the original coordinate list. Hence the matrix $[R]$ and the

$$\begin{bmatrix} \sin \varphi \cos \psi + \cos \varphi \sin \psi \cos \theta & \sin \varphi \sin \psi & \cos \varphi \cos \psi \\ -e(\sin \varphi \sin \psi - \cos \varphi \cos \psi \cos \theta) & e \cos \varphi \sin \psi & e \sin \psi \cos \theta \\ -\cos \varphi \sin \psi & \cos \varphi \cos \psi & \cos \theta \end{bmatrix}.$$

matrix $[R_s] = [S] [R]$ define indistinguishable molecular orientations and are entirely equivalent. Correspondingly, the sets of molecular parameters e, φ, ψ, θ and $e_s, \varphi_s, \psi_s, \theta_s$ satisfying the relation

$$[R(e_s, \varphi_s, \psi_s, \theta_s)] = [S] [R(e, \varphi, \psi, \theta)]$$

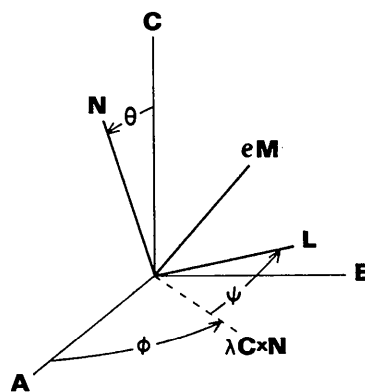


Fig. 1. Definition of Eulerian angles φ, ψ, θ relating molecular axes L, M, N to reference axes A, B, C fixed in the unit cell. The A axis may be imagined either to project forward out of the paper ($\lambda = +1$) or to recede behind the paper ($\lambda = -1$). In either case the angles are:

Angle	Measured from	to	In positive sense about	Range (revolutions)
φ	A	$\lambda C \times N$	λC	0 to 1
ψ	$\lambda C \times N$	L	λN	0 to 1
θ	C	N	$C \times N$	0 to $\frac{1}{2}$

where $\lambda = [\text{ABC}]$; *i.e.* $+1$ if A, B, C form a right-handed axial system, -1 if left-handed.

are equivalent under the symmetry operation [S]. Values of $e_s, \varphi_s, \psi_s, \theta_s$ equivalent to the set e, φ, ψ, θ are given in Table 1 for some commonly encountered molecular symmetry operations. It is an awkward consequence of the unsymmetrical way in which the several axes enter into the definitions of the Eulerian angles that a simple interchange of axial labels can radically alter the expressions for equivalent parameter sets corresponding to a given symmetry operation. Any axis of higher than twofold symmetry is conveniently taken to lie along N. If a molecule possesses more than one such axis, the expressions for $e_s, \varphi_s, \psi_s, \theta_s$ become far more complicated and, correspondingly, less useful.

Table 1. Parameter sets $e_s, \varphi_s, \psi_s, \theta_s$ corresponding, under various molecular symmetry operations, to reference set e, φ, ψ, θ

Letters in parentheses following Hermann-Mauguin symbols for point-group operations identify directions of symmetry axes or of normals to symmetry planes.

$\bar{1}$	$-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta$
$2(L)$	$e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta$
$2(M)$	$e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta$
$2(N)$	$e, \varphi, \frac{1}{2} + \psi, \theta$
$m(L)$	$-e, \varphi, \frac{1}{2} + \psi, \theta$
$m(M)$	$-e, \varphi, \psi, \theta$
$m(N)$	$-e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta$
$k^j(N)\dagger$	$e, \varphi, ej/k + \psi, \theta$
$\bar{k}^j(N)\dagger$	$-e, \frac{1}{2} + \varphi, -ej/k - \psi, \frac{1}{2} - \theta$ (j odd)

$\dagger k^j(N)$ is a rotation through $\omega = 2\pi j/k$ radians about the N axis, the positive sense of rotation being taken so that the coordinates l, m, n are transformed to $l \cos \omega - m \sin \omega, l \sin \omega + m \cos \omega, n$; $\bar{k}^j(N)$ is the same rotation combined, for j odd, with inversion in the molecular origin. A single k -fold rotation axis entails $k-1$ distinct symmetry operations k^j ($j=1, 2, \dots, k-1$). A \bar{k} inversion axis entails, if k is odd, k operations \bar{k}^j and $k-1$ operations k^j ; if k is even, $\frac{1}{2}k$ operations \bar{k}^j and $\frac{1}{2}k-1$ operations k^j .

For a molecule of given symmetry, suitably oriented with respect to the molecular axes L, M, N, we extract from Table 1 the appropriate parameter sets corresponding to the several point-group operations and so compile a list of parameter sets $e_s, \varphi_s, \psi_s, \theta_s$ that are equivalent by virtue of the molecular symmetry. For example, with a molecule of symmetry $2/m$, oriented with its twofold axis along L, the point-group operations 1, $2(L)$, $m(L)$, and $\bar{1}$ correspond to the four equivalent parameter sets:

$$\begin{aligned} & e, \varphi, \psi, \theta; \\ & e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta; \\ & -e, \varphi, \frac{1}{2} + \psi, \theta; \\ & -e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta. \end{aligned}$$

The coordinates u, v, w have been omitted from this discussion since we always choose the molecular origin so that they are not affected by any of the point-group operations of the molecule.

Space-group symmetry

We turn next to the effect of crystal symmetry. Suppose the lattice has been defined by specification of the cell dimensions $a, b, c, \alpha, \beta, \gamma$ and the space group by tabulation of the coordinates of equivalent positions in the unit cell. Given these crystallographic parameters, the assignment of chemical labels and coordinates to the atoms in one asymmetric unit will completely determine the structure (except for possible enantiomorphism; see below). The converse, however, is not true; alternative sets of coordinates may describe the same structure. Such alternative sets of coordinates may be related by three types of transformation:

- a shift of origin, consistent with the table of coordinates of equivalent positions;
- reversal or interchange of unit-cell axes, consistent with the coordinates of equivalent positions and with the cell dimensions;
- replacement of every atom by a symmetry-related atom.

The admissible shifts of origin comprise arbitrary displacements along any polar axes as well as translations by particular submultiples of the lattice vectors, depending on the space group. Thanks to the indeterminacy in choice of origin, the position of the molecular centre may be arbitrarily restricted to a region that is invariably smaller than the full unit cell, *i.e.* the molecular coordinates u_i never need to scan the entire range $0 \leq u_i < 1$. Thus in space group $P2$ the coordinates of equivalent positions are generally referred to an origin on the diad axis. But they do not restrict the position of the origin along this axis and, furthermore, four diad axes pass through each unit cell, any one of which may contain the origin. We are thus free to specify our origin by arbitrarily restricting the molecular coordinates to the region

$$0 \leq u < \frac{1}{2}, v = 0, 0 \leq w < \frac{1}{2}.$$

An example of (b) is the simultaneous reversal of the **a** and **c** axes of a monoclinic unit cell. This transformation, which changes the signs of all x and z coordinates, may equally be regarded as an example of (c), if the space group is, *e.g.*, $P2$, or of (a) and (c) combined, if it is $P2_1$. But in general (b) is more inclusive than (c), *i.e.* the equivalences deducible from transformations of type (b) include all those deducible from (c) plus, frequently, others not permitted by (c). Thus, for all monoclinic space groups the pertinent (b) type transformations comprise all the operations of point group $2/m$ (reversal of **b**, or of **a** and **c**, or of all three), while (c) is restricted by the point group of the particular structure, which may be 2 or m or $2/m$. Accordingly we may disregard (c) and derive all the relevant equivalences from a consideration of (a) and (b) transformations alone.

Our problem, then, is to catalogue, for a given space group, the translations and rotations of the crystal axes that leave invariant the cell dimensions and the coor-

dinates of equivalent positions. These two items of input data together specify the magnitudes and directions of all the lattice vectors and the nature and location, within the unit cell, of all the symmetry elements. The set of axial transformations under which these symmetry specifications are invariant defines a special kind of derivative symmetry for the space group. More general than the symmetry of the crystal structure itself, it is the symmetry the structure would acquire if all its atoms were removed and only its symmetry elements left behind, like the grin of the vanishing Cheshire cat. The full symmetry of the space group is, of course, always included in this derivative symmetry, since the space-group operations themselves must leave all symmetry elements invariant; thus the space group is necessarily a subgroup of its derivative symmetry group, which we may call its 'Cheshire' group. This conclusion justifies our previous generalization that every (c) type

transformation, which represents a space-group operation, is matched by an equivalent (b) type transformation, which is an operation of the Cheshire group.

The Cheshire groups

With a small effort we can derive the Cheshire group for any space group. The results appear in Table 2, where the 230 space groups are classified according to their corresponding Cheshire groups. Each Cheshire group is characterized by its Hermann-Mauguin symbol, referred to its own unit cell, and by the axes of this cell defined in terms of the space-group axes **a**, **b**, **c**.

Those Cheshire groups that derive from polar space groups have unit cells with one or more axes of vanishing length. These define degenerate 'lattices', to which we have assigned the symbol Z^n , where the integer n denotes the number of vanishing axes. These

Table 2. *The 230 space groups classified by corresponding Cheshire groups*

a, **b**, **c** are the axes of the conventional crystallographic unit cell, hexagonal axes in the trigonal and hexagonal systems; ϵ is an infinitesimal quantity, used in defining vanishing axes of the Cheshire-group unit cell.

Cheshire group and unit cell	Corresponding space groups
$P\bar{1}$	$P\bar{1}$
$Z^3\bar{1}$	$P1$
$P2/m$	$P2/m, P2_1/m, C2/m, P2/c, P2_1/c, C2/c$
Z^{12}/m	$P2, P2_1, C2$
$Z2^2/m$	Pm, Pc, Cm, Cc
$Pmmm$	$P222, P222_1, P2_12_12, P2_12_12_1, C222_1, C222, I222, I2_12_12_1, Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnm, Pmnm, Pbcn, Pbca, Pnma, Cmcm, Cmca, Cmmm, Cccm, Cmca, Ccca, Fmmm, Immm, Ibam, Ibca, Imma$
$Pnnn$	$Fddd$
$Immm$	$F222$
Z^1mmm	$Pmm2, Pmc2_1, Pcc2, Pma2, Pca2_1, Pnc2, Pmn2_1, Pba2, Pna2_1, Pnn2, Cmm2, Cmc2_1, Ccc2, Amm2, Abm2, Ama2, Aba2, Fmm2, Imm2, Iba2, Ima2$
Z^1ban	$Fdd2$
$P4_222$	$P4_122, P4_12_12, P4_322, P4_32_12$
$Z^{14}22$	$P4_1, P4_3$
$P4/mmm$	$P\bar{4}, P4/m, P4_2/m, P4/n, P4_2/n, I4/m, P422, P42_12, P4_222, P4_22_12, I422, P\bar{4}2m, P\bar{4}2c, P\bar{4}2_1m, P\bar{4}2_1c, P\bar{4}2m, P\bar{4}2c, P\bar{4}2_1m, P\bar{4}2_1c, P4/mmm, P4/mcc, P4/nbm, P4/nnc, P4/mbm, P4/mnc, P4/nmm, P4/ncc, P4_2/mmc, P4_2/mcm, P4_2/nbc, P4_2/nmm, P4_2/mbc, P4_2/mnm, P4_2/nmc, P4_2/ncm, I4/mmm, I4/mcm$
$P4_2/nmm$	$I4_1/a, I4_122, I\bar{4}2d, I4_1/amd, I4_1/acd$
$I4/mmm$	$I\bar{4}, I\bar{4}m2, I\bar{4}c2$
Z^{14}/mmm	$P4, P4_2, I4, P4mm, P4bm, P4_2cm, P4_2nm, P4cc, P4nc, P4_2mc, P4_2bc, I4mm, I4cm$
Z^{14}/nbm	$I4_1, I4_1md, I4_1cd$
$R\bar{3}m$	$R\bar{3}, R32, R\bar{3}m, R\bar{3}c$
$Z^1\bar{3}1m$	$R3, R3m, R3c$
$P6_222$	$P3_121, P6_122, P6_422$
	$P3_112$
$P6_422$	$P3_221, P6_522, P6_222$
	$P3_212$
Z^1622	$P6_1, P6_5, P6_2, P6_4$
	$P3_1, P3_2$
$P6/mmm$	$P\bar{3}, P321, P\bar{3}1m, P\bar{3}1c, P\bar{3}m1, P\bar{3}c1, P6/m, P6_3/m, P622, P6_322, P\bar{6}2m, P\bar{6}2c, P6/mmm, P6/mcc, P6_3/mcm, P6_3/mmc$
	$P312, P\bar{6}, P6m2, P\bar{6}c2$
Z^{16}/mmm	$P31m, P31c, P6, P6_3, P6mm, P6cc, P6_3cm, P6_3mc$
	$P3, P3m1, P3c1$
$Ia3$	$Pa3$
$I4_132$	$P4_332, P4_132$
$Pm3m$	$Fm3, F432, Fm3m, Fm3c$
$Pn3m$	$Fd3, F4_132, Fd3m, Fd3c$
$Im3m$	$P23, I23, Pm3, Pn3, Im3, P432, P4_232, I432, P\bar{4}3m, I\bar{4}3m, P\bar{4}3n, Pm3m, Pn3n, Pm3n, Pn3m, Im3m$
	$F23, F\bar{4}3m, F\bar{4}3c$
$Ia3d$	$P2_13, I2_13, Ia3, I4_132, I\bar{4}3d, Ia3d$

axes, though having no length, do have direction and are indicated in Table 2 with the aid of the infinitesimal ε . The Z^1 lattice consists of an array, primitive in every case, of parallel lines, the Z^2 lattice of a set of parallel planes, and the Z^3 lattice of a three-dimensional continuum. In all we find there are 30 distinct Cheshire groups; of these 20 are identical with ordinary space groups and 10 are continuous groups with Z -type lattices.

To make use of Table 2 we first locate, in the column headed 'Space groups', the particular space group with which we are concerned. To the left of this entry we then find the corresponding Cheshire group, with its unit cell. Our next step is to draw up a table of coordinates of equivalent positions for the Cheshire group, most conveniently by referring to *International Tables for X-ray Crystallography* (1952), and transform these to the original unit-cell axes. In doing so we must take heed to choose a consistent origin for space group and Cheshire group so that the symmetry elements common to both groups are properly coincident when the two unit cells are superimposed with matching origins. The transformed coordinates of equivalent positions x_t, y_t, z_t then define, for the given space group, all possible alternative ways of assigning atomic coordinates to the same structure.

As an example of the procedure, consider the space group $I4_122$. Table 2 assigns to this space group the Cheshire group $P4_2/nmm$ with a unit cell $\frac{1}{2}(\mathbf{a}-\mathbf{b}) \times \frac{1}{2}(\mathbf{a}+\mathbf{b}) \times \frac{1}{2}\mathbf{c}$. We can write the axes of this unit cell as $M_{ij}\mathbf{a}_j$, thus defining the transformation matrix

$$M = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix}.$$

We suppose our origin has been chosen at the point 222 so that the equivalent positions for $I4_122$ are (*International Tables*):

$$\begin{aligned} &(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + \\ &x, y, z; \bar{x}, \bar{y}, z; \bar{x}, \frac{1}{2} + y, \frac{1}{4} - z; x, \frac{1}{2} - y, \frac{1}{4} - z; \\ &y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \bar{y}, \frac{1}{2} + x, \frac{1}{4} + z; y, \frac{1}{2} - x, \frac{1}{4} + z. \end{aligned}$$

The corresponding origin in $P4_2/nmm$ must then be at one of the points 222 or $\bar{4}2m$ (which is a supergroup of 222). The latter alternative must be chosen so that the 4_1 axis of $I4_122$, at $\frac{1}{4}, \frac{1}{4}, z$, may coincide with an equivalent symmetry element (in the guise of a 4_2 axis at $0, \frac{1}{2}, z$) of $P4_2/nmm$ (Fig. 2). With this choice of origin, the equivalent positions of $P4_2/nmm$ may be written:

$$\begin{aligned} &x', y', z'; \bar{x}', \bar{y}', z'; \frac{1}{2} + x', \frac{1}{2} + y', \frac{1}{2} - z'; \frac{1}{2} - x', \frac{1}{2} - y', \frac{1}{2} - z' \\ &\bar{x}', y', \bar{z}'; x', \bar{y}', \bar{z}'; \frac{1}{2} - x', \frac{1}{2} + y', \frac{1}{2} + z'; \frac{1}{2} + x', \frac{1}{2} - y', \frac{1}{2} + z' \\ &\bar{y}', x', \bar{z}'; y', \bar{x}', \bar{z}'; \frac{1}{2} - y', \frac{1}{2} + x', \frac{1}{2} + z'; \frac{1}{2} + y', \frac{1}{2} - x', \frac{1}{2} + z' \\ &y', x', z'; \bar{y}', \bar{x}, z'; \frac{1}{2} + y', \frac{1}{2} + x', \frac{1}{2} - z'; \frac{1}{2} - y', \frac{1}{2} - x', \frac{1}{2} - z' \end{aligned}$$

The use of primes serves to remind us that these coordinates are referred to the axes of the Cheshire-group unit cell. To transform them to the space-group cell

axes $\mathbf{a}, \mathbf{b}, \mathbf{c}$, we regard each coordinate set in the above list as a row vector and *postmultiply* by the matrix $[M]$. We thus obtain:

$$\begin{aligned} &\frac{1}{2}(x' + y'), \frac{1}{2}(y' - x'), \frac{1}{2}z'; \\ &-\frac{1}{2}(x' + y'), \frac{1}{2}(x' - y'), \frac{1}{2}z'; \\ &\frac{1}{2} + \frac{1}{2}(x' + y'), \frac{1}{2}(y' - x'), \frac{1}{4} - \frac{1}{2}z'; \\ &\frac{1}{2} - \frac{1}{2}(x' + y'), \frac{1}{2}(x' - y'), \frac{1}{4} - \frac{1}{2}z'; \end{aligned}$$

etc. The form of the first coordinate set in this list suggests the obvious substitution:

$$x = \frac{1}{2}(x' + y'), y = \frac{1}{2}(y' - x'), z = \frac{1}{2}z',$$

which leads to the transformed coordinate list:

$$\begin{aligned} &x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, y, \frac{1}{4} - z; \frac{1}{2} - x, \bar{y}, \frac{1}{4} - z; \\ &y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \frac{1}{2} + y, x, \frac{1}{4} + z; \frac{1}{2} - y, \bar{x}, \frac{1}{4} + z; \\ &\bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; \frac{1}{2} - y, x, \frac{1}{4} + z; \frac{1}{2} + y, \bar{x}, \frac{1}{4} + z; \\ &x, \bar{y}, z; \bar{x}, y, z; \frac{1}{2} + x, \bar{y}, \frac{1}{4} - z; \frac{1}{2} - x, y, \frac{1}{4} - z. \end{aligned}$$

This list is incomplete, however, in that it comprises the equivalent coordinate sets corresponding to only one unit cell of the Cheshire group, *i.e.* to one quarter of the crystallographic unit cell. To indicate explicitly the presence in the full unit cell of four Cheshire-group lattice points, we add their coordinates at the head of the list, which now becomes:

$$\begin{aligned} &(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + \\ &x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, y, \frac{1}{4} - z; \frac{1}{2} - x, \bar{y}, \frac{1}{4} - z; \\ &y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \frac{1}{2} + y, x, \frac{1}{4} + z; \frac{1}{2} - y, \bar{x}, \frac{1}{4} + z; \\ &\bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; \frac{1}{2} - y, x, \frac{1}{4} + z; \frac{1}{2} + y, \bar{x}, \frac{1}{4} + z; \\ &x, \bar{y}, z; \bar{x}, y, z; \frac{1}{2} + x, \bar{y}, \frac{1}{4} - z; \frac{1}{2} - x, y, \frac{1}{4} - z. \end{aligned}$$

This is the complete list of equivalent coordinate sets x_t, y_t, z_t for the space group $I4_122$. It specifies 64 alternative ways of assigning atomic coordinates to any structure belonging to this space group. We note that the list includes, as it must, the 16 equivalent positions of $I4_122$ tabulated above.

We can systematize the illustrated procedure, for example to adapt it to computer manipulation, by writing the coordinates x_t, y_t, z_t that are equivalent, under a given Cheshire-group operation, to the reference coordinates x, y, z in the form

$$(x_t, y_t, z_t) = (xyz) [T] + (p_t q_t r_t).$$

The full list of matrices $[T]$ and vectors $(p_t q_t r_t)$ defines the particular Cheshire group. From *International Tables* we normally obtain, taking care about choice of origin, the corresponding quantities $[T']$ and $(p'_t q'_t r'_t)$ referred to the axes $M_{ij}\mathbf{a}_j$ of the Cheshire-group unit cell. Transformation to the unit-cell axes \mathbf{a}_j is readily effected by means of the relations:

$$\begin{aligned} T &= [M^{-1}] [T'] [M], \\ (p_t q_t r_t) &= (p'_t q'_t r'_t) [M]. \end{aligned}$$

In the case of a polar space group, we disregard the degeneracy of the Cheshire-group lattice and derive

the equivalent coordinate sets as though for the corresponding non-degenerate lattice. Thus, for the Cheshire group Z^{12}/m we use the equivalent positions of $P2/m$ and transform with the aid of the matrix

$$[M] = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix}.$$

The fact that in the limit, as ε approaches zero, the matrix $[M]$ becomes singular, causes no embarrassment.

Several properties of Cheshire groups, though almost trivial, deserve explicit mention. First, the operations of the Cheshire group, unlike those of the corresponding space group, are not applicable to the coordinates of individual atoms but must transform the coordinates of all atoms simultaneously. While we may have several alternative choices of unit-cell axes, we must be consistent about referring all our atoms to the same axes.

Second, since the unit cell of the Cheshire group is usually smaller than that of its parent space group, the supergroup-subgroup relation between them may

not always be instantly apparent. In fact it is readily enough verified, though possibly unfamiliar, that, for example, the space group $P2_12_12_1$ with unit cell $\mathbf{a} \times \mathbf{b} \times \mathbf{c}$ is indeed a subgroup of its Cheshire group $Pmmm$ with unit cell $\frac{1}{2}\mathbf{a} \times \frac{1}{2}\mathbf{b} \times \frac{1}{2}\mathbf{c}$.

Third, among the transformations that may occur in the several Cheshire groups, we have allowed improper rotations, which convert a right-handed into a left-handed coordinate system. Thus we are permitting our crystal axial system to have either chirality, *i.e.* a given list of atomic coordinates may describe either of two enantiomorphous structures. Such a convention is appropriate to our present purpose only because enantiomorphous structures are, in fact, hardly ever distinguishable in the trial-structure stage of a crystallographic study.

An alternative point of view, less offensive to purists, might insist on right-handed crystal axes but regard an enantiomorphous pair of trial structures as constituting a single model. The Cheshire-group operation (permitted for all but the eleven enantiomorphous pairs of space groups) that changes the signs of all x, y, z coordinates would then be interpreted, not as a

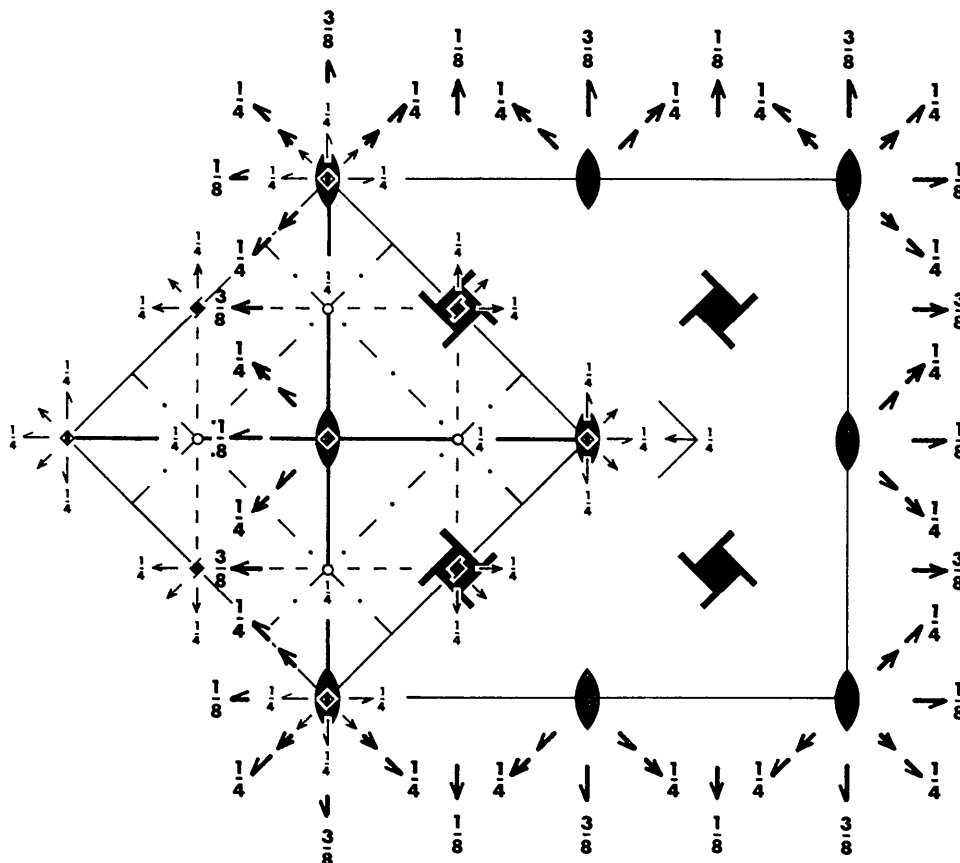


Fig. 2. Superposed unit cells of space group $I4_122$ and of its Cheshire group $P4_2/nmm$, in c -axis projection. Large, bold symbols denote symmetry elements of space group, small symbols those of Cheshire group. Height designations for Cheshire-group symmetry elements are in fractions of corresponding lattice vector, which is $\frac{1}{2}c$; similarly 4_2 screw axis of Cheshire group has translation component half this lattice vector, *i.e.* $c/4$.

reversal of the crystal axes, but as an interchange of the two structures comprising the same model. This interpretation would alter none of our results, except to simplify the caption to Fig. 1 by eliminating the parameter λ , but it would logically complicate the definition of a Cheshire group, forcing us to view its symmetry operations as hybrids of (proper) axial rotations combined with transformations of the trial structure.

In this connexion, it is important to recognize that the application of Cheshire-group symmetry to the generation of trial structures is legitimate only if the criterion by which these trial structures are to be judged itself conforms to that symmetry. If, for example, our

$$[A] = \begin{bmatrix} 1/a & 0 & 0 \\ (\cos \alpha \cos \beta - \cos \gamma)/va \sin \beta & \sin \beta/vb & (\cos \beta \cos \gamma - \cos \alpha)/vc \sin \beta \\ -\cot \beta/a & 0 & 1/c \sin \beta \end{bmatrix},$$

criterion is a comparison of observed and calculated structure amplitudes and the observed amplitudes are unequal for pairs of reflexions with indices hkl and $\bar{h}\bar{k}\bar{l}$, then the situation is not symmetric under a reversal of all three crystal axes and the equivalences we have derived are no longer appropriate. We may restore the assumed symmetry either by averaging the amplitudes of all pairs of inversion-related reflexions or, more laboriously, by testing each trial structure twice with hkl and $\bar{h}\bar{k}\bar{l}$ reflexions interchanged. A less trivial situation arises with those space groups for which the diffraction symmetry, even in the absence of anomalous dispersion, is lower than the point-group symmetry of the corresponding Cheshire group. For example, the tetragonal space groups $P4$, $P4_2$, and $I4$ all correspond to the Cheshire group Z^4/mmm although their diffraction symmetry is only $4/m$. If structure-factor comparisons were used to test trial structures in any of these space groups, the full Cheshire-group symmetry would not be preserved unless the test of each model allowed for the possible interchange of reflexions hkl and $\bar{h}\bar{k}\bar{l}$. We have nevertheless preferred to base our general procedure on the full Cheshire-group symmetry, rather than on the diffraction symmetry, for two main reasons. First, even if the final comparison of structure amplitudes must be performed twice (or more times) for each model, this is a far more economical procedure than calculating structure factors independently for twice as many (or more) models. Second, for other common ways of testing trial structures, e.g. by estimating intermolecular packing energies, the Cheshire-group symmetry is entirely appropriate.

Equivalent molecular parameters

Having derived the Cheshire-group equivalences for a particular space group, we must next express these equivalences in terms of the molecular parameters $e \varphi \psi \theta u v w$. Before we can do so we must define the reference axes $\mathbf{A}, \mathbf{B}, \mathbf{C}$ to which the Eulerian angles

are referred, *i.e.* we must specify the explicit form of the matrix $[A]$ appearing in equation (1). The convention we shall now adopt is to define $\mathbf{A}, \mathbf{B}, \mathbf{C}$ as orthogonal unit axes oriented with $\mathbf{A} \parallel \mathbf{a}, \mathbf{B} \parallel \mathbf{b}^*, \mathbf{C} \cdot \mathbf{c} > 0$. With this definition the axes $\mathbf{A}, \mathbf{B}, \mathbf{C}$ are parallel to the crystal axes $\mathbf{a}, \mathbf{b}, \mathbf{c}$ in most cases where these are fixed by symmetry. The trigonal and hexagonal systems (for both of which we take $\mathbf{a}, \mathbf{b}, \mathbf{c}$ to be hexagonal axes) are exceptional, with \mathbf{B} lying 30° away from \mathbf{b} . Note, too, that if $\mathbf{a}, \mathbf{b}, \mathbf{c}$ form a left-handed system, so do $\mathbf{A}, \mathbf{B}, \mathbf{C}$, the expression for $\mathbf{b}^* = \mathbf{c} \times \mathbf{a}/[\mathbf{abc}]$ having then a negative denominator.

We can now write the matrix $[A]$, and its inverse $[A^{-1}]$, explicitly as

$$[A^{-1}] = \begin{bmatrix} a & 0 & 0 \\ b \cos \gamma & vb/\sin \beta & b(\cos \alpha - \cos \beta \cos \gamma)/\sin \beta \\ c \cos \beta & 0 & c \sin \beta \end{bmatrix},$$

where

$$v = |[\mathbf{abc}]|/abc = (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}}.$$

To proceed, let us suppose that the coordinate set x_t, y_t, z_t , related to the set x, y, z by the Cheshire-group transformation

$$(x_t y_t z_t) = (xyz) [T] + (p_t q_t r_t), \quad (2)$$

corresponds to the set of molecular parameters $e_t, \varphi_t, \psi_t, \theta_t, u_t, v_t, w_t$, *i.e.* that it is related to them by the analog of equation (1):

$$(x_t y_t z_t) = (lmn) [R(e_t, \varphi_t, \psi_t, \theta_t)] [A] + (u_t v_t w_t). \quad (3)$$

Since this relation must hold for any l, m, n , we obtain, on substituting equations (1) and (3) into equation (2):

$$[R(e_t, \varphi_t, \psi_t, \theta_t)] [A] = [R(e, \varphi, \psi, \theta)] [A] [T]$$

and

$$(u_t v_t w_t) = (uvw) [T] + (p_t q_t r_t).$$

Of these two equations, the second has the trivial significance that the coordinates of the molecular origin transform under a Cheshire-group operation just as those of any other point. But the first provides the more important relation

$$[R(e_t, \varphi_t, \psi_t, \theta_t)] = [R(e, \varphi, \psi, \theta)] [A] [T] [A^{-1}],$$

from which we can deduce, by simple if occasionally tedious algebra, the form of the parameters $e_t, \varphi_t, \psi_t, \theta_t$ for any Cheshire-group operation whose transformation matrix $[T]$ is given. We may often avoid much of the tedium by simplifying the matrices $[A]$ and $[A^{-1}]$ in accordance with the lattice symmetry appropriate to the particular crystal system; after this simplification

it frequently happens that $[A]$ commutes with $[T]$ and hence

$$[R(e_t, \varphi_t, \psi_t, \theta_t)] = [R(e, \varphi, \psi, \theta)] [T].$$

The rules just presented permit us to construct complete tables of equivalent molecular parameters for all the Cheshire groups. Since these tables depend on the choice of origin and on the definition of the axes **A, B, C**, they probably do not merit listing here in full. Instead we tabulate (as we did, in Table 1, for the molecular symmetry operations) the equivalent molecular parameters corresponding to the most common individual Cheshire-group transformations. With the axes **A, B, C** chosen as above and with the Eulerian angles defined as in Fig. 1, the symmetry operations occurring in the majority of Cheshire groups lead to linear transformations of the Eulerian angles, *i.e.* the transformed angles $\varphi_t, \psi_t, \theta_t$ are found to be linear functions of the untransformed angles φ, ψ, θ . For these operations the explicit expressions for the transformed molecular parameters are given in Table 3. The omitted operations, for which the transformations of the Eulerian angles are non-linear (in fact non-algebraic), are all confined to the cubic space groups, to which the procedures now to be outlined are not readily applicable. An example will indicate how Table 3 can aid in the preparation of the full list of equivalent parameter sets for any non-cubic space group.

Table 3. *Cheshire-group equivalences for symmetry operations occurring in non-cubic crystal systems*

Each row gives the set of molecular parameters $e_t, \varphi_t, \psi_t, \theta_t, u_t, v_t, w_t$ related by the indicated Cheshire-group symmetry operation to the reference set $e, \varphi, \psi, \theta, u, v, w$. The positive sense of rotation about $[001]$ is taken as that of increasing φ ; rotation through an angle ω transforms the coordinates of a point from X, Y, Z to $X \cos \omega - Y \sin \omega, X \sin \omega + Y \cos \omega, Z$.

I	$-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$
2[100]	$e, \frac{1}{2} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, u, \bar{v}, \bar{w}$
2[010]	$e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$
2[001]	$e, \frac{1}{2} + \varphi, \psi, \theta, \bar{u}, \bar{v}, w$
2[110]	$e, \frac{1}{2} + \gamma - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, v, u, \bar{w}$
2[1\bar{1}0]	$e, \gamma - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{v}, \bar{u}, \bar{w}$
$m(100)$	$-e, -\varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, w$
$m(010)$	$-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$
$m(001)$	$-e, \varphi, -\psi, \frac{1}{2} - \theta, u, v, \bar{w}$
$m(110)$	$-e, \gamma - \varphi, \frac{1}{2} - \psi, \theta, \bar{v}, \bar{u}, w$
$m(1\bar{1}0)$	$-e, \frac{1}{2} + \gamma - \varphi, \frac{1}{2} - \psi, \theta, v, u, w$
3[001]	$e, \frac{1}{3} + \varphi, \psi, \theta, \bar{v}, u - v, w$
3 ⁻¹ [001]	$e, \frac{2}{3} + \varphi, \psi, \theta, v - u, \bar{u}, w$
3[001]	$-e, \frac{5}{6} + \varphi, -\psi, \frac{1}{2} - \theta, v, v - u, \bar{w}$
3 ⁻¹ [001]	$-e, \frac{1}{6} + \varphi, -\psi, \frac{1}{2} - \theta, u - v, u, \bar{w}$
4[001]	$e, \frac{1}{4} + \varphi, \psi, \theta, \bar{v}, u, w$
4 ⁻¹ [001]	$e, \frac{3}{4} + \varphi, \psi, \theta, v, \bar{u}, w$
4[001]	$-e, \frac{3}{4} + \varphi, -\psi, \frac{1}{2} - \theta, v, \bar{u}, \bar{w}$
4 ⁻¹ [001]	$-e, \frac{1}{4} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{v}, u, \bar{w}$
6[001]	$e, \frac{1}{6} + \varphi, \psi, \theta, u - v, u, w$
6 ⁻¹ [001]	$e, \frac{5}{6} + \varphi, \psi, \theta, v - u, w$
6[001]	$-e, \frac{2}{3} + \varphi, -\psi, \frac{1}{2} - \theta, v - u, \bar{u}, \bar{w}$
6 ⁻¹ [001]	$-e, \frac{1}{3} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{v}, u - v, \bar{w}$

Consider again the space group $I4_122$, for which we have already derived the 64 equivalent sets of fractional coordinates x_t, y_t, z_t . To these correspond 16 distinct $[T]$ matrices, each of which is represented by one of

the rows of Table 3. We can select the pertinent rows either by noting the forms of the expressions for x_t, y_t, z_t and matching these (disregarding the constants p_t, q_t, r_t) against the expressions for u_t, v_t, w_t in the table or by identifying the Cheshire-group symmetry operations (or their point-group analogs) and locating their descriptions in column 1 of the table. Starting, for example, with the coordinate set \bar{x}, \bar{y}, z in our list of Cheshire-group equivalents for $I4_122$, we recognize this as arising from a diad axis along **c** and matching row 4 in Table 3, where we find the parameter set

$$e, \frac{1}{2} + \varphi, \psi, \theta, \bar{u}, \bar{v}, w.$$

Similarly, the coordinate set $\frac{1}{2} + y, x, \frac{1}{4} + z$ further along in our list corresponds (if we disregard the translation components) to a reflexion plane parallel to $(1\bar{1}0)$ and to the parameters in row 11 of the table:

$$-e, \frac{1}{2} + \gamma - \varphi, \frac{1}{2} - \psi, \theta, v, u, w.$$

Substituting $\gamma = \frac{1}{4}$, as required by the tetragonal lattice, and adding the translation components p_t, q_t, r_t , we obtain the parameter set

$$-e, \frac{3}{4} - \varphi, \frac{1}{2} - \psi, \theta, \frac{1}{2} + v, u, \frac{1}{4} + w.$$

Proceeding in this way we eventually derive the full list of equivalent parameter sets:

$$\begin{aligned} &-, -, -, -, (0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + \\ &e, \varphi, \psi, \theta, u, v, w; \\ &e, \frac{1}{2} + \varphi, \psi, \theta, \bar{u}, \bar{v}, w; \\ &-e, \varphi, -\psi, \frac{1}{2} - \theta, \frac{1}{2} + u, v, \frac{1}{4} - w; \\ &-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \frac{1}{2} - u, \bar{v}, \frac{1}{4} - w; \\ &e, \frac{3}{4} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, v, u, \bar{w}; \\ &e, \frac{1}{4} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{v}, \bar{u}, \bar{w}; \\ &-e, \frac{3}{4} - \varphi, \frac{1}{2} - \psi, \theta, \frac{1}{2} + v, u, \frac{1}{4} + w; \\ &-e, \frac{1}{4} - \varphi, \frac{1}{2} - \psi, \theta, \frac{1}{2} - v, \bar{u}, \frac{1}{4} + w; \\ &-e, \frac{1}{4} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{v}, u, \bar{w}; \\ &-e, \frac{3}{4} + \varphi, -\psi, \frac{1}{2} - \theta, v, \bar{u}, \bar{w}; \\ &e, \frac{1}{4} + \varphi, \psi, \theta, \frac{1}{2} - v, u, \frac{1}{4} + w; \\ &e, \frac{3}{4} + \varphi, \psi, \theta, \frac{1}{2} + v, \bar{u}, \frac{1}{4} + w; \\ &-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w; \\ &-e, -\varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, w; \\ &e, \frac{1}{2} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \frac{1}{2} + u, \bar{v}, \frac{1}{4} - w; \\ &e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \frac{1}{2} - u, v, \frac{1}{4} - w. \end{aligned}$$

The translations indicated at the top of the list are, of course, to be added to the coordinates u_t, v_t, w_t ; they do not affect the other parameters $e_t, \varphi_t, \psi_t, \theta_t$.

Combining molecular and crystallographic symmetry

Having seen how to derive separately the equivalent parameter sets arising from the molecular and from the crystallographic symmetry, we are ready to combine the two. This may be accomplished by a straightforward substitution of one set of equivalents into the

other. Two examples may serve to illustrate the general procedure.

Consider first a molecule of symmetry $2/m$ occupying a general position in the space group $P2_1/c$. If we take the molecular origin at the inversion centre and L along the twofold symmetry axis of the molecule, we have (see above) the following parameter sets $e_s, \varphi_s, \psi_s, \theta_s$ related by the molecular symmetry:

- (a) e, φ, ψ, θ ;
- (b) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta$;
- (c) $-e, \varphi, \frac{1}{2} + \psi, \theta$;
- (d) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta$.

The Cheshire group, according to Table 2, is $P2/m$ with unit cell $\frac{1}{2}\mathbf{a} \times \frac{1}{2}\mathbf{b} \times \frac{1}{2}\mathbf{c}$. With the aid of Table 3 the equivalent parameter sets $e_t, \varphi_t, \psi_t, \theta_t, u_t, v_t, w_t$ are readily found to be:

- (1) $e, \varphi, \psi, \theta, u, v, w$;
- (2) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$; (line 1 of Table 3)
- (3) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$; (line 3)
- (4) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$. (line 8)

If we had followed strictly the procedure set out above for the space group $I4_122$, we should have tabulated explicitly, at the top of this list, the eight Cheshire-group translations per crystallographic unit cell. It is simpler, however, in the present instance, merely to note the fact that the coordinates u, v, w may be restricted, in accordance with the periodicity of the Cheshire group, to the ranges

$$0 \leq u < \frac{1}{2}, 0 \leq v < \frac{1}{2}, 0 \leq w < \frac{1}{2}.$$

We now form the direct product of the two symmetry groups by substituting, in turn, each of the parameter sets $e_s, \varphi_s, \psi_s, \theta_s$ of the first group for the variables e, φ, ψ, θ appearing in the expressions $e_t, \varphi_t, \psi_t, \theta_t$ of the second. In this way we obtain the complete list of equivalent parameter sets $e_{st}, \varphi_{st}, \psi_{st}, \theta_{st}, u_t, v_t, w_t$ as follows:

- (a1) $e, \varphi, \psi, \theta, u, v, w$;
- (a2) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$;
- (a3) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$;
- (a4) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$;
- (b1) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, u, v, w$;
- (b2) $-e, \varphi, \frac{1}{2} + \psi, \theta, \bar{u}, \bar{v}, \bar{w}$;
- (b3) $e, \frac{1}{2} - \varphi, -\psi, \theta, \bar{u}, v, \bar{w}$;
- (b4) $-e, -\varphi, \psi, \frac{1}{2} - \theta, u, \bar{v}, w$;
- (c1) $-e, \varphi, \frac{1}{2} + \psi, \theta, u, v, w$;
- (c2) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$;
- (c3) $-e, -\varphi, \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$;
- (c4) $e, \frac{1}{2} - \varphi, -\psi, \theta, u, \bar{v}, w$;
- (d1) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, u, v, w$;
- (d2) $e, \varphi, \psi, \theta, \bar{u}, \bar{v}, \bar{w}$;
- (d3) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, \bar{w}$;
- (d4) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, u, \bar{v}, w$.

The letter and the numeral preceding each parameter set identify, respectively, the molecular and the crystallographic equivalences *via* which it has been derived. The last three columns indicate a systematic method of selecting, by a process of successive restriction, a suitable scanning range in the space of the seven molecular parameters. Consider these parameters in turn, from left to right. If we fix the parameter e at the value $+1$, we effectively restrict our attention to eight of the sixteen parameter sets listed, *i.e.* to those checked in the column headed ' $e = +1$ '. For the second parameter φ there remain the four alternative expressions $\varphi, -\varphi, \frac{1}{2} + \varphi, \frac{1}{2} - \varphi$. By selecting the range $0 \leq \varphi \leq \frac{1}{4}$ we discard three of these, leaving the parameter sets (a1) and (d2). These have identical expressions for ψ and for θ so we pass over these two parameters and choose finally $0 \leq u \leq \frac{1}{4}$, remembering that the Cheshire-group periodicity makes the values \bar{u} and $\frac{1}{2} - u$ equivalent. The parameter set (a1) is now the sole survivor out of the original list of 16 equivalent sets. The range to be scanned (the asymmetric unit in our multidimensional space) is:

$$\begin{aligned} e &= +1, \\ 0 &\leq \varphi \leq \frac{1}{4}, \\ 0 &\leq \psi < 1, \\ 0 &\leq \theta \leq \frac{1}{2}, \\ 0 &\leq u \leq \frac{1}{4}, \\ 0 &\leq v < \frac{1}{2}, \\ 0 &\leq w < \frac{1}{2}. \end{aligned}$$

This range, which is not, of course, the only one we might have selected (any more than the asymmetric unit of a crystal has uniquely defined boundaries) is complete in that any structure having the given cell dimensions, space group, and molecular dimensions can be represented by a set of parameter values lying within the indicated limits.

- | | | |
|----------|-----------------------------------|-----------------------------|
| $e = +1$ | $0 \leq \varphi \leq \frac{1}{4}$ | $0 \leq u \leq \frac{1}{4}$ |
| ✓ | ✓ | ✓ |
-
- (a1) $e, \varphi, \psi, \theta, u, v, w$;
 - (a2) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$;
 - (a3) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$;
 - (a4) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$;
 - (b1) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, u, v, w$;
 - (b2) $-e, \varphi, \frac{1}{2} + \psi, \theta, \bar{u}, \bar{v}, \bar{w}$;
 - (b3) $e, \frac{1}{2} - \varphi, -\psi, \theta, \bar{u}, v, \bar{w}$;
 - (b4) $-e, -\varphi, \psi, \frac{1}{2} - \theta, u, \bar{v}, w$;
 - (c1) $-e, \varphi, \frac{1}{2} + \psi, \theta, u, v, w$;
 - (c2) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$;
 - (c3) $-e, -\varphi, \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$;
 - (c4) $e, \frac{1}{2} - \varphi, -\psi, \theta, u, \bar{v}, w$;
 - (d1) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, u, v, w$;
 - (d2) $e, \varphi, \psi, \theta, \bar{u}, \bar{v}, \bar{w}$;
 - (d3) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, \bar{w}$;
 - (d4) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, u, \bar{v}, w$.

As a second example, consider a molecule of symmetry 2 in space group $Pca2_1$. Taking **L** along the molecular diad axis, we have, for the equivalent parameter sets $e_s, \varphi_s, \psi_s, \theta_s$ under the molecular symmetry:

- (a) e, φ, ψ, θ ;
 (b) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta$.

The Cheshire group, according to Table 2, is Z^1mmm with unit cell $\frac{1}{2}\mathbf{a} \times \frac{1}{2}\mathbf{b} \times c$. Accordingly, the equivalent parameter sets $e_t, \varphi_t, \psi_t, \theta_t, u_t, v_t, w_t$ are, with some assistance from Table 3:

- (1) $e, \varphi, \psi, \theta, u, v, w$;
 (2) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$; (line 1)
 (3) $e, \frac{1}{2} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, u, \bar{v}, \bar{w}$; (line 2)
 (4) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$; (line 3)
 (5) $e, \frac{1}{2} + \varphi, \psi, \theta, \bar{u}, \bar{v}, w$; (line 4)
 (6) $-e, -\varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, w$; (line 7)
 (7) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$; (line 8)
 (8) $-e, \varphi, -\psi, \frac{1}{2} - \theta, u, v, \bar{w}$. (line 9)

Again, we simply take note of the Cheshire-group periodicity by restricting the ranges of the coordinates u, v, w to the interval

$$0 \leq u < \frac{1}{2}, 0 \leq v < \frac{1}{2}, w = 0.$$

As before, we now substitute each of the molecular equivalents $e_s, \varphi_s, \psi_s, \theta_s$ in turn into each of the Cheshire group equivalents $e_t, \varphi_t, \psi_t, \theta_t, u_t, v_t, w_t$ and so obtain the complete list of equivalent parameter sets $e_{st}, \varphi_{st}, \psi_{st}, \theta_{st}, u_t, v_t, w_t$:

- (a1) $e, \varphi, \psi, \theta, u, v, w$;
 (a2) $-e, \frac{1}{2} + \varphi, -\psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, \bar{w}$;
 (a3) $e, \frac{1}{2} - \varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, u, \bar{v}, \bar{w}$;
 (a4) $e, -\varphi, \frac{1}{2} + \psi, \frac{1}{2} - \theta, \bar{u}, v, \bar{w}$;
 (a5) $e, \frac{1}{2} + \varphi, \psi, \theta, \bar{u}, \bar{v}, w$;
 (a6) $-e, -\varphi, \frac{1}{2} - \psi, \theta, \bar{u}, v, w$;
 (a7) $-e, \frac{1}{2} - \varphi, \frac{1}{2} - \psi, \theta, u, \bar{v}, w$;
 (a8) $-e, \varphi, -\psi, \frac{1}{2} - \theta, u, v, \bar{w}$;
 (b1) $e, \frac{1}{2} + \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, u, v, w$;
 (b2) $-e, \varphi, \frac{1}{2} + \psi, \theta, \bar{u}, \bar{v}, \bar{w}$;
 (b3) $e, -\varphi, -\psi, \theta, u, \bar{v}, \bar{w}$;
 (b4) $e, \frac{1}{2} - \varphi, -\psi, \theta, \bar{u}, v, \bar{w}$;
 (b5) $e, \varphi, \frac{1}{2} - \psi, \frac{1}{2} - \theta, \bar{u}, \bar{v}, w$;
 (b6) $-e, \frac{1}{2} - \varphi, \psi, \frac{1}{2} - \theta, \bar{u}, v, w$;
 (b7) $-e, -\varphi, \psi, \frac{1}{2} - \theta, u, \bar{v}, w$;
 (b8) $-e, \frac{1}{2} + \varphi, \frac{1}{2} + \psi, \theta, u, v, \bar{w}$.

Working again from left to right, we restrict the ranges of the successive parameters, as indicated in the last three columns, to obtain the scanning range:

$$\begin{aligned} e &= +1, \\ 0 &\leq \varphi \leq \frac{1}{4}, \\ -\frac{1}{4} &\leq \psi \leq \frac{1}{4}, \\ 0 &\leq \theta \leq \frac{1}{2}, \\ 0 &\leq u < \frac{1}{2}, \\ 0 &\leq v < \frac{1}{2}, \\ w &= 0. \end{aligned}$$

In this example, because of the polar **c** axis, the space to be scanned is of five dimensions rather than six.

While the manner in which we have chosen to restrict the ranges of the several parameters is essentially an arbitrary one, there is often a computational advantage in restricting, as far as possible, the Eulerian angles rather than the coordinates of the molecular origin. This is because the generation and testing of each new molecular orientation usually entail several operations that can be omitted when a molecule of fixed orientation is simply translated to a new position in the unit cell.

Molecules in special positions

We have thus far considered situations where the molecule occupies a general position of the space group, but the same procedure, with important simplifications, is readily applicable to molecules in special positions. The most obvious simplification is that the requirements of the site symmetry immediately constrain the molecule in position and, often, in orientation so that several of the molecular parameters have only a limited choice of discrete values available to them. For example, site symmetry $\bar{1}$ fixes the molecular coordinates

$$e = +1 \quad 0 \leq \varphi \leq \frac{1}{4} \quad -\frac{1}{4} \leq \psi \leq \frac{1}{4}$$

$$\begin{array}{ccc} \checkmark & \checkmark & \checkmark \end{array}$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

$$\checkmark$$

u, v, w ; site symmetry 2 fixes two of these coordinates as well as two of the Eulerian angles. Consequently the number of dimensions to be scanned is drastically

reduced. An incidental further simplification occurs in the procedure for deriving the equivalent parameter sets in that we can disregard those molecular point-group operations that are part of the crystallographic site symmetry. If, for example, a molecule of symmetry $2/m$ is known to occupy a special position of site symmetry $\bar{1}$, we may, in constructing the table of equivalent parameter sets $e_s, \varphi_s, \psi_s, \theta_s$, replace the true molecular point group by one of its subgroups 2 or m , leaving the inversion centre to be implied by the space-group symmetry in conjunction with the specification of the molecular coordinates.

We can illustrate this matter by referring to the example, treated explicitly above, of a molecule of symmetry $2/m$ in the space group $P2_1/c$. With the molecule in a general position, *i.e.* with four molecules per unit cell, we derived a list of sixteen equivalent parameter sets $e_{st}, \varphi_{st}, \psi_{st}, \theta_{st}, u_t, v_t, w_t$ in the Cheshire-group unit cell of $\frac{1}{2}\mathbf{a} \times \frac{1}{2}\mathbf{b} \times \frac{1}{2}\mathbf{c}$. If we now substitute in that list the coordinate values $u=v=w=0$, appropriate to a structure with two molecules per unit cell in special

positions of site symmetry $\bar{1}$, the sixteen parameter sets reduce to eight distinct sets occurring twice over. And these are just the eight equivalent parameter sets we could have obtained if we had considered explicitly only the molecular symmetry operations 1 and 2 (or, alternatively, 1 and m) in tabulating the molecular equivalences.

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A New Interpretation of the Fourier Coefficients of Debye-Scherrer Lines from Small Distorted Crystals

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Equations are derived which express the mean distortion and the particle size coefficient of small distorted crystals in the Fourier coefficients of broadened X-ray diffraction powder lines. To this end the distribution function $\varphi(t, L)$ for the distortions L of the cells, which are at a distance t apart, is expanded into a Fourier series and it is assumed that $\varphi(t, L) = 0$ for $|L| \geq d/2$ (d is the interplanar spacing between the reflecting planes). The sums of infinite series of Fourier coefficients of all orders of a reflexion appear in the equations. The problem of the incomplete evaluation caused by the limited number of orders which can be measured in practice is discussed. Finally, as it is assumed in this analysis that the distortion coefficient is a constant for all values of the reciprocal coordinate of the line profile, the small error introduced into the equations by this approximation is calculated.

Introduction

The method most widely used for determining particle size and strains in polycrystalline materials from X-ray diffraction line broadening is that of Warren & Averbach (1952). For small distorted crystals in which no stacking faults occur, they derived the equation

$$\log_e A_n^{\text{rs}}(t) = \log_e V(t) - 2\pi^2 s_n^2 \langle L_t^2 \rangle.$$

In this equation t is a distance normal to the reflecting planes. $A_n^{\text{rs}}(t)$ represents the real part of the Fourier

transform of the intensity profile of the n th order of reflexion, $i_n(s_0)$, which has been corrected for continuous factors. $V(t)$ has the following meaning: for a crystal of volume V , $VV(t)$ is the volume common to the crystal and its 'ghost' shifted a distance t . Further, s_n is the reciprocal-lattice point coordinate, and s_0 is that with origin at the reciprocal lattice point. $\langle L_t^2 \rangle$ equals $\int \varphi(t, L) L^2 dL$ (and likewise $\langle L_t \rangle = \int \varphi(t, L) L dL$). Function $\varphi(t, L)$ is the normalized distribution function for the distortion L at the distance t . Thus $t+L$ is the distance between two cells in the distorted crystal, projected on the direction perpendicular to the reflecting planes. In the ideal crystal this distance is t . The mean values of L^2 and L depend on t and for ease of

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