Symmetry of the Lattice-Energy Functional of a Molecular Crystal

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Abstract

In calculating the lattice-energy hypersurface by the systematic variation of the molecular rigid-body parameters and the lattice constants, the ranges to be scanned depend on the molecular symmetry and on the space group. A generalization of Hirshfeld's approach [Hirshfeld (1968). *Acta Cryst.* A**24**, 301–311] applicable to the case of variable lattice constants is suggested. The symmetry of the multidimensional parameter space is defined by the direct product of the molecular point group and a normalizer $N_A(F)$ of the space group F. The normalizer $N_A(F)$ is a group of affine transformations of the crystal axes that leave invariant the coordinates of equivalent positions. An asymmetric unit of the parameter space is obtained through keeping the lattice constants within such ranges that satisfy the Niggli reduced-cell conditions.

Introduction

In molecular-packing analysis, the most stable crystal is usually determined through minimization of the static lattice energy with respect to the set of structural variables specifying the crystal configuration (Kitaigorodskii, 1973). Considering a crystal with one molecule per crystallographic asymmetric unit, one may define any possible crystal structure by specification of its symmetry, the three molecular centre-of-mass coordinates, t_x, t_y, t_z, the three Eulerian angles, φ, θ, ψ, and the six lattice constants, $a, b, c, \alpha, \beta, \gamma$.

A consistent application of packing analysis involves mapping of the lattice-energy hypersurface by systematic variation of the structural variables, or construction of a grid of trial structures serving as starting points for subsequent minimization. Owing to crystal symmetry different sets of the twelve parameters may describe the same crystal configuration. The problem of ranges to be scanned, which take into account the symmetry equivalences, then arises. A particular case of this problem has been discussed by Hirshfeld (1968) who derived the symmetry relations between the molecular parameters t_x, t_y, t_z, φ, θ, ψ for a crystal with fixed cell dimensions. Hirshfeld's considerations were intended mainly for application in trial-and-error

solutions of the phase problem. They were also employed in structure determinations by molecular-packing analysis when the cell dimensions were available from experiment (Williams, 1969; Dzyabchenko, Zavodnik & Belsky, 1979).

In lattice-energy calculations with variable lattice constants a more general approach is called for. This is the subject of the present work. It concerns only triclinic, monoclinic and orthorhombic crystals while those of higher symmetry are treated in terms of Hirshfeld's original theory. The results can be directly applied in calculations of the global lattice-energy minimum, and may also be useful whenever a comparison of crystal structures is made, say, when comparing isomorphous structures.

Invariant transformations of the unit-cell axes

The equivalent sets of structural variables are produced by two factors (Hirshfeld, 1968): firstly, the (non-crystallographic) molecular point symmetry, and, secondly, the invariance of the crystal structure with respect to transformations of the crystal axes. Of these transformations, Hirshfeld considered the rotations (and rotatory reflections) of the axes that leave invariant the table of coordinates of equivalent positions, with the unit-cell dimensions being unchanged. The full list of such transformations defines the so-called Cheshire group. The Cheshire group is a symmetry-group derivative from a given space group. It may be readily obtained by considering the symmetry of a three-dimensional pattern representing the space group. In other words, in deriving the Cheshire group the original space group is treated as a 'structure' whose elements are the space-group symmetry elements.

In our case, the requirement that the unit-cell dimensions must be invariant under axial transformations should be rejected. The general rule is then formulated as *a set of transformations of the crystal axes that leave invariant the coordinates of equivalent positions*. There are three types of transformations which fulfil this rule:

    (*a*) a shift of origin;

    (*b*) reversal and/or interchange of unit-cell axes;

(c) replacement of unit-cell axes by their linear combinations (in monoclinic and triclinic crystals).

Transformations (a) alter the molecular parameters t_x, t_y, t_z, φ, θ, ψ while leaving the unit-cell dimensions unchanged; (b) change the unit-cell constants although the cell parallelepiped remains, as a whole, invariant; (c) distort this parallelepiped (while the lattice, of course, remains invariant). The (c)-type transformation obviously includes (b). Examples of combined transformations of types (a) and (b) and (a) and (c) in a crystal with space group $P2_1$ are shown in Fig. 1.

We now write any transformation of type (a), (b) or (c) or their combination as an affine operator (S,τ) which involves a linear unit-cell transformation

$$\begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} = S \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix},$$

with the matrix

$$S = \begin{pmatrix} n_{11} & n_{12} & n_{13} \\ n_{21} & n_{22} & n_{23} \\ n_{31} & n_{32} & n_{33} \end{pmatrix},$$

where n_{ij} are integers; and a shift of the origin τ, whose components are fractions of the unit-cell edges $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$.

On going from $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ to $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$ the fractional coordinates $\mathbf{x}$ transform as

$$\mathbf{x}' = (S^{-1})^T \mathbf{x} - \tau, \tag{1}$$

where $(S^{-1})^T$ is the transposed inverse of S. If the transformation S origin is shifted with respect to the space-group origin by $\mathbf{x}_0$ a somewhat different expression should be used:

$$\mathbf{x}' = (S^{-1})^T (\mathbf{x} - \mathbf{x}_0) + \mathbf{x}_0 - \tau, \tag{1a}$$

instead of (1).

The problem is to derive the group $\{S, \tau\}$ of the unit-cell transformations that leave invariant the equivalent coordinates of a given space group. We shall call this group the affine normalizer $N_A(F)$ of the space

Fig. 1. Examples of invariant unit-cell transformations in a crystal with space group $P2_1$: $\mathbf{a}' = -\mathbf{c}$, $\mathbf{c}' = \mathbf{a}$; $\mathbf{a}'' = -\mathbf{a} - \mathbf{c}$, $\mathbf{c}'' = -2\mathbf{a} - \mathbf{c}$.

group F, since its properties are consistent with the definition of a normalizer in group theory (Kuroš, 1967). The space group F is a subgroup of its normalizer $N_A(F)$ (its normal divisor) in the complete group of affine transformations. Note that in this terminology the Cheshire group is also a normalizer of the space group, but in the complete group of movements.

For space groups of the tetragonal, hexagonal and cubic systems the normalizers N_A are identical to the corresponding Cheshire groups. The subsequent consideration is thus limited to the space groups of lower symmetry, i.e. of the orthorhombic, monoclinic and triclinic systems.

Orthorhombic crystals

To derive the normalizer N_A of an orthorhombic space group we consider again the symmetry of the corresponding space-group pattern. The actual dimensions of this pattern are now ignored while the type of symmetry element and its direction is significant. Consequently, we may take the cell dimensions a, b, c of equal length to obtain the highest derivative symmetry. The symmetry of the resulting space-group pattern drawn in cubic axes defines a derivative group which we call the extended Cheshire group, since it has a close analogy with Hirshfeld's Cheshire group but includes extra symmetry. The 59 orthorhombic space groups are classified in Table 1 according to their extended Cheshire groups. Hirshfeld's Cheshire groups are also given in this table for comparison. Each extended Cheshire group is specified 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 $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. According to Hirshfeld (1968) we use the symbol Z^1 to designate degenerate primitive 'lattices' with an axis of vainishing length ε. Such lattices are derived from polar space groups in which arbitrary shifts of origin are admitted.

An extended Cheshire group provides a set of unit-cell transformations $\{S, \tau\}$ which form the normalizer. Although we have derived this set using cubic axes it will obviously be the same for an arbitrary orthorhombic cell, while the geometric sense of operations (S,τ) is altered. Namely, the elements of the so-called space homology (Mikheyev, 1961) appear instead of the corresponding symmetry elements. We can now conclude that the normalizer N_A of an orthorhombic space group is in fact the space-homology group isomorphous to the extended Cheshire group. The complete theory of the space-homology groups as well as their terminology is insufficiently developed at present. Thus, the extended Cheshire group provides a convenient way to define the affine normalizer in terms of conventional symmetry groups.
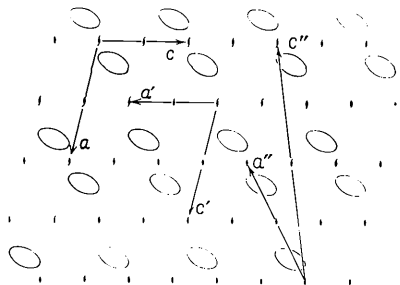
Triclinic and monoclinic crystals

In oblique crystal systems, where transformations of general type (c) take place, the description of the affine normalizer through an isomorphous symmetry group is insufficient. [Note that such a description is possible only for a part of type-(c) transformations, if we draw the space-group pattern in specially chosen non-orthogonal axes. For example, the derivative symmetry of the space group $P2_1/m$ in hexagonal axes is $P2/m$ $6/m\ 2/m$. The operation 6^1 in this group with $S = 1\ 0\ 1/\ 0\ 1\ 0/-1\ 0\ 0$ then corresponds to the type-(c) transformation $\mathbf{a'} = \mathbf{a} + \mathbf{c}$, $\mathbf{b'} = \mathbf{b}$, $\mathbf{c'} = -\mathbf{a}$ in $P2_1/m$. However, the use of non-orthogonal axes results in the loss of some important operations of the normalizer, which appear as derivative symmetry elements of the space-group pattern taken in cubic axes. Thus, the operation $S = 1\ 0\ 0/0\ 1\ 0/0\ 0\ -1$ is absent in $P2/m$ $6/m\ 2/m$ and present in $P2/m\ 4/m\ 2/m$, the derivative symmetry group of $P2_1/m$ in cubic axes.] Fortunately, the invariant properties of the two triclinic and 13 monoclinic space groups are quite simple owing to a limited number of available symmetry elements, and they can be written in terms of constraints imposed on matrices S and vectors τ.

In the triclinic space groups, $P1$ and $P\bar{1}$, the only requirement on S is that the number of lattice points within a unit cell should be invariant, $i.e.$

$$\det (S) = \pm 1.$$

The three components of τ may assume arbitrary real values in $P1$ which allows arbitrary shifts of the space-group origin. In $P\bar{1}$ the components of τ, τ_x, τ_y, τ_z are $k/2$, $l/2$, $m/2$ ($k,l,m = 0, \pm 1, \pm 2, ...$), respectively, since the shortest displacement of the space-group origin is 1/2 along each cell axis.

In the space groups of the monoclinic system (b-axis unique) the integers n_{12}, n_{21}, n_{23}, n_{32} are zeros and $n_{22} = \pm 1$. In addition to the general requirement $\det (S) = \pm 1$ there may exist further conditions for the remaining n_{ij} depending on the presence of a glide plane and/or face-centering translation. These conditions are summarized in Table 2.

Calculation of the equivalent sets of structural variables

We first derive a law by which the Cartesian coordinates are transformed on going from one set of unit-cell axes, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, to another set, $\mathbf{a'}$, $\mathbf{b'}$, $\mathbf{c'}$. Let $A = A(a,b,c,\alpha,\beta,\gamma)$ be a matrix which relates the fractional coordinates $\mathbf{x}$, referred to $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, to the Cartesian coordinates $\mathbf{X}$, so

$$\mathbf{X} = A\mathbf{x}$$

Table 2. *The invariant unit-cell transformations* (S, τ) *forming the affine normalizers* N_A *of the space groups of monoclinic system*

General condition:

$$\det (S) = \pm 1,$$

where $S = n_{11}\ 0\ n_{13}/0\ \pm 1\ 0/n_{31}\ 0\ n_{33}$, n_{ij} are integers. $k,l,m = 0, \pm 1, \pm 2, ...$; e,f,g are arbitrary real numbers.

Space group	Conditions for n_{ij}	τ_x, τ_y, τ_z
$P2, P2_1$		$k/2, f, m/2$
Pm	None	$e, l/2, g$
$P2/m, P2_1/m$		$k/2, l/2, m/2$
Pc	n_{11}, n_{33} odd, n_{31} even	$e, l/2, g$
$P2/c, P2_1/c$		$k/2, l/2, m/2$
$C2$		$k/2, f, m/2$
Cm		$e, l/2, g$
$C2/m$	n_{11}, n_{33} odd, n_{13} even	$k/2, l/2, m/2$
Cc		$e, l/2 + n_{31}/4, g$
$C2/c$		$k/2 + n_{31}/4, l/2 + n_{31}/4, m/2$

Table 1. *The 59 orthorhombic space groups classified by the corresponding affine normalizers written in terms of extended Cheshire groups*

$\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are the axes of the conventional crystallographic unit cell. The extended Cheshire group is defined as a true derivative symmetry group if $|\mathbf{a}| = |\mathbf{b}| = |\mathbf{c}|$. For an arbitrary orthorhombic cell it represents an isomorphous space-homology group through the set of operations $\{S,\tau\}$. ε is an infinitesimal quantity used in defining vanishing axes of the derivative unit cell.

If the space-group origin is chosen following *International Tables for X-ray Crystallography* (1952) then it coincides with the extended Cheshire-group origin, $i.e.$ $\mathbf{x}_0 = 0$ in equation (1a) (see text), everywhere except $Fdd2$ and $Imma$, for which the components of $\mathbf{x}_0$ are 1/4,0,0 (or 0,1/4,0).

Extended Cheshire group	Unit cell	Cheshire group (Hirshfeld, 1968)	Corresponding space groups
$Pmmm$	$a/2 \times b/2 \times c/2$	$Pmmm$	$Pmma, Pnna, Pmna, Pcca, Pbcm, Pbcn, Pnma, Cmcm, Cmca, Ccca$
Z^1mmm	$a/2 \times b/2 \times \varepsilon c$	Z^1mmm	$Pmc2_1, Pma2, Pca2_1, Pnc2, Pmn2_1, Pna2_1, Cmc2_1, Amm2, Abm2, Ama2, Aba2, Ima2$
$P4/mmm$	$a/2 \times b/2 \times c/2$	$Pmmm$	$P2_12_12, C222, Pccm, Pban, Pbam, Pccn, Pnnm, Pmmn, Cmmm, Cccm, Cmma, Ibam$
Z^14/mmm	$(a-b)/4 \times (a+b)/4 \times \varepsilon c$	Z^1mmm	$Cmm2$
Z^14/mmm	$a/2 \times b/2 \times \varepsilon c$	Z^1mmm	$Pmm2, Pcc2, Pba2, Pnn2, Ccc2, Fmm2, Imm2, Iba2$
Z^14/nbm	$a/2 \times b/2 \times \varepsilon c$	Z^1ban	$Fdd2$
$P4_2/mmc$	$a/2 \times b/2 \times c/2$	$Pmmm$	$P222_1, C222_1, Imma$
$Pm3$	$a/2 \times b/2 \times c/2$	$Pmmm$	$Pbca$
$Pm3m$	$a/2 \times b/2 \times c/2$	$Pmmm$	$P222, I222, Pmmm, Pnnn, Fmmm, Immm$
$Pm3n$	$a/2 \times b/2 \times c/2$	$Pmmm$	$P2_12_12_1, I2_12_12_1, Ibca$
$Pn3m$	$a/2 \times b/2 \times c/2$	$Pnnn$	$Fddd$
$Im3m$	$a/2 \times b/2 \times c/2$	$Immm$	$F222$

and

$$x = A^{-1}X. \qquad (2)$$

For the primed axes similar equations can be written:

$$X' = A'x',$$

$$x' = A'^{-1}X', \qquad (3)$$

where $A' = A(a',b',c',\alpha',\beta',\gamma')$ is a matrix obtained by substitution of the new lattice constants into the expressions for the matrix A elements. Substituting (2) and (3) into (1) we obtain

$$A'^{-1}X' = (S^{-1})^T A^{-1}X - \tau,$$

or

$$X' = A'(S^{-1})^T A^{-1}X - A'\tau. \qquad (4)$$

The new lattice constants a', b', c', α', β', γ' can in general be derived from the corresponding metric matrix

$$G' = SGS^T, \qquad (5)$$

where

$$G = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

is the metric matrix written in the axes a, b, c. Equation (5) describes the transformational properties of the metric tensor (*International Tables for X-ray Crystallography*, 1959) written in matrix notation.

Suppose now that the molecular structure is defined by a set of Cartesian atomic coordinates X_i^0. Any possible molecular position is then given by

$$X = RX^0 + At, \qquad (6)$$

where the matrix R specifies rotation of the orthogonal molecular axes through the Eulerian angles φ, θ, ψ; t is a vector whose components are the molecular centre fractional coordinates t_x, t_y, t_z. We assume here temporarily that both proper and improper rotations are defined by means of an additonal two-valued parameter e, which specifies the chirality of the molecular axes (Hirshfeld, 1968). Thus, $R = R(e,\varphi,\theta,\psi)$. Substituting (6) into (4), we get

$$X' = A'(S^{-1})^T A^{-1}RX^0 + A'(S^{-1})^T t - A'\tau.$$

An equation similar to (6) can be written for the coordinates X' on introducing the equivalent set of variables:

$$X' = R'X^0 + A't'.$$

Since the two last equations must hold for any X^0 we get

$$R' = A'(S^{-1})^T A^{-1}R \qquad (7)$$

and

$$t' = (S^{-1})^T t - \tau. \qquad (8)$$

These relations express the effect of any unit-cell transformation (S,τ) on the rotation R and shift of the molecular origin t.

The equation which describes the effect of molecular symmetry may be taken directly from Hirshfeld (1968):

$$R' = RM. \qquad (9)$$

Here M is a matrix of the point-group symmetry operation which relates the coordinates X^0 and $X^{0'}$ of any pair of symmetry-identical atoms within the molecule.

It is convenient to combine (7) and (9) to give

$$R(\varphi',\theta',\psi') = A'(S^{-1})^T A^{-1}R(\varphi,\theta,\psi)M. \qquad (10)$$

The parameter e in (10) is dropped since the requirement

$$\det(S)\det(M) > 0 \qquad (11)$$

is implied to hold for all possible combinations of S and M. The list of S for a given space group is provided by the corresponding normalizer. The condition (11) ensures that the resulting rotation S is proper. All combinations of S and M for which (11) does not hold should be rejected, since they generate the same equivalent structures but of opposite chirality.

For a general transformation S, which changes the lattice constants, the equivalent Eulerian angles cannot be explicitly derived but can be calculated numerically from the matrix R' elements using (7) or (10).

If S leaves the lattice constants invariant, so that $A' = A$, (7) reduces to that given by Hirshfeld (1968), and there exist explicit relations between equivalent sets of Eulerian angles for any symmetry operation of non-cubic space groups.

It may be shown that for S of diagonal form, (10) is simplified radically:

$$R' = SRM.$$

This equation shows that in a triclinic crystal the Eulerian angles are transformed by a diagonal-matrix operation S in the same manner as in an orthorhombic crystal under the action of the corresponding twofold axis, mirror plane or inversion centre.

Asymmetric unit in space of structural variables

Let us suppose that the intermolecular potential is defined and our aim is to map, for a given space group and molecular geometry, the lattice-energy surface by systematic variation of all structural variables. The problem is to choose such scanning ranges within which all possible structures will be generated and none of them will occur twice owing to symmetry. In other words, an asymmetric unit in the space of structural variables is to be determined.

Hirshfeld (1968) has described a way of choosing an asymmetric unit in the space of the molecular parameters t_x, t_y, t_z, φ, θ, ψ. His procedure is applicable in our case too, provided that the extra equivalences due to the variability of the lattice constants are taken into account.

It is now convenient to consider separately the equivalent sets of the lattice constants a, b, c, α, β, γ. The list of equivalent lattice-constant sets gives all possible unit cells, each of which is suitable for deriving the equivalent structural-variable sets with Hirshfeld's procedure. The aim is to impose such constraints upon the lattice constants which would ensure generation of only one unit cell.

In the triclinic case a convenient choice of the cell is the Niggli reduced cell (Niggli, 1928) which provides a unique description of the lattice (Santoro & Mighell, 1970). The conditions which define the Niggli cell can be written in the following form.

I. Main conditions:

(a) $a \leq b \leq c$;

(b) $-b/2c \leq \cos \alpha \leq 0$, $-a/2c \leq \cos \beta \leq 0$, $-a/2b \leq \cos \gamma \leq a/2b$;

(c) if $\gamma > \pi/2$ then $c \leq d$,

where

$$d = (a^2 + b^2 + c^2 + 2ab \cos \gamma + 2ac \cos \beta + 2bc \cos \alpha)^{1/2}.$$

II. Special conditions:

1. $\gamma \geq \pi/2$

(a) if $a = b$ then $\alpha \leq \beta$,

(b) if $b = c$ then $\beta \leq \gamma$,

(c) if $\cos \alpha = -b/2c$ then $\gamma = \pi/2$,

(d) if $\cos \beta = -a/2c$ then $\gamma = \pi/2$,

(e) if $\cos \gamma = -a/2b$ then $\beta = \pi/2$,

(f) if $c = d$ then $a \leq -2c \cos \beta - b \cos \gamma$;

2. $\gamma < \pi/2$

(a) if $a = b$ then $\alpha \leq \beta$,

(b) if $b = c$ then $\beta \leq \pi - \gamma$,

(c) if $\cos \alpha = -b/2c$ then $\cos \beta \leq - b \cos \gamma/2c$,

(d) if $\cos \beta = -a/2c$ then $\cos \alpha \leq - a \cos \gamma/2c$,

(e) if $\cos \gamma = a/2b$ then $\cos \alpha \leq a \cos \beta/2b$.

The main conditions define the reduced cell by the three shortest non-coplanar lattice translations **a**, **b**, **c**. The special conditions remove ambiguities which may exist in particular cases of strict equality in the main conditions (Santoro & Mighell, 1970).

We can now regard the above conditions as the scanning ranges, with certain hierarchy of the lattice constants implied. Namely, the lattice constant c is altered first, assuming the values c_{min}, ..., c_i, ..., c_{max}. [The choice of the proper range (c_{min}, c_{max}) depends on the intermolecular potential and the molecular dimensions.] The second constant, b, is restricted above

by c_i, the current value of c. Consequently, a should not exceed the current value of b. The ranges for the interaxial angles are further specified by the current values of the conjugate cell edges.

The case $\gamma \geq \pi/2$ involves some difficulty because the shortest ranges for α, β, γ are not expressed in an explicit form. The optimum way to surmount this difficulty in computations is to assume the ranges in accordance with Ia and Ib, rejecting any trial set of the lattice constants if the condition Ic is not satisfied.

The lattice-constant-range conditions for monoclinic crystals are given in Table 3. They were derived assuming the reduced monoclinic cell defined by two shortest lattice translations, a and c, and considering the conditions from Table 2.

In the orthorhombic case we note that the list of equivalent lattice-constant sets is defined by the point group of the extended Cheshire group. The corresponding ranges for a, b, c, which may be also regarded as conditions to define the 'reduced' orthorhombic cell, are given in Table 4 for all point groups corresponding to the extended Cheshire groups of Table 1.

Keeping the lattice constants within above ranges eliminates all equivalent lattice-constant sets except the reference one. The subsequent treatment, leading to the ranges for the molecular parameters t_x, t_y, t_z, φ, θ, ψ, should be done following essentially Hirshfeld's paper. The procedure is to write down the equivalent sets of molecular parameters using all combinations of the Cheshire-group operations with the molecular point-symmetry operations. These sets are then successively eliminated through restrictions on the parameter ranges (Hirshfeld, 1968).

An elucidation is necessary in a boundary case, i.e. when one or more lattice constants is exactly equal to

Table 3. *Lattice-constant-range conditions for monoclinic crystals*

Space group	Range conditions
$P2, P2_1, Pm, P2/m, P2_1/m$	$a \leq c;\ -a/2c \leq \cos \beta \leq 0$
$Pc, P2/c, P2_1/c$	$\left.\begin{array}{c} -c/2a \\ -a/c \end{array}\right\} \leq \cos \beta \leq 0$
$C2, Cm, Cc, C2/m, C2/c$	$\left.\begin{array}{c} -a/2c \\ -c/a \end{array}\right\} \leq \cos \beta \leq 0$

Table 4. *Lattice-constant-range conditions for orthorhombic crystals*

Point group of the extended Cheshire group (from Table 1)	Range conditions
mmm	None
$4/mmm$	$a \leq b$
$m3$	$a \leq b;\ a \leq c$
$m3m$	$a \leq b \leq c$

its limiting value. In this case the derivative symmetry group may be of higher order than that given by Hirshfeld, due to extra symmetry of the lattice. Consider, for instance, the space group $P2_1/m$ with its lattice-constant ranges $a \leq c, -a/2c \leq \cos \beta \leq 0$ (Table 3). In the general case ($a < c, -a/2c \leq \cos \beta < 0$) the derivative group is the Cheshire group $P2/m$ (Hirshfeld, 1968) but it turns to $Pmmm$ if $a < c$ and $\beta = 90°$. Further, for $a = c$ the derivative group is $P2/m$ $4/m$ $2/m$, if $\beta = 90°$, and $P2/m$ $6/m$ $2/m$, if $\beta = 120°$. These groups should be taken instead of $P2/m$ in the corresponding boundary case to derive the molecular parameter ranges.

Thus the boundary case is treated as the general one but requires a 'boundary' derivative group. Since there are too many situations to be considered, we do not systematize them, assuming that obtaining a derivative symmetry group is a trivial procedure for a crystallographer and may be readily undertaken, if necessary, for a particular boundary situation.

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SHORT COMMUNICATIONS

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Imaging of polytypes and stacking faults in tetrahedral compounds. By A. F. MOODIE and H. J. WHITFIELD,

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Abstract

The resolution attained with a JEOL 200CX electron microscope in top-entry configuration has allowed the direct elucidation of the structure of tetrahedrally bonded compounds. Computer simulation methods were used to calculate through-focus series of images at a range of thicknesses and the conditions for which structural features are interpretable on an atomic scale have been ascertained. In particular, various polytypes are differentiated and stacking faults are intuitively interpreted.

A wide variety of compounds crystallize as stacking variants of the diamond lattice. For nearly all of these compounds, ranging from silicon carbide to the quaternary chalcogenides, it is easily seen that, in order to identify specific polytypes directly from electron micrographs, a first requirement is a minimum resolution of about 2.5 Å.

There are, of course, many other requirements, most of which are well known. Using a JEOL 200CX electron microscope in a configuration specifically chosen to maxi-

mize the resolution of lattice images, we have found that all conditions can be satisfied at an accelerating voltage of 200 kV. This is illustrated in Figs. 1(b), (c) with images of 3,3 stacking (*i.e.* pseudo 6H polytype) and 3,4 stacking (*i.e.* pseudo 21R polytype) of the compound CuAsSe (Whitfield, 1981). Our measured value of C_s is somewhat less than 1 mm so that the standard expression for resolution at the Scherzer focus gives a value of 2.3 Å.

As might be anticipated from the micrographs, the technique can be extended much further, for instance to the direct imaging of the intergrowth of polytypes (Fig. 2). Standard multislice calculations (Fig. 1a) have been used in establishing the interpretation. In this example, correspondence between the observed and calculated image is not exact, in that one row of spots in the observed image is somewhat brighter than the rest. This arises from a slight tilt about the c axis, a delicate effect which transforms a glide line into a reflexion line. Effects of this type will be discussed in a forthcoming publication.

The particular material chosen for illustration would appear to be unpromising, since the periodicity in the