The Symmetry of Phases in the Reciprocal Lattice

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The usefulness of Buerger's geometrical treatment for the deduction of the phases associated with symmetry-related reciprocal-lattice points is illustrated by the derivation of the phase relations between reflexions hkl and $\bar{k}hl$ for the 68 space groups of the tetragonal system. This information is supplementary to that given in *International Tables for X-ray Crystallography*. Its use in data processing for Fourier summation is illustrated.

Introduction

The independent development of the symmetry of reciprocal space given in the paper by Bienenstock & Ewald (1962) is a landmark in the theoretical development of crystallography. However, the reference to the method developed by Buerger (1949), for deducing the symmetry of the reciprocal lattice with points weighted with the structure factors, does less than justice to its practical importance. The method is not, as stated, based on deductions from the explicit structure factor expressions but on the type and arrangement of the space-group symmetry elements as laid out in the diagrams of Vol. I of *International Tables for X-ray Crystallography* (1952).

These diagrams are necessarily familiar to crystallographers and a method which uses them as a starting point has considerable practical advantages.

To illustrate the power and simplicity of the method the symmetry relations between reciprocal-lattice points hkl and $\bar{k}hl$ for the 68 space groups of the tetragonal system are derived and listed below. These relations are not given in the *International Tables* and at present have a practical importance in computing Fourier syntheses.

The absolute values of F_{hkl} are related by the *Laue symmetry* elements (the point-group symmetry + a centre if not already present) passing through the origin of the reciprocal lattice. If the corresponding space-group symmetry elements also pass through the origin and have no translation components, then the phases of the F's are related by the *point-group symmetry* (as distinct from the Laue symmetry, when these differ). In addition, $\alpha_{hkl} = -\alpha_{\bar{h}\bar{k}\bar{l}}$ in all cases.* If, however, the space-group symmetry elements contain translational components or do not pass through the origin, then the symmetry of the phases becomes more complicated and, in particular, depends on the indices hkl.

The essential problem of reciprocal-lattice symmetry is, therefore, the relation between phases in such cases.

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* Phase differences arising from anomalous dispersion are, of course, excluded from this discussion.

By application of Buerger's method to an axis of symmetry parallel to c which cuts the ab plane at $xa + yb$, the relation between the reciprocal lattice point hkl and its symmetry axis equivalent $h'k'l'$ reduces to:

$$\alpha_{h'k'l'} = \alpha_{hkl} + 2\pi\{pl/q + (h' - h)x + (k' - k)y\}$$

where p is the power of the operation of the symmetry axis and c/q is the translation component.

This expression can be readily adapted to other symmetry elements, but is the relevant form for the present purpose.

Application to the tetragonal space groups

For the points hkl, $\bar{k}hl$, related by a 90° rotation about a tetrad axis (a right-handed rotation of a screw axis, if the translation is upwards) and the relevant values of x and y, we have:

$$
\begin{aligned}
\alpha_{\bar{k}hl} &= \alpha_{hkl} + (nl - 2k)\tfrac{1}{2}\pi && \text{for } x = y = \tfrac{1}{4} \\
&= \alpha_{hkl} + (nl - 2h)\tfrac{1}{2}\pi && \text{for } x = \tfrac{1}{4},\ y = -\tfrac{1}{4} \\
&= \alpha_{hkl} + (nl - h - k)\tfrac{1}{2}\pi && \text{for } x = \tfrac{1}{4},\ y = 0 \\
&= \alpha_{hkl} + (nl + 2h - 2k)\tfrac{1}{2}\pi && \text{for } x = 0,\ y = \tfrac{1}{2}
\end{aligned}
$$

$n = 0$ for a 4 axis; 1 for 4_1; 2 for 4_2; 3 for 4_3 axes. For a $\bar{4}$ axis at the origin, point-group symmetry combined with $\alpha_{\bar{h}\bar{k}l} = -\alpha_{hkl}$ gives $\alpha_{\bar{k}hl} = -\alpha_{hkl}$. A $\bar{4}$ axis displaced from the origin should not be used in determining phase symmetry because the movement of the inversion centre is involved as well as the position of the axis. In such cases another fourfold axis can always be found for determining phase symmetry. In the body-centred space groups, both 4_1 and 4_3 axes may be found and it is essential to distinguish which is being used for the derivation of the symmetry relation.

Using these expressions, the phase relations for all the space groups can be written down by inspection of the diagrams of the symmetry elements.

Table 1 gives these relations as derived directly from the above expressions. In Table 2 the relations have been reduced to the most convenient form and

Table 1. *Phase relations for tetragonal space groups*

Row no.	Phase angle hkl	Phase angle k̄hl	Space group numbers*
1	α	α	75, 79, 83, 87, 89, 97, 99, 100, 103, 104, 107, 108, 123, 124, 125(422),† 126 (422), 127, 128, 139, 140
2	α	$-\alpha$	81, 82, 85($\bar{4}$), 86($\bar{4}$), 88($\bar{4}$), 111 to 122, 129($\bar{4}m2$), 130($\bar{4}$), 133($\bar{4}$), 134($\bar{4}2m$), 138($\bar{4}$), 141($\bar{4}m2$), 142($\bar{4}$)
3	α	$\alpha + l\pi/2$	76, 91
4	α	$\alpha + l\pi$	77, 84, 93, 101, 105, 106, 131, 132, 135
5	α	$\alpha + l(3\pi/2)$	78, 95
6	α	$\alpha + k\pi$	85($\bar{1}$), 125(2/m), 126($\bar{1}$), 129(2/m), 130($\bar{1}$)
7	α	$\alpha + (3l - 2k)\frac{1}{2}\pi$	80, 98, 109, 110
8	α	$\alpha + (l-k)\pi$	133($\bar{1}$), 134(2/m), 137($\bar{1}$), 138($\bar{1}$)
9	α	$\alpha + (l-h)\pi$	86($\bar{1}$)
10	α	$\alpha + (h-k)\pi$	90
11	α	$\alpha + (l+h-k)\pi$	94, 102, 136
12	α	$\alpha + (l-h-k)\frac{1}{2}\pi$	141(2/m), 142($\bar{1}$)
13	α	$\alpha + (3l-h-k)\frac{1}{2}\pi$	88($\bar{1}$)
14	α	$\alpha + (l+2h-2k)\frac{1}{2}\pi$	92
15	α	$\alpha + (3l+2h-2k)\frac{1}{2}\pi$	96

* From Vol. I of *International Tables* (1952).

† The symbols in brackets after a space group number give the position of the origin when two alternatives are given in the Tables.

extended to second- and third-power rotations for those cases where this is not a trivial deduction from the first power. In rows 7, 12 and 13, which contain only body-centred space groups, use has been made of the relation between the indices and, in general, the relations $n - m = n + m$ (modulo 2) and $n - 2m = n + 2m$ (modulo 4) have been extensively used. No attempt has been made to distinguish between centrosymmetric and non-centrosymmetric

space groups. For the former, with the origin at a centre, α is either 0 or π and will take the values $n\pi/4$ when the (standard) origin is not at a centre (*International Tables*, 1952, p. 356). However, all the space groups in rows 6, 8, 9, 12 and 13 have a centre at the origin and all the space groups in rows 3, 5, 7, 10, 14 and 15 are non-centrosymmetric. The rest, rows 1, 2, 4 and 11, are mixed, but if the space group is centrosymmetric the origin is always at a centre unless given otherwise. In row 2 the origins are all at $\bar{4}$ and therefore not at centres.

An attempt to deduce the phase relationships from the structure-factor expressions for space group 141 (I$4_1/amd$, origin at $2/m$), for example, should convince anyone of the efficacy of Buerger's method. The checking of the relations when found is far more laborious than the derivation from the diagram of the symmetry elements.

Use in Fourier summation

The main use of these and similar phase symmetry relations is in deriving more extensive data from the unique structure factors produced by a least-squares refinement program. This is necessary to prepare data for a Fourier program and may be done as an initial stage by the program itself (directly or by the equivalent modification of the summation process), as in the case of the Mills (1961) Fourier program for space groups up to No. 74 (the end of the ortho-rhombic space groups). If this facility is not available the unique data must be processed beforehand. In the case of Mills's Mercury program, space groups 75 to 88, which are without symmetry elements along x and y, have to be reduced to monoclinic space groups. For space groups 85 and 86 this involves taking different axes, and three quadrants of the tetragonal reciprocal lattice are involved. For the rest, only a change of axis *notation* and the generation of a second tetragonal quadrant are required, apart from re-sorting for efficient use of the Fourier program. In producing programs for this data-processing, the different symmetry relations involved in these space groups can be obtained from Tables 1 and 2.

Table 2. *Phase relations reduced to convenient form*

Row no	Phase angles hkl	Phase angles k̄hl	Phase angles h̄kl	Phase angles kh̄l
6*	α	$\alpha + k\pi$	$\alpha + (h+k)\pi$	$\alpha + h\pi$
7†‡	α	$\alpha + (2h+l)\frac{1}{2}\pi$	α	$\alpha + (2h+l)\frac{1}{2}\pi$
8*	α	$\alpha + (k+l)\pi$	$\alpha + (h+k)\pi$	$\alpha + (h+l)\pi$
9*	α	$\alpha + (h+l)\pi$	$\alpha + (h+k)\pi$	$\alpha + (k+l)\pi$
10‡	α	$\alpha + (h+k)\pi$	α	$\alpha + (h+k)\pi$
11	α	$\alpha + (h+k+l)\pi$	α	$\alpha + (h+k+l)\pi$
12*†	α	$\alpha + (h+k+3l)\frac{1}{2}\pi$	$\alpha + (h+l)\pi$	$\alpha + (h+3k+l)\frac{1}{2}\pi$
13*†	α	$\alpha + (h+k+l)\frac{1}{2}\pi$	$\alpha + (h+l)\pi$	$\alpha + (3h+k+l)\frac{1}{2}\pi$
14‡	α	$\alpha + (2h+2k+l)\frac{1}{2}\pi$	$\alpha + l\pi$	$\alpha + (2h+2k+3l)\frac{1}{2}\pi$
15‡	α	$\alpha + (2h+2k+3l)\frac{1}{2}\pi$	$\alpha + l\pi$	$\alpha + (2h+2k+l)\frac{1}{2}\pi$

* All the space groups in these rows have a centre at the origin.

† These rows contain only body-centred space groups. No other rows except 1 and 2 contain body-centred space groups.

‡ These rows contain only non-centrosymmetric space groups.

Similar considerations apply to some degree to all the tetragonal space groups. Even those which can be reduced to orthorhombic symmetry require the symmetry relations across the diagonal plane.

Table 3. *Modification of the two parts A and B of F_{hkl}*

Case		n	$A_{h'k'l'}$	$B_{h'k'l'}$
1	{	0	A	B
		1	$-A$	$-B$
2	{	0	A	B
		1	$-B$	A
		2	$-A$	$-B$
		3	B	$-A$
3		—	A	$-B$

The phase-symmetry relations are of the form

$$\alpha_{h'k'l'} = \alpha_{hkl} + n\pi \qquad (1)$$

or

$$\alpha_{h'k'l'} = \alpha_{hkl} + n\tfrac{1}{2}\pi \qquad (2)$$

or

$$\alpha_{h'k'l'} = -\alpha_{hkl} . \qquad (3)$$

For either case (1) or (2) n is computed and the result taken modulo 2 for case (1) and modulo 4 for case (2). In some autocode systems a logical product instruction exists to do this directly. This value of n is then used to instruct the machine to modify the values of the two parts, A and B, of F_{hkl} (which will have been fed in as data) to produce the correct values for $F_{h'k'l'}$. The modifications are given in Table 3.

References

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The Likelihood Ratio Method for the Precise and Accurate Determination of Lattice Parameters for Tetragonal and Hexagonal Crystals*

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The Likelihood Ratio Method (LRM) for the precise and accurate determination of lattice parameters has been described (Beu, Musil, and Whitney, 1962) as it applies to crystals of cubic symmetry. This report gives the basic equations for the applications of the LRM to crystals of tetragonal and hexagonal symmetry.

Introduction

The Likelihood Ratio Method (LRM) for the precise and accurate determination of lattice parameters has been described (Beu, Musil & Whitney, 1962) as it applies to crystals of cubic symmetry. This report gives the basic equations for the application of the LRM to crystals of tetragonal and hexagonal symmetry. To save space, the reader is referred to the previous paper (Beu, Musil & Whitney, 1962) for the definition of terms not defined in this report and for a statistical analysis of the problem.

Discussion

The development of the LRM is given below for the tetragonal case only. The development for the hexagonal case is identical if the expression $4/3(h_i^2 + h_i k_i + k_i^2)$ is substituted for $(h_i^2 + k_i^2)$ wherever the latter expression appears. The development of the LRM for tetragonal and hexagonal crystals is very similar to that for cubic crystals and most of the derivation details can be inferred from the cubic case;

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