THE CRYSTALLOGRAPHIC SYMMETRIES DETERMINABLE BY X-RAY DIFFRACTION

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The problem of how to determine the symmetry of a given crystal has been an important one from the early days of the science of crystallography. Symmetry requires the various properties of a crystal to be equivalent in symmetrically equivalent directions. Accordingly, the general nature of a test for the presence or absence of a particular kind of symmetry is to subject the possibly symmetrical directions of a crystal to some physical or chemical action and then ascertain whether the crystal's response is equivalent in these directions or not.

Unfortunately, some tests inherently involve certain symmetry themselves and this prevents one from judging whether the symmetry resulting from such a test derives from the crystal or from the test. This kind of dilemma occurs in testing the symmetry of a crystal by its diffraction effects. When a crystal diffracts x-rays whose wave-length is not in the immediate neighborhood of an absorption edge of one of the chemical elements in the crystal, the diffraction effects are inherently centrosymmetrical. This was pointed out by Friedel¹ as early as 1913, only a year after the discovery of the diffraction of x-rays by crystals made by von Laue and his students.^{2, 3, 4} The cause of this lies in the impossibility of experimentally observing the phases of the x-ray diffraction spectra. Thus, if a set of planes hkl "reflects" x-rays with amplitude $|F_{hkl}|$ and phase φ , the set of planes $\bar{h}\bar{k}\bar{l}$ "reflects" with identical amplitude $|F_{hkl}|$, but with phase $-\varphi$. Since the amplitudes (in the form of intensities, or F^2 's) but not the phases of the reflections can be experimentally observed, diffraction effects are inherently centrosymmetrical, and, even though a crystal does not have a center of symmetry, its diffraction effects do display a center. Therefore, although there are 32 symmetry combinations possible in crystals, only 11 symmetry combinations can be distinguished by the symmetry of their diffraction effects. None of these 11 sets uniquely characterizes any of the 32 crystal classes (i.e., the 32 combinations of symmetry possible for crystals).

One might suppose that this feature provides an ultimate limitation on the detection of symmetry by x-ray diffraction. But in 1919 Niggli⁵ showed that the space group symmetry elements which involve translation components could be identified by the characteristic missing spectra which they caused to occur in the diffraction effects. Later the writer^{6, 7} showed that by combining the information from Friedel's law and Niggli's "ex-

tinctions" (missing spectra), a total of 120 "diffraction groups" could be distinguished. The total number of space groups, or kinds of internal symmetry which are possible in crystals, is 230. Most of the diffraction groups include several space groups, namely, those from the several centrosymmetrical crystal classes which have the same Niggli extinctions. But 59 of these diffraction groups embrace only a single space group (counting enantiomorphous pairs as one space group) and consequently 59 out of the 219 space groups (excluding enantiomorphous duplicates) can be distinguished by a mere qualitative inspection of the diffraction data.

At the 1946 meeting of the American Society for X-Ray and Electron Diffraction, the writer announced⁸ that all space groups except those pairs differing solely by an inversion could be distinguished by diffraction means provided that the spectra are considered on a quantitative basis. In the light of this discovery, Niggli's extinctions, which amounted to *intensity* = 0 for certain special spectra, were seen to be merely a qualitatively obvious special case of a much more general control of spectral intensity by the crystal symmetry. It thus became clear that the key to crystal symmetry was contained in the diffraction spectra of the crystal.

In the same paper⁸ the writer showed that the key to the structure of the crystal also lay fallow in the spectra, and one device for finding the structure, namely, the *implication* method, was suggested. This was an astonishing result which was received with incredulity by nearly everyone, because it was a well-established belief⁹ that, since the phases of the diffraction cannot be observed, there is not necessarily a solution for a crystal structure from diffraction data alone.

Some more recent developments make it possible to treat the determinability of crystal symmetry by x-ray diffraction data on a more straightforward basis. The electron density of a crystal at a selection of points xyz is related to the complex amplitudes, F_{hkl} , of the diffraction spectra hkl by

$$\rho(xyz) = \sum_h \sum_k \sum_l F_{hkl} e^{2\pi i(hx + ky + lz)}. \quad (1)$$

Patterson^{10, 11} showed that another function, not involving the complex F 's, but rather their observable squares, bears a simple relation to (1). Patterson's function,

$$A(uvw) = \sum_h \sum_k \sum_l F_{hkl}^2 e^{2\pi i(hu + kv + lw)}, \quad (2)$$

has maxima where vectors with components u, v, w span maxima in (1). Thus, if maxima occur at $x_1y_1z_1$ and $x_2y_2z_2$ in (1), then maxima occur in (2) at $\pm uwv$, where

$$\left. \begin{aligned} u &= x_2 - x_1 \\ v &= y_2 - y_1 \\ w &= z_2 - z_1 \end{aligned} \right\}. \quad (3)$$

Of course, maxima occur in (1) where the electron density is high, i.e., at atom locations.

The relation involved between (1) and (2) can be rendered more evident if points are substituted for atoms in the crystal structure.¹² Then (1) is transformed into a collection of points called the *fundamental set*, and (2) is transformed into another collection of points called the *vector set*. To derive the vector set from the fundamental set, the vectors between all pairs of points in the fundamental set are drawn, then the vectors are re-assembled at a common origin. The collection of points at the ends of the reassembled vectors constitutes the vector set.

It is an easy matter to find the vector set for any given fundamental set. The writer has recently shown¹² that it is also possible to find the fundamental set for any vector set. But the vector set is a representation of (2), simplified so that the maxima become points,¹³ and the fundamental set is a representative of (1), similarly simplified. This implies that if (2) can be solved, (1) can be derived from it. The interesting consequence of this is that, although (1) cannot be computed from diffraction data because of the unobservability of the phase component of the complex F 's, (2) involves F 's and therefore does not require a knowledge of these phase components. Therefore, in principle, crystal structures are solvable from diffraction data alone.

An immediate consequence of this conclusion is that all crystal symmetries are determinable from diffraction data, for the symmetry of a crystal is an incidental aspect of its structure. Furthermore, since the symmetry of the fundamental set and the crystal are the same, and since the fundamental set is derivable from the vector set, it follows that the key to the symmetry of the crystal is in its vector set.

Actually, vector sets display fewer possible symmetries than the fundamental sets, since the former must all be centrosymmetrical. The writer has shown another way of looking at this.¹² When the vectors between points in the fundamental set are transferred to the origin of the vector set, the translation components of the symmetry elements relating the vectors are lost to the symmetry of the vector set, although other components are retained. In this way it can be shown that, although the symmetries of the fundamental sets comprise the 230 space groups, there are only 24 space group symmetries possible in vector sets. But in this degeneration of actual symmetry, the key to the symmetry of the original fundamental set is not lost. The translation components of the vectors between all atoms in the fundamental set which are symmetrically equivalent,

when transferred to the vector set, cause a concentration of points at the ends of these vectors at loci characteristic of the lost translation. The principal key to crystallographic symmetry is these concentrations in vector space. These are discovered for any crystal by computing the full three-dimensional Patterson synthesis (2). The unaided computation of this synthesis is so laborious that it has very rarely been carried out to date. But with the recent development of the Pepinsky Fourier synthesizer,¹⁴ this full synthesis has now become quite practical.

The writer has tabulated the symmetrical concentrations for the 230 space groups. The tabulation shows that all space groups are uniquely

TABLE 1

PAIRS OF SPACE GROUPS NOT DISTINGUISHABLE BY LOCATIONS OF SYMMETRICAL IMAGES
THE ENANTIOMORPHOUS PAIRS

$\begin{Bmatrix} C3_1 \\ C3_2 \end{Bmatrix}$	$\begin{Bmatrix} P1 \\ P\bar{1} \end{Bmatrix}$	$\begin{Bmatrix} C\bar{6} \\ C6/m \end{Bmatrix}$	$\begin{Bmatrix} I222 \\ I2_12_12_1 \end{Bmatrix}$
$\begin{Bmatrix} C3_121 \\ C3_221 \end{Bmatrix}$	$\begin{Bmatrix} C3 \\ C\bar{3} \end{Bmatrix}$		$\begin{Bmatrix} I23 \\ I2_13 \end{Bmatrix}$
$\begin{Bmatrix} C3_112 \\ C3_212 \end{Bmatrix}$	$\begin{Bmatrix} R3 \\ R\bar{3} \end{Bmatrix}$		
$\begin{Bmatrix} P4_1 \\ P4_2 \end{Bmatrix}$	$\begin{Bmatrix} P4 \\ P\bar{4} \end{Bmatrix}$		
$\begin{Bmatrix} P4_12 \\ P4_22 \end{Bmatrix}$	$\begin{Bmatrix} I4 \\ I\bar{4} \end{Bmatrix}$		
$\begin{Bmatrix} P4_12_1 \\ P4_22_1 \end{Bmatrix}$			
$\begin{Bmatrix} C6_1 \\ C6_2 \end{Bmatrix}$			
$\begin{Bmatrix} C6_2 \\ C6_4 \end{Bmatrix}$			
$\begin{Bmatrix} C6_122 \\ C6_222 \end{Bmatrix}$			
$\begin{Bmatrix} C6_222 \\ C6_422 \end{Bmatrix}$			
$\begin{Bmatrix} P4_132 \\ P4_232 \end{Bmatrix}$			

characterized by these concentrations except for the pairs shown in table 1. There are four kinds of categories where the concentrations determine pairs of space groups instead of a single space group. Each category is listed as a column in table 1. Column one contains the 11 pairs of enantiomorphous space groups. Column two contains 4 pairs of space groups, each pair containing a cyclical group of the first sort and the corresponding cyclical group of the second sort. Columns three and four contain three more pairs which cannot be placed in either of the other categories.

Now, all space groups except the 19 pairs shown in table 1 can be distinguished merely by the locations of the concentrations. But by taking into account some obvious aspects of the *patterns* in the concentrations, all space groups except the 11 enantiomorphous pairs in the first column of table 1 can be distinguished. Thus, in the pairs $P4$, $P\bar{4}$ and $I4$, $I\bar{4}$ the first member of each pair contains satellites⁸ while the second does not. (A satellite is merely a duplication of the pattern motif enlarged and rotate 45° in this case.) The members of the pairs are therefore easily distinguished by the qualitative appearance of the patterns in the concentration. In the first member of the pairs $I222$, $I2_12_12_1$ and $I23$, $I2_13$, the patterns in the three orthogonal (axial) planar concentrations are simple projections of one another. For the second member of the pairs, the corresponding patterns are also projections of one another, but with origins shifted $\frac{1}{4}\frac{1}{4}0$ etc. The members of these pairs can therefore also be distinguished by the qualitative appearance of the patterns in the concentrations. It remains to distinguish between members of the three pairs $P1$, $P\bar{1}$; $R3$, $R\bar{3}$; and $C3$, $C\bar{3}$. These can be distinguished if it is possible to distinguish points of weight 1 and weight 2, since the first and second members of these pairs differ in exactly this way.⁸ This can readily be done provided that the x-ray diffraction data from which the Patterson synthesis (2) has been made is on an absolute basis. Then, the total number of electrons within each peak is of the form z_1z_2 for the first member of each pair and $2z_1z_2$ for the second member of each pair, where z_1 and z_2 are the atomic numbers of atoms 1 and 2 in the crystal structure. For peaks in the symmetrical concentration loci of $R3$, $R\bar{3}$, $C3$ and $C\bar{3}$, this condition reduces to peaks of z^2 and $2z^2$, where z is the atomic number of an atom in the structure.

Thus, an incidental consequence of the conclusion that crystal structures are solvable from diffraction data is that all space groups can be distinguished from diffraction data except that one cannot distinguish between members of the enantiomorphous pairs. A rather similar but less general conclusion has been reached on other grounds. Wilson¹⁵ has recently shown that the presence or absence of an inversion center (not detectable by observation of relative intensities, which results only in distinguishing the 11 centrosymmetrical crystal classes) can be discerned by a quantitative statistical analysis of all spectra produced by the crystal. Rogers¹⁶ then pointed out that this additional feature could be used to modify the writer's diffraction symbols. When the possibility of distinguishing centrosymmetrical zones is taken into account, this permits distinguishing all but the 11 enantiomorphous pairs and the following four pairs of space groups:

$$\left\{ \begin{array}{l} I_{222} \\ I_{2,2,2_1} \end{array} \right\} \quad \left\{ \begin{array}{l} I_{23} \\ I_{2,3} \end{array} \right\} \quad \left\{ \begin{array}{l} C_{3lm} \\ C_{3ml} \end{array} \right\} \quad \left\{ \begin{array}{l} C_{\bar{3}lm} \\ C_{3ml} \end{array} \right\}$$

Since these four pairs *can* be distinguished by the vector set method, the latter is more powerful. Of course, it has this greater power because the patterns themselves are examinable in the concentration loci, and because the loci are correlated with the lattice (which accounts for distinguishing the last two pairs above).

¹ Friedel, G., "Sur les symétries cristallines que peut révéler la diffraction des rayons Röntgen," *Compt. rend.*, **157**, 1533-1536 (1913).

² Friedrich, W., Knipping, P., and Laue, M., "Interferenz-Erscheinungen bei Röntgenstrahlen," *Sitzber. math.-physik. Klasse Akad. Wiss. München*, **1912**, 303-322.

³ Laue, M., "Eine quantitative Prüfung der Theorie für die Interferenz-Erscheinungen bei Röntgenstrahlen," *Ibid.*, **1912**, 363-373.

⁴ Laue, M., "Röntgenstrahlinterferenzen," *Physik. Z.*, **14**, 1075-1079 (1913).

⁵ Niggli, Paul, *Geometrische Kristallographie des Discontinuums*, Gebrüder Borntraeger, Leipzig, 1919, pp. 482-503.

⁶ Buerger, M. J., "The Application of Plane Groups to the Interpretation of Weissenberg Photographs," *Z. Krist.*, **A91** (1935), especially pp. 287-288.

⁷ Buerger, M. J., *X-Ray Crystallography*, John Wiley & Sons, New York, 1942, pp. 510-516.

⁸ Buerger, M. J., "The Interpretation of Harker Syntheses," *J. Applied Phys.*, **17**, 579-595 (1946).

⁹ Buerger, M. J., reference 7, p. 2.

¹⁰ Patterson, A. L., "A Fourier Series Method for the Determination of Interatomic Distances in Crystals," *Phys. Rev.*, **46**, 372-376 (1934).

¹¹ Patterson, A. L., "A Direct Method for the Determination of the Components of Interatomic Distances in Crystals," *Z. Krist.*, **A90**, 517-542 (1935).

¹² Buerger, M. J., "Vector Sets," *Acta Cryst.*, **3**, 87-97 (1950).

¹³ It is possible to derive a vector set from any (2) (or to derive the fundamental set from (1)) by a pin-point-focussing process. To do this each $F_{\mathbf{hkl}}^2$ is divided by $f_{1,\mathbf{hkl}}^2$ (or each $F_{\mathbf{hkl}}$ is divided by $f_{1,\mathbf{hkl}}$), where $f_{1,\mathbf{hkl}}$ is the scattering power of atom 1, selected to be pinpointed for spectrum hkl , at the temperature of the experimental determination of $F_{\mathbf{hkl}}^2$.

¹⁴ Pepinsky, R., "An Electronic Computer for X-ray Crystal Structure Analyses," *J. Applied Phys.*, **18**, 601-604 (1947).

¹⁵ Wilson, A. J. C., "Possible X-ray Determination of a Center of Symmetry," *Research*, **2**, 246 (1949).

¹⁶ Rogers, D., "Determination of Space Groups by Intensity Statistics, *Ibid.*, **2**, 342-343 (1949).