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Symmetry relations between structure factors.

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It is known (Buerger, 1949) that the relationships between structure factors generated by space-group operations may be described by the use of the operations of the point group isomorphous with the space group considered, and of phase factors related to the translational components of the space-group elements. However, none of the existing space-group tables lists all independent relations, nor does there appear to exist a simple derivation of them (see, however, MacGillavry (1950) and Patterson (1952)). Such a derivation is given in the following, and an example provided.

Let C_j be any space-group operation relating the vector $\mathbf{r}$ to $C_j\mathbf{r} = \mathbf{t}_j + A_j . \mathbf{r}$, where $\mathbf{t}_j$ is the translational component of the operation and A_j is a dyadic corresponding to the proper or improper rotation isomorphous with C_j. The value of $\mathbf{t}_j$ depends on the position of the origin relative to the plane, axis, or center of A_j. For proper or improper rotations the conjugate dyadic A_{jC} is equal to the inverse dyadic A_j^{-1}, which relation insures invariance of distances (see, for example, Zachariasen (1945)).

Consider the structure factor

$$F_{\mathbf{h}} = \int_{\text{unit cell}} \varrho(\mathbf{r}) \exp\,(2\pi i \mathbf{h}.\mathbf{r}) dV\,,$$

in usual notation. Since $\varrho(C_j\mathbf{r}) = \varrho(\mathbf{r})$,

$$\begin{aligned} F_{\mathbf{h}} &= \int \varrho(\mathbf{r}) \exp\,[2\pi i(\mathbf{h}.C_j\mathbf{r})] dV \\ &= \exp 2\pi i(\mathbf{h}.\mathbf{t}_j) \int \varrho(\mathbf{r}) \exp\,[2\pi i(\mathbf{h}.A_j.\mathbf{r})] dV\,. \end{aligned}$$

The integral may be interpreted as structure factor $F_{\mathbf{h}^{(j)}}$, where $\mathbf{h}^{(j)} = \mathbf{h}.A_j = A_j^{-1}.\mathbf{h}$ is related to $\mathbf{h}$ by the inverse of the operation A_j.

Thus

$$F_{\mathbf{h}^{(j)}} = \exp\,(-2\pi i \mathbf{h}.\mathbf{t}_j) F_{\mathbf{h}}\,.$$

To obtain all independent relations between the structure factors only those operations C_j need be considered whose rotational components completely generate the point group isomorphous to the space group. This means that from a knowledge of the Hermann–Mauguin symbol all independent relations may be derived. If the symbol is redundant, relations which are dependent result.

The form of the relations depends on the choice of the origin. If the proper components of $\mathbf{t}_j$ are in doubt, consideration of the parameters related by the operation C_j will provide them, as will be apparent in the following example.

Example.—Space group *Pn3n*; origin at center of symmetry.

In self explanatory notation:

Type of operation	$C_j(x, y, z)$	$\mathbf{t}_j$	$F_{hkl} \doteq$
$n_{[0, x, y]}$	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}+z$	$0, \frac{1}{2}, \frac{1}{2}$	$(-1)^{k+l}F_{\bar{h}kl}$
$3_{[x, x, x]}$	y, z, x	$0, 0, 0$	F_{lhk}
$n_{[x, x, z]}$	$\frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}+z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$(-1)^{h+k+l}F_{khl}$
$4_{[\frac{1}{4}, \frac{1}{4}, z]}$	$\frac{1}{2}-y, x, z$	$\frac{1}{2}, 0, 0$	$(-1)^{h}F_{k\bar{h}l}$
$4_{[\frac{1}{4}, \frac{1}{4}, z]}$	$y, \frac{1}{2}-x, z$	$0, \frac{1}{2}, 0$	$(-1)^{k}F_{\bar{k}hl}$

Since the point group isomorphous with *Pn3n* contains 47 operations different from identity there will be 47 relations among structure factors. However, only the relations of the first three lines of the table are independent: for instance, those of lines 4 and 5 follow from combination of lines 2 and 3, while $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$ is a consequence of lines 1 and 2. Note the importance, in lines 4 or 5, of the fact that the indices *hkl* are related by the dyadic inverse to the one which (except for $\mathbf{t}_j$) relates the parameters. Since line 5 deals with the inverse of the operation of line 4 the indices $k\bar{h}l$ on line 4 are related to *hkl* in the same way as the parameters on line 5 are related to x, y, z (except for $\mathbf{t}_j$), and inversely.

References

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The accuracy of structures determined by powder methods, with reference to the Ag–Zn ζ structure.

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It is gratifying to find that the qualitative X-ray examination carried out by Bergman & Jaross (1955) on powder specimens and on orientated aggregates of 'single crystal' domains leads to an approximate structure for the Ag–Zn ζ phase which, in so far as it goes, is in agreement with the more detailed structure given by Edmunds & Qurashi (1951) and based on measured intensities of X-ray powder reflexions. Nevertheless, the suggestion of Bergman & Jaross, that a structure determined from X-ray powder data alone will in general be less reliable than one derived from work on single crystals, needs some reply; and, moreover, it should be made clear that these authors did not in fact use the single-crystal method in the accepted sense of the term.

The main weakness of the powder method lies in the fact that, for structures of any complexity, so many reflexions overlap that it is not possible to use Fourier methods of analysis, the Fourier coefficients being indeterminate. This objection does not apply when other methods, such as that of steepest descents, are used and, when the final solution has been found, it should be as reliable as one derived from single-crystal data provided the number of reflexions measured is large compared with the number of atomic parameters to be determined. In many instances the accuracy may exceed that attainable with a single crystal since it is often impossible adequately to correct the intensities, usually found by visual estimation, for the absorption in a single crystal of irregular shape. This absorption correction is an important factor for an alloy composed of such heavy atoms as zinc and silver.

To the comment that the procedure of Edmunds & Qurashi was rather lengthy, it may be answered that the refining and testing of a structure by any method is usually lengthy. More details of procedure than usual were given as these were considered to be useful contributions on the application of the methods of steepest descent and of irregular absences. Approximate atomic parameters comparable with the *final* values of Bergman & Jaross were obtained early in the investigation, but it was found that there existed a range of co-ordinates which gave very nearly the same X-ray intensities and which, though not equally probable, were possible on grounds of packing.

References

Bergman, G. & Jaross, R. W. (1955). *Acta Cryst.* **8**, 232.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

Journal of Electronics

Messrs Taylor and Francis announce the publication as from July 1955 of a new periodical, *Journal of Electronics*, which is to appear under the editorship of J. Thomson, with N. F. Mott as consultant editor. It is the policy of the journal to publish original work in electron science 'interpreted to mean the description of the behaviour of electrons in the free state or in states where their binding energy is low'.

The journal is published in the same format as the *Philosophical Magazine*, with which it is associated; the first part consists of 102 pages and contains nine articles, all by British authors. Subsequent parts will appear at two-monthly intervals and the volume will contain six parts. The price is 20*s*. per part or 110*s*. per volume.

A.C.A. Publications

The American Crystallographic Association has decided on the following prices for its publications:

(*a*) Monograph No. 1 (Buerger): $2·00.
Monograph No. 2 (Wrinch): $2·00.
Monograph No. 3 (Hauptman & Karle): $1·50.
Monograph No. 4 (Bravais): $2·00.
(*b*) Back programs and abstracts of meetings; bibliographies: $1·00 each.

These prices are valid for anyone, whether a member of A. C. A. or not. Six months after this announcement the items under (*b*) will be destroyed.

Orders, accompanied by the payment, should be sent without delay to the Polycrystal Book Service, 84 Livingston Street, Brooklyn 1, N.Y., U.S.A.

Liège International Fair

L'Association des Ingénieurs sortis de l'École de Liège announces that at the Liège International Fair, to be held in May 1956, it will organize a section devoted to the industrial applications of the electron microscope. Further information may be obtained from the General Secretary of the Association, 22 rue Forgeur, Liège, Belgium.

The Geometrical Basis of Crystal Chemistry

The following corrections should be made in the above series of papers by A. F. Wells:

Part 1 (*Acta Cryst.* (1954), **7**, 535).

Table 2: Add 14 in last column for Nets 1, 2 and 5; add 12 in the appropriate column for Nets 2 and 6.

Table 3: For $I4/amd$ read $I4_1/amd$.

Part 5 (*Acta Cryst.* (1955), **8**, 32).

Fig. 6 and preceding text: The 'uniform' Net 21 of Part 1 has the symbol $12^2.14$, so that replacement of the points by triangles does not give a net 3.24^2. The series of Fig. 6 terminates at 3.20^2.

A simplified computation technique for structure refinement by means of two-dimensional F_o-F_c synthesis

An error occurs in the short communication by E. Harnik (*Acta Cryst.* (1955), **8**, 363). The expression in the fifth line of the article should read:

$$D(u, w) = D(x/a, z/c) = \Sigma_h \Sigma_l (F_o-F_c)_{hl} \cos 2\pi(hx/a+lz/c)\ .$$