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# The Use of Symmetry for Calculating Structure Semi-Invariants I. Primitive Space Groups

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A simple method to deduce the equivalent origins, the number of origin-fixing reflexions and the semi-invariant structure factors, starting from 'equivalent positions' is given for all primitive space groups. The method can be usefully applied to computer routines. Note that only the rotation matrices are essential for this purpose.

## Introduction

In recent years, in connexion with the considerable increase in power and use of direct methods, we have felt that a systematic way of deducing semi-invariant structure factors, equivalent origins and the number of origin-fixing reflexions starting from symmetry transformations ('equivalent general positions') might be particularly useful. Although some computer programs for apparently working out the problem do exist (Hall, 1970), they attempt to solve it in a somewhat empirical way; for this reason, and as a result of a working period spent together at a meeting of the C.E.C.A.M. in Paris (September–October 1970) we considered the whole problem from theoretical beginning to practical applications, starting from primitive space groups.

## Equivalent origins

A general space-group transformation, relating one point position $\mathbf{x}=x_1\mathbf{a}_1+x_2\mathbf{a}_2+x_3\mathbf{a}_3$ to an equivalent position $\mathbf{x}'$, can be represented by:

$$\mathbf{x}'=\mathbf{M}\,\mathbf{x}+\mathbf{t}\,, \tag{1}$$

where $\mathbf{M}$ is a rotation matrix and $\mathbf{t}$ a translation vector; a change in origin will lead to the expression:

$$\mathbf{y}'=\mathbf{N}\,\mathbf{y}+\mathbf{u}\,, \tag{1a}$$

where $\mathbf{y}',\mathbf{y},\mathbf{N}$ and $\mathbf{u}$ correspond to $\mathbf{x}',\mathbf{x},\mathbf{M}$ and $\mathbf{t}$ respectively, referred to the new origin.

If the two origins are 'equivalent', the structure-factor expressions must have the same functional form (Hauptman & Karle, 1953, 1956, 1959, 1961). This will be true when, for each transformation, the rotation matrices $\mathbf{M}$ and $\mathbf{N}$ coincide and each component of a translation vector $\mathbf{t}$ differs from the corresponding one $\mathbf{u}$ only by integer numbers, *i.e.*

$$\mathbf{N}=\mathbf{M}\quad \mathbf{u}\equiv\mathbf{t}(\mathrm{mod}\,\boldsymbol{\omega})\;. \tag{2}$$

As in Hauptman & Karle (1953, 1956, 1959, 1961) $\boldsymbol{\omega}$ is a vector with arbitrary integer components. Calling $\mathbf{s}$ the vector 'origin shift', and substituting $\mathbf{y}=\mathbf{x}-\mathbf{s}$ and $\mathbf{y}'=\mathbf{x}'-\mathbf{s}$ in (1*a*), we have:

$$\mathbf{x}'=\mathbf{N}\mathbf{x}+(\mathbf{I}-\mathbf{N})\mathbf{s}+\mathbf{u}\,, \tag{3}$$

where $\mathbf{I}$ is the unit $3\times3$ matrix.

Comparing (3) with (1), and considering that these expressions must be equal for every value of $\mathbf{x}$, leads to:

$$\mathbf{N}=\mathbf{M};\quad \mathbf{u}=\mathbf{t}+(\mathbf{M}-\mathbf{I})\,\mathbf{s}\,. \tag{4}$$

Comparing (4) with (2), the condition for $\mathbf{s}$ to connect two equivalent origins is:

$$(\mathbf{M}-\mathbf{I})\mathbf{s}=\boldsymbol{\omega}\,. \tag{5}$$

A relation of type (5) must hold simultaneously for all $\mathbf{M}$ rotation matrices in the space group. Let us denote $\mathbf{m}_i$ as a vector corresponding to a row of one $\mathbf{M}-\mathbf{I}$ matrix in the space group. If a shift $\mathbf{s}$ connects two equivalent origins, it follows that for all $\mathbf{m}_i$'s in the group:

$$\mathbf{m}_i\mathbf{s}=\omega\,, \tag{6}$$

where $\omega$ is an integer number.

Let us choose, from our matrices $\mathbf{M}-\mathbf{I}$ in the group, a set of three non-coplanar row vectors, $\mathbf{m}_i$; if this is possible (as for all non-polar groups‡) we can consider three vectors, $\mathbf{d}_j$, defined by the relationship $\mathbf{m}_i\mathbf{d}_j=\delta_{ij}$. Let us denote by $\mathbf{M}'$ the matrix (non-singular) whose

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‡ In polar groups, where all $3\times3$ $M'$ matrices are singular, one or more $\mathbf{d}_j$'s are undetermined and *any* shift along the polar directions is a shift between equivalent origins (and then a $\mathbf{d}_j$). The $\mathbf{d}_j$'s corresponding to non-polar directions can be obtained from the inversion of an $n\times n$ $\mathbf{M}'$ matrix ($n<3$), applying the same arguments as for non-polar cases.

rows are the three $\mathbf{m}_i$ vectors; this matrix may, or may not, necessarily be one $\mathbf{M}-\mathbf{I}$ matrix in the group (most $\mathbf{M}-\mathbf{I}$ matrices are singular). If $\mathbf{D}$ is the matrix whose columns are the $\mathbf{d}_j$ vectors, it follows that:

$$\mathbf{M}'\mathbf{D}=\mathbf{I};\quad \mathbf{D}=(\mathbf{M}')^{-1}, \tag{7}$$

where $\mathbf{I}$ is the unit $3\times 3$ matrix.

From (6) and the Appendix, (*b*), it is evident that any possible shift $\mathbf{s}$ between 'equivalent' origins must be a linear combination, with integer coefficients, of these $\mathbf{d}_j$ vectors, which determine a lattice of possible equivalent origins. This can be most easily seen in space group $P\bar{1}$, where the only non-singular matrix $\mathbf{M}'$ that can be built is $\mathbf{M}'=-2\mathbf{I}$; the lattice of equivalent origins is then determined by the three vectors:

$$\mathbf{d}_1=\begin{bmatrix}-\frac{1}{2}\\0\\0\end{bmatrix},\quad \mathbf{d}_2=\begin{bmatrix}0\\-\frac{1}{2}\\0\end{bmatrix},\quad \mathbf{d}_3=\begin{bmatrix}0\\0\\-\frac{1}{2}\end{bmatrix}$$

as is universally known.

If more symmetry elements are present, the $\mathbf{d}_j$'s obtained as above from *any* $\mathbf{M}'$ matrix may not form integer scalar products with all the remaining $\mathbf{m}_i$ rows in the group; in this case, the lattice determined by these $\mathbf{d}_j$'s does not consist entirely of really 'equivalent' origins. It can be proved [see Appendix, (*e*), (*f*), (*g*), (*h*)] that the $\mathbf{d}_j$'s which are compatible with all symmetry transformations in a space group can be obtained from inverting *any one* among the possible non-singular $\mathbf{M}'$ matrices whose determinants are the smallest in absolute value.

### Tests for semi-invariance and number of 'origin-defining' reflexions

Let us now consider a general shift, $\mathbf{s}=\sum\omega_j\mathbf{d}_j$, between equivalent origins. For a structure factor $F_\mathbf{h}$, the phase shift $\Delta\varphi$ is given by:

$$\Delta\varphi=2\pi\mathbf{hs}=2\pi\sum\omega_j\mathbf{hd}_j\,, \tag{8}$$

where $\omega_j$ are, as usual, integer numbers. For some reflexions, taking any one of the three $\mathbf{d}_j$'s, we have $\mathbf{hd}_j=$integer; therefore, any shift between equivalent origins changes the phase value by an integer multiple of $2\pi$. The phases of these reflexions are 'semi-invariant' or 'invariant' (Hauptman & Karle, 1953, 1956, 1959, 1961): in this treatment, the difference between 'semi-invariant' and 'invariant' phases is not considered necessary, because we prefer to treat the operation 'centre of symmetry' in the same way as any other operation.

The phases of all reflexions that are not semi-invariant will depend, accordingly, on our choice of origin. Let us imagine a 'known' structure with appropriate phases assigned to all reflexions, and consider the origin shifts necessary to change some of the phases to certain prescribed values. We end up with a system of three equations:

$$\begin{aligned}\omega_1\mathbf{h}_1\mathbf{d}_1+\omega_2\mathbf{h}_1\mathbf{d}_2+\omega_3\mathbf{h}_1\mathbf{d}_3&=\Delta\varphi_{\mathbf{h}_1}/2\pi\\ \omega_1\mathbf{h}_2\mathbf{d}_1+\omega_2\mathbf{h}_2\mathbf{d}_2+\omega_3\mathbf{h}_2\mathbf{d}_3&=\Delta\varphi_{\mathbf{h}_2}/2\pi\\ \omega_1\mathbf{h}_3\mathbf{d}_1+\omega_2\mathbf{h}_3\mathbf{d}_2+\omega_3\mathbf{h}_3\mathbf{d}_3&=\Delta\varphi_{\mathbf{h}_3}/2\pi\,,\end{aligned} \tag{9}$$

where the unknowns are the three (integer) components $\omega_i$ of the vector 'origin shift'. $F_{\mathbf{h}_1}$, $F_{\mathbf{h}_2}$ and $F_{\mathbf{h}_3}$ are the so-called 'origin-defining' reflexions. From (9) it is evident that in no case are these reflexions more than three in number, the phases of all others being determined by the known structure and the $\omega_i$'s. The system (9) can be solved (for the three $\omega_i$'s) when:

(*a*) No phase of $F_{\mathbf{h}_i}$ is semi-invariant,
(*b*) There are no correlations among the $\mathbf{h}_i$'s [see Appendix, (*c*)],
(*c*) No $\mathbf{d}_j$ is a lattice translation,
(*d*) There are no correlations among the $\mathbf{d}_j$'s [see Appendix, (*d*)].

Whereas (*a*) and (*b*) above give general indications about how to choose the indices $\mathbf{h}_i$ of the origin-fixing reflexions, (*c*) and (*d*) result in suppressing one or more equations in the system (9), *i.e.* the number of these origin-fixing reflexions.

### Examples

*Space group $P\bar{6}m2$*

Let us first consider (*a*) of the Appendix, and use for this example only two rotation matrices, $\mathbf{M}_1$ and $\mathbf{M}_2$, since all the others in the group can derive from these by multiplication:

$$\mathbf{M}_1=\begin{bmatrix}0&-1&0\\1&-1&0\\0&0&-1\end{bmatrix},\quad \mathbf{M}_2=\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix}.$$

It follows that

$$\mathbf{M}_1-\mathbf{I}=\begin{bmatrix}-1&-1&0\\1&-2&0\\0&0&-2\end{bmatrix},\quad \mathbf{M}_2-\mathbf{I}=\begin{bmatrix}-1&-1&0\\-1&-1&0\\0&0&0\end{bmatrix}.$$

Examining the rows of $\mathbf{M}_1-\mathbf{I}$ and $\mathbf{M}_2-\mathbf{I}$, the only nonsingular matrix $\mathbf{M}'$ that we can build is $\mathbf{M}'=\mathbf{M}_1-\mathbf{I}$. Inverting $\mathbf{M}'$ we have:

$$\mathbf{D}=\begin{bmatrix}-\frac{2}{3}&\frac{1}{3}&0\\-\frac{1}{3}&-\frac{1}{3}&0\\0&0&-\frac{1}{2}\end{bmatrix}.$$

The $\mathbf{d}_j$'s are the columns of $\mathbf{D}$. Since $\mathbf{d}_1-\mathbf{d}_2=\begin{bmatrix}-1\\0\\0\end{bmatrix}=\mathbf{t}$,

where $\mathbf{t}$ indicater a lattice translation, only two reflexions are necessary to define the origin. The semi-invariant $F_\mathbf{h}$'s must be such as to have $\mathbf{hd}_1$ or $\mathbf{hd}_2=$integer (one condition implies the other, because $\mathbf{d}_1-\mathbf{d}_2=\mathbf{t}$) and $\mathbf{hd}_3$=integer. Therefore, for semi-invariance, $h+k=3n$ and $l$ is even.

*Space group P*622

Here, too, we can consider only two rotation matrices:

$$\mathbf{M}_1=\begin{bmatrix}1 & -1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{bmatrix},\quad \mathbf{M}_2=\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & -1\end{bmatrix},$$

so that

$$\mathbf{M}_1-\mathbf{I}=\begin{bmatrix}0 & -1 & 0\\ 1 & -1 & 0\\ 0 & 0 & 0\end{bmatrix},\quad \mathbf{M}_2-\mathbf{I}=\begin{bmatrix}-1 & 1 & 0\\ 1 & -1 & 0\\ 0 & 0 & -2\end{bmatrix}.$$

The nonsingular matrix $\mathbf{M}'$ with the smallest absolute value of the determinant (=2) is:

$$\mathbf{M}'_s=\begin{bmatrix}0 & -1 & 0\\ 1 & -1 & 0\\ 0 & 0 & -2\end{bmatrix}\qquad \mathbf{D}=\mathbf{M}_s'^{-1}=\begin{bmatrix}-1 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & -\frac{1}{2}\end{bmatrix}.$$

Of the three $\mathbf{d}'_j$s (the columns of $\mathbf{D}$), two are lattice translations. Only one reflexion is therefore necessary to define the origin; the semi-invariant $F'_{\mathbf{h}}$s must have $l$=even.

*Space group P*23

Here, three matrices $\mathbf{M}_1$, $\mathbf{M}_2$ and $\mathbf{M}_3$ can be considered:

$$\mathbf{M}_1=\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 1 & 0 & 0\end{bmatrix};\quad \mathbf{M}_2=\begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{bmatrix};$$

$$\mathbf{M}_3=\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}.$$

Using rows of the corresponding $\mathbf{M}_i-\mathbf{I}$'s, a non-singular matrix $\mathbf{M}'$ whose determinant is the smallest in absolute value (=2) can be built, such as:

$$\mathbf{M}'=\begin{bmatrix}-1 & 1 & 0\\ 0 & -1 & 1\\ 0 & 0 & -2\end{bmatrix};\qquad \mathbf{D}=\mathbf{M}'^{-1}=\begin{bmatrix}-1 & -1 & -\frac{1}{2}\\ 0 & -1 & -\frac{1}{2}\\ 0 & 0 & -\frac{1}{2}\end{bmatrix}.$$

Of the three $\mathbf{d}_j$'s, two are integer and, therefore, lattice translations. Therefore one origin-defining reflexion can be chosen. The semi-invariant reflexions are the ones with $h+k+l=$ even.

*Space group P*2

Here, the only rotation matrix $\mathbf{M}_1$ (differing from identity) is:

$$\mathbf{M}_1=\begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{bmatrix};\quad \mathbf{M}'=\mathbf{M}_1-\mathbf{I}=\begin{bmatrix}-2 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -2\end{bmatrix}.$$

Since the group is polar, $\mathbf{M}'$ is singular. Referring to the non-polar directions, $x$ and $z$, we can build a $2\times2$ $\mathbf{M}'$ matrix $(=-2\mathbf{I})$ and invert it. Consequently, the $\mathbf{d}_j$'s are:

$$\mathbf{d}_1=\begin{bmatrix}-\frac{1}{2}\\ 0\\ 0\end{bmatrix},\ \mathbf{d}_2=\begin{bmatrix}0\\ 0\\ -\frac{1}{2}\end{bmatrix},\ \mathbf{d}_3=\begin{bmatrix}0\\ \text{any}\\ 0\end{bmatrix}\ (d_{32}\text{ undetermined})$$

Besides having $h$=even, $l$=even, the semi-invaiiant reflexions must have $k=0$, because of the particular nature of $\mathbf{d}_3$. Three origin-defining reflexions can be chosen.

## APPENDIX

(*a*) When a rotation matrix $\mathbf{C}$ is the product of two matrices $\mathbf{A}$ and $\mathbf{B}$, then any vector $\mathbf{d}_j$ giving integer scalar products with all rows of $(\mathbf{A}-\mathbf{I})$ and $(\mathbf{B}-\mathbf{I})$ gives integer products with all rows of $(\mathbf{C}-\mathbf{I})$.

*Proof*: We have:

$(\mathbf{A}-\mathbf{I})\ \mathbf{d}_j=\boldsymbol{\omega}_1$; $(\mathbf{B}-\mathbf{I})\mathbf{d}_j=\boldsymbol{\omega}_2$; $(\mathbf{B}-\mathbf{A})\ \mathbf{d}_j=\boldsymbol{\omega}_2-\boldsymbol{\omega}_1=\boldsymbol{\omega}_3$, where $\boldsymbol{\omega}_i$ are vectors with integer components. We can also write: $(\mathbf{AB}-\mathbf{I})\ \mathbf{d}_j=(\mathbf{A}+\mathbf{I})\ (\mathbf{B}-\mathbf{I})\ \mathbf{d}_j-(\mathbf{B}-\mathbf{A})\ \mathbf{d}_j=(\mathbf{A}+\mathbf{I})\boldsymbol{\omega}_2-\boldsymbol{\omega}_3$. Since the elements of $\mathbf{A}$ are integers the result is obvious.

(*b*) All the possible shifts $\mathbf{s}$ between equivalent origins are linear combinations, with integer coefficients, of the $\mathbf{d}_j$ vectors, as obtained from the inversion of one $\mathbf{M}'$ matrix.

*Proof*: Since the matrix $\mathbf{D}=(\mathbf{M}')^{-1}$ is not singular, any vector can be expressed as $\mathbf{s}=\sum p_j\mathbf{d}_j$. Since $\mathbf{m}_i\mathbf{d}_j=\delta_{ij}$, it follows that $\mathbf{s}\ \mathbf{m}_j=p_j$. Therefore, if one or more $p_j$'s are not integer, $\mathbf{s}$ does not give an integer product with at least one $\mathbf{m}_i$ and the new origin is not equivalent to the 'old' one.

(*c*) Kinds of correlation between $\mathbf{h}_i$ in the system (9):

(i) *The* $\mathbf{h}_i$ *are linearly dependent*. For instance, if $\mathbf{h}_1=a\mathbf{h}_2+b\mathbf{h}_3$, the first of equations (9) becomes:

$$\omega_1(a\mathbf{h}_2\mathbf{d}_1+b\mathbf{h}_3\mathbf{d}_1)+\omega_2(a\mathbf{h}_2\mathbf{d}_2+b\mathbf{h}_3\mathbf{d}_2)+\ldots=\Delta\varphi_{\mathbf{h}_1}/2\pi,$$

the coefficients of the unknowns in the first equation becoming linear combinations of the coefficients in the other equations.

(2) *The* $\mathbf{h}_i$*'s are linearly dependent modulo* $\mathbf{h}'$, *where the phase of* $F_{\mathbf{h}'}$ *is semi-invariant*. For instance, if $\mathbf{h}_1=a\mathbf{h}_2+b\mathbf{h}_3+\mathbf{h}'$, considering that $\mathbf{h}'\mathbf{d}_1=0$ (mod 1), the result is as in the preceding case.

(3) *The* $\mathbf{h}_i$*'s, when transformed by a symmetry operation in the group, are linearly dependent* (*modulo* $\mathbf{h}'$). For instance, if $\mathbf{h}_1=a(\mathbf{h}_2\mathbf{M})+b\mathbf{h}_3+\mathbf{h}'$, where $\mathbf{M}$ is a rotation matrix of some symmetry operation, and $a$ is integer, we have, for the first equation in (9):

$$\omega_1(a\mathbf{h}_2\mathbf{M}\mathbf{d}_1+b\mathbf{h}_3\mathbf{d}_1+\mathbf{h}'\mathbf{d}_1)+\omega_2(a\mathbf{h}_2\mathbf{M}\mathbf{d}_2+b\mathbf{h}_3\mathbf{d}_2+\mathbf{h}'\mathbf{d}_1)+\ldots=\Delta\varphi_{\mathbf{h}_1}/2\pi.$$

Since $(\mathbf{M}-\mathbf{I})\mathbf{d}_j=\boldsymbol{\omega}$, *i.e.* $\mathbf{M}\mathbf{d}_j=\boldsymbol{\omega}+\mathbf{d}_j$, and $a\mathbf{h}_2\boldsymbol{\omega}+\mathbf{h}'\mathbf{d}_1=0$ (mod 1), the demonstration proceeds as for case (2). This case is obviously the generalization of the two preceding cases.

(*d*) The correlations (if any) between $\mathbf{d}_j$'s in the system (9) can always be reduced to the form:

$$\mathbf{d}_i \pm \mathbf{d}_j = \mathbf{t}, \quad \text{or} \quad \mathbf{d}_1 \pm \mathbf{d}_2 \pm \mathbf{d}_3 = \mathbf{t}\,,$$

where $\mathbf{t}$ is a lattice translation.

*Proof*: First of all, since the matrix $\mathbf{D}=(\mathbf{M}')^{-1}$ is not singular, any $\mathbf{d}_j$ is not a linear combination, as such, of the others. Since a lattice translation is a possible shift between equivalent origins, $\mathbf{t}$ must be a linear combination of the $\mathbf{d}_j$'s with integer coefficients [see point (*b*)]. The components of each $\mathbf{d}_j$ will be, in general, fractional. For a centric group, the $\mathbf{d}_j$'s themselves will be linear combinations, with integer coefficients, of the $\mathbf{d}_j$ vectors proper to group $P\overline{1}$ (otherwise the operation 'centre-of-symmetry' would not be satisfied by all the origins); since any operation corresponding to a rotation of 180° around one axis behaves – in this respect – just as a centre of symmetry for the directions which are perpendicular to it, we can always arrive at the same situation as for a centric case for non-polar directions of non-centric groups of any system but hexagonal/trigonal with a $\overline{6}$ or 3 axis. Accordingly, the non-zero components of every $\mathbf{d}_j$ will be either integer or $\pm\frac{1}{2}$. For the latter (hexagonal/trigonal) groups, considering the partitioning of rotation matrices as specified in point (*h*), which leads to a $2\times2$ matrix whose determinant is 3, two of the $\mathbf{d}_j$'s will have their non-zero elements equal to $\pm\frac{1}{3}$ or $\pm\frac{2}{3}$. Consequently, when all non-integer components are $\pm\frac{1}{2}$, for any product $a_j\mathbf{d}_j$ we have: $a_j\mathbf{d}_j=\mathbf{t}'$ (where $\mathbf{t}'$ is an integer vector, *i.e.* a lattice translation) if $a_j$ is even, or $a_j\mathbf{d}_j=\mathbf{t}'-\mathbf{d}_j$ when $a_j$ is odd. When the components are $\pm\frac{1}{3}$ or $\pm\frac{2}{3}$, we have $a_j\mathbf{d}_j=\mathbf{t}'$ if $a_j$ is a multiple of 3, or $(a_j\pm1)\mathbf{d}_j=\mathbf{t}'$ in all other cases. This results in having either $\mathbf{d}_j=\mathbf{t}$, or $\mathbf{d}_i\pm\mathbf{d}_j=\mathbf{t}$, or $\mathbf{d}_1\pm\mathbf{d}_2\pm\mathbf{d}_3=\mathbf{t}$, as we wanted to show.

Another possible correlation between $\mathbf{d}_j$'s might be the following: $\mathbf{d}_i=a\mathbf{M}\mathbf{d}_j+b\mathbf{d}_k$, where $\mathbf{M}$ is the rotation matrix relative to a symmetry operation in the space group and $a$, $b$ are integer numbers. From (5), we obtain: $\mathbf{M}\mathbf{d}=\boldsymbol{\omega}+\mathbf{d}_j$($\mathbf{d}_j$ itself being a possible origin shift $\mathbf{s}$), and the results are as in the preceding cases.*

(*e*) For any system but the hexagonal/trigonal one, the absolute value of any possible determinant of a non-singular $\mathbf{M}'$ matrix is $2^n$ $(n=1,2,3)$.

*Proof*: Let us adopt the symbol $\begin{vmatrix} r_1 \\ r_2 \\ r_3 \end{vmatrix}$ for a determinant of a matrix, whose rows are $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$. Then:

$$\begin{vmatrix} r_1+r \\ r_2+r \\ r_3+r \end{vmatrix} = \begin{vmatrix} r_1 \\ r_2 \\ r_3 \end{vmatrix} + \begin{vmatrix} r_1' \\ r_2 \\ r_3 \end{vmatrix} + \begin{vmatrix} r_1 \\ r_2' \\ r_3 \end{vmatrix} + \begin{vmatrix} r_1' \\ r_2' \\ r_3 \end{vmatrix} + \begin{vmatrix} r_1 \\ r_2 \\ r_3' \end{vmatrix} + \begin{vmatrix} r_1' \\ r_2 \\ r_3' \end{vmatrix} + \begin{vmatrix} r_1 \\ r_2' \\ r_3' \end{vmatrix} + \begin{vmatrix} r_1' \\ r_2' \\ r_3' \end{vmatrix}\,.$$

Every row of an $\mathbf{M}'$ matrix can be written as the sum of a row $\mathbf{r}_i$ of a rotation matrix $\mathbf{M}$ and a row $\mathbf{r}_i'$ of $-\mathbf{I}$; in all groups except in the hexagonal/trigonal system, $\mathbf{r}_i$ can be only a unit vector $\pm[100]$, $\pm[010]$, $\pm[001]$, as (of course) $\mathbf{r}_i'$. Consequently, each of the eight determinants in the sum will be either $\pm1$ or zero; in the latter case, two rows must be equal (in absolute value). If one determinant is zero, then another one at least must be zero, because for any choice of two rows, these rows are common to two determinants. For the same reason, if two determinants are non-zero, they must be either equal or opposite in sign. This makes the absolute value of $|M'|$ either zero or $2^n$, with a maximum of 8.

(*f*) If the determinants of all possible non-singular $\mathbf{M}'$ matrices are multiples of the smallest one by integer numbers, then the $\mathbf{d}_j$'s obtained from inverting any $\mathbf{M}'$ matrix whose determinant is the smallest (in absolute value) form integer products with any row $\mathbf{m}_i$ of all other possible $\mathbf{M}'$ matrices in the group.

*Proof*: Let us suppose that a product $\mathbf{m}_i\mathbf{d}_j=m/n$, where $m$ is not divisible by $n$. Then, replacing the row $\mathbf{m}_j$ in the $\mathbf{M}'$ matrix whose determinant is supposed to be the smallest with $\mathbf{m}_i$, we would obtain a new $\mathbf{M}'$ matrix, whose determinant is $m/n$ times the smallest one, against our hypothesis.

(*g*) If the $\mathbf{d}_j$'s obtained from inverting one $\mathbf{M}_1'$ matrix give integer products with all rows $\mathbf{m}_i$ of another $\mathbf{M}_2'$ matrix, then $|M_2'|=n|M_1'|$, where $n$ is integer.

*Proof*: If $\mathbf{m}_i\mathbf{d}_j=k_{ij}$, we have $\mathbf{m}_i=\sum k_{ij}\mathbf{m}_j'$, where $\mathbf{m}_j'$ is a row of $\mathbf{M}_1'$. Consequently, $|M_2'|=|K||M_1'|$, where $\mathbf{K}$ is the matrix, whose elements are the $k_{ij}$'s. If all these elements are integer, $|K|$ is integer $(=n)$.

(*h*) The $\mathbf{d}_j$'s compatible with all symmetry transformations in the group can be obtained from inverting any one among the possible non-singular $\mathbf{M}'$ matrices whose determinants are the smallest in absolute value.

*Proof*: For non-hexagonal/trigonal space groups, applying points (*e*) and (*f*), the conclusion is obvious. For hexagonal/trigonal groups, however, point (*e*) cannot be applied, because in some rotation matrices $\mathbf{M}$ one row of the kind $[1\overline{1}0]$ or $[\overline{1}10]$ is present.

All rotation matrices $\mathbf{M}_1$ in the hexagonal/trigonal system can be partitioned as follows:

$$\mathbf{M}_i = \left[\begin{array}{c:c} A & C \\ \hdashline C' & B \end{array}\right],$$

where $\mathbf{A}$ and $\mathbf{B}$ are $2\times2$ and $1\times1$ matrices respectively, and $\mathbf{C},\mathbf{C}'$ have their elements all equal to zero.† A rotation of 120° around the $c$ axis is always part of the group; for this operation,

$$\mathbf{A}=\begin{bmatrix} 0 & \overline{1} \\ 1 & \overline{1} \end{bmatrix}\;;\quad \mathbf{A}-\mathbf{I}=\begin{bmatrix} \overline{1} & \overline{1} \\ 1 & \overline{2} \end{bmatrix}\;;\quad |A-I|=3\,.$$

* In agreement with the equations from which it has been derived (the equations depend only on rotation matrices $\mathbf{M}_i$), the symmetry of the $\mathbf{d}_j$ lattice is the one of the corresponding space group without screw and glide translations; strange as it may seem, whereas $\mathbf{d}_j=\mathbf{M}\mathbf{d}_i$ is a possible origin shift, it is not generally true that $\mathbf{d}_j=\mathbf{M}\mathbf{d}_i+\mathbf{t}$ is another possible origin shift (consider, for instance, the space group $P4_12_12$).

† We point out here that for some space groups, such as $P312$ and $P321$, which correspond to the same point group (32), the sets of rotation matrices are different.

Let us indicate, by $\mathbf{A}_m$, the $\mathbf{A}$ matrix corresponding to the minimum rotation around the $c$ axis. The groups with 6 or $\bar{3}$ axes must contain either binary (180°) rotation or inversion respectively; one $\mathbf{A}$ matrix is therefore $-\mathbf{I}_{(2\times2)}$, and the determinant of the corresponding $\mathbf{A}-\mathbf{I}$ is $-4$. Because of points ($a$) and ($g$), the determinant of $\mathbf{A}_m-\mathbf{I}$ cannot be other than $\pm1$, since 3 and $-4$ must be integer multiples of it. Therefore, in this case the application of point ($f$) becomes possible, as for non-hexagonal space groups. For groups with a $\bar{6}$ or 3 axis, this symmetry element can be alone [and then we can apply points ($a$) and ($g$)] or combined with other symmetry elements. In the latter case, each new symmetry element is relative to a series of rotation matrices, one of which (let us call it $\mathbf{R}_o$) has rows as in non-hexagonal groups (see *International Tables for X-ray Crystallography*, 1952); the others are combinations of this operation and rotations around $c$. Let us now examine which $\mathbf{A}$ matrices can be related to $\mathbf{R}_o$. Omitting singular matrices, the identity, and $-\mathbf{I}$ (which would bring us back to $\bar{3}$ or 6 axes), and moreover considering that, since $a$ and $b$ are oblique, no rotations are possible which leave either $x$ or $y$ unchanged, we end up with:

$$\pm\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \quad \pm\begin{bmatrix}0 & 1\\\bar{1} & 0\end{bmatrix},$$

the rows of the corresponding $\mathbf{A}-\mathbf{I}$ matrices being only $\pm[\bar{1}1]$ and $[\bar{1}\bar{1}]$. The latter is already a row of the $\mathbf{A}-\mathbf{I}$ matrix corresponding to a rotation of 120°; the former rows, if present, can be combined with the row $[1\bar{2}]$ (of the 120° rotation) to give a new $2\times2$ matrix, whose determinant is $\pm1$. Consequently, we can always build a matrix $\mathbf{M}'$ such that the determinants of all the others are its integer multiples, making the application of ($f$) possible even in this case.

The fundamental part of this theory was developed at the C.E.C.A.M. meeting on direct methods (September–October 1970), where a computer routine working essentially to this scheme was written (in *FORTRAN* language). Accordingly, we want to thank the Italian Consiglio Nazionale delle Ricerche and the French Conseil National de la Récherche Scientifique for making it possible to carry out this work. The kind hospitality at C.E.C.A.M., extended by Dr Carl Moser, is also gratefully appreciated. We thank Dr Gremlich and Professor Wondratschek for useful criticism.

### References

HALL, S. R. (1970). *Symmetry considerations in the Application of Structure Invariants in Relations,* Nato Advanced Study Institute on Direct and Patterson Methods. Parma, Italy.

HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal.* A.C.A. Monograph No. 3. New York: Polycrystal Book Service.

HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45.

HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 93.

HAUPTMAN, H. & KARLE, J. (1961). *Acta Cryst.* **14**, 217.

*International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.

*Acta Cryst.* (1972). A**28**, 155

# Calculation of the Intensity of Secondary Scattering of X-rays by Noncrystalline Materials. II. Moving Sample Transmission Geometry

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Equations that require numerical integration over only one variable were derived for calculating the intensity of secondary scattering of X-rays for noncrystalline samples in the case of a transmission geometry, in which the sample is rotated so that the incident and diffracted beams are always at equal angles with respect to a normal to the faces of the slab of sample. Tables are given that allow the intensity ratios of secondary-to-primary scattering to be determined without making lengthy calculations.

## Introduction

The first paper of this series (Dwiggins & Park, 1971) gives the background material, general theory, and nomenclature section needed to follow this paper.

The transmission geometry is best visualized by considering a slab of sample in a reflection geometry diffractometer to be rotated by 90° from the reflection position when the instrument is set for zero total scattering angle. It is then apparent that the incident and diffracted X-ray beams will form equal scattering angles with a normal to the sample faces at all scattering angles. In comparison with the more usual transmission geometry, where the sample remains fixed and normal to the incident X-ray beam, this type of transmission geometry has the advantages that the