

Let us set:

$$\vec{OM} = \sqrt{NW},$$

\vec{MC} : vector normal to the plane (V_1, V_2) .

By Pythagoras's theorem, we have:

$$X_m^2 = |\vec{OC}|^2 = N|\mathbf{W}|^2 - |\vec{MC}|^2 = N - |\vec{MC}|^2.$$

By elementary geometry and equation (3) we have:

$$|\vec{MC}|^2 = \left(\frac{\text{volume of } (V_1, V_2, \sqrt{NW})}{\text{surface of } (V_1, V_2)} \right)^2 = N \frac{D_3}{D_2}. \quad (B.7)$$

By a straightforward generalization, we have:

$$|\vec{MC}|^2 = N \frac{D_{m+1}}{D_m}. \quad (B.7a)$$

Therefore:

$$Q_m = N \frac{D_m - D_{m+1}}{D_m} = N - N \frac{D_{m+1}}{D_m} = N - |\vec{MC}|^2 = X_m^2.$$

We conclude:

$$Q_m = X_m^2 \quad (B.8)$$

is the square of the modulus of the projection of \mathbf{W} upon the 'sub-space' $(V_1 \dots V_m)$.

(D) Proof of inequality (15a)

Clearly

$$|\vec{MC}|^2 \leq N|\mathbf{W}|^2 = N.$$

Therefore, from (B.7a), we obtain

$$\frac{D_{m+1}}{D_m} \leq 1. \quad (B.9)$$

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The Strengthening of Direct Methods of Crystal Structure Determination by use of Data from Isomorphous Compounds

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A new set of relations between structure factors corresponding to an isomorphous pair is established: inequalities, convolution equations, probabilities. These relations may enhance the power of direct methods for the determination of phases.

The aim of this paper is to establish relations between structure factors belonging to pairs of isomorphous crystals. The theory can be applied also to a set of dif-

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fraction data obtained for the same crystal by X-ray and neutron diffraction respectively. These relations can be considered as the extension to isomorphous

pairs of the so-called direct methods for solving crystal structures: inequalities, Sayre's equation, theory of probability.

1. Inequalities

The unitary structure factors for an isomorphous pair will be denoted by:

$$U_{\mathbf{H}} = \sum_{j=1}^N n_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (1)$$

$$U'_{\mathbf{H}} = \sum_{j=1}^N n'_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (1a)$$

$$\text{with } \sum_j n_j = \sum_j n'_j = 1, \quad (2)$$

where n' is a complex or a real number,
 n is a real, strictly positive number,
 N is the number of atoms in the unit cell.

(a) Inequalities arising from Cauchy's inequality

These inequalities are an extension of the Harker & Kasper (1948) inequalities. We recall first the Cauchy's inequality (3) verified by any pair of sets of complex numbers a_j and b_j ($j=1, \dots, n$):

$$\left| \sum_{j=1}^N a_j b_j \right|^2 \leq \left[\sum_{j=1}^N |a_j|^2 \right] \left[\sum_{j=1}^N |b_j|^2 \right]. \quad (3)$$

We now consider a centrosymmetrical isomorphous pair; the unitary structure factors are given by:

$$U_{\mathbf{H}} = \sum_{j=1}^N n_j \cos(2\pi \mathbf{H} \cdot \mathbf{r}_j), \quad (4)$$

$$U'_{\mathbf{H}} = \sum_{j=1}^N n'_j \cos(2\pi \mathbf{H} \cdot \mathbf{r}_j). \quad (4a)$$

Let us apply Cauchy's inequality by setting:

$$a_j = n'_j/n_j^{\frac{1}{2}} \quad b_j = n_j^{\frac{1}{2}} \cos(2\pi \mathbf{H} \cdot \mathbf{r}_j). \quad (5)$$

We obtain:

$$\left| \sum_j (n'_j/n_j^{1/2}) n_j^{1/2} \cos(2\pi \mathbf{H} \cdot \mathbf{r}_j) \right|^2 \leq \left[\sum_j |n'_j|^2/n_j \right] \left[\sum_j n_j \cos^2 2\pi \mathbf{H} \cdot \mathbf{r}_j \right]$$

or

$$\left| \sum_j n'_j \cos(2\pi \mathbf{H} \cdot \mathbf{r}_j) \right|^2 \leq A \sum_j n_j \left(\frac{1 + \cos 4\pi \mathbf{H} \cdot \mathbf{r}_j}{2} \right)$$

with

$$A = \sum_j \frac{|n'_j|^2}{n_j}. \quad (6)$$

By using (1), we obtain finally:

$$|U'_{\mathbf{H}}|^2 \leq A \left(\frac{1}{2} + \frac{1}{2} U_{2\mathbf{H}} \right). \quad (7)$$

This inequality enables one to obtain information about the phase of $U_{2\mathbf{H}}$ by using the knowledge of the modulus of $U'_{\mathbf{H}}$. By following the same reasoning we obtain similar inequalities for different space groups. For example, in space group $P2_1$, by setting:

$$a_j = \frac{n'_j}{n_j^2} \exp(2\pi i k y_j),$$

$$b_j = n_j^{1/2} \{ \exp[2\pi i (h x_j + l z_j)] + (-1)^k \exp[-2\pi i (h x_j + l z_j)] \}$$

we obtain:

$$|U'_{hkl}|^2 \leq A \left(\frac{1}{2} + \frac{1}{2} (-1)^k U_{2h,0,2l} \right). \quad (8)$$

(b) Determinants associated with isomorphous pairs

The inequalities of § (a) may be derived from more general inequalities involving determinants, in the same way as the Harker-Kasper inequalities may be derived from Karle-Hauptman determinants. In order to establish these inequalities, we use the N -dimensional Hilbert space, described by Kitaigorodski (1961).* However, the m th vector is now defined differently, as follows:

$$p \leq m-1: \quad \mathbf{V}_p = \sum_j [n_j^{1/2} \exp(2\pi i \mathbf{H}_p \cdot \mathbf{r}_j)] \mathbf{e}_j; \quad (9)$$

$$p = m: \quad \mathbf{W} = \mathbf{V}_m = \sum_j \left[\frac{n'_j}{n_j^{1/2}} \exp(2\pi i \mathbf{H}_m \cdot \mathbf{r}_j) \right] \mathbf{e}_j. \quad (10)$$

We then form the scalar products:

$$(\mathbf{V}_p \cdot \mathbf{V}_q) = \sum_j n_j \exp[2\pi i (\mathbf{H}_p - \mathbf{H}_q) \cdot \mathbf{r}_j] = U_{pq}$$

$$p, q = 1 \dots m-1$$

$$(\mathbf{V}_p \cdot \mathbf{V}_p) = \sum_j n_j = 1$$

$$(\mathbf{V}_p \cdot \mathbf{W}) = \sum_j n'_j \exp[2\pi i (\mathbf{H}_p - \mathbf{H}_m) \cdot \mathbf{r}_j] = U'_{pm}$$

$$p = 1, \dots, m-1$$

$$(\mathbf{W} \cdot \mathbf{W}) = A \quad (A \text{ is given by equation 6}).$$

With these scalar products we construct the following determinant of order m denoted by I_m (I for 'isomorphous pair').

$$I_m = \begin{vmatrix} U_{11} & U_{12} & \dots & U'_{1m} \\ U_{21} & U_{22} & \dots & U'_{2m} \\ \dots & \dots & \dots & \dots \\ U_{m1} & U_{m2} & \dots & A \end{vmatrix} \geq 0.$$

I_m is a Gram determinant; therefore:

$$\begin{array}{ll} \text{for } m \geq N+1 & I_m = 0, \\ \text{for } m \leq N & I_m \geq 0. \end{array}$$

Remark

If both n_j and n'_j are positive, the role of $U_{\mathbf{H}}$ and $U'_{\mathbf{H}}$ can be inverted in all equations derived in this paper.

2. Algebraic equations

By generalization of the reasoning which leads to the Sayre's (1952) equation, we obtain a similar relation for isomorphous pairs; in this paper we will use the form given by Hughes (1953). We introduce the normalized structure factor $E_{\mathbf{H}}$ defined by

* Also Tsoucaris (1970).

$$E_{\mathbf{H}} = \sum_{j=1}^n g_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (12)$$

$$\sum_{j=1}^N g_j^2 = \sum_{j=1}^N g_j'^2 = 1, \quad \overline{|E_{\mathbf{H}}|^2}^{(\mathbf{H})} = \overline{|E_{\mathbf{H}}'|^2}^{(\mathbf{H})} = 1.$$

The g_j 's are related to the n_j 's or f_j 's (atomic scattering factors) by:

$$g_j = \frac{n_j}{(\sum_j n_j^2)^{1/2}} = \frac{f_j}{(\sum_j f_j^2)^{1/2}}$$

and the horizontal bar means 'average value of the expression underneath' when \mathbf{H} sweeps all reciprocal space.

By multiplying $E_{\mathbf{K}}$ and $E_{\mathbf{H}-\mathbf{K}}$, and averaging over \mathbf{K} (\mathbf{H} being kept constant) we obtain:

$$\overline{E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}}^{(\mathbf{K})} = \sum_{j=1}^N g_j g_j' \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) = G_{\mathbf{H}}. \quad (13)$$

$G_{\mathbf{H}}$ is the Fourier coefficient corresponding to the product of the electron densities $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$.

In the general case, $G_{\mathbf{H}}$ is not simply related to $E_{\mathbf{H}}$ or $E_{\mathbf{H}}'$; in the same way, the expression

$$\overline{E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}}^{(\mathbf{K})}$$

is not simply related to $E_{\mathbf{H}}$ unless all atoms are equal.

In our problem, if all atoms in $\rho(\mathbf{r})$ [not necessarily in $\rho'(\mathbf{r})$] are equal, we have:

$$G_{\mathbf{H}} = N^{-1/2} E_{\mathbf{H}}' = \overline{E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}}^{(\mathbf{K})}. \quad (14)$$

Equation (14) suggests that the relationship (in the centrosymmetrical case):

$$E_{-\mathbf{H}}' E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}' \sim \text{positive} \quad (15)$$

is likely to be true even if it is not strictly required by the inequalities. To answer in a quantitative way the question 'How probable is it that (15) holds?' the theory of probability is used.

3. Statistical relations

By using the mathematical apparatus described in the paper by Tsoucaris (1970), we obtain the following approximate expression for the probability P_+ that (15) holds:

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh \left[\frac{1}{\sqrt{N}} |E_{\mathbf{H}}' E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}| \right]. \quad (16)$$

Equation (16) is still approximately true for the general case where the atoms in $\rho(\mathbf{r})$ are unequal (see Cochran & Woolfson, 1955).

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Sesquioxyde de Plomb, Pb_2O_3 . I. Détermination de la Structure

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The structure proposed for lead sesquioxide by Byström (1947) is incorrect. The space group found in the present work is $P2_1/a$ with four Pb_2O_3 in the unit cell; the unit-cell dimensions are: $a=7.814$, $b=5.625$, $c=8.466$ Å (all ± 0.003 Å); $\beta=124^\circ 48' \pm 5'$. The structure has been determined by means of X-ray and neutron-diffraction powder data, and refined by a full-matrix least-squares method. The Pb^{4+} ions are surrounded by six oxygen atoms forming deformed octahedra, with an average Pb-O distance of 2.18 Å. These octahedra share edges and corners to form a two-dimensional framework parallel to (001). These layers are interconnected by Pb^{2+} ions having sixfold coordination, with Pb-O separations ranging from 2.30 to 3.00 Å. The three shortest distances $\text{Pb}^{2+}-\text{O}^{2-}$ give rise to a Pb^{2+} coordination reminiscent of the threefold coordination of Pb^{2+} in Pb_3O_4 .

Introduction

Le sesquioxyde de plomb, Pb_2O_3 , fut préparé pour la première fois par Clark, Schieltz & Quirke (1937) par synthèse hydrothermale. Gross (1941) proposa pour ce composé une maille monoclinique ayant pour paramètres: $a=7,03$, $b=5,62$, $c=3,93$ Å et $\beta=82^\circ$ avec $Z=2$ et $P2_1/m$ ou $P2_1$ comme groupe spatial. Byström

(1944) adopte les hypothèses de Gross et propose une structure dans laquelle les atomes de plomb occupent deux positions $2(e)$ du groupe spatial $P2_1/m$; l'atome d'oxygène ayant un facteur de diffusion trop faible par rapport à celui de l'atome de plomb, il lui est impossible de déterminer les positions des atomes d'oxygène, par comparaison des intensités calculées et observées; il propose cependant des positions en tenant compte