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A General Theory of Inequalities Based on a Matrix of Karle & Hauptman's Type

Shigeo Naya

Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo-ken, Japan

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A general theory of inequalities based on a matrix of Karle & Hauptman's type is given, which is formulated by a somewhat different method from that given in our previous paper (Oda, Naya & Taguchi, 1961). It is shown that inequalities so far reported by different authors can be easily derived from the present theory.

1. Introduction

Since Harker & Kasper (1948) first derived their inequalities to be imposed among structure factors, this problem has been treated by a number of authors; i.e. Gillis (1948), MacGillavry (1950), Karle & Hauptman (1950), Goedkoop (1950, 1952), Okaya & Nitta (1952), de Wolff & Bouman (1954), von Eller (1955, 1960), Bouman (1956) and Löfgren (1960), etc.

In the two papers reported by the present author and others (Taguchi & Naya, 1958; Oda, Naya & Taguchi, 1961), we derived a non-negative matrix of Karle & Hauptman's type which was based upon a matrix-representation of Fourier series as follows:

$$\boldsymbol{F} = \frac{1}{N^3}\sum_{\mathbf{h}=0}^{N-1} F_{\mathbf{h}}\boldsymbol{C}^{\mathbf{h}}, \tag{1}$$

where $\boldsymbol{C}^{\mathbf{h}}$ expresses a direct product of three matrices $\boldsymbol{C}^h$, $\boldsymbol{C}^k$ and $\boldsymbol{C}^l$,

$$\boldsymbol{C}^{\mathbf{h}} = \boldsymbol{C}^h \times \boldsymbol{C}^k \times \boldsymbol{C}^l, \quad h, k, l = 0, 1, 2, \ldots, N-1\,,$$

$$\boldsymbol{C} = \begin{bmatrix} 0 & & & & 1 \\ 1 & 0 & & & \\ & 1 & 0 & & \\ & & & \ddots & \\ & & & 1 & 0 \end{bmatrix}. \tag{2}$$

$\boldsymbol{C}$ is a regular representation of a cyclic group of order N, with N large. Starting from expression (1) and reducing $\boldsymbol{F}$ by symmetry based on a matrix-theoretical treatment, we obtained a general form of inequalities which is in harmony with that of Goedkoop (1952). This corresponds to a generalization of the method given by Bouman (1956) for the case of $P_{\bar{1}}$, and gives us a 'fundamental form of inequalities' applicable to any given space group. However, some of the inequalities reported by different authors could not be derived by this method.

In the present paper, we shall show a more generalized theory of inequalities based on a matrix of Karle & Hauptman's type by a somewhat different method from that given in our previous paper. First, we shall utilize the geometrical considerations to derive inequalities involving the structure factors, as shown by von Eller (1955, 1960). The results obtained by the present method will not only give the fundamental form of inequalities reported by the author and others in the previous paper, but also will cover inequalities of other types found by different authors.

2. Mathematical preliminary

2·1. *Properties of non-negative matrix*

Let us note that any non-negative matrix has the following properties.

(I) The trace of any non-negative matrix is always non-negative.

(II) The product of any two non-negative matrices is also non-negative, if they can be diagonalized by a same transformation.

(III) The product of any matrix and its transposed and complex-conjugate is always non-negative.

2·2. *Selection-operator for the structure factor*

We shall introduce a selection-operator $\tilde{\boldsymbol{C}}^{\mathbf{h}_i}$ which picks up a structure factor $F_{\mathbf{h}_i}$ from (1) by the following operation.

$$\text{tr.}\,\{\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{F}\} = F_{\mathbf{h}_i}, \quad \tilde{\boldsymbol{C}}^{\mathbf{h}_i} = \boldsymbol{C}^{-\mathbf{h}_i}, \tag{3}$$

where symbol $\sim$ stands for a transposed and complex-conjugate matrix. Equation (3) holds always, since

$$\text{tr.}\,\{\boldsymbol{C}^{\mathbf{h}}\} = \begin{cases} 0, & \mathbf{h} \neq 0\,, \\ N^3, & \mathbf{h} = 0\,, \end{cases} \tag{4}$$

from (2), and

$$\text{tr.}\,\{\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{F}\} = \text{tr.}\left\{\frac{1}{N^3}\sum_{\mathbf{h}=0}^{N-1} F_{\mathbf{h}}\boldsymbol{C}^{\mathbf{h}}\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\right\}$$
$$= \frac{1}{N^3}\sum_{\mathbf{h}=0}^{N-1} F_{\mathbf{h}}\,\text{tr.}\,\{\boldsymbol{C}^{\mathbf{h}-\mathbf{h}_i}\} = F_{\mathbf{h}_i}\,, \tag{5}$$

from (1) and (4). For the sake of simplicity, we shall write $\text{tr.}\,\{\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{F}\}$ as $\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\rangle$, hence

$$\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\rangle = F_{\mathbf{h}_i}\,. \tag{6}$$

2·3. *Introduction of a unitary space*

Since N^3 different $\boldsymbol{C}^{\mathbf{h}_i}$ are linearly independent with each other by the nature of cyclic group (2), the selection-operators $\boldsymbol{C}^{\mathbf{h}_i}$ introduced in 2·2 are also recognized as base vectors belonging to a N^3-dimensional vector space. In this vector space, let us introduce a 'metric' representing the square of length of any vector $\boldsymbol{Q}$ as follows.

$$\langle|\boldsymbol{Q}|^2\rangle \equiv \langle\tilde{\boldsymbol{Q}}\boldsymbol{Q}\rangle , \tag{7}$$

where $\boldsymbol{Q}$ is expressed by a linear combination of the base vectors $\boldsymbol{C}^{\mathbf{h}_i}$ and $\langle\ldots\rangle$ means tr. $\{\ldots\boldsymbol{F}\}$ like that of equation (6). Expression (7) is always non-negative by virtue of (I), (II) and (III) given in 2·1. Thus we can construct a N^3-dimensional unitary space U of which the base vectors are given by N^3 linearly independent $\boldsymbol{C}^{\mathbf{h}_i}$ and the metrical distinction is shown by (7). The scalar product of any two base vectors $\boldsymbol{C}^{\mathbf{h}_i}$ and $\boldsymbol{C}^{\mathbf{h}_j}$ belonging to space U is now given by $\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{C}^{\mathbf{h}_j}\rangle$. Using equation (6), it follows that

$$\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{C}^{\mathbf{h}_j}\rangle = F_{\mathbf{h}_i-\mathbf{h}_j} . \tag{8}$$

Equation (8) corresponds to a metric tensor which was considered by von Eller (1955, 1960).†

2·4. *Consideration of symmetry*

Let us consider the case where the factor group is expressed by

$$\{\boldsymbol{S}_0\equiv\boldsymbol{E},\ \boldsymbol{S}_1,\ \ldots,\ \boldsymbol{S}_p,\ \ldots,\ \boldsymbol{S}_{m-1}\},\ \boldsymbol{E}=(1|0),$$
$$\boldsymbol{S}_p=(\boldsymbol{R}_p|\mathbf{t}_p),\ p=0,1,\ldots,m-1 , \tag{9}$$

where $\boldsymbol{R}_p$ and $\mathbf{t}_p$ indicate the rotational and translational parts of the pth operation, m being the order of group. We shall summarize some relations which can be applied to any space group.

(I) The following relations hold among the structure factors.

$$F_{\mathbf{h}_i}=F_{\boldsymbol{R}_p\mathbf{h}_i}e^{-2\pi i\mathbf{h}_i\mathbf{t}_p},\ p=0,1,\ldots,m-1 . \tag{10}$$

(II) If $\boldsymbol{S}_q=\boldsymbol{S}_p\boldsymbol{S}_r$, we have the relation

$$\boldsymbol{R}_q=\boldsymbol{R}_p\boldsymbol{R}_r,\quad \mathbf{t}_q=\mathbf{t}_p\boldsymbol{R}_r+\mathbf{t}_r . \tag{11}$$

(III) Using (6) and (10), we obtain

$$\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p\mathbf{h}_i}e^{-2\pi i\mathbf{h}_i\mathbf{t}_p}\rangle=\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p\mathbf{h}_i}\rangle e^{-2\pi i\mathbf{h}_i\mathbf{t}_p}$$
$$=F_{\boldsymbol{R}_p\mathbf{h}_i}e^{-2\pi i\mathbf{h}_i\mathbf{t}_p}=F_{\mathbf{h}_i},\ p=0,1,\ldots,m-1 . \tag{12}$$

Hence, we can introduce m different selection-operators for the same structure factor $F_{\mathbf{h}_i}$ as follows.

$$\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p\mathbf{h}_i}e^{-2\pi i\mathbf{h}_i\mathbf{t}_p}\rangle=\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\rangle=F_{\mathbf{h}_i},\ p=0,1,\ldots,m-1 . \tag{13}$$

(IV) If $\boldsymbol{S}_q=\boldsymbol{S}_p\boldsymbol{S}_r$, using (11) and (13), the scalar product of two base vectors

$$\boldsymbol{C}^{\boldsymbol{R}_p\mathbf{h}_i}e^{2\pi i\mathbf{h}_i\mathbf{t}_p}\ \text{and}\ \boldsymbol{C}^{\boldsymbol{R}_q\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_q}$$

is given by

$$\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p\mathbf{h}_i-\boldsymbol{R}_q\mathbf{h}_j}e^{-2\pi i(\mathbf{h}_i\mathbf{t}_p-\mathbf{h}_j\mathbf{t}_q)}\rangle$$
$$=\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p(\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j)}e^{-2\pi i(\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j)\mathbf{t}_p}e^{2\pi i\mathbf{h}_j\mathbf{t}_r}\rangle$$
$$=\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_r}\rangle=F_{\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_r}. \tag{14}$$

Hence, for given p and q, we obtain

$$\langle\tilde{\boldsymbol{C}}^{\boldsymbol{R}_p\mathbf{h}_i}e^{-2\pi i\mathbf{h}_i\mathbf{t}_p}\boldsymbol{C}^{\boldsymbol{R}_q\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_q}\rangle$$
$$=\sum_{r=0}^{m-1}\delta_{\boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1},1}\langle\tilde{\boldsymbol{C}}^{\mathbf{h}_i}\boldsymbol{C}^{\boldsymbol{R}_r\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_r}\rangle$$
$$=\sum_{r=0}^{m-1}\delta_{\boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1},1}F_{\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_r}, \tag{15}$$

where

$$\delta_{\boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1},1}=\begin{cases}1, & \boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1}=1 ,\\ 0, & \boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1}\neq 1 .\end{cases} \tag{16}$$

2·5. *Regular representation of a point group and its reduction*

Let $\boldsymbol{P}(\boldsymbol{R}_r)$ be a regular representation for an element $\boldsymbol{R}_r$ of a point group. Then the $\boldsymbol{R}_p\boldsymbol{R}_q$ element of the matrix $\boldsymbol{P}(\boldsymbol{R}_r)$ is given by

$$\boldsymbol{P}_{\boldsymbol{R}_p\boldsymbol{R}_q}(\boldsymbol{R}_r)=\delta_{\boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1},1} . \tag{17}$$

$\boldsymbol{P}(\boldsymbol{R}_r)$ can be transformed to an irreducible form by a unitary matrix $\boldsymbol{O}$. Namely

$$\boldsymbol{O}\boldsymbol{P}(\boldsymbol{R}_r)\boldsymbol{O}^{-1}=\sum_{\mu=1}^{l}{}^{+}n_\mu\boldsymbol{P}_\mu(\boldsymbol{R}_r) , \tag{18}$$

with a relation

$$\sum_{\mu=1}^{l}n_\mu^2=m , \tag{19}$$

where $\sum^+$ means the direct sum of the matrices, $\boldsymbol{P}_\mu(\boldsymbol{R}_r)$ being the μth irreducible representation obtained from the reduction of the regular representation $\boldsymbol{P}(\boldsymbol{R}_r)$, n_μ its dimensions and l the number of classes.

3. Derivation of a general type of inequalities

3·1. *Unitary space U and inequalities*

Inequalities can be taken as the expressions to represent the geometrical natures of a unitary space U introduced in 2·3. The most characteristic expression for the geometrical nature is a bilinear form which represents that the square of length of any vector in space U must be always non-negative. This statement expresses the characters of the unitary space, as a necessary and sufficient condition. However, we shall note here that this statement comes from the character of U itself which does not depend on the ways of choice of the base vectors.

Let us consider n base vectors $\boldsymbol{C}^{\mathbf{h}_i}(i=1,2,3,\ldots,n)$. Any n-dimensional vector $\boldsymbol{Q}$ which has components $x^{\mathbf{h}_i}$ with respect to these base vectors $\boldsymbol{C}^{\mathbf{h}_i}$ is expressed by†

† The base vectors considered by von Eller are normalized, which correspond exactly to $\boldsymbol{C}^{\mathbf{h}_i}/\sqrt{\langle 1\rangle}=\boldsymbol{C}^{\mathbf{h}_i}/F_0^{\frac{1}{2}}$.

† Note that $x^{\mathbf{h}_i}$ is a contravariant component where $\mathbf{h}_i$ means a suffix.

$$Q = \sum_{i=1}^{n} C^{\mathbf{h}_i} x^{\mathbf{h}_i}. \quad (20)$$

The square of length of the vector Q must be non-negative; that is,

$$\langle |Q|^2 \rangle = \left\langle \left| \sum_{i=1}^{n} C^{\mathbf{h}_i} x^{\mathbf{h}_i} \right|^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \tilde{C}^{\mathbf{h}_i} C^{\mathbf{h}_j} \rangle x^{\mathbf{h}_i *} x^{\mathbf{h}_j}$$
$$= \sum_{i=1}^{n} \sum_{j=1}^{n} F_{\mathbf{h}_i - \mathbf{h}_j} x^{\mathbf{h}_i *} x^{\mathbf{h}_j} \geq 0 \,. \quad (21)$$

(21) is Karle & Hauptman's bilinear form. Let us consider n base vectors $e_{\mathbf{r}_i}$ $(i = 1, 2, \ldots, n)$ defined by

$$e_{\mathbf{r}_i} = \frac{1}{\sqrt{N^3}} \sum_{\mathbf{h}_k=0}^{N=1} C^{\mathbf{h}_k} e^{-2\pi i \mathbf{h}_k \mathbf{r}_i / N}, \quad i = 1, 2, \ldots, n \,. \quad (22)$$

Any n-dimensional vector Q which has components $x^{\mathbf{r}_i}$ with respect to these new base vectors $e_{\mathbf{r}_i}$ is expressed by

$$Q = \sum_{i=1}^{n} e_{\mathbf{r}_i} x^{\mathbf{r}_i} \,. \quad (23)$$

Similarly, the square of length of the vector Q must be non-negative.

$$\langle |Q|^2 \rangle = \left\langle \left| \sum_{i=1}^{n} e_{\mathbf{r}_i} x^{\mathbf{r}_i} \right|^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \tilde{e}_{\mathbf{r}_i} e_{\mathbf{r}_j} \rangle x^{\mathbf{r}_i *} x^{\mathbf{r}_j}$$
$$= \sum_{i=1}^{n} \varrho_{\mathbf{r}_i} |x^{\mathbf{r}_i}|^2 \geq 0 \,, \dagger \quad (24)$$

where

$$\varrho_{\mathbf{r}_i} = \sum_{\mathbf{h}_k=0}^{N-1} F_{\mathbf{h}_k} e^{2\pi i \mathbf{h}_k \mathbf{r}_i / N}, \quad i = 1, 2, \ldots, n \,. \quad (25)$$

(24) represents directly that the electron densities are non-negative.

Now, let T_i $(i = 1, 2, \ldots, n)$ be a set of linearly independent n base vectors which are selected arbitrarily in unitary space U. T_i has the following form.

$$T_i = \sum_{k=0}^{s-1} \gamma_i^k C^{\mathbf{h}_k}, \quad i = 1, 2, \ldots, n \,, \quad (26)$$

where γ_i^k is an arbitrary constant and s an integer $(s \geq n)$. Similarly to (20), any vector Q is expressed by

$$Q = \sum_{i=1}^{n} T_i x^i. \quad (27)$$

Consequently, we have

$$\langle |Q|^2 \rangle = \left\langle \left| \sum_{i=1}^{n} T_i x^i \right|^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \tilde{T}_i T_j \rangle x^{i*} x^j \geq 0 \,. \quad (28)$$

From the principal determinants of (28), we can obtain the inequalities of the following type.

$$\begin{vmatrix} T_{11} & T_{12} & \ldots & T_{1n'} \\ T_{21} & T_{22} & \ldots & T_{2n'} \\ \cdot & \cdot & \ldots & \cdot \\ T_{n'1} & T_{n'2} & \ldots & T_{n'n'} \end{vmatrix} \geq 0, \quad n' = 1, 2, \ldots, n, \quad (29)$$

† See Appendix I.

where

$$T_{ij} \equiv \langle \tilde{T}_i T_j \rangle \,. \quad (30)$$

The consequences (21), (24), (28) and (29) are the equivalent statements to each other representing the characters of the unitary space.

Let $\{T_{ij}\}$ and $\{F_{\mathbf{h}_k - \mathbf{h}_l}\}$ be the matrices belonging to the same subspace. Then the matrix $\{T_{ij}\}$ can be obtained by a unitary transformation from Karle & Hauptman's matrix $\{F_{\mathbf{h}_k - \mathbf{h}_l}\}$, if $\{\gamma_i^k\}$ is unitary. But $\{\gamma_i^k\}$ is not always necessary to be unitary. Moreover, $\{T_{ij}\}$ and $\{F_{\mathbf{h}_k - \mathbf{h}_l}\}$ need not belong to the same subspace. Accordingly, in some cases, it will not be easy to find $\{T_{ij}\}$ by a simple transformation from Karle & Hauptman's matrix.†

We can also express some of the characters of space U by utilizing other methods of geometrical considerations. In fact, some of these have been considered by von Eller (1955, 1960). (See Appendix II for a few of these examples.) In such a case, one might arrive at inequalities somewhat different in appearance. This comes from nothing but the necessary consequences which arise from the characters of the unitary space.

(29) represents a general type of inequalities for the case of P_1.

3·2. *General type of inequalities*

Introduction of symmetry. Let $(T_1^p, \ldots, T_i^p, \ldots, T_n^p)$ be a new set of the n base vectors which are derived by a symmetry operation $S_p = (R_p | \mathbf{t}_p)$ from a set of n base vectors $(T_1, \ldots, T_i, \ldots, T_n)$. The base vectors T_i^p here have the following form.

$$T_i^p = \sum_{k=0}^{s-1} \gamma_i^k C^{R_p \mathbf{h}_k} e^{2\pi i \mathbf{h}_k \mathbf{t}_p}, \quad T_i^0 \equiv T_i,$$
$$i = 1, 2, \ldots, n,$$
$$p = 0, 1, \ldots, m-1 \,. \quad (31)$$

Any vector Q corresponding to (27) is now given by

$$Q = \sum_{i=1}^{n} \sum_{p=0}^{m-1} T_i^p x_p^i. \quad (32)$$

The square of length of the vector (32) must be non-negative; that is,

$$\langle |Q|^2 \rangle = \left\langle \left| \sum_{i=1}^{n} \sum_{p=0}^{m-1} T_i^p x_p^i \right|^2 \right\rangle$$
$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{p=0}^{m-1} \sum_{q=0}^{m-1} \langle \tilde{T}_i^p T_j^q \rangle x_p^{i*} x_q^j \geq 0 \,, \quad (33)$$

which is a bilinear form corresponding to (28).

Reduction. Using (15), (17) and (31), we can transform $\langle \tilde{T}_i^p T_j^q \rangle$ to

† We shall note, however, that T_{ij} relates to $F_{\mathbf{h}_k - \mathbf{h}_l}$ in the following way.

$$T_{ij} = \sum_{k=0}^{s-1} \sum_{l=0}^{s-1} \gamma_i^{k*} \gamma_j^l F_{\mathbf{h}_k - \mathbf{h}_l}, \quad i, j = 1, 2, \ldots, n \,.$$

$$\langle \tilde{T}_i^p T_j^q \rangle = \sum_{k=0}^{s-1} \sum_{l=0}^{s-1} \gamma_i^{k*} \gamma_j^l \langle \tilde{C}^{R_p h_k} e^{-2\pi i h_k t_p} C^{R_q h_l} e^{2\pi i h_l t_q} \rangle$$
$$= \sum_{r=0}^{m-1} \delta_{R_p R_r R_q^{-1}, 1} \sum_{k=0}^{s-1} \sum_{l=0}^{s-1} \gamma_i^{k*} \gamma_j^l \langle \tilde{C}^{h_k} C^{R_r h_l} e^{2\pi i h_l t_r} \rangle$$
$$= \sum_{r=0}^{m-1} P_{R_p R_q}(R_r) \langle \tilde{T}_i T_j^r \rangle . \quad (34)$$

Therefore, (33) can be expressed as follows.

$$\langle |Q|^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{p=0}^{m-1} \sum_{q=0}^{m-1} \sum_{r=0}^{m-1} P_{R_p R_q}(R_r) \times \langle \tilde{T}_i T_j^r \rangle x_p^{i*} x_q^j \geq 0 . \quad (35)$$

Using the m-dimensional column vectors

$$\mathbf{x}^i = \begin{bmatrix} x_0^i \\ \vdots \\ x_p^i \\ \vdots \\ x_{m-1}^i \end{bmatrix}, \quad i=1, 2, \ldots, n , \quad (36)$$

and introducing

$$\mathbf{X}^i = O \mathbf{x}^i, \quad i=1, 2, \ldots, n , \quad (37)$$

by unitary matrix O given by (18), we can transform (35) to

$$\sum_{i=1}^{n} \sum_{j=1}^{n} (\tilde{\mathbf{x}}^i \cdot \sum_{r=0}^{m-1} P(R_r) \langle \tilde{T}_i T_j^r \rangle \cdot \mathbf{x}^j)$$
$$= \sum_{i=1}^{n} \sum_{j=1}^{n} (\tilde{\mathbf{X}}^i \cdot \sum_{\mu=1}^{l}{}^{+} n_\mu \left\{ \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_i T_j^r \rangle \right\} \cdot \mathbf{X}^j) \geq 0 . \quad (38)$$

The second one of (38) indicates a bilinear form reduced into the direct sum of different irreducible representations with respect to $P(R_r)$ (see Appendix III for a set of the base vectors by which the bilinear form becomes (38) directly in contrast to (33)).

Inequalities. Putting

$$T_{ij}^{(\mu)} \equiv \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_i T_j^r \rangle, \quad \mu=1, 2, \ldots, l , \quad (39)$$

it follows from (38) that the hypermatrices having ij elements given by (39) must be non-negative. Hence we obtain

$$\text{princ. subdet.} \begin{bmatrix} T_{11}^{(\mu)} & T_{12}^{(\mu)} & \ldots & T_{1n}^{(\mu)} \\ T_{21}^{(\mu)} & T_{22}^{(\mu)} & \ldots & T_{2n}^{(\mu)} \\ \cdot & \cdot & \ldots & \cdot \\ T_{n1}^{(\mu)} & T_{n2}^{(\mu)} & \ldots & T_{nn}^{(\mu)} \end{bmatrix} \geq 0, \mu=1, 2, \ldots, l, \quad (40)$$

which is a general type of inequalities applicable to any given space group. It should be noted that inequalities (40) characterized by terms of irreducible representations of a point group was derived as a necessary consequence of (33), which is a natural extention of (28) to any space group.

3·3. *Some comments*

Let us give here some comments which will be used later in the application of (39) and (40).

Elements $T_{ij}^{(\mu)}$. When a given point group is a commutative group, all of the irreducible representations are one-dimensional. But, when a given point group is not commutative, some of the irreducible representations are not one-dimensional. In such cases, the corresponding $T_{ij}^{(\mu)}$ becomes a matrix. In the case of P_1, of course, we have

$$T_{ij}^{(1)} = T_{ij} = \langle \tilde{T}_i T_j \rangle, \; T_i \equiv T_i^0 = \sum_{k=0}^{s-1} \gamma_i^k C^{h_k}. \quad (41)$$

In the case of $P_{\bar{1}}$ which has one-dimensional irreducible representations:

$$P_1(R_0)=1, \; P_1(R_1)=1, \quad \text{for totally symmetric representation,}$$
$$P_2(R_0)=1, \; P_2(R_1)=-1, \quad \text{for anti-symmetric representation,} \quad (42)$$

where $R_0=1$ and $R_1=I$ (the operation of inversion), we have

$$T_{ij}^{(1)} = \sum_{r=0}^{1} P_1(R_r) \langle \tilde{T}_i T_j^r \rangle = \langle \tilde{T}_i T_j \rangle + \langle \tilde{T}_i T_j^1 \rangle \equiv T_{ij}^{(+)}, \quad (43)$$

$$T_{ij}^{(2)} = \sum_{r=0}^{1} P_2(R_r) \langle \tilde{T}_i T_j^r \rangle = \langle \tilde{T}_i T_j \rangle - \langle \tilde{T}_i T_j^1 \rangle \equiv T_{ij}^{(-)}, \quad (44)$$

or, in a compact form,

$$T_{ij}^{(\pm)} = \langle \tilde{T}_i T_j \rangle \pm \langle \tilde{T}_i T_j^1 \rangle , \quad (45)$$

where

$$T_i = \sum_{k=0}^{s-1} \gamma_i^k C^{h_k}, \; T_j^1 = \sum_{l=0}^{s-1} \gamma_j^l C^{R_1 h_l} = \sum_{l=0}^{s-1} \gamma_j^l C^{-h_l}. \quad (46)$$

We shall show few other examples of $T_{ij}^{(\mu)}$ in Appendix IV.

Inequalities of lower degree. Let

$$P_\mu(R_r), \; \mu=1, 2, \ldots, t, \; (t \leq l)$$

be one-dimensional irreducible representations. Since $T_{ij}^{(\mu)} (\mu=1, 2, \ldots, t)$ is one-dimensional, we can easily obtain the following inequalities from the determinants of the first and second degrees of (40).

$$T_{11}^{(\mu)} \geq 0, \text{ or } \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_1 T_1^r \rangle \geq 0, \; \mu = 1, 2, \ldots, t , \quad (47)$$

and

$$\begin{vmatrix} T_{11}^{(\mu)} & T_{12}^{(\mu)} \\ T_{21}^{(\mu)} & T_{22}^{(\mu)} \end{vmatrix} = T_{11}^{(\mu)} T_{22}^{(\mu)} - |T_{12}^{(\mu)}|^2 \geq 0 , \quad (48)$$

or

$$\left\{ \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_1 T_1^r \rangle \right\} \left\{ \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_2 T^r \rangle \right\} \geq \left| \sum_{r=0}^{m-1} P_\mu(R_r) \langle \tilde{T}_1 T_2^r \rangle \right|^2 , \quad \mu=1, 2, \ldots, t . \quad (49)$$

In the case of $T_2 = 1$ in (49), the inequalities except the one for the case of totally symmetric representation are trivial equations.† Therefore (49) becomes as

$$\frac{1}{m}\langle 1\rangle\left\{\sum_{r=0}^{m-1}\langle\tilde{T}_1 T_1^r\rangle\right\} \geq |\langle T_1\rangle|^2. \tag{50}$$

Similarly, in the case of $T_3=1$, the inequality obtained from the determinants of the third degree of (40) becomes as

$$\left[\langle 1\rangle\left\{\sum_{r=0}^{m-1}\langle\tilde{T}_1 T_1^r\rangle\right\} - m|\langle T_1\rangle|^2\right] \times \left[\langle 1\rangle\left\{\sum_{r=0}^{m-1}\langle\tilde{T}_2 T_2^r\rangle\right\} - m|\langle T_2\rangle|^2\right] \geq \left|\langle 1\rangle\left\{\sum_{r=0}^{m-1}\langle\tilde{T}_1 T_2^r\rangle\right\} - m\langle\tilde{T}_1\rangle\langle T_2\rangle\right|^2. \tag{51}$$

Let us consider the case where $P_\mu(R_r)$ is not necessarily one-dimensional. Even in this case, we can derive a similar expression to (47) from the trace of a non-negative matrix $T_{11}^{(\mu)}$ as follows.

$$\text{tr. } T_{11}^{(\mu)} = \sum_{r=0}^{m-1}\chi_\mu(R_r)\langle\tilde{T}_1 T_1^r\rangle \geq 0\,, \tag{52}$$

where $\chi_\mu(R_r) \equiv \text{tr. } P_\mu(R_r)$ represents the so-called simple character. Combining (50) and (52), we obtain

$$\frac{1}{m}\langle 1\rangle\left\{\sum_{r=0}^{m-1}\chi_\mu(R_r)\langle\tilde{T}_1 T_1^r\rangle\right\} \geq |\langle T_1\rangle|^2\delta_{\mu 1}\,. \tag{53}$$

4. Inequalities given by different authors

4·1. *Inequalities of lower degree*

Okaya & Nitta. We shall use the totally symmetric representation ($\mu=1$) of the linear inequalities (47) for the case of $P\bar{1}$. In this case, from (43), we have

$$T_{11}^{(1)} = \langle\tilde{T}_1 T_1\rangle + \langle\tilde{T}_1 T_1^1\rangle \geq 0\,, \tag{54}$$

where

$$T_1 = \sum_{k=0}^{s-1}\gamma_1^k C^{\mathbf{h}_k},\ T_1^1 = \sum_{k=0}^{s-1}\gamma_1^k C^{-\mathbf{h}_k},\ (\mathbf{h}_0 \equiv 0)\,. \tag{55}$$

(*a*) Putting $\gamma_1^0=1$, $\gamma_1^1=\pm m$ and otherwise $\gamma_1^k=0$, we obtain $T_1 = 1 \pm mC^{\mathbf{h}_1}$ and $T_1^1 = 1 \pm mC^{-\mathbf{h}_1}$. Substituting these in (54), we have

$$\begin{aligned} T_{11}^{(1)} &= \langle(1\pm m\tilde{C}^{\mathbf{h}_1})(1\pm mC^{\mathbf{h}_1})\rangle + \langle(1\pm m\tilde{C}^{\mathbf{h}_1})(1\pm mC^{-\mathbf{h}_1})\rangle \\ &= \langle 1\pm m\tilde{C}^{\mathbf{h}_1}\pm mC^{\mathbf{h}_1}+m^2\tilde{C}^{\mathbf{h}_1}C^{\mathbf{h}_1}\rangle \\ &\quad + \langle 1\pm m\tilde{C}^{\mathbf{h}_1}\pm mC^{-\mathbf{h}_1}+m^2\tilde{C}^{\mathbf{h}_1}C^{-\mathbf{h}_1}\rangle \\ &= (2+m^2)F_0+m^2F_{2\mathbf{h}_1}\pm 4mF_{\mathbf{h}_1} \geq 0\,, \end{aligned} \tag{56}$$

or

$$(2+m^2)F_0+m^2F_{2\mathbf{h}_1} \geq 4m|F_{\mathbf{h}_1}|\,. \tag{57}$$

(*b*) Putting $\gamma_1^1=1$, $\gamma_1^2=\pm m$ and otherwise $\gamma_1^k=0$, we obtain from (54) and (55) that

$$(1+m^2)F_0+F_{2\mathbf{h}_1}+m^2F_{2\mathbf{h}_2}\pm 2m(F_{\mathbf{h}_1+\mathbf{h}_2}+F_{\mathbf{h}_1-\mathbf{h}_2}) \geq 0\,, \tag{58}$$

or in a form replaced by $\mathbf{h}_1+\mathbf{h}_2=\mathbf{k}_1$ and $\mathbf{h}_1-\mathbf{h}_2=\mathbf{k}_2$,

$$(1+m^2)F_0+F_{\mathbf{k}_1+\mathbf{k}_2}+m^2F_{\mathbf{k}_1-\mathbf{k}_2} \geq 2m|F_{\mathbf{k}_1}+F_{\mathbf{k}_2}|\,. \tag{59}$$

(*c*) Putting $\gamma_1^0=r$, $\gamma_1^1=\pm p$ and $\gamma_1^2=\pm q$ and otherwise $\gamma_1^k=0$, we obtain from (54) and (55) that

$$\begin{aligned}(2r^2+p^2+q^2)F_0+p^2F_{2\mathbf{h}_1}+q^2F_{2\mathbf{h}_2} \\ +2pq(F_{\mathbf{h}_1+\mathbf{h}_2}+F_{\mathbf{h}_1-\mathbf{h}_2}) \geq 4r|pF_{\mathbf{h}_1}+qF_{\mathbf{h}_2}|\,.\end{aligned} \tag{60}$$

Harker & Kasper. We shall use quadratic inequalities (49) and (50) for the case of $P\bar{1}$. $T_{ij}^{(\mu)}$ is given by (43) and (44), or by (45).

(*a*) Putting $\gamma_1^1=1$ and otherwise $\gamma_1^k=0$, and substituting $T_{11}^{(1)}$ given by (43) in (50), we have

$$F_0(F_0+F_{2\mathbf{h}_1}) \geq 2F_{\mathbf{h}_1}^2\,. \tag{61}$$

(*b*) Putting $\gamma_1^1=1$, $\gamma_1^2=\pm 1$ and otherwise $\gamma_1^k=0$, and substituting $T_{11}^{(1)}$ given by (43) in (50), we can obtain

$$F_0(F_0+\tfrac{1}{2}F_{2\mathbf{h}_1}+\tfrac{1}{2}F_{2\mathbf{h}_2}\pm F_{\mathbf{h}_1-\mathbf{h}_2}\pm F_{\mathbf{h}_1+\mathbf{h}_2}) \geq (F_{\mathbf{h}_1}\pm F_{\mathbf{h}_2})^2. \tag{62}$$

(*c*) Putting $\gamma_1^1=1$, $\gamma_2^2=1$ and otherwise $\gamma_1^k=\gamma_2^k=0$, and substituting $T_{ij}^{(\pm)}(i,j=1,2)$ given by (45) in (49), we have

$$(F_0\pm F_{\mathbf{k}_1+\mathbf{k}_2})(F_0\pm F_{\mathbf{k}_1-\mathbf{k}_2}) \geq (F_{\mathbf{k}_1}\pm F_{\mathbf{k}_2})^2, \tag{63}$$

in a form replaced by $\mathbf{h}_1+\mathbf{h}_2=\mathbf{k}_1$ and $\mathbf{h}_1-\mathbf{h}_2=\mathbf{k}_2$.

Gillis. At first sight, the inequalities found by Gillis do not seem to be derived easily from (40). However, we shall show some examples of deriving these from the present theory. Here we shall use quadratic inequalities (49) and (50) for the case of $P\bar{1}$.

(*a*) Putting $\gamma_1^0=1$, $\gamma_1^2=1$ and otherwise $\gamma_1^k=0$, and substituting $T_{11}^{(1)}$ given by (43) in (50), we have

$$\tfrac{1}{2}F_0(3F_0+4F_{\mathbf{h}_2}+F_{2\mathbf{h}_2}) \geq (F_0+F_{\mathbf{h}_2})^2. \tag{64}$$

Putting $\mathbf{h}_2=2\mathbf{h}_1$ and comparing (64) with (61), we have

$$F_0^3(3F_0+4F_{2\mathbf{h}_1}+F_{4\mathbf{h}_1}) \geq 8F_{\mathbf{h}_1}^4\,. \tag{65}$$

(*b*) Putting $\gamma_1^0=1$, $\gamma_1^1=\pm 1$, $\gamma_2^0=1$, $\gamma_2^2=\pm 1$ and otherwise $\gamma_1^k=\gamma_2^k=0$, and substituting $T_{ij}^{(1)}(i,j=1,2)$ given by (43) in the totally symmetric representation of (49), we have

$$\begin{aligned}(3F_0\pm 4F_{\mathbf{h}_1}+F_{2\mathbf{h}_1})(3F_0\pm 4F_{\mathbf{h}_2}+F_{2\mathbf{h}_2}) \\ \geq 4(F_0+\tfrac{1}{2}F_{\mathbf{h}_1-\mathbf{h}_2}+\tfrac{1}{2}F_{\mathbf{h}_1+\mathbf{h}_2}\pm F_{\mathbf{h}_1}\pm F_{\mathbf{h}_2})^2.\end{aligned} \tag{66}$$

Putting $\mathbf{h}_1=\mathbf{k}_1+\mathbf{k}_2$ and $\mathbf{h}_2=\mathbf{k}_1-\mathbf{k}_2$, and comparing (66) with (62), we can obtain

† In the case of $T_2=1$, all terms of $T_2{}^r$ for different r ($r=0, 1, \ldots, m-1$) equal with each other, and are not linearly independent. Hence, with relation

$$\sum_{r=0}^{m-1}P_\mu(R_r) = m\delta_{\mu 1}\,,$$

(49) becomes trivial except $\mu=1$.

$$F_0^3(3F_0 \pm 4F_{\mathbf{k}_1+\mathbf{k}_2}+F_{2\mathbf{k}_1+2\mathbf{k}_2})(3F_0 \pm 4F_{\mathbf{k}_1-\mathbf{k}_2}+F_{2\mathbf{k}_1-2\mathbf{k}_2}) \geq 4(F_{\mathbf{k}_1} \pm F_{\mathbf{k}_2})^4. \quad (67)$$

We shall derive inequalities for structure factors based on $P1$ using (49), however putting $F_{\mathbf{h}}=F_{-\mathbf{h}}$. In this case, $\boldsymbol{T}_{ij}^{(1)}$ $(i, j=1, 2)$ is given by (41).

(*c*) Putting $\gamma_1^1=1$, $\gamma_1^2=1$, $\gamma_2^0=1$, $\gamma_2^3=1$ and otherwise $\gamma_1^k=\gamma_2^k=0$, and substituting $\boldsymbol{T}_{ij}^{(1)}$ in (49), we have

$$4(F_0+F_{\mathbf{h}_1-\mathbf{h}_2})(F_0+F_{\mathbf{h}_3}) \geq (F_{\mathbf{h}_1}+F_{\mathbf{h}_2}+F_{\mathbf{h}_1-\mathbf{h}_3}+F_{\mathbf{h}_2-\mathbf{h}_3})^2. \quad (68)$$

In the special case of $\mathbf{h}_2=-\mathbf{h}_1$ and $\mathbf{h}_3=2\mathbf{h}_1$, (68) becomes as

$$4(F_0+F_{2\mathbf{h}_1})^2 \geq (3F_{\mathbf{h}_1}+F_{3\mathbf{h}_1})^2, \quad (69)$$

or

$$2(F_0+F_{2\mathbf{h}_1}) \geq |3F_{\mathbf{h}_1}+F_{3\mathbf{h}_1}|\,. \quad (70)$$

Karle & Hauptman. Let us use inequality (51) for the case of $P1$. $\boldsymbol{T}_{ij}^{(1)}$ is given by (41). Putting $\gamma_1^1=1$ $\gamma_2^2=1$ and otherwise $\gamma_1^k=\gamma_2^k=0$, and substituting $\boldsymbol{T}_{ij}^{(1)}$ in (51), we have

$$\{F_0^2-|F_{\mathbf{h}_1}|^2\}\{F_0^2-|F_{\mathbf{h}_2}|^2\} \geq |F_0F_{\mathbf{h}_1-\mathbf{h}_2}-F_{\mathbf{h}_1}F_{-\mathbf{h}_2}|^2. \quad (71)$$

de Wolff & Bouman. Let us use (51) for the case of $P\bar{1}$. $\boldsymbol{T}_{ij}^{(1)}$ is given by (43). Putting $\gamma_1^1=1$, $\gamma_2^2=1$ and otherwise $\gamma_1^k=\gamma_2^k=0$, and substituting $\boldsymbol{T}_{ij}^{(1)}$ in (51), we have

$$\{F_0(F_0+F_{2\mathbf{h}_1})-2F_{\mathbf{h}_1}^2\}\{F_0(F_0+F_{2\mathbf{h}_2})-2F_{\mathbf{h}_2}^2\} \geq \{F_0(F_{\mathbf{h}_1-\mathbf{h}_2}+F_{\mathbf{h}_1+\mathbf{h}_2})-2F_{\mathbf{h}_1}F_{\mathbf{h}_2}\}^2. \quad (72)$$

MacGillavry. We shall use inequality (50) for the case of any given space group. In this case,

$$\boldsymbol{T}_{11}^{(1)}=\sum_{r=0}^{m-1}\langle \boldsymbol{T}_1\boldsymbol{T}_1^r\rangle,\ \boldsymbol{T}_1=\sum_{k=0}^{s-1}\gamma_1^k\boldsymbol{C}^{\mathbf{h}_k},$$
$$\boldsymbol{T}_1^r=\sum_{k=0}^{s-1}\gamma_1^k\boldsymbol{C}^{\boldsymbol{R}_r\mathbf{h}_k}e^{2\pi i\mathbf{h}_k\mathbf{t}_r}. \quad (73)$$

(*a*) Putting $\gamma_1^1=1$ and otherwise $\gamma_1^k=0$, and substituting (73) in (50), we have

$$\frac{1}{m}F_0\left\{\sum_{r=0}^{m-1}F_{(1-\boldsymbol{R}_r)\mathbf{h}_1}e^{2\pi i\mathbf{h}_1\mathbf{t}_r}\right\} \geq |F_{\mathbf{h}_1}|^2. \quad (74)$$

(*b*) Putting $\gamma_1^1=1$, $\gamma_1^2=\pm1$ and otherwise $\gamma_1^k=0$, and substituting (73) in (50), we have

$$\frac{1}{m}F_0\sum_{r=0}^{m-1}\{F_{(1-\boldsymbol{R}_r)\mathbf{h}_1}e^{2\pi i\mathbf{h}_1\mathbf{t}_r}+F_{(1-\boldsymbol{R}_r)\mathbf{h}_2}e^{2\pi i\mathbf{h}_2\mathbf{t}_r} \pm 2Re(F_{\mathbf{h}_1-\boldsymbol{R}_r\mathbf{h}_2}e^{2\pi i\mathbf{h}_2\mathbf{t}_r})\} \geq |F_{\mathbf{h}_1} \pm F_{\mathbf{h}_2}|^2. \quad (75)$$

Goedkoop (1950). We shall use inequality (53) for the case of any given space group. Putting $\gamma_1^1=1$ and otherwise $\gamma_1^k=0$, we can obtain from (53)

$$\frac{1}{m}F_0\left\{\sum_{r=0}^{m-1}\chi_\mu(\boldsymbol{R}_r)F_{(1-\boldsymbol{R}_r)\mathbf{h}_1}e^{2\pi i\mathbf{h}_1\mathbf{t}_r}\right\} \geq |F_{\mathbf{h}_1}|^2\delta_{\mu1}\,. \quad (76)$$

Löfgren. We shall use inequality (50) for the case of any given space group.

Putting $\gamma_1^k=\gamma(\mathbf{h}_k)$, $k=0, 1, 2, \ldots, s-1$, and substituting (73) in (50), we have

$$\frac{1}{m}F_0\sum_{r=0}^{m-1}\left\{\sum_{k=0}^{s-1}|\gamma(\mathbf{h}_k)|^2F_{(1-\boldsymbol{R}_r)\mathbf{h}_k}e^{2\pi i\mathbf{h}_k\mathbf{t}_r} + 2Re\left(\sum_{k>l=0}^{s-1}\sum\gamma^*(\mathbf{h}_k)\gamma(\mathbf{h}_l)F_{\mathbf{h}_k-\boldsymbol{R}_r\mathbf{h}_l}e^{2\pi i\mathbf{h}_l\mathbf{t}_r}\right)\right\} \geq \left|\sum_{k=0}^{s-1}\gamma^*(\mathbf{h}_k)F_{\mathbf{h}_k}\right|^2. \quad (77)$$

4·2. *Inequalities of general form*

Karle & Hauptman. We shall use inequalities (40) for the case of $P1$; i.e. inequalities (29). Putting $\gamma_i^k=\delta_i^k$ and substituting $\boldsymbol{T}_{ij}^{(1)}$ given by (41) in (29), we obtain

$$\begin{vmatrix} F_{\mathbf{h}_1-\mathbf{h}_1} & F_{\mathbf{h}_1-\mathbf{h}_2} & \cdots & F_{\mathbf{h}_1-\mathbf{h}_{n'}} \\ F_{\mathbf{h}_2-\mathbf{h}_1} & F_{\mathbf{h}_2-\mathbf{h}_2} & \cdots & F_{\mathbf{h}_2-\mathbf{h}_{n'}} \\ \cdot & \cdot & \cdots & \cdot \\ F_{\mathbf{h}_{n'}-\mathbf{h}_1} & F_{\mathbf{h}_{n'}-\mathbf{h}_2} & \cdots & F_{\mathbf{h}_{n'}-\mathbf{h}_{n'}} \end{vmatrix} \geq 0\,,\quad n'=1, 2, \ldots . \quad (78)$$

Bouman. We shall use inequalities (40) for the case of $P\bar{1}$. Putting $\gamma_i^k=\delta_i^k$ and substituting $\boldsymbol{T}_{ij}^{(\pm)}$ (corresponding to $\mu=1, 2$) given by (45) in (40), we can obtain that

$$\begin{vmatrix} F_{\mathbf{h}_1-\mathbf{h}_1} \pm F_{\mathbf{h}_1+\mathbf{h}_1} & F_{\mathbf{h}_1-\mathbf{h}_2} \pm F_{\mathbf{h}_1+\mathbf{h}_2} & \cdots & F_{\mathbf{h}_1-\mathbf{h}_{n'}} \pm F_{\mathbf{h}_1+\mathbf{h}_{n'}} \\ F_{\mathbf{h}_2-\mathbf{h}_1} \pm F_{\mathbf{h}_2+\mathbf{h}_1} & F_{\mathbf{h}_2-\mathbf{h}_2} \pm F_{\mathbf{h}_2+\mathbf{h}_2} & \cdots & F_{\mathbf{h}_2-\mathbf{h}_{n'}} \pm F_{\mathbf{h}_2+\mathbf{h}_{n'}} \\ \cdot & \cdot & \cdots & \cdot \\ F_{\mathbf{h}_{n'}-\mathbf{h}_1} \pm F_{\mathbf{h}_{n'}+\mathbf{h}_1} & F_{\mathbf{h}_{n'}-\mathbf{h}_2} \pm F_{\mathbf{h}_{n'}+\mathbf{h}_2} & \cdots & F_{\mathbf{h}_{n'}-\mathbf{h}_{n'}} \pm F_{\mathbf{h}_{n'}+\mathbf{h}_{n'}} \end{vmatrix} \geq 0,\quad n'=1, 2, \ldots . \quad (79)$$

Goedkoop (1952). We shall use inequalities (40) for the case of any given space group.

Putting $\gamma_i^k=\delta_i^k$, we can obtain the elements $\boldsymbol{T}_{ij}^{(\mu)}$ from (39) as follows.

$$\boldsymbol{T}_{ij}^{(\mu)}=\sum_{r=0}^{m-1}\boldsymbol{P}_\mu(\boldsymbol{R}_r)F_{\mathbf{h}_i-\boldsymbol{R}_r\mathbf{h}_j}e^{2\pi i\mathbf{h}_j\mathbf{t}_r} \equiv \boldsymbol{F}_{ij}^{(\mu)},\quad \mu=1, 2, \ldots, l\,. \quad (80)$$

From (40) with (80), we have

$$\text{princ. subdet.}\begin{bmatrix} \boldsymbol{F}_{11}^{(\mu)} & \boldsymbol{F}_{12}^{(\mu)} & \cdots & \boldsymbol{F}_{1n}^{(\mu)} \\ \boldsymbol{F}_{21}^{(\mu)} & \boldsymbol{F}_{22}^{(\mu)} & \cdots & \boldsymbol{F}_{2n}^{(\mu)} \\ \cdot & \cdot & \cdots & \cdot \\ \boldsymbol{F}_{n1}^{(\mu)} & \boldsymbol{F}_{n2}^{(\mu)} & \cdots & \boldsymbol{F}_{nn}^{(\mu)} \end{bmatrix} \geq 0\,,\quad \mu=1, 2, \ldots, l\,. \quad (81)$$

which is a form in close relationship with that of Goedkoop (1952), (Oda, Naya & Taguchi, 1961).

5. Conclusion

We have derived a general type of inequalities (40). This theory shows that (40) contains not only the 'fundamental form of inequalities' (81) given in our previous paper, but also covers all the inequalities of other types so far found by different authors. One might arrive at the same results from a different approach. However, we intended to show explicitly that expression (40) can also be derived from a matrix of Karle & Hauptman's type, and that the inequality relations to be imposed among structure factors can be reduced entirely to the geometrical characters of the unitary space.

In conclusion, we shall note that various inequalities can be derived using other irreducible representations, and we hope that some useful inequalities will be derived from this theory for particular space group for practical purpose. The methods presented in this paper may also be applied to other fields of crystallography.

APPENDIX I

The scalar product between two base vectors $\boldsymbol{e}_{\mathbf{r}_i}$ and $\boldsymbol{e}_{\mathbf{r}_j}$ given by (22) becomes

$$\langle \boldsymbol{e}_{\mathbf{r}_i}\boldsymbol{e}_{\mathbf{r}_j}\rangle = \frac{1}{N^3}\sum_{\mathbf{h}_k=0}^{N-1}\sum_{\mathbf{h}_l=0}^{N-1}\langle \tilde{\boldsymbol{C}}^{\mathbf{h}_k}\boldsymbol{C}^{\mathbf{h}_l}\rangle e^{2\pi i\mathbf{h}_k\mathbf{r}_i/N}e^{-2\pi i\mathbf{h}_l\mathbf{r}_j/N}$$
$$= \frac{1}{N^3}\sum_{\mathbf{h}_k=0}^{N-1}\sum_{\mathbf{h}_l=0}^{N-1} F_{\mathbf{h}_k-\mathbf{h}_l} e^{2\pi i(\mathbf{h}_k\mathbf{r}_i-\mathbf{h}_l\mathbf{r}_j)/N}. \qquad \text{(I–1)}$$

Using the periodic condition for $F_\mathbf{h}$ (Taguchi & Naya, 1958) and remembering that

$$\varrho_{\mathbf{r}_i} = \sum_{\mathbf{h}_k=0}^{N-1} F_{\mathbf{h}_k} e^{2\pi i\mathbf{h}_k\mathbf{r}_i/N}, \qquad \text{(I–2)}$$

and

$$\frac{1}{N^3}\sum_{\mathbf{h}_k=0}^{N-1} e^{2\pi i\mathbf{h}_k(\mathbf{r}_i-\mathbf{r}_j)/N} = \delta_{\mathbf{r}_i\mathbf{r}_j}, \qquad \text{(I–3)}$$

we can easily transform (I–1) to

$$\sum_{\mathbf{h}_k=0}^{N-1} F_{\mathbf{h}_k-\mathbf{h}_l} e^{2\pi i(\mathbf{h}_k-\mathbf{h}_l)\mathbf{r}_i/N}\cdot\frac{1}{N^3}\sum_{\mathbf{h}_l=0}^{N-1} e^{2\pi i\mathbf{h}_l(\mathbf{r}_i-\mathbf{r}_j)/N}$$
$$= \sum_{\mathbf{h}_k-\mathbf{h}_l=0}^{N-1} F_{\mathbf{h}_k-\mathbf{h}_l} e^{2\pi i(\mathbf{h}_k-\mathbf{h}_l)\mathbf{r}_i/N}\delta_{\mathbf{r}_i\mathbf{r}_j} = \varrho_{\mathbf{r}_i}\delta_{\mathbf{r}_i\mathbf{r}_j}. \qquad \text{(I–4)}$$

APPENDIX II

For the sake of simplicity, we shall introduce an Euclidian space E as considered by von Eller, so that all $F_\mathbf{h}$ become real.

(I) Any normalized base vector is expressed by

$$\boldsymbol{D}_i = \frac{\boldsymbol{T}_i}{\langle \tilde{\boldsymbol{T}}_i\boldsymbol{T}_i\rangle^{\frac{1}{2}}}, \quad \langle \tilde{\boldsymbol{D}}_i\boldsymbol{D}_i\rangle = 1, \quad i=1, 2, \ldots . \qquad \text{(II–1)}$$

The scalar product of two normalized base vectors $\boldsymbol{D}_1$ and $\boldsymbol{D}_2$ gives the direction cosine between these two vectors. Obviously

$$-1 \le \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_2\rangle \le 1 . \qquad \text{(II–2)}$$

(II) Let φ_{12}, φ_{23} and φ_{31} be the angles between any two of three normalized base vectors $\boldsymbol{D}_1$, $\boldsymbol{D}_2$ and $\boldsymbol{D}_3$ respectively. Namely,

$$\varphi_{ij} = \cos^{-1}\langle \tilde{\boldsymbol{D}}_i\boldsymbol{D}_j\rangle, \quad i \neq j = 1, 2, 3 . \qquad \text{(II–3)}$$

φ_{12}, φ_{23} and φ_{31} represent also the three sides of a spherical triangle. Accordingly, it follows

$$\begin{aligned} 0 \le \varphi_{12}+\varphi_{23}+\varphi_{31} &\le 2\pi , \\ \varphi_{12} &\le \varphi_{23}+\varphi_{31} , \\ \varphi_{23} &\le \varphi_{31}+\varphi_{12} , \\ \varphi_{31} &\le \varphi_{12}+\varphi_{23} , \end{aligned} \qquad \text{(II–4)}$$

similarly to von Eller.

(III) Now let us consider the square of volume of a n-dimensional parallel-polyhedron:

$$\begin{vmatrix} 1 & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_2\rangle & \ldots & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_n\rangle \\ \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_1\rangle & 1 & \ldots & \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_n\rangle \\ \cdot & \cdot & \ldots & \cdot \\ \langle \tilde{\boldsymbol{D}}_n\boldsymbol{D}_1\rangle & \langle \tilde{\boldsymbol{D}}_n\boldsymbol{D}_2\rangle & \ldots & 1 \end{vmatrix}, \quad n=1, 2, \ldots, \qquad \text{(II–5)}$$

which is constructed by n base vectors $\boldsymbol{D}_1, \boldsymbol{D}_2, \ldots, \boldsymbol{D}_n$. By simple geometrical considerations, it follows that (II–5) is not only more than zero and less than unity for each degree n of the determinants, but also they decrease as the degree n increases. Namely,

$$1 \ge \begin{vmatrix} 1 & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_2\rangle \\ \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_1\rangle & 1 \end{vmatrix} \ge \begin{vmatrix} 1 & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_2\rangle & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_3\rangle \\ \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_1\rangle & 1 & \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_3\rangle \\ \langle \tilde{\boldsymbol{D}}_3\boldsymbol{D}_1\rangle & \langle \tilde{\boldsymbol{D}}_3\boldsymbol{D}_2\rangle & 1 \end{vmatrix} \ge \ldots$$
$$\ldots \ge \begin{vmatrix} 1 & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_2\rangle & \ldots & \langle \tilde{\boldsymbol{D}}_1\boldsymbol{D}_n\rangle \\ \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_1\rangle & 1 & \ldots & \langle \tilde{\boldsymbol{D}}_2\boldsymbol{D}_n\rangle \\ \cdot & \cdot & \ldots & \cdot \\ \langle \tilde{\boldsymbol{D}}_n\boldsymbol{D}_1\rangle & \langle \tilde{\boldsymbol{D}}_n\boldsymbol{D}_2\rangle & \ldots & 1 \end{vmatrix} \ge \ldots \ge 0 . \qquad \text{(II–6)}$$

APPENDIX III

We shall use the following base vectors which are expressed by a linear combination of $\boldsymbol{T}_i^p$.

$$\boldsymbol{T}_{i\,;\,\beta}^{(\mu)\cdot\,\alpha} = \sqrt{(n_\mu/m)}\sum_{p=0}^{m-1}[\boldsymbol{P}_\mu(\boldsymbol{R}_p)]_{\alpha\beta}\boldsymbol{T}_i^p, \quad \begin{aligned} i&=1, 2, \ldots, \\ \mu&=1, 2, \ldots, l , \end{aligned} \qquad \text{(III–1)}$$

where the coefficients $[\boldsymbol{P}_\mu(\boldsymbol{R}_p)]_{\alpha\beta}$ represent the $\alpha\beta$ element of the μth irreducible representation for the elements $\boldsymbol{R}_p$ of the point group. The scalar product of two base vectors $\boldsymbol{T}_{i\,;\,\beta}^{(\mu)\cdot\,\alpha}$ and $\boldsymbol{T}_{j\,;\,\delta}^{(\nu)\cdot\,\gamma}$ becomes to be

$$\langle \tilde{\boldsymbol{T}}_{i\,;\,\beta}^{(\mu)\cdot\,\alpha}\cdot\boldsymbol{T}_{j\,;\,\delta}^{(\nu)\cdot\,\gamma}\rangle =$$
$$\sqrt{(n_\mu n_\nu/m^2)}\sum_{p=0}^{m-1}\sum_{q=0}^{m-1}[\boldsymbol{P}_\mu(\boldsymbol{R}_p)]_{\alpha\beta}^*[\boldsymbol{P}_\nu(\boldsymbol{R}_q)]_{\gamma\delta}\langle \tilde{\boldsymbol{T}}_i^p\boldsymbol{T}_j^q\rangle . \qquad \text{(III–2)}$$

Using (34),

$$[\boldsymbol{P}_\nu(\boldsymbol{R}_q)]_{\gamma\delta}\langle \tilde{\boldsymbol{T}}_i^p \boldsymbol{T}_j^q \rangle = \sum_{r=0}^{m-1} \delta_{\boldsymbol{R}_p\boldsymbol{R}_r\boldsymbol{R}_q^{-1},1} \left(\sum_{\varepsilon=1}^{n_\nu} [\boldsymbol{P}_\nu(\boldsymbol{R}_p)]_{\gamma\varepsilon} [\boldsymbol{P}_\nu(\boldsymbol{R}_r)]_{\varepsilon\delta} \right) \langle \tilde{\boldsymbol{T}}_i \boldsymbol{T}_j^r \rangle \,, \qquad \text{(III–3)}$$

and using the orthogonality relation for the irreducible representation,

$$\sum_{p=0}^{m-1} [\boldsymbol{P}_\mu(\boldsymbol{R}_p)]^*_{\alpha\beta} [\boldsymbol{P}_\nu(\boldsymbol{R}_p)]_{\gamma\varepsilon} = (m/n_\mu)\,\delta_{\mu\nu}\delta_{\alpha\gamma}\delta_{\beta\varepsilon}\,. \qquad \text{(III–4)}$$

Substituting (III–3) and (III–4) in (III–2), we can obtain that

$$\langle \tilde{\boldsymbol{T}}_{i\ \ ,\beta}^{(\mu)\cdot\alpha} \cdot \boldsymbol{T}_{j\ \ ,\delta}^{(\nu)\cdot\gamma} \rangle = \left\{ \sum_{r=0}^{m-1} [\boldsymbol{P}_\mu(\boldsymbol{R}_r)]_{\beta\delta} \langle \tilde{\boldsymbol{T}}_i \boldsymbol{T}_j^r \rangle \right\} \delta_{\mu\nu}\delta_{\alpha\gamma}\,. \qquad \text{(III–5)}$$

Namely, for each case of given i and j, the scalar products of the base vectors shown by (III–1) just equal to the $\beta\delta$ element of (39) when $\mu=\nu$ and $\alpha=\gamma$, and equal to zero when $\mu\neq\nu$ or $\alpha\neq\gamma$ (i.e. the base vectors are orthogonal with each other). In order to derive his inequalities, Goedkoop (1950) used a relation similar to this for the case of $i=j$ of (III–2). But, at first sight, the necessity of the introduction of the base vectors (III–1) characterized by terms of the irreducible representation of the point group seems to be less obvious than those shown in 3·2.

APPENDIX IV

Example 1. $P2_1/c$

The factor group is expressed by

$$S_0=(\boldsymbol{R}_0|\mathrm{t}_0),\ S_1=(\boldsymbol{R}_1|\mathrm{t}_1),\ S_2=(\boldsymbol{R}_2|\mathrm{t}_2),\ S_3=(\boldsymbol{R}_3|\mathrm{t}_3)\,, \qquad \text{(IV–1)}$$

where

$$\boldsymbol{R}_0=1,\ \boldsymbol{R}_1=\boldsymbol{I},\ \boldsymbol{R}_2=\boldsymbol{U},\ \boldsymbol{R}_3=\boldsymbol{IU}\,, \qquad \text{(IV–2)}$$

and

$$\mathrm{t}_0=\mathrm{t}_1=0,\ \mathrm{t}_2=\mathrm{t}_3=\begin{Bmatrix}0\\ \frac{1}{2}\\ \frac{1}{2}\end{Bmatrix}. \qquad \text{(IV–3)}$$

$\boldsymbol{I}$ represents the operation of inversion with respect to the origin and $\boldsymbol{U}$ the operation of two-fold rotation with respect to the b-axis. The point group:

$$(\boldsymbol{R}_0, \boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3)=(1, \boldsymbol{I}, \boldsymbol{U}, \boldsymbol{IU}) \qquad \text{(IV–4)}$$

is a commutative group of the order four and its irreducible representations which are one-dimensional are given by

$$\begin{aligned}
&\boldsymbol{P}_1(\boldsymbol{R}_0)=\boldsymbol{P}_1(\boldsymbol{R}_1)=\boldsymbol{P}_1(\boldsymbol{R}_2)=\boldsymbol{P}_1(\boldsymbol{R}_3)=1\,,\\
&\boldsymbol{P}_2(\boldsymbol{R}_0)=\boldsymbol{P}_2(\boldsymbol{R}_1)=1,\ \boldsymbol{P}_2(\boldsymbol{R}_2)=\boldsymbol{P}_2(\boldsymbol{R}_3)=-1\,,\\
&\boldsymbol{P}_3(\boldsymbol{R}_0)=\boldsymbol{P}_3(\boldsymbol{R}_2)=1,\ \boldsymbol{P}_3(\boldsymbol{R}_3)=\boldsymbol{P}_3(\boldsymbol{R}_1)=-1\,,\\
&\boldsymbol{P}_4(\boldsymbol{R}_0)=\boldsymbol{P}_4(\boldsymbol{R}_3)=1,\ \boldsymbol{P}_4(\boldsymbol{R}_1)=\boldsymbol{P}_4(\boldsymbol{R}_2)=-1\,. \qquad \text{(IV–5)}
\end{aligned}$$

Using (IV–2), (IV–3) and (IV–5), we can easily obtain $\boldsymbol{T}_{ij}^{(\mu)}$ ($\mu=1, 2, 3, 4$) from (39).

Example 2. $P42$

The point group is expressed by

$$(\boldsymbol{R}_0, \boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, \boldsymbol{R}_4, \boldsymbol{R}_5, \boldsymbol{R}_6, \boldsymbol{R}_7) \equiv (1, \boldsymbol{U}_4, \boldsymbol{U}_4^2, \boldsymbol{U}_4^3, \boldsymbol{U}_2, \boldsymbol{U}_2\boldsymbol{U}_4, \boldsymbol{U}_2\boldsymbol{U}_4^2, \boldsymbol{U}_2\boldsymbol{U}_4^3)\,, \qquad \text{(IV–6)}$$

where $\boldsymbol{U}_4$ represents the four-fold rotation with respect to the c-axis and $\boldsymbol{U}_2$ the two-fold rotation with respect to the b-axis. The non-commutative group (IV–6) of order eight has the following five classes.

$$(1),\ (\boldsymbol{U}_4^2),\ (\boldsymbol{U}_4, \boldsymbol{U}_4^3),\ (\boldsymbol{U}_2, \boldsymbol{U}_2\boldsymbol{U}_4^2),\ (\boldsymbol{U}_2\boldsymbol{U}_4, \boldsymbol{U}_2\boldsymbol{U}_4^3)\,. \qquad \text{(IV–7)}$$

Hence, the five different irreducible representations are obtained.

The relation (19) is expressed by

$$1^2+1^2+1^2+1^2+2^2=8\,. \qquad \text{(IV–8)}$$

Accordingly, we have the four different irreducible representations of one-dimension and one irreducible representation of two-dimensions. Each of them is given as follows.

$$\begin{aligned}
&\boldsymbol{P}_1(\boldsymbol{R}_0)=\boldsymbol{P}_1(\boldsymbol{R}_1)=\boldsymbol{P}_1(\boldsymbol{R}_2)=\boldsymbol{P}_1(\boldsymbol{R}_3)\\
&\qquad=\boldsymbol{P}_1(\boldsymbol{R}_4)=\boldsymbol{P}_1(\boldsymbol{R}_5)=\boldsymbol{P}_1(\boldsymbol{R}_6)=\boldsymbol{P}_1(\boldsymbol{R}_7)=1\,,\\
&\boldsymbol{P}_2(\boldsymbol{R}_0)=\boldsymbol{P}_2(\boldsymbol{R}_1)=\boldsymbol{P}_2(\boldsymbol{R}_2)=\boldsymbol{P}_2(\boldsymbol{R}_3)=1,\\
&\qquad\boldsymbol{P}_2(\boldsymbol{R}_4)=\boldsymbol{P}_2(\boldsymbol{R}_5)=\boldsymbol{P}_2(\boldsymbol{R}_6)=\boldsymbol{P}_2(\boldsymbol{R}_7)=-1\,,\\
&\boldsymbol{P}_3(\boldsymbol{R}_0)=\boldsymbol{P}_3(\boldsymbol{R}_2)=\boldsymbol{P}_3(\boldsymbol{R}_4)=\boldsymbol{P}_3(\boldsymbol{R}_6)=1,\\
&\qquad\boldsymbol{P}_3(\boldsymbol{R}_1)=\boldsymbol{P}_3(\boldsymbol{R}_3)=\boldsymbol{P}_3(\boldsymbol{R}_5)=\boldsymbol{P}_3(\boldsymbol{R}_7)=-1\,,\\
&\boldsymbol{P}_4(\boldsymbol{R}_0)=\boldsymbol{P}_4(\boldsymbol{R}_2)=\boldsymbol{P}_4(\boldsymbol{R}_5)=\boldsymbol{P}_4(\boldsymbol{R}_7)=1,\\
&\qquad\boldsymbol{P}_4(\boldsymbol{R}_1)=\boldsymbol{P}_4(\boldsymbol{R}_3)=\boldsymbol{P}_4(\boldsymbol{R}_4)=\boldsymbol{P}_4(\boldsymbol{R}_6)=-1\,,
\end{aligned}$$

$$\boldsymbol{P}_5(\boldsymbol{R}_0)=\begin{bmatrix}1&0\\0&1\end{bmatrix},\ \boldsymbol{P}_5(\boldsymbol{R}_1)=\begin{bmatrix}i&0\\0&-i\end{bmatrix},$$

$$\boldsymbol{P}_5(\boldsymbol{R}_2)=\begin{bmatrix}-1&0\\0&-1\end{bmatrix},\ \boldsymbol{P}_5(\boldsymbol{R}_3)=\begin{bmatrix}-i&0\\0&i\end{bmatrix},$$

$$\boldsymbol{P}_5(\boldsymbol{R}_4)=\begin{bmatrix}0&1\\1&0\end{bmatrix},\ \boldsymbol{P}_5(\boldsymbol{R}_5)=\begin{bmatrix}0&-i\\i&0\end{bmatrix},$$

$$\boldsymbol{P}_5(\boldsymbol{R}_6)=\begin{bmatrix}0&-1\\-1&0\end{bmatrix},\ \boldsymbol{P}_5(\boldsymbol{R}_7)=\begin{bmatrix}0&i\\-i&0\end{bmatrix}. \qquad \text{(IV–9)}$$

Using (IV–6) and (IV–9), we can easily obtain $\boldsymbol{T}_{ij}^{(\mu)}$ ($\mu=1, 2, 3, 4, 5$) from (39).

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The Crystal Structure of Sodium Bicarbonate

BY RONALD L. SASS AND RONALD F. SCHEUERMAN

Department of Chemistry, Rice University, Houston, Texas, U.S.A.

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The atomic parameters in sodium bicarbonate are redetermined. The resulting bicarbonate ion structure differs significantly from that found in other salts. The bicarbonate ion was found to have C_{2v} symmetry (excluding the hydrogen atom), with C–O bond distances equal to 1·346, 1·264 and 1·263 Å. The hydrogen bond distance between adjacent bicarbonate ions is 2·595 Å. These dimensions are compared with those in related compounds.

Introduction

The bicarbonate salts are a rather interesting series of compounds which illustrate the effects of crystal packing on the internal structure of covalently bonded molecules. Three such salts which have been studied by X-ray diffraction are potassium bicarbonate (Nitta, Tomiie & Hoo Koe, 1952), sodium sesquicarbonate (Brown, Peiser & Turner-Jones, 1949) and sodium bicarbonate (Zachariasen, 1933). These systems each crystallize by utilizing a different hydrogen bonding scheme and show marked differences in the carbon-oxygen lengths of the anion. The solution of the structure of sodium bicarbonate was obtained, however, by using the assumption that planar trigonal carbonate groups exist in the cyrstal with all carbon-oxygen distances equal to 1·27 Å. This assumption was not valid and only an approximately correct structure resulted. It is the object of the work reported in this paper to collect new diffraction data and to reexamine the atomic parameters of this structure.

Experimental

Small needle-like crystals of sodium bicarbonate were obtained by slow evaporation of the aqueous solution in an atmosphere of carbon dioxide. The resulting crystals were mounted in the usual manner with the axis of rotation corresponding to the needle axis. Several crystals had to be examined before one was found which did not exhibit twinning. The dimensions of this crystal were approximately 0·1 mm. in diameter × 2 mm.

Oscillation and rotation photographs showed the Laue symmetry to be C_{2h}–$2/m$. Systematic absences led to the space group assignment of C_{2h}^5–$P2_1/c$, in agreement with Zachariasen (in his paper Zachariasen used the related unit cell having symmetry C_{2h}^5–$P2_1/n$). The unit cell dimensions obtained, compared with those of Zachariasen, are shown below.

This investigation	Zachariasen ($P2_1/c$)
$a = 3·51 \pm 0·01$ Å	$a = 3·53 \pm 0·03$ Å
$b = 9·71 \pm 0.01$	$b = 9·70 \pm 0·04$
$c = 8·05 \pm 0·01$	$c = 8·11 \pm 0·04$
$\beta = 111°\ 51'$	$\beta = 112°\ 25'$
$a:b:c = 0·361:1:0·829$	$a:b:c = 0·364:1:0·836$

The above axial ratios may be compared to the values of $a:b:c = 0·3582:1:0·8253$ determined optically by Groth (1908). Assuming four molecules per unit cell, the calculated density is 2·19 g.cm.$^{-3}$, compared to the experimental density of 2·22 g.cm.$^{-3}$ reported by Groth (1908) and 2·20 g.cm.$^{-3}$ listed in the International Critical Tables (1926).

Multiple film Weissenberg photographs of the $h = 0$, 1, and 2 layers were recorded using Cu $K\alpha$ radiation. The intensities of the various reflections were estimated visually in the usual manner with the aid of an intensity strip. Correlation of the intensities of the various sets of film was made by comparison to a photograph which contained fifteen minute exposures of a twenty-five degree portion of each layer; absorption was neglected.

Treatment of data

A Fourier projection down the a axis was calculated using the magnitudes of the structure factors obtained from our intensity data and signs based on