References

PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
PAULING, L. (1949). *Proc. Roy. Soc. A*, **196**, 343.
THEWLIS, J. (1951). *Nature, Lond.* **168**, 198.
THEWLIS, J. (1952). *Acta Cryst.* **5**, 790.
THEWLIS, J. (1954). In preparation.
TUCKER, C. W., JR. (1950). U.S. Atomic Energy Commission Declassified Document No. 2957.
TUCKER, C. W., JR. (1951). *Acta Cryst.* **4**, 425.
TUCKER, C. W., JR. (1952). *Acta Cryst.* **5**, 395.
TUCKER, C. W., JR. & SENIO, P. (1952). Knolls Atomic Power Laboratory Report No. 844.
TUCKER, C. W., JR. & SENIO, P. (1953). *Acta Cryst.*, **6**, 753.
WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 397.

Acta Cryst. (1954). **7**, 328

A Fundamental Set of Structure-Factor Inequalities

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Among all inequalities between the structure factors related by a given restriction on the indices, the fundamental set is defined as a set of independent inequalities from which all others can be derived. The present paper deals with the problem of finding this set for the structure factors U_H, $U_{H'}$, U_{2H}, $U_{2H'}$, $U_{H-H'}$ and $U_{H+H'}$ for a centrosymmetric structure. Starting from a more restricted problem, viz. to establish relations between some known inequalities, a new inequality is found:

$$(U_{H+H'}+U_{H-H'}-2U_HU_{H'})^2 \leqq (1+U_{2H}-2U_H^2)(1+U_{2H'}-2U_{H'}^2).$$

It is shown that various known inequalities containing the same U's can be derived from this relation combined with three different versions of Harker & Kasper's inequality $(U_H\pm U_{H'})^2 \leqq (1\pm U_{H+H'})(1\pm U_{H-H'})$.

The general problem is solved by calculating the extreme values of $U_{H+H'}$ for arbitrary variations of a positive charge distribution in the unit cell, provided the other five U's remain constant. The above four inequalities are found anew, so these constitute the fundamental set.

A convenient graphical representation is obtained by plotting the extreme values of $U_{H+H'}$ as a function of $U_{H-H'}$ for given values of the other U's. Finally Karle & Hauptman's inequality $(U_{H\pm H'}-U_HU_{H'})^2 < (1-U_H^2)(1-U_{H'}^2)$ is discussed, and is found to be the analogue of the new inequality for the asymmetric case.

1. Introduction

Since Harker & Kasper (1948) derived the first inequalities between structure factors, many new inequalities have been found. The diversity of these relations leads to the following questions:

Let us consider inequality relations, based on the positiveness of the electron density, between structure factors belonging to a given set.

(*A*) Can all possible relations of this kind be enumerated in an explicit way? This question will be treated in a forthcoming paper, using Karle & Hauptman's (1950) method of generating inequalities (cf. also § 5).

(*B*) Are the explicitly known inequalities independent of each other? If one of them can be derived from another, clearly this one can be discarded.

(*C*) Can a set of independent inequalities be found from which all others can be derived? This set will obviously be of considerable importance, so we shall call it the *fundamental set* of inequalities for the given structure factors. This set may, of course, be stated in algebraically different forms. The limits which it imposes on U-values are, however, unique (cf. also § 4), so the above definition is essentially unambiguous.

Grison (1951) has given an answer to question (*B*), and his answer, though erroneous in itself, will lead us to a new way of tackling this problem. An approach to (*C*) has led to the development of a theory which confirms and strengthens the results which have been derived in answering (*B*).

We consider unitary structure factors, U_H, defined by

$$U_H = \sum_i n_i \exp 2\pi i(hx_i+ky_i+lz_i) = \sum_i n_i \exp 2\pi i(\mathbf{h}, \mathbf{r}_i)\,,$$

where n_i is the atomic number of the ith atom, divided by the sum of the atomic numbers in the cell, so that

$$\sum_i n_i = 1 ,$$

and x_i, y_i, z_i are its parameters. We now confine ourselves to centrosymmetrical structures and to relations between U_H, $U_{H'}$, U_{2H}, $U_{2H'}$, $U_{H+H'}$ and $U_{H-H'}$, because only these structure factors occur in the inequalities which have been used and/or discussed by previous authors:

$$\varepsilon_1 \equiv 1+\tfrac{1}{2}U_{2H}+\tfrac{1}{2}U_{2H'}+U_{H+H'}+U_{H-H'} -(U_H+U_{H'})^2 \geqslant 0 , \quad (1)$$

$$\varepsilon_2 \equiv 1+\tfrac{1}{2}U_{2H}+\tfrac{1}{2}U_{2H'}-U_{H+H'}-U_{H-H'} -(U_H-U_{H'})^2 \geqslant 0 , \quad (2)$$

$$\varepsilon_3 \equiv 1+U_{H+H'}+U_{H-H'}+U_{H+H'}U_{H-H'} -(U_H+U_{H'})^2 \geqslant 0 , \quad (3)$$

$$\varepsilon_4 \equiv 1-U_{H+H'}-U_{H-H'}+U_{H+H'}U_{H-H'} -(U_H-U_{H'})^2 \geqslant 0 , \quad (4)$$

$$\varepsilon_5 \equiv 1+U_{2H}+U_{2H'}+U_{2H}U_{2H'} -(U_{H+H'}+U_{H-H'})^2 \geqslant 0 , \quad (5)$$

$$\varepsilon_6 \equiv 1-U_{2H}-U_{2H'}+U_{2H}U_{2H'} -(U_{H+H'}-U_{H-H'})^2 \geqslant 0 , \quad (6)$$

$$\varepsilon_7 \equiv (1-U_H^2)(1-U_{H'}^2)-(U_{H+H'}-U_HU_{H'})^2 \geqslant 0 , \quad (7)$$

$$\varepsilon_8 \equiv (1-U_H^2)(1-U_{H'}^2)-(U_{H-H'}-U_HU_{H'})^2 \geqslant 0 . \quad (8)$$

The first six expressions have been found by Harker & Kasper (1948), the last two by Karle & Hauptman (1950). We may add

$$G_H \equiv 1+U_{2H}-2U_H^2 \geqslant 0 ,$$

the first inequality found by Harker & Kasper. We have omitted the linear inequalities of Okaya & Nitta (1952), as these are less powerful than (3) and (4) (Sakurai, 1952).*

2. A new inequality

In establishing the connexion between some inequalities, Grison uses the relation

$$U_{H+H'}+U_{H-H'}-2U_HU_{H'} \geqslant 0 ,$$

which is derived by subtracting two inequalities. This is not permissible; the result, however, might be true, so the first thing to do is to investigate

$$G_1 \equiv U_{H+H'}+U_{H-H'}-2U_HU_{H'} = \sum_j n_j [\cos 2\pi(\mathbf{h}+\mathbf{h}', \mathbf{r}_j)+\cos 2\pi(\mathbf{h}-\mathbf{h}', \mathbf{r}_j)] -2\sum_i n_i \cos 2\pi(\mathbf{h}, \mathbf{r}_i) . \sum_j n_j \cos 2\pi(\mathbf{h}', \mathbf{r}_j) .$$

This may be written, using $\Sigma n_i = 1$, as

$$G_1 = 2\sum_{i,j} n_in_j \cos 2\pi(\mathbf{h}, \mathbf{r}_j) \cos 2\pi(\mathbf{h}', \mathbf{r}_j) -2\sum_{i,j} n_in_j \cos 2\pi(\mathbf{h}, \mathbf{r}_i) \cos 2\pi(\mathbf{h}', \mathbf{r}_j)$$

$$= \sum_{i,j} n_in_j [\cos 2\pi(\mathbf{h}, \mathbf{r}_j)-\cos 2\pi(\mathbf{h}, \mathbf{r}_i)] \times [\cos 2\pi(\mathbf{h}', \mathbf{r}_j)-\cos 2\pi(\mathbf{h}', \mathbf{r}_i)] .$$

The identity between these two expressions may be proved by commuting i and j in the first expression for G_1. Now from the second expression it is seen at once that G_1 may be positive or negative, so the alleged inequality used by Grison is not valid. This second expression, however, invites us to apply the inequality of Cauchy. If we put

$$a_p = \sqrt{(n_in_j)} . [\cos 2\pi(\mathbf{h}, \mathbf{r}_j)-\cos 2\pi(\mathbf{h}, \mathbf{r}_i)] ,$$
$$b_p = \sqrt{(n_in_j)} . [\cos 2\pi(\mathbf{h}', \mathbf{r}_j)-\cos 2\pi(\mathbf{h}', \mathbf{r}_i)] ,$$

then, from

$$(\Sigma a_pb_p)^2 \leqslant \Sigma a_p^2 . \Sigma b_p^2 ,$$

we have

$$(U_{H+H'}+U_{H-H'}-2U_HU_{H'})^2 \leqslant (1+U_{2H}-2U_H^2).(1+U_{2H'}-2U_{H'}^2) . \quad (9)$$

We shall prove later that this inequality is rather powerful; at present we only draw attention to the right side, which contains two non-negative factors. We denote them as before by G_H and $G_{H'}$ and further introduce $G_2 = U_{2H}+U_{2H'}-2U_{H+H'}U_{H-H'}$.

3. Relations between the inequalities

The expressions G_1 and G_2 are obtained by subtracting inequalities. Accordingly we will try to express our inequalities in G_H, $G_{H'}$, G_1 and G_2. Then it is easily verified that

$$\varepsilon_1 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}+G_1 \geqslant 0 , \quad (1a)$$
$$\varepsilon_2 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-G_1 \geqslant 0 , \quad (2a)$$
$$\varepsilon_3 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-\tfrac{1}{2}G_2+G_1 \geqslant 0 , \quad (3a)$$
$$\varepsilon_4 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-\tfrac{1}{2}G_2-G_1 \geqslant 0 , \quad (4a)$$
$$\varepsilon_7 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-U_{H+H'}G_1-\tfrac{1}{2}G_2 \geqslant 0 , \quad (7a)$$
$$\varepsilon_8 = \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-U_{H-H'}G_1-\tfrac{1}{2}G_2 \geqslant 0 , \quad (8a)$$
$$\varepsilon_9 = G_HG_{H'}-G_1^2 \geqslant 0 ; \quad (9a)$$

or

$$|G_1| \leqslant \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'} , \quad (1,2b)$$
$$|G_1| \leqslant \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-\tfrac{1}{2}G_2 , \quad (3,4b)$$
$$U_{H\pm H'}G_1 \leqslant \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-\tfrac{1}{2}G_2 , \quad (7,8b)$$
$$|G_1| \leqslant \sqrt{(G_HG_{H'})} . \quad (9b)$$

As $2|\sqrt{(ab)}| \leqslant |a|+|b|$, it is seen at once that (9b)

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* *Note added in proof*, 22 *February* 1954.—Our attention has been drawn to the relation

$$(1\pm U_H)^{3/2} \leqq 2{\cdot}38(\tfrac{1}{2}\pm\tfrac{3}{8}U_H+\tfrac{3}{56}U_{2H})$$

derived by Gillis (1948). The ensuing lower limit of U_{2H} lies above the one given by $G_H \geqq 0$. The latter boundary value can, however, be realized (namely by taking $\cos 2\pi\mathbf{H}.\mathbf{r}_j = U_H$ for all j). In this case Gillis's inequality is violated. Gillis's error is caused by the use of only three terms of a series development of $|\cos^3 \varkappa|$ in his derivation.

implies (1, 2). From (3) and (4), (7) and (8) may be derived:

$$|U_{H\pm H'}| \leqslant 1 ,$$

so

$$|U_{H\pm H'}G_1| \leqslant \tfrac{1}{2}G_H+\tfrac{1}{2}G_{H'}-\tfrac{1}{2}G_2 .$$

Then *a fortiori* (7, 8*b*) is true.

We have omitted (5) and (6). We find, however,

$$\begin{aligned}\varepsilon_5 &= (G_HG_{H'}-G_1^2)+2(U_H\surd G_{H'}-U_{H'}\surd G_H)^2 \\ &\qquad +4U_HU_{H'}\{\surd(G_HG_{H'})-G_1\} \\ &= (G_HG_{H'}-G_1^2)+2(U_H\surd G_{H'}+U_{H'}\surd G_H)^2 \\ &\qquad -4U_HU_{H'}\{\surd(G_HG_{H'})+G_1\}\end{aligned}$$

by writing

$$1+U_{2H} = G_H+2U_H^2, \quad \text{etc.}$$

Hence inequality (5) follows from (9); for if the sign of $U_HU_{H'}$ is positive, the relation is proved with the help of the first expression of ε_5, in the other case with the second one.

The inequality (6) has a somewhat lonely position between the others (cf. §§ 4 and 5). We may mention here that (7) and (8) may also be derived from (6) and (9):

If

$$\begin{aligned}A &= \surd(1-U_{2H}).\surd(1-U_{2H'}) \\ &\qquad + \surd(1+U_{2H}-2U_H^2).\surd(1+U_{2H'}-2U_{H'}^2) ,\end{aligned}$$

then, from the inequality of Cauchy,

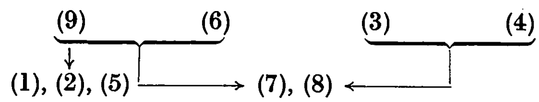
$$A \leqslant 2\surd\{(1-U_H^2)(1-U_{H'}^2)\}$$

and, from (6) and (9),

$$\begin{aligned}A &\geqslant |U_{H+H'}-U_{H-H'}|+|U_{H+H'}+U_{H-H'}-2U_HU_{H'}| \\ &\geqslant 2|U_{H\pm H'}-U_HU_{H'}| .\end{aligned}$$

By eliminating A the inequalities of Karle & Hauptman are found again.

Our results are schematically represented by



No relations exist between (9), (6), (3) and (4). This is easily seen for the last two. As G_2 is the same as G_1 for a different choice of H and H', its sign may be positive or negative; therefore no relation exists between (1), (2) and (3), (4), and it does not seem probable that (3) and (4) could be derived from (9) or (6). This does not concern us here, as the next sections will show the exact relation between these four.

4. The extremum approach

Inequalities have, so far, been obtained by showing that certain combinations of U-values cannot occur. Conversely, one may try to determine which combinations *can* occur. This amounts to an investigation of the extreme values which one structure factor (say $U_{H+H'}$) can assume when a distribution of positive charges in the unit cell is varied in such a way that certain others (in our case U_H, $U_{H'}$, U_{2H}, $U_{2H'}$ and $U_{H-H'}$) remain constant. If we express the maximum value thus found, $\hat{U}_{H+H'}$, as a function of the other U's, then for every structure the inequality

$$U_{H+H'} \leqslant \hat{U}_{H+H'}(U_H, U_{H'}, \ldots)$$

obtains, and similarly for the minimum value.

Since these inequalities determine *all* possible combinations of the six U's, any other inequality containing the same U's must be derivable from the previous ones; so they form the fundamental set defined in § 1.

We will show that the extremum values can be realized, so the fundamental set defines all possible values of $U_{H+H'}$. An advantage of this method is that it gives the results in a logical order: if we drop a restriction, the ensuing inequality (though a fundamental one for the reduced set of U's) can never be more stringent than the general one.

The solution of the variation problem for $U_{H+H'}$ is as follows: Lagrange's method for calculating conditional extremes is applied to a charge distribution of a given number of atoms. We ascribe to the ith atom the charge fraction n_i and the coordinates $\mathbf{r}_i$. Introducing $x_i = \cos 2\pi\mathbf{h}.\mathbf{r}_i$ and $y_i = \cos 2\pi\mathbf{h}'.\mathbf{r}_i$, we wish to derive the extreme values of

$$U_{H+H'} \equiv \Sigma n_i[x_iy_i-\surd\{(1-x_i^2)(1-y_i^2)\}]$$

with the conditions

$$\begin{aligned}&U_{H-H'} = \Sigma n_i[x_iy_i+\surd\{(1-x_i^2)(1-y_i^2)\}] , \\ &U_H = \Sigma n_ix_i, \; U_{H'} = \Sigma n_iy_i , \\ &V_H \equiv \tfrac{1}{2}(1+U_{2H}) = \Sigma n_ix_i^2, \; V_{H'} = \Sigma n_iy_i^2, \; 1 = \Sigma n_i .\end{aligned}$$

The condition $n_i > 0$ need not be introduced at once, because it can at most rule out certain solutions of the variation problem without changing the remaining ones. Both the n_i's and the summations apply to the asymmetric unit only, since the centrosymmetric character is already expressed in the formulas. Adding the six expressions to $U_{H+H'}$, multiplied by the Lagrange coefficients ϱ, $\varkappa$, λ, $\frac{1}{2}\mu$, $\frac{1}{2}\nu$, τ, we restate the problem by deriving the extreme values of

$$\begin{aligned}\varphi = \Sigma n_i[&(1+\varrho)x_iy_i+(\varrho-1)\surd\{(1-x_i^2)(1-y_i^2)\} \\ &+\varkappa x_i+\lambda y_i+\tfrac{1}{2}\mu x_i^2+\tfrac{1}{2}\nu y_i^2+\tau] .\end{aligned}$$

Putting the derivatives of φ with regard to x_i, y_i and n_i equal to zero, we get three sets of equations. We shall denote $\surd\{(1-y_i^2)/(1-x_i^2)\}$ by t_i; then the sets are

$$(1+\varrho)y_i+(1-\varrho)x_it_i+\mu x_i+\varkappa = 0 , \qquad (A)$$

$$(1+\varrho)x_i+(1-\varrho)y_i/t_i+\nu y_i+\lambda = 0 , \qquad (B)$$

$$\begin{aligned}&(1+\varrho)x_iy_i+(\varrho-1)\surd\{(1-x_i^2)(1-y_i^2)\}+\tfrac{1}{2}\mu x_i^2 \\ &\qquad +\tfrac{1}{2}\nu y_i^2+\varkappa x_i+\lambda y_i+\tau = 0 . \qquad (C)\end{aligned}$$

From these equations and the six conditional equations the extreme values can be calculated. The character of the extreme values can be ascertained with the help of the total differential of φ for the extreme value. Using (A), (B) and (C), we find

$$\Delta^2\varphi = \tfrac{1}{2}\Sigma n_i\{(\Delta x_i)^2[(1-\varrho)t_i/(1-x_i^2)+\mu] + (\Delta y_i)^2[(1-\varrho)/t_i(1-y_i^2)+\nu]+2(\Delta x_i)(\Delta y_i) \times [(1+\varrho)-(1-\varrho)x_iy_i/\sqrt{\{(1-x_i^2)(1-y_i^2)\}}]\}\,. \quad (D)$$

If the extremum is a maximum, this differential must be negative for all values of (Δx_i) and (Δy_i) allowed by the conditions.

We choose from all equations (A), (B), (C) those pertaining to two arbitrary atoms, say 1 and 2. Eliminating $\varkappa$, λ, μ, ν and τ from these six equations, we find

$$(1-\varrho)(t_1-t_2)[1-x_1x_2-(1-y_1y_2)/t_1t_2] = 0\,. \quad (E)$$

This equation can be satisfied by

$$1-\varrho = 0\,, \quad (E_1)$$

or by

$$t_1-t_2 = 0\,, \quad (E_2)$$

or by

$$1-x_1x_2-(1-y_1y_2)/t_1t_2 = 0\,. \quad (E_3)$$

Now it is readily seen that if for atoms 1 and 2 we assume $t_1 = t_2$, the same relation (E_2) must obtain for the other atoms; for x_1, y_1, x_2, y_2 may be eliminated from (A), (B) and (E_2), and from this a relation between the Lagrange coefficients can be found. The equation (E_3) would give another relation, and (E_1) is the relation $\varrho = 1$. If two relations existed between the Lagrange coefficients, it would not be possible to calculate the coefficients from the arbitrarily given structure factors. Our problem has three separate solutions, which we have to consider separately. We shall from now assume that the number of atoms is at least three.

(E_1)—The equations (A) and (B) must be valid for all atoms, so they must be identical. This gives two connections between the Lagrange coefficients. We find the solution by multiplying the equations (A) by n_i, n_ix_i and n_iy_i, and summing. These equations can be expressed with the given structure factors; we find:

The extreme value $\hat{U}_{H+H'}$ is given by

$$G_1^2 \equiv (\hat{U}_{H+H'}+U_{H-H'}-2U_HU_{H'})^2 = (1+U_{2H}-2U_H^2) \times (1+U_{2H'}-2U_{H'}^2) \equiv G_HG_{H'}\,.$$

The atomic parameters obey the relation

$$(x-U_H)/\sqrt{G_H} = \pm(y-U_{H'})\sqrt{G_{H'}}$$
$$\nu = 4/\mu = \mp2\sqrt{G_H}/\sqrt{G_{H'}}\,.$$

Now (D) may be calculated and takes the form

$$\Delta^2\varphi = -\Sigma n_i[\Delta x_i\sqrt{(-\mu)}-\Delta y_i/\sqrt{(-\mu)}]^2\,.$$

To the upper sign in the equation for the atomic parameters corresponds $\hat{G}_1 = +\sqrt{(G_HG_{H'})}$, then $\Delta^2\varphi$ is never positive; this value is a maximum. To the lower sign corresponds a minimum. So

$$-\sqrt{(G_HG_{H'})} \leqslant G_1 \leqslant \sqrt{(G_HG_{H'})}\,.$$

This is the inequality (9). We must remark that this result holds only if all n_i have the same sign, in our case positive or zero. If some n's were negative, the extreme value would be neither a maximum, nor a minimum.

(E_2)—This relation leads to

$$\sqrt{(1-y^2)}/\sqrt{(1-x^2)} = C\,.$$

By the same device as used in the first case, we find

$$C = \pm\sqrt{(1-U_{2H})}/\sqrt{(1-U_{2H'})}\,,$$

and from the same equation we find the extreme values

$$U_{H-H'}-\hat{U}_{H+H'} = \pm\sqrt{\{(1-U_{2H})(1-U_{2H'})\}}\,,$$

the positive sign belonging to the positive sign of C. If we now express y by x and insert this expression in the equations (A) and (B), we get two quadratic equations for x, and, as there are more than two atomic parameters, these equations must be identically satisfied. This gives the values $\varrho = -1$, $\mu = -2C$, $\nu = -2/C$ and enables us to write down the total differential (D). The result is that $\hat{U}_{H+H'}$ is a minimum, if the positive sign of C obtains and if all n's are non-negative. To the negative sign of C belongs the maximum. From this the inequality (6) is found.

(E_3)—This case is treated in the same way as (E_2). The equation can be written

$$\frac{(1-x_1x_2)^2}{(1-y_1y_2)^2} = \frac{(1-x_1^2)(1-x_2^2)}{(1-y_1^2)(1-y_2^2)}\,.$$

By subtracting the denominators and the numerators and equalling the new fraction to the first, we find that either $(1-xy)/(y-x)$ or $(1+xy)/(y+x)$ must be a constant.

The first expression may be written

$$(1-xy)/(y-x) = \tfrac{1}{2}(M+1/M)\,.$$

Solving for M and summing the result over all values of x_i, y_i after having multiplied with n_i, the extremum is found to be

$$(1-\hat{U}_{H+H'})(1-U_{H-H'}) = (U_{H'}-U_H)^2\,,$$
$$M = (1-U_{H-H'})/(U_{H'}-U_H)\,.$$

As (A) and (B) must be identically satisfied, it is possible to evaluate the coefficients:

$$\mu = \nu = 0, \quad \text{and} \quad \varrho = M^2\,.$$

Then it can be shown from equation (D) that $\hat{U}_{H+H'}$ is a maximum (non-negative n_i).

In the same way the second expression gives a minimum, defined by

$$(1+\hat{U}_{H+H'})(1+U_{H-H'}) = (U_{H'}+U_H)^2\,.$$

So far we have obtained as possible extreme values of $U_{H+H'}$ three expressions for the maximum and three for the minimum, which, taken together, are exactly identical with the inequalities (9), (6), (4) and (3). A further examination of these extreme values will be given in § 5. The fact that no additional expressions are obtained is, however, sufficient to prove that this set is the fundamental one.

It does not seem likely that the 'extremum' method would lead to a simple generalization for arbitrary sets of structure factors. Presumably certain sets are to be preferred because they lead to essentially new inequalities; the set which we have chosen in a heuristic way seems to be one of these.

We have succeeded in establishing a relation between the above results and those of Karle & Hauptman's method (1950) by choosing the indices in their determinant $|F_{H_p-H_q}|$ as follows:

$$H_1 = 0;\ H_2 = H;\ H_3 = -H;\ H_4 = H';\ H_5 = -H',$$

and applying an orthogonal transformation. The striking correspondence between the two results suggests that a systematic derivation of fundamental sets will eventually be possible by introducing this notion in Karle & Hauptman's method of generating inequalities.

5. A graphical representation

The mutual relations between the extreme values of $U_{H+H'}$ may be understood from an inspection of the $(U_{H+H'}, U_{H-H'})$ plane. Sakurai (1952) has shown that the relation (3) may be represented by a hyperbola in this plane. The admissible points are situated above this hyperbola. In the same way (4) may be represented by another hyperbola, and (6) and (9) by two pairs of parallel lines, corresponding to the maximum and minimum values. We have added the relations (7) and (8), defining a square, and also (1) and (2). If we choose a value of $U_{H-H'}$ in this plane, then the intersections with the curves belonging to the fundamental set denote the six possible extreme values. Now we will prove that only the lowest maximum and the highest minimum satisfy the condition $n_i > 0$. For, if a higher maximum could be attained, then by shifting the atomic parameters and keeping the n's constant, we must exceed the value belonging to the lowest maximum. But this value will now not be a maximum, so the atomic parameters cannot lie on the corresponding curve. This is impossible, because we can show that not only are the inequalities obtained from the curves derived in § 4, but conversely the extreme values can only be obtained under the conditions of this curve, provided that the n's are non-negative. We will prove this for the inequality (9); the other inequalities may be treated in the same way.

From § 2 it is seen that, putting

$$a_p = \sqrt{(n_i n_j)}.(x_j - x_i),\ b_p = \sqrt{(n_i n_j)}.(y_j - y_i),$$

the relation $G_1^2 = G_H G_{H'}$ may be written

$$\Sigma a_p^2 \Sigma b_p^2 - (\Sigma a_p b_p)^2 = 0 .$$

This is a determinant and may be written

$$\sum_{p,q} \begin{vmatrix} a_p a_q \\ b_p b_q \end{vmatrix}^2 = 0 .$$

Now if some n's are positive, some negative, some squares of these determinants may be negative. But if all density fractions have the same sign (without loss of generality we may put a positive sign) all the determinants will be real, their squares cannot be negative, and so, from the relation mentioned above, they must be zero. This condition can be written

$$a_p/b_p = C ,$$

or

$$x_j - x_i = C(y_j - y_i) .$$

If we multiply this relation by n_i, then by summing the equation is reduced to

$$x_j - U_H = C(y_j - U_{H'}) .$$

Multiplying by $n_j x_i$ and summing leads to

$$C = G_H/G_1 = \pm\sqrt{G_H}/\sqrt{G_{H'}} ,$$

the same relations as obtained in § 4.

The higher maxima could only be realized by mixed signs of n, and then they would not be real maxima at all, as may be seen from § 4. So, only the heavy lines in the diagram represent real extremes. They can be reached by putting the atomic parameters on the corresponding curves in the x, y plane. The net result is, therefore, that each point of the space

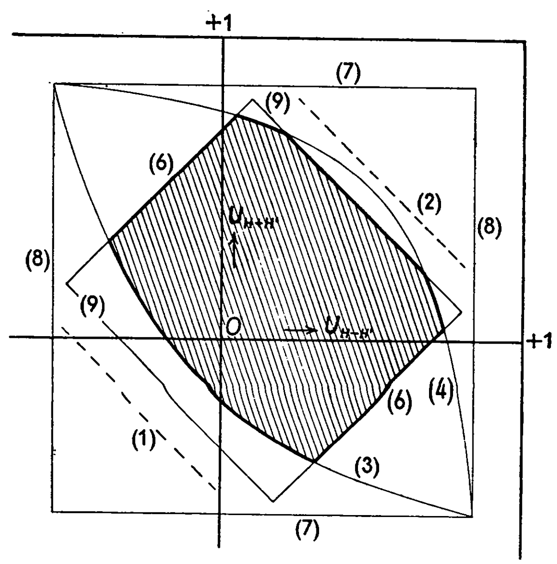


Fig. 1. Extreme values of $U_{H+H'}$ as a function of $U_{H-H'}$ for $U_H = 0{\cdot}70$, $U_{H'} = 0{\cdot}20$, $U_{2H} = 0{\cdot}29$, $U_{2H'} = 0{\cdot}32$, according to various inequalities. The fundamental set (3), (4), (6) and (9) delimits the area of all possible combinations of $U_{H+H'}$ and $U_{H-H'}$ (shaded region).

between the heavy lines corresponds to a possible combination of $U_{H+H'}$ and $U_{H-H'}$.

The square, defined by (7) and (8), the inequalities of Karle & Hauptman, and the set of lines defined by (1) and (2) include the allowed region entirely. The corners of the square coincide with the intersections of the hyperbolas. This is to be seen immediately from (7a) and (8a), (3a) and (4a). For these points $G_1 = 0$. So these inequalities do not belong to the fundamental set. The inequality of Karle & Hauptman, however, is important for asymmetric structures, as will be shown in the next section.

6. Asymmetric structures

If we consider

$$g_+ = U_{H+H'} - U_H U_{H'} ,$$

we find that it may be written

$$g_+ = \tfrac{1}{2} \sum_{i,j} n_i n_j \left[\exp 2\pi i(\mathbf{h}, \mathbf{r}_j) - \exp 2\pi i(\mathbf{h}, \mathbf{r}_i)\right] \times \left[\exp 2\pi i(\mathbf{h}', \mathbf{r}_j) - \exp 2\pi i(\mathbf{h}', \mathbf{r}_i)\right] .$$

If we apply the inequality of Cauchy in the same way as we did in the proof of (9), we find

$$|U_{H+H'} - U_H U_{H'}|^2 \leqslant (1-|U_H|^2)(1-|U_{H'}|^2) , \quad (10)$$

the relation of Karle & Hauptman. If we write

$$g_1 = 1-|U_H|^2, \; g_2 = 1-|U_{H'}|^2$$

then (10) may be written

$$|g_+| \leqslant \sqrt{(g_1 g_2)} . \quad (10a)$$

The same relation obtains for g_-, which is g_+ after replacing H' by $-H'$.

The relation (10) plays the same part here as does the new inequality (9) for centrosymmetrical structures. We mention without proof, that the inequalities of Harker & Kasper, valid for asymmetric structures, namely

$$|U_H \pm U_{H'}|^2 \leqslant 2(1+\mathrm{Re}\, U_{H-H'}) ,$$

can be derived from (10). Hence the latter implies all known inequalities for asymmetric structures. Combined with its transcription for $U_{-H'}$, it constitutes the fundamental set for U_H, $U_{H'}$, $U_{H+H'}$ and $U_{H-H'}$.

For centrosymmetric structures, however, application of these inequalities leads to the rather poor results (7, 8) in comparison with (3) and (4), which form the fundamental set in this special case (cf. Fig. 1).

References

GILLIS, J. (1948). *Acta Cryst.* **1**, 76.
GRISON, E. (1951). *Acta Cryst.* **4**, 489.
HARKER, D. & KASPER, E. (1948). *Acta Cryst.* **1**, 70.
KARLE J. & HAUPTMAN, H. (1950). *Acta Cryst.* **3**, 181.
OKAYA, Y. & NITTA, I. (1952). *Acta Cryst.* **5**, 564.
SAKURAI, K. (1952). *Acta Cryst.* **5**, 697.

Acta Cryst. (1954). **7**, 333

'Mean Strains' in Worked Aluminium

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Experiments have been carried out to investigate the cause of the relative radial displacements of adjacent diffraction spots on some X-ray microbeam back-reflexion photographs of rolled polycrystalline aluminium. Among other causes, it is possible that the displacements are due to the existence, within the material, of particles in which the lattice spacing is different from the average value. From the present experiments it is concluded that a few reflexions from such particles have been found. The stresses required to produce strains of the observed magnitude are of the order of the yield stress of the material.

1. Introduction

It is possible to resolve the continuous Debye–Scherrer rings on normal X-ray back-reflexion photographs of deformed polycrystalline aluminium into discrete reflexions by the use of the X-ray microbeam technique (Kellar, Hirsch & Thorp, 1950). A feature of the microbeam photographs is that not all the reflexions of given indices lie on a ring of definite radius: adjacent reflexions are often displaced radially from one another, and variations in the magnitude of the displacements from point to point give an appearance of waviness around the ring. The effect is very often most marked on photographs of lightly deformed specimens taken with relatively large beam diameters ($\sim 100\,\mu$) (see Hirsch & Kellar, 1952). When smaller X-ray beam

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