A New Method for Phase Determination. The 'Maximum Determinant Rule'

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The joint probability of a set of structure factors involved in a Karle–Hauptman determinant is evaluated. For equal atoms, under conditions to be specified, the theory leads to the conclusion: among all combinations of phases compatible with the condition of non-negativity of a Karle–Hauptman determinant, the most probable combination is that which maximizes this determinant. This 'maximum determinant rule' can be used as a basis for the practical determination of phases. Special cases and further properties of the determinants are also obtained from the main expression for the joint probability.

The aim of this paper is the development of a method allowing the simultaneous determination of a large number of structure invariants. This method is based upon a new probability relation between structure factors obtained by use of the theory of 'conditional joint probabilities'.

The final formula [equation (8)] can be expressed very simply in terms of *Karle–Hauptman determinants.* Thus, this formula establishes a connection between *inequality theory* (Harker & Kasper, 1948; Karle & Hauptman, 1950) and the *probability concept* [initiated by Hauptman & Karle (1953) and further developed by several authors: Bertaut, Cochran, Woolfson, Kitaigorodski, Klug].

The practical possibilities can be summarized by the following statement, valid under conditions to be specified below:

Among all combinations of phases compatible with the condition of non-negativity of the Karle–Hauptman determinant, the most probable combination is the one that leads to the maximum value of this determinant. Thus, the 'maximum determinant method' allows the *simultaneous* determination (in the statistical sense) of a large number of phases.

The above theory, which involves the definition of a new determinant is given in §§ 1 and 2.

As this determinant has a fundamental role, its properties are studied in § 3. A geometrical interpretation in Hilbert space allows a simple formulation of these properties.

In § 4 we deal with some special cases and we show that several statistical theories developed by Wilson, Cochran & Woolfson, and Karle & Hauptman (the 'unified algebraic approach') can be very simply deduced from the general formula (8).

1. Conditional joint probabilities

(A) Definition of the a priori conditions

The essential difference between the work of previous authors on structure factor probabilities and the present study lies in the notion of '*conditional* joint probability'.

The problem can be stated as follows: let us consider m normalized structure factors denoted by $E_1 \ldots E_p \ldots E_m$ which are considered as random variables; we are seeking the probability law (or 'probability density' or 'distribution law'),

$$p(E_1 \ldots E_m),$$

under the condition that other structure factors (to be defined below) have values fixed and known *a priori.*

We now give explicitly the relationship between the reciprocal lattice vectors corresponding to the m structure factors $E_1 \ldots E_m$ (random variables) and those corresponding to the fixed structure factors.

For simplicity, we assume that all atoms are identical. The normalized structure factor $E_\mathbf{H}$ is then given by:

$$E_\mathbf{H} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) ;\qquad (1)$$

$\mathbf{H}$: reciprocal lattice vector,
$\mathbf{r}_j$: vector defining the position of the jth atom,
N: number of atoms in the unit cell.

The unitary structure factors are given by:

$$U_\mathbf{H} = E_\mathbf{H}/\sqrt{N} .\qquad (2)$$

For reasons that will become apparent later, let us set:

$$E_p = E_{\mathbf{L}+\mathbf{H}_p}, \quad p = 1, \ldots m ;$$

$\mathbf{H}_p$ are fixed vectors,
$\mathbf{L}$ is a random vector (*i.e.* it sweeps out all reciprocal space).

Therefore, $(\mathbf{L}+\mathbf{H}_p)$ are also random vectors. The families of m random variables $E_1 \ldots E_m$ are generated by considering vector $\mathbf{L}$ as sweeping out all reciprocal space: as a consequence, the 'figure' formed by the m points $\mathbf{L}+\mathbf{H}_p$ moves randomly in reciprocal space, in the sense that this 'figure' sweeps out all reciprocal space (keeping a constant orientation).

We also notice that to each pair of E's, say $E_p = E_{\mathbf{L}-\mathbf{H}_p}$ and $E_q = E_{\mathbf{L}+\mathbf{H}_q}$, corresponds one fixed reciprocal

vector $\mathbf{H}_p - \mathbf{H}_q$ such that:

$$(\mathbf{L} + \mathbf{H}_p) - (\mathbf{L} + \mathbf{H}_q) = \mathbf{H}_p - \mathbf{H}_q .$$

We now give the fundamental condition which governs the probability we are seeking:

We assume that the $m(m-1)/2$ unitary structure factors corresponding to the fixed reciprocal vectors $(\mathbf{H}_p - \mathbf{H}_q)$ have values which are fixed and known *a priori*.

$$U_{\mathbf{H}_p - \mathbf{H}_q} = U_{pq} = \text{constant} \quad p,q = 1, \ldots m . \quad (3)$$

It is perhaps important to emphasize that this *a priori* lack of knowledge is not an obstacle for practical determination of crystal structures, as a process of recurrent determination of phases will be described later.

(B) Interpretation of the conditions

The connection between the above conditions [equation (3)] and familiar notions in crystal analysis will appear in the following remarks:

(a) The $m(m-1)/2$ correlation coefficients between the m random variables $E_1 \ldots E_m$ are given by the Sayre equation:

$$\overline{E_\mathbf{K} E_{\mathbf{H}-\mathbf{K}}}^{(\mathbf{K})} = U_\mathbf{H} ; \quad (4)$$

H: fixed vector,
K: random vector.

The notation of the left-hand member means 'average over $\mathbf{K}$'.

The above statement is obvious if we make the following change of notation:

$$\mathbf{K} = \mathbf{L} + \mathbf{H}_p ,$$
$$\mathbf{H} = \mathbf{H}_p - \mathbf{H}_q .$$

Then, equation (4) becomes:

$$\overline{E_p E_q{}^*} = \overline{E_{\mathbf{L}+\mathbf{H}_p} E_{-\mathbf{L}-\mathbf{H}_q}}^{(\mathbf{L})} = U_{\mathbf{H}_p - \mathbf{H}_q} \ (p,q = 1, \ldots m) . \quad (4a)$$

The left-hand side of (4a) is, by definition, the correlation coefficient between the random variables E_p and E_q.

If $p = q$, we obtain from (4a) the obvious relation:

$$|\overline{E_p}|^2 = \overline{|E_{\mathbf{L}+\mathbf{H}_p}|^2}^{(\mathbf{L})} = U_0 = 1 . \quad (5)$$

(b)The correlation coefficients U_{pq} form, in the usual probability terminology, the 'covariance matrix', the determinant of which is a Karle–Hauptman determinant.
We recall that

$$D_m = \det(U_{pq}) \geq 0 . \quad (6)$$

The above two statements can be summarized as follows:

For p, $q = 1 \ldots m$, there are m^2 Sayre's relations given by (4a); the right-hand sides of these equations form a non-negative Karle–Hauptman determinant D_m of order m.

(C) Definition of the Δ_{m+1} determinant

Let us consider a new determinant obtained from D_m by adding a last column and line, formed by the m structure factors $E_1 \ldots E_m$ (the last element is set equal to N, number of atoms in the unit cell). This determinant of order $m+1$, divided by N, is also a Karle–Hauptman determinant, but it will be denoted differently, by Δ_{m+1}, in order to emphasize the random character of its value, as it depends upon the reciprocal random vector $\mathbf{L}$ (in contrast with D_m whose elements are assumed to be fixed).

Summarizing, the Δ_{m+1} determinant contains all structure factors involved simultaneously in the above theory:

The m structure factors $E_{\mathbf{L}+\mathbf{H}_p}$ of the last column (and line) of Δ_{m+1} are considered as random variables.

The right-hand sides of the m^2 Sayre's equations:

Table 1. *Values of Δ_{m+1}/D_m and corresponding probability for a particular vector* $\mathbf{L}$ *of jamine* $(m = 16)$

p	$|E_p|$	Correct			Incorrect			
1	2·03							
2	2·89	+						
3	2·35	+						
4	1·86	+						
5	0·37	+						
6	2·22	+			All signs positive			
7	0·87	+						
8	1·88	+						
9	0·99	+						
10	3·36	+						
11	1·20	+						
12	0·49	+	+	+	−	+	+	+
13	0·72	+	+	−	+	+	−	+
14	0·63	−	+	+	+	−	−	+
15	2·60	+	+	+	+	+	+	+
16	1·23	−	−	−	−	+	+	+
Δ_{m+1}/D_m		0·368	0·252	0·211	0·139	0·117	0·064	0·07
$p(\Delta_{m+1})$		0·9960	0·0036	0·0004	~0	~0	~0	~0

Possible combinations of signs of $E_1 E_p U_{p1}$

D_m (fixed values of U_{pq})   Random variables

$$\Delta_{m+1} = \frac{1}{N} \begin{vmatrix} 1 & U_{12} & . & . & U_{1p} & U_{1q} & . & . & U_{1m} & E_{L+H_1} \\ U_{21} & 1 & . & . & U_{2p} & U_{2q} & . & . & U_{2m} & E_{L+H_2} \\ . & . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . & . \\ U_{p1} & U_{p2} & . & . & 1 & U_{pq} & . & . & U_{pm} & E_{L+H_p} \\ U_{q1} & U_{q2} & . & . & U_{qp} & 1 & . & . & U_{qm} & E_{L+H_q} \\ . & . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . & . \\ U_{m1} & U_{m2} & . & . & U_{mp} & U_{mq} & . & . & 1 & E_{L+H_m} \\ E_{-H_1-L} & E_{-H_2-L} & . & . & E_{-H_p-L} & E_{-H_q-L} & . & . & E_{-H_m-L} & N \end{vmatrix}$$

$$\overline{E_{L+H_p} E^*_{L+H_q}}{}^{(1)} = U_{H_p-H_q} = U_{pq} = \text{constant}; \qquad (7)$$

L: random vector,
H_p, H_q: fixed vectors, $p, q = 1, \ldots m$,
D_m: $\det(U_{pq}) \geq 0$.

form the non-negative Karle–Hauptman determinant D_m, which is a principal minor of Δ_{m+1}.

(D) Result

To obtain the probability $p(E_1 \ldots E_m)$, we could use the classical method of the 'characteristic function'. However, the result is directly obtainable by the application of the central limit theorem. The conditions for the validity of this theorem are:

1. The number of atoms N in the unit cell is very large.
2. The positions of the atoms in the asymmetric unit cell are mutually independent.

The probability law corresponding to the above conditions is an m-dimensional Laplace–Gauss law, involving the definite positive hermitian form (or quadratic form in the centrosymmetrical case), Q:

centrosymmetrical

$$p(E_1 \ldots E_m) = (2\pi)^{-m/2} D_m^{-1/2} \exp\left(-\tfrac{1}{2}Q_m\right) \quad (8a)$$

non-centrosymmetrical

$$p(E_1 \ldots E_m) = (2\pi)^{-m} D_m^{-1/2} \exp\left(-Q_m\right) \quad (8b)$$

where Q_m is given by either of the following equivalent expressions:

$$Q_m = E^+[U^{-1}]E, \qquad (9)$$

$$Q_m = \sum_{p=1}^{m} \sum_{q=1}^{m} D_{pq} E_p E_q^* \qquad (9a)$$

$$Q_m = N \frac{D_m - \Delta_{m+1}}{D_m}; \qquad (9b)$$

E: m dimensional column vector of which the components are $(E_1 \ldots E_m)$,
E^+:   transpose of E,
[U]:   matrix of elements U_{pq},
$[U^{-1}]$:   inverse matrix of matrix [U],
D_{pq}:   element of $[U^{-1}]$,
N: number of atoms in the unit cell,
D_m and Δ_{m+1}: Karle–Hauptman determinants.

In the non-centrosymmetrical case, the notation $p(E_1 \ldots E_m)$ (where E's are complex variables) represents, in fact, the joint probability

$$p(A_1, B_1, \ldots A_m, B_m),$$

where A and B are respectively the real and imaginary part of E:

$$E_1 = A_1 + iB_1, \text{ etc.}$$

It is important to emphasize that the hermitian form Q_m, and consequently, the probability law depends only upon the value of two Karle–Hauptman determinants D_m and Δ_{m+1}. The proof of (9b) is given in Appendix A.

Special case of (8)

Let us suppose now that all E's except one, E_p, are known. Then, by elementary manipulations (see Fortet, 1965) we can obtain from (8) the (unidimensional) distribution law of E_p; it is a Gaussian law:

$$p(E_p) = \frac{1}{\sqrt{2\pi}\sigma_p} \exp\left[-\frac{(E_p - \bar{E}_p)^2}{2\sigma_p^2}\right] \qquad (10)$$

with a mean value:

$$\bar{E}_p = \sum_{q \neq p} D_{pq} E_p E_q^* \qquad (11)$$

and a variance σ_p^2:

$$\sigma_p^2 = 1/D_{pp} . \qquad (12)$$

2. Application to the phase problem: The maximum determinant method

Let us assume that the moduli of all structure factors appearing in Δ_{m+1} are fixed. Then, the value of Δ_{m+1} depends only on the phases of the structure invariants T_p:

$$T_p = E_1 E_p^* U_{p1}$$
$$= E_{L+H_1} E_{-L-H_p} U_{H_p - H_1} \quad (p = 2, \ldots m) ,$$

not on the phases of the individual structure factors E_p (Kitaigorodski, 1961).

Let us also notice that the maximum value of the conditional joint probability (8) is obtained when Δ_{m+1} is a maximum; indeed, keeping in mind that all U_{pq}'s are constant, we can write:

$$p(E_1 \ldots E_m) = \text{constant} \times \exp\left(N \frac{\Delta_{m+1}}{D_m}\right) .$$

We are now able to state the following rule: *the most probable values of the phases of the structure invariants T_p corresponding to E_p are those which lead to the maximum value of the Δ_{m+1} determinant.*

We write schematically:

$$[\Delta_{m+1}]_{\text{most probable set of phases}} = \text{maximum} . \qquad (13)$$

This 'maximum determinant rule' is the basis of a practical method for the determination of crystal structures, to be described in a forthcoming paper. It has been successfully applied to solving the structure of trigonellin hydrate (De Rango, 1969).

It is important to emphasize that for centrosymmetrical structures, the signs of the structure invariants determined by this rule may be positive or negative; the statistical methods developed previously allow one only to infer, with a certain probability, that the sign of the invariants is positive.

Also, for non-centrosymmetrical structures, previous formulae (*e.g.* Cochran, 1955) lead to a probable value for the phase of T_p which is always equal to 0, whereas the above rule may yield a value which is not necessarily 0 (as a result of the assumed knowledge of the phases of U_{pq}).

Numerical test of the 'maximum determinant rule'

It is important to show, for an actual structure, that there are effectively cases where *the maximum value of Δ_{m+1} is obtained for a negative value of the invariants $E_H E_K E_{-H-K}$.*

The following data corresponding to the structure of jamine (Karle & Karle, 1964) are extracted from the thesis of De Rango (1969). For a determinant of order

17, there are only a few combinations compatible with the inequality $\Delta_{m+1} \geq 0$. The correct combination yields the maximum value of Δ_{m+1} (Table 1).

The probability p_j for occurrence of the jth combination is given by the formula:

$$P_j = [p(E_1 \ldots E_m)]_j / \sum_i [p(E_1 \ldots E_m)]_i \qquad (14)$$

where $[p(E_1 \ldots E_m)]_i$ denotes the value of the probability density (8) corresponding to the ith combination of phases compatible with the inequality $\Delta_{m+1} \geq 0$.

It is remarkable that the probability for the correct combination is almost equal to 1, although the 'contrast' between the different values of Δ_{m+1} is quite small.

In conclusion, if the inequality theory indicates that only combinations of phases yielding a non-negative Karle–Hauptman determinant are possible, the conditional joint probability theory states, that among all possible combinations, the most probable is that which leads to the maximum value of this determinant.

3. Properties of the Δ determinants

(A) Inequalities

The main result [equation (8)] can be usefully interpreted in terms of Hilbert or Euclidean geometry (Appendix B). We recall that D_m, as well as Δ_{m+1}, are special cases of the Gram determinant (Gantmacher, 1966; Goedkoop, 1953). The theory of Gram determinants yields also the following result, which, to the knowledge of this author, does not seem to have been pointed out in the crystallographic literature.

A Karle–Hauptman determinant D_{m+1} of order $m+1$ is limited on *both* sides:

$$D_m \geq D_{m+1} \geq 0 . \qquad (15)$$

Therefore, the sequence of Karle–Hauptman determinants D_m, as m increases, forms a *non-increasing series.*

For equal atoms we have $\Delta_{m+1} = D_{m+1}$, so that equation (15) can be written as (15a):

$$D_m \geq \Delta_{m+1} \geq 0 . \qquad (15a)$$

In the case of *unequal atoms*, Δ_{m+1} is not defined by (7), but by (B.6). However, with this new definition of Δ_{m+1}, equation (15a) is still valid, although $\Delta_{m+1} \neq D_{m+1}$.

(B) Average value of the Δ_{m+1} determinant

We now pose the question: for a given D_m what is the average value of Δ_{m+1} when L sweeps out uniformly all reciprocal space? In other words, what is the 'expected value' of Δ_{m+1} when L is picked out arbitrarily?

Using Sayre's equation (4a), we obtain for the hermitian form Q:

$$\overline{Q_m}^{(L)} = \sum_{p,q=1}^m D_{pq} \overline{E_p E_q^*}^{(L)} = \sum_{p,q=1}^m D_{pq} U_{pq} = m .$$

The last equality follows from the fact that D^{pq} and U_{pq} are, respectively, elements of the matrices $[U^{-1}]$ and $[U]$.

Recalling that:

$$\overline{Q_m}^{(L)} = N\left(1 - \frac{\overline{\Delta_{m+1}}^{(L)}}{D_m}\right),$$

we obtain:

$$\overline{\Delta_{m+1}}^{(L)} = \left(1 - \frac{m}{N}\right)D_m \qquad m \leq N. \qquad (16)$$

This equation may be a practical guide for searching the combination of phases which maximize Δ_{m+1}.

Remark

For the limiting case $m = N$ we obtain:

$$\overline{\Delta_{m+1}} = \Delta_{N+1} = 0$$

as it should, according to the Gram theory (Goedkoop, 1953).

4. Special cases

It is interesting to apply the general theory given in § 1, where m has any value, to special cases ($m = 1, 2, 3$) which have already been studied by previous authors.

m = 1. Wilson's statistics

Clearly equation (8) reduces to Wilson's distribution because, for $m = 1$:

$$Q_1 = |E_H|^2 \qquad D_1 = 1 .$$

$m = 2$

(a) *Correction term in Woolfson's 'hyperbolic tangent' formula*

After a convenient notation change we can write for equal atoms:

$$\Delta_{m+1} = \Delta_3 = \begin{vmatrix} 1 & U_H^* & E_K^* \\ U_H & 1 & E_{H-K}^* \\ E_K & E_{H-K} & N \end{vmatrix} .$$

In the centrosymmetrical case, the conditional joint probability is given by:

$$p(E_K, E_{H-K} \mid U_H) =$$
$$\frac{1}{2\pi}\frac{1}{\sqrt{1-U_H^2}} \exp\left[-\frac{E_K^2 + E_{H-K}^2 - 2U_H E_K E_{K-H}}{2(1-U_H^2)}\right] . \qquad (17)$$

Following the reasoning of Cochran & Woolfson (1955), we obtain for the probability that the structure invariants are positive:

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{|E_K E_{H-K} E_H|}{\sqrt{N}(1-U_H^2)} . \qquad (18)$$

These authors used also the concept of conditional joint probability (for $m = 2$), but formula (18) differs from Woolfson's familiar formula by the factor $(1-U_H^2)$ which is neglible only if $|U_H| \ll 1$.

A numerical test of equation (18) is given by Fig. 1 for the reflexion 214 of jamine.

(b) *Extension of Friedel's law*

Applying equation (10) for the centrosymmetrical case, we can write for the probability law of E_{K-H}, under the supplementary condition that E_K is fixed, as well as U_H:

$$p(E_{H-K} \mid U_H, E_K) =$$
$$\frac{1}{\sqrt{2\pi}\sqrt{1-U_H^2}} \exp\left[-\frac{(E_{H-K} - U_H E_K)^2}{2(1-U_H^2)}\right] . \qquad (19)$$

Suppose now that $|U_H| \to 1$. Then, the above equations show that:

$$E_{H-K} \to s_H E_K \qquad |E_{H-K}| = |E_K| \qquad (20)$$

where s_H is the sign of U_H.

This means that, if all atoms diffract in phase for the reflexion H, then the end of vector H/2 is a center of symmetry ($s_H = 1$) or antisymmetry ($s_H = -1$) in reciprocal space. Obviously, for the moduli of the structure factors, H/2 is a cenret of symmetry. Naturally, for values of $|U_H|$ less than 1, but still considerable, H/2 is a 'pseudo-center' of symmetry. This is illustrated in Fig. 2 which represents the reciprocal space points $hk0$ of kyanite (De Rango, Tsoucaris & Zelmer, 1966); reflections 500 and $\overline{1}40$ can be considered as pseudo-centers of symmetry. If H is the null vector, then equation (20) amounts to Friedel's law:
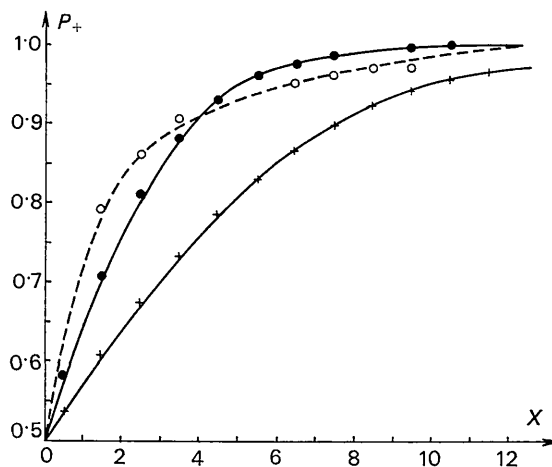
$$|E_{-K}| = |E_K| .$$

Fig. 1. Statistical distribution of the invariants $E_H E_K E_{H-K}$ for all reflexions of jamine corresponding to a fixed H ($h = 2$, $k = 1$, $l = 4$) with $|U_H| = 0.70$.

$+$ (P$_+$) Woolfson $= \tfrac{1}{2} + \tfrac{1}{2} \tanh \dfrac{X}{6.92}$

$\bullet$ (P$_+$) equation (18) $= \tfrac{1}{2} + \tfrac{1}{2} \tanh \dfrac{X}{3.53}$.

$\bigcirc$ $\qquad\qquad$ = experimental points

Remark

This pseudosymmetry phenomenon holds also for non-centrosymmetrical structures.

m = 3. The 'unified algebraic approach'

From the general law (8) one can compute the average value of *any* function of the variables $(E_1, \ldots E_m)$.

For $m = 3$, the calculation of the average of the function given below leads to the 'unified algebraic' formula of Karle & Hauptman (1957) (non-centrosymmetrical case):

$$E_1 = E_L \quad E_2 = E_{L-H} \quad E_3 = E_{L-K}$$
$$M = (|E_L|^2 - 1) \quad (|E_{L-H}|^2 - 1) \quad (|E_{L-K}|^2 - 1)$$

$$\bar{M}^{(L)} = \int \int \int Mp(E_1, E_2, E_3) dE_1 dE_2 dE_3$$

$$\bar{M}^{(L)} = 2N^{-3/2} \{ \mathrm{Re}(E_H E_H E_{-H-K}) - N^{-1/2} \\ \times (|E_H|^2 + |E_K|^2 + |E_{H+K}| - 2) \}. \quad (21)$$

The knowledge of the complete probability law [equation (8)], instead of the 'average equation' (21) can provide a better approach to the determination of structure invariants from the moduli of *all* structure factors.

APPENDIX A

We shall prove that:

$$E^+[U^{-1}]E = N \frac{D_m - \Delta_{m+1}}{D_m}.$$

Let us develop the Δ_{m+1} determinant given by equation (7) along the elements of the last column, then along the elements of the last line:

$$\Delta_{m+1} = \frac{1}{N} \left\{ \sum_{p=1}^{m} \sum_{q=1}^{m} (-1)^{p+q+1} \delta_{pq} E_p E_q^* + ND_m \right\}$$

where δ_{pq} denotes the minor order $m-1$ obtained from D_m by suppressing the pth line and qth column.

The above equation can be written as:

$$N(D_m - \Delta_{m+1}) = \sum_{p=1}^{m} \sum_{q=1}^{m} (-1)^{p+q} \delta_{pq} E_p E_q^*.$$

However, the elements of $[U^{-1}]$ are:

$$D_{pq} = [U^{-1}]_{pq} = (-1)^{p+q} \delta_{pq}/D_m.$$

Therefore:

$$N \frac{D_m - \Delta_{m+1}}{D_m} = \sum_{p=1}^{m} \sum_{q=1}^{m} D_{pq} E_p E_q^*$$
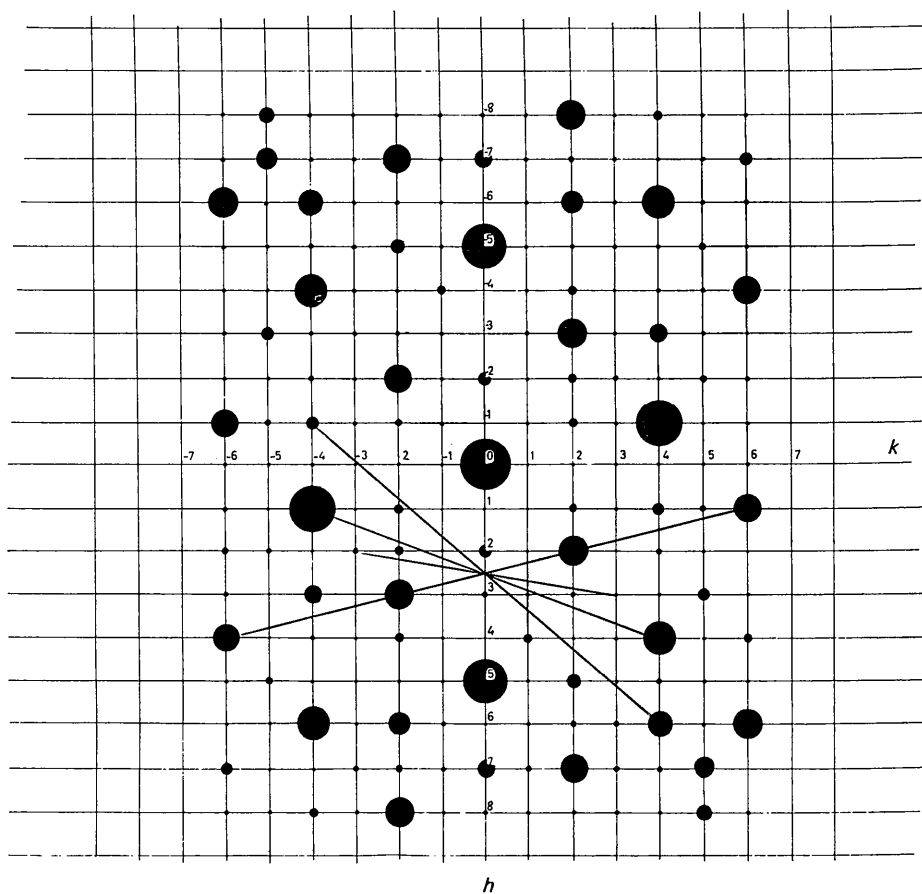
which is (9b).

h

Fig. 2. Weighted reciprocal lattice points *hk*0 of kyanite. The point $h = 2 \cdot 5$ $k = 0$ is a 'pseudo-inversion' centre as a consequence of the large value of $|U_{500}|$.

APPENDIX B

Geometrical interpretation and further properties of Δ_{m+1} (Gram) determinants

The results of the main paper can be usefully interpreted in terms of Hilbert or Euclidian space geometry. This space has been introduced in crystallography by von Eller (1955) and Kitaigorodski (1961, p. 151). Here we consider the general case of unequal atoms:

$$E_H = \sum_{j=1}^{N} g_j \exp (2\pi i H . r_j)$$

$$\sum_{j=1}^{N} g_j = 1 \quad g_j = \frac{f_j}{\sqrt{\sum_j f_j^2}}$$

where f_j is the atomic scattering factor.

(A) Recap of the definition of a Gram determinant

Let us consider m arbitrary nodes of reciprocal space corresponding to the vectors:

$$H_p (p = 1, 2, \ldots m) .$$

To each node of reciprocal space we shall assign an N-dimensional vector:

$$V_p = \sum_{j=1}^{N} [g_j \exp (2\pi i H_p . r_j)] e_j \qquad (B.1)$$

where the expression in square brackets is the jth (complex) coordinate of V_p; e_j is one of the orthonormal unit vectors in N-dimensional space.

Vectors V_p are orthonormal; as their length is given by:

$$(V_p . V_p) = \sum_j g_j^2 = 1 .$$

The scalar product

$$(V_p . V_q) = \sum_{j=1}^{n} g_j^2 \exp [2\pi i (H_p - H_q)]$$

$$= G_{H_p - H_q} = G_{pq} . \qquad (B.2)$$

G_{pq} is just the structure amplitude of the node $(H_p - H_q)$ corresponding to the 'square structure' $\varrho^2(r)$.

The determinant D_m whose general element is given by $(B.2)$ is, by definition, a Gram determinant. In crystallography, with the above definition of D_m, this is a Karle–Hauptman determinant corresponding to the 'square' $\varrho^2(r)$ structure (for equal atom structures, obviously, $G_{pq} = U_{pq}$).

In terms of Hilbert space (or Euclidian space in centrosymmetrical structures) geometry, it can be proved (Gantmacher, 1966, p. 254) that D_m is equal to the square of the hypervolume of the parallelepiped, defined by the m vectors V_p, which is non-negative:

$$D_m = [\text{Volume } (V_1, \ldots V_m)]^2 \geq 0 . \qquad (B.3)$$

(B) Definition of the Δ_{m+1} determinant

To the sequence of m (fixed) vectors V_p we add now a last vector W which depends upon the random reciprocal lattice vector L:

$$W = \frac{1}{\sqrt{N}} \sum_j [\exp (-2\pi i L . r_j)] e_j . \qquad (B.4)$$

Obviously:

$$(V_p . W) = \frac{1}{\sqrt{N}} \sum_j g_j \exp [2\pi i (H_p + L) . r_j]$$

$$= E_{L+H_p} / \sqrt{N} = E_p / \sqrt{N} . \qquad (B.5)$$

The Δ_{m+1} determinant is also a Gram determinant:

$$\Delta_{m+1} = \frac{1}{N} \begin{vmatrix} 1 & . & . & G_{1m} & E_1 \\ . & . & . & . & . \\ G_{m1} & . & . & 1 & E_m \\ E_1^* & . & . & E_m^* & N \end{vmatrix} \geq 0 .$$

$$(B.6)$$

Consequently, Δ_{m+1} is equal to the hypervolume in Hilbert space of the parallelepiped defined by the $m + 1$ vectors $(V_1, \ldots V_p, \ldots V_m, W)$.

(C) Geometrical interpretation of the conditional probability law [equation (8)]

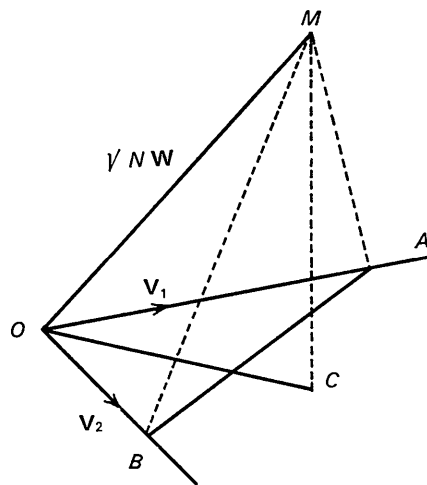For clearness we refer to the case $m = 2$ in Euclidian space but the result is perfectly general (Fig. 3).

Fig. 3. Particular case ($m = 3$) of Euclidian space

$$V_1 . V_2 = U_{12} = U_{H_1 - H_2}$$

$$\overrightarrow{OA} = \sqrt{N} V_1 . W = E_1 = E_{L+H_1}$$

$$\overrightarrow{OB} = \sqrt{N} V_2 . W = E_2 = E_{L+H_2}$$

$$|\overrightarrow{OC}| = Q = N \left(1 - \frac{D_3}{D_2}\right)$$

The probability density $p(E_1, E_2)$ depends solely on the length X_m of $\overrightarrow{OC}$.

Let us set:

$$\overrightarrow{OM} = \sqrt{N}\mathbf{W},$$

$\overrightarrow{MC}$: vector normal to the plane $(\mathbf{V}_1, \mathbf{V}_2)$.

By Pythagoras's theorem, we have:

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

By elementary geometry and equation (3) we have:

$$|\overrightarrow{MC}|^2 = \left(\frac{\text{volume of } (\mathbf{V}_1, \mathbf{V}_2, \sqrt{N}\mathbf{W})}{\text{surface of}(\mathbf{V}_1, \mathbf{V}_2)}\right)^2 = N\frac{\Delta_3}{D_2}. \quad (B.7)$$

By a straightforward generalization, we have:

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

Therefore:

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

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' $(\mathbf{V}_1 \ldots \mathbf{V}_m)$.

(D) *Proof of inequality* (15a)

Clearly

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

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

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

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