not yet been evaluated in detail (Sörum, 1943); whether it is that of diopside or one closely related to it needs still to be determined. There is little doubt, however, that the coordination of vanadium is tetrahedral, and chains of the formula $(VO_3)_n^{n-}$ are formed by sharing corners. The transition from the γ phase appears to result from the disruption of the closely coordinated sheets into these isolated units which will require additional alkali metal ions, not necessarily in a fixed proportion, to link together in the diopside grouping.

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A Unified Algebraic Approach to the Phase Problem. I. Space Group P1̄

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A unified algebraic approach to the phase problem is described, which, under certain limitations, yields explicit formulas for determining the sign of any structure factor. Some of these formulas correspond to those previously derived and throw additional light on them, while others provide a useful addendum to these relations. The unified algebraic approach provides, in general, a basis for deriving phase-determining relations in all the space groups.

1. Introduction

Probability methods utilizing the concept of the joint distribution yield formulas which lead to procedures for phase determination in the centrosymmetric space groups (Hauptman & Karle, 1953 (Monograph I)), and in those non-centrosymmetric space groups (Karle & Hauptman, 1956) which are characterized by having all components of the seminvariant modulus (Hauptman & Karle, 1956) equal to two. For certain structure seminvariants these methods also prove useful in some of the remaining space groups. However we have been unable, by means of the joint probability distribution, to obtain formulas for the remaining structure

seminvariants. We have therefore found it necessary to attack the problem from a different point of view which complements the probability approach and throws additional light on the probability formulas already obtained.

The present algebraic approach is based on a formula for the product of an arbitrary number of suitably normalized structure factors. An algebraic approach has been foreshadowed by Hughes (1953) and by Bullough & Cruickshank (1955) in their derivations of certain phase-determining formulas. Our present approach is a unified one in that it can be applied to all the space groups, non-centrosymmetric as well as centrosymmetric. In a forthcoming publication (Karle

& Hauptman, 1957) the application to space group $P1$ will be described in detail. In addition, not only does the method corroborate the probability formulas already obtained, but it leads to many new and important relationships in these same space groups. It is also shown by these algebraic methods that, under special circumstances, the results of the probability theory are not merely probably correct but are in fact exactly true. At the same time these methods also clearly show to what extent the simple phase-determining formulas might be adversely affected by special arrangements of the atoms in any space group.

The formulas to be derived in this paper have exact validity only in the case that the structure consists of N identical point atoms. This restriction, however, is easily removed. In fact the joint distribution will play an important role in modifying these relationships for the case of unequal atoms. However, we defer the treatment of unequal atoms and special positions to forthcoming publications. This permits the presentation of the present results in their simplest forms.

2. Phase-determining formulas

We list here for convenience all formulas derived in this paper which will be seen to include and supplement those described in our Monograph I.

$$E_{2\mathbf{h}} = -N^{3/2}\langle(E_{\mathbf{k}}^2-1)(E_{\mathbf{h}+\mathbf{k}}^2-1)\rangle_{\mathbf{k}}+2N^{1/2}(E_{\mathbf{h}}^2-1). \quad (2\cdot1)$$

$$E_{\mathbf{h}}E_{\mathbf{h}_1}E_{\mathbf{h}+\mathbf{h}_1} = \frac{N^{3/2}}{8}\langle(E_{\mathbf{k}}^2-1)(E_{\mathbf{h}'+\mathbf{k}}^2-1)(E_{\mathbf{h}+\mathbf{h}_1+\mathbf{k}}^2-1)\rangle_{\mathbf{k}}$$

$$+\frac{1}{N^{1/2}}(E_{\mathbf{h}}^2+E_{\mathbf{h}_1}^2+E_{\mathbf{h}+\mathbf{h}_1}^2-2)$$

$$+\frac{1}{2N^{1/2}}(E_{\mathbf{h}}E_{\mathbf{h}+2\mathbf{h}_1}+E_{\mathbf{h}_1}E_{\mathbf{h}_1+2\mathbf{h}}+E_{\mathbf{h}+\mathbf{h}_1}E_{\mathbf{h}-\mathbf{h}_1})$$

$$-\frac{1}{N}(E_{2\mathbf{h}}+E_{2\mathbf{h}_1}+E_{2(\mathbf{h}+\mathbf{h}_1)}), \quad \mathbf{h}' = \mathbf{h} \text{ or } \mathbf{h}_1. \quad (2\cdot2)$$

$$\left(E_{\mathbf{h}}^2-\frac{1}{2}+\frac{2}{N}\right)E_{2\mathbf{h}}$$

$$= \frac{N^{3/2}}{8}\langle(E_{\mathbf{k}}^2-1)(E_{\mathbf{h}+\mathbf{k}}^2-1)(E_{2\mathbf{h}+\mathbf{k}}^2-1)\rangle_{\mathbf{k}}$$

$$+\frac{1}{N^{1/2}}(2E_{\mathbf{h}}^2+E_{2\mathbf{h}}^2-2)+\frac{1}{N^{1/2}}E_{\mathbf{h}}E_{3\mathbf{h}}-\frac{1}{N}E_{4\mathbf{h}}. \quad (2\cdot2a)$$

$$E_{2\mathbf{h}} = N\langle E_{2\mathbf{k}}(E_{\mathbf{h}+\mathbf{k}}^2-1)\rangle_{\mathbf{k}}. \quad (2\cdot3)$$

$$E_{\mathbf{h}}E_{\mathbf{h}_1} = \frac{N}{2}\langle E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}_1\pm\mathbf{k}}(E_{\mathbf{k}}^2-1)\rangle_{\mathbf{k}}$$

$$+\frac{3}{4N^{1/2}}(E_{\mathbf{h}+\mathbf{h}_1}+E_{\mathbf{h}-\mathbf{h}_1}). \quad (2\cdot4)$$

$$E_{\mathbf{h}}E_{\mathbf{h}_1} = \frac{N}{2}\langle E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}_1+\mathbf{k}}(E_{\mathbf{k}}^2-1)\rangle_{\mathbf{k}}$$

$$+\frac{1}{2N^{1/2}}E_{\mathbf{h}+\mathbf{h}_1}+\frac{1}{N^{1/2}}E_{\mathbf{h}-\mathbf{h}_1}. \quad (2\cdot4a)$$

$$E_{\mathbf{h}}E_{\mathbf{h}_1} = \frac{N}{2}\langle E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}_1-\mathbf{k}}(E_{\mathbf{k}}^2-1)\rangle_{\mathbf{k}}$$

$$+\frac{1}{N^{1/2}}E_{\mathbf{h}+\mathbf{h}_1}+\frac{1}{2N^{1/2}}E_{\mathbf{h}-\mathbf{h}_1}. \quad (2\cdot4b)$$

$$E_{\mathbf{h}} = N\langle E_{\mathbf{h}+2\mathbf{k}}(E_{\mathbf{h}+\mathbf{k}}^2-1)\rangle_{\mathbf{k}}. \quad (2\cdot3a)$$

$$E_{\mathbf{h}} = N^{1/2}\langle E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle_{\mathbf{k}}. \quad (2\cdot5)$$

$$\langle E_{\mathbf{k}}^2\rangle_{\mathbf{k}} = 1. \quad (2\cdot5a)$$

Of these formulas, $(2\cdot1)$ has been previously derived by Cochran (1954) and $(2\cdot5)$ by Hughes (1953) (although the latter was foreshadowed by Sayre (1952)). Equation $(2\cdot5a)$ is the case $\mathbf{h} = 0$ of $(2\cdot5)$. Equation $(2\cdot3)$ has already been used, but not in this exact form, in our Monograph I (1953). The remaining equations are new, although Vaughan (1956) has obtained, by means of the Patterson superposition method, an approximate formula which resembles $(2\cdot2)$. Equation $(2\cdot2a)$ is obtained from $(2\cdot2)$ by setting $\mathbf{h}_1 = \mathbf{h}$. Equation $(2\cdot4)$ is an obvious consequence of $(2\cdot4a)$ and $(2\cdot4b)$, while $(2\cdot3)$ is derivable from $(2\cdot3a)$. It is to be emphasized that, under hypotheses to be stated, these formulas are exact, not merely probable, relationships among the structure factors.

3. Analysis

3·1. The preliminary formulas

We start with the definition of the normalized structure factor $E_{\mathbf{h}}$ for $P\bar{1}$ (Monograph I, 1953, equation $(3\cdot14)$).* If there are N point atoms per unit cell with no atom at a special position, this reduces to

$$E_{\mathbf{h}} = \frac{2}{N^{1/2}}\sum_{j=1}^{N/2}\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j, \quad (3\cdot01)$$

where $\mathbf{r}_j$ is the position vector of the jth atom. Equation $(3\cdot01)$ is the case $q = 1$ of the more general definition

$$E_{\mathbf{h}_1\mathbf{h}_2\ldots\mathbf{h}_q} = \frac{2^q}{N^{q/2}}\sum_{\substack{j_1+j_2+\ldots+j_q \\ 1}}^{N/2}\prod_{i=1}^{q}\cos 2\pi\mathbf{h}_i\cdot\mathbf{r}_{j_i}. \quad (3\cdot02)$$

Employing $(3\cdot01)$ to compute $E_{\mathbf{h}_1}E_{\mathbf{h}_2}$ and $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$, we readily derive in turn the two preliminary formulas

$$E_{\mathbf{h}_1\mathbf{h}_2} = E_{\mathbf{h}_1}E_{\mathbf{h}_2}-\frac{1}{N^{1/2}}(E_{\mathbf{h}_1+\mathbf{h}_2}+E_{\mathbf{h}_1-\mathbf{h}_2}), \quad (3\cdot03)$$

---

* In practice $E_{\mathbf{h}}$ is obtained from $F_{\mathbf{h}}$ by means of $E_{\mathbf{h}} = F_{\mathbf{h}}\Big/\Big(\sum_{j=1}^{N}f_{j\mathbf{h}}^2\Big)^{\frac{1}{2}}$, where $F_{\mathbf{h}}$ is the crystal structure factor and $f_{j\mathbf{h}}$ is the atomic scattering factor.

$$E_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} = E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3} - \frac{1}{N^{1/2}}(E_{\mathbf{h}_1+\mathbf{h}_2}E_{\mathbf{h}_3} + E_{\mathbf{h}_1-\mathbf{h}_2}E_{\mathbf{h}_3}$$
$$+ E_{\mathbf{h}_1+\mathbf{h}_3}E_{\mathbf{h}_2} + E_{\mathbf{h}_1-\mathbf{h}_3}E_{\mathbf{h}_2} + E_{\mathbf{h}_2+\mathbf{h}_3}E_{\mathbf{h}_1} + E_{\mathbf{h}_2-\mathbf{h}_3}E_{\mathbf{h}_1})$$
$$+ \frac{2}{N}(E_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3} + E_{\mathbf{h}_1+\mathbf{h}_2-\mathbf{h}_3} + E_{\mathbf{h}_1-\mathbf{h}_2+\mathbf{h}_3} + E_{\mathbf{h}_1-\mathbf{h}_2-\mathbf{h}_3}) .$$
$$(3\cdot04)$$

3·2. The final formulas

We prove in detail only the typical formula (2·4a) and merely indicate the proofs of the remaining equations.

From (3·01) we find

$$\overset{4}{\underset{i=1}{\Pi}} E_{\mathbf{h}_i} = \frac{16}{N^2} \overset{N/2}{\underset{j,\,j',\,j'',\,j'''}{\Sigma}} \cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_{j'}$$
$$\times \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_{j''} \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j'''} \quad (3\cdot05)$$
$$= R_1 + R_2 + R_2' + R_3 + R_4 , \quad (3\cdot06)$$

where

$$R_1 = \frac{16}{N^2} \overset{N/2}{\underset{j=1}{\Sigma}} \cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_j$$
$$\times \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_j , \quad (3\cdot07)$$

$$R_2 = \frac{16}{N^2} \overset{N/2}{\underset{j\neq j'}{\Sigma}} \{\cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_j$$
$$\times \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j'} + 3 \text{ similar terms} \} , \quad (3\cdot08)$$

$$R_2' = \frac{16}{N^2} \overset{N/2}{\underset{j\neq j'}{\Sigma}} \{\cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_{j'}$$
$$\times \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j'} + 2 \text{ similar terms} \} , \quad (3\cdot09)$$

$$R_3 = \frac{16}{N^2} \overset{N/2}{\underset{j\neq j'\neq j''}{\Sigma}} \{\cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_{j'}$$
$$\times \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j''} + 5 \text{ similar terms} \} , \quad (3\cdot10)$$

$$R_4 = \frac{16}{N^2} \overset{N/2}{\underset{j\neq j'\neq j''\neq j'''}{\Sigma}} \cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_2 \cdot \mathbf{r}_{j'}$$
$$\times \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_{j''} \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j'''} . \quad (3\cdot11)$$

By elementary trigonometric manipulations it is easily verified that

$$R_1 = \frac{2}{N^2} \overset{N/2}{\underset{j=1}{\Sigma}} \{\cos 2\pi(\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3+\mathbf{h}_4) \cdot \mathbf{r}_j + \dots$$
$$+ \cos 2\pi(\mathbf{h}_1-\mathbf{h}_2-\mathbf{h}_3-\mathbf{h}_4) \cdot \mathbf{r}_j \} , \quad (3\cdot12)$$

$$R_2 = \frac{4}{N^2} \overset{N/2}{\underset{j\neq j'}{\Sigma}} \{[\cos 2\pi(\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3) \cdot \mathbf{r}_j + \dots$$
$$+ \cos 2\pi(\mathbf{h}_1-\mathbf{h}_2-\mathbf{h}_3) \cdot \mathbf{r}_j] \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j'}$$
$$+ 3 \text{ similar terms} \} , \quad (3\cdot13)$$

$$R_2' = \frac{4}{N^2} \overset{N/2}{\underset{j\neq j'}{\Sigma}} \{[\cos 2\pi(\mathbf{h}_1+\mathbf{h}_2) \cdot \mathbf{r}_j + \cos 2\pi(\mathbf{h}_1-\mathbf{h}_2) \cdot \mathbf{r}_j]$$
$$\times [\cos 2\pi(\mathbf{h}_3+\mathbf{h}_4) \cdot \mathbf{r}_{j'} + \cos 2\pi(\mathbf{h}_3-\mathbf{h}_4) \cdot \mathbf{r}_{j'}]$$
$$+ 2 \text{ similar terms} \} , \quad (3\cdot14)$$

$$R_3 = \frac{8}{N^2} \overset{N/2}{\underset{j\neq j'\neq j''}{\Sigma}} \{[\cos 2\pi(\mathbf{h}_1+\mathbf{h}_2) \cdot \mathbf{r}_j$$
$$+ \cos 2\pi(\mathbf{h}_1-\mathbf{h}_2) \cdot \mathbf{r}_j] \cos 2\pi\mathbf{h}_3 \cdot \mathbf{r}_{j'}$$
$$\times \cos 2\pi\mathbf{h}_4 \cdot \mathbf{r}_{j''} + 5 \text{ similar terms} \} . \quad (3\cdot15)$$

Next we specialize (3·06) by means of the substitutions

$$\mathbf{h}_1 \to \mathbf{h}-\mathbf{k}, \quad \mathbf{h}_2 \to \mathbf{h}_1-\mathbf{k}, \quad \mathbf{h}_3 \to \mathbf{k}, \quad \mathbf{h}_4 \to \mathbf{k} , \quad (3\cdot16)$$

and average both sides over all vectors $\mathbf{k}$. By imposing the condition that no four different vectors $\mathbf{r}_j, \mathbf{r}_{j'}, \mathbf{r}_{j''}, \mathbf{r}_{j'''}$ in the asymmetric unit be rationally dependent,* i.e. that there exist no four integers m_i, $i = 1, 2, 3, 4$, not all zero, such that

$$m_1\mathbf{r}_j + m_2\mathbf{r}_{j'} + m_3\mathbf{r}_{j''} + m_4\mathbf{r}_{j'''} = \mathbf{r} , \quad (3\cdot17)$$

where the three components of $\mathbf{r}$ are integers, it is readily verified that

$$\langle R_2\rangle_\mathbf{k} = \langle R_3\rangle_\mathbf{k} = \langle R_4\rangle_\mathbf{k} = 0 . \quad (3\cdot18)$$

Furthermore, it is easily seen that

$$\langle R_1\rangle_\mathbf{k} = \frac{2}{N^2} \overset{N/2}{\underset{j=1}{\Sigma}} \{\cos 2\pi(\mathbf{h}+\mathbf{h}_1) \cdot \mathbf{r}_j + 2 \cos 2\pi(\mathbf{h}-\mathbf{h}_1) \cdot \mathbf{r}_j \} , \quad (3\cdot19)$$

and

$$\langle R_2'\rangle_\mathbf{k} = \frac{4}{N^2} \overset{N/2}{\underset{j\neq j'}{\Sigma}} \{\cos 2\pi(\mathbf{h}_1-\mathbf{h}_2) \cdot \mathbf{r}_j$$
$$+ 2 \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j \cos 2\pi\mathbf{h}_1 \cdot \mathbf{r}_{j'} \} . \quad (3\cdot20)$$

Substituting these values of $\langle R_1\rangle_\mathbf{k}$, $\langle R_2\rangle_\mathbf{k}$, $\langle R_2'\rangle_\mathbf{k}$, $\langle R_3\rangle_\mathbf{k}$, $\langle R_4\rangle_\mathbf{k}$ into (3·06), employing (3·01) and (3·03), and solving for $E_\mathbf{h}E_{\mathbf{h}_1}$, we find

$$E_\mathbf{h}E_{\mathbf{h}_1} = \frac{N}{2} \langle E_{\mathbf{h}-\mathbf{k}}E_{\mathbf{h}_1-\mathbf{k}}E_\mathbf{k}^2\rangle_\mathbf{k}$$
$$+ \frac{1}{2N^{1/2}} E_{\mathbf{h}+\mathbf{h}_1} - \frac{N-2}{2N^{1/2}} E_{\mathbf{h}-\mathbf{h}_1} . \quad (3\cdot21)$$

Next, we use (2·5), an immediate consequence of (3·03), to obtain

$$\langle E_{\mathbf{h}-\mathbf{k}}E_{\mathbf{h}_1-\mathbf{k}}(E_\mathbf{k}^2-1)\rangle_\mathbf{k}$$
$$= \langle E_{\mathbf{h}-\mathbf{k}}E_{\mathbf{h}_1-\mathbf{k}}E_\mathbf{k}^2\rangle_\mathbf{k} - \frac{1}{N^{1/2}} E_{\mathbf{h}-\mathbf{h}_1} . \quad (3\cdot22)$$

Finally, substituting from (3·22) into (3·21) and replacing $\mathbf{k}$ by $-\mathbf{k}$, we obtain (2·4a).

In order to prove (2·4b) we make use of the substitutions

$$\mathbf{h}_1 \to \mathbf{h}+\mathbf{k}, \quad \mathbf{h}_2 \to \mathbf{h}_1-\mathbf{k}, \quad \mathbf{h}_3 \to \mathbf{k}, \quad \mathbf{h}_4 \to \mathbf{k} , \quad (3\cdot23)$$

---

* This condition may be replaced by the less stringent requirement that no two position vectors in the asymmetric unit and no two interatomic vectors in the whole unit cell be rationally dependent.

instead of (3·16), in (3·06) and proceed as before.

Equation (2·1) is the special case $\mathbf{h} = \mathbf{h}_1$ of (2·4a).

In order to derive (2·2) we expand $\prod\limits_{i=1}^{6} E_{\mathbf{h}_i}$ as in (3·05)–(3·15) and then specialize the result by means of the substitutions

$$\mathbf{h}_1 \to \mathbf{k}, \ \mathbf{h}_2 \to \mathbf{k}, \ \mathbf{h}_3 \to \mathbf{h}_1 + \mathbf{k}, \ \mathbf{h}_4 \to \mathbf{h}_1 + \mathbf{k},$$
$$\mathbf{h}_5 \to \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{k}, \ \mathbf{h}_6 \to \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{k} . \quad (3·24)$$

If we impose the condition that no six different position vectors be rationally dependent, average over $\mathbf{k}$, and make use of (3·01), (3·03), (3·04), and (2·1), we finally obtain (2·2) after a somewhat lengthy analysis similar to (3·18)–(3·22).

Finally, (2·3a) is derivable by a similar analysis from the product $\prod\limits_{i=1}^{3} E_{\mathbf{h}_i}$.

4. Applications

A procedure for phase determination has already been described in our Monograph I. The formulas here derived are useful in supplementing this procedure in two important ways. First, additional formulas are now available for obtaining the signs of the $E_{2\mathbf{h}}$'s from intensities alone. Secondly, once the sign of an $E_{\mathbf{h}}$, which is linearly independent modulo 2, has been arbitrarily specified, these formulas yield the signs of the E's which are linearly dependent modulo 2 on $E_{\mathbf{h}}$.

While in principle (2·1) yields the sign of $E_{2\mathbf{h}}$, as a practical matter (2·2a) is likely to be more useful. Furthermore, once the signs of several $E_{2\mathbf{h}}$'s have been thus determined, (2·2), (2·3), (2·4), (2·4a), or (2·4b) may be used to obtain the signs of other $E_{2\mathbf{h}}$'s.

Next, once the sign of an $E_{\mathbf{h}}$, linearly independent modulo 2, has been arbitrarily specified, then (2·2), (2·4), (2·4a), or (2·4b) may be used to determine the signs of the remaining E's which are linearly dependent modulo 2 on $E_{\mathbf{h}}$. Naturally, in applying these formulas, use is made of the signs of the $E_{2\mathbf{h}}$'s previously determined. In particular, taking $\mathbf{h} \equiv \mathbf{h}_1$ (mod 2) in (2·4), (2·4a), and (2·4b), $\mathbf{k}$ ranges over all vectors such that $\mathbf{k} \equiv \mathbf{h} \equiv \mathbf{h}_1$ (mod 2). Of course, in order to fix the origin uniquely, the signs of three structure factors, constituting a linearly independent set modulo 2 (Monograph I), must be specified arbitrarily.

Finally, as in our Monograph I, once a sufficient number of signs has been thus determined, (2·3a) and (2·5) are used to determine the remaining signs.

5. Concluding remarks

Although the averages appearing in the formulas of § 2 are to be taken over all vectors $\mathbf{k}$, it is clear that

in practice these averages must be computed from a finite sample. Naturally, the question concerning the reliability of the means so computed is important and merits further study. In this way standards of significance may be set up and suitable levels of rejection can be established.

In this paper the algebraic method has been applied to products up to the sixth order. However, it is apparent that the same procedures may be applied to higher-order products and may conceivably lead to more powerful formulas. For example a formula for $E_{2\mathbf{h}}^3$ may be contained within the tenth-order product.

Except for (2·2) and (2·2a), which require that no six position vectors be rationally dependent, all our formulas have exact validity provided that no four position vectors be rationally dependent (see (3·17)). Even if this requirement is only approximately fulfilled it is clear that these formulas have approximate validity and are useful for determining phases. It should be noted that the requirement that no four position vectors be rationally dependent implies that no two interatomic vectors coincide and that no atom have three rational coordinates, in particular that no atom occupy a special position.

Our formulas imply that a structure consisting of N identical point atoms is uniquely determined by the magnitudes of its structure factors provided that no four position vectors are rationally dependent. In short we have proven the following:

THEOREM.—A centrosymmetric structure consisting of N identical point atoms per unit cell and such that no four position vectors in the asymmetric unit are rationally dependent has no centrosymmetric homometric mate (Patterson, 1944).

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