

where E is the structure factor on a scale $\langle E^2 \rangle = 1$.

Turning first to Σ_1 : it is immediately apparent that this is equivalent to the coefficient of a sharpened Patterson with the peak at the origin removed. It is well known that a Patterson of a structure having a center of symmetry contains a set of 'rotational' peaks corresponding to the vectors *across* the center of symmetry. These peaks correspond to an image of the structure on twice the scale. A detailed calculation (Vand & Pepinsky, 1953, 1954) indicates that the Hauptman-Karle statistical formulae are simply making use of the above property of the Patterson function in order to obtain the bias for the probability of sign of a structure factor. It unfortunately follows that when the statistical formulae are used *jointly*, nothing else than a Patterson is obtained, *whatever the number of structure factors used*. Therefore the solution converges to the highest peaks of the Patterson, and the statistical method becomes successful only when the highest peaks of the Patterson resemble the image of the structure on twice the scale. This seldom occurs in practice, however, since the wanted *rotational* peaks have half the weight of the *non-rotational* peaks. It follows that the only structures which can be solved in space group $P\bar{1}$ are those with two atoms per cell. We have tried to apply the method to a four-atom structure, and have obtained—as theoretically predicted—an incorrect solution resembling the Patterson rather than the structure itself.

Turning now to Σ_4 : we see that this is equivalent to a convolution in reciprocal space, and therefore to a product in Patterson space. This product turns out to be nothing else than a square of Patterson density. This sharpens the Patterson peaks, but brings out the unwanted peaks much higher than the wanted rotational peaks. It therefore can be concluded that if Σ_1 leads jointly to an incorrect structure, then Σ_4 certainly leads jointly to an incorrect structure. The claim that the formulae represent a solution for the space group $P\bar{1}$ is therefore fallacious.

The above considerations need to be modified when other elements of symmetry are present. We have shown (Vand & Pepinsky, 1953) that the statistical formulae then become equivalent to Patterson-Harker sections. If these sections resemble the image of the structure on twice the scale, the statistical formulae become successful; but the Harker sections then become so, too. This is the case with naphthalene, used as an example of the power of their method by Hauptman & Karle. In this respect, their method does not represent anything of greater power

than that of previously known methods. On the contrary, the intelligent use of Harker maps permits one to distinguish and allow for non-Harker peaks, whereas the statistical method conceals their influence in the mathematics involved.

This note is not meant to belittle entirely the value of the formulae derived by Hauptman & Karle. In fact, their approach has led us to derivations of maps which are superior to Harker maps for the purposes of structure determination. For example, one of the functions for space group $P2_1/c$ is a map having

$$U_{2h,0,2l} \sum_k (-1)^{k+l} (E_{hkl}^2 - 1)$$

as Fourier coefficients. This map shows non-Harker peaks considerably suppressed. Details of the derivations and properties of these functions have been made available elsewhere, along with a full account of all the above matters (Vand & Pepinsky, 1953).

Our conclusions are in full agreement with those obtained independently by Cochran & Woolfson (1954), which appear elsewhere in this issue of *Acta Crystallographica*. We are grateful to these authors for permitting us to see their communication before its publication.

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A note on the solution of the phase problem. By H. HAUPTMAN and J. KARLE, *U.S. Naval Research Laboratory, Washington 20, D.C., U.S.A.*

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A routine solution of the phase problem, valid for all 92 centrosymmetric space groups, is described in our Monograph (Hauptman & Karle, 1953). The evidence for its validity we felt was overwhelming. The mathematical development is exact and rigorous, and is not challenged in the above notes (Cochran & Woolfson, 1954; Vand & Pepinsky, 1954). The probability theory yields the correct

structure invariants and seminvariants. The final formulas are capable of independent justification by means of a simple geometric interpretation. Finally, the application of these formulas to the naphthalene structure was successful. We consider this application non-trivial because no advantage was taken of the special properties of this simple structure, and only a small fraction of the

total power of the formulas was used. Owing to the fact that the probability distribution for the normalized structure factor E is always approximately

$$\frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}E^2\right),$$

all structures are equally vulnerable to the attack by probability methods.

In view of these considerations, we looked forward, with the appearance of the Monograph, to a period of cooperation with crystallographers interested in applying the method, since the very essence of the scientific method consists in the direct confrontation of a plausible theory with an experimental problem. Indeed, we have recently enjoyed the privilege of cooperating with Christ, Clark & Evans (1954) in their study of the structure of colemanite, and the successful application of these methods is described in the note which follows.

In view of the successful solution of the colemanite structure, the appearance of the previous two notes is unfortunate since they tend to discourage further applications of method.

With regard to the note of Cochran & Woolfson (1954), there is no logical basis for their interpretation of the validity of our formulas in terms of the Patterson function. Furthermore, while they implicitly admit the existence of a bias in the separate terms of Σ_4 , they conclude that this bias can never be revealed, no matter how many terms Σ_4 may contain. This conclusion contradicts well known laws of probability and is in disagreement with column 5 of Table 14 in the Monograph.

The note of Vand & Pepinsky (1954) is vague and logically disconnected. Their claim that our formulas are approximate is misleading because, as implied on the top of p. 39 of the Monograph, any desired accuracy can be obtained by using a sufficient number of terms in the series expansion of (3.03). Naturally we listed only those terms which in our experience appeared to be required. In any event, it is difficult to understand how more accurate general distributions can be obtained from empirical tables.

Their claim that our formulas are related to the Patterson function in the way they describe has not been justified and, in view of the theoretical derivation and the experimental verification of our formulas, their claim

cannot be justified. Also, it is not at all clear how individual formulas admittedly having the correct bias can lead to incorrect answers when a sufficient number of structure factors are used jointly.

For $P\bar{1}$, it is true that Σ_1 contains only one term, and consequently is unimportant as a phase-determining formula for this space group. For the other space groups, however, Σ_1 contains several terms and is an important phase-determining relation. Thus Σ_1 is included in the formulas for $P\bar{1}$ merely for completeness; the term Σ_4 , which may contain hundreds of terms, is much more important. The terms Σ_2 and Σ_3 are also very important in the intermediate stages of the phase-determining procedure. It is therefore difficult to understand why these terms have been omitted from their consideration while the unimportant Σ_1 occupies a central position in their note. Furthermore, it should be noted that in $P\bar{1}$, Σ_1 and Σ_4 apply only to those structure factors whose indices h, k, l are all even.

The general impression given by the note of Vand & Pepinsky is that our solution of the phase problem 'does not represent anything of greater power than that of previously known methods' (e.g. the use of Harker maps), whereas they claim to have discovered new formulas of greater power. Their example of such a formula is the coefficient of $U_{2h,0,2l}$ in their last equation. They apparently failed to realize that this is identical with our equation (4.41) on p. 63 of the Monograph and has been used by us to help determine the signs of $E_{2h,0,2l}$ for naphthalene. (Note that they refer to $P_{2_1/c}$ instead of our $P_{2_1/a}$.)

In conclusion we would welcome further opportunities to cooperate with other crystallographers in applying these methods to the study of structures in the various centrosymmetric space groups.

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The structure of colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, determined by the direct method of Hauptman & Karle.* By C. L. CHRIST, JOAN R. CLARK and H. T. EVANS, JR., *U.S. Geological Survey, Washington, D.C., U.S.A.*

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The present note describes the preliminary structure of colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, obtained through the use of the direct method of crystal-structure determination given by Hauptman & Karle (1953).

In order to compute the E_{hkl}^2 's required by the method, 3084 F_{hkl}^2 's (including 1056 non-observed F_{hkl}^2 's), obtained by visual estimation, were used to determine the

$K(s)$ curve (Karle & Hauptman, 1953). Using all 3084 E_{hkl}^2 's the signs of the 2028 non-zero F_{hkl} 's were calculated. For 183 (9%) of these non-zero terms the sign was indeterminate. However, only the sums Σ_1 , Σ_2 , and Σ_3 were used in the sign determinations, and only a small percentage of the total available number of contributors to each of these sums was used. It seems clear from this that at least most of the remaining 183 signs could have been obtained using the full power of the method had it been necessary for this preliminary investigation.

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