A WEIGHTING FUNCTION TO RESOLVE THE TWO-FOLD AMBIGUITY IN THE PHASE DETERMINED BY THE ANOMALOUS DISPERSION METHOD IN CRYSTAL STRUCTURE ANALYSIS

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INTRODUCTION

THE importance of the anomalous dispersion method in solving the structure of non-centrosymmetric crystals with suitable heavy atoms has been well recognized in recent years. With a proper choice of the wavelength and heavy atom it is possible to measure the Bijvoet difference of a large number of reflections. It is then possible to determine the phase of a reflection but for a two-fold ambiguity.[1,2] Various methods proposed[1,3] to resolve this ambiguity are (*i*) to use a pair of isomorphous crystals in which the anomalous scatterers form the replaceable group of atoms; (*ii*) to use both the phases and compute a double-phased synthesis. This is the same as the β-anomalous synthesis proposed by Ramachandran and Raman[4]; (*iii*) to use the phase closer to the phase of the heavy-atom contribution to the structure factor. This method has been successfully used by Raman,[5] Dale *et al.*[6] and Chopra *et al.*[7]

However, since the presence of anomalous scatterers (*i.e.*, heavy atoms) in a crystal biases the phase angle distribution to be closer to the heavy atom phase, the double-phased synthesis in which the two ambiguities are given equal weights is not consistent with the statistical theory. So also, the method (*iii*) in which one ambiguity is given unit weight and the other zero weight is also not fully compatible with statistical considerations. Thus, we are naturally led to work out a weighting function in which the two ambiguities are given weights depending on their probabilities of occurrences. Such a weighting function is derived below.

DERIVATION OF THE WEIGHTING FUNCTION

We consider a non-centrosymmetric crystal containing P anomalous scatterers of the same type and Q normal scatterers (*i.e.*, light atoms) in the unit cell. Let N $(= P + Q)$ be the total number of atoms in the unit cell. The two ambiguous phases obtained by the anomalous dispersion method are shown in Fig. 1, in which

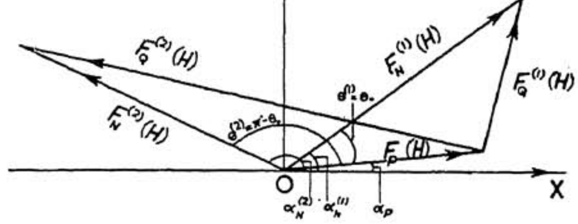

FIG. 1. Argand diagram showing the two-fold ambiguity in the phase determined by the anomalous dispersion method.

θ_0 is the acute one of the two possible values for $\alpha_N - \alpha_P$, which are obtained by solving the triangle for the Bijvoet difference. The other value will obviously be $\pi - \theta_0$. The structure factor equation of a reflection H, corresponding to the two ambiguous values can be written as

$$F_N{}^{(i)}(\mathbf{H}) = F_P(\mathbf{H}) + F_Q{}^{(i)}(\mathbf{H}) \qquad (1)$$

where $i (= 1, 2)$ refers to the ambiguities θ_0 and $\pi - \theta_0$ for $\alpha_N - \alpha_P$. Since the probabilities for the events $F_Q{}^{(i)}$ to occur are known to be[8]

$$P[F_Q{}^{(i)}] = \left(\frac{1}{\pi\sigma_Q{}^2}\right) \exp\left[-\frac{|F_Q{}^{(i)}|^2}{\sigma_Q{}^2}\right] \qquad (2)$$

where

$$\sigma^2{}_Q = \sum_{j=1}^{Q} f_{Qj}{}^2,$$

it is clear from Equations (1) and (2) that the probabilities of occurrence of the events $F_N{}^{(i)}$ for a given F_P, are given by

$$P[F_N{}^{(i)}; F_P] = \left(\frac{1}{\pi\sigma_Q{}^2}\right) \exp\left[-\frac{|F_N{}^{(i)} - F_P|^2}{\sigma_Q{}^2}\right]. \qquad (3)$$

Since $|F_N{}^{(1)}| = |F_N{}^{(2)}| = |F_N|$, say, we can write Equation (3) as

$$P[F_N{}^{(i)}; F_P] = K \exp[-X \cos \theta^{(i)}] \qquad (4)$$

where we have used the simplifying notations

$$K = \left(\frac{1}{\pi\sigma_Q{}^2}\right) \exp\left[-\frac{(|F_N|^2 + |F_P|^2)}{\sigma_Q{}^2}\right]$$

$$X = \frac{2|F_N||F_P|}{\sigma_Q{}^2} \quad \text{and} \quad \theta^{(i)} = \alpha_N{}^{(i)} - \alpha_P. \qquad (5)$$

It is clearly seen that

$$\theta^{(1)} = \theta_0,$$
$$F_N{}^{(1)} = |F_N| \exp i\alpha_N{}^{(1)} = |F_N| \exp i(\alpha_P + \theta_0) \qquad (6a)$$

and

$$\theta^{(2)} = \pi - \theta_0,$$
$$F_N{}^{(2)} = |F_N| \exp i\alpha_N{}^{(2)} = |F_N| \exp. i(\alpha_P + \pi - \theta_0). \qquad (6b)$$

Now, each $F_N{}^{(j)}$ may be weighted with its probability of occurrence, taking the total weight assigned for all events to be unity. The weighted structure factor $F_N{}^W$ will then be given by

$$F_N{}^W = \left\{\frac{\sum_{i=1}^{2} F_N{}^{(i)} P[F_N{}^{(i)}; F_P]}{\sum_{i=1}^{2} P[F_N{}^{(i)}; F_P]}\right\}. \qquad (7)$$

Using Equations (4) and (6) in Equation (7) and simplifying the resulting expression, we get

$$F_N{}^W = [|F_N| \exp i\alpha_P] \times [\cos\theta_0 \tanh(X \cos\theta_0) + i \sin\theta_0]. \qquad (8)$$

Since $|F_N| \exp i\alpha_P$ is the coefficient used in the conventional heavy-atom method, we may write

$$F_N{}^W = W\,|F_N| \exp i\alpha_P \qquad (9)$$

where the weighting function W is given by

$$W = \cos\theta_0 \tanh(X\cos\theta_0) + i \sin\theta_0 = |W| \exp i\alpha_W \qquad (10)$$

where

$$|W| = [\{\cos\theta_0 \tanh(X\cos\theta_0)\}^2 + \sin^2\theta_0]^{\frac{1}{2}}$$

and

$$\alpha_W = \tan^{-1}\left\{\frac{\tan\theta_0}{\tanh(X\cos\theta_0)}\right\}. \qquad (11)$$

This weighting function can be readily computed from the known positions of the anomalous scatterers, the known contents of the unit cell and the measured Bijvoet difference. Since the weighting function derived here is a complex quantity, it leads to a correction in the amplitude as well as a change in the phase of the structure amplitude.

It is obvious that the weighted structure amplitude given by Equation (9) is statistically the best that can be used in a Fourier, making use of anomalous dispersion data. It is also clearly superior to the usual weighted synthesis[9] using only the heavy-atom phase. Investigations regarding the power of this weighting function and details regarding tests of its usefulness will appear elsewhere.

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Note added in proof.—Since this note was sent to press, a short communication by G. A. Sim (*Acta Cryst*, 1964, 17, 1072) has come to the attention of the authors in which similar results have been derived.

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