conventional standards. Since these data are the justification for everything else, they should be easily accessible to the reader.

(*b*) The $(\Delta F)^2$ difference Patterson map for *each* derivative used, whether it was interpretable by itself or not. The map should have marked on it the locations of the vectors expected from the heavy atom sites as finally adopted.

(*c*) A summary of the manner in which the heavy atom sites were deciphered, and in particular how those derivatives whose difference Patterson maps were uninterpretable in isolation were pulled into the analysis.

(*d*) ΔF difference maps for each derivative using phases or signs obtained from other unrelated derivatives. The parameters of these derivatives should be as they were before any refinement in combination with the derivative in question.

(*e*) Mean figures of merit and other refinement criteria such as the Kraut R factor for each derivative separately (or for pairs of derivatives in three dimensions), and for the final combination of all derivatives before and after refinement.

(*f*) Commentary on any unusual features of the refinement, such as the previously mentioned wiping out of the erronium site, which would permit one to judge the derivatives.

The opportunities for self-deception in a low resolution analysis are limitless. If the fundamental difference Patterson maps are interpretable, then their publication should be a matter of record. If some are *not* interpretable, and if the derivatives are used in the phase analysis, then publication of the maps becomes a matter of obligation. Enough supplementary information should then be provided to convince the average crystallographer that the derivatives are valid *in spite of* the uninterpretability of the difference Patterson maps. In view of the difficulties of interpreting the final structure, the onlooker may legitimately ask, 'If you don't know where you are going, how do you know when you are there?' The only answer is that the course of analysis must be so transparent and so obvious that *any* end product, no matter how unexpected in appearance, will be accepted.

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The Effect of Errors in the Intensities on the Phase Angles Determined by the Isomorphous Replacement Method

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Expressions are derived to estimate the error in phase angle α determined by the isomorphous replacement method due to the systematic and random errors in the intensities. When α is small, the error in α is fairly large whereas when α approaches 90°, the error is small and reasonably constant. This is compared with the case of phases obtained by the anomalous dispersion method.

The evaluation of phases by the isomorphous replacement method requires the intensities in absolute values. However, in practice there are always some errors: systematic ones like scale factor, absorption *etc.*, and random errors which occur during the estimation of the intensities. But it is possible to examine the problem analytically and arrive at the magnitude of errors that can occur in the determined phase angles as attempted here.

We take two isomorphous crystals in which the replaceable groups are centrosymmetrically related in pairs. Let F_1 and F_2 be the structure factors of a particular reflexion (hkl) for these two crystals. Now we know that

$$F_1^2 = F_2^2 + (\Delta F)^2 + 2F_2\Delta F \cos\alpha\,, \tag{1}$$

where α is the phase angle attached to $|F_2|$ and ΔF is the difference between the contributions of the replaceable group to F_1 and F_2.

Random errors

Now from the law of variances,

$$\sigma^2(\cos\alpha) = \left[\left(\frac{\partial\cos\alpha}{\partial F_1}\right)^2 \sigma^2(F_1) + \left(\frac{\partial\cos\alpha}{\partial F_2}\right)^2 \sigma^2(F_2)\right] \tag{2}$$

and the variance

$$\sigma(\alpha) = -\sigma(\cos\alpha)/\sin\alpha \tag{3}$$

where $\sigma(F_1)$ and $\sigma(F_2)$ are the variances in F_1 and F_2.

Now from (1) we get

$$\frac{\partial\cos\alpha}{\partial F_1} = \frac{F_1}{F_2}\cdot\frac{1}{\Delta F} \tag{4}$$

and

$$\frac{\partial\cos\alpha}{\partial F_2} = -\left(\frac{F_2+\Delta F\cos\alpha}{F_2\,.\,\Delta F}\right). \tag{5}$$

Substituting (4) and (5) in (2) and (3) we get

$$\sigma^2(\alpha) = \frac{F_1^2}{(\Delta F\sin\alpha)^2}\left(\frac{F_1^2}{F_2^2}\,\frac{\sigma^2(F_1)}{F_1^2} + \frac{(F_2+\Delta F\cos\alpha)^2}{F_1^2}\,\frac{\sigma^2(F_2)}{F_2^2}\right). \tag{6}$$

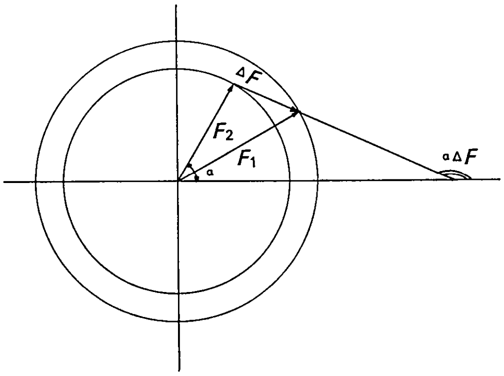

Fig. 1. Diagram for case of non-centrosymmetrically disposed replaceable groups.

Thus knowing the ratios $\sigma(F_1)/F_1$ and $\sigma(F_2)/F_2$ it is possible to estimate $\sigma(\alpha)$. In order to analyse the variation of $\sigma(\alpha)$ with α, we make the assumption that $\sigma(F_1)/F_1 \simeq \sigma(F_2)/F_2$ and that they are equal to ε. Then

$$\sigma^2(\alpha) = \frac{\varepsilon^2 F_1^2}{(\Delta F\sin\alpha)^2}\left[\left(\frac{F_1}{F_2}\right)^2 + \left(\frac{F_2+\Delta F\cos\alpha}{F_1}\right)^2\right]. \tag{7}$$

Now it is clear that when α is very small $\sigma(\alpha)$ is fairly large, while when α approaches 90°, $\sigma(\alpha)$ is small and could be estimated.

Systematic errors

Let K_1F_1 and K_2F_2 be the absolute values. Then

$$K_1^2F_1^2 = K_2^2F_2^2 + (\Delta F)^2 + 2K_2F_2\Delta F\cos\alpha\,; \tag{8}$$

on differentiating K_1 and K_2 with respect to α, we get

$$2K_2F_2F_1^2K_1\frac{dK_1}{d\alpha} = F_2[2F_2^2K_2^2 + 2K_2F_2\Delta F\cos\alpha]\frac{dK_2}{d\alpha} - 2K_2^2F_2^2\Delta F\sin\alpha\,. \tag{9}$$

Substituting (8) in (9) we get

$$2K_2F_2F_1^2K_1\frac{dK_1}{d\alpha} = F_2[K_2^2F_2^2 + K_1^2F_1^2 - (\Delta F)^2]\frac{dK_2}{d\alpha} - 2K_2^2F_2^2\Delta F\sin\alpha\,. \tag{10}$$

i.e.

$$2K_2F_2\Delta F\sin\alpha d\alpha = \left(\frac{dK_2}{K_2}\right)[K_2^2F_2^2 + K_1^2F_1^2 - (\Delta F)^2] - \left(\frac{dK_1}{K_1}\right)2K_1^2F_1^2\,. \tag{11}$$

Thus, knowing the values (dK_1/K_1) and (dK_2/K_2) we can estimate $d\alpha$ the error in α. Here also we notice that as in random errors when α is small $d\alpha$ is quite large, whereas when α approaches 90° $d\alpha$ is reasonably small and fairly constant.

This analysis makes it clear that the 'danger zone' is in the region of small values of α and this is in perfect accordance with the earlier findings (Amirthalingam & Grant, 1963) in the case of the anomalous dispersion method where the 'danger zone' is found to be when α is nearing 90°, because the already known vector ΔF here is normal to ΔB of the latter case.

In a similar fashion, expressions are derived for random and systematic errors for the general case when the replaceable groups are non-centrosymmetrically disposed. The $\sin\alpha$ and $\cos\alpha$ in (7) and (11) are now replaced by $\sin\theta$ and $\cos\theta$ where $\theta = (\alpha_{\Delta F} - \alpha)$; $\alpha_{\Delta F}$ being the phase angle attached to ΔF (see Fig. 1).

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