Acta Cryst. (1974). A30, 574

A Note on the Probability Distribution of Phases in a Non-centrosymmetric Crystal with a Degree of Centrosymmetry*

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(*Received* 18 *March* 1974; *accepted* 21 *March* 1974)

The probability distribution of the magnitude of the phase angles in a non-centrosymmetric crystal with a degree of centrosymmetry is worked out for a structure with similar atoms. Curves showing the probable fractional number of reflexions for which the magnitude of the phase angles would deviate from the centrosymmetric values of 0 or π by any given amount α_0 are also obtained for crystals with different degrees of centrosymmetry.

In a recent paper the probability distribution of X-ray intensities in a non-centrosymmetric crystal (containing a large number of atoms of similar scattering power) with a degree of centrosymmetry† has been worked out (Parthasarathy & Parthasarathi, 1974, hereafter referred to as PP, 1974). In this note we shall study the probability distribution of the phase angles (denoted by α) of structure factors in such a crystal. This study is interesting, since of the amplitude and phase, the latter plays the dominant role in building up the maxima of the electron density distribution at the atomic sites in a Fourier synthesis (Ramachandran & Srinivasan, 1970). The theoretical distribution of α obtained here also enables one to study quantitatively the effect of the degree of centrosymmetry on the distribution of phase angles.

Derivation of the probability distribution of α

The probability distribution of the phase angle α could be obtained from the joint distribution of the normalized structure amplitude y and α derived in the earlier paper (PP, 1974). Thus from equation (13) of PP (1974) we obtain

$$P(\alpha)=\int_0^\infty \exp\left[-y^2\left(\frac{1-D\cos 2\alpha}{1-D^2}\right)\right]\frac{y\mathrm{d}y}{\pi\sqrt{1-D^2}}$$

$$=\frac{\sqrt{1-D^2}}{2\pi(1-D\cos 2\alpha)}, \quad -\pi<\alpha<\pi \qquad (1)$$

where

$$D=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}\rangle\,. \qquad (2)$$

Since (1) is an even function of α, the probability density function of the magnitude of α will be given by

$$P(|\alpha|)=\frac{\sqrt{1-D^2}}{\pi(1-D\cos 2\alpha)}, \quad 0<\alpha\leq\pi. \qquad (3)$$

From (3) we obtain the cumulative function of $|\alpha|$ to be

$$N(|\alpha|)=\frac{1}{\pi}\sin^{-1}\left\{\sqrt{\frac{(1+D)\sin^2\alpha}{1-D\cos 2\alpha}}\right\} \text{ for } \alpha\leq\pi/2$$

$$=1-\frac{1}{\pi}\sin^{-1}\left\{\sqrt{\frac{(1+D)\sin^2\alpha}{1-D\cos 2\alpha}}\right\} \text{ for } \alpha>\pi/2\,. \qquad (4)$$

Discussion of the results

It is known that for a crystal containing a large number of similar atoms the phases of the structure factors of reflexions follow a uniform distribution in the range $-\pi$ to π if the crystal is ideally non-centrosymmetric (abbreviated by the symbol *NC*), and if the crystal is ideally centrosymmetric (abbreviated by the symbol *C*) the phases are equally likely to be either 0 or π. Thus the distribution of the magnitude of the phase angle will be given by [see equation (30) of Parthasarathy, 1965]

$$P(|\alpha|)=\frac{1}{\pi}\,, \quad 0\leq\alpha\leq\pi \text{ for } NC$$

$$=\tfrac{1}{2}\delta(\alpha)+\tfrac{1}{2}\delta(\alpha-\pi) \text{ for } C\,. \qquad (5)$$

It would be interesting to study in the present *NC'* case the fraction of reflexions for which $|\alpha|$ deviates much from the centrosymmetric values of 0 or π, for example the fraction of reflexions for which $|\alpha|$ takes values in the range 30 to 150°. The relevant quantity for this study is therefore the probability that the phase-angle magnitude takes a value in the interval $(\alpha_0,\pi-\alpha_0)$ (where α_0 is an acute angle) and we shall denote this by Pr $(\alpha_0,\pi-\alpha_0)$. From the symmetry of the $P(\alpha)$ curve about $\alpha=\pi/2$ it can be readily shown from (3) and (4) that

$$\Pr(\alpha_0,\pi-\alpha_0)=\int_{\alpha_0}^{\pi-\alpha_0}P(|\alpha|)\mathrm{d}\alpha=1-2N(\alpha_0)$$

$$=1-\frac{2}{\pi}\sin^{-1}\left\{\sqrt{\frac{(1+D)\sin^2\alpha_0}{1-D\cos 2\alpha_0}}\right\},$$

$$0\leq\alpha_0\leq\pi/2\,. \qquad (6)$$

* Contribution No. 374 from the Centre of Advanced Study in Physics, University of Madras, Madras-600025, India.

† This type of crystal is denoted by the symbol *NC'* in this note.

It is seen that (6) leads to the expected results, namely, Pr $(\alpha_0, \pi-\alpha_0)=1$ and 0 when $\alpha_0=0$ and $\pi/2$ respectively. For $D=0$ (*i.e.* large $\langle|\Delta\mathbf{r}|\rangle$) (6) leads to the result

$$\Pr(\alpha_0, \pi-\alpha_0)=1-\frac{2}{\pi}\alpha_0 \qquad (7)$$

which is to be expected for the *NC* case in view of the uniform distribution of phase angles [see equation (5)].

The probability functions $P(|\alpha|), N(|\alpha|)$ and Pr $(\alpha_0, \pi-\alpha_0)$ all depend on the parameter D which in turn is a function of the magnitude $H(=2\sin\theta/\lambda)$ of the position vector of the reciprocal-lattice points and the quantity $\langle|\Delta\mathbf{r}|\rangle$ defining the degree of centrosymmetry *via* the relation (Luzzati, 1952)

$$D=\exp\left[-\frac{\pi^3}{4}H^2\langle|\Delta\mathbf{r}|\rangle^2\right]. \qquad (8)$$

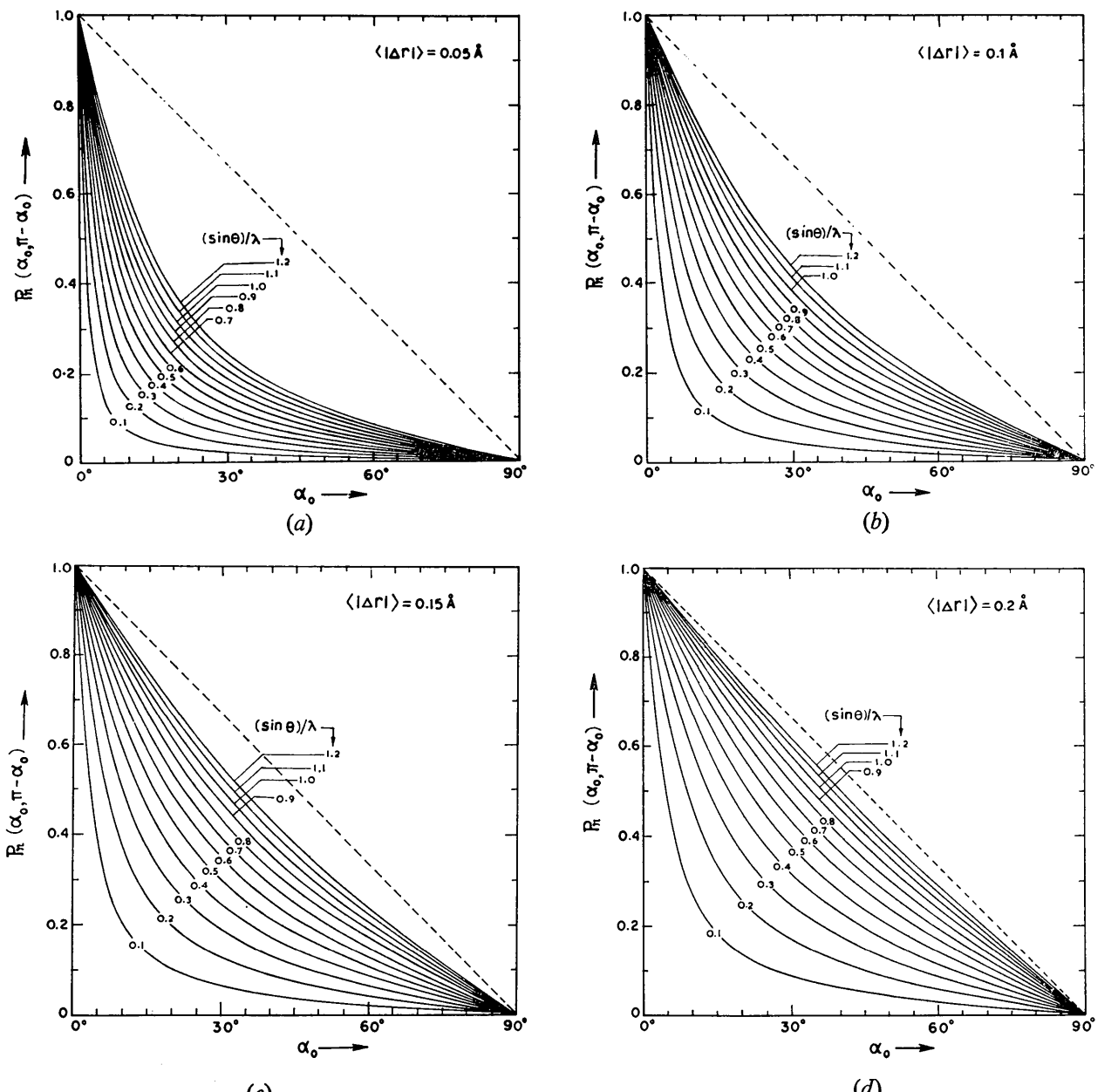

Fig. 1. Fractional number of reflexions Pr $(\alpha_0, \pi-\alpha_0)$ for which the magnitude of the phase angles lie in the range α_0 to $\pi-\alpha_0$ as a function of α_0 for crystals with different degree of centrosymmetry. (*a*) to (*d*) correspond to the cases with $\langle|\Delta r|\rangle=0{\cdot}05$, 0·1, 0·15 and 0·2 Å respectively. The number near each curve denotes the value of (sin θ)/λ. The dotted line corresponds to the ideally non-centrosymmetric (*NC*) case.

The functional dependence of $\Pr(\alpha_0, \pi-\alpha_0)$ on α_0 is shown in Fig. 1 (*a* to *d*) for $(\sin\theta)/\lambda = 0{\cdot}1, 0{\cdot}2, \ldots 1{\cdot}2$ when $\langle|\Delta\mathbf{r}|\rangle$ has values 0·05, 0·10, 0·15 and 0·2 Å respectively.

The following points may be noted for making use of Fig. 1 in actual cases: (i) The value of $\Pr(\alpha_0, \pi-\alpha_0)$ read from a *given* curve corresponding to a *given* value of $(\sin\theta)/\lambda$ represents the fraction with reference to reflexions in that range of $(\sin\theta)/\lambda$. Thus for example, if n denotes the total number of reciprocal-lattice points in the range $0{\cdot}05 \le (\sin\theta)/\lambda \le 0{\cdot}15$ for a given crystal, then for the case $\langle|\Delta\mathbf{r}|\rangle = 0{\cdot}1$ Å and $\alpha_0 = 30°$, we have $\Pr(\alpha_0, \pi-\alpha_0) = 0{\cdot}04$. Thus under the above conditions the actual number of reflexions lying in the $(\sin\theta)/\lambda$ range 0·05 to 0·15 and having phases whose values deviate from the centrosymmetric values of 0 or π by more than 30° will be $0{\cdot}04 \times n$; (ii) From the consideration given above it is clear that the value of $\langle|\Delta\mathbf{r}|\rangle$ must be known *a priori* in order to make use of Fig. 1. The value of $\langle|\Delta\mathbf{r}|\rangle$ for a given crystal exhibiting a degree of centrosymmetry could be estimated by a procedure discussed in the previous paper (PP, 1974).

It is seen from Fig. 1 that in a given crystal (*i.e.* $\langle|\Delta\mathbf{r}|\rangle$ is fixed) the percentage of reflexions for which the magnitude of the phase angles would lie in any given range, say $30° \le \alpha \le 150°$, is more for the high-angle than for the low-angle reflexions. For example when $\langle|\Delta\mathbf{r}|\rangle \simeq 0{\cdot}1$ Å, only 4% of the reflexions have phase angle distributed in the range 30 to 150° when $(\sin\theta)/\lambda = 0{\cdot}1$ while it is as high as 17% when $(\sin\theta)/\lambda = 0{\cdot}4$. The deviation of the phase angles from the centrosymmetric values of 0 or π is thus more effectively exhibited for the reflexions with $(\sin\theta)/\lambda > 0{\cdot}1$. This property might possibly be exploited for refinement of such structures by a modified Fourier synthesis and this problem is under investigation.

One of the authors (V.P.) would like to thank the Council of Scientific and Industrial Research, New Delhi, India, for financial assistance.

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Acta Cryst. (1974). A**30**, 576

A Contribution to the Determination of a Correct System of Signs of Structure Factors for Centrosymmetric Crystals

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(*Received* 8 *January* 1974; *accepted* 26 *February* 1974)

To find a solution of the phase problem of centrosymmetric crystals, it is as a rule necessary to find among many possible solutions a correct system of signs of the structure factors. This paper describes the procedure used for finding a correct solution based on a comparison of the theoretical and empirical distribution functions of the positive signs of structure products.

1. Introduction

When solving the phase problem of centrosymmetric crystals by using direct methods it is usually necessary to decide at the end of the calculation which of the suggested sets of signs of the structure factors is the correct one (Karle & Karle, 1966; Ahmed, 1969; Woolfson, 1971, *etc.*). There exist several different procedures for determining which of the suggested solutions is the likeliest to be the correct one.

Schenk (1973*a*) has described an effective procedure for determining the correct set of signs using Harker–Kasper type relations.

Riche (1973) suggested for these purposes the so-called phase function based on the Sayre–Hughes formula.

It has been the objective of this paper to show how to create criteria suited for the determination of a correct system of signs of the structure factors based in the so-called statistical relationship (*e.g.* Hauptman & Karle, 1953; Cochran & Woolfson, 1955; Karle & Gilardi, 1973).

2. Consistency test

As a rule, sign relationships of the statistical type may be rearranged into a form in which the probability $P_{+\text{theor}}$ of the positive sign of the structure product* is

* The structure product is such a product of structure factors $\prod_{i=1}^{n} F_{\mathbf{H}_i}^{a_i}$ for which the corresponding linear combination of their phases $\sum_{i=1}^{n} a_i . \varphi_{\mathbf{H}i}$ is a structure seminvariant.