

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

II. The Case of a Crystal with Type-II Degree of Centrosymmetry

BY S. PARTHASARATHY AND V. PARTHASARATHI

Centre of Advanced Study in Physics,* University of Madras, Guindy Campus, Madras-600025, India

(Received 22 April 1975; accepted 22 May 1975)

The nomenclature and parameters needed for characterizing two different types of degrees of centrosymmetry in a non-centrosymmetric crystal are introduced. The probability distribution of the phase angles of reflexions for the type-II case is worked out and this is used to obtain the probable fraction 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 corresponding to different type-II degrees of centrosymmetry.

Introduction

A non-centrosymmetric crystal may exhibit a degree of centrosymmetry due to two independent causes (Srinivasan, Swaminathan & Chacko, 1972; Srinivasan, 1965). In this note we shall, after introducing the nomenclature, notation and parameters, derive the probability distribution of the phase angles of reflexions for the type-II case. This distribution is also used to discuss (under specific conditions) whether it would be more difficult to refine the structure of a non-centrosymmetric crystal with type-I or type-II degrees of centrosymmetry.

Nomenclature, notation and parameters for characterizing the degrees of centrosymmetry of a non-centrosymmetric crystal

Consider a non-centrosymmetric crystal (space group $P1$) containing a large number (N) of similar atoms in the unit cell. Suppose the structure has an approximate centre of symmetry. Thus, if we choose the centroid of the unit cell to be the origin, the positions of these N atoms could be written as \mathbf{r}_j ($j=1$ to $N/2$) and $-\mathbf{r}_j + \Delta\mathbf{r}_j$ ($j=1$ to $N/2$) where the $\Delta\mathbf{r}_j$'s are mutually independent random vectors which are independent of the \mathbf{r}_j 's. We shall define the degree of centrosymmetry exhibited by such a type of non-centrosymmetric crystal to be type I. The probability distributions of intensities and phases of reflexions for such a case have been derived earlier (Parthasarathy & Parthasarathi, 1974; Parthasarathi & Parthasarathy, 1974; hereafter PP1 and PP2 respectively) by assuming the $\Delta\mathbf{r}_j$'s to obey a Gaussian distribution. Evidently the quantity $\langle |\Delta\mathbf{r}| \rangle$ ($= [1/(N/2)] \sum |\Delta\mathbf{r}_j|$) is a good measure of the degree of centrosymmetry in such a crystal. It is related to the parameter D [$= \langle \cos 2\pi H \cdot \Delta\mathbf{r} \rangle$, see equation (5) of PP1] which takes the values 0 and 1 for the ideally non-centrosymmetric and ideally centrosymmetric cases respectively.

A non-centrosymmetric crystal can also exhibit a degree of centrosymmetry when its unit cell consists of two groups of atoms such that one group consisting of N_c atoms is centrosymmetric and the other consisting of $N_n (= N - N_c)$ atoms is ideally non-centrosymmetric. A molecule consisting of a benzene ring with a non-centrosymmetric group of atoms attached to it and crystallizing in space group $P1$ is an example. We define the degree of centrosymmetry exhibited by such a crystal to be type II. Evidently the degree of centrosymmetry in such a crystal depends on the relative proportions of atoms in the N_c and N_n parts. A good measure of the degree of centrosymmetry in this case (*i.e.* similar-atom case) could therefore be the quantity r defined by

$$r = N_c / (N_c + N_n) = N_c / N. \quad (1)$$

It is obvious that r assumes the values 0 and 1 for the ideally non-centrosymmetric and ideally centrosymmetric cases respectively and has intermediate values which correspond to different degrees of centrosymmetry. Though the probability distribution of X-ray intensities for this situation has been worked out by Srinivasan (1965) and Parthasarathy (1966), that for the phases is not available. Owing to the importance of phases in crystal structure analysis this distribution is worked out in the next section by making use of the property of normal variates.

For brevity we shall use the symbols NC , NC' and NC'' to denote an ideally non-centrosymmetric crystal, a non-centrosymmetric crystal with type-I degree of centrosymmetry and a non-centrosymmetric crystal with type-II degree of centrosymmetry respectively.

Derivation of the probability distribution of the phase angles

Define the origin to be at the centre of the N_c group of atoms. From the structure-factor relation,

$$F_N = F_{N_c} + F_{N_n} = A_N + iB_N = |F_N| \exp(i\alpha), \quad (2)$$

* Contribution No. 399.

it follows that*

$$\langle |F_N|^2 \rangle = \langle |F_{Nc}|^2 \rangle + \langle |F_{Nn}|^2 \rangle, \text{ i.e. } \sigma_N^2 = \sigma_{Nc}^2 + \sigma_{Nn}^2. \quad (3)$$

Since all the atoms in the unit cell are assumed to be similar,

$$\sigma_{Nc}^2/\sigma_N^2 = N_c/N = r, \quad \sigma_{Nn}^2/\sigma_N^2 = N_n/N = 1-r. \quad (4)$$

From (2) it follows that

$$A_N = A_{Nc} + A_{Nn}, \quad B_N = B_{Nn}. \quad (5)$$

Since the N_c group is taken to satisfy the requirements of the centric and the N_n group the acentric Wilson distribution, it follows from Wilson (1949) that A_{Nc} and A_{Nn} are normally distributed with parameters $(0, \sigma_{Nc}^2)$ and $(0, \frac{1}{2}\sigma_{Nn}^2)$ respectively. Since the N_c and N_n groups are independent, A_{Nc} and A_{Nn} are independent variables and hence their sum $A_{Nc} + A_{Nn} = (A_N)$ will also be normally distributed with parameters $(0, \sigma_{Nc}^2 + \frac{1}{2}\sigma_{Nn}^2)$ (see p. 212 of Cramér, 1962). Hence we have

$$P(A_N) = [2\pi(\sigma_{Nc}^2 + \frac{1}{2}\sigma_{Nn}^2)]^{-1/2} \exp[-A_N^2/2(\sigma_{Nc}^2 + \frac{1}{2}\sigma_{Nn}^2)]. \quad (6)$$

Since $B_N = B_{Nn}$, the p.d.f. of B_N will be that of B_{Nn} which has a normal distribution with parameter $(0, \frac{1}{2}\sigma_{Nn}^2)$ (see Wilson, 1949). That is

$$P(B_N) = (\pi\sigma_{Nn}^2)^{-1/2} \exp[-B_N^2/\sigma_{Nn}^2]. \quad (7)$$

From (6) and (7) we obtain the joint p.d.f. of A_N and B_N to be

$$P(A_N, B_N) = \frac{1}{\pi\sigma_{Nn}\sqrt{\sigma_{Nn}^2 + 2\sigma_{Nc}^2}} \times \exp\left[-\frac{A_N^2}{\sigma_{Nn}^2 + 2\sigma_{Nc}^2} - \frac{B_N^2}{\sigma_{Nn}^2}\right]. \quad (8)$$

Transforming to plane polar coordinates $(|F_N|, \alpha)$ we obtain from (8)

$$P(|F_N|, \alpha) = \frac{|F_N|}{\pi\sigma_{Nn}\sqrt{\sigma_{Nn}^2 + 2\sigma_{Nc}^2}} \times \exp\left[-|F_N|^2\left(\frac{\cos^2 \alpha}{\sigma_{Nn}^2 + 2\sigma_{Nc}^2} + \frac{\sin^2 \alpha}{\sigma_{Nn}^2}\right)\right]. \quad (9)$$

The joint p.d.f. of $y_N (= |F_N|/\sigma_N)$ and α will therefore be

$$P(y_N, \alpha) = \frac{y_N}{\pi\sqrt{1-r^2}} \exp\left[-y_N^2\left(\frac{\cos^2 \alpha}{1+r} + \frac{\sin^2 \alpha}{1-r}\right)\right] \\ = \frac{y_N}{\pi\sqrt{1-r^2}} \exp\left[-y_N^2\left(\frac{1-r \cos 2\alpha}{1-r^2}\right)\right]. \quad (10)$$

A comparison of (10) with (13) of PP1 shows that these two equations are identical in the functional form. The quantity r of the present case plays the same role

as D in (13) of PP1. It follows that $P(|\alpha|)$ and $Pr(\alpha_0, \pi - \alpha_0)$ [which represents the fractional number of reflexions for which the magnitude of the phase angles would lie in the interval $(\alpha_0, \pi - \alpha_0)$] for the present case could be readily obtained respectively from (3) and (6) of PP2 by replacing D by r . Thus we have,

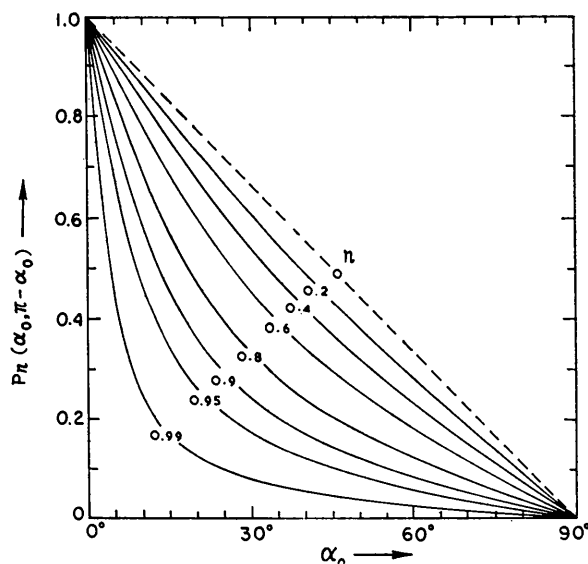


Fig. 1. Representation of $Pr(\alpha_0, \pi - \alpha_0)$ as a function of α_0 for a non-centrosymmetric crystal with different type-II degrees of centrosymmetry. The broken line corresponds to the ideally non-centrosymmetric crystal.

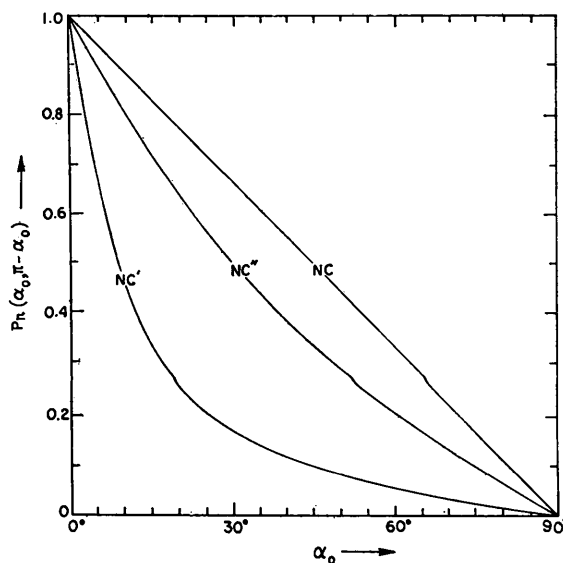


Fig. 2. Comparison of the function $Pr(\alpha_0, \pi - \alpha_0)$ for typical non-centrosymmetric crystals with type-I and type-II degrees of centrosymmetry. The curve marked NC' is for the type-I case corresponding to $S=0.4 \text{ \AA}^{-1}$ and $\langle |Dr| \rangle = 0.1 \text{ \AA}$, that marked NC'' is for the type-II case with $r=0.5$ and that marked NC is for the ideally non-centrosymmetric case.

* $\sigma_{Nc}^2 = \sum_{j=1}^{N_c} f_j^2$, $\sigma_{Nn}^2 = \sum_{k=1}^{N_n} f_k^2$, $\sigma_N^2 = \sum_{i=1}^N f_i^2$.

$$P(|\alpha|) = \frac{\sqrt{1-r^2}}{\pi(1-r \cos 2\alpha)}, \quad 0 \leq \alpha \leq \pi \quad (11)$$

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

$$0 \leq \alpha_0 \leq \pi/2. \quad (12)$$

Discussion of the results

The functional dependence of $Pr(\alpha_0, \pi - \alpha_0)$ on α_0 is shown in Fig. 1 for different values of r (which is a measure of the type-II degree of centrosymmetry). It is interesting to see that even when 50% of the atoms in the unit cell have a centrosymmetric configuration (*i.e.* $r \simeq 0.5$) the distribution of the phase angles is much closer to the distribution expected for the ideally non-centrosymmetric case than for the ideally centrosymmetric case. It is useful to note that though $Pr(\alpha_0, \pi - \alpha_0)$ for the type-I case is a function of $(\sin \theta)/\lambda$ ($=S$, say), it is independent of S for the type-II case considered here since r is practically a constant for a given crystal.

It would be interesting to make a comparative study of the variation of $Pr(\alpha_0, \pi - \alpha_0)$ as a function of α_0 for typical non-centrosymmetric crystals with type-I and type-II degrees of centrosymmetry. We shall consider, for example, a non-centrosymmetric crystal with type-I degree of centrosymmetry having $\langle |\Delta r| \rangle = 0.1 \text{ \AA}$ and a non-centrosymmetric crystal with type-II degree of

centrosymmetry with $r=0.5$. Since $Pr(\alpha_0, \pi - \alpha_0)$ for the former is a function of S , we shall set $S=0.4 \text{ \AA}^{-1}$ which is a typical value for Cu $K\alpha$ radiation. The relevant curves are shown in Fig. 2. It is seen that while for the type-II case about 55% of the reflexions have phases in the interval 30° to 150° (whatever the value of S), for the type-I case only about 20% of the reflections (for $S=0.4 \text{ \AA}^{-1}$ and $\langle |\Delta r| \rangle = 0.1 \text{ \AA}$) have phases in the interval 30° and 150° . Thus, under the conditions stated above, the type-I case would be more difficult to refine than the type-II case.

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

References

- CRAMÉR, H. (1962). *Mathematical Methods of Statistics*. New Delhi: Asia Publishing House.
- PARTHASARATHI, V. & PARTHASARATHY, S. (1974). *Acta Cryst.* **A30**, 574–576.
- PARTHASARATHY, S. (1966). *Z. Kristallogr.* **123**, 77–80.
- PARTHASARATHY, S. & PARTHASARATHI, V. (1974). *Acta Cryst.* **A30**, 310–315.
- SRINIVASAN, R. (1965). *Curr. Sci.* **34**, 529–530.
- SRINIVASAN, R., SWAMINATHAN, P. & CHACKO, K. K. (1972). *Curr. Sci.* **41**, 768–769.
- WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

Acta Cryst. (1976). **A32**, 59

General Theory of Coincidence-Site Lattices, Reduced 0-Lattices and Complete Pattern-Shift Lattices in Arbitrary Crystals

BY Y. IWASAKI

Research Laboratories, Kawasaki Steel Corporation, Kawasaki-cho, Chiba, Japan

(Received 1 May 1975; accepted 14 June 1975)

The definition of a lattice and its superlattice is given algebraically. A coincidence site lattice (CSL) is defined as an intersection lattice of any two crystal lattices, and a complete pattern-shift lattice (DSCL) as the set theoretically smallest lattice containing both crystal lattices as superlattices. In the case where the two lattices are related by a non-singular matrix (having non-zero determinant), the so-called 0-lattice may be generated from the two crystal lattices. Any translation of the 0-lattice by all the vectors of one of the crystal lattices forms a lattice, *i.e.* a reduced 0-lattice. As a result of the theory of groups and numbers, the reduced 0-lattice (abbreviated to ROL) is homomorphic to the DSCL. It is shown that the factor group of all cosets of lattice 1 in the DSCL (in the ROL) is isomorphic with the factor group of all cosets of the CSL in lattice 2 (in the 0-lattice). The volume of a unit cell is derived for all the lattices generated by the two crystal lattices. Secondly, the reciprocal of a lattice is introduced and the reciprocity between the CSL and the DSCL determined by the reciprocals of the two crystal lattices is shown as a special case of a theorem mentioned about modules over a ring. Finally a complete diagram of relationships between *b*-lattices and 0-lattices for direct lattices and reciprocal lattices is given.

Introduction

Since Bollman's 0-lattice theory (Bollmann, 1967 *a, b*, 1970; Bollmann & Perry 1969; Warrington & Boll-

mann, 1972) was derived, many theoretical studies of the coincidence-site lattice (CSL) and the complete pattern-shift lattice (DSCL) have been made. In particular, Grimmer has recently developed a general