

SHORT COMMUNICATIONS

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Acta Cryst. (1983). **A39**, 818

Phase relationships in the chiral space groups $P4_1$ and $P4_3$. Correction of an error in *International Tables for X-ray Crystallography*, Vol. I. By J. KROON and W. M. G. F. PONTENAGEL, *Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands*

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Abstract

Corrections are given to phase relationships for space groups $P4_1$ and $P4_3$ listed in *International Tables for X-ray Crystallography* [Vol. I. (1969). Birmingham: Kynoch Press].

The entries $l = 4n + 1$ and $l = 4n + 3$ to the phase relationships between $\alpha(\bar{h}kl)$ and $\alpha(khl)$ in space groups $P4_1$ and $P4_3$ listed in *International Tables for X-ray Crystallography* (1969) should be interchanged. This leads to the following phase relations:

$$\begin{aligned} \alpha(\bar{h}kl) &= \pi + \alpha(h\bar{k}l) = \frac{1}{2}\pi + \alpha(khl) & [P4_1: l = 4n + 1; P4_3: l = 4n + 3] \\ \alpha(\bar{h}kl) &= \pi + \alpha(h\bar{k}l) = \frac{3}{2}\pi + \alpha(khl) & [P4_1: l = 4n + 3; P4_3: l = 4n + 1]. \end{aligned}$$

The same corrections should be made in the paper on the discrimination between two enantiomorphously related space groups (Kroon, Pontenagel, Krabbendam & Peerdeman, 1982). They do not affect, however, the validity of the procedure suggested in that article.

References

- International Tables for X-ray Crystallography* (1969). Vol. I, 3rd ed., pp. 415–416, 417. Birmingham: Kynoch Press.
KROON, J., PONTENAGEL, W. M. G. F., KRABBENDAM, H. & PEERDEMAN, A. F. (1982). *Acta Cryst.* **A38**, 170.

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An alternative approach to the quantitative determination of grain-size distribution in X-ray diffraction?

A comment. By E. F. BERTAUT, *Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166 X, 38042 Grenoble CEDEX, France*

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Abstract

The paper by Zhao, Lu & Lagally [*Acta Cryst.* (1982), **A38**, 800–802] is commented on and compared with a previous paper by Bertaut [*Acta Cryst.* (1950), **3**, 14–18].

In a recent publication with the title above, the authors (Zhao, Lu & Lagally 1982, abbreviated ZLL) quote my paper (in French, Bertaut, 1950) which relates the distribution of particle size m to the profile of Debye–Scherrer lines according to equation (22).

$$\frac{\partial^2 t(m)}{\partial m^2} = g(m). \quad (22)$$

Here $g(m)$ is the distribution function of size m and $t(m)$ is the Fourier transform of the observed intensity profile $I(X)$. The paper also states (Bertaut, 1950) that the size distribution $g(m)$ can be obtained directly by Fourier transforming $X^2 I(X)$, that is, the intensity multiplied by X^2 .

ZLL rediscover this equivalence, after the lecture in Guinier's fine book (Guinier, 1963), call it an 'alternative approach' and obtain $g(m)$ in model calculations using Gaussian and Lorentzian functions $I(X)$.

Let us translate here the French text following (22) in view of another problem which in our mind is most important.

'One may ask the question if it is not possible to replace an always uncertain double differentiation in m space by a simpler operation in X space on $I(X)$, prior to its Fourier transformation.

Indeed the theory of Fourier integrals establishes the following correspondences

$$\begin{aligned} I(X) &\rightarrow t(m) \\ 2\pi i X I(X) &\rightarrow \frac{\partial t(m)}{\partial m} \\ -4\pi^2 X^2 I(X) &\rightarrow \frac{\partial^2 t(m)}{\partial m^2}. \end{aligned} \quad (23)$$

Thus the Fourier transform of $X^2I(X)$ would lead directly to the size distribution function. This equivalence sheds new light on the experimental difficulty to be solved. The asymptotic behaviour of the intensity is of primordial importance: even if for X large, $I(X)$ takes small values, its product by X^2 may be non-negligible. Thus one replaces one difficulty by another one.⁷

This problem of the effect of finite summation on $g(m)$ has been considered from a theoretical point of view (Bertaut, 1952, 1963). In a paper with the title *Correction of oscillations in the distribution functions of particle size obtained from diffraction profiles*, my co-workers (de Bergevin & Germi, 1972) consider the problem from an experimental point of view and get satisfactory plots of $g(m)$ taking advantage of the measurement of the second moment

$$\int X^2 I(X) dX / \int I(X) dX$$

(Wilson, 1962; Langford, 1968) and adjusting $g(m)$ so that $g(0) = 0$.

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On evaluating the standard deviation of U_{eq} .* By VERNER SCHOMAKER† and RICHARD E. MARSH, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA*

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Abstract

For roughly isotropic and orthic cases the variance of U_{eq} is about one-sixth of the average of the variances of U_{11} , U_{22} , and U_{33} , *i.e.* only about one-half of what would be estimated on ignoring the covariances of the diagonal elements of U .

For some time, *Acta Crystallographica* has required that, except in special cases, the anisotropic Gaussian quadratic amplitudes be deposited as supplementary material and replaced in the published paper by 'equivalent' isotropic measures, U_{eq} (or B_{eq}). Another requirement, now removed at least for U_{eq} and B_{eq} (*Notes for Authors*, 1983, p. 181), has been that all derived measures of any kind should be accompanied by their e.s.d.'s, although the computer programs used in many crystallographic laboratories do not permit ready access to the covariances $\text{cov}(U_{ij}, U_{kl})$ that are necessary for a proper evaluation of $\sigma_{U_{eq}}$. Moreover, in none we know of are the covariances regularly so used, despite the well-known need for them and Waser's thorough reminder (Waser, 1973); instead, the usual practice, it seems, is to estimate $\sigma_{U_{eq}}$ from the readily available e.s.d.'s, $\sigma_{U_{ij}}$, ignoring the covariances.

We derive simple expressions for variances and co-

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One should notice that de Bergevin & Germi (1972) consider from the start the Fourier transform of $X^2I(X)$.

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- BERGEVIN, F. DE & GERMI, P. (1972). *J. Appl. Cryst.* **5**, 416–420.
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variances of the *principal* values of U and proceed to expressions for $\sigma_{U_{eq}}$. Our expressions for the variances and covariances extend somewhat those derived rather less directly and under more restrictive assumptions by Scheringer (1966) and Hirshfeld & Shmueli (1972, H & S), and our expressions for $\sigma_{U_{eq}}$ may prove useful in practice even when the underlying assumptions are hardly valid, but the main point to be made is that $\sigma_{U_{eq}}$ is substantially smaller than the usual estimates, the covariances being substantially negative.

We assume that the atoms are of Gaussian shape, so that each U is the sum of parts due to the (known) atom shape and to the crystal disorder (if the Gaussian atom approximation is good, the e.s.d.'s and covariances of a total U will be just those of its disorder, *i.e.* 'thermal' part); use Cartesian coordinates aligned with the principal axes of U for the atom of interest at the moment; and move the origin of coordinates to the position of that atom. Its contribution to an F is then

$$F_s = \exp \left[- \sum_{k=1}^3 u_k s_k^2 / 2 \right] \\ = \exp [-(at^2 + bv^2 + cw^2) / 2],$$

where, taking advantage of $U_{ij} = 0$ for $i \neq j$, we omit one or both indices, writing $u_k = U_{11}, U_{22}, U_{33} = a, b, c$; $s_k = t, v, w$; and $|s| = 4\pi(\sin \theta) / \lambda$. For unit weights it is then easy to form the least-squares matrix B , its inverse B^{-1} , and the correlation matrix, appropriately replacing the usual summation over all reflections by integration over all s :