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Absorption corrections for neutron diffraction.

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Abstract

The transmission factors tabulated by Rouse, Cooper, York & Chakera [*Acta Cryst.* (1970), A**26**, 682–691] for $\mu r < 1$ can be expressed as the product of two factors: a scale factor and a Debye–Waller factor. In the case of a sphere or a cylinder, the absorption corrections then reduce to simple adjustments of these parameters at the end of the refinement, instead of tedious corrections to the data itself. The results are of particular use for powder data. A printing error in the original paper is also corrected.

Absorption corrections are usually made by reference to a tabulation of the transmission factor A_{hkl}, or by the use of computer programs to correct the raw data. For example, Rouse, Cooper, York & Chakera (1970) have produced a table particularly suited to neutron diffraction, where usually $\mu r < 1$. Of course the use of such tables is tedious, and when computer programs are available it is not always clear what the effect will be of errors in the measurement of the absorption coefficient μ, the crystal radius r, or even the different approximations used to calculate A_{hkl}.

Rouse *et al.* also give an analytical approximation for A_{hkl}, where the error does not exceed 0·0035 for $\mu r < 1$ ($1 > A_{hkl} > 0{\cdot}1965$):

$$A_{hkl} = \exp[-(a_1 + b_1 \sin^2\theta)\mu r - (a_2 + b_2 \sin^2\theta)(\mu r)^2],$$

where the coefficients are:

	Cylinder	Sphere
a_1	1·7133	1·5108
b_1	−0·0368	−0·0315
a_2	−0·0927	−0·0951
b_2	−0·3750	−0·2898.

(Note that there is a printing error for b_2 in the original paper.) Clearly this expression can be rewritten as

$$A_{hkl} = k\exp[-\Delta B(\sin\theta/\lambda)^2],$$
$$k = \exp[-a_1\mu r + a_2(\mu r)^2],$$
$$\Delta B = \lambda^2[b_1\mu r + b_2(\mu r)^2],$$

where k is a scale factor and ΔB is an overall Debye–Waller factor.

Then, unless absolute measurements are being made, the absorption correction for spherical or cylindrical samples can be performed at the end of the refinement simply by adding $\Delta B\cos\gamma^*$ to all the B_{ij}, where γ^* is the angle between the reciprocal-lattice axes i and j.

The result is of particular use for neutron powder diffraction where the product μr can be obtained simply by measuring the transmission through a fine slit placed in front of the sample. For example, a value of $\mu r = 0{\cdot}579$ was obtained for a 16 mm diameter sample of $CsPbCl_3$, giving $\Delta B = 0{\cdot}27$. Even for a weakly absorbing sample of deuteronaphthalene, we found $\mu r = 0{\cdot}274$ and hence $\Delta B = 0{\cdot}07$. In most cases, absorption corrections are not made for neutron powder diffraction, and this results in significant underestimations of the Debye–Waller factors, even for apparently weakly absorbing materials. Given the ease with which the above formulae can be applied, there is now no excuse for not making these corrections.

The concurrence of M. J. Cooper with these comments on his original paper is acknowledged.

Reference

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Errors in coordinates, bond lengths, and bond angles.

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Abstract

Standard deviations in bond lengths and bond angles are related to standard deviations in atomic coordinates according to published equations [Cruickshank (1959). *International Tables for X-ray Crystallography.* Vol. II, pp. 331–332]. These equations were derived for an idealized model in which the distribution of coordinate errors is isotropic. Tests show that typical structures exhibit only moderate deviations from this model, and so the calculated standard deviations are accurate. Furthermore, the standard deviation in a bond angle φ (in degrees) can be well approximated by the expression $\sigma(\varphi) \sim 81\,[\sigma(R)/R]_{\rm r.m.s.}$, where the quantity in square brackets is the root-mean-square value of $\sigma(R)/R$ for

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the two bonds forming the angle. Tests on typical published results show that this equation usually estimates $\sigma(\varphi)$ to within the round-off error in the reported value.

Numerical estimates of the standard deviations of bond lengths and angles are usually provided by conventional computer programs from variances and covariances of atomic coordinates. Nevertheless, it remains of interest to find analytic relations among these measures of error in order to provide a check of the calculations, to estimate quantities that have not been calculated, or to predict the accuracy needed in atomic coordinates to obtain a desired accuracy in bond lengths or angles. In fact this problem has been solved (Cruickshank, 1959) but the wide range of applicability and the usefulness of the results appear to have been generally overlooked. This communication indicates the nature of the derivation, points out a useful approximation suitable for 'back-of-an-envelope' calculations, and reports tests of the results.

The simple relations among the various errors are derived from an idealized model in which the standard deviation of the position of a given atom is the same in any direction and the errors in the coordinates of different atoms are uncorrelated. It is not necessary to assume that the standard deviations in coordinates are the same for different atoms.

A straightforward analysis of the propagation of errors leads to Cruickshank's relation for the standard deviation in the distance R_{np} between atom n and atom p:

$$\sigma(R_{np}) = (\sigma_n^2 + \sigma_p^2)^{1/2}, \tag{1}$$

where σ_n is the standard deviation in any coordinate (Cartesian, not fractional) of atom n, and similarly for atom p. This result is essentially obvious: it arises from the fact that the variance in the interatomic distance is merely the sum of the variances of the positions of the end atoms along their line of centers, provided the errors are uncorrelated.

A straightforward but tedious analysis of the propagation of errors leads to Cruickshank's result for the standard deviation in the angle φ determined by three atoms m, n, and p:

$$\sigma(\varphi) = \left[\frac{\sigma_m^2 + \sigma_n^2}{R_{nm}^2} + \frac{\sigma_p^2 + \sigma_n^2}{R_{np}^2} - \frac{2\sigma_n^2 \cos\varphi}{R_{nm}R_{np}}\right]^{1/2}, \tag{2}$$

where the terms have been rearranged to indicate their magnitudes and significance. The third term can usually be neglected, either because φ is near 90° or because the center atom n is a heavy atom with small σ_n. The first two terms are just double the mean squared relative standard deviation in the two bonds forming the angle:

$$\left\langle\frac{\sigma(R)^2}{R^2}\right\rangle \equiv \frac{1}{2}\left[\frac{\sigma(R_{nm})^2}{R_{nm}^2} + \frac{\sigma(R_{np})^2}{R_{np}^2}\right]. \tag{3}$$

Then equation (2) simplifies to the approximate form

$$\begin{aligned}\sigma(\varphi) &= 2^{1/2}\,\langle\sigma(R)^2/R^2\rangle^{1/2}\\ &= 2^{1/2}[\sigma(R)/R]_{\text{r.m.s.}}\end{aligned} \tag{4a}$$

(with the use of an obvious abbreviation) or, expressed in degrees,

$$\sigma(\varphi) = 81\,[\sigma(R)/R]_{\text{r.m.s.}}. \tag{4b}$$

It is interesting to note that it is not the relative standard deviation $\sigma(\varphi)/\varphi$, but rather the absolute standard deviation $\sigma(\varphi)$ that is proportional to the relative standard deviation of a bond length.

The assumption of isotropic errors and the estimates provided by equations (1), (2), and (4*b*) were tested against a sample of reported results. Five papers from different countries were selected from one issue of *Acta Crystallographica*. It is not always apparent what computer programs were used for the calculation of distances, angles, and their errors; however, all probably made use of the complete variance–covariance matrix for the atomic coordinates. In each case four or five atoms were chosen, and the bond lengths and angles involving them were examined. The comparisons are summarized in Table 1.

For each atom the standard deviation in a coordinate was taken as the r.m.s. value of the standard deviations along the three crystallographic axes:

$$\sigma_n = [(\sigma_x^2 + \sigma_y^2 + \sigma_z^2)/3]^{1/2}, \tag{5}$$

where σ_x is the product of the standard deviation in the fractional coordinate and the axial length, and so on. For one atom the deviation from the assumption of isotropic error is measured by

$$\left[\frac{(\sigma_x - \sigma_n)^2 + \ldots}{3\sigma_n^2}\right]^{1/2}. \tag{6}$$

The arithmetic mean of these quantities, for the atoms considered, is reported in Table 1 as the 'mean deviation from

Table 1. *Tests of approximations*

	(1)*	(2)	(3)	(4)	(5)
Mean deviation from isotropic error (%)	21	16	6	15	5
Maximum deviation (%)	33	25	15	33	12
Worst case, $\sigma(R)$ from equation (1) (Å)	0·0038	0·060	0·014	0·0052	0·0043
$\sigma(R)$ reported (Å)	0·003	0·05	0·02	0·005	0·005
Worst case, $\sigma(\varphi)$ from equation (4*b*) (°)	0·15	0·61	1·41	0·36	0·33
$\sigma(\varphi)$ from equation (2) (°)	0·16	0·69	1·49	0·40	0·38
$\sigma(\varphi)$ reported (°)	0·1	0·8	1·5	0·3	0·4

* References: (1) Calvo, Gillespie, Vekris & Ng (1978); (2) Fitzgerald & Jensen (1978); (3) Hughes, Mortimer & Truter (1978); (4) Kojić-Prodić & Rogić (1978); (5) Wijmenga, Numan & Vos (1978).

isotropic error'. The 'maximum deviation' is the largest value of $|\sigma_x - \sigma_n|/\sigma_n$, or the analogous fraction for the y or z coordinate, of any atom.

Estimates of $\sigma(R)$ from equation (1) were typically within the round-off error; the poorest agreement noted between calculated and reported values is given in Table 1. The same can be said for the estimates of $\sigma(\varphi)$, from equation (4*b*); the poorest agreement found is included in the table. The corresponding value of $\sigma(\varphi)$ calculated from equation (2) is also given for these cases; it is not markedly superior to the approximate value from equation (4*b*).

The assumption of isotropic uncorrelated errors appears to be satisfactory for typical crystal structure determinations, and the error estimates provided by equations (1) and (4*b*) are surprisingly good.

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Extinction in single crystals of UO_2.

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Abstract

The measurements of nuclear neutron diffraction intensities for a single crystal of UO_2 by Faber & Lander [*Phys. Rev. B* (1976), **14**, 1151–1164] have been re-analysed using both the Cooper–Rouse and Becker–Coppens extinction formalisms. The results indicate that this crystal is type I in nature, not type II as was suggested by Faber & Lander, and this conclusion is essentially the same as that obtained for a different single crystal of UO_2 used in our earlier study of the wavelength dependence of extinction in this material [Sakata, Cooper, Rouse & Willis (1978). *Acta Cryst.* A**34**, 336–341]. The analysis of the Faber & Lander data gave a value for the scattering-length ratio $b_U/b_O = 1{\cdot}448$ (2).

Introduction

In a recent study of the magnetic structure of UO_2 Faber & Lander (1976) carried out a series of accurate neutron diffraction measurements on a single crystal of UO_2 at three different temperatures, *viz* 300, 80 and 4·2 K. In analysing their data they assumed the model for extinction given by Zachariasen (1967) and found this adequate to describe the extinction results for the purpose of their study. However, they concluded that the high value they obtained for the mosaic-spread parameter g, *i.e.* about 1000, suggested a type II extinction, as defined by Zachariasen (1967).

Recently we have carried out an independent neutron diffraction study of the wavelength dependence of extinction in UO_2 (Sakata, Cooper, Rouse & Willis, 1978), analysing our results on the basis of the improvements to the Zachariasen extinction model derived by Cooper & Rouse (1970) and Becker & Coppens (1974). This study led to the conclusion that these formalisms gave similar results for the crystal studied and indicated a type I extinction in this case. Since almost every recent study of extinction has indicated type I extinction or a tendency to type I extinction we have therefore carried out an analysis of the Faber & Lander data to determine whether the extinction type in their crystal was any different from that in the one we studied.

Results of the new analysis

Detailed experimental results for the nuclear scattering in the Faber & Lander (1976) experiment were kindly supplied by these authors and were re-analysed using the Harwell *TAILS* computer program (see Sakata, Cooper, Rouse & Willis, 1978). In order to determine the most suitable model for the extinction in this crystal the data were analysed using the following models:

(1)	Cooper–Rouse	
(2)	Becker–Coppens	type I Gaussian (secondary)
(3)	Becker–Coppens	type I Lorentzian (secondary)
(4)	Becker–Coppens	type II (secondary)
(5)	Becker–Coppens	mixed-type Gaussian (secondary)
(6)	Becker–Coppens	mixed-type Lorentzian (secondary)
(7)	Becker–Coppens	general (mixed-type Lorentzian plus primary).

The Cooper–Rouse model gave reasonable agreement, with values of the effective domain radius which do not differ significantly for the three temperatures. The Becker–Coppens type II model gave a fit which is significantly worse than that for the type I models, particularly for the most severely extinguished reflections. Of the type I models, that using a Lorentzian mosaic-spread function gave slightly better overall agreement than that using a Gaussian mosaic-

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