

Short Communications

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Acta Cryst. (1969). A25, 488

The importance of thermal diffuse scattering in the comparison of X-ray and neutron diffraction data.

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(Received 8 August 1968)

A careful consideration of thermal diffuse scattering (TDS) is necessary in comparing X-ray and neutron diffraction data from crystals of the same material, because of the errors which it can cause in the integrated Bragg intensities. It is extremely unlikely that these errors will be the same in the two cases. The use of a three-crystal spectrometer for an 'elastic' neutron diffraction measurement results in only a small reduction in the TDS contribution to the integrated intensity.

Attempts have recently been made to determine deviations from spherical symmetry of atomic charge distributions in small organic molecules, by comparison of the results of X-ray and neutron diffraction experiments (*e.g.* Coppens 1967, 1969*a, b*; Hamilton 1969). X-ray diffraction measurements determine only the atomic charge density and deviations from spherical symmetry may displace the centroid of this density from the atomic nuclear position. In order to study these deviations it is necessary, therefore, to determine the nuclear positions by other means, such as neutron diffraction.

When comparing the results of X-ray and neutron diffraction measurements it is clearly essential to take proper account of the thermal motion of the atoms and a careful consideration of thermal diffuse scattering (TDS) will be necessary. The peaking of the TDS under the Bragg peaks can give rise to appreciable errors in the observed integrated Bragg intensity when a conventional background subtraction is made; these errors may be as much as 25 to 30% for some reflexions in a typical experiment at room temperature. It has been shown that neglect of these errors will result in an underestimation of the diagonal terms (U_{ii}) in the thermal motion tensors (Cooper, 1969). For elastically isotropic crystals (Nye, 1957) this is equivalent to an error in the mean temperature parameters (Cooper & Rouse, 1968). However, for anisotropic crystals the error in the thermal parameters would be expected to differ with direction in the crystal, especially for non-cubic crystals, and so may lead to spurious anisotropic effects in the apparent charge density. A method has recently been published for calculating isotropic TDS corrections for cubic crystals (Cooper & Rouse, 1968) and this method has now been extended to provide anisotropic corrections for crystals of any symmetry (Rouse & Cooper, 1969). Provided the incident neutrons are much faster than the velocity of sound in the crystal and the temperature is not too low, the TDS cross-section will be the same for neutrons and X-rays (Willis, 1969; Cooper, 1969). However, because of the different scattering factors and the different resolution functions, it is extremely unlikely that the errors resulting from ignoring TDS can be made to be the same in the two cases.

Hamilton (1968) has advocated the use of a three-crystal neutron spectrometer in an 'elastic' diffraction measure-

ment, as described by Caglioti (1964), to reject the TDS. However, it must be emphasized that near the Bragg peak, where the intensity is greatest, the TDS arises from acoustic modes of vibration with very small energy, so that complete rejection is certainly impossible, as Caglioti has shown. The use of an analyser will sharpen the TDS peak to some extent (see Caglioti, 1964, Fig. 7), but it will also reduce the TDS which is normally corrected for in the background measurement, as has been pointed out by Young (1968). The resultant error through ignoring TDS may thus still be comparable to that for a two-crystal diffraction measurement.

In order to emphasize this I have estimated the ratio of the TDS corrections for the three-crystal 'elastic' and two-crystal diffraction measurements for several examples. The ratio of the TDS corrections has been estimated using a spherical model for the scanning volume in reciprocal space (see Cooper & Rouse, 1968) and a Gaussian energy resolution function (Cooper & Nathans, 1967). An equivalent scan range of $\pm 1^\circ$ at $\theta = 45^\circ$ has been used together with energy resolutions of 2 and 4 meV full-width at half-height; the energy resolution of a three-crystal spectrometer is typically within this range (see *e.g.* Caglioti, 1964; Cooper & Nathans, 1967). Since for low energy phonons the energy is proportional to the wave vector q , the energy resolution gives rise to a probability function of the form:

$$P(\mathbf{q}) = P(0) \exp(-Aq^2).$$

For a spherical volume the ratio α_3/α_2 , where $\alpha = I_{\text{TDS}}/I_{\text{BRAGG}}$ and α_3 and α_2 are for a three-crystal and a two-crystal diffraction measurement respectively, is then, for a peak scan:

$$\begin{aligned} \frac{\alpha_3}{\alpha_2} &= \int \frac{P(\mathbf{q})}{q^2} (4\pi q^2 d\mathbf{q}) \bigg/ \int \frac{1}{q^2} (4\pi q^2 d\mathbf{q}) \\ &= \int \exp(-Aq^2) d\mathbf{q} \bigg/ \int d\mathbf{q}. \end{aligned}$$

The values of this ratio for a conventional background corrected scan are listed in Table 1 for lead (Brockhouse, Arase, Caglioti, Rao & Woods, 1962), iron (Minkiewicz, Shirane & Nathans, 1967) and nickel (Birgeneau, Cordes, Dolling & Woods, 1964).

Table 1. α_3/α_2 for background corrected scan ($\pm 1^\circ$ at $\theta=45^\circ$) for various crystals

Resolution (full-width at half-height)	α_3/α_2		
	Lead	Iron	Nickel
4 meV	1.00	0.86	0.76
2 meV	0.93	0.50	0.39

It is clear from these results that, in general, extremely high resolution is required in order to make any appreciable reduction in the TDS correction, and for soft materials, such as the organic crystals referred to earlier, little improvement can be made. In any case, it will still be necessary to calculate the TDS correction for an 'elastic' diffraction measurement and the energy resolution function will have to be included in the integration. In addition, the use of an analyser will reduce the Bragg intensity and it is doubtful whether the reduction which can be achieved in the TDS correction will be sufficient, on its own, to make the use of the analyser worthwhile.

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Acta Cryst. (1969) **A25**, 489

Treatment of accidentally absent reflexions in least-squares refinement of crystal structures. By A. J. DUNNING, *Unilever Research Laboratory, Port Sunlight, Cheshire, England* and V. VAND,* *Materials Research Laboratory and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.*

(Received 4 November 1968 and in revised form 9 December 1968)

An improved method of including accidentally absent reflexions in the least-squares refinement of crystal structures, so as to accelerate the initial convergence of the procedure, is discussed. It is shown that when the calculated structure factors of these reflexions are less than the observed threshold value they determine nothing more about the structure, and should not be included in expressions for either the standard deviations or the shifts during refinement of atomic parameters.

In a least-squares refinement of a crystal structure, corrections Δx_i to variable parameters x_i (coordinates, temperature factors, etc.) are computed by expanding the formula for a structure factor, $F(hkl)$, into a Taylor series in x_i . After neglecting non-linear terms, a least-squares matrix is formed. If non-diagonal terms are neglected,

$$\Delta x_i = \frac{\sum w \Delta F (\delta F_c / \delta x_i)}{\sum w (\delta F_c / \delta x_i)^2}, \quad (1)$$

where the sums extend over all measured reflexions, and $\Delta F = |F_o| - |F_c|$, where F_o is the observed structure factor and F_c is the structure factor calculated from the initial parameters, x_i . Both F_o and F_c may differ from the true value F_i of the structure. The statistical weight of a structure factor is given by $w = 1/\sigma^2$, where σ is the standard deviation of F_o .

In general there are three classes of reflexion:

Class 1. Well-observed reflexions, to which a value of w can be assigned based on an error analysis of the system, and which can be incorporated into the least-squares procedure without further question.

Class 2. Accidentally absent reflexions which are smaller in magnitude than some instrumental threshold, F_{lim} , in which case we know that $0 \leq |F_o| < F_{lim}$ with uniform probability distribution in the interval.

Class 3. Totally unobserved reflexions, such as those outside the sphere of reflexion, or those which are known to be zero owing to symmetry requirements.

Class 3 reflexions should be given zero weight, which is equivalent to leaving them out of the calculation altogether.

The question of how to treat the class 2 reflexions arises. The knowledge of a limit obviously carries some useful information about the structure, and it therefore appears that such reflexions should be included in the refinement procedure. However, as they represent a probability distribution of errors which is no longer normal, the usual least-squares procedure breaks down. Previous authors, however, have incorporated these reflexions in the least-squares procedure as though their errors were normally distributed.

Hamilton (1955) discussed the treatment of unobserved reflexions, averaging over their intensities. Truter, Cruickshank & Jeffrey (1960) used, in principle, a similar procedure in the analysis of nitrogen perchlorate for a centro-

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