Acta Cryst. (1968). A**24**, 405

The Correction of Measured Integrated Bragg Intensities for First Order Thermal Diffuse Scattering

BY M. J. COOPER AND K. D. ROUSE

Ceramics Division, Atomic Energy Research Establishment, Harwell, Berks., England

(*Received* 14 *August* 1967)

The correction for the contribution of first-order thermal diffuse scattering to the measured integrated Bragg intensities of cubic single crystals has been derived by Nilsson (*Ark. Fys.* (1957) **12**, 247). Nilsson's formulation applies to diffractometer measurements using an ω scan (crystal rotating, detector stationary) and involves the approximation of an infinite slit height. In this paper the corresponding result for a $\theta-2\theta$ scan (detector coupled 2:1 to the crystal) is given and a further analytical method which approximates the volume scanned in reciprocal space to a sphere is discussed. The analysis for both ω and $\theta-2\theta$ scans is extended in order to eliminate some of the approximations involved in the other methods; the limitations of the various methods are discussed and the results of example calculations are presented.

Introduction

One of the corrections necessary when accurate structure factors are to be derived from Bragg intensity measurements is that for the thermal diffuse scattering (TDS) which peaks beneath the Bragg peak and so is included in the observed intensity. The standard derivation of this correction for measurements on cubic single crystals has been given by Nilsson (1957). However, Nilsson's formulation is applicable directly only for ω scans (crystal rotating, detector stationary) and great care must also be taken in view of the approximations involved. It is the purpose of this paper to present the corresponding result for a θ–2θ scan (detector coupled 2:1 to the crystal) and to extend the analysis in order to eliminate some of the approximations involved in the Nilsson formulation.

Nilsson method

Nilsson (1957) derives the total observed intensity for an imperfect cubic single crystal as:

$$I=I_0(1+\alpha)\,, \tag{1}$$

where I_0 is the true Bragg intensity and αI_0 is the contribution to the observed intensity from TDS.

Ignoring multi-phonon scattering

$$\alpha=\frac{4\pi k_B T}{3\lambda^3}\sin 2\theta\,\sin^2\theta\kappa\sigma\,, \tag{2}$$

where κ is a function of the elastic constants and is given approximately by

$$\kappa_{\text{approx}}=\frac{\frac{1}{5}b_1(c_{11}+c_{12})+c_{44}(2c_{11}+c_{44})}{\frac{1}{105}b_1^2b_2+\frac{1}{5}b_1(c_{11}+c_{12})c_{44}+c_{11}c_{44}^2} \tag{3}$$

with

$$\left.\begin{aligned}b_1&=c_{11}-c_{12}-2c_{44}\\ b_2&=c_{11}+2c_{12}+c_{44}\end{aligned}\right\} \tag{4}$$

and the following quantities in equation (2) have their usual meanings: k_B, Boltzmann's constant; T, absolute temperature; θ, Bragg angle; λ, wavelength.

The derivation of α is simplified by averaging the TDS over a spherical surface in reciprocal space centred on the relevant reciprocal lattice point and σ is then obtained by integrating the inverse square of the wave vector, q, of the phonon over the volume in reciprocal space appropriate to the type of scan used:

$$\sigma=\frac{1}{\pi k\sin 2\theta}\int\frac{dxdydz}{|q|^2}\,, \tag{5}$$

where $k=2\pi/\lambda$.

The expression for α given in equation (2) has been derived for the high temperature limit when each mode has energy k_BT. In addition the expression for κ_{approx} in equation (3) is valid only if b_1 is close to zero, *i.e.* the elastic constants are almost isotropic (for $b_1=0$, κ_{approx} is exactly correct). κ has been derived for other conditions by Schwartz (1964) but in the present paper we shall assume equations (2) and (3) to be valid.

Nilsson shows that σ can be evaluated analytically if the detector aperture is taken to be infinite in the vertical direction. It is convenient to define a point in reciprocal space by the three angles u, v and w in real space: u is the displacement of the crystal from the Bragg setting, *i.e.* the increase in the angle between the incident beam and the reflecting planes from the value θ: v and $w+\delta 2\theta$ are the vertical and horizontal divergence angles respectively of the scattered beam with respect to the direction of the Bragg scattered beam, v being measured upwards and w towards increasing 2θ, and $\delta 2\theta$ is the increase in detector angle at a point during the scan. The Bragg reciprocal lattice point then corresponds to $u=v=w=0$ and we can define a scan range from u_1 to u_2 and a rectangular slit aperture by the limits v_1, v_2, w_1 and w_2. The expression for σ given by Nilsson for an ω scan is then:

$$\sigma_1 = \frac{w_2}{2\sin^2\theta}\left[f\left(\frac{2u_2\sin^2\theta}{w_2}\right) - f\left(\frac{2u_1\sin^2\theta}{w_2}\right)\right] - \frac{w_1}{2\sin^2\theta}\left[g\left(\frac{2u_2\sin^2\theta}{w_1}\right) - g\left(\frac{2u_1\sin^2\theta}{w_1}\right)\right] - (u_2-u_1)\ln\left(-\frac{w_1}{w_2}\right), \quad (6)$$

where

$$f(x) = x\ln[(1-x)\sin\theta + \sqrt{x^2-2x\sin^2\theta+\sin^2\theta}] - x + \sin\theta\ln[x-\sin^2\theta+\sqrt{x^2-2x\sin^2\theta+\sin^2\theta}] \quad (7)$$

and $g(x)$ is obtained from $f(x)$ if $\sin\theta$ is replaced by $-\sin\theta$.

This expression for σ assumes that w_1 is negative and w_2 positive, as they must be for a normal peak scan. However, this condition on the signs of w_1 and w_2 may be relaxed for a background measurement, in which case we must modify equation (6) as follows. If w_1 and w_2 are both positive we must replace $g(x)$ by $f(x)$ in the second square bracket and put $+w_1/w_2$ instead of $-w_1/w_2$ in the last term; if w_1 and w_2 are both negative we must replace $f(x)$ by $g(x)$ in the first square bracket and again put $+w_1/w_2$ instead of $-w_1/w_2$ in the last term.

Since this derivation has assumed an infinite slit height it is likely to overestimate the TDS contribution quite appreciably for a single calculation. As Nilsson points out, the additional contribution will tend to be cancelled out by a similar contribution to the TDS included in the background calculation, which will be subtracted from the peak intensity. However, some additional contribution will always remain and this may still be quite large if the background measurement is not very close to the Bragg peak. We shall discuss this quantitatively in a later section.

Other analytical methods

(a) θ–2θ scan with infinite slit height

For a θ–2θ scan the volume swept out in reciprocal space will, in general, differ markedly from that swept out during an ω scan (Fig. 1). We have therefore derived the corresponding result for a θ–2θ scan, assuming an infinite vertical aperture and integrating analytically as in the Nilsson case. The resultant expression for σ is

$$\sigma_2 = \frac{w_2}{2\cos^2\theta}\left[F\left(\frac{2u_2\cos^2\theta}{w_2}\right) - F\left(\frac{2u_1\cos^2\theta}{w_2}\right)\right] - \frac{w_1}{2\cos^2\theta}\left[G\left(\frac{2u_2\cos^2\theta}{w_1}\right) - G\left(\frac{2u_1\cos^2\theta}{w_1}\right)\right] - (u_2-u_1)\ln\left(-\frac{w_1}{w_2}\right), \quad (8)$$

where

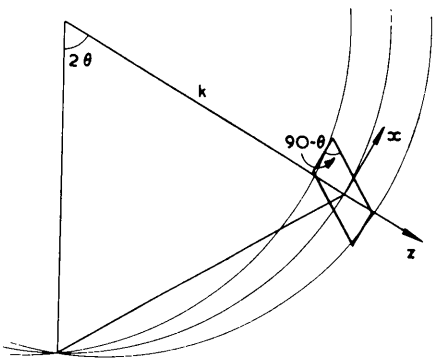
$$F(x) = x\ln[(1+x)\cos\theta + \sqrt{x^2+2x\cos^2\theta+\cos^2\theta}] + \cos\theta\ln[x+\cos^2\theta+\sqrt{x^2+2x\cos^2\theta+\cos^2\theta}] \quad (9)$$

and $G(x)$ is obtained from $F(x)$ if $\cos\theta$ is replaced by $-\cos\theta$. Changes in sign of w_1 and w_2 require the same changes as for the ω scan case, replacing $F(x)$ by $G(x)$ or $G(x)$ by $F(x)$ as required; equation (8) is for w_1 negative and w_2 positive.

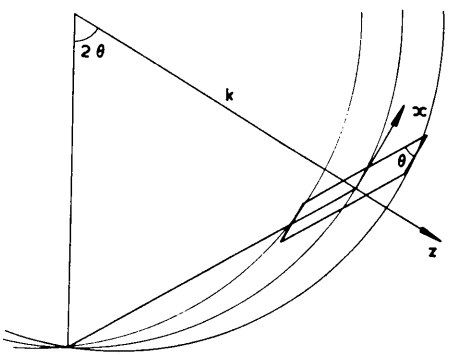
Overestimation of the TDS contribution will again occur in the same way as for the ω scan case.

(b) Spherical volume

A much simpler correction can be derived by considering the integration for σ to be carried out over a sphere centred on the reciprocal lattice point (Pryor, 1966). This avoids the need to consider an infinite slit height by approximating the appropriate volume to a sphere so that we may expect to obtain a better approximation to the TDS for a single calculation. The integration can be carried out immediately giving



(a)



(b)

Fig. 1. Diagrams of reciprocal space illustrating the volume swept out for (*a*) ω scan, (*b*) θ–2θ scan. The orthogonal coordinates (x,y,z) in reciprocal space are defined for the ω scan by $x = kw - z\tan\theta$, $y = kv$, $z = 2ku\sin\theta\cos\theta$ and for the $\theta-2\theta$ scan by $x = kw + z\cot\theta$, $y = kv$, $z = 2ku\sin\theta\cos\theta$.

$$\sigma_3 = \frac{2\lambda}{\pi \sin 2\theta} \quad q_m = \frac{2u'}{\sin 2\theta}, \tag{10}$$

where q_m is the maximum value of the wave vector of the phonon, *i.e.* the radius of the sphere, and u' is an effective scan range. In general the best value of u' will not be equal to the actual scan range $(u_2 - u_1)$ since the true volume depends on the dimensions of the detector aperture. u' must therefore be estimated from a detailed consideration of the true volume or alternatively it can be estimated by fitting the value of σ_3 to that of σ_1 or σ_2, corrected as necessary for finite slit height and background contribution, at a suitable value of θ (*e.g.* 45°) and allowing for any change in scan range from reflexion to reflexion. Provided that an appropriate value of u' is used this method may give a good approximation to the TDS contribution over quite a large range of θ.

As before a correction may be necessary for TDS included in the background measurement. For this method the most convenient way is to consider a stationary background count at the extremities of the scan range and assume that the TDS measured at these points corresponds to that calculated at the surface of the sphere, which is in fact $\frac{1}{3}$ of the contribution to the peak measurement. The validity of this procedure will of course depend on the true shape of the volume concerned.

It may be noted that if the scan range is the same for all reflexions this method gives an expression for α which is proportional to $\sin^2\theta$ for a given wavelength and temperature. The true Bragg intensity, I_0, is given by

$$I_0 = I_A \exp(-2B \sin^2\theta/\lambda^2), \tag{11}$$

where B is the mean temperature factor (Buerger, 1960) and I_A is the value at 0°K (assuming no zero-point motion). If α is small we can approximate equation (1) to the exponential form:

$$I \simeq I_0 \exp(\alpha), \tag{12}$$

so that for a spherical volume and small α we can write

$$\alpha \simeq 2\Delta B \sin^2\theta/\lambda^2. \tag{13}$$

Hence, provided that conditions are such that the spherical volume approximation with u' constant is valid and the TDS corrections are small, the effect of TDS is equivalent to a decrease $(-\Delta B)$ in the mean temperature factor. Under these conditions structure factors derived ignoring TDS effects will be fairly reliable but the temperature factor will be in error.

Numerical methods

In general the methods of evaluating σ described above all involve uncertain approximations. In order to avoid these it is necessary to integrate the expression given in equation (5) over the exact volume in reciprocal space corresponding to the experimental scan and this can only be done readily by using numerical methods.

We can define the following orthogonal coordinates of a point in reciprocal space corresponding to a θ–2θ scan (Fig. 1(*b*)]:

$$\begin{aligned} x &= kw + z\cot\theta \\ y &= kv \\ z &= 2ku\sin\theta\cos\theta, \end{aligned} \tag{14}$$

where u, v and w are the angular displacements defined earlier.

Hence we can write equation (5) in the form

$$\sigma = \frac{1}{\pi}\int_{u_1}^{u_2}\int_{v_1}^{v_2}\int_{w_1}^{w_2} \frac{dudvdw}{4u^2\cos^2\theta + 4uw\cos^2\theta + w^2 + v^2}. \tag{15}$$

Integrating first over v we obtain

$$\sigma = \frac{1}{\pi}\int_{u_1}^{u_2}\int_{w_1}^{w_2} \frac{1}{\sqrt{4u^2\cos^2\theta + 4uw\cos^2\theta + w^2}} \left[\tan^{-1}\left(\frac{v}{\sqrt{4u^2\cos^2\theta + 4uw\cos^2\theta + w^2}}\right)\right]_{v_1}^{v_2} dudw \tag{16}$$

$$= \frac{1}{\pi}\int_{u_1}^{u_2}\int_{w_1}^{w_2}\frac{1}{a}\left[\tan^{-1}(v/a)\right]_{v_1}^{v_2} dudw. \tag{17}$$

A similar result is obtained for an ω scan [Fig. 1(*a*)] for which $x = kw - z\tan\theta$ and we must replace $a^2 = 4u^2\cos^2\theta + 4uw\cos^2\theta + w^2$ in equations (15) to (17) by $b^2 = 4u^2\sin^2\theta - 4uw\sin^2\theta + w^2$. It can be seen that this result corresponds to the definition of σ given by Nilsson, putting $v = \varphi\cos\theta$, and Nilsson's equation (6) is obtained by putting $v_2 = -v_1 = \infty$ and integrating over u and w analytically.

Retaining finite limits on v we must integrate over u and w numerically. Great care must be exercised since the integrand becomes singular at the Bragg reciprocal lattice point $(u = w = 0)$. However, this singularity can be avoided by putting

$$\tan^{-1}\left(\left|\frac{v}{a}\right|\right) = \frac{\pi}{2} - \tan^{-1}\left(\left|\frac{a}{v}\right|\right), \tag{18}$$

so that

$$\sigma_4 = \int_{u_1}^{u_2}\int_{w_1}^{w_2}\frac{dudw}{a} - \frac{1}{\pi}\int_{u_1}^{u_2}\int_{w_1}^{w_2}\frac{1}{a}\left[\tan^{-1}\left(\frac{a}{v}\right)\right]_{v_1}^{v_2} dudw \tag{19}$$

for v_1 negative, v_2 positive.

The first term is that corresponding to an infinite slit height and has been evaluated earlier and the second term does not have the singularity and so can be evaluated numerically.

The authors have written a computer program to determine the TDS correction using this method and details of this are available elsewhere (Rouse & Cooper, 1968). The numerical integration is performed by Gaussian quadrature for a minimum of six points for both u and w and is repeated increasing the number of points for both by one. This process is continued until

two successive evaluations agree to within 0·1%. In the authors' experience the number of points required has never exceeded eleven.

Resolution effects

The analysis in the previous sections has assumed that divergence of the incident beam and the mosaic spread of the crystal are negligible: in practice allowance for these factors may be desirable. A detailed consideration of instrumental resolution is extremely complex (see *e.g.*, Cooper & Nathans, 1967) introducing several other parameters into the calculations. The resolution function of the diffractometer can be considered as a probability distribution in reciprocal space giving the probability of detection of the radiation as a function of the scattering vector when the instrument has been set to measure a scattering process corresponding to a particular scattering vector. The introduction of this general probability distribution, however, prevents us from obtaining an integral which can be evaluated analytically. Hence we are unable to avoid the singularity which occurs at the Bragg reciprocal lattice point.

To overcome this limitation we must write the probability over the volume concerned as a function of the crystal misset only, as for mosaic spread, and take it to be unity between certain limits of v and w. This allows us to overcome the singularity as before, leaving an additional integration over the 'mosaic spread' to be evaluated numerically. We should however increase the effective aperture dimensions to allow for the divergence of the incident beam. The effective aperture dimensions and the 'mosaic spread' function should then be estimated experimentally for each reflexion using crystal (ω) and detector (2θ) scans.

Discussion

From the considerations of the earlier sections it is clear that if accurate corrections for TDS are required these should be evaluated by means of numerical integration over the relevant volume in reciprocal space. Although the use of analytical methods may often provide satisfactory results considerable care is required in view of the approximations concerned. To illustrate this we shall consider some quantitative examples, ignoring for the moment any resolution effects.

We shall consider first the X-ray measurements of James & Brindley (1928) on potassium chloride, which were taken by Nilsson as an example. Following Nilsson we have calculated the TDS parameter α [see equation (1)] for an infinite slit height at 20 °C. These calculations reproduce the values given by Nilsson for the peak scans but differ slightly on the background corrected values. This is possibly due to greater accuracy in the present calculations, since σ' in Nilsson's Table 2 should be a smooth function of θ. The α values are given in Table 1 together with the values obtained by numerical integration for the following angular dimensions (peak: $u_2=-u_1=1{\cdot}25°$, $w_2=-w_1=0{\cdot}75°$, $v_2=-v_1=0{\cdot}75°$; background: $u_1=-0{\cdot}25°$, $u_2=2{\cdot}25°$, $w_1=1{\cdot}25°$, $w_2=2{\cdot}75°$, $v_2=-v_1=0{\cdot}75°$). Since no values of these parameters are quoted in the original paper we have used those given by Nilsson and assumed that the detector has a square aperture. Although this may

Table 1. *TDS correction parameters* (α) *for potassium chloride at* 20 °C

hkl	θ	α_1 Infinite slit peak only	α_2 Infinite slit peak − background	α_3* Finite slit peak − background	α_4 Spherical volume	α_5 $A\bar{B}$ = 0·16 Å²
400	13·0°	0·047	0·037	0·033	0·036	0·033
600	19·7	0·127	0·097	0·079	0·081	0·076
444	22·9	0·177	0·129	0·109	0·108	0·102
800	26·7	0·248	0·179	0·147	0·146	0·139
10,0,0	34·2	0·405	0·282	0·227	0·226	0·224
666	35·7	0·438	0·298	0·244	0·244	0·244

* Best values

Table 2. *TDS correction parameters* (α) *for barium fluoride at* 400 °C

hkl	θ	α_1 ω scan Infinite slit	α_2 $\theta-2\theta$ scan Infinite slit	α_3 Sphere (Infinite slit)	α_4* $\theta-2\theta$ scan Finite slit	α_5 Sphere (Finite slit)	α_6 $A\bar{B}$ = 0·16 Å²
511	25·5°	0·084	0·072	0·091	0·056	0·069	0·065
711	36·3	0·173	0·162	0·173	0·123	0·131	0·127
733	42·8	0·228	0·224	0·227	0·170	0·172	0·171
911	49·1	0·275	0·284	0·282	0·216	0·214	0·215
933	55·6	0·308	0·334	0·336	0·257	0·255	0·262
377	59·1	0·317	0·353	0·362	0·274	0·275	0·286
577	66·9	0·338	0·428	†	0·328	†	†

* Best values
† Not calculated because of change in scan range.

not represent the true experimental conditions it will provide a useful case for comparison with the infinite slit height results.

It can be seen that for these conditions the values (α_2) given by Nilsson result in errors of up to 5% in the corrected intensities. We have also listed the values α_4 for a spherical volume fitted to the numerical calculation (α_3) at the 666 reflexion; and in addition the values $\alpha_5 = \exp[2\Delta B(\sin^2\theta)/\lambda^2]$, where ΔB has the value 0·16 Å^2 chosen to give agreement with α_3 at the same reflexion. It can be seen that for this range of data the error in the intensities resulting from ignoring the TDS correction is always less than 1% although there will be a resultant error in the mean temperature factor of the order of 0·16 Å^2, compared with the value 0·20 Å^2 given by Nilsson (1957) on the basis of the infinite slit height calculations.

As a second example we shall consider some recent accurate neutron diffraction measurements on barium fluoride (Cooper, Rouse & Willis, 1968), in particular several representative measurements which were made at 400°C. In Table 2 we list the TDS parameters calculated in six ways. α_1 to α_4 correspond to σ_1 to σ_4 respectively, being the parameters obtained for (1) ω scan, infinite slit height, (2) θ–2θ scan, infinite slit height, (3) spherical volume, fitted to infinite slit height at $\theta = 45°$, and (4) θ–2θ scan, finite slit height. α_5 is for a spherical volume fitted to the finite slit height at $\theta = 45°$ and $\alpha_6 = \exp[2\Delta B(\sin^2\theta)/\lambda^2]$ with a value of $\Delta B = 0{\cdot}16$ Å^2. The neutron measurements were made with a θ–2θ scan with a range of $u_2 = -u_1 = 1{\cdot}2°$ in θ and a slit of angular aperture $v_2 = -v_1 = 1{\cdot}62°$, $w_2 = -w_1 = 1{\cdot}12°$ (except for 577 for which the scan range was $u_2 = -u_1 = 1{\cdot}6°$). Background measurements were made with a similar scan with the crystal offset from the Bragg peak; the figures given in the Table refer to the peak scan only.

If we compare firstly the values of α_1, α_2 and α_3 we see that the differences between the values calculated for an ω scan and for a θ–2θ scan with an infinite aperture are relatively small for $\theta < 50°$ but increase rapidly for $\theta > 50°$. $\alpha_1 = \alpha_2$ at $\theta = 45°$ and α_3 has been fitted to this value. The effective scan range for the spherical calculation is then $\pm 1{\cdot}94°$ and it can be seen that α_3 is a good approximation to α_2 for $\theta < 45°$ and to α_1 for $\theta > 45°$ and up to at least 60°.

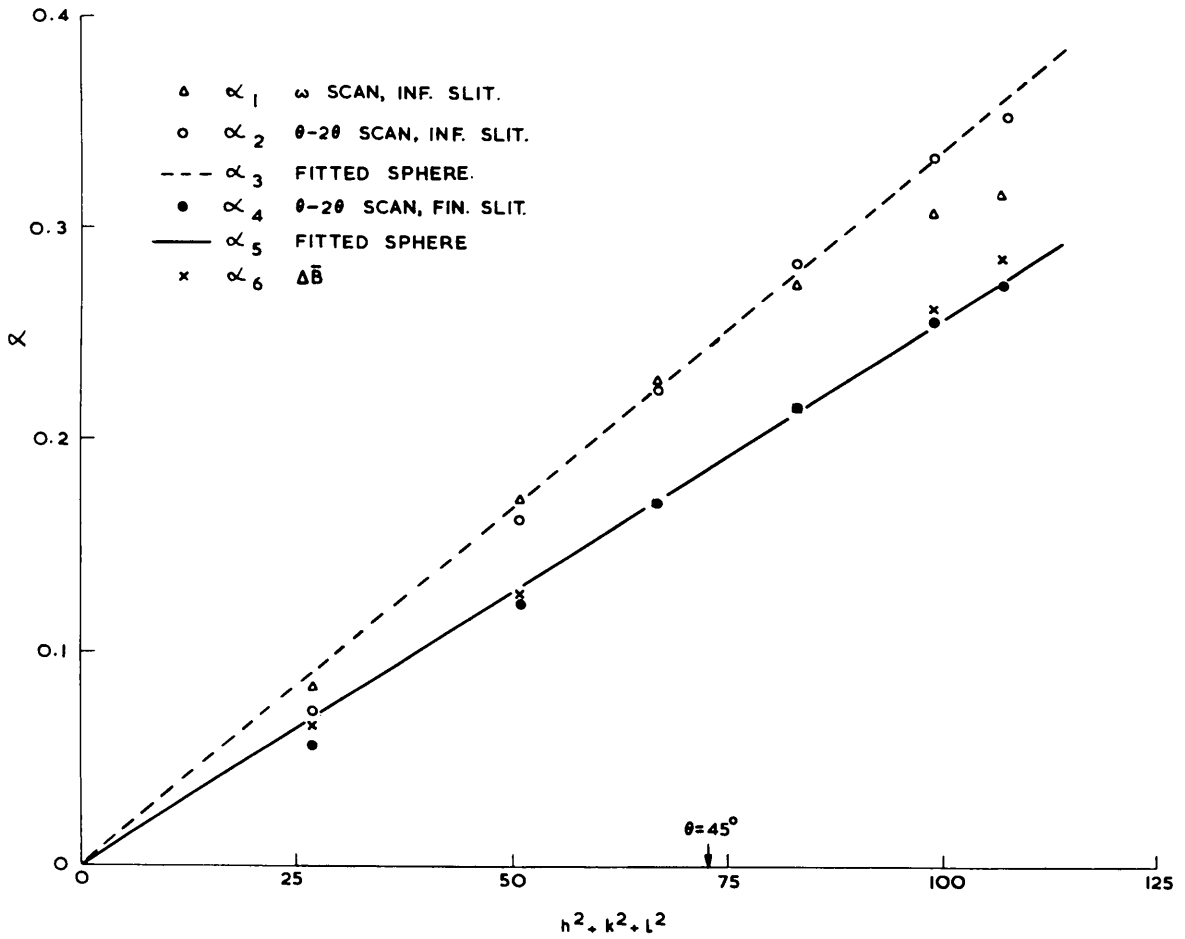


Fig. 2. TDS correction parameters for barium fluoride at 400°C as a function of $h^2 + k^2 + l^2$ ($\propto \sin^2\theta/\lambda^2$).

α_4 is the corresponding value calculated for the finite aperture (θ–2θ scan) and it can be seen that the approximation of an infinite slit in this case gives an error of the order of 30% in the TDS contribution to the peak scan. The values obtained for a spherical volume (α_5) are in this case also quite good approximations for $\theta > 40°$; the effective scan range being $\pm 1{\cdot}47°$. A sphere of equal volume would give an effective scan range of $\pm 1{\cdot}43°$ resulting in values of α 3% lower than α_5. These effective scan ranges may be compared with the true scan range of $\pm 1{\cdot}2°$; a spherical volume using the true scan range would thus give values of α of the order of 20% too small in this case. The error in the intensities resulting from ignoring the TDS correction would again be less than about 1% with a corresponding error in the mean temperature factor. The relative agreement between the various α values is also illustrated in Fig. 2.

We have also estimated the 'mosaic spread' effect for the barium fluoride measurements. The full width at half height of the measured peaks varied from 0·2° up to 0·8° resulting in a reduction of the TDS correction between 1% and 10%. This can therefore be an important factor particularly if the width of the measured peaks changes rapidly with the scattering angle and passes through a focusing position.

The authors are indebted to Dr B.T.M.Willis for numerous and valuable discussions and for access to his unpublished review on Lattice Vibrations and the Accurate Determination of Structure Factors for the Elastic Scattering of Neutrons and X-rays.

References

BUERGER, M. J. (1960). *Crystal Structure Analysis*, p. 232. New York: John Wiley.
COOPER, M. J. & NATHANS, R. (1967). *Acta Cryst.* **23**, 357.
COOPER, M. J., ROUSE, K. D. & WILLIS, B. T. M. (1968). To be published.
JAMES, R. W. & BRINDLEY, G. W. (1928). *Proc. Roy. Soc.* A**121**, 155.
NILSSON, N. (1957). *Ark. Fys.* **12**, 247 .
PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138.
ROUSE, K. D. & COOPER, M. J. (1968). Atomic Energy Research Establishment Report R 5725.
SCHWARTZ, L. H. (1964). *Acta Cryst.* **17**, 1614.

Acta Cryst. (1968). A**24**, 410

A Neutron Diffraction Determination of the Crystal Structures of Thiourea and Deuterated Thiourea above and below the Ferroelectric Transition

BY MARGARET M. ELCOMBE AND J. C. TAYLOR

Solid State Physics Section, Australian Atomic Energy Commission, Lucas Heights, Sutherland, N.S.W. Australia

(*Received* 13 *November* 1967 *and in revised form* 22 *December* 1967)

The structures of thiourea, $SC(NH_2)_2$, and deuterated thiourea, $SC(ND_2)_2$, have been determined at room and liquid nitrogen temperatures from three-dimensional neutron diffraction data. No significant structural change on deuteration has been found. N–H···S hydrogen bonds occur in both materials at both temperatures with N–S distances of 3·35–3·43 Å and N–H–S angles of 169–171° and, apart from these hydrogen atoms, the molecules are planar to within 0·010 Å. An analysis of the thermal parameters of the atoms in each molecule in terms of rigid vibration parameters shows that at liquid nitrogen temperature the molecules are fairly rigid whereas at room temperature there are serious deviations from rigidity. Excellent agreement has been found between the thermal vibrations of the molecules at room temperature and the observed structure change to the lower ferroelectric state. A qualitative theory of the ferroelectric nature of thiourea is proposed which explains the observed temperature variation of the spontaneous polarization and coercive field in the lower ferroelectric region, in terms of a variable molecular orientation and a single hydrogen bond which is switched from one sublattice to the other during ferroelectric reversal.

1. Introduction

On cooling from room temperature, thiourea, $SC(NH_2)_2$, passes through at least five different phases, two of which are ferroelectric (Goldsmith & White, 1959). The ferroelectric phases occur in the temperature ranges 179–173 °K and < 169 °K. Substitution of deuterium for hydrogen raises the temperature of the three major dielectric anomalies by 16°, 16°, and 11°. The coercive field is small, 200 volts.cm^{-1} at 120 °K.

An X-ray diffraction study of the room temperature structure of thiourea has been made by Kunchur & Truter (1958) using photographic data, and again by Truter (1967) using counter data. The structure at 293 °K is orthorhombic with space group *Pnma* and lattice parameters $a = 7{\cdot}655$, $b = 8{\cdot}537$, $c = 5{\cdot}520$ Å, all