multiple reflexions are likely to co-exist or reflect two aspects of the internal structure.

MASLEN: Can you comment on the broad modulation observable in the Si curve in addition to the sharp peaks?

POST: The specimen referred to had been ground and had a fairly substantial mosaic spread, probably mainly in the surface layers. Moon & Shull have carried out calculations and we have examined two cases. It appears possible to explain the widths observed on the basis of those geometrical considerations, at least for mosaic crystals. For perfect crystals, the situation is of course different.

WEISS: Now is probably the time for crystallographers to accept, at the beginning of a crystal study, that multiple diffraction effects exist, and are important, and to seek to satisfy themselves as to their magnitude in the specific case they have on hand. One way which would be useful would be to look for their effect on space-group forbidden reflexions.

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The Correction of Measured Structure Factors for Thermal Diffuse Scattering

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Correction of X-ray intensities for thermal diffuse scattering (TDS) is necessary, though difficult in practice. Existing calculations for the TDS correction are reviewed and the hitherto neglected resolution function, $R(\mathbf{q})$, of the diffractometer is discussed. It is concluded that overcorrection for inelastic scattering results when $R(\mathbf{q})$ is ignored. Computation of accurate corrections requires a knowledge of the elastic constants of the material, experimental measurement of $R(\mathbf{q})$ for several reflexions and considerable machine programming and computing time.

1. Introduction

I undertook to give this paper with some reluctance, since my periods of interest in accurate measurement of structure factors and in lattice dynamics have scarcely overlapped. Consideration of both at the same time has proved to be a useful exercise however, and has convinced me that the correction of X-ray intensities for thermal scattering is both necessary, and difficult in practice. I am therefore advocating a tedious correction which I never applied to my own data!

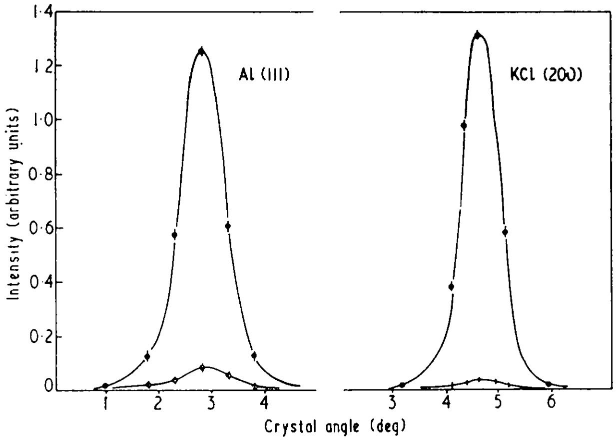


Fig. 1. Bragg intensity and diffuse intensity determined by the method of Butt & O'Connor (1967). Reproduced from their paper.

The theory of X-ray scattering by lattice vibrations has been reviewed elsewhere (Cochran, 1966; Smith, 1966) and will not be considered in detail. Bragg scattering is the process in which the X-ray photon is scattered without change of energy, so that the wavelength is unaltered. This scattering is superimposed on a background of Compton scattering and possibly fluorescence scattering which we do not consider since the intensity varies slowly in reciprocal space and is easily subtracted off. Thermal scattering is the process in which the incident radiation is scattered inelastically, the incident photon exchanging one or more quanta of vibrational energy (phonons) with the crystal. The change in energy (or wavelength) of the scattered radiation is only a few parts per million, ordinarily negligible. It is however enough to distinguish elastically and inelastically scattered radiations when the technique of Mössbauer spectroscopy is used (Butt & O'Connor, 1967). Fig. 1 shows the elastically and inelastically scattered components from Al (111 reflexion) and from KCl (200 reflexion). The intensity of thermal scattering is seen to be by no means negligible, even for these low-angle reflexions. Fig. 1 can be misleading: to gain intensity the experiment had to be done with poor geometrical resolution and as a result the inelastic and elastic components appear equally 'peaked' at a reciprocal lattice point, which is not at all the case.

Lattice vibrations can be distinguished as acoustic modes, for which the (circular) frequency $\omega_j(\mathbf{q})$ is proportional to the wave number q for small values of q, and optic modes for which $\omega_j(\mathbf{q})$ remains relatively high for all values of $\mathbf{q}$. The index j distinguishes different branches of the spectrum such as transverse acoustic, longitudinal optic *etc.* For a general value of $\mathbf{q}$ there are 3 acoustic modes and $3n-3$ optic modes, where n is the number of atoms per unit cell. Thermal (*i.e.* inelastic) scattering can be distinguished as one-phonon, two-phonon *etc.* processes according to the number of phonons absorbed or emitted. One-phonon scattering by acoustic modes is quite strongly peaked at reciprocal lattice points, the intensity varying as $1/q^2$ for small $\mathbf{q}$, where the wave vector $\mathbf{q}$ is also the distance from the reciprocal lattice point. This component of the intensity is roughly proportional to $KT/m\theta_D^2$, where $K=(4\pi \sin \theta)/\lambda$, T is the absolute temperature, m the mass per unit cell and θ_D the Debye temperature. Two-phonon scattering by acoustic modes is less strongly peaked, the intensity varying more slowly than $1/q$ and being roughly proportional to $(KT/m\theta_D^2)^2$. Higher-order processes are generally of negligible intensity, while scattering processes involving optic modes do not vary rapidly in intensity with $\mathbf{q}$ and can be subtracted off by a background measurement. Table 1, compiled from data kindly provided by Dr T. Smith, shows the (calculated) relative intensities of different scattering processes for NaF at a few different points in reciprocal space. These numbers confirm that normally it will be necessary to calculate a correction only for one-phonon scattering by acoustic modes. Fortunately the intensity of this component, unlike the others, can be calculated without a detailed knowledge of the dynamics of the crystal; it does however involve the elastic constants.

2. The correction in an idealized situation

The considerations of this section apply to a small crystal and a four-circle diffractometer, but the situation is idealized in that both the crystal and the X-ray source are treated as points in relation to the other dimensions involved. Symbols which appear frequently, other than those already defined in the previous section, are as follows:

$$\mathbf{K}=\mathbf{k}-\mathbf{k}_0 \tag{2·1}$$

is the scattering vector, the difference between the wave vectors of the scattered and incident radiation. $\mathbf{H}$ is a vector to a reciprocal lattice point, $F(\mathbf{H})$ the corresponding structure factor. N is the number of unit cells in the crystal, each of volume v. k_B is Boltzmann's constant. The cross section for Bragg scattering is (see for example Cochran, 1966)

$$\frac{d\sigma_0}{dS}=\frac{(2\pi)^3N}{v}|F(\mathbf{H})|^2\delta(\mathbf{K}-\mathbf{H})\,. \tag{2·2}$$

Here $d\sigma_0$ is a measure of the photons scattered per second into a solid angle dS in the direction $\mathbf{k}$. The δ-function satisfies the conditions

$$\delta(\mathbf{K})=0 \text{ for } \mathbf{K}\neq 0\,, \int \delta(\mathbf{K})d^3K=1 \tag{2·3}$$

and shows that this intensity is concentrated entirely at reciprocal lattice points, *i.e.* the Bragg reflecting condition, $\mathbf{K}=\mathbf{H}$, must be satisfied. Suppose the detector slits subtend (small) horizontal and vertical angles ψ_1 and ψ_2 at the specimen, and the latter is rotated through a (small) angle Ω about a vertical axis which takes it through the reflecting position with angular velocity ω in the recording time τ. The 'total count recorded' is then

$$E_0=\int_0^\tau \sigma_0 dt,$$

that is

$$E_0=\frac{(2\pi)^3N|F(\mathbf{H})|^2}{v}\iint \delta(\mathbf{K}-\mathbf{H})d\psi_1 d\psi_2 dt \tag{2·4}$$

since $dS=d\psi_1 d\psi_2$. Fig. 2 shows the volume swept out in reciprocal space, and also that the element of volume is

$$d^3K=(Kd\Omega)\,(kd\psi_1)\,(kd\psi_2)\cos \zeta\,. \tag{2·5}$$

Table 1. *Theoretical diffuse intensities for* NaF *at room temperature*

h	k	l	I_1	I_2	I_3	I_{4+}	Total	Compton intensity
			n-phonon intensities, $n=1,2\ldots.$					
4	0·2	0	119·6	6·05	0·36	0·01	126·02	11·87
4	0·4	0	34·13	3·54	0·31	0·02	38·00	11·92
4	0·6	0	18·55	2·70	0·30	0·03	21·57	11·96
4	0·8	0	13·58	2·34	0·29	0·03	16·23	12·02
4	1·0	0	12·13	2·24	0·29	0·03	14·69	12·09
4	1·2	0	12·87	2·34	0·29	0·03	15·53	12·16
6	0·2	0	61·86	7·02	0·93	0·10	69·90	14·42
6	0·4	0	17·68	4·09	0·80	0·13	22·71	14·43
6	0·6	0	9·65	3·10	0·76	0·16	13·67	14·44
6	0·8	0	7·10	2·67	0·73	0·17	10·67	14·45
6	1·0	0	6·39	2·54	0·71	0·18	9·81	14·46
6	1·2	0	6·83	2·64	0·73	0·17	10·37	14·48
6	1·4	0	8·93	3·03	0·77	0·16	12·90	14·50
6	1·6	0	15·76	3·96	0·84	0·15	20·71	14·54
6	1·8	0	53·08	6·73	0·97	0·12	60·96	14·58

h,k,l are the components of $\mathbf{K}$ in units of $2\pi/a$.

Combining equations (2·5) and (2·4), and using $k = 2\pi/\lambda$, $K = (4\pi \sin\theta)/\lambda$ and $\omega = d\Omega/dt$ we get the familiar result (James, 1948)

$$E_0 = \frac{N\lambda^3|F(\mathbf{H})|^2}{v\omega \sin 2\theta}\,. \qquad (2\cdot6)$$

The corresponding cross section for one-phonon scattering by acoustic modes of small wave vector is, to a good approximation

$$\frac{d\sigma_1}{dS} = \frac{(2\pi)^3|F(\mathbf{H})|^2}{v} \times \sum_{\mathbf{q}j} \frac{[K\,.\,\mathbf{e}_j(\mathbf{q})]^2 k_{\mathrm{B}}T}{m\omega_j^2(\mathbf{q})}\,\delta(\mathbf{K}+\mathbf{q}-\mathbf{H})\,. \qquad (2\cdot7)$$

Here $\mathbf{e}_j(\mathbf{q})$ is a unit vector in the direction of polarization of an acoustic mode. As a convenient abbreviation we introduce

$$J(\mathbf{q}) = \sum_j \frac{[\mathbf{K}\,.\,\mathbf{e}_j(\mathbf{q})]^2 k_{\mathrm{B}}T}{\varrho\omega_j^2(\mathbf{q})} \qquad (2\cdot8)$$

where $\varrho = m/v$ is the density of the crystal. $J(\mathbf{q})$ gives the intensity distribution in the vicinity of a reciprocal lattice point $\mathbf{H}$. The total count recorded from this scattering process is therefore, by analogy with (2·4),

$$E_1 = \frac{(2\pi)^3|F(\mathbf{H})|^2}{v^2}\iint \sum_{\mathbf{q}} J(\mathbf{q})\delta(\mathbf{K}+\mathbf{q}-\mathbf{H})d\psi_1 d\psi_2 dt\,. \qquad (2\cdot9)$$

where the sum is to be taken over those wave vectors which can contribute, namely those which lie inside the volume in reciprocal space swept out in the course of the measurement, shown in Fig. 2. (We shall refer to this as the 'range of measurement'). However the density of wave vectors in reciprocal space is $(Nv)/(2\pi)^3$, and we can replace the sum by an integral

$$\sum_{\mathbf{q}} \rightarrow \frac{Nv}{(2\pi)^3}\int d^3q\,. \qquad (2\cdot11)$$

(Clearly d^3q and d^3K are equal since $\mathbf{K}+\mathbf{q}=\mathbf{H}$, a constant.) Thus we finally obtain the basic result

$$\alpha = \frac{1}{(2\pi)^3}\int J(\mathbf{q})d^3q \qquad (2\cdot12)$$

where $J(\mathbf{q})$ is given by equation (2·8) and the integral is over the range of measurement.

Expression (2·12) could be programmed for numerical evaluation. $J(\mathbf{q})$ is determined by the elastic constants, for example for a cubic crystal $\varrho\omega_j^2(\mathbf{q})$ and $\mathbf{e}_j(\mathbf{q})$ are determined by the equation (James, 1948)

$$(c_{11}q_x^2 + c_{44}(q_y^2+q_z^2) - \varrho\omega^2)e_x + (c_{12}+c_{44}) \times (q_xq_ye_y + q_xq_ze_z) = 0 \qquad (2\cdot13)$$

and two similar equations in which the indices are cyclically permuted. Alternatively expressed, each $\varrho\omega_j^2(\mathbf{q})$ is an eigenvalue and each $\mathbf{e}_j(\mathbf{q})$ the corresponding eigenvector of the following matrix,

$$\left.\begin{matrix} c_{11}q_x^2 + c_{44}(q_y^2+q_z^2) & (c_{12}+c_{44})q_xq_y & (c_{12}+c_{44})q_xq_z \\ (c_{12}+c_{44})q_yq_x & c_{11}q_y^2 + c_{44}(q_x^2+q_z^2) & (c_{12}+c_{44})q_yq_z \\ (c_{12}+c_{44})q_zq_x & (c_{12}+c_{44})q_zq_y & c_{11}q_z^2 + c_{44}(q_x^2+q_y^2) \end{matrix}\right\}\,. \qquad (2\cdot14)$$

Comparing equations (2·9) and (2·4) we see that

$$\alpha = \frac{E_1}{E_0} = \frac{1}{Nv}\sum_{\mathbf{q}} J(\mathbf{q}) \qquad (2\cdot10)$$

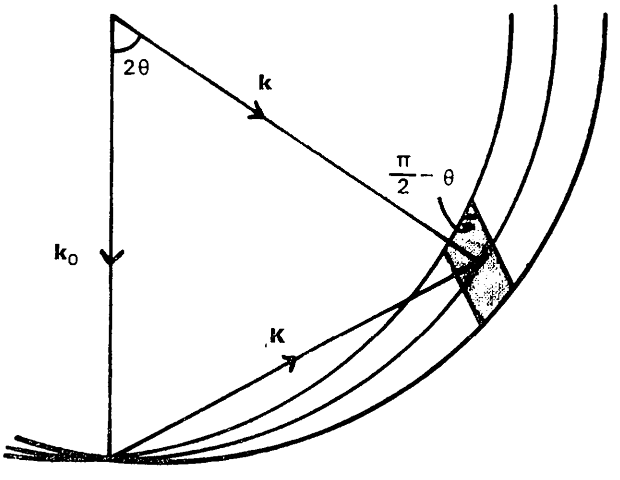


Fig. 2. The 'range of measurement' in reciprocal space for an Ω-scan.

Isodiffusion contours, surfaces on which $J(\mathbf{q})$ is constant, are illustrated by James (1948). They are not spherical, even for a crystal such as sodium or an alkali halide. A further complication is that the range of measurement, over which the integral (2·12) is to be evaluated, is not the same for every reciprocal lattice point. It is therefore not surprising that the tedious numerical calculation outlined in this paragraph has not so far been made.

3. Review of existing calculations

The integral (2·12) has been evaluated analytically by Nilsson (1957), making a number of approximations, and more exactly by Cooper & Rouse (1968) by a combination of analytical and numerical methods. The major approximation made by these authors is that $J(\mathbf{q})$ is isotropic, and can be written $J(q)$. Alternatively expressed, it is as if all acoustic modes had the same velocity, independent of directions of propagation and polarization, so that

$$\varrho\omega_j^2(\mathbf{q}) = cq^2\,. \qquad (3\cdot1)$$

Nilsson (1957) evaluated the 'best' value of the elastic constant c in terms of the actual elastic constants of a cubic crystal. The relation is not a simple one; however if $c_{11}=c_{12}+2c_{44}$, it reduces to the more obvious one,

$$3/c=1/c_{11}+2/c_{44}\,. \tag{3·2}$$

With the approximation of a single elastic constant, equation (2·8) reduces to

$$J(q)=\frac{K^2k_{\rm B}T}{cq^2} \tag{3·3}$$

and therefore

$$\alpha=\frac{K^2k_{\rm B}T}{(2\pi)^3c}\int\frac{d^3q}{q^2}\,. \tag{3·4}$$

The integral is still difficult to evaluate because the 'range of measurement' is a parallelepiped. Pryor (1966) suggested replacing the parallelepiped by a sphere of radius q_m, so that

$$\alpha=\frac{K^2k_{\rm B}Tq_m}{2\pi^2c}\,. \tag{3·5}$$

The volume is determined by equation (2·5), so one expects q_m to be determined by the condition

$$\left(\frac{2\pi}{\lambda}\right)^3(\sin 2\theta)\Omega\psi_1\psi_2=\frac{4\pi}{3}\,q_m^3\,. \tag{3·6}$$

In fact Cooper & Rouse (1968) found that in two instances the spherical approximation gave results in good agreement with their exact evaluation of (3·4), provided that q_m was kept constant at a value corresponding to about $\theta=45°$ in equation (3·6).

The background reading E' obviously includes a contribution E_1' from the scattering by acoustic modes. The corrected reading is

$$E_0=(E-E')-(E_1-E_1') \tag{3·7}$$

and we write

$$\alpha'=\frac{E_1'}{E_0}\,. \tag{3·8}$$

α' is also given by equation (2·12), the integral being over a range of measurement which of course does not include the reciprocal lattice point. Alternatively, if the background is measured with the crystal stationary at the end of the range of Ω, for the same recording time,

$$\frac{\alpha'}{\alpha}=\frac{\langle J'\rangle}{\langle J\rangle}\,, \tag{3·9}$$

where $\langle J\rangle$ is the average of $J(\mathbf{q})$ over the volume of the parallelepiped, and $\langle J'\rangle$ is the average over the area which is one end of the parallelepiped. Pryor's approximation enables one to estimate that

$$\alpha'\simeq\tfrac{1}{3}\alpha\,. \tag{3·10}$$

Table 2. *Values of α–α' for* KCl *at room temperature*

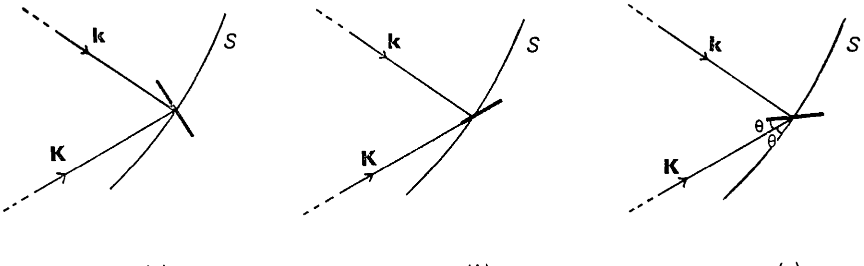
$h\ k\ l$	$\theta°$	$\alpha-\alpha'$†	$\alpha-\alpha'$*
4 0 0	13·0	0·033	0·036
6 0 0	19·7	0·079	0·081
4 4 4	22·9	0·109	0·108
8 0 0	26·7	0·147	0·146
10 0 0	34·2	0·227	0·226
6 6 6	35·7	0·244	0·244

† Cooper & Rouse (1968).
* Pryor (1966).

Table 2, column 3, shows the values of α–α' calculated by Cooper & Rouse (1968) for KCl at 20 °C, with $\Omega=2{\cdot}5°$, $\psi_1=\psi_2=1{\cdot}5°$. Column 4 shows the results of the spherical approximation, with q_m fixed at a value which makes the figures agree for the 666 reflexion. These results confirm Nilsson's (1957) conclusion that α–α' is nearly proportional to $\sin^2\theta$. It follows that the result of *not* applying the correction is to deduce too small a value of B in the expression for the Debye–Waller factor,

$$F=F_0\exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right]. \tag{3·11}$$

For KCl, the value of B deduced originally was 1·15 Å^{-2}, correction of the measurements for thermal scattering raised this to 1·31 Å^{-2}.



(a) (b) (c)

Fig. 3. (*a*) The effect of mosaic spread is to make the resolution function finite on a disc perpendicular to **K**. (*b*) The effect of wavelength spread is to extend the resolution function along a line parallel to **K**. (*c*) The effect of the finite size of the source is to make the resolution function finite on a disc perpendicular to the plane of the diagram and inclined to **K** at an angle θ. S is a section of the reflecting sphere.

4. The resolution function

The approximation that $J(q)$ is isotropic may not be the most serious approximation made in the work described in § 3. In practice the correct expression for α is not equation (2·12), but the same expression with $J(\mathbf{q})$ replaced by $J_R(\mathbf{q})$, where

$$J_R(\mathbf{q}) = \frac{1}{(2\pi)^3} \int R(\mathbf{q}')J(\mathbf{q}-\mathbf{q}')d^3q' \; . \qquad (4·1)$$

$R(\mathbf{q})$ is the resolution function. (See for example Als-Nielsen & Dietrich, 1967). It satisfies the normalizing condition

$$\frac{1}{(2\pi)^3} \int R(\mathbf{q})d^3q = 1 \qquad (4·2)$$

and is itself the result of convoluting at least four separate functions. These arise from the effects of mosaic spread, of wavelength spread, of finite source dimensions and of finite specimen dimensions. Each is considered in turn with the other three absent.

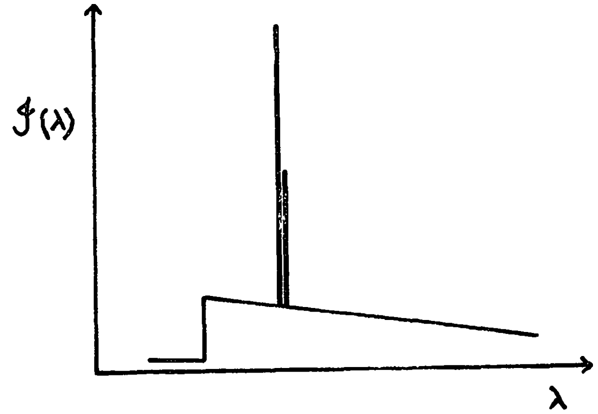


Fig. 4. Schematic representation of the intensity distribution when filtered radiation is used.

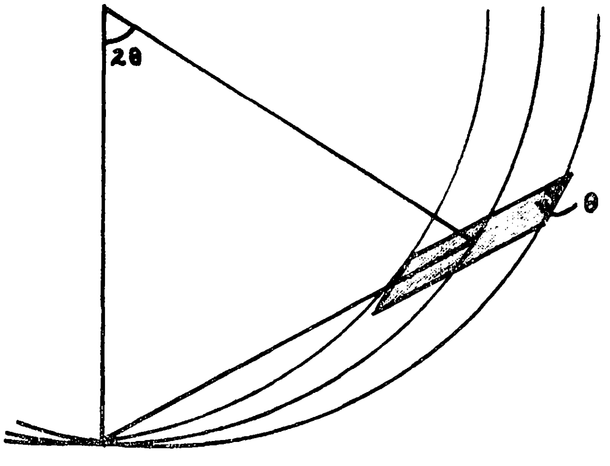


Fig. 5. The 'range of measurement' in reciprocal space for an Ω-2θ scan.

The effect of mosaic spread is to make $R(\mathbf{q})$ finite in a plane perpendicular to $\mathbf{K}$, with a distribution depending on the distribution of misorientations which constitutes the mosaic spread. The width of $R(\mathbf{q})$ is proportional to K, see Fig. 3(*a*). This effect will usually be relatively unimportant, the height of the spots on the zero layer of a single-crystal photograph does not increase noticeably with increasing 2θ, whatever the orientation of the crystal.

The incident radiation will usually have $K\alpha_1$ and $K\alpha_2$ wavelength components, and a proportion of white radiation with a sharp cut-off on the low wavelength side (Fig. 4). The resolution function is finite on a straight line parallel to $\mathbf{K}$, with $R(q)$ proportional to $I(\Delta\lambda)$, where $q = K\Delta\lambda/\lambda$ [Fig. 3(*b*)]. The gradual separation of $R(q)$ into α_1 and α_2 components may or may not be important, depending on the characteristic radiation used and the range of 2θ. Since the intensity of white radiation will usually vary almost linearly with $\Delta\lambda$, a satisfactory correction for white radiation can be made experimentally as follows. Counts are recorded using an $\Omega - 2\theta$ scan (detector moving with angular velocity 2ω). The 'range of measurement' is then the parallelepiped shown in Fig. 5. Taking the background as the average of that at the two extremities of the range, results in the white radiation being subtracted out. This method breaks down when the dispersion is small, so that the background position on the low angle side is on the wrong side of the absorption edge, or so close to it that the intensity is reduced by the geometrical contributions to the resolution function. In this situation it may be possible to make a correction based on the background reading on the high-angle side only, but further consideration of the correction for white radiation lies outside the scope of this paper. We may note however that any correction computed from $I(\Delta\lambda)$, ignoring the geometrical contributions to the resolution function, will be inadequate since these smear out the idealized distribution shown schematically in Fig. 4.

Next let us suppose the specimen remains a point, but the X-ray source is a uniform rectangle subtending horizontal and vertical angles f_1 and f_2 at the specimen. The effect in reciprocal space is to make $R(\mathbf{q})$ a uniform rectangular disc of height kf_2 and width kf_1 inclined at an angle θ to the vector $\mathbf{K}$ [see Fig. 3(*c*)]. (Note that in this situation the angular velocity of the reflected beam is ω.)

With the X-rays originating from a point, the effect of having a vertical needle-shaped specimen subtending an angle s_2 at the source, is to make $R(\mathbf{q})$ a vertical line of length ks_2. One can say little beyond this, because of absorption in a specimen with extension in a horizontal direction. Evidently $R(\mathbf{q})$ will not then be centrosymmetric. In the absence of absorption, the width of the reflected beam decreases with increasing

2θ. This focusing effect is quite noticeable on single-crystal photographs.

Clearly when these effects operate simultaneously, as they do in practice, one can only say that $R(\mathbf{q})$ will have vertical extension $\sim k(f_2+s_2)$, and a horizontal section through it might be as shown schematically in Fig. 6. When the specimen is a sphere, $R(\mathbf{q})$ will vary systematically with 2θ and while it is probably impracticable to compute it, it can be measured for a few reflexions covering the range of 2θ used. This could be done for a particular reflexion by taking a series of perhaps ten photographs, with the films at the detector slits, and the specimen stationary in ten successive settings for Ω. A photometer trace of each film is then a vertical section through $R(\mathbf{q})$ in a nearly planar segment of the reflecting sphere. This method assumes that Bragg intensity in characteristic radiation can be distinguished from thermal scattering and white radiation on a 'still' photograph with sufficient accuracy to give $R(\mathbf{q})$ for the Bragg peak, which is what we require.

5. Discussion

A correction which can be as large as 25% should not be ignored, and the correction will be largest for materials with relatively low elastic constants, such as molecular crystals. It is some comfort that $\alpha-\alpha'$ is likely to vary systematically with $\sin\theta$ so that failure to make a correction can be largely 'taken up' in the Debye–Waller factor. The extent to which this remains true for a material as anisotropic as most molecular crystals are in their elastic properties has not been investigated. It seems likely that when $R(\mathbf{q})$ is ignored in calculating $\alpha-\alpha'$, a considerable over-correction results. The effect of $R(\mathbf{q})$ is to smear out each δ-function, over a region not much smaller than the volume which we have called the range of measurement. This must have the effect of making α' and α more nearly equal. Computation of *accurate* corrections requires a knowledge of the elastic constants, experimental measurement of $R(\mathbf{q})$ for several reflexions and considerable machine programming and computing time. It might be easier to cool the crystal to 4°K!

I am grateful to Dr Cooper for a preprint and for helpful discussions, and to Dr Smith for supplying the data given in Table 1.

References

ALS-NIELSEN, J. & DIETRICH, O. W. (1967). *Phys. Rev.* **153**, 706 and 711.
BUTT, N. M. & O'CONNOR, D. A. (1967). *Proc. Phys. Soc.* **90**, 247.
COCHRAN, W. (1966). *Phonons in perfect lattices and in Lattices with Point Imperfections.* Ed. R. W. H. STEVENSON. Edinburgh: Oliver & Boyd. p. 153.
COOPER, M. J. & ROUSE, K. D. (1968). *Acta Cryst.* A**24**, 405.
JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.
NILSSON, N. (1957). *Ark. Fys.* **12**, 247.
PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138.
SKELTON, E. F. & KATZ, J. L. (1968). *Acta Cryst.* In the press.
SMITH, T. (1966). *Phonons in Perfect Lattices and in Lattices with Point Imperfections.* Ed. R. W. H. STEVENSON. p. 161. Edinburgh: Oliver & Boyd.

DISCUSSION

WILLIS: There are 3 elastic constants for a cubic crystal, but 21 for a triclinic one. How much of a problem is this?

COCHRAN: The phonon frequencies and eigenvectors will still be determined from a 3×3 matrix, but the matrix elements will depend on the elastic constants in a more complicated way than for a cubic crystal. Measurement of the elastic constants presents something of problem; in principle they can be deduced from X-ray measurements, in practice ultrasonic methods have given more accurate results. Brillouin scattering can now also be used.

MASLEN: How important is the contribution of internal modes likely to be to the X-ray scattering?

COCHRAN: Internal modes are a special case of optic modes. Their contribution will be rather accurately subtracted by making a background measurement, *i.e.* they contribute equally to α and to α'.

MILLEDGE: One can calculate a difference Fourier between a molecule at rest and the molecule in vibration. How helpful is this in correcting for TDS?

COCHRAN: Not very, since, as ordinarily done, it treats the molecules as vibrating independently and therefore does not give the contribution of acoustic modes.

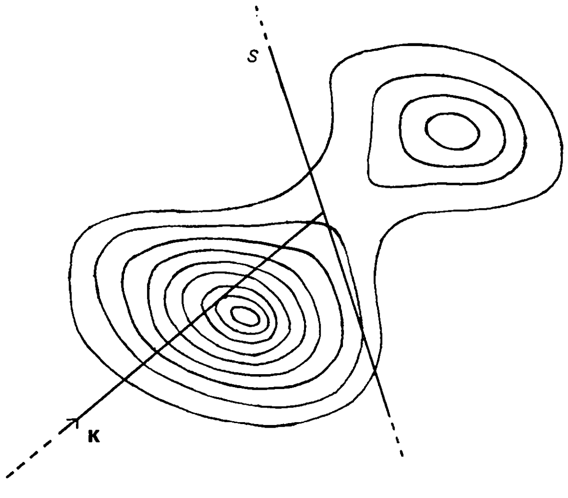


Fig. 6. An estimate of the appearance of a horizontal section through the resolution function in a particular instance, taking into account the effects mentioned in the text, except for white radiation. In the absence of these effects the function would contract to a δ-function at the point **K**.

KATZ: We have made corrections for TDS by calculation of the intensity at up to 60000 points in the parallelepiped of reciprocal space which represents the range of measurement. The effect of replacing the parallelepiped by a sphere, and of Nilsson's approximation of taking the slit height to be infinite, was investigated. The latter can lead to errors of 30%.

COCHRAN: Yes, I don't think that anyone will want to make that particular approximation.

ROUSE & COOPER: The assumption of isotropy made in the original Cooper–Rouse treatment gives a good approximation to the TDS correction for a cubic crystal. This is because the TDS peaks at the Bragg reciprocal lattice point and therefore a large proportion of the TDS intensity is included in the inscribed sphere contained within the volume of integration and centred on this point. The contribution from the remaining volume will give rise to an anisotropic contribution to the TDS intensity, since it depends on the direction of the scattering vector as well as its magnitude. However, this anisotropy will, in general, be small except at large scattering angles when the inscribed sphere becomes a small fraction of the volume of integration.

We have now extended our treatment* to crystals of any symmetry, from cubic to triclinic, retaining the dependence of the TDS intensity on direction. Although the expressions are easy to formulate, they are extremely difficult to evaluate, because they involve the numerical integration of a triple integral which becomes singular within the range of integration. When this problem is overcome we shall be able to compute the correction parameter α for any crystal for which the appropriate elastic constants are known.

A detailed consideration of instrumental resolution is extremely complex and we would agree with Professor Cochran that the only really satisfactory way of taking this into account is to measure it experimentally.

KATZ: A correction procedure has been developed by Dr Earl F. Skelton and myself (Skelton & Katz, 1968) to account for first order thermal diffuse scattering (TDS) contributions to integrated Bragg intensity measurements. It is believed that this correction is applicable for an arbitrary type of integrated intensity scan and that it can be applied to a monatomic crystal of any symmetry. In developing the final expressions, several approximations were necessary: Perhaps the two most important of these are (1) the high temperature approximation and (2) the mean velocity approximation.

In the high temperature approximation, it is assumed that the average energy of a normal mode of vibration can be represented by kT, where k is Boltzmann's constant and T is the absolute temperature of the crystal. Although this condition is fulfilled in general when T is in excess of the Debye temperature (Θ), for the low frequency modes, which contribute to the TDS in the immediate vicinity of a Bragg reflection, this approximation can be applied even for cases when $T < \Theta$.

In the mean velocity approximation it is assumed that, for the absolute value of each lattice wave considered ($|\bar{g}|$), all directions of propagation occur. It is presumed that the error introduced by this approximation will be minimized by the $|\bar{g}|^{-2}$-term which appears in the first order TDS function.

In order to assay the size of the errors generated by these two approximations, a typical integrated intensity measurement was considered for the 511 reflection of Cu. The calculation of the TDS/Bragg scattering ratio was first performed by summing over a grid of 68920 points superimposed over the appropriate volume in reciprocal space; the result was 0·038195. Then the high temperature approximation was introduced and the calculation repeated; the result was 0·038180. Finally, the expressions were simplified by introduction of the mean velocity approximation; the result using the modified expressions was 0·0399. For this particular situation then, the high temperature approximation caused an error of less than 0·04% and the mean velocity approximation resulted in an error of less than 5%. These errors seem quite modest in consideration of the labor saved through their application, *e.g.*, the first calculation took almost 20 minutes on a C.D.C.-3800, whereas the last computation was performed in less than 30 seconds.

Note added by W. Cochran

A recent paper which I would have mentioned had I been aware of it in time is that by S. Göttlicher (1968). *Acta Cryst.* **B24**, 122. Göttlicher has shown that a correction for TDS which avoids some of the approximations made hitherto still has the effect of changing only the Debye–Waller factor, for sodium chloride.

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* Cooper, M. J., Rouse, K. D. & Willis, B. T. M. To be published.