

As an application measurements on LiF and NaCl were performed. Studying different orders of reflexion of the same crystal one gets information on the size distribution of the mosaic blocks as a function of the distance from the surface. It was found that in the 3 crystals examined the sizes were much larger on the surface than below it. This can easily be explained by recrystallization processes under the influence of water vapour, which takes place mostly on the surface of the crystals. The influence of secondary extinction was remarkable for the strong reflexions (up to 80%), while the fraction of 1-phonon scattering had to be taken into consideration only for the high orders of reflexion (up to 13%). These results are of general importance to eliminate systematic errors in absolute intensity measurements. In this way more correct data for atom factors and electron-density maps (time average) are attainable.

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The Anisotropy of Thermal Diffuse Scattering

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In order to correct X-ray integrated intensities for thermal diffuse 1-phonon scattering, the influence of the anisotropy of the lattice vibrations was examined. Using an oscillating-crystal technique with a long slit between source and goniometer, it is shown that the anisotropy of the three-dimensional intensity function of the 1-phonon scattering is smeared out by means of a twofold integration, such that an isotropic approximation can be applied. In all cases under investigation (NaCl, LiF) the systematic error was less than 1% of the total integrated intensity of a reflexion if this approximation was applied. An elegant criterion is given to test the applicability of the spherically symmetric isotropic approximation.

1. Introduction

In order to calculate structural amplitudes from measured absolute X-ray intensities one has to correct the integrated intensities for thermal diffuse scattering (TDS). A method for the determination of the fraction of the TDS 1-phonon scattering, after Bradaczek & Hosemann (1968) and Urban & Hosemann (1972) is based on a synthesis of the measured line-profiles. This synthesis requires the knowledge of the relative shape of TDS. Neglecting many-phonon scattering, the shape of the thermal diffuse 1-phonon scattering curve may be calculated in the 'harmonic approximation' from the knowledge of the elastic constants (Born & Huang, 1954; Wooster, 1962; Maradudin, Montroll & Weiss, 1963). The intensity distribution round a reciprocal-lattice point is in general anisotropic. Measuring the line profile of a reflexion by the method of Bradaczek & Hosemann means scanning a two-dimensional intergral of the intensity function of a single

crystal. If the 1-phonon scattering is isotropic, the twofold integration leads to analytic functions; if an anisotropic model is used all the calculations are much more complicated. In the following we show that under special experimental conditions the influence of anisotropy on TDS for NaCl and LiF can be neglected. A method for testing whether the isotropic or the anisotropic model has to be used will be given.

2. The shape of thermal diffuse 1-phonon scattering

It is well known (*e.g.* Maradudin *et al.*, 1963) that the shape of the 1-phonon scattering near a reciprocal-lattice point is proportional to:

$$\sin^2 \theta \sum_{j=1}^3 \frac{\cos^2 \Phi_j(k)}{\rho V_j^2 |k|^2} \quad (1)$$

[ρ : density (g.cm⁻³), V_j : velocity of the j -mode lattice vibration; $\Phi_j(k)$: angle between the polarization vector \mathbf{j} of the acoustic wave and the reciprocal vector \mathbf{b} ($|\mathbf{b}| =$

$2 \sin \theta / \lambda$, λ being the wavelength of the radiation used); \mathbf{k} : reciprocal vector, indicating the distance from the reciprocal-lattice point \mathbf{b}_0 ($|\mathbf{b}_0| = 2 \sin \theta_0 / \lambda$); 2θ : scattering angle; θ_0 : Bragg angle of the centre of the reflexion].

For convenience we put each $V_j = \text{constant}$. Then this approximation holds for the acoustic modes of the elastic waves near the reciprocal-lattice point \mathbf{b}_0 . In order to evaluate the term $\sum \cos^2 \Phi_j / \varrho V_j^2$, we start with the wave-equation (Born & Huang, 1954; Wooster, 1962), which also only holds for small wave-vectors \mathbf{k} ,

$$\varrho V^2 \mathbf{u}_\alpha = \sum_{\beta} \left\{ \sum_{\gamma, \lambda} c_{\alpha\beta\gamma\lambda} f_\gamma f_\lambda \right\} \mathbf{u}_\beta$$

$[\mathbf{u}$: oscillation vector of the lattice points; f_γ : directional cosine of the wave-vector \mathbf{k} ; $c_{\alpha\beta\gamma\lambda}$: elastic constants ($\alpha, \beta, \gamma, \lambda = 1, 2, 3$)].

Introducing the matrix A

$$A_{\beta\alpha} = \sum_{\gamma, \lambda} c_{\alpha\beta\gamma\lambda} f_\gamma f_\lambda,$$

one obtains

$$\varrho V^2 \mathbf{u}_\alpha = \sum_{\beta} A_{\beta\alpha} \mathbf{u}_\beta. \quad (2a)$$

From equation (2a) one can calculate the eigenvalues of the equation using

$$|A - D| = 0 \quad (2b)$$

where

$$D = \begin{pmatrix} \varrho V^2 & 0 & 0 \\ 0 & \varrho V^2 & 0 \\ 0 & 0 & \varrho V^2 \end{pmatrix}.$$

With these eigenvalues one can calculate the eigenvectors \mathbf{u} and one obtains,

$$\cos \Phi_j = \frac{\mathbf{b} \cdot \mathbf{u}_j}{|\mathbf{b}| |\mathbf{u}_j|}, \quad |\mathbf{b}| = \frac{2 \sin \theta}{\lambda}.$$

3. Integration of the TDS

In order to compare the shape of the TDS curve with measured line profiles one has to integrate equation (1) in two directions. The integration area depends on the particular experimental conditions. We used an oscillating crystal technique with a long slit in the primary beam (see Fig. 1). The area of integration then lies on the surface of a cylinder with radius

$$r = \frac{2}{\lambda} \sin \frac{2\theta_0 + \beta}{2} \quad (3a)$$

where β is given by the intersection of the cylinder with the Ewald sphere in the goniometer plane [Fig. 1(a)]. The oscillating amplitude is τ_0 the radius of the goniometer R and the length of the primary beam L on the film, and the maximum angle ξ_0 according to Fig. 1(b) is given by

$$\text{tg } \xi_0 = \frac{L}{2R}.$$

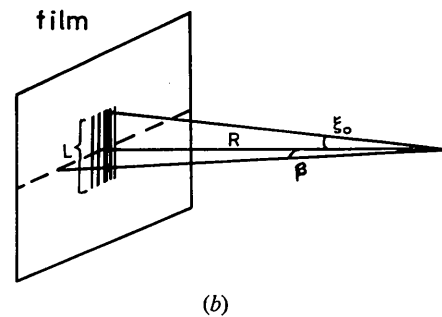
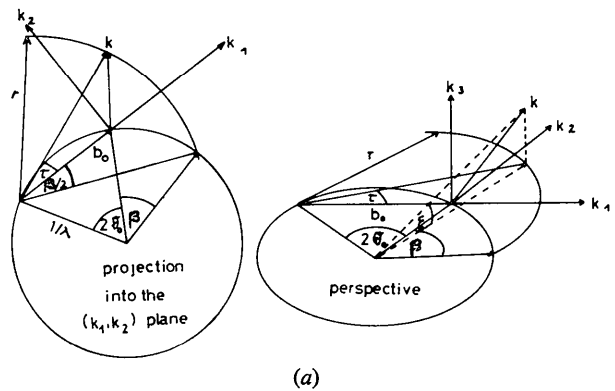


Fig. 1(a). Reciprocal space for the definition of the angular coordinates τ , β , ξ . k_1 , k_2 , k_3 are orthogonal coordinates of \mathbf{k} . Projection on the film describing the angular coordinates ξ_0 , β .

The integration then runs over ξ and τ as a function of β . To register the line profiles, a film was put in a fixed position perpendicular to the reflected beam, while the sample was oscillated. [For a more detailed description of the technique used see Urban & Hosemann (1972)].

The cylinder coordinates are given by r , τ , k_3 with

$$k_3 = \frac{1}{\lambda} \text{tg } \xi. \quad (3b)$$

The surface element of the r cylinder is:

$$df = r d\tau dk_3 = \frac{2}{\lambda^2} \sin \frac{2\theta_0 + \beta}{2} \frac{1}{\cos^2 \xi} d\tau d\xi.$$

As can be seen from Fig. 1(a), the position of the maximum of the profile is shifted to larger θ values with increasing r and the oscillation must be adjusted so that $-\tau_0 - \beta/2 \leq \tau \leq \tau_0 - \beta/2$.

The shape of the TDS curve is defined by

$$I_{\text{TDS}}(\beta) \sim \int_{-\xi_0}^{\xi_0} \int_{-\tau_0 - \beta/2}^{\tau_0 - \beta/2} \sin \left(\frac{2\theta_0 + \beta}{2} \right) \frac{1}{\cos^2 \xi} \times \left\{ \sin^2 \left(\frac{2\theta_0 + \beta}{2} \right) + \sin^2 \xi/2 \right\} \sum_{j=1}^3 \frac{\cos^2 \Phi_j}{\varrho V_j^2 |k|^2} d\xi d\tau. \quad (4)$$

The evaluation of equation (4) requires a computer, because one has to evaluate equations (2a) and (2b) for a large number of reciprocal points \mathbf{k} . We used an ICT 1909 computer and found the calculation time to be

several hours per reflexion. We also tried to make the calculation using an isotropic model although $\sum \frac{\cos^2 \Phi_j}{\rho V_j^2}$ shows a large anisotropy (see Fig. 2). It was hoped that the twofold integration over df would smear out the anisotropy to such an extent that, within the errors of measurement, the isotropic approximation would give the same result.

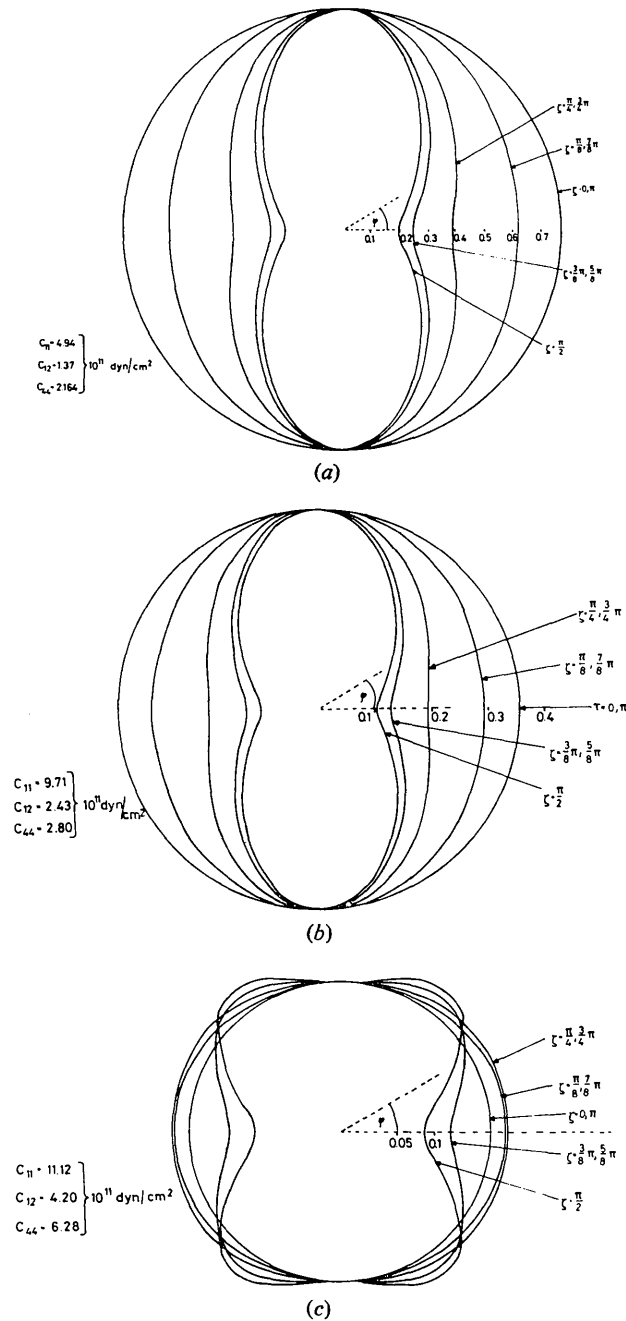


Fig. 2. Spherical diagrams of $g(\zeta, \varphi)$ of the $h00$ reflexions. (a) NaCl (b) NaF (c) LiF. Anisotropy: $\sum_{j=1}^3 \frac{\cos^2 \Phi(\mathbf{k}_j)}{V_j^2}$.

4. The anisotropy of TDS

The large anisotropy of the term

$$g(\zeta, \varphi) = \sum_{j=1}^3 \frac{\cos^2 \Phi_j}{\rho V_j^2}(\mathbf{k}) \quad (4b)$$

can be seen in the polar diagrams of Fig. 2 for source reflexions ($h00$). ζ and φ are the polar angles, $\zeta=0$ is the $[001]$ direction and $\zeta=\pi/2$; $\varphi=0$ the $[100]$ direction of the cubic crystal. The function was calculated using equations (2a) and (2b) with the tabulated elastic constants for NaCl, LiF and NaF. In the polar diagrams (Fig. 2) the distance from the centre to each curve is directly proportional to $g(\zeta, \varphi)$.

5. The isotropic approximation

For convenience in the further calculations we introduce the following three approximations.

1. $\sum_j \frac{\cos^2 \Phi_j}{\rho V_j^2} = c$, c being a constant.

Since the contribution of 1-phonon scattering to the integral intensity of the reflexion can be obtained by the analysis of the relative shape of line profiles, the value of c is of no interest.

2. The two-dimensional integration is not carried out along the r cylinder [Fig. 1(a)] but along a tangential plane with the element $df_1 = dk_2 \cdot dk_3$; k_1, k_2, k_3 are orthogonal coordinates of k .

3. $\sin^2 \theta = \sin^2 \left(\frac{2\theta_0 + \beta}{2} \right) + \sin^2 \frac{\zeta}{2}$ is replaced by $\sin^2 \theta_0$.

The limits of the integration in the coordinates k_2, k_3 are

$$k_2^0 = \frac{\sin \theta_0}{\lambda} \operatorname{tg} \tau_0,$$

$$k_3^0 = \frac{L}{2r}.$$

Using these approximations equation (4) reduces to

$$I_{\text{TDS}}(k_1) \simeq \int_{-k_2}^{k_2} \int_{-k_3^0}^{k_3^0} \frac{1}{k_1^2 + k_2^2 + k_3^2} dk_2 dk_3. \quad (5)$$

To compare equation (4) with equation (5), one has to express k_1 in terms of β [see Fig. 1(a)], such that

$$k_1 = \frac{\operatorname{tg} \beta \cos \theta_0}{\lambda}.$$

For large enough values of k_2^0 (large oscillation angles τ_0) the k_2 integration limit can be put equal to infinity and this leads to the expression,

$$I_{\text{TDS}}(k_1) = \ln \left[\frac{k_3^0 + \sqrt{k_1^2 + k_3^{02}}}{-k_3^0 + \sqrt{k_1^2 + k_3^{02}}} \right]. \quad (6)$$

This function is compared for several reflexions of LiF and NaCl with the anisotropic solution of equation (4), (Fig. 3). The constant c is chosen so that the functions are practically identical in the outer domain. This kind

of fitting is of practical interest since the outer tails of experimentally observed line profiles are essentially proportional to I_{TDS} .

The calculated and approximated I_{TDS} curves are in good agreement, except for small values of k_1 (or β). Since the isotropic approximation does not take into account that, according to Fig. 2, the I_{TDS} function is more extended for the $h00$ reflexions in all directions orthogonal to $[100]$, the integral value of the approximated and fitted I_{TDS} is systematically too small in these areas, but as can be seen from Fig. 3, the deviation is less than 10%. Since the correction of the integrated intensities for 1-phonon scattering of the reflexions 333, 600, 444 and 800 is of the order of 10%, the approximation contributes a systematic error of less than 1% to the total integral intensity, which is negligible in absolute terms.

We can conclude that the isotropic model is a good enough approximation under our experimental conditions for the eliminating of I_{TDS} from integrated intensities for LiF and NaCl.

6. Advantages of the isotropic approximation

As we have seen in the preceding section, the isotropic approximation was valid for the elimination of the

1-phonon contribution to the integrated intensity of a reflexion, and had the great advantage that, instead of tedious calculations with a computer, an elegant analytic expression [equation (6)] could be used. If, however, in the experiment the k_2 integration is not performed over a large enough range, numerical corrections can easily be introduced but we will not discuss these in detail here.

If this approximation is valid, one only has to discuss two experimental intensity values in the tail of the observed line profile, one not too near the centre so that the profile is practically proportional to I_{TDS} and the other not too far from the centre so that it can be separated from the background. The synthesis of the calculated intensity can then easily be performed and the independent parameters varied until the outer tail fits the observed profile* within the errors of experiment.

In this section we now give an elegant way to test whether or not approximation is applicable. Firstly, from the elastic constants are calculated the function

$$h(\zeta, \varphi) = \left[\frac{1}{b_0^2} \int_F \frac{b^2 g(\zeta, \varphi) df}{|k|^2} \right] k_1 = \text{const.} \quad (7)$$

* See for details Urban & Hosemann (1972).

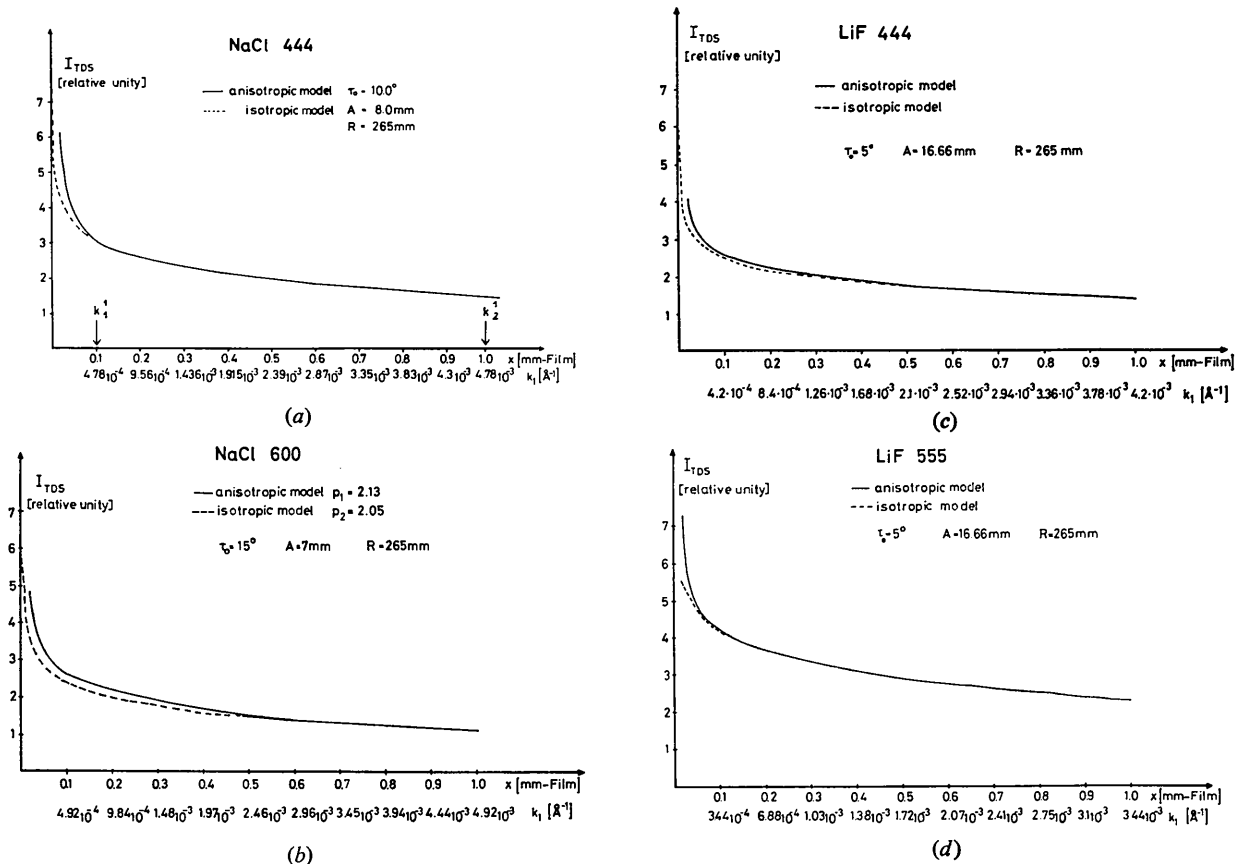


Fig. 3. One-phonon scattering I_{TDS} (calculated), —, and its isotropic approximation, - - - - . (a) NaCl 444, (b) NaCl 600, (c) LiF 444, (d) LiF 555.

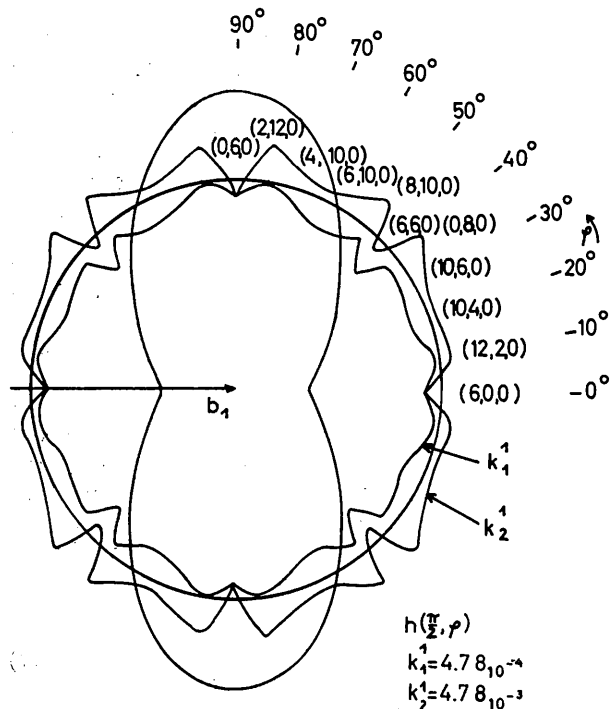


Fig. 4. The function $h(\pi/2, \varphi)$ defined by equation (7) for several $hk0$ reflexions of NaCl.

The area F of integration in the k_2k_3 plane has to be kept constant in \mathbf{b} space for all reflexions. This integral is evaluated for two different k_1 values, which are the same for all reflexions and have the positions mentioned above so as to give a practicable synthesis of the line profile.

In our experiments the k_1 values were chosen to be

$$4,78 \times 10^{-4} \text{ \AA}^{-1} \text{ and } 4,78 \times 10^{-3} \text{ \AA}^{-1},$$

[see Fig. 3(a)]. In Fig. 4 the function $h(\pi/2, \varphi)$ is plotted in polar coordinates for several reflexions of NaCl. Within $\pm 10\%$ the h function shows spherical symmetry. As mentioned previously the isotropic approximation can now be used to calculate the correction for 1-phonon scattering to an accuracy of about 1% (or less) of the total integrated intensity of a reflexion.

7. Summary

Using a special experimental technique after Bradaczek & Hosemann (1968) and Urban & Hosemann (1972) to

analyse X-ray line profiles, the relative intensity distribution of the thermal diffuse 1-phonon scattering was calculated for NaCl and LiF from tabulated elastic constants. Since these calculations are tedious and require long computer times we looked for a criterion which clearly defines the validity of an isotropic approximation, which has the advantage of using an analytic expression for I_{TDS} which can easily be handled without long computing times. Although the thermal diffuse scattering is anisotropic, it was demonstrated that under our special experimental conditions, an isotropic model is applicable for NaCl and LiF after a twofold integration in reciprocal space. The integration was performed over the oscillation angle of the crystal and the length of the primary beam for two special k values of interest for the line profile analysis. The deviation from spherical symmetry is less than 10%. The calculated approximation for I_{TDS} is practically identical with the exact function for $k_1 \geq 5 \times 10^{-4} \text{ \AA}^{-1}$. Only in the core of the line profile is there a small deviation, where the integrated intensities of I_{TDS} deviate by less than 10%.

It has been shown that by this method it is possible to eliminate the contribution of the 1-phonon scattering with a systematic error of less than 1% of the total integrated intensity. In a spherical diagram (Fig. 4) the relative intensities of TDS for many reflexions is shown.

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