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The Influence of Thermal Diffuse Scattering, Secondary Extinction and Crystallite Size Distribution on X-ray Line Profiles

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A method is given for correcting the integral intensities of X-ray reflexions from platelets of single crystals or powders for secondary extinction and thermal diffuse scattering (TDS). The line profiles are calculated as folding integrals from theoretical functions considering the crystallite size distribution, the total absorption, and TDS. By means of variation of the unknown parameters (fraction of TDS to the overall intensity, mean crystallite size and their polydispersity, and absorption coefficient, secondary extinction included) the calculated function has to fit the measured line profile. A detailed description of this method according to Bradaczek and Hosemann is given after introducing some modifications such as collimation errors of the primary beam and anisotropy of the lattice vibrations. The method is applied to measured line profiles of NaCl and LiF single crystals.

Introduction

From absolute X-ray intensities the structural amplitudes cannot be obtained with accuracies better than 1% until the present (Jennings, 1969). The reasons for this are systematic errors such as insufficient corrections of absorption (primary and secondary extinction) and of thermal diffuse scattering. The influence of these corrections on the measured integral intensities can be considerable. It is therefore necessary to measure these corrections. By the method of Bradaczek & Hosemann (1968) one obtains directly the true absorption coefficient, the influence of thermal diffuse scattering, and the crystallite size distribution function by means of a line-profile analysis. Contrary to the known methods (Bragg, James & Bosanquet, 1921), where the angular distribution of the mosaic blocks influences the profile of the rocking curve, here the reflexions will be measured by means of a film in a fixed position. In the present paper this method is refined and applied to the line-profile analysis of NaCl and LiF single crystals. By careful development and analysis of several films of the same reflexion much more information is available than by counter meas-

urements with different slit widths after Göttlicher (1968). To get the same amount of information with electronic methods one has to use narrow counter slits with slit widths of $\sim 10^{-2}$ mm. If only 6 points of the line profile are taken into account with an accuracy of 4% a rough calculation shows that the film has a registration time which is comparable with the electronic registration. In order to make a line-profile analysis according to our method one needs more data per reflexion. The electronic registration then obviously offers no advantage. Our new method emphasizes the importance of the film method and of film material with a high reproducibility and constancy of the gradation characteristics.

The experimental arrangement

For the investigation of reflexions, monochromated Mo $K\alpha_1$ radiation was used. A plane Ge-dendrite, which was given us by Červinka, Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia, was used as monochromator (reflexion 111). The slit system $B1, B2, B3$ (Fig. 1) limited the primary beam and cut away fractions of $K\alpha_2$. It is desirable to have a sharp primary beam with a small divergence, small enough to eliminate the collimation error. The slit-system was mounted on the Siemens horizontal goniometer 'with ω-scan'. The data
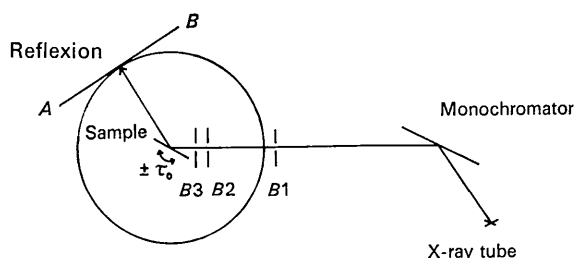

Fig. 1. Apparatus with the oscillation angle τ_0 of the crystal and the X-ray film for determinating the line profile. The film is in a fixed position in the plane AB.
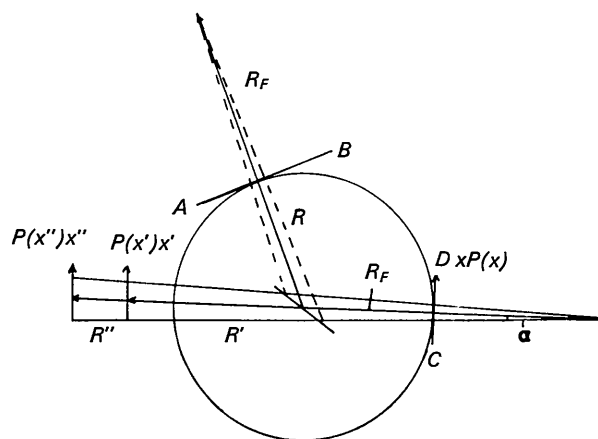

Fig. 2. Construction for eliminating the divergence.

of the primary beams were: half-width at a distance $R = 265$ mm from the centre of the goniometer, $H = 1.356 \times 10^{-1}$ mm. At this point the divergence between 1.87×10^{-4} and 1.07×10^{-2} degrees. To eliminate the angular distribution of the mosaic blocks the sample oscillated with the maximum angle of $\pm \tau_0$ over the mean reflexion angle θ_0. The film was, as mentioned above, in a fixed position. The angular distribution of the mosaic blocks now has no influence on the line profile since the intensity is integrated point by point over time.

Photographic method

For the registration of a line profile the X-ray film gives the advantage that one gets the whole line profile during one measuring process. In order to register the whole intensity distribution of the reflexion with one exposure several film plates (up to six) were put one after another and weakened by intermediate Al filters. To reduce the error of the measurement several film packets were used.

The film-material was 'X-ray film with clear base' manufactured by Doneo (Dupont). The linearity of the density compared with the registered X-ray intensity was 0·8 D per layer. Therefore, the maximal density was 1·6 D, 0·8 D per layer. We did not make a separate investigation of the fluctuations in the layer (i.e. fluctuation per cm²). But we always registered errors of 4 to 5% in the line-profiles of the same reflexion of the same crystal from film to film although nothing had been changed in the experimental conditions and well defined developing conditions were used (constant and exact developing time, fresh developer, controlled temperature). These errors were obviously due to the fluctuation of the photochemical properties of the film material used.

The measurement of the line profile by means of a film is an excellent method, which is preferable to the counter method because of its simplicity and brevity. It is therefore of high interest to improve the accuracy of the film material.

Elimination of collimation error

The influence of an even small divergence of the primary beam on the profile of a reflexion in most cases of our investigations was not negligible. Not taking into account this effect, one would get mean crystallite sizes and absorption coefficients, which are too big. The correction for divergence was performed in the following way. Let $P(x')$ and $P(x'')$ be the profile of the primary beam at the distances R' and R'' from the centre of the goniometer (Fig. 2). From these one has to calculate $P(x)$ in the plane CD. Since the primary beam is 'reflected' from the crystal the same function $P(x)$ describes the collimation error in the plane AB of the film. Let R_F be the distance of the focal point from the centre of the goniometer and α be the angle

of divergence. The width d of the primary beam may be calculated from

$$\operatorname{tg} \alpha = \frac{d}{R_F + R} = \frac{d'}{R_F + R'} = \frac{d''}{R_F + R''} \cdot$$

Hence

$$R_F = \frac{d'' R' - d' R''}{d' - d''} \cdot$$

If one has measured the line profiles of the primary beam $P(x')$ and $P(x'')$ at the distances R' and R'', one can calculate this profile on the plane AB of the film at the point x by

$$x = \frac{x''(R' + R) - x'(R'' + R)}{R' - R''} \tag{1}$$

if one puts $x' = d'$ and $x'' = d''$ into equation (1).

Components of the line profile

The method described in this paper does not differ much from the one described by Bradaczek & Hosemann (1968). The differences will be mentioned below. The components of the line-profile are:

I. Influence of lattice vibrations (0- and many-phonon scattering). In this paper only 0- and 1-phonon scattering were taken into account. For not too high orders of reflexion, and temperatures small compared with the melting point, the 2-phonon scattering and all higher processes can be neglected. There is no doubt that our method principally can be extended to 2-phonon scattering and so on. Hence, the non-systematic experimental errors should be much more diminished. We will call the intensity distribution function of the 1-phonon scattering I_{TDS}.

II. Line broadening by the primary beam P. This function has to be measured and is taken as a known function into the calculation after transformation to the variable x according to equation (1).

III. Influence of mosaic size distribution on the intensity function. This may be I_s.

IV. The absorption. By the absorption, the reflexions become asymmetric. This function we call I_u.

In order to simplify the calculations, we introduce coordinates, which differ from the coordinate x on the film. The systems are connected in a simple way. With the help of Ewald's construction one gets (Fig. 3):

$$k_1 = \frac{x}{R\lambda} \cos \theta_0 \tag{1a}$$

where R = radius of the goniometer, x = film coordinate, λ = wavelength of the X-rays, θ_0 = Bragg angle.

In the above mentioned system one gets for the line profile

$$I_{\text{calc}}(k_1) = \alpha_1 I_0(k_1) + \alpha_2 I_1(k_1) . \tag{2}$$

I_{calc}, I_0, and I_1 are normalized to 1 with respect to their maxima. With the definition of the convolution (folding) operation
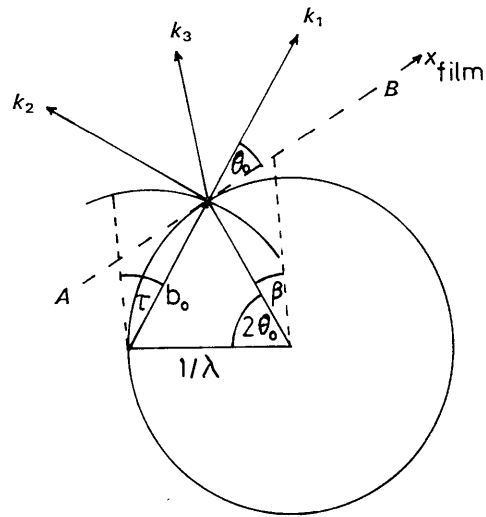

Fig. 3. Ewald's construction· Definition of the system (k_1, k_2, k_3). k_3 was drawn perspectively and is perpendicular to the drawing plane.

$$\widehat{fg}(z) = \int f(x) \, g(z - x) \mathrm{d}x$$

one obtains

$$I(k_1) = I_0(k_1) + I_1(k_1) \tag{3}$$

with

$$I_0(k_1) = P(k_1) \frown I_s(k_1) \frown I_u(k_1)$$

$$I_1(k_1) = I_0(k_1) \frown I_{\text{TDS}}(k_1) . \tag{4}$$

I_u, I_0, and I_1 are non-dimensional; P, I_s, and I_{TDS} have the dimension of length.

$P(k_1)$ means the measured primary beam in the coordinates k_1 given by equation (1a) and corrected by (1)].

$I_s(k_1)$ is the intensity profile depending on the crystallite size distribution, which may be approximated after Hosemann & Bagchi (1962). The mean mass statistical crystallite size $2\bar{y}$ and the polydispersity g are defined as follows:

$$\bar{\bar{y}} = y_0 \frac{\Gamma[(n+2)/2]}{\Gamma[(n+1)/2]}$$

$$g = \frac{(\bar{\bar{y}^2} - \bar{\bar{y}}^2)^{1/2}}{\bar{\bar{y}}} = \left\{ \frac{K(n+1)^2}{K(n)K(n+2)} - 1 \right\}^{-1/2}$$

$$\simeq (2n+2)^{-1/2}$$

$$\frac{1}{K(n)} = \tfrac{1}{2} \Gamma[(n+1)/2] . \tag{6}$$

Thus one obtains for I_s

$$I_s(k_1) = \bar{y} \left(1 + \frac{4\pi^2}{5} y_0^2 k_1^2 \right)^{-(n+2)/2} . \tag{6a}$$

$I_u(k_1)$ takes in account the absorption in the crystal as mentioned above (Bradaczek & Hosemann, 1968).

$$I_u(k_1) = \begin{cases} \exp\left[-u\dfrac{R\lambda}{\cos\theta_0}k_1\right] & k_1 \geq 0 \\ 0 & \text{otherwise}, \end{cases} \tag{7}$$

$u = \dfrac{2\mu}{\sin 2\theta_0}$, $\mu =$ true absorption coefficient including secondary extinction.

$I_{TDS}(k_1)$ is the thermal diffuse scattering (only 1-phonon scattering). Only the acoustic branches of the frequency spectrum have been taken into consideration. With the velocity V_j of the acoustic wave of the branch j for a special value $|k|$, one gets for the circular frequency ω_j

$$\omega_j(k) = 2\pi V_j |k| .$$

The one-phonon scattering in the reciprocal point $\mathbf{b} = \mathbf{b}_0 + \mathbf{k}$ is, according to Laval (1941, 1954) and Wooster (1962), proportional to

$$\sin^2\theta \sum_{j=1}^{3} \frac{\cos^2 \Phi_j}{\varrho V_j^2 |k|^2} . \tag{8}$$

$\mathbf{b}_0$ is the reciprocal vector of the centre of the reflexion according to Bragg's equation.

$$b_0 = \frac{2\sin\theta_0}{\lambda} \tag{8a}$$

where ϱ is the density (g.cm^{-3}) and Φ_j is the angle between the polarization vector $\mathbf{j}$ and $\mathbf{b}_0$ (Fig. 4).

To get $I_{TDS}(k_1)$ in connexion with the oscillating technique with a long slit of the primary beam parallel to k_3, one has to integrate over the plane of a cylinder with the radius r and the axis through $b_0 = 0$ and parallel to k_3 (Fig. 4). One obtains

$$r = \frac{2}{\lambda} \sin \frac{2\theta_0 + \beta}{2} .$$

It is possible to calculate the plane element of the r cylinder after introducing the angular system τ, β, ξ (Fig. 4) with

$$k_3 = \frac{1}{\lambda} \text{tg}\,\xi .$$

For the plane element df we obtain

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

With the above mentioned approximations for the one-phonon scattering we can express I_{TDS} as follows:

$$I_{TDS} = C \int_{-\xi_0}^{+\xi_0} d\xi \int_{(-\beta/2)-\tau_0}^{(-\beta/2)+\tau_0} d\tau \frac{2}{\lambda^2} \sin \frac{2\theta_0 + \beta}{2} \frac{1}{\cos^2 \xi}$$

$$\times \left[\sin^2\left(\frac{2\theta_0 + \beta}{2}\right) + \sin^2 \xi/2\right] \sum_{j=1}^{3} \frac{\cos^2 \Phi_j(k)}{\varrho V_j^2 |k|^2} . \tag{9}$$

$$C = \frac{4\tilde{k}T}{\lambda^2} \tag{9a}$$

where $\tilde{k}$ is the Boltzmann constant and T is the absolute temperature.

The fraction of one-phonon scattering to the overall intensity can be eliminated, as we will see later, by knowing only the relative shape of the line profile. In equation (9) τ_0 means the maximal oscillating angle of the crystal. With the length A of the primary beam one obtains

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

The term $\sum \dfrac{\cos^2 \Phi_j}{\varrho V_j^2}$ can be evaluated by means of the elastic constants (Wooster, 1962; Maradudin, Montroll & Weiss, 1963). In the case of LiF and NaCl the influence of the anisotropy of the lattice vibrations on the function $I_{TDS}(\beta)$ is negligible (Hosemann & Urban, 1972).

Adaptation of I_{calc} to the observed line-profile I_{obs}

In (2) α_1 and α_2 are not independent of each other. Let $I_{calc}(k_1^0) = 1$ be the maximum of the function I_{calc}, whose position is at $k_1 = k_1^0$. With $\alpha_2 = \alpha$ one obtains

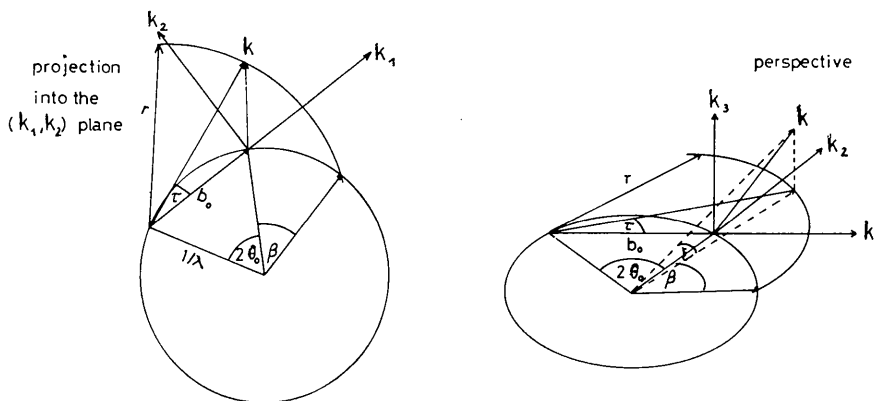$$\alpha_1 = \frac{1 - \alpha I_1(k_1^0)}{I_0(k_1^0)} . \tag{10}$$

Fig. 4. Definition of the angular system $\tau\beta\xi$.

By variation of the parameters μ, α, g, and $\bar{\bar{y}}$ one has to fit I_{calc} to the observed intensity function I_{obs}, whose maximum value again is normalized to unity. But first of all one has to make a background correction of I_{obs} and I_{calc}. Over the region of the line profile of I_{obs} this background was found to be constant if no overlapping occurred with other reflexions. k_1^1 is the point where I_{obs} could no longer be separated from the background, hence where $I_{\text{obs}}(k_1)$ is practically constant for $|k_1| \geq k_1^1$ within the errors of experiment. Even at the same point k_1^1, I_{calc} has to be set zero to coincide with I_{obs} (see Fig. 5). For the constant background one obtains from the above-mentioned theoretical calculations (equations 2 to 10):

$$B = I_{\text{calc}}(k_1^1) \tag{11}$$

Sometimes it may happen that the background is not constant over the whole profile. In this case one uses a linear interpolation for the background, using the right and left flank at k_1^1 and k_1^2, where I_{obs} could no longer be separated from the background. In the same manner one uses a linear background correction for I_{calc}.

$$B(k_1) = \frac{I_{\text{calc}}(k_1^1) \; k_1^2 - I_{\text{calc}}(k_1^2) \; k_1^1}{k_1^2 - k_1^1}$$
$$+ \frac{I_{\text{calc}}(k_1^2) - I_{\text{calc}}(k_1^1)}{k_1^2 - k_1^1} k_1 \; . \tag{11a}$$

Using the formulae (11) and (11a) for the background one obtains

$$I'_{\text{calc}}(k_1) = \frac{1 - \alpha I_1(k_1^0)}{I_0(k_1^0)} I_0(k_1) + \alpha I_1(k_1) - B(k_1) \; . \tag{12}$$

To compare I_{obs} with I'_{calc}, I'_{calc} has to be normalized again to unity in its maximum.

$$I'_{\text{calc}} = \frac{1}{1 - B(k_1)} I'_{\text{calc}} \simeq I_{\text{obs}} \; . \tag{13}$$

The integral fraction ε of thermal diffuse 1-phonon scattering is given by the integral of the second term on the right hand side of equation (12) divided by the integral of the left hand term, not forgetting to subtract from α $I_1(k_1)\mathrm{d}k_1$ the calculated 'background' $I_1(k_1^1)$ at the end of the integration range;

$$\varepsilon = \frac{\alpha \int [I_1(k_1) - I_1(k_1^1)]\mathrm{d}k_1}{(1 - B) \int I'_{\text{calc}}(k_1)\mathrm{d}k_1} \; . \tag{14a}$$

If the open parameters g, $\bar{\bar{y}}$, μ, and α are well adjusted so that equation (13) holds, we finally get a value of ε by normalized intensity functions

$$\varepsilon = \frac{\alpha \int [I_1(k_1) - I_1(k_1^1)]\mathrm{d}k_1}{(1 - B) \int I_{\text{obs}} \, \mathrm{d}k_1} \; . \tag{14b}$$

This value can be controlled without knowledge of α with non-normalized I functions. We directly obtain from (3)

$$\varepsilon = \frac{\int [I_1(k_1) - I_1(k_1^1)]\mathrm{d}k_1}{\int [I(k_1) - I(k_1^1)]\mathrm{d}k_1} \; . \tag{15}$$

Putting $I(k_1) = I_{\text{max}}(k_1) \; \bar{I}(k_1)$ we get from equation (2): $I_1 = \alpha \; I_{\text{max}}\bar{I}_1$. Introducing the background correction from equation (12), one obtains at the position of the maximum of I_1:

$$\alpha = \frac{[I_{1\text{max}}(k_1) - I_1(k_1^1)] \; (1 - B)}{[I_{\text{max}}(k_1) - I(k_1^1)]} \; . \tag{16}$$

With the help of equations (12) and (13) firstly the normalized observed line profiles I_{obs} were synthesized
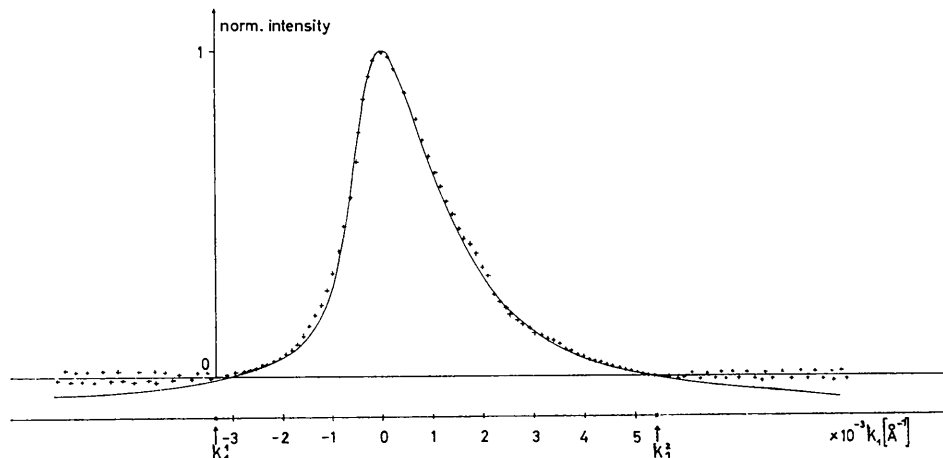

Fig. 5. Synthesized ($-$) and experimental ($+$) line profiles of NaCl 444. k_1^1 and k_1^2 are the points, where I_{obs} could not be separated from the background. The fitting parameters are $\varepsilon = 9 \cdot 2\%$, $2\bar{\bar{y}} = 1100$ Å, $g = 70\%$, $\mu = 17 \cdot 0$ cm^{-1}.

and suitable parameters g, $\bar{\bar{y}}$, μ, and α were found. Since I_u alone is asymmetric, the parameter μ can be found unequivocally. The parameter $\bar{\bar{y}}$ is independent too of the other parameters, since it only influences the width of the centre of the reflexion. For the parameters α and g one sometimes finds different solutions, since for instance a combination of a large α with a small g produces large intensities in the tail, as well as the combination of small values of α with large g. This ambiguity was removed with equation (16), which selects the right value of α. Since one always has to deal with several solutions, the four parameters in our experiments could be calculated only with an accuracy of 10% for $\bar{\bar{y}}$, α and g, and 3% for μ. All calculations have been done with a computer of the type ICT 1909.

The above mentioned method differs slightly from that of Bradaczek & Hosemann (1968):

(a) The divergence of the primary beam was taken in account.

(b) The maxima of I_0 and I_1 do not coincide for finite absorption. The shift for finite absorption was considered.

(c) The anisotropy of the lattice vibrations was taken into consideration.

(d) The background correction was made before the final normalization.

Experimental results

Using the above described method, single crystals of LiF and NaCl were analysed. An example of the fitted line-profile of NaCl 444 can be seen in Fig. 5. Table 1 shows the results for 3 crystals (NaCl 100 and 111 and LiF 111). For all crystals examined we found that the mean crystallite size decreases with increasing order of reflexion. Obviously the reason for this effect is that with increasing orders of reflexion deeper regions of the crystal contribute to the line profile. Obviously the examined crystals recrystallize in the surface layers, hence the size of mosaic blocks remains smaller in deeper domains. The whole absorption coefficient μ is given by

$$\mu = \mu_0 + \gamma \qquad (17)$$

where μ_0 is the total linear absorption coefficient without secondary extinction and γ is the fraction of secondary extinction.

As can be seen from Table 1 the influence of secondary extinction γ for the strong reflexions is remarkable. The reflexions NaCl 600, 444, and 800 alone have a negligibly small γ. In all cases the polydispersity g of the crystallites was within the errors of experiment in the order of 70%.

Summary

A method for analysing line profiles after Bradaczek & Hosemann (1968) was slightly modified. This was done by taking into account the divergence of the primary beam and the anisotropy of the lattice vibrations. A shift of the maxima of the 0- and 1-phonon scattering by the absorption in the crystal was found. This effect was taken into consideration.

The advantage of this method compared with other published treatments consists in a measurement of the line profiles as exactly as is possible. A primary beam of high monochromaticity and low divergence is used and the collimation error carefully eliminated. A synthetic line profile with some variable parameters is calculated with an ICT 1909 computer by means of convolution integrals of theoretically well-established intensity functions I_u, I_s, and I_{TDS}, which take into account the absorption in the crystal, the particle size effect, and the 1-phonon scattering. For the latter, tabulated elastic constants are used. The four free parameters are varied until the normalized synthetic line profiles fit the observed profile. From this the total absorption coefficient, including the secondary extinction, and the amount of 1-phonon scattering can be obtained directly. As a secondary result the weight-averaged size of the mosaic blocks and their polydispersity is obtained.

Table 1. *Results of the line profile analysis of* LiF *and* NaCl

NaCl $\mu_0 = 16{\cdot}95$ cm^{-1}

Reflexion	ε (%) Experimental	Theoretical	γ (cm^{-1})	$2\bar{y}$ (Å)	g (%)	τ_0 (degrees)
111	0	0·6	5	2200	70	6
200	0·5	0·9	6·5	2400	70	7·5
222	3	3·5	9	1700	70	10
400	2·1	2·7	3	1400	70	15
333	13·5	12·9	5	900	70	10
600	9	9·3	0	950	70	15
444	9·2	11·3	0	1100	70	10
800	11·7	13·9	0	950	70	15

LiF $\mu_0 = 3{\cdot}006$ cm^{-1}

Reflexion						
333	0		0·6	1900	70	5
444	20·1		0·5	2100	70	5
555	20·2		0·1	1100	70	5

As an application measurements on LiF and NaCl were performed. Studying different orders of refleixon 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:

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

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