

Preliminary analysis of the 10,10,0 rocking curve shown in Fig. 2 indicates a scattering factor per atom of  $0.83 \pm 0.02$  e. At present the precision of measurement is not limited by the 10,10,0 measurement itself but by small, and so far unexplained, deviations between theoretical and experimental rocking curves for the lower-order Bragg reflections which we use to determine the crystal thickness using the known values of the X-ray optical constants (Tanemura & Kato, 1972; Aldred & Hart, 1973*a,b*). When this problem has been resolved we anticipate that the high-order scattering factors will be determined to 0.1% or so. At that precision not only the core scattering itself but also the temperature variation of the Debye-Waller factor becomes theoretically interesting. Further work is in progress.

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## The Consequences of the Neglect of TDS Correction for Temperature Parameters

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### Abstract

The importance of carrying out TDS corrections is emphasized. Their relative effect on the derived temperature parameter values is discussed and shown to rely primarily on the experimental conditions and not on the softness of the crystal.

### 1. Introduction

In accurate analyses of charge density distributions from X-ray diffraction data there has recently been a tendency to utilize shorter wavelengths of X-rays such as Ag K $\alpha$  radiation to improve the resolution of charge density maps synthesized by Fourier methods from observed X-ray data. Such studies clearly require correction for thermal diffuse scattering (TDS) contributions to the Bragg peaks since these often amount to more than 35%.

The consequences of the neglect of TDS correction

on structure analysis have been discussed by Harada & Sakata (1974) on the basis of their general formalism of TDS correction. They predicted that while the position parameters are little affected, thermal parameters are modified in such a way that the principal axes of the thermal ellipsoids change their directions. Furthermore, it was emphasized that TDS correction was particularly important for soft materials because in this case the correction factor is larger. This statement, however, was not intended to imply that it is unnecessary to correct for possible TDS if the crystal is sufficiently hard. It will in fact be shown that the relative reduction of the temperature parameters due to neglect of TDS correction is almost the same for any crystal, largely independent of its hardness and depending mainly on the experimental conditions under which the Bragg intensities were measured: the size and shape of the counter aperture, the scan width, the wavelength of the radiation used and the unit-cell dimension of the crystal.

In this paper we discuss this problem theoretically on the basis of the formalism of Harada & Sakata (1973, 1974) and then endeavour to test our findings in four different cases.

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## 2. The effect of TDS on the temperature parameters

Within the framework of kinematical scattering theory, the integrated Bragg intensity  $I(\text{obs})$  from an ideal mosaic single crystal is given by

$$I(\text{obs}) = (1 + \alpha - \alpha') I(B), \quad (1)$$

where  $I(B)$  is the contribution from true Bragg scattering,  $\alpha I(B)$  is the contribution from the TDS under the Bragg peak and  $\alpha' I(B)$  is the TDS already subtracted in the course of background correction. The correction factor  $\alpha$  is expressed in quadratic form in terms of the Miller indices  $h$ ,  $k$  and  $l$ , provided that the TDS which contributes to the integrated Bragg intensity consists of only one-phonon scattering,

$$\alpha = \tilde{\mathbf{h}} \Delta \mathbf{\beta} \mathbf{h}, \quad (2)$$

where  $\Delta \mathbf{\beta}$  is the symmetric TDS tensor, representing anisotropy of the TDS in reciprocal space and  $\mathbf{h}$  is a column vector whose elements are  $h$ ,  $k$  and  $l$ . Since  $\alpha'$  is of the same form as  $\alpha$ , (1) can be rewritten as

$$I(\text{obs}) = (1 + k\alpha) I(B), \quad (3)$$

where  $k$  is a proportionality constant. Although the value of  $k$  has as yet not been unequivocally determined, two values, 0.74 and 0.67, have been proposed by Harada & Sakata (1973)\* and Willis (1969), respectively.

Let us compare the situations with and without TDS corrections. Since in both cases the integrated intensities are treated as proportional to the square of the structure factors, we have

$$I(\text{obs}) = s \left| \sum_{\kappa} f_{\kappa} \exp(-w_{\kappa}^{\text{eff}}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_{\kappa}^{\text{eff}}) \right|^2 \quad (4)$$

$$I(B) = s' \left| \sum_{\kappa} f_{\kappa} \exp(-w_{\kappa}^{\text{true}}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_{\kappa}^{\text{true}}) \right|^2, \quad (5)$$

where  $f_{\kappa}$  is the atomic scattering amplitude of the  $\kappa$ th atom,  $w_{\kappa}^{\text{eff}}$  and  $\mathbf{r}_{\kappa}^{\text{eff}}$  represent the exponent of the temperature factor and the position vector for the  $\kappa$ th atom obtained from the data which has not been corrected for TDS, respectively (we have omitted the Lorentz and polarization factors).  $w_{\kappa}^{\text{true}}$  and  $\mathbf{r}_{\kappa}^{\text{true}}$  are values obtained from the data corrected for TDS. The scale factors are denoted by  $s$  and  $s'$ . As is well known,  $w_{\kappa}$  is expressed in terms of Miller indices in a quadratic form similar to (2),

$$w_{\kappa} = \tilde{\mathbf{h}} \mathbf{\beta}_{\kappa} \mathbf{h}, \quad (6)$$

where  $\mathbf{\beta}_{\kappa}$  is the temperature-parameter tensor whose form is uniquely assigned if the symmetry of the  $\kappa$ th atomic site is specified in the limit of the harmonic approximation of thermal vibration. Such a tensor

\* Sakata & Harada (1976) cited 0.72 as the value of  $k$  but it should read 0.74.

form, however, breaks down if anharmonicity is included. We continue our discussion of the problem within the harmonic approximation.

Although the TDS correction factor  $\alpha$  may exceed 0.3 for higher-order Bragg reflections, we use the approximation

$$\frac{1}{(1 + k\alpha)} = \exp(-k\alpha). \quad (7)$$

By substituting (4), (5) and (7) in (3) and equating  $s$  and  $s'$ , we obtain the following relations

$$w_{\kappa}^{\text{true}} \simeq w_{\kappa}^{\text{eff}} + \frac{k}{2} \alpha$$

or

$$\mathbf{\beta}_{\kappa}^{\text{true}} \simeq \mathbf{\beta}_{\kappa}^{\text{eff}} + \frac{k}{2} \Delta \mathbf{\beta} \quad (8)$$

and

$$\mathbf{r}_{\kappa}^{\text{true}} \simeq \mathbf{r}_{\kappa}^{\text{eff}}. \quad (9)$$

As discussed previously (Harada & Sakata, 1974), this indicates that within our approximation the position parameters  $\mathbf{r}_{\kappa}$  are not affected significantly even if the TDS correction is not applied to the data, but temperature parameters  $\mathbf{\beta}_{\kappa}$  are modified by the amount  $(k/2) \Delta \mathbf{\beta}$ . It should be noted that the tensor form of  $\mathbf{\beta}_{\kappa}$  obeys the site symmetry of the  $\kappa$ th atomic location, while that of  $\Delta \mathbf{\beta}$  is independent of the atomic species and dependent only on the crystal system. Therefore, the directions of the principal axes of the thermal ellipsoids would, without TDS correction, be different from their true directions. This would have especially serious consequences for charge-density analyses.

In (8)  $\mathbf{\beta}_{\kappa}^{\text{true}}$  is a quantity proportional to the mean-square atomic displacement due to the presence of phonons in the crystal. It is therefore conveniently expressed as a sum of two terms: contributions from acoustic phonons and from optic phonons. Thus, (8) may be rewritten as

$$\mathbf{\beta}^{\text{true}} = \mathbf{\beta}^{\text{true}}(\text{acoustic}) + \mathbf{\beta}^{\text{true}}(\text{optic}), \quad (10)$$

where

$$\mathbf{\beta}^{\text{true}}(\text{acoustic}) = \mathbf{\beta}^{\text{eff}}(\text{acoustic}) + \frac{k}{2} \Delta \mathbf{\beta} \quad (11)$$

if we restrict ourselves to the main contribution to  $\Delta \mathbf{\beta}$ , which is due to the acoustic term.

The components of  $\Delta \mathbf{\beta}$  and  $\mathbf{\beta}^{\text{true}}(\text{acoustic})$  in the notation of Harada & Pedersen (1968) and Harada & Sakata (1974) are defined by

$$\Delta \beta_{lm} = \sum_p \sum_q \sigma_{pl} \sigma_{qm} T_{pq} \quad (12)$$

$$\beta_{lm}^{\text{true}}(\text{acoustic}) = \sum_p \sum_q \sigma_{pl} \sigma_{qm} T'_{pq} \quad (13)$$

with

$$T_{pq} = \frac{k_B T}{(2\pi)^3} \int_{\text{scan volume}} \frac{(\mathbf{A}^{-1})_{pq}}{q^2} d^3 q \quad (14)$$

and

$$T'_{pq} = \frac{k_B T}{(2\pi)^3} \int_{\text{Brillouin zone}} \frac{(\mathbf{A}^{-1})_{pq}}{q^2} d^3 q, \quad (15)$$

where  $(\mathbf{A}^{-1})_{pq}$  is an element of a  $3 \times 3$  symmetric tensor which is determined from the elastic constants and the direction cosines of the wave vector;  $\mathbf{q}$  is the wave vector of the phonon and  $\sigma_{pl}$  is the element of a  $3 \times 3$  matrix used to transform the rectangular coordinate system in which the elastic constants are usually defined into the crystallographic coordinate system. The difference between  $T_{pq}$  and  $T'_{pq}$  is in the region over which the integral is taken: in  $T_{pq}$  the integral should be taken over the scan volume swept out in reciprocal space in the course of a measurement, while in  $T'_{pq}$  the integral is over the entire Brillouin zone. Substituting (12) and (13) in (11), we have

$$\begin{aligned} \beta_{lm}^{\text{eff}}(\text{acoustic}) &= \beta_{lm}^{\text{true}}(\text{acoustic}) - \frac{k}{2} \Delta \beta_{lm} \\ &= \sum_p \sum_q \sigma_{pl} \sigma_{qm} T'_{pq} \left( 1 - \frac{k}{2} \frac{T_{pq}}{T'_{pq}} \right). \end{aligned} \quad (16)$$

Let us define

$$\Delta_{pq} \equiv \frac{k}{2} \frac{T_{pq}}{T'_{pq}} \quad (17)$$

for the correction to the  $p, q$  element of the tensor  $\mathbf{T}'$ . Since  $\Delta_{pq}$  is almost independent of the element  $p, q$ , as will be proven in the next section, writing  $\Delta_{pq}$  as  $\Delta$ , we have

$$\begin{aligned} \beta_{lm}^{\text{eff}}(\text{acoustic}) &= \beta_{lm}^{\text{true}}(\text{acoustic}) - \frac{k}{2} \Delta \beta_{lm} \\ &= (1 - \Delta) \beta_{lm}^{\text{true}}(\text{acoustic}). \end{aligned} \quad (18)$$

### 3. Estimation of $\Delta_{pq}$

The elements of the tensor  $\Delta$ , which are correction terms for the corresponding elements of  $\mathbf{T}'$ , are given by (17). Both the Brillouin zone and the scan volume swept out in reciprocal space in the course of a measurement may be approximated by spheres of equivalent volumes having radii  $q_{ZB}$  and  $q_s$ , respectively. Replacing  $(\mathbf{A}^{-1})_{pq}$  by its average value  $\langle (\mathbf{A}^{-1})_{pq} \rangle$  and taking it out of the integrals in (14) and (15) [cf. Nilsson (1957)], we obtain

$$T_{pq} = \frac{k_B T}{2\pi^2} \langle (\mathbf{A}^{-1})_{pq} \rangle q_s \quad (19)$$

and

$$T'_{pq} = \frac{k_B T}{4\pi^2} \langle (\mathbf{A}^{-1})_{pq} \rangle q_{ZB}. \quad (20)$$

Hewat (1972) has suggested that the phonon dispersion relation  $\omega(\mathbf{q})$  is much better approximated by a sine curve than by the Debye model [which has been used in the derivation of (13)]. This is because the frequently made assumption that the shape of  $\omega(\mathbf{q})$  is not important for large  $\mathbf{q}$  is not justified, *i.e.* the contribution of acoustic modes near the zone boundary to  $w_{\kappa}^{\text{true}}$  may be quite significant. The introduction of this dispersion relation results in an additional factor  $2 \ln 2$  and (20) is therefore replaced by

$$T'_{pq} = \frac{k_B T}{2\pi^2} \langle (\mathbf{A}^{-1})_{pq} \rangle q_{ZB} \ln 2. \quad (21)$$

Since TDS occurs primarily from scattering by long-wavelength phonons, consideration of the shape of  $\omega(\mathbf{q})$  in conjunction with  $\mathbf{T}$  is not necessary and so using (19) and (21) in (17) gives

$$\Delta = \frac{k q_s}{2 \ln 2 \times q_{ZB}}, \quad (22)$$

where the subscripts on  $\Delta_{pq}$  are now superfluous. This result is quite important in that it provides a measure of the relative change of the temperature parameters resulting from correction for TDS. A significant feature of it is that it is independent of the elastic constants (and therefore the softness of the crystal).

The contribution of optic modes to  $w_{\kappa}^{\text{true}}$  can be significant and the effect can be estimated by extending the first Brillouin zone to the second or higher zone (see Fig. 1) depending on the number of atoms in the unit cell. We may therefore replace  $q_{ZB}$  by  $q'_{ZB}$ , the radius appropriate to the extended zone. In the case of two atoms per unit cell, for example, the volume of the extended Brillouin zone becomes twice that of the original zone and so  $q'_{ZB}$  is  $2^{1/3} q_{ZB}$ . Thus the final expression for the correction including optic effects is

$$\Delta' = \frac{k q_s}{2 \ln 2 \times q'_{ZB}}. \quad (23)$$

This correction term is easily calculated and depends, for a given crystal, only on the experimental technique used to scan the Bragg peaks, *i.e.* the mode of scan, the scan width, the size and shape of the detector aperture, the Bragg angle ( $\theta$ ) and the wavelength of the incident radiation ( $\lambda$ ). Fig. 2 demonstrates the results for a small real cell (*a*) and a large real cell (*b*) with the same scan volume in each case. The magnitude of the relative effect on the temperature parameters is determined by the respective ratios  $q_s/q'_{ZB}$ . For the small unit cell the relative effect on the temperature parameters is small, whereas for the large unit cell the relative effect is considerable.

Table 1. Details for comparison of experimental and theoretical  $\Delta'$  values for each of four studies

The size of the detector aperture is given with the width first in each case.

	Experimental conditions			Lattice parameters		Results					
	Scan mode	Scan width ( $^\circ\theta$ )	Detector aperture ( $^\circ$ )	$a$ (Å)	$c$ (Å)	$q_s$ (Å $^{-1}$ )	$q_{zB}$ (Å $^{-1}$ )	$\Delta'$	$\Delta'_{\text{obs}}$	$\delta\bar{B}$ (Å $^2$ )	$\delta\bar{B}_{\text{obs}}$ (Å $^2$ )
KCl	$\omega$	2.5	1.5 × 1.5	6.290	—	0.1702	0.6197	0.116	0.105	0.22	0.20
CdS	$\omega-2\theta$	3.0	2.0 × 1.5	4.136	6.713	0.1991	0.8413	0.100	0.057	0.13	0.08
CdSe	$\omega-2\theta$	3.0	2.0 × 1.5	4.299	7.010	0.1991	0.8081	0.104	0.072	0.15	0.11
BaF $_2$	$\omega-2\theta$	2.4	2.2 × 3.2	6.196	—	0.1682	0.6291	0.099	0.066	0.08	0.05

#### 4. Comparison of experiment and theory

Equation (23) was used to calculate  $\Delta'$  for four different studies involving single crystals at room temperature as described below. The relevant experimental conditions under which diffracted intensities were recorded are given in Table 1. In all cases except BaF $_2$ , Mo  $K\alpha$  characteristic X-radiation ( $\lambda = 0.7107$  Å) was used. In the BaF $_2$  study the incident radiation was neutrons ( $\lambda = 1.038$  Å). The detector apertures were either square or rectangular and the dimensions given in Table 1 are the angles subtended by the aperture at the crystal.

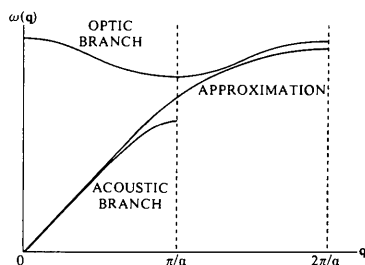


Fig. 1. Optic and acoustic branches of the dispersion relation for a diatomic linear lattice, showing extension of the zone. The lattice parameter is  $a$ .

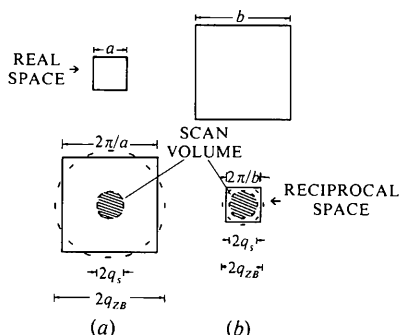


Fig. 2. Demonstration of the relative effects of TDS on the temperature parameters for: (a) a small unit cell and (b) a large unit cell. The scan volume is the same in both cases.

The scan volume can be calculated using one of the formulae given by Sakata & Harada (1976), which depend on  $\theta$  and result in  $q_s$  being dependent on  $\sin^{1/3} 2\theta$ , a slowly varying function in the region of interest. The values of  $q_s$  are obtained by setting  $\theta = 45^\circ$  and are given in Table 1, along with values of  $q_{zB}$ ,  $\Delta'$  and  $\Delta'_{\text{obs}}$  (the observed value of  $\Delta'$ ). The lattice parameters used in the calculations of  $q_{zB}$  were those of: Donnay & Donnay (1963) for KCl and BaF $_2$ ; National Bureau of Standards (1955) for CdS; National Bureau of Standards (1957) for CdSe. In all cases we set  $k = 0.74$ .

The calculations for KCl are based on the study by James & Brindley (1928), the results of which have been used more recently [*e.g.* Kashiwase (1965) and Willis (1969)]. The experimental conditions listed in Table 1 for KCl are those used by Willis (1969) [see also Nilsson (1957) and Cooper & Rouse (1968)]. The value of  $\Delta'$  for KCl represents an increase in the temperature parameter of approximately 13% as a result of including TDS corrections. This is in excellent agreement with the findings of Nilsson (1957), who obtained a temperature-parameter value of 1.885 Å $^2$  after correcting the data for the contributions from TDS, calculated on the basis of an infinite slit height for the detector (*cf.* 1.688 Å $^2$  originally). It should be noted that a slight error is involved in this calculation of  $\Delta'$  because James & Brindley's (1928) background measurements were not recorded at the ends of the scans.

The calculations for CdS, CdSe and BaF $_2$  are based on studies by Stevenson, Milanko & Barnea (1983), Stevenson & Barnea (1983) and Cooper, Rouse & Willis (1968), respectively. In these three cases there is approximate agreement between  $\Delta'$  and  $\Delta'_{\text{obs}}$ . The value of  $\Delta'_{\text{obs}}$  for BaF $_2$  is based on the comparison of two methods used to calculate TDS correction factors (Willis, 1969).

By using (3), (5) and (7) it is possible to obtain the following approximation [see, for example, Willis (1969)]:

$$k\alpha = 2(\delta\bar{B}) \sin^2 \theta / \lambda^2, \quad (24)$$

where  $\delta\bar{B}$  is the change in the 'overall' temperature parameter, as a result of correcting for TDS effects.

Table 1 also lists values of  $\delta\bar{B}$  and  $\delta\bar{B}_{\text{obs}}$ , the changes in the 'overall' temperature parameters, in accordance with  $\Delta'$  and  $\Delta'_{\text{obs}}$  respectively. In carrying out a linear least-squares fit of the CdS TDS correction factors (Merisalo & Kurittu, 1978) according to (24), the value of  $\delta\bar{B}$  is found to be approximately  $0.10 \text{ \AA}^2$  (cf.  $\delta\bar{B}$  and  $\delta\bar{B}_{\text{obs}}$  in Table 1).

We can rewrite (24), in terms of  $\Delta'$ , as

$$k\alpha = 2\bar{B}^{\text{true}} \Delta' \sin^2 \theta / \lambda^2 = 2\bar{B}^{\text{eff}} \Delta' \sin^2 \theta / [\lambda^2(1 - \Delta')], \quad (25)$$

where  $\bar{B}^{\text{eff}}$  and  $\bar{B}^{\text{true}}$  are the 'overall' temperature parameters before and after correction for TDS, respectively. Equation (25) can be used to obtain approximate values of the TDS correction factors without knowing the elastic constants, whose effect is included in the temperature parameters. The accuracy of such correction factors is largely dependent on the accuracy of  $\Delta'$  and so a more rigorous calculation than is given by (23) is recommended. Accurate calculations of TDS correction factors can involve large amounts of computing time (to evaluate surface or volume integrals numerically for each reflection), especially for large data sets. Calculation of a small number of these correction factors at a variety of Bragg angles may, after comparison with (25), yield a suitable value of  $\Delta'$  with which (25) could be used to obtain the other correction factors [a similar approach has been used by Willis (1969)].

It is worthy of note that, within the above formalism, it is possible to derive approximate values of temperature parameters, which can be given by

$$B_{lm} \simeq 8k_B T \langle (\mathbf{A}^{-1})_{lm} \rangle q'_{zB} \ln 2. \quad (26)$$

As an example, the values of  $\langle (\mathbf{A}^{-1})_{lm} \rangle$  were evaluated by numerical integration using the TDS correction program of Sakata, Stevenson & Harada (1983) for CdS. The elastic constants used were those of Berlincourt, Jaffe & Shiozawa (1963). The calculated value of the 'overall' temperature parameter for CdS was  $1.04 \text{ \AA}^2$ , cf.  $1.345(4) \text{ \AA}^2$  from experiment (Stevenson, Milanko & Barnea, 1983).

The main factors which limit the usefulness of the foregoing approach are: the approximate way in which the Brillouin zone is extended to include the effects of optic modes, the approximations to the shape of the phonon dispersion curves (particularly in the vicinity of the Brillouin zone boundary) and the use of spherical volumes for the Brillouin zone and scan volume. In particular, Table 1 shows that  $\Delta'_{\text{obs}}$  is lower than  $\Delta'$  in each case. This trend is more pronounced if the value of

$\Delta'_{\text{obs}}$  for KCl is replaced by a value based on  $\delta\bar{B}_{\text{obs}} = 0.16 \text{ \AA}^2$  (Cooper & Rouse, 1968), i.e.  $\Delta'_{\text{obs}} = 0.087$ . This systematic discrepancy may be characteristic of one or more of the limitations mentioned above.

## 5. Discussion and conclusions

The agreement between theory and experiment for the four cases presented in the previous section is reasonable when the nature of the approximations made in deriving (23) are considered. Clearly, the use of (23) requires further testing, on a variety of crystals, in order to determine its range of applicability and usefulness. Such a test, for a crystal and experimental conditions where the relative effect of TDS on the temperature parameters is smaller, would be particularly timely, since, in all the examples considered thus far this relative effect is quite significant. Unfortunately, suitable studies where all necessary details are given, including the change in the derived temperature parameters as a result of correcting for TDS and the experimental conditions under which intensities were recorded, are few.

The use of (25) and (23) serves as an indication of the size of the TDS corrections and the relative effect such corrections have on the derived values of temperature parameters. The validity of these equations depends on a number of factors including the shapes of the Brillouin zone and scan volume and the contribution of optic modes to the temperature parameters.

Equation (23) indicates the importance of applying TDS corrections in all cases, since their relative effect on temperature parameters is primarily dependent on the experimental conditions under which data is collected and not necessarily on the softness of the crystal under investigation.

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\* It should be noted here that  $B$  is defined in the unit of  $\text{\AA}^2$  while the elements of  $\beta_{\mathbf{k}}$  in (6) are dimensionless quantities [see, for example, Willis & Pryor (1975)]. Both  $B$  and  $\beta$  are, however, used as so-called 'temperature parameters', although their definitions are slightly different.

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## X-ray Diffraction Under Specular Reflection Conditions. Ideal Crystals

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### Abstract

The theory of X-ray diffraction by ideal crystals under the conditions when the incident and diffracted beams are directed at small angles to the entrance surface of a crystal has been developed. Besides the diffracted wave propagating inside the crystal (*i.e.* Laue-case diffraction) there are two specular reflected waves arising from incident and diffracted waves respectively. Such a diffraction scheme has been recently put into practice [Marra, Eisenberger & Cho (1979). *J. Appl. Phys.* **50**, 6927–6933]. It is found that at small glancing angles of incidence there exist directions in which the intensity of the reflected diffracted wave is close to the incident wave intensity, while both the specular reflected wave and diffracted wave intensities are close to zero. The analytical expressions are obtained for the diffraction curve shape. It is shown that for diffraction curve measurements high collimation through the glancing angle of incidence of X-rays on the crystal,  $\Phi$ , is sufficient. There is no need to provide collimation through parameter  $\alpha$  denoting deviation from exact Bragg conditions. Owing to the rigid relation between  $\alpha$ ,  $\Phi$  and the angle of emergence of the reflected diffracted wave from the entrance surface of the crystal,  $\Phi'$ ,

$$\Phi^2 = \alpha + \Phi'^2,$$

when measuring the intensity of the reflected diffracted wave as a function of  $\Phi$ , the intensity is obtained as a function of  $\alpha$ . Measurement of  $\Phi'$  with the accuracy of about 30'' corresponds to accuracy through  $\alpha$  of about

0.1''. These facts sufficiently simplify the performance of experiment and open wide prospects for studies of crystal structure of thin subsurface layers with unique accuracy.

### 1. Introduction

The use of extremely asymmetric X-ray diffraction techniques requires the account of the specular reflection phenomenon. This problem has been studied in detail for both Bragg-case (Farwig & Schürmann, 1967; Kishino, 1971; Rustichelli, 1975) and Laue-case diffraction (Farwig & Schürmann, 1967; Kishino, Noda & Kohra, 1972; Bedynska, 1973, 1974; Härtwig, 1976, 1977). In the Laue case the specular reflection effect would essentially increase the intensity of anomalously transmitted waves in the  $T$  beam. In the Bragg case a decrease in penetration depth due to specular reflection leads to an appreciable increase in the integral reflection coefficient with the position and shape of the Bragg peak being essentially changed. Consideration of the specular reflection phenomenon does not appear to be restricted only to asymmetric diffraction schemes.

A new diffraction scheme has been recently described (Marra, Eisenberger & Cho, 1979). In this scheme, the incident-beam glancing angle was chosen in such a way as to allow the Laue-case diffraction condition to be realized. On the other hand, both the incident and diffracted beams made small angles with