acht speziellen Punktlagen (a)–(h) zur gleichen Kon-figurationslage. Von den 8! möglichen Permutationen dieser Punktlagen ist wegen der Koppelung zwar nur $\frac{1}{30}$ zulässig; das sind aber immerhin noch 1344.

In diesem Zusammenhang sei auf eine Arbeit von Boyle & Lawrenson (1973) hingewiesen, in welcher alle die Permutationen der Punktlagen explizit angegeben werden, welche einer Translation in der Automorphis-mengruppe entsprechen, alle übrigen Permutationen aber unberücksichtigt bleiben.

Die hier vorgelegte Arbeit beruht auf Unter-suchungen, die von uns im Fachbereich Geowissen-schaften der Philipps-Universität Marburg mit Unter-stützung durch die Deutsche Forschungsgemeinschaft durchgeführt wurden. Der deutschen Forschungsge-meinschaft gilt daher unser besonderer Dank.

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Thermal Diffuse X-ray Scattering for Small Samples and Small Coherent Scattering Domains

BY J. P. URBAN

Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

The influences of sample size and mosaic block size upon X-ray thermal diffuse scattering have been investigated. Surface and edge vibrational modes were incorporated into the Debye spectrum. Two additional terms, which depend on the surface/volume and edge-length/volume ratios, appear therefore in the expression for the scattered intensity. The TDS contributions of the volume and surface terms to the integrated Bragg intensity are calculated numerically.

Introduction

Various authors have performed studies of the thermal diffuse scattering contributions to X-ray reflexions. The most recent of this is the refined model of Walker & Chipman (1972). But in all of these studies, the in-fluences of mosaic particle size and sample size (in the case of powders the powder grain size) have been neg-lected. These influences become important for mosaic and grain sizes below $\simeq 250$ Å.

The influence of particle size on the Debye–Waller factor has been studied by Schoening (1968), whose work is based on the complete counting of vibrational frequencies through the introduction of surface and edge terms into the Debye spectrum. These additional terms were used first by Bolt (1939), Maa (1939) and Roe (1941).

The influences of the additional surface terms on the expression for the integrated one-phonon scattering of acoustic modes are discussed in the present paper. Furthermore, the effect of the size of coherent scatter-ing domains will be considered.

It is useful to write the scattered X-ray intensity in terms of multiple-phonon processes:

$$I(\mathbf{b}) \propto I_0(\mathbf{b}) + I_1(\mathbf{b}) + \ldots . \qquad (1)$$

$I_0(\mathbf{b})$ and $I_1(\mathbf{b})$ are the zero- and one-phonon intensity functions, which can be written as:

$$I_0(\mathbf{b}) = N/V_{\mathrm{el}}\delta(\Delta\mathbf{b}) \qquad (1a)$$

and

$$I_1(\mathbf{b}) = \tfrac{1}{2} \sum_{jk} G_{kj}\{I_0(\mathbf{b}+\mathbf{k}) + I_0(\mathbf{b}-\mathbf{k})\} \qquad (1b)$$

where

$$G_{kj} = 4\pi^2 b^2 \cos^2 \xi_{kj} k_B T/\omega_{kj}^2 N m_{\mathrm{el}} \qquad (1c)$$

and $\delta(\Delta\mathbf{b})$ is a three-dimensional δ function.

$\mathbf{k}$ = wave vector of the phonons, $|\mathbf{k}| = 1/\lambda_{\mathrm{phon}}$
V_{el} = volume of the elementary cell
m_{el} = mass of the elementary cell
N = number of the elementary cells in the crystal
ω_{kj} = frequency of a phonon of wave vector $\mathbf{k}$ and polarization j

T = absolute temperature
k_B = Boltzmann constant
$\mathbf{b}$ = vector in reciprocal space, $|\mathbf{b}| = 2 \sin \theta/\lambda$
θ_0 = Bragg angle
$\Delta\mathbf{b}$ = $\mathbf{b} - \mathbf{b}_0$
ξ_{kj} = angle between polarization vector of phonon $(\mathbf{k}, j)$
      with $\mathbf{b}$.

Introducing the density of states in $\mathbf{k}$ space, ϱ_k, the sum over $\mathbf{k}$ in equation $(1b)$ can be replaced by an integral:

$$I \propto N/V_{\mathrm{el}}\delta(\Delta\mathbf{b}) + \tfrac{1}{2} \sum_j \int G_{kj}\{I_0(\mathbf{b}+\mathbf{k}) + I_0(\mathbf{b}-\mathbf{k})\}\varrho_k \mathrm{d}V_k . \tag{2}$$

After integration, equation (2) becomes

$$I \propto N/V_{\mathrm{el}}\delta(\Delta\mathbf{b}) + N/V_{\mathrm{el}} \sum_j G_{\Delta bj}\varrho_{\Delta b}; \tag{3}$$

$\varrho_{\Delta b}$ is the density of states ϱ_k for $\mathbf{k} = \Delta\mathbf{b}$.

Higher orders than one-phonon scattering have been neglected. In order to obtain the density of states, ϱ_k, the modified Debye spectrum accounting for surface and edge effects is introduced (Maradudin, Montroll & Weiss, 1963):

$$g(\omega)\mathrm{d}\omega = \left(\frac{4\pi V\omega^2}{(2\pi)^3 c_3} + \frac{\pi S\omega}{2(2\pi)^2 c_2} + \frac{L}{2\pi 8 c_1} \right) \mathrm{d}\omega; \tag{4}$$

V is the volume of the crystal, S its surface area and L the edge length. According to Schoening (1968) the c's can be related to an average velocity c_m which depends on the longitudinal and transverse acoustic phonon velocities c_l and c_t.

The assumption of a linear-chain dispersion relation for the acoustic frequencies (Walker & Chipman, 1972) leads to the following equation for the frequencies:

$$\omega_{jk} \simeq 2\pi\bar{v}_{jk}|\mathbf{k}| \quad \text{with} \quad \bar{v}_{jk} \simeq \bar{v}_j \sin (\pi k/2k_m)/(\pi k/2k_m). \tag{5}$$

$\bar{v}_j$ is the average velocity for small wave vectors.

k_m is the radius of the first Brillouin zone, which has been replaced by a sphere of equal volume as the correct Brillouin zone.

$\bar{v}_j$ can be related to the c's by the following equations:

$$\bar{v}_j^3 = c_3 , \quad \bar{v}_j^2 = \beta_1 c_2 , \quad \bar{v}_j = \beta_2 c_1$$

with

$$\beta_1 = (1 + 2c_l^2/c_t^2)/(1 + 2c_l^3/c_t^3)^{2/3} \simeq 1\cdot 35 \tag{5a}$$

$$\beta_2 = (1 + 2c_l/c_t)/(1 + 2c_l^3/c_t^3)^{1/3} \simeq 1\cdot 80 . \tag{5b}$$

The factors β_1 and β_2 are not very sensitive to changes of the ratio c_l/c_t. In the range $1\cdot 5 \le c_l/c_t \le 2\cdot 5$ β_1 and β_2 can be replaced by mean values as indicated in equations $(5a)$ and $(5b)$.

If $g(k)\mathrm{d}k$ is the number of states in a shell between k and $k + \mathrm{d}k$, the density of states in k space is

$$\varrho_k = V + S\beta_1/(8|k|) + L\beta_2/(32\pi k^2) \tag{6}$$

with

$$g(k)\mathrm{d}k = 4\pi k^2 \varrho_k \mathrm{d}k .$$

The contribution of one-phonon scattering to the integrated Bragg intensity

If equation (6) is substituted in equation (3), the following expression for the scattered intensity is obtained:

$$I \propto N/V_{\mathrm{el}}\delta(\Delta\mathbf{b})$$
$$+ N/V_{\mathrm{el}} \sum_j G_{\Delta bj}[V + S\beta_1/(8\Delta b) + L\beta_2/(32\pi\Delta b^2)] . \tag{7}$$

The sum over j can be replaced by a mean value and, for cubic crystals, can be approximated by

$$\sum_j G_{\Delta bj} \simeq \frac{b_0^2 k_B T}{N V_{\mathrm{el}}\Delta b^2} \left(\frac{1}{c_{11}} + \frac{4}{c_{11} - c_{12}} \right)$$
$$\times \left(\frac{k_m}{\displaystyle\int_0^{k_m} \frac{\sin \dfrac{\pi|\Delta b|}{2k_m}}{\dfrac{\pi\Delta b}{2k_m}} \mathrm{d}\Delta b} \right)^2 ; \tag{8}$$

c_{11}, c_{12} are the elastic constants.

With equation (8), equation (7) becomes:

$$I \propto \delta(\Delta\mathbf{b}) + \frac{\alpha_v}{\pi\Delta b^2} + \frac{\beta_1\alpha_v S}{8\pi V|\Delta b|^3} + \frac{L\beta_2\alpha_v}{32\pi^2 V\Delta b^4} ; \tag{9}$$

α_v is a constant and independent of Δb and can be written as:

$$\alpha_v = \pi b_0^2 k_B T 1\cdot 28/3 \left(\frac{1}{c_{11}} + \frac{4}{c_{11} - c_{12}} \right) 10^{24} \tag{9a}$$

where the following units have to be used:

c_{kl} in dyn/cm^2, k_B in erg/°C, T in °K and b_0 in Å^{-1}.

Because of the finite size of the particles, restrictions on the frequency spectrum must be introduced. The maximum phonon wavelength can be expressed in terms of the size of the sample:

$$\lambda_{\max}/2 \simeq D \quad (D = \text{linear dimension of the sample}) .$$

Except for the first term, equation (9) holds only for $k_0 \le |\Delta\mathbf{b}| \le k_m$ with $k_0 = 1/D$. Outside this range $I - \delta(\Delta\mathbf{b}) = 0$. The function $\delta(\Delta\mathbf{b})$ is, however, defined for all values of $\Delta\mathbf{b}$.

In general, the sample shows a mosaic structure, which is mirrored in a broadening of the function described by equation (9). This broadening can be introduced by means of a convolution of equation (9) with a suitable function I_p, which is an average of the squared Fourier transform of a mosaic shape function.

The average must be taken over all coherent domains (mosaics) in the sample. To account for this, equation (9) should be modified to

$$I^* = \widehat{I_p I} . \tag{10}$$

In the following, equation (10) will be applied to powder samples. In order to take care of the different

orientations of the powder grains, equation (10) must be integrated over a sphere of radius b centred at $b = 0$. The observed scattering intensity function for powder samples, I_{sc} [i.e. apart from constant factors it is the function I^* in equation (10) averaged over the powder grain orientations], becomes

$$I_{sc} \propto \int \widehat{I_p} \left[\delta(\Delta\mathbf{b}) + \frac{\alpha_v}{\pi \Delta b^2} + \frac{\beta_1 \alpha_v S}{8\pi V |\Delta b|^3} \right.$$
$$\left. + \frac{L\beta_2 \alpha_v}{32\pi^2 V \Delta b^4} \right] dS_b, \quad (11)$$

where dS_b is the surface element of the sphere. It has to be born in mind that the second, third, and fourth terms are non-zero only in a restricted range ($k_0 \leq |\Delta\mathbf{b}| \leq k_m$).

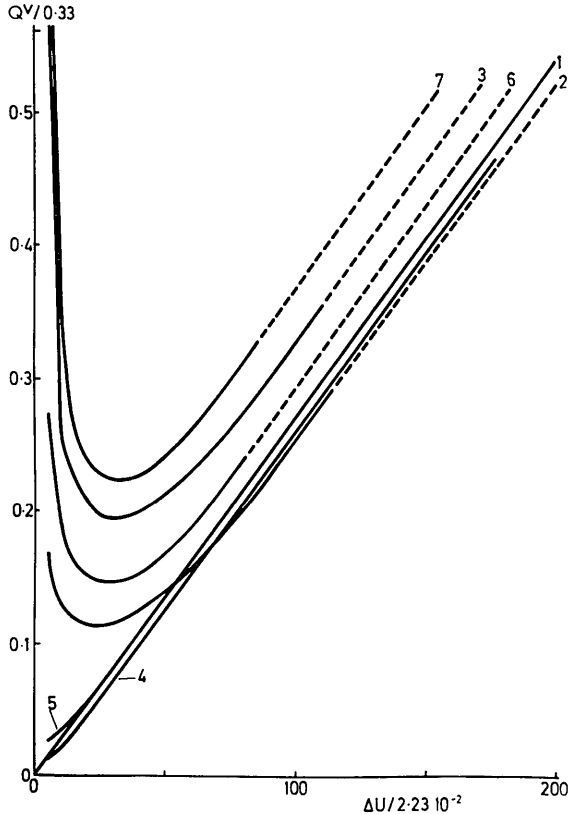With the approximation that the integration and convolution can be interchanged,

Fig. 1. Volume TDS. Q^v as a function of Δu. $n = 6$.

curve	k_m^*	k_0^*	μ^*
1	0·14···0·55	0	∞
2	0·14	$5·77 \times 10^{-3}$	$4·55 \times 10^3$
3	0·14	0	$4·55 \times 10^3$
4	0·14···0·55	$5·77 \times 10^{-4}$	$4·55 \times 10^5$
5	0·14···0·55	0	$4·55 \times 10^5$
6	0·55	$5·77 \times 10^{-3}$	$4·55 \times 10^3$
7	0·14	0	$4·55 \times 10^3$

$$I_{sc} \propto \int_{S^*} \widehat{I_p dS_b} \left[\delta(\Delta\mathbf{b}) + \frac{\alpha_v}{\pi} \int_{\tilde{S}} \frac{1}{\Delta b^2} \, dS_b \right.$$
$$\left. + \frac{\beta_1 \alpha_v S}{8\pi V} \int_{\tilde{S}} \frac{1}{|\Delta b|^3} \, dS_b + \frac{L\beta_2 \alpha_v}{32\pi^2 V} \int_{\tilde{S}} \frac{1}{\Delta b^4} \, dS_b \right]. \quad (12)$$

The area S^* corresponds to the surface of the sphere of radius b, while $\tilde{S}$ is the area on this sphere where $k_0 \leq |\Delta b| \leq k_m$. $\tilde{S}$ accounts for the restricted magnitudes of the phonon wavelengths.

$$\int_{\tilde{S}} \Delta b^{-2} dS_b = \pi \frac{b}{b_0} \ln \frac{b^2 + b_0^2 - 2bb_0 \cos \varphi_0}{b^2 + b_0^2 - 2bb_0 \cos \varphi_1}$$
$$= \pi \frac{b}{b_0} I_{TDS}^V \quad (13a)$$

$$\int_{\tilde{S}} |\Delta b|^{-3} dS_b = 2\pi \frac{b}{b_0} \{(b^2 + b_0^2 - 2bb_0 \cos \varphi_1)^{-1/2}$$
$$- (b^2 + b_0^2 - 2bb_0 \cos \varphi_0)^{-1/2}\} = 2\pi \frac{b}{b_0} I_{TDS}^S \quad (13b)$$

$$\int_{\tilde{S}} \Delta b^{-4} dS_b = \pi \frac{b}{b_0} \{(b^2 + b_0^2 - 2bb_0 \cos \varphi_1)^{-1}$$
$$- (b^2 + b_0^2 - 2bb_0 \cos \varphi_0)^{-1}\} = \pi \frac{b}{b_0} I_{TDS}^E. \quad (13c)$$

The functions I_{TDS}^V, I_{TSD}^S and I_{TDS}^E represent the main TDS-intensity dependence on Δb for the volume, surface and edge components. The factors $\pi b/b_0$ and $2\pi b/b_0$, in (13a, c) and (13b) respectively, are much less dependent on Δb than the functions $I_{TDS}^{V,S,E}$. I_{TDS}^S and I_{TDS}^E are additional terms, which have been introduced through the extension of the density of states ϱ_k, equation (6), with surface and edge terms considered in the vibrational spectrum. I_{TDS}^V, however, is the usual TDS intensity in the Debye theory.

$$\tan \varphi_0 = \begin{cases} \dfrac{\sqrt{k_m^2 4b_0^2 - (b_0^2 - b^2 + k_m^2)^2}}{b^2 - k_m^2 + b_0^2} & \text{for } |\Delta\mathbf{b}| \leq k_m \\ 0 & \text{otherwise} \end{cases}$$

$$\tan \varphi_1 = \begin{cases} \dfrac{\sqrt{k_0^2 4b_0^2 - (b_0^2 - b^2 + k_0^2)^2}}{b^2 - k_0^2 + b_0^2} & \text{for } |\Delta\mathbf{b}| \leq k_0 \\ 0 & \text{otherwise}. \end{cases}$$

A suitable approximation for I_p can be introduced by assuming spherical coherent regions of mean radius $\bar{y}$ and polydispersity g, where the polydispersity of the spherical regions is defined by:

$$g = [\overline{\bar{y}^2} - \bar{y}^2]^{1/2}/\bar{y}.$$

The double dashes indicate the mass statistical averages. For the mass statistics a Maxwellian distribution has been assumed (Hosemann & Bagchi, 1962). The integration over dS_b leads to the following functions:

$$\tilde{I}_p = \int_{S^*} I_p dS_b = \begin{cases} \dfrac{\pi b}{\mu b_0} \ln \dfrac{(b+b_0)^2 + 1/\mu}{(b-b_0)^2 + 1/\mu} & \text{for } n=4 \\[2ex] \dfrac{\pi b}{\mu b_0} \{\exp[-\mu(b-b_0)^2] \\ \qquad -\exp[-\mu(b+b_0)^2]\} \\ \hfill \text{for } n=\infty \\[2ex] \dfrac{\pi b}{\mu^{(n-2)/2} b_0^{(n-4)/2}} \{[1/\mu + (b-b_0)^2]^{-(n/2-2)} \\ \quad -[1/\mu + (b+b_0)^2]^{-(n/2-2)}\} \\ \hfill \text{for } 4 < n < \infty \end{cases}$$

(13d)

with

$$\mu = \frac{4\pi^2}{5} \left[\frac{\Gamma\left(\dfrac{n+1}{2}\right)}{\Gamma\left(\dfrac{n+2}{2}\right)} \right]^2 \bar{y}^2$$

and

$$g = \left[\frac{\Gamma\left(\dfrac{n+3}{2}\right) \Gamma\left(\dfrac{n+1}{2}\right)}{\Gamma\left(\dfrac{n+2}{2}\right)^2} - 1 \right]^{1/2}.$$
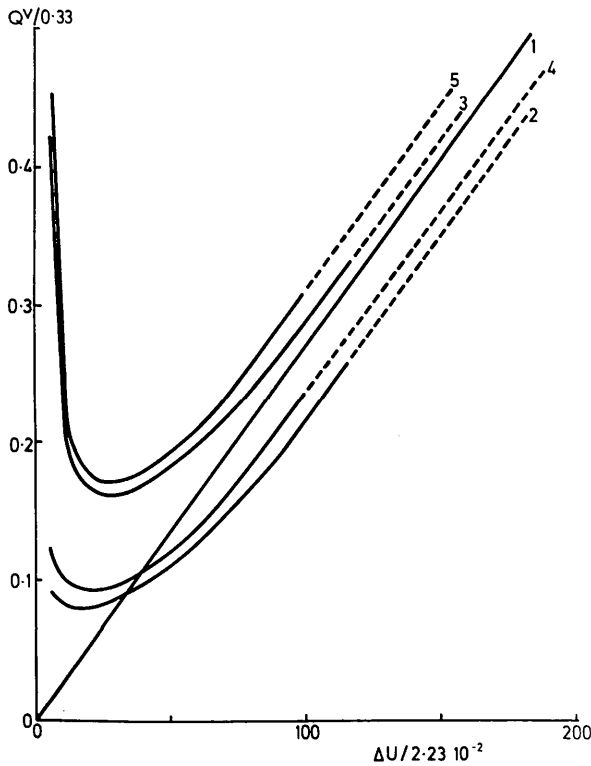
Finally, with the functions $\tilde{I}_{TDS}^{V,S,E}$ introduced through the definition

$$\tilde{I}_{TDS}^{V,S,E} = (b/b_0) I_{TSD}^{V,S,E} \tilde{I}_p,$$ (14a)

the scattered intensity can be written as:

$$I_{sc} \propto \tilde{I}_p + \alpha_v \tilde{I}_{TDS}^V + \alpha_s \tilde{I}_{TDS}^S + \alpha_E \tilde{I}_{TDS}^E$$ (14)

where

$$\alpha_s = \frac{\beta_1 S \alpha_v}{4V}, \quad \alpha_E = \frac{\beta_2 L \alpha_v}{32\pi V}.$$

A background correction has to be performed in order to take care of the finite range of the observable reflexions. If $\Delta b_2 - \Delta b_1$ is the experimentally obtained spread of the peak, the background functions F_p and F_{TDS} can be introduced by assuming a linear background.

$$F = \frac{\tilde{I}(\Delta b_1) - \tilde{I}(\Delta b_2)}{\Delta b_1 - \Delta b_2} (\Delta b - \Delta b_1) + \tilde{I}(\Delta b_1).$$ (15)

The ratios of the different integrated TDS components to the integral Bragg intensity in the range $\Delta b_1 - \Delta b_2$ are:
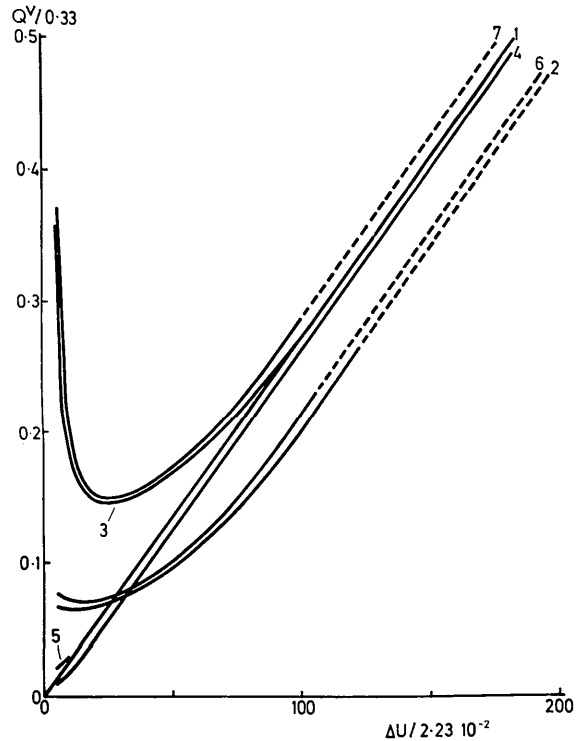

Fig. 2. Volume TDS. Q^v as a function of Δu. $n=7$.

Curve	k_m^*	k_0^*	μ^*
1	0·14···0·55	0	∞
2	0·14	$5\cdot77 \times 10^{-3}$	$3\cdot95 \times 10^3$
3	0·14	0	$3\cdot95 \times 10^3$
4	0·55	$5\cdot77 \times 10^{-3}$	$3\cdot95 \times 10^3$
5	0·55	0	$3\cdot95 \times 10^3$

Fig. 3. Volume TDS. Q^v as a function of Δu. $n=8$.

Curve	k_m^*	k_0^*	μ^*
1	0·14···0·55	0	∞
2	0·14	$5\cdot77 \times 10^{-3}$	$3\cdot5 \times 10^3$
3	0·14	0	$3\cdot5 \times 10^3$
4	0·14···0·55	$5\cdot77 \times 10^{-4}$	$3\cdot5 \times 10^5$
5	0·14···0·55	0	$3\cdot5 \times 10^5$
6	0·55	$5\cdot77 \times 10^{-3}$	$3\cdot5 \times 10^3$
7	0·55	0	$3\cdot5 \times 10^3$

$$E^{V,S,E} = \alpha_{V,S,E} \frac{\int_{\Delta b1}^{\Delta b2} (\tilde{I}_{TDS}^{V,S,E} - F_{TDS}^{V,S,E}) \, d\Delta b}{\int_{\Delta b1}^{\Delta b2} (\tilde{I}_p - F_p) d\Delta b} . \qquad (16)$$

In most cases, the contribution of the edge term is negligible and therefore will not be considered further.

With a new dimensionless coordinate $u = \Delta b / b_0$ introduced, equation (16) can be rewritten in a form which is more suitable for a general treatment:

$$E^{V,S} = A_{V,S} \frac{\int_{u_1}^{u_2} (\tilde{I}_{TDS}^{V,S}(u) - F_{TDS}^{V,S}(u)) du}{\int_{u_1}^{u_2} [\tilde{I}_p(u) - F_p(u)] du} = A_{V,S} Q^{V,S} \qquad (17)$$

with

$$A_v = \alpha_v b_0, \qquad A_s = \alpha_v \beta_1 S / (4V)$$

$$\tilde{I}_{TDS}^{V}(u) = \ln \frac{(1+u)^2 + 1 - 2(1+u) \cos \varphi_0}{(1+u)^2 + 1 - 2(1+u) \cos \varphi_1} I_p(u) \qquad (18a)$$

$$\tilde{I}_{TDS}^{S}(u) = \{[(1+u)^2 + 1 - 2(1+u) \cos \varphi_1]^{-1/2}$$

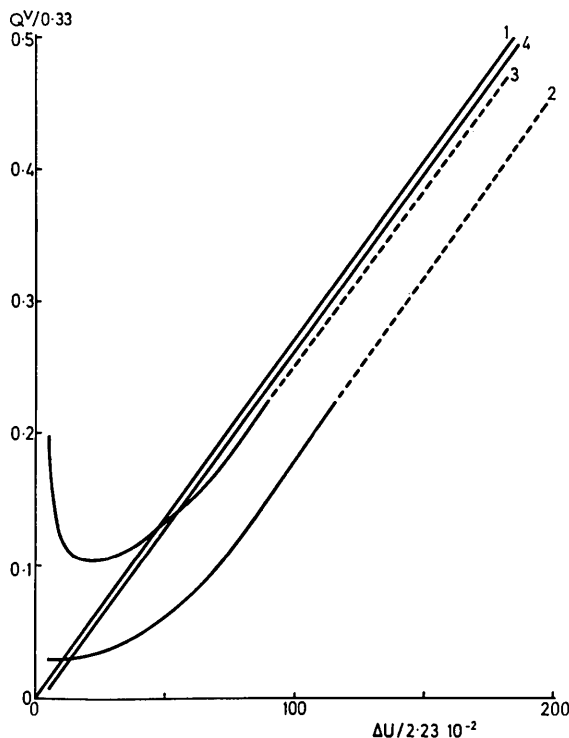$$- [(1+u)^2 + 1 - 2(1+u) \cos \varphi_0]^{-1/2}\} \tilde{I}_p(u) . \qquad (18b)$$

In order to obtain the integrated contributions of the TDS terms to the integrated Bragg intensity, only the functions $Q^{V,S}$ need to be calculated. Later, the proper parameters for A_v and A_s for the individual sample and reflexion must be introduced. For the calculation of the functions $Q^{V,S}$, different sets of parameters have been used; the parameters being $n, \mu^*, k_0^*, k_m^*, \Delta u = u_2 - u_1$. $(\mu^* = \mu b_0^2, k_0^* = k_0 / b_0, k_m^* = k_m / b_0)$.

The functions Q^v and log Q^s are plotted in Figs. 1–5 as functions of Δu for various sets of parameters, where for simplicity $|u_1| = |u_2|$. In Figs. 1–4, curves for different parameters n are plotted, i.e. $n = 6, 7, 8, \infty$. In each figure different parameter sets (k_0^*, k_m^*, μ^*), but with equal values of n, belong to the different curves.
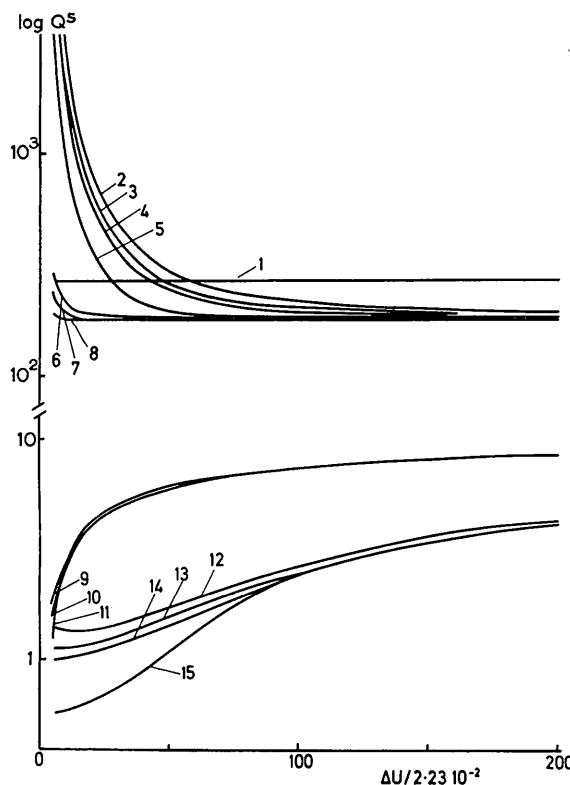

Fig. 5. Surface TDS. logQ^s as a function of Δu. $k_m^* = 0.14 \cdots 0.55$

Curve	n	k_0^*	μ^*	
1	$6 \cdots \infty$	0	∞	
2	6	0	4.55×10^3	
3	7	0	3.95×10^3	
4	8	0	3.50×10^3	
5	∞	0	1.48×10^4	$\bar{y} \ll D = \infty$
6	6	0	4.55×10^5	
7	8	0	3.50×10^5	
8	∞	0	1.48×10^6	
9	6	5.77×10^{-4}	4.55×10^5	
10	8	5.77×10^{-4}	3.50×10^5	
11	∞	5.77×10^{-4}	1.48×10^6	
12	6	5.77×10^{-3}	4.55×10^3	$D/2 = \bar{y}$
13	7	5.77×10^{-3}	3.95×10^3	
14	8	5.77×10^{-3}	3.50×10^3	
15	∞	5.77×10^{-3}	1.48×10^4	

Fig. 4. Volume TDS. Q^v as a function of Δu. $n = \infty$.

Curve	k_m^*	k_0^*	μ^*
1	$0.14 \cdots 0.55$	0	$1.48 \times 10^6 \cdots \infty$
2	$0.14 \cdots 0.55$	5.77×10^{-3}	1.48×10^4
3	$0.14 \cdots 0.55$	0	1.48×10^4
4	$0.14 \cdots 0.55$	5.77×10^{-4}	1.48×10^6

It can be seen that in the calculated range, the function Q^s is independent of the radius of the reduced Brillouin zone of k_m^*. The surface term depends only on the polydispersity parameter n, the mosaic size parameter μ^*, the sample size parameter k_0^*, and the spread Δu. The volume term is independent of k_m^* only for $n=\infty$. For high spreads Δu, $Q^v(\Delta u)$ becomes linear in Δu for all parameters. The volume component Q^v for the particular case of infinity grain and mosaic sizes is a linear function of Δu, as can be seen in Figs. 1–4. Deviations from the straight line can be found for finite grain and mosaic sizes for small spreads Δu. The reason for this behaviour is that the Bragg peak has a spread bigger than the range of Δu employed here. Therefore, for very small grain and mosaic sizes, Q^v decreases with increasing Δu until it goes through a minimum, and then it increases again becoming linear for large Δu. The minimum occurs where the Bragg contribution, calculated over the spread Δu, is nearly 100% of the total Bragg contribution over the full spread $\Delta u=\infty$. Any further increase of Δu does not affect the Bragg contribution. Increasing the grain and mosaic sizes shifts the position of the minimum to smaller Δu values, until the minimum disappears. This typical behaviour can be seen for all calculated parameters n.

The surface components Q^s are again most sensitive to the size of Δu for small Δu. Since the function $\tilde{I}^s_{TDS}(u)$ [equation (18b)] decreases more rapidly with increasing Δu than $\tilde{I}^v_{TDS}(u)$ [equation (18a)], it can be expected that in extreme cases (Δu and μ^* very small and k_0^* very big) the surface component may become dominant. For high Δu spreads, the function Q^s becomes constant. The functions $\tilde{I}^s_{TDS}$ and $\tilde{I}_v$ tend to zero when this happens.

In this treatment the overlap contribution due to neighbouring reflexions has not been considered. This can be easily obtained by additional calculations of the $Q^{v,s}$ corresponding to the proper range of the additional reflexions which contribute to the intensity. In this case, the multiplicity of the individual reflexions and their relative weights should be considered.

Table 1 provides a practical example for the calculation of the TDS contributions. The 521 reflexion of tungsten powder has been investigated with the following sets of room-temperature parameters: $2(\theta_2-\theta_1)=1°$ and $4°$, $n=\infty$ and 6, mean mosaic radii $\bar{y}=25$, 250 and ∞ Å and powder grain sizes $D/2=25$, 250 and ∞ Å. It can be seen that for small values of $D/2=25$ Å and $\bar{y}=25$ Å the surface contribution becomes comparable with the volume contribution, and for the spread $2(\theta_2-\theta_1)=1°$ with $n=\infty$, then E^s is bigger than E^v ($E^s=0.8\%$, $E^v=0.5\%$). With increasing D, the surface contribution decreases. This is reasonable since the factor A_s depends on the surface/volume ratio.

Table 1. TDS contributions for tungsten 521 powder reflexion at $T=293°K$

$D/2$ [Å]	$\bar{y}$ [Å]	$2(\theta_2-\theta_1)$ [degrees]	$E^v[\%]$		$E^s[\%]$	
			$n=\infty$	$n=6$	$n=\infty$	$n=6$
25	25	1	0·5	1·6	0·8	1·4
25	25	4	2·5	3·5	2·1	2·6
$>10^6$	25	1	1·4	2·7	0	0
$>10^6$	25	4	3·5	4·5	0	0
250	250	1	0·8	0·8	0·4	0·4
250	250	4	3·5	3·5	0·7	0·7
$>10^6$	250	1	0·9	0·9	0	0
$>10^6$	250	4	3·7	3·7	0	0
$>10^6$	>250	1	0·9	0·9	0	0
$>10^6$	>250	4	3·7	3·7	0	0

Conclusion

The contributions of surface effect and mosaic-block size terms to the thermal diffuse scattering have been considered. For small powder grains (of the order of $D/2 \simeq 25$ Å) these influences cannot be neglected; here, an additional surface term, which can be introduced through the addition of surface vibrational modes to the Debye spectrum, becomes comparable with the usual volume term. Calculated correction terms for the surface influences have been plotted. Independently of the sample and the reflexion order, they can be used as corrections in many situations. The volume term shows a complicated dependence upon the grain size, the mosaic size and polydispersity. Although the plotted curves may be used for a correction of the volume TDS, large errors may occur in this procedure, and an individual calculation of the function Q^v, [equation (17)], would be preferable.

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