

the axis of the objective, at a distance of about 10 cm from the object. The exposure was about 8 seconds. The image reconstruction was obtained through an eyepiece $10\times$, 0.4 N.A. The ratio between the intensities of the two beams does not seem to be critical but there are some differences in the details using the reference beam stronger or weaker than the reflected beam. The reference beam was constant in intensity and the relative intensities were varied by rotating a polaroid on the beam entering the Opakilluminator.

An enlargement of the hologram is shown in Fig. 2. A photograph of the image reconstructed from Fig. 2 through the eyepiece is shown in Fig. 3. The actual enlargement of the apparatus with the lenses used is $100\times$. On the photograph the total enlargement is about $150\times$. The subject is a point-bottomed trigon. Also in Fig. 2 it is possible to recognize broadly the shape of the trigon since the reference beam was weaker than the light reflected from the diamond. Fig. 4 is the same trigon reconstructed from another hologram, whose reference beam was stronger and with an inclination slightly different to the axis of the objective.

We have applied this method also to the inspection of metallic surfaces. Fig. 5 is the microscopic reconstructed image by holography of a part of the number 7 of the date 1967 in relief on an Italian 50 lire coin; the actual enlargement on the photograph is in this case $120\times$.

By this method some microscopical details may be enhanced in respect to the classical optical methods. If the slope of the surface labelled with two asterisks in Fig. 3 is examined by phase contrast microscopy and interferometry, its stepped nature can be detected, but hardly any information is obtained regarding the fine irregularities of the edges of the steps and they seem to be almost rectilinear. By the method of reconstructing the image one can detect in addition that in the area with the asterisks the edges are a little waved. The wall of the trigon is also waved, as one can see in the region marked with an arrow in the reconstructed image of Fig. 4, and the edges of the trigon are represented by broken lines since they are stepped. The results are satisfying even at this early stage of the work and we think it is possible to improve the method.

We both wish to thank Professor Malvano and Professor Sanero for their interest in this work.

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The Debye-Waller Factor for Small Cubes and Thin Films

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The dependence of the Debye-Waller factor on the size of cubes and plates is calculated by assuming the Debye theory, but using the frequency distribution which incorporates a term that is proportional to the surface area. The ratio of B for small particles to B for large particles is less than 0.01 for cubes with 10^9 atoms or more and for plates which are more than 330 atoms thick. The inclusion or exclusion of the zero point energy terms has a large influence on the size correction which has to be applied to small particles and thin films.

Introduction

Comparison of the Debye-Waller factors for small and large crystallites can give some information about the specific surface vibrations in small particles. However, before this can be obtained it is necessary to apply a size correction to the frequency distribution for volume vibrations. This correction is calculated here for small crystallites and thin films belonging to the cubic system, using the Debye theory. Although the Debye theory of lattice vibrations is a simplification which is justifi-

able at low temperatures, experimental results are often expressed in terms of this theory because it leads to one single parameter, the Debye temperature, which is 'characteristic' of every material.

Bolt (1939), Maa (1939) and Roe (1941) were first to show that the correct counting of the vibrational frequencies introduces surface and edge terms in the frequency distribution for a Debye solid. Later Montroll (1950) estimated that the size effect in specific heat measurements would become noticeable for non-metallic powders and thin films at 1°K. Recently Marshall

& Wilenzick (1966) have drawn attention to a size correction which has to be applied in Mössbauer experiments with small particles. Thiel (1967) has published a critical discussion of the size effect.

It will be shown here that the inclusion or exclusion of the zero point energy (z.p.e.) vibrations in the evaluation of a particular diffraction experiment has a large influence on the size correction which has to be applied. It should be emphasized that specific surface or interface vibrations are not included in the correction term calculated below.

For a cubic crystal with N atoms of mass m in the crystal of volume V , surface area S and edge length L , the Debye-Waller factor $\exp(-2B\lambda^{-2}\sin^2\theta)$, can be expressed in terms of the frequency distribution $g(\nu)$ as follows:

$$B = \frac{2h}{3Nm} \int_{\text{all } \nu_s} g(\nu) \frac{1}{\nu} \left[\frac{1}{\exp(h\nu/kT) - 1} + \frac{1}{2} \right] d\nu \quad (1)$$

where

$$g(\nu)d\nu = \left(\frac{4\pi V\nu^2}{c_3} + \frac{\pi S\nu}{2c_2} + \frac{L}{8c_1} \right) d\nu.$$

In $g(\nu)$ the term which is proportional to L is relatively small and will not be taken into account. The c 's are related to an average wave velocity c_m which is defined in terms of the longitudinal, c_l , and transverse, c_t , wave velocities by

$$c_m = [\frac{1}{3}(c_l^{-3} + 2c_t^{-3})]^{-1/3}.$$

The relations are

$$c_3^{-1} \equiv c_l^{-3} + 2c_t^{-3} = 3c_m^{-3}$$

$$c_2^{-1} \equiv c_l^{-2} + 2c_t^{-2} = 3\gamma c_m^{-2}$$

with

$$\gamma = \frac{1}{3}(1 + 2c_l^2/c_t^2) [3/(1 + 2c_l^3/c_t^3)]^{2/3}.$$

The factor γ is nearly unity, being 0.973 for $c_l/c_t = 1.5$ and 0.923 for $c_l/c_t = 2.5$.

It is customary and justified for large crystallites to take the limits of integration in (1) as zero and ν_D , with the largest frequency ν_D given by $3N = \int_0^{\nu_D} g(\nu) d\nu$.

In the present case the lower limit of zero in (1) leads to a divergent integral for the surface term. This difficulty can be overcome when it is realized that the integral is an approximation to a sum over all frequencies and that, except for the three degenerate modes at $\nu=0$, there is a finite smallest frequency, ν_s , which depends on the dimensions of the crystal. The implications of the use of this integral with a non-zero lower limit have been discussed by Thiel (1967).

Cubical crystallites

The Debye frequency distribution can be derived for a cube assuming clamped surfaces or mixed boundary conditions (Sommerfeld, 1945). It does not apply to a finite body with force-free surfaces. Debye used the

solution for a 'sufficiently' large force-free sphere, but had to obtain his frequency distribution from a high frequency approximation. For a cube with clamped surface the lowest frequency is $\nu_s = \frac{1}{2}c_m V^{-1/3}$ where the lowest wave velocity has been approximated by the average velocity c_m . The lowest velocity would be c_t which is smaller than c_m by factors 0.915 or 0.883 for $c_l/c_t = 1.5$ or 2.5 respectively. On the other hand ν_s would be somewhat larger for a cube with free surfaces, e.g. for a sphere it is larger by factors 2.95, 2.28 or 1.35 depending on the mode of vibration (Love, 1944). In the following calculations $\nu_s = \frac{1}{2}c_m V^{-1/3}$.

The largest frequency, ν_L , can be obtained from a third-order equation which follows from $\int_{\nu_s}^{\nu_L} g(\nu) d\nu = 3N$.

Neglecting the terms of the order of $N^{-2/3}$, i.e. setting $\nu_s = 0$ for the purpose of evaluating ν_L , ν_L becomes (Montroll, 1950):

$$\begin{aligned} \nu_L &= \left(\frac{9Nc_3}{4\pi V} \right)^{1/3} \left[1 - \frac{S\pi}{36c_2N} \left(\frac{9Nc_3}{4\pi V} \right)^{2/3} \right] \\ \nu_L &= c_m \left(\frac{3}{4\pi v_a} \right)^{1/3} \left[1 - \frac{\gamma\pi}{2n} \left(\frac{3}{4\pi} \right)^{2/3} \right], \quad (2) \end{aligned}$$

where the atomic volume v_a , the average velocity c_m and $n = N^{1/3}$ have been introduced.

Equation (1) now becomes [using the temperatures $\theta_s = h\nu_s/k$, $\theta_L = h\nu_L/k$ and θ_L^∞ , the latter being the Debye temperature for large crystals ($n \rightarrow \infty$, $\theta_s \rightarrow 0$)]

$$\begin{aligned} B &= A \left\{ \frac{T^2}{\theta_L^2} \int_{\theta_s/T}^{\theta_L/T} x \left[\frac{1}{\exp(x) - 1} + \frac{1}{2} \right] dx + \frac{\gamma b T}{n\theta_L} \right. \\ &\quad \left. \times \left(1 - \frac{\gamma b}{2n} \right)^{-1} \int_{\theta_s/T}^{\theta_L/T} \left[\frac{1}{\exp(x) - 1} + \frac{1}{2} \right] dx \right\} \quad (3) \end{aligned}$$

where

$$A = \left(1 - \frac{\gamma b}{2n} \right)^3 \frac{6h^2}{km\theta_L}$$

$$b = \pi \left(\frac{3}{4\pi} \right)^{2/3}$$

$$\theta_L = \theta_L^\infty \left(1 - \frac{\gamma b}{2n} \right)$$

$$\theta_s = \theta_L^\infty \left(\frac{4\pi}{3} \right)^{1/3} \frac{1}{2n}$$

$$\theta_L^\infty = \frac{c_m h}{k} \left(\frac{3}{4\pi v_a} \right)^{1/3}.$$

Except for A , which is temperature independent, (3) depends on θ_L/T , the crystal size n and γ , which can vary between 0.973 and 0.923.

It is instructive to divide B into its components and to consider the ratio of the surface to volume components. Writing

$$B/A = B_{0vol} + B_{tvol} + B_{0surt} + B_{tsurt}$$

in obvious notation (the letters *o* and *t* referring to the zero-point-energy and thermal contributions respectively), this ratio becomes

$$R = (Bo_{\text{surf}} + Bt_{\text{surf}}) / (Bo_{\text{vol}} + Bt_{\text{vol}})$$

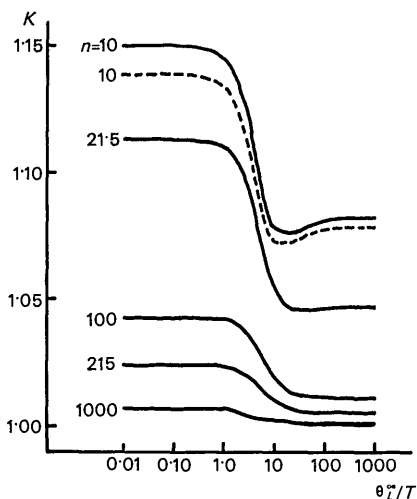


Fig. 1. *K*, which is the ratio of *B* for small cubes with n^3 atoms to *B* for large cubes, is plotted against θ_L^∞/T where θ_L^∞ is the Debye temperature for large cubes. The zero point energy terms are included. $\gamma = 0.973$ except for the broken line, which is for $\gamma = 0.923$.

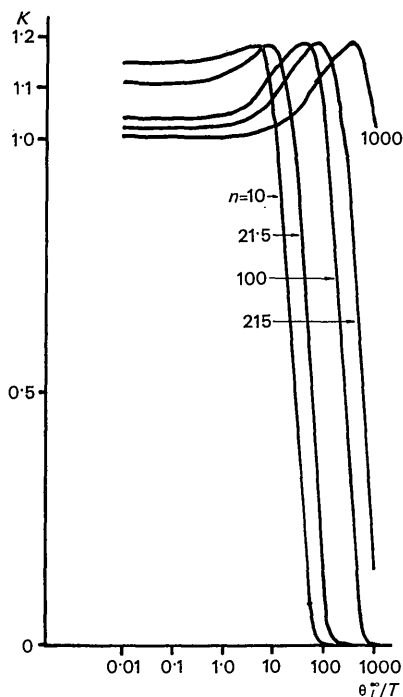


Fig. 2. Same as Fig. 1 except that the zero point energy terms are excluded.

The components and good approximations, taking $\gamma = 1$, $b = 1.2$, $\theta_L/\theta_s = n$ and $\gamma b/2n < 1$, are as follows:

$$Bo_{\text{vol}} = \frac{1}{4}(1 - \theta_s^2/\theta_L^2) \approx \frac{1}{4}$$

$$Bt_{\text{vol}} = \frac{T^2}{\theta_L^2} \int_{\theta_s/T}^{\theta_L/T} \frac{x}{\exp(x) - 1} dx$$

$$Bo_{\text{surf}} = \frac{1}{2} \gamma b n^{-1} \left(1 - \frac{\gamma b}{2n}\right)^{-1} \left(1 - \frac{\theta_s}{\theta_L}\right) \approx 0.6/n$$

$$Bt_{\text{surf}} = \gamma b n^{-1} \left(1 - \frac{\gamma b}{2n}\right)^{-1} \frac{T}{\theta_L} \ln \frac{1 - \exp(-\theta_L/T)}{1 - \exp(-\theta_s/T)}$$

At low temperatures $R = Bo_{\text{surf}}/Bo_{\text{vol}} \approx 2.4/n$ because the thermal terms tend to zero. At high temperatures $R = Bt_{\text{surf}}/Bt_{\text{vol}} \approx 1.2n^{-1} \ln n$ because now the z.p.e. terms which are temperature independent are relatively small. It is noteworthy that the relative surface contribution is larger at high than at low temperatures. This feature is due to the z.p.e. terms.

If only the thermal contributions are considered the situation is different. The low temperature ratio, $Bt_{\text{surf}}/Bt_{\text{vol}}$, is $1.2\{1 - n \exp[-(\theta_L - \theta_s)/T]\}^{-1} \approx 1.2$ and the high temperature ratio is about $1.2n^{-1} \ln n$, as above. Now the low temperature ratio is considerably larger than the high temperature ratio.

Diffraction data taken at two temperatures are usually evaluated by plotting the logarithm of the ratio of the intensities at these temperatures against $\lambda^{-2} \sin^2\theta$. The slope of this plot is a measure of the difference in the thermal components of *B* at the two temperatures. On the other hand, comparison of the theoretical and experimental atomic scattering factors allows the calculation of the total *B*. Therefore two ratios of *B* for small particles to *B* for large particles were computed by either including or excluding the z.p.e. terms. With the z.p.e. terms the ratio is

$$K = \frac{BS(\text{small particles})}{BL(\text{large particles})} = \left(1 - \frac{\gamma b}{2n}\right)^2 \times \frac{BSo_{\text{vol}} + BSt_{\text{vol}} + BSo_{\text{surf}} + BSt_{\text{surf}} + B'}{BLo_{\text{vol}} + BLt_{\text{vol}}}, \quad (4)$$

where

$$BLt_{\text{vol}} = \frac{T^2}{\theta_L^{\infty 2}} \int_0^{\theta_L/T} \frac{x}{\exp(x) - 1} dx$$

$$BLo_{\text{vol}} = \frac{1}{4}$$

and *B'* is zero for cubes but it is required for thin films. Without z.p.e. terms *K* is the same as (4) except that $BSo_{\text{vol}} = BSo_{\text{surf}} = BLo_{\text{vol}} = 0$. The results for *K* are given in Fig. 1 and Fig. 2.

Thin monocrystalline films

The neglect of the dispersion and anisotropy of the wave velocities and of the condition for force-free boundaries makes the application of the Debye theory quite risky. Nevertheless, in terms of a Debye solid,

the frequencies of the lattice waves travelling normal to the thin plate have a sizable lower bound, whilst those belonging to waves travelling along the plate approach zero more closely. An estimate of the lowest frequency of the waves travelling normal to a plate of thickness L_z is $\nu_s = \frac{1}{2}c_m/L_z$.

The characteristic properties of waves in plates are most noticeable for wavelengths that are long compared with the thickness of the plate. For an infinitely extended free plate the wave velocities for the fundamental branch can be described in terms of c_l and c_t which are the velocities in an infinite medium. Longitudinal waves of long wavelengths travel parallel to the plate with phase velocity $0.945 c_l$ (for Poisson's ratio $= \frac{1}{4}$; Tolstoy & Usdin, 1953) and perpendicular to the plate with c_l . Transverse waves with displacements normal to the plate (waves of flexure) propagate along the plate with a velocity which approaches zero for long wavelengths. Transverse waves with displacements in the plate travel with c_t . The wave velocities in an infinite elastic plate which is welded to a semi-infinite elastic continuum are different from those in free plates (Tolstoy & Usdin, 1953). The longitudinal wave of long wavelength now becomes a wave which travels along the plate with the velocity of Rayleigh waves in the substrate. Transverse waves of long wavelengths with displacements normal to the plate propagate along the plate with the shear velocity of the substrate. It is obvious that a 'soft' film on a 'hard' substrate would have to be treated differently from the reverse case.

Using the Debye theory for a quadratic thin plate with surface area $S = 2L^2 + 4qL^2 \approx 2L^2$ ($q \ll 1$) and having $N_x N_y N_z$ ($N_x = N_y = N_z/q$) atoms in the volume $V = qL^3$, the expression for ν_L [equation (2)] and B [equation (3)] have to be modified as follows. Everywhere n has to be replaced by $3N_z$ except in the equation for θ_s . The modification for θ_s depends on the choice for ν_s . Using one single lower cut-off ν_s for all modes irrespective of their directions of propagation is obviously wrong, because for waves travelling normal to the plate the lowest frequency is $\nu_s = \frac{1}{2}c_m/qL$, and for waves travelling in the plate it is $\nu_s = \frac{1}{2}c_m/L$. By using the larger ν_s a fraction of about N_z^{-3} of low frequency modes is not included in the integrals in (3).

The question of what to take for the lower limit ν_s was approached in two ways. Firstly, $\nu_s = \frac{1}{2}c_m/qL$ was taken in all expressions and the remaining modes between 0 and ν_s were summed individually by assuming $q = 10^{-3}$. In this case n in the expression for θ_s has to be replaced by N_z , and the additional term

$$B' = \frac{k\theta_L}{9hN} \left(1 - \frac{\gamma b}{6N_z}\right)^{-3} \times \sum_{\text{remaining modes}} \frac{1}{\nu_i} \left[\frac{1}{\exp(h\nu_i/kT) - 1} + \frac{1}{2} \right]$$

has to be included in (4). Secondly, the same ν_s was used for the surface terms BSO_{surf} and BSI_{surf} , but not for the volume terms BSO_{vol} and BSI_{vol} which were

integrated from zero. For the surface terms the remaining modes between 0 and ν_s were again summed individually assuming $q = 10^{-3}$, the sum being $\frac{1}{2}B'$. For both cases the ratio, K , of B for thin films to B for infinitely thick films was calculated by either including or excluding the z.p.e. terms.

In Fig. 3, which shows K for plates with z.p.e. terms, the full lines refer to the first choice for ν_s and the broken lines to the second, as discussed above. The curves for K without z.p.e. terms are similar to those for cubes (Fig. 2) but are not reproduced here because the mixing of integration and summation in (4) leads to numerical uncertainties. These errors are particularly large for K without z.p.e. at low temperatures because K is the ratio of two quantities which individually approach zero as the temperature decreases.

Discussion

When the z.p.e. terms are included in the size correction the curves in Fig. 1 show that the correction is less than 1% for cubical particles of $N = 10^9$ atoms or more. For smaller particles the correction can become quite large and never vanishes at any temperature. At low temperatures the correction is determined by the ratio of the z.p.e. terms which is smaller than the ratio of the thermal terms at high temperatures. The size correction is, therefore, decreasing with decreasing temperature.

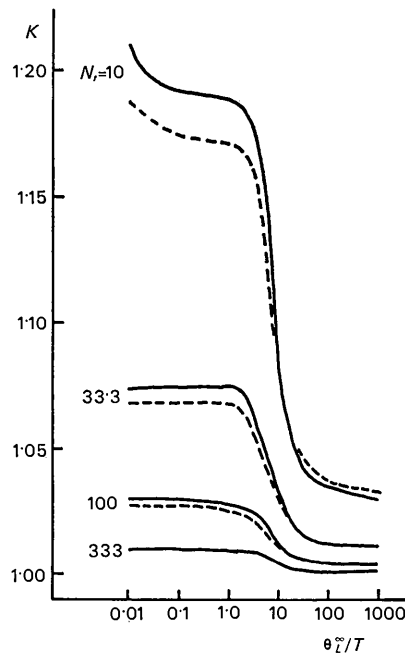


Fig. 3. K for quadratic plates with a thickness of N_z atoms. The zero point energy terms are included. Broken and full lines refer to different summing of the low frequency modes as described in the text.

The size correction without the z.p.e. terms is shown in Fig. 2. The curves in Fig. 1 and Fig. 2 coincide at high temperatures because the z.p.e. terms are relatively unimportant. As the temperature decreases the correction without z.p.e. terms (Fig. 2) increases, because the thermal contribution of the surface terms increases relative to the volume terms. This follows from the frequency distribution $g(\nu)$ in which the volume term is proportional to ν^2 and the surface term proportional to ν . On further lowering of the temperature the correction falls to zero since at these very low temperatures long wavelength modes which are possible in the large particles cannot exist in the small particle.

The influence of γ on the resulting curves is small. This is seen from Fig. 1, where the broken line is for $\gamma=0.923$ whilst the other lines are for $\gamma=0.973$. In the other Figures $\gamma=0.973$.

For thin films the thickness correction is qualitatively similar to that for cubical particles as may be seen from Fig. 3. These curves include the B' terms which are the contributions of the low frequency modes omitted in the integrals. Because B' has been calculated with a thickness to length ratio of 10^{-3} , the curves are not as general as those for cubes. In particular this is the case for $N_z=10$ and 33.3. For the thicker films the influence of B' is small.

As expected, the correction for films is smaller than that for cubes with an edge length equal to the film thickness. At high temperatures it is somewhat larger than $\frac{1}{3}$ of that for cubes. The correction without z.p.e. terms for films is uncertain for low temperatures. At high temperatures it is the same as that which includes the z.p.e. terms. As the temperature decreases it first increases and then decreases in a manner which is qualitatively similar to that for cubes.

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The Resolution Function in Neutron Diffractometry. III. Experimental Determination and Properties of the 'Elastic Two-Crystal' Resolution Function*

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The experimental determination of the resolution function of a two-crystal neutron diffractometer is discussed. The form of the Bragg reflexion profiles observed for a perfect crystal using conventional scanning modes is considered in detail and their application to the measurement of diffuse elastic scattering is discussed.

1. Introduction

In earlier papers we have discussed the derivations of the resolution function for a three-crystal neutron diffractometer (paper I; Cooper & Nathans, 1967) and for a two-crystal neutron diffractometer for elastic scattering (paper II; Cooper & Nathans, 1968) in terms of a matrix notation involving the parameters of the system.

Although the matrix formulation is convenient for calculating the resolution function for a particular set of Gaussian instrumental parameters, it does not give us any direct or simple indication of the form of the dependence of the resolution function on the various parameters, and the extraction of this information from the matrix elements becomes complex. In addition it does not give us a clear indication of how well we can

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