

## Neutron Diffraction Study of the Debye–Waller Factor for Aluminum

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Measurements of the relative intensities of Bragg reflexions from aluminum single crystals, at a series of temperatures in the range 300 to 860°K, have confirmed earlier determinations by X-ray diffraction methods of the temperature dependence of the Debye–Waller factor [ $\exp(-B \sin^2 \theta/\lambda^2)$ ]. The change with temperature is much greater than that expected from thermal expansion arguments; it is discussed in terms of the harmonic and anharmonic approximations to the thermal vibration state of a real crystal. The measured phonon dispersion relations for aluminum have been used to calculate  $B$  for comparison with the observed values. Certain features of the calculation which are relevant to the calculation of  $B$  for other materials are outlined.

### 1. Introduction

The theory of lattice dynamics based on the harmonic approximation (Born & Huang, 1954) cannot account for many thermal properties of real crystals (Cowley, 1963). Such features as thermal expansion, for example, require that derivatives of the interaction potential higher than the second be taken into account, and several authors have suggested that an examination of vibration phenomena at elevated temperatures may provide useful information regarding these anharmonic contributions. Two well-known and important thermal parameters which could be used in this way are the specific heat and the Debye–Waller factor. For the specific heat, the relevant theory has been given by Leibfried & Ludwig (1961) while for diffraction phenomena it has been given by Kashiwase (1965) and by Maradudin & Flinn (1963). Maradudin & Flinn give the Debye–Waller factor,  $\exp(-B \sin^2 \theta/\lambda^2)$ , and the equivalent, temperature dependent, Debye temperature  $\Theta_M(T)$ , directly in terms of derivatives of the interaction potentials.

The harmonic theory predicts a value of  $\Theta_M$  which is constant with increasing temperature, and several authors (Zener & Bilinsky, 1936; Paskin, 1957) have attempted to explain the observed temperature dependence of  $\Theta_M$  by including thermal expansion effects. In a number of cases, however, this correction has been insufficient to account fully for the observed behaviour and a further correction, proposed by Marshall & Stuart (1961), utilizes the fact that the temperature variation of the elastic constants and of the  $\Theta_M$  of a crystal have their origin in the same anharmonic effects. This correction was found to give good agreement with the measured  $\Theta_M$  values for lead but not with those of aluminum (Chipman, 1960).

In view of this discrepancy, it was decided to re-examine the temperature dependence of the Debye–

Waller factor of aluminum and to test the expansion correction and the Marshall & Stuart modification of it. At the same time, methods of measuring and calculating  $B$  factors and of correcting for temperature diffuse scattering have been investigated.

For aluminum, X-ray diffraction methods have been used previously to measure the Debye–Waller factor or  $\Theta_M$  and to investigate the variation of  $\Theta_M$  with temperature (James, Brindley & Wood, 1929; Owen & Williams, 1947; Chipman, 1960; Flinn & McManus, 1963; Nicklow & Young, 1966). The most accurate investigation at elevated temperatures has been that of Chipman (1960). Usually, one of two possible methods has been employed in these investigations. In one the integrated intensity of a particular reflexion is measured at a series of temperatures and  $\Theta_M$  is calculated from the ratio of the intensities at two different temperatures. This scheme has the advantage of being relatively insensitive to those sources of error which vary from reflexion to reflexion such as extinction and misalignment, but the method presupposes a knowledge of the  $\Theta_m$  versus  $T$  relationship which is being measured.

In the other method a complete set of intensities at a particular temperature can give  $B$  from the slope of a 'Wilson plot', that is by plotting  $\ln(I_0 \sin 2\theta)$  versus  $\sin^2 \theta/\lambda^2$ . However, this method is sensitive to errors such as extinction, misalignment, and (in the case of powder measurements) preferred orientation, and for X-ray diffraction measurements the method requires a knowledge of the theoretical atomic scattering factor curve. With neutrons, however, the scattering length is independent of scattering angle and in the absence of extinction and other errors an accurate measurement of  $B$  should be possible from a direct analysis of neutron diffraction intensities.

This paper reports the results of such an investigation of the variation with temperature of the Debye–

Waller factor for aluminum by means of a neutron diffraction study using single-crystal specimens in the temperature range from 300 to 860°K. Aluminum is well suited to an investigation of this kind since it has a low capture cross-section for neutrons. This allows neutron diffraction experiments with relatively large samples and, hence, high diffracted intensities, without serious absorption corrections. In addition, the Debye temperature is reasonably low ( $\sim 400^\circ\text{K}$ ) and large reductions in diffraction intensities are obtained at moderately high temperatures.

In § 2, details of the experimental procedure are presented together with the results of the measurements, while the results of a calculation of  $B$  and  $\Theta_m$  from an analysis of published phonon dispersion curves for aluminum are given in § 3.

## 2. Experimental details and results

The neutron diffraction intensity measurements described here were made with a single-crystal neutron spectrometer at the A.A.E.C.'s Dido-type reactor HIFAR. The neutron wavelength was  $1.10 \text{ \AA}$  and the intensity of the monochromatic beam at the specimen was  $2 \times 10^5 \text{ n.cm}^{-2}\text{sec}^{-1}$ . Cylindrical specimens approximately 2 mm in diameter by 2 mm long were trepanned from a large single crystal by means of a spark cutter. The parent crystal was obtained from L. Light and Co., England, with a stated purity of 99.995%. The cylindrical specimens were mounted in a small vacuum furnace on a three-circle goniometer. Complete sets of three-dimensional intensity data were collected in the  $\theta, 2\theta$  scanning mode out to the 620 reflexion at a series of temperatures from 300 to 860°K. The spectrometer was controlled by a monitor counter in the incident monochromatic beam. After the accumulation of a pre-set number of monitor counts the total detector count was punched onto paper tape and the counter moved 2 minutes to the next position. For each reflexion, the number of counts was always adequate for a statistical accuracy of at least 1%, but for various experimental reasons the reproducibility of equivalent reflexions was at times only within 5%. Part of this error was thought to be due to a lack of rigidity in the specimen mounting.

Initially, considerable difficulty was encountered in fixing the specimens securely to the furnace (under conditions of widely varying temperature and repeated thermal cycling) without causing deformation of the crystal and subsequent recrystallization at high temperatures. The final arrangement is shown schematically in Fig. 1. The vacuum jacket was made from 0.005-in vanadium foil. The scattering from vanadium is wholly incoherent, which removes the necessity to correct for Bragg reflexion from the container. The cylindrical single-crystal specimen was pushed into the split, accurately machined, 0.005-in-wall, polycrystalline aluminum tube as shown, and the base of this holder was crimped and cemented to the pyrophyllite thermal

stand-off piece which contained the heater element. Since the specimen and holder have the same thermal expansion coefficient, no difficulty was encountered from either sample movement or deformation. Power to the heater was provided by a stabilized D.C. source and at equilibrium the specimen temperature was constant to within  $2^\circ\text{K}$ . Power dissipation was of the order of one to two watts per  $100^\circ\text{C}$ .

The chromel-alumel thermocouple was connected to a recorder to indicate the specimen temperature. However, the absolute temperature measurements were made by measuring the position of the 004 reflexion at each temperature by the Bond (1960) technique and using published values of the thermal expansion of aluminum (Hidnert & Krider, 1952) to establish the specimen temperature within about  $5^\circ\text{K}$ .

In the analysis of the measured intensities some of the low angle reflexions were obviously affected by extinction and an attempt was made to estimate the magnitude of the effect. Extinction was worse after the sample had been annealed during high temperature measurements, and the thermal history of the specimen was taken into account in estimating the extinction coefficients, at different temperatures, of the various reflexions.

In metal crystals which have not received special care during growth and handling, such as the aluminum crystals used in the present work, the dislocation density is usually so large that effects due to primary extinction can be safely ignored. Under these condi-

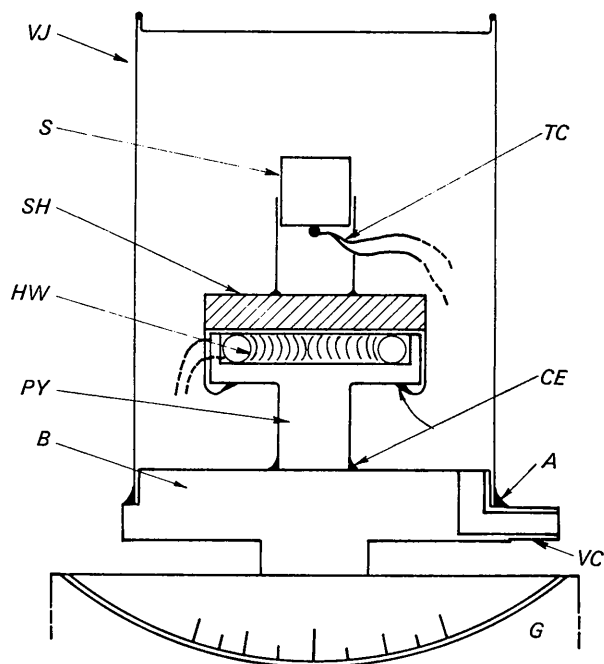


Fig. 1. Schematic section of single-crystal goniometer furnace: VJ vacuum jacket; S single-crystal specimen; SH polycrystalline aluminum specimen holder; HW heater winding; PY pyrophyllite thermal stand-off; B stainless steel base; TC thermocouple; CE high-temperature cement; A 'Araldite' vacuum seal; VC vacuum connection; G goniometer arc.

tions secondary extinction is, to a first approximation (James, 1954), equivalent to an increase in the absorption coefficient at the reflecting angle, the increase varying from reflexion to reflexion. The absorption and secondary extinction correction factor to the measured intensities,  $I_{obs}$ , for the present equatorial neutron reflexions is (Hamilton, 1957):

$$I_{obs}/I_{calc} = E_{s,a} = \exp[-(\mu + \sigma)D], \quad (1)$$

where:

$\mu$  = linear absorption coefficient (negligible for aluminum)

$\sigma = QW(\Delta\theta)$

$Q = \lambda^3 F^2 / V_c^2 \sin 2\theta$

$F = 4b \exp(-B \sin^2\theta/\lambda^2)$  for f.c.c. element

$b$  = scattering amplitude per nucleus

$V_c$  = unit-cell volume

$W(\Delta\theta) = 1/(2\eta/\pi)$

$\eta$  = mosaic spread parameter

and  $D$  = average path length of beam through crystal.

For each reflexion,  $D$  was calculated from the specimen shape and orientation following the procedure described by Busing & Levy (1957), but extended to three-dimensions, using an IBM 7040 computer\*.

The mosaic spread parameter after appropriate annealing treatments was measured by comparing the aluminum half-peak widths measured on a Bond X-ray spectrometer (Bond, 1960) with the width measured at a similar  $2\theta$  using a highly perfect silicon crystal. This procedure was carried out with two crystals cut from different parts of the parent crystal and  $\eta$  was found

to vary from 30' in the 'as-cut' condition to 5' after annealing for several days at 860°K.

For the computation of  $Q$ , initial values of  $B$  at the various temperatures were obtained from the high angle reflexions (004 to 620) by a least-squares method in which  $B$  and the scale factor  $K$  were variable parameters in the relationship:

$$I_0 \sin 2\theta = K \exp(-2B \sin^2\theta/\lambda^2),$$

(Pryor & Sabine, 1964).

The values obtained for  $E_{s,a}$  confirmed the assumption that the high angle data were not significantly affected by extinction, all having  $E_{s,a} > 0.95$ . In view of this fact, and considering the possible uncertainties arising from large corrections to the low angle data ( $E_{s,a}$  for the 111 reflexion being as low as 0.68) it was decided to use only the 004 to 620 reflexions in determining  $B$ . Willis (1962) has shown that for values of  $E_{s,a}$  less than about 0.75, the approximation of treating secondary extinction as an absorption correction is of questionable validity. The results of measurements at three of the temperatures are shown on a Wilson plot in Fig. 2 where the uncorrected intensities are denoted by open symbols.

In addition to the problem with extinction, it was also found in the analysis that a constant scale factor was not obtained. The variation was of the order of 5 to 10% but quite random. The reasons for this effect are not known.

The values obtained from the above procedure,  $B'$ , are plotted as a function of temperature in Fig. 3 (curve 2). The measured intensities used to calculate  $B$  in this manner include a contribution from the thermal diffuse scattering (TDS) which peaks under the

\* I am indebted to Dr G. W. Cox for allowing me to modify his absorption program to include extinction corrections.

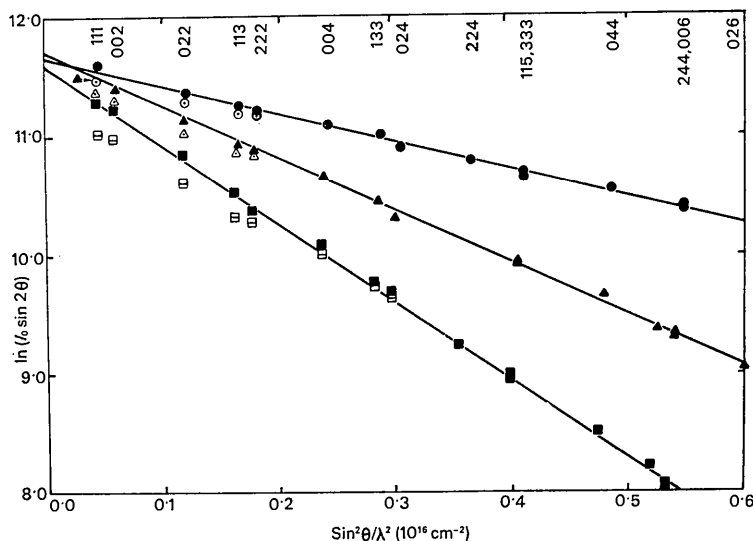


Fig. 2. Wilson plot of aluminum neutron diffraction data taken at three temperatures. The solid curves are the least-mean-squares fit to the data with  $\sin^2 \theta/\lambda^2 > 0.2 \text{ \AA}^{-2}$ . Open symbols: measured intensities. Closed symbols: corrected for secondary extinction.

	$T$ (°K)	$B$ ( $10^{-16} \text{ cm}^2$ )	$K$
—○—	378	$1.085 \pm 0.04$	$1.14 \times 10^5$
—△—	657	$2.18 \pm 0.06$	$1.19 \times 10^5$
—□—	863	$3.281 \pm 0.04$	$1.08 \times 10^5$

Bragg peaks (Nilsson, 1956; Chipman & Paskin, 1959), and a correction to the intensities for this effect is necessary. Since an exact calculation of the TDS contribution to each of the Bragg peaks is difficult, a correction due to Pryor has been used. Pryor (1966) showed that a correction factor  $\Delta B$  to the measured  $B$  for single crystals is given by

$$\Delta B = \frac{16\pi k T}{\rho \lambda C_t^2} \frac{2\delta\theta}{9} (2 + C_t^2/C_l^2), \quad (2)$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature,  $2\delta\theta$  is the counter aperture,  $\rho$  the density,  $\lambda$  the wavelength and  $C_t$  and  $C_l$  are average transverse and longitudinal velocities. These average velocities can be calculated from the elastic constants. In making this correction, the elastic constants reported by Sutton (1953) were used. Values of  $B$  corrected in this way for TDS are also shown in Fig. 3 (curve 1). The Debye diffraction temperature,  $\Theta_m$ , was obtained in an iterative procedure from the Debye-Waller formula (Waller, 1923):

$$B = \frac{6h^2 T}{mk\Theta_m^2} \left\{ \frac{1}{x} \int_0^x \mu(e^\mu - 1)^{-1} d\mu + \frac{x}{4} \right\}, \quad (3)$$

where  $x = \Theta_m/T$ . The values of  $\Theta_m$  corresponding to the corrected  $B$ 's are shown in Fig. 4. The solid curve is the result of a least-squares fit to these  $\Theta_m$ . The solid curves through the  $B$  and  $B'$  values in Fig. 3 were obtained from the  $\Theta_m - T$  curves by means of (3).

### 3. Calculation of $B$ , $\Theta_m$ and $C_v$

To calculate theoretical values of  $B$  and the related Debye temperature,  $\Theta_m$ , an analysis was carried out, in terms of a Born-von Karman general force constant model, of the phonon dispersion curves for aluminum measured at 80 and 300°K by Stedman & Nilsson

(1965). Recently, details of a very precise investigation of these dispersion curves by Gilat & Nicklow (1966) have been published, and only brief details of the present calculations will be given, in order to illustrate certain features found in a comparison of the two studies.

A least-squares analysis of the measured dispersion curves, using the method of Squires (1963, 1964) for 4th nearest neighbours, gave a satisfactory fit, the average deviation from the measured frequencies being less than 1.5%, except near the zone boundary for the  $[\xi\xi\xi]T$  branch where the deviation was as large as 8%.

Using the force constants obtained in this analysis, the standard root sampling technique (Flinn, McManus & Rayne, 1961) was employed to calculate the frequencies at a large number of points in the irreducible 1/48th of the first Brillouin zone. With suitable weight-

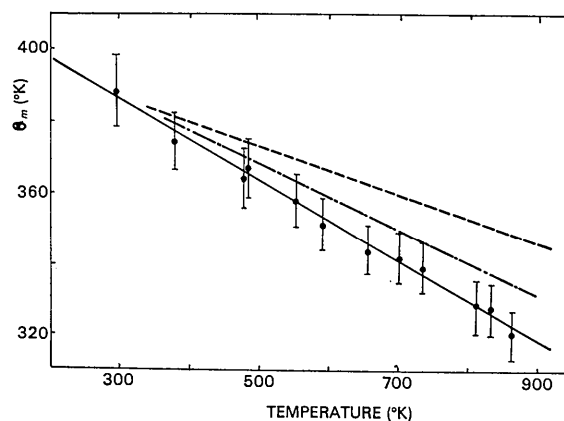


Fig. 4.  $\Theta_m$  of aluminum as a function of temperature. The solid curve is the least-mean-squares fit to the measured  $\Theta_m$ . The dashed curve is the variation predicted by volume change and the dot-dashed curve is due to Marshall & Stuart (see text).

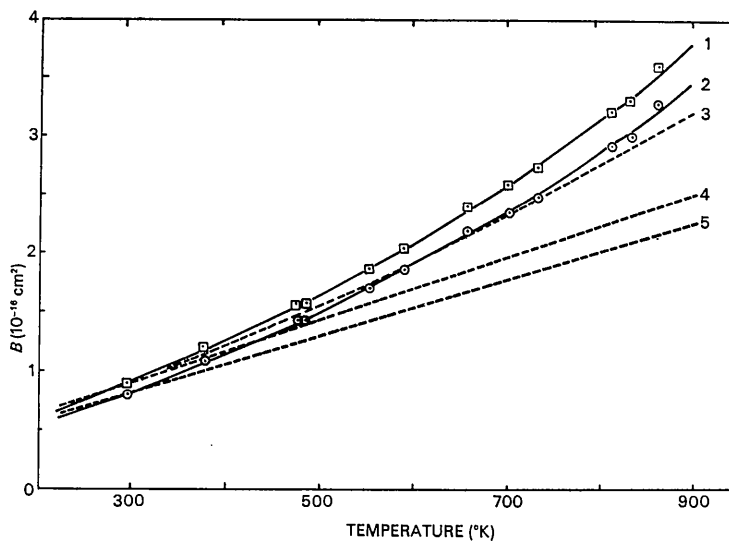


Fig. 3. Measured and calculated values of  $B(T)$  for aluminum. Curve 1, measured  $B$  corrected for TDS; Curve 2, as measured; Curve 3, Paskin (1957); Curves 4 and 5, from 300 and 80°K frequency distributions (Gilat & Nicklow, 1966).

ing according to the symmetry of each particular phonon wave vector, the phonon frequency distributions,  $g(\omega)$ , were assembled for both the 80°K and 300°K cases. These frequency distributions were used to calculate both  $B$  and the specific heat,  $C_v$ , as functions of temperature from the expressions:

$$B = \frac{8\pi^2\hbar}{3mN} \sum_{ij} \frac{1}{\omega_{ij}} \left\{ \frac{1}{2} + [\exp(\xi_{ij}) - 1]^{-1} \right\}, \quad (4)$$

and

$$C_v = k \sum \xi_{ij}^2 \exp(\xi_{ij}) [\exp(\xi_{ij}) - 1]^{-2}, \quad (5)$$

where  $\xi_{ij} = \frac{\hbar\omega_{ij}}{kT}$ ,  $i=1, 2$  or  $3$  and  $j=1, 2, \dots, N$ .

In their analysis, Gilat & Nicklow (1966) (referred to as GN) used an 8th neighbour axially symmetric force constant model and an extrapolation technique (Gilat & Raubenheimer, 1966) to obtain extremely detailed and accurate frequency spectra. These were similar to those obtained in the present calculation but gave much finer details of the spectrum shape. It is of interest to compare the results of their calculation, in which each distribution function contained a sample of  $3.58 \times 10^7$  frequencies, with the present calculation using the standard root sampling technique where computing time limited the possible sample size to a maximum of about  $5 \times 10^5$  frequencies.

At a temperature of 300°K, using their frequency distribution calculated from 300°K dispersion curves, GN calculated a value of  $0.89 \times 10^{-16}$  cm<sup>2</sup> for  $B$ , in excellent agreement with the measured value corrected for TDS. The present calculation, using a distribution of  $5.12 \times 10^5$  frequencies, gave a value 7% lower than this figure. In calculating  $B$  the final result was governed by the number of frequencies in the sample, because, with a coarse sampling mesh, relatively few of the phonon wave vectors near the origin of the Brillouin zone are considered. The low frequencies corresponding to these wave vectors are important in the calculation of  $B$  because the frequency appears as  $1/\omega_{ij}$  in the summation shown in (4). In calculating the specific heat and its associated Debye temperature,  $\Theta_D$ , a different weighting of the frequencies results from (5) and a dependence of  $\Theta_c$  on the frequency sample size is not observed.

These effects are illustrated in Table 1, where values of  $B$ ,  $\Theta_m$  and  $\Theta_c$  obtained with different frequency sample sizes are shown together with the results of GN. The steady trend of the  $B$  values indicates that a larger sampling than the present maximum of  $5.12 \times 10^5$  frequencies would reduce the 7% difference between the present calculation and that of GN. It would appear that in calculating  $B$  from the dispersion relations, adequate sampling may be as important as obtaining a very close fit to the experimental dispersion curves.

In calculating the specific heat, it is obvious that only a modest sampling is required for the convergence of  $\Theta_c$ . However, although convergence was readily achieved, the resulting  $\Theta_c$  was extremely sensitive to the force constant model chosen in the region below 80°K where better than qualitative agreement with measured values of the specific heat (Giauque & Meads, 1941) was not obtained with the present model.

In Fig. 3, values of  $B(T)$  obtained by GN from 300 and 80°K frequency distributions are shown (curve 4 and curve 5 respectively), together with the experimental values of  $B(T)$  corrected for TDS (curve 1).  $B(300)$  is predicted correctly by the 300°K  $g(\omega)$  while the 80°K  $g(\omega)$  gives a value which is in error by 9% at this temperature. At 80°K, however, the situation is reversed and  $B(80)$  is given by the 80°K frequency distribution (Gilat & Nicklow, 1966). Above room temperature the calculations do not predict the non-linear nature of the temperature dependence of  $B$  and the agreement with the measured value becomes progressively worse at higher temperatures. It would be expected that a set of dispersion curves taken at an elevated temperature would lead to better agreement with the present high temperature results than that obtained from 80 and 300°K frequency distributions.

#### 4. Discussion

Chipman (1960) has made accurate X-ray measurements of  $\Theta_m$  and the variation of  $\Theta_m$  with temperature. At 300°K he chose a  $\Theta_m$  of  $390 \pm 10$ °K as the most likely value. This is in excellent agreement with our result of  $386 \pm 10$ °K at the same temperature when the TDS correction is included. Chipman's value is repre-

Table 1. Variation of  $B$ ,  $\Theta_m$ ,  $C_v$  and  $\Theta_c$  with varying frequency distribution sample size

Number of frequencies	$B^{(c)}$	$T=80^\circ\text{K}^{(a)}$			$B$	$T=300^\circ\text{K}^{(b)}$		
		$\Theta_m$ (°K)	$C_v^{(d)}$	$\Theta_c$ (°K)		$\Theta_m$ (°K)	$C_v$	$\Theta_c$ (°K)
$3.21 \times 10^3$	0.3109	420.6	0.944	392.4	0.8083	407.5	2.29	394.8
$8.00 \times 10^3$	0.3097	421.8	0.933	395.1	0.8040	408.7	2.29	397.3
$6.40 \times 10^4$	0.3139	4.7.8	0.933	395.1	0.8219	404.0	2.29	397.3
$5.12 \times 10^5$	0.3160	415.8	0.933	395.1	0.8308	401.7	2.29	397.3
$3.58 \times 10^{7(e)}$	0.325	407	—	392	0.890	390	—	396

(a) From 80°K frequency distribution

(b) From 300°K frequency distribution

(c) In units of  $10^{-16}$  cm<sup>2</sup>

(d) In units of ergs (°K.g.atom)<sup>-1</sup>

(e) Gilat & Nicklow (1966)

sentative of other X-ray determinations of  $\Theta_m$  (James *et al.*, 1929; Owen & Williams, 1947; Flinn & McManus, 1963; Nicklow & Young, 1966), since they are all within 5% of his result. As would be expected, there is no significant difference between the X-ray value and the neutron diffraction value reported here.

The measured temperature variation of  $\Theta_m$  is again in excellent agreement with Chipman's value. For the neutron results  $(d/dT) \ln \Theta_m = -3.10 \times 10^{-4}$ , compared with  $-3.1 \times 10^{-4}$  for the X-ray measurements. This temperature variation (as measured now by both neutrons and X-rays) is far in excess of that predicted by a consideration of volume expansion alone in the manner of Paskin (1957) as both Chipman (1960) and Marshall & Stuart (1961) reported. Marshall & Stuart proposed a relation in terms of the variation with temperature of the elastic constants to account for the temperature variation of  $\Theta_m$ . This was:

$$\frac{d}{dT} (\ln \Theta_m) = \frac{1}{2} \frac{d}{dT} (\ln C_{44}) + \beta/6, \quad (6)$$

where  $\beta$  is the volume coefficient of expansion.

This relation predicted a value for  $(d/dT) \ln \Theta_m$  of  $-2.4 \times 10^{-4}$ . The volume correction alone yields a value for aluminum of  $-1.6 \times 10^{-4}$  so that compared with the measured value of  $3.1 \times 10^{-4}$  for  $(d/dT) \ln \Theta_m$  the Marshall & Stuart correction was a distinct improvement on that given by the volume correction. The  $\Theta_m$  versus  $T$  curves predicted in both of these cases are shown in Fig. 4. Since in the case of lead the relation (6) gave good agreement (Marshall & Stuart, 1961) with the value of  $(d/dT) \ln \Theta_m$  measured by Chipman (1960) it was surprising that better agreement was not obtained with the aluminum results.

The Marshall & Stuart relation can be forced into agreement with the measured slope by a suitable choice of  $(d/dT) \ln C_{44}$ . Marshall & Stuart used the room temperature elastic constant variation cited by Huntington (1958). Sutton (1953) has measured the elastic constants of aluminum up to about 800°K and the variation of  $\ln C_{44}$  with temperature is non-linear.

The room temperature slope measured by Sutton is in agreement with that cited by Huntington in giving a value for  $(d/dT) \ln \Theta_m$  of  $-2.4 \times 10^{-4}$  from (6). At about 630°K however, Sutton's measured slope gives a value for  $(d/dT) \ln \Theta_m$  of  $3.18 \times 10^{-4}$ , which is only a few per cent away from the slope found in this investigation. Purely empirically it may be observed that this temperature is about midway between the low temperature  $\Theta_m$  of aluminum of about 400°K and its melting temperature,  $T_m$ , of 930°K. In the previously mentioned case of Pb, the midpoint between its  $\Theta_m$  of 90°K and  $T_m$  of 600°K is only slightly above room temperature, and the 300°K slope of the Pb elastic constants when used in (6) by Marshall & Stuart gave a value for  $(d/dT) \ln \Theta_m$  within a few per cent of the value measured by Chipman. Thus it would appear that the Marshall & Stuart relationship for the tem-

perature variation of  $\Theta_m$  could be a useful approximation provided that a suitable average slope for the temperature variation of  $C_{44}$  can be chosen.

The failure of the volume correction alone (curve 3 in Fig. 3) to account for the observed temperature variation of  $B$  indicates that in aluminum, at elevated temperatures, intrinsic anharmonic effects are appreciable. In their paper on the anharmonic contribution to the Debye-Waller factor, Maradudin & Flinn (1963) derived a relationship for  $B$  of the form:

$$B(T) = K_1 T + K_2 T^2 + K_3 T^3 \cdot f(Q). \quad (7)$$

Applying their results to the model of a lead crystal with 1st neighbour interactions, they concluded that the  $T^3$  contribution to  $B(T)$  should be negligible.

An analysis of the measured  $B(T)$  relationship for aluminum in terms of (7) is not strictly valid since the measurements were derived from the relationship

$$I_0 \sin 2\theta = K \exp(-2B \sin^2\theta/\lambda^2),$$

using the assumption that  $B$  is independent of  $\theta$ . If this point is disregarded and the measured curve is fitted with a polynomial in powers of  $T$ , then a better fit to the measured curve is obtained by the inclusion of a  $T^3$  term rather than only  $T$  and  $T^2$  terms (average deviation from the measured curve of 0.2% compared to 1%). Using this best fit 3rd degree polynomial, the  $T^3$  contribution would amount to 28% of  $B(T_m)$  for aluminum.

For Pb,  $B(T)$  can be derived from the measurements of Chipman (1960) or from those of Alexopoulos, Boskovits, Mourikis & Roilos (1965). This curve, too, is best fitted by the inclusion of a  $T^3$  term. The contribution from this term at the melting temperature of lead would amount to 23% of  $B$ . These figures indicate, at least, that a  $K_3 T^3$  contribution to  $B(T)$  for Al and Pb may not be negligible.

An analysis of the  $K$  parameters in terms of derivatives of the interaction potentials is beyond the scope of this paper. The difficulties involved in an analysis of this sort are illustrated by the attempt of Maradudin & Flinn, cited above, to use their result to predict the behaviour of lead. Using the approximations and physical property measurements necessary to evaluate their  $2M$  relationship they would arrive at the result (*cf.* their equations 6.11 and 4.9) that the total anharmonic effects are less than that due to expansion alone. Similar problems are evident in the application of the results of Kashiwase (1965) to crystals other than certain of the alkali halides.

## 5. Conclusion

The results of this investigation have confirmed the X-ray measurements of the temperature variation of the Debye-Waller factor of aluminum, and a possible explanation is put forward for the failure of the Marshall & Stuart correction to the harmonic relation in the case of aluminum.

Reliable values of the  $B$  factor for simple crystals can be calculated from an accurate set of dispersion relations at a particular temperature, provided due care is exercised in fitting these dispersion curves, and an adequate frequency sampling is taken.

Present knowledge of interatomic forces does not allow a direct calculation of the anharmonic contributions to the Debye-Waller factor; it may be possible to derive information concerning these forces from the measured high temperature behaviour of  $B$  in certain cases.

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#### References

- ALEXOPOULOS, K., BOSKOVITS, J., MOURIKIS, S. & ROLOS, M. (1965). *Acta Cryst.* **19**, 349.  
 BOND, W. L. (1960). *Acta Cryst.* **13**, 814.  
 BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices*. Oxford Univ. Press.  
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.  
 CHIPMAN, D. R. (1960). *J. Appl. Phys.* **31**, 2012.  
 CHIPMAN, D. R. & PASKIN, A. (1959). *J. Appl. Phys.* **30**, 1992.  
 COWLEY, R. A. (1963). *Advanc. Phys.* **12**, 421.  
 FLINN, P. A. & MCMANUS, G. M. (1963). *Phys. Rev.* **132**, 2458.  
 FLINN, P. A., MCMANUS, G. M. & RAYNE, J. A. (1961). *Phys. Rev.* **123**, 809.  
 GIAUQUE, W. F. & MEADS, P. F. (1941). *J. Amer. Chem. Soc.* **63**, 1897.  
 GILAT, G. & NICKLOW, R. M. (1966). *Phys. Rev.* **143**, 407.  
 GILAT, G. & RAUBENHEIMER, L. J. (1966). *Phys. Rev.* **144**, 390.  
 HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629.  
 HIDNERT, P. & KRIDER, H. S. (1952). *J. Res. Nat. Bur. Stands.* **48**, 209.  
 HUNTINGTON, H. B. (1958). *Solid State Physics*, **7**, 213.  
 JAMES, R. W. (1954). *The Optical Principles of the Diffraction of X-rays*, p.275. London: Bell.  
 JAMES, R. W., BRINDLEY, G. W. & WOOD, R. G. (1929). *Proc. Roy. Soc. A*, **125**, 401.  
 KASHIWASE, Y. (1965). *J. Phys. Soc., Japan*, **20**, 320.  
 LEIBFRIED, G. & LUDWIG, W. (1961). *Solid State Physics*, **12**, 275.  
 MARADUDIN, A. A. & FLINN, P. A. (1963). *Phys. Rev.* **129**, 2529.  
 MARSHALL, W. & STUART, R. N. (1961). *Inelastic Scattering of Neutrons in Solids and Liquids*, p.75. Vienna: I.A.E.A.  
 NICKLOW, R. M. & YOUNG, R. A. (1966). To be published.  
 NILSSON, N. (1956). *Ark. Fys.* **12**, 247.  
 OWEN, E. A. & WILLIAMS, R. W. (1947). *Proc. Roy. Soc. A*, **188**, 509.  
 PASKIN, A. (1957). *Acta Cryst.* **10**, 667.  
 PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138.  
 PRYOR, A. W. & SABINE, T. M. (1964). *J. Nucl. Mat.* **14**, 275.  
 SQUIRES, G. L. (1963). *Ark. Fys.* **25**, 21.  
 SQUIRES, G. L. (1964). *Ark. Fys.* **26**, 223.  
 STEDMAN, R. & NILSSON, G. (1965). *Inelastic Scattering of Neutrons in Solids and Liquids*, Vol.I, p.211. Vienna: I.A.E.A.  
 SUTTON, P. M. (1953). *Phys. Rev.* **91**, 816.  
 WALLER, I. (1923). *Z. Phys.* **17**, 398.  
 WILLIS, B. T. M. (1962). *Pile Neutron Research in Physics*, p.455. Vienna: I.A.E.A.  
 ZENER, C. & BILINSKY, S. (1936). *Phys. Rev.* **50**, 101.

*Acta Cryst.* (1967). **23**, 191

## An Iterative Method of Slit-Correcting Small Angle X-ray Data

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An iterative method has been developed for correcting experimental small-angle X-ray data simultaneously for the effects of height and width smearing. The advantages of the method are that it does not require the differentiation of an experimental curve, that the height and width weighting functions are completely arbitrary, that the corrected curve remains well defined at small values of the scattering angle, and that the method is designed for use with digital computers. The method may also be applied to the solution of other similar integral equations.

### Introduction

In order to obtain sufficient scattered intensity in a small-angle X-ray experiment one normally uses a slit collimation system. The observed intensity in this case

is not that obtained with a pinhole collimator, but is the pinhole intensity averaged (smeared) over an angular range which is defined by the slit geometry.

Guinier & Fournet (1947) and DuMond (1947) solved the smearing equation for the case of infinitely high and negligibly narrow slits. Their method was modified by Kratky, Porod & Kahovec (1951) for use

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