

## The Temperature Dependence of the Debye–Waller Factor of Magnesium

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The temperature dependence of the average Debye–Waller factor for magnesium was measured by means of neutron diffraction spectrometry. The experimental results obtained in the temperature range from 5 to 256 K are compared with theoretical calculations, using the harmonic and quasi-harmonic approximations and results of previous experiments.

### 1. Introduction

The temperature dependence of the Debye–Waller factor for crystals with a cubic structure has been widely investigated experimentally and many theoretical approaches have been proposed in order to explain the experimental results (Willis, 1969). In the past decade there has been a growing interest in similar studies of crystals with a hexagonal close-packed structure. Until recently the most extensively studied elements were beryllium (Schiffer, Parks & Heberle, 1964; Housley, Dash & Nussbaum, 1964), zinc (Barron & Munn, 1967; Skelton & Katz, 1968), and holmium (Skelton, 1969). The Debye–Waller factor for magnesium was known at 86 and 293 K from the early measurements of Brindley & Ridley (1938). Watanabe, Iwasaki & Ogawa (1971) made an X-ray determination of the Debye–Waller factor of magnesium at four temperatures between 92 and 300 K. We measured the temperature dependence of the Debye–Waller factor of magnesium powder between 5 and 256 K by means of neutron diffraction and compared the experimental results with the theoretical predictions (Sledziewska-Blocka & Rajca, 1974) based on a simple phenomenological model (Czachor, 1970; Czachor & Rajca, 1971).

The experimental procedure and possible systematic errors are discussed in § 2. The data analysis and the results are described in § 3. In § 4 the model is described and the experimental results are compared with previous experiments and theory.

### 2. Experimental procedures

The measurements were made with the neutron diffractometer at the 10 MW steady-state reactor DR 3 at Risø. Monochromatic neutrons were obtained by reflexion from a (111) plane of a germanium single crystal with a mosaic of 15'. The wavelength used was  $1.651 \pm 0.005$  Å, and the contamination of the incident

neutron beam due to reflexion from the (333) plane was less than 0.3%. Soller collimators with an angular spread of 20' were placed both in front of and behind the sample.

Powder diffraction measurements were carried out between 5 and 256 K. The temperature was measured with germanium and platinum resistance thermometers in the low-temperature regions and with a copper–constantan thermocouple at higher temperatures. The sample temperature was kept constant within  $\pm 2$  K. The Koch-Light Laboratories Ltd, England, supplied the 99.9% pure magnesium powder with a grain size of less than 200  $\mu\text{m}$ . The sample was enclosed in a thin-walled cylindrical container which was sealed in a helium atmosphere to avoid oxidation of the magnesium powder.

Control measurements were carried out in order to detect evidence of preferred orientation and thermal hysteresis in the powdered sample. They showed that the diffraction patterns were reproducible within the limits of statistical fluctuations.

Two important experimental effects are temperature dependent and may give rise to systematic errors in the relative change of the Debye–Waller factor. The first is the effect of extinction, which was assumed to be negligible in the powdered sample. The second effect is the thermal diffuse scattering (TDS). To estimate the TDS we used the method developed by Beg, Aslam, Butt, Khan & Rolandson (1974). The energy distribution of the TDS can be expressed in terms of an effective sound velocity in the sample. The total thermal diffuse scattering under a Bragg peak is then calculated by integrating the TDS distribution over energy. The effective sound velocities were estimated from the phonon-dispersion relations (Iyengar, Venkataraman, Rao, Vijayaraghavan & Roy, 1963). The calculations showed that the total TDS contribution to the 110 Bragg peak decreases almost linearly from  $\sim 1.5\%$  at 300 K to  $\sim 0.2\%$  at 4.2 K. The TDS contributions to the 010, 002, 011 and 012 reflexions are smaller than 1% below 300 K. The TDS contribution to the scattering is thus within the experimental accuracy. From these calculations and from the con-

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trol measurements mentioned it can be deduced that the influence of the systematic experimental errors is negligible.

### 3. Data analysis and results

Fig. 1 shows a typical diffraction pattern obtained at 245 K. Five Bragg reflexions from magnesium and two from the aluminum sample container were resolved. In order to determine the integrated intensities of the magnesium Bragg peaks the following assumptions were made:

1. the shape of the individual Bragg peaks is described by a Gaussian function of the scattering angle,

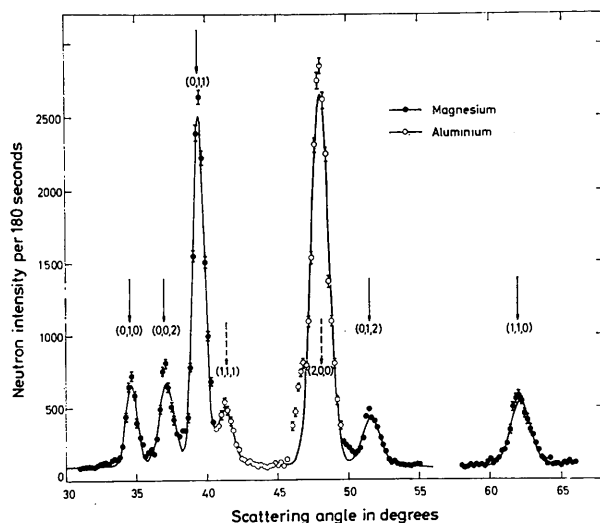


Fig. 1. Neutron diffraction pattern for magnesium obtained at 245 K. The solid line is the result of a least-squares fit to a sum of Gaussian distribution functions and a linear background. Bragg peaks due to the aluminum sample container are indicated by the dashed arrows and unfilled points.

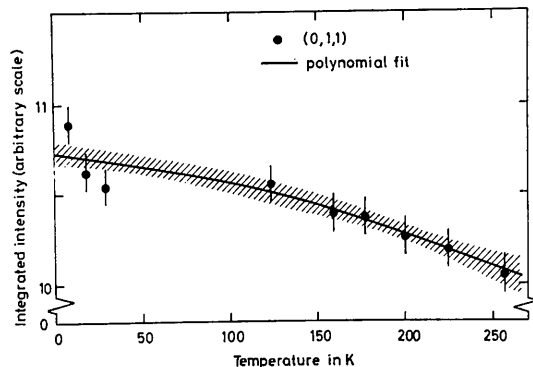


Fig. 2. Temperature dependence of the integrated intensity for an 011 Bragg peak. The solid line is the result of a least-squares fit to a polynomial, and the hatched area shows the 67% confidence limits.

2. the background is a linear function of the scattering angle, and

3. the experimental errors are given solely by the statistical errors.

Under these assumptions a least-squares fit of the experimental points to the sum of Gaussian distributions and a linear background were obtained. For each temperature the experimental data were divided into three parts. The first part of the diffraction pattern including the 111 aluminum peak ( $31^\circ < 2\theta < 44^\circ$ ) were fitted to the sum of four Gaussian distributions and a linear background. In the second ( $44^\circ < 2\theta < 55^\circ$ ) and third ( $58^\circ < 2\theta < 66^\circ$ ) parts the experimental points were fitted to two and one Gaussian distribution functions, respectively, and a linear background. The fitting procedure is simple for the well-resolved 110 Bragg peak, but somewhat more complicated for the 012 Bragg peak which is situated on the edge of the 200 aluminum peak from the sample container. The two peaks were therefore fitted together.

The integrated intensities and the error estimates determined from the least-squares fit were obtained for the five magnesium peaks at several different temperatures between 5 and 256 K. For each Bragg peak a least-squares fit to a polynomial was obtained for the temperature dependence of the integrated intensity,  $I_{\mathbf{H}}(T)$ . The best fits were obtained for first or second-order polynomials:

$$I_{\mathbf{H}}(T) = b_0 + b_1 T + b_2 T^2. \quad (1)$$

The  $b_i$  values and their estimated errors are given in Table 1. Fig. 2 shows a typical example of the measured integrated intensities and the polynomial for the 011 reflexion.

Table 1. Coefficients  $b_i$  to  $I_{\mathbf{H}}(T)$  as described by equation (1) and estimated errors

$\mathbf{H}$	$b_0$	$b_1$	$b_2$	$\Delta b_0$	$\Delta b_1$	$\Delta b_2$
010	2391.2	-0.49	0	30.9	0.18	-
002	3250.1	-1.40	0.004	50.2	0.87	0.003
011	10723.5	-1.14	-0.006	75.8	1.63	0.006
012	1908.7	-0.82	0	30.0	0.19	-
110	3422.7	-2.06	0	41.8	0.25	-

The temperature dependence of the integrated intensities for the individual Bragg reflexions as described by (1) may be used to determine the temperature dependence of the relative change of the Debye-Waller factor. The integrated intensity of a Bragg reflexion for a cylindrical powdered sample is given by

$$I_{\mathbf{H}}(T) = I_{\mathbf{H}}^0 \exp[-2W_{\mathbf{H}}(T)] \\ = K \frac{j_{\mathbf{H}} \lambda^3 |F_{\mathbf{H}}^0|^2}{\sin \theta_{\mathbf{H}}(T) \sin 2\theta_{\mathbf{H}}(T)} \exp[-2W_{\mathbf{H}}(T)], \quad (2)$$

where  $K$  is a scaling factor and  $\lambda$  the incident neutron wavelength.  $j_{\mathbf{H}}$  is the multiplicity factor of the  $\mathbf{H}$  reflexion given by the Miller indices  $hkl$ .  $\theta_{\mathbf{H}}(T)$  is the

Bragg angle, and  $F_{\mathbf{H}}^0$  is the structure factor for the rigid crystal lattice. The attenuation of the intensity due to the thermal motion of the atoms is described by  $\exp[-2W_{\mathbf{H}}(T)]$  – the usual Debye-Waller factor. As  $a(T)/a(0) \leq 1.006$  for  $T < 300$  K we neglect the lattice contraction in the further analysis. In the harmonic approximation  $W_{\mathbf{H}}(T)$  may then be expressed by

$$W_{\mathbf{H}}(T) = B_{\mathbf{H}}(T) \cdot \sin^2(\theta_{\mathbf{H}})/\lambda^2. \quad (3)$$

For the h.c.p. structure  $B_{\mathbf{H}}$  may be written in the form suggested by Blackman (1956),

$$B_{\mathbf{H}}(T) = B_a(T) \cdot \sin^2 \varphi_{\mathbf{H}} + B_c(T) \cdot \cos^2 \varphi_{\mathbf{H}}, \quad (4)$$

where  $\varphi_{\mathbf{H}}$  is the angle between the scattering vector and the hexagonal axis.

The  $c/a$  ratio for magnesium is very close to that for the ideal h.c.p. structure, and the distribution of nearest neighbours is almost isotropic. It may therefore be argued that  $B_{\mathbf{H}}(T)$  is almost isotropic ( $B_a \approx B_c$ ) as well. This actually agrees with the calculations in the harmonic and quasi-harmonic approximations by Sledziewska-Blocka & Rajca (1974). These calculations are based on a simple phenomenological model of the lattice dynamics of crystals with hexagonal close-packed structure (Czachor, 1970; Czachor & Rajca, 1971). The model is of the Born-von Karman type and is essentially equivalent to the quasi-harmonic approximation. Two nearest-neighbour interactions are included. For nearest neighbours in the basal plane ( $z=0$ ) the interaction is assumed to be of a general form. The force matrix for the interactions with nearest neighbours in adjacent hexagonal planes ( $z = \pm c/2$ ) is similar to a central-force matrix, where the diagonal force constant ( $xx$ ) is assumed to be zero, and where the remaining force constants are restricted by symmetry. In such a model all force constants may be deduced from the elastic constants determined by experiment.

The applicability of the model was tested by calculating the phonon-dispersion relations for magnesium at 300 K along the three principal symmetry directions. The calculated dispersion relations agreed with the results of neutron scattering within 4%. Within the same model we calculated the temperature dependence of the specific heat. For temperatures between 10 K and 700 K the results of calculations in the quasi-harmonic approximation agree with the measured specific heat of magnesium within 4%.

The model calculations showed furthermore that the relative difference between  $B_a$  and  $B_c$  is less than 1% below 300 K. Therefore it was assumed, in the analysis of the present experimental data, that  $B_{\mathbf{H}}(T) \equiv B(T)$  and thus  $B_{\mathbf{H}}(T)$  is independent of the Miller indices. The relative change in  $B(T)$ ,  $\Delta B(T)$ , is then given by

$$\begin{aligned} \Delta B(T) &= B(T) - B(0) \\ &= \frac{\lambda^2}{2 \sin^2 \theta_{\mathbf{H}}} \cdot \{[\ln [J_{\mathbf{H}}(0)] - \ln [J_{\mathbf{H}}(T)]]\}. \quad (5) \end{aligned}$$

For all five magnesium peaks  $\Delta B(T)$  was then calculated by means of (5), using the measured  $I_{\mathbf{H}}(T)$  and the values of  $I_{\mathbf{H}}$  for  $T=0$  determined from the polynomials (1). The differences between the individual  $\Delta B(T)$  functions are within one standard deviation. A mean value  $\Delta B(T)$  and the error were calculated from these five values, according to Squires (1968):

$$\begin{aligned} \overline{\Delta B}(T) &= \frac{\sum_{i=1}^5 \left( \frac{\Delta B_i(T)}{\sigma_i^2} \right)}{\sum_{i=1}^5 \left( \frac{1}{\sigma_i^2} \right)} \\ \text{and } \frac{1}{\sigma^2} &= \sum_{i=1}^5 \left( \frac{1}{\sigma_i^2} \right). \quad (6) \end{aligned}$$

The temperature dependence of  $B(T) = \overline{\Delta B}(T) + B_{\text{th}}(0)$  is shown in Fig. 3.  $B(T)$  was obtained using the theoretical value of  $B_{\text{th}}$  at absolute zero  $B_{\text{th}}(0) = 0.35 \text{ \AA}^2$ . For comparison Fig. 3 also shows  $B(T)$  calculated by the harmonic (dot-dashed) and quasi-harmonic (dashed) approximations as well as the experimental values obtained by Brindley & Ridley (1938) and Watanabe *et al.* (1971).

#### 4. Discussion

The present experimental determination of the temperature dependence of the average Debye-Waller factor (or  $B$ ) for hexagonal close-packed magnesium in the temperature range from 5 to 256 K shows (Fig. 3) that the theoretical results obtained in the quasi-harmonic approximation, as well as Brindley & Ridley's (1938) experimental results, agree with the

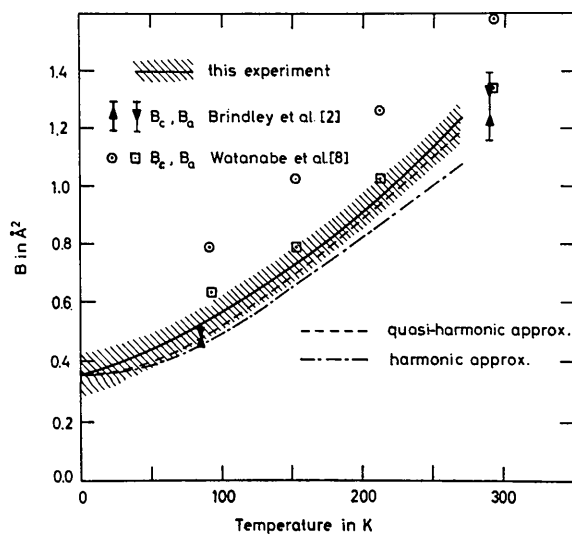


Fig. 3. The temperature dependence of  $\bar{B}$ . The solid line and the hatched area show the experimental determination of  $\bar{B}$  and the 67% confidence limit. The dashed and the dot-dashed lines are the calculated results obtained in the quasi-harmonic and harmonic approximations respectively. The error bars on Brindley & Ridley's experimental results are estimated by Sledziewska-Blocka & Rajca (1974).

experimental values to within one standard deviation. Above 70 K the calculation based on the harmonic approximation lies outside this error limit. The solid line in Fig. 3 shows the average value of  $B(T)$ . From the experimental results at 256 K we estimate  $B_a/B_c \sim 1.05$ , which is within the experimental accuracy (hatched area). Similarly, the pronounced anisotropy in  $B(T)$  obtained by Brindley & Ridley (1938) is not fully justified if one takes the experimental errors which were estimated by Sledziewska-Blocka & Rajca (1974) into account.

However, the X-ray results of Watanabe *et al.* (1971) on a single-crystal sample differ considerably from our results and show a much larger anisotropy of  $B$  than that calculated by Sledziewska-Blocka & Rajca (1971). The absolute values of  $B$  obtained by Watanabe *et al.* (1971) is about 30% larger than the  $B$  values obtained by us at 93 K, but the temperature dependence agrees with the present measurements. One explanation of the pronounced difference in the absolute values of  $B$ :  $B = B_w$  obtained by Watanabe *et al.* (1971) and  $B = B_s$  obtained in the present work – could be as follows. At each temperature  $B_w(T)$  was determined from a logarithmic plot of the measured integrated intensities versus  $(\sin \theta/\lambda)^2$ . The integrated intensities were corrected for thermal diffuse scattering, which amounts to 40% for large values of  $(\sin \theta/\lambda)^2$  (Watanabe *et al.*, 1971). No details of how the corrections for thermal diffuse scattering were made are given in the paper, but too large TDS corrections will lead to too large values of  $B$ . It therefore seems plausible that the large values of  $B(T)$  and the pronounced anisotropy of  $B_w(T)$  is caused by an overestimation of the thermal diffuse scattering.

In the present investigation, however,  $\Delta B_s(T)$  was determined from the integrated intensities of Bragg reflexions for which the thermal diffuse scattering was less than 2% below 300 K. The thermal diffuse scattering was therefore neglected in the determination of  $\Delta B_s(T)$ .  $B_s(T)$  shown in Fig. 3 was then calculated as  $B_{th}(0) + \Delta B_s(T)$  where  $B_{th}(0)$  is the value of  $B$  at absolute zero calculated from the elastic constants and

the lattice parameters of magnesium (Sledziewska-Blocka & Rajca, 1974). Since this model calculation of the phonon-dispersion relations and the specific heat capacity agree with experiment within 4%, the estimate of  $B_{th}(0)$  is assumed to be accurate within this limit.

The calculations in the quasi-harmonic approximation show that the anisotropy in  $B$  increases with temperature. Measurements above 300 K could therefore be of interest.

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