

Temperature Dependence of the Debye–Waller Factor for Magnesium Measured by Energy-Dispersive Diffractometry

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(Received 2 October 1978; accepted 22 January 1979)

Abstract

The Debye–Waller factor for powdered magnesium was measured in the temperature range 293 to 700 K by the energy-dispersive X-ray method. The results are compared with published theoretical calculations based on the quasi-harmonic and the anharmonic approximations. Anisotropy was found in the behaviour of the temperature factor $B(T)$, with excellent agreement in the a axis direction between the experimental and theoretical calculations within the quasi-harmonic approximation. In the c axis direction, however, the experimental values at increasing temperature exceed the theoretical values, even in the anharmonic approximation.

1. Introduction

The energy-dispersive X-ray diffraction method was used to study the temperature dependence of the Debye–Waller factor for hexagonal, close-packed magnesium in the temperature range 293–700 K.

Theoretical calculations by Czachor (1970), and Czachor & Rajca (1971) of lattice vibration were used by Sledziewska-Blocka & Rajca (1972) to evaluate the temperature factor in the temperature interval 0–700 K, taking into account the anisotropy of the temperature factor $B_{\mathbf{H}}(T)$.[†] Experimentally, the Debye–Waller factor for magnesium was measured by Brindley & Ridley (1938) and Watanabe, Iwasaki & Ogawa (1971) with X-ray diffraction, and by Sledziewska-Blocka & Lebech (1976) with neutron diffraction, but only in the temperature interval 0–300 K. We have measured the temperature dependence of the Debye–Waller factor for magnesium powder between 293 and 700 K by X-ray diffraction, and compared the experimental results with the theoretical predictions mentioned above. The experimental procedure is described

in §2, the results and data analysis are discussed in §3, which is followed by a comparison between theory and experiment in §4.

2. Experimental

A tungsten, fine-focus Philips diffraction tube was used to produce an incident white X-ray beam. The tube was provided with stabilized (0.01%) current and voltage from a Philips generator, type 1130. The wavelengths (photon energy) of the X-rays scattered by the powdered sample through a fixed scattering angle $2\theta_0$ were measured by a Princeton Gamma Tech Ultrapure Germanium detector (150 eV FWHM at 5.9 keV).

A special oven was constructed for the measurements; this had a temperature stability of ± 1 K in the temperature interval 300–900 K. 99.99% pure magnesium powder, supplied by Goodfellow Metals, with a grain size of less than 50 μm was used as sample material. The sample was enclosed in a thin-walled quartz capillary tube and sealed in an argon atmosphere to avoid oxidation of the magnesium powder. To avoid texture, the magnesium sample was rotated during the measurements. A typical diffraction pattern obtained at 293 K and $2\theta_0 = 17^\circ$ is shown in Fig. 1. The reflections 012, 110, 013 and the double one 020/021 were selected for measurement.

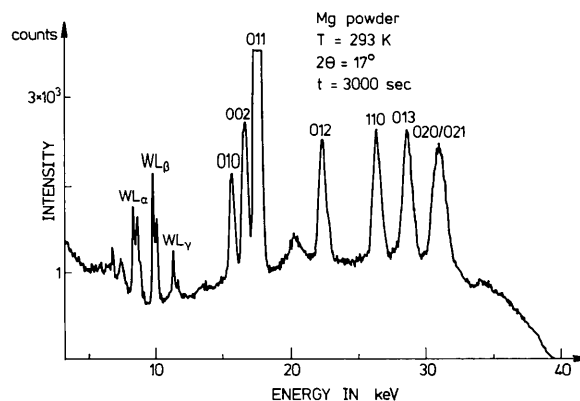


Fig. 1. X-ray diffraction pattern for magnesium at 293 K. The four Bragg reflections used are 012, 110, 013 and 020/021.

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[†] The Debye–Waller factor is written in the form $\exp(-2W_{\mathbf{H}})$, where $W_{\mathbf{H}} = B_{\mathbf{H}}(T)/4d_{\mathbf{H}}^2(T)$, $d_{\mathbf{H}}$ is the interplanar spacing at temperature T , and \mathbf{H} is the abbreviation for the reflection indices.

In order to obtain reasonable intensity, the four peaks selected have to be measured at an energy that is as close as possible to the maximum in the distribution of the *Bremsstrahlung*. At the same time, the distribution is rather flat close to its maximum, and thus the change of the incident intensity resulting from the small shift of the peaks with increasing temperature (caused by thermal expansion of the lattice) can be neglected. Unfortunately, the quartz tube, which was necessary because of heating to 700 K, caused a rather high background compared with the integrated intensities of the Bragg reflections used.

3. Results

As already mentioned, the integrated intensities were measured for the Bragg reflections 012, 110, 013 and the double peak 020/021, as shown in Fig. 2. From the assumptions that each Bragg peak is described by a Gaussian function and that the background below each peak is a linear function of energy, a least-squares fit of the experimental results to a Gaussian function was used to determine the integrated intensities for the four peaks in question at discrete temperatures between 293 and 700 K.

These results were then used to fit a smooth curve (a polynomial) to the intensities (solid lines shown in

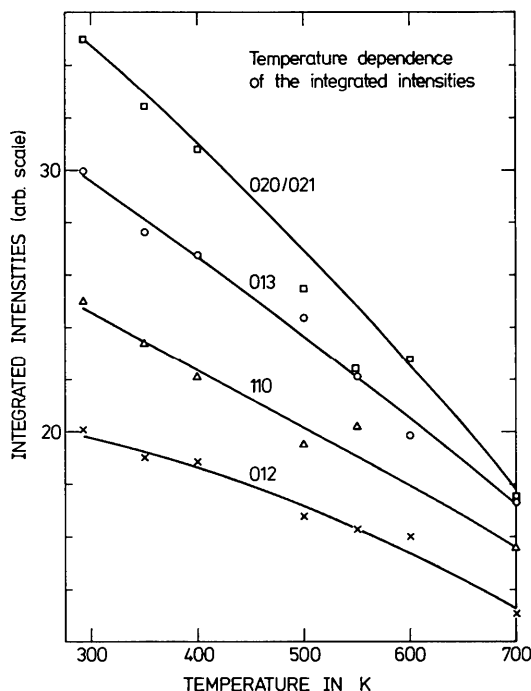


Fig. 2. Temperature dependence of the integrated intensities of the Bragg reflections used. The experimental results are fitted to a polynomial (solid lines).

Fig. 2). The parameters of these fits were used to determine the temperature factor $B_H(T)$ from the relation

$$B_H(T) = B_H(T_0) + 2d_H^2(T)[\ln I_H(T_0) - \ln I_H(T)], \quad (1)$$

where $I_H(T)$ denotes the integrated intensity at temperature T . In the case of the double peak 020/021, the value $d = (d_{020} + d_{021})/2$ was used. Two intensity measurements were considered, one performed at an arbitrary reference temperature T_0 , and the other at a different temperature T . When writing (1) it was assumed that $d_H(T_0) = d_H(T)$, which even for the highest temperature gives an error of 2% that is much smaller than other errors at this temperature.

For the h.c.p. structure, B_H may be written in the following form

$$B_H(T) = B_a(T) \sin^2 \theta_H + B_c(T) \cos^2 \theta_H, \quad (2)$$

where θ_H is the angle between the scattering vector and the hexagonal axis. As shown by Sledziewska-Blocka & Lebeck (1976), it is reasonable to assume that at room temperature (293 K) B_H is almost isotropic ($B_a \approx B_c$). Therefore, at $T_0 = 293$ K we chose a value $B_H(293 \text{ K}) = 1.25 \text{ \AA}^2$, independent of the Miller indices, in agreement with the earlier measurements.

An effect influencing the determination of integrated intensities is thermal diffuse scattering (TDS). However,

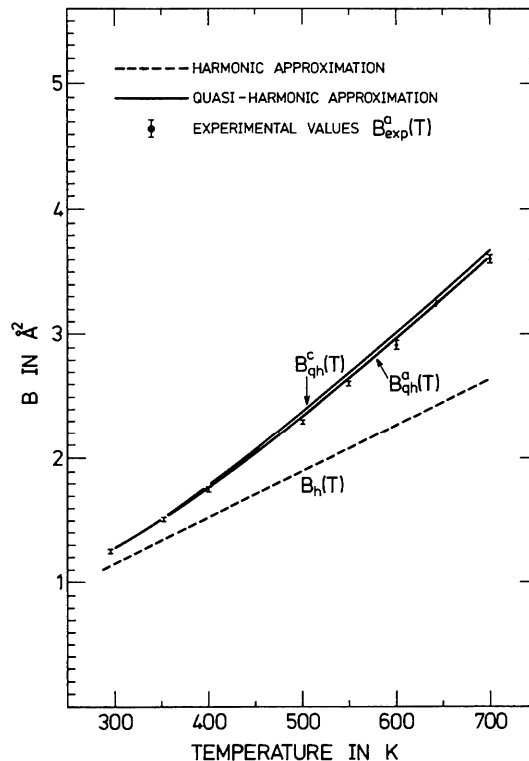


Fig. 3. The temperature dependence of $B_{110}(T)$ as evaluated from the 110 Bragg peak. The experimental results are compared with the theoretical calculations in the quasi-harmonic approximation.

by using the method of Uno & Ishigaki (1975) in the case of white X-ray diffraction, and taking account of the h.c.p. structure by the method of Skelton (1976), we calculated that the correlation is rather modest even at 700 K (<1%). Therefore, the correction is negligible compared with the statistical accuracy of the intensities.

4. Comparison between theory and experiment

The temperature-dependent part of the Debye-Waller factor (B_H) for hexagonal, close-packed magnesium in the temperature range 293 to 700 K is shown in Figs. 3 and 4.

Fig. 3 shows the calculation of $B_{110}(T)$ as determined from the 110 reflection. The experimental results are compared with the theoretical calculations of

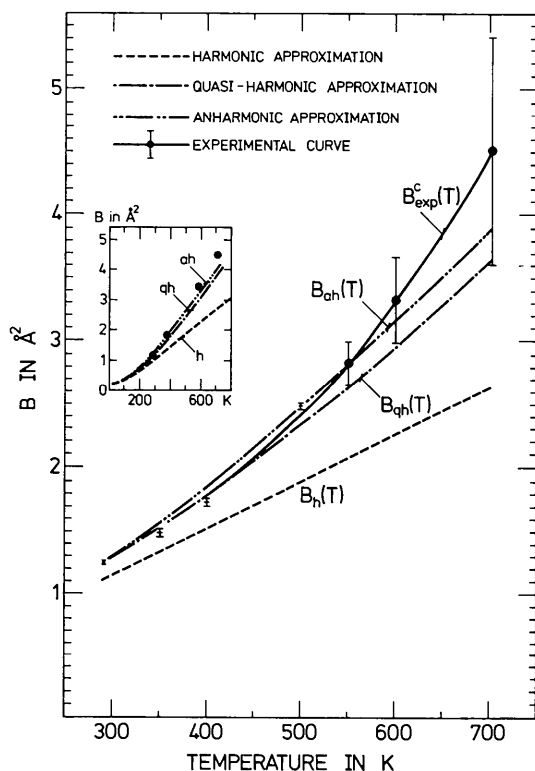


Fig. 4. The temperature dependence of $B_c(T)$ calculated from the 020/021, 013, 110 and 012 Bragg reflections. Comparison is made with theoretical calculations in both the quasi-harmonic and the anharmonic approximations. The insert shows how our results fit to the theoretical calculations in the temperature interval 0–700 K.

Sledziwska-Blocka & Rajca (1972, 1974) in the quasi-harmonic approximation, and the agreement with the theoretical values of $B_a(T)$ is excellent. Calculations of $B_c(T)$ from measurements of scattering in the c direction (the 002 peak) caused too much trouble because of the great fluctuation in the intensity measurements at low photon energies, or at small scattering angles. Hence, the temperature factor $B_c(T)$ was evaluated from calculations of $B_H(T)$ in directions involving both the a and c axes. In Fig. 4 we have calculated $B_a(T)$ and $B_c(T)$ from all the measured Bragg reflections by (2). The results are compared in this figure with theoretical calculations in both the quasi-harmonic and the anharmonic approximation. From the figure we conclude that B_c seems to increase faster than calculated, even in the anharmonic model. However, in this case, the statistical accuracy of the four reflections used has great influence on the accuracy, as can be seen from the error bars.

It is concluded from this experiment that the temperature dependence of the Debye-Waller factor $B_a(T)$ is in agreement with recent calculations in the quasi-harmonic approximation, and that the anharmonic effect in $B_c(T)$ seems to be more pronounced than the lattice-dynamical force-model predicts.

We would like to thank Professor B. Buras and Dr B. Lebeck for encouragement and discussions. This work would not have been possible without the financial support of Danish Natural Sciences Research Council, which we gratefully acknowledge.

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