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Debye Temperature of MgO Powder by Elastic Neutron Scattering

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The Debye–Waller exponent B and the Debye temperature Θ_D for a powdered sample of MgO has been determined at room temperature by elastic neutron scattering using a triple-axis spectrometer. Detailed calculations were performed to estimate the thermal diffuse scattering (TDS) under the Bragg peaks. The TDS contribution proved to be negligible. The value obtained for B is $0{\cdot}354 \pm 0{\cdot}008$ Å^2 which corresponds to a Θ_D of 743 ± 8 K. The Θ_D value obtained here for a powdered sample is about two percent lower than the corresponding value obtained from the inelastic neutron scattering for a single-crystal sample.

1. Introduction

The characteristic Debye temperature Θ_D of magnesium oxide has been obtained previously by specific-heat measurements in the temperature range 20 K to 300 K for a powdered sample by Giauque & Archibald (1937) and for single-crystal samples by Parks & Kelley (1926) and Barron, Berg & Morrison (1959). Peckham (1967) has measured the phonon-dispersion relations in a single crystal of MgO by coherent inelastic neutron scattering. Sangster, Peckham & Saunderson (1970), and Singh & Upadhaya (1973) have calculated the temperature dependence of the Debye temperature by the modified shell models in the harmonic approximation, employing neutron scattering data. The Θ_D values thus obtained increase slowly with temperature above 200 K and reach the asymptotic value near 700 K, whereas the specific-heat measurements show a decrease in Θ_D near room temperature. In the temperature region from 100 K to 300 K the Θ_D values obtained from the neutron scattering data are lower than those found from the specific-heat measurements of Baron, Berg & Morrison (1959) by about 5 K. The measurements of Giauque & Archibald (1937) on a powder sample give Θ_D values systematically lower than those from single crystals over the whole temperature range.

In the present experiment the Debye–Waller exponent B for the magnesium oxide powder has been determined at room temperature by elastic neutron scattering. MgO crystallizes in the NaCl-type structure with lattice constant $a=4{\cdot}213$ Å. The neutron scattering lengths for magnesium and oxygen are nearly equal (Willis, 1973), and consequently the intensity of the Bragg reflexions with odd Miller indices is 500 times smaller than the even-index Bragg intensities. Therefore the odd-index reflexions are practically unobserved and the problem of the overlapping Bragg peaks is absent over the observed angular range, resulting in a much better resolution than that normally obtained for powder samples.

2. Experimental procedure and the analysis

The neutron diffraction pattern was recorded at room temperature using a triple-axis spectrometer at the DR3 reactor with an incident neutron wavelength of 1·183 Å. Pyrolytic graphite crystals were used as monochromator and analyser, the analyser resolution being 4·9 meV. A magnesium oxide slab sample (AnalaR grade) with thickness corresponding to a total neutron transmission of 92% was used. $\theta{:}2\theta$ scans were performed with the monochromator and analyser in the parallel geometry.

The structure factors for the observed peaks were evaluated by taking into account the multiplicity of planes, total attenuation in the sample and the geometrical effects in the usual manner (Bacon, 1962; Caglioti & Tochetti, 1965). Detailed calculations were performed to estimate the thermal diffuse scattering (TDS) under the Bragg peaks. In an experiment using a triple-axis spectrometer TDS is considerably reduced owing to the energy resolution (Caglioti, 1964). Beg, Aslam, Butt, Khan & Rolandson (1974) have considered the problem of TDS for a powder experiment with a triple-axis spectrometer, where the coherent inelastic scattering processes involving phonons of lower than the analyser resolution are important. They have derived the one-phonon scattering surfaces for phonon energies $h\omega \ll k_BT$ near a reciprocal-lattice point τ as

$$\left(\frac{1-d}{d}\right)\left(z-\frac{\Delta}{1-d}\right)^2-q^2-\frac{\Delta^2}{1-d}=0\,, \tag{1}$$

where z and q are cylindrical coordinates with z in the τ direction and $q(\ll\tau)$ along the momentum vector;

$$d=\frac{m^2\tau^2c^2}{4\hbar^2K^4}$$

$$\Delta=2K\sin\theta-\tau\,, \tag{2}$$

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m is the neutron mass, c the effective sound velocity in the material, and K is the incident neutron wave vector. Δ is a particular offset position under the Bragg peak. For $d < 1$ the scattering surface is a hyperboloid which gives a TDS peak centred at the Bragg position. For sound velocities which give $d > 1$, (1) represents an ellipsoid and the TDS contributes only to the flat background under the peak.

Equation (1) is a quadratic in q and takes into account both the phonon emission and absorption processes. In the high-temperature limit ($h\omega \ll k_BT$) the one-phonon coherent cross section for both the processes is taken to be same and can be written as (Willis, 1969; Beg *et al.*, 1974)

$$\sigma(q) = \frac{N|F(Q)|^2}{2M} Q^2 k_B T \, 1/c^2 \cdot \frac{1}{q^2} \tag{3}$$

where M is the mass per unit-cell and N is the number of unit cells in the crystal,

$$1/c^2 = \frac{1}{3} \sum_{j=1}^{3} \frac{1}{\langle V_q \rangle_j^2}, \tag{4}$$

V_q, j is the sound velocity of a mode with polarization j. When c is evaluated only the phonon branches with small sound velocities, so that $d < 1$, are considered.

The TDS peak originates from a small q space in the first Brillouin zone around τ. To obtain the relative TDS intensity the inelastic scattering is normalized to the Bragg-scattering cross section for $Q = \tau$. The Bragg-scattering cross section is given by

$$\sigma_0 = N v_z |F(Q)|^2 \cdot \delta(Q - \tau) \tag{5}$$

where $\int \delta(Q - \tau) dv_z = 1$; v_z is the volume of the Brillouin zone. The thermal diffuse scattering for a given Δ value within the peak width was calculated by integrating the one-phonon cross section analytically over the q values for both phonon emission and absorption defined by the scattering surface within the first Brillouin zone and within the instrumental resolution. The total TDS under a peak was evaluated by integrating the TDS contributions on both sides of the peak position over Δ (Beg *et al.*, 1974). The TDS normalized to the elastic cross section gave the necessary correction to the observed Bragg intensity.

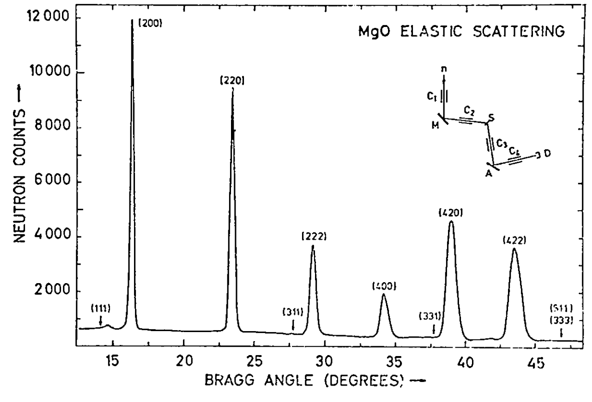

Fig. 1. The elastic scattering pattern for MgO measured with a triple-axis neutron spectrometer using a wavelength = 1·183 Å. The insert shows the schematic geometry of the apparatus. M – pyrolytic graphite monochromator (004) planes. A – pyrolytic graphite analyser (002) planes. S – sample. $C_2 = 0{\cdot}53°$, $C_3 = 0{\cdot}43°$.

3. Results and discussion

The elastic neutron scattering pattern for MgO is shown in Fig. 1. The expected positions of the odd-index reflexions are also indicated. The Debye–Waller exponent B for MgO is found from a least-squares fit to be $0{\cdot}354 \pm 0{\cdot}008$ Å. The observed and calculated structure factors are compared in Table 1, which also gives the calculated TDS corrections. The R value obtained for the fit is 0·16% which is excellent for a powder neutron scattering experiment. The main reasons for the small R value were as follows: (*a*) The good counting statistics, the improved resolution due to the absence of odd reflexions and the focusing effect in the triple-axis spectrometer. A thin sample (92% transmission) was used, which also reduces the experimental errors. (*b*) For MgO only the even-index reflexions are observable by neutron scattering, all having the same scattering length ($b_{Mg} + b_O$). Therefore the results are free of any errors in the neutron scattering length. (*c*) MgO has a high Debye temperature and therefore the sound velocities are large (average longitudinal velocity $\simeq 0{\cdot}9 \times 10^6$ cm s^{-1}) and according to equation (3), the TDS is small. For reflexions with indices above 200 only the transverse branches [for $d < 1$ in (2)] contribute to TDS. With the elastic constants given by Chung (1963) the calculated TDS at room temperature varies from 0·06% for the 200 peak to 0·26% for the 400 peak. For all peaks the TDS is less than half the statistical error and the inelastic scattering correction alters the B value by 0·0004 Å^2 which is negligible. The absence of TDS also helped to achieve the good R value.

Table 1. *The observed and calculated structure factors for* MgO *elastic reflexions*

The thermal diffuse scattering contributions to the peak intensities are also shown.

hkl	Observed intensities (total neutron counts)	Constant × exp $(-B \sin^2 \theta/\lambda^2)$ F_o	F_c	TDS %
200	71594	61·466	61·350	0·06
220	74288	60·046	60·134	0·13
222	34691	58·759	58·940	0·23
400	20906	57·758	57·765	0·26
420	72522	56·733	56·616	0·20
422	65969	55·469	55·488	–

$R = 0{\cdot}16\%$ $\quad B = 0{\cdot}354 \pm 0{\cdot}008$ Å^2

The B value obtained above corresponds to a Debye temperature of (743 ± 8) K at 293 K. The Θ_D is compared with the results of other authors in Table 2. The specific heat measurements quoted in Table 2 extend over a temperature range from 2·5 K to 300 K and from those data only the values at 293 K are tabulated. The specific-heat measurements of Barron *et al.* (1959) extend only up to 270 K and an extrapolated value at 293 K is given for that work. The measurements of Barron *et al.* (1959) and of Parks & Kelley (1926), on single crystals, agree with each other within the experimental accuracy and an average value of (756 ± 4) K is obtained from their specific heat data. The value of Θ_D for a single crystal, obtained in the effective harmonic approximation from the inelastic neutron scattering data, is also in agreement with specific-heat data at 293 K.

Table 2. *Debye temperature of* MgO *at* 293 K

Reference	Method*	Θ_D (K)
Barron, Berg & Morrison (1959)	Specific heat. SC.	$757 \pm 5°$†
Parks & Kelley (1926)	Specific heat. SC.	754 ± 7
Giauque & Archibald (1937)	Specific heat. P.	735 ± 5
Sangster, Pekham & Saunderson (1970)	Inelastic neutron scattering, shell model. SC.	761
Singh & Upadhaya (1972)	Shell model. SC.	761
Present work	Neutron Diffraction. P.	743 ± 8

* SC: Single Crystal, P: Powder.
† Extrapolated value.

The Debye temperature obtained by Giauque & Archibald (1937) for a powder sample at 293 K is about 3% lower than the corresponding single-crystal value. It had been suggested (Jura & Garland, 1952) that the difference could be due to the particle size. Barron *et al.* (1959) have estimated that the above effect leads to a lowering of Θ_D by only about $\frac{1}{3}$% and they could not account for the observations of Giauque & Archibald (1937).

To estimate the difference between the Θ_D values from the single-crystal and powder samples, the present results can realistically be compared only with the previous inelastic neutron scattering work. This is because, for temperatures greater than $\Theta_D/3$, the value of Debye temperature obtained from the specific-heat measurements is affected by anharmonicity much more than that from the neutron scattering measurements (Barron, 1963). This comparison gives a difference of about 2% for the two samples, which is comparable with that obtained from the specific heat experiments. It is therefore suggested that more detailed theoretical calculations be performed to evaluate the difference between the single crystal and the powder sample Debye-temperature values.

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