Room-Temperature Debye–Waller Factors of Magnesium Oxide*

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From bulk thermodynamic data a precise value is derived for the Debye equivalent temperature for the Debye–Waller effect: $\Theta^M(293) = 804.5 \pm 4$ K. This agrees with the temperature dependence of X-ray Bragg intensities measured by Baldwin & Tompson [*J. Chem. Phys.* (1964), **41**, 1420–1426], but rules out many pairs of values for $B(Mg)$ and $B(O)$ obtained from angular dependence of X-ray Bragg intensities. Only the results of Lawrence [*Acta Cryst.* (1973), A**29**, 94–95] are fully consistent. These give $B(O)$ slightly larger than $B(Mg)$, in agreement with shell-model calculations. Combining the thermodynamic error limits with Lawrence's gives at 293 K $B(Mg) = 0.296 \pm 0.009$ Å^2, $B(O) = 0.330 \pm 0.012$ Å^2. This gives for even-index neutron peaks $B^{eff} = 0.314 \pm 0.010$ Å^2, compared with a recent powder measurement of $B^{eff} = 0.354 \pm 0.008$ Å^2 which is incompatible with the thermodynamic data [unless $B(O)/B(Mg) \simeq 3$]. The discrepancy, though small, cannot be due to particle-size effects.

Thermodynamic information

Debye equivalent temperatures describing Debye–Waller effects cannot be compared directly with those describing heat capacities. Because the frequency distribution of a real crystal is not of the Debye form, different Θ's must be defined for different crystal properties; in general they have different values and temperature variations. Debye–Waller factors and thermodynamic properties can, however, be related through the quasi-harmonic theory of crystal vibrations, by a method which applies to any vibrational spectrum and so does not depend on the Debye model (Barron, Leadbetter, Morrison & Salter, 1966, hereafter referred to as I). Allowance is made in the theory for the effect of thermal expansion, but not for further anharmonic effects; it is therefore most reliable at comparatively low temperatures far below the melting point.

For a cubic crystal in which each atom has an isotropic mean-square displacement $B_\kappa/8\pi^2$, the sum $\sum_\kappa m_\kappa B_\kappa$ depends only on the vibrational frequency distribution and so can be related to the heat capacity. We define an equivalent Debye temperature, $\Theta^M(T)$, such that the corresponding Debye spectrum gives the correct $\sum_\kappa m_\kappa B_\kappa$ at temperature T. Equation (4.7) of I gives an expression for $\Theta^M(T)$, valid above about $\Theta/6$; this depends only on the high-temperature limits Θ^M_∞ and Θ^C_∞, where Θ^C is the equivalent temperature for the heat capacity.

Θ^C_∞, Θ^M_∞ and the low temperature limit Θ^M_0 depend on the moments $\langle v^2 \rangle$, $\langle v^{-2} \rangle$ and $\langle v^{-1} \rangle$ of the frequency spectrum ($v = \omega/2\pi$). For magnesium oxide these were obtained from the heat capacity by Barron, Berg & Morrison (1959, table 4), for the equilibrium

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volume at $T = 0$, V_0. The methods of §4 of I then give at V_0

$$\Theta^M_0 = 779 \pm 3 \text{ K}, \qquad \Theta^M_\infty = 810.5 \pm 1.0 \text{ K}, \qquad (1)$$

$$\Theta^C_\infty = 783 \pm 10 \text{ K}, \qquad \Theta^M(293) = 810.1 \pm 1.0 \text{ K}, \qquad (2)$$

where the range of possible values for Θ^C_∞ has been slightly increased from the original estimate. For correction to V_{293} we use the thermal expansion results of White & Anderson (1966); the small temperature variation of the Grüneisen functions implies we may take $\gamma = 1.6 \pm 0.1$ for all characteristic temperatures, and equation (5·3) of I then gives $\Theta^M(293) = 804.5 \pm 1$ K. A further correction to $\Theta^M(293)$ due to additional anharmonic effects cannot be estimated rigorously; it is likely to be of the same order as the volume correction, but not so large (Maradudin & Flinn, 1963; Willis, 1969). We therefore take it as ± 3 K, and get finally

$$\Theta^M(293) = 804.5 \pm 4 \text{ K}, \qquad (3)$$

corresponding to an average temperature factor weighted by the atomic masses

$$\tilde{B} = [m_O B(O) + m_{Mg} B(Mg)]/(m_O + m_{Mg}) =$$
$$= 0.3085 \pm 0.0030 \text{ Å}^2, \qquad (4)$$

where 1 Å $= 0.1$ nm. The high precision arises because $\langle v^{-2} \rangle$ depends on the heat capacity in a temperature range of high accuracy ($\sim 0.2\%$), and it provides a powerful check of direct determinations of temperature factors.

Temperature dependence of X-ray scattering

By analysing the temperature dependence of X-ray Bragg reflexions, Baldwin & Tompson (1964) derived $\Theta^M(333) = 802 \pm 5$ K, where the error limits are estimated from their Fig. 6. This is in complete agreement with the thermodynamic data, for which the methods described above give $\Theta^M(333) = 803 \pm 4$ K; we note also

that Θ^M varies little with temperature in this range, as required by the analysis of Baldwin & Tompson. We thus confirm their belief that the difference between their Θ^M and the thermodynamic Θ^C was a property of the vibrational spectrum and not due to experimental error.

Angle-dependence of X-ray scattering

Sanger (1969) quotes widely differing room-temperature values of Θ^M derived from several different X-ray measurements and one neutron measurement. They all differ greatly from that of (3) except for Sanger's own value, obtained with a single crystal which had been damaged by neutron-irradiation to reduce extinction. For this crystal at 300 K he found

$$B(\text{Mg}) = 0.346 \pm 0.009 \text{ Å}^2, \quad B(\text{O}) = 0.315 \pm 0.010 \text{ Å}^2, \quad (5)$$

giving $\Theta^M(300) = 768 \pm 12$ K; the discrepancy with (3) is small but significant.

Lawrence (1973a) reduced the effects of extinction by considering only higher-order reflexions from his single crystal. At a temperature of 293 ± 3 K (private communication) he obtained:

$$B(\text{Mg}) = 0.30 \pm 0.01 \text{ Å}^2, \quad B(\text{O}) = 0.34 \pm 0.02 \text{ Å}^2. \quad (6)$$

These give $\tilde{B} = 0.316 \pm 0.01 \text{ Å}^2$, fully consistent with the thermodynamic value of (3). Additional reasons for preferring them to Sanger's values are that they were obtained from an undamaged crystal, and that the measurements were a preliminary to a systematic study of the effects of extinction (Lawrence, 1973b). We therefore provisionally accept Lawrence's values as the best at present available. Combining his limits of error with those of (3), and also allowing for his uncertainty in temperature, gives at 293 K

$$B(\text{Mg}) = 0.296 \pm 0.009 \text{ Å}^2, \quad B(\text{O}) = 0.330 \pm 0.012 \text{ Å}^2. \quad (7)$$

Theoretical values

The best lattice dynamical model for magnesium oxide appears to be that of Singh & Upadhyaya (1972), who used a shell model modified to take account of three-body forces. With only seven adjustable parameters this model gave remarkably good agreement with several different types of experimental measurement. In particular, agreement with elastic constants and phonon frequencies measured by inelastic neutron scattering confirms that the model gives a good representation of the vibrational frequencies. Singh & Upadhyaya did not calculate Debye–Waller effects, but their close agreement with the measured heat capacities [see the graph of $\Theta^C(T)$ in their Fig. 3] implies a value for Θ^M close to that of (3). Similar remarks apply to the breathing-shell model of Sangster, Peckham & Saunderson (1970).

Separate Debye–Waller factors have been calculated for the models listed in Table 1, where RI denotes a

Table 1. *Debye–Waller factors for theoretical models of magnesium oxide*

Model	T (K)	$B(\text{Mg})$ (Å^2)	$B(\text{O})$ (Å^2)	$\tilde{B}$ (Å^2)	Θ^M (K)
RI[1]	300	0.355	0.28	0.325	788
SM[2]	300	0.287	0.350	0.312	807
TSM[3]	295	0.331	0.361	0.343	758

References: (1) Groenewegen & Huiszoon (1972). (2) Sanger (1969). (3) Sneh & Dayal (1975).

rigid ion model, SM a simple shell model and TSM a shell model with three-body forces. The last of these ought to be the best, but unfortunately Sneh & Dayal (1975) used slightly different assumptions and input data from Singh & Upadhyaya (1972) and did not check that their model still agreed with the phonon dispersion curves. The value of $\Theta^M(295)$ calculated from their results shows that they are not strictly consistent with the frequency distribution. Peckham's (1967) shell model, used by Sanger (1969) in his Debye–Waller calculations, gives a fair fit to the dispersion curves, but not so good as that of Singh & Upadhyaya (1972); it is to be preferred to the rigid ion model, but cannot be regarded as wholly reliable.

To sum up, there is no wholly satisfactory calculation of the separate Debye–Waller factors. The model of Singh & Upadhyaya (1972) establishes the close consistency of phonon dispersion curves with the experimental heat capacity, and hence the validity of the calculation from thermodynamic data. All models of Table 1 agree that $B(\text{Mg})$ and $B(\text{O})$ are of roughly the same magnitude, and the two shell models that $B(\text{Mg}) < B(\text{O})$, in agreement with Lawrence's experimental values.

Neutron-scattering measurements

Beg (1976) has made precise measurements of intensities of six Bragg peaks for MgO powder (AnalaR) at 293 K. The scattering lengths are almost equal (Scherm, 1972):

$$b(\text{Mg}) = 0.516 \times 10^{-12} \text{ cm}, \quad b(\text{O}) = 0.575 \times 10^{-12} \text{ cm}; (8)$$

consequently, only even-index peaks were observable. For these Beg obtained an effective temperature factor, $B^{\text{eff}} = 0.354 \pm 0.008 \text{ Å}^2$, from which he deduced a Debye temperature of 743 ± 8 K significantly different from that of (3).

In discussing this discrepancy, we must first note that Beg's Debye temperature must be defined differently from Θ^M, because B^{eff} is not the same as $\tilde{B}$: $-2B^{\text{eff}}$ is the slope of a graph of

$$\ln |b(\text{O}) \exp [-B(\text{O}) \sin^2 \theta / \lambda^2] + b(\text{Mg}) \exp [-B(\text{Mg}) \sin^2 \theta / \lambda^2]|^2 \quad (9)$$

plotted against $\sin^2 \theta / \lambda^2$. For the range of Beg's experiment the exponents are small, and the graph should

be only very slightly curved. B^{eff} is thus given by the initial slope:

$$B^{eff} = [b(O)B(O) + b(Mg)B(Mg)]/[b(O) + b(Mg)] . \quad (10)$$

This is a different average from (3), and calculations show that Beg's value for B^{eff} could be consistent with the thermodynamic data if $B(O)$ were about three times as large as $B(Mg)$. However, the X-ray measurements and theoretical calculations discussed above rule out this explanation. For example, the values of (7) give $B^{eff} = 0.314 \pm 0.010$ Å^2.

Beg makes the interesting suggestion that a difference between the Debye–Waller effect in single-crystal and powder samples might arise from particle-size effects. Size effects on the vibrational spectrum of magnesium oxide have been investigated by inelastic neutron scattering (Rieder & Hörl, 1968) and in theoretical models (Genzel & Martin, 1972; Chen, Alldredge & De Wette, 1973); size effects in the heat capacity are discussed by Barron et al. (1959). The data are insufficient to establish definitive experimental quantities and to relate them to theory, and in particular there appears to be no thorough investigation, experimental or theoretical, of the Debye–Waller effect in small particles. However, all the evidence indicates that even for particles as small as 1000 Å in linear dimensions the reduction of a Debye temperature due to size effects is of the order of 1% or less. Therefore, unless the powder used by Beg was unusually fine (the AnalaR magnesium oxide powder in this Laboratory has particle dimensions ~ 3 μm), the discrepancy between his results and the X-ray and thermodynamic data cannot be due to particle-size effects. Its cause remains obscure.

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