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Mean-Square Atomic Displacements in Zinc

BY T. H. K. BARRON AND R. W. MUNN

Department of Theoretical Chemistry, The University, Bristol, England

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The mean-square atomic displacements $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ are calculated in the range 0–600°K from thermodynamic and inelastic neutron-scattering data. Thermodynamic data alone give $\langle 2u_x^2+u_z^2\rangle$, which is separated into its components $2\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ with the aid of the lattice-dynamical model of DeWames, Wolfram & Lehman and the neutron-diffraction data on which it is based. Earlier values derived from the Debye–Waller effect in X-ray scattering are discussed briefly.

Introduction

For a hexagonal close-packed structure, the intensity of a Bragg reflexion varies as exp $(-2M)$, with

$$M=8\pi^2(\sin\theta/\lambda)^2[\langle u_x^2\rangle \sin^2\psi+\langle u_z^2\rangle\cos^2\psi]\ ; \qquad (1)$$

here θ is the Bragg angle, λ is the wavelength of the radiation, $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ are the mean-square atomic displacements in directions parallel and perpendicular to the hexagonal axis,* and ψ is the angle between the hexagonal axis and the normal to the reflecting plane (Zener, 1963; Blackman, 1956). Table 1 lists various published values of $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ for zinc, derived mainly from X-ray data. Although there is fair agreement between some of the measurements, they do not provide definitive values for $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ and their likely errors. In this paper we use thermodynamic and inelastic neutron-scattering data to derive such definitive values for $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$.

Use of thermodynamic data

From thermodynamic data we can calculate the total mean-square amplitude $\langle 2u_x^2+u_z^2\rangle$ as a function of both temperature and strain, without recourse to any force-constant model (Feldman & Horton, 1963; Salter, 1965; for a simple review see Barron, Leadbetter, Morrison & Salter, 1966). $\langle 2u_x^2+u_z^2\rangle$ is conveniently represented by an equivalent Debye temperature $\Theta^M(T;a,c)$; this is defined as the characteristic temperature of that Debye distribution which gives the actual value of $\langle 2u_x^2+u_z^2\rangle$ at temperature T and lattice parameters a,c. Comprehensive tables relating $\langle u_x^2+u_y^2+u_z^2\rangle$ and Θ^M are available (Benson & Gill, 1966). From the results of an analysis of the heat capacity of zinc (Barron & Munn, 1966) we find that the low- and high-temperature expansions (Salter, 1965) for $\Theta^M(T;a_0,c_0)$ are respectively

$$\Theta^M(T;a_0,c_0)=221[1+0{\cdot}93(T/100)^2-3{\cdot}6(T/100)^4+\ldots]\ , \qquad (2)$$

and

$$\Theta^M(T;a_0,c_0)=224{\cdot}5[1+0{\cdot}0026(100/T)^4-0{\cdot}0012(100/T)^6+\ldots]\ , \qquad (3)$$

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* Maradudin & Flinn (1963) have shown that for an anharmonic crystal the Debye–Waller factors do not depend only on the mean-square atomic displacements, so that equation (1) is ideally not strictly true. However, their calculations indicate that this effect is normally negligible.

where a_0 and c_0 denote the equilibrium strain at zero temperature; a_T and c_T will be used to denote the equilibrium strain at temperature T. The convergence of such series is made more rapid by an Euler transformation (Sack, Maradudin & Weiss, 1961); here we use

$$t = (100/T)^2/[3 + (100/T)^2]\,. \qquad (4)$$

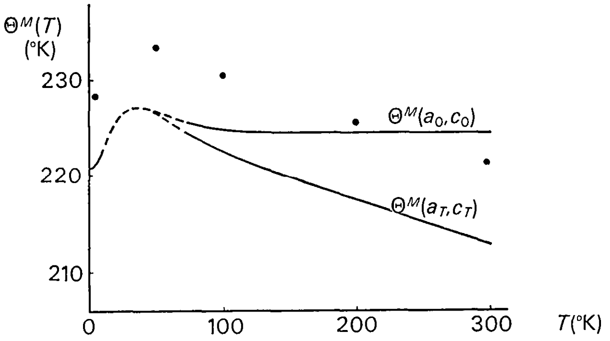

Fig. 1. Temperature dependence of characteristic Debye temperatures for zinc. Full lines: from low- and high-temperature expansions; dashed lines: interpolation; ● $\Theta^M(a_T,c_T)$ from DeWames, Wolfram & Lehman (1965), corrected for the effect of thermal expansion.

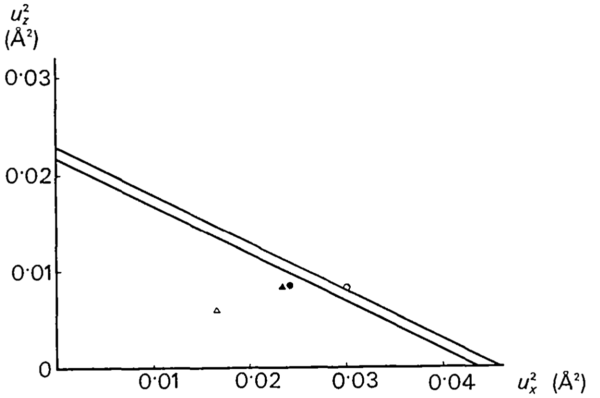

Fig. 2. Comparison of published values for $\langle u_x{}^2\rangle$ and $\langle u_z{}^2\rangle$ at 298°K with the thermodynamic value for $\langle 2u_x{}^2 + u_z{}^2\rangle$. The straight lines correspond to the limits in equation (6). ● DeWames, Wolfram & Lehman (1965); △ Ryba (1960); ▲ Wollan & Harvey (1937); ○ Jauncey & Bruce (1937).

From the series in t equivalent to (2) and (3) and from a graphical interpolation at intermediate temperatures we obtain the values of $\Theta^M(T;\, a_0, c_0)$ shown in Fig. 1. The values of $\Theta^M(T;\, a_T, c_T)$ in Fig. 1 are derived from $\Theta^M(T;\, a_0, c_0)$ by means of the relation

$$\Theta^M(a_T, c_T)/\Theta^M(a_0, c_0) = (a_0/a_T)^{2\gamma_\perp(-2)}\,(c_0/c_T)^{\gamma_\parallel(-2)}\;; \qquad (5)$$

here $\gamma_\perp(-2)$ and $\gamma_\parallel(-2)$ are Grüneisen parameters which can be calculated with the use of thermal expansion and other thermodynamic data (Barron & Munn, 1966). Equation (5) is strictly valid for zinc only above 100°K, but its use at lower temperatures introduces negligible errors.

The estimated errors in Θ^M are ± 2°K at low temparatures, and ± 3°K at intermediate and high temperatures. At low temperatures the errors come mainly from uncertainties in the heat-capacity analysis, but at room temperature constant-volume anharmonic effects may already be appreciable. Study of other constant-volume effects in a variety of solids suggests that for zinc the effect on Θ^M is unlikely to exceed about 30% of the effect due to thermal expansion.

At 298°K we find that $\langle 2u_x^2 + u_z^2\rangle = (0{\cdot}0446 \pm 0{\cdot}0012)$ Å². One of the published sets of values in Table 1 differs widely from this figure, and none of them falls strictly within the limits of error. This is illustrated in Fig. 2, where to be consistent with the thermodynamic result the true values of $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$ (in Å²) must lie between the straight lines

$$2\langle u_x^2\rangle + \langle u_z^2\rangle = 0{\cdot}0446 \pm 0{\cdot}0012\,. \qquad (6)$$

Thermodynamic data alone can tell us no more, and further information is needed to estimate the individual values of $\langle u_x^2\rangle$ and $\langle u_z^2\rangle$.

Table 1. *Values for mean-square atomic displacements along the principal axes of zinc derived from published data, and corresponding equivalent Debye temperatures*

Reference	T (°K)	$\langle u_x{}^2\rangle$ (Å²)	$\langle u_z{}^2\rangle$ (Å²)	$\langle 2u_x{}^2 + u_z{}^2\rangle$ (Å²)	$\Theta^M(a_T,c_T)$ (°K)
Jauncey & Bruce (1937)*	100	0·00329	0·00861	0·0152	223·0
	200	0·00557	0·0158	0·0270	226·3
	298	0·00811	0·0299	0·0461	209·2
	370	0·01064	0·0481	0·0694	189·4
	550	—	0·0785	—	—
Wollan & Harvey (1937)†	85	0·00279	0·00798	0·0136	222·1
	295	0·00836	0·0234	0·0401	223·3
Ryba (1960)†	293	0·00596	0·0165	0·0284	265·6
	673	0·0237	0·0545	0·102	210·4
DeWames, Wolfram & Lehman (1965)‡	298	0·00848	0·0242	0·0412	221·5

* From the intensity of diffuse scattering from single crystals.
† From the temperature dependence of the intensity of Bragg reflexions.
‡ From a theoretical model fitted to neutron diffraction data.

Use of neutron-scattering data

From coherent inelastic scattering of neutrons the frequencies of individual branches of the vibrational spectrum of a solid can be obtained as functions of wave-number. These results must be fitted to a force-constant model before mean-square displacements can be calculated. For zinc several models with short-range forces have been used, and although no such model can be wholly valid (Holas, 1965), reasonable fits have been obtained with most of the experimental dispersion curves (Borgonovi, Caglioti & Antal, 1963; Maliszewski, Rosolowski, Sledziewska & Czachor, 1965; De Wames, Wolfram & Lehman, 1965; Gupta & Dayal, 1966). The chief failing of the short-range-force models is that they do not reproduce the strong dispersion for transverse waves propagating in directions perpendicular to the hexagonal axis with the atoms vibrating parallel to this axis. The models overestimate the frequencies of these modes and consequently overestimate Θ^M by an appreciable amount, since modes of this type contribute quite strongly to the Debye–Waller effect. This can be seen in Fig. 1, where the set of points, obtained from the model of DeWames *et al.* (1965) corrected to the equilibrium strain at each temperature, lies consistently above the true curve obtained thermodynamically.

Modes in which the atoms are vibrating approximately parallel to the hexagonal axis contribute primarily to $\langle u_z^2\rangle$ rather than to $\langle u_x^2\rangle$. This suggests that the shortcomings of the model affect $\langle u_z^2\rangle$ more seriously than $\langle u_x^2\rangle$, and that a reasonable estimate of the true values will be provided by the $\langle u_x^2\rangle$ calculated by DeWames *et al.* and the corresponding $\langle u_z^2\rangle$ consistent with the thermodynamic data. At 298 °K this gives

$$\langle u_x^2\rangle=(0\cdot0085\pm0\cdot0005)\ \text{Å}^2\,,\qquad \langle u_z^2\rangle=(0\cdot0276\pm0\cdot0015)\ \text{Å}^2\,, \quad (7)$$

where the uncertainty in $\langle u_x^2\rangle$ is rather arbitrarily taken as about a fifth of the difference between the value of $\langle 2u_x^2+u_z^2\rangle$ calculated from the model and the value calculated thermodynamically. The ratio $\langle u_z^2\rangle/\langle u_x^2\rangle$ is 3·25, in agreement with the suggestion from Mössbauer-effect measurements that $\langle u_z^2\rangle/\langle u_x^2\rangle\geq2$ (Housley & Nussbaum, 1965).

From the calculations of DeWames *et al.* we can obtain $\langle u_x^2\rangle$ at other temperatures below 298 °K, and extrapolation above 298 °K is straightforward because $\langle u_x^2\rangle$ is already approaching its limiting high-temperature behaviour.* We cannot make direct use of these values for $\langle u_x^2\rangle$ because they refer to a model which is fitted to room-temperature data and does not allow for thermal expansion. There is no wholly satisfactory way of calculating the strain dependence of $\langle u_x^2\rangle$ from thermodynamic data, but an estimate can be obtained from the crude approximation that $\langle u_z^2\rangle$ is affected only by expansion along the hexagonal axis and $\langle u_x^2\rangle$ only by expansion perpendicular to the axis. It then follows that the change in $\langle u_x^2\rangle$ due to altering the lattice parameter a is half the corresponding change in $\langle 2u_x^2+u_z^2\rangle$ and so can be calculated from the strain dependence of Θ^M:

$$\Theta^M(T;\,a_{298},c_T)=\Theta^M(T;\,a_T,c_T)\,(a_T/a_{298})^{2\gamma_\perp(-2)}\,.\quad(8)$$

With this approximation we obtain the values of $\langle u_x^2\rangle$ in Table 2, where the errors include a 50% uncertainty in the strain correction. $\langle u_z^2\rangle$ is then obtained by subtracting $2\langle u_x^2\rangle$ from $\langle 2u_x^2+u_z^2\rangle$.

Table 2. *Mean-square atomic displacements along the principal axes of zinc as functions of temperature*

T (°K)	$\langle u_x^2\rangle$ (Å^2)	$\langle u_z^2\rangle$ (Å^2)	$\langle 2u_x^2+u_z^2\rangle$ (Å^2)
0	0·0020 ± 0·00015	0·0036 ± 0·0003	0·0076 ± 0·0003
50	0·0023 ± 0·0002	0·0050 ± 0·0004	0·0097 ± 0·0003
85	0·0029 ± 0·0003	0·0071 ± 0·0007	0·0129 ± 0·0004
100	0·0033 ± 0·0003	0·0087 ± 0·0008	0·0153 ± 0·0005
200	0·0058 ± 0·0005	0·0175 ± 0·0011	0·0291 ± 0·0007
300	0·0085 ± 0·0005	0·0278 ± 0·0015	0·0446 ± 0·0012
370	0·01055 ± 0·0009	0·0352 ± 0·0020	0·0563 ± 0·0016
400	0·0115 ± 0·0010	0·0390 ± 0·0030	0·0620 ± 0·0019
500	0·0147 ± 0·0016	0·0513 ± 0·005	0·0807 ± 0·0032
550	0·0164 ± 0·0022	0·0576 ± 0·006	0·0904 ± 0·0038
600	0·0184 ± 0·0028	0·064 ± 0·007	0·101 ± 0·005
673	(0·022)*	(0·076)*	(0·120)*

* Definite limits of error cannot be ascribed so near to the melting point (692 °K).

Comparison with X-ray data

The available X-ray data are listed in Table 1. The pioneer studies of Brindley (1936) on the anisotropy of the atomic scattering factors f_T employed inadequate theories and for this reason his values for the mean-square displacements are not quoted (they are in fact seriously in error). The best-established values based on X-ray measurements appear to be those obtained at room temperature by Jauncey & Bruce (1937) from a study of diffuse scattering (see James (1948) for a critical discussion), since these were shown also to give a good account of Brindley's measurements. It is satisfactory that these values are in fair agreement with Table 2. On the other hand, the temperature dependence of $\langle u_z^2\rangle$ found by Jauncey & Bruce is in much poorer agreement.

Of the two direct measurements of Debye–Waller factors (from the temperature dependence of Bragg intensities), those of Ryba (1960) appeared originally in an unpublished thesis, and the values quoted in Table 1 are taken from *International Tables for X-ray Crystallography* (1962). Although his absolute values at room temperature differ markedly from those of Wollan & Harvey (1937), the ratio $\langle u_z^2\rangle/\langle u_x^2\rangle$ is about the same (2·75) in each set of measurements. Remarking on this, *International Tables* suggested that the discrepancy might have arisen because 'Wollan & Harvey scaled their intensities to correspond with the

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* If an equivalent Debye temperature $\Theta_\perp{}^M(T)$ is defined for $\langle u_x{}^2\rangle$, it is found to be effectively constant for $T\gtrsim298$ °K.

early absolute data which are probably incorrect'. Rather surprisingly, however, it is now apparent that Wollan & Harvey's final results are by far the closer to the true values.

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The Crystal Structure of Beraunite

BY L. FANFANI AND P. F. ZANAZZI

Istituto di Mineralogia dell'Università di Perugia, Italy

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Beraunite, a basic hydrated iron phosphate, crystallizes in the monoclinic space group $C2/c$ with $a_0=20{\cdot}646\pm0{\cdot}005$, $b_0=5{\cdot}129\pm0{\cdot}007$, $c_0=19{\cdot}213\pm0{\cdot}005$ Å, $\beta=93°37'\pm4'$ and $Z=8$. Crystallochemical considerations and a chemical analysis of the ratio Fe^{II}/Fe^{III} suggest the formula

$$Fe^{II}_{0{\cdot}5}\,Fe^{III}_{2{\cdot}5}\,(OH)_{2{\cdot}5}\,(PO_4)_2.3H_2O$$

as the most representative for the mineral.

The intensities from $h0l$ to $h4l$ were collected by Weissenberg techniques. The analysis of the crystal structure was carried out by interpretation of the Patterson function and by three-dimensional Fourier syntheses. An isotropic refinement gave a final R index of 0·066 for 898 measured reflexions.

Fe and P show the usual octahedral and tetrahedral coordination respectively. The average bond length is 2·01 Å for Fe–O and 1·54 Å for P–O.

The crystal structure can be outlined as a three-dimensional framework of Fe and P coordination polyhedra with empty channels along the screw axes, where free water molecules are located. The existence of thick sheets normal to **a** explains the good cleavage {100}.

Introduction

Beraunite is a hydrated basic phosphate of iron, which occurs in secondary iron deposits and as an alteration product of primary phosphates in pegmatites.

The mineral was first found by A. Breithaupt in 1841. Bořicky (1867) assigned it to the monoclinic system from morphological studies and gave the first chemical analysis. Later Frondel (1949), on the basis of a small but significant content of ferrous iron revealed by the analysis, suggested that beraunite, like dufrenite and rockbridgeite, is properly a basic phosphate of both divalent and trivalent iron with a ratio Fe/P of 5:4. Beraunite was also studied from morphological, optical and chemical points of view under the name eleonorite (Nies, 1877; Streng, 1881; König, 1890); Fischer in 1956