

Mean Square Vibration Amplitudes in Zinc

D. W. Field

Department of Physics, University of Adelaide; present address:
Department of Physics, Queensland Institute of Technology,
George Street, Brisbane, Qld 4000.

Abstract

The structure factors of 98 independent reflections have been determined by measurement of the integrated intensities for X-ray diffraction from a zinc single crystal at 295 K. The mean square vibration amplitudes found for the two principal directions are compared with other recent measurements. The X-ray Debye temperature determined from the data is 207 ± 3 K at 295 K.

A measurement of the intensities of X-rays diffracted from the hexagonal close-packed metal zinc has been carried out at room temperature and the mean square thermal vibration amplitudes in the two principal directions have been determined. No previous comprehensive single-temperature X-ray diffraction study has been reported in the literature.

A single cylindrical crystal of zinc was grown by sucking molten zinc into a thin-walled (0.01 mm) glass capillary. The diameter of the crystal was measured to be 0.3172 ± 0.0048 mm. The crystal was oriented about a non-symmetry $[101]$ axis, which avoided major multiple diffraction errors and which coincided almost exactly with the cylinder axis, thus obviating anisotropic absorption corrections. Integrated intensities were measured for reflections up to $(\sin \theta)/\lambda \sim 1.28 \text{ \AA}^{-1}$ on a Stoe two-circle automatic diffractometer operating in the ω - 2θ mode. A graphite monochromator was used to obtain the $\text{MoK}\alpha$ wavelength used.

Zinc crystallizes in a hexagonal close-packed structure, space group $P6_3/mmc$ (No. 194), with two atoms per unit cell at sites of non-centric symmetry $\bar{6}m2$. The only special extinction condition is such that, for reflections with $h-k = 3n$, only those with l even are allowed. The coordination is such that each atom has six nearest neighbours at 2.66 \AA in the $\langle 100 \rangle$ directions and six others at 2.91 \AA . The structure factor in the absence of any crystal-field effects may be written

$$F(hkl) = A(hkl) \exp[-\{\beta_{11}(h^2 + k^2 + hk) + \beta_{33}l^2\}], \quad (1)$$

where

$$A(hkl) = \sum_{j=1}^2 f_j(hkl) \cos\{2\pi(hx_j + ky_j + lz_j)\},$$

β_{11} and β_{33} are the two independent anisotropic temperature factor coefficients and the other symbols have their usual meanings. Mean square vibration amplitudes for the principal a and c directions may be determined from β_{11} and β_{33} as (e.g.

Willis and Pryor 1975)

$$\langle u_a^2 \rangle = \frac{3}{4} \beta_{11} a^2 / 2\pi^2, \quad \langle u_c^2 \rangle = \beta_{33} c^2 / 2\pi^2.$$

The measured intensities were corrected for Lorentz-polarization, absorption, anomalous dispersion and thermal diffuse scattering effects, the last by the anisotropic first-order method of Rouse and Cooper (1969) using the elastic constants of Alers and Neighbours (1958). Relativistic scattering factors $f(hkl)$ were calculated from the nine-parameter-fit tables of Doyle and Turner (1968). The lattice constants used throughout were $a = 2.6648 \text{ \AA}$ and $c = 4.9467 \text{ \AA}$, taken from Brown (1954). A calculation was performed of the angular position of every other reciprocal lattice point with respect to the reflecting sphere when each reciprocal lattice point was exactly on the sphere, in order to determine the possible effect of simultaneous diffraction. Where strong simultaneous diffraction was possible, measurements were deleted if they differed significantly from the mean of symmetry-related reflection intensities.

Values of the temperature-factor coefficients were obtained by a least squares fit of the structure-factor expression (1) to the measured intensities. Extinction was present, and the first nine reflections were neglected in the analysis for this reason. A discrepancy index R was calculated for the present data, with the definition

$$R = \left(\sum_{i=10}^{98} \alpha_i^{-2} (F_{oi} - F_{ci})^2 \right)^{\frac{1}{2}} / \left(\sum_{i=10}^{98} \alpha_i^{-2} F_{oi}^2 \right)^{\frac{1}{2}},$$

where F_{oi} and F_{ci} are the i th observed and calculated structure factors respectively and α_i is the standard error for the i th structure factor. The value of R obtained was 2.3%. An X-ray Debye temperature θ_D was also calculated by the usual means from the mean square vibration amplitude averaged over all directions.

Table 1. Mean square vibration amplitudes and Debye temperatures for zinc

Source ^A	T (K)	θ_D (K)	$\langle u_a^2 \rangle$ (\AA^2)	$\langle u_c^2 \rangle$ (\AA^2)	ε
1	295	—	0.0084	0.017	2.0
2	296	—	0.0076	0.0231 ± 0.0016	3.0
3	298	—	0.00973	0.0278	2.85
4	298	213 ± 3	0.0085 ± 0.0005	0.0276 ± 0.0015	3.25
5	300	206 ± 3	0.0112 ± 0.0003	0.0259 ± 0.001	2.31 ± 0.15
6	295	207 ± 3	0.01028 ± 0.00022	0.02582 ± 0.00022	2.51 ± 0.08

^A References: 1, Housley and Nussbaum (1965); 2, Kundig *et al.* (1965); 3, DeWames *et al.* (1965); 4, Barron and Munn (1967); 5, Skelton and Katz (1968); 6, Present work.

The values obtained for β_{11} and β_{33} from the analysis were:

$$\beta_{11} = 0.0381 \pm 0.0007, \quad \beta_{33} = 0.0208 \pm 0.0001.$$

The results for θ_D , $\langle u_a^2 \rangle$, $\langle u_c^2 \rangle$ and $\varepsilon = \langle u_c^2 \rangle / \langle u_a^2 \rangle$ from this experiment and from other recent measurements or calculations for temperatures near 295 K are compared in Table 1.

Measurements made prior to 1965 are summarized in the paper by Barron and Munn (1967). Mostly they differ considerably from the results of the two most

recent experiments. Of the data reviewed in Table 1, those of Housley and Nussbaum (1965) and Kundig *et al.* (1965) were obtained from measurements of the Mossbauer effect. The values attributed to DeWames *et al.* (1965) were calculated by Kundig *et al.* from the data presented in the paper by DeWames *et al.* on a 'modified axially symmetric' lattice dynamical model of zinc. The values of Barron and Munn (1967) were derived from thermodynamic data and the DeWames *et al.* model, while those of Skelton and Katz (1968) were obtained from a study of the temperature dependence of the X-ray diffraction intensities.

As can be seen from Table 1, the values determined from the Mossbauer experiments are less reliable or accurate than the X-ray measurements. This is supposed (Skelton and Katz 1968) to be due to a greater binding force between the impurity (cobalt) and host atoms than between the host zinc atoms themselves. The two most recent X-ray measurements agree excellently for all values except that for $\langle u_a^2 \rangle$, for which, nevertheless, both are larger than the model values. The individual mean square amplitudes of Barron and Munn are based on their estimate of $\langle u_a^2 \rangle$ from the calculation of DeWames *et al.*, an estimate differing from that of Kundig *et al.* from the same calculation. However, Barron and Munn have derived from thermodynamic data alone a value for $2\langle u_a^2 \rangle + \langle u_c^2 \rangle$ of $0.0446 \pm 0.0012 \text{ \AA}^2$ which is in excellent agreement with the present measurement of $0.0464 \pm 0.0007 \text{ \AA}^2$.

Acknowledgments

This work was supported in part by the Australian Research Grants Committee. I am grateful to B. Bednarz for stimulating discussion.

References

- Alers, G. A., and Neighbours, J. R. (1958). *J. Phys. Chem. Solids* **7**, 58–64.
- Barron, T. H. K., and Munn, R. W. (1967). *Acta Crystallogr.* **22**, 170–3.
- Brown, J. R. (1954). *J. Inst. Met.* **83**, 49–52.
- DeWames, R. E., Wolfram, T., and Lehman, G. W. (1965). *Phys. Rev.* **138**, A717–28.
- Doyle, P. A., and Turner, P. S. (1968). *Acta Crystallogr. A* **24**, 390–7.
- Housley, R. M., and Nussbaum, R. H. (1965). *Phys. Rev.* **138**, A753–4.
- Kundig, W., Ando, K., and Bommel, H. (1965). *Phys. Rev. A* **139**, 889–91.
- Rouse, K. D., and Cooper, M. J. (1969). *Acta Crystallogr. A* **25**, 615–21.
- Skelton, E. F., and Katz, J. L. (1968). *Phys. Rev.* **171**, 801–8.
- Willis, B. T. M., and Pryor, A. W. (1975). 'Thermal Vibrations in Crystallography' (Cambridge Univ. Press).

