

## Debye-Waller Factors of $\alpha$ -Iron and Sodium

Jyoti Prakash, L. P. Pathak and M. P. Hemkar

Department of Physics, University of Allahabad, Allahabad-2, India.

### Abstract

The Debye-Waller exponents for  $\alpha$ -iron and sodium are calculated at different temperatures using the Behari-Tripathi (1969) modified angular-force model, which takes into account the effect of electron-ion interactions. The computation uses Blackman's sampling technique. The results are compared with existing experimental data. They are found to agree satisfactorily up to a certain temperature, above which they become progressively lower than the corresponding experimental values.

### Introduction

The Debye-Waller factor  $\exp(-2W)$  expresses the effect of thermal motion on the wave intensity of scattered X-rays and on the results of Mössbauer effect experiments. The quantity  $2W$  (the so-called Debye-Waller exponent) is directly related to the mean square displacement of the atoms in the crystal. It has been correlated with a number of phenomena in solid state physics such as neutron scattering, electrical conductivity and the melting of crystals. The Debye-Waller exponent has usually been calculated by applying the Debye model to the lattice vibrations of a crystal, and is expressed as a known function of the characteristic temperature  $\Theta$ . This method of calculation has been shown to be inadequate (Herbstein 1961) and the Debye parameters it yields are in poor agreement with those obtained from calorimetric and other experimental data. This result is not surprising since the actual vibration spectrum of a solid is far from being of the Debye type. It is therefore of interest to compute the Debye-Waller factor by using a more realistic lattice dynamical model than the Debye model.

The past decade has seen considerable development, both theoretically and experimentally, in the lattice dynamics of crystals, with a corresponding increase of interest in the study of the Debye-Waller factor. Flinn *et al.* (1961) reported a determination of the Debye-Waller factor for copper from X-ray intensity measurements from 4 to 500 K and interpreted their results in terms of a central-force model with first- and second-nearest neighbour interactions. A similar application to aluminium was made by Flinn and McManus (1963). Dewames *et al.* (1963) have discussed, in the light of the experiments of Flinn *et al.*, the Debye-Waller factors for copper as predicted by various force models. The Debye-Waller factor has also been worked out by Barron and Smith (1966) and by Feldman (1969) for nickel. The former used the Birgeneau *et al.* (1964) fourth-nearest neighbour model and calculated the Debye-Waller factor at  $T = 300$  K, while the latter used a fourth-nearest neighbour

Begbie–Born model, a fifth-nearest neighbour axially symmetric model and a first-nearest neighbour Begbie–Born model.

In the present paper, we report a calculation of the temperature dependence of the Debye–Waller factors for  $\alpha$ -iron and sodium, both b.c.c. metals, by using the modified noncentral force model proposed by Behari and Tripathi (1969). This model takes into account Clark *et al.* (1964) type angular forces and Sharma and Joshi (1963) type volume forces. It has been found that this model offers a fairly reasonable account of the lattice dynamical behaviour of copper (Behari and Tripathi 1969) and of many other cubic metals (Behari and Tripathi 1970; Gupta and Tripathi 1971; Behari 1972; Bose *et al.* 1972). In recent studies, we have utilized this model to explain many other solid state phenomena in a number of cubic metals (Prakash and Hemkar 1973, 1974a, 1974b; Prakash *et al.* 1974).

### Theory

In the harmonic approximation, the Debye–Waller exponent is related to the mean mean-square displacement of the atoms and is given by (James 1954)

$$2W = \langle |\mathbf{K} \cdot \mathbf{u}(n)|^2 \rangle, \quad (1)$$

where  $\mathbf{u}(n)$  is the displacement of the  $n$ th atom and  $\mathbf{K}$  is the difference between the initial and final wave vectors of the wave. From a knowledge of both the time dependence of the atomic displacements and the average energy of the phonon in mode  $\mathbf{q}$ , the amplitude  $U_{\mathbf{q}}$  of mode  $\mathbf{q}$  can be written as

$$|U_{\mathbf{q}}|^2 = (n_{\mathbf{q}} + \frac{1}{2}) \hbar / mN\omega_{\mathbf{q}}. \quad (2)$$

Here  $m$  is the mass of the atom,  $N$  is the total number of unit cells in the crystal,  $\omega_{\mathbf{q}}$  is the frequency of the normal mode of wave vector  $\mathbf{q}$ , and  $n_{\mathbf{q}}$  is the average occupation number of the  $\mathbf{q}$  lattice mode and is given by

$$n_{\mathbf{q}} = \{ \exp(\hbar\omega_{\mathbf{q}}/kT) - 1 \}^{-1}, \quad (3)$$

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. With the help of equations (1) and (2), we obtain

$$2W = (\hbar/mN) \sum_{\mathbf{q},j} (\mathbf{K} \cdot \mathbf{e}_{\mathbf{q},j})^2 (n_{\mathbf{q},j} + \frac{1}{2}) / \omega_{\mathbf{q},j}, \quad (4)$$

where  $j$  is the polarization index and  $\mathbf{e}_{\mathbf{q},j}$  is the polarization vector of the  $(\mathbf{q}, j)$  lattice mode. The summation over  $\mathbf{q}$  extends over all normal vibrations of the crystal.

For a monatomic cubic crystal, the polarization factor  $(\mathbf{K} \cdot \mathbf{e}_{\mathbf{q},j})^2$  may be replaced by its average value outside the summation, and equation (4) then reduces to

$$2W = \frac{8\pi^2 \hbar}{3mN} \left( \frac{\sin \theta}{\lambda} \right)^2 \sum_{\mathbf{q},j} \frac{1}{\omega_{\mathbf{q},j}} \coth \left( \frac{\hbar\omega_{\mathbf{q},j}}{2kT} \right), \quad (5)$$

where  $\theta$  is the glancing angle of incidence and  $\lambda$  the wavelength of the incident wave.

### Numerical Computation

We have evaluated the Debye–Waller exponent at different temperatures for  $\alpha$ -iron and sodium from equation (5) by using Blackman's technique to sample the

frequencies for a discrete subdivision in wave vector space. For this purpose, it was necessary to determine the characteristic frequencies at a suitable number of points in an irreducible section of the first Brillouin zone. In order to limit the amount of computation and yet avoid too many approximations, we have considered an evenly distributed mesh of 1000 wave vectors in the first Brillouin zone. From Born's cyclic boundary condition and considerations of lattice symmetry, these 1000 points reduce to 47 (including the origin) lying within 1/48th part of the Brillouin zone. The 3000 frequencies corresponding to the 1000 points in the zone were obtained from the solution of the Behari-Tripathi secular equation for a b.c.c. lattice. These frequencies represent the complete vibration spectrum. In evaluating the summation in equation (5), we divided the whole vibration spectrum into a number of frequency intervals and assigned appropriate weights to each interval. The term corresponding to  $q = 0$  was omitted from the summation as it refers to a nonvibrating lattice in which the Debye-Waller exponent vanishes. The numerical values for the relevant elastic constants, the density and the lattice parameter used in the calculations are given in Table 1.

Table 1. Physical constants for  $\alpha$ -iron and sodium

Metal	Elastic constants ( $10^{10}$ Pa*)			Lattice parameter ( $10^{-10}$ m)	Density ( $\text{g cm}^{-3}$ )
	$C_{11}$	$C_{12}$	$C_{44}$		
$\alpha$ -Iron†	23.350	13.550	11.800	7.87	2.86
Sodium‡	0.808	0.664	0.586	1.0014	4.24

\* Note that 1 Pa (pascal)  $\equiv$  10 dyn  $\text{cm}^{-2}$ .

† Constants obtained from Rayne and Chandrasekhar (1961).

‡ Constants obtained from Daniels (1960) and Sharma and Joshi (1963).

### Comparison with Experiments

Comparison of the calculated and experimental Debye-Waller factors may be made in terms of a temperature parameter  $Y$  defined by

$$Y = \log_{10} e (\lambda/\sin \theta)^2 (2W_{T_0} - 2W_T), \quad (6)$$

where  $2W_T$  and  $2W_{T_0}$  are the values of the Debye-Waller exponent for temperatures  $T$  and  $T_0$  respectively. This quantity is independent of  $\lambda$  and  $\theta$ . Experimental values of  $Y$  are directly accessible from the measured X-ray intensities of Bragg reflections. The ratio of the measured X-ray intensities  $I_T$  and  $I_{T_0}$  of a given Bragg reflection at temperatures  $T$  and  $T_0$  respectively are given by

$$I_T/I_{T_0} = \exp(-2W_T)/\exp(-2W_{T_0}), \quad (7)$$

and hence we have

$$Y = (\lambda/\sin \theta)^2 \log_{10}(I_T/I_{T_0}). \quad (8)$$

The calculated values of  $Y$  were evaluated from equation (6) with the help of equation (5). The results for  $\alpha$ -iron and sodium at different temperatures with reference to a standard temperature are plotted in Fig. 1 together with experimental values.

**$\alpha$ -Iron**

The temperature variation of the Debye–Waller factor for  $\alpha$ -iron has been studied through both X-ray diffraction (Ilyine and Kritskaya 1955; Haworth 1960; Herstein and Smuts 1963) and  $\gamma$ -ray resonant absorption experiments (Debrunner and Morrison 1964). Haworth's measurements were made over the classical high-temperature range and so are most suitable for the present comparison with theory. Unfortunately, these results possess a large scatter which Haworth attributed to statistical changes in the distribution of the reflected particles. These results are shown in Fig. 1 for  $T_0 = 286$  K along with the data of Debrunner and Morrison. The calculated results show satisfactory agreement with the experimental values only up to about 600 K, but above this temperature the observed decrease in the intensity of reflections becomes greater than that expected theoretically.

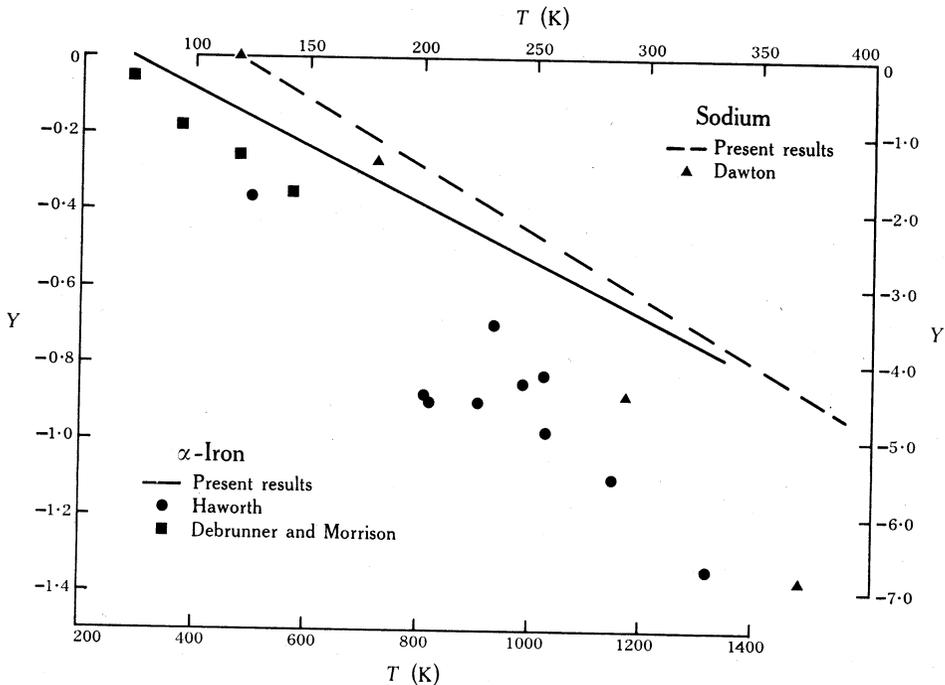


Fig. 1. Split diagram showing the temperature variation of the Debye–Waller temperature parameter  $Y$  for  $\alpha$ -iron (with  $T_0 = 286$  K) and sodium (with  $T_0 = 117$  K). The axes at the bottom left-hand corner of the graph refer to  $\alpha$ -iron and those at the top right-hand corner refer to sodium.

**Sodium**

The effect of temperature on the intensities of X-ray reflections from a single crystal of sodium was studied experimentally by Dawton (1937) in the temperature range 117–368 K. He measured intensity ratios  $I_{117}/I_T$  at three different temperatures 180, 291 and 368 K for a chilled crystal. These ratios were found for the (400), (310), (220), (200) and (110) reflections, and Dawton recommended the (400), (310) and (220) reflections as being the most reliable. The average value of

$$(\lambda/\sin \theta)^2 \log_{10}(I_T/I_{T_0})$$

for the above three planes for  $T_0 = 117$  K has been plotted against temperature in Fig. 1. The agreement between the theoretical and experimental values of  $Y$  is good only in the lower temperature range. For temperatures above 200 K, the experimental values are higher than the theoretical ones, and the discrepancy gradually increases with the rise of temperature.

### Discussion

The present investigation shows that the Debye-Waller temperature parameter  $Y$ , as obtained from the modified angular-force model of Behari and Tripathi (1969) offers a satisfactory explanation for the observed temperature variation of the X-ray intensities of Bragg reflections below a certain temperature. However, at higher temperatures, the experimental values of  $2W$  are consistently higher than the theoretical, and this discrepancy increases with the temperature. Such discrepancies at high temperatures are not unexpected, and may be attributed to the neglect of lattice expansion (Zener and Bilinsky 1936) and other anharmonic effects (Hahn and Ludwig 1961; Cowley 1963; Maradudin and Flinn 1963; Slater 1965; Wolfe and Goodman 1969). Anharmonic contributions vary mostly as the square of the absolute temperature and become predominant at high temperatures. Also the elastic constants vary with temperature, e.g. in the case of sodium,  $C_{44}$  changes by almost 30%; but we have taken no account of this in the present calculations.

The difference between the calculated and experimental values of the temperature factor can be understood from the fact that there is a decrease in the characteristic frequency at high temperatures owing to thermal expansion. This effect depends upon the Grüneisen parameter which varies with temperature. Several attempts (Owen and Williams 1947; Spreadborough and Christian 1959; Haworth 1960) have been made to estimate this effect in terms of the Grüneisen parameter, but a detailed discussion has not been possible. At higher frequencies,  $2W$  depends on the lattice frequencies as the summation over  $q, j$  of  $\omega_{q,j}^{-2}$ . The lower-frequency peaks in the frequency distribution therefore contribute much more to the value of  $2W$  than do the higher-frequency peaks. Studies by various workers on the lattice dynamics of metals show that the frequency spectrum can be approximated by two peaks, of which the lower-frequency one usually covers the much larger area. It is this peak that largely governs the intensity of X-ray lines. Since the value and temperature variation of the Grüneisen parameter for this peak are not known, no quantitative assessment of the effect of thermal expansion on the X-ray intensities is possible. It seems that more elaborate studies are needed to relate this parameter to anharmonicity in lattice vibrations. However, as things now stand, it emerges from the present study that the temperature variation of the Debye-Waller factors of  $\alpha$ -iron and sodium can be explained satisfactorily by the Behari-Tripathi lattice dynamical model.

### Acknowledgments

The authors record their sincere thanks to Professor Vachaspati, Head of the Physics Department, University of Allahabad, for encouragement and for providing facilities for the study. One of them (J.P.) also wishes to thank the Council of Scientific and Industrial Research, India, for the award of a Senior Research Fellowship.

## References

- Barron, H. W. T., and Smith, T. (1966). *J. Phys. Chem. Solids* **27**, 1951.
- Behari, J. (1972). *Indian J. Phys.* **46**, 315.
- Behari, J., and Tripathi, B. B. (1969). *Phys. Lett. A* **29**, 313.
- Behari, J., and Tripathi, B. B. (1970). *Aust. J. Phys.* **23**, 311.
- Birgeneau, R. J., Cordes, J., Dolling, G., and Woods, A. D. B. (1964). *Phys. Rev.* **136**, A1359.
- Bose, G., Gupta, H. C., and Tripathi, B. B. (1972). *J. Phys. F* **2**, 426.
- Clark, B. C., Gazis, D. C., and Wallis, R. F. (1964). *Phys. Rev.* **134**, A1486.
- Cowley, R. A. (1963). *Advan. Phys.* **12**, 421.
- Daniels, W. B. (1960). *Phys. Rev.* **119**, 1246.
- Dawton, R. H. V. M. (1937). *Proc. Phys. Soc. London* **49**, 294.
- Debrunner, P., and Morrison, R. J. (1964). *Rev. Mod. Phys.* **36**, 463.
- Dewames, R. T., Wolfram, T., and Lehman, G. W. (1963). *Phys. Rev.* **131**, 528.
- Feldman, J. L. (1969). *J. Phys. Chem. Solids* **30**, 367.
- Flinn, P. A., and McManus, G. M. (1963). *Phys. Rev.* **132**, 2458.
- Flinn, P. A., McManus, G. M., and Rayne, J. A. (1961). *Phys. Rev.* **123**, 809.
- Gupta, H. C., and Tripathi, B. B. (1971). *Indian J. Pure Appl. Phys.* **9**, 1034.
- Hahn, H., and Ludwig, W. (1961). *Z. Phys.* **161**, 404.
- Haworth, C. W. (1960). *Phil. Mag.* **5**, 1229.
- Herbstein, F. H. (1961). *Advan. Phys.* **10**, 313.
- Herbstein, F. H., and Smuts, J. (1963). *Phil. Mag.* **8**, 367.
- Ilyine, V. A., and Kritskaya, V. K. (1955). Proc. 4th Symp. on Metallography and Physics of Metals, p. 294.
- James, R. W. (1954). 'The Optical Principles of the Diffraction of X-rays', p. 193 (Bell and Sons: London).
- Maradudin, A. A., and Flinn, P. A. (1963). *Phys. Rev.* **129**, 2529.
- Owen, E. A., and Williams, R. W. (1947). *Proc. Roy. Soc. London A* **188**, 509.
- Prakash, J., and Hemkar, M. P. (1973). *J. Phys. Soc. Jap.* **34**, 1583.
- Prakash, J., and Hemkar, M. P. (1974a). *Aust. J. Phys.* **27**, 129.
- Prakash, J., and Hemkar, M. P. (1974b). *J. Phys. F* **4**, 1015.
- Prakash, J., Pathak, L. P., and Hemkar, M. P. (1974). *J. Phys. F* **4**, 1107.
- Rayne, J. A., and Chandrasekhar, B. S. (1961). *Phys. Rev.* **122**, 1714.
- Sharma, P. K., and Joshi, S. K. (1963). *J. Chem. Phys.* **39**, 2633.
- Slater, L. S. (1965). *Advan. Phys.* **14**, 1.
- Spreadborough, J., and Christian, J. W. (1959). *Proc. Phys. Soc. London* **74**, 609.
- Wolfe, G. A., and Goodman, B. (1969). *Phys. Rev.* **178**, 1171.
- Zener, C., and Bilinsky, S. (1936). *Phys. Rev.* **50**, 101.