Debye–Waller Factors of α-Iron and Sodium. II*
Willis's Anharmonic Theory

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Abstract

An application of Willis's anharmonic theory has been made to improve the earlier calculations of the Debye–Waller factors of α-iron and sodium reported in Part I, and to estimate the effect of including anharmonic terms in the crystal potential. The calculations have been compared with the existing experimental data in terms of the Debye–Waller factor temperature parameter Y. The agreement between the calculated values and the experimental results is now shown to be quite good over a wide range of temperature.

Introduction

Results of previous calculations of the Debye–Waller factors of α-iron and sodium reported in Part I (Prakash *et al.* 1975) agreed well with the experimental observations only up to a certain temperature, above which the theoretical values were found to be lower than the experimental data. The most likely reason for this discrepancy appears to be the neglect of anharmonic effects, which become significant at higher temperatures, as shown by Hahn and Ludwig (1961), Krivoglaz and Tekhonova (1961), Cowley (1963), Maradudin and Flinn (1963) and Kashiwase (1965). Experimental evidence in support of such a modified treatment is due to Steyart and Taylor (1964), Rouse *et al.* (1968) and Cooper *et al.* (1968).

Hahn and Ludwig (1961) studied the effect of anharmonic vibration on the thermal scattering of X-rays from crystals for temperatures above the Debye temperature. In their theory, the anharmonic effect was given in terms of a temperature-dependent dispersion relation instead of the temperature-independent dispersion relation which is used in the usual formula for X-ray thermal scattering by crystals. Maradudin and Flinn (1963) considered a monatomic crystal with atoms arrayed at lattice points of a cubic Bravais lattice, and they obtained anharmonic contributions to the Debye–Waller factor that were proportional to both the square and cube of the absolute temperature in the classical limit. Their calculations are extremely lengthy, and nowhere was a comparison with experiment made. More recently, Willis (1969) adopted the fashionable approach to the problem by treating the crystal as an Einstein solid, in which each atom vibrates in a potential field which is unaffected by the motion of the neighbouring atoms. He extended this analysis to crystals with rocksalt, diamond and fluorite type structures, and he obtained good agreement with experiments in KCl and BaF_2. His theory has further been applied by our group (Chandra *et al.* 1972; Prakash *et al.* 1973) to investigate the effect of lattice

anharmonicity on the Debye–Waller factors of KBr and NaF respectively, and it has been found to show fairly good agreement with experiment. In the present paper, we have applied the same technique to the cubic metals α-iron and sodium. The interest in the present calculations arises from the fact that experimental values for the Debye–Waller factor temperature parameter Y were found to be considerably higher than the theoretical harmonic values reported in Part I.

Theory

From the kinematic theory of diffraction, the X-ray scattering amplitude for the scattering of X-rays from a monatomic crystal is proportional to

$$A(Q) = \sum_{l} f \exp[iQ.\{r(l)+u(l)\}], \tag{1}$$

where Q is the scattering vector ($Q = 4\pi\lambda^{-1}\sin\theta$, λ being the wavelength of the X-rays), f is the X-ray atomic scattering factor of the atom at rest, $r(l)$ is the radius vector defining the equilibrium position of the lth atom and $u(l)$ is the displacement of the lth atom from its equilibrium position. The summation is understood to extend over all N atoms of the solid.

The differential scattering cross section $d\sigma/d\Omega$, representing the intensity of scattering into unit solid angle for unit incident beam, is given by $\langle AA^* \rangle$, that is,

$$d\sigma/d\Omega = \sum_{l}\sum_{l'} ff' \exp[iQ.\{r(l)-r(l')\}]$$

$$\times \langle\exp[iQ.\{u(l)-u(l')\}]\rangle. \tag{2}$$

The angle brackets $\langle\ \rangle$ represent the average value over a period of time which is longer than the period of the vibration of the atom, and the displacements $u(l)$ are time dependent. In the classical or high-temperature limit, this time average is evaluated as an ensemble average using

$$\langle\exp[iQ.\{u(l)-u(l')\}]\rangle$$

$$= \frac{\iiint\ldots\int \exp[-V/k_BT]\exp[iQ.\{u(l)-u(l')\}]\,dx_1\,dx_2\,dx_3\ldots dx_{3N}}{\iiint\ldots\int \exp[-V/k_BT]\,dx_1\,dx_2\,dx_3\ldots dx_{3N}}, \tag{3}$$

where V and k_B are the potential energy of the total system of coupled oscillators and the Boltzmann constant respectively, and the integration is carried out over the $3N$ cartesian coordinates dx_i of the N atoms in the crystal. The Debye–Waller factor is related to the differential cross section for Bragg scattering $(d\sigma/d\Omega)_0$, and is given by those terms in equation (3) which are independent of l and l'. Thus the effect of thermal motion on the Bragg intensity is equivalent to multiplying the scattering amplitude of the lth atom by the temperature factor $T(Q)$, defined by

$$T(Q) = \exp\{-W(Q)\} = \langle\exp\{iQ.u(l)\}\rangle. \tag{4}$$

In the harmonic approximation, the average $\langle\exp\{iQ.u(l)\}\rangle$ obeys a gaussian distribution, so that we have

$$2W = \langle\{Q.u(l)\}^2\rangle. \tag{5}$$

However, anharmonicity introduces additional terms in W which are of higher order than quadratic in Q. For an Einstein solid, we can obtain $\langle \exp\{iQ \cdot u(l)\} \rangle$ by weighting each possible value of $\exp\{iQ \cdot u(l)\}$ by its thermodynamic probability, using the equation

$$\langle \exp\{iQ \cdot u(l)\} \rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\{-V/k_B T\} \exp\{iQ \cdot u(l)\}\, du_1\, du_2\, du_3}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\{-V/k_B T\}\, du_1\, du_2\, du_3}, \quad (6)$$

where u_1, u_2 and u_3 are the cartesian coordinates of the displacement $u(l)$, and V is the potential energy of the lth atom vibrating as an anharmonic oscillator in the average force field of its neighbours. The temperature factor $T(Q)$ can be reduced to the standard form by expanding the potential energy with the help of Taylor's theorem in terms of the coordinates u_1, u_2 and u_3. In the harmonic approximation, the potential expansion terminates at the quadratic and is of the form

$$V = V_0 + \tfrac{1}{2}\alpha(u_1^2 + u_2^2 + u_3^2), \quad (7)$$

where the parameter α is related to the mean square displacement $\langle u^2(l) \rangle$ of the atom in this potential (which is same in all directions) by

$$\alpha = k_B T / \langle u^2(l) \rangle. \quad (8)$$

Anharmonic contributions to V are represented by adding higher-order terms to the right-hand side of equation (7). These anharmonic terms are either isotropic or anisotropic. By considering the potential expansion up to quartic terms, a general expression for the potential of the lth atom in a cubic crystalline field is given by

$$V(u_1, u_2, u_3) = V_0 + \tfrac{1}{2}\alpha r^2 + \beta u_1 u_2 u_3 + \gamma r^4 + \delta(u_1^4 + u_2^4 + u_3^4 - \tfrac{3}{5}r^4). \quad (9)$$

Here $r^2 = u_1^2 + u_2^2 + u_3^2$ and α, β, γ and δ are the potential parameters. For a cubic monatomic lattice with $m3m$ symmetry, we have $\beta = 0$ and hence

$$V = V_0 + \tfrac{1}{2}\alpha r^2 + \gamma r^4 + \delta(u_1^4 + u_2^4 + u_3^4 - \tfrac{3}{5}r^4). \quad (10)$$

The thermal expansion is taken into account by assuming the potential parameters to vary with temperature in accordance with

$$\alpha/\alpha_0 = \gamma/\gamma_0 = \delta/\delta_0 = (1 - 2\gamma_G \chi T), \quad (11)$$

where α_0, γ_0 and δ_0 are the temperature-independent parameters, γ_G is the Grüneisen parameter and χ is the volume expansion coefficient.

If the displacement $u(l)$ is such that the anharmonic terms in equation (10) are small compared with $k_B T$, we can write

$$\exp\{-V(u_1, u_2, u_3)/k_B T\} = \exp\{-V_0/k_B T\} \exp\{-\tfrac{1}{2}\alpha r^2/k_B T\}$$
$$\times \{1 - \gamma r^4/k_B T - \delta(u_1^4 + u_2^4 + u_3^4 - \tfrac{3}{5}r^4)/k_B T\}. \quad (12)$$

Inserting this expression into equation (6) and replacing $Q \cdot u(l)$ by

$$2\pi a^{-1}(h_1 u_1 + h_2 u_2 + h_3 u_3),$$

where a is the lattice parameter and h_1, h_2 and h_3 are the Miller indices, we obtain a final expression for the temperature factor as

$$\exp\{-W(Q)\} = N \exp\{-\tfrac{1}{2}Q^2\alpha^{-1}k_B T\}$$

$$\times \left[1 - 15 k_B T \gamma\alpha^{-2} + 10(k_B T)^2 (2\pi/a)^2 \gamma\alpha^{-3}(h_1^2 + h_2^2 + h_3^2)\right.$$

$$- (k_B T)^3 (2\pi/a)^4 \gamma\alpha^{-4}(h_1^2 + h_2^2 + h_3^2)^2$$

$$\left. - (k_B T)^3 (2\pi/a)^4 \delta\alpha^{-4}\{h_1^4 + h_2^4 + h_3^4 - \tfrac{3}{5}(h_1^2 + h_2^2 + h_3^2)^2\}\right], \qquad (13)$$

with

$$N = \{1 - 15 k_B T \gamma\alpha^{-2}\}^{-1}.$$

The explicit temperature dependence of the temperature factor follows by considering equations (11) and (13). The Einstein treatment then leads to the following expression for the exponent of the Debye–Waller factor:

$$2W = (2\pi/a)^2(h_1^2 + h_2^2 + h_3^2)[1/\alpha_0] k_B T + (2\pi/a)^2(h_1^2 + h_2^2 + h_3^2)[2\gamma_G \chi/\alpha_0 k_B](k_B T)^2$$

$$- (2\pi/a)^2(h_1^2 + h_2^2 + h_3^2)[20\gamma_0/\alpha_0^3](k_B T)^3 + (2\pi/a)^4(h_1^2 + h_2^2 + h_3^2)[2\gamma_0/\alpha_0^4](k_B T)^3$$

$$- (2\pi/a)^4(h_1^2 h_2^2 + h_2^2 h_3^2 + h_3^2 h_1^2 - \tfrac{1}{3}h_1^4 - \tfrac{1}{3}h_2^4 - \tfrac{1}{3}h_3^4)[12\delta_0/5\alpha_0^4](k_B T)^3, \qquad (14)$$

where the quantities in square brackets are independent of temperature. Here the first term is the harmonic contribution to $2W$; the second term is the thermal expansion correction to the harmonic contribution; the third and fourth terms are the isotropic anharmonic contributions due to the quartic component of the potential; and the last term is the anisotropic contribution to $2W$. For the metals under consideration, the contributions of the last two terms to $2W$ are quite small except at very high temperatures and for high values of $(\sin\theta)/\lambda$. Thus, neglecting the quartic terms in equation (14) and writing $\exp(-x) \approx 1-x$ for $x \ll 1$, we find that the temperature factor is approximately given by

$$T(Q) \approx \exp\{-\tfrac{1}{2}\alpha_0^{-1} k_B T(1 + 2\chi\gamma_G T)(1 - 20k_B T\gamma_0 \alpha_0^{-2})Q^2\}$$

or

$$B(T) \approx B_h(T)\{1 + T(2\chi\gamma_G - 20k_B \gamma_0 \alpha_0^{-2})\}, \qquad (15)$$

where $B(T)$ is the isotropic B-factor at temperature T, which is given by

$$T(Q) = \exp\{-B(T)\lambda^{-2}\sin^2\theta\}, \qquad (16)$$

while $B_h(T)$ is the harmonic B-factor at temperature T, given by

$$B_h(T) = 8\pi^2 \alpha_0^{-1} k_B T. \qquad (17)$$

Thus, in the harmonic approximation, the B value is proportional to T, but in the anharmonic approximation an extra term appears in the expression which is proportional to T^2. This term consists of two parts: one due to thermal expansion and the other due to the quartic modification of the potential.
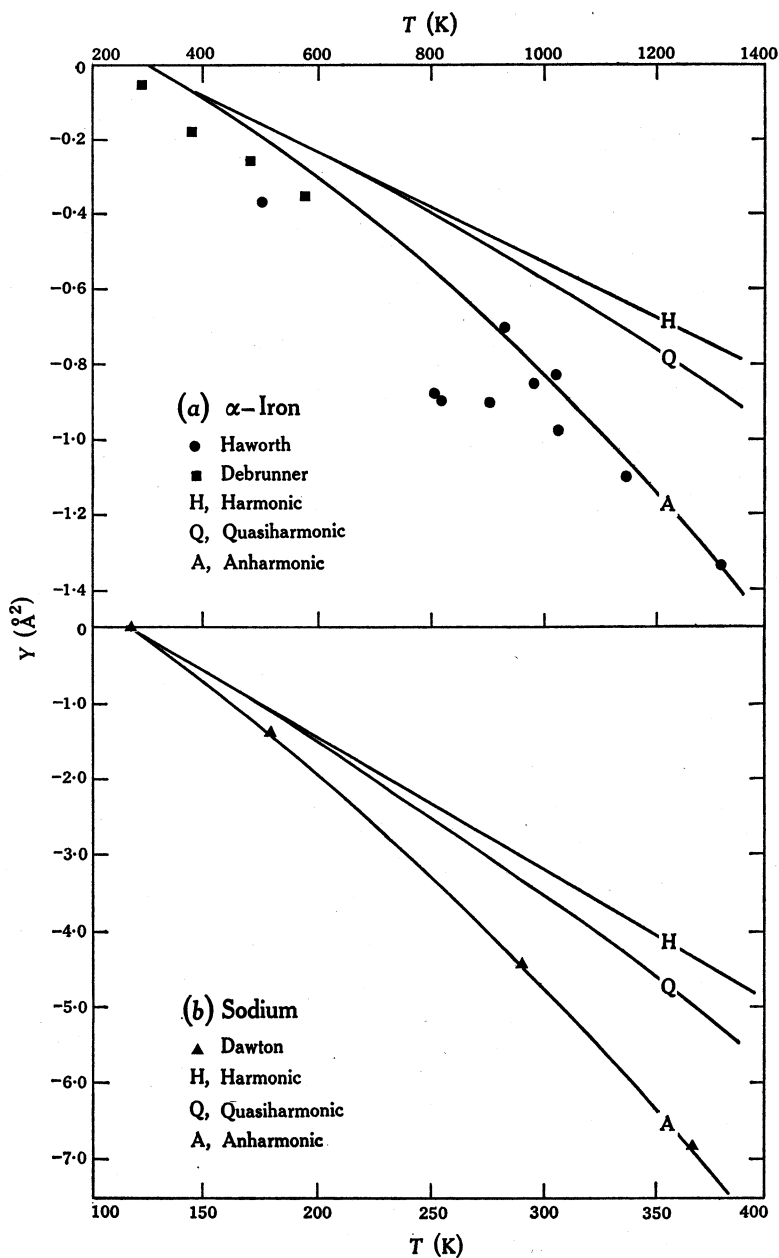
Fig. 1. Comparison of the present theoretical curves with experimental data for the temperature variation of the Debye–Waller temperature parameter Y for (a) α-iron and (b) sodium.

Comparison with Experiment

Comparison between the present calculated values and the experimental results is made here in terms of the Debye–Waller factor temperature parameter Y given by

$$Y = (\lambda/\sin\theta)^2 \log_{10}(I_T/I_{T_0}) = 0\cdot 86\{B(T_0) - B(T)\}, \tag{18}$$

where I_T and I_{T_0} are the experimentally measured intensities of a particular reflection at temperatures T and T_0 respectively. The calculated Y, T curves are compared with the experimental results for α-iron and sodium in Figs 1a and 1b respectively. In these figures, the curves labelled H show the theoretical variation according to the harmonic theory, and are based on the calculations of Part I. The curves labelled Q were obtained after applying the quasiharmonic correction to $B_h(T)$ by retaining the thermal expansion term, but putting $\gamma_0\alpha_0^{-2} = 0$ in equation (15). The curves labelled A represent the anharmonic form of Willis's (1969) equation (15), and they were drawn by choosing $\gamma_0\alpha_0^{-2}$ in such a way as to make the anharmonic curves pass through the experimental points at the highest temperatures, where the influence of anharmonicity is greatest. The harmonic parameter α_0 is calculated from equation (17). In calculating the Q and A curves, the Grüneisen constants for the metals were taken from Slater (1939) and the temperature dependence of the thermal expansion coefficients taken from Gray (1963).

α-Iron

Measurements of the temperature variation of the Debye–Waller factor of α-iron have been made both through X-ray diffraction techniques (Ilyine and Kritskaya 1955; Haworth 1960; Herbstein and Smuts 1963) and γ-ray resonant absorption experiments (Debrunner and Morrison 1964). Haworth's measurements were made over the classical high-temperature range and so are preferable for comparison with the present theory. These results, however, possess a large scatter which Haworth attributed to statistical changes in the distribution of the reflected particles. These results are shown in Fig. 1a for $T_0 = 286$ K along with the data of Debrunner and Morrison. The anharmonic curve was allowed to pass through the experimental point at $T = 1321$ K. The calculated harmonic parameter α_0 and anharmonic parameter γ_0 are $134\cdot 4$ J m^{-2} and $-2\cdot 745 \times 10^{22}$ J m^{-4} respectively. The agreement of the calculated values of Y with experiment is fairly good throughout the temperature range studied.

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 the three 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 amongst these, the (400), (310) and (220) reflections as the most reliable. The average values of Y for the above three planes with $T_0 = 117$ K have been plotted against temperature in Fig. 1b. The anharmonic curve was allowed to pass through the experimental point at $T = 368$ K. The calculated harmonic parameter α_0 and anharmonic parameter γ_0 are $5\cdot 98$ J m^{-2} and $-1\cdot 28 \times 10^{20}$ J m^{-4} respectively. The theoretical results agree satisfactorily with the experimental values.

Discussion

Comparison of the theoretical plots with the experimental values reveals that the anharmonicity for the Debye–Waller factors of α-iron and sodium is explained to a great extent by the inclusion of quartic anharmonic contributions to the Debye–Waller exponent $-2W$, along with the harmonic contribution and the thermal expansion correction. The quartic contribution represented by the difference between the curves Q and A is much more for these metals than the thermal expansion contribution represented by the difference between the curves H and Q. This is contrary to the situation in the case of KCl, where the quasiharmonic values were found by Kashiwase (1965) and Willis (1969) to be in good agreement with the experimental data of James and Brindley (1928). However, a critical appraisal of the anharmonic theory requires more precise experimental data. Nevertheless, we have shown conclusively that anharmonic effects are accounted for satisfactorily by using an Einstein model of the crystal.

Acknowledgments

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