TEMPERATURE VARIATION OF DEBYE-WALLER FACTORS OF B.C.C. METALS

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The temperature variation of Debye-Waller factors for five bcc metals-sodium, α-iron, chromium, molybdenum and tungsten have been studied using the lattice dynamical model which considers short range pairwise forces effective up to second neighbours, long range screened Coulomb forces on the lines of Krebs and describes the ionic lattice to be in equilibrium in a medium of electrons. Computational results have been compared with the existing experimental data in terms of the temperature parameter Y of the Debye-Waller factor, the effective characteristic temperature Θ_M and the mean square displacement $\overline{u^2}$ of the atoms. The calculated results have been found to be in very good agreement with the available experimental data.

1. Introduction

It has been shown experimentally that there is a reduction in the intensity of X-ray diffraction maxima with the rise of temperature on account of thermal vibrations in a crystal. The effect was first considered theoretically by Debye [1] and subsequently modified by Waller [2] who showed that this decrease could be expressed by an experimental factor $\exp(-2W)$. Blackman [3] has shown that measurements of the effect of temperature on the diffraction of X-rays and neutrons as described by the Debye-Waller (D–W) factor, $\exp(-2W)$, can be used to obtain information on the vibrational spectrum of solids. Study of the temperature dependence of this effect, or rather the change in mean square amplitude of vibration with temperature is very important for the understanding of many temperature dependent crystal properties. In the past, considerable interest has been shown in the experimental study of the thermal variation of the D–W factors of metals by means of X-ray and neutron diffraction, e. g. Ref. [4]. Several authors [5–9] have used different phenomenological models to compute the exponent $(2W)$ using their vibration spectra. But the main drawback with these approaches is that they do not satisfy the symmetry requirements of the lattice in the sense that the computed frequencies are

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not periodic in the reciprocal space due to the neglect of the translational invariance of the lattice, and further, none of the above models satisfy the crystal equilibrium. In addition to this, in computing the D–W factor, the term corresponding to the zero phonon wave vector ($q = 0$) has not been considered by these workers, since the value of the wavevector in this case corresponds to a nonvibrating lattice for which the D–W exponent vanishes and, therefore, the contribution of the central part of the Brillouin zone (BZ) has not been taken into account. It would, therefore, be preferable to compute the D–W factors using a more realistic lattice dynamical model.

Quite recently, Kulshrestha and Upadhyaya [10] suggested a new lattice dynamical model for cubic metals. This model overcomes the above shortcoming by including electron-ion interaction on the basis of the Krebs [11] theory to the ion-ion interaction through second neighbour pair potential [12] as the bare electron ion interaction reduces the effect of long range Coulomb interaction to the short range forces between the ions [13]. Also the model describes the crystal in equilibrium under zero external stress as has been emphasized by Thomas [14] that the elastic constant theory applies only to the solid in equilibrium and that an equilibrium condition must be imposed explicitly for empirical models for lattice cohesion. In recent studies we have successfully used this model to interpret various lattice dynamical properties, e. g. phonon dispersion, frequency spectrum, Debye temperature, thermal expansion, and transport properties of cubic metals. The present paper reports on the study of temperature variation of the D–W factor, characteristic Debye temperature, and mean square displacement of atoms in five bcc metals viz., sodium, α-iron, chromium, molybdenum and tungsten.

2. Theory

The contribution to W consists of two parts:

(*i*) the phonon-dependent part (W') which is obtained from knowledge of the whole vibration spectra, and

(*ii*) the contribution from the central part (W'') of the BZ, corresponding to $\boldsymbol{q} \to 0$, is evaluated in the Debye approximation.

Thus the D–W factor exponent W may be written as

$$2W = 2W' + 2W''. \tag{1}$$

Part (*i*): In the harmonic approximation, the exponent of the D–W factor is related to the mean square displacement of the atoms and is given by James [15]

$$2W = \langle |\boldsymbol{S} \cdot \boldsymbol{u}(n)|^2 \rangle, \tag{2}$$

where $\boldsymbol{u}(n)$ is the displacement of the n^{th} atom and $\boldsymbol{S}$ is the difference between the unit wave vectors of the scattered and incident wave. From a knowledge of the nature of the time dependence of atomic displacements and the average energy of phonons in the mode $\boldsymbol{q}$, the amplitude A_q of mode $\boldsymbol{q}$ can be expressed as

$$|A_q|^2 = \frac{(n_q + \frac{1}{2})\hbar}{mN\omega_q}, \tag{3}$$

where m is the mass of the atom, N is the total number of unit cells in the crystal, ω_q is the angular frequency of the normal mode of wave vector q and n_q is the average occupation number of the q lattice mode and is given by the Planck relation

$$n_q = \left\{\exp\left[\frac{\hbar\omega_q}{k_B T}\right] - 1\right\}^{-1}, \tag{4}$$

where k_B is the Boltzmann constant and T the absolute temperature. Relation (2) can be written in terms of the eigenvectors and eigenvalues of the vibrational spectrum as (writing W', the phonon dependent part, in place of W),

$$2W' = \frac{\hbar}{mN} \sum_{q,p} \frac{(S \cdot e_{q,p})^2 (n_{q,p} + \frac{1}{2})}{\omega_{q,p}}, \tag{5}$$

where $e_{q,p}$ is the polarization vector for the p^{th} polarization of the q^{th} lattice mode, and $\omega_{q,p}$ is the angular frequency of the q, p lattice mode. From consideration of the cubic symmetry of the lattice [16], the factor $(S \cdot e_{q,p})^2$ may be replaced by its average value outside the summation, so that Eq. (5) reduces to

$$2W' = \frac{16\pi^2 \hbar}{3mN} \left(\frac{\sin\theta}{\lambda}\right)^2 \sum_{q,p} \frac{1}{\omega_{q,p}} (n_{q,p} + \tfrac{1}{2}), \tag{6}$$

where θ is the Bragg angle and λ the wavelength of the incident radiation.

Part (*ii*): Since all the modes are acoustic for a monatomic lattice, the angular frequency ω is zero when $q = 0$. Following Barron and Smith [7], we have avoided this singularity in the sum by replacing the contribution to the sum at $q = 0$ with an integration of the energy term, (E/ω^2) (of the mode of lattice vibration)

$$E = \hbar\omega[n_q + \tfrac{1}{2}], \tag{7}$$

over a sphere of volume equal to $\dfrac{1}{20 \times 20 \times 20}$ of the BZ near $q = 0$. It is assumed that the frequency in this region is given by the average velocity times the wave vector.

The zero phonon contribution (W'') is then written as

$$W'' = \frac{a^3}{3m} [D(C_L) + 2D(C_T)] \left[\frac{\sin\theta}{\lambda}\right]^2, \tag{8}$$

where

$$D(C) = \frac{1}{C^2} \int_0^{2\pi k_{max}} 4\pi^2 \hbar c k dk [n_q + \tfrac{1}{2}], \tag{9}$$

C_L is the average velocity for the longitudinal phonons and C_T is that for the transverse phonons in this region, k_{max} is the radius of the sphere of integration and is given by

$$\frac{4\pi}{3} k_{max}^3 = \tfrac{1}{8000} \text{ (volume of BZ)}$$

or

$$k_{\max} = \frac{1}{20a}\left(\frac{3}{2\pi}\right)^{1/3}, \tag{10}$$

$D(C)$ can be reduced to

$$D(C) = p\left(\frac{1}{x}\int_0^x \frac{t\,dt}{e^t - 1}\right) + \tfrac{1}{4}\,px, \tag{11}$$

where

$$p = \frac{4\pi^2 k_B T k_{\max}}{C^2}, \qquad x = \frac{4\pi^2 \hbar C k_{\max}}{k_B T}, \tag{12}$$

and

$$t = \frac{2\pi\hbar k C}{k_B T}.$$

The value of the integral in expression (11) can be substituted from standard tables.

From Eq. (2), the mean square of the total displacements of an atom from the average position is given by

$$\overline{u^2} = \frac{3W}{8\pi^2}\left(\frac{\lambda}{\sin\theta}\right)^2, \tag{13}$$

The temperature dependence of the D–W factor, considering a Debye model of the solid, can be written as

$$2W = \frac{48\pi^2\hbar^2 T}{m k_B \Theta_M^2}\left(\Phi(x) + \frac{x}{4}\right)\left(\frac{\sin\theta}{\lambda}\right)^2, \tag{14}$$

where Θ_M is the Debye characteristic temperature, $x = \Theta_M/T$ and $\Phi(x)$ is the Debye integral function defined as

$$\Phi(x) = \frac{1}{x}\int_0^x \frac{z\,dz}{\exp(z) - 1}, \tag{15}$$

with

$$z = \frac{\hbar\omega}{k_B T}.$$

The above formula has been used by different workers for interpreting the experimental data from X-ray reflections for the evaluation of the D–W factors.

3. *Numerical computation*

The evaluation of D–W factor exponent $2W$ from Eqs. (1), (6) and (8) at different temperatures has been done by Blackmann's sampling technique [18] for a discrete subdivision in wave-vector space. To have a fairly large survey of frequencies, we have considered a mesh of evenly spaced 8000 wave vectors in the first BZ obtained by dividing the first BZ into $20\times20\times20$ miniature cells with axes $\frac{1}{20}$ of the length of the reciprocal lattice cell. Symmetry considerations reduce these 8000 points to only 256 non equivalent points including the origin, lying within an irreducible 1/48 part of the first BZ. The secular equation determining the vibrational frequencies of metals was solved for all these points and each frequency so obtained was weighted according to the symmetrically equivalent points. The value of maximum frequency was then obtained and 50 equal intervals were made and the number of frequencies lying within each of the intervals were counted after duly assigning proper weights to them. Thus the histogram of the vibrational spectrum

TABLE I

Lattice constant and elastic constants for cubic metals used in the computation

Metal	Lattice constant (Å)	Elastic constants (10^{11} dyn/cm^2)			Reference
		C_{11}	C_{12}	C_{44}	
sodium	4.2400	0.808	0.664	0.586	[34]
α-iron	2.8662	23.310	13.550	11.780	[35]
chromium	2.8792	35.000	6.780	10.080	[36]
molybdenum	3.1468	44.077	17.243	12.165	[37]
tungsten	3.1650	52.327	20.453	16.072	[37]

was obtained. The mid point of each frequency step was taken as the representative of any particular interval whose statistical weight was given by the number of frequencies lying in it. Using this histogram, the D–W factor exponent $2W = 2W'+2W''$ at various temperatures was calculated from Eqs. (6) and (8). The mean square displacements of atoms and the effective characteristic temperature Θ_M at different temperatures were evaluated from Eqs. (13) and (14), respectively. The elastic constants and other relevant parameters for the metals used in the calculations are given in Table I.

4. *Comparison with the experimental results*

The results have been compared with the experimental data in terms of the D–W temperature parameter defined as

$$Y = \left(\frac{\lambda}{\sin\theta}\right)^2 (2W_0 - 2W_T)\times\log_{10}e, \tag{16}$$

where W_0 and W_T are the values of W at temperatures T_0 and T, respectively. The parameter Y is independent of λ and θ, being completely determined by the vibrational spectrum,

and is easily found from the X-ray intensities of the Bragg reflections. If I_T and I_0 are the meassured integrated intensities of a given reflection from the crystal at temperature T and T_0, respectively, then

$$\frac{I_T}{I_0} = \frac{\exp(-2W_T)}{\exp(-2W_0)}, \tag{17}$$

which gives

$$\left(\frac{\lambda}{\sin\theta}\right)^2 \log_{10}\left(\frac{I_T}{I_0}\right) = \left(\frac{\lambda}{\sin\theta}\right)^2 (2W_0 - 2W_T) \times \log_{10} e = Y. \tag{18}$$

The numerical values of Y, $\overline{u^2}$ and Θ_M at different temperatures for sodium, α-iron, chromium, molybdenum and tungsten are presented in Fig. 1–5 respectively. For comparison the corresponding values deduced from various X-ray measurements have also been plotted.

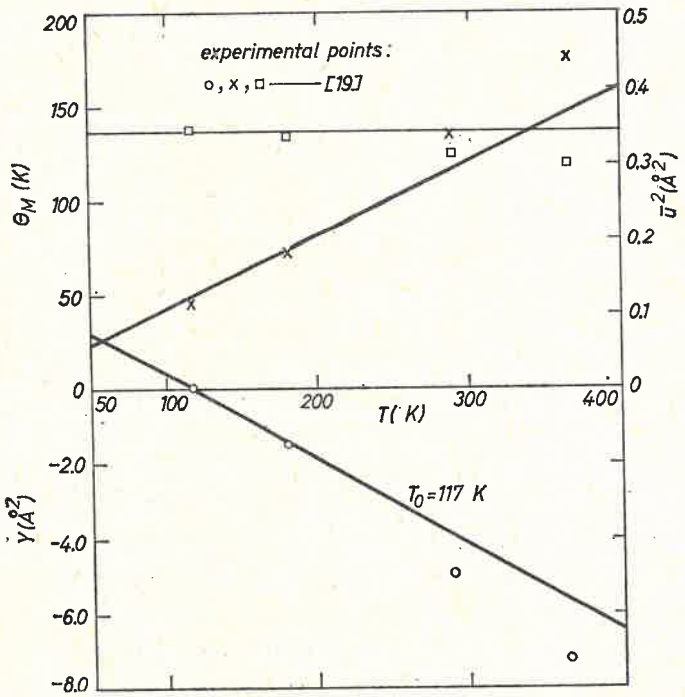

Fig. 1. Variation of Y, $\overline{u^2}$ and Θ_M with temperature for sodium; solid curves — present calculation

(A) Sodium: The effect of temperature on the intensities of X-ray reflections from a single crystal of sodium has been experimentally studied by Dawton [19] in the temperature range 117–370 K. He has measured the intensity ratio (I_{117}/I_T) at three different temperatures 180, 291 and 368 K for a chilled crystal. These ratios were found for (400), (310), (220), (200) and (110) reflections but Dawton suggests that among these the observa-

tions for the (400), (310) and (220) reflections are the most reliable. The average of the values of $(\lambda/\sin\theta)^2 \log_{10}(I_T/I_0) = Y$, $\overline{u^2}$ and Θ_M for the above three planes with $T_0 = 117$ K has been plotted in Fig. 1. The theoretical results are found to agree very well with the experimental measurements.

(B) α-iron: The temperature dependence of the D–W factor for α-iron has been studied by X-ray diffraction [20–22] and γ-ray resonant absorption experiment [23]. The X-ray measurements of Haworth [21] covered the temperature range 286–1190 K by making integrated intensities and peak heights measurements for the diffraction line (220) for an iron spectrum. The results show large scatter associated with crystal changes brought about by prolonged annealing. The observed X-ray intensity measurements for iron by Ilyina and Kristakaya [20], and Herbstein and Smuts [22] refer only to room

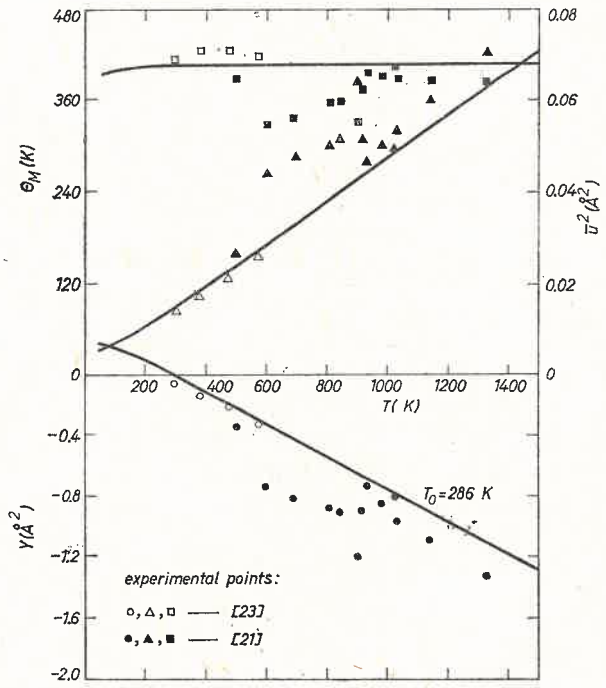

Fig. 2. Temperature variation of Y, $\overline{u^2}$ and Θ_M for α-iron; solid curves — present calculation

temperature and are, therefore, not selected for the present comparison with our computed values. The experimental observations of Haworth [21] are plotted in Fig. 2 along with a few experimental measurements of Debrunner and Morrison [23] in the temperature range 293 to 573 K. The theory agrees very well with the low temperature observations [23] but appears to be in somewhat disagreement with the observations of Haworth [21], and the discrepancy may be attributed to large scatter in the experimental points which is particularly striking in the temperature range 600–1000 K and hence these measurements can not be heavily relied upon for our present comparison.

(C) Chromium: The integrated X-ray intensity measurements for a single crystal of chromium at different temperatures have been reported by Wilson et al. [24] for the temperature range 100 to 520 K. These are corrected for thermal diffuse scattering as well as changes in the lattice parameters. These experimental measurements have been expressed

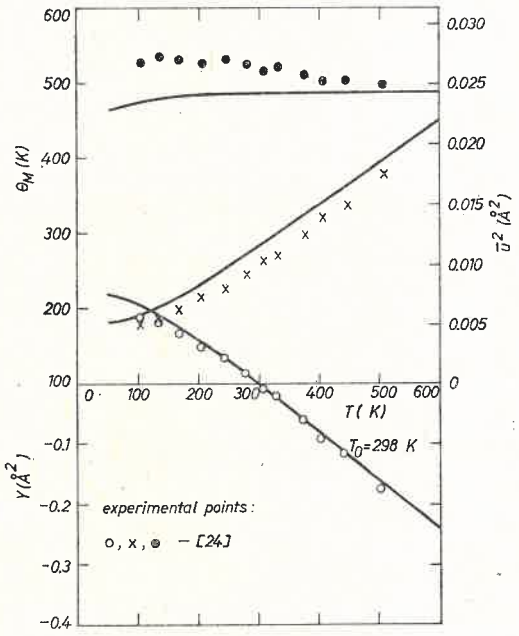

Fig. 3. Temperature dependence of Y, $\overline{u^2}$ and Θ_M for chromium; solid curves — present calculation

in terms of the characteristic Debye temperature Θ_M. For the purpose of the present comparison, we have calculated the values of $\left(\frac{\lambda}{\sin\theta}\right)^2 \log_{10}\left(\frac{I_T}{I_0}\right) = Y$ as a function of temperature from the corresponding value of Θ_M. The values of Y, $\overline{u^2}$ and Θ_M deduced from the measurements of Wilson et al. [24] are plotted in Fig. 3 with $T_0 = 298$ K. A reasonably satisfactory agreement in the theoretical values of Y, $\overline{u^2}$ and Θ_M with the experimental observations is obtained.

(D) Molybdenum: The temperature dependence of the intensities of X-ray reflection for a molybdenum crystal was experimentally studied by Korsunskii [25] in the temperature range 100—400 K, by measuring the intensity ratio I_{291}/I_T for the (232) and (322) reflection planes. The measured values of $\left(\frac{\lambda}{\sin\theta}\right)^2 \log_{10}\left(\frac{I_T}{I_0}\right) = Y$ for these two planes, with reference temperature $T_0 = 291$ K and the corresponding values of $\overline{u^2}$ and Θ_M along with the theoretically calculated values are shown in Fig. 4. The theoretical values of Y, $\overline{u^2}$ and Θ_M agree quite satisfactorily with the experimental ones.

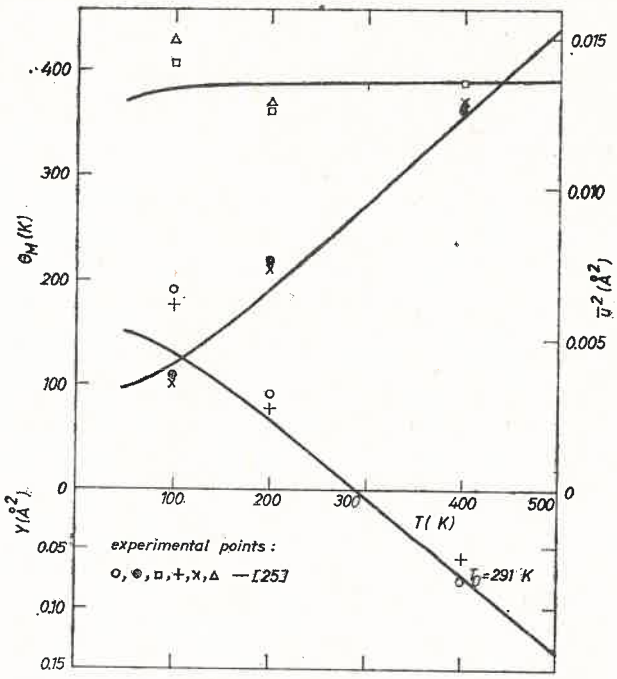

Fig. 4. Temperature variation of Y, $\overline{u^2}$ and Θ_M for molybdenum; solid curves — present calculations

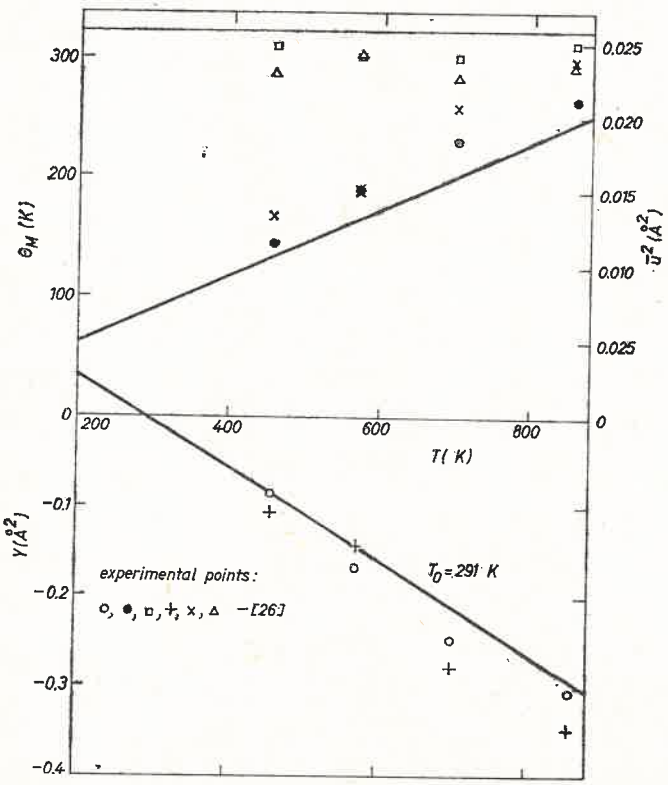

Fig. 5. Temperature variation of Y, $\overline{u^2}$ and Θ_M for tungsten; solid curves — present calculations

(E) Tungsten: Geshko [26] has studied the temperature variation of the D–W factor by X-ray intensity measurements in the temperature range 400—850 K for the (310) and (321) reflection planes of a tungsten crystal. We have plotted the measured values of $\left(\frac{\lambda}{\sin\theta}\right)^2 \log_{10}\left(\frac{I_T}{I_0}\right) = Y$, with reference temperature $T_0 = 291$ K, and the corresponding values of $\overline{u^2}$ and Θ_M along with the theoretically calculated values in Fig. 5. Reasonably satisfactory agreement between theory and experiment is observed.

5. *Discussion*

The present study shows that the D-W temperature parameter Y obtained from the model of Kulshrestha and Upadhyaya [10] provides a satisfactory explanation of the observed temperature variation of the X-ray intensities of Bragg reflections up to a certain temperature. In the high temperature region the experimental values of Y are consistently higher than the theoretical ones. This discrepancy between the theoretical results and the experimental data may be attributed to the neglect of the temperature variation of the vibrational frequencies [27] and to other anharmonic effects [28–33]. Moreover, the temperature variations of the elastic constants and lattice parameter have not been taken into account in the present study. With an increase in temperature, the normal-mode frequencies decrease because of thermal expansion. This effect depends upon the Gruneisen parameter which varies with temperature. However, a detailed study incorporating the Gruneisen parameter and the anharmonicity in lattice vibrations, though very much desired for the interpretation of the D-W factor of solids, has not yet been attempted. As things stand, it emerges from the present study that the temperature variation of the D-W factor of bcc metals can be very satisfactorily explained by the present model. Our results are undoubtly superior enough to eclipse those obtained earlier for various existing lattice dynamical models.

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