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Debye-Waller factors of BCC transition metals

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The Debye-Waller exponents for molybdenum and tungsten are calculated at different temperatures by using the modified angular force model of Clark *et al* which, together with the central and angular forces, also accounts for the effect of electron-ion interaction on the lattice vibrations. The vibrational modes of frequencies are summarised by the use of Blackman's sampling technique and the results for the Debye-Waller factor are compared with the experimental data in terms of a temperature parameter $Y = \log_{10}e(\lambda/\sin\theta)^2 (2W'_{T_0} - 2W_T)$. The theoretical values obtained here compare well with the experimental results.

1 Introduction

The effect of thermal motion of the atoms on the intensity of scattered X-ray waves and the Mossbauer effect experiments can be envisaged by the study of an exponential factor e^{-2W}, often referred to as Debye-Waller factor. The exponent $2W$ is directly related to the mean-square displacement of the atoms and provides a direct tool for the study of a large number of phenomena in solid-state physics such as neutron scattering, electrical conductivity and melting of crystals. The Debye model for the vibrational spectrum of the lattice has usually been applied for estimation of the factor $2W$ in terms of a known function involving the characteristic temperature Θ. This method is now shown to be inadequate (Herbstein 1961), since the phonon frequencies derived from the Debye model of the solid is found to be far from the real spectrum of the lattice vibration. It would therefore be preferable to compute the Debye-Waller factor by using a more realistic lattice dynamical model than the hypothetical Debye one.

In the recent past a considerable attention is being paid for the theoretical and experimental study of the lattice dynamics of crystals with a corresponding increase of interest in the study of Debye-Waller factor. Flinn et al (1961) have reported an experimental determination of the Debye-Waller factor for copper from X-ray intensity measurements in the temperature range 4–500°K and interpreted their results in terms of a central force model with first and second nearest neighbour interactions. Flinn & McManus (1963) have followed the same technique for the study of aluminium. The Debye-Waller factor of copper has also been discussed by Dewames *et al* (1963) by using the various force models in the light of experimental findings of Flinn *et al*. Barron *et al* (1966) and Feldman (1966) have worked out the Debye-Waller factor for nickel. While Barron *et al* make the use of fourth neighbour model by Birgeneau *et al* (1964)

for the computation of Debye-Waller exponent at T - 300°K, Feldman uses the fourth neighbour Begbieborn model, a fifth neighbour axially symmetric model and a first neighbour Begbie-born model. Quite recently, Goel & Such (1974) have studied the Debye-Waller factors of noble metals silver and gold using the modified deLaunnay model.

In the present paper, we have used the modified non-central force model of Behari & Tripathi (1969) for the study of temperature dependence of the Debye-Waller factors in molybdenum and tungsten, both BCC metals. The force model takes into account the Clark-Gazis & Wallis (1964) type angular forces and Sharma & Joshi (1963) type volume forces. It has been found that this model explains satisfactorily the lattice dynamical behaviour of copper (Behari & Tripathi 1969) and many other cubic metals (Behari & Tripathi 1970, Gupta & Tripathi 1971, Behari, 1972, Prakash & Hemkar 1973, Prakash *et al* 1974 and Pathak *et al* 1975).

2. Theory

In the harmonic approximation, the Debye-Waller exponent $2W$ is directly related to the mean square displacement of the atoms and can be given as (James 1964).

$$2W = <|(S-S_0)\,u(n)|^2>,$$

where $u(n)$ is the displacement of nth atom, S_0 the incident wave-vector and S the scattered wave vector. Considering the time dependence of the atomic displacements and the average energy of mode q phonon, the amplitude u_q can be written as

$$|u_q|^2 = \frac{(n_q+\frac{1}{2})\hbar}{mN\omega_q} \qquad \ldots (2)$$

Here, m is the atomic mass, N the total number of unit cells in the crystal, n_q the average occupation number of lattice mode q given by

$$n_q = \left[\exp\left(\frac{\hbar\omega_q}{k_BT}\right)-1\right]^{-1}. \qquad \ldots (3)$$

Here k_B is the Boltmann constant and T the absolute temperature. Now one can get from the eqs. (1–3)

$$2W = \frac{\hbar}{4N}\sum_{q,j}\frac{|(S-S_0).e_{q,j}|^2.(n_{q,j}+\frac{1}{2})}{\omega_{q,j}} \qquad \ldots (4)$$

where j is the polarization index and $e_{q,j}$ the polarization vector of the lattice mode (q, j). The summation over q extends over all normal vibrations of the crystal. For a monatomic cubic crystal, the polarization factor $[(S-S_0).e_{q,j}]^2$ may be replaced by its average value so that the eq. (4) reduces to

$$2W = \frac{8\pi^2\hbar}{3mN}\left(\frac{\sin\theta}{\lambda}\right)^2 \sum_{q,j} \frac{1}{\omega_{q,j}} \operatorname{Coth}\left(\frac{\hbar\omega_{q,j}}{2k_BT}\right). \quad \ldots (5)$$

where θ is the glancing angle of incidence and λ the wave-length of the incident wave.

For the Debye model of the solid, the temperature dependence of the Debye-Waller exponent can be written as

$$2W = \frac{48\pi^2\hbar^2T}{mk_B\Theta_M^2}\left[\phi(x)+\frac{x}{4}\right]\left(\frac{\sin\theta}{\lambda}\right)^2, \quad \ldots (6)$$

where Θ_M is the effective X-ray characteristic temperature. $\phi(x)$ is the usual Debye integral function and $x = \Theta_M/T$.

3. Numerical Computation

For the estimation of Debye-Waller exponent $2W$, it is necessary to determine the frequency spectrum of lattice vibration at a suitable number of points in an irreducible section of the first Brillouin zone. For this purpose, we have used the Blackman's (1955) root sampling technique for a discrete sub-division of the wave vector space. In order to keep the frequencies within limit and to avoid too much approximations, we have divided the first brillouin zone into evenly spaced 1000 miniature cells. Consideration of Born's cyclic boundary condition and symmetry property of the lattice reduces the 1000 points to 47 only, including the origin, lying within 1/48 part of the Brillouin zone. The 3000 frequencies corresponding to 1000 points in the zone are computed from the solutions of secular equation formed by the dynamical matrix of Behari and Tripathi for bcc structure. These frequencies corresponds to the complete vibrational spectrum of the system. For the evaluation of the summation (5), the whole frequency spectrum is divided into a number of intervals and properly weighted frequencies are counted in each interval. The term corresponding to $q = 0$ is neglected in the summation because this value of the wave vector refers to a static lattice for which the Debye-Waller factor vanishes to zero. The elastic constants and other pertinent data for the metals used in the calculation are given in table 1.

Table 1. Physical Constants for molybdenum and tungsten

Metal	Elastic constants (10^{11} dyn/cm^2)			Lattice parameter (10^{-8} cm)	Reference
	C_{11}	C_{12}	C_{44}		
Molybdenum	40·077	17·243	12·165	3·14	(*a*)
Tungsten	52·327	20·453	16·072	3·16	(*b*)

(*a*) Woods A. D. & Chen S. H. 1964 *Solid State Comm.* **2**, 233

(*b*) Chen S. H & Brockhouse B. N 1964 *Solid State Comm.* **2**, 73.

4. Comparison with Experiments

The comparison of the calculated values of $2W$ with the experimental results on Debye-Waller factor is made in terms of a temperature parameter Y defined by

$$Y = \log_{10}e \left(\frac{\lambda}{\sin\theta} \right)^2 (2W_{T_0} - 2W_T), \qquad \ldots \quad (6)$$

where $2W_T$ and $2W_{T_0}$ are the values of Debye-Waller exponent for temperatures T and T_0 respectively. This factor is independent of λ and θ and is directly accessible from the measured X-ray intensities of the Bragg reflection. If I_T and I_{T_0} are the experimentally measured intensities of a given reflection at temperatures T and T_0 respectively, we have

$$\frac{I_T}{I_{T_0}} = \frac{\exp(-2W_T)}{\exp(-2W_{T_0})}. \qquad (7)$$

This gives

$$Y = \left(\frac{\lambda}{\sin\theta} \right)^2 \log_{10} \frac{I_T}{I_{T_0}} = \log_{10}e \left(\frac{\lambda}{\sin\theta} \right)^2 (2W_{T_0} - 2W_T) \quad \ldots \quad (8)$$

The right hand side of the above equation is calculated for different temperatures with the help of eq. (5). For the purpose of comparison we have also calculated the Debye-Waller factor parameter Y from the Debye's theory, using the eq. (6), with $\Theta_M = 450$°K for molybdenum and $\Theta_M = 400$°K for tungsten. The computed values and the experimental results of Y for the molybdenum and tungsten are shown in Figures. 1 and 2 with reference to a standard temperature.

4.1. *Molybdenum*

Korsunshii (1971) has studied the temperature dependence of the Debye-Waller exponent $2W$ in terms of parameter Y for molybdenum in low temperature range 100–400°K by the observations made on the X-ray reflections for the planes (232) and (322). These results are shown in Figure 1 with reference

temperature T_0 291 K. The calculated values for the parameter Y from the modified angular force model show a good agreement with the experimental

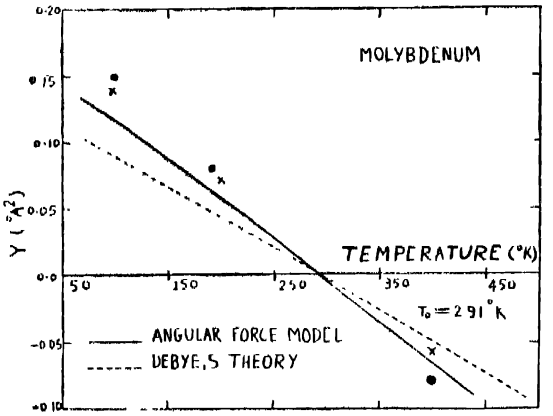

Fig. 1. Variation of Y with temperature for molybdenum ●, experimental data of Korsunskii for (232) plane; ×, experimental data of Korsunskii for (322) plane.

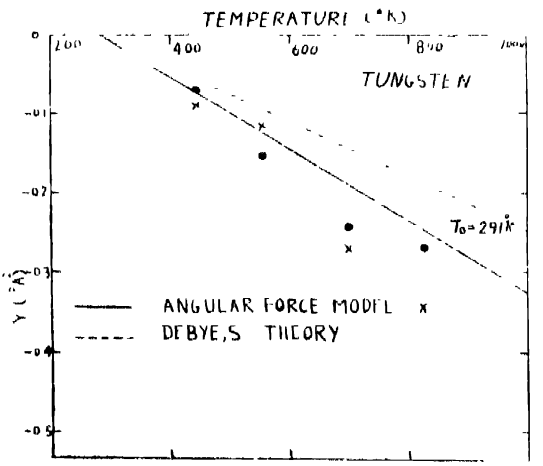

Fig. 2. Variation of Y with temperature for tungsten ●, experimental data of Geshko for (310) plane; ×, experimental data of Geshko for (321) plane.

results for whole the temperature range of experimental observations. However, the results obtained from the Debye's theory are much lower than that expected from the experimental findings.

4.2 *Tungsten*

The temperature variation of the intensity of X-ray reflections for (310) and (321) planes of the tungsten crystal was studied by Geshko (1963) for the

temperature range 400–850°K. The results are shown in Figure 2 with reference temperature $T_0 = 291$°K, together with the computed values of Debye-Waller temperature parameter Y. The calculated results show a satisfactory agreement with the experimental values only upto about 600°K, but above this temperature the observed decrease in the intensity of reflections becomes greater than that expected theoretically and the discrepancy gradually increases with the rise of temperature. It is also seen that our calculated values based on modified angular force model are much closer to the experimental values than those computed from the Debye's theory.

5. Discussion

The theoretical results obtained for the Debye-Waller temperature parameter Y from the modified angular force model of Behari and Tripathi offers a reasonable explanation for the observed decrease of the X-ray intensities of Bragg reflections below a certain temperature. However, at higher temperatures, the X-ray intensity of reflections decreases rapidly than that expected from the theory. Such discrepancies at higher temperature are not unexpected, as the neglect of lattice expansion (Zener & Bilinsky 1936) and other anharmonic effects (Hahn & Ludwig 1961, Cowley 1963, Maradudin & Flinn 1963, Slater 1965, Wolfe & Goodmann 1969, Willis 1969), can widely effect the frequency consideration. Anharmonic contributions vary mostly as the square of the absolute temperature and is more effective at higher temperatures. The temperature variation of the elastic constants has also been neglected in the present study.

The observed discrepancy between the computed and the experimental results for the temperature factor can be attributed to the fact that the characteristic frequency decreases due to thermal expansion at high temperatures. This effect depends upon the Grüneisen constant, a temperature dependent parameter. Several workers (Owen & Williams 1947, Spreadborough & Christian 1959, Haworth 1960) have tried to summarize this effect in terms of the Gruneisen parameter, but a detailed discussion has not yet been possible. At higher frequencies, the Debye-Waller factor $2W$ depends on the summation over q, j of $\omega_{q,j}^{-2}$. Hence, the lower frequency peaks in the frequency spectrum contribute much more to the value of $2W$ than that from the higher frequency peaks. As it is clear from the observations on the lattice dynamics of metals by several workers that the frequency spectrum can be approximated by two peaks, of which the low frequency peak usually covers the much larger area. It is this peak that gives a major contribution to govern the intensity of X-ray reflections. Since the values and temperature dependence of the Grüneisen parameter for this peak are not known, no quantitative estimation of the effect of thermal expansion on the X-ray intensities is possible. It seems that a more detailed study incorporating the Grüneisen parameter and the anharmonicity in lattice vibrations

is much needed for the clear interpretation of the Debye-Waller factor of the solids

A comparative study of the experimental results and the theoretical values shows that the results obtained from the angular force model are much closer to the experimental results than that obtained from the Debye's theory. It shows how sensitive the Debye-Waller factor is on the details of phonon spectrum. The more realistic the dynamical approach consistent with the physical situation of the lattice, the better the results obtained for the parameter Y. However, as the things stand, it emerges from the present study that the temperature variation of the Debye-Waller factors of molybdenum and tungsten can be explained satisfactorily by the Behari-Tripathi lattice dynamical model.

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