CHAPTER - SEVEN

DEBYE-WALLER FACTOR OF HCP METALS

7.1 INTRODUCTION:

The intensity of x-ray diffraction maxima decreases with rise in temperature because of thermal vibrations of scattering atoms. This effect was first considered theoretically by Debye [1] who showed that this decrease could be expressed by an exponential factor $e^{-2w}$, where the quantity $2w$ is often referred as Debye-Waller exponent. The treatment was reconsidered by Waller [2] who found that the value of $2w$ was twice that given by Debye.

Because of its inherent relationship with lattice vibrations, the Debye Waller factor enters into a large number of solid state problems and thus provides a direct tool for the study of various lattice dynamical properties such as neutron scattering, mean square displacement of the atoms, electrical conductivity, melting phenomenon in solids and thermal resistivity. This factor has usually been calculated by using Debye model for the lattice vibration in solid in terms of Debye characteristic temperature $\theta$. But the calculated values do not agree with the experimental data satisfactorily. This is due to fact that theory of lattice dynamics based on Debye approximation is inadequate. It is therefore preferable to compute
the Debye-Waller factor by using a more appropriate dynamical model than that of Debye.

During the past two decades a little has been done on temperature variation of Debye-Waller factor of transition and rare earth metals.

A theoretical model has been applied by Ramanand and Ramji Rao [3] to calculate Debye-Waller factor for hcp scandium. These authors also reported the mean square displacement amplitude of atomic displacements and verified the results by evaluating the Lindmann [4] parameter which relates the Debye temperature of the solid to the melting temperature.

In this chapter, we have also calculated the Debye Waller factor and mean square displacement of atom for some hcp metals and mean square displacement of atoms for some hcp metals on the basis of model which has been described in detail in previous chapters. For the numerical computation at low temperatures, the contribution from the central part of the Brillouin zone, corresponding to $\bar{q} \rightarrow 0$ is also taken into account.

7.2 DEBYE WALLER FACTOR IN THE HARMONIC APPROXIMATION:

The total effect of the thermal motion of scattering atoms on the Bragg intensity can be estimated quantitatively by multiplying the scattering amplitude of such atom with a temperature parameter given by

$$\exp \left[ - W(\bar{Q}) \right] = \langle \exp \left( i \bar{Q} \cdot \bar{\mathbf{u}}(n) \right) \rangle$$

(7.1)
Where \( \vec{Q} \) is the scattering vector, \( \vec{u} \) (n) the displacement of nth atom from equilibrium position and \( W(\vec{Q}) \) the Debye-Waller temperature factor. The angular bracket \(< >\) shows the time average of the function. For the harmonic approximation the time average \( < \exp|\vec{q} \cdot \vec{u}(n)|> \) in equation (7.1) obeys a Gaussian distribution and gives the relation

\[
2W = <(|\vec{s} - \vec{s}_0| \cdot \vec{u}(n)|^2 >
\]

(7.2)

Where \( \vec{s}_0 \) and \( \vec{s} \) are the incident and scattering vectors respectively and are related to the scattering vector \( \vec{Q} \) by relation \( \vec{s} - \vec{s}_0 = \vec{Q} \). Taking the time dependence of the atomic displacements and the average energy of phonon mode \( \vec{q} \) the amplitude \( |\vec{u}_q|^2 \) for the mode \( \vec{q} \) can be given as

\[
|\vec{u}_q|^2 = (n_q + \frac{\hbar}{m_q} N\omega_q)
\]

(7.3)

Where \( n_q \) is the average occupation number corresponding to mode \( \vec{q} \), \( m_q \) the atomic mass, \( N \) the total number of normal modes vibrations and \( \omega_q \) the angular frequency for the normal mode of wavevector \( \vec{q} \). The value of \( n_q \) is given as

\[
n_q = \left[\exp\left(\frac{\hbar\omega_q}{k_B T}\right) - 1\right]^{-1}
\]

(7.4)

From \( k_B \) is the Boltzmann constant and \( T \) the absolute temperature.
From equation (7.2) and (7.3)

\[ 2W = \frac{\hbar}{m_A N} \sum_{i,j} \left[ (\vec{s} - \vec{s}_o) \cdot \vec{e}_{\bar{q},j} + \frac{1}{2} \right] \frac{1}{\omega_{\bar{q},j}} \]  

(7.5)

Here \( j \) is the polarization index and \( \vec{e}_{\bar{q},j} \) the polarization vector of the lattice mode \((\bar{q},j)\). For monotomic crystal the factor \([ (\vec{s} - \vec{s}_o) \vec{e}_{\bar{q},j} ]\) may be replaced by its average value outside the summation so that equation (6.12) gives

\[ 2W = \frac{\hbar}{2m_A N} \sum_{i,j} \left| (\vec{s} - \vec{s}_o) \cdot \vec{e}_{\bar{q},j} \right|^2 \coth \left[ \frac{\hbar \omega(\bar{q},j)}{2K_BT} \right] \]

or

\[ 2W = \frac{8\pi^2 \hbar}{6m_A N} \left( \frac{\sin \Theta}{\lambda} \right)^2 \sum_{i,j} \frac{1}{\omega(\bar{q},j)} \coth \left( \frac{\hbar \omega_{\bar{q},j}}{2K_BT} \right) \]  

(7.6)

Where \( \Theta \) is the glancing angle of incident and \( \lambda \) the wavelength of the incident wave. The summation in equation (7.6) extend over the entire vibrational frequencies corresponding to all wave vector except the ones where \( \bar{q} \rightarrow 0 \). At this point \( \upsilon \) is zero for all three acoustic modes for hcp structure. Other three modes however e.g. \( L_0 \), \( T_{0,1} \) and \( T_{0,1} \) have finite values.

The zero phonon contribution \((2w_o)\) to the Debye – Waller is given by

\[ 2W_o = \frac{80}{60 m_A} [D(\upsilon_L) + 2D(\upsilon_T)] \left( \frac{\sin \Theta}{\lambda} \right)^2 \]  

(7.7)

Where

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\[
D(V) = \frac{1}{2\Omega^2} \int_0^{q_m} \hbar v q \, dq \left[ \exp\left(\frac{\hbar \omega}{K_B T}\right)^{-1} + \frac{1}{2} \right]
\]  
(7.8)

and \( \Omega = \frac{\sqrt{3}a^2 c}{4} \) is the atomic volume for hcp structure, \( v_T \) is the average velocity for the transverse phonon and \( v_L \) for longitudinal phonons in this region. \( q_m \) is the radius for the sphere of integration and is given by

\[
\frac{4}{3} \pi q_m^3 = \frac{1}{1000} \quad \text{(Volume of Brillouin zone)}
\]

\[
= \frac{1}{1000} \left( \frac{16\pi^3}{\sqrt{3}a^2 c} \right) \quad \text{for hcp structure} \quad \text{(7.9)}
\]

\( D(v) \) can be reduced to

\[
D(v) = R \left( \frac{\int_0^{\eta'} \eta' \, d\eta'}{e^{q/v} - 1} \right) + \frac{Ry}{4}
\]

(7.10)

Where

\[
R = 2\pi K_B T q_m / v^2
\]

\[
Y = 2\pi \hbar v q m / K_B T
\]

and

\[
\eta' = \hbar q v / K_B T
\]

The value of integral contained in the expression for \( D(v) \) can be evaluated from the standard tables.

From the equation (7.2) the mean square displacement of an atom can be given as

\[
u^{-2} = \frac{3}{8\pi^2} \left( \frac{\lambda}{\sin \Theta} \right)^2 \text{ W}
\]

(7.11)
For a Debye model of the solid, the temperature dependence of the Debye-Waller exponent $2W$ can be expressed as

$$2W = \frac{48 \pi^2 \hbar^2 T}{m K_B \Theta^2} \left[ \phi(x) + \frac{x}{4} \right] \left( \frac{\sin \Theta}{\lambda} \right)^2 \tag{7.12}$$

Where $\Theta$ is the Debye characteristic temperature, $x = \theta / T$

$\phi(x)$ is the Debye integral function, given by

$$\phi(x) = \frac{1}{x} \int_0^x \frac{z \, dz}{e^z - 1} \tag{7.13}$$

$Z = \hbar \omega / K_B T$

### 7.3 COMPUTATION TECHNIQUE:

The Debye-Waller exponent $2W$ be evaluated by knowing the frequency spectrum of lattice vibrations at suitable number of points (84) in an irreducible section of first Brillouin zone. We have used Blackman's technique for this purpose. The first Brillouin zone has been frequencies corresponding to 1000 miniature cells. 6000 frequencies corresponding to 1000 points in the zone are computed using the secular determinant.

For sampling purpose, the whole frequency spectrum is divided into small intervals and all frequencies falling into these intervals are computed with their proper statistical weights. This gives a frequency distribution function which has been used for calculation $2w$ using equation (7.6). Since zero phonon contribution becomes quite significant, particularly at low temperature, we have
used expression (7.7) for evaluating the contribution from central part of the Brillouin zone corresponding to $\bar{q} \rightarrow 0$. The mean square displacement $u^2$ and the effective characteristic temperature $\theta$ have been evaluated from the equations (7.11) and (7.12) respectively.

The Debye-Waller factor temperature parameter $Y$ is given by the relation

$$Y = \log_{10} e \left( \frac{\lambda}{\sin \Theta} \right)^2 (2W_T - 2W_0) \quad (7.14)$$

Where $2W_T$ and $2W_0$ are the values of Debye-Waller exponents at temperature $T$ and $T_0$ respectively. This quantity is directly accessible from the measured intensities of Bragg's reflection in X-Ray diffraction experiments. If $I_T$ and $I_{T_0}$ are the measured intensities of certain diffraction line at temperature $T$ and $T_0$ respectively, we have following relation

$$\frac{I_T}{I_{T_0}} = \frac{\exp(-2w)}{\exp(-2w_0)} \quad (7.15)$$

Thus we get

$$Y = \left( \frac{\lambda}{\sin \Theta} \right)^2 \log_{10} \left( \frac{I_T}{I_{T_0}} \right) \quad (7.16)$$

The present model has been used to calculate mean square displacement $u^2$ of several hcp transition and rare earth metals. Such results have been shown in Table 7.1.
The computed results of $Y, u^{-2}$ and $\Theta$ at different temperature for hexagonal close packed metals have been plotted in Figures 6.11 - 6.16.

7.4 LINDEMANN'S MELTING CRITERIA:

As the amplitudes of vibrations become large at high temperatures, it is necessary to include the anharmonic terms in the vibrations. Eventually a temperature is reached where the amplitude is too large to be contained by the interatomic forces and the lattice breaks up. Lindemann’s [4] hypothesis is that the melting temperature of a material is attained when the root mean square amplitude of atomic vibration becomes a critical fraction of the nearest neighbour distance. It was proposed that this fraction, the so called Lindemann parameter, might be same for all metals. However in various hcp transition and rare earth metals, it has been observed that this fraction indeed is not constant but depends upon the location of the elements in the periodic table. Similar results were also obtained for II-VI and III-V compound.

No comparison between calculated and measured data on $Y, u^{-2}$ would be made as the experimental results on these properties have not been made available so far. In the case of zirconium [5, 6] and yttrium [7] calculated Debye characteristic temperature has been found in agreement with the experimental data available at low temperature. Measured Debye characteristic temperature as plotted as the function of temperature shows abnormal behaviour beyond 120 K in the case of scandium [8]. Low temperature data in the case of hafnium [5, 6]
Figure 7.1 Temperature variation of Y, $U^2$ and $\Theta$ for Holmium and O Experimental.
Figure 7.2 Temperature variation of $Y$, $U^2$ and $\Theta$ for Zirconium and O Experimental.
Figure 7.3 Temperature variation of $Y$, $U^2$ and $\Theta$ for Yttrium and O Experimental.
Figure 7.4 Temperature variation of $Y$, $U^2$ and $\Theta$ for Hafnium and O Experimental.
Figure 7.5 Temperature variation of $Y$, $U^2$ and $\Theta$ for Scandium and O Experimental.
Figure 7.6 Temperature variation of $Y$, $U^2$ and $\Theta$ for Terbium and $O$ Experimental.
shows deviation of the order of 5% from the calculated value at 80 K. In the case of rare earth metals like holmium [9] and terbium [10] magnetic contribution to the specific heat is very small as compared to lattice contribution at higher temperature. For such metals observed Debye characteristic temperature shows very good agreement with calculated values.

Despite the paucity of experimental results we feel that the present semi-first-principle lattice dynamical model provides an adequate interpretation of the Debye-Waller factors in the case of rare earth and transition hcp metals. However, a detailed study of the lattice vibrations incorporating the effect of lattice expansion and anharmonicity is essential in order to gain better insight into the melting process in these metals.
REFERENCES

1. Debye P. Ann. Phys. 43 (1914),

2. Waller I. Z. Phys. 7 398 (1923)


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