

Temperature Variation of Debye-Waller Factor and Mean Square Displacement for bcc Metals Using Density Based Pseudopotential

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The variation of Debye-Waller factors and mean square displacements at different temperatures for simple bcc metals Li, Na, Rb and Cs is studied using pseudopotential proposed by Fiolhais et al. Comparison of computed theoretical values with experimental results is made and discussed. A reasonable agreement is found between our results and experimental data.

Keywords: Debye-Waller factor, Mean square displacement, Pseudopotential.

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1. INTRODUCTION

The study of lattice dynamics has continuously evolved as a large and significant branch of condensed matter physics. It has been a subject of considerable interest to physicists for the understanding of various physical properties of solids like elastic, electrical, thermodynamic etc. [1]. In the past, the vibrations of lattice was investigated in detail for the intention of describing the basis of macroscopic behavior of solids, but now a days experimental techniques are becoming sufficiently stronger to examine the detailed motions of vibrating atoms. Enhanced X-ray and neutron scattering techniques have been very beneficial in this direction [2, 3].

The theoretical investigations of lattice dynamic properties are important as it determines the temperature variation of many physical properties of solids like temperature variation of Debye temperature, specific heats, isothermal and adiabatic bulk moduli, thermal expansion, entropy, thermal pressure etc. It also describes quantitatively the interaction between ions of a solid [4-6]. Several forms of pseudopotential (local and non-local) have been used successfully for the theoretical study of lattice vibrations for different types of metals (simple, alkali, transition and polyvalent cubic metals) [7]. During literature survey, it has been observed that different researchers have used different phenomenology and philosophy in the construction and determination of pseudopotential. Also, the predictivity and capability of such pseudopotential for comprehensive study of physical properties at extreme environment is still to be verified [8]. Recently, Fiolhais et al. [9] have proposed density-based pseudopotential with two set of parameters (universal and individual). They have also verified that individual set of parameters are good working and such facts are also verified by Bhatt et al. [10-12]. Very recently, Priyank et al. [13] have used such form of pseudopotential to examine superconducting state parameters and their pressure dependence for some simple metals. The study of temperature variation of the thermodynamic properties using individual set of parameters up to room temperature has not been carried out

yet. Encouraged by this fact, the present study is concerned with a structured local pseudopotential developed by Fiolhais et al. to carry out the temperature variation of Debye-Waller factor (W_T) and mean square displacement (\bar{U}^2) of some bcc simple metals (Li, Na, Rb and Cs). Since these solid state parameters are directly related, it is clearly relevant for several phenomena of condensed matter physics such as electrical resistivity, volume or pressure dependence of melting temperatures [14, 15].

It is observed that the intensity of a wave scattered from a crystal depends on temperature. It is lower than its absolute zero value by a temperature dependent exponential factor referred as Debye-Waller factor related to the mean square displacements of the atoms in a crystal [7]. Although, many researchers have used different methods and philosophies to study these properties, there is still lack of work done for simple metals. So, the purpose of this work is to study the temperature dependence of above mentioned properties for some simple metals.

2. THEORY

In the harmonic approximation, the Debye-Waller exponent $2W_T$ is directly related with the mean square displacement of the atoms given as [7],

$$2W_T = \frac{\hbar}{4\pi^2 MN} \sum_{\mathbf{q}, j} \frac{(\mathbf{K} \cdot \hat{\mathbf{e}}_{\mathbf{q}, j})^2}{v_{\mathbf{q}, j}} \cdot \left\{ \frac{1}{2} + \frac{1}{\exp\left\{\frac{\hbar v_{\mathbf{q}, j}}{k_B T}\right\} - 1} \right\}, \quad (2.1)$$

where M is the mass of the atom, N is the total number of unit cells in the crystal, \mathbf{K} is the difference of the initial and final wave vectors of X-rays, $v_{\mathbf{q}, j}$ is the frequency of a phonon with the wave vector \mathbf{q} and polarization j , $\hat{\mathbf{e}}_{\mathbf{q}, j}$ is the polarization vector of the (\mathbf{q}, j) lattice mode, and the summation extends over the all normal modes. For a monatomic cubic crystal, the polarization factor $(\mathbf{K} \cdot \hat{\mathbf{e}}_{\mathbf{q}, j})^2$ can be replaced by its average value outside the summation so that (2.1) becomes,

$$2W_T = \frac{2\hbar}{3MN} \left(\frac{\sin\theta}{\lambda}\right)^2 \sum_{\mathbf{q}, j} \frac{1}{v_{\mathbf{q}, j}} \coth\left\{\frac{\hbar v_{\mathbf{q}, j}}{2k_B T}\right\}. \quad (2.2)$$

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If $g(v)$ is the phonon frequency distribution function that gives the number of vibration modes between v and $v + dv$,

$$2W_T = \frac{8\pi^2 h}{3MN} \left(\frac{\sin\theta}{\lambda}\right)^2 \int_0^{v_{max}} \frac{g(v)}{v} \coth\left\{\frac{hv}{2k_B T}\right\} dv, \quad (2.3)$$

where Q is the glancing angle and λ is the incident radiation wavelength. The mean square displacement of the atoms in the crystal in the harmonic approximation is determined by [1],

$$\bar{U}^2 = \frac{3}{8\pi^2} \left(\frac{\lambda}{\sin\theta}\right)^2 W_T. \quad (2.4)$$

In order to calculate frequency distribution $g(v)$ (phonon density of states) we have used Blackman's technique [7]. In the present communication, a mesh of evenly spaced 64000 wave vectors in the first Brillouin zone is considered. For the calculation of phonon frequencies, diagonalising the dynamical matrix is required. For such study one has to use wave vectors in off-symmetric directions. To generate a set of wave vectors, an irreducible sector of Brillouin zone (1/48 portion) is defined for a bcc lattice by set of equations,

$$(q_x + q_y) \leq 1; (q_y + q_z) \leq 1; (q_z + q_x) \leq 1, \quad (2.5)$$

$$q_x \leq 1; q_y \leq 1; q_z \leq 1.$$

Dividing q_x , q_y and q_z axes into z equal intervals and writing,

$$q_x = \frac{P_x}{z}; q_y = \frac{P_y}{z}; q_z = \frac{P_z}{z}, \quad (2.6)$$

then Eq. (2.5) becomes

$$(P_x + P_y) \leq z; (P_y + P_z) \leq z; (P_z + P_x) \leq z, \quad (2.7)$$

$$P_x \leq z; P_y \leq z; P_z \leq z,$$

where P_x , P_y and P_z are integers such that $(P_x + P_y + P_z)$ is even. Every point is weighed by symmetry according to the number of points corresponding to it. Care must be taken to give the proper weights to points lying on the Brillouin zone's edges, surfaces and corners.

In the entire zone, the overall number of points is z^3 . We took $z = 40$ in the current study. Thus, the total number of points in the entire zone was $(40)^3 = 64000$ and approximately the total number of frequencies are 2,00,000.

3. RESULTS AND DISCUSSION

As we have discussed earlier, we have used Fiolhais pseudopotential with individual set of parameters and calculated phonon frequencies and phonon density of states $g(v)dv$ using method discussed in section 2. Once phonon density of states is obtained, we have calculated temperature variation of W_T and \bar{U}^2 (Eq. (2.3)). We have compared our results with results due to Peng et al. [15] obtained using experimentally derived phonon density of states. The comparison of experimental and theoretical results shows that our results are consistent in nature.

The temperature variations of W_T and \bar{U}^2 along with the experimental results due to Peng et al. [15] are shown in Fig. 1, which reveals the excellent agreement between computed and experimental results. Fig. 2- Fig. 4

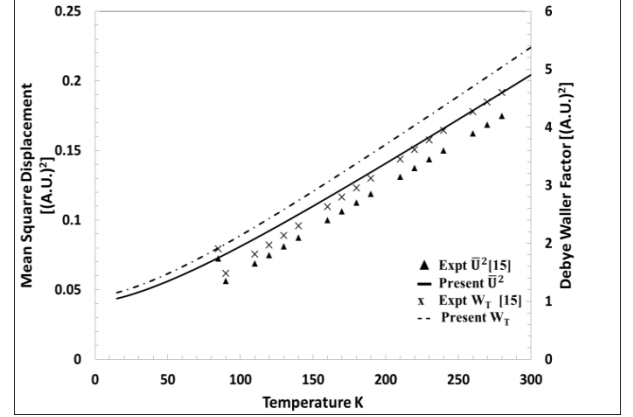


Fig. 1 – Temperature variations of W_T and \bar{U}^2 for Li

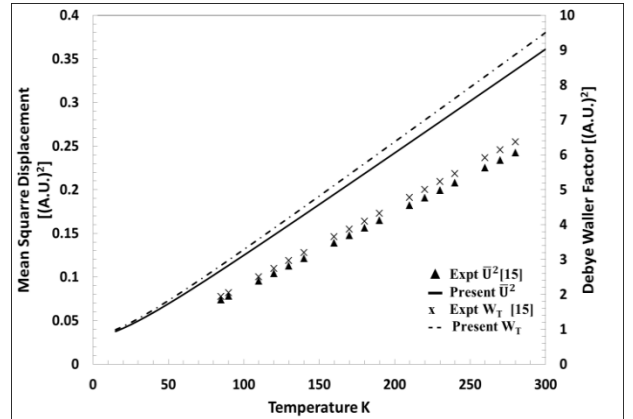


Fig. 2 – Temperature variations of W_T and \bar{U}^2 for Na

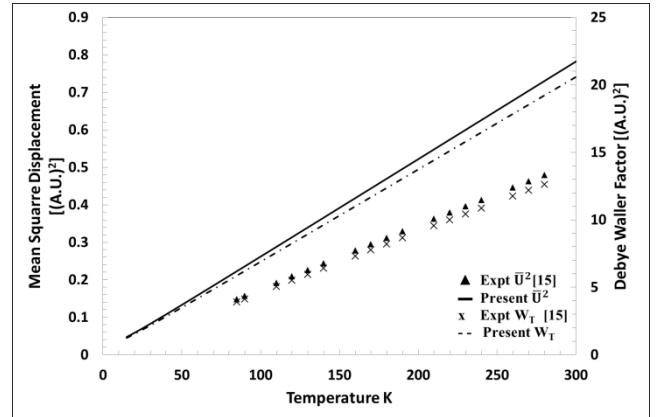


Fig. 3 – Temperature variations of W_T and \bar{U}^2 for Rb

represent the temperature variations of W_T and \bar{U}^2 for Na, Rb and Cs.

In case of Na, Rb and Cs, at lower temperatures, the agreement between experimentally measured and computed Debye-Waller factors is better which means the harmonic approximation works better at lower temperatures. One of the reasons of this disagreement at higher temperatures may be due to computed values of phonon frequencies in non-symmetric directions. Surprisingly, the peak value of $g(v)$ for these metals are not occurring exactly at the value of maximum frequency observed in symmetric directions. In order to improve computed results, we have also repeated the present study with $z = 80$ in Eq. (2.7) but we did not find any change in the calculated

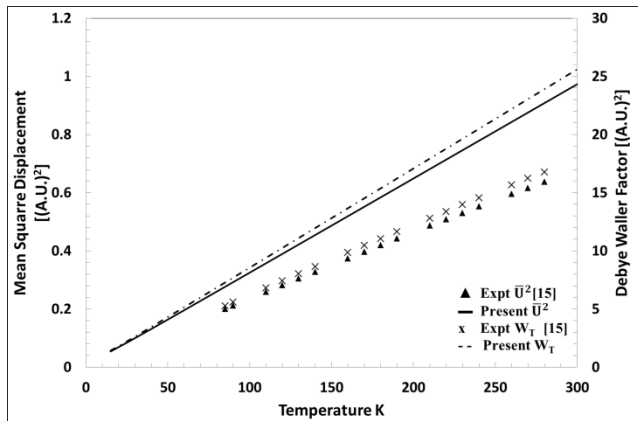


Fig. 4 – Temperature variations of W_T and \bar{U}^2 for Cs

values of phonon density of states. The maximum deviation at high temperature is more than 25 %, which requires further detailed investigation. We have also carried out this study using universal set of parameters, but results using individual parameters are better than former ones.

4. CONCLUSIONS

The study of temperature variations of Debye-Waller factor and mean square displacement are important in dynamical electron diffraction calculations. In reality, for most of the crystals the values of Debye-Waller factor are not available. At same time, experimental values of such factor are available at a given temperature using X-

ray diffraction and neutron scattering. In such circumstances, it is necessary to carry out study of such factors using theoretical approach. Keeping this fact in our mind, in the present study we have used most effective density-based pseudopotential due to Foilhais et al. with individual set of parameters. The present study reveals the versatility of present pseudopotential for the study of thermodynamic functions from temperature range 0 K to melting temperature. The present study has proven once again that the present form of local pseudopotential is mathematically simple, physically transparent and results generated using them are sometimes comparable and more accurate in comparison with first principles method. The important point emerging from the present theoretical study is that even the excellent agreement between calculated phonon frequencies and experimental results may not give correct frequency distribution.

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