Temperature Dependent Lattice Mechanical Properties of Some fcc Transition Metals

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(Received November 13, 2003)

A simple pseudopotential model is used for the calculation of the temperature dependence of the lattice mechanical properties which depend on the phonon density of states, such as the lattice heat capacity $C_V$, the Debye temperature $\theta_D$, the harmonic contribution to the free energy, the thermal pressure, the isothermal bulk modulus corrected to the fourth order and volume, the thermal expansion coefficient $\beta$, $\beta B_T^2 \Omega/3Nk_B^2$, the Debye-Waller factor, the mean-square displacement, the Debye-Waller temperature parameter, and the X-ray characteristic temperature $\theta_M$ of Cu, Ag, Au, Ni, Pd, Pt, Rh, and Ir. The contribution of d-like electrons is taken into account by introducing a repulsive short range Born-Mayer-like term. The theoretical results are compared with the experimental findings wherever possible. A good agreement between the theoretical investigations and the experimental findings demonstrates the capability of our model potential for successfully explaining the lattice vibrations and the related properties of some cubic transition metals.

PACS numbers: 65.40.Ba, 63.70.+h

I. INTRODUCTION

In our previous work [1] a simple pseudopotential model of a transition metal was proposed to account for the d-electron interaction. This model was successfully exploited for the calculation of the binding energy, the equations of state, the ion-ion interaction, phonon dispersion curves (q-space and r-space analysis), the phonon densities of states, the mode Grüneisen parameters, and the dynamical elastic constants. The results were in reasonable agreement with the experiments and showed a consistent improvement over other theoretical findings, thus confirming the applicability and capability of our model potential for the investigation of such properties.

During our literature survey we have found that very few attempts have been made to calculate the properties which depend on the phonon density of states [2–6] using pseudopotential theory. The reason may be that, in the calculation of the phonon dispersion curve, limited $q$ vectors in the major symmetry direction are required, while in the calculation of the phonon density of states a large number of $q$ vectors distributed throughout the Brillouin zone are required. It is possible that for all the vectors the results may not be equally good, and this is reflected in the calculation of the phonon density of states. Such results have been reported in the literature in the past for copper [7–9].

In the present paper we have further exploited the previously calculated phonon
density of state for the calculation of the lattice heat capacity $C_V$, the Debye temperature $\theta_D$, the harmonic contribution to the free energy, the thermal pressure, the isothermal bulk modulus corrected to the fourth order and the volume, the thermal expansion coefficient $\beta$, $\beta B T \Omega / 3 N k_B^2$, the Debye-Waller factor, the mean-square displacement, the Debye-Waller temperature parameter, and the X-ray characteristic temperature $\theta_M$ of Cu, Ag, Au, Ni, Pd, Pt, Rh, and Ir.

II. LATTICE HEAT CAPACITY $C_V$

The previously calculated [1] phonon density of states $g(\nu)$ is used in the present calculation of the lattice contribution to the various thermodynamic properties. The $g(\nu)$ curves are usually measured by inelastic neutron, infrared, and Raman scattering experiments only with quite a low resolution. The low-frequency behavior of the phonons is corrected with the elastic properties of the solid, whereas the high-frequency optical modes typically reflect the interactions between nearest neighbors. Therefore theoretical investigations of the phonon density of states can provide insight into both macroscopic properties of the solids as well as the microscopic dynamics of the atoms. The phonon density of states curves in the present study were obtained by using the root sampling technique in which 1685 $q$ values were used to calculate the frequencies in $(1/48)^{th}$ part of the Brillouin zone. The temperature dependence of the lattice heat capacity $C_V$ is calculated using the theoretical phonon density of states $g(\nu)$ as earlier reported [1], along with the following relation [6,10] in the temperature range 0–300 K:

$$\frac{C_V}{3R} = \int_{0}^{\nu_{\text{max}}} \left( \frac{h \nu}{k_B T} \right)^2 \frac{e^{h \nu/k_B T}}{(e^{h \nu/k_B T} - 1)^2} g(\nu) d\nu,$$

where $R$ is the real gas constant.

The results obtained for various metals are shown in Figs. 1-(a) to 8-(a). Only the experimental results for the specific heat $C_V$ for Cu, Ag, Au, and Pd are available. Our present values of Cu, Ag, and Pd are in excellent agreement with experimental findings, while for Au discrepancies are found at lower temperatures. The results for the remaining metals are predictive in nature.

III. DEBYE TEMPERATURE

The concept of the Debye temperature, $\theta_D$, has played an important role in the field of thermophysical properties of materials ever since its introduction. It is basically a measure of the vibrational response of the material and, therefore, intimately connected with properties like the specific heat, thermal expansion, and vibrational entropy [11]. The Debye temperature is not a strictly determined parameter; various estimates may be obtained through well established empirical or semi-empirical formulae, relating $\theta_D$ with
FIG. 1: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B_T \Omega / 3 N k_B^2$, and (d) the Debye temperature for Copper.

FIG. 2: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B_T \Omega / 3 N k_B^2$, and (d) the Debye temperature for Silver.
FIG. 3: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B T \Omega/3N k_B^2$, and (d) the Debye temperature for Gold.

FIG. 4: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B T \Omega/3N k_B^2$, and (d) the Debye temperature for Nickel.
FIG. 5: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B_T \Omega / 3N k_B^2$, and (d) the Debye temperature for Palladium.

FIG. 6: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B_T \Omega / 3N k_B^2$, and (d) the Debye temperature for Platinum.
FIG. 7: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B T / 3 N k_B^2$, and (d) the Debye temperature for Rhodium.

FIG. 8: Temperature variation of (a) the specific heat $C_V$, (b) the thermal pressure, (c) $\beta B T / 3 N k_B^2$, and (d) the Debye temperature for Iridium.
various macroscopic properties [12]. The Debye temperature $\theta_D$ can be found by using the standard tables for $C_V/3R$ versus $\theta_D/T$ [13].

The Debye temperature gives an opportunity to check the validity of the computed phonon density of states. The results obtained in the temperature range 0–100 K for various metals are shown in Figs. 1-(d) to 8-(d). Gupta [14] has discussed the details of the experimental data for the Debye temperature. Our present findings show excellent agreement with the experimental values as well as with the other such theoretical findings [3, 6] except for Cu, Rh, and Ir, and then only for less than 25 K.

IV. HARMONIC CONTRIBUTION TO THE FREE ENERGY

The harmonic contribution to the free energy in terms of the frequency distribution function is given by [2, 10]

$$E_H = 3N \int_0^{\nu_{\text{max}}} \left\{ \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/k_BT} - 1} \right\} g(\nu) d\nu.$$  \hspace{1cm} (2)

At room temperature the value of the free energy is shown in Table 1. Our present findings for the harmonic contribution to the free energy have been compared with other such theoretical findings [23, 24] and agree well. To the best of our knowledge experimental data for this property is not available.

<table>
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<tr>
<th>Elements</th>
<th>Zero point free energy in Ryd./elec.</th>
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<tr>
<td></td>
<td>Present</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00220</td>
</tr>
<tr>
<td>Ag</td>
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<td>Au</td>
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<td>Pt</td>
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</tr>
<tr>
<td>Rh</td>
<td>0.00295</td>
</tr>
<tr>
<td>Ir</td>
<td>0.00245</td>
</tr>
</tbody>
</table>

V. THERMAL PRESSURE

Thermal pressure arises from the vibrational part of the free energy. In the harmonic approximation, the thermal pressure can be given as [10]

$$P^*(\Omega, T) = - \left( \frac{\partial E_H}{\partial \Omega} \right)_T.$$  \hspace{1cm} (3)
In order to find $P^*$, the volume derivatives of the phonon frequencies are required. These are related to the mode Gr"uneisen parameter as [1, 10]

$$\gamma_{q,\lambda} = -\frac{d \ln \nu_{q,\lambda}}{d \ln \Omega} = -\frac{\Omega}{\nu_{q,\mu}} \frac{d \nu_{q,\lambda}}{d \Omega}. \quad (4)$$

Here $\gamma_{q,\lambda}$ is known as the mode Gr"uneisen parameter associated with the mode $(q, \lambda)$ and has been reported in our previous work [1]. Using the above equation, $P^*$ is given by

$$P^*(\Omega, T) = \frac{1}{\Omega} \sum_{q,\lambda} h\nu_{q,\lambda} \gamma_{q,\lambda} \left( n_{q,\lambda} + \frac{1}{2} \right). \quad (5)$$

In terms of the frequency distribution function it is [10]

$$P^*(\Omega, T) = \frac{3N}{\Omega} \int_0^{\nu_{\text{max}}} h\nu \gamma_{q,\lambda} \left\{ \frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1} \right\} g(\nu) d\nu, \quad (6)$$

where $N$ is the Avogadro number. The total pressure, corrected to the third order, is given by

$$P_T(\Omega, T) = P_0(\Omega) + P^*(\Omega, T), \quad (7)$$

where $P_0(\Omega)$ is the pressure at 0 K. The results for the thermal pressure using Eq. (7) in the temperature range 0–300 K are shown in the Figs. 1–8(b), for various metals.

VI. ISOTHERMAL BULK MODULUS ($B_T$) CORRECTED TO THE FOURTH ORDER

The following relation can be used obtain the isothermal bulk modulus [10]:

$$B_T(\Omega, T) = B_0(\Omega) + B^*(\Omega, T). \quad (8)$$

Here $B_0(\Omega)$ is the bulk modulus at 0 K and

$$B^*(\Omega, T) = \frac{3N}{\Omega} \int_0^{\nu_{\text{max}}} h\nu \left\{ \xi_{q,\lambda} \left( \frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1} \right) - \gamma_{q,\lambda}^2 \frac{h\nu}{k_B T} \right\} \times \left\{ \frac{1}{(e^{h\nu/k_B T} - 1)^2} + \frac{1}{e^{h\nu/k_B T} - 1} \right\} g(\nu) d\nu. \quad (9)$$

Figs. 9–11 show the isothermal bulk modulus in the temperature range 0–300 K for various metals. The experimental results for the isothermal bulk modulus for only Cu, Ag, and Au are available. At low temperatures our results show some discrepancy, otherwise it shows good agreement, while for the rest of the metals our present findings are predictive in nature.
FIG. 9: Isothermal bulk-modulus $B_T$ for Cu, Ag, and Au.

FIG. 10: Isothermal bulk-modulus $B_T$ for Ni, Pd, and Pt.
VII. VOLUME THERMAL EXPANSION COEFFICIENT $\beta$

The volume thermal expansion coefficient in terms of the frequency distribution curves is given by [10]

$$
\frac{\beta B_T}{3 k_B} = \frac{3N}{\Omega} \int_0^{\nu_{\text{max}}} \gamma_{q,\lambda} \left( \frac{\hbar \nu}{k_B T} \right)^2 \left\{ \frac{1}{(e^{\hbar \nu/k_B T} - 1)^2} + \frac{1}{e^{\hbar \nu/k_B T} - 1} \right\} g(\nu) d\nu.
$$

The present findings for the volume thermal expansion coefficient $\beta$ are shown in Figs. 12–14 in the temperature range 0–300 K for various metals. Here also the experimental data for only Cu, Ag, and Au are available. It was found that our present results agree extremely well with the experimental data for Cu, Ag, and Au. The results of $\beta B_T \Omega/3Nk_B^2$ versus temperature are shown in Figs 1-(c) to 8-(c) in the temperature range 0–300 K for various metals.

VIII. DEBYE-WALLER FACTOR AND MEAN SQUARE DISPLACEMENT

Despite the importance of the Debye-Waller factor in dynamical electron diffraction calculations, accurate values of the Debye-Waller factors are not readily available for most crystals. Recently Peng et al. [25] computed the Debye-Waller factor for 44 elemental crystals over the temperature range from 1 to 1000 K, or to the melting temperature,
FIG. 12: Volume thermal expansion coefficient $\beta$ for Cu, Ag, and Au.

FIG. 13: Volume thermal expansion coefficient $\beta$ for Ni, Pd, and Pt.
whichever is smaller. They derived the Debye-Waller factors from the experimentally determined phonon density of states. We have also derived the Debye-Waller factor from the phonon density of states in the following way [2, 3, 4, 26]:

$$2W = \frac{8\pi^2 h}{3MN} \left( \frac{\sin \theta}{\lambda} \right)^2 \int_0^{\nu_{\text{max}}} \frac{g(\nu)}{\nu} \coth \left( \frac{h\nu}{2k_BT} \right) d\nu.$$  \hspace{1cm} (11)

The calculated values of the Debye-Waller factor in the temperature range 0–1000 K for various metals are given in Figs. 15–17. The present values of the Debye-Waller factor show significant improvements over those of Pandya et al. [3, 4] and are found to be relatively close to the experimental findings of [25]. So far the experimental values of Rh and Ir for the mean-square displacement are not available; our values are predictive in nature. The following relation relates the mean square displacement to the Debye-Waller factor [2, 3, 4, 26]:

$$\bar{u}^2 = \frac{3}{8\pi^2} \left( \frac{\lambda}{\sin \theta} \right)^2 W.$$  \hspace{1cm} (12)

Figs. 18–20 show a comparison of our results with those of Peng et al. [25] for the mean-square displacement evaluated in the temperature range 0–1000 K for various metals. The present result shows a significant improvement compared to the results of Pandya et al. [3, 4]. Overall a good agreement between theory and experiment has been found.
FIG. 15: Debye-Waller factor for Cu, Ag, and Au.

FIG. 16: Debye-Waller factor for Ni, Pd, and Pt.
FIG. 17: Debye-Waller factor for Rh and Ir.

FIG. 18: Mean-square displacement for Cu, Ag, and Au.
FIG. 19: Mean-square displacement for Ni, Pd, and Pt.

FIG. 20: Mean-square displacement for Rh and Ir.
IX. DEBYE-WALLER TEMPERATURE PARAMETERS

A comparison of the calculated and experimental values of the Debye-Waller factor can also be made in terms of the Debye-Waller temperature parameter [2, 3, 4, 26]

\[ Y = \log_{10} e \left( \frac{\lambda}{\sin \theta} \right)^2 \left( 2W_{T_0} - 2W_T \right), \]  

(13)

where \( 2W_T \) and \( 2W_{T_0} \) are the values of the Debye-Waller factors at the temperatures \( T \) and \( T_0 \); these quantities are independent of \( \lambda \) and \( \theta \). Figs. 21–23 show the results of the Debye-Waller temperature parameter evaluated in the temperature range 0–1000 K. Our results for these quantities are comparable to those of the experiment [25] as well as those of the theoretical findings [2, 26] and are superior to [3].

X. X-RAY CHARACTERISTIC TEMPERATURE \( \theta_M \)

The X-ray characteristic temperature can be obtained as [26]

\[ \theta_M^2 = \frac{24\pi^2 \hbar^2 T}{Mk_B TW} \left\{ \varphi(x) + \frac{x}{4} \right\} \left( \frac{\sin \theta}{\lambda} \right)^2. \]  

(14)

\[ \theta_M^2 = \frac{24\pi^2 \hbar^2 T}{Mk_B TW} \left\{ \varphi(x) + \frac{x}{4} \right\} \left( \frac{\sin \theta}{\lambda} \right)^2. \]  

FIG. 21: Debye-Waller temperature for Cu, Ag, and Au.
FIG. 22: Debye-Waller temperature for Ni, Pd, and Pt.

FIG. 23: Debye-Waller temperature for Rh and Ir.
Here, $\theta_M$ is the effective X-ray characteristic temperature, $\varphi(x)$ is the usual Debye integral function given by [26]

$$
\varphi(x) = \frac{1}{x} \int_{0}^{x} \left( \frac{\nu}{\nu_{max}} \right) \frac{1}{e^{\nu/\nu_{max}} - 1} d\nu ,
$$

and

$$
x = \frac{\theta_M}{T} .
$$

The present findings for the X-ray characteristic temperature $\theta_M$ are shown in Fig. 24. Our present investigations of Cu, Ag, Au, and Ni are compared with the experimental findings, while for the rest of the metals the experimental data are not available. Our results for Cu, Ag, Au, and Ni agree extremely well with the experimental results and also with the theoretical investigations of Mohammed et al. [26].

XI. CONCLUSION

The calculations of the thermal properties are statistical properties; they require a knowledge of a great many phonons in the nonsymmetry directions. Thus agreement with
these properties tests the validity of our model for the reproduction of phonons in the nonsymmetry directions. We are aware that very few measurements [7–9] are available for phonon frequencies in the nonsymmetry directions, and, until the time when such measurements are available, we can only compare our theoretical results with statistical properties. This study is consistent with some of the earlier studies on the lattice mechanical properties of the fcc metals by Pandya et al. [2–5] and Antonov et al. [6]. Very recently using the ab initio density functional theory and the density functional perturbation theory along with the quasi-harmonic approximation, Narasimhan and Gironcoli [29] have calculated the thermal properties of Cu, viz. temperature dependence of the lattice constant, the coefficient of thermal expansion, the bulk modulus, the pressure derivative of the bulk modulus, the Grüneisen parameters, and the phonon contributions to the specific heats at constant volume and constant pressure. Their results also deviated from the experimental findings, in particular the phonon dispersion curves, Grüneisen parameters, the bulk modulus, and coefficient the of linear thermal expansion have much more deviation than the other such properties. Kirchhoff et al. [30] have reported the various properties of Au using a tight-binding molecular dynamic simulation. They have calculated the temperature dependence of the lattice constant, the mean square displacement, the phonon density of states, and the phonon dispersion curves. Their results for the phonon dispersion curve and the phonon density of states deviate greatly from the experimental findings. Xie et al. [31] have also reported a large number of thermal properties of Silver using ab initio molecular dynamics. The results could not avoid a reasonable deviation from the experimental findings. Quong and Li [32] have studied some thermal properties using first principle calculations of Al, Li, and Na. Their results are excellent.

The results so obtained are also comparable to those obtained from the most sophisticated methods [29–32], which are intricate and require lengthy calculations along with large computer time. The approach we suggest is simpler and less time consuming. Thus, the method can readily be used with relative ease and accuracy. Further, the earlier applications [3–5] of pseudopotentials were limited to fitting with experimental phonon frequencies at some symmetry points in the Brillouin zone. In the light of the above facts, the successful application of the present study proves the capability of reproducing a large number of physical properties of the d and f-shell metals.

References


