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Thermodynamic properties of Copper using parameter free Pseudopotential in harmonic approximation

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ABSTRACT:

Using parameter free local pseudopotential (first principles pseudopotential) in harmonic approximation, we have carried out theoretical study of temperature variation of thermodynamic properties of Copper. We have investigated predictivity of present approach by carrying out temperature variation of thermal expansion (β), isothermal and adiabatic bulk moduli (B_T& B_S), specific heats (C_p& C_v) and gruneisen parameter (γ). Our computed results are found to be in good agreement with experimental findings which suggests that even local pseudopotential can be used successfully for the description of thermodynamic properties at extreme environment (high temperature and high pressure).

KEYWORDS: pseudopotential, harmonic approximation, thermodynamic properties, copper

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INTRODUCTION:

The study of thermodynamic properties of materials is subject of interest in many branches of science like Astrophysics, Nuclear Physics, Earth Sciences and Biological Sciences.Such study is helpful for the understanding of many microscopic properties of the materials. For such studies, in the recent past many experimental methods and theoretical models are developed.In the experimental studies there are lot of limitations to perform experiments at extreme environments (High Temperatures and High Pressures). While in case of theoretical studies one has to study interactions between vibrational ions and free electrons. In order to understand thermodynamic properties theoretically, one has to find out free energy of the lattice ions due to vibrations. It has been observed that with increase in temperature one has to account anharmonic effects which are computationally lengthy.

Transition metals are complicated and pose some challenges for theoretical researchers due to their unusual chemical and electronic properties. Pseudopotential theory has been proven as a successful tool for describing thermodynamics of the crystal at extreme environments for transition metals and even for f-shell metals with good degree of success [1, 2]. Local pseudopotential proposed by Pandya et. al. [3]has been used to study thermodynamic properties in harmonic approximation. Priyank et. al. [4] have also applied harmonic theory with improved lattice dynamical model due to Antonov et. al. [5] for the theoretical study of thermal expansion in case of ten FCC transition metals. Recently we have proposed method to study phonon frequencies of Cu in highly symmetric directions[6]. In such calculation we proposed a method in which pseudopotential used is parameter free. The vibrational frequencies are found to be in good agreement with having maximum deviation of 10% variation.

Encouraged by the predictivity and success of our method we, in the present communication, extend it for the study of thermodynamic properties in harmonic approximation. For such studies one must have knowledge of phonon density of states which we have obtained by calculating phonon frequencies at number of points in the brillouin zone.

THEORY:

Once phonon density states are known the free energy due to lattice ions can be computed as [7],

$$E_H = 3N \int_0^{\omega_{max}} \left\{ \hbar\omega + \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \right\} g(\omega) d\omega \qquad (1)$$

where, N is the Avogadro number, ω_{max}= maximum frequency of the frequency distribution, k_B is Boltzmann constant and $g(\omega)$ is the normalized phonon density of states. Using above equation, the specific heat associated with lattice vibration in harmonic approximation is defined as,

$$C_V = \left(\frac{\partial E_H}{\partial T}\right)|_{\Omega=\Omega_0} \quad (2)$$

where, Ω_0=crystal volume at 0K. In terms of frequency distribution above equation takes the following form[7],

$$\frac{C_v}{3R} = \int_0^{\omega max}\left[\frac{(\frac{\hbar\omega}{k_BT})^2 \exp(\frac{\hbar\omega}{k_BT})}{[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1]^2}\right]g(\omega)d\omega \quad (3)$$

where, R is a gas constant. The thermal pressure arises from the vibrational part of the free energy. In harmonic approximation, thermal pressure is [7],

$$P^*(\Omega,T) = -(\frac{\partial E_H}{\partial \Omega})|_T \quad (4)$$

In terms of frequency distribution,

$$P^*(\Omega,T) = \frac{3N}{\Omega}\int_0^{\omega max}\hbar\omega\gamma\{\frac{1}{2} + \frac{1}{[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1]}\}g(\omega)d\omega \quad (5)$$

The bulk modulus at temperature T is defined as [7],

$$B^*(\Omega,T) = \Omega\left(\frac{\partial^2 E_H}{\partial \Omega^2}\right)|_T \quad (6)$$

In terms of frequency distribution,

$$B^*(\Omega,T) = \frac{3N}{\Omega}\int_0^{\omega max}\hbar\omega[\xi(\frac{1}{2} + \frac{1}{[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1]}) - \gamma^2\left(\frac{\hbar\omega}{k_BT}\right)]x\{\frac{1}{[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1]^2} + \frac{1}{[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1]}\}g(\omega)d\omega \quad (7)$$

where, ξ=concavity parameter and γ=Gruneisen parameter. The thermal expansion (β) measures change in volume of the crystal at constant pressure due to the change in temperature. β can be found by calculating the factor $\frac{\beta B_T \Omega}{3N{k_B}^2}$. The specific heat at constant pressure C_P is calculated by using following equation[7],

$$B_S - B_T = \frac{T\Omega}{C_V}[\beta B_T]^2 \quad (8)$$

and

$$\frac{B_S}{C_P} = \frac{B_T}{C_V} \qquad (9)$$

where B_S= adiabatic bulk modulus and B_T = isothermal bulk modulus.

RESULTS AND DISCUSSION:

We have computed phonon frequencies of Copper in symmetric directions using Kumar's pseudopotential [8]. The frequency spectra of the lattice vibrations is computed by the numerical sampling of the frequencies according to the Blackmann's technique. We have considered a mesh of evenly spaced 64000 wavevectors in the first Brillouin zone. The details of the calculations may be found in [9]. The presently computed results of C_V using equation (3) as a function of temperature is plotted and compared with theoretical results of Vyas [9] in Fig. 1.

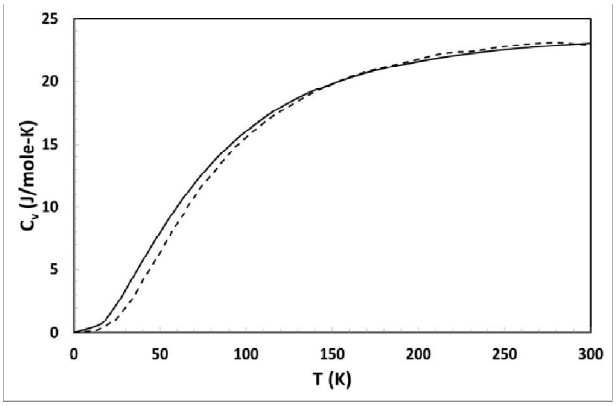

Figure 1: Specific heat C_V as a function of temperature for Cu. The dotted line --- represents theoretical results due to Vyas [9].

Here we would like to comment that pseudopotential used by Vyas contains five parameters including two Born-Mayer type repulsive potentials. In our case both the parameters of the potential (r_c and r_m) are approximated by experimental ionic and atomic radii.

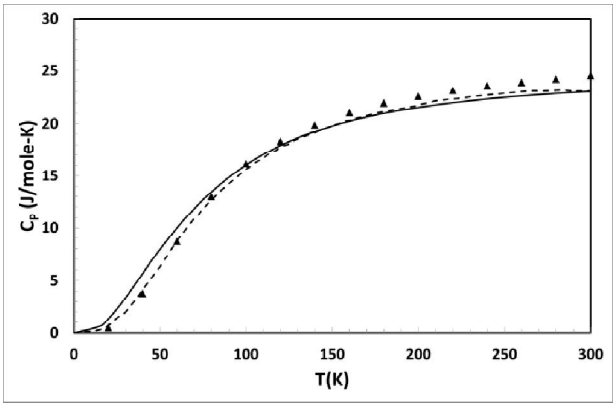

Figure 2: Specific heat C_P as a function of temperature for Cu. The dotted line --- represents theoretical resultsdue to Vyas [9] and experimental results are indicated by solid triangles ▲quoted from Wallace [7].

Specific heat at constant pressure is experimentally measureable. From Fig. 2 one can find that presently obtained results are in excellent agreement with experimental findings.

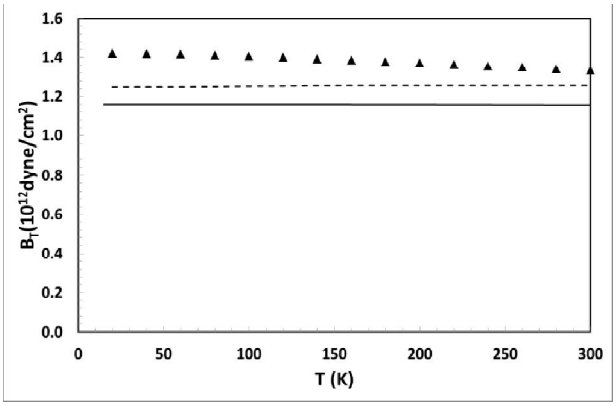

Figure 3: Isothermal bulk modulus B_T as a function of temperature for Cu. The dotted line --- represents theoretical results due to Vyas[9] and experimental results are indicated by solid triangles ▲ quoted from Wallace [7].

The isothermal bulk modulus B_T as a function of temperature upto room temperature is plotted and compared with experimental [7] and theoretical results due to Vyas [9]. It is clear from the figure with increase in temperature, theoretical results are in good agreement with experimental findings with having 13% variation. Thus in the present scheme, temperature effect is accounted properly and one can extend such studies for higher temperatures. The adiabatic bulk modulus- B_S is compared with theoretical results of Vyas in Fig. 4. The numerical values of B_S and $B_T$are decreasing with temperature which is not observable from graph.

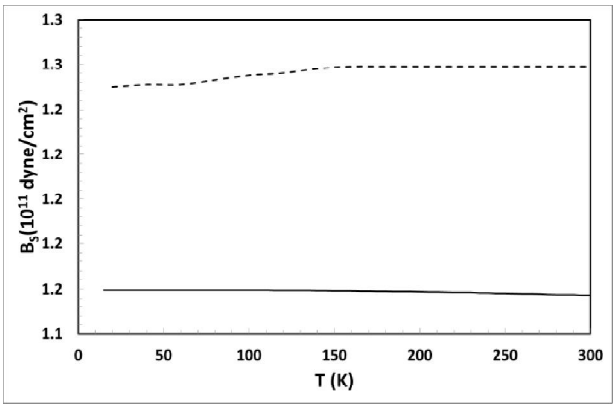

Figure 4: Adiabatic bulk modulus B_S as a function of temperature for Cu. The dotted line --- represents theoretical results due to Vyas 9

Thermal expansion is quite sensitive to the macroscopic dynamical quantities such as phonon frequencies, mode gruineisen parameter and concavity parameter. With the knowledge of temperature variation of B_T using equation $\frac{\beta B_T \Omega}{3Nk_B{}^2}$ we find thermal expansion β.

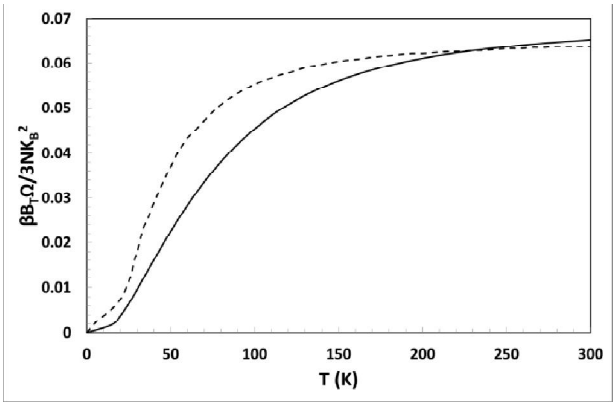

Figure 5: The temperature variation of the quantity $\beta B_T\Omega/3NK_B{}^2$ for Cu. The dotted line --- represents theoretical results due to Vyas [9].

The results of thermal expansion are quite satisfactory with the experimental results due to Wallace [7]. Instead of presenting temperature variation of β, we present temperature variation of $\frac{\beta B_T \Omega}{3Nk_B{}^2}$ (Fig.5). The variation of thermal pressure with temperature is shown in Fig. 6.

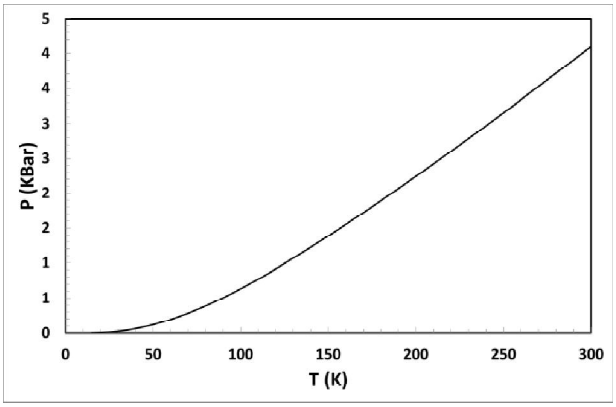

Figure 6:Thermal Pressure P as a function of temperature for Cu.

CONCLUSION:

The parameter free local pseudopotential due to Kumar is found to be successful for describing almost all the thermodynamic properties in harmonic approximation. Present approach is better than Vyas in the sense that his pseudopotential contains five parameters which are obtained from zero pressure condition and overall agreement with phonon frequency at zone boundary. As we have discussed earlier, in the present calculation we have used experimental values of parameters. Thus such theoretical study is identical to highly sophisticated first principles calculations.

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