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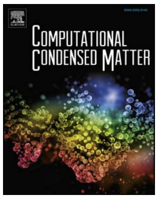

Grüneisen parameter and equations of states for copper – High pressure study

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ABSTRACT

A consistent computational scheme is proposed for calculating various thermophysical properties under simultaneous high temperature and high pressure condition in conjunction with first principles density functional theory, whereas anharmonic contribution is added perturbatively. We have demonstrated that the Grüneisen parameter γ_{th} can be calculated from the knowledge of *ab initio* binding energy, and separate volume dependence of γ_{th} is required. Taking copper as a prototype, we have calculated static and dynamic equation of states and some thermodynamic properties along the shock Hugoniot. Present study reveals the importance of anharmonic effect on various thermal properties by examining Grüneisen parameter. Computed high pressure melting curve confirms this assertion and concludes the non-negligible contributions of temperature dependence of Grüneisen parameter.

1. Introduction

Thermodynamically, equation of state (EOS) is the relation between any of the two macroscopic quantities like pressure (*P*), temperature (*T*), volume (*V*), (≡ density, ρ), entropy (*S*), enthalpy (*H*) keeping the third quantity constant; of which relations $P \equiv P_T(V)$ and $V \equiv V_T(P)$ are extensively studied experimentally and theoretically [1–3]. Due to the development in static high pressure experimental techniques to pressures up to 400 GPa and dynamic shock condition to pressure greater than 1 TPa and temperature higher than few tens of kilo Kelvin is possible to attain. Correspondingly, newer and newer theoretical models have come up [4–7] to understand and explain these isotherms. Though, the statistical mechanics offer rigorous physical foundation for these EOS in terms of classical partition function; however, in practice the evaluation of vibrational response of a crystal to total free energy at high temperature and high pressure environment till date is computationally daunting task. For metallic system, such as copper, contribution from thermally excited electrons should also be accounted for. At temperatures near or above the Fermi temperature (e.g. for copper, $T_F = 8.12 \times 10^4$ K) electronic contribution can be treated separately when classical partition function is used to compute Helmholtz free energy. *Ab initio* all-electron energy-band structure [8] methods to compute electronic free energy, $F_{el}(V, T)$, at each point in *V*-*T* plane are quite cumbersome. In the present study, we have therefore used an interpolation scheme (described in section-II) proposed by McCloskey [9] which connects low-temperature and low-pressure free-electron Sommerfeld term to ultrahigh pressure Thomas-Fermi (TF) results to account for electronic excitations. The thermal contribution due to lattice-vibration is included through quasiharmonic (QH) Mie-Grüneisen (MG) EOS. Since MG-EOS requires volume dependent thermodynamic Grüneisen parameter γ_{th} a *priory*, different parametric relations are proposed for $\gamma_{th}(V)$. The parameters of these equations are usually fitted to known EOS [3,10,11]. We show in the present study that such fitting procedure can be avoided and based on well justified assumptions for γ_{th} as a function of volume, it can be obtained from the knowledge of binding energy [12–15].

In the previous paper [16], henceforth we call it paper-I, we have investigated various thermal properties of silver, and the role played by anharmonicity in determining these properties at high temperature but zero pressure condition. In the present study, we examine the role of compression on some thermodynamic properties under simultaneous high pressure and high temperature environment for solid copper. In particular, we combine first principles density functional perturbation theory (DFPT) based lattice contribution to MG-EOS in addition to lowest order perturbative term to account for anharmonic free energy along with contributions from thermally excited electrons. Though anharmonicity reduces with pressure; present results for γ_{th} show its

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importance along strong shock condition. Thus, the main objective of the present study is to report systematic results for static and dynamic EOS and some thermodynamic properties along the shock Hugoniot. Temperature along the principal shock Hugoniot is also determined. Furthermore, high pressure melting curve is deduced within the Lindemann's criterion to explore the sensitivity of temperature-dependent Grüneisen parameter.

The paper is organized as follows. In the next section, we present theoretical background with necessary equations to formulate the problem. Section-III highlights comparison of present findings with other experimental and theoretical results – where available. Based on this comparison, important inferences are drawn to conclude the paper in the final section.

2. Theoretical formulation

Classically, ignoring electron-phonon interaction, the total free energy [16] can be written as a sum of (i) cold energy $E_C(V)$, (ii) QH lattice-vibrational energy $F^l_{QH}(V,T)$, (iii) electronic free energy $F_{el}(V,T)$ and (iv) anharmonic energy $F_{An}(V,T)$.

$$F(V,T) = E_C(V) + F^l_{QH}(V,T) + F_{el}(V,T) + F_{An}(V,T). \tag{1}$$

The total isothermal pressure can be obtained through thermodynamic relation, $P(V) = -\left(\frac{dF(V,T)}{dV}\right)_T$. Thus, $P(V) = P_C(V) + P^l_{QH}(V,T) + P_{el}(V,T) + P_{An}(V,T)$. The cold energy and hence the cold pressure (P_C) is derived by solving Kohn-Sham energy functional using ultrasoft pseudopotential within the GGA due to Perdew-Burke-Ernzenhof. The *ab initio* calculation for phonon dynamics were performed using PWSCF and PHONON code [17]. The pseudopotential was generated using Vanderbilt code with [Ar] $3s^2 3p^6$ as the core state. To tackle in the expansion of the augmentation charges for such non-norm-conserving pseudopotential a relatively high cut-off of 900 Ry was used, while a plane wave basis set with a cut-off of 90 Ry was used after checking the convergence for electronic SCF. Total energies were then calculated self-consistently within the density functional theory (DFT). Phonon dynamical matrices were computed using 4 × 4 × 4 $\vec{q}$-point mesh; while dense 14 × 14 × 14 regular k-point mesh was implemented to Fourier interpolates these matrices. Force constants so deduced are then used to compute p-dos. The Methfessel-Paxton (MP) scheme with smearing parameter equals to 0.06 Ry was used to tackle convergence problem due to free electrons. Total energy (E_{tot}) at various volumes so deduced is then fitted to third order Birch-Murnaghan (BM) EOS to derive equilibrium volume V_0 ($\equiv$ lattice constant, a_0), bulk modulus B_0 and its first order pressure derivative B'. Present results are: $a_0 = 6.8273$ a.u. (6.8219), $B_0 = 148.7$ GPa (142.3), and $B' = 4.11$ (3.91, 4.1, 4.8, 5.3, 5.59, 5.44). Experimental findings are shown in parenthesis, which are quoted from Ref. [18]. The cohesive (cold) energy curve is derived using the relation $E_C(V) = E_{tot}(V) - E_{atom}$, where E_{atom} is obtained with $V = 10V_0$ such that practically it represents a single isolated atom. Results for cohesive energy are fitted to third order Birch-Murnaghan (BM) EOS to determine the cold pressure.

For lattice-vibrational part, we differentiate the second term in Eq. (1) with respect to volume to get,

$$P^l_{QH}(V,T) = \frac{3N}{V}\int_0^{\omega_{max}} \omega\gamma_i(\omega_{\lambda,\vec{q}})\left\{\frac{1}{2} + \frac{1}{exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\right\} g(\omega)d\omega, \tag{2}$$

where $\gamma_i(\omega_{\lambda,\vec{q}})$ represents dynamic mode-Grüneisen parameter and $g(\omega)$ denotes p-dos, while all the other physical quantities have usual meaning [16]. Equation (2) can be solved in principle by finding volume dependent phonon frequency $\omega_{\lambda,\vec{q}}(V)$ and using the phonon–density-of-state (p-dos) in the first Brillouin Zone (BZ) at each temperature, where use can be made,

$$\gamma_i(V) = -\left(\frac{dln\omega_{\lambda,\vec{q}}(V)}{dlnV}\right). \tag{3}$$

However, this procedure is mathematically tedious and seldom used in practice without imposing some plausible approximations. More tractable form is possible; if one assumes all $\gamma_i(V)$'s are equal. In fact, previous all studies indicate that the result based on this assumption agree well with experimental and simulation findings [3,19,20]. With this point of view, in Eq. (2), $\gamma_i(V)$ can be assumed independent of index λ and $\vec{q}$. It can be written as volume only dependent thermodynamic Grüneisen parameter, i.e. $\gamma_i(V) \equiv \gamma_{th}(V)$. Thus, solving Eq. (2) requires to know $\gamma_{th}(V)$, which can be computed as follows. Recently, Wang and his co-workers [6,12,21] have proposed and later by the other researchers [13–15] have used a way to compute generalized force constant $k(V)$ for vibrating lattice ions.

$$k(V) = \frac{1}{a_0^{2\lambda}}\frac{\partial}{\partial a_0}a_0^{2\lambda}\left(\frac{\partial E_C(V)}{\partial a_0}\right). \tag{4}$$

Here, a_0 denotes equilibrium lattice constant and a parameter λ determines the degree of anharmonicity. Commonly adopted different choices for λ; namely, −1.0, 0, +1.0, +1.5, corresponds, respectively, to different literature expressions for Grüneisen parameter: due to Slater [22], due to Dugdale and MacDonald [23], due to Vashchenko and Zubarev [24], and that due to improved *free-volume* theory by Stacy [1]. In general, λ can also be treated as adjustable parameter [14,25,26] and volume dependent, however. With this generalized force constant and by assuming lattice ions are performing quasiharmonic vibrations, their *mean* vibrational frequency can be estimated as follows,

$$\omega(V) \approx \left[\frac{k(V)}{M}\right]^{\frac{1}{2}}. \tag{5}$$

Here, M is the mass of lattice ion. Now, replacing $\omega_{\lambda,\vec{q}}(V)$ in Eq. (3) by Eq. (5); an ionic or lattice part of Grüneisen parameter is written as,

$$\gamma_l(V) = \frac{-V_0}{\omega(V_0)}\left(\frac{d\omega(V)}{dV}\right). \tag{6}$$

$$\gamma_l(V,\lambda) = \frac{-a_0}{6}\left[\frac{\frac{d^3E_C}{da_0^3} + \frac{2\lambda}{a_0}\frac{d^2E_C}{da_0^2} + \frac{dE_C}{da_0}}{\frac{d^2E_C}{da_0^2} + \frac{2\lambda}{a_0}\frac{dE_C}{da_0}}\right]. \tag{7}$$

In Refs. [6,12,16], it was demonstrated that the choice λ = −1.0 gives better thermal expansion coefficient, and we retain the same in the present study also. It is also to be noted that expression (7) is equivalent to the following equation (8) for $\gamma_{th}(V)$ written explicitly in terms of pair-potential $\phi(R)$ and its derivatives for a particular choice of λ = +1.0.

$$\gamma_l(V) = \frac{-1}{6}\frac{\left[\sum_i C_i\left\{\frac{-2}{R}\phi'(R) + 2\phi''(R) + R\phi'''(R)\right\}\right]}{\left[\sum_i C_i\left\{\frac{-2}{R}\phi'(R) + \phi''(R)\right\}\right]}, \tag{8}$$

where we have used $E_c(V) \equiv \frac{1}{2}\sum\phi(R)$. Here, $|\vec{R}| \equiv R$ represents the magnitude of direct lattice vectors for fcc structure and C_i denotes the co-ordination number of i^{th} shell. Thus, Eq. (7) represents the most general definition of $\gamma_{th}(V)$, and has more general appeal than Eq. (8). For instance, current all *state-of-art* calculations give binding energy, while pair-potential can be derived only approximately [27,28] from the total energy functional. Furthermore, volume dependence of γ_{th} is now intrinsically incorporated in Eq. (6) and no separate parametric expression is required. With these line of arguments, the lattice contribution to total pressure $P^l_{QH}(T)$ is now given as,

$$P^l_{QH}(V,T) = \gamma_l(V)\left[\frac{3N}{V}\int_0^{\omega_{max}} \omega\left\{\frac{1}{2} + \frac{1}{exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\right\} g(\omega)d\omega\right], \tag{9}$$