Theoretical Study of Static and Dynamic Equation of State of Cerium and Ytterbium

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Abstract

Theoretical study of the dynamic equation of state or shock Hugoniot plays a key role in describing behaviour of materials under simultaneous high temperature and high pressure that are very difficult to achieve in the experiments. Schock Hugoniot is locus of all possible states that arises due to a single shock from a given initial state, generally explained by thermodynamic variables like pressure, volume and internal energy or enthalpy. Anharmonicity aroused due to lattice ions and thermally excited electrons should be accounted properly at such high temperature and high pressure. In the present study, a conjunction scheme of a local form of the pseudopotential proposed by Krasko and Gruski (KG) and mean field potential (MFP) has been used to account anharmonic effects due to lattice vibrations. The anharmonicity due to thermally excited electrons has been included using Mermin functional. Static as well as dynamic equation of states along with temperature along principal Hugoniot of rare earth elements cerium and ytterbium have been studied theoretically. The conjunction scheme is found to be capable to account for anharmonicity at extreme environment such as high temperature and high pressure.

Keywords: Pseudopotential, Rare Earth Elements, Equation of State, Shock Hugoniot.
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Introduction

Equation of state (EOS) relates various state functions of materials like pressure, volume and temperature that is used to study thermodynamic behaviour of materials and modelling of interior of planets and stars [1].

To study behaviour of materials under simultaneous high temperature and high pressure produced due to shock wave, Dynamic equation of state or shock-Hugoniot is used which is fundamental relationship between pressure, volume and energy of a materials. Shock waves are sudden variations in pressure, density and internal energy of material that occur due to localised rapid release of energy [2]. Shock wave phenomenon has found its applications in shock welding and dynamic compaction of materials. Shock wave data are found useful not only in the measurement of densities of materials at high pressure but also in the study of terrestrial planets and the solid satellites [3]. These data can further be utilized to design systems like infantry helmets and ship hulls facades that are exposed to explosive or projectile loading [2]. Such facts lead to requirement of theoretical models that can be used to describe behaviour of transition and f-shell metals especially at high temperature and high pressure that are very difficult to achieve experimentally.

Due to complicated electronic and structural behaviour of

transition and f-shell metals, use of local pseudopotential for comprehensive study of their physical properties is very difficult to implement.

Though, the non-local and norm conserving pseudopotentials are found to be better but their mathematical complexity is a major hurdle in implementing them computationally for comprehensive studies of physical properties of materials. During, literature survey, we found that local pseudopotential has been used efficiently to explore properties of simple, transition and f-shell metals at extreme environment [4-8]. It is also important to note that limited efforts have been made to study physical properties of f-shell metals especially at extreme environment using pseudopotential theory [7-8].

Theory

The Helmholtz free energy at given volume (Ω) and temperature (T) is used to calculate thermodynamic properties of a material that is given by following equation [7]-

$$F(\Omega,T) = E_c(\Omega_0) + F_{ion}(\Omega,T) + F_{eg}(\Omega,T) \qquad (1)$$

Second order perturbation theory using pseudopotential due to Krasko and Gruski (KG) [9] has been used to find cold energy $E_c(\Omega_0)$. The pseudopotential used in the present study has following form in the q space [7,9].

$$V_{ion}(Q) = \left(\frac{8\pi Z}{\Omega Q^2}\right)\left(\frac{(2a-1)(Qr_c)^2-1}{[(Qr_c)^2+1]^2}\right) \qquad (2)$$

The pseudopotential has two adjustable parameters a and the core radius- r_c. Exchange and correlation function due to Hubbard [10] and Sham [11] has been used to screen the pseudopotential following equation has been used to calculate ionic contribution $F_{ion}(\Omega,T)$ to the Helmholtz free energy [7]

$$F_{ion}(\Omega,T) = -k_BT\left[\left(\frac{3}{2}\right)ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + ln\{v_f(\Omega,T)\}\right] \qquad (3)$$

Where $v_f(\Omega,T) = 4\pi\int exp\left[\frac{-g(r,\Omega)}{k_BT}\right]r^2dr$

Here, m is ionic mass and k_B is Boltzmann constant. The, mean field potential (MFP) as a function of cold energy- $E_c(\Omega_0)$ as suggested by Wang and Li [12] is given by

$$g(r,\Omega) = \frac{1}{2}[E_c(R_0+r) + E_c(R_0-r) - 2E_c(R_0)] + \left(\frac{\lambda}{2}\right)\left(\frac{r}{R_0}\right)[E_c(R_0+r) - E_c(R_0-r)] \qquad (4)$$

In equation 4, r defines deviation of lattice ion from its equilibrium position while R_0 is the lattice constant corresponding to equilibrium volume ($\Omega = \Omega_0$). The parameter λ has three possible integral values -1, 0 and +1 that correspond to three different choices of Gruneisen parameters due to Slater, Dugdale and MacDonald and Vashchenko and Zubarev respectively [12]. We have taken $\lambda = +1$ in the present study; because it reproduces good result of physical properties of different classes of metals [4-8]

We have calculated P-Ω relation at 300 K by following equation [13].

$$P = -\left[\frac{\partial F(\Omega,T)}{\partial\Omega}\right]_{T=300K} \qquad (5)$$

The internal energy or enthalpy is defined as [7, 12]

$$E_H(\Omega,T) = E_c(\Omega) + \xi(\Omega,T)k_BT \qquad (6)$$

With, $\xi(\Omega,T) = \frac{3}{2} + \left(\frac{\partial ln v_f(\Omega,T)}{\partial lnT}\right)_\Omega$

Further, Rankin-Hugoniot equation is used to calculate pressure-P_H and temperature-T_H along Hugoniot that is obtained from conservation laws of mass, momentum and energy [4-6],

$$(E_H - E_0) = \frac{1}{2}(P_H + P_0)(\Omega_0 - \Omega_H) \qquad (7)$$

Here, ρ, P and E represent density, pressure and enthalpy respectively. Suffix 0 and H represent quantities in the un-shocked and shocked region respectively.

Results and Discussion

On the line of many previous studies [4-8], the pseudopotential parameter a is kept equal to 3 to reduce number of adjustable parameters from two to one. The second pseudopotential parameter r_c has been fitted using zero pressure condition. The values of r_c for Ce and Yb are 0.569 a. u. and 0.572 a.u. respectively [7].

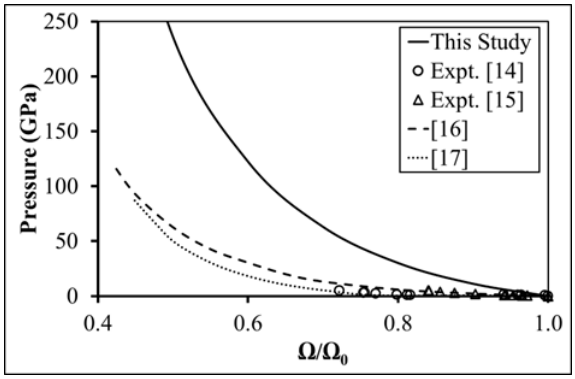

Figure 1: 300 K isotherm of Ce.

Equation of state of Ce and Yb at 300 K along with other experimental and theoretical results [14-19] are shown in Fig.1 and Fig.2 respectively. Static EOS at 300 K of Ce and Yb are in reasonably good agreement with experimental and other theoretical results. At higher pressure results deviate from other reported experimental and theoretical results. Such variation may be due to the fact that the parameter λ involved in the equation 4 is kept equal to 1. Some studies [20-22] suggest that the parameter λ is temperature and

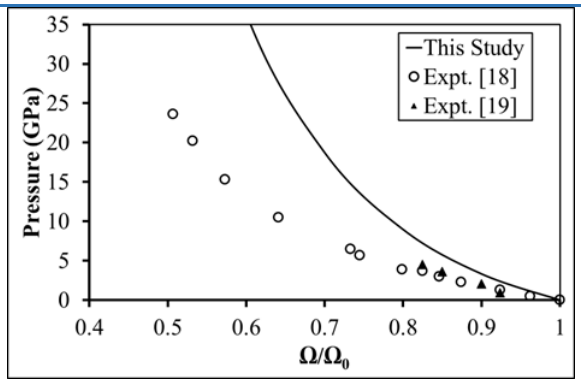

Figure 2: 300 K isotherm of Yb.

volume dependent. Therefore, results of EOS of Ce and Yb at 300 K can be improved by making temperature and volume dependent.

Static EOS is used to find shock Hugoniot and temperature along principal Hugoniot using iterative method [4-6]. The calculated shock wave pressure (P_H) of Ce as a function of reduced volume (Ω_H/Ω_0) and available experimental [23-24] as well as other theoretical results [16-17] are shown in Fig 3. Fig. 4 presents Shock Hugoniot of Yb along with experimental results [23].

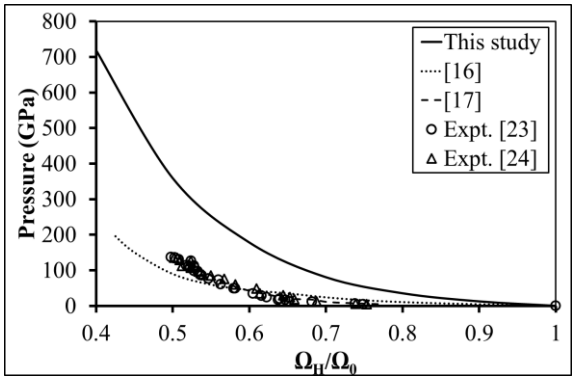

Figure 3: Shock Hugoniot of Ce.

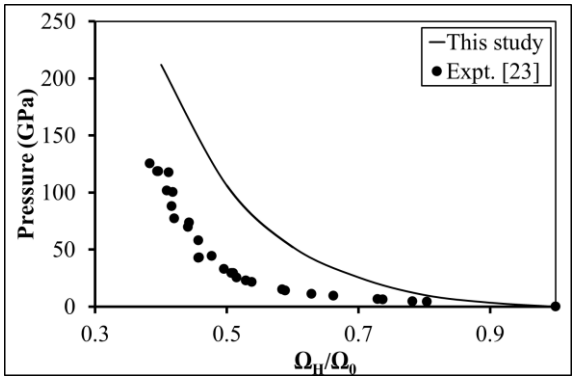

Figure 4: Shock Hugoniot of Yb.

Temperature along principal Hugoniot (T_H) of Ce and Yb as a function of reduced volume (Ω_H/Ω_0) are shown in Fig 5 and Fig. 6 respectively.

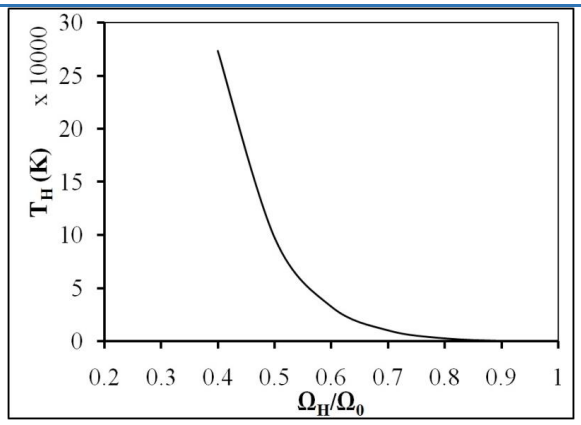

Figure 5: Temperature along principle Hugoniot of Ce.

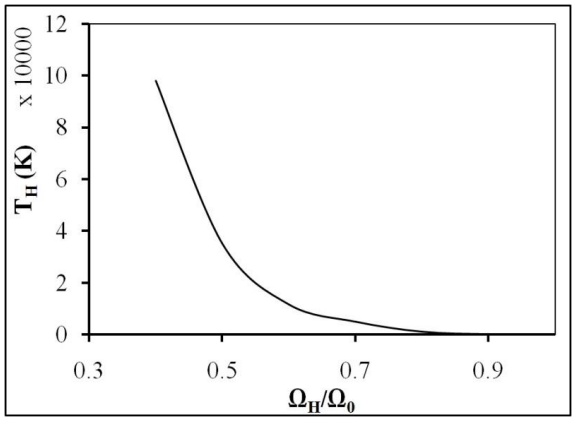

Figure 5: Temperature along principle Hugoniot of Yb.

We could not compare the results of temperature along principal Hugoniot with others because no experimental or theoretical study have been found in literature.

It is important to point out that the parameter $\boldsymbol{\lambda}$ depends on volume, temperature and material as suggested in some studies [20-21]**.** Therefore, the results obtained in the present study can be improved by accounting anharmonicity properly at high temperature by making λ temperature and volume dependent [23] instead of using extra anharmonic contribution to the Helmholtz free energy as suggested in reference [25].

Conclusion

Local form of the KG pseudopotential in conjunction with MFP accounts the anharmonicity due to lattice vibrations and thermally excited electrons at high temperature. Presently used conjunction scheme does not require an additional Born-Mayer type of potential to accounts core-core repulsion and valency has also not been adjusted in the present study. Observed deviation in the theoretical results with experimental results especially at high temperature may have aroused because of the constant value of parameter $\boldsymbol{\lambda}$ which is appearing in the equation of $\mathbf{F_{ion}}$(see equation 3 and 4). Thus, due to its computational simplicity and reliability, the present conjunction scheme of local

pseudopotential and MFP can be used for theoretical study of thermodynamic properties of transition metals and f-shell metals.

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