High-pressure study of Na: A mean-field potential approach

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Study of anharmonicity through Grüneisen parameter is carried out for elemental Na at finite temperatures and pressures. The mean-field potential (MFP) approach has been employed in conjunction with the local pseudopotential to evaluate Helmholtz free energy at elevated temperatures and pressures. The calculated pressure and temperature variation of thermodynamic Grüneisen parameter ($\gamma_{th}$), pressure dependence of isothermal bulk modulus ($B_T$) and total free energy at $T = 300$-K have been calculated. Results obtained are satisfactorily compared with the experimental and other first principles data.

Keywords: Helmholtz free energy, Grüneisen parameter, Bulk modulus, High-pressure

1 Introduction

Because of the single $s$-electron in the valence band, the alkali metals are considered simple metals with the band structures that differ very slightly from those of free-electron systems. However, when alkali metals are subjected to high compressions they show unexpected complexity. The high-pressure complexity in the crystal structure and melting curve of heavier alkali metals (Rb and Cs) have been attributed to $s\rightarrow d$ transitions in the electronic structures. Since $s$-wave functions are more extended in space than $d$ functions, compression induces the $s$-like states to rise in energy relative to the $d$-like levels leading to a transfer of $s$-conduction electron to $d$-states. However, light alkali metals, namely Li and Na, do not fit into this explanation as Li has no $d$-bands and Na has $3s$ conduction band far below the $3d$ band. For instance, high-pressure low symmetry phases of Li and Na, and melting curve of Na can’t be explained with the same argument. This makes the high-pressure behaviour of light alkali metals an important subject of current experimental and theoretical study. On experimental side, there are certain difficulties, primarily, in keeping the samples at very high $P$-$T$ conditions due to high reactivity of these metals. On the other hand, complete ab initio theoretical investigations are still restricted to ambient conditions due to mathematical complexity and are carried out with well-defined approximations only.

Thermodynamic properties at high temperatures and equations of states of alkali, alkaline earth and simple polyvalent metals with the proposed coupling scheme (i.e. MFP + local pseudopotential) have been studied earlier. In the present paper, the new possibilities of calculating high-pressure bulk properties of light alkali metal Na have been explored. The total energy curves at 0-K and 300-K, pressure variation of isothermal bulk modulus ($B_T$), a quantity that influences the slope of the total energy curve and therefore decisive for other bulk properties; thermodynamic Grüneisen parameter ($\gamma_{th}$) at high-temperature and high-pressure, which describes the volume (=pressure) dependence of the phonon frequencies for elemental Na have been obtained.

2 Theory

Total Helmholtz free energy of the crystalline solid, neglecting electron-phonon interaction, can be written as,

$$F(V,T)=E_C(V)+F_{ion}(V,T)+F_{eg}(V,T) \quad \ldots(1)$$

where $E_C$ represents static 0-K total binding energy. $F_{ion}$ and $F_{eg}$ are the vibrational free energy of the lattice ion and Helmholtz free energy due to thermal excitation of electron gas, respectively. Recently, Wang and Li, have proposed the mean-field potential (MFP) approach for evaluating contribution of vibrating lattice ions in terms of cold energy $E_C$, which they have obtained employing first principles method, namely FP-LAPW, within generalised gradient approximation (GGA). In present study...
$E_C(V)$ in Eq. (1) is calculated using second-order pseudopotential formalism with the local pseudopotential (with the individual set of parameters) due to Fiolhais et al.\textsuperscript{11} (see Ref. 6 for more details). Having obtained $F(V,T)$, equilibrium volume at different temperatures and pressures were obtained with minimization criterion (i.e. zero pressure condition). Volume thermal-expansion ($\beta$), bulk modulus ($B_T$) and thermodynamic Grüneisen parameter ($\gamma_{th}$) can be calculated numerically using standard thermodynamic equations.

$$\beta_p(V,T) = \frac{1}{V} \left( \frac{\partial V(T)}{\partial T} \right)_V$$ \hspace{1cm} ... (2)

$$\beta_T(V,T) = V \left( \frac{\partial^2 F(V,T)}{\partial V^2} \right)_V$$ \hspace{1cm} ... (3)

$$\gamma_{th}(V,T) = \left( \frac{VB_T(V,T)\beta_p(V,T)}{C_V(V,T)} \right)$$ \hspace{1cm} ... (4)

3 Results and Discussion

The total energy curve at 0-K and room temperature (300-K) as a function of bcc lattice constant shown in the Fig. 1, compared satisfactorily with the first principles results due to Wang and Fang\textsuperscript{12}, and experimental datum from Kittel\textsuperscript{13}. Wang and Fang\textsuperscript{12} have obtained $E_C$ in Eq. (1) using FP-LAPW within GGA. It is clear from the graphs that as temperature increases dip in energy $\rightarrow$ lattice constant curve shifts downward as well as towards right. Our results at 0-K are in close confirmation to the experimental datum relative to first principles calculation of Wang and Fang\textsuperscript{12}.

Pressure variation of isothermal bulk modulus is depicted in Fig. 2. An excellent result for isothermal bulk modulus is obtained for the entire range of pressure that studied. Christensen and Novikov\textsuperscript{2}, through first principles calculations, have demonstrated that Na above 80 GPa pressure transfers to fcc (which is lower in energy by $\sim$5 meV/atom) and remains up to $\approx$130 GPa, and then to lower symmetry state. Such small energy differences between these structures cannot be estimated using the present scheme. Therefore, bcc-phase for complete pressure range has been considered. In Fig. 2, results for $B_T$ at higher pressures (>65 GPa) is compared nicely with the \textit{ab initio} results of Christensen and Novikov\textsuperscript{2} (not shown in the figure) for bcc-phase of Na. Straub and Wallace\textsuperscript{14} have coupled molecular dynamics (MD) method with the pseudopotential perturbation formulation. They have determined potential parameters by requiring agreement between theory and experiment for the crystal binding energy and its first two volume derivatives at 0-K and zero pressure. Considering that the bulk modulus increases more than an order of magnitude, our results are considered good in agreement with these theoretical and experimental findings due to Aleksandrov \textit{et al.}\textsuperscript{15}.

![Fig. 1 — Presently calculated total energy curve at 0-K (solid line) and 300-K (broken line) along with the \textit{ab initio} results due to Wang & Fang\textsuperscript{12} (dotted line), while experimental point is due to Kittel\textsuperscript{13}.](image1)

![Fig. 2 — Pressure variation of $B_C$: Present calculation (solid line), MD results (broken line) due to Straub and Wallace\textsuperscript{14}, experimental data (diamond) are due to Aleksandrov \textit{et al.}\textsuperscript{15}.](image2)
Lattice anharmonicity (at finite temperatures and pressures) leads to a volume dependence of the phonon frequencies, that is described by the mode Grüneisen parameters, $\gamma_i=-(\partial \ln \omega_i / \partial \ln V)$, and mechanical Grüneisen parameter is defined as the average of the $\gamma_i$ over the first Brillouin zone. At relatively low temperature (i.e. $T < \theta_D$, where $\theta_D$ is the Debye temperature for Na, $\theta_D = 158$-K), $\gamma_i$ are all different, but at elevated temperature (i.e. $T > \theta_D$), it is a reasonable assumption to treat all $\gamma_i$ to be equal, which is known as thermodynamic Grüneisen parameter. According to Grüneisen, the volume dependence of the phonon frequencies can be estimated by the single parameter ($\gamma_{th}$) and thereby is the measure of the anharmonicity. Temperature and pressure variations of the same are shown in Figs 3 and 4, respectively. Relatively weak temperature dependence (i.e. only slightly increases with temperature) is consistent with the Grüneisen hypothesis. Also shown in the Fig. 3 are the experimental results due to Boehler\textsuperscript{16} (from the graph of Ref. 16, p. 6760 for $P = 0$ kbar), extending well into liquid regime. Deviation in $\gamma_{th}$ observed at 300-K is about 10%.

Grüneisen gamma as a function of pressure is the key ingredient in determining thermophysical properties at high-pressure environment, particularly, high-pressure melting curve and equations of state (EOS), (both static as well as shock Hugoniot). Present study results are excellent in comparison to the other theoretical and experimental results (Fig. 4). At low pressures it decreases rapidly and then flattens and decreases slowly on compression. Thus, it is reasonable to treat gamma almost constant at moderately high pressures. Wang and Fang\textsuperscript{12} have plotted the graph of $\gamma_{th}(V_0/V) \rightarrow$ pressure assuming $\gamma_{th}/V$ to be constant, which in this study are converted for $\gamma_{th} \rightarrow$ pressure using their EOS for comparison. Low pressure experimental points are due to Boehler\textsuperscript{16} and dotted line is due to Straub and Wallace\textsuperscript{14}. The results of this study lie between the first principles estimates and the experimental ones. Maximum deviation is found to be 11\% with the experimental data. Trend observed for all the results is same which justifies the present conjunction scheme.

4 Conclusions

It has been demonstrated that simple coupling scheme of combining local pseudopotential with the recently proposed MFP approach can produce good bulk properties of elemental Na at high pressures. Good results for high-temperature Grüneisen parameter and total energy ($F$) at 300-K reveal that associated anharmonicity is accounted correctly. Isothermal bulk modulus and Grüneisen parameter at high pressures are also in confirmation with the other theoretical and experimental data. Thus, Fiolhais’ local pseudopotential with MFP approach is capable of producing good quality results for thermophysical properties and can be considered as good working proxy to the other reliable first principles approaches, at least for simple metals. It is also to be noted that no fitting to any of the physical quantity has been made
during the course of calculation except following zero pressure condition, in determining equilibrium volume at each temperature and pressure. Looking to good quality results for $\gamma_h \rightarrow$ pressure, we have calculated several other thermophysical properties at high-pressure environment for Na and remaining alkali metals, and results are found in good agreement with the other results.

References