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Role of Quasiharmonic Gruneisen Parameter in Determining Solid-Liquid Phase Boundary

Abstract

Diamond Anvil Cell (DAC) and first principles density functional theory have substantially influenced and developed our understanding regarding high pressure behaviour of materials in general; and the structural phase transition, in particular. Of which the study of solid-liquid phase boundary under compression is of greater importance as it involves order (crystalline) to disorder (statistical character) phase as well as the vital temperature dependent anharmonic effects. As a result of such complexity, the two-phase melting scenario is seldomly used to estimate high pressure melting curve. One phase melting theory includes, for example, the dislocation mediated melting, the Lindemann criterion, etc.; are efficiently used to drive T-P phase relation. A common practice using Lindemann melting law in conjunction with Grüneisen parameter (γ) is that the volume (\equiv pressure) variation of γ for each phase is incorporated empirically with parameters are fitted to known equation of state and its asymptote. Such procedure is necessary to predict low melting slopes for bcc phase of the metals. In the present study, however, we propose that volume variation for γ can be calculated consistently from the pair-potential that is based on the local pseudopotential; and hence the melting curve can be deduced. Corresponding pressure is estimated employing third-order Birch-Murnaghan EOS added with thermal contribution to cold pressure. Results for Grüneisen parameter and solid-liquid phase boundary for prototype simple metals, viz; Al (fcc) and Na (bcc), are compared and discussed with literature findings, which validate the present scheme.

Keywords: Lindemann criterion, Pseudopotential, Grüneisen parameter

Introduction

Study of thermodynamic properties of materials at high- P is challenging even with *state-of-art* experimental and first principles density functional theory. Some metals have a simple *nearly free-electron* (NFE) behaviour at low pressure; but at high- P their behaviour is complex and involves structural phase transition (SPT). Of which the study of solid-liquid phase boundary under compression; high- P melting curve, is of greater importance, e.g., in geophysics. Melting point of materials involves effect of ordered crystal phase and disordered fluid phase along with the vital T -dependent anharmonic effects. Gregoryanz et al. [I] have determined P -dependence of melting temperature for Na using high- P /high- T X-ray diffraction technique. Authors in Ref. [II, III] have used two-phase thermodynamic model to estimate high- P melting curve. In the present study, we derive high- P melting curve using single-phase model in conjunction with quasiharmonic Grüneisen parameter γ_{th} . Results are compared and discussed.

Theory and Formulation

The theory of melting was first proposed by Lindemann in terms of the mean square average amplitude of vibrations which was rewritten by Gilveri [V] in terms of γ_{th} as,

$$\frac{d\ln T_m}{d\ln V} = -2 \left(\gamma_{th}(V) - \frac{1}{3} \right). \quad \dots(1)$$

On solving above equation, we get,

$$T_m = T_m^0 \exp \int_{\eta=1}^{\eta} \left[-\frac{2}{\eta} \left(\gamma_{th}(V) - \frac{1}{3} \right) \right] d\eta, \quad \dots(2)$$

Where T_m is melting temperature at compression $\eta = V/V_0$ and $\gamma_{th}(V)$ is a Grüneisen parameter. Subscript and superscript '0' indicate quantities at zero-pressure equilibrium condition. If we assume γ_{th} independent of volume then Eq. (1) becomes

$$T_m(V) = T_m^0 \left(\frac{V_m^0}{V} \right)^{2(\gamma_{th}-\frac{1}{3})}. \quad \dots(3)$$

Thus, knowing normal melting temperature T_m^0 , one can deduce melting temperature at compression η in terms of γ_{th} . The $\gamma_{th}(V)$ can be calculated from the knowledge of pair-potential $\varphi(R)$ among the particles.

$$\gamma_{th}(V) = -\frac{1}{6} \frac{\sum_i C_i \left(-\frac{2}{R} \varphi'(R) + 2\varphi''(R) + R \varphi'''(R) \right)_{R_i}}{\sum_i C_i \left(\frac{2}{R} \varphi'(R) + \varphi''(R) \right)_{R_i}}. \quad \dots(4)$$

Here, C_i is Coordination number of i^{th} neighbour, R is interatomic distance at volume V and primes on $\varphi(R)$ indicate derivatives of it. We consider NFE model as weak interaction between valence electrons and the core; thus the pair potential.

$$\varphi(R) = \frac{Ze^2}{R} - \frac{2Z^2e^2}{\pi} \int c(q) \frac{\sin qR}{qR} dq. \quad \dots(5)$$

We have used third-order BM-EOS for cold pressure, while thermal contribution to it is $P_{th} = 3k_B T \frac{\gamma_{th}(V)}{V}$.

Results and Discussion

The melting curve of Al (fcc) and Na (bcc) are obtained to pressure up to 100 GPa and 125 GPa respectively, using QHA for γ_{th} . Melting curve for Al and Na are shown and compared in figures 1-4. It can be seen from the graphs that at low- P melting data are in good agreement with other values. At high- P , our results for Na with volume dependent

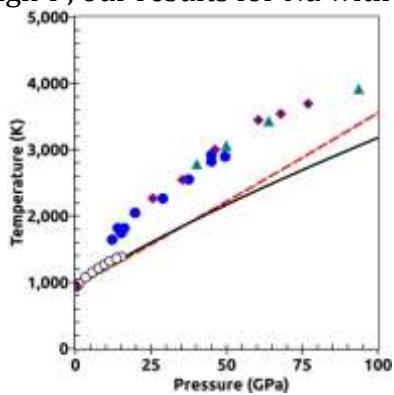


Fig.1 Melting curve for Al: Solid line-Eq.(1), Dashed line-Eq.(2) ◆-[VII], ●-[VIII], ▲-[IX], ○-[VI]

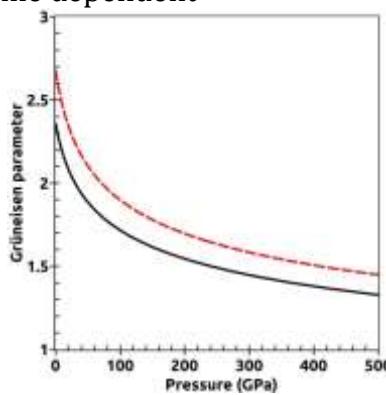


Fig.2 Pressure variation of γ_{th} for Al, Solid line-at V_0 , and Dashed line - V_m^0 .

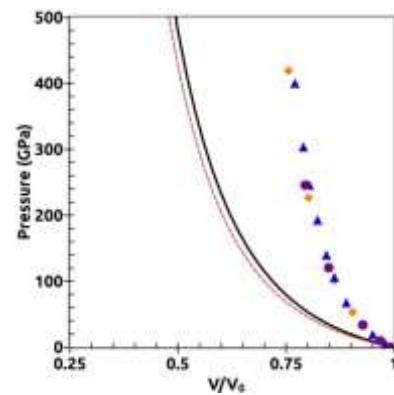


Fig.3 EOS for Al: solid line - BM-EOS, Dashed line - BM-EOS+ P_{th} , ◆ - [IV], ▲ - [IV], ● - [IV],

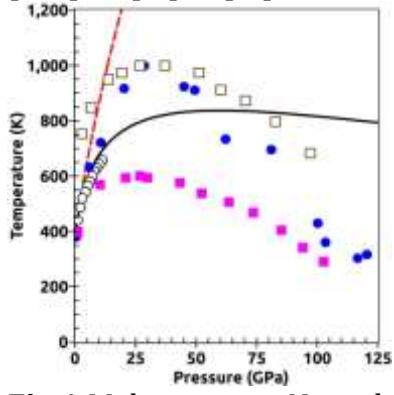


Fig.4 Melting curve Na: solid line-Eq(1), Dashed line-Eq(2), ■-[X], □-[XI], ●-[I], ○-[XII]

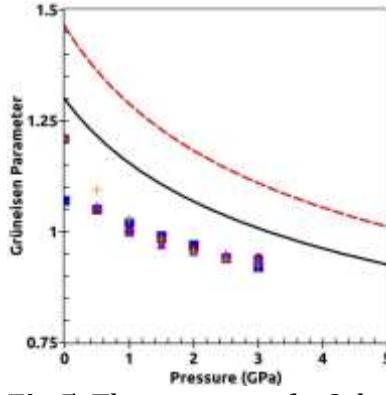


Fig.5 The same as fig.3 but for Na. + -[XIII], ▲-[XIV], ■-[XV], ●-[XVI], (+,▲,■- at 298 K)

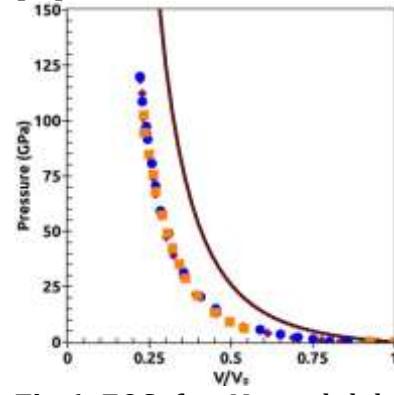


Fig.6 EOS for Na: solid line-BM-EOS, Dashed line-BM-EOS+ P_{th} , ■-[XVII], ◆ - [XVIII], ● - [XIX],

γ_{th} show observed trend, giving peak-structure ($T_m^{\text{Peak}} = 863.90$ K at 62.21 GPa) but they differ by more than 20%. The decrease in T_m is due to an overlap of the valence electron band and core electrons which significantly changes the electronic states. At high- P simple cubic structure is destroyed resulting in anomalous melting scenario. Nevertheless, results using harmonic expression

for γ_{th} are unphysical, and giving monotonous increase in T_m with pressure. Since Al remains stable in closed packed fcc structure up to the studied highest- P , it shows continuous increase in T_m with pressure, Fig.1. Discrepancy observed can be attributed to poorer estimate for total pressure, as discussed below. Figs. 2-5 show variation of γ_{th} with pressure. Our calculations show that the values of γ_{th} at ambient condition is 2.365 and 2.674 at melting point for Al and 1.298 and 1.462 at T_m for Na. In Figs. 3, 6 present and compare EOS with other findings for Al and Na, respectively. Softer EOS observed in the case of Al is responsible for lower estimate for melting slope in Fig.1.

Conclusion

We have studied high Pressure melting temperature for fcc Al and bcc phase of Na using QHA and HA γ_{th} . Results are in good agreement with reported data when QH- γ_{th} is used compared to H- γ_{th} . In particular, we could show peak-structure melting curve for Na, whereas poor estimate in P - V results give slightly inferior melting slope for Al. Decrease in γ_{th} is in accordance with reported trend, which validates the use of pair-potential formalism to determine $\gamma_{th}(V)$. The present approach avoids any fitting procedure to find $\gamma_{th}(V)$ thus validate the use of the local pseudopotential under compressed state. We conclude that single-phase melting can be used to estimate T_m as a function of P .

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