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The Study of low pressure melting curves using modified Morse potential- Cu and Ag as a test case

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***Abstract*— In the present communication, the volume and hence pressure dependence of melting temperature of Cu and Ag have been studied using explicit volume dependence of Gruneisen parameter. The Gruneisen parameter as a function of compressed volume has been calculated by using modified Morse potential. The analytical form of pressure dependence of melting temperature, which has been derived using Lindeman's criterion for melting and Debye's theory has been used. Our computed results are compared with experimental findings and other available theoretical results and good agreements are observed.**

***Index Terms*— Copper and Silver, Lindeman's criterion, melting curve and Morse potential**

INTRODUCTION

In the study of melting curve (melting temperature versus compressed volume or melting temperature versus pressure) has great technological importance. In such study the central problem is to understand how melting of solid takes place and to determine the temperature at which melting occurs. During literature survey, it has been observed that lots of efforts have been made to study melting curves theoretically [1-5] as well as experimentally [6-10]. Disagreements are observed in the results of melting temperature studied using experimental as well as theoretical methods [2]. Number of theoretical models based on different philosophy are proposed to understand phenomena of melting among which two in particular deserve special considerations. These are the Lindeman's criterion and Born's criterion. The Lindeman criterion is based on the concept that melting occurs when the root mean square displacement of the atoms reaches a critical fraction of the nearest neighbor distance, so it relates to a vibrational instability. The Born criterion instead is related to an elastic instability i.e melting occurs when the shear modulus vanishes and the crystal no longer has the rigidity to withstand melting. Experimentally high pressure melting curves for Cu, Ta, Mo, W, V, Ti, Cr, Al, Mg, Sr, Ca, Ba, MgO and Fe have been measured using diamond anvil cell experiment [2]. On the other hand lots of theoretical studies have been carried out very recently using different theoretical approaches. Melting temperature is also studied using molecular dynamics simulations. In such calculations, simulation for particular material is carried out based on modelling of interatomic interactions.

Looking to all above facts, in the present communication, we have studied melting curves of Cu and Ag upto Compression (Ω/Ω_0=0.84) using modified Morse type potential for interatomic interactions, which has following form,

$$V(r) = \frac{D_0}{(1-2b)}\left[\exp\left(-2a(r-r_0)\sqrt{b}\right) - 2b\exp\left(-a(r-r_0)/\sqrt{b}\right)\right] \quad \ldots\ldots (1)$$

Such form of the potential and potential parameters were determined by MacDonald and MacDonald [11]. In equation (1), r_0 is the nearest neighbor distance, a is hardness parameter, D_0 is Dissociation energy and b is dimensionless parameter. They have determined potential parameters using following procedure. They have taken r_0 from Varshani and Bloore [12]. D_0 was obtained by fitting sublimation energy. The parameter a was obtained from value of Debye temperature θ_D at zero degree kelvin and melting temperature T_m. They have studied thermodynamic properties of some fcc monoatomic crystal at high temperature using above form of potential [11] (Thermodynamic parameters and potential's parameters are given in [11]). Using equation (1), we have computed first, second and third derivatives $V'(r)$, $V''(r)$ and $V'''(r)$ respectively. Then Gruneisen parameter and its volume and pressure dependence has been calculated using following relations [13].

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$$\gamma = -\frac{1}{6}\frac{\left[\sum_l C_l\left[-\left(\frac{2}{r}\right)V'(r)+2V''(r)+rV'''(r)\right]_{r=r_l}\right]}{\left[\sum_l C_l\left[\left(\frac{2}{r}\right)V'(r)+V''(r)\right]_{r=r_l}\right]} \quad \ldots\ldots (2)$$

Here C_l is the coordination number for l^{th} coordination sphere of radius r_l.

THEORY OF MELTING

For the study of melting temperature as a function of volume, we follow the method as discussed in [6]. In Debye's model simplifying contributions from the acoustical modes, the mean square displacement $\langle u^2 \rangle$ at temperature T higher than Debye's temperature θ_D is expressed as,

$$\langle u^2 \rangle = \frac{9\hbar^2 T}{M k_b \theta_D^2} \quad \ldots\ldots (3)$$

We define Lindeman's criterion for melting χ_m as the ratio of two times the root mean square displacement of the melting point to the nearest neighbor distance.

$$\chi_m = 2\sqrt{\frac{\langle u^2 \rangle}{r_1}} \quad \ldots\ldots (4)$$

By combining above equations (3) and (4), we get

$$T_m = \frac{\chi_m^2}{36\hbar^2} M k_b \theta_D^2 r_1^2 \quad \ldots\ldots (5)$$

Considering the volume dependence of Debye's temperature θ_D and the nearest neighbor distance $r_1 \sim \Omega^{1/3}$ as a criterion for melting χ_m, Soma et al [6] obtained the following differential equation for T_m,

$$\frac{d(\ln T_m)}{d(\ln \Omega)} = -2\gamma + \frac{2}{3} \quad \ldots\ldots (6)$$

Where Υ is volume dependent Gruneisen parameter (which is taken as constant in Debye's model). The differential equation (6) can be solved by satisfying the melting T_m (Ω/Ω_0=1) under atmospheric pressure with the crystal volume Ω_0,

$$\frac{T_m(y)}{T_m(1)} = \exp\left[2\int_y^1 \frac{\gamma(y)-\frac{1}{3}}{y}dy\right] \quad \ldots\ldots (7)$$

Where $y = \Omega/\Omega_0$,
$T_m(y)$ = melting temperature at pressure P (at a volume Ω) and
$T_m(1)$ =melting temperature at zero pressure (at a volume Ω_0)

RESULT AND DISCUSSIONS

Using equation (2), we have calculated Υ at crystal volume Ω_0 (at zero pressure) shown in Table 1 [14] along with experimental results obtained by using different methods. We have also compared our theoretical results of $\Upsilon=\Upsilon_0$ (at zero pressure) with other theoretical findings in the same Table.

TABLE 1: Comparison of calculated Gruneisen parameters with experimental findings and other theoretical results for Cu and Ag.

Metal	Present values	Experimental values [14]	Other
Cu	1.4308	1.97,1.96,2.00±0.08, 2.93, 2.00±0.06	1.93[13], 1.19[16], 1.84[15], 1.73[17]
Ag	1.5514	2.46,2.44,2.36±0.12,0.32, 2.29	3.28[13], 1.26[16], 2.22[15], 2.14[17]

For both the metals presently calculated values are not matching well with experimental values but they fall within the range of experimental uncertainties. Here we would like to point out that, experimental values are also

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scattered. For both the metals, the computed Υ_0 agree well with theoretical results of Harrison and Wills, who have used transition metal pair potential (TMPP). The volume variation of Υ Upto 16% compressions i.e Ω/Ω_0=0.84 are displayed in Fig (1). Once volume variation of Υ is studied, we calculate melting temperature T_m as a function of compressed volume using equation (7). The melting temperature T_m against compressed volume (Ω/Ω_0) and T_m against pressure for Cu and Ag are shown in figures (2-3). We have computed T_m against Ω/Ω_0 and finally converted into pressure by using well known Vinet equation of state (EOS) and it has the following form. From figures 3(a) and 3(b) it is clearly observed that our computed results agree well with experimental results for both the metals at low pressure. We have also compared our results with theoretical results of [1]. In their calculations they have derived equation for the calculation of melting temperature and Υ_0 is fitted to the value obtained by first principles. They have adjusted parameter q for such fitting and Vinet's equation of state (EOS) to convert compressed volume into pressure. We would like to point out here in the present calculation no such fitting procedure is used for calculation of Υ. From the physics of interactions we have determined volume and hence pressure dependence of Υ and T_m.

$$P = 3K_0\left(\frac{\Omega}{\Omega_0}\right)^{-2/3}\left[1-\left(\frac{\Omega}{\Omega_0}\right)^{1/3}\right]\exp\left\{\frac{3}{2}\left(K_0^{'}-1\right)\times\left[1-\left(\frac{\Omega}{\Omega_0}\right)^{1/3}\right]\right\} \quad \ldots\ldots (8)$$

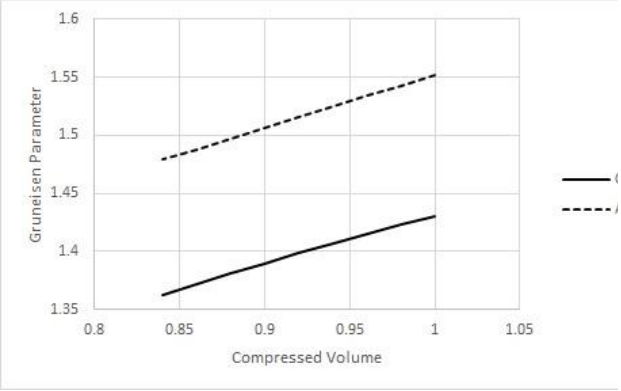

FIG (1): Volume variation of Gruneisen parameter.

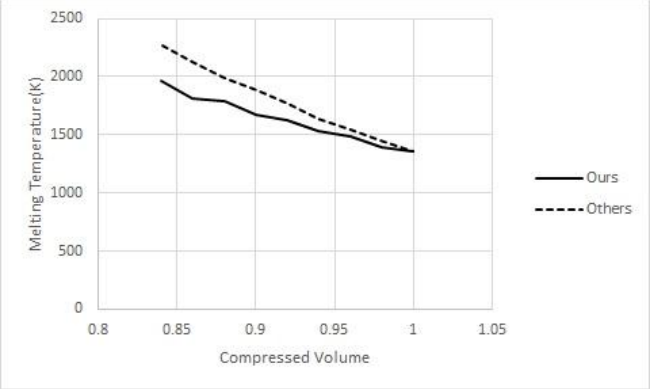

FIG 2(a): Melting temperature as a function of compressed volume for Cu. The solid line is due to present result and dotted line is due to [1].

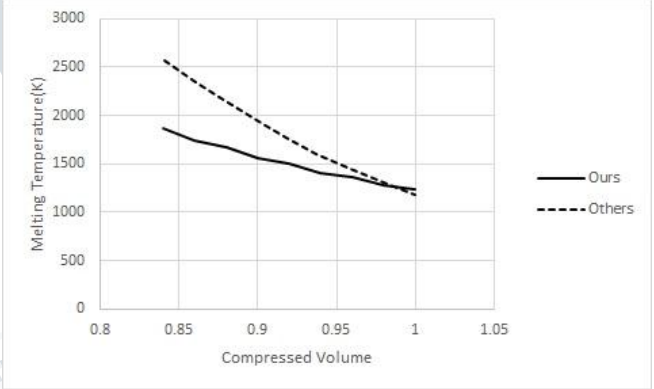

FIG 2(b): Melting temperature as a function of compressed volume for Ag. The solid line is due to present result and dotted line is due to [1].

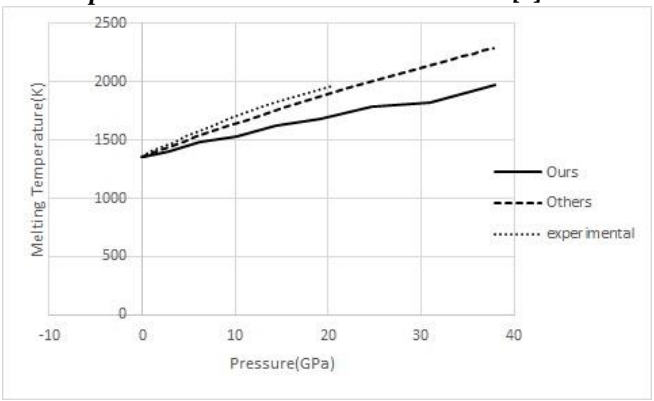

FIG 3(a): Melting temperature versus Pressure (GPa) for Cu is shown in above figure. The solid line is due to present result and dotted line is due to [1].

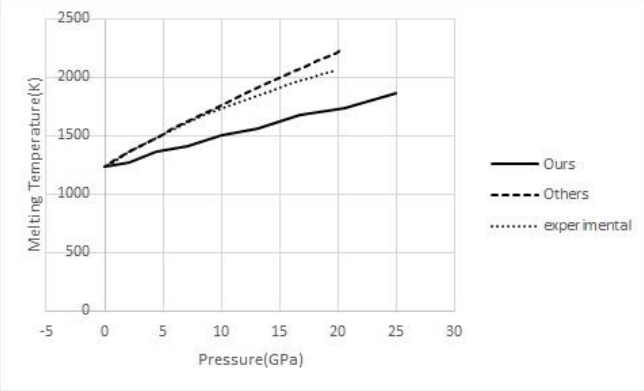

FIG 3(b): Melting temperature versus Pressure (GPa) for Ag is shown in above figure. The solid line is due to present result and dotted line is due to [1].

CONCLUSION

From the present study we conclude that for the study of pressure dependence of melting the Modified Morse potential without any adjustment of Υ can be used successfully. Present approach is very simple computationally and can be extended for the study of high pressure melting curves of remaining transition metals. The use of pseudopotential theory for the study of melting temperature has some limitations. In pseudopotential method potential parameters have to be determined and due to the use of different exchange and correlation functions, results are varying about 20%.

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