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Melting of metals under pressure

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ABSTRACT

Lindemann's formula of melting is extended in terms of bulk modulus and Grüneisen parameter to study the pressure dependence of melting temperature, $T_m(P)$ of metals. The formalism is applied to study $T_m(P)$ of noble and transition metals, di-, tri- and tetravalent (Ag, Au, Cu, Mn, Mg, Zn, CD, In, Pb and Al) metals over a wide range of pressures up to 12 GPa. The computed melting temperatures of the metals under pressure using our semi-empirical relation is in good agreement with the experimental data.

1. Introduction

Properties of metals under elevated conditions of temperature and pressure are important for their thermo-physical characterization. These are useful in the fields of material physics, geophysics and astrophysics. Because of the lack of microscopic information such as inter-atomic forces and atomic distributions, theoretical calculations of the melting curves based on the first principle theory lag behind. Given the complexities involved with experimental and theoretical determination of melting temperature, $T_m(P)$ at high pressures, it is of considerable interest [1] to develop empirical relations that can satisfactorily be used to determine $T_m(P)$ at high pressures. Such approaches are also useful to extrapolate $T_m(P)$ at high pressures from the available low pressure data. Simon's semi-empirical equation has proved to be quite successful for large varieties of substances, but the major difficulties appear to be that of (i) uncertainty in fitting Simon's parameters and (ii) identifying the physical properties that are responsible for the dependence of T_m in the higher pressure region.

A number of attempts were made in the past for the empirical evaluation of the magnitude of T_m, the most famous and in many ways most successful is that of Lindemann [2]. Lindemann's picture of melting suggests that the amplitude of atomic vibrations increases with increasing temperature and melting occurs when the amplitude of vibrations reaches a critical fraction, y_m, of the mean atomic radius R_a. The quantity y_m may readily be estimated [3] with the aid of the Debye model in terms of characteristic temperature θ_D. The critical value of y_m has been found to vary between 0.11 and 0.23 [4]. This has been successfully used to evaluate the melting temperature of metals at normal pressure.

In the present work, a semi-empirical approach based on Lindeman's concept is used to compute the melting point of metals, $T_m(P)$, over a wide range of pressures. We have reformulated Lindemann's formula to compute $T_m(P)$ in terms of bulk modulus, the Grüneisen parameter and their first derivative with pressure. All these factors can be independently determined and hence the formalism is independent of any fitting parameter. It has also been applied [5] successfully to evaluate the pressure dependence of the melting of minerals and rocks such as alumina, Heusler alloy and gabbro. Under the simplified version of the formalism, Simon's empirical constants have been readily related to the bulk modulus and the Grüneisen parameter. We have applied the formalism to compute $T_m(P)$ of Ag, Au, Cu, Mn, Mg, Zn, Cd, In, Pb and Al. These metals differ quite substantially in their melting points at atmospheric pressure. Recently Errandonea [6] has measured the melting curves for metals up to 12 GPa using Bridgman-type cell which has made it possible to compare our semi-empirical values with the measured values.

Formalism leading to the modified version of Lindemann's expression in terms of bulk modulus and the Grüneisen parameter is given in Section 2. Results and discussions for the pressure dependence of the melting temperature of ten metals are given in Section 3, followed by summary and conclusion in Section 4.

2. Theoretical formulation

It was proposed by Lindemann [2] that the amplitude of the atomic vibrations increases with increasing temperature and that

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melting occurs when the amplitude of vibrations reaches a critical fraction, y_m, of the mean atomic radius R_a. Lindemann's original formula, in association with the approximate expression of Mott and Jones [3] for the mean square amplitude of vibration of each atom, can be written in the form:

$$T_m = \left(\frac{2\pi}{3h} y_m R_a \theta_D\right)^2 M k_B \tag{1}$$

where θ_D is the Debye temperature and M is the atomic mass. θ_D occurs as one of the important ingredients in Eq. (1). It is very useful to characterize the atomic vibrations in solids [7] as well as in liquids [8]. It may be noted that if the observed specific heat data at low temperature is exactly fitted to the Debye formula, then θ_D is constant. Mott and Jones [3], however, argued that for vibrational distribution other than Debye distribution, θ_D should depend on temperature, T, and pressure, P.

On replacing $R_a[=(3M/4\pi\rho)^{1/3}]$ and M in Eq. (1), one gets

$$T_m = \text{const}\, \Omega^{2/3} \theta_D^2 \tag{2}$$

where Ω is the atomic volume. Taking the pressure derivative of the above equation

$$\frac{d(\ln T_m)}{dP} = \frac{2}{B_T}\left(\xi - \frac{1}{3}\right) \tag{3}$$

where the bulk modulus $B_T = -\Omega(\partial P/\partial \Omega)_T$ and the Grüneisen parameter, $\xi = -(\partial(\ln\theta_D)/\partial(\ln\Omega))$. B_T and ξ in Eq. (3) are pressure dependent. For the need of a better analytical expression for $B_T(P)$ and $\xi(P)$, it can be expanded in terms of P:

$$\xi(P) = \xi_0 + a_1 P + a_2 P^2 + \cdots \tag{4}$$

$$B_T(P) = B_0 + b_1 P + b_2 P^2 + \cdots \tag{5}$$

ξ_0 and B_0 are the values at normal melting point and at zero pressure (atmospheric pressure). Taking into account the linear terms of Eqs. (4) and (5), one can readily solve Eq. (3) to get

$$\frac{T_m}{T_0} = \left[1 + \frac{b_1 P}{B_0}\right]^n \exp\left(\frac{2a_1 P}{b_1}\right) \tag{6}$$

with

$$n = \frac{2b_1\xi_0 - 2a_1 B_0}{b_1^2} - \frac{2}{3b_1}, \quad a_1 = \left(\frac{\partial \xi}{\partial P}\right) \quad \text{and} \quad b_1 = \left(\frac{\partial B}{\partial P}\right) \tag{7}$$

Eq. (6) suggests that the basic inputs to calculate $T_m(P)$ are the bulk modulus, the Grüneisen parameter and their derivatives with pressure. Experimental values of the bulk modulus are amply available for a large group of metals. However, very few data exist for ξ and its pressure gradient. In its absence, the coefficient can even be treated as a fitting parameter. On the other hand some of the existing measurements [9,10] indicate that the dependence of ξ on P is very small. If we take $a_1=0$, then Eq. (6) simplifies considerably to

$$\frac{T_m}{T_0} = \left[1 + \frac{b_1 P}{B_0}\right]^{2/b_1(\xi_0 - (1/3))} \tag{8}$$

Eq. (8) is a simplified version to compute the pressure dependence of melting temperature subjected to the condition that the bulk modulus of the material depends linearly on pressure and the Grüneisen parameter remains invariant.

It is of interest to compare Eq. (8) to one of the most important and extensively used Simon's empirical relations:

$$\frac{T_m}{T_0} = \left[1 + \frac{P}{X}\right]^Y \tag{9}$$

It suggests that Simon's constant X and Y can readily be related to bulk modulus and the Grüneisen parameter respectively as

$$X = \left(\frac{B_0}{b_1}\right), \quad \text{and} \quad Y = \frac{2}{b_1}\left(\xi_0 - \frac{1}{3}\right) \tag{10}$$

Eq. (6) or its simplified version Eq. (8) can be readily used to evaluate the melting temperature with increasing pressure provided the bulk modulus, the Grüneisen parameter and their gradients with pressure are known. Most of these physical parameters have been determined experimentally. However, the data for the Grüneisen parameter is scarce, and in that case we have determined it from the thermodynamic relation [11]:

$$\xi_0 = \frac{\beta}{\rho\, c_P \kappa_S} \tag{11}$$

where β (K^{-1}) is the coefficient of volume expansion, ρ (kg m^{-3}) is the density and C_P (J kg^{-1} K^{-1}) is the heat capacity at constant pressure. The values of these quantities are taken from [12,13]. The adiabatic compressibility, κ_S (Pa^{-1}), appearing in Eq. (11) is determined from the relation:

$$\kappa_S = \frac{1}{\rho(v_p^2 - (3/4)v_s^2)} \tag{12}$$

v_p and v_s are the primary (longitudinal) and secondary (transverse) acoustic wave velocities respectively.

3. Results and discussions

Below we present the pressure dependence of the melting curves of ten metals obtained from semi-empirical Eq. (8). Results are compared with the experimental data available in literature [6].

3.1. Noble and transition metals (Ag, Au, Cu and Mn)

Silver, copper and gold share certain attributes like having one *s*-orbital electron on top of a filled *d*-electron shell and possessing high ductility and electrical conductivity. Inter-atomic interactions in these elements are slightly contributed by the filled *d*-shells compared to the dominant contributions from the *s*-electrons through metallic bonds. This explains their low hardness and high ductility. T_m for Ag, Au and Cu at atmospheric pressure are respectively, 1234.78 K, 1337.18 K and 1357.62 K, which are comparatively higher than those for the other metals.

At the macroscopic scale, introduction of extended defects in Cu to the crystal lattice, such as grain boundaries, hinders flow of the material under applied stress thereby increasing its hardness. For this reason, copper is usually supplied in a fine-grained polycrystalline form, which has greater strength than monocrystalline forms. It has the ability to remain in a face centered (fcc) structure up to pressures higher than 100 GPa. Contrary to noble metals, Mn is chemically reactive, harder and brittle. Its melting temperature, $T_m = 1497$ K, is quite high at atmospheric pressure. Due to its reactive nature it has large industrial applications. Contrarily, gold is chemically one of the least reactive solid elements. The metal therefore occurs often in free elemental (native) form, as nuggets or grains in rocks, in veins and in alluvial deposits. Silver has large industrial applications due to its high electrical and thermal conductivities. It is very ductile, malleable (slightly higher than gold), monovalent coinage metal, with a brilliant white metallic luster that can take a high degree of polish.

We have applied Eq. (8) to compute $T_m(P)$ for Ag and Au for pressures up to 8 GPa and for Cu up to 16 GPa. The computed values are plotted in Fig. 1(a–c). The bulk modulus B, its first