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An equation of state for alkali metals

Sayyadul Arafin*, Ram N. Singh

Department of Physics, College of Science, Sultan Qaboos University, Box:36, Al-Khoudh 123, Oman

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ABSTRACT

Semi-empirical equations of state based on Lindemann's law have been developed to determine the pressure (P) dependence of the melting temperature (T_m) of Li, K, Rb and Cs. The basic inputs are Grüneisen parameter and the bulk modulus. T_m–P variations exhibit maximum melting temperature with concave downwards. The maximum in T_m for Cs is found to occur at pressure of 2.2 GPa whereas for Li, K and Rb it falls in the range of 7–9.5 GPa. The predicted values of T_m as a function of pressure, based on the present empirical relation, fit quite well with the available experimental data. The empirical relation can also be used to extrapolate T_m at higher pressure from the values available at lower pressures.

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1. Introduction

Alkali metals (Li, Na, K, Rb and Cs) are highly reactive and have large number of industrial applications, including alkalides and biological roles as electrolytes. These fall under the category of low melting temperature metals varying in the range 301.59 K (Cs) to 453.69 K (Li) at ambient conditions. It is of great interest to investigate the effect of high pressure on the melting curve. The general character of the melting phenomenon at lower pressure is the same as for other substances i.e. melting curve rises with increasing pressure but the behavior at higher pressure is not well understood.

Recent experimental results for Na and Li [1,2] suggest that at lower pressure, T_m increases with P and then decreases with increasing pressure exhibiting a maximum for T_m–P variation. In the present work we investigate the characteristics of melting curves of Li, K, Rb and Cs as a function of pressure and examine the maxima and the critical point of the curves. The comparative study of the behavior of these metals under pressure has special significance because the effects of pressure on these metals are excessively large, for example, Cs is by far the most compressible solid element. The energy density on compressions becomes comparable to the bonding energies resulting in significant changes in the electronic states, chemical bonding and the packing of condensed phases. Alkali metals are found [3–6] to transform at high pressure into structurally complex and poorly conducting states as a result of changes in the electronic structure due to s–p or s–d hybridization. Several authors [7–9] have experimentally determined the *bcc–fcc* transitions in Rb, K and Cs at higher pressure.

We used here an empirical approach based on Lindemann criterion of melting to determine T_m as a function of pressure. Such an approach has been successfully applied to different class of materials [10–12]. The basic inputs are the Grüneisen parameter (ξ) and the bulk modulus (B). ξ and B have been expanded here in terms of pressure which allows us to obtain analytical relation for T_m in terms of pressure. The computed results are in very good agreement with the available experimental data [2,13]. We observe that T_m–P variation of all the alkali metals exhibits maximum at a pressure around which the *bcc–fcc* transformation occurs. Section 2 covers the formulation for obtaining the analytical relations for T_m as a function of P. The computed values of the results are given and discussed in Section 3 which is followed by conclusion in Section 4.

2. Formalism

2.1. Melting temperature in terms of bulk modulus (B) and Grüneisen parameter (ξ)

The present empirical method is based on Lindemann's melting law which has been extended by expressing the bulk modulus, B and the Grüneisen parameter, ξ as a function of pressure. Grüneisen parameter is a property of materials that establishes a link between thermal behavior and the elastic response to thermally induced stress of the material. It measures the anharmonic interactions and is of considerable interest for theoretical and experimental studies of materials whereas the bulk modulus determines the ability of the materials to undergo compression.

It was proposed by Lindemann [14] that the amplitude of the lattice vibrations increases with increasing temperature and that melting occurs when the amplitude of vibrations reaches a critical

* Corresponding author.
E-mail address: sayfin@squ.edu.om (S. Arafin).

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fraction, y_m, of the mean atomic radius R_a. Lindemann's original formula, in association with the approximate expression of Mott and Jones [15] 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, R_a is the atomic radius and M is the atomic mass. The variation of Θ_D with atomic volume can be expressed in terms of Grüneisen parameter

$$\xi = -\frac{\partial(\ln \theta_D)}{\partial(\ln \Omega)} = -\frac{\Omega}{\theta_D}\frac{\partial \theta_D}{\partial \Omega} \tag{2}$$

On replacing $R_a=(3M/4\pi\rho)^{1/3}$ and M in Eq. (1), carrying out some algebra with the help of Eq. (2) one gets an expression for pressure variation of T_m in terms of bulk modulus, B and Grüneisen parameter, ξ [10,11]

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

where $B = \Omega(\frac{\partial P}{\partial \Omega})_T$ is the bulk modulus of the material. B and ξ in Eq. (3) are pressure dependent.

2.1.1. Linear dependence of B and ξ on pressure

For want of better analytical expression, we have considered pressure variation of ξ and B in terms of linear equations of the form

$$\xi(P) = \xi_0 + a_1 P \tag{4}$$

and

$$B(P) = B_0 + b_1 P \tag{5}$$

ξ_0 and B_0 are the bulk modulus and the Grüneisen parameter at zero pressure. a_1 and b_1 are the 1st derivatives of Grüneisen parameter and the bulk modulus respectively. Without going into derivation of the equation, which can be found in [10–12], T_m(P) can be expressed as

$$T_m(P) = T_{m0}\left\{\left(1+\frac{b_1}{B_0}P\right)^{n'} exp\left(\frac{2a_1}{b_1}P\right)\right\} \tag{6}$$

$$with\ \ n' = \frac{2}{b_1}\left(\xi_0 - \frac{a_1 B_0}{b_1} - \frac{1}{3}\right) \tag{7}$$

T_{m0}, ξ_0 and B_0 the melting temperature, Grüneisen parameter and bulk modulus are at ambient condition respectively; a_1 and b_1 are the pressure derivatives of Grüneisen parameter, $(\partial\xi/\partial P)$ and the bulk modulus, $(\partial B/\partial P)$ respectively. If the Grüneisen parameter is assumed to be independent of P, then Eq. (6) simplifies to

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

Eq. (8) is a simplified version to compute the pressure dependence of the melting temperature subject 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 relation,

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

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

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

To find the pressure, P_m at which T_m becomes maximum, we differentiate Eq. (6) with respect to P and set it equal to zero. This leads to the relation

$$P_m = \frac{1}{a_1}\left(\frac{1}{3} - \xi_0\right) = \frac{\left(\frac{1}{3} - \xi_0\right)}{\frac{\partial \xi}{\partial P}} \tag{11}$$

For most metals ξ_0 is greater than 1/3. Hence the pressure derivative of Grüneisen parameter, a_1 must be negative. It suggests that Grüneisen parameter, ξ decreases with pressure which is in agreement with available results [16].

2.1.2. Non-linear dependence of ξ and B on pressure

In this case of non-linear variation of ξ and B with pressure, P, we have considered equations up to second order in P which may be written as

$$\xi(P) = \xi_0 + a_1 P + a_2 P^2 \tag{12}$$

$$B(P) = B_0 + b_1 P + b_2 P^2 \tag{13}$$

Higher order terms in Eqs. (12) and (13) could be considered but it would pose a great hindrance in formulating an analytical solution. Integration of Eq. (3) leads to

$$ln\left(\frac{T_m}{T_0}\right) = 2\int_0^P \frac{\xi dP}{B(P)} - \frac{2}{3}\int_0^P \frac{dP}{B(P)} \tag{14}$$

To solve the above integral equation analytically we substitute Eqs. (12) and (13) in Eq. (14) and get

$$ln\left(\frac{T_m}{T_0}\right) = I_1 + I_2 + I_3 \tag{15}$$

$$\text{with}\ \ I_1 = 2\left(\xi_0 - \frac{1}{3}\right)\int_0^P \frac{dP}{B(P)} \tag{16}$$

$$I_2 = 2a_1 \int_0^P \frac{P dP}{B(P)} \tag{17}$$

$$\text{and}\ \ I_3 = 2a_2 \int_0^P \frac{P^2 dP}{B(P)} \tag{18}$$

It is possible to integrate I_1, I_2 and I_3 analytically for two conditions (i) $b_1^2 < 4B_0 b_2$ and (ii) $b_1^2 > 4B_0 b_2$. We provide below explicit expressions satisfying these two conditions:

2.1.2.1. Solution for condition I: if $b_1^2 < 4B_0 b_2$. The integrals I_1, I_2 and I_3 (Eqs. (16)–(18)) stand for:

$$I_1 = \left[\frac{2}{\sqrt{4B_0 b_2 - b_1^2}}\, arctan\, \frac{b_1 + 2b_2 P}{\sqrt{4B_0 b_2 - b_1^2}}\right]\Bigg|_0^P \tag{19}$$

$$I_2 = \left[\frac{1}{2b_2}\, ln\, B(P) - \frac{b_1}{2b_2} I_1\right]\Bigg|_0^P \tag{20}$$

$$I_3 = \left[\frac{P}{b_2} - \frac{1}{2b_2^2}\, ln\, \frac{B(P)}{B_0} + \frac{b_1^2 - 2B_0 b_2}{2b_2^2} I_1\right]\Bigg|_0^P \tag{21}$$

The above integrals are to be evaluated between the limits 0 and P. After substituting Eqs. (19)–(21) in Eq. (15), we obtain an

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