

## STUDY OF MELTING TEMPERATURE OF METALS: PRESSURE DEPENDENCE

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**Abstract.** *The melting temperature of metals are studied using the statistical moment method, going the quasi-harmonic approximations. The melting temperature of metals are calculated as a function of the pressure. We discuss the pressure dependence of melting temperatures of Ce, Fe metals and compare the present results with those of the experimental results.*

### I. INTRODUCTION

High-pressure behaviour of materials is of great interest from the viewpoints of geophysics [1] as well as of solid states sciences and technologies. The study of the phase stabilities and phase diagrams under extreme (high-pressure) conditions has also become quite interesting in recent years since the many geophysical and technological applications. It is the purpose of the present paper to study the pressure dependence of the melting temperatures of metals by the basis on the statistical moment method (SMM) [2-6].

In order to determine theoretically the melting temperatures of metals we will use the equilibrium condition of the solid phases. In particular, we will use the limiting condition for the absolute crystalline stability in order to find the melting temperatures  $T_m$  under the hydrostatic pressure. Rigorously speaking, melting temperatures of the solid phases are defined as the temperature points at which the solid and the liquid states coexist in the thermally equilibrium condition [7]. Since the treatments of liquid phases are rather complicated [1-8], the most of the previous studies have been performed on the basis of the properties of the solid phases (starting with the Lindermann's formula) theorized in terms of the lattice instability [10, 11], free energy of dislocation motions, or a simple order-disorder transition [7].

In the present study, we use the SMM to investigate the equation of state and melting temperatures of metals. We will calculate the pressure dependence of the nearest neighbor distance and the melting temperature of metals.

## II. EQUATION OF STATES AND MELTING TEMPERATURES OF METALS BY STATISTICAL MOMENT METHOD

### II.1. Pressure versus volume relation

The pressure versus volume relation of the lattice is [2, 3]

$$Pv = -a \left[ \frac{1}{6} \frac{\partial U_0}{\partial a} + \theta x \coth x \frac{1}{2k} \frac{\partial k}{\partial a} \right], \quad (1)$$

where  $x = \frac{\hbar\omega}{2\theta}$ ,  $\theta = k_B T$ ,  $\omega$  is the vibrational frequencies of atoms,  $P$  denotes the hydrostatic pressure and  $v$  is the atomic volume  $v = \frac{V}{N}$  of the crystal, being  $v = \frac{4}{3\sqrt{3}}a^3$  for the bcc lattice. Using Eq.(1), one can find the nearest neighbor distance  $a$  at pressure  $P$  and temperature  $T$ . However, for numerical calculations, it is convenient to determine firstly the nearest neighbor distance  $a(P, 0)$  at pressure  $P$  and at absolute zero temperature  $T = 0$ . For  $T = 0$  temperature, Eq.(1) is reduced to

$$Pv = -a \left[ \frac{1}{6} \frac{\partial U_0}{\partial a} + \frac{\hbar\omega_0}{4k} \frac{\partial k}{\partial a} \right]. \quad (2)$$

For simplicity, we take the effective pair interaction energy in metal systems as the power law, similar to the Lennard - Jones

$$\varphi(r) = \frac{D}{(n-m)} \left[ m \left( \frac{r_0}{r} \right)^n - n \left( \frac{r_0}{r} \right)^m \right], \quad (3)$$

where  $D, r_0$  are determined to fit to the experimental data (e.g., cohesive energy and elastic modulus). For bcc metals we take into account the first nearest, second, third, fourth and fifth nearest neighbor interactions. Using the effective pair potentials of Eq.(3), it is straightforward to get the interaction energy  $U_0$  and the parameter  $k$  in the crystal as

$$U_0 = \frac{D}{(n-m)} \left[ mA_n \left( \frac{r_0}{a} \right)^n - nA_m \left( \frac{r_0}{a} \right)^m \right] \quad (4)$$

$$\begin{aligned} k &= \frac{1}{2} \sum_i \left( \frac{\partial^2 \varphi_{i0}}{\partial u_{i\beta}^2} \right)_{eq} \\ &= \frac{Dnm}{2a^2(n-m)} \left\{ \left[ (n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \right] \left( \frac{r_0}{a} \right)^n - \left[ (m+2)A_{m+4}^{a_{ix}^2} \right] \left( \frac{r_0}{a} \right)^m \right\} \\ &= m_0 \omega_0^2, \end{aligned} \quad (5)$$

where  $m_0$  is the mass of particle,  $\omega_0$  is the frequency of lattice vibration, and Eq.(2) can be transformed to the form for bcc and fcc metals:

$$P \frac{4}{3\sqrt{3}} r_0^3 = c_1 y^{n+3} - c_2 y^{m+3} + \frac{c_3 y^{n+4} - c_4 y^{m+4}}{\sqrt{c_5 y^n - c_6 y^m}}, \quad (6)$$

$$P \frac{r_0^3}{\sqrt{2}} = c_1 y^{n+3} - c_2 y^{m+3} + \frac{c_3 y^{n+4} - c_4 y^{m+4}}{\sqrt{c_5 y^n - c_6 y^m}}, \quad (7)$$

where  $y = \frac{r_0}{a}$ ,

$$\begin{aligned}
c_1 &= A_n \frac{Dnm}{6(n-m)} \\
c_2 &= A_m \frac{Dnm}{6(n-m)} \\
c_3 &= \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} (n+2) \left[ (n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \right] \frac{1}{r_0} \\
c_4 &= \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} (m+2) \left[ (m+2)A_{m+4}^{a_{ix}^2} - A_{m+2} \right] \frac{1}{r_0} \\
c_5 &= (n+2)A_{n+4}^{a_{ix}^2} - A_{n+2} \\
c_6 &= (m+2)A_{m+4}^{a_{ix}^2} - A_{m+2}
\end{aligned} \tag{8}$$

where  $A_n, A_m \dots$  are the structural sums for the given crystal and defined by

$$A_n = \sum_i \frac{Z_i}{\nu_i^n}; \quad A_m = \sum_i \frac{Z_i}{\nu_i^m}; \quad A_n^{a_{ix}^2} = \frac{1}{a^2} \sum_i \frac{Z_{ix} a_{ix}^2}{\nu_i^n}$$

here  $Z_i$  is the coordination number of  $i^{\text{th}}$  nearest neighbor atoms with radius  $r_i$  (for bcc lattice  $r_k = \nu_k a_0$ ;  $\nu_1 = 1, Z_1 = 8$ ;  $\nu_2 = \sqrt{\frac{4}{3}}, Z_2 = 6$ ;  $\nu_3 = \sqrt{\frac{8}{3}}, Z_3 = 12$ ;  $\nu_4 = \sqrt{\frac{11}{3}}, Z_4 = 24$ ; ...).

In principle Eqs.(6,7) permits to find the nearest neighbor distance  $a(P, 0)$  at zero temperature and pressure  $P$ . Using the Maple program and the values of parameters  $D$  and  $r_0$  determined by the experimental data [12]. Eqs.(6,7) can be solved, we find the values of the nearest neighbor distance  $a(P, 0)$  at temperature  $T = 0$  and pressure  $P$ . Calculated results for the nearest neighbor distance  $a(P, 0)$  of Ce, Dy and Fe metals at zero temperature and pressure  $P$  are presented in the Table 1.

## II.2. Pressure versus volume relation

In this subsection, we discuss the pressure dependence of melting temperatures of metals by the basis on the statistical moment method. The expression of the pressure  $P$  (1) can be write in the form

$$P = -\frac{a}{6v} \frac{\partial U_0}{\partial a} + \frac{3\gamma_G \theta}{v}, \tag{9}$$

where the Grüneisen constant  $\gamma_G$  is given by

$$\gamma_G = -\frac{a}{6k} \frac{\partial k}{\partial a} x \coth x. \tag{10}$$

From the limiting condition of the absolute stability for the crystalline phase

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \text{ie.,} \quad \left(\frac{\partial P}{\partial a}\right)_T = 0. \quad (11)$$

One can find the limiting temperature  $T_S$  for the crystalline stability. This limiting temperature  $T_S$  can be give in the third order approximation as

$$T_S \approx T_S(0) + \left(\frac{\partial T}{\partial P}\right)_a P + \frac{1}{2} \left(\frac{\partial^2 T}{\partial P^2}\right)_a P^2 + \frac{1}{6} \left(\frac{\partial^3 T}{\partial P^3}\right)_a P^3 + \dots \quad (12)$$

where

$$T_S(0) = \frac{a}{18k_B\gamma_G} \frac{\partial U_0}{\partial a}. \quad (13)$$

In deriving Eq.(12), the thermodynamic relation  $\left(\frac{\partial P}{\partial T}\right)_a \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$  is used. From the equation of states (9), it is easy to find the following expressions

$$\left(\frac{\partial T}{\partial P}\right)_a = \frac{vP}{3k_B\gamma_G} \left[1 - \frac{T}{\gamma_G} \left(\frac{\partial \gamma_G}{\partial T}\right)_a\right], \quad (14)$$

$$\left(\frac{\partial^2 T}{\partial P^2}\right)_a \approx -\frac{v^2}{(3k_B\gamma_G)^2 T} + \frac{v}{3k_B\gamma_G T} \left(\frac{\partial T}{\partial P}\right)_a, \quad (15)$$

$$\left(\frac{\partial^3 T}{\partial P^3}\right)_a \approx \left(\frac{v}{3\theta\gamma_G}\right)^2 \left(\frac{\partial T}{\partial P}\right)_a + \frac{v}{3\theta\gamma_G T} \left[T \left(\frac{\partial^2 T}{\partial P^2}\right)_a - \left(\frac{\partial T}{\partial P}\right)_a^2\right]. \quad (16)$$

From the Eqs.(12), (14), (15) and (16), we find the expression of the limiting temperature  $T_S$  as

$$T_S(P) \approx T_S(0) + \frac{Pv}{3k_B\gamma_G} \left\{1 - \frac{T_S(0)}{\gamma_G} \left(\frac{\partial \gamma_G}{\partial T}\right)_a \left[1 + \frac{Pv}{6k_B T_S(0)\gamma_G}\right]\right\} + \left(\frac{v}{3k_B\gamma_G}\right)^2 \frac{P^3}{6T_S^2(0)} \left(\frac{\partial T}{\partial P}\right)_a - \frac{P^3 v}{18k_B\gamma_G T_S^2(0)} \left[\left(\frac{v}{3k_B\gamma_G}\right)^2 + \left(\frac{\partial T}{\partial a}\right)_a^2\right]. \quad (17)$$

After the nearest neighbor distance  $a$  is known [2-4], we can find both harmonic and inharmonic vibration parameters  $k, \omega, \frac{\partial k}{\partial a}, \frac{\partial \omega}{\partial a}, \dots$ . Therefore, Eq.(13) permits us to determine the limiting temperature of absolute stability  $T_S(0)$  at pressure  $P = 0$ .

The above Eq.(17) can be used to find the limiting temperature  $T_S(P)$  at pressure  $P$  in an interactive manner: Firstly, we calculate the limiting temperature at zero pressure  $T_S(0)$ . Then,  $T_S(0)$  value is used to calculate  $\gamma_G(T_S(0), P)$  and at pressure  $P$  and limiting temperature  $T_S(0)$  and the limiting temperature  $T_S(P)$  is obtained by using the right-hand side of Eq.(17).

### III. RESULTS AND DISCUSSIONS

In order to check the validity of the present SMM for the study of the melting temperature of the metallic systems described herein, we performed calculations for pure rare earth metals Ce and Fe. When the SMM is used to evaluate the limiting temperature of crystalline materials, it is very important to satisfy the self consistency conditions between the equilibrium lattice spacing, the related thermodynamic quantities  $\gamma_G$  and  $U_0$ . In such a calculation, the melting temperature  $T_m$  is approximated quite well by the limiting temperature  $T_S$

$$T_m \approx T_S \quad (18)$$

Table 1: Calculated results for the nearest neighbor distance  $a(P, 0)$  at zero temperature and pressure  $P$

| $P(\text{GPa})$ | 0      | 5      | 10     | 20     | 30     |
|-----------------|--------|--------|--------|--------|--------|
| <i>Ce</i>       | 3.0445 | 2.9619 | 2.8909 | 2.7946 | 2.7279 |
| <i>Dy</i>       | 3.1571 | 3.0861 | 3.0353 | 2.9630 | 2.9108 |
| <i>Fe</i>       | 2.4318 | 2.4227 | 2.4144 | 2.3996 | 2.3753 |

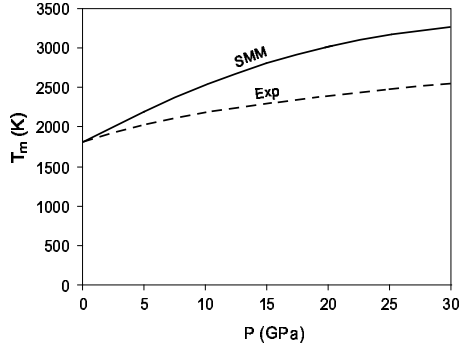


Fig.1. Melting temperatures of Fe

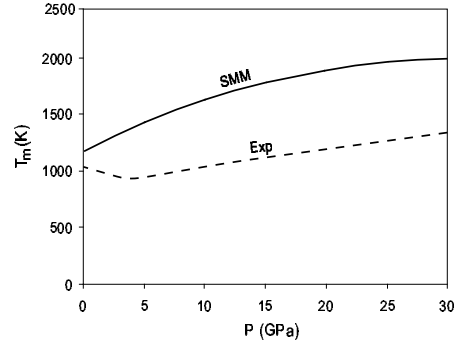


Fig.2. Melting temperatures of Ce

In Fig.1 we present the pressure dependence of the melting (limiting) temperatures of Fe and in Fig.2 present the pressure dependence of the melting (limiting) temperatures of Ce, by solid lines, in comparison with the corresponding experimental results, by dashed lines. One can see in Fig.1, that the melting temperatures of Fe increase with the hydrostatic pressure, in agreement with the experimental results [13].

Table 2: Calculated pressure dependence of nearest neighbor distance  $a(P, T_S)(\text{\AA})$  and melting temperature  $T_m(\text{K})$  for Fe metal.

| $P(\text{GPa})$ | 0      | 1      | 2      | 3      | 4      | 5      | 6      |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| $a(P, 0)$       | 2.4318 | 2.4299 | 2.4281 | 2.4263 | 2.4245 | 2.4227 | 2.4210 |
| $a(P, T_S)$     | 2.4772 | 2.4745 | 2.4720 | 2.4695 | 2.4670 | 2.4645 | 2.4622 |
| $T_S(P)$        | 1810.0 | 1888.2 | 1965.9 | 2042.9 | 2118.9 | 2194.0 | 2267.8 |
| <i>Exp</i> [13] | 1812.0 | 1873.0 | 1908.0 | 1943.0 | 1978.0 | 2013.0 | 2033.0 |

One can see in Table 2 that the calculated pressure dependence, increasing rates, of the melting temperatures for Fe metal are very sensitive to the material, in good agreement with the corresponding experimental results [14].

#### IV. CONCLUSION

The SMM calculations are performed by using the effective pair potential for the Fe, Ce and Dy metals. The use of the simple potentials is due to the fact that the purpose of the present study is to gain a general understanding of the effects of the inharmonic of the lattice vibration and pressure on the melting temperature for the bcc and fcc metals. The melting temperatures of Ce, Dy bcc metals and Fe fcc metal at a wide range of pressure calculated by using the SMM are generally in good agreement with the experimental results.

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