Melting Temperature of Lithium, Sodium and Potassium at High Pressures

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Abstract

Based on Lindemann's law and the Debye model, the melting temperature T_m of metals has been argued. It's found that the melting temperature appears to be decided finally by the second Grüneisen parameter q,which is assumed to have a power form of volume in the preset work. Hence we can obtain a new expression of T_m different from that of the prior works. Good agreement between theory and experiment is found.

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1. Introduction

Determination of the pressure dependence of the melting temperature is of great importance for understanding structures of solids (Schlosser et al 1989; Fang and Chen 1994; Kechin 1995; Anderson 1998; Fang 1998; Kaver and Jeanloz 1998; Boehler et al 2001; Kechin 2001; Wang et al 2001; Chauhan and Singh 2002; Zubov et al 2003; Liu and Chen 2005; Asanuma et al 2010; Chauhan et al 2011). According to Lindemann's law, the relationship between the melting temperature T_m and the Debye temperature θ_D is given by $T_m = CV_m^{\frac{2}{3}}\theta_D^2$, where C is a constant which depends on the material, V_m is the volume at T_m. In the Debye model of a solid, the Grüneisen parameter $\gamma = -\frac{\partial \ln \theta_D}{\partial \ln V}$ .In the meantime, the second Grüneisen paramete $q = (\frac{\partial \ln \gamma}{\partial \ln V})_T$.

Both Schlosser et al (1989) and Fang et al (1994) assume that, for metals, $\frac{\gamma}{V} = const.$, so $q = 1$.But q itself is often a function of volume (Jeanloz 1989; Anderson et al 1992; Nie 2000). In this paper, we shall choose q as

$$q = q_0 x^{3n} \qquad (1)$$

for the alkali metals, where n is a positive constant, $x = (\frac{V_m}{V_{R0}})^{\frac{1}{3}}$, q_0 and V_{R0} are the second Grüneisen parameter and volume at zero pressure and room temperature T_R, respectively, and V_m is the volume at arbitrary melting temperature T_m.Then we can get a new expression for T_m with pressure. We shall compare this pressure dependence of melting temperature T_m with experimental data.

2. Theory

From the above analyses, we can get

$$T_m = T_{m0}(\frac{x}{\xi})^{2+6\gamma_0(\frac{q_0}{n}-1)} \exp\left\{\frac{2q_0\gamma_0}{n^2}\xi^{3n}[1-(\frac{x}{\xi})^{3n}]\right\} \qquad (2)$$

where γ_0 is the Grüneisen parameter at zero pressure room temperature, $\xi = (\frac{V_{m0}}{V_{R0}})^{\frac{1}{3}}$ and T_{m0} is melting temperature at zero pressure .

In order to find the relation between T_m and the pressure $P(T_m, V_m)$, we shall search for the relation between $P(T_m, V)$ and x. According to Birch equation concerning thermal effects (Nie and Chen 1999):

$$P(T_m, V) = P(T_R, V) + \alpha(0, T_R)B(0, T_R)(T_m - T_R) \quad (3)$$

$$P(T_R, V) = \frac{3B(0, T_R)}{2}(x^{-7} - x^{-5})\left\{1 + \frac{3}{4}[B'(0, T_R) - 4](x^{-2} - 1)\right\} \quad (4)$$

where $\alpha(0, T_R)$, $B(0, T_R)$ and $B'(0, T_R)$ are the volume thermal expansion coefficient , the isothermal bulk modulus and its first – order pressure derivative at zero pressure and room temperature, respectively. ξ in Eq.(2) can get from Eqs. (3) and (4) while letting $P(T_{m0}, V) = 0$.

3. Results and Discussions

With the method mentioned above, we fitted the experimental data on the melting temperature under a high pressure for alkali metals (Li, Na and K). The values of the parameters $\alpha(0, T_R), B(0, T_R), B'(0, T_R)$ at T_R (Boehler 1983) are listed in Table 1, the values of γ_0, q_0 and n obtained by the fitting are listed in Table 2.

To compare the fitting accuracy, we calculate the melting temperature T_m of Li, Na and K versus *P* with Eqs. (2) and (3) using the parameters listed in Table 2. The calculated results in this paper (Eq.(2))、Eq.(5) by Fang (1998), and the experimental data (Leudemann and Kennedy 1968) are all listed in Table 3 (RMSD stands for the root mean square deviations of T_m).

(1) From Table 3, we can find that Eq.(2) is one of the accurate representations for the pressure dependence of the melting temperature of alkali metals, which can be obtained by combining Lindemann's law with the Debye model and the Birch EOS, with the assumption that *q* is a function of volume. The results agree well with the experiment.

(2) Fang (1998) has used another method to obtain the pressure dependence of melting temperature of the alkali metals :

$$P = \frac{C_2 T_m}{1 - C_1(T_m - T_{m0})} \ln \frac{T_m}{T_{m0}} \quad (5)$$

He compared the results with Simon's empirical relation

$$P = a[(\frac{T_m}{T_{m0}})^c - 1] \quad (6)$$

and melting relation presented by Schlosser et al.(1989)

$$T_m = T_{m0} x^2 (1 + \beta P)^{2\gamma_0/\alpha} \quad (7)$$

All these relations yield good agreement for Li, Na and K.at low pressures. When the pressure is larger than 15Gpa, they deviate from each other. And Eq.(5) is more close to experiment than Eqs.(6) and (7).

In Table 3 , we calculate values of the root mean square deviations (RMSD) of T_m for Li, Na and K by Eqs.(2) and (5),we can see that results from Eq.(2) tend to reality more than Eq.(5).

Besides, in deducing Eq.(5),Fang (1998) has used the linear relationship for the change of volume V_m along the melting curve

$$V_m = V_{m0}[1 - C_1(T_m - T_{m0})] \quad (8)$$

It's pointed that Eq.(8) might be imperfect, especially at very high pressures (Fang 1998). (3) While assuming γ / V is a constant, Fang and Chen (1994) has presented another expression of T_m for metals as

$$T_m = T_{m0}(\frac{x}{\xi})^2 \exp\left\{2\gamma_0\xi^3[1-(\frac{x}{\xi})^3]\right\} \quad (9)$$

We can get Eq.(9) easily while choosing $q_0 = n = 1$ in Eq. (2). But from Table 2 we see that $q_0 \neq n \neq 1$. Therefore Eq.(9) is just obtained as a approximation. We prefer q to be a function of volume as Eq.(1). That might be a new method to predict the high temperature second Grüneisen parameter q for alkali metals.

(4) Kechin (1995; 2001) has predicted that the melting curve equation at high pressure is

$$T_m = T_{m0}(1+\Delta P/a)^b \exp(-c\Delta P) \quad (10)$$

where $\Delta P = P - P_0$. Eq.(10) supports Tammann's hypothesis that all materials have a maximum melting temperature at high pressures. The present Eq.(2) is just the right agreement with this point of view, while Eq.(5) isn't satisfied with Tammann's hypothesis (see Fig.1). Moreover, Dass (1995) has studied the melting maximum in alkali metals. It's found that the melting maximum occurs at 86, 377 and 72 kbar for Li, Na and K, respectively. From Fig.1, we can see that our results are in good agreement with these conclusions.

Table 1. Values of $\alpha(0,T_R), B(0,T_R), B'(0,T_R)$ at T_R=298K (Boehler 1983)

Solid	$\alpha(0,T_R)(10^{-3}K^{-1})$	$B(0,T_R)(10^8 Pa)$	$B'(0,T_R)$
Li	0.158	112.7	3.58
Na	0.208	62.1	3.86
K	0.246	30.9	3.83

Table 2. Fitting values of γ_0, q_0 and n

solid	$T_{m0}(K)$ [19]	γ_0	q_0	n
Li	453.5	0.6933	1.644	1.0250
Na	371.0	0.9785	0.816	0.6031
K	336.0.	1.1230	1.327	0.7747

Table 3. Calculated values of T_m through Eqs. (2), (5) and the experimental data (Leudemann and Kennedy 1968) for Li, Na and K

P	Li			Na			K		
(10^8 Pa)	(2)	(5)	[19]	(2)	(5)	[19]	(2)	(5)	[19]
0	454.2	453.5	453.5	371.2	371.0	371.0	337.8	336.0	336.0
5	468.8	470.9	470.0	411.6	408.2	412.0	394.8	408.4	401.0
10	480.4	482.8	481.0	439.3	437.5	440.0	437.0	447.0	435.0
15	489.5	491.5	490.0	462.3	461.6	462.0	465.9	472.1	464.0
20	497.1	498.2	496.0	482.2	482.0	482.0	487.2	489.8	485.0
25	503.0	503.5	502.0	499.0	499.7	499.0	504.3	503.2	503.0
30	507.9	507.9	508.0	514.3	515.2	514.0	515.9	513.7	516.0
35	512.2	511.5	512.0	528.1	528.9	528.0	525.7	522.1	527.0
40	515.6	514.5	516.0	541.6	541.2	541.0	533.1	529.0	535.0
45	518.3	517.2	519.0	551.9	552.3	553.0	538.8	534.8	541.0
50	520.6	519.4	521.0	562.1	562.4	563.0	543.0	539.8	545.0
55	522.4	521.4	523.0	570.5	571.6	571.0	546.2	544.0	549.0
60	523.8	523.2	524.0	579.2	580.1	580.0	548.9	547.7	550.0
65	525.1	524.7	525.0	587.7	587.9	588.0	550.0	551.0	551.0
70	525.7	526.1	526.0	594.6	595.1	595.0	551.5	553.9	552.0
75	526.2	527.4	526.0	601.1	601.8	602.0	551.7	556.4	553.0
80	526.7	528.5	527.0	608.0	608.0	608.0	551.7	558.8	553.0
RMSD	0.615	1.310		0.556	1.210		2.218	5.409	

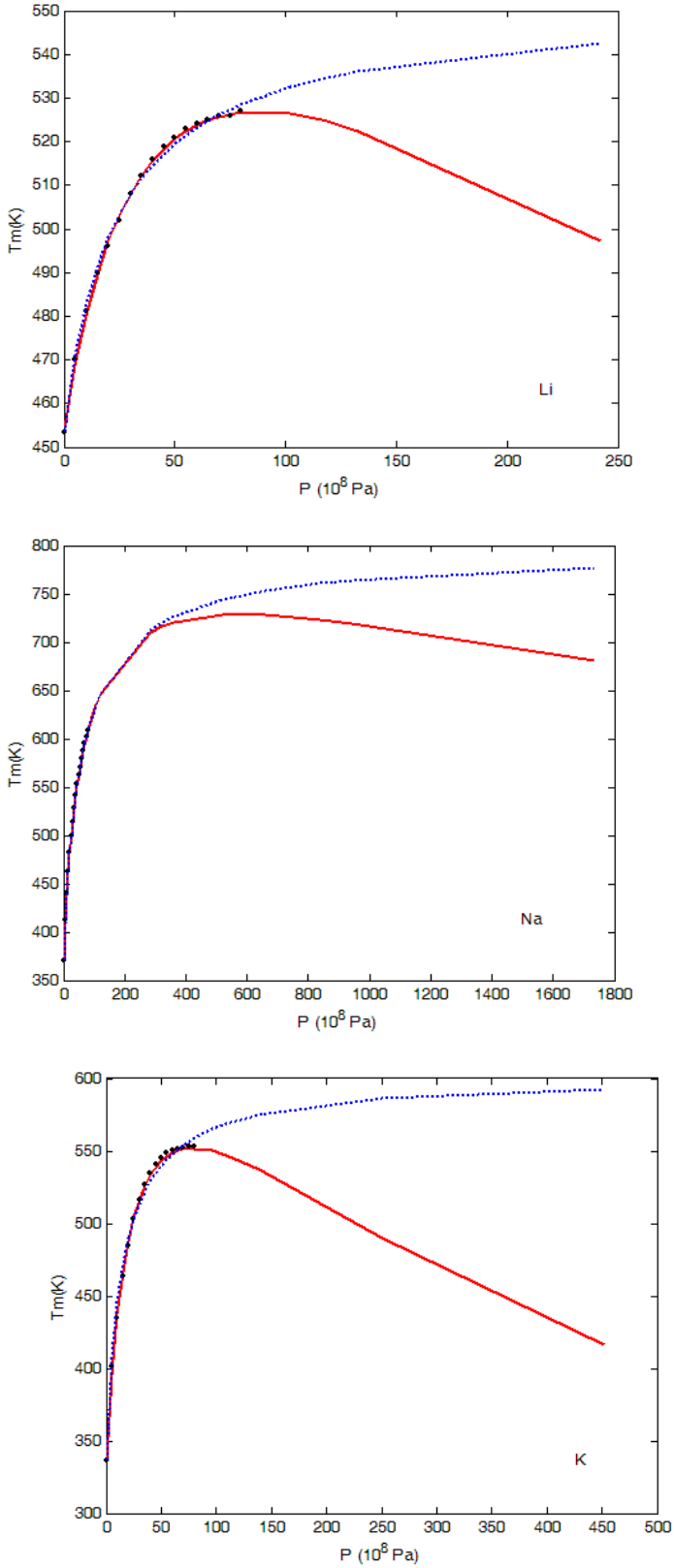

Fig.1. Melting curves of Li, Na and K. The dashed line: Eq.(5), the solid line: the present work, and the solid circles (·) : the experimental data (Leudemann and Kennedy 1968).

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References

Anderson,O.L. (1998), The Grüneisen parameter for iron at outer core conditions and the resulting conductive heat and power in the core. Physics of the Earth and Planetary Interiors,109, 179-197.

Anderson,O. L., Isaak, D., Oda, H. (1992). High-temperature elastic constant data on minerals relevant to geophysics. Reviews of Geophysics, 30, 57-90.

Asanuma, H., Ohtani, E., Sakai, T.,Terasaki,H.,Kamada,S.,Kondo,T.,Kikegawa,T.(2010), Melting of iron-silicon alloy up to the core-mantle boundary pressure: implications to the thermal structure of the Earth's core, Physics and Chemistry of Minerals,37,353-359

Boehler, R. (1983), Melting temperature, adiabats, and Grüneisen parameter of lithium, sodium and potassium versus pressure. Physical Review B, 27, 6754-6762.

Boehler, R. Ross, M. Soderlind, P., Boercker,D.B. (2001), High-pressure melting curves of Argon, Krypton, and Xeon: Deviation from corresponding states theory. Physical Review Letters, 86, 5731-5734.

Chauhan, R.S., Singh,C.P. (2002). Analysis of melting for alkali halides based on the potential energy curve. Physica B, 324, 151-156.

Chauhan,R.S., Snehlata, K., Singh,C.P. (2011). Defects induced melting in alkali halides. Physica B, 406, 567-570.

Dass, N. (1995), Melting maximum in alkali metals. Physical Review B, 52, 3023-3025.

Fang, Z. H. (1998), A new universal relation for the pressure dependence of the melting temperature of solids. Physics Status Solidi (b), 207, 89-94.

Fang, Z. H., Chen, L.R. (1994), A simplified treatment to calculate the melting temperature of metals under a high pressure. Journal of Physics: Condensed Matter, 6, 6937-6940.

Jeanloz, R. (1989), Shock wave equation of state and finite strain theory. Journal of Geophysical Research, 94, 5873-5886.

Kaver, A., Jeanloz, R. (1998), High-pressure melting curve of platinum, Journal of Applied Physics, 83, 7553-7559.

Kechin V.V. (1995), Thermodynamically based melting-curve equation, Journal of Physics: Condensed Matter, 7, 531-535.

Kechin,V.V. (2001), Melting curve equations at high pressure. Physics Review B, 65, 052102.

Leudemann ,H.D., Kennedy, G.C. (1968), Melting curves of lithium, sodium and potassium, and Rubidium to 80 kilobars. J.Geophys. Res 73, 2795-2805.

Liu, Q. Chen, L.R. (2005). A simple melting theory applied to alkali halide, alkaline-earth chalcogenide, and alkali chalcogenide compounds.Canadian Journal of Physics, 83,653-660.

Nie, C. H. (2000), Volume and temperature dependence of the second Grüneisen parameter of NaCl. Physics Status Solidi (b), 219, 241-244.

Nie,C.H., Chen, L.R. (1999),Comparison of three temperature –dependent eqution of state of condensed matter. Physics Status Solidi (b), 215, 957-962.

Schlosser, H., Vinet, P. , Ferrante, J. (1989), Pressure dependence of the melting temperature of metals. Physical Review B, 40, 5929-5935.

Wang, Z.W., Lazor, P., Saxena, S.K. (2001), A simple model for assessing the high pressure melting of metals: nickel, aluminum and platinum, Physica B 293, 408-416.

Zubov,V.I., Rodrigues,C.G., Zubov, I.V. (2003), On a possible melting curve of C_{60} fullerite, Physics Status Solidi (b), 238, 110-114.