Short communication

Volume and pressure-dependent thermodynamic properties of sodium

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ABSTRACT

In this work, the volume and pressure effects on thermodynamic quantities including Grüneisen parameter and melting temperature of sodium have been studied of to 65 GPa. The volume dependence of Grüneisen parameter of sodium has been firstly analyzed. Based on this result and the Lindemann criterion of melting we derived the analytical expression of volume-dependent melting temperature. Combining with Vinet equation-of-state, the melting curve of sodium at high pressure has been proposed. Numerical calculations were performed for solid sodium up to pressure 65 GPa. Theoretical calculations are compared with available experimental data showing the good and reasonable agreements in the pressure range 0−30 GPa. This research proposes the good volume- and pressure-dependent Grüneisen parameter as well as the potential of Lindemann criterion approach on predicting high-pressure melting of materials.

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The investigation of thermodynamic properties of materials under extreme condition is one of the interesting subjects in physics because of its importance in studying shock physics, planetary science, astrophysics, geophysics and nuclear physics. In recent years, with the development of diamond-anvil cell technology the researchers are able to perform the experiments in ultra-high pressures (up to hundreds of GPa) [1−4]. Consequently, the investigation of thermodynamic properties of materials under high pressure is a topical and scientific significance.

Sodium is a light alkali metal with the single *s* electron in the valence band. Under compression, this metal exhibits unexpected complexity accompanied by series of structural phase transition into lower symmetry. One of the complexity properties of sodium is its melting temperature [1,5]. In the recent experiment by x-ray diffraction techniques, the melting curve of sodium has been investigate up to 130 GPa [1]. Gregoryanz and collaborations found the maximum of the melting curve at 31 GPa and 1000 K in body-centered cubic phase and the steep decrease of the melting in face-centered cubic phase. They also found the abnormally low melting above 100 GPa accompanied by the new low-symmetry solid phases.

In present paper, we are going to investigate the volume- and pressure-dependent thermodynamic properties of sodium including Grüneisen parameter and melting problem. Thanks to the combination of the Lindemann melting criterion [6] and the volume-dependent Grüneisen parameter, we carried out the relatively simple analytical expression of melting temperature as a function of volume compression $\eta = V/V_0$. Combining derived result with the Vinet equation-of-state [7], the pressure-dependent melting temperature of sodium up to 65 GPa will be calculated numerically. Our results are compared with recent experimental and theoretical studies when possible.

On studying the volume dependence of phonon frequencies ω_i, Grüneisen [8] proposed the parameter γ_G, so-called Grüneisen parameter, which was defined as [9] $\gamma_G = -\sum \frac{\partial \ln \omega_i}{\partial \ln V} = -\frac{\partial \ln \omega_0}{\partial \ln V}$, where V is crystal volume and ω_i are phonon frequencies which depend only on volume V. At low pressure, the Grüneisen parameter of material can be seen as constant which does not depend on pressure variation. However, previous experiments and theories [10−13] showed that it will reduce gradually when pressure increases. In order to evaluate the volume (and pressure) effect on Grüneisen parameter, many great ideas had been put forward. Graf et al. assumed the Grüneisen parameter had the quite well described power-law form as $\gamma_G = \gamma_0 \eta^q$, where γ_0, V_0, and η are Grüneisen parameter, crystal volume at ambient conditions and isothermal volume compression ratio $\eta = V/V_0$, respectively. The value of q belongs to studied material, usually, $q > 0$. Using this model, they had successfully investigated the Grüneisen parameter and Debye−Waller factor of copper and gold at high pressure [9].

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By supposing the second Grüneisen parameter q had the form of $q = q_0\eta^n$, Nie derived the volume-dependent expression of γ_G as $\gamma_G = \gamma_0 \cdot \exp\left[\frac{q_0}{n}(\eta^n - 1)\right]$, where q_0 is the zero pressure second Grüneisen parameter. Nie applied this equation to experimental data of lithium, sodium and potassium and sodium chloride, and the reasonable agreement between theory and experiment was found. However, this expression still does not well describe the volume dependence of Grüneisen parameter of materials.

Recently, through the consideration of low- and ultra-high-pressure limits, Burakovsky et al. have modeled the Grüneisen parameter of solid as [14].

$$\gamma_G = \frac{1}{2} + \gamma_1\eta^{1/3} + \gamma_2\eta^q, \tag{1}$$

where $\gamma_1, \gamma_2, q = \text{const}, q>1$. In order to obtain the above analytic form for γ_G, Burakovsky et al. assumed that [14]: i) $\gamma_G \to 1/2$ as $\eta \to 0$; ii) γ_G is an analytic function of $\eta^{1/3}$, essentially the interatomic distance; iii) the first-order coefficient of the Taylor-Maclaurin series expansion for γ_G is nonzero. The third term on the right-hand side of Eq. (1) represents the contribution of the quadratic and higher-order terms in the power series. In present paper, this expression will be applied to investigate the Grüneisen parameter as well as melting temperature of sodium. The values of γ_1, γ_2, and q will be determined by fitting Eq. (1) with experimental data.

To the best of our knowledge, up to now, there is only one experiment performed by Boehler to determine the temperature-dependent Grüneisen parameter based on the adiabatic bulk modulus of sodium up to 3 GPa [10]. Fitting the equation (1) to the experimental Grüneisen parameter data of Boehler, one could derive the values of $\gamma_1 = 0.4801$, $\gamma_2 = 0.2291$, and $q = 13.7253$. Using the parameters derived above we calculate the Grüneisen parameter of sodium up to 3 GPa. Our results have been presented in Table 1. Previous theoretical calculations as well as experimental data of γ_G have also been showed for comparison. As can be seen in this table, all of the reported data propose the decrease of Grüneisen parameter with the increasing of pressure. Our calculations are in very good agreement with those observed experimentally and better than those obtained by other authors [11–13]. Consequently, the validity of Eq. (1) can be actually confirmed and can be used to investigate the melting temperature of sodium.

In the following part of paper, the melting behavior of sodium under pressure up to 65 GPa will be discussed. As shown in the recent high-pressure high-temperature synchrotron diffraction measurements [1], up to 65 GPa, the solid sodium is in phase I with body-centered cubic structure and its melting curve has a maximum at 31 GPa and 1000 K.

In pursuance of melting of materials, the most widespread theory has been used for the melting instability is the Lindemann melting criterion. This criterion has been proposed as [6]: Melting is going to occur when the ratio between mean-square vibration and square of nearest-neighbor distance reaches a threshold value.

Lindemann criterion of melting was naturally derived to the following equation [16].

$$\frac{\partial \ln(T_m)}{\partial V} = \frac{2}{V}\left(\frac{1}{3} - \gamma_G\right), \tag{2}$$

where γ_G is Grüneisen parameter in Debye model defined as $\gamma_G = -\partial \ln\theta_D/\partial \ln V$.

Substituting Eq. (1) into Eq. (2) and taking the integral, one could carry out the analytical formula of melting T_m as a function of volume compression $\eta = V/V_0$ as

$$T_m = T_0\eta^{-1/3}\exp\left\{6\gamma_1\left(1 - \eta^{1/3}\right) + \frac{2\gamma_2}{q}(1 - \eta^q)\right\}, \tag{3}$$

in the above equation, T_0 is the melting temperature at ambient conditions.

Taking into account Eq. (3), the melting temperatures of sodium metal under high pressure can be evaluated numerically. It is obviously that indispensable input parameters required to determine melting temperature T_m as a function of volume compression η are T_0, γ_1, γ_2 and q. Melting temperature T_0 at ambient conditions can be gathered from experiments while the values of γ_1, γ_2 and q could be obtained by fitting Eq. (1) with experimental data [10].

In order to derive the pressure dependence of melting temperature T_m, we take into account the relation between pressure P and volume compression $\eta = V/V_0$ from well-established and up-to-date Vinet EOS formulation [7]. This EOS has form as

$$P = 3K_0\eta^{-2/3}\left(1 - \eta^{1/3}\right)\exp\left\{\frac{3}{2}\left(K_0' - 1\right)\left(1 - \eta^{1/3}\right)\right\}, \tag{4}$$

where K_0 and K_0' are the isothermal bulk modulus and its first pressure derivative at ambient pressure, respectively. The values of $K_0 = 5.35$ GPa and $K_0' = 5.0$ are reported in literature [20] and [21], respectively. By combining Eq. (3) with (4), we evaluate numerically melting temperature of sodium under high pressure. In Fig. 1 the melting curve T_m of sodium has been displayed up to 65 GPa. Our results are compared with those of experimental data of Luedemann and Kennedy [17] (□ marks), Zha and Boehler [18] (★ marks), and Gregoryanz et al. [1] (◆ marks). The well-fitted function of the experimental melting temperature data $T_m(P) = 417.6186 + 33.5913P - 0.5883P^2 + 0.002511P^3$ done by Arafin and Singh [19] is also plotted for comparison. As can be seen in Fig. 1, up to 30 GPa melting curve in current work is in very good consistent with recent high-pressure high-temperature synchrotron diffraction measurements of Gregoryanz et al. [1]. Beyond 30 GPa, experimental melting temperature shows a surprising decrease. While the experimental melting curve gets the maximum at 31 GPa and about 1000 K where the structural phase transition from body-centered cubic to face-centered cubic occurs, our determinations continue increasing with the increasing of pressure.

Table 1
Pressure dependence of the Grüneisen parameter γ_G of sodium.

P (GPa)	η [15]	Exp [10]	Kumari&Dass [11]	Fang [12]	Cui&Yu [13]	This work
0.0	1.000	1.21	1.07	1.21	1.2100	1.2092
0.5	0.931	1.05	1.05	1.12	1.1163	1.0473
1.0	0.878	1.00	1.02	1.06	1.0471	0.9953
1.5	0.837	0.98	0.99	1.00	0.9949	0.9713
2.0	0.803	0.96	0.97	0.96	0.9523	0.9575
2.5	0.775	0.94	0.94	0.93	0.9177	0.9483
3.0	0.750	0.94	0.92	0.90	0.8870	0.9415