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Pressure dependence of the melting temperature of rare-gas solids

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Abstract. According to Lindemann's law and the Debye model and with the assumption that the volume derivative $q (= d \ln \gamma / d \ln V)$ of the Grüneisen parameter γ is a constant depending on the material, we present a new expression for the analysis of the experimental data for the melting temperature of solids under a high pressure. The test on rare-gas solids (Ne, Ar, Kr and Xe) shows that the calculated results are in good agreement with the corresponding experimental data.

1. Introduction

The Grüneisen parameter γ is generally regarded as only a volume-dependent parameter. However, there exist several different expressions in the literature for this parameter [1–3]. In fact the knowledge of the Grüneisen parameter γ is still imperfect at present. It has been noted that, to a good approximation, the ratio γ/V of the Grüneisen parameter γ to the volume is a constant for some solids [4]. Recently, with the assumption that γ/V is a constant, we calculated the melting temperatures under a high pressure for seven metals (Al, Ag, Au, Cu, Na, K and Rb) using Lindemann's law and the Debye model [5]. The calculated results on the melting temperature versus pressure are in good agreement with the experimental values. However, we have found that, if the same calculation procedure is applied to rare-gas solids, then the deviations between the calculated results and the experimental data are too large. It seems to us that the assumption that the ratio γ/V is a constant is perhaps not suitable for rare-gas solids. In fact, if we introduce the volume derivative of the Grüneisen parameter γ given by

$$q = d \ln \gamma / d \ln V \quad (1)$$

then the fact that γ/V is a constant is equivalent to $q = 1$. Yet the value of q is generally not just equal to unity [6]. Therefore, in this paper we take q as an adjustable parameter which depends on the material. With this assumption we obtain another expression for the melting temperature of a solid under a high pressure using Lindemann's law and test it on rare-gas solids (Ne, Ar, Kr and Xe).

2. Pressure dependence of the melting temperature of solids

According to Lindemann's law, the relationship between the melting temperature T_m and Debye temperature Θ_D is given by

$$T_m = C V_m^{2/3} \Theta_D^2 \quad (2)$$

where C is a constant which depends on the material and V_m is the volume at the temperature T_m . The Grüneisen parameter γ is given in the Debye model by

$$\gamma = -\partial(\ln \Theta_D)/\partial(\ln V) \quad (3)$$

and hence

$$(\partial \Theta_D / \partial V)_T = -\gamma \Theta_D / V. \quad (3a)$$

Assuming that q is a constant which depends on the material, then the following expression is given by (1):

$$\gamma/\gamma_0 = (V/V_0)^q \quad (4)$$

where γ_0 and V_0 are the Grüneisen parameter and the volume, respectively, at zero pressure and melting temperature. Hence, the following expression is given by equations (2)–(4):

$$T_m = T_{m0} \left(\frac{V}{V_0} \right)^{2/3} \exp \left\{ \frac{2\gamma_0}{q} \left[1 - \left(\frac{V}{V_0} \right)^q \right] \right\} \quad (5)$$

where T_{m0} is the zero-pressure melting point. If we write

$$\xi = (V_0/V_r)^{1/3} \quad X_r = (V/V_r)^{1/3} \quad C_1 = 2\gamma_0/q$$

where V_r is the volume at zero pressure and the reference temperature, then equation (5) can be written

$$T_m = T_{m0} X_r^2 \exp\{C_1[1 - (X_r/\xi)^{3q}]\}/\xi^2. \quad (5a)$$

The pressure $P(T, V)$ has been found experimentally to be related to the isothermal pressure $P(T_r, V)$ at the reference temperature T_r by [7]

$$P(T, V) = P(T_r, V) + \alpha(T_r) B_0(T_r)(T - T_r) \quad (6)$$

where $\alpha(T_r)$ is the volume thermal expansion coefficient at T_r and $P = 0$, and $P(T_r, V)$ is given by the Vinet *et al* [8] equation

$$P(T_r, V) = [3B_0(T_r)(1 - X_r)/X_r^2] \exp\{\frac{3}{2}[B'_0(T_r) - 1](1 - X_r)\} \quad (7)$$

where $B_0(T_r)$ and $B'_0(T_r)$ are the bulk modulus and its first pressure derivative, respectively, at zero pressure and the reference temperature. Substituting equation (7) into (6) and letting $P(T_{m0}, V) = 0$, we can obtain ξ and then the values of q and C_1 can be obtained by fitting the experimental data on the melting temperature under a high pressure of the solid with equations (5a) and (6). The theoretical curve of T_m versus P can be plotted with equations (5a) and (6) using the values of q and C_1 obtained by the fitting.

3. The calculation results on rare-gas solids

With the method mentioned above, we fitted the experimental data on the melting temperature under a high pressure for rare-gas solids (Ne, Ar, Kr and Xe). The values of the parameters $\alpha(T_r)$, $B_0(T_r)$ and $B'_0(T_r)$, which are necessary for the fitting, are all listed in table 1. The values of C_1 and q obtained by the fitting are also listed in table 1.

To compare the fitting accuracy we calculated the melting temperature of the four rare-gas solids under a high pressure with equations (5a) and (6) using the parameters listed in table 1. The calculated results are reported in tables 2–5. For comparison, the experimental data on the melting temperature under a high pressure are also listed in tables 2–5. Some experimental points are not listed to avoid the repetition due to a small variation in pressure. From tables 2–5 we can see that the agreement between the theoretical calculated results and the experimental values is very good.

Table 1. The experimental values of $\alpha(T_r)$, $B_0(T_r)$, $B'_0(T_r)$ and the fitting values of C_1 and q .

Solid	T_r (K)	$\alpha(T_r)$ [9] (10^{-3} K^{-1})	$B_0(T_r)$ (GPa)	$B'_0(T_r)$	C_1	q
Ne	20	4.110	0.827 [10]	8.5 [10]	3.862	1.938
Ar	75	1.770	1.410 [11]	8.4 [11]	3.378	2.480
Kr	75	1.029	1.580 [11]	7.6 [11]	4.164	1.421
Xe	150	1.020	1.480 [11]	8.8 [11]	4.393	1.583

Table 2. The melting temperature of Ne under a high pressure.

P (10^8 Pa)	T (K)	
	Experimental [12]	This work
0.000 43	24.555	24.555
0.629 24	33.146	32.145
1.355 19	41.530	40.635
2.027 81	48.498	47.981
2.653 64	54.513	54.395
3.243 80	59.874	60.077
3.794 96	64.665	65.128
4.370 26	69.477	70.123
4.951 52	74.168	74.936
5.555 66	78.900	79.690
6.002 54	82.311	83.093
6.702 55	87.520	88.154
7.548 04	93.165	94.083
7.988 15	96.716	96.835
8.456 69	99.962	99.838
9.234 65	105.253	104.579
9.928 11	109.870	108.648

4. Discussion

(1) Starting from Lindemann's law and using the assumption that q ($= d \ln \gamma / d \ln V$) is a constant we obtained equation (5a). From table 2–5 we can see that the theoretical results are in good agreement with the experimental data, which indicated that the assumption that q is a constant is a good approximation for the four rare-gas solids.

(2) The parameter q ($= d \ln \gamma / d \ln V$) is a useful quantity for studying the high-temperature and high-pressure equation of state of solids. However, the parameter q has been given very different values by various workers. Thus Dhoble and Verma [14] on the basis of a thermodynamic analysis reported values of q which are significantly higher than 1 but closer to 2, Boehler and Kennedy [15] derived a value of q somewhat smaller than 1 from their experiment. Chang [16] assumed that $q \ll 1$, and Anderson [17] assumed it to be of the order of unity. Using an interionic potential approach, Kaur *et al* [18] found in general that $q < 1$ and Sharma and Shukla [19] found values ranging from 1 to 2.9. The results obtained in this work show that, for rare-gas solids, q is of the order of unity which is consistent with the results presented by Sharma and Shukla.

(3) With the assumption that the ratio γ/V is a constant. Schlosser and Ferrante [20]

Table 3. The melting temperature of Ar under a high pressure.

P (10^8 Pa)	T (K)	
	Experimental [13]	This work
0.000	83.2	83.2
2.420	137	130
5.037	182	180
5.487	188	189
6.330	197	206
7.790	226	225
9.218	245	247
10.383	262	263
11.514	278	278
12.053	284	285
12.395	288	290
12.602	291	292
13.128	299	298
14.600	317	315
18.274	360	354

Table 4. The melting temperature of Kr under a high pressure.

P (10^8 Pa)	T (K)	
	Experimental [12]	This work
0.000 73	115.773	115.773
0.788 27	138.284	137.720
1.324 95	152.379	151.881
1.863 18	165.790	165.476
2.388 24	178.297	178.240
2.917 30	190.430	190.528
3.471 70	202.696	202.981
4.087 42	215.874	216.267
4.687 63	228.302	228.763
5.302 93	240.685	241.088
5.939 79	253.150	253.422
6.594 43	265.674	265.662
7.318 88	279.160	278.743
8.008 52	291.695	290.754

obtained the following expression using Lindemann's law:

$$T_m = T_{m0} X^2 \exp[2\gamma_0(1 - V/V_0)]. \quad (8)$$

The following equation, similar in form to the isothermal Tait equation, was chosen for the variation in pressure with volume along the melting curve

$$\frac{V}{V_0} = 1 - \frac{1}{\alpha} \ln \left(1 + \frac{\alpha p}{B_0} \right) \quad (9)$$

where B_0 was identified with the isothermal bulk modulus of the solid at the zero-pressure melting point. Combining equations (8) and (9) and taking α and γ_0 as the two fitting parameters, they fitted and calculated the melting temperature of rare-gas solids under a high pressure. The fitting accuracy is also very good. However, it should be mentioned that

Table 5. The melting temperature of Xe under a high pressure.

P (10^8 Pa)	T (K)	
	Experimental [13]	This work
0.00	161.4	161.4
1.95	224	228
2.48	245	241
2.84	250	257
3.55	277	273
3.95	288	286
4.15	291	293
5.07	322.5	315
6.87	363	368

strictly there is an inconsistency in this derivation. Whatever the value of this adjustable parameter α , equation (9) implies that the initial slope of the p - V melting curve is determined by the isothermal bulk modulus, but of course this curve is not an isotherm. Therefore, it seems that the physical meaning of the procedure is a little vague.

(4) The assumption that q is a constant depending on the material is made in this paper but the assumption that q is exactly equal to 1 (i.e. $\gamma/V = \text{constant}$) was made in [20]. For rare-gas solids the calculated results obtained in this work and in [20], respectively, are all in good agreement with the experimental data. However, which assumption is in the end more reasonable physically needs to be tested further.

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