A NOTE ON THE MELTING OF IRON UNDER HIGH PRESSURE

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Abstract. Using new experimental data on the pressure dependence of the melting temperature of iron, the value of the high temperature limit of the Grüneisen parameter, γ_o, has been derived. The calculation has been performed within the theory of melting of metals recently proposed by Schlosser *et al.*, (1989, *Phys. Rev.*, **B40**, 5929), with and without modifications due to taking into account the pressure dependence of the ratio γ/V. The results of both calculations are in agreement with values quoted in recent literature. Possible causes of the discrepancies are discussed. A change of γ occuring at $P \cong 120$–130 GPa indicates the occurence of a phase transition, whose existence is confirmed within a particular semiclassical theory of dense matter.

Introduction

The pressure dependence of the melting temperature of solids is of particular planetological importance, because of the interest in the determination of the depth under the surface (i.e., the pressure) at which melting of various materials can be expected. Apart from that, predicting the melting temperature of a real material starting from first principles of solid-state physics is an extremely complex problem.

The purpose of this letter is to analyze recent experimental data on the melting of iron under high pressure, because there are strong indications that it is one of the major constituents of the Earth's core (Mulargia, 1986; Anderson, 1986; Stacey *et al.*, 1989). We shall in particular be interested in γ_0, the value of the Grüneisen parameter at the melting temperature under zero pressure. The calculations will be performed within the theory of the pressure dependence of the melting temperature of metals proposed by Schlosser *et al.* (1989).The theory will be somewhat improved, so as to take into account the volume dependence of ratio γ/V. A brief review of the main ideas of this theory in its original form (that is, assuming that γ/V is pressure independent) and in the modified form (with γ/V being a function of the volume) is presented in the following section. The third part contains the determination of γ_0 within the original and modified forms of the theory, while the fourth section is devoted to the interpretation of the results.

The Theory

The initial point of the theory of Schlosser *et al.* is Lindemann's law, which relates the melting temperature T_m and Debye's temperature Θ_D,

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$$T_m = CV^{2/3}\Theta_D^2, \tag{1}$$

where C is a material dependent constant.

In Debye's model of a solid, the Grüneisen parameter γ is a function of volume and temperature

$$\gamma = -\,\partial \ln \Theta_D / \partial \ln V. \tag{2}$$

It follows that

$$(\partial\,\Theta_D/\partial V)_T = -\,\gamma\,\Theta_D/V. \tag{3}$$

High pressure experiments (both static and dynamical) have shown that the ratio γ/V is a constant for a given material (Eliezer, Ghatak and Hora, 1986). This means that

$$(\partial\Theta_D/\partial V)_T = -\,\gamma_0\Theta_D/V, \tag{4}$$

which can be solved to give

$$\Theta_D = \Theta_{D0}\exp(\gamma_0 \Delta V/V_0)\,; \tag{5}$$

where $\Delta V = V_0 - V$. Combining Equations (5) and (1), we find that

$$T_m = T_{m0}X^2\exp(2\gamma_0\Delta V/V_0)\,, \tag{6}$$

where T_{m0} is the zero pressure melting temperature. $X = (V/V_0)^{1/3}$ and γ_0 is the zero pressure Grüneisen parameter measured at T_{m0}. It has earlier been shown (Schlosser and Ferrante, 1989) that

$$\Delta V/V_0 = (1/\alpha)\ln(1+\beta P)\,, \tag{7}$$

where $\alpha = B_0' + 1$ and $\beta = \alpha/B_0$. In application to iron, this expression fits the experimental data with a relative error of 0.49% for $P \leq 270$ GPa (Schlosser and Ferrante, 1989). Equation (6) can be linearized by introducing the transformations $T' = (T_m/T_{m0}X^2)$ and $P' = 1 + \beta P$, which reduce it to

$$\ln T' = (2\gamma_0/\alpha)\ln p'\,. \tag{7a}$$

If the ideas outlined above are correct, and in a region of pressure in which there are no phase transitions, a plot of $\ln T'$ versus $\ln P'$ should be a straight line with a slope of $2\gamma_0/\alpha$. Any deviations from linearity indicate the existence of a phase transition.

It could be objected that the assumption concerning the constancy with pressure of the ratio γ/V, which is built in the calculation outlined above, is not quantitatively justified. Accordingly, the region of pressure in which the theory is applicable is not clearly defined.

Experiments have shown that, in the limiting case of high compressions, the Grüneisen parameter depends on the volume (i.e., the pressure, in the following way (Eliezer, Ghatak and Hora, 1986):

$$\gamma = \gamma_0 V/V_0 + (2/3)(1 - V/V_0). \tag{8}$$

Introducing Equation (8) into Equation (3), one gets the following expression for the volume dependence of the Debye temperature

$$(\partial\Theta_D/\partial V)_T = -[\gamma_0/V_0 + (2/3V) - (2/3V_0)]\,\Theta_D. \tag{9}$$

Integrating Equation (9) and performing some simple algebra, we can show that

$$\Theta_D/\Theta_{D0} = \exp[(\gamma_0 - 2/3)\,\Delta V/V_0 - (2/3)\ln(1 - V/V_0)]. \tag{10}$$

Applying Equation (1) to two different values of pressure, and combining this with Equation (10), we find that the final expression for the pressure dependence of the melting temperature of metals becomes

$$T_m = T_{m0}X^2(1 - \Delta V/V_0)^{-4/3}\exp[2(\gamma_0 - 2/3)\Delta V/V_0], \tag{11}$$

where all the symbols have been previously defined.

Introducing the primed variables $T' = (T_m/T_{m0}X^2)$ and $P' = 1 + \beta P$, one obtains the following form of the pressure dependence of the melting temperature of metals:

$$T' = \exp\{2[(\gamma_0 - 2/3)\Delta V/V_0 - (2/3)\ln(1 - \Delta V/V_0)]\}. \tag{12}$$

Taking logarithms of both sides of Equation (12), so as to transform it in a form comparable with Equation (7a), one arrives at the equation

$$\ln T' = 2\{(\gamma_0 - 2/3)(1/\alpha)\ln P' - (2/3)\ln[1 - (1/\alpha)\ln P']\}, \tag{13}$$

where Equation (7) and the definition of P' have been used. Expression (13) can be transformed to the following final form:

$$\ln T' = 2[\gamma_0/\alpha - 2/(3\alpha)]\ln P' - (2/3)\ln[1 - (1/\alpha)\ln P']. \tag{13a}$$

This equation describes the pressure dependence of the melting temperature of metals. It represents an improvement of the theory proposed by Schlosser *et al.* (1989), because it takes into account the pressure dependence of the ratio γ/V. The form of this dependence is experimentally justified (Eliezer, Ghatak and Hora, 1986). The second term on the right side of Equation (13a) has the form of $\ln(1 - (1/\alpha)x)$, with $x = \ln P'$. Developing it into Taylor's series, and limiting the development to fifth order, we get the expression for the melting temperature of a metal of the form:

$$\ln T' = (2/3\alpha)(3\gamma_0 - 1)\ln P' + (1/3)(\ln P'/\alpha)^2 + (1/6)(\ln P'/\alpha)^4 + \\ + (2/15)(\ln P'/\alpha)^5 + (1/9)(\ln P'/\alpha)^6 + \cdots. \tag{14}$$

The first term in Equation (14) corresponds to the original result of Schlosser *et al.*, while the following appear as a consequence of the pressure dependence of the ratio γ/V. The relative importance of th correction terms can be estimated by forming the ratio of Equations (14) and (7a).

In this way, it follows that

$$(\ln T')_{\text{modif}}/(\ln T')_{\text{orig}} = 1 - 1/3\,\gamma_0 + (1/6\gamma_0)(\ln P'/\alpha) + \\ + (1/9\gamma_0)(\ln P'/\alpha)^2 + (1/12\gamma_0)(\ln P'/\alpha)^3 + \cdots . \tag{15}$$

This indicates that the relative importance of the correction terms is an increasing function of the applied pressure; the validity of the results obtained within the original form of the theory of Schlosser *et al.* thus increases with $\ln P'/\alpha \Rightarrow 0$.

In the following section, Equations (7a) and (14) will be applied to experimental data on the melting of iron under high pressure, with the aim of determining the value of the Grüneisen parameter.

The Value of γ_0

Experimental data on the pressure dependence of the melting temperature of iron, obtained in laser-heated diamond-anvil cells, are presented in the following table.

TABLE 1

P(GPa)	$T_m(K)$	References
0	1809	Wallace, 1991
65	2650 ± 100	Boehler *et al.*, 1990
100	2800 ± 100	Boehler *et al.*, 1990
120	3000 ± 100	Boehler *et al.*, 1990
133	4800 ± 200	Williams *et al.*, 1991
243	6700 ± 400	Williams *et al.*, 1991
330	7600 ± 500	Williams *et al.*, 1987

Transforming to the primed variables (P, T) and fitting all the data in Table I by a least-squares straight line gives

$$2\gamma_0/\alpha = 0.54 \pm 0.23 ,$$

which can hardly be regarded as a result of acceptable precision. More precise results can be obtained by separating the data into two groups: $P \leq 120$ GPa and $P \geq 133$ GPa, and fitting them by two separate straight lines. In this way, one gets the following values of the ratio $2\gamma_0/\alpha$:

$$2\gamma_0/\alpha = 0.3059 \pm 0.0002 , \quad P \leq 120 \text{ GPa} ;$$
$$2\gamma_0/\alpha = 0.677 \pm 0.002 , \quad P \geq 133 \text{ GPa} .$$

By use of the value of α determined in (Schlosser and Ferrante, 1989), which is, according to that paper, valid for $P \leq 270$ GPa, the final results for the Grüneisen parameter γ_0 are:

$$\gamma_0 = 1.21 \pm 0.05 , \quad P \leq 120 \text{ GPa} ;$$
$$;\gamma_0 = 2.67 \pm 0.05 , \quad P \geq 133 \text{ GPa} .$$

A calculation of γ_0 has also been performed within the modified theory of Schlosser *et al.*, in which the volume dependence of the ratio γ/V has been included, as described in the preceeding section. Data presented in Table I were numerically fitted by least-squares polynomials of various orders and the standard deviations were determined for each of them. Because of the form of Equation (14) only those polynomials in which $\ln P'$ had a positive coefficient could be retained for further consideration. The best results (in the sense of minimizing the standard deviation, and the fitting polynominal being of a smallest possible degree) were obtained with the following expressions:

in the interval $0 \leq P(\text{GPa}) \leq 120$,

$$\ln T' = 0.0003 + 0.2715 \ln P' + 0.0153 (\ln P')^2 ; \tag{16}$$

and, in the range $133 \leq P(\text{GPa}) \leq 330$,

$$\ln T' = 0.2210 \ln P' + 0.916 (\ln P')^3 - 0.0188 (\ln P')^4) . \tag{17}$$

By comparing these polynominals with the form of Equation (14), and using the value of α determined in (Schlosser and Ferrante, 1989) one finally gets the following values of the Grüneisen parameter of iron:

$$0 \leq P(\text{GPa}) \leq 120 , \quad \gamma_0 = 1.41 \pm 0.17 ;$$
$$133 \leq P(\text{GPa}) \leq 330 , \quad \gamma_0 = 1.20 \pm 0.11 .$$

The errors were determined from the numerically obtained values of the standard deviations of Equations (16) and (17).

Discussion

In this letter we have determined the value of the Grüneisen parameter of iron. The calculation was performed within the theory of the pressure dependence of the melting temperature of metals proposed by Schlosser *et al.* (1989).

The result, $\gamma_0 = 1.21 \pm 0.05$ for $P \leq 120$ GPa, is in excellent agreement with existing low-temperature data (Baron *et al.*, 1980; Wallace, 1991). On the other hand, (Wallace, 1991) mentions $\gamma = 1.7$ as the high temperature limit of the Grüneisen parameter of iron. The obvious difference between these two values can be explained by the difference in methods by which the two results were obtained. The result of the present letter is a direct product of an analysis of experimntal data within a particular theory of the pressure dependence of the melting temperature of metals. The value quoted used in (Wallace, 1991) as the high temperature limit of γ is a result of a calculation involving the frequency distribution of phonons and an averaging over the Brillouin zone; at the melting point, both of these data are not neccessarily known with sufficient precision.

The change by a factor of almost 2 in the value of γ_0 between 120 and 133 GPa is, according to (Schlosser *et al.*, 1989) a sign of the occurrence of a high-pressure phase transition. Experimentally, it corresponds to a solid-liquid transition at the melting line of iron (Williams *et al.*, 1991). It would be interesting to check for the the existence of a phase transition in iron in this interval of pressure in a room-temperature diamond-anvil cell experiment. The existence of such a transition can be predicted within the classical theory of dense matter proposed by Savić and Kašanin (1962/65) (for a recent review of the applicability of this theory, see Čelebonović, 1992b).

The theory of Schlosser *et al.* was modified in the present letter by the inclusion of the pressure dependence of the ratio γ/V. (For work relating the volume dependence of γ/V with the elastic moduli of a material see Gerlich, 1992). Values of γ calculated with such a modified theory are given in Equation (18). It is obvious that they are smaller and mutually closer than those obtained by the original theory. Mathematically, such a change of behaviour is due to a particular form of the volume dependence of γ/V used in the present work, which physically reflects changes in the form of the interatomic interaction potential in a solid under increasing pressure (Sherman and Wilkinson, 1980; Mimkes, 1992).

There still occurs a change between 120 and 133 GPa, but the 'strength' of the transition (measured by the relative change in the value of γ) is much weaker than in the original theory of Schlosser *et al.* Which of the two sets of values of γ is a more realistic approximation of iron can only be decided by high-pressure experiments, similar to those analyzed in the present work, but performed at more finely distributed values of pressure.

On the theoretical side, it would be interesting to modify the theory used in the present calculation by including in it a different form of the volume dependence of γ/V (such as Jeanloz, 1989).

Conclusions

By a simple analysis of recent experimental data on the melting of iron under high pressure, the high temperature limit of the Grüneisen parameter of iron was determined. The calculation was performed with and without taking into account the volume dependence of the ratio γ/V. Differences with values appearing in recent literature were noted and partially explained. A phase transition occurs in iron between 120 and 133 GPa. Some suggestions for further work were given.

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