The melting curve of gold up to 1500 kbar

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Abstract. The melting temperature $T_m$ of gold has been determined from ambient pressure to 1500 kbar using statistical moment method (SMM) and the Lindemann criterion. The equation of the melting curve obtained is a quadratic polynomial of the melting temperature $T_m$, with coefficients that are explicitly dependent on pressure $P$. Simple number calculation and easily verify. Numerical results for the melting temperature of gold up to 1500 kbar are in good agreement with the experimental data and the theoretical results of other authors.

1. Introduction

So far predictions of high-pressure melting curves of metals are still inadequate due to the differences between experimental measurements as well as theoretical methods. Other than some metals such as copper, its melting curves has been studied quite a lot, the molten studies of gold are few [1-5, 16].

The melting temperature of gold, silver, and copper as a function have been determined to 65 kbar by differential thermal analysis [1] and high-pressure apparatus using a recently developed low-friction cell [2]. Good agreement exits between shock-wave data, ultrasonic data, and static measurement on the relationship between $P$ and $V$ for these metal. On the basis of extrapolation of the linear melting relationship, it is possible to construct a melting curves for these three metals to 200 or more kbar. The melting curves of $Au, Cu, Ag$ and some other metals have been measured up to 120 kbar using a Bridgman-type cell [3]. The reported results suggest that the electric structure of an element might play a key role in determining the pressure dependence of its melting curves. Recently, melting of gold obtained from X-ray diffraction (XRD) measurement up to 1060 kbar [16]. On the theoretical side, melting of the metals under high pressures have been studied by various methods such as: First-principles calculations [6]; ab initio calculations [7,8]; Molecular dynamics simulation [9,16]. Using the Lindemann’s formula of melting and the pressure-dependent Gruneisen parameter, in [4] has obtained the analytical expression of melting of temperature of silver, gold, and copper metals as a function of volume compression. In [19], the melting curves of gold determined using the Lindemann criterion calculated from the atomic mean-square displacements obtained by ab initio simulations.

The statistical moment method (SMM) has also been used in the melting study of metals [5,10]. In [5], the authors obtained the equations of the melting curves of $Au, Cu$ and $Ag$ metals with simple analytic form, but the pressure is only calculated to 40 kbar. In general, the results of the study on melting of materials under high pressure by experimental as well as theory are quite complicated, there are many adjustment parameters and difficult to verify.
In this paper, the melting temperature $T_m$ of gold has been determined from ambient pressure to 1500 kbar using the statistical moment method (SMM) and the Lindemann criterion. The equation of the melting curve obtained is a quadratic polynomial of the melting temperature $T_m$ with coefficients that are explicitly dependent on the pressure $P$. Simple number calculation and easily verify. Numerical results for the melting temperature of gold up to 1500 kbar are in good agreement with the experimental data and the theoretical results of other authors.

2. Theory
2.1. The mean square amplitude of atomic vibrations and the lattice spacing of metals.
Using the SMM, the mean square amplitude of atomic vibrations about their equilibrium position, $<u^2>$, obtained in the form [11,12] (expressions of (1) to (5))

$$<u^2> = \frac{\theta}{k_0} \left[ 1 + \frac{\gamma_0 \theta}{(k_0)^2} + 6 \left( \frac{\gamma_0 \theta}{(k_0)^2} \right)^2 \right]$$  \hspace{1cm} (1)

where $\theta = k_B T$, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature; $k_0$, $\gamma_0$ are pressure dependent coefficients, calculated at temperature 0K, determined by the following expressions:

$$k = \frac{1}{2} \sum_i \left( \frac{\partial^2 \varphi_{0i}}{\partial u_{ix}^2} \right)_{eq} ; \gamma = \frac{1}{12} \sum_i \left[ \left( \frac{\partial^4 \varphi_{0i}}{\partial u_{ix}^4} \right)_{eq} + 6 \left( \frac{\partial^3 \varphi_{0i}}{\partial u_{ix}^3 \partial u_{iy}^2} \right)_{eq} \right]$$  \hspace{1cm} (2)

where $\varphi_{0i}$ is the interaction potential between the two atoms on the 0 and $i$ nodes of the lattice; $u_{ix}$ and $u_{iy}$ are the displacements of the atoms at node $i$ in the directions $x, y$ respectively.

The lattice spacing of metals are calculated according to the formula [11]:

$$a = a_0 + \Delta r$$  \hspace{1cm} (3)

where $a_0$, $\Delta r$ are the lattice spacing at 0K, pressure $P$, and the average displacement of atomic at temperature $T$, pressure $P$, respectively.

The lattice spacing, $a_0$, is determined from the equation of state at 0K, the pressure $P$:

$$\frac{P v_0}{a_0} = \frac{1}{6} \frac{\partial u_0}{\partial a_0} + \frac{\hbar \omega_0}{4 \sqrt{m^* k_0}} \frac{\partial k_0}{\partial a_0}$$  \hspace{1cm} (4)

where $v_0 = \frac{V_0}{N}$ is the volume of unit cell in crystal lattice of metal at the absolute zero temperature and pressure $P$; $m^*$ is the atomic mass; $u_0$ is interaction energy of the atom at the node 0 with other atoms on the lattice nodes of metal; $u = \sum_i \varphi_{0i}(a_i)$.

The average displacement $\Delta r$ of atomic at temperature $T$, pressure $P$:

$$(\Delta r)^2 = \frac{\gamma_0 \theta^2}{k_0^3} \left[ 1 + \frac{73 \gamma_0^2 \theta^2}{18 k_0^4} \right]$$  \hspace{1cm} (5)

The above general results take into account the an-harmonic effects of thermal lattice vibration and high temperature (above room temperature).

2.2. Lindemann’s criterion and the melting curves of gold
On study the melting of materials, Lindemann argued that, melting temperature of a material is attained when the root mean square amplitude of atomic vibration about their equilibrium positions becomes a critical fraction of the nearest neighbor separation. This fraction $\delta_1$ is called the Lindemann parameter. In the approximation of the Einstein model, the melting temperature $T_m$ is given by the Lindemann law is expressed [13,21] (expressions of (6), (7)):
\[ T_m = C_L MV^2 \nu_E^2 \]  \hspace{1cm} (6)

where \( \nu_E \) is the Einstein characteristic frequency, \( V \) is the molar volume, and \( M \) is the atomic mass. \( C_L \) is a constant to be determined empirically. In the approximation of Debye model, the Lindemann parameter \( \delta_L \) at the melting temperature \( T_m \) is given by the relation:

\[ \delta_L^2 = \frac{<-u>^2}{r^2} = \frac{9h^2T_m}{Mk_B r^2 \theta_D^2} \]  \hspace{1cm} (7)

where \( <-u>^2 \) is the mean square amplitude of vibration; \( r \) is the nearest neighbor interatomic distance; \( h \) is the planck constant divided by \( 2\pi \) and \( \theta_D \) the Debye temperature. It has been found that \( \delta_L \) has different values for different classes of solids. However, for a given family of solids \( \delta_L \) is nearly constant.

Calculating the melting temperature \( T_m \) by (6) or (7) is a fairly complex problem, taking into account the an-harmonic effects of thermal lattice vibration. In this paper, using results (1)-(5) and (7), we calculated the equation of the melting curve of the metals in the following general form:

\[ \frac{\theta}{k_0} \left[ 1 + \frac{\gamma_0 \theta}{(k_0)^2} + 6 \left( \frac{\gamma_0 \theta}{(k_0)^2} \right)^2 \right] = \delta_L^2 \left[ a_0 + \sqrt{\frac{\gamma_0 \theta^2}{k_0}} \left[ 1 + \frac{73}{18} \frac{\gamma_0 \theta^2}{k_0^4} \right] \right] \]  \hspace{1cm} (8)

3. Results and discussion

To calculate the \( u_0, k_0, \gamma_0 \), parameters determined by the expression (2), we must know the potential interaction between atoms in the metal. In discussing the thermodynamic of metals and alloys, the Lennar-Jones potential has been very successful [14]. In the view of this, we will use the Lennar-Jones potential of Au:

\[ \varphi(r) = \frac{D}{n - m} \left[ m \left( \frac{r}{r_0} \right)^n - n \left( \frac{r}{r_0} \right)^m \right] \]  \hspace{1cm} (9)

where \( D = \frac{468.4}{k_B}(K); r_0 = 2.8751A^0; n = 10.5; m = 5.5 \)

Using the expressions of the parameters \( k_\alpha, \gamma_\alpha \) calculated for the fcc lattice in [5,20] are based on the derivative formulas given by [15], we have obtained the equation of state at 0K, pressure \( P \) and the equation of the melting curve of Au by the formulas in section 2.

In [5,18], the equation of state at the absolute zero temperature and under pressure \( P \) of Au have the following form:

\[ 0.0213Py^{13.5} - 0.019y^{14.25} + 0.137y^{9.25} + 11.62y^5 - 0.243y^{4.25} - 10.96 = 0 \]  \hspace{1cm} (10)

where \( y = \frac{a_0}{r_0} \), the pressure \( P \), and the lattice parameter \( a_0(P,0), a(P,T) \) are in kbar\((10^8Pa)\), \( A^0(10^{-10}m) \), respectively.

Equation of the melting curve of Au under pressure \( P \), calculated from the general equation (8) is a quadratic polynomial of the melting temperature, \( T_m \), and has explicitly dependent factors on pressure [5]:

\[ 2.82 \times 10^{-4}y^{21}(1 + 0.65y^5)T_m^2 + y^{10.5}T_m - (3346.6 - 1582.2y^5) = 0 \]  \hspace{1cm} (11)

where \( y \) is the solution of equation (10).

However, the melting temperature of gold calculated by (10) and (11) only match experimental data up to 100kbar [5].
Using equations (4) and (10), we obtain another approximate solution of gold with the following polynomial form:

$$y = 0.9905(1 - 5.85 \times 10^{-4} P^{0.755}) + 2.8 \times 10^{-7} P^{1.637}$$  \hspace{1cm} (12)

The results of the calculation of $y$ by equation (10) and expression (12) have differences less than 2% with pressure up to 1500 kbar (150 Gpa), but using expression (12) for the results of calculating the melting temperature of gold is consistent with experiment up to 1000 kbar and especially simple.

The melting temperature of $Au$ is pressure dependent, which is a positive solution of equation (11), having the following simple form:

$$T_m = \frac{-C_2 + \sqrt{C_2^2 - 4C_1C_3}}{2C_1}$$  \hspace{1cm} (13)

where,

$$C_1 = 2.82 \times 10^{-4} y^{21}(1 + 0.65y^5); \ C_2 = y^{10.5}; \ and \ C_3 = -(3346.6 - 1582.2y^5)$$  \hspace{1cm} (14)

The values of the melting temperature at different pressures given in Table 1 are calculated directly from expressions (12) to (14), very simple and do not need the assistance of any computational software. In Table 2, the values of the pressure that we used to calculate $T_m$ in this work match with the values of the pressure to calculate $T_m$ used in the experiment [16] and theory [16], for comparison.

Table 1. The values of melting temperature $T_m$ of $Au$ at pressures to 1500 kbar.

| P(kbar) | Cal.(K) | Exp.[16] | Cal.[16] | P(kbar) | Cal.(K) | Exp.[16] | Cal.[16] |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 30.5    | 1464    | -       | 1300±100| 582     | 3083    | -       | 3300±100 |
| 49      | 1532    | 1523±50 | -       | 633     | 3224    | 3227±75 | -       |
| 122     | 1768    | 1776±75 | -       | 775     | 3554    | 3580±75 | -       |
| 147     | 1844    | -       | 1900±100| 800     | 3673    | -       | 3900±100 |
| 191     | 1975    | 2000±75 | -       | 859     | 3827    | 3705±75 | -       |
| 238     | 2113    | 2121±75 | -       | 1060    | 4331    | 4330±75 | -       |
| 254     | 2159    | -       | 2100±100| 1070    | 4355    | -       | 4671±100 |
| 343     | 2414    | 2426±75 | -       | 1100    | 4426    | -       | -       |
| 347     | 2425    | -       | 2500±100| 1200    | 4655    | -       | -       |
| 426     | 2648    | -       | 2900±100| 1300    | 4871    | -       | -       |
| 460     | 2744    | 2840±75 | -       | 1400    | 5072    | -       | -       |
| 516     | 2900    | 3029±75 | -       | 1500    | 5257    | -       | -       |

Melting temperature of $Au$ at pressure up to 1500 kbar is given in Table 1 and shows in Figure 1. Table 2 and Figure 2 show melting temperature of $Au$ at pressures up to 60 kbar. Experimental values and other theoretical calculations are also shown in the Figures for comparison. With pressures from 0 to 60 kbar, our calculated results fit well with experiment Akella et al. [1], Mirwald et al. [2], and Errandonea [3], and the results calculated by other authors [4,17]. With pressures from 0 to 1070 kbar, our melting curve fit well with the experimental data and values calculated by the ab initio molecular dynamics (AIMD)
Table 2. The values of melting temperature $T_m$ of Au at pressures to 60 kbar.

| $P$(kbar) | 10  | 20  | 30  | 40  | 50  | 60  |
|-----------|-----|-----|-----|-----|-----|-----|
| $T_m$(K)  | 1379| 1423| 1463| 1500| 1535| 1570|

Figure 1. Melting curve of gold up to 1500 kbar determined in this work, the experimental and theoretical points obtained in [16]. Results of [4] (short dash) and [19] (long dash) are also displayed for comparison.

Figure 2. Melting curve of gold up to 60 kbar determined in this work and the experimental points obtained in [1,16]. Results of [4] (short dash) and [19] (long dash) are also displayed for comparison.
simulations within the two phase approach (TPA) published by Weck et al. [16]. Theoretical results calculated by Hieu et al. [4] and Smirnov et al. [19] also fit quite well this experimental curve. However, the results for [4] are lower than the experimental values and calculated by us, while the results of [19] and [16] are higher than the experimental values and calculated by us. In particular, the calculations above are very complex.

With pressures from 1070 to 1500 kbar, our melting curve fit well with the Theoretical results calculated by Hieu et al. [4], Smirnov et al. [19], and Weck et al. [16].

Equation of the melting curve of gold, Eq.(12) is very simple and has no adjustment parameters, but the numerical results for the melting temperature of gold up to 1500 kbar are in good agreement with the experimental data and the theoretical results of other authors. Thus can be used to determine the pressure \( P \) when measuring the melting temperature \( T_m \) of gold. In addition, this conformance is an example of the Lindemann criterion that can be applied well to study melting of metals at high pressure.

4. Conclusion
Using a more precise solution of the equation of state of gold at pressure \( P \) and 0K, we have extended the previous gold’s melting curve equation, with pressure up to 1500 kbar. This equation is a quadratic polynomial of the melting temperature \( T_m \), with coefficients that are explicitly dependent on pressure \( P \). Simple number calculation and easily verify. Numerical results for the melting temperature of gold up to 1500 kbar are in good agreement with the experimental data and the theoretical results of other authors. The results obtained in this paper are new and has not been published, can be used to determine the pressure \( P \) when measuring the melting temperature \( T_m \) of gold. In addition, this conformance is an example of the Lindemann criterion that can be applied well to study melting of metals at high pressure.

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