High temperature and high pressure equation of state of gold

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Abstract. High-temperature and high-pressure equation of state (EOS) of Au has been developed using measured data from shock compression up to 240 GPa, volume thermal expansion between 100 and 1300 K and 0 GPa, and temperature dependence of bulk modulus at 0 GPa from ultrasonic measurements. The lattice thermal pressures at high temperatures have been estimated based on the Mie–Grüneisen–Debye type treatment with the Vinet isothermal EOS. The contribution of electronic thermal pressure at high temperatures, which is relatively insignificant for Au, has also been included here. The optimized EOS parameters are $K_{0\text{T}} = 6.0$ and $q = 1.6$ with fixed $K_{0} = 167$ GPa, $\gamma_0 = 2.97$, and $\Theta_0 = 170$ K from previous investigations. We propose the present EOS to be used as a reliable pressure standard for static experiments up to 3000 K and 300 GPa.

1. Introduction
Au is often used as an internal pressure calibrant for high pressure studies, since it is stable over wide temperature and pressure ranges, chemically inert, reasonably compressible, and gives a simple x-ray diffraction pattern. However, there has been much debate on the temperature-pressure-volume (T-P-V) equation of state (EOS) of Au, even at room temperature. Estimated pressure differences between proposed EOSs [1-5] at 300 K often reach more than 10 %, and the differences increase substantially with increasing temperature. The use of an accurate pressure scale is particularly critical for the study of the properties in the deep Earth. Measured high temperature and high pressure phase boundaries, for example, directly depend on the pressure scale used for estimation.

Here we develop an accurate pressure scale of Au applicable at high temperatures and high pressures, without relying on any pressure scale. We derive the high temperature and pressure EOS using the Mie–Grüneisen–Debye type treatment including the electronic thermal pressure, based on measured data from shock compression, volume thermal expansion, and temperature dependence of bulk modulus. We propose to use the present EOS of gold as a reliable pressure scale applicable to static experiments at high temperatures and high pressures up to 3000 K and 300 GPa.

2. Equation of state analysis
The pressure of a metal at a fixed $V$ is written as a function of $T$ as described previously [6, 7]

$$P(V,T) = P(V, 300 \text{ K}) + P_{\text{TH}}(V,T) + P_{\text{el}}(V,T).$$

In this expression, $P(V, 300 \text{ K})$ is the pressure at 300 K, and $P_{\text{TH}}(V,T)$ and $P_{\text{el}}(V,T)$ are the lattice and the electronic thermal pressures, respectively. Here the thermal pressure is defined as the increase in pressure caused by heating from 300 K to $T$ at constant $V$. $P(V,300 \text{ K})$ is expressed by the Vinet equation, given as

$$P(V,300 \text{ K}) = 3 K_{0\text{T}} (V/V_0)^{2/3}\{1-(V/V_0)^{1/3}\}\exp\{3/2(K_{0\text{T}} - 1)[1-(V/V_0)^{1/3}]\},$$

$K_{0\text{T}} = 6.0$ and $q = 1.6$ with fixed $K_{0} = 167$ GPa, $\gamma_0 = 2.97$, and $\Theta_0 = 170$ K from previous investigations. We propose the present EOS to be used as a reliable pressure standard for static experiments up to 3000 K and 300 GPa.
where \( V_0 \) and \( K_{0T} \) is the volume and the isothermal bulk modulus at 300 K and 0 GPa, and \( K'_{0T} \) is the pressure derivative of \( K_{0T} \). \( P_d(V,T) \) is taken from first-principles electronic structure calculations using density functional theory by Tsuchiya and Kawamura [8], who have reported that \( P_d(V,T) \) is nearly independent of volume and relatively insignificant for Au, with only 0.01 and 0.5 GPa at 1000 K and 5000 K, respectively, and 2.4 GPa even at 8000 K.

\[ P_{TH}(V,T) = \left( \frac{\gamma}{V} \right) [E_{TH}(V,T) - E_{TH}(V,300 \text{ K})] \]  

where \( \gamma \) is the Grüneisen constant and is assumed to be a function of volume only, independent of temperature, and is often approximated [2, 7, 9] as,

\[ \gamma = \gamma_0 (V/V_0)^q \]  

in which \( \gamma_0 \) is the value at \( V_0 \), and \( q \) is a fitting constant. \( E_{TH}(V,T) \) can be calculated using the Debye model,

\[ E_{TH}(V,T) = [9nRT/(\Theta/T)^3] \int_0^{\Theta/T} z^{3}(e^z - 1)dz \]

where \( n = 1 \) for Au, \( R \) is the gas constant, and \( \Theta \) is the Debye temperature, with \( \Theta \) being written as

\[ \Theta = \Theta_0 \exp(\gamma_0/\gamma) \]

(6)

when \( \gamma \) is expressed by equation (4); \( \Theta_0 \) is the Debye temperature at \( T = 300 \text{ K} \) and \( P = 0 \text{ GPa} \). Hence, we can estimate the \( T-P-V \) relation of Au using the five key parameters \( K_{0T}, K'_{0T}, \gamma_0, q, \) and \( \Theta_0 \). Of these \( \Theta_0 \) was fixed at 170 K from previous works [1, 2, 10], \( K_{0T} \) taken at 167 GPa [2, 3, 5] from ultrasonic measurements, and \( \gamma_0 \) fixed at 2.97 from ref. [11] based on the equation \( \gamma_0 = a K_{0S} V/C_P \), where \( a, K_{0S}, \) and \( C_P \) are the volume thermal expansivity, the adiabatic bulk modulus, and the heat capacity at constant pressure at 300 K and 0 GPa, respectively. The remaining two parameters, \( K'_{0T} \) and \( q \), were optimized in this study using shock compression data up to 240 GPa [12, 13] including the recent measurements by ref. [13], measured volume thermal expansion data up to 1300 K and 0 GPa [14, 15], and temperature dependence of the isothermal bulk modulus [11], converted from the measured adiabatic bulk modulus from ultrasonic measurements, at 0 GPa. The isothermal bulk modulus at temperature \( T \) was obtained using the Vinet equation for each isotherm. A more detailed and general description of the analysis is described previously [7].

3. Results and discussion

The optimized EOS parameters are listed in table 1, together with the values obtained by previous works [1–3, 10] for comparison. The \( K'_{0T} \) values by refs. [1, 2] are reestimated here based on the Vinet EOS, using their reported data, for comparison. The difference in \( K'_{0T} \) between refs. [2] and [3] is simply due to the difference in ruby pressure scales used for their measurements, refs. [16] and [3], respectively. Our \( K'_{0T} \) of 6.0 (table 1) agrees with the value by ref. [3], supporting the ruby scale developed by [3]. Both refs. [2] and [10] give much smaller \( q \) values, compared to the present work.

| Parameters          | this study | refs. [3, 10] | ref. [2] | ref. [1] |
|---------------------|------------|---------------|---------|---------|
| \( V_0 / \text{cm}^3 \text{ mol}^{-1} \) | 10.215(Fix) | 10.215        | 10.215  | 10.215  |
| \( K_{0T} / \text{GPa} \) | 167(Fix)   | 167\textsuperscript{a} | 167(3)  | 166.7(5.0) |
| \( K'_{0T} \)        | 6.0        | 6.0\textsuperscript{a} | 5.26\textsuperscript{b} | 5.72\textsuperscript{b} |
| \( \Theta_0 / \text{K} \) | 170(Fix)   | 170           | 170     | 170     |
| \( \gamma_0 \)       | 2.97(Fix)\textsuperscript{c} | 2.97          | 2.97(5) | 2.95(43) |
| \( q \)              | 1.6        | 0.6(3)        | 1.0(1)  | 1.7(7)  |

\textsuperscript{a} From ref. [3]

\textsuperscript{b} The \( K'_{0T} \) values were reestimated here using the Vinet EOS.

We give in figure 1 the calculated Hugoniot of Au based on the present EOS parameters listed in table 1, together with experimental data [12, 13] for comparison. The agreement between the
calculated and measured Hugoniot data is satisfactory over a wide \( P \) range up to 240 GPa. As figure 2 shows, the calculated volume thermal expansion also agrees very well with the observed values \([14, 15]\) up to 1300 K. Figure 3 gives a comparison between the observed and calculated temperature dependence of bulk modulus at 0 GPa. Our calculated \( \frac{dK}{dT} \) again compares well with the measured data based on ultrasonic experiments \([11]\), however, the EOS by \([10]\) results in a smaller \( \frac{dK}{dT} \) slope, due to their use of much smaller \( q \) value of 0.6 (table 1), as previously pointed out by ref. \([17]\).

Hirose et al. \([18]\) have made simultaneous volume measurements of Au and MgO by synchrotron X-ray diffraction combined with laser heated diamond-anvil cell (DAC) experiments, at \( P \) between 10 and 146 GPa and \( T \) from 300 to 2330 K. We reestimated the measured pressures by ref. \([18]\) using their reported cell parameters of both Au and MgO, based on the present Au EOS and the MgO EOS derived by the MD simulation by ref. \([19]\). We find that as table 2 shows, the Au pressures based on the present EOS agree very well with the MgO pressures using the EOS by ref. \([19]\), with the differences less than 2 GPa over wide \( T \) and \( P \) ranges up 2330 K and 122 GPa; the 4.0 GPa difference at 300 K and more than 140 GPa might be partly due to non-hydrostatic pressure effects in their DAC experiments. Since the present Au EOS and the MgO EOS by ref. \([19]\) were obtained using completely different techniques and without relying any pressure scale, the excellent consistency between the Au and MgO pressures over wide \( T \) and \( P \) ranges listed in table 2 gives us much credibility in the two pressure scales at high temperatures and high pressures.

Table 3 gives the \( T-P-V \) EOS of Au at \( T \) up to 3000 K, and \( P \) up to near 260 GPa, estimated by the present analysis. As our 300 K EOS parameters, \( K_0T \) and \( K'_0T \), agree with the data by \([3]\) as shown in
Table 1, the pressures at 300 K, given in Table 3, are the same as those by ref. [3].

Table 2. Observed unit cell parameters of MgO and Au at high pressures, using the data by ref. [18].

| $T$ (K) | $a$(MgO) (Å) | $P$(MgO) (GPa) | $a$(Au) (Å) | $P$(Au) (GPa) | $P$(MgO) − $P$(Au) (GPa) |
|---------|---------------|----------------|---------------|----------------|-----------------------------|
| 300     | 4.12964(58)   | 10.71          | 4.00755(46)   | 10.31          | 0.40                        |
| 300     | 4.05996(47)   | 22.17          | 3.94795(44)   | 21.79          | 0.38                        |
| 300     | 3.98991(45)   | 36.37          | 3.88790(43)   | 36.62          | -0.25                       |
| 300     | 3.89763(43)   | 60.05          | 3.81218(42)   | 61.16          | -1.11                       |
| 300     | 3.89589(43)   | 60.56          | 3.81201(42)   | 61.22          | -0.66                       |
| 300     | 3.81984(42)   | 85.42          | 3.75389(40)   | 85.57          | -0.15                       |
| 300     | 3.76549(41)   | 106.67         | 3.70978(40)   | 107.92         | -1.25                       |
| 300     | 3.73469(40)   | 120.20         | 3.68509(39)   | 122.11         | -1.91                       |
| 300     | 3.69014(39)   | 141.85         | 3.64819(39)   | 145.85         | -4.00                       |
| 1600    | 3.86714(21)   | 76.9           | 3.7930(20)    | 76.8           | 0.1                         |
| 1610    | 3.86779(21)   | 76.7           | 3.7946(9)     | 76.3           | 0.4                         |
| 1720    | 3.86820(18)   | 77.4           | 3.7951(11)    | 76.8           | 0.6                         |
| 1960    | 3.86944(10)   | 78.6           | 3.7957(11)    | 78.1           | 0.5                         |
| 1340    | 3.7827        | 105.2          | 3.7237        | 106.8          | -1.6                        |
| 2330    | 3.7767        | 114.0          | 3.7254        | 112.1          | 1.9                         |
| 1780    | 3.7727        | 112.1          | 3.7182        | 112.4          | -0.3                        |
| 1800    | 3.7713        | 112.8          | 3.7168        | 113.3          | -0.5                        |
| 1960    | 3.7723        | 113.5          | 3.7186        | 113.3          | 0.2                         |
| 1970    | 3.7743        | 112.7          | 3.7207        | 112.3          | 0.4                         |
| 2070    | 3.7692        | 115.4          | 3.7152        | 115.8          | -0.4                        |
| 2080    | 3.7683        | 115.8          | 3.7158        | 115.5          | 0.3                         |

*a* Estimated based on the MgO pressure scale by ref. [19].

*b* Estimated based on the Au pressure scale obtained in this study.

Table 3. Pressures (GPa) of Au at different volumes and temperatures.

| $V/V₀$ | $T$ = 300 K | 500 K | 1000 K | 2000 K | 3000 K |
|--------|------------|-------|--------|--------|--------|
| 1.00   | 0.0        | 1.44  | 5.06   | 12.35  | 19.67  |
| 0.95   | 9.98       | 11.37 | 14.88  | 21.95  | 29.05  |
| 0.90   | 24.03      | 25.37 | 28.76  | 35.60  | 42.48  |
| 0.85   | 43.72      | 45.01 | 48.29  | 54.89  | 61.54  |
| 0.80   | 71.34      | 72.57 | 75.73  | 82.10  | 88.51  |
| 0.75   | 110.18     | 111.36| 114.38 | 120.51 | 126.68 |
| 0.70   | 165.13     | 166.24| 169.14 | 175.01 | 180.93 |
| 0.65   | 243.54     | 244.60| 247.36 | 252.97 | 258.64 |

Figure 4 compares the present EOS with the other EOSs by refs. [2, 4, 10, 11, 18, 20] at temperatures of 1000, 2000, and 3000 K, and pressures up to 180 GPa. As shown in figure 4, the EOS by ref. [4] agrees very well with our EOS, with the differences between the two being less than 0.6 GPa over wide $T$ and $P$ ranges up to 3000 K and 180 GPa. The EOS by ref. [4] was constructed semiempirically to reproduce available $T$-$P$-$V$ data as well as thermodynamic data using more than 20 EOS parameters. The EOS by ref. [20] also compares well with our EOS, with the maximum difference between the two being 2.2 GPa in the $T$, $P$ ranges shown in figure 4. The EOS by either ref.
[2] or ref. [11] increasingly underestimates pressure with increasing $P$ compared with the present EOS at all temperatures. The EOS by ref. [18] gives higher pressures than the others at high temperature and high pressures, as shown in figure 4.

Figure 4. Pressure differences, $P - P_{\text{present}}$, between the present EOS of Au and the EOSs by DO (refs. [4]), T (ref. [20]), SDK (ref. [2]), AIY (ref. [11]), F (ref. [10]), and H (ref. [18]). Note the data by T and F at 1000 K and the data by DO and T at 3000 K both nearly overlap on the figure. Dotted lines show $P - P_{\text{present}} = 0$.

References
[1] Heinz D L, and Jeanloz R 1984 J. Appl. Phys. 55 885
[2] Shim S-H, Duffy T S, and Takemura K 2002 Earth Planet. Sci. Lett. 203 729
[3] Dewaele A, Loubeyre P, and Mezouar M 2004 Phys. Rev. B 70, 094112
[4] Dorogokupets P I, and Oganov A R 2007 Phys. Rev. B 75, 024115
[5] Takemura K, and Dewaele A 2008 Phys. Rev. B 78 104119
[6] Holmes N C, Moriarty J A, Gathers G R, and Nellis W J 1989 J. Appl. Phys. 66 2962
[7] Matsui M, Ito E, Katsura T, Yamazaki D, Yoshino T, Yokoyama A, and Funakoshi K 2009 J. Appl. Phys. 105 013505
[8] Tsuchiya T, and Kawamura K 2002 Phys. Rev. B 66, 094115
[9] Brown J M 1999 J. Appl. Phys. 86, 5801
[10] Fei Y, Ricolleau A, Frank M, Mibe K, Shen G, and Prakapenka V 2007 Proc. Natl. Acad. Sci. U.S.A. 104 9182
[11] Anderson O L, Isaak D G, and Yamamoto S 1989 J. Appl. Phys. 65 1534
[12] Marsh S P 1980 LASL Shock Hugoniot Data, University of California Press, Berkley, California
[13] Yokoo M, Kawai N, Nakamura K G, and Kondo K 2008 Appl. Phys. Lett. 92 051901
[14] Nix F C, and MacNair D 1941 Phys Rev. 60 597
[15] Suh I-K, Ohta H, and Waseda Y 1988 J. Mater. Sci. 23 757
[16] Mao H K, Xu J, and Bell P M 1986 J. Geophys. Res. 91, 4673
[17] Dorogokupets P I, and Dewaele A 2007 High Pressure Res. 27 431
[18] Hirose K, Sata N, Komabayashi T, and Ohishi Y 2008 Phys. Earth Planet. Inter. 167 149
[19] Matsui M, Parker S C, and Leslie M 2000 Am. Mineral. 85, 312
[20] Tsuchiya T 2003 J. Geophys. Res. 108 doi:10.1029/2003JB002446