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Equation of State for Gold*

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Abstract: A modified calculative formula for the thermal pressure is proposed and the equation of state (EOS) is obtained accordingly for gold. We compared this EOS with the other two common EOS using the experimental data for gold. The results show that the new EOS is better than the other two EOS at high temperature.

Key words: equations of state; gold; the thermal pressure; Grüneisen parameter

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1 Introduction

The equation of state (EOS) of solids can be expressed generally as

$$p(V,T)=p(V,T_0)+p_{\rm th}(V,T) \tag{1}$$

where T_0 is the reference temperature; the first term $p(V,T_0)$ on the right-hand side is the pressure for isothermal compression and is expressed by a suitable isothermal EOS, such as the Birch-Murnaghan EOS[1-2], the Vinet EOS etc.[2-3]; the second term $p_{\rm th}(V,T)$ on the right represents the thermal pressure produced from T_0 to T. It has been found that the thermal pressure is linear in T for many solids above the Debye temperature. It is commonly written as

$$p_{\rm th}(V,T)=\alpha B_T(T-T_0) \tag{2}$$

where α and B_T are the thermal expansion coefficient and the isothermal bulk modulus respectively. It is a good assumption for many solids that the product (αB_T) is constant with various volumes, i. e. $\alpha B_T=\alpha_0 B_0$. Then substituting Eq. (2) into Eq. (1), we get the following p-V-T relation in solids

$$p(V,T)=p(V,T_0)+\alpha_0 B_0(T-T_0) \tag{3}$$

where α_0 and B_0 are the values of α and B_T at temperature T_0 respectively. The applications of Eq. (3) have been reported frequently in the literature [2-4]. However, in case of gold, Anderson et al. pointed out that the thermal pressure should be depended on volume compression. It means that the product (αB_T) may not be a constant, so they modified Eq. (2) as[1]

$$p_{\rm th}=\left[\alpha_0 B_0+\left(\frac{\partial B_T}{\partial T}\right)_V\ln\frac{V_0}{V}\right](T-T_0) \tag{4}$$

where V is the volume at zero pressure and temperature T_0. Substituting Eq. (4) into Eq. (1), Anderson et al. derived the following EOS for gold

$$p(V,T)=p(V,T_0)+\left[\alpha_0 B_0+\left(\frac{\partial B_T}{\partial T}\right)_V\ln\frac{V_0}{V}\right](T-T_0) \tag{5}$$

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Using Eq. (5), Anderson et al. calculated the pressures at different compressions and temperatures for gold. However, the results calculated by Eq. (5) show that the theoretical values of pressure are less than the corresponding experimental data reported by Heinz and Jeanloz[5]. Therefore the above modification is not satisfactory. We try to modify the thermal pressure term in this paper to find a better EOS for gold.

2 Method of Analysis

Grüneisen parameter is one of the important physics quanta that characterizes the vibration of crystal lattice. More recently, Cui and Chen got an expression for Grüneisen parameter γ in the following form[6]

$$\frac{\gamma}{\gamma_0}=\left(\frac{V_0}{V}\right)^{B'_0}\exp\left[(\delta_0+1)\left(\frac{V}{V_0}-1\right)\right] \tag{6}$$

where γ_0 and B'_0 are, respectively γ determined and the first pressure derivation of B_T at zero pressure and T_0, δ_0 is Anderson-Grüneisen parameter δ_T at zero pressure and T_0.

According to the famous Grüneisen relation, γ can be written as[7]

$$\gamma=\frac{\alpha B_T V}{C_V} \tag{7}$$

where C_V is the heat capacity at constant volume, which may be regarded as to be stable at high temperature. Eqs. (6) and (7) yield the following expression for the product (αB_T)

$$\alpha B_T=\alpha_0 B_0\left(\frac{V_0}{V}\right)^{B'_0+1}\exp\left[(\delta_0+1)\left(\frac{V}{V_0}-1\right)\right] \tag{8}$$

Taking Eq. (8) into account, another expression for the thermal pressure can be obtained from Eq. (2)

$$p_{\mathrm{th}}=\alpha_0 B_0\left(\frac{V_0}{V}\right)^{B'_0+1}\exp\left[(\delta_0+1)\left(\frac{V}{V_0}-1\right)\right](T-T_0) \tag{9}$$

Substituting Eq. (9) into Eq. (1), we get an EOS for the p-V-T relation for gold as follows

$$p(V,T)=p(V,T_0)+\alpha_0 B_0\left(\frac{V_0}{V}\right)^{B'_0+1}\exp\left[(\delta_0+1)\left(\frac{V}{V_0}-1\right)\right](T-T_0) \tag{10}$$

3 Discussion

For the convenience of comparison, we use the Birch-Murnaghan EOS to evaluate the first term $p(V,T_0)$ appeared in Eqs. (3), (5) and (10), as has been done by Anderson et al. The Birch-Murnaghan EOS can be expressed in the following form

$$p(V,T_0)=\frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3}-\left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1-\frac{3}{4}(4-B'_0)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\} \tag{11}$$

The necessary input parameters for the calculation are: $\alpha_0=42.78\times10^{-6}\ \mathrm{K}^{-1}$, $B_0=166.65$ GPa, $B'_0=5.4823$, and $\delta_0=8.061$ which values are all taken from Ref. [1]. Here the reference temperature T_0 is fixed at 300 K. The results of pressure calculated from Eqs. (3), (5) and (10) against the compressions for gold are listed in Table 1 at different temperatures along with the corresponding experimental data. We have also calculated the average relative deviations between p_{cal} and p_{exp} at different temperatures in Table 2. From Table 2, we can see that the average relative deviations between p_{cal} and p_{exp} in Eq. (10) is the smallest comparing with Eqs. (3) and (5).

Table 1 Values of pressure in gold (in GPa) at different compression and temperature. The pressure values (in GPa) listed in the first line are given by this work with Eq. (10), the second are the experimental data[5], the third obtained by Eq. (3), and the fourth reported by Anderson et al. who used Eq. (5)

T/(K)	V/V_0																
	0.98	0.96	0.94	0.92	0.90	0.88	0.86	0.84	0.82	0.80	0.78	0.76	0.74	0.72	0.70	0.68	0.66
500	4.94	8.95	13.53	18.75	24.70	31.48	39.22	48.06	58.17	69.74	82.99	98.21	115.71	135.87	159.16	186.12	217.42
	4.96	8.99	13.58	18.80	24.75	31.54	39.27	48.10	58.19	69.74	82.79	98.16	115.62	135.75	158.99	185.90	217.14
	4.99	9.04	13.65	18.89	24.87	31.67	39.42	48.28	58.40	69.97	83.22	98.43	115.92	136.07	159.33	186.27	217.53
	4.94	8.94	13.50	18.70	24.62	31.37	39.08	47.88	57.93	69.44	82.64	97.79	115.21	135.29	158.49	185.32	216.54
1 000	8.40	12.32	16.81	21.96	27.85	34.58	42.29	51.10	61.19	72.76	86.02	101.26	118.79	139.01	162.37	189.41	220.82
	8.50	12.48	17.01	22.18	28.08	34.81	42.49	51.27	61.31	72.80	85.97	101.11	118.52	138.59	161.77	188.63	219.81
	8.56	12.61	17.22	22.46	28.44	35.24	43.00	51.85	61.97	73.54	86.79	102.00	119.49	139.64	162.99	189.84	221.10
	8.39	12.28	16.72	21.79	27.59	34.21	41.78	50.44	60.36	71.73	84.78	99.78	117.05	136.97	160.00	186.70	217.72
1 500	11.86	15.68	20.09	25.17	31.00	37.69	45.35	54.14	64.22	75.78	89.05	104.31	121.88	142.15	165.57	192.71	224.22
	12.05	15.98	20.46	25.58	31.42	38.10	45.73	54.45	64.43	75.87	88.99	104.07	121.43	141.44	164.57	191.37	222.49
	12.13	16.18	20.79	26.03	32.01	38.81	46.57	55.42	65.54	77.11	90.36	105.57	123.06	143.21	166.47	193.41	224.67
	11.85	15.61	19.93	24.88	30.55	37.04	44.48	53.01	62.79	74.02	86.92	101.77	118.89	138.65	161.52	188.05	218.90
2 000	15.32	19.05	23.38	28.38	34.15	40.79	48.42	57.18	67.24	78.80	92.08	107.36	124.97	145.28	168.78	196.00	227.62
	15.60	19.47	23.90	28.97	34.77	41.39	48.97	57.63	67.56	78.95	92.02	107.04	124.34	144.50	167.37	194.11	225.18
	15.70	19.75	24.36	29.60	35.58	42.38	50.14	58.99	69.11	80.68	93.93	109.14	126.63	146.78	170.04	196.98	228.24
	15.30	18.95	23.15	27.97	33.51	39.88	47.19	55.58	65.22	76.30	89.06	103.76	120.72	140.33	163.04	189.40	220.08
2 500	18.78	22.41	26.66	31.59	37.30	43.89	51.48	60.22	70.27	81.82	95.11	110.41	128.05	148.42	171.98	199.29	231.02
	19.15	22.97	27.35	32.37	38.11	44.68	52.20	60.82	70.70	82.03	95.04	110.01	127.25	147.16	170.17	196.86	227.87
	19.27	23.32	27.93	33.17	39.15	45.95	53.71	62.56	72.68	84.25	97.50	112.71	130.20	150.35	173.61	200.55	231.81
	18.76	22.28	26.36	31.06	36.48	42.71	49.89	58.15	67.65	78.59	91.20	105.57	122.56	142.01	164.56	190.76	221.26
3 000	22.23	25.78	29.94	34.80	40.45	47.00	54.55	63.26	73.29	84.84	98.14	113.46	131.14	151.56	175.19	202.58	234.42
	22.70	26.47	30.80	35.76	41.45	47.97	55.44	64.01	73.83	85.11	98.07	112.98	130.17	150.02	172.98	199.61	230.56
	22.84	26.89	31.50	36.74	42.72	49.52	57.28	66.13	76.25	87.82	101.07	116.28	133.77	153.92	177.18	204.12	235.38
	22.21	25.62	29.57	34.15	39.44	45.55	52.59	60.71	70.08	80.88	93.34	107.75	124.40	143.70	166.08	192.11	222.44

Table 2　The average relative deviations between p_{cal} and p_{exp} in Eqs. (3), (5) and (10) at different temperatures

Equation	Average relative deviations (%)					
	500 K	1 000 K	1 500 K	2 000 K	2 500 K	3 000 K
(3)	0.36	0.97	1.46	1.88	2.28	2.63
(5)	0.43	1.45	2.30	3.05	3.72	4.32
(10)	0.16	0.54	0.84	1.08	1.30	1.48

From Table 1, we can see that the difference among the three equations (Eqs. (3), (5) and (10)) is very small; the values of pressure from all of the three equations are in good agreement with the corresponding experimental data from temperature 500～1 500 K. However, the calculations of Eq. (5) modified by Anderson et al. are systematically less than the corresponding data while the Eq. (3) overestimated the pressure values with increasing temperature and decreasing compression. It is shown that the agreement between the calculated results given by our Eq. (10) and the experimental data is very good till the temperature up to 3 000 K, only at $V/V_0<0.7$ our results are just a little bigger than the data reported by Heinz and Jeanloz. In order to clearly show the difference in the results obtained with these equations, we have plotted the pressure p (given by Eqs. (3), (5) and (10)) versus compression V/V_0 curves for gold at temperature 3 000 K along with the corresponding experimental data (see Fig. 1). So, as far as the gold is considered Eq. (10) is slightly better than Eq. (3) and Eq. (5).

It should be pointed out here that we haven't considered the electronic contribution to the thermal pressure in this paper, since it is small under low temperature condition discussed here. As is well known in metal, the contribution of the electronic degree of freedom to the thermal pressure becomes important with increasing temperature. However, as for gold is considered, till the temperature up to 3 000 K the electronic thermal pressure is only 0.12 GPa and its pressure dependency is quite small too[8-9]. So the electronic thermal pressure can be rationally neglected here.

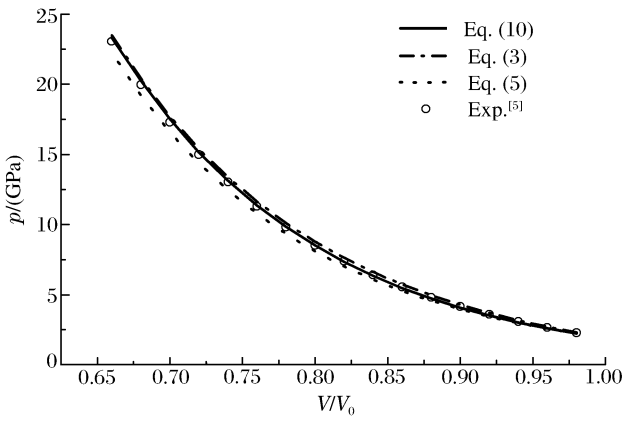


Fig. 1　The curves of p against V/V_0 for Au at $T=3\,000$ K

In brief, we have proposed a straightforward analysis of thermal pressures for gold whose experimental data are available in the case of high temperatures-high pressures. The predicted values are in good agreement with the experiment. Because the basis of Eq. (10), i. e., Eq. (6), is restricted[6], whether Eq. (10) can be applied to more pressure ranges and more classes solids need further investigation, which will be discussed in our future paper. As for as the case of very high pressures so much as $V\to 0$ is concerned, it is beyond of the field of our study and the theory of Thomas-Fermi can deal well with it[10].

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贵金属金的状态方程

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摘要: 提出了一个热压强的计算公式, 从而获得金的状态方程。并结合实验数据与文献中常用的其它两个状态方程进行了比较。结果发现, 修正后的状态方程与实验数据吻合很好, 略优于其它两个状态方程。

关键词: 状态方程; 金; 热压; Grüneisen 参数

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