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Thermal expansion of metals Cu, Au and Ag at higher temperature and under pressure.

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Abstract. The thermodynamic properties of metals are studied using the moment method in the statistical dynamics, which allows us to take into account the anharmonicity of thermal lattice vibrations, going beyond the quasi-harmonic approximation. Within the fourth-order moment approximation, the free energy, equation of state and thermal expansion of the metals with fcc structure are given explicitly in terms of the effective pair potentials and the second- and fourth-order vibrational coefficients. Applying to Cu, Au and Ag metals, we calculate these properties at higher temperature and under pressure in simple analytic form. Numerical results for the lattice spacing, linear thermal expansion coefficient, pressure-volume dependence of these metals in different temperatures and pressures agree with the experiments and got better calculations than other authors.

1. Introduction

The *ab* initio density functional theory have enabled us to get detailed information on the ground state properties of material [1, 2]. However, it is still difficult to calculate properties if materials at high temperature and high pressures require the allowance for an-harmonic effects which are very essential in these regions. The simplest way to use the QH Debye-Gruneisen theory [3]. However, the results obtained in such a way are not always satisfactory. It is noted that the Debye form of harmonic approximation is rather crude theory. The applicability of the QH method to study of particular metals is often restricted by the isotropic Debye mode and the asumption of the mean sound velocity v [4]. Calculate lattice spacing and thermal expansion coefficient of some metals in the form of polynomials of temperature has also been done on the basic of experimental results [15,16], however, only at zero pressure. In this article, we go beyond the quasi-harmonic approximation of the lattice vibrations by using the moment method in statistical dynamics to derive the Helmholtz free energy of metals. The temperature dependence of the lattice spacing and the linear thermal expansion coefficient are calculated by minimizing the free energy with respect to the volume of the system. Due to their simplicity, pair potentials are often used for genetic studies of trends among a given class of metallic materials. Within the fourth-order moment approximation, the free energy, equation of state and thermal expansion of the metal with fcc structure are given explicitly in term of the effective pair potentials and the second- and fourth-order vibrational coefficients. Applying to Cu, Au, and Ag metals, we calculate the equation of state and the thermodynamic quantities at higher temperature and under pressure for these metals. Numerical results for the lattice spacing, linear thermal expansion coefficient, pressure-volume dependence of these metals in different temperatures and pressures agree with experiments and got better calculations than other authors [8, 13, 17].

2. Theory

We use the moment method in the statistical dynamics, calculated the displacement in the case of no external force, the Helmholtz free energy, and thermodynamic quantities of metal system [5, 6].

The atomic displacement in the limit of zero of supplemental force:

$$(\Delta r)^2 = \frac{[-C_2 + \sqrt{C_2^2 - 4C_1C_3}]}{2C_1} \tag{1}$$

where

$$C_1 = 3\gamma, \quad C_2 = 3k\left[1 + \frac{\gamma\theta^2}{k^2}(X+1)\right], \quad C_3 = -\frac{2\gamma\theta^2}{k^2}\left(1 + \frac{X}{2}\right) \tag{2}$$

with:

$X = xcothx, x = \frac{\hbar\omega}{2\theta}; k, \gamma$ are the sum of the second- and fourth-order derivatives of the effective pair potential φ_{0i} and defined by the following formulas:

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

The lattice spacing of metal is counted from the formula

$$a = a_0 + \Delta r, \tag{4}$$

where a_0 is the lattice spacing of metal at the absolute zero temperature and pressure P.

The Helmholtz free energy of the metal in the following form:

$$\psi = U_0 + \psi_0 + \psi_1 \tag{5}$$

where ψ_0 denotes the free energy in the harmonic approximation and ψ_1 the an-harmonicity contribution to the free energy,

$$\psi_0 = 3N\theta\left[x + ln\left(1 - e^{-2x}\right)\right] \tag{6}$$

$$\psi_1 = 3N\frac{\theta^2}{k^2}\left[\gamma_2 X^2 - \frac{2}{3}\gamma_1\left(1 + \frac{X}{2}\right)\right] + 6N\frac{\theta}{k^4}\left[\frac{4}{3}\gamma_2^2 X\left(1 + \frac{X}{2}\right) - 2\gamma_1(\gamma_1 + 2\gamma_2)\left(1 + \frac{X}{2}\right)(1 + X)\right] \tag{7}$$

with

$$\gamma_1 = \frac{1}{48}\sum_i \left(\frac{\partial^4\varphi_{0i}}{\partial u_{ix}^4}\right)_{eq}, \gamma_2 = \frac{1}{8}\sum_i \left(\frac{\partial^4\varphi_{0i}}{\partial u_{ix}^2\partial u_{iy}^2}\right)_{eq} \tag{8}$$

The equation of state for metals is derived from the thermodynamic relation

$$P = -\left(\frac{\partial\psi}{\partial V}\right)_T = -\frac{a}{3V}\left(\frac{\partial\psi}{\partial a}\right)_T \tag{9}$$

At the absolute zero temperature and pressure P, the equation of state for metal in the following form

$$-\frac{Pv_0}{a_0} = \frac{1}{6}\frac{\partial u_0}{\partial a_0} + \frac{\hbar\omega_0}{4\sqrt{m^* k_0}}\frac{\partial k_0}{\partial a_0}, \tag{10}$$

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.

The linear thermal expansion coefficient of metal is determined by

$$\alpha_T = \frac{1}{a_0}\left(\frac{\partial a}{\partial_T}\right)_P = \frac{1}{a_0}\left(\frac{\partial(\Delta r)}{\partial T}\right)_P \tag{11}$$

3. Results and Discussion

By using the moment method in statistical dynamics, we calculate the equation of state, lattice spacing, linear thermal expansion coefficient of metals Cu, Au and Ag with fcc structure. In discussing the thermodynamic properties of metals and alloys, the Lennar-Jones potential has been very successful [7, 8]. In the view of this, we will use the Lennar-Jones potentials for all three Cu, Au and Ag metals. The parameters of Lennar-Jones potentials that used in the current calculations are presented in Table 1.

Table 1. Lennard-Jones potential parameters D and r_0 of Cu, Au and Ag [9]

$Metals$	n	m	$r_0(A^0)$	$\frac{D}{k_B(K)}$
Cu	9	5.5	2.5487	3401.1
Au	10.5	5.5	2.8751	4683.0
Ag	9.5	5.5	2.8760	3325.6

Using the derivatives of the interatomic potentials [10] and the vibrational parameters $k, \gamma_1, \gamma_2, \gamma$, one can determine the equation of state at the absolute zero temperature under pressure P and lattice spacing, linear thermal expansion coefficient of the metals at higher temperature and under pressure in polynomial form.

In equations and expressions from (12) to (17), $y = y(P,0) \equiv a_0(P,0)$; the pressure P, lattice spacing $a(P,T)$, and temperature T are measured in unit of $kbar(10^8 Pa), A^0(10^{-10}m)$, and K, respectively.

3.1. Copper

The equation of state at the absolute zero temperature and under pressure P of the metal Cu have the following form:

$$5.124.10^{-6}Py^{12} - 0.97.10^{-4}y^{10.5} + 0.016y^7 + 16.94.y^{3.5} - 446.21 = 0 \tag{12}$$

The lattice spacing of the metal Cu at the temperature T under pressure P have the following form:

$$a(P,T) = y(P,0)\{1 + 2.266.10^{-9}TQ(P)[1 + 0.575.10^{-14}T^2R(P)]\}, \tag{13}$$

with

$Q(P) = y^9 + 0.026y^{12.5}; \quad R(P) = y^{18} + 0.06y^{21.5} - 2.04.10^{-3}y^{25}$

where $y(P,0)$ is the solution of the equation (12), dependence on the pressure P.

The calculated lattice spacing and linear thermal expansion coefficient of the metal Cu at different pressures as the polynomial functions of the temperature T are presented in Table 2.

Table 2. The lattice spacing and linear thermal expansion coefficient of metal Cu as the polynomial functions of the temperature T at different pressures.

$P(kbar)$	$y(P,0)(A^0)$	$a(P,T)(A^0)$	$\alpha_T(P,T).10^5(K^{-1})$
0	2.5299	$2.5299(1+1.606.10^{-5}T+1.983.10^{-12}T^3)$	$1.606(1+3.705.10^{-7}T^2)$
10	2.5244	$2.5244(1+1.570.10^{-5}T+1.878.10^{-12}T^3)$	$1.570(1+3.588.10^{-7}T^2)$
20	2.5191	$2.5191(1+1.536.10^{-5}T+1.785.10^{-12}T^3)$	$1.536(1+3.486.10^{-7}T^2)$
30	2.5141	$2.5141(1+1.505.10^{-5}T+1.696.10^{-12}T^3)$	$1.505(1+3.381.10^{-7}T^2)$

The calculate lattice spacing and linear thermal expansion coefficient of the metal Cu at pressure $P=0$ are presented in Table 3 and shown in Fig. 1.

Table 3. The calculated lattice spacing and linear thermal expansion coefficient of the metal Cu at pressure $P=0$.

$T(K)$	300	400	500	600	700	800	900	1000
$a(A^0)$	2.5421	2.5464	2.5508	2.5553	2.5600	2.5649	2.5700	2.5755
$exp.$[12]	2.5510							
$cal.$[8, 13]	2.5358		2.5462		2.5574	2.5633	2.5696	2.5761
$\alpha_T.10^5(K^{-1})$	1.66	1.70	1.76	1.82	1.9	1.99	2.09	2.20
$exp.$[11]	1.68	1.77	1.83	1.89	1.94	2.0		2.15
$exp.$[14]	1.67	1.73	1.79	1.86	1.94	2.01	2.09	2.18

Fractional change of volume $\frac{\Delta V}{V_0}=\frac{V(0,T)-V(P,T)}{V(0,T)}=1-\left[\frac{a(P,T)}{a(0,T)}\right]^3$ at 300K of metal Cu are presented in Table 4 and show in Fig. 3.

Table 4. Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Cu.

$P(kbar)$	5	10	15	20	25	30
$Cal.$	0.0035	0.0069	0.0102	0.0134	0.0165	0.0196
$Exp.$[11]	0.0035	0.0070	0.0104	0.0137	0.0169	0.0201
$Cal.$[8, 13]	0.0027	0.0054	0.0080	0.0105	0.0131	0.0156

3.2. Gold

The equation of state at the absolute zero temperature and under pressure P of the metal Au have the following form:

$$4.355.10^{-6}Py^{13.5}-3.1.10^{-6}y^{14.25}+4.74.10^{-3}y^{9.25}+37.21y^5-1.79y^{4.25}-7142.4=0 \quad (14)$$

The lattice spacing of the metal Au at the temperature T under pressure P have the following form:

$$a(P,T) = y(P,0)\{1 + 1.352.10^{-10}TQ(P)[1 + 0.127.10^{-16}T^2R(P)]\}, \tag{15}$$

with

$$Q(P) = y^{10.5} + 0.003y^{15.5}; \quad R(P) = y^{21} + 0.0075y^{26} - 2.1.10^{-5}y^{31}$$

where $y(P,0)$ is the solution of the equation (14), dependence on the pressure P.

The calculated lattice spacing and linear thermal expansion coefficient of metal Au at different pressures as the polynomial functions of the temperature T are presented in Table 5.

Table 5. The lattice spacing and linear expansion coefficient of metal Au as the polynomial functions of the temperature T at different pressures.

$P(kbar)$	$y(P,0)(A^0)$	$a(P,T)(A^0)$	$\alpha_T(P,T).10^5(K^{-1})$
0	2.8710	$2.8710(1 + 1.382.10^{-5}T + 1.213.10^{-12}T^3)$	$1.382(1 + 2.634.10^{-7}T^2)$
10	2.8659	$2.8659(1 + 1.352.10^{-5}T + 1.144.10^{-12}T^3)$	$1.352(1 + 2.538.10^{-7}T^2)$
20	2.8609	$2.8609(1 + 1.322.10^{-5}T + 1.080.10^{-12}T^3)$	$1.322(1 + 2.451.10^{-7}T^2)$
30	2.8561	$2.8561(1 + 1.295.10^{-5}T + 1.022.10^{-12}T^3))$	$1.295(1 + 2.367.10^{-7}T^2)$

The calculated lattice spacing and linear thermal expansion coefficient of the metal Au at pressure $P = 0$ are presented in Table 6 and shown in Fig. 1.

Table 6. The calculated lattice spacing and linear thermal expansion coefficient of the metal Au at pressure $P = 0$

$T(K)$	300	400	500	600	700	800	900	1000
$a(A^0)$	2.8830	2.8871	2.8913	2.8956	2.900	2.9045	2.9092	2.9142
$exp.$[12]	2.8838							
$cal.$[8, 13]	2.8454		2.8550		2.8651	2.8703	2.8757	2.8812
$\alpha_T.10^5(K^{-1})$	1.41	1.44	1.47	1.51	1.56	1.62	1.68	1.75
$exp.$[11]	1.41	1.45	1.5	1.54	1.59	1.65		1.79
$exp.$[14]	1.41	1.45	1.5	1.55	1.60	1.65	1.71	1.77
$Cal.$[8, 13]	1.48	1.53	1.58	1.64	1.70	1.76		1.90

Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Au are presented in Table 7 and show in Fig. 4.

3.3. Silver

The equation of state at the absolute zero temperature and under pressure P of the metal Ag have the following form:

$$4.714.10^{-6}Py^{12.5} - 0.41.10^{-5}y^{11.75} + 1.9.10^{-3}y^{7.75} + 29.95y^4 - 0.212y^{3.75} - 2020.3 = 0 \tag{16}$$

Table 7. Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Au.

$P(kbar)$	5	10	15	20	25	30
$Cal.$	0.0028	0.0056	0.0084	0.0110	0.0137	0.0162
$Exp.$[11]	0.0028	0.0056	0.0083	0.0110	0.0137	0.0162
$Cal.$[8, 13]	0.0029	0.0057	0.0086	0.0113	0.0140	0.0167

The lattice spacing of the metal Ag at the temperature T under pressure P have the following form:

$$a(P,T) = y(P,0)\{1 + 0.496.10^{-9}TQ(P)[1 + 1.957.10^{-16}T^2R(P)]\} \tag{17}$$

with

$$Q(P) = y^{9.5} + 9.6.10^{-3}y^{13.5}; \quad R(P) = y^{19} + 0.023y^{23} - 2.5.10^{-4}y^{27}$$

where $y(P,0)$ is the solution of the equation (16), dependence on the pressure P.

The calculated lattice spacing and linear thermal expansion coefficient of the metal Ag at different pressures as the polynomial functions of the temperature T are presented in Table 8.

Table 8. The lattice spacing and linear expansion coefficient of metal Ag as the polynomial functions of the temperature T at different pressures.

$P(kbar)$	$y(P,0)(A^0)$	$a(P,T)(A^0)$	$\alpha_T(P,T).10^5(K^{-1})$
0	2.8674	$2.8674(1 + 1.815.10^{-5}T + 2.468.10^{-12}T^3)$	$1.815(1 + 4.080.10^{-7}T^2)$
10	2.8589	$2.8589(1 + 1.756.10^{-5}T + 2.270.10^{-12}T^3)$	$1.756(1 + 3.879.10^{-7}T^2$
20	2.8510	$2.8510(1 + 1.701.10^{-5}T + 2.101.10^{-12}T^3)$	$1.701(1 + 3.705.10^{-7}T^2)$
30	2.8435	$2.8435(1 + 1.652.10^{-5}T + 1.949.10^{-12}T^3))$	$1.652(1 + 3.540.10^{-7}T^2)$

The calculated lattice spacing and linear thermal expansion coefficient of the metal Ag at pressure $P = 0$ are presented in Table 9 and shown in Fig. 2.

Table 9. The calculated lattice spacing and linear thermal expansion coefficient of the metal Ag at pressure $P = 0$

$T(K)$	300	400	500	600	700	800	900	1000
$a(A^0)$	2.8832	2.8887	2.8943	2.9002	2.9063	2.9127	2.9194	2.9265
$exp.$[12]	2.8891							
$cal.$[8, 13]	2.8634		2.8754		2.8882	2.8951	2.9023	2.9100
$\alpha_T.10^5(K^{-1})$	1.88	1.93	2.00	2.08	2.18	2.29	2.42	2.56
$exp.$[11]	1.92	2.00	2.06	2.14	2.23	2.34		2.62
$exp.$[14]	1.88	1.95	2.02	2.10	2.20	2.31	2.43	2.56
$Cal.$[8, 13]	1.92	2.01	2.17	2.23	2.35	2.48		2.80

Table 10. Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Ag.

$P(kbar)$	5	10	15	20	25	30
$Cal.$	0.0048	0.0094	0.0138	0.0181	0.0222	0.0262
$Exp.$[11]	0.0047	0.0094	0.0138	0.0182	0.0224	0.0262
$Cal.$[8, 13]	0.0040	0.0081	0.0121	0.0158	0.0195	0.0231

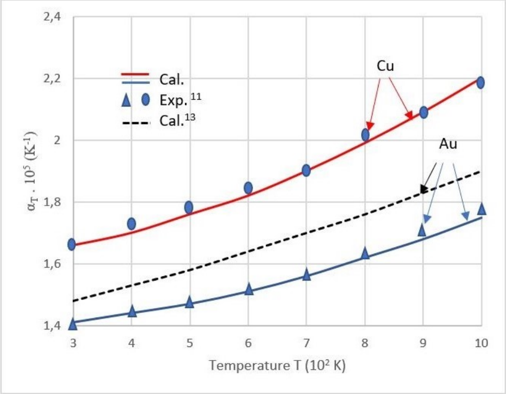

Figure 1. The linear thermal expansion coefficient of metals Cu, Au at pressure $P = 0$.

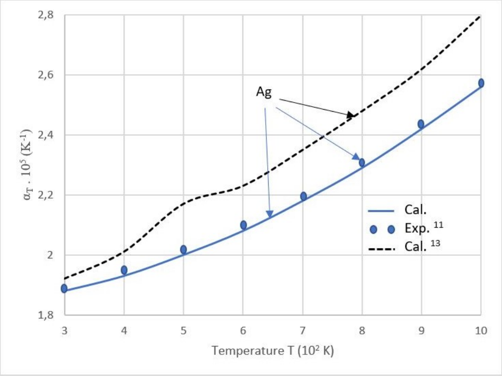

Figure 2. The linear thermal expansion coefficient of metals Ag at pressure $P = 0$.

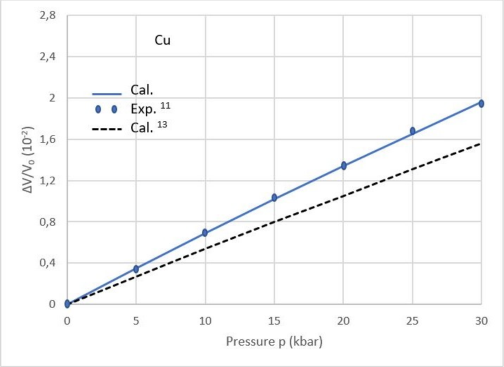

Figure 3. Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Cu.

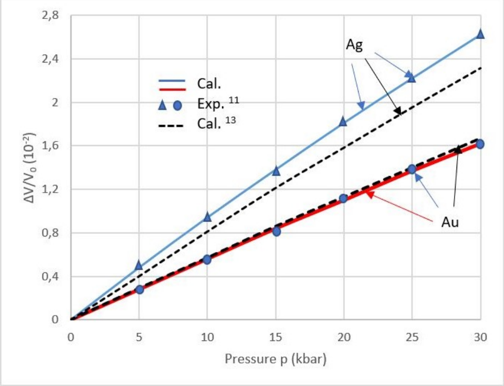

Figure 4. Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Au, Ag

Fractional change of volume $\frac{\Delta V}{V_0}$ at 300K of metal Ag are presented in Table 10 and show in Fig. 4.

From the numerical results in Tables 3, 4, 6, 7, 9, 10, we calculate the relative errors for lattice spacing, linear thermal expansion coefficient, fractional $\frac{\Delta V}{V_0}$ of metals Cu, Au and Ag (as well as in study [8, 13]), in comparison with the experiment, respectively, they are smaller:

$0.35\%(0.59\%); 2.1\%(\text{Does not have}); 2.5\%(22.4\%); (Cu)$

$0.0028\%(1.33\%); 1.9\%(9.9\%); 1.2\%(3.1\%); (Au)$

$0.02\%(0.89\%); 0.02\%(6.8\%); 1.1\%(12.9\%); (Ag)$

By comparison of these pairs show that: The results that obtained in this study of thermal expansion of metals Cu, Au and Ag give us appropriate numerical results to the experiment, in a wide range of temperature, from room to melting temperature and pressure up to $30Kbar$, in which much better than those in study [8, 13].

4. Conclusions

Beside the simplicity of expressions and numerical calculations of the lattice spacing and linear thermal expansion coefficient, the numerical results that we studied agree with experiment and better than other studies that we knew [8, 13, 17]. These results in which obtained are new, can be considered as a contribution in study of thermodynamic properties of metals. These results are able to describe the thermal expansion of Cu, Au and Ag at higher temperature and pressure with relative errors in comparison with experiment when calculating lattice spacing, linear thermal expansion coefficient and fractional $\frac{\Delta V}{V_0}$, respectively, less than $0.35\%; 2.1\%$ and 2.5% (to Cu); $0.0028\%; 1.9\%$ and 1.2% (to Au); $0.02\%; 0.02\%$ and 1.1% (to Ag) within a wide range of temperature, from room to melting temperature and pressure up to $30Kbar$.

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