Thermal expansion for ordered Cu₃Au alloy at higher temperature and under pressure.

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Abstract. The thermodynamic properties of alloys are studied using the statistical moment method (SMM), which allows us to take into account the anharmonicity of the thermal lattice vibration. Within the forth-order moment approximation, the free energy, equation of state and lattice spacing of the binary ordered alloys with cubic structure are given explicitly in terms of the effective pair potentials and the second-and fourth-order vibrational coefficients. Applying to ordered Cu₃Au alloy, we determine these properties at higher temperature and under pressure in simple analytic form. Numerical results for the lattice parameter, pressure-volume dependence of this alloy in different temperatures and pressures are in good agreement with experiments, better than other calculations.

1. Introduction

The study of the an-harmonic properties in the partly ordered state of the alloy Cu₃Au below the order-disorder transition have been made for the thermal expansion behaviour and the iso-thermals at various temperatures and compared with the experimental data [1], the quasi-harmonic free energy expression has been derived from the Bragg-Williams approximations considered the nearest neighbour interactions only.

The recent developments of ab initio density functional theory have enabled us to get detailed information on the ground state properties of materials [2,3], especially at the absolute zero temperature. However, it is still difficult and problematic to calculate the properties of materials at finite temperatures, finite pressures and excited states. Calculate lattice spacing and thermal expansion coefficient of some metals and alloys in the form of polynomials of temperatures has also been done on the basis of experimental result [12,14,15]. However, in these studies only survey at zero pressure. In this present 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 alloys. 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 use for genetic studies of trends among a given class of metallic materials. Within the fourth-order moment approximation and general formulas calculated the free energy of the alloys in [4,11], the free energy, equation of state and the lattice spacing of ordered alloys with fcc structure are given explicitly in terms of the effective pair potentials and the second-and fourth-order vibration coefficient. Applying to ordered Cu₃Au alloy, we determined these properties at higher temperature and under pressure.
in simple analytic form. Numerical results for the lattice spacing, \( P - V \) dependence in different temperatures and pressures are in good agreement with the experiments, better than other calculations.

2. Theory

By using the general formulas calculated the free energy of the alloy in [4,11], we calculate the free energy expression of binary ordered alloys with cubic structure are given explicitly in terms of the effective pair potentials and second-and forth-ordered vibration constants as:

\[
\psi_{AB} = 3N \left[ C_A \left( \frac{u_{0A}}{6} + \psi_{0A} \right) + C_B \left( \frac{u_{0B}}{6} + \psi_{0B} \right) \right] + \\
3N \left[ \frac{\theta (k_B - k_A)^2}{k_A k_B} - \frac{2\omega^2}{3} \right] P_{AB} + \\
3N \left( C_A \frac{m_A}{k_A^2} + C_B \frac{m_B}{k_B^2} \right) \theta^2 - TS_{conf}
\]

with:

\[
k_{\alpha} = \frac{1}{2} \sum_i \left( \frac{\partial^2 \varphi_{\alpha i}}{\partial u_{ix}^2} \right)_{eq}, \quad \gamma_{1\alpha} = \frac{1}{48} \sum_i \left( \frac{\partial^4 \varphi_{\alpha i}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq}, \quad \gamma_{2\alpha} = \frac{1}{8} \sum_i \left( \frac{\partial^4 \varphi_{\alpha i}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq}
\]

In the above eq. (2), the summations on \( i \) run over the neighbour sites of site of \( \alpha \) atoms in metal \( \alpha (\alpha = A, B) \), \( \varphi_{\alpha i} \) is interaction potential between atom \( \alpha \) and atom of site \( i \); \( u_{0\alpha} \) in eq. (1) denotes the effective pair interaction of \( \alpha \) atoms with other atoms in metal \( \alpha \) and \( \psi_{0\alpha} \) the Helmholtz free energy in the harmonic approximation of the atom \( \alpha \) in metal \( \alpha \):

\[
u_{0\alpha} = \sum_i \varphi_{\alpha i} (r_{\alpha i}); \quad \psi_{0\alpha} = 3N\theta \left[ x_{\alpha} + \ln (1 - e^{-2x_{\alpha}}) \right]
\]

where:

\[
x_{\alpha} = \frac{\hbar \omega_{\alpha}}{2\theta}, \quad \omega_{\alpha} = \sqrt{\frac{k_{\alpha}}{m^*}}, \quad m^* = C_A m_A + C_B m_B
\]

with \( m_{\alpha} \) is the mass of atom \( \alpha \).

In the above eq. (1), \( C_{\alpha}, \omega \) and \( P_{AB} \) are concentrations of \( \alpha \) atoms, order energies and probability of two atoms \( A \) and \( B \) next to each other respectively, \( S_{conf} \) is the configurational entropy, \( \theta = kT \), \( k \) and \( T \) are Boltzmann’s constant and temperature in K respectively.

The atomic displacement in the limit of zero of supplemental force in ordered \( AB \) alloy calculated by the general formula:

\[
\Delta r = \sum_{\alpha\beta} v_{\beta} P_{\alpha} y_{\alpha}^\beta
\]

where \( y_{\alpha}^\beta \) is displacement of atom \( \alpha \) in the sub-lattice \( \beta (\beta = a, b) \), \( v_{\beta}, P_{\alpha}^\beta \) are the concentrations of sub-lattice \( \beta \) and the probabilities of finding an \( \alpha \) atom \( (\alpha = A, B) \) in the sub-lattice \( \beta \).

From (1) we calculated the displacement of the atom in the ordered \( AB \) alloy as:

\[
\Delta r = C_A y_A + C_B y_B + \frac{P_{AB}}{4} \left[ y_A \left( 2 + \frac{\gamma_{0B}}{\gamma_{0A}} - \frac{3k_{0B}}{k_{0A}} \right) + y_B \left( 2 + \frac{\gamma_{0A}}{\gamma_{0B}} - \frac{3k_{0A}}{k_{0B}} \right) \right]
\]
with: \( \gamma_\alpha = 4 (\gamma_{1\alpha} + \gamma_{2\alpha}) \), \( y_\alpha \) is the displacement of the \( \alpha \) atom in metal \( \alpha \) in the limit of zero of supplemental force \([5]\) as:

\[
y^2_\alpha = \left[ -C_{2\alpha} + \sqrt{C^2_{2\alpha} - 4C_{1\alpha}C_{3\alpha}} \right] \frac{2C_{1\alpha}}{2C_{1\alpha}}
\]

(7)

where:

\[
C_{1\alpha} = 3\gamma_\alpha, C_{2\alpha} = 3k_\alpha \left[ 1 + \frac{\gamma_\alpha}{k_\alpha} (X_\alpha + 1) \right], C_{3\alpha} = -\frac{2\gamma_\alpha}{k_\alpha^2} \left( 1 + \frac{X_\alpha}{2} \right)
\]

(8)

with \( X_\alpha = x_\alpha \coth x_\alpha \).

The lattice spacing of alloy is counted from the formula:

\[
a = a_0 + \Delta r
\]

(9)

with \( a_0 \) is the lattice spacing of alloy the absolute zero temperature and pressure \( p \).

The equation of state for alloys is derived from the thermodynamic relation:

\[
P = -\left( \frac{\partial \psi}{\partial V} \right)_T = -\frac{a}{3V} \left( \frac{\partial \psi}{\partial a} \right)_T
\]

(10)

At the absolute zero temperature and pressure \( P \), the equation of state for alloy in the following form:

\[
- \frac{Pv_0}{a_0} = C_A \left( \frac{1}{6} \frac{\partial u_{0A}}{\partial a_0} + \frac{\hbar \omega_{0A}}{4\sqrt{m^* k_{0A}}} \frac{\partial k_{0A}}{\partial a_0} \right) + C_B \left( \frac{1}{6} \frac{\partial u_{0B}}{\partial a_0} + \frac{\hbar \omega_{0B}}{4\sqrt{m^* k_{0B}}} \frac{\partial k_{0B}}{\partial a_0} \right)
\]

(11)

where \( v_0 = \frac{V_0}{N} \) is the volume of unit cell in crystal lattice of alloy at the absolute zero temperature and pressure \( P \).

The linear thermal expansion coefficient of alloy is determined by:

\[
\alpha_T = \frac{1}{a_0(P,0)} \left( \frac{\partial a(P,T)}{\partial T} \right)_P = \frac{1}{a_0} \left( \frac{\partial (\Delta r)}{\partial T} \right)_P
\]

(12)

3. Results and discussion

By using of the statistical moment method (SMM), we calculated the equilibrium lattice spacing for ordered \( Cu_3Au \) alloy with \( Ll_2 \) structure. In discussing the thermodynamic properties of metals and alloys, the Lennard-Jones potential has been very successful. It has also been used to calculate mechanical properties of a wide variety of metals and alloys, including lattice defects \([7,8]\). In view of this, we will use the Lennard-Jones potential \( \varphi_{AB}(r) \) for the \( A - B \) atom pair in alloys determined by pairs of \( A - A \) and \( B - B \) atoms and order energy \( \omega \) as:

\[
\varphi_{AB}(r) = \left[ \frac{\varphi_{AA}(r) + \varphi_{BB}(r)}{2} \right] - \omega . \text{ Here, } A \text{ and } B \text{ represent } Cu \text{ and } Au \text{ atoms in ordered } Cu_3Au \text{ alloy. The Lennard-Jones potential } \varphi_{\alpha\alpha}(r) \text{ for interaction between atoms in metal } \alpha \text{ as:}
\]

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

here \( D, r_0, n \) and \( m \) are the parameters of potential and have concrete values depending on each metal. For metals \( Cu, Au \), values of potential parameters are given in Table 1.

Using the derivatives of the interatomic potentials \([10]\) and the vibrational parameters \( k_\alpha, \gamma_{1\alpha}, \gamma_{2\alpha}, \gamma_\alpha (\alpha = Cu, Au) \), one can calculate the equation of state at the absolute zero temperature under pressure \( P \) and lattice spacing, linear thermal expansion coefficient for the ordered \( Cu_3Au \).
Table 1. Lennard-Jones potential parameters $D, r_0$ of $Cu, Au$ metals [9]

| Metals | $D/k (K)$ | $r_0 (A^0)$ | $n$  | $m$  |
|--------|-----------|-------------|------|------|
| $Cu$   | 3401.1    | 2.5487      | 9    | 5.5  |
| $Au$   | 4683.0    | 2.8751      | 10.5 | 5.5  |

The equation of state for ordered $Cu_3Au$ alloy at the absolute zero temperature under pressure $P$:

$$0.2835.10^{-6}P y^{10.25} + 1.0125y^{10.75} - 0.018y^{10} - 13.05y^{7.25} - 72.36y^{5.75} + 1.83y^5 - 1.42y^{3.75} - 46.4 = 0 \quad (13)$$

The lattice spacing for ordered $Cu_3Au$ alloy at the temperature $T$ under pressure $P$:

$$a(P,T) = y(P,0) \left\{ 1 + 0.303.10^{-9}TQ(P) \left[ 1 + 10^{-14}T^2 R(P) \right] \right\} \quad (14)$$

with:

$$Q(P) = 4.185y^9 + 0.084y^{10.5} + 0.109y^{12.5} + 2.51.10^{-4}y^{15.5}$$

and:

$$R(P) = 1.035y^{18} + 1.43.10^{-3}y^{21} + 0.063y^{21.5} - 2.07.10^{-3}y^{25} + 1.1.10^{-5}y^{26} - 3.0.10^{-8}y^{31}.$$  

where $y = y(P,0)$ is the solution of the equation (13), dependence on the pressure $P$.

In equation (13) and expression (14), $y = y(P,0) \equiv a_0(P,0)$; the pressure $P$, lattice spacing $a(P,T)$, and temperature $T$ are measured in unit of kbar($10^8Pa$), $A^0(10^{-10}m)$, and $K$, respectively.

The dependence of lattice spacing and thermal expansion coefficient for alloy $Cu_3Au$ on temperature $T$ and pressure $P = 0$ are respectively have the following form:

$$a(0,T) = 2.6358 \left( 1 + 1.474.10^{-5}T + 6.230.10^{-12}T^3 \right) \quad (15)$$

$$\alpha_T(0,T) = 1.474 \left( 1 + 12.68.10^{-7}T^2 \right) \quad (16)$$

The calculated lattice spacing and linear thermal expansion coefficient for the ordered $Cu_3Au$ alloy at different pressures as a polynomial function of the temperature $T$ are presented in Table 2.

Table 2. The lattice spacing and thermal expansion coefficient for ordered $Cu_3Au$ alloy as the polynomial functions of the temperature at different pressures.

| $P$(kbar) | $y(P,0)(A^0)$ | $a(P,T)(A^0)$ | $\alpha_T(P,T).10^5(K^{-1})$ |
|-----------|-------------|--------------|-------------------------------|
| 100       | 2.5841      | 2.5841(1 + 1.194.10^{-5}T + 3.868.10^{-12}T^3) | 1.194(1 + 9.920.10^{-7}T^2) |
| 200       | 2.5477      | 2.5477(1 + 1.030.10^{-5}T + 2.720.10^{-12}T^3) | 1.030(1 + 7.920.10^{-7}T^2) |
| 300       | 2.5193      | 2.5193(1 + 0.915.10^{-5}T + 2.040.10^{-12}T^3) | 0.915(1 + 6.690.10^{-7}T^2) |

The calculated lattice spacing for ordered $Cu_3Au$ alloy at pressure $P = 0$ are presented in Table 3 and show in Fig.1 and compared with the experimental results [1, 13] is in
good agreement the compared with the calculations by the moment method [11] and by the quasi-harmonic approximation [1], while that obtained by the quasi-harmonic approximation shows strong nonlinear behaviour at higher temperatures, in qualitative disagreement with experiments.

The theoretical pressure - volume dependence at corresponding temperatures show in Table 4 and Fig.2 in this Cu$_3$Au alloy bellow the transition temperature. From Fig.2 where the calculated values of $\frac{V}{V_0} = \left(\frac{a(P,T)}{a(0,T)}\right)^3$ have been plotted as a function of pressure $P$ for alloy Cu$_3$Au at two temperatures 300 and 650K, it becomes apparent the theoretical pressure - volume dependence in this ordered alloy. Where the compressibility decreases with increasing pressure the plots at two temperatures show considerable nonlinearity in the behaviour, is in agreement with calculations by the quasi-harmonic approximation [1].

Table 3. The lattice spacing and linear thermal expansion coefficient for ordered Cu$_3$Au alloy at pressure $P = 0$.

| $T$(K) | 300  | 373  | 473  | 573  | 623  | 643  | 658  |
|-------|------|------|------|------|------|------|------|
| $a(A^0)$ | Cal. | 2.6479 | 2.6511 | 2.6559 | 2.6612 | 2.6640 | 2.6651 | 2.6660 |
| Exp.[1, 13] | 2.6507 | 2.6538 | 2.6580 | 2.6623 | 2.6648 | 2.6660 | 2.6671 |
| Cal.[1] | 2.6479 | 2.6504 | 2.6541 | 2.6596 | 2.6635 | 2.6660 | 2.6692 |
| $\alpha T$(K$^{-1}$).10$^5$ | Cal. | 1.642 | 1.734 | 1.892 | 2.087 | 2.199 | 2.246 | 2.283 |

Table 4. $P - V$ isotherms (theoretical) at the temperature 300K and 650K for the ordered Cu$_3$Au alloy.

| $P$(kbar) | 50  | 100 | 150 | 200 | 250 | 300 |
|-----------|-----|-----|-----|-----|-----|-----|
| $\frac{V}{V_0}$ | 300K | 0.9663 | 0.9397 | 0.9178 | 0.8992 | 0.8829 | 0.8685 |
| 650K | 0.9637 | 0.9354 | 0.9123 | 0.8927 | 0.8758 | 0.8609 |

4. Conclusion
We have presented the thermodynamic quantities for the ordered Cu$_3$Au alloy at higher than room temperature but below the order-disorder transition in polynomial form base general formulas of the moment method in statistical dynamic. The lattice spacing, thermal lattice expansion for the Cu$_3$Au alloy as the polynomial functions of the temperature $T$.

The calculated lattice spacing for the ordered Cu$_3$Au alloy at pressure $P = 0$ by a polynomial function of the temperature are in good agreement with experiments, better than other calculations [1,11], while that obtained by the quasi-harmonic approximate shows strong nonlinear behaviour at higher temperature, in qualitative disagreement with experiments. The calculated theoretical pressure-volume dependence at corresponding temperatures agrees with calculations by the quasi-harmonic approximation [1].

Consequently, the theoretical results obtained for ordered Cu$_3$Au alloys have a better applicability due to their simplicity but effectiveness. Besides, calculating lattice spacing is an important basis in study the theory of order, heat capacity and other thermodynamic properties of this alloy.
Figure 1. The temperature dependence of the lattice spacing of the Cu₃Au alloy.

Figure 2. The $P-V$ behaviour in Cu₃Au alloy at temperatures 300K and 650K.

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