

Research Article

Critical Temperature for Ordered-Disordered Phase Transformation in Cu₃Au under Pressure

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We use the statistical moment method to study the dependence of the critical temperature T_c for Cu₃Au on pressure in the interval from 0 to 30 kbar. The calculated mean speed of changing critical temperature to pressure is 1.8 K/kbar. This result is in a good agreement with the experimental data.

1. Introduction

The ordered-disordered phase transformation in Cu₃Au under pressure has been studied by experimental methods such as electrical-resistance measurements made while the sample is at high temperature and under pressure [1] and the X-ray diffraction and resistance measurement. The transitional process in the Cu₃Au alloy from the disordered to the ordered state and the relaxation process in the phase change in Cu₃Au have been investigated by measuring the time dependence of the X-ray superstructure line width and the electrical resistivity [2]. The ordering kinetics of the order-disorder phase transition in Cu₃Au has been investigated by X-ray diffraction [3].

A coarse-grained model for a Cu₃Au system undergoing an order-disorder transition is constructed. The model is characterized by a Ginzburg-Landau Hamiltonian with a three-component order parameter and the symmetry of the Cu₃Au system. The ordering dynamics of this model subjected to a temperature quench are then studied by use of Langevin dynamics. The model is analyzed with a generalization of the recently developed first-principles theory of unstable thermodynamic systems [4]. The ordered-disordered phase transition in alloy Cu₃Au also is investigated theoretically by applying statistical methods for ordered phenomena such as the Kirkwood method, the pseudopotential method,

and the pseudochemical method [5, 6]. However, these works only considered the dependence of ordered parameter on temperature and considered the critical temperature at zero pressure.

In this paper, the dependence of critical temperature on pressure in alloy Cu₃Au is studied by using the model of effective metals and the statistical moment method (SMM). We obtained a rather simple equation describing this dependence. Our numerical calculations are in a good agreement with the experimental data.

2. Helmholtz Free Energy of Cu₃Au Alloy by Using the SMM

Using the thermodynamic theory of alloy in [5, 7], we analyze the ordered alloy Cu₃Au into a combination of four effective metals Cu^{*}1, Cu^{*}2, Au^{*}1, and Au^{*}2. Then, the Helmholtz free energy of alloy Cu₃Au can be calculated through the Helmholtz free energy of these effective metals and has the form

$$\begin{aligned} \psi_{\text{Cu}_3\text{Au}} = & \frac{1}{4} \left(P_{\text{Cu}}^{(1)} \psi_{\text{Cu}^*1} + 3P_{\text{Cu}}^{(2)} \psi_{\text{Cu}^*2} + P_{\text{Au}^*1}^{(1)} \psi_{\text{Au}^*1} \right. \\ & \left. + 3P_{\text{Au}^*2}^{(2)} \right) - TS_c, \end{aligned} \quad (1)$$

where $P_\alpha^{(\beta)}$ ($\alpha = \text{Cu, Au}; \beta = 1, 2$) is the probability so that the atom α occupies the lattice site of β -type and these probabilities are determined in [8], ψ_{Cu^*1} , ψ_{Cu^*2} , ψ_{Au^*1} , and ψ_{Au^*2} are the Helmholtz free energy of effective metals Cu^{*}1, Cu^{*}2, Au^{*}1, and Au^{*}2, respectively, and S_c is the configurational entropy.

The Helmholtz free energy of effective metals $\alpha * \beta$ ($\alpha = \text{Cu, Au}; \beta = 1, 2$) is calculated by the SMM analogously as for pure metals [9] and is equal to

$$\begin{aligned} \psi_{\alpha*\beta} &= 3R \left\{ \frac{u_{\alpha*\beta}}{6k_B} \right. \\ &\quad \left. + T \left\{ X_{\alpha*\beta} + \ln \left[1 - \exp(-2X_{\alpha*\beta}) \right] \right\} \right\}, \\ u_{\alpha*\beta} &= u_\alpha + \frac{P_{\alpha\alpha'}}{C_\alpha} (\Delta_{\alpha\alpha'}^{(0)} - 2\omega), \end{aligned} \quad (2)$$

$$X_{\alpha*\beta} \sqrt{\frac{k_{\alpha*\beta}}{m_{\alpha*\beta}}}, \quad k_{\alpha*\beta} = k_\alpha + 3 \frac{P_{\alpha\alpha'}}{C_\alpha} \Delta_{\alpha\alpha'}^{(2)},$$

where u_α, k_α are parameters of the pure metal α [9], $P_{\alpha\alpha'}$ is the probability so that the atom of α -type and the atom of α' -type ($\alpha, \alpha' = \text{Cu, Au}; \alpha \neq \alpha'$) are side by side, and ω is the ordered energy and is determined by [6]

$$\omega = \frac{1}{2} (\varphi_{\text{Cu-Cu}} + \varphi_{\text{Au-Au}}) - \varphi_{\text{Cu-Au}}, \quad (3)$$

where $\varphi_{\text{Cu-Cu}}$, $\varphi_{\text{Au-Au}}$, and $\varphi_{\text{Cu-Au}}$ are the interaction potential between atoms Cu-Cu, Au-Au, and Cu-Au, respectively, on same distance and $\Delta_{\alpha\alpha'}^{(0)}$ and $\Delta_{\alpha\alpha'}^{(2)}$ are the difference of interaction potentials and the difference of derivatives of second degree for interaction potential to displacement of atom pairs $\alpha' - \alpha'$ and $\alpha - \alpha$, respectively, on same distance a .

Substituting (2) into (1), we obtain the expression of the Helmholtz free energy for alloy Cu₃Au as follows:

$$\begin{aligned} \psi_{\text{Cu}_3\text{Au}} &= \frac{1}{4} (3\psi_{\text{Cu}} + \psi_{\text{Au}}) \\ &\quad + 6R \left[3T \left(\frac{X_{\text{Cu}}}{k_{\text{Cu}}} - \frac{X_{\text{Au}}}{k_{\text{Au}}} \right) \Delta_{\text{Cu-Au}}^{(2)} - \frac{\omega}{k_B} \right] P_{\text{Cu-Au}} \\ &\quad - TS_c, \end{aligned} \quad (4)$$

where $X_\alpha = x_\alpha \coth x_\alpha$, $x_\alpha = (\hbar/2k_B T) \sqrt{k_\alpha/m_\alpha}$ ($\alpha = \text{Cu, Au}$), m_α is the mass of atom α , ψ_{Cu} and ψ_{Au} are the Helmholtz free energies of pure metals Cu and Au, respectively, and the configurational entropy of alloy has the form [6]

$$\begin{aligned} S_c &= -\frac{R}{4} \left(P_{\text{Cu}}^{(1)} \ln P_{\text{Cu}}^{(1)} + 3P_{\text{Cu}}^{(2)} \ln P_{\text{Cu}}^{(2)} + P_{\text{Au}}^{(1)} \ln P_{\text{Au}}^{(1)} \right. \\ &\quad \left. + 3P_{\text{Au}}^{(2)} \ln P_{\text{Au}}^{(2)} \right). \end{aligned} \quad (5)$$

3. Critical Temperature for Cu₃Au Alloy under Pressure

The ordered-disordered phase transition in alloy Cu₃Au is the phase transition of first type [8], where the following relations are satisfy simultaneously:

$$\left(\frac{\partial \psi_{\text{Cu}_3\text{Au}}}{\partial \eta} \right)_{\eta=\eta_0} = 0, \quad (6)$$

$$(\psi_{\text{Cu}_3\text{Au}})_{\eta=\eta_0} = (\psi_{\text{Cu}_3\text{Au}})_{\eta=0}, \quad (7)$$

where η is the equilibrium long-range ordered parameter at the temperature T and pressure p and is determined from condition (6) and η_0 is the equilibrium long-range ordered parameter at the critical temperature T_c .

The probabilities $P_\alpha^{(\beta)}$ and $P_{\alpha\alpha'}$ are represented through the ordered parameter η by the following relations [6, 8]:

$$\begin{aligned} P_{\text{Au}}^{(1)} &= \frac{1}{4} + \frac{3}{4}\eta, \\ P_{\text{Au}}^{(2)} &= \frac{1}{4} - \frac{1}{4}\eta, \\ P_{\text{Cu}}^{(1)} &= \frac{3}{4} - \frac{3}{4}\eta, \\ P_{\text{Cu}}^{(2)} &= \frac{3}{4} + \frac{1}{4}\eta, \\ P_{\text{AuCu}} &= \frac{3}{16} + \frac{1}{16}\eta^2 + \varepsilon_{\text{AuCu}}, \end{aligned} \quad (8)$$

where $\varepsilon_{\text{AuCu}}$ is the correlational parameter. This parameter has small value and is ignored.

Substituting (4) into (6) and (7), paying attention to (8), and carrying out some calculations, we obtain two equations in order to determine η_0 and T_c as follows:

$$\begin{aligned} \left[3 \left(\frac{X_{\text{Cu}}}{k_{\text{Cu}}} - \frac{X_{\text{Au}}}{k_{\text{Au}}} \right) \Delta_{\text{Cu-Au}}^{(2)} - \frac{\omega}{k_B T} \right] \eta &= -\frac{1}{4} \\ \cdot \ln \frac{(1+3\eta)(3+\eta)}{(1-\eta)(3-3\eta)}, \end{aligned} \quad (9)$$

$$\begin{aligned} \left[3 \left(\frac{X_{\text{Cu}}}{k_{\text{Cu}}} - \frac{X_{\text{Au}}}{k_{\text{Au}}} \right) \Delta_{\text{Cu-Au}}^{(2)} - \frac{\omega}{k_B T} \right] \eta_0^2 &= \frac{2}{3} \left[3 \ln 3 \right. \\ \left. - 4 \ln 4 - \left(\frac{3}{4} - \frac{3}{4}\eta_0 \right) \ln \left(\frac{3}{4} - \frac{3}{4}\eta_0 \right) \right. \\ \left. - 3 \left(\frac{3}{4} + \frac{1}{4}\eta_0 \right) \ln \left(\frac{3}{4} + \frac{1}{4}\eta_0 \right) \right] \end{aligned} \quad (10)$$

$$\begin{aligned} &- \left(\frac{1}{4} + \frac{3}{4}\eta_0 \right) \ln \left(\frac{1}{4} + \frac{3}{4}\eta_0 \right) \\ &- 3 \left(\frac{1}{4} - \frac{1}{4}\eta_0 \right) \ln \left(\frac{1}{4} - \frac{1}{4}\eta_0 \right) \Big] - \Delta(a, T_c), \end{aligned}$$

where $\Delta(a, T_c) = (2/RT)[\psi_{\text{Cu}}(a) - \psi_{\text{Cu}}(a')] + (2/3RT)[\psi_{\text{Au}}(a) - \psi_{\text{Au}}(a')]$ and a and a' are the lattice parameters

TABLE 1: Solutions of (13) at different pressures ($\omega/k_B = 910.6\text{K}$).

p (kbar)	0	5	10	15	20	25	30
a (10^{-10} m)	2.7618	2.7591	2.7563	2.7536	2.7509	2.7480	2.7453
T_c (K)	665	676	686	695	704	711	718

of alloy Cu₃Au at the critical temperature T_c in the ordered zone and the disordered zone, respectively.

From (9) we find the dependence of η on temperature and pressure as follows:

$$\frac{\omega}{k_B T} = \frac{1}{4\eta} \ln \frac{(1+3\eta)(3+\eta)}{(1-\eta)(3-3\eta)} + 3 \left[\left(\frac{X_{\text{Cu}}}{k_{\text{Cu}}} - \frac{X_{\text{Au}}}{k_{\text{Au}}} \right) \Delta_{\text{Cu-Au}}^{(2)} \right]_{T,p}. \quad (11)$$

Second term in right side of (10) depends on temperature and pressure. At phase transition point in (9), $T = T_c$ and $\eta = \eta_0$. Therefore, from (9) and (10) we find the equation in order to determine η_0 as follows:

$$\begin{aligned} -\eta_0 \ln \frac{(1+3\eta_0)(3+\eta_0)}{3(1-\eta_0)^2} &= -4\Delta(a, T_c) + \frac{8}{3} \left[3 \ln 3 \right. \\ &\quad - 4 \ln 4 - \left(\frac{3}{4} - \frac{3}{4}\eta_0 \right) \ln \left(\frac{3}{4} - \frac{3}{4}\eta_0 \right) \\ &\quad - 3 \left(\frac{3}{4} + \frac{1}{4}\eta_0 \right) \ln \left(\frac{3}{4} + \frac{1}{4}\eta_0 \right) \\ &\quad - \left(\frac{1}{4} + \frac{3}{4}\eta_0 \right) \ln \left(\frac{1}{4} + \frac{3}{4}\eta_0 \right) \\ &\quad \left. - 3 \left(\frac{1}{4} - \frac{1}{4}\eta_0 \right) \ln \left(\frac{1}{4} - \frac{1}{4}\eta_0 \right) \right]. \end{aligned} \quad (12)$$

Because the parameters a and a' are somewhat different, $\Delta(a, T_c)$ has very small contribution to (12). Therefore, $\Delta(a, T_c)$ approximately does not depend on temperature and pressure and is determined at the critical point and zero pressure.

Using the expressions of ψ_α and a in [9, 10] at the temperature $T = T_c = 665\text{ K}$ and pressure $p = 0$, we obtain $\Delta(a, T_c) = 0.6526\eta_0^2$.

Substituting this value of $\Delta(a, T_c)$ into (12), we find the ordered parameter $\eta_0 = 0.37$. Substituting this value of η_0 into (11), the dependence of critical temperature T_c on pressure has the form

$$k_B T_c = \left\{ 1.207 + 3 \left[\left(\frac{X_{\text{Cu}}}{k_{\text{Cu}}} - \frac{X_{\text{Au}}}{k_{\text{Au}}} \right) \Delta_{\text{Cu-Au}}^{(2)} \right]_{T_c, p} \right\}^{-1} \omega. \quad (13)$$

4. The Results and Discussion

At the critical temperature T_c ($\sim 100\text{ K}$), X_{Cu} , X_{Au} are very near unit and we can take $X_{\text{Cu}} = X_{\text{Au}} = 1$. On the other hand,

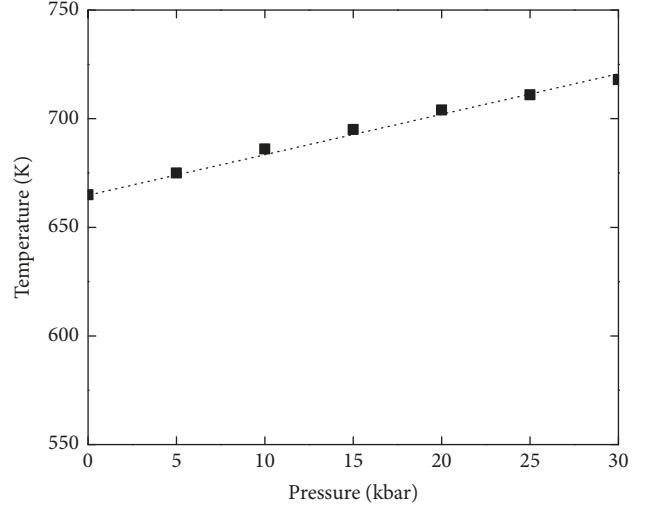


FIGURE 1: The dependence of the critical temperature T_c for alloy Cu₃Au on pressure.

from [11] we find $\Delta_{\text{Cu-Au}}^{(2)} = (1/6)(k_{\text{Au}} - k_{\text{Cu}})$. So, (13) has the following simple form:

$$\frac{k_B T_c}{\omega} = \left[1.207 + \frac{1}{2} \frac{(k_{\text{Au}} - k_{\text{Cu}})^2}{k_{\text{Au}} k_{\text{Cu}}} \right]^{-1}. \quad (14)$$

Applying the potential Lennard-Jones ($n - m$) [12] to interactions Cu-Cu and Au-Au and the expression of k_α in [11], we have

$$\frac{(k_{\text{Au}} - k_{\text{Cu}})^2}{k_{\text{Au}} k_{\text{Cu}}} = A a^{2.5} X(a) + \frac{1}{A a^{2.5} X(a)} - 2, \quad (15)$$

where $A = 0.052$, $X(a) = (1 - 0.02a^{3.5})/(1 - 0.002a^6)$, a is measured in unit of 10^{-10} m.

From (14), (15) and the equation of parameter a for alloy Cu₃Au in [10], we find the dependence of the critical temperature T_c on pressure. Our numerical calculations of the dependence of $T_c(p)$ with the values of pressure from 0 to 30 kbar are given in Table 1 and represented in Figure 1.

From Figure 1 we see that, in the interval of pressure from 7 to 21 kbar, the critical temperature T_c depends near linearly on pressure with the mean speed of changing $\Delta T/\Delta p \approx 1.8\text{ K/kbar}$. This result agrees with experiments [1], where the rate of change of the critical temperature with pressure is 2.1 K/kbar from 7 to 21 kbar. The kinetics of the order transformation below T_c are adequately described by the homogeneous reaction rate equation and an activation volume of $6.8\text{ cm}^3/\text{mole of atoms}$. The magnitude of this activation volume indicates that the formation of vacancies on the

gold sublattice is the rate-limiting step in the homogeneous ordering process.

If ignoring the second term in right side of (11) (this term depends on pressure and temperature), we obtain the expression of ordered parameter η calculated by other statistical methods [8].

In conclusion, the obtained dependence of critical temperature on pressure (see (14)) in alloy Cu₃Au has simple analytic form and numerical result in a good agreement with the experimental data.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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