ORDER-DISORDER PHASE TRANSITION IN Cu_3Au UNDER PRESSURE

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Abstract. *The dependence of the critical temperature T_c for alloy Cu_3Au on pressure in the interval from 0 to 30 kbar is studied by the statistical moment method. 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.*

I. INTRODUCTION

The order-disorder phase transition in alloy Cu_3Au under pressure is studied by experimental methods such as the measurement of resistance for specimen at high temperature and under pressure [1] and the X-ray diffraction and resistance measurement [2, 3].

The order-disorder phase transition in alloy Cu_3Au also is investigated theoretically by applying statistical methods for order phenomena such as the Kirkwood method, the pseudopotential method and the pseudochemical method [4, 5, 6]. However, these works only considered the dependence of order parameter on temperature and considered the critical temperature at zero pressure.

In this paper, the dependence of critical temperature on pressure in alloy Cu_3Au 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.

II. CALCULATION OF HELMHOLTZ FREE ENERGY FOR Cu_3Au ALLOY

In order to apply our thermodynamic theory of alloy in [5, 7], we analyze the order alloy Cu_3Au into a combination of four effective metals $Cu*1, Cu*2, Au*1$ and $Au*2$. Then, the Helmholtz free energy of alloy Cu_3Au can be calculated through the Helmholtz free energy of these effective metals and has the form:

$$\Psi_{Cu_3Au} = \frac{1}{4}\left(P_{Cu}^{(1)}\Psi_{Cu^*1} + 3P_{Cu}^{(2)}\psi_{Cu^*2} + P_{Au}^{(1)}\Psi_{Au^*1} + 3P_{Au}^{(2)}\Psi_{Au^*2}\right) - TS_C, \qquad (1)$$

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

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

$$\Psi_{\alpha^*\beta} = 3R\left\{ \frac{u_{\alpha^*\beta}}{6k_B} + T\left[X_{\alpha^*\beta} + \ln(1 - e^{-2X_{\alpha^*\beta}}) \right] \right\}, \tag{2}$$

$$u_{\alpha^*\beta} = u_\alpha + \frac{P_{\alpha\alpha'}}{C_\alpha}\left(\Delta_{\alpha\alpha'}^{(0)} - 2\omega \right); X_{\alpha^*\beta} = \frac{\hbar}{2\theta}\sqrt{\frac{k_{\alpha^*\beta}}{m_{\alpha^*\beta}}};$$

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

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 ($\alpha, \alpha' = Cu, Au; \alpha \neq \alpha'$) are side by side, ω is the order energy and is determined by [8]: $2\omega = (\varphi_{CuCu} + \varphi_{AuAu}) - 2\varphi_{CuAu}$, where $\varphi_{CuCu}, \varphi_{AuAu}, \varphi_{CuAu}$ are the interaction potential between atoms $Cu - Cu, Au - Au$ and $Cu - Au$ on same distance, respectively; $\Delta_{\alpha\alpha'}^{(0)}, \Delta_{\alpha\alpha'}^{(2)}$ are the difference of interaction potentials and the difference of derivatives of second degree for interaction potential to displacement of atom pairs α'-α', α-α on same distance a, respectively. Substituting (2) and (3) into (1), we obtain the expression of the Helmholtz free energy for alloy Cu₃Au as follows:

$$\Psi_{Cu_3Au} = \frac{1}{4}(3\Psi_{Cu} + \Psi_{Au})$$
$$+ 6R\left[3T\left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}} \right)\Delta_{CuAu}^{(2)} - \frac{\omega}{k_B} \right]P_{CuAu} - TS_C, \tag{4}$$

where $X_\alpha = x_\alpha cthx_\alpha, x_\alpha = \frac{\hbar}{2\theta}\sqrt{\frac{k_\alpha}{m_\alpha}}, (\alpha = Cu, Au), m_\alpha$ is the mass of atom α; Ψ_{Cu}, Ψ_{Au} are the Helmholtz free energies of pure metals Cu and Au, respectively, S_C is the configurational entropy of alloy Cu_3Au and has the form [6]:

$$S_C = -\frac{R}{4}\left[P_{Cu}^{(1)}\ln P_{Cu}^{(1)} + 3 P_{Cu}^{(2)}\ln P_{Cu}^{(2)} + P_{Au}^{(1)}\ln P_{Au}^{(1)} + 3 P_{Au}^{(2)}\ln P_{Au}^{(2)} \right]. \tag{5}$$

III. CALCULATION OF CRITICAL TEMPERATURE FOR ALLOY Cu_3Au UNDER PRESSURE

The order-disorder phase transition in alloy Cu_3Au is the phase transition of first type [8], where the following relations are satisfy simultaneously:

$$\left.\frac{\delta\Psi_{Cu_3Au}}{\delta\eta}\right|_{\eta=\eta_0} = 0; \tag{6}$$

$$\Psi_{Cu_3Au}\big|_{\eta=\eta_0} = \Psi_{Cu_3Au}\big|_{\eta=0}, \tag{7}$$

where η is the parameter of equilibrium long order at the temperature T and pressure p and is determined from the condition (6) and η_0 is the parameter of equilibrium long order at the critical temperature T_c. The probabilities $P_\alpha^{(\beta)}$ and $P_{\alpha\alpha'}$ are represented through the order parameter η by the following relations [8, 6]:

$$P_{Au}^{(1)} = \frac{1}{4} + \frac{3}{4}\eta; \ P_{Au}^{(2)} = \frac{1}{4} - \frac{1}{4}\eta; \ P_{Cu}^{(1)} = \frac{3}{4} - \frac{3}{4}\eta; \ P_{Cu}^{(2)} = \frac{3}{4} + \frac{1}{4}\eta, \tag{8}$$

$$P_{AuCu} = \frac{3}{16} + \frac{\eta^2}{16} + \varepsilon_{AuCu}, \tag{9}$$

where ε_{AuCu} is the correlational parameter. This parameter has small value and is ignored. Substituting (4) into (6) and (7), paying attention to (8) and (9) and carrying out some calculations, we obtain two equations in order to determine η_0 and T_c as follows:

$$\left[3\left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}}\right)\Delta_{CuAu}^{(2)} - \frac{\omega}{k_B T}\right]\eta = -\frac{1}{4}\ln\frac{(1+3\eta)(3+\eta)}{(1-\eta)(3-3\eta)}, \tag{10}$$

$$\left[3\left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}}\right)\Delta_{CuAu}^{(2)} - \frac{\omega}{k_B T}\right]\eta_0^2 = \frac{2}{3}\left[3\ln 3 - 4\ln 4 - \left(\frac{3}{4} - \frac{3\eta_0}{4}\right)\ln\left(\frac{3}{4} - \frac{3\eta_0}{4}\right)\right.$$

$$\left. - 3\left(\frac{3}{4} + \frac{\eta_0}{4}\right)\ln\left(\frac{3}{4} + \frac{\eta_0}{4}\right) - \left(\frac{1}{4} + \frac{3\eta_0}{4}\right)\ln\left(\frac{1}{4} + \frac{3\eta_0}{4}\right) - 3\left(\frac{1}{4} - \frac{\eta_0}{4}\right)\ln\left(\frac{1}{4} - \frac{\eta_0}{4}\right)\right]$$

$$- \Delta(a, T_c), \quad (11)$$

where $\Delta(a, T_c) = \frac{2}{RT}\left(\Psi_{Cu}(a) - \Psi_{Cu}(a')\right) + \frac{2}{3RT}\left(\Psi_{Au}(a) - \Psi_{Au}(a')\right)$, a and a' are are the lattice parameters of alloy Cu_3Au at the critical temperature T_c in the order zone and the disorder zone, respectively.

From Eq. (10) we find the dependence of η on temperature and pressure as follows:

$$\frac{\omega}{k_B T} = \frac{1}{4\eta}\ln\frac{(1+3\eta)(3+\eta)}{(1-\eta)(3-3\eta)} + 3\left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}}\right)\Delta_{CuAu}^{(2)}\bigg|_{T,P} \tag{12}$$

Second term in right side of Eq.(12) depends on temperature and pressure. At phase transition point in Eq.(10), $T = T_c$ and $\eta = \eta_0$. Therefore, from (10) and (11) we find the equation in order to determine η_0 as follows:

$$- \eta_0 \ln\frac{(1+3\eta_0)(3+\eta_0)}{3(1-\eta_0)^2} = -4\Delta(a, T_c) + \frac{8}{3}\left[3\ln 3 - 4\ln 4 - \left(\frac{3}{4} - \frac{3\eta_0}{4}\right)\ln\left(\frac{3}{4} - \frac{3\eta_0}{4}\right)\right.$$

$$\left. - 3\left(\frac{3}{4} + \frac{\eta_0}{4}\right)\ln\left(\frac{3}{4} + \frac{\eta_0}{4}\right) - \left(\frac{1}{4} + \frac{3\eta_0}{4}\right)\ln\left(\frac{1}{4} + \frac{3\eta_0}{4}\right) - 3\left(\frac{1}{4} - \frac{\eta_0}{4}\right)\ln\left(\frac{1}{4} - \frac{\eta_0}{4}\right)\right]$$

$$\tag{13}$$

Because the parameters a and a', are somewhat different, $\Delta(a, T_c)$ has very small contribution to Eq.(13). 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 Ψ_α and a in [9, 10] at the temperature $T = T_c = 665K$ and pressure $p = 0$, we obtain $\Delta(a, T_c) = 0.6526\eta_0^2$.

Substituting this value of $\Delta(a, T_c)$ into Eq. (13), we find the order parameter $\eta_0 = 0.37$. Substituting this value of η_0 into Eq. (12), the dependence of critical temperature T_c on pressure has the form:

$$k_B T_c = \left[1,207 + 3\left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}}\right)\Delta_{CuAu}^{(2)}\bigg|_{T_c,P}\right]^{-1}\omega, \tag{14}$$

IV. DISSCUSION OF OBTAINED RESULTS

At the critical temperature $T_c(\sim 10^2 K)$, X_{Cu}, X_{Au} are very near unit and we can take $X_{Cu} = X_{Au} = 1$.

On the other hand, from [11] we find: $\Delta_{CuAu}^{(2)} = \dfrac{k_{Au} - k_{Cu}}{6}$.

So, Eq. (14) has the following simple form:

$$\frac{k_B T_c}{\omega} = \left[1,207 + \frac{1}{2}\frac{(k_{Au} - k_{Cu})^2}{k_{Cu}k_{Au}}\right]^{-1}, \tag{15}$$

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

$$\frac{(k_{Cu} - k_{Au})^2}{k_{Cu}k_{Au}} = Aa^{2,5}X(a) + \frac{1}{Aa^{2,5}X(a)} - 2, \tag{16}$$

where $A = 0,052; X(a) = \dfrac{1 - 0,02a^{3,5}}{1 - 0,002a^6}; a$ is measured by $\mathring{A}$ $(10^{-10}m)$.

From Eqs. (15), (16) and the equation of parameter a for alloy Cu_3Au 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 Table1 and represented in Figure 1.

Table 1. Solutions of Eqs. (15) at different pressures $\left(\dfrac{\omega}{k_B} = 910,6K\right)$

p(Kbar)	0	5	10	15	20	25	30
a($\mathring{A}$)	2,7618	2,7591	2,7563	2,7536	2,7509	2,7480	2,7453
$T_c(K)$	665	676	686	695	704	711	718

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 $\dfrac{\Delta T}{\Delta p} \approx 1,8$ K/kbar. This result agrees with experiments [1].
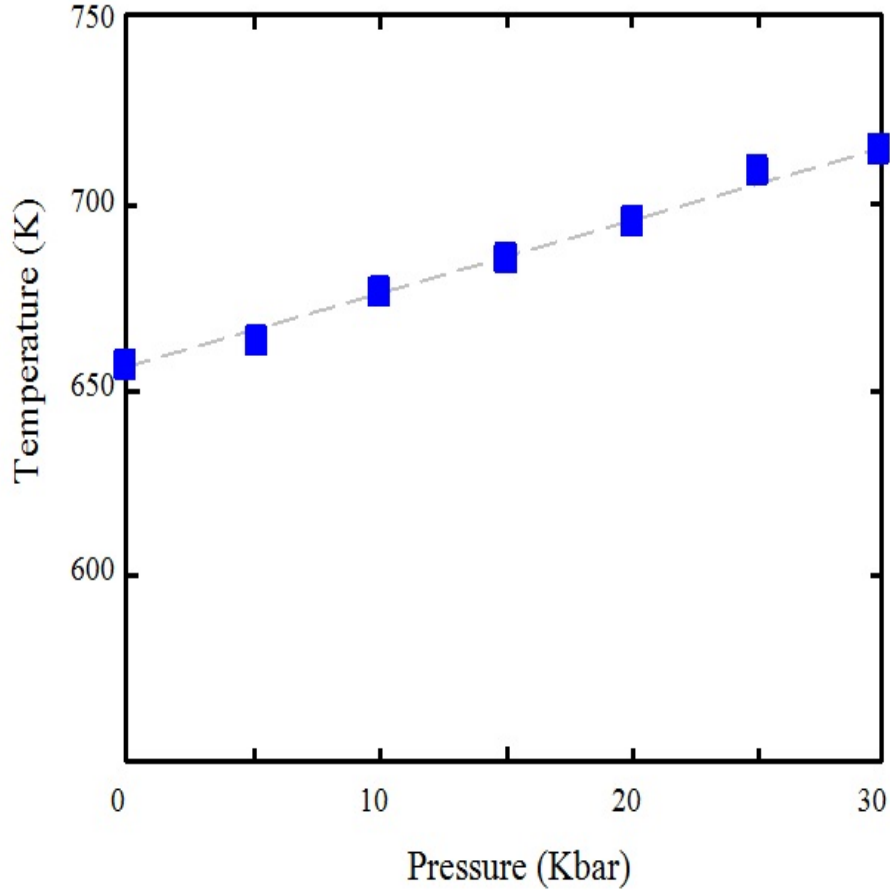
Fig. 1. The dependence of the critical temperature T_c for alloy Cu_3Au on pressure.

If ignoring the second term in right side of Eq. (12) (this term depends on pressure and temperature), we obtain the expression of order parameter calculated by other statistical methods [8].

In conclusion, the obtained dependence of critical temperature on pressure (equation (15)) in alloy Cu_3Au has simple analytic form and the numerical result in a good agreement with the experimental data.

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