ORDER-DISORDER PHASE TRANSITION IN Cu₃Au UNDER PRESSURE

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Abstract. The dependence of the critical temperature $T_c$ for alloy Cu₃Au 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 Cu₃Au 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 Cu₃Au 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 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.

II. CALCULATION OF HELMHOLTZ FREE ENERGY FOR Cu₃Au ALLOY

In order to apply our thermodynamic theory of alloy in [5, 7], we analyze the order 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:

$$\Psi_{Cu₃Au} = \frac{1}{4} \left( P_C^{(1)} \Psi_{Cu*1} + 3 P_C^{(2)} \Psi_{Cu*2} + P_A^{(1)} \Psi_{Au*1} + 3 P_A^{(2)} \Psi_{Au*2} \right) - TSC,$$

(1)
where \( P^{(\beta)}_\alpha (\alpha = Cu, Au; \beta = 1, 2) \) is the probability so that the atom \( \alpha \) occupies the knot of \( \beta \)-type and these probabilities are determined in [8], \( \Psi_{Cu^*1}, \Psi_{Cu^*2}, \Psi_{Au^*1} \) and \( \Psi_{Au^*2} \) 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:

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

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

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

where \( u_\alpha, k_\alpha \) are parameters of the pure metal \( \alpha [9], P_{\alpha\alpha'} \) is the probability so that the atom of \( \alpha \)-type and the atom of \( \alpha' \)-type (\( \alpha, \alpha' = Cu, Au; \alpha \neq \alpha' \)) are side by side, \( \omega \) is the order energy and is determined by [8]:

\[
2\omega = (\varphi_{Cu}Cu + \varphi_{Au}Au) - 2\varphi_{CuAu},
\]

where \( \varphi_{Cu}Cu, \varphi_{Au}Au, \varphi_{CuAu} \) 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 \( \alpha' - \alpha', \alpha - \alpha \) 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:

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

where \( X_\alpha = x_\alpha \text{cthx}_\alpha, x_\alpha = \frac{h}{2\theta} \sqrt{\frac{k_\alpha}{m_\alpha}}, (\alpha = Cu, Au) \), \( m_\alpha \) is the mass of atom \( \alpha \); \( \Psi_{Cu}, \Psi_{Au} \) are the Helmholtz free energies of pure metals \( Cu \) and \( Au \), respectively, \( S_C \) is the configurational entropy of alloy \( Cu_{3}Au \) and has the form [6]:

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

### III. Calculation of Critical Temperature for Alloy \( Cu_{3}Au \) Under Pressure

The order-disorder phase transition in alloy \( Cu_{3}Au \) is the phase transition of first type [8], where the following relations are satisfy simultaneously:

\[
\delta \Psi_{Cu_{3}Au} \bigg|_{\eta = \eta_0} = 0;
\]

\[
\Psi_{Cu_{3}Au} \bigg|_{\eta = \eta_0} = \Psi_{Cu_{3}Au} \bigg|_{\eta = 0},
\]
where \( \eta \) is the parameter of equilibrium long order at the temperature \( T \) and pressure \( p \) and is determined from the condition (6) and \( \eta_0 \) is the parameter of equilibrium long order at the critical temperature \( T_c \). The probabilities \( P^{(\beta)}_a \) and \( P^{(\alpha)}_{aa'} \) are represented through the order parameter \( \eta \) by the following relations [8, 6]:

\[
P^{(1)}_{Au} = \frac{1}{4} + \frac{3}{4} \eta; \quad P^{(2)}_{Au} = \frac{1}{4} - \frac{1}{4} \eta; \quad P^{(1)}_{Cu} = \frac{3}{4} - \frac{3}{4} \eta; \quad P^{(2)}_{Cu} = \frac{3}{4} + \frac{1}{4} \eta.
\]

\[
P_{AuCu} = \frac{3}{16} + \frac{3}{16} \varepsilon_{AuCu},
\]

where \( \varepsilon_{AuCu} \) 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 \( \eta_0 \) and \( T_c \) as follows:

\[
\left[ 3 \left( \frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}} \right) \Delta^{(2)}_{CuAu} - \frac{\omega}{k_BT} \right] \eta_0 = -\frac{1}{4} \ln \left( \frac{(1 + 3\eta)(3 + \eta)}{(1 - \eta)(3 - 3\eta)} \right),
\]

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

\[
\left[ 3 \left( \frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}} \right) \Delta^{(2)}_{CuAu} - \frac{\omega}{k_BT} \right] \eta_0^2 = \frac{2}{3} \ln 3 - 4 \ln 4 - \left( \frac{3}{4} - \frac{3\eta_0}{4} \right) \ln \left( \frac{3}{4} - \frac{3\eta_0}{4} \right)
\]

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

\[
- \Delta(a, T_c),
\]

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 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 \( \eta \) on temperature and pressure as follows:

\[
\frac{\omega}{k_BT} = \frac{1}{4\eta} \ln \left( \frac{(1 + 3\eta)(3 + \eta)}{(1 - \eta)(3 - 3\eta)} \right) + 3 \left( \frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}} \right) \Delta^{(2)}_{CuAu} \bigg|_{T,P}
\]

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 \( \eta_0 \) as follows:

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

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

\[
(13)
\]
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 $\Psi_\alpha$ and $a$ in [9, 10] at the temperature $T = T_c = 665 K$ and pressure $p = 0$, we obtain $\Delta(a, T_c) = 0.6526\eta_0^2$.

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

$$k_B T_c = \left[1,207 + 3 \left(\frac{X_{Cu}}{k_{Cu}} - \frac{X_{Au}}{k_{Au}}\right) \frac{\Delta^{(2)}_{C_{Cu,Au}}}{T_c, P}\right]^{-1} \omega, \quad (14)$$

IV. DISCUSSION 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: $\Delta^{(2)}_{C_{Cu,Au}} = \frac{k_{Au} - k_{Cu}}{6}$.

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

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

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

$$\frac{(k_{Cu} - k_{Au})^2}{k_{Cu}k_{Au}} = Aa^{2.5}X(a) + \frac{1}{Aa^{2.5}X(a)} - 2, \quad (16)$$

where $A = 0.052; X(a) = \frac{1 - 0.02a^{3.5}}{1 - 0.002a^5}; a$ is measured by \( \Lambda (10^{-10} m) \).

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 Table 1 and represented in Figure 1.

<table>
<thead>
<tr>
<th>p(Kbar)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a(\AA)$</td>
<td>2.7618</td>
<td>2.7591</td>
<td>2.7563</td>
<td>2.7536</td>
<td>2.7509</td>
<td>2.7480</td>
<td>2.7453</td>
</tr>
<tr>
<td>$T_c(K)$</td>
<td>665</td>
<td>676</td>
<td>686</td>
<td>695</td>
<td>704</td>
<td>711</td>
<td>718</td>
</tr>
</tbody>
</table>

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 $\frac{\Delta T}{\Delta p} \approx 1.8 \text{ K/kbar}$. This result agrees with experiments [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.

REFERENCES


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