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ORDER THEORY OF ALLOY $\beta - CuZn$

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Abstract. *By applying the model of pair interaction, the model of central atom, the method of coordination sphere and the statistical moment method, we calculate the free energy of $\beta - CuZn$ ordered alloy and determine the dependence of ordered parameter and lattice constant on pressure and temperature for this alloy. The obtained results have simple analytic, easy to calculate form and our numerical results are in good agreement with the experimental data*

I. INTRODUCTION

The ordered alloy $\beta - CuZn$ (still called brass) is a material which has rather special property relating to the distribution law of Cu and Zn atoms on lattice knots (the order) and is characterized by the ordered parameter. The experimental data [1] shows that in the range of temperature from 0 to 742 K, when the temperature increases, the ordered parameter decreases and reachs to zero (responding to the non-ordered state or disordered state) when the temperature reachs to 742 K. This temperature is called the critical temperature T_c. In this range of temperature (called the ordered zone), when the temperature increases, the specific heat increases and increases very quickly at temperatures near the critical temperature T_c. The experiments [1, 3, 5] also show that the ordered parameter and the critical temperature of $\beta - CuZn$ ordered alloy depend on pressure. There are many different theoretical methods in studying the above mentioned properties of $\beta - CuZn$ ordered alloy such as the Bragg - Williams method, the Kirkwood method and the pseudochemical method [1, 2, 3]. The obtained results explained many properties of this alloy. However, the dependence of lattice parameter and specific heat on temperature and pressure is not taken account Therefore, the numerical results are in not good agreement with experiments. The dependence of ordered parameter, ordered temperature and lattice parameter on pressure for $CuZn$ alloy is considered by methods of molecular dynamics [4, 5]. However, the obtained results have usually a complicated and non-analytic form. In present paper, we investigate the $\beta - CuZn$ ordered alloy and obtain some results in simple analytic form in order to describe the dependence of ordered parameter and lattice parameter on temperature and pressure and the dependence

of critical temperature on pressure. Our numerical calculations are compared with the experimental data and other calculations of other authors.

II. LATTICE PARAMETER AND ORDERED PARAMETER FOR $\beta - CuZn$ ORDERED ALLOY

II.1. Free energy of $\beta - CuZn$ ordered alloy

Free energy of $\beta - CuZn$ alloy is determined by

$$\Psi_{CuZn} = N f_{CuZn}, \tag{1}$$

where, N and f_{CuZn} are respectively the number of atoms and the mean free energy per atom in $\beta - CuZn$ alloy. Applying the expression of free energy for ordered double alloy in [6. 7] to the $\beta - CuZn$ ordered alloy, we obtain the following expression:

$$f_{CuZn} = \frac{f_{Cu} + f_{Zn}}{2} + \left[\frac{3\theta(k_{Zn} - k_{Cu})^2}{4k_{Zn}k_{Cu}} - 4\omega\right] P_{CuZn} - Ts_c, \tag{2}$$

where, f_{Cu} , k_{Cu} , f_{Zn} and k_{Zn} are the mean free energy per atom and the potential parameter in metals Cu and Zn respectively; s_c and ω are configuration entropy per atom and the ordered energy respectively in $\beta - CuZn$ alloy; $\theta = kT$; k is the Boltzmann constant and T is the absolute temperature. According the definition in [1], the expression of entropy s_c of $\beta - CuZn$ alloy has the form

$$s_c = -k \sum_{\alpha\beta} \nu_\beta P_\alpha^\beta ln P_\alpha^\beta = -k\big[(1+\eta)ln(1+\eta) + (1-\eta)ln(1-\eta)\big] \tag{3}$$

II.2. Lattice parameter of $\beta - CuZn$ ordered alloy

The lattice parameter of $\beta - CuZn$ alloy at pressure P and temperature T is determined from the formula:

$$a = a_0 + y, \tag{4}$$

where a_0 and y are the lattice parameter and the mean displacement of atom from equilibrium position respectively in $\beta - CuZn$ alloy at pressure P and temperature $0K$. Applying the equation determing the lattice parameter for ordered double alloy in [8] to $\beta - CuZn$ alloy, we find the equation of state for $\beta - CuZn$ alloy at pressure p and temperature $0K$ in order to calculate the lattice parameter a_0 as follows:

$$\begin{aligned} -P\delta a_0^2 =& \frac{1}{12}\frac{\partial}{\partial a_0}\big(u_{Cu}(a_0) + u_{Zn}(a_0)\big) \\ &+ \frac{\hbar}{8}\left(\frac{1}{\sqrt{m_{Cu}k_{0Cu}}}\frac{\partial k_{0Cu}}{\partial a_0} + \frac{1}{\sqrt{m_{Zn}k_{0Zn}}}\frac{\partial k_{0Zn}}{\partial a_0}\right) + \Delta^{(1)}(a), \end{aligned} \tag{5}$$

where $\Delta^{(1)}(a) = \dfrac{kT}{4}\dfrac{\partial}{\partial a}\dfrac{(k_{Zn} - k_{Cu})^2}{k_{Zn}k_{Cu}} P_{CuZn}; \delta, u_\alpha(a_0)$ is the coefficient depending on the crystal structure and the mean interaction potential energy per atom in metal α. The

displacement y is found through the displacements y_{Cu} and y_{Zn} of atoms in metals Cu and Zn in the form [8]:

$$y = 0.5(y_{Cu} + y_{Zn}) + \Delta_2, \tag{6}$$

here Δ_2 is a adjustable number depending on the ordered parameter η and the temperature and has small value in comparison with y_α.

II.3. Equations of ordered parameter and critical temperature

The equilibrium long - ordered parameter η is determined from the following condition of equilibrium:

$$\frac{\partial \Psi}{\partial \eta} = 0 \tag{7}$$

Substituting Ψ from Eqs. (1) and (2) into (7) and performing calculations, we obtain the equation of long-ordered parameter for $\beta - CuZn$ alloy as follows:

$$\left[\frac{3kT}{16}\frac{(k_{Zn} - k_{Cu})^2}{k_{Zn}k_{Cu}} - \omega\right]\eta = -\frac{kT}{2} ln \frac{1+\eta}{1-\eta} \tag{8}$$

The disordered-ordered transition in $\beta - CuZn$ alloy is the transition of second type [1] and then the disordered-ordered transition temperature (the critical temperature T_c) is calculated from the following condition for transition of second type:

$$\eta \to 0 \text{ when } T \to T_c - 0 \text{ and } \eta = 0 \text{ when } T > T_c \tag{9}$$

From (9) we see that at temperature T very near T_c , the ordered parameter $\eta << 1$. So at temperature very near T_c , the right-side of (8) has the form:

$$-\frac{kT}{2} ln \frac{1+\eta}{1-\eta} = -kT\eta \tag{10}$$

From (8) and (10) we derive the equation of critical temperature T_c for $\beta - CuZn$ alloy as follows:

$$T_c = \frac{\omega}{k}\frac{2}{\dfrac{3(k_{Zn} - k_{Cu})^2}{8k_{Zn}k_{Cu}} + 2}. \tag{11}$$

III. NUMERICAL CALCULATIONS AND DISCUSSION

Applying the modified Lennard Jones potential (n-m) to the interaction between atoms α [9]:

$$\varphi(a) = \frac{D}{n-m}\left[m\left(\frac{r_0}{a}\right)^n - n\left(\frac{r_0}{a}\right)^m\right], \tag{12}$$

where the potential parameters for metals Cu and Zn are given in Table 1.

Table 1. Parameters D, r_0, n and m in metals Cu and Zn.

Metals	$D/k(K)$	$r_0(A^0)$	n	m
Cu	3401.0	2.5487	9.0	5.5
Zn	1681.5	2.7622	10.0	5.5

From general formulae of quantities u_α , k_α and y_α in [10] and using the potential form (12) with parameter given in Table 1, we can transform equations (16), (17), (19) and (22) into more simple forms. The lattice parameter of $\beta - CuZn$ alloy is determined by the following expression :

$$a_{CuZn} = a_0 \left[1 + 10^{-9}(2.9a_0^9 + 1.14a_0^{10} + 0.013a_0^{12.5} + 0.0033a_0^{14.5})T\right], \tag{13}$$

where a_0 is counted from the equation:

$$5.214 \times 10^{-6} P a_0^{13} - 5.12 \times 10^{-6} a_0^{13} - 0.49 \times 10^{-4} a_0^{11.5} + 3.54 \times 10^{-3} a_0^{8.5} + 0.008a_0^8 + 15.1a_0^{4,5} - 0.61a_0^4 - 223.1a_0 - 578.35 = 0, \tag{14}$$

where the pressure P is deremined in kbar.

The ordered parameter of $\beta - CuZn$ alloy at pressure P and temperature T is determined from the equation :

$$\frac{1}{\eta} ln \frac{1+\eta}{1-\eta} + \frac{0.685}{a_0} \frac{1 - 0.0052a_0^{4.5}}{1 - 0.0213a_0^{3.5}} + 0.09a_0 \frac{1 - 0.0213a_0^{3.5}}{1 - 0.0052a_0^{4.5}} - 0.5 - \frac{2\omega}{kT} = 0, \tag{15}$$

where a depending on pressure and temperature is calculated from (13) and (14).

The critical temperature T_c of $\beta - CuZn$ alloy is found from the equation:

$$T_c = \frac{2\omega}{k} \left[\frac{0.685}{a^0} \frac{1 - 0.00521a^{4.5}}{1 - 0.0213a^{3.5}} + 0.09a_0 \frac{1 - 0.0213a^{3.5}}{1 - 0.00521a^{4.5}} + 1.5 \right]^{-1} \tag{16}$$

Numerical calculations from equations from (13) to (16) are summarized in Tables 2 .

Table 2. Lattice parameter and ordered parameter of $\beta - CuZn$ alloy at different temperatures and pressures ($\frac{\omega}{k} = 777.64K$)

$P(Kbar)$	$T(K)$	0	100	200	300	400	500	600	700
0	$a(A^0)$	2.6271	2.6380	2.6488	2.6597	2.6705	2.6814	2.6923	2.7031
	η	1.0000	1.0000	0.9991	0.9870	0.9466	0.8616	0.7074	0.3996
	Exp. [1]	1.00	1.00	1.00	0.99	0.95	0.89	0.74	0.41
50	$a(A^0)$	2.5923	2.6017	2.6110	2.6204	2.6297	2.6391	2.6485	2.6578
	η	1.0000	1.0000	0.9991	0.9872	0.9472	0.8637	0.7134	0.4216
100	$a(A^0)$	2.5631	2.5734	2.5818	2.5901	2.5984	2.6068	2.6151	2.6234
	η	1.0000	1.0000	0.9991	0.9872	0.9476	0.8649	0.7168	0.4331

The dependence of lattice parameter and ordered parameter on temperature and pressure is plotted in Figures 1 and 2. Numerical results show that at constant pressure, the ordered parameter decreases when the temperature increases. At pressure $P = 0$, our numerical calculations are in good agreement with experiments. The change of ordered parameter in term of temperature at high pressures is slower than that at small pressures. This phenomenon can be explained by paying attention to that the change of ordered parameter relates to the permutation of atoms of different types on lattice knots. At high pressures and at same temperature, this permutation is prevented more strongly. These results are in good agreement with experiments and that of other authors [3, 5]. In summary, the ordered phenomena of $\beta - CuZn$ alloy are described rather fully through equations from (13) to (16). These equations have simple analytic form.

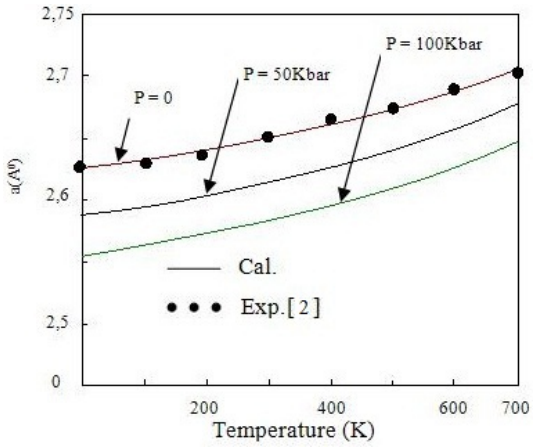

Fig. 1. Dependence of lattice parameter on temperature and pressure of $\beta - CuZn$ alloy

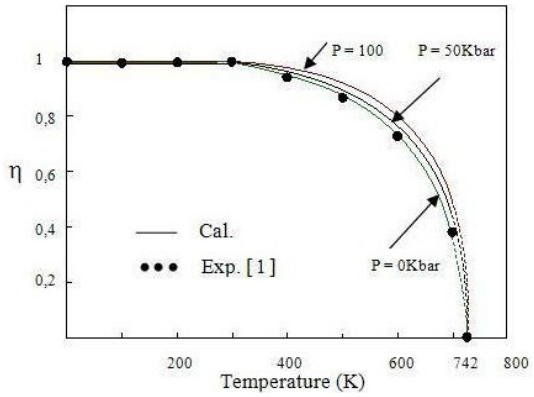

Fig. 2. Dependence of ordered parameter on temperature and pressure of $\beta - CuZn$ alloy

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