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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 order parameter and lattice constant on pressure and temperature for this alloy. The obtained results have simple analytical, easy to calculate form and our numerical results are in good agreement with the experimental data.*

I. INTRODUCTION

The order 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 order parameter. The experimental data [1] shows that in the range of temperature from 0 to 742 K, when the temperature increases, the order parameter decreases and reachs to zero (responding to the non-order state or disorder state) at 742 K. This temperature is called the critical temperature T_c. In this range of temperature (called the order zone), when the temperature increases, the specific heat increases very quickly at temperatures near the critical temperature T_c. The experiments [1, 3, 5] also show that the order parameter and the critical temperature of $\beta-$CuZn order alloy depend on pressure. There are many different theoretical methods in studying the above mentioned properties of $\beta-$CuZn order alloy such as the Bragg - Williams method, the Kirkwood method and the pseudochemical method [1–3]. 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 order parameter, critical 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 order alloy and obtain some results in simple analytical form in order to describe the dependence of order 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 the results of other authors.

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

II.1. Free energy of $\beta-$CuZn order 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 order double alloy in [6. 7] to the $\beta-$CuZn order 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,P_{CuZn} is the probability so that two atoms Cu and Zn are side by side; 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 order 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

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

where, P_α^β is the probability of finding atom α ($\alpha = Cu, Zn$) in the sub-lattice the $\beta(\beta = a, b)$; ν_β denotes the concentration of atoms in the sub-lattice β; η is the equilibrium long range order parameter.

II.2. Lattice parameter of $\beta-$CuZn order 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 order 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:

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

where $\delta, u_\alpha(a_0)$ 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]:

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

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

II.3. Equations of order parameter and critical temperature

The equilibrium long-range order 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-range order 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 disorder-order transition in $\beta-$CuZn alloy is the transition of second kind [1] and then the disorder-order transition temperature (the critical temperature T_c) is calculated from the following condition for transition of second kind:

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

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 (5), (6), (8) and (11) into more simple forms. The lattice parameter of $\beta-$CuZn alloy is determined by the following expression :

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

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; a_0 and a is deremined in A^0.

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

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

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:

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

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

Table 2. Lattice parameter and order 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 order parameter on temperature and pressure is plotted in Figures 1 and 2. Numerical results show that at constant pressure, the order parameter decreases when the temperature increases. At pressure $P = 0$, our numerical calculations are in good agreement with experiments. The change of order 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 order 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 analytical form.

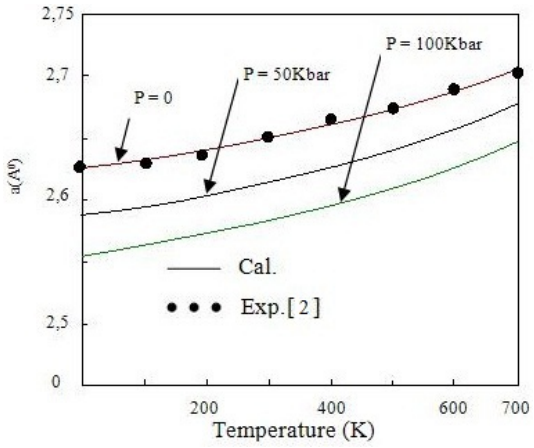

Fig. 1. Dependence of lattice parameter on temperature and pressure of $\beta-$CuZn alloy

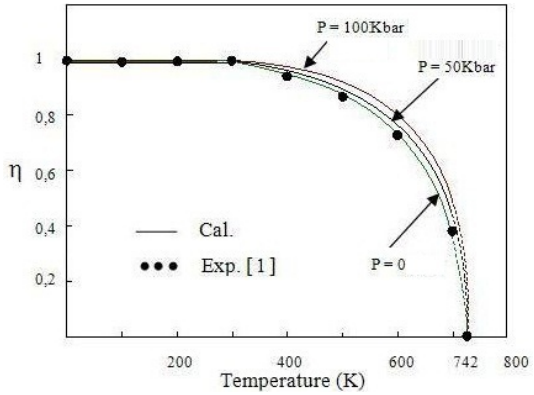

Fig. 2. Dependence of order parameter on temperature and pressure of $\beta-$CuZn alloy

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