INVESTIGATION OF THERMODYNAMIC PROPERTIES OF BINARY A - B ALLOYS BY THE MOMENT METHOD

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Abstract. *By the moment method the thermodynamic quantities of binary A - B alloys with f.c.c structure are considered. The analytic expression of thermodynamic quantities for the binary A - B alloys as the isothermal compressibility χ_T, the linear thermal expansion coefficient α, the specific heat at constant volum C_v... are obtained. The obtained results are applied to Al - based binary alloys $(AlCu, AlNi)$, Cu- based binary alloys $(CuAl)$ and Ni - based binary $(NiAl)$... and compared with the experimental data.*

I. INTRODUCTION

It is known that if the free energy of a system is known, we can find the thermodynamic properties. So it is very important to determine the free energy ψ although it is not easy to find ψ. For idial system one can determine the exact expression of ψ_0. But on general one can only find the expression for ψ by an approximate theory.

At first, we shall restrict ourselves to the simplest case of pairwise interactions. To calculate ψ of binary A B alloys we shall use the quasi-chemical approximation for the multi - component systems [1, 2, 3]. We denote the potential of interaction of an atom of component A with that of component B φ_{AB}, and the numbers of atoms in these component by N_A and N_B. The Gibbs free energy of such system can be written [2] as

$$G = \sum_{A} N_A \mu_{AA} + \sum_{A<B} \overline{N}_{AB} M_{AB} - k_B T ln W(\{\overline{N}_A\}, \{\overline{N}_{AB}\}), \tag{1}$$

Here N_{AB} is the number of the nearest - neighbor pairs formed by the atoms of the A - th and B-th components:

$$M_{AB} = \frac{2\mu_{AB} - \mu_{AA} - \mu_{BB}}{n_1}, \tag{2}$$

where n_1 is the (first) coordination number; $\mu_{AB} = \mu|\varphi_{AB}|$ is the chemical potential of the pure AB subsystem, i.e., of the imagine one - component system in which all atoms interact with each other by the potential φ_{AB} and k_B is the Boltzman's constant.

The values N_{AB} and the statistical weight W obey [1] condition

$$2N_{AA} + \sum_B N_{AB} = n_1 N_A, \tag{3}$$

$$\sum_{\{N_{AB}\}} W(\{N_A\}, \{N_{AB}\}) = \frac{(\sum_A N_A)!}{\prod_A (N_A)!}. \tag{4}$$

In the considered case where the concentration of one component is small (for example $N_B << N_A$) the quasi - chemical approximation leads to a random distribution of the pairs and we have

$$\overline{N}_{AB} \approx \frac{n_1 N_A N_B}{N_A + N_B}, \overline{N}_{AA} \approx \frac{n_1 N_A^2}{2(N_A + N_B)}, \overline{N}_{AB} \approx \frac{n_1 N_B^2}{2(N_A + N_B)}. \tag{5}$$

Substituting (5) into (1) and taking into account (4) we get

$$G = G_A + N_B(2\mu_{AB} - \mu_{AA}) - k_B T ln \frac{(N_A + N_B)!}{N_A! N_B!}, \tag{6}$$

where G_A is Gibbs free energy of metal A. In this paper, using the obtained in [4] results for the Gibbs free energy G_A of metal A and (6) we investigate the thermodynamic properties of binary $A - B$ alloys with face -centered cubic structures. The analytic expressions for the thermodynamic quantities as the thermal expansion coefficient α, the specific heats C_v and C_p, ete. are obtained. The obtained results are compared with the experimental data.

II. THE EXPRESSION OF THE THERMODYNAMIC QUANTITIES FOR THE BINARY $A - B$ ALLOYS WITH F.C.C STRUCTURES.

At first we can find the Gibbs free energy of alloys in the approximation form analogous to (6)

$$G = G_A + N_B g_B^f - TS_C, \tag{7}$$

where g_B^f is the Gibbs energy change on substituting a single particle B and

$$S_C = k_B ln \frac{(N_A + N_B)!}{N_A! N_B!}, \tag{8}$$

is the entropy of mixing.

If only take into account the interaction of particles being on first coordination sphere, we can find

$$g_B^f = G - G_A = -(1 + n_1)\psi_{AA} + \psi_{BA} + n_1 \psi_{AB} + P\Delta V, \tag{9}$$

where ΔV is the volume change on substituting a particle B, n_1 is the number of particles being on first coordination sphere, ψ_{AA} is the Helmholtz free energy of a particle of A metal in [4] $(N\psi_{AA} = \psi_A$ and $N_A + N_B = N), \psi_{BA}$ is the Helmholtz free energy of an atom B with atoms A being on two first and second coordination spheres, i.e., of an atom of the imagined one - component system in which all atoms interact with each other by the potential $\varphi_{BA}, \varphi_{AB}$ is the Helmholtz free energy of an atom A with an atom B being on the first coordination sphere in the imagined system in which all atoms interact with each other by the potential φ_{AA} rule out an atom B on the first coordination sphere interact with other ones by the potential φ_{AB}.

Substituting (9) into (7) we have found the Helmholtz free energy ψ of binary AB alloys (in the case of the pressure $P = 0$)

$$\psi = \left[N - N_B(1 + n_1)\right]\psi_{AA} + N_B\left(\psi_{BA} + n_1\psi_{AB}\right) - TS_C, \tag{10}$$

where ψ_{AA} is determined by the moment method and equal to [4]

$$\begin{aligned} \psi_{AA} &= 3\{\frac{u_0^A}{6} + \theta[x + ln(1 - e^{-2x})]\}, \\ u_0^A &= \sum_i \varphi A_i A_0(|a_i|); \quad x = \frac{\hbar\omega}{2\theta}; \quad \theta = k_B T, \\ m\omega^2 &= k_A = \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{A_i A_0}}{\partial u_{i\beta}^2}\right)_{eq} \quad ; \quad \beta = x, y, z \end{aligned} \tag{11}$$

and $\varphi_{A_i A_0}$ is the interaction potential energy between zero-th and i - th particles of A metal. ψ_{BA} has a form analogous to (11) but parameter k in this case has the form

$$k_{BA} = \frac{1}{2}\sum \left(\frac{\partial^2 \varphi_{A_i B_0}}{\partial u_{i\beta}^2}\right)_{eq} \quad \text{and} \quad u_0^{BA} = \sum_i \varphi_{A_i B_0}(|a_i|). \tag{12}$$

Note that the interaction potential between i - th particle A and B one is often used in the approximate form [5]

$$\varphi_{AB}(r) \approx \frac{1}{2}\left[\varphi_{AA}(r) + \varphi_{BB}(r)\right]. \tag{13}$$

Therefore, we can determine ψ_{AB} analogously as (11) with the aid of (13), but parameter k and u_0 are equal to

$$\begin{aligned} k_{AB} &= k_A + \frac{1}{4}\left[\left(\frac{\partial^2 \varphi_{BB}(r_1)}{\partial u_{i\beta}^2}\right)_{eq} - \left(\frac{\partial^2 \varphi_{AA}(r_1)}{\partial u_{i\beta}^2}\right)_{eq}\right], \\ u_0^{AB} &= u_0^A + \frac{1}{2}\left[\varphi_{BB}(r_1) - \varphi_{AA}(r_1)\right], \end{aligned} \tag{14}$$

here the radius of the k - th coordination sphere is determined by $r_k = \nu_k a$, in which r_1 is the first coordination sphere (in the case of f.c.c lattice ν_k equal to $\nu_1 = 1, \nu_2 = \sqrt{2}$) and a is the nearest neighbor distance at temperature T.

If the displacement of the particle from equilibrium position of perfect metal A is denoted by y_0 [4], the displacement of the particle from equilibrium position of the pure AB subsystem i.e., of the imagined one - component system in which all atoms with the corresponding free energy ψ_{BA}(or ψ_{AB} is denote by y_1(or y_2), then expressions of the corresponding nearest neighbors distances at temperature T are equal to

$$\begin{aligned} a_A &= a_0 + y_0 \\ a_{BA} &= a_0 + y_1, \\ a_{AB} &= a_0 + y_2, \end{aligned} \tag{15}$$

here a_0 is the distance a at temperature O K and determined from experiment..

By the moment method, the displacement of the particle of the metal A is considered and is equal to [4]

$$\begin{aligned} y_0^2 &= \frac{2}{3}\frac{\gamma.\theta^2}{k^3}.A, \\ A &= a_1 + \frac{\gamma^2\theta^2}{k^4}a_2 + \frac{\gamma^3\theta^3}{k^6}a_3 + \frac{\gamma^4\theta^4}{k^8}a_4, \\ a_1 &= 1 + \frac{x\mathrm{cth}x}{2}, \\ a_2 &= \frac{13}{3} + \frac{47}{6}x\mathrm{cth}x + \frac{23}{6}x^2\mathrm{cth}^2x + \frac{1}{2}x^3\mathrm{cth}^3x, \\ a_3 &= -\left(\frac{25}{3} + \frac{121}{6}x\mathrm{cth}x + \frac{50}{3}x^2\mathrm{cth}^2x + \frac{16}{3}x^3\mathrm{cth}^3x + \frac{1}{2}x^4\mathrm{cth}^4x\right), \\ a_4 &= \frac{43}{3} + \frac{93}{2}x\mathrm{th}x + \frac{169}{3}x^2\mathrm{cth}^2x + \frac{83}{3}x^3\mathrm{cth}^3x + \frac{22}{3}x^4\mathrm{cth}^4x + \frac{1}{2}x^5\mathrm{cth}^5x, \end{aligned} \tag{16}$$

where the parameter k has the form (11)

$$\gamma = \frac{1}{12}\sum_i \left[\left(\frac{\partial^4\varphi_{A_iA_0}}{\partial u_{i\beta}^4}\right)_{eq} + 6\left(\frac{\partial^4\varphi_{A_iA_0}}{\partial u_{i\beta}^2\partial u_{i\gamma}^2}\right)_{eq}\right] \equiv \gamma_A, \tag{17}$$

and the terms $\left(\frac{\partial^2\varphi_{A_iA_0}}{\partial u_{i\beta}^2}\right)_{eq}$, $\left(\frac{\partial^4\varphi_{A_iA_0}}{\partial u_{i\beta}^4}\right)_{eq}$ and $\left(\frac{\partial^4\varphi_{A_iA_0}}{\partial u_{i\gamma}^2\partial u_{i\beta}^2}\right)_{eq}$ are determined as in [6]. With the aid of (13) and (17) the expression of the displacement of the particle y_1 (or y_2) has a form analogous to (16), but the parameter k in this case has the form (12) or (14) and the parameter γ has the corresponding form

$$\begin{aligned} \gamma_{BA} &= \frac{1}{2}(\gamma_A + \gamma_B) \\ \gamma_{AB} &= \gamma_A + \frac{1}{24}\left[\left(\frac{\partial^4\varphi_{BB}(r_1)}{\partial u_{i\beta}^4}\right)_{eq} - \left(\frac{\partial^4\varphi_{AA}(r_1)}{\partial u_{i\beta}^4}\right)_{eq}\right] + \\ &\quad + \frac{1}{4}\left[\left(\frac{\partial^4\varphi_{BB}(r_1)}{\partial u_{i\beta}^2\partial u_{i\gamma}^2}\right)_{eq} - \left(\frac{\partial^4\varphi_{AA}(r_1)}{\partial u_{i\beta}^2\partial u_{i\beta}^2}\right)_{eq}\right] \end{aligned} \tag{18}$$

We notice that the nearest neighbor distance a of the binary AB alloy is approximately equal to the distances a_A, a_{AB} or a_{BA}. Besides, from (10) we see that the Helmholtz free energy ψ is a function of the nearest neighbor distance a. Thus, expanding this function on the nearest neighbor distance a in second order approximation, we find the following expressions

$$\psi_{AA}(a) = \psi_{AA}(a_A) + \frac{1}{2}\left(\frac{\partial^2\psi_{AA}}{\partial a^2}\right)_T \times (a - a_A)^2,$$
$$\psi_{BA}(a) = \psi_{BA}(a_{BA}) + \frac{1}{2}\left(\frac{\partial^2\psi_{BA}}{\partial a^2}\right)_T \times (a - a_{BA})^2, \quad (19)$$
$$\psi_{AB}(a) = \psi_{AB}(a_{AB}) + \frac{1}{2}\left(\frac{\partial^2\psi_{AB}}{\partial a^2}\right)_T \times (a - a_{AB})^2.$$

From the definition of the isothermal bulk modulo B_T with $B_T = V_0\left(\frac{\partial^2\psi}{\partial V^2}\right)_T$, the results (10), (19) and minimizing ψ : $\left(\frac{\partial\psi}{\partial a}\right)_{T,P,N} = 0$, we can find the equilibrium distance a of binary AB alloy at temperature T

$$a = \frac{(N_A - n_1 N_B)B_T^A.a_A^2 + N_B B_T^{BA}.a_{BA}^2 + n_1 N_B B_T^{AB} \times a_{AB}^2}{(N_A - n_1 N_B])B_T^A.a_A + N_B B_T^{BA}.a_{BA} + n_1 N_B B_T^{AB} \times a_{AB}} \quad (20)$$

Using the thermodynamic relations and the expression of the Helmholtz free energy (10), we obtain the expressions of the isothermal compressibility χ_T, the linear thermal expansion coefficient α, the specific heats C_v and C_p of binary AB alloy. Where, the isothermal compressibility has the form

$$\chi_T = \frac{3\left(\frac{a}{a_0}\right)^3}{2P + \frac{\sqrt{2}}{a}\frac{1}{3N}\left(\frac{\partial^2\psi}{\partial a^2}\right)_T} = \frac{3\left(\frac{a}{a_0}\right)^3}{2P + \frac{\sqrt{2}}{a}.\chi_T^*} \quad (21)$$

here

$$\chi_T^* = \frac{1}{3N}\left(\frac{\partial^2\psi}{\partial a^2}\right)_T = [1 - C_B(1 + N_1)]\chi_T^{*A} + C_B(\chi_T^{*BA} + n_1\chi_T^{*AB}),$$
$$\chi_T^{*A} \equiv \frac{1}{3N}\left(\frac{\partial^2(N\psi_{AA})}{\partial a^2}\right)_T, \quad \chi_T^{*BA} \equiv \frac{1}{3N}\left(\frac{\partial^2(N\psi_{BA})}{\partial a^2}\right)_T, \quad (22)$$
$$\chi_T^{*AB} \equiv \frac{1}{3N}\left(\frac{\partial^2(N\psi_{AB})}{\partial a^2}\right)_T \text{ and } C_B = \frac{N_B}{N}.$$

From the definition of the thermal expansion coefficient, it is easy to derive the following formula

$$\alpha = -\frac{\sqrt{2}}{3a^2}k_B\chi_T.\frac{1}{3N}\left(\frac{\partial^2\psi}{\partial a.\partial\theta}\right) = [1 - C_B(1 + n_1)]\alpha^A + C_B(\alpha^{BA} + n_1\alpha^{AB}), \quad (23)$$

where α^A is the linear thermal expansion coefficient of the metal A [4];

$$\alpha^{BA} \approx -\frac{\sqrt{2}}{3a^2}k_B\chi_T.\frac{1}{3N}\left(\frac{\partial^2\psi_{BA}}{\partial a.\partial\theta}\right)$$
$$\text{and } \alpha^{AB} \approx -\frac{\sqrt{2}}{3a^2}k_B\chi_T.\frac{1}{3N}\left(\frac{\partial^2\psi_{AB}}{\partial a.\partial\theta}\right). \quad (24)$$

Applying the Gibbs - Helmholtz relation and using (10) we find the expression for the energy of binary AB alloy and so the specific heat at constant volume C_v has the form

$$C_v = \left[1 - C_B(1 + n_1)\right]C_v^A + C_B\left[C_v^{BA} + n_1 C_v^{AB}\right] \tag{25}$$

in which C_v^A is the specific heat at constant volume of metal A [4]. According to the above obtained results, in order to find C_v^{BA} or C_v^{AB}, we must use the expressions of the parameters k, γ defined by (12) (14) and (18) corresponding to the free energy ψ_{BA} or ψ_{AB}. The specific heat at constant pressure C_p and the adiabatic compressibility χ_s are determined from the known thermodynamic relations

$$C_p = C_v + \frac{9TV\alpha^2}{\chi_T}; \quad \chi_s = \frac{C_v}{C_p}\chi_T. \tag{26}$$

At last, the isothermal and adiabatic bulk moduli B_T and B_s of binary AB alloy are equal to

$$B_T = 1/\chi_T; \quad BS = 1/\chi_s. \tag{27}$$

III. NUMERICAL RESULTS FOR AlCu, AlNi, CuAl AND NiAl ALLOYS

The interaction potential between two atoms of a metal is often used in the form of the $n - m$ one [7]

$$\varphi(r) = \frac{D}{(n-m)}\left[m\left(\frac{r_0}{r}\right)^n - n\left(\frac{r_0}{r}\right)^m\right], \tag{28}$$

where D, r_0 are determined from the experimental data and n, m are determines by the empirical way (in Table 1) [7].

The obtained results in Section 2 are applied to study Al - based binary alloys $(AlCu, AlNi)$, Cu - based binary alloys $(CuAl)$ and Ni - based binary alloys $(NiAl)$ with f.c.c structure ($n_1 = 12$). Using (28), Table 1 and (11), (12), (14), (17 and 18), we obtain the values of parameters k, γ. Therefore, from these results and (11) (15) (16), (20) $\div$ (27) we obtain the values of the compressibility χ_T, linear thermal expasion coefficient α and constant - pressure specific heat C_P at pressure $P = 0$. The results for $AlCu, AlNi, CuAl$ and $NiAl$ alloys are summarized in Tables 3, 4.

In the case of Al, Cu and Ni pure metals (the concentration of atoms $B : C_B = 0$), the obtained results well coincide with the experimental data (Tables 2, 4).

For $AlCu, AlNi, CuAl$ and $NiAl$ alloys ($C_B < 0,1$) the calculated results for α and C_P also coincide well with the experimental data (Tables 3, 4).

Metal	n	m	$r_0(A^0)$	**D/KB(^{0}B)**
Al	12.0	4.5	2.8541	**2995.6**
Cu	9.0	5.5	2.5487	**4125.7**
Ni	8.5	5.5	2.4780	**4762.0**

Table 1: Experimental values of parameters D, r_0 [7]

Metal	T(^{0}K)	100	200	300	400	500	600	800	**1000**	**1200**
Al	Cp (Cal/mol.K)	2.99	5.07	5.69	5.99	6.18	6.34	6.65		
	Cp_{exp}[8]	-	-	-	6.13	6.42	6.72	7.31		
Cu	Cp (Cal/mol.K)	3.80	5.37	5.78	5.97	6.08	6.17	6.32	**6.47**	**6.63**
	Cp_{exp}[8]	-	-	-	6.01	6.16	6.31	6.61	**6.91**	**7.21**
Ni	Cp (Cal/mol.K)	3.40	5.20	5.68	5.89	6.01	6.10	6.24	**6.37**	**6.62**
	Cp_{exp}[8]	-	-	-	6.76	7.47	8.37	7.44	**7.80**	**8.7**

Table 2: The specific heat at constant pressure Cp of metal

C_B	Alloys	AlCu	NiAl	CuAl
0.045	Cp (Cal/mol.K)	6.08	5.83	
	Cp_{exp}[9]	6.58	6.87	
0.08	Cp (Cal/mol.K)			5.85
	Cp_{exp}[9]			6.43

Table 3: The specific heat at constant pressure Cp of alloys at Temperature 400^{0}K

Alloys	C_B	T^{0}K	100	300	400	500	800	1000	1200
AlCu	0	$\alpha.10^{-5}$/K	1.18	2.32	2.50	2.65	3.18		
		α_{exp}[8]	1.22	2.32	2.49	2.64	3.38		
	0.045	$\alpha.10^{-5}$/K	1.44	2.321	2.47	2.60	3.06	3.59	
		α_{exp}[9]		2.30	2.40	2.50			
	0.099	$\alpha.10^{-5}$/K	1.76	2.33	2.44	2.54	2.92	3.36	
		α_{exp}[8]		2.20	2.38				
CuAl	0	$\alpha.10^{-5}$/K	1.06	1.66	1.74	1.80	1.97	2.10	2.26
		α_{exp}[8]	1.05	1.68	1.77	1.83	2.00	2.25	2.34
	0.05	$\alpha.10^{-5}$/K	0.93	1.66	1.75	1.82	2.01	2.15	2.31
		α_{exp}[9]			1.80				
	0.08	$\alpha.10^{-5}$/K	0.85	1.66	1.75	1.83	2.03	2.17	2.34
		α_{exp}[9]		1.66	1.74	1.82			
AlNi	0.034	$\alpha.10^{-5}$/K	1.34	2.29	2.45	2.59	3.05	3.58	
		α_{exp}[8]		2.19	2.37				
NiAl	0	$\alpha.10^{-5}$/K	0.84	1.43	1.50	1.56	1.69	1.78	2.01
		α_{exp}[8]	0.62	1.27	1.38	1.52	1.68	1.78	
	0.045	$\alpha.10^{-5}$/K	0.74	1.44	1.52	1.58	1.73	1.82	
		α_{exp}[9]		1.30					

Table 4: Thermal expansion coefficient α of alloys

In conclusion, it should be noted that the moment method really to investigate the thermodynamic properties of binary alloys with face - centered cubic structure. These results are right still for other cubic ones. However, we must notice that their parameter are determined by other formulae.

In the following paper we shall use the results of this paper for the invetgation of the thermodynamic properties of alloys with other cubic structure.

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NGHIÊN CỨU CÁC TÍNH CHẤT NHIỆT ĐỘNG CỦA HỢP KIM ĐÔI THAY THẾ A- B BẰNG PHƯƠNG PHÁP MÔMEN

Khoa Vật lý - Đại học Sư phạm - ĐHQG Hà Nội

Bằng phương pháp mômen, các đại lượng nhiệt động của hợp kim thay thế AB có cấu trúc lập phương tâm diện đã được nghiên cứu. Biểu thức giải tích của các đại lượng nhiệt động như hệ số nén đẳng nhiệt χ_T, hệ số dãn nở nhiệt α, nhiệt dung iêng đẳng tích C_v,... của hợp kim thay thế AB đã thu nhận được. Các kết quả lý thuyt được áp dụng cho các hợp kim đôi Al (AlCu, AlNi) hợp kim đôi gốc Cu (Cu Al) và N (Ni Al)... và so sánh với số liệu thực nghiệm.