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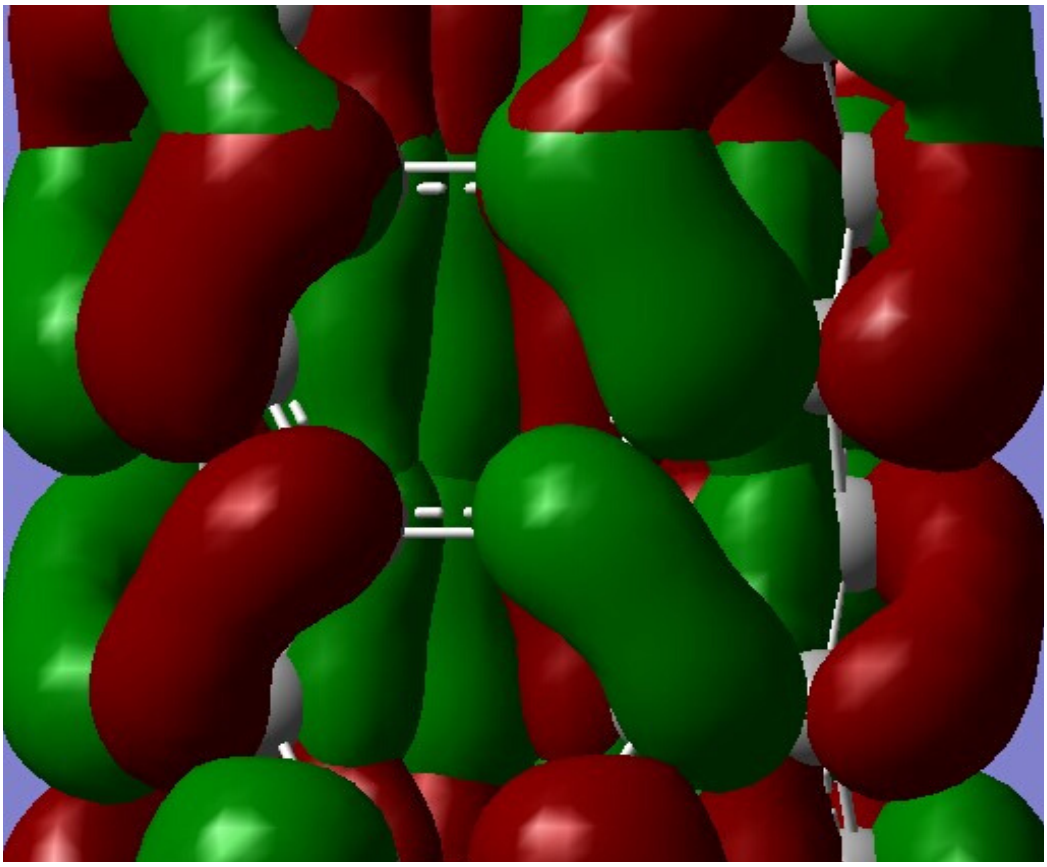

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Thermodynamics of liquid Gallium-Zinc alloy

Research Article

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Abstract: This research explores mixing behavior of Ga-Zn system throughComplex Formation Model. The variables affecting to temperature are the interaction energy parameters in which the properties under investigation are projected. The study has inspected through different thermodynamic properties such as free energy of mixing, heat of mixing and entropy of mixing. Theoretical results are in a good acceptance with the corresponding literaturedata and support a homocoordinating tendency in Ga-Zn liquid alloys.

Keywords: Thermodynamic properties • Complex formation model • Segregation

1. Introduction

Gallium lies on group IIIB in the periodic table. It is proficiently applicable as a thermometric liquid and in doping semi-conductors and production of solid-state devices like transistors. Huge amounts of zinc are used to produce die castings. These applications of the components of liquid alloys studied make them good candidates for the current kind of study. In manufacturing semiconductor devices, Gallium alloys play the pivotal role. And it is promising materials for lead free solders, because they have the traits of low melting point, good wetting properties, adhesion and oxidation resistance [1–3].Ga-Zn alloy possesses the constituents of different Gallium based multi component alloys i.e. applied in semiconducting industry. This research is significant for the study of the energetics of ternary systems such as Ga-Sn-Zn, Al-Ga-Zn, etc. It is specified that, this system is intensified low melting eutectic which is mentioned in literature [4–6].

The Ga-Zn system is analyzed through positive interaction energy, amplifying the formation of two phase structure, as presented by its simple eutectic phase diagram. The preliminary research of the empirical factors such as electronegativity difference (= 0) and size ratio $\Omega_{Ga}/\Omega_{Zn} \approx 1.19$ (Ω is atomic volume) [7, 8]. Ga-Zn system presents the values which are the characteristics for segregating alloys. However, the determining role is ascribed to the size ratio values. It purposes a limited solubility in the solid state and hence the presence of an eutectic reaction.

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Thermodynamics of Ga-Zn system is examined through various experimental methods. There are numerous findings obtained applying EMF measurements. Besides this, there are some other results derived by thermodynamic calculation based on various theoretical models [9]. Numerous investigations have been performed for different system through various approaches [10–14]. This paper presents the results of thermodynamic analysis of Ga-Zn alloys according to Conformal Solution Model. The outcomes are analyzed and compared with literature data to explicate the accuracy of this method in thermodynamic description of the presented binary system.

2. Modelling

If c is the atomic concentration of A atoms then (1-c) is atomic concentration for B atoms and such that $uA + vB = A_uB_v$ (u and v are small integer) then, number of A atoms, N_A = c. Number of B atoms, N_B = (1-c) , so that total number of atoms, $N = N_A + N_B$. When components A and B are blended together to form a binary $A - B$ solution, thermodynamic properties are changed. The liquid alloy is assumed to be composed of three species; A atom, B atom and chemical complex A_uB_v, ternary mixture also called conformal solution. The number of free atoms will be reduced due to compound formation in the melt. Now for n_1 gm atoms of A, n_2 gm atoms of B and n_3 gm atoms of A_uB_v,

$$n_1 = c - un_3 \; and \; n_2 = (1 - c) - vn_3 \tag{1}$$

The total number of atoms after mixing,

$$n = n_1 + n_2 + n_3 \tag{2}$$

$$= 1 - (u + v - 1)n_3 \tag{3}$$

The free energy of mixing of the binary A-B mixture can be written as,

$$G_M = -n_3g + G' \tag{4}$$

Here, $-n_3g$ represents lowering of free energy due to compound formation, g is the formation energy of complex. G' is the free energy of mixing of the ternary mixture of A, B and A_uB_v. If the ternary mixture is an ideal solution,

$$G' = RT \sum n_i ln \left(\frac{n_i}{n}\right) \tag{5}$$

If the effects of differences in sizes of the various constituents in the mixture cannot be ignored and the interaction ω_{ij} are small but not zero, the theory of regular solutions in the zeroth approximation [15] or the conformal solution approximation [16] is valid. For regular solution

$$G' = RT \sum n_i ln \left(\frac{n_i}{n}\right) + \sum \omega_{ij} \left(\frac{n_i n_j}{n}\right) \tag{6}$$

This equation is also referred to as conformal solution approximation. where $\omega_{ij} = 0 (for i = j)$ are termed as the interaction energies and by definition are independent of concentration, although they depend upon temperature and pressure. Now the expression for free energy of mixing G_M for the compound forming binary alloy is

$$G_M = -n_3 g + RT \sum_{i=1}^{3} n_i ln\left(\frac{n_i}{n}\right) + \sum\sum_{i<j}\left(\frac{n_i n_i}{n}\right)\omega_{ij} \tag{7}$$

The expression for heat of mixing HMis given by [17],

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_P \tag{8}$$

$$H_M = -n_3 g + RT\sum_{1}^{3} n_i ln\left(\frac{n_i}{n}\right) + \sum_{i<j}\sum\left(\frac{n_i n_j}{n}\right)\omega_{ij} - T\frac{\partial}{\partial T}\left[-n_3 g + RT\sum_{i=1}^{3} n_i ln\left(\frac{n_i}{n}\right) + \sum_{i<j}\sum\left(\frac{n_i n_j}{n}\right)\omega_{ij}\right] \tag{9}$$

$$= -n_3\left[g - T\left(\frac{\partial g}{\partial T}\right)_P\right] + \sum_{i<j}\sum\left(\frac{n_i n_j}{n}\right)\left[\omega_{ij} - T\left(\frac{\partial \omega_{ij}}{\partial T}\right)_P\right] \tag{10}$$

The expression for entropy of mixing SM can be obtained as [17],

$$S_M = n_3\frac{\partial g}{\partial T} - R\sum_{i=1}^{3} n_i ln\frac{n_i}{n} - \sum_{i<j}\sum\frac{n_i n_j}{n}\frac{\partial \omega_{ij}}{\partial T} \tag{11}$$

The equilibrium value of n_3 at a given pressure and temperature is given by

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,N,C} = 0 \tag{12}$$

Substituting the value of GM from Eq. 7 and after some algebraic calculation

$$ln\left(n_3 n^{u+v-1} n_1^{-u} n_2^{-v}\right) + Y = \frac{g}{RT} \tag{13}$$

which is the equilibrium equation, where

$$Y = \left[\frac{n_1 n_2}{n^2}(u+v-1) - u\frac{n_2}{n} - v\frac{n_1}{n}\right]\frac{\omega_{12}}{RT} + \left[\frac{n_2 n_3}{n^2}(u+v-1) - v\frac{n_3}{n} + \frac{n_2}{n}\right]\frac{\omega_{23}}{RT} + \left[\frac{n_1 n_3}{n^2}(u+v-1) - u\frac{n_3}{n} + \frac{n_1}{n}\right]\frac{\omega_{13}}{RT}$$

3. Results and Discussion

Ga-Zn system has a eutectic point at 3.7 wt% Zn and at temperature of 25°C. The hexagonal (Zn) terminal solid solution has a maximum solubility of 2.36 wt% Ga at 260°C, while the orthorhombic (Ga) solid solution has a maximum solubility of 0.8 wt% Zn at 20°C [9]. Available experimental data [18] on the thermodynamic

properties as well as phase diagram information [18] have been used for the calculation of the order energy parameters for the Ga-Zn liquid phase by the CFM in a weak approximation. For the given temperatures the Gibbs free energy are negative and exhibit a flat minimum of -0.567 at the composition, $c = 0.45$.]. Accordingly, the Ga-Zn compound was postulated as energetically less favored and the preferential arrangements of Ga and Zn constituent atoms does not so favor the formation of Ga-Zn complexes ($\mu = 1, v = 1$) in the liquid alloys. Keeping in mind the Ga-Zn phase diagram and the applications related to the different melting intervals of Ga-Zn alloys, all calculations have been done at T = 750 K. The optimized data set of the Gibbs energy of mixing of liquid Ga-Zn alloys together with the enthalpy of mixing and Ga and Zn activity data [18] have been used to calculate the interaction energy parameters at T =750 K. The calculated interaction energy parameters for liquid Ga-Zn alloy, expressed in RT units at T = 750 K are; $g = 0.721$, ω_{12} = -6.091, $\omega_{13} = 1.942$, $\omega_{23} = 1.808$

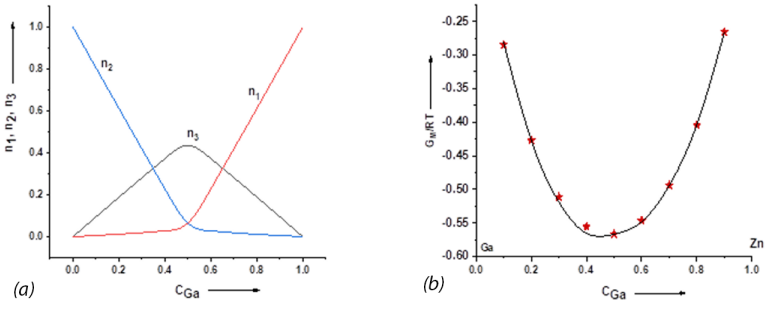

Figure 1. (a) Number of complexes (n_1, n_2, n_3) Vs concentration (c_{Ga}) of liquid Ga-Zn alloy at 750 K, (b) Free energy of mixing (GM/RT) Vs concentration (c_{Ga}) of liquid Ga-Zn alloy at 750 K [Theoretical(–) and experimental($\star$) values [18]].

Equilibrium relation Eq. 13 along with Eqs. 1 and 3 are used to compute the number of complexes, n_3, as a function of concentration. The values of interaction energy parameters are adjusted to give the concentration dependence of G_M which fits well with the corresponding thermodynamic data. The curves describing the Gibbs free energy of mixing of the Ga-Zn liquid phase are almost not symmetric with respect to the equiatomic composition. The concentration dependence of the equilibrium values of chemical complexes, n_3, at $T = 750K$ exhibits the symmetry at the same composition, $c = 0.5$, with the maximum value of about 0.4365 (Fig. 1). With an increase in temperature, the inter-atomic forces become weaker, and the corresponding maximum value of n_3 decreases. Using the order energy parameters calculated at $T = 750K$, the enthalpy of mixing, H_M and the entropy of mixing SM have been evaluated by Eqs. 10 and 11, respectively. The experimental data on the enthalpy of mixing measured at temperatures $T = 750K$ [18] have been used to calculate the variation in order energy parameters with temperature. The computed values of the derivatives are

$$\frac{1}{R}\frac{\partial g}{\partial t} = 1.224, \quad \frac{1}{R}\frac{\partial \omega_{12}}{\partial t} = 7.159, \quad \frac{1}{R}\frac{\partial \omega_{13}}{\partial t} = 0.444, \quad \frac{1}{R}\frac{\partial \omega_{23}}{\partial t} = 0.662 \tag{14}$$

A comparison between the calculated values of H_M and S_M by the CFM with the literature data [18] of liquid Ga-Zn alloy displays a good agreement between the two types of data (Fig. 2(a) and Fig. 2(b)).

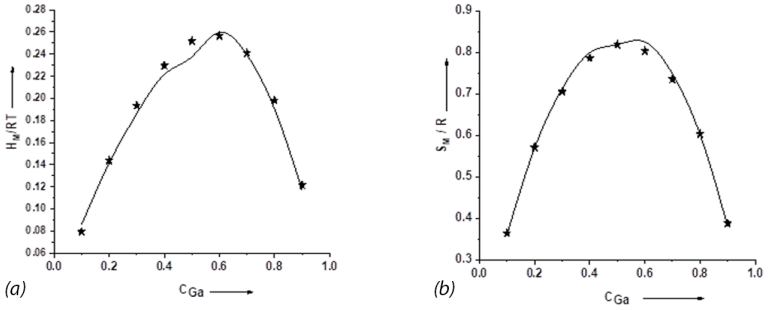

Figure 2. (a) Heat of mixing (H_M/RT), (b) Entropy of mixing (S_M/R) Vs concentration (c_{Ga}) of liquid Ga-Zn alloy at 750 K. [Theoretical(–) and experimental($\star$) values [18]]

4. Conclusions

Thermodynamic properties of Ga-Zn liquid alloy have been theoretically investigated by the CFM in a weak approximation. The thermodynamic data on mixing are used to obtain the interaction energy parameters, which are speculated to be invariant in all calculations. With the use same interaction parameters, the investigation of surface, transport and structural properties can be done further [14, 19–24]. The results obtained in the present work assure the applicability of this approach for a complete description of the thermodynamic of binary system which exhibit similar mixing properties. Moreover, it is found to be a useful tool in the interpretation of experimental results as well as in experimental planning.

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