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Structural Properties of Ga-Zn Liquid Alloys at 750 K by Molecular Interaction Volume Model

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Abstract

The Structural properties like concentration-concentration structure factor also known as concentration fluctuations and short-range order parameter of Ga-Zn liquid alloys at 750 K have been studied theoretically. The theoretical model employed is well known statistical mechanical model i.e. molecular interaction volume model (MIVM). The investigative expressions are utilized to explore the thermodynamic functions such as excess free energy of mixing, free energy of mixing and activity, and structural properties i.e. concentration fluctuations and short-range order parameter for Ga-Zn liquid alloys at 750 K. The theoretical data of thermodynamic functions and structural properties are found to be in well agreement with the corresponding experimental data available in the literature. The results show the segregating nature of Ga-Zn liquid alloys at 750 K.

Keywords: *MIVM model; concentration fluctuations; excess free energy of mixing; activity; short-range order parameter.*

1. Introduction

The Ga-Zn system is a eutectic alloy having it's melting point smaller than the melting point of pure Ga metal [1]. Therefore, Ga-Zn alloys have potential applications in electronic industries, computer chips, batteries, wearable sensors etc, as coolant material in nuclear industries [2, 3]. This led several investigators to study the thermophysical properties of Ga-Zn and GaZn-based ternary alloys such as Al-Ga-Zn, As-Ga-Zn, Ga-Zn-Sn etc [3, 4. 5, 6, 7].

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The Phase diagram [1] represents the segregating nature of Ga-Zn liquid alloys at 750 K because excess free energy of mixing, G_M^E and heat of mixing, H_M are positive [8] in the entire concentration region, x = 0.1 to 0.9. Again, G_M^E exhibits asymmetry while free energy of mixing, G_M indicates symmetry in Ga-Zn liquid alloys at 750 K. Therefore, Ga-Zn system is still an acceptable choice for the theoretical investigation.

In present investigation, MIVM model [9] has been employed for the assessment of the structural properties like concentration fluctuations, $S_{cc}(0)$ [10, 11] and short-range order parameter, α_1 [12, 13] on assuming the interaction between the constituent atoms. For this, the G_M^E, G_M, activity, $a_q(q = Ga \,\&\, Zn)$, $S_{cc}(0)$ and α_1 are deduced in the framework of MIVM model. The MIVM model [9] has been utilized successfully to study the thermodynamic behavior of several binary alloys like Zn-Bi, Ti-Al, Au-Cu, Au-Ni etc [14, 15, 16] and ternary alloys like Au-Sn-Bi, Au-Sn-Zn, Ag-Au-Cu etc [17, 18, 19].

2. Formalism

2.1 Structural properties like concentration–concentration structure factor, $S_{cc}(0)$ and short-range order parameter α_1 of binary liquid alloys

For the understanding of atomic interaction between the constituent atoms of a binary liquid alloy, the concentration fluctuations [20, 21] and α_1 [12, 13] play a vital role. In terms of free energy of mixing, G_M, the $S_{cc}(0)$ can be represented as [20]

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial x_i^2}\right)^{-1}_{T,P,N} = RT\left(\frac{\partial^2 G_M}{\partial x_j^2}\right)^{-1}_{T,P,N} \quad (1)$$

where, $G_M = G_M^E + G_M^{id}$ (2)

$$\Rightarrow G_M = G_M^E + RT\left[x_i \ln x_i + x_j \ln x_j\right] \quad (3)$$

with G_M^E = excess free energy of mixing of the binary liquid alloys. Using MIVM model [9], The expression for G_M^E is given by

$$\frac{G_M^E}{RT} = x_i \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}}\right) + x_j \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i A_{ji} lnA_{ji}}{x_i + x_j A_{ji}} + \frac{Z_j A_{ij} lnA_{ij}}{x_j + x_i A_{ij}}\right) \quad (4)$$

where, x_i and x_j = compositions of the metal i and j respectively, A_{ij} and A_{ji} = model parameters known as energy interaction parameters, Z_i and Z_j = coordination numbers in first shell for pure metal i and j respectively. The energy interaction parameters may be given by [7]

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$$A_{ji} = \exp\left[-\frac{\varepsilon_{ji}-\varepsilon_{ii}}{kT}\right] \text{ and } A_{ij}=\exp\left[-\frac{\varepsilon_{ij}-\varepsilon_{jj}}{kT}\right] \quad (5)$$

where, ε_{ii}, ε_{jj} and ε_{ji} stand represent potential energies for $i-i$, $j-j$ and $i-j$ pairs respectively, T and k represent absolute temperature and Boltzmann constant respectively. It is necessary to mention that $\varepsilon_{ij} = \varepsilon_{ji}$.

Equations (1), (3) and (4) provide

$$Scc(0) = \frac{x_i x_j}{1+x_i x_j f(x_i x_j)} \quad (6)$$

where,

$$f(x_i, x_j) = \frac{V_{mj}A_{ji}-V_{mi}}{x_i V_{mi}+x_j V_{mj}A_{ji}} + \frac{V_{mi}A_{ij}-V_{mj}}{x_j V_{mj}+x_i V_{mi}A_{ij}} + \frac{V_{mj}A_{ji}(V_{mj}A_{ji}-V_{mi})}{(x_i V_{mi}+x_j V_{mj}A_{ji})^2}$$
$$+\frac{V_{mi}A_{ij}(V_{mi}A_{ij}-V_{mj})}{(x_j V_{mj}+x_i V_{mi}A_{ij})^2}+\left[\frac{Z_i A_{ji}{}^2 \ln A_{ji}}{(x_i+x_j A_{ji})^3}+\frac{Z_j A_{ij}{}^2 \ln A_{ij}}{(x_j+x_i A_{ij})^3}\right] \quad (7)$$

For ideal solution, $G_M = G_M^{id}$ hence equations (6) and (7) yield

$$S_{cc}^{id}(0) = x_i x_j \quad (8)$$

Again, the $S_{cc}(0)$ can be represented in terms of activity [20] are represented by

$$S_{cc}(0) = a_i x_j \left(\frac{\partial a_i}{\partial x_i}\right)^{-1} = a_j x_i \left(\frac{\partial a_j}{\partial x_j}\right)^{-1} \quad (9)$$

The $S_{cc}(0)$ determined from equation (9) is regarded as experimental data of $S_{cc}(0)$ [8, 20] if the experimental data of activity is employed

It is pointed out that the positive deviation of $S_{cc}(0)$ from $S_{cc}^{id}(0)$ represents the ordered nature of the binary alloy i.e. dissimilar ($i-j$) atoms or molecules coupled together as the closest neighbors Similarly, the negative deviation of $S_{cc}(0)$ from $S_{cc}^{id}(0)$ refers to the segregating nature of the binary alloy i.e. dissimilar ($i-i$ or $j-j$) atoms or molecules link together as the closest neighbors [8].

The SRO in terms of $S_{cc}(0)$ is expressed as [8]

$$\alpha_1=\frac{S-1}{S(Z-1)+1} \text{ with } S=\frac{S_{cc}(0)}{S_{cc}^{id}(0)} \quad (10)$$

where, Z = coordination number in first neighbor shell.

Equation (10) illustrates that for segregating system, ordered system and ideal solution, α_1 may be positive, negative or zero respectively.

In MIVM model, the activity coefficients of pure metals i and j of a binary melt are respectively, expressed as

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$$\ln\gamma_i=\ln\left(\frac{V_{mi}}{x_iV_{mi}+x_jV_{mj}A_{ji}}\right)+x_j\left(\frac{V_{mj}A_{ji}}{x_iV_{mi}+x_jV_{mj}A_{ji}}-\frac{V_{mi}A_{ji}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right)-\frac{x_j^2}{2}\left(\frac{Z_iA_{ji}^2\ln A_{ji}}{\left(x_i+x_jA_{ji}\right)^2}+\frac{Z_jA_{ij}\ln A_{ji}}{\left(x_j+x_iA_{ij}\right)^2}\right) \tag{11}$$

and

$$\ln\gamma_j=\ln\left(\frac{V_{mj}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right)-x_i\left(\frac{V_{mj}A_{ji}}{x_iV_{mi}+x_jV_{mj}A_{ji}}-\frac{V_{mi}A_{ij}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right)-\frac{x_i^2}{2}\left(\frac{Z_jA_{ij}^2\ln A_{ij}}{\left(x_j+x_iA_{ij}\right)^2}+\frac{Z_iA_{ji}\ln A_{ji}}{\left(x_i+x_jA_{ji}\right)^2}\right) \tag{12}$$

For the element i, the first co-ordination number is calculated from the relation [7]

$$Z_i=\frac{4\sqrt{2\pi}}{3}\left(\frac{r_{mi}^3-r_{oi}^3}{r_{mi}-r_{oi}}\right)\rho_i r_{mi}\exp\left(\frac{\Delta H_{mi}(T_{mi}-T}{Z_CRT_{mi}}\right) \tag{13}$$

where, ΔH_{mi}, the enthalpy at melting temperature at T_{mi}, $\rho_i=N_iV_i=$ molecular number density = $\frac{0.6022}{V_{mi}}$, r_{mi} and r_{oi} = initial value as well as first peak value of radial distribution function for constituent i in liquid state near T_{mi}, R = molar gas constant and Z_C represents the co-ordination number for closed packed structure which is normally taken to be 12. The radial distances may be represented by

$$r_{oi}=0.918d_{\mathrm{cov},i} \text{ and } r_{mi}=\sigma_i \tag{14}$$

where, d_{cov} represents atomic covalent diameter and σ_i the atomic diameter.

In infinite dilute solution region like x_i or $x_j\to 0$, the activity coefficients of metals i and j may be given by [tao]

$$\ln\gamma_i^{\infty}=1-\ln\left(\frac{V_{mj}A_{ji}}{V_{mi}}\right)-\frac{V_{mi}A_{ji}}{V_{mj}}-\frac{1}{2}\left(Z_i\ln A_{ji}+Z_jA_{ij}\ln A_{ij}\right) \tag{15}$$

and

$$\ln\gamma_j^{\infty}=1-\ln\left(\frac{V_{mi}A_{ij}}{V_{mj}}\right)-\frac{V_{mj}A_{ji}}{V_{mi}}-\frac{1}{2}\left(Z_j\ln A_{ij}+Z_iA_{ji}\ln A_{ji}\right) \tag{16}$$

From activity coefficient the activity of the component i and j can be determined from the relations [8]

$$a_i=\gamma_ix_i \tag{17a}$$

$$a_j=\gamma_jx_j \tag{17b}$$

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3. Results and Discussions

3.1 G_M^E , G_M , activity, $a_q(q=i,j)$ of Ga-Zn melts at 750 K

The analytical equations for G_M^E, G_M, and activity, $a_q(q=i,j)$ are employed to assess the thermodynamic properties of Ga-Zn melts at 750 K. The necessary parameters related to pure Ga and Zn are presented in Table 1[22]. The z_i and z_j of Ga and Zn are determined from equation (6) which are presented in Table 2. The parameters A_{ji} and A_{ij} are evaluated on solving equations (15) and (16) simultaneously by Newton - Rapson method. The γ_i^∞ and γ_j^∞ i.e. infinite dilute activity coefficients for Ga and Zn are shown in Table 2[1]. The approximated values of A_{ji} and A_{ij} are slightly altered to acquire a good unison between the theory and experiment [1] for G_M^E of Ga-Zn melts at 750 K. The best fit values of A_{ji} and A_{ij} are also incorporated in Table 2.

Table 1 Required parameters for the pure metals [22]

Metal, i	ΔH_{mi} (KJ/mol)	σ_i (×10^{-8}cm)	r_{oi} (×10^{-8} cm)	V_{mi} (cm^3/mol)
Ga	5.59	2.78	2.38	11.4[1+0.92×10^{-4}(T-303)]
Zn	7.28	2.66	2.16	9.94[1+1.5×10^{-4}(T-693)]

Table 2 Estimated values of A_{ij} , A_{ji} , z_i and z_j for the constituents of Ga-Zn molten alloys at 750 K

$i-j$	T(K)	A_{ij}	A_{ji}	z_i	z_j	γ_i^∞	γ_j^∞
Ga-Zn	750	1.0835	0.8207	9.43	9.34	2.252	1.557

The Theoretical values of $\frac{G_M^E}{RT}$ and $\frac{G_M}{RT}$ calculated from equations (3) and (4) as a function of Ga for Ga-Zn alloys at 750 K show excellent agreement with the correlated experimental values [1] as illustrated in Fig. 1. In complete composition region, x_{Cd} = 0.1 to 0.9, the values of G_M^E are positive having maximum values i.e. 0.1306 (Theory) at x_{Ga} = 0.45 and 0.1276 (Experiment) at x_{Ga} = 0.4. Again, $\frac{G_M}{RT}$ is minimum at x_{Ga} = 0.50 i.e. - 0.5633 (Theory) and - 0.566 (Experiment). Hence, the present theoretical investigation successfully reveals the asymmetry in $\frac{G_M^E}{RT}$ and symmetry in $\frac{G_M}{RT}$ as well as segregating nature of Ga-Zn alloys at 750 K.

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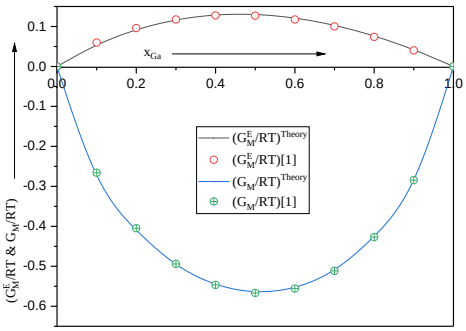

Fig. 1 (G_M^E/RT & G_M/RT) vs x_{Al} for Al-Sn alloy at 750 K

The activity coefficients γ_{Ga} and γ_{Zn} are evaluated from equations (11) and (12) respectively in terms of the concentration of Ga. The theoretical data of γ_{Ga} and γ_{Zn} are utilized to determine a_{Ga} and a_{Zn} respectively using equations (17a) and (17b) for Ga-Zn alloys at 750 K, which are shown in Fig. 2. A well harmony is noticed between theory and experiment [1]. The observed positive departures of a_{Ga} and a_{Zn} from ideal behavior [1] refers to the segregating nature of Ga-Zn alloys at 750 K. The similarity between theory and experiment provides the validity of A_{ji} and A_{ij} .

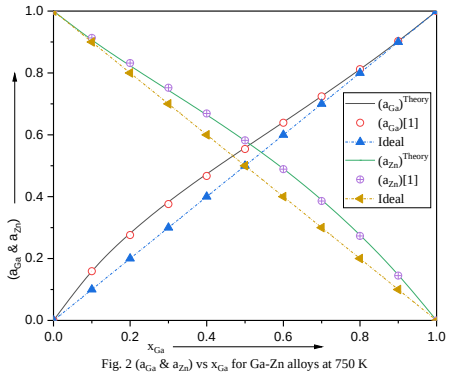

Fig. 2 (a_{Ga} & a_{Zn}) vs x_{Ga} for Ga-Zn alloys at 750 K

3.2 $S_{cc}(0)$, and α_1, of Ga-Zn liquid alloys at 750 K

The expressions (6) and (7) are employed to determine $S_{cc}(0)$ relative to the concentration of Ga for Ga-Zn alloys at 750 K. The theoretical data of $S_{cc}(0)$ are depicted in Fig. 3 along with $S_{cc}^{id}(0)$ and experimental values of $S_{cc}(0)$ [1]. A well uniformity is observed between the theory and experiment. It is noticed that $S_{cc}(0) > S_{cc}^{id}(0)$ in the complete composition region which indicates the segregation in Ga-Zn alloys at 750 K [8]. Again, both the theoretical and experimental values of $S_{cc}(0)$ are maximum at x_{Ga} = 0.5 i.e. 0.342 (Theory) and 0.336 (Experiment). Hence, the symmetric behavior of Ga-Zn alloys at 750 K is explained theoretically.

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Equation (10) is utilized to assess the concentration dependence of α_1 for Ga-Zn alloys at 750 K on using Z = 10. The theoretical data of α_1 relative to the concentration of Ga are presented in Fig 3. In whole range of composition i.e. x_{Ga} = 0.1 to 0.9, α_1 is positive at each composition and having maximum value of 0.0277 at x_{Ga} = 0.5 which indicates the segregation in Ga-Zn liquid alloys at 750 K [23].

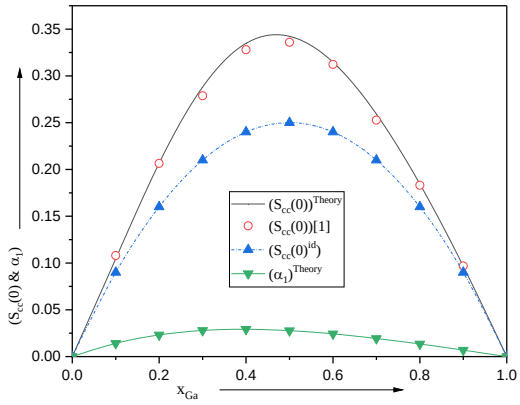

Fig. 3 ($S_{cc}(0)$ & α_1) vs x_{Ga} for Ga-Zn alloys at 750 K

4. Conclusions

In present work, the concentration dependent properties such as G_M^E, G_M, activity, $S_{cc}(0)$ and α_1 for Ga-Zn liquid alloys 750 K have been successfully explored. The results show the segregation in Ga-Zn melts at 750 K. The asymmetry in G_M^E, and symmetries G_M and $S_{cc}(0)$ for Ga-Zn melts at 750 K are successfully reproduced.

Therefore, MIVM model is an appropriate and reliable model to study the structural behavior of segregating liquid alloys.

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