Thermodynamics and surface properties of liquid Ga-X (X = Sn, Zn) alloys

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The mixing behaviour of Ga-Sn and Ga-Zn segregating alloy systems has been investigated by the Quasi-Chemical Approximation (QCA) in the frame of the Quasi-Lattice Theory (QLT) combined with a statistical mechanical theory. Assuming the order energy parameters as temperature dependent, various thermodynamic quantities are calculated at different temperatures. Thermodynamic properties of both systems deviate positively from the Raoult's law. The energetics of mixing in liquid alloys has been analysed through the study of surface properties (surface tension and surface composition) and microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter). Theoretical results are in a good agreement with the corresponding literature data and support a weak demixing tendency in Ga-Sn and Ga-Zn liquid alloys.
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1. Introduction

The Ga-Sn and Ga-Zn systems have been studied extensively as subsystems of different Ga-based multicomponent alloys applied in semiconducor industry. Thermodynamic and electrical properties of both systems have been considered by many authors, but only few articles are related to their surface properties and moreover, nun of them considered in detail intrinsic relation between the thermodynamic and surface properties.

The atomic interactions and the related energies of the bonds between the A and B constituent atoms of a binary alloy play a key role in elucidating the mixing behaviour of two metals. From this point of view the energetically preferred heterocoordinated A-B atoms as nearest neighbours over self-coordinated A-A and B-B, or vice versa lead to the alloy classification into either compound forming [1–8] or segregating binary alloys [9–12].

The Ga-Sn and Ga-Zn systems are characterised by a positive interaction energy, indicating the formation of two-phase structures, as shown by their simple eutectic phase diagrams [13]. Preliminary investigation of the Hume-Rothery empirical factors such as valence differences (=0; 1; 2 and =0; 1) [9], electronegativity difference (= −0.2 and =0) [14] and size ratio (=1.46 and 1.19) [15] for the Ga-Sn and Ga-Zn systems, respectively, indicate values that are characteristic for segregating alloys [9], but the decisive role can be attributed to the size ratio values, $V_{Sn}/V_{Ga} \approx 1.46$ and $V_{Ga}/V_{Zn} \approx 1.19$ that suggest a limited solubility in the solid state, and hence the presence of an eutectic reaction [16, 17]. The activities and the enthalpy of mixing of Ga-Sn and Ga-Zn molten alloys deviate positively from the ideal

values, and thus both alloy systems belong to the class of liquid alloys that exhibit a tendency towards segregation. The concentration dependence of thermodynamic and surface properties as well as the microscopic functions of liquid Ga-Sn and Ga-Zn alloys have been investigated by the Quasi-Chemical Approximation (QCA). For segregating alloys the size effects have an appreciable influence on their surface properties [9,16]. The magnitude of these effects increases together with a tendency of a system to phase separation. In the frame of the present formalism, a simple model developed by Prasad *et al.* has also been used to analyse the impact of size factors on the surface properties [18].

2. Theory

2.1. The QCA model: thermodynamic and surface properties

The generalised mathematical formalism treats an alloy as a pseudoternary mixture of *A* atoms, *B* atoms and $A_\mu B_\nu$ (μ and ν are small integers) group of atoms or clusters with the stoichiometry of intermetallics present in the solid state, all in chemical equilibrium with one another. The absence of clusters in the melt reduces the model to the QCA for regular solutions [3, 4]. The grand partition function for the bulk, Ξ^b, of a binary A-B alloy consisting of N_A (=NC_A) and N_B(=NC_B) atoms of elements A and B, respectively, where the total number of atoms, N, is equal to $N_A + N_B$, is expressed by:

$$\Xi^b = \sum_E q_A^{N_A}(T) q_B^{N_B}(T)$$
$$\times \exp[(\mu_A N_A + \mu_B N_B - E)/k_B T] \quad (1)$$

where $q_i^{N_i}(T)$ and μ_i are atomic partition function and chemical potential of i-th component ($i = A, B$), k_B is Boltzman's constant, T is the absolute temperature and E is the configurational energy of the alloy. The interface between a bulk liquid and its equilibrium vapour is reduced to a monolayer [19, 20] and the order energy, ω, is taken as an invariant property of the system. For the regular solution model, ω is expressed by:

$$\omega = Z\left[\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)\right] = a + bT \quad (2)$$

where ε_{ij}, i, $j = A$, B are bonding energies of $i - j$ bond, Z is the coordination number, a and b are the interaction energy parameters that can be calculated from thermodynamic data. Assuming the same type of packing for the atoms of the bulk and surface phases, the reduced coordination of the surface monolayer with respect to the bulk phase can be expressed in terms of the surface coordination fractions, p and q, defined as the fractions of the total number of nearest neighbours of an atom in its own layer and that in the adjoining layer. As a consequence, $p + 2q = 1$. For a closed-packed structure the values of these parameters usually are taken as 1/2 and 1/4, respectively [20]. Guggenheim demonstrated that the partition function approach from a statistical-mechanical theory and the QLT lead to similar results [20], as it was later confirmed by two models, i.e. "the surrounded atom" model, developed by Mathieu *et al.* [21] and "the central atom" model, introduced by Lupis and Eliot [22]. Both models have been developed in the frame of the QCA that takes into account the energies of the different configurations and the probabilities associated with them as well as the average atomic order effect. The liquid phase structure is described by the statistical entity of cluster formed by a central atom and its nearest neighbour shell [23]. A special case of the models mentioned above is the QCA for regular solution which assumes the additivity of pair wise interactions in the melt. This model describes quite well the mixing behaviour of liquid binary alloys in which the complex formation does not take place. In particular, for the bulk regular alloys, the solution of Equation 1 is given as the ratio of activity coefficients of alloy components, γ:

$$\ln \gamma = \frac{Z(1-C)}{2C} \cdot \frac{(\beta + 2C - 1)}{(\beta - 2C + 1)} \quad (3)$$

where the auxiliary variable β is defined by:

$$\beta = [4C(1-C)\exp(2\omega/Zk_BT) + (1-2C)^2]^{1/2} \quad (4)$$

with the interaction energy, ω, given in Equation 2. The activity coefficients can be easily obtained by the Fowler-Guggenheim method, as reported in [24, 25]:

$$\gamma_A = \left\{\frac{\beta - 1 + 2C}{C(1+\beta)}\right\}^{\frac{1}{2}Z} \quad (5)$$

$$\gamma_B = \left\{\frac{\beta + 1 - 2C}{(1-C)(1+\beta)}\right\}^{\frac{1}{2}Z} \quad (6)$$

Taking into account the basic thermodynamic relations for the excess Gibbs energy of mixing, G_M^{xs},

$$G_M^{xs} = RT(C \ln \gamma_A + (1 - C) \ln \gamma_B) \quad (7)$$

and the Gibbs energy of mixing, G_M:

$$G_M = G_{ID} + G_M^{xs} \quad (8)$$

as well as the entropy of mixing, S_M, given by:

$$S_M = -\left(\frac{\partial G_M}{\partial T}\right)_P \quad (9)$$

combined with other thermodynamic equations of the QLT-formalism [20], the enthalpy of mixing can be expressed by:

$$H_M = -\frac{8RTC^2(1-C)^2 \exp\left(\frac{2\omega}{Zk_BT}\right)}{(\beta - 1 + 2C)(1 + \beta)(\beta + 1 - 2C)}$$
$$\times \left(\frac{1}{k_B}\frac{d\omega}{dT} - \frac{\omega}{k_BT}\right) \quad (10)$$

The order energy parameters, a and b, can be calculated using the experimental data on the thermodynamic properties [11].

Once the grand partition function for the bulk is solved, it is possible to express the grand partition function for the surface, Ξ^s, in the same form as given in Equation 1 with the subscript and superscript s refer to the corresponding quantities of the surface phase. Under the hypothesis that the bulk and surface phases are in thermodynamic equilibrium ($\mu_i = \mu_i^s$), the surface tension for regular alloys can be obtained from:

$$\sigma = \sigma_A + \frac{k_BT(2 - pZ)}{2\alpha} \ln \frac{C^s}{C}$$
$$+ \frac{Zk_BT}{2\alpha}\left[p \ln \frac{(\beta^s - 1 + 2C^s)(1 + \beta)}{(\beta - 1 + 2C)(1 + \beta^s)}\right.$$
$$\left. - q \ln \frac{(\beta - 1 + 2C)}{(1 + \beta)C}\right] \quad (11a)$$

$$\sigma = \sigma_B + \frac{k_BT(2 - pZ)}{2\alpha} \ln \frac{(1 - C^s)}{(1 - C)}$$
$$+ \frac{Zk_BT}{2\alpha}\left[p \ln \frac{(\beta^s + 1 - 2C^s)(1 + \beta)}{(\beta + 1 - 2C)(1 + \beta^s)}\right.$$
$$\left. - q \ln \frac{(\beta + 1 - 2C)}{(1 + \beta)(1 - C)}\right] \quad (11b)$$

where β^s is the function obtained by Equation 4 substituting the bulk concentration C by the surface concentration C^s, σ_i, ($i = A$, B) are the surface tensions of pure components and α is the mean surface area of the alloy [26].

2.2. Microscopic functions

The extensive experimental material on densities and heat of formation of binary molten alloys allows to predict the dependence of fluctuation structure factors over the whole concentration range that is not easy accessible for the diffraction experiments [27]. The Bhatia-Thornton's formalism [28] makes it possible to visualize the nature of mixing and the degree of order in the melt in terms of chemical order [29] and segregation [9] by two microscopic functions. The first one, the concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, describes the nature of mixing of liquid alloys indicating chemical order and segregation [30] and it is also directly related to thermophysical properties [5, 9]. The $S_{cc}(0)$ can be expressed by G_M, or by the activity, a_i ($i = A, B$), as:

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

$$= C_B a_A \left(\frac{\partial a_A}{\partial C_A} \right)^{-1}_{T,P,N}$$

$$= C_A a_B \left(\frac{\partial a_B}{\partial C_B} \right)^{-1}_{T,P,N} \tag{12}$$

For ideal mixing the energy parameters, ω, given by Equation 2 is equalto zero, and Equation 12 becomes:

$$S_{cc}(0, id) = C(1 - C) \tag{13}$$

The mixing behaviour of liquid binary alloys can be deduced from the deviation of $S_{cc}(0)$ from $S_{cc}(0, id)$. The presence of chemical order is indicated by $S_{cc}(0) < S_{cc}(0, id)$; on the contrary, if $S_{cc}(0) > S_{cc}(0, id)$, the segregation and demixing in liquid alloys take place.

The degree of order and segregation in the melt can be quantified [31, 32] by the second microscopic function, the Warren-Cowley short-range order parameter, α_1. In the frame of QLT, the α_1 and $S_{cc}(0)$ are related to each other through the β-function (Equation. 4) [3]. The Warren-Cowley short-range order parameter, α_1, can be expressed also by the β-function (Equation 4), as:

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{14}$$

The parameter α_1 takes the values between -1 and 1; the negative values indicate the ordering in the melt, and complete ordering is manifested by $\alpha_1^{min} = -1$. On the contrary, positive values of α_1 indicate segregation, whereas the phase separation takes place if $\alpha_1^{max} = 1$.

3. Results and discussion

The Ga-Sn and Ga-Zn systems are characterised by low-melting eutectics at 8.5 at.% Sn and 3.7 at.% Zn, and at temperatures of 292 and 298 K, respectively [13]. To understand the energetics of Ga-Sn and Ga-Zn liq-uid alloys, their phase diagrams and various thermodynamic functions have been analysed. The optimised data set related to the excess Gibbs energy of mixing (G_M^{xs}) of Ga-Sn liquid phase [33, 34] together with the enthalpy of mixing [35], the Gibbs free energy of mixing [35, 36] and the activity experimental data [35, 36] are taken as input data to determine the interaction energy parameters, a and b. The calculations were performed over the whole concentration range at temperatures of 1000, 1073 and 1200 K and then the optimised values of interaction energy parameters are used to describe the same thermodynamic quantities as well as the surface properties at $T = 723$ K. In the case of the Ga-Zn system, the enthalpy of mixing [35, 37], the excess Gibbs energy of mixing (G_M^{xs}) of the liquid phase [38] as well as its optimised value [38, 39] and the activity data [35] are used to calculate the interaction energy of the system at temperatures of 1100, 950 and 723 K. For both the binary systems mentioned above, the thermodynamic data available in the literature are used to be directly inserted in the QLT-formalism [20, 24, 25]. In order to compare the mixing behaviour of these systems, the graphical presentation of thermodynamic quantities for both systems is given at 723 K (Figs 1–4). In particular, as concern the Ga-Sn system, for a comparison with literature data [40], some of results are also presented at $T = 1073$ K (Figs 1 and 3). For both systems the Gibbs free energy of mixing and the enthalpy of mixing curves (Figs 1 and 2) are almost symmetric around the equiatomic composition. Assuming the energetic term as an invariant of the system [3,4], the order energies, ω, for the Ga-Sn and Ga-Zn systems at $T = 723$ K have been calculated from the corresponding experimental data and their values in $k_B T$ units, are 0.57 and 0.54 respectively. For the metallic systems considered here the coordination number, Z, in the liquid phase was taken as 10 [20, 27]. A comparison between calculated and experimental values for these liquid alloys shows a good agreement between two types of data.
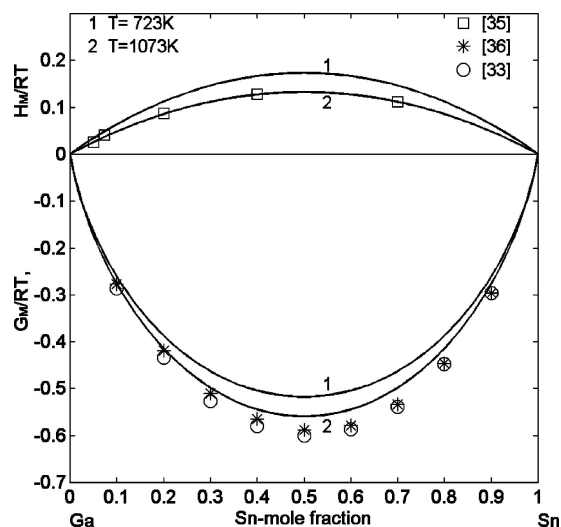

Figure 1 Concentration dependence of H_M/RT and G_M/RT for molten Ga-Sn alloys calculated at $T = 1073$ K together with experimental data [33, 35, 36] (curves no.1) and the extrapolted data at $T = 723$ K (curve no. 2).
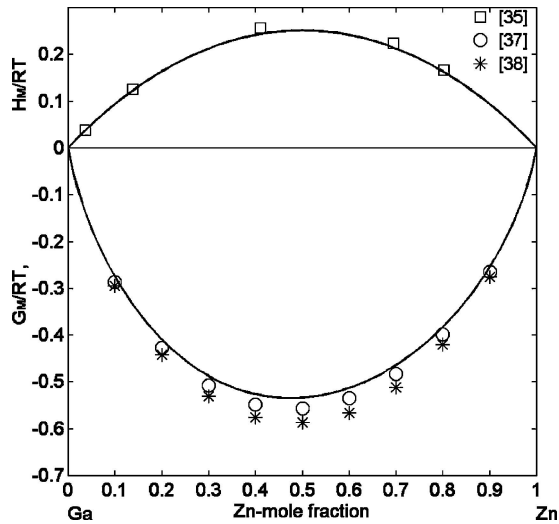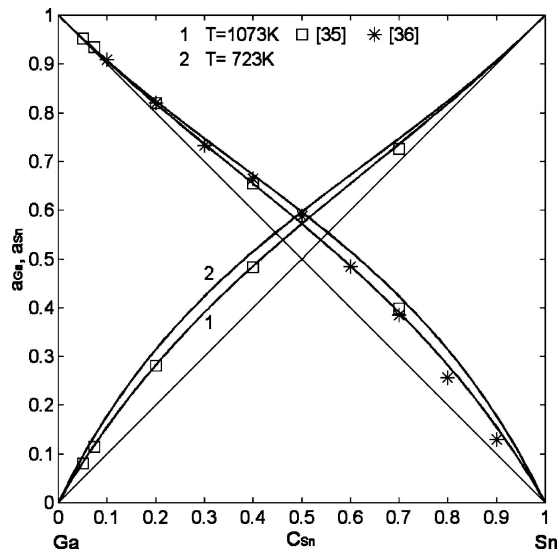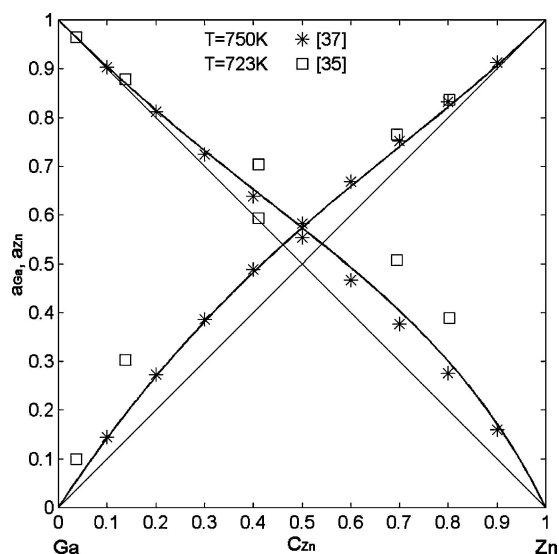
Figure 2 Concentration dependence of H_M/RT and G_M/RT for molten Ga-Zn alloys calculated at $T = 723$ K together with experimental data [35, 37, 38].

3.1. Surface properties: surface tension and surface segregation

Surface properties of Ga-Sn and Ga-Zn liquid alloys have been considered in the framework of QLT. Subtracting Equation 11b from Equation 11a, the obtained equation has been solved numerically with respect to the surface composition, C_i^s. The calculated values of surface composition suggest the segregation of Sn-atoms and Ga-atoms to the surface at all bulk concentrations of liquid Ga-Sn (Fig. 5) and Ga-Zn (Fig. 6) alloys, respectively. The same type of calculation was performed using the Prasad's model that takes into account the size ratio value [18]. The surface composition of the Ga-Sn system obtained by the Prasad's model exhibits more pronounced effect of this factor on the Sn-segregation (Fig. 5), that can be attributed to its larger value respect to that in the case of the Ga-Zn system (Fig. 6). The curves describing Ga-surface enrichment on Ga-Zn liquid alloys calculated by the QLT and by the
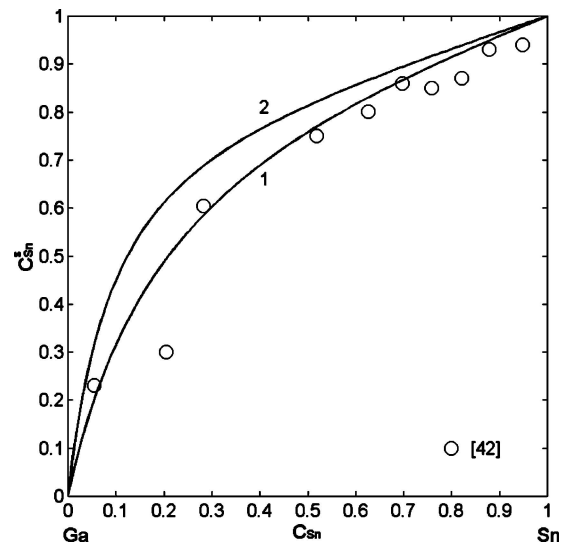

Figure 3 Concentration dependence of activities for molten Ga-Sn alloys calculated at $T = 1073$ K together with experimental data [35, 36] (curves no. 1) and the extrapolted data at $T = 723$ K (curve no. 2).

Figure 5 Surface composition (C_{Sn}^s) vs. bulk composition (C_{Sn}) for Ga-Sn liquid alloys at temperature $T = 723$ K and the experimental data measured by [42] at $T = 773$ K (1—the QCA; 2—Prasad's model).
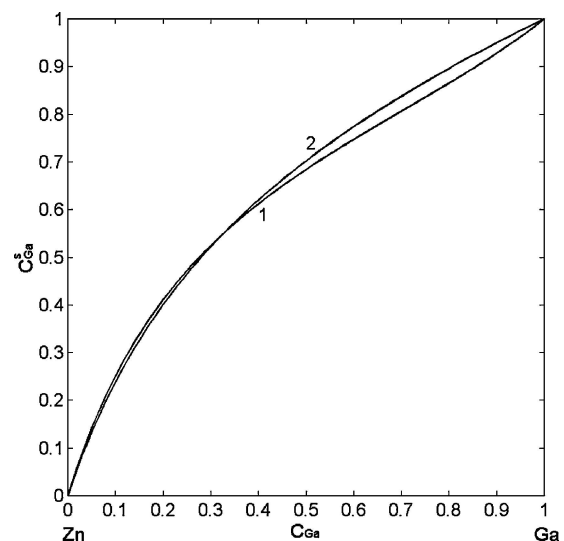

Figure 4 Concentration dependence of activities for molten Ga-Zn alloys calculated at $T = 723$ K together with experimental data [35, 37].

Figure 6 Surface composition (C_{Ga}^s) vs. bulk composition (C_{Ga}) for Ga-Zn liquid alloys at temperature $T = 723$ K (1 – the QCA; 2 – Prasad's model).

Prasad's model are very close to each other and differ slightly only for the compositions containing more than 40 at.% Ga (Fig. 6). The surface segregation of Sn in Ga-Sn liquid alloys has been experimentally investigated at $T = 623$ K [41] and $T = 773$ K [42], and the last data set is also comparable with our theoretical results, as it is shown in Fig. 5. Moreover, the present theoretical data computed at $T = 723$ K are slightly higher than the experimental results obtained at $T = 773$ K [42], this agrees with the fact that the extent of segregation decreases with an increase in temperature.

Reliable reference data for the surface tension of pure metals are the prerequisites that are necessary to predict correctly both the surface tension and surface composition of molten alloys. The large scatter among the surface tension experimental data reported in the literature [43] can be attributed to the presence of trace impurities, such as oxygen and sulphur that affects to a great extent the surface tension of liquid metals. Surface tension data of Ga, Sn and Zn were taken from Keene [43]. Once the surface composition, C_i^s, is known, the surface tension of Ga-Sn and Ga-Zn liquid alloys have been calculated by inserting these values into one of proposed equations, Equations 11a or 11b. The surface tension isotherms of the Ga-Sn system computed at $T = 723$ K by the QLT and by the Prasad's model [18] are shown in Fig. 7 together with the literature experimental data [44, 45]. The size effects on the surface tension and surface segregation are reciprocal, and thus the surface tension isotherm obtained by [18] is lower than that calculated by the QLT, confirming the previous considerations related to the Sn-segregation on the surface of Ga-Sn melts. As shown in Fig. 7, the literature surface tension data agree better with the corresponding data calculated by the Prasad's model. The agreement between two experimental sets seems to be good over the whole concentration range, except for the surface tension data related to the Sn-rich alloys and pure Sn.

As concerns Ga-Zn alloy system, the size effects on its surface properties can be neglected and the surface tension was calculated at $T = 723$ K only by the QLT. Theoretical results together with the surface tension ex-
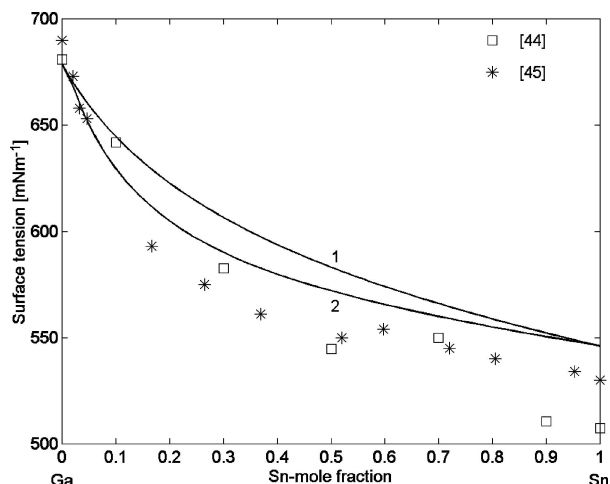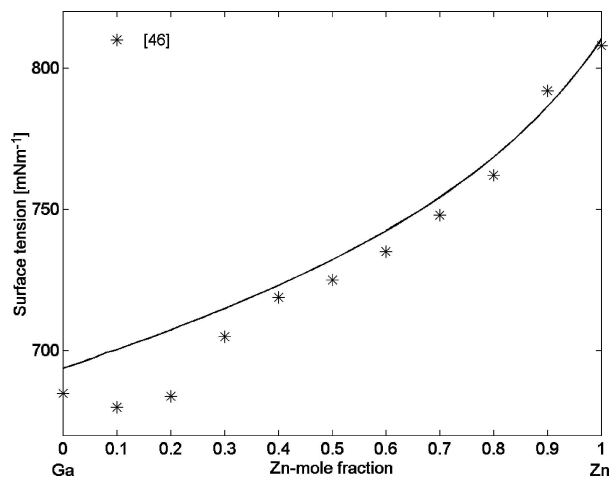

Figure 8 Surface tension of Ga-Zn liquid alloys calculated by the QCA at $T = 723$ K.* refers to experimental data [46].

perimental data [46] are given in Fig. 8, exhibiting a good agreement over the whole concentration range, except the surface tension data of the Ga-rich alloys and pure Ga.

3.2. Microscopic functions: concentration fluctuations in the long-wavelength limit and chemical short-range order parameter

The ordering phenomena in both systems, Ga-Sn and Ga-Zn have been analysed by concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, and CSRO parameter, α_1, as functions of bulk compositions. The excess Gibbs energy terms, G_M^{xs}, for the Ga-Sn, [33] and Ga-Zn [38,39] liquid alloys combined with corresponding experimental data [35,36] and [35,37], respectively, were used to calculate their Gibbs energies of mixing, G_M, at $T = 723$ K, and consequently these data were used in Equation 12 for calculations of the $S_{cc}(0)$. In order to verify the reliability of order energy parameters, $\omega = a + bT$, (Equation 2), and taking the second equation for the $S_{cc}(0)$ calculations using the activity (Equation 12), the microscopic functions related to the Ga-Sn and Ga-Zn systems were also calculated by this equation, exhibiting very small differences between the theoretical curves obtained by (Equation 12). The deviation of the $S_{cc}(0)$ from its ideal values, $S_{cc}(0, id)$ (Equation 13) is used as an indicator to determine the mixing tendency in binary alloys expressed in terms of ordering or segregation.

The $S_{cc}(0)$ values for the Ga-Sn system at $T = 723$ K (Fig. 9) clearly indicate that $S_{cc}(0) > S_{cc}(0, id)$ in the whole concentration range. This implies a tendency for homocoordination, i.e. like atoms Ga-Ga and Sn-Sn tend to pair as nearest neighbours. The $S_{cc}(0)$ curve exhibits the maximum value of about 0.347 at $C_{Sn} = 0.54$. The position of maximum coincides with that reported by [40], obtained by the Self Aggregating Model (SAM), having the lower value of about 0.31, as calculated at $T = 1073$ K. Similar $S_{cc}(0)$ behaviour was observed for the Ga-Zn liquid phase, with the $S_{cc}(0)$ values (Fig. 10) close to those of the Ga-Sn system. The
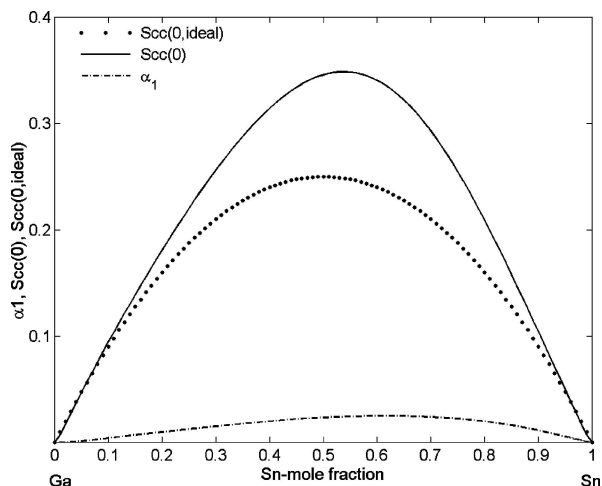

Figure 7 Surface tension of Ga-Sn liquid alloys at $T = 723$ K. □,* refer to experimental data [44, 45], respectively (1 – the QCA; 2 – Prasad's model).

Figure 9 Concentration fluctuations in the long-wavelength limit ($S_{CC}(0)$ and $S_{CC}(0, id)$) and Chemical short-range order parameter (α_1) vs. bulk composition (C_{Sn}) of liquid Ga-Sn alloys at $T = 723$ K.

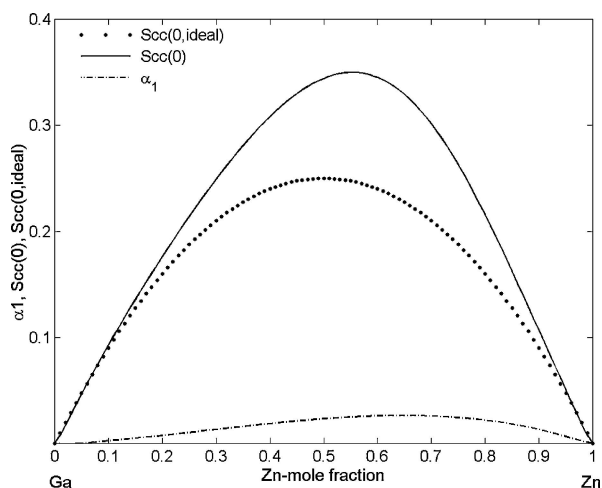*Figure 10* Concentration fluctuations in the long-wavelength limit ($S_{CC}(0)$ and $S_{CC}(0, id)$) and Chemical short-range order parameter (α_1) vs. bulk composition (C_{Zn}) of liquid Ga-Zn alloys at $T = 723$ K.

positive values of the Warren-Cowley short range order parameter, α_1, for the Ga-Sn (Fig. 9) and Ga-Zn (Fig. 10) melts support a tendency of both systems towards segregation.

4. Conclusion

The mixing behaviour of Ga-Sn and Ga-Zn liquid alloys have been analysed by the two models: the QCA, which does not take into account the effect of size factor on surface properties and the Prasad's model with the size effect. For segregating alloys, such as the Ga-Zn system, having the size ratio value close to 1, the effects of size on their mixing properties can be neglected. On the contrary, for the segregating systems such as the Ga-Sn, with the size ratio of 1.5 or higher, the size effect on mixing behaviour becomes significant and its contribution must be considered. Thermodynamic and surface properties as well as the microscopic functions of Ga-Sn and Ga-Zn liquid alloys indicate a weak demixing tendency in both systems, as described reasonably well by the QCA.

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