Thermodynamic and surface properties of Ge-Ga and Ge-Sb liquid alloys

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Thermodynamic and surface properties of Ge–Ga and Ge–Sb liquid alloys have been studied using statistical mechanical formulations based on complex formation and that based on the concept of layered structure near the interface. The study showed that low level of complex formation of the form Ge_2Sb exists in Ge–Sb toward the Ge-rich end of the concentration range and the surface properties of Ge–Ga are almost equal to their corresponding bulk equivalent.

Keywords: Liquid alloys; Surface properties

1. INTRODUCTION

The activities of Ge–Ga and Ge–Sb liquid alloys show very slight departures from Raoult's law at low concentration of Ge. This behaviour may lead to a quick assumption that the thermodynamic properties of these alloys may not be too far from one another and their behaviours may be close to ideal. Close examination of other thermodynamic quantities for these alloys shows that while Ge–Ga exhibited symmetry in its free energy of mixing and heat of mixing, Ge–Sb shows slight departure from symmetry in its free energy of mixing and manifests a positive heat of mixing which is asymmetrical about equiatomic composition. From the behaviour of the thermodynamic quantities for these alloy systems, it can be said that though the activities of Ge–Sb alloys are very close to ideal, their general thermodynamic behaviour is far from ideal to be of interest. It becomes worthwhile therefore to seek for a greater understanding of the thermodynamic properties of these alloys and their relative influence on the surface properties of the alloys, knowing that these alloys are of interest due to their potential applications in the semiconductor industry.

Some theoretical and experimental studies on the thermodynamic properties of Ge–Ga and Ge–Sb had been carried out by some authors [1–5]. These studies had focused more on the determination of the thermodynamic properties and calculation

of phase diagrams for these alloys. However, the studies had not incorporated the study of local order and estimation of surface properties in the alloys. Surface properties have become a subject of interest to many authors [6–8], this is likely because the study of surface properties leads to a better understanding and improvement on metallurgical processes and material design. In addition, surface studies lead to a better understanding of surface-related phenomena such as heterogeneous catalysis, epitaxial growth, corrosion and wettability at solder joints.

The statistical formulations of Prasad *et al*. [9] based on the concept of layered structure near the interface for the determination of surface properties gave a link between surface properties and the bulk thermodynamic properties of liquid metallic binary alloys. The expression obtained relates the surface tension of the liquid binary alloy to the activity coefficient of the alloy components in the bulk. Interestingly, these formulations determine surface properties not from energetics and factors based on geometry only but also has as input valuable thermodynamic data such as the activity coefficient of the alloy components in the bulk. The obvious implication of this is that it is possible to observe the effect of bulk thermodynamic properties on surface properties.

In this article, we employ the quasi chemical model [10] to describe the thermodynamic properties observed in the Ge–Ga and Ge–Sb liquid alloys. This will be extended to determine the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ and the chemical short range order (CSRO) in the alloys. The activity coefficients and energetics determined from the thermodynamic calculations will be used in the formulation of Prasad *et al*. to estimate the surface properties of these alloys. In addition to giving an insight into the surface behaviour of these alloys, this study will reveal to a large extent the large disparities in the properties of these alloys whose activities appear very close in value at higher Ge concentration.

In the section that follows, the basic equations for the calculations are outlined. Section 3 discusses the thermodynamic properties of the alloys. The results of the calculations on surface properties are given in Section 4 and conclusions are presented in Section 5.

2.   THEORETICAL CONCEPTS

The fundamental idea about the quasi chemical model is that the thermodynamic properties of a compound forming A–B alloy can be explained by treating the alloy as pseudo ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes. Details of the formulations are given in [10].

The excess free energy of mixing G_m^{es} is related to the free energy G_m by the expression,

$$G_m^{es} = G_m - RT[x \ln x + (1-x)\ln(1-x)] \tag{1}$$

here, x is the concentration of atom A, and R is the universal gas constant. The quasi chemical expression for the excess free energy of mixing G_m^{es} is given as:

$$\frac{G_m^{es}}{RT} = z \int_0^x [\ln \sigma + (2kT)^{-1}(P_{aa}\Delta\epsilon_{aa} - P_{bb}\Delta\epsilon_{bb})]dx + \psi \tag{2}$$

where z is the co-ordination number, k, the Boltzman constant and $\ln \sigma$ is

$$\ln \sigma = \frac{1}{2} \ln \frac{(1-x)(\beta + 2x - 1)}{x(\beta - 2x + 1)} \tag{3}$$

with

$$\beta = [1 + 4x(1-x)(\eta^2 - 1)]^{1/2} \tag{4}$$

and

$$\eta^2 = \exp\left(\frac{2w}{zkT}\right) \exp\left(\frac{2P_{ab}\Delta\epsilon_{ab} - P_{aa}\Delta\epsilon_{aa} - P_{bb}\Delta\epsilon_{bb}}{kT}\right) \tag{5}$$

w, $\Delta\epsilon_{ab}$, $\Delta\epsilon_{aa}$, $\Delta\epsilon_{bb}$ are the interaction parameters with w denoting the interchange energy and $\Delta\epsilon_{ij}$ being the change in the energy if the ij bond is in the complex $A_\mu B_\nu$. P_{ij} denotes the probability that the bond is part of the complex and the expressions are given as follows:

$$P_{ab} = x^{\mu-1}(1-x)^{\nu-1}[2 - x^{\mu-1}(1-x)^{\nu-1}] \tag{6}$$

$$P_{aa} = x^{\mu-2}(1-x)^{\nu}[2 - x^{\mu-2}(1-x)^{\nu}], \quad \mu \geq 2 \tag{7}$$

$$P_{bb} = x^{\mu}(1-x)^{\nu-2}[2 - x^{\mu}(1-x)^{\nu-2}], \quad \nu \geq 2 \tag{8}$$

The constant ψ is determined from the requirement that $G_m = 0$ at $x = 1$.

The heat of mixing H_m is obtained from the equation

$$H_m = G_m + TS_m \tag{9}$$

where $S_m = -(\partial G_m/\partial T)_p$ is the entropy of mixing. Considering the interaction parameters as temperature dependent, the derivative of the excess free energy of mixing becomes

$$\frac{1}{R}\frac{\partial G_m^{es}}{\partial T} = z \int_0^x \left[\ln \sigma + T\frac{\partial}{\partial T}\ln \sigma + \frac{1}{2k}\left(P_{aa}\frac{\partial\Delta\epsilon_{aa}}{\partial T} + P_{bb}\frac{\partial\Delta\epsilon_{bb}}{\partial T}\right)\right]dx + \psi \tag{10}$$

where,

$$\frac{\partial}{\partial T}\ln \sigma = \frac{1}{\sigma^2}\left[\frac{(1-x)(1-2x)(\partial\beta/\partial T)}{x(\beta - 2x + 1)^2}\right] \tag{11}$$

and

$$\frac{\partial\beta}{\partial T} = \left[2x(1-x)\frac{\partial\eta^2}{\partial T}\right]\beta^{-1} \tag{12}$$

and

$$\frac{\partial \eta^2}{\partial T} = \frac{2\eta^2}{zkT^2}[z(-2P_{ab}\Delta\epsilon_{ab} + P_{aa}\Delta\epsilon_{aa} + P_{bb}\Delta\epsilon_{bb}) - w]$$
$$+ \frac{2\eta^2}{zkT}\left[z\left(2P_{ab}\frac{\partial\Delta\epsilon_{ab}}{\partial T} - P_{aa}\frac{\partial\Delta\epsilon_{aa}}{\partial T} - P_{bb}\frac{\partial\Delta\epsilon_{bb}}{\partial T}\right) + \frac{\partial w}{\partial T}\right] \quad (13)$$

The activities of the metals are obtained by

$$a_m = x\gamma_m \quad (14)$$

where x is the concentration of the species and γ_m is its activity coefficient given by

$$\gamma_m = \left\{\frac{\beta - 1 + 2x}{x(1 + \beta)}\right\}^{(1/2)z} \quad (15)$$

where β is as defined in Eq. (4).

The concentration–concentration fluctuations in the long wavelength limit $S_{cc}(0)$ has been shown to be given by

$$S_{cc}(0) = x(1 - x)\left\{1 + \frac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \Omega\right\}^{-1} \quad (16)$$

where Ω is the expression given below

$$\Omega = \frac{zx(1 - x)}{2\beta kT}\Theta \quad (17)$$

and

$$\Theta = \left[2(1 - 2x)P'_{ab}\Delta\epsilon_{ab} + (\beta - 1 + 2x)P'_{aa}\Delta\epsilon_{aa} - (\beta + 1 - 2x)P'_{bb}\Delta\epsilon_{bb}\right] \quad (18)$$

where the prime on P denotes the first derivative with respect to x. The Warren–Cowley [11,12] short range order parameter α_1 for the first nearest neighbours is expressed as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \quad (19)$$

In the model for studying surface properties, a statistical mechanical approach which derives from the concept of a layered structure near the interface was used by Prasad et al. [9] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension σ by the expression

$$\Xi^s = \exp\left(\frac{-A\sigma}{kT}\right) = \exp\left(\frac{-N^s\sigma\xi}{kT}\right) \quad (20)$$

where A is the surface area and ξ is the mean area of the surface per atom and is defined as $\xi = A/N^s$, and N^s is the total number of atoms at the surface. k is the Boltzmann constant.

Prasad *et al.* [9] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\sigma = \sigma_A + \frac{kT}{\xi} \ln \frac{x_A^s}{x_A} - \frac{kT}{\xi} \ln \gamma_A + [p(x_B^s)^2 + q(x_B)^2] \frac{w}{\xi} \tag{21}$$

$$\sigma = \sigma_B + \frac{kT}{\xi} \ln \frac{x_B^s}{x_B} - \frac{kT}{\xi} \ln \gamma_B + [p(x_A^s)^2 + q(x_A)^2] \frac{w}{\xi} \tag{22}$$

where σ_A and σ_B are surface tension values for the pure components A and B respectively. x_i and x_i^s are the bulk and surface concentrations of the alloy components respectively. γ_A and γ_B are the bulk activity coefficients of the alloy components. w is the interchange energy.

The surface $S_{cc}(0)$ can be written as [9]

$$S_{cc}^s(0) = x_A^s x_B^s \left[1 + \left(\frac{z^s}{2\beta^s} \right)(1 - \beta^s) \right]^{-1} \tag{23}$$

where

$$\beta^s = \left\{ 1 + 4x_A^s x_B^s \left[\exp\left(\frac{2w}{z^s kT} \right) - 1 \right] \right\}^{1/2} \tag{24}$$

Here, z^s is the coordination number of the surface atoms which is obtained from $z^s = (p + q)z$ and z is the coordination number in the bulk.

3. RESULTS AND DISCUSSIONS ON THERMODYNAMIC PROPERTIES

To apply the quasi chemical model to the liquid alloys Ge–Ga and Ge–Sb using the activity data, free energy of mixing and heat of mixing data, the expressions to be used are already given in the previous section. Next, the interaction parameters for each of the alloys have to be determined. Here the interaction parameters of interest include w, $\Delta\epsilon_{ab}$, $\Delta\epsilon_{aa}$, $\Delta\epsilon_{bb}$ and their derivatives $\partial w/\partial T$, $\partial\Delta\epsilon_{ab}/\partial T$, $\partial\Delta\epsilon_{aa}/\partial T$ and $\partial\Delta\epsilon_{bb}/\partial T$. Suitable values of μ and ν which predict the complexes formed were chosen from conjectures or based on phase diagrams where available. The equation for the activity, free energy of mixing and heat of mixing were solved and the interaction parameters were fine tuned such that they reproduce simultaneously and to a reasonable extent the experimental activity, free energy of mixing and heat of mixing. In this work, there are no formed compounds indicated in the phase diagrams of Ga–Ge and Ga–Sb [13], hence the values of μ and ν were taken from conjecture. The values of μ and ν and their corresponding interaction parameters which reproduced simultaneously to a reasonable extent the measured free energy of mixing,

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heat of mixing and the activity for the alloys Ge–Ga and Ge–Sb at a temperature of 1273 K are given in Table I.

Figures 1a, 2a and 3 give the plots of the calculated values of activity, free energy of mixing and heat of mixing respectively for Ge–Ga liquid alloy. The points are experimental values derived from [5] for activity and free energy of mixing while the data for the heat of mixing were obtained from [3]. It is obvious from the figures that the calculated values reproduced fairly well the measured thermodynamic data of the

TABLE I   Interaction parameters for the Ge–Ga and Ge–Sb liquid alloys

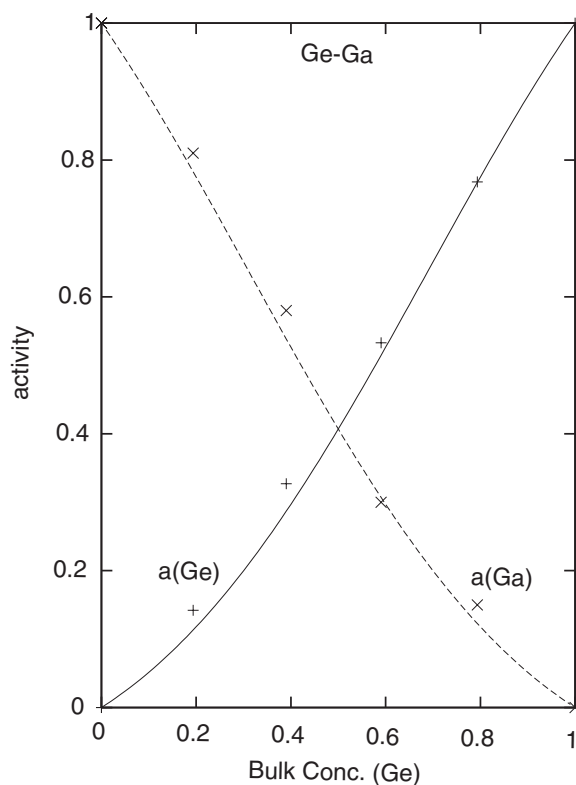|	μ	v	w/kT	$\Delta\epsilon_{ab}/kT$	$\Delta\epsilon_{aa}/kT$	$\Delta\epsilon_{bb}/kT$	$1/kT \times \partial w/\partial T$ (K^{-1}) $(\times 10^{-4})$	$1/kT \times \partial\Delta\epsilon_{ab}/\partial T$ (K^{-1}) $(\times 10^{-6})$	$1/kT \times \partial\Delta\epsilon_{aa}/\partial T$ (K^{-1}) $(\times 10^{-5})$	$1/kT \times \partial\Delta\epsilon_{bb}/\partial T$ (K^{-1})
Ge–Ga	1	1	−0.81	0.00	0.00	0.00	−4.50	0.00	0.00	0.00
Ge–Sb	2	1	−0.83	0.02	−0.16	0.00	−6.50	−7.00	−5.00	0.00

FIGURE 1   (a) Activity *vs* Bulk Conc. of Ge for Ge–Ga liquid alloy. Solid lines represent calculated activity values for Ge. (- - -) represents calculated activity values for Ga. (+++) represents experimental activity values for Ge at 1273 K. (× × ×) represents experimental activity values for Ga at 1273 K; (b) Activity *vs* Bulk Conc. of Ge for Ge–Sb liquid alloy. Solid lines represent calculated activity values for Ge. (---) represents calculated activity values for Sb. (+++) represents experimental activity values for Ge at 1273 K. (× × ×) represents experimental activity values for Sb at 1273 K.
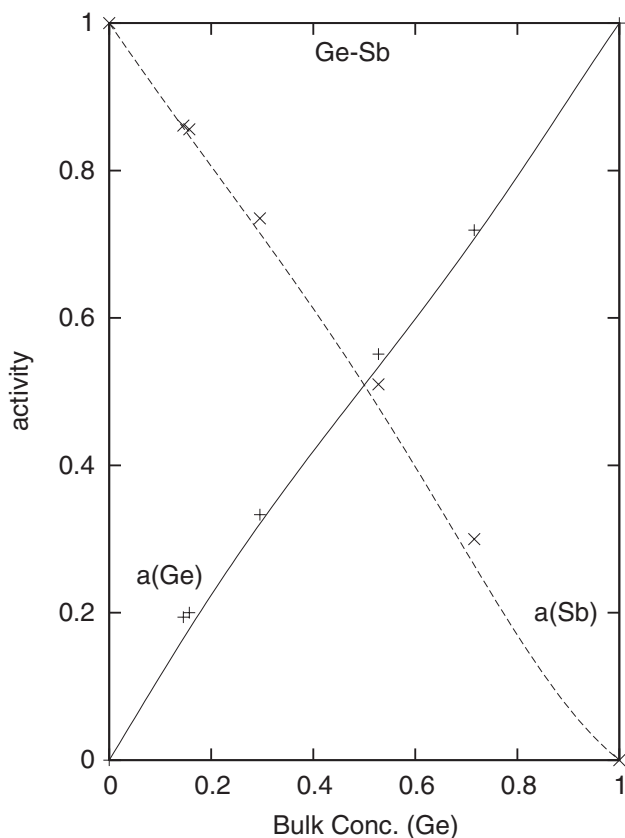
FIGURE 1   Continued.

alloy at the given temperature. These thermodynamic quantities for Ge–Ga were repro-
duced by assuming a regular alloy configuration for the melt with $\mu = 1$ and $\nu = 1$.
Under this condition, all the interaction parameters become zero except for w
and $\partial w/\partial T$. The Gibb's free energy of mixing and heat of mixing for the Ge–Ga
liquid alloys showed perfect symmetry about equiatomic concentration and with the
interaction parameters given in Table I, the measured values were reproduced almost
perfectly. This justifies the assumption of a regular alloy configuration for the alloy.

On the other hand, Figs. 1(b), 2(b) and 3 show the plot for the activity, free energy of
mixing and heat of mixing for Ge–Sb alloy. The experimental data for activity and free
energy of mixing were derived from [5] while the experimental data for heat of mixing
was obtained from [3]. The assumption of a regular alloy configuration was unable to
reproduce simultaneously the measured thermodynamic data. However, an assumption
of the existence of the complex of the form Ge_2Sb which gives that $\mu = 2$ and $\nu = 1$, not
only reproduced simultaneously and to a reasonable extent the measured thermody-
namic values for the alloy but it also reproduced the asymmetry observed in the meas-
ured values of free energy of mixing and heat of mixing as can be observed from the
figures. It can therefore be inferred that though no form of compounds were suggested
in the liquid phase of Ge–Sb phase diagrams [13], some level of interactions strong
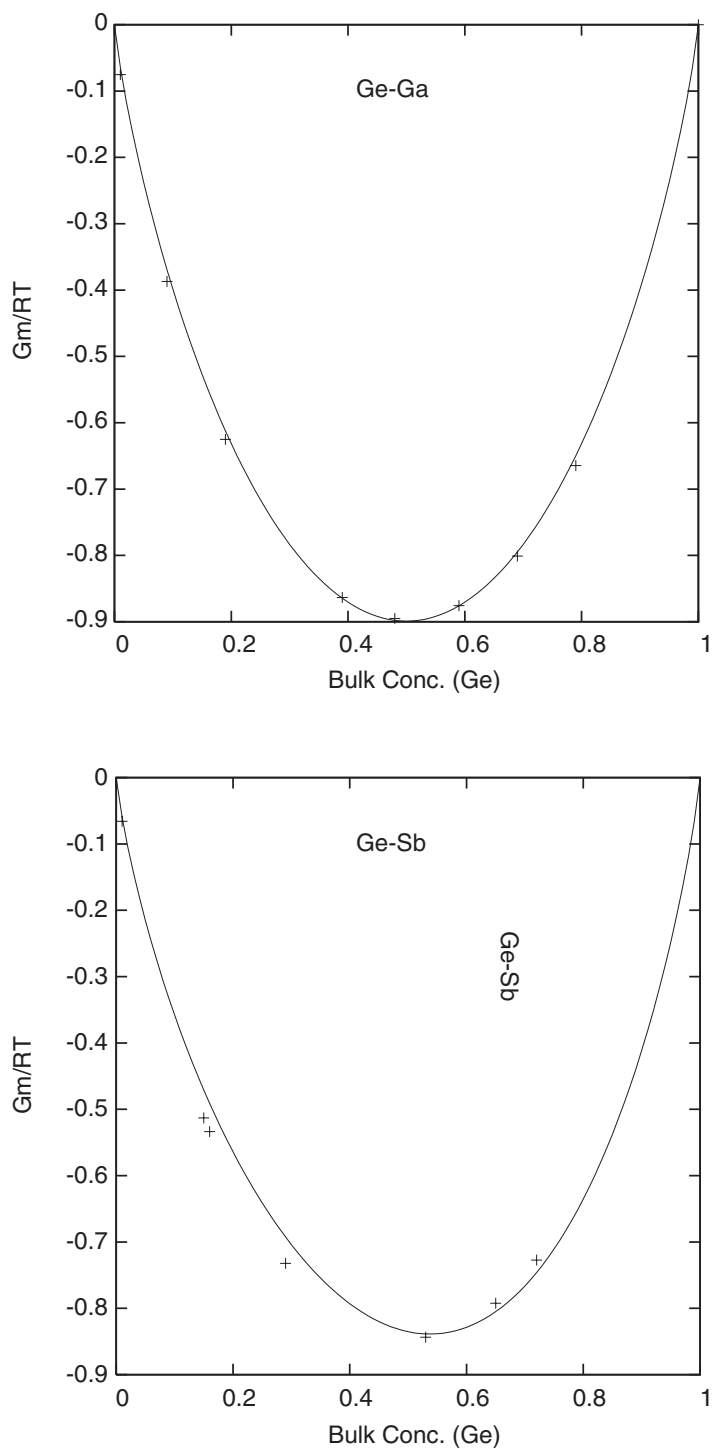enough to influence thermodynamic properties exist in the liquid alloy.

FIGURE 2   (a) *Gm/RT vs* Bulk Conc. of Ge for Ge–Ga liquid alloy. Solid lines represent calculated values. Points represent experimental values at 1273 K; (b) *Gm/RT vs* Bulk Conc. of Ge for Ge–Sb liquid alloy. Solid lines represent calculated values. Points represent experimental values at 1273 K.
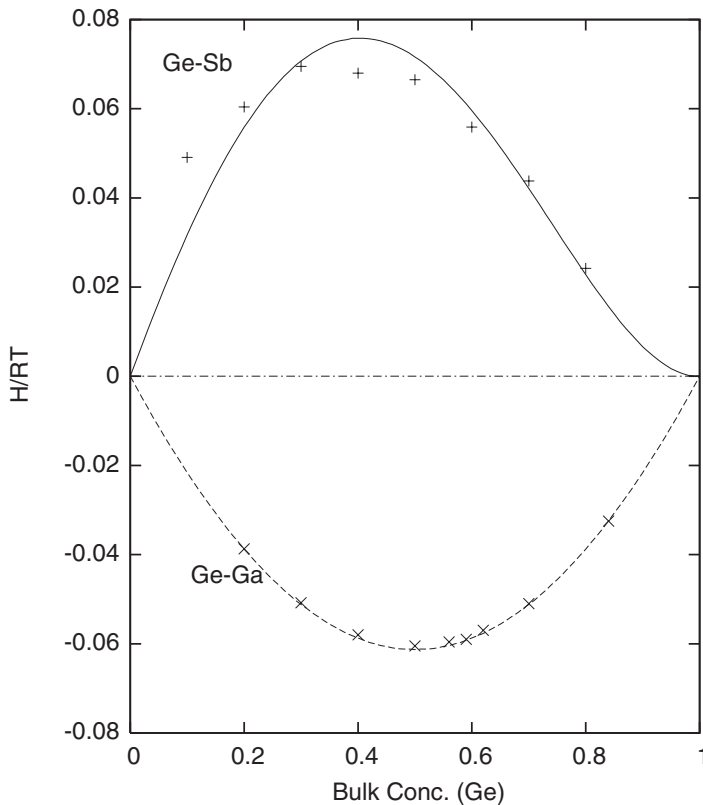
FIGURE 3 H/RT *vs* Bulk Conc. of Ge for Ge–Ga and Ge–Sb liquid alloys. Solid lines represent calculated values for Ge–Sb. (- - -) represents calculated values for Ge–Ga. (+ + +) represents experimental values for Ge–Sb at 1273 K. (× × ×) represents experimental values for Ge–Ga at 1273 K.

To investigate the extent of interactions, the phenomenon of ordering, and the strength of any complexes formed in the liquid alloys, the quantities of interest are the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ and the Warren–Cowley short range order parameter α_1. The expressions for the $S_{cc}(0)$ and α_1 using the quasi chemical model has been derived in [10] and given in equation (16) and (19) respectively. The same interaction parameters which reproduced fairly well the activity, free energy of mixing and heat of mixing data were used in the calculation of the $S_{cc}(0)$ and α_1. The experimental $S_{cc}(0)$ can be derived from measured thermodynamic data by using the relation

$$S_{cc}(0) = \frac{RT}{(\partial^2 G_m/\partial x^2)} \tag{25}$$

which is further simplified as

$$S_{cc}(0) = \frac{x(1-x)}{x(\partial \ln \gamma_m/\partial x) + 1} \tag{26}$$

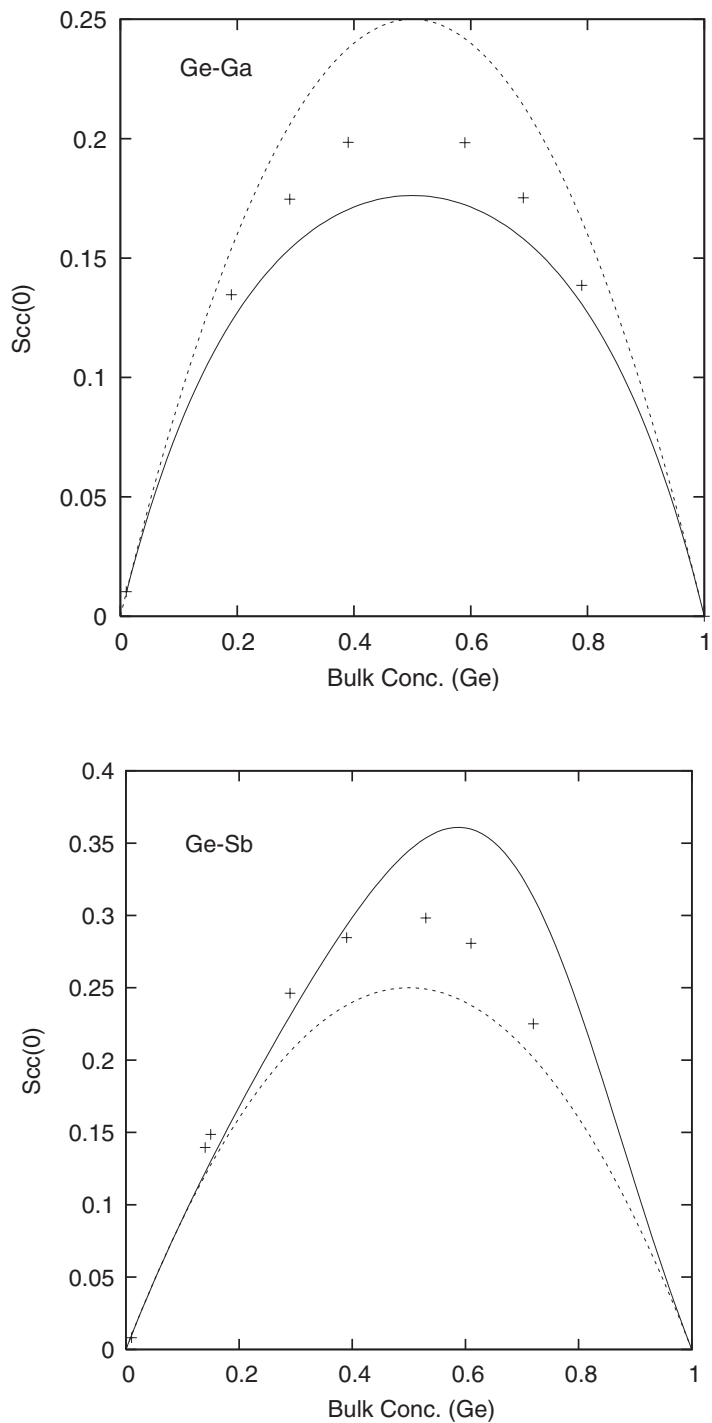where γ_m is the activity coefficient for the alloy component.

FIGURE 4   (a) Bulk $S_{cc}(0)$ *vs* Bulk Conc. of Ge for Ge–Ga liquid alloy. Solid lines represent calculated values. (+++) represents experimental values. (- - -) represents ideal values; (b) Bulk $S_{cc}(0)$ *vs* Bulk Conc. of Ge for Ge–Sb liquid alloy. Solid lines represents calculated values. (+++) represents experimental values. (- - -) represent ideal values.
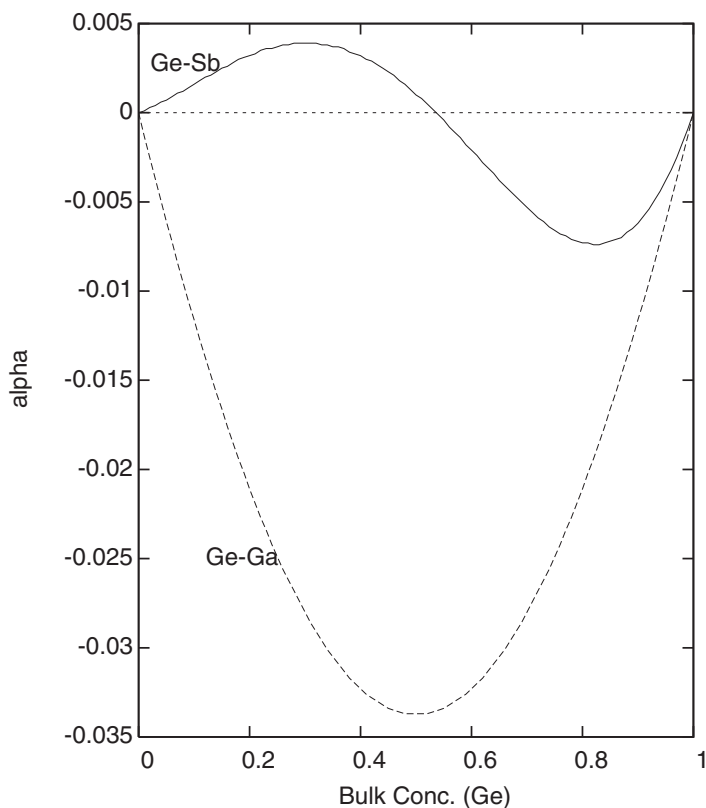
FIGURE 5 α_1 *vs* Bulk Conc. of Ge for Ge–Ga and Ge–Sb liquid alloys. Solid lines represent calculated values for Ge–Sb. (- - -) represents calculated values for Ge–Ga.

The calculated and experimental $S_{cc}(0)$ for Ge–Ga and Ge–Sb are shown in Fig. 4(a) and (b) respectively. The $S_{cc}(0)$ for Ge–Ga still showed full symmetry about equiatomic concentration. The calculated values showed an underestimation of the experimental $S_{cc}(0)$. For Ge–Sb, the calculated values showed an overestimation of the experimental $S_{cc}(0)$. In general, the $S_{cc}(0)$ values showed that Ge–Ga has a tendency to heterocoordination while Ge–Sb to homocoordination. However, when the values of the $S_{cc}(0)$ are compared to the ideal values, it can be said that the levels of interactions in these alloys are low. The Warren–Cowley short range order parameter α_1 gives more insight into the level of interaction. It should be noted that for complete ordering or heterocoordination α_1 has a value of -1 and for complete phase segregation or homocoordination, the value of α_1 is $+1$. Figure 5 gives the values of the calculated α_1 for both alloys. The Ge–Ga alloy is ordered throughout the concentration range. The level of order is relatively low with $\alpha_1^{\min} \approx -0.034$ at about the equiatomic concentration. Ge–Ga liquid alloy can thus be considered to have an almost even distribution of alloy components. On the other hand, α_1 for Ge–Sb showed segregation tendency with $\alpha_1^{\max} \approx 0.004$ at the lower concentration of Ge and some level of order with $\alpha_1^{\min} \approx -0.007$ at higher concentration of Ge. This low level of order suggests that the Ge–Sb liquid alloy is not phase segregating throughout the composition range, however the assumed complex Ge_2Sb exists in very small amount at the Ge-rich end.

4.   RESULTS AND DISCUSSION ON SURFACE PROPERTIES

The surface compositions and surface tensions of Ge–Ga and Ge–Sb were computed numerically from the expressions in Eqs. (21) and (22). The activity coefficients for the A and B atoms for each alloy were computed from the expression in Eq. (14) using the energy parameters given in Table I. The surface coordination fractions p and q are taken as those for close-packed structures with $p = 0.5$ and $q = 0.25$ for all the systems considered. The surface tension (σ_i) and atomic volume (Ω_i) at the melting temperatures of the components of the alloy systems were taken from [14], (where i denotes the components A or B of the alloy). However, to obtain the surface tension and atomic volumes at the working temperature of 1273 K for Ge–Ga and Ge–Sb, the relationship on the temperature dependence of surface tension and atomic volume as given in [15] are used

$$\sigma_i = \sigma_{im} + (T - T_m)\frac{\partial \sigma_i}{\partial T} \qquad (27)$$

and

$$\Omega_i = \Omega_{im}[1 + \theta(T - T_m)] \qquad (28)$$

where θ is the thermal coefficient of expansion, Ω_{im}, σ_{im} are the atomic volumes and surface tension of the alloy components at their melting temperature T_m and T is the working temperature in Kelvin. The values of $\partial \sigma_i/\partial T$ and θ for the pure alloy components were obtained from [14]. The atomic surface area ξ_i for each atomic species of the different alloy systems was calculated following the relation [16]

$$\xi_i = 1.102\left(\frac{\Omega_i}{N}\right)^{2/3} \qquad (29)$$

and the mean surface area ξ is then given as

$$\xi = \sum_i x_i \xi_i \qquad (30)$$

where N is Avogadro number and x_i are the concentrations of the alloy components.

Figure 6 shows the plot of surface concentration of Ge against its bulk concentration for Ge–Ga and Ge–Sb liquid alloys. The plot for Ge–Ga is almost a straight line. This implies that the concentration of Ge in the bulk of Ge–Ga liquid alloy is almost equal to the concentration of Ge at the surface. A direct deduction from this is that the properties of Ge–Ga in the bulk is not too different from its properties at the surface. The plot for Ge–Sb liquid alloy showed that for every bulk concentration, there are more Ga atoms present at the surface. There is no incidence of complete segregation to the surface by the atoms of any of the alloy components.

The calculated surface tension values for Ge–Ga and Ge–Sb are shown in Fig. 7. There are no experimental values of surface tension for these alloys at present to compare with the calculated values. The surface tension values for Ge–Ga alloy shows a
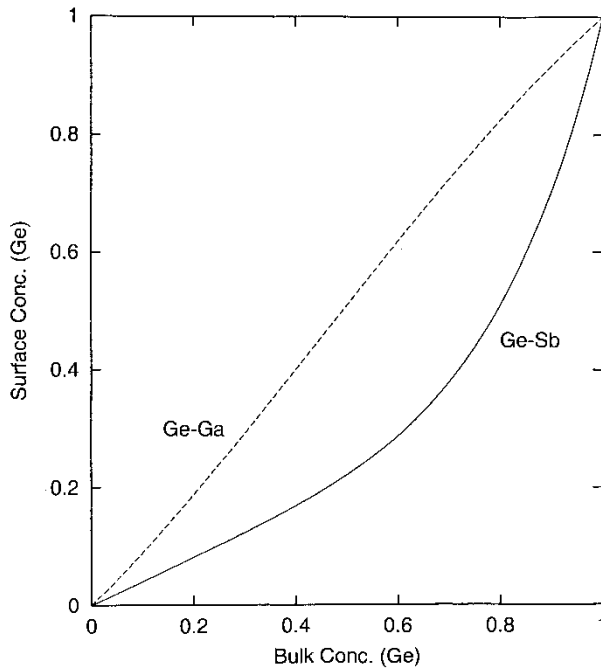
FIGURE 6 Surface Conc. of Ge *vs* Bulk Conc. of Ge for Ge–Ga and Ge–Sb liquid alloys. Solid lines represent calculated values for Ge–Sb. (- - -) represents calculated values for Ge–Ga.
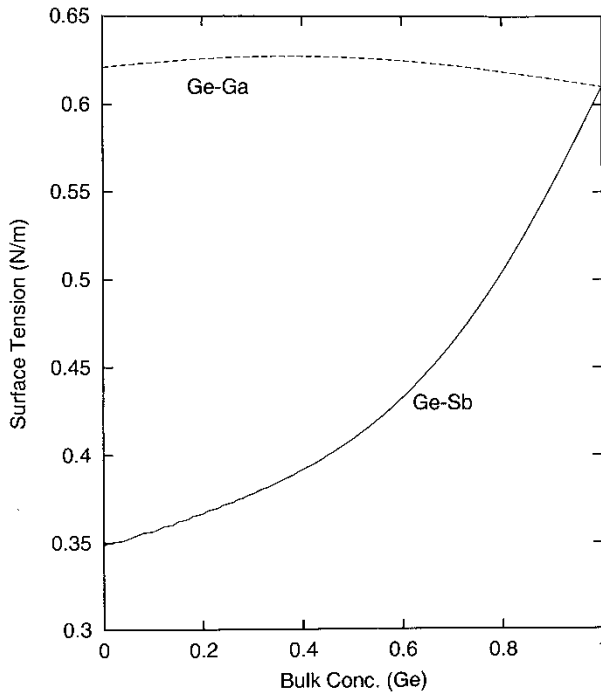

FIGURE 7 Surface tension *vs* Bulk Conc. of Ge for Ge–Ga and Ge–Sb liquid alloys. Solid lines represent calculated values for Ge–Sb. (- - -) represents calculated values for Ge–Ga.
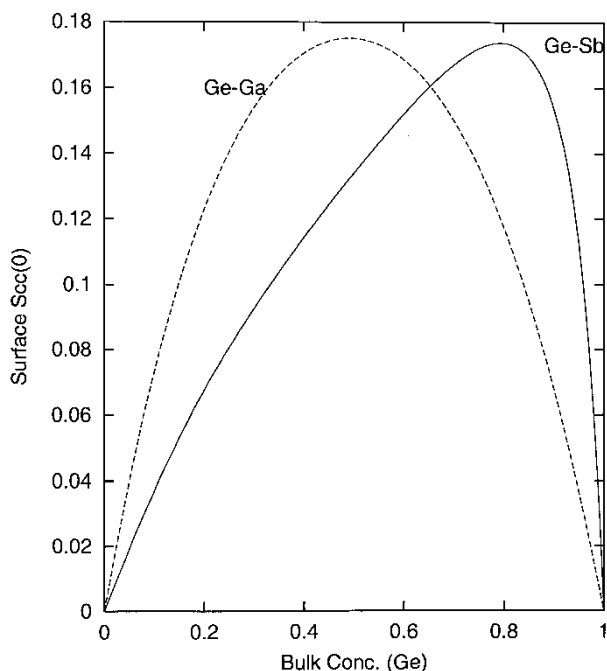
FIGURE 8   Surface $S_{cc}(0)$ *vs* Bulk Conc. of Ge for Ge–Ga and Ge–Sb liquid alloys. Solid lines represent calculated values for Ge–Sb. (- - -) represents calculated values for Ge–Ga.

slight increase from the value of the surface tension of pure Ga before decreasing gradually to the surface tension value of pure Ge. The curve only shows relatively little departure from ideal hence supporting the regular alloy behaviour of Ge–Ga. On the other hand, the surface tension curve for Ge–Sb shows clear departure from ideal behaviour.

The surface concentration fluctuation at the long wavelength limit $S_{cc}^s(0)$ for the two alloys are shown in Fig. 8. It is of interest to note that the surface $S_{cc}^s(0)$ for Ge–Ga is symmetric about equiatomic composition and is almost equal to the bulk $S_{cc}(0)$. This to a large extent confirms that the properties of Ge–Ga in the bulk is almost equal to its properties at the surface. However, while the surface $S_{cc}^s(0)$ for Ge–Sb tilts towards the Ge-rich side as was also observed in the bulk $S_{cc}(0)$, its magnitude is far lower than the values in the bulk.

5.   CONCLUSION

The study of the thermodynamic and surface properties of Ge–Ga and Ge–Sb shows that Ge–Ga has the properties of a regular alloy and its surface properties are very close to the bulk properties. On the other hand, the thermodynamic properties of Ge–Sb liquid alloy can be described by assuming the presence of some compounds of the form Ge_2Sb. This compound must be dilute and probably exists towards the Ge-rich end.

Acknowledgements

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