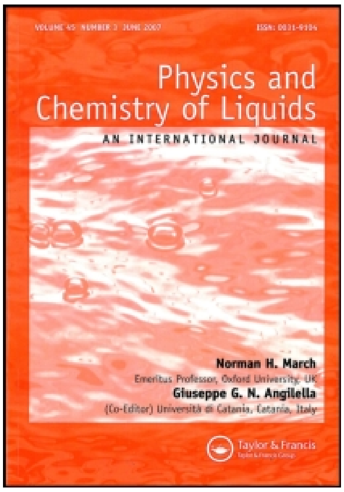

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Ordering Phenomena in Na-Ga and Na-Sn Molten Alloys

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ORDERING PHENOMENA IN Na–Ga AND Na–Sn MOLTEN ALLOYS

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The quasilattice approximation (QLA) has been applied to study the alloying behaviour of Na–Ga and Na–Sn molten alloys by assuming the formation of complexes of the form Na_5Ga_8 and Na_4Sn_3. This has been used to obtain the concentration dependence of the free energy of mixing, the long wavelength limit of the concentration–concentration fluctuations and the ordering parameter α_1.

Our calculations yield for both alloys, qualitative agreement with experiment about the concentrations at which phase separation or compound formation occurs in the alloy. In the case of Na–Ga, however, because of the relatively large asymmetry in the concentration dependence of its free energy of mixing and possibly the nature of the complex chosen, the calculated results when compared with experiment are not as good as that for Na–Sn.

For Na–Ga, we have also calculated the higher order conditional probabilities using the four atom cluster model (FACM) this has made it possible to calculate another value for α_1. A comparison of the two values of α_1 computed, enables us to obtain better insight to the limit of applicability of each of the models.

KEY WORDS: Activity, chemical complexes, concentration fluctuations, ordering.

1 INTRODUCTION

The study of thermodynamic quantities and by extension ordering phenomena has engaged the attention of physicists for the past few years. These investigations were initially mainly from the point of view of experiment[1] and theoretical formulations/models[2–5]. In recent times, computer simulations[6] have further helped to gain more insight into the problem.

For binary alloys, severe limitations in explaining results usually come up in situations were there is formation of complexes and ideally one has to seek recourse to computationally more demanding methods like the Car-Parrinello[7] type of simulations. The present paper is an attempt to explain ordering phenomena in Na–Ga and Na–Sn alloys using the Bhatia-Hargrove[2] model put in a more tractable form by Singh[3]. The model has been used to a large extent[8–11] in explaining the thermodynamic properties of molten alloys with considerable success.

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The distinct idea of the model is that one can understand some essential thermodynamic properties of binary molten alloys using information obtainable about the long wavelength limit of the concentration–concentration structure factor $S_{cc}(0)$ and conditional probabilities calculated therefrom. Na–Ga and Na–Sn alloys exhibit some features which make them interesting from a theoretical viewpoint. Their pecularities are as follows;

For Na–Ga, as far as one is aware, the study of most of its electronic properties are not very extensive in the literature. EMF measurements have been made, however[12], and they indicate that this alloy system behaves anomalously, its entropy of mixing is negative over a considerable part of its concentration range and its free energy of mixing G_M/RT is asymmetric with a minimum at $C_{\mathrm{Na}} = 0.385$ corresponding to the most stable solid compound $\mathrm{Na_5Ga_8}$. The activities of sodium and gallium a_{Na} and a_{Ga} have also been measured and are reported in the paper.

Furthermore, the experimentally determined $S_{cc}(0)$ vs. concentration curve for Na–Ga molten alloys shows a strong tendency for phase separation over most of its concentration range. Because of the above mentioned points, it seems clear that the application of an empirical, well tested method to its thermodynamics would be worthwhile.

In the case of Na–Sn on the other hand, experimental measurements abound in the literature on a lot of its electronic properties like thermopower[13], Knight shift[14], magnetic susceptibility[15], stability function[16], resistivity[21] and *ab-initio* molecular dynamic simulations[7] of its structure.

All these experiments however indicate an important face which is that there is still a lot of controversy about the most prominent complex to describe the alloy though $\mathrm{Na_4Sn_3}$[13] appears to be the most stable form at temperatures above the liquidus.

We have applied the quasilattice approximation QLA to obtain interaction parameters, chosen to reproduce experimental G_M/RT values and have computed its concentration dependence for Na–Ga and Na–Sn alloys. The interaction parameters have further been used to compute $S_{cc}(0)$ and the Warren-Cowley short-range order parameter α_1 for the alloys.

α_1 can also be obtained from a knowledge of conditional probabilities[17,18]. Here what one does is to enumerate the occupation of neighbouring sites by the atoms of the constituents in the compound-forming liquid alloy. A two atom cluster model (TACM) consisting of atoms interacting via pairwise interaction was first used by Singh and Mishra[19] to obtain the excess free energy of mixing, concentration fluctuations and the chemical short-range order parameters for some liquid metals.

More recently Singh[17] has extended the above idea to the four atom cluster model (FACM) with a view to obtaining higher order conditional probabilities encompassing atomic distributions in nearest neighbour shells. The FACM unlike the QLA depends on only one parameter ω (the order energy) which has also been used for calculating surface properties[20].

Calculation of α_1 using the FACM requires a knowledge of the activity ratio a_B/a_A where A and B are the individual components of the alloy AB. Since the values are available for Na–Ga alloys[12], we have computed α_1 for it and compared the result from FACM with that of QLA in an attempt to assess the limit of applicability of each model.

The present paper thus has the following layout. In Section 2, we summarise the essential equations required for the application of the QLA and the FACM; in Section 3.1 we discuss our results of the QLA as applied to Na–Ga and Na–Sn by assuming the existence of the complexes Na_5Ga_8 and Na_4Sn_3 respectively. In Section 3.2 we make a comparison of results for FACM and QLA as applied to Na–Ga molten alloys. In the final section we make some concluding remarks.

2 THE MODELS AND THEIR FORMULATION

In the present section, we shall give summaries of essential parts of each model sufficient to perform the calculations. For more details, one can obtain information on the quasilattice/Bhatia-Hargrove approximations from Ref. [2–3] while a more detailed discussion of the FACM is given in Ref.[17].

2.1 *The Quasilattice Approximation (QLA)*

This quasilattice approximation starts by assuming that the properties of an A–B alloy can be treated theoretically if one considers it to be a pseudoternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes, μ and ν being relatively small numbers all in chemical equilibrium with one another and with the atoms located on lattice sites. One can then assume that in general, the binary alloy contains in all N atoms, of which Nc are A atoms and $N(1-c)$ are B atoms. On the assumption of chemical complexes $A_\mu B_\nu$, the binary alloy can be assumed to consist of n_1 individual A atoms, n_2 individual B atoms and n_3 complexes. From the conservation of atoms, one has

$$n_1 = Nc - \mu n_3, \quad n_2 = N(1-c) - \nu n_3 \tag{1}$$

and $n = n_1 + n_2 + n_3 = N - (\mu + \nu - 1)n_3$. The Gibbs free energy of mixing of the binary alloy can be expressed as

$$G_M = -n_3 g + RT\left[n_1 \ln\left(\frac{n_1}{N}\right) + n_2 \ln\left(\frac{n_2}{N}\right) + n_3 \frac{(\ln(\mu+\nu)n_3)}{N}\right] + \sum_{i<j}\sum n_i n_j V_{ij}/\mathrm{N} \tag{2}$$

In Eq. (2), the first term $-n_3 g$ represents the lowering of the free energy of mixing due to the formation of complexes $A_\mu B_\nu$, with g representing the free energy of formation of the complex. The V_{ij}'s$(i, j = 1, 2, 3)$ are average interaction energies and by definition independent of concentration, although they may depend on temperature and pressure.

The equilibrium values of n_3 at a given temperature and pressure is obtained from the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,N,c} = 0. \tag{3}$$

From Eqs. (2) and (3), the equilibrium value of n_3 is given by the equation

$$n_1^{\mu} n_2^{\nu} = (\mu + \nu) n_3 e^{-(\mu+\nu-1)} e^{(Y - g/RT)} N^{\mu+\nu-1}, \tag{4}$$

where

$$Y = \frac{[(n_1 - \mu n_3)V_{13} + (n_2 - \nu n_3)V_{23} - (\mu n_2 + \nu n_1)V_{12}]}{NRT}. \tag{5}$$

Within the model, the concentration-concentration fluctuations in the long wavelength limit $S_{cc}(0)$, by definition, is given by the expression

$$S_{cc}(0) = \frac{RT}{(\partial^2 G_M / \partial c^2)_{T,P,N;}} \tag{6}$$

this can be expressed for this approximation as[3]

$$S_{cc}(0) = \left[\sum_{i=1}^{3} (n_i')^2/n_i + 2/RT \sum_{i<j}\sum n_i' n_j' V_{ij}\right]^{-1}, \tag{7}$$

where n_i' in Eq. (7) refers to the derivative of n_i with respect to c.

A measure of the tendency to compound formation or phase separation in a molten alloy is given by the Warren-Cowley short-range order parameter (α_1)[22,23]. This is an important indicator of the degree of ordering in a binary alloy. For nearest neighbour sites α_1 can be defined as:

$$\alpha_1 = 1 - \frac{P_{AB}}{(1-c)}, \tag{8}$$

where P_{AB} is the conditional probability of finding a B atom nearest to a given A atom. It can easily be shown that the limiting values of α_1 lie in the range.

$$\frac{-c}{1-c} \leqslant \alpha_1 \leqslant 1 \quad c \leqslant \frac{1}{2} \tag{9}$$

$$\frac{-(1-c)}{c} \leqslant \alpha_1 \leqslant 1 \quad c \geqslant \frac{1}{2} \tag{10}$$

For equiatomic composition ($c = 1/2$), one has $-1 \leqslant \alpha_1 \leqslant 1$. The minimum possible value of α_1 i.e. $\alpha_1^{\min} = -1$ represents the complete ordering of pairs of nearest neighbour atoms in the A–B configuration whereas $\alpha_1^{\max} = +1$ suggests segregation leading to the formation of A–A pairs or B–B pairs in the alloy. $\alpha_1 = 0$ corresponds to a random distribution. A more convenient expression for α_1 from a computational point of view is the relationship derived from Eq. (8) and used previously[9]. It is given by

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1}, \tag{11}$$

where

$$S = \frac{S_{CC}(0)}{c(1-c)}, \tag{12}$$

Z being the coordination number of the alloy. These are the essential equations for this model.

2.2 The Four Atom Cluster Model (FACM)

The model is a little different from the QLA in that it does not assume the formation of complexes. It simply assumes that one has N atoms of which $N_A = (NC_A)$ are A atoms and $N_B = (NC_B)$ are B atoms. It is then possible to express the grand partition function Ξ of the alloy as

$$\Xi = \sum_E q_A^{N_A}(T)\, q_B^{N_B}(T)\, e^{\beta(\mu_A N_A + \mu_B N_B)} e^{-\beta E} \tag{13}$$

where $q_i(T)$ are the partition functions of atoms i (A or B) associated with inner and vibrational degrees of freedom, μ_A and μ_B are the chemical potentials and E is the configurational energy. Equation (13) can be solved by resorting to some simplifying assumptions eventually[17,18]; one can define parameters P_{ij} and ε_{ij} (the bond energies for ij nearest neighbour bonds) such that

$$P_{ij} = e^{-\beta\varepsilon_{ij}}, \quad ij = A, B \tag{14}$$

Further simplifications[17] lead to an expression of the form

$$\sigma^{12} - B_1\sigma^9 - B_2\sigma^6 - B_3\sigma^3 - B_4 = 0 \tag{15}$$

where

$$\sigma = \phi(P_{AA}/P_{BB})^{1/2} \tag{16}$$

$$B_1 = \frac{(1-3x)}{\eta^3} \tag{17}$$

$$B_2 = \frac{3x(1-x)}{\eta^4} \tag{18}$$

$$B_3 = \frac{3x^2(1 - x/3)}{\eta^3} \tag{19}$$

$$B_4 = x^3 \tag{20}$$

$$x = \frac{(1-c)}{c} \quad \text{and} \quad \eta = \exp\left(\frac{\beta\omega}{Z}\right) \tag{21}$$

ϕ being a constant which has to be eliminated from the final result. $\omega = Z[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2]$, is called the interchange or order energy for the alloy. With the activity ratio as earlier defined i.e. $a = a_B/a_A$, one can obtain an expression[17] which connects a to σ. It is given by

$$cf_1(a,\sigma) = (1-c)f_2(a,\sigma) \tag{22}$$

where $f_1(a,\sigma)$ and $f_2(a,\sigma)$ are defined as

$$f_1(a,\sigma) = a^4\sigma^{4ZL} + 3a^3\sigma^{3ZL}/\eta^3 + 3a^2\sigma^{2ZL}/\eta^4 + a\sigma^{ZL}/\eta^3 \tag{23}$$

and

$$f_2(a,\sigma) = a^3\sigma^{3ZL}/\eta^3 + 3a^2\sigma^{2ZL}/\eta^4 + 3a\sigma^{ZL}/\eta^3 + 1 \tag{24}$$

where $ZL = Z - 3$. Equation (22) can thus be solved to determine the activity ratio for a binary alloy using the value of σ obtained from the numerical solution of Eq. (15).

Even in the framework of this model, the probability of finding an A atom or B atom on any lattice site still depends on the nature of atoms already present on the neighbouring sites. We define (A,A,A,A) as the probability that all four lattices sites of the cluster are occupied by atoms A and similarly others. Some other probabilities (i,j,k,l) say, can further be reduced[17] to higher-order conditional probabilities (HOCP) (i/iji) (the probability of finding i atom on a given lattice site while the other three sites in the cluster are occupied by i, j and i atoms) and similarly others. With this in mind, one can express the probability P_{AB} as,

$$P_{AB} = (A/B) = \frac{(A/BB)}{(B/AB) + (A/BB)} \tag{25}$$

In terms of HOCP one can write[17]

$$(A/BB) = \frac{(A/BBB)}{(B/ABB) + (A/BBB)} \tag{26}$$

$$(B/AB) = \frac{(B/AAB)}{(B/AAB) + (A/BBB)} \tag{27}$$

and it is possible to write $(B/ABB) = 1 - (A/ABB)$. These equations are only useful to us, if we are able to express them in terms of a and σ. These derivations can also be found in[17,18] and one ends up with the results

$$(A/BBB) = \frac{1}{1 + a\sigma^{ZL}\, e^{(3\beta\omega/Z)}} \tag{28}$$

$$(A/ABB) = \frac{1}{1 + a\sigma^{ZL}\, e^{(\beta\omega/Z)}} \tag{29}$$

and

$$(B/\mathrm{AA}B) = \frac{a\sigma^{ZL}\, e^{-(\beta\omega/Z)}}{1 + a\sigma^{(ZL)}\, e^{(-\beta\omega/Z)}}. \tag{30}$$

Equation (25) can thus be solved from knowledge of a and σ obtained from Eqs. (22–24) and the solutions substituted in Eq. (8) to obtain α_1 from the FACM.

The essential equations for each model have thus been given and can now be used for our calculations.

3 RESULTS AND DISCUSSION

3.1 *Results from QLA*

In applying the QLA, the first step is to determine the interaction parameters g and the V_{ij}'s. The values of μ and ν for each alloy are those for the most stable complexes observed experimentally. One proceeds by solving Eq. (4) for n_3 and then fits the interaction parameters using Eq. (2) such that they reproduce to a considerable extent the experimentally measured free energy of mixing. The values obtained for the interaction parameters in the case of Na–Ga and Na–Sn are given in Table 1.

Plots of calculated and experimental values of the free energy of mixing as well as n_1, n_2 and n_3 are given in Figures 1 and 2 for Na–Ga and Na–Sn alloys. From a perusal of the graphs, one observes that our calculated G_M/RT with the interaction parameters gives qualitatively good results for Na–Ga while the results for Na–Sn are in excellent agreement with experiment. Experimental G_M/RT values for Na–Ga are taken from Reference [12] for the concentration range $0 < C_{\mathrm{Na}} \leqslant 0.8$, while that of Na–Sn is from Reference [16] and covers the whole range. The fitted value of g/RT is very high for Na–Sn compared to that of Na–Ga, the high value indicating

Table 1 Values of μ, ν and the interaction parameters for Na–Ga and Na–Sn molten alloys.

Alloy	*Temp (K)*	μ	ν	g/RT	V_{12}/RT	V_{13}/RT	V_{23}/RT
Na–Ga	843	5	8	2.00	1.42	−10.00	−2.00
Na–Sn	673	4	3	22.75	−5.95	0.5	−0.75

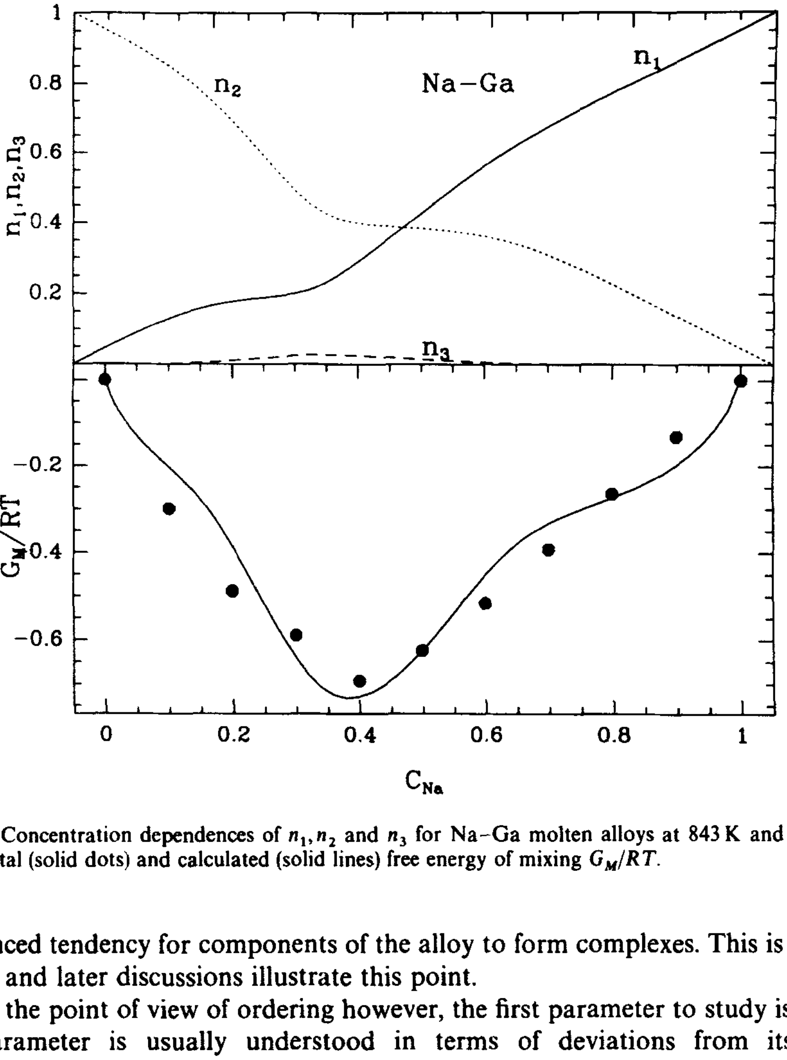

Figure 1 Concentration dependences of n_1, n_2 and n_3 for Na–Ga molten alloys at 843 K and also the experimental (solid dots) and calculated (solid lines) free energy of mixing G_M/RT.

pronounced tendency for components of the alloy to form complexes. This is indeed the case and later discussions illustrate this point.

From the point of view of ordering however, the first parameter to study is $S_{cc}(0)$. This parameter is usually understood in terms of deviations from its ideal value given by $S_{cc}^{\mathrm{id}} = c(1-c)$. $S_{CC}(0)$ is a response function and stability requires it to be positive. A strong response to a concentration-concentration stimulus shows that the system is near phase separation while a weak one indicates compound formation. Put in another form we can write.

$$S_{cc}(0) = \begin{cases} < S_{cc}^{\mathrm{id}}(0) & \text{Heterocoordination(CF)} \\ > S_{cc}^{\mathrm{id}}(0) & \text{Homocoordination(PS).} \end{cases} \tag{31}$$

For the two alloys being investigated, plots of $S_{cc}(0)$ as a function of concentration are given and it is thus easy to make comparison with those values computed using Eq. (7). The plots are shown in Figures 3 and 4. From the graphs, one observes that qualitative agreement is obtained as compared to experiments with the positions of

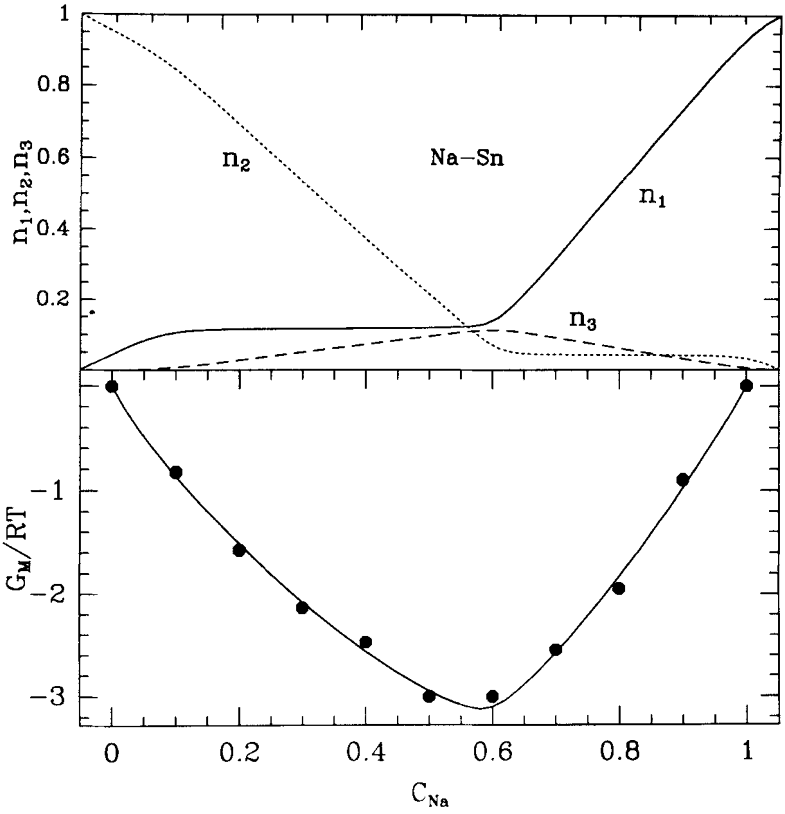

Figure 2 Same as in Figure 1 but for Na–Sn at 673 K.

compound formation (CF) and phase separation (PS) in the two alloys although the results for Na–Sn are again much better than those for Na–Ga. In fact, except for the heights of our calculated peaks being higher than the experimental values and a slight phase shift, our calculations for Na–Sn could be said to be in excellent agreement with experiment.

For Na–Ga, even the experimental $S_{cc}(0)$ have a peculiar behaviour. It is compound forming in the ranges $0 \leqslant C_{Na} \leqslant 0.475$ and $C_{Na} \geqslant 0.8$ in between these concentration ranges, it phase separates and shows a strong inclination for demixing. The poor agreement of computed results with experiments may signify a need to use some other model for this kind of alloy. The more recent models of Singh *et al.*[24,25] which they applied to demixing molten alloys could most probably give better quantitative agreement with experiment.

A better insight into the nature of ordering in molten alloys can be obtained by calculating the Warren-Cowley short-range order parameter α_1. In Figure 5 we give a graphical illustration of our results for the two alloys, essentially α_1 (negative) implies CF while positive values of α_1 shows a tendency for PS. The plot indicates that Na–Sn is expectedly compound forming throughout the whole concentration

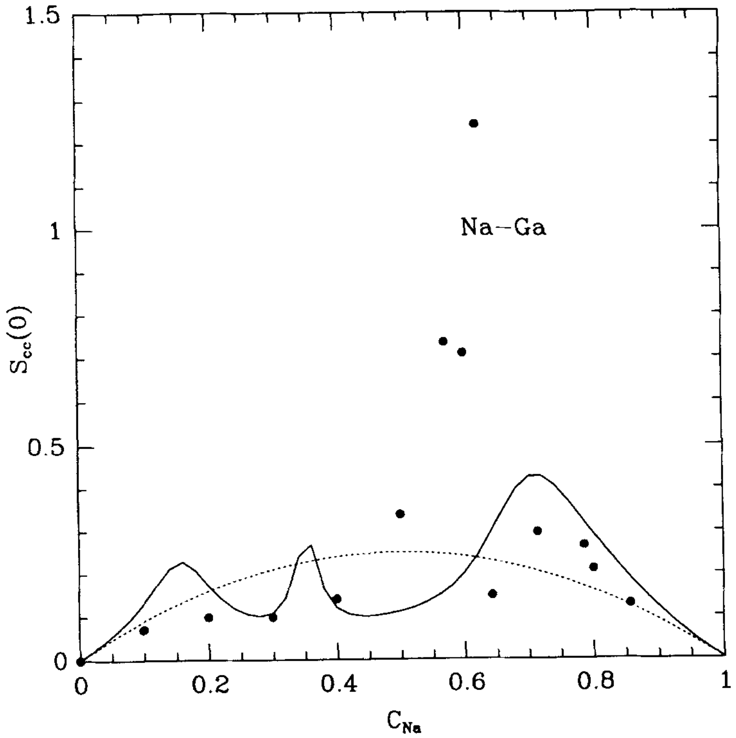

Figure 3 Experimental (solid dots) and calculated $S_{cc}(0)$ for Na–Ga alloys, also the ideal values (dashes).

range and the ability of the complex chosen to illustrate experimental results is a probable indication of its correctness.

For Na–Ga however, the result is again fairly complicated, it shows an equal likelihood of homocoordination and heterocoordination. This is at variance with available experimental results and once again signifies a need for an improved model. The graph however interestingly indicates the formation of a complex very close to Na_5Ga_8, the one chosen.

In concluding this section, one can say that the QLA is able to explain all the essential concentration dependence of compound formation observed in Na–Sn. The model fails for Na–Ga and for this reason among other considerations, one has endeavoured to use a FACM in an attempt to obtain better agreement with experiment regarding α_1 and also to make a comparison of the two models.

3.2 *Results for Na–Ga from FACM*

Table 2 shows results for Na–Ga obtained from FACM with $Z = 10$ (as assumed in QLA), the optimised value of $\omega = +0.0095\,\mathrm{eV}$. A positive value of α_1 as indicated from FACM indicates that Na–Ga is a self-coordinated system, i.e. like atoms tend to pair as nearest neighbours.

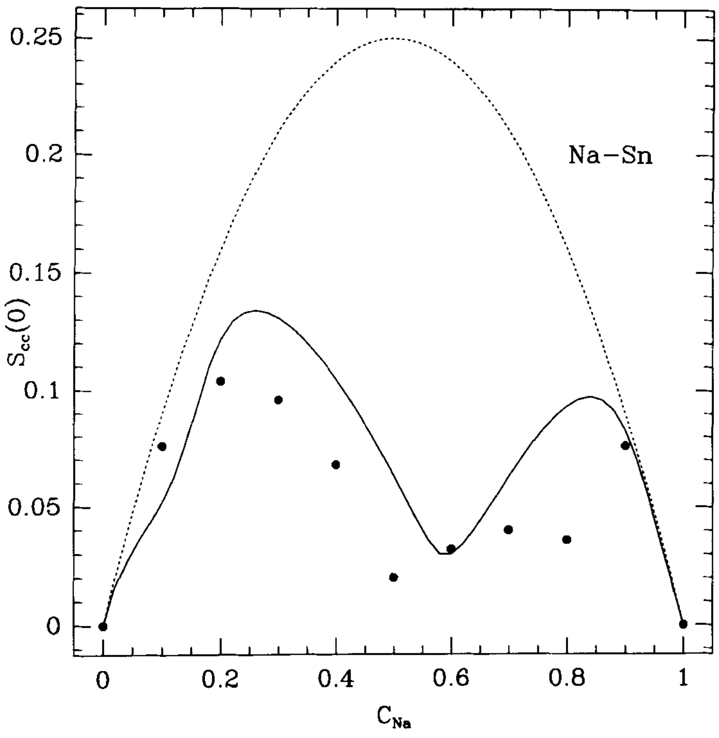

Figure 4 Same as in Figure 3 but for Na–Sn.

From the table it can be observed that the model always gives α_1 that is symmetric about the equiatomic composition. Though the model is easier from a numerical point of view (since it depends on only one parameter), the above mentioned point implies that it will have a problem in explaining results for alloys like Na–Ga where the activity shows a significant departure from Raoult's law. Our calculations (not shown here) indicate that the model works very well for In–Ga molten alloys[26], for which the departure of the experimental activity ratio from Raoult's law is minimal.

The model though gives an indication of weak phase separation throughout the concentration range. It does, however, have the failing that it cannot describe both compound formation and demixing tendencies experimentally observed for the alloys. Part of the peculiarity of the $S_{cc}(0)$ it predicts may be ascribed to the size effect $\Omega_{Na}/\Omega_{Ga} \approx 2$; the deviation could also be due to Ga since Na is a simple well behaved metal which has been extensively studied using pseudopotential theory.

Singh and Sommer[24] have recently proposed a simple model to explain the behaviour of demixing liquid alloys where the existence of polyatomic self associates (cluster like atoms are considered). It would be of interest to apply such concepts to Na–Ga.

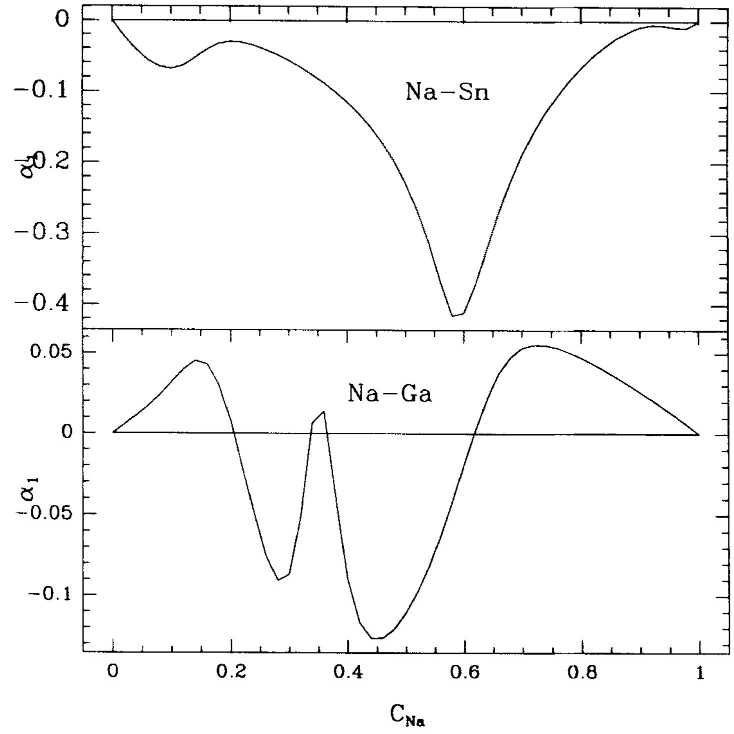

Figure 5 Ordering Parameter α_1 for Na-Ga and Na-Sn as calculated from the QLA.

Table 2 Computed and observed activity ratio $a = a_{Ga}/a_{Na}$ for Na-Ga molten alloys, also α_1 from QLA and FACM.

C_{Na}	a^{exp}	a^{FACM}	α_1^{FACM}	α_1^{QLA}
0.1	14.667	8.108	0.0024	0.032
0.2	4.167	3.699	0.0042	0.008
0.3	1.400	2.215	0.0056	−0.087
0.4	0.636	1.462	0.0064	−0.090
0.5	0.375	1.000	0.0066	−0.111
0.6	0.313	0.684	0.0064	−0.019
0.7	0.286	0.452	0.0056	0.053
0.8	0.286	0.270	0.0042	0.048
0.9	0.278	0.123	0.0024	0.026

4 CONCLUSION

The quasilattice approximation has been applied to study the alloying behaviour of Na-Ga and Na-Sn alloys by fitting their free energies using complexes which are expected to be the most stable for each alloy. The fitted parameters have further been used to study ordering phenomena in the molten alloys.

Good agreement is obtained for the concentration dependence of the thermodynamic properties of Na–Sn within QLA; for Na–Ga the agreement could at best be said to be semi-quantitative. With a view to obtaining improvements in the results for Na–Ga, we have applied the FACM model to calculate its activity ratio and from there have investigated ordering using α_1. Though the FACM does better (in that it indicates weak homocoordination throughout the whole concentration range), the results are however still somewhat at variance with experiments where partial heterocoordination is observed. It follows therefore that the model still has some shortcomings when applied to Na–Ga. Our calculations further indicate that the FACM always gives results for α_1 that are symmetrical about the equiatomic composition.

We conclude by saying that calculations for Na–Ga signify the need to proceed to more sophisticated models suitable for demixing binary alloys and possibly the recent work of Singh & Sommer[24] may be useful in this respect.

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