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ALLOYS ALONG THE LINE OF PHASE SEPARATION**

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ALONG THE LINE OF PHASE SEPARATION**

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Abstract

We have investigated the energy of formation for AgIn liquid binary alloys along the solid-liquid phase separation line. A microscopic theory based on the first order perturbation has been applied. The interionic interaction and a reference liquid are the fundamental components of the theory. These are described by a local pseudopotential and the hard sphere liquids, respectively. The results of calculations reveal a characteristic feature that the energy of formation becomes minimum at the equiatomic composition, and thus indicates maximal mix-ability at this concentration. The energy of formation at a particular thermodynamic state that is at $T = 1173$ K predicts the experimental trends fairly well.

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1 Introduction

In this work, we have presented the results of calculations for the energy of formation for AgIn liquid binary alloys. The calculations are performed in two different physical situations. One is near the melting temperatures of the alloys, and another is at an elevated temperature. Note that the melting temperatures for alloys with different concentrations are different, and these lie at different points along the solid-liquid phase separation line.

Recently, an increasing attraction toward the study of different properties of liquid binary alloys is observed [1-6]. Very recently, Khaleque et al. [5] showed that the additive hard sphere theory in conjunction with a local pseudopotential was adequate to reproduce observed data [7] for the partial as well as total static structure factors for AgIn liquid binary alloys along the phase separation line. Following the work of Ref. [6] Bhuiyan et al. [1] performed calculations for atomic transport properties for AgIn liquid binary systems. Bhuiyan et al. [1] found a reasonably good agreement when compared with corresponding experimental data [8]. Being encouraged by the above successes we have been motivated in this work. As far as we know some authors [9] attempted, in the past, to study this property at a particular temperature, but none of them attempted to study near the melting temperatures of the concerned alloys.

So far several theories have been advanced to study the energy of formation for the liquid binary alloys. Among them (i) the quasi lattice theory [10], (ii) the general microscopic theory (GMT) [11], (iii) the computer simulations [12] and the empirical linear free energy theory [13] etc. are commonly used. In the quasi lattice theory the activity is expressed (via the Gibbs free energy) in terms of the average interionic interaction energy and the formation energy of mixing and, these two are then determined by fitting to the experimental data for activity. The linear free energy theory as developed by Sverjensky and Molling [13] is an empirical theory, and applicable only when the solute concentration is very low [14]. The simulations are computationally expensive. The GMT is based on the electronic theory of metals and the static structure factors obtainable from the knowledge of interionic pair interactions [11]. Each term in the GMT is clearly understandable from the physical point of view. Moreover, the GMT is relatively simple for numerical calculations and has proved to be successful for some liquid simple metal alloys [11]. Since we are concerned with liquid less simple alloys, we have employed it in the present work.

The essential ingredients of the GMT are the knowledge of the partial interionic interactions and partial pair correlation functions. For the interionic interactions we use the Bretonnet-Silbert (BS) model of local form [15]. The reason is that the BS model is able to take into account the effects of the sd-hybridization (sometimes known as the sd-mixing) properly. Since the components of AgIn alloys belong to the group of less simple metals having the effects of sd-hybridization, the BS model is logistically important for them.

The theory of hard spheres (HS) liquids is well established now. In addition, the hard

sphere liquid closely represents the liquid simple metals when the effective hard sphere diameter (HSD) is properly chosen [16]. Moreover, the HS expressions for the free energy are available in the literature. So it is quite natural to choose an effective HS liquid as a reference for the perturbative calculations for the concerned systems.

This paper is organized in the following way. Theories related to our calculations for the energy of formation are briefly described in section 2. The results of calculations are presented and discussed in section 3. We conclude this paper in section 4.

2 Theory

Theories relevant to the present calculations for energy of formation namely the first order perturbation theory for the free energy, the theory for the partial interionic interactions and for partial pair distribution functions are briefly presented below.

2.1 Energy of formation for liquid binary alloys

Within the first order perturbation theory the Helmholtz free energy for an alloy may be written, in general, as

$$F = F_{HS} + F_{eg} + F_{TAIL} \quad (1)$$

where F_{HS} , F_{eg} and F_{TAIL} denote free energy per atom of the reference HS liquid, free energy of the electron gas in metals and the free energy due to the tail part of the potential, respectively. Symbolically

$$\begin{aligned} \frac{F_{HS}}{k_B T} &= \sum_i \left[-\ln(\Lambda_i^3 v) + \ln C_i \right] - \frac{3}{2} \left(\frac{5}{3} - y_1 + y_2 + y_3 \right) \\ &+ (3y_2 - 2y_3)/(1 - \eta) + \frac{3}{2} \left(1 - y_1 - y_2 - \frac{y_3}{3} \right) / (1 - \eta)^2 \\ &+ (y_3 - 1) \ln(1 - \eta) \end{aligned} \quad (2)$$

where

$$\Lambda_i = \left\{ \frac{2\pi\hbar^2}{m_1^{C_1} m_2^{C_2} k_B T} \right\}^{\frac{1}{2}} \quad (3)$$

$$\eta = \sum_i \eta_i ; \quad \eta_i = \frac{C_i \pi \rho_i \sigma_{ii}^3}{6} \quad (4)$$

$$y_1 = \sum_{j>i} \Delta_{ij} (\sigma_{ii} + \sigma_{jj}) / (\sigma_{ii} \sigma_{jj})^{\frac{1}{2}} \quad (5)$$

$$y_2 = \sum_{j>i} \Delta_{ij} \sum_k \left(\frac{\eta_k}{\eta} \right) (\sigma_{ii} \sigma_{jj})^{\frac{1}{2}} / \sigma_{kk} \quad (6)$$

$$y_3 = \left[\sum_i \left(\frac{\eta_i}{\eta} \right)^{\frac{2}{3}} C_i^{\frac{1}{3}} \right]^3 \quad (7)$$

$$\Delta_{ij} = \left[(\eta_i \eta_j)^{\frac{1}{2}} / \eta \right] \left[(\sigma_{ii} - \sigma_{jj})^2 / \sigma_{ii} \sigma_{jj} \right] (C_i C_j)^{\frac{1}{2}} \quad (8)$$

In the above equations C_i , ρ_i , m_i and σ_{ii} denote the atomic concentration, ionic number density, ionic mass and the hard sphere diameter of the i th component, respectively.

$$\frac{F_{TAIL}}{k_B T} = D \sum_{ij} C_i C_j M_{ij} \quad (9)$$

where

$$D = \frac{2\pi\rho}{k_B T}$$

$$M_{ij} = \int_{\sigma}^{\infty} v_{ij}(r_{ij}) g_{ij}^{HS}(r, \sigma_{ij}, \rho) r^2 dr \quad (10)$$

In equation (10)

$$\rho = \frac{\rho_1 \rho_2}{(C_1 \rho_2 + C_2 \rho_1)} \quad (11)$$

The contribution of the electron gas to the free energy may be written as (in Rydberg units)

$$F_{eg} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.031 \ln r_s - 0.115 \quad (12)$$

where r_s is the dimensionless parameter defined as

$$r_s = \left(\frac{3}{4\pi\rho Z} \right)^{\frac{1}{3}} / a_0 \quad (13)$$

a_0 being the first Bohr radius. Finally, the energy of formation reads

$$\begin{aligned} \Delta F &= F - \sum_i C_i F^{(i)} \\ &= \Delta F_{HS} + \Delta F_g + \Delta F_{TAIL} \end{aligned} \quad (14)$$

In the above equation $F^{(i)}$ denotes the free energy of the elemental components.

2.2 The effective partial pair potentials

The local pseudopotential for metallic systems may be modeled by the superposition of the sp and d-band contributions [15]

$$W(r) = \begin{cases} \sum_{m=1}^2 B_m \exp(-r/ma) & \text{if } r < R_C \\ -Z/r & \text{if } r > R_C \end{cases} \quad (15)$$

where a , R_C and Z are softness parameter, core radius and the effective s-electron occupancy number, respectively. The term inside the core of equation (15) is deduced from the d-band

scattering phase shift by using an inverse scattering approach. The term outside the core is just the Coulomb interaction between a positive ion and an electron. The coefficients in the core are

$$\begin{aligned} B_1 &= \frac{Z}{R_C} (1 - 2a/R_C) \exp(R_C/a) \\ B_2 &= \frac{2Z}{R_C} (a/R_C - 1) \exp(R_C/a) \end{aligned} \quad (16)$$

The effective interionic interaction finally reads

$$v_{ij}(r) = \frac{Z_i Z_j}{r} \left[1 - \frac{2}{\pi} \int dq F_{ij}^N \frac{\sin(qr)}{q} \right] \quad (17)$$

where i and j represent the ionic species i and j . In equation (17) F_{ij}^N is the normalized energy wave number characteristics

$$\begin{aligned} F_{ij}^N &= \left[\frac{q^2}{\pi a \rho \sqrt{Z_i Z_j}} \right]^2 W_i(q) W_j(q) \\ &\times \left[1 - \frac{1}{\epsilon(q)} \right] \left[\frac{1}{1 - G(q)} \right] \end{aligned} \quad (18)$$

In the above equation $W_i(q)$ denotes the unscreened form factor. $\epsilon(q)$ and $G(q)$ are dielectric function and the local field factor, respectively. These are taken from Ichimaru and Utshumi [17] because their theory satisfies the compressibility sum rule and the short range correlation conditions.

2.3 Partial pair correlation functions for HS binary liquids

The Ashcroft and Langreth (AL) partial structural structure factors $S_{ij}(q)$ are calculated in line with their original work [18]. The essential ingredients in calculating the structure factors are the concentrations of two spheres in the mixture and the effective HSD. The effective HSD are determined by using the linearized Weeks-Chandler-Andersen (LWCA) perturbation theory [19]. The expressions for the AL partial structural factors are given in [18]. The corresponding pair correlation functions may be obtained by the Fourier transform of $S_{ij}(q)$ in the following way

$$g_{ij}(r) = 1 + \frac{1}{(2\pi)^3 \rho \sqrt{C_i C_j}} \int_0^\infty (S_{ij} - \delta_{ij}) \exp(i\mathbf{q}\cdot\mathbf{r}) d^3r \quad (19)$$

3 Results and Discussions

The results of calculations for the energy of formation are presented and discussed in this section. As we mentioned earlier the calculation for free energy requires the knowledge of the effective pair potentials and the pair distribution functions. In calculating the effective pair potentials we take the values for R_C , and a , from the work of Bhuiyan et al. [1]. The rest of the necessary inputs are listed in Table-I.

Table-I: Input values for number densities $\rho_i(\text{\AA}^{-3})$, hard sphere diameters for pure $\sigma_i(\text{\AA})$ and for alloys $\sigma_{ii}(\text{\AA})$. C_1 denotes the atomic concentration of Ag.

C_1	T(K)	ρ_1	ρ_2	σ_1	σ_2	σ_{11}	σ_{22}
0.1	517	0.0558	0.0366	2.600	2.820	2.630	2.800
0.2	623	0.0553	0.0362	2.584	2.815	2.603	2.780
0.5	780	0.0545	0.0356	2.568	2.808	2.570	2.713
0.7	973	0.0535	0.0349	2.533	2.799	2.540	2.665
0.9	1173	0.0523	0.0342	2.510	2.794	2.510	2.620

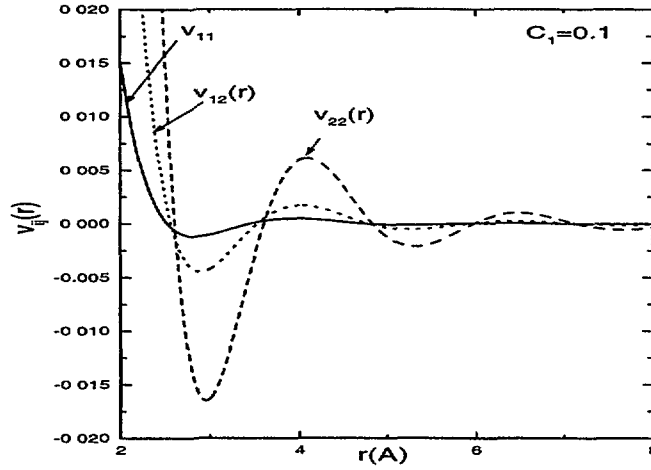


Figure 1: Partial pair potentials for $C_1 = 0.1$.

Figures from 1 to 3 show the profile of effective partial pair potentials for concentrations $C_1 = 0.1, 0.5$ and 0.9 , respectively. It is noticed that at each thermodynamic state V_{22} has a deeper potential well than V_{11} . The reason of it would be clear if we have a closer look at equation (15). The Coulomb term is directly proportional to Z and the well gets deeper as Z increases. Since the value of Z for In is 3 and that for Ag is 1 so the well for In is deeper. It is also noticed that the depth of the well for V_{22} decrease with increasing concentration of Ag, C_1 , while that for V_{11} increases slowly. It happens, as expected, due to the transfer of charge from In to Ag ion in the alloy state (we shall discuss about it below). This trend fairly justifies the internal accuracy of our calculations.

Figures from 4 to 6 display the partial pair distribution functions, $g_{ij}(r)$, for the effective reference HS liquids. For $C_1 = 0.1$ the principal peak for $g_{22}(r)$ is much larger than that for $g_{11}(r)$, and the corresponding trends become opposite for $C_1 = 0.9$. This is due to the fact that

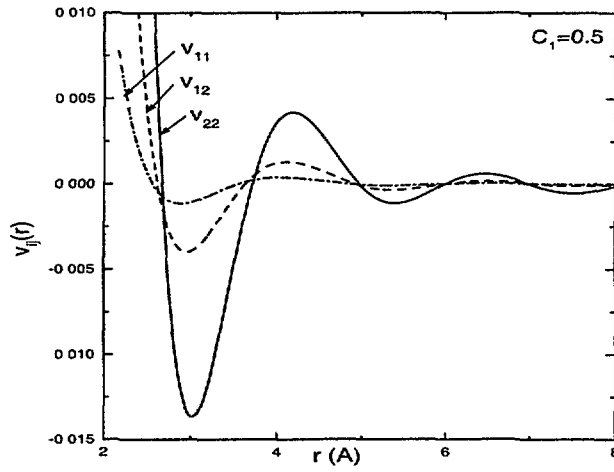


Figure 2: Partial pair potentials for $C_1 = 0.5$.

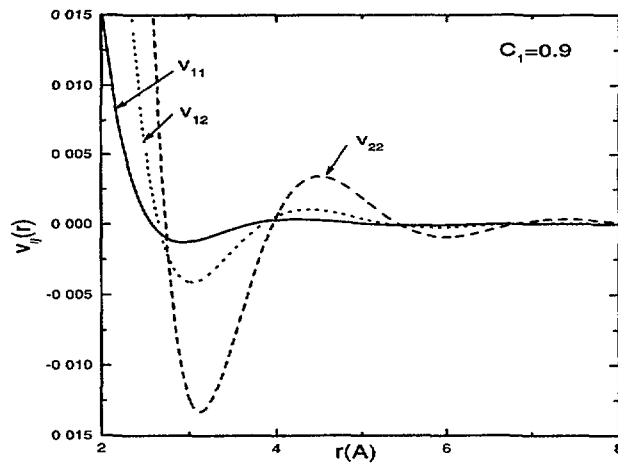


Figure 3: Partial pair potentials for $C_1 = 0.9$.

at the former concentration the alloy is rich in In so the probability of finding an indium ion from another one is larger. According to this argument the situation would reverse in the case of Ag rich alloys (say for $C_1 = 0.9$). This scenario is exactly reflected in Figure 6. For $C_1 = 0.5$ the principal peak values for g_{11} and g_{22} should be equal according to the previous statistical argument, but, a closer look reveals a small difference in height. That is the peak for g_{22} is somewhat higher than that for g_{11} . This is due to the effect of larger HSD for In. We note that the values of HSD for Ag expands and that for In shrinks for all alloys when compared with corresponding elemental values (see table-I). The underlying reason of it may be attributed to the fact of charge transfer from In to Ag in the alloy state.

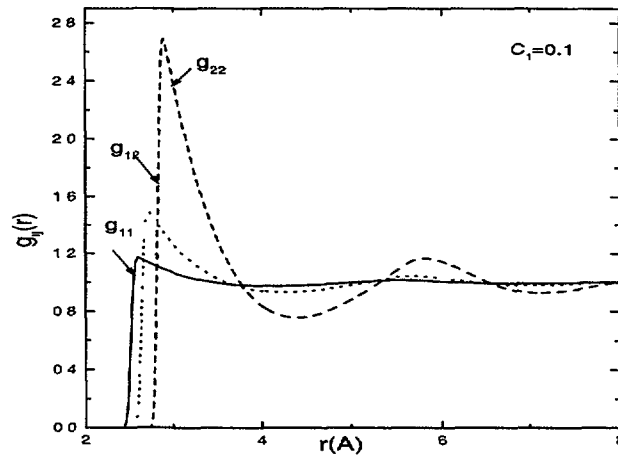


Figure 4: Partial pair correlation functions for $C_1 = 0.1$.

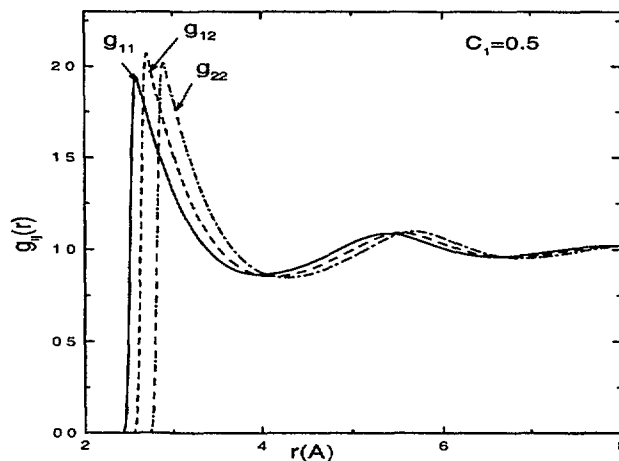


Figure 5: Partial pair correlation functions for $C_1 = 0.5$

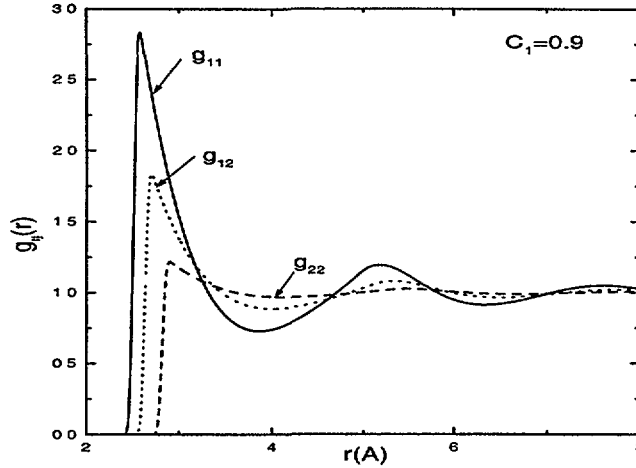


Figure 6: Partial pair correlation functions for $C_1 = 0.9$.

Table-II: Total free energy, F and the energy of formation along the line of phase separation.

C_1	T(K)	$F^{(1)}$ (eV)	$F^{(2)}$ (eV)	F (eV)	ΔF (eV)
0.1	517	-0.925	-1.321	-1.348	-0.0659
0.2	623	-1.015	-1.418	-1.427	-0.0895
0.5	780	-1.154	-1.566	-1.492	-0.1320
0.7	973	-1.352	-1.759	-1.586	-0.1115
0.9	1173	-1.566	-1.971	-1.673	-0.0659

Now let us turn to the results of calculation for the energy of formation along the solid-liquid phase separation line. The phase diagram for AgIn shows that the melting point increases with increasing C_1 [20]. So it is obvious to expect that the free energy of the concerned alloys would increase with increasing Ag concentration along the phase separation line. The calculated results for the free energy of the elemental systems and of the alloy (presented in Table-II) correctly predict these trends (see column 3, 4 and 5). But the most striking behaviour reveals when we examine the energy of formation along the phase separation line (see Figure 7). The energy of formation goes to a minimal value around the equiatomic composition and becomes larger for both In and Ag rich alloys, despite different compositions represent different thermodynamic states. This result fairly indicates that the mix-ability of AgIn alloys is maximum at the equiatomic composition.

To compare theoretical results for the energy of formation with the available experimental data we have performed calculations at an elevated temperature $T = 1173$ K. These results are presented in Figure 8 and 9. From Figure 8 we observe that the two components of the free energy namely F_{eg} and F_{TAIL} (see eqn. (1)) increase with increasing Ag concentration, but the third component namely the F_{HS} has the minimal value around the equiatomic concentra-

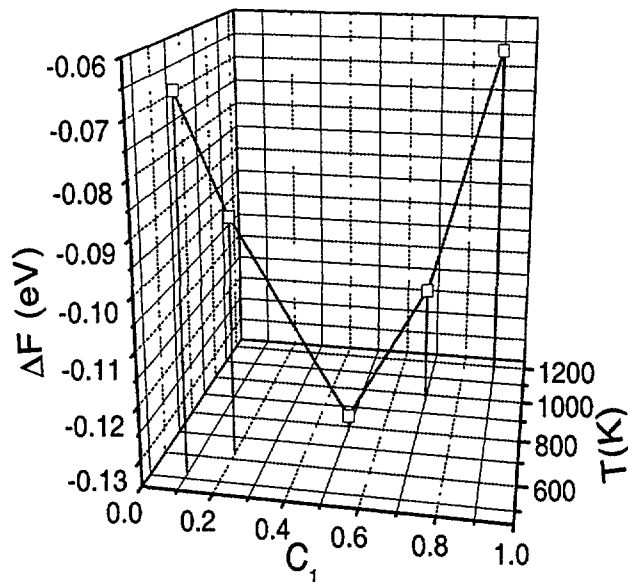


Figure 7: Energy of formation as a function of Concentration and temperature along the line of phase separation.

tion, and gradually increase on both sides. As a result the total free energy of the alloy shows somewhat asymmetry about the equiatomic composition. Unfortunately we do not have experimental data to compare with the calculated total free energy. Figure 9 shows that the GMT results underestimate the energy of formation. But as far as the trends across the concentration range is concerned the agreement is fairly good. We attribute the cause of this discrepancy to the limitations of the pseudopotential theory for the interionic interactions together with the limitations of the additive HS theory.

4 Conclusions

The energy of formation for AgIn liquid binary alloys has been investigated near the melting temperatures close to the solid-liquid phase separation line. This property has also been investigated at an elevated temperature $T = 1173$ K. The energy of formation has been found to be negative for all concerned alloys in both situations. Theoretical results predict that a mixture of any proportion of liquid Ag and In form an alloy at any temperatures above the melting temperatures. This is broadly supported by experiments [20]. The most interesting feature that has emerged from our calculations is that, the energy of formation calculated near the melting temperatures becomes minimum for the alloy of an equiatomic composition, although the temperature and material density are different for different compositions.

Theoretical results for the energy of formation at $T=1173$ K has been found to be lower than

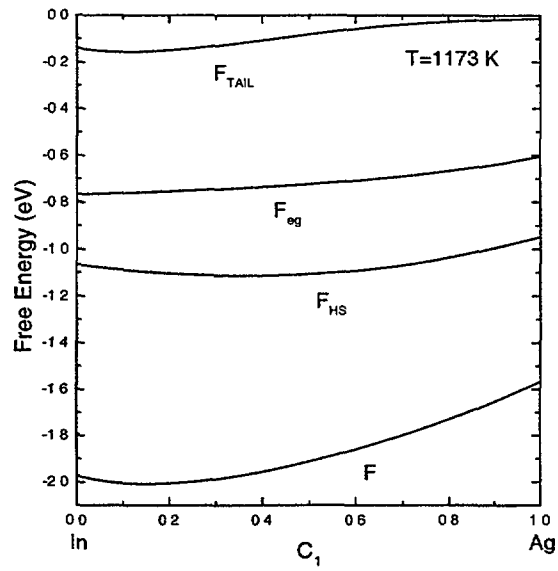


Figure 8: Free energy for AgIn liquid binary alloys at $T=1173$ K.

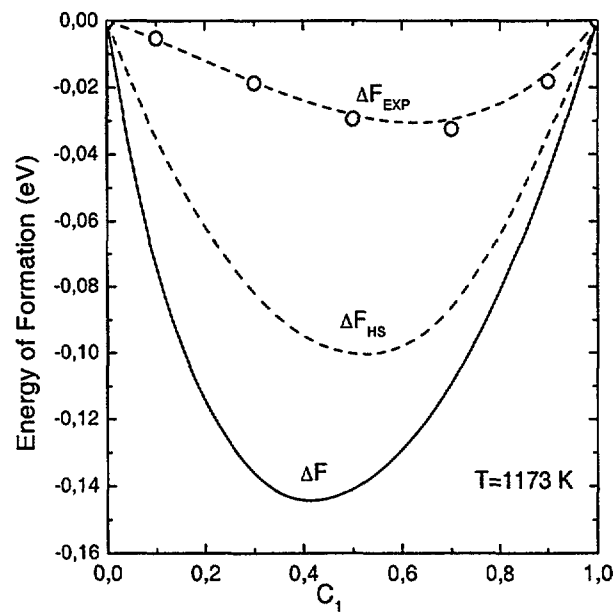


Figure 9: Energy of formation for AgIn liquid binary alloys at $T=1173$ K.

those of the experimental ones. But the qualitative trends of symmetry around the equiatomic concentration is found to be fairly good. The results of some works [21,22] indicate that the pseudopotential perturbation theory becomes less reliable in some alloys as the valency difference is increased. As far as the energy of formation is concerned the AgIn liquid binary alloys seems to have similar problems due to the valency difference between Ag and In. Another cause of discrepancy may be due to the limitation of the additive hard sphere theory. Theories like the embedded atom method [23] for interionic interactions together with the non-additive HS theory might improve the results. This work is in progress.

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