

# Energy of formation for $\text{Ag}_x\text{In}_{1-x}$ and $\text{Ag}_x\text{Sn}_{1-x}$ liquid binary alloys

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## Abstract

We have investigated the free energy of formation for  $\text{Ag}_x\text{In}_{1-x}$  and  $\text{Ag}_x\text{Sn}_{1-x}$  liquid binary alloys at temperatures 1173 and 1250 K, respectively. 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. The interionic interaction is described by a local pseudopotential. A liquid of hard spheres (HS) of two different effective diameters and charges is used to describe the reference system. The results of the calculations for energy of formation agree very well with the available experimental data. Our calculations also reveal that a simple perturbative approach along with appropriate effective pair potentials can produce nearly quantitative results for the concerned alloys.

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## 1. Introduction

We have systematically investigated the free energy of formation for  $\text{Ag}_x\text{In}_{1-x}$  and  $\text{Ag}_x\text{Sn}_{1-x}$  liquid less simple binary alloys at 1173 and 1250 K, respectively. To understand the mixing behaviour of two elemental systems forming a binary alloy has been a subject of considerable interest to physicists, chemists and metallurgist. This is due to the fact that the interionic interaction in an alloy largely differs from those of the constituent elemental systems and consequently the physical properties of alloys deviate from those of the parent elements. The study of energy of formation is important not only to understand this property alone but also to understand other characteristic properties such as compound formation, phase separation or segregation etc. of binary alloys.

Recently an increasing attraction toward the study of different physical properties of binary alloys is observed [1–6]. Among these alloys  $\text{Ag}_x\text{In}_{1-x}$  has drawn a special attention due to some of its characteristic properties, for example the presence of pseudogap in the density of states

and deviation of its magnetic susceptibility from the linearity at some concentration [6]. In addition, recent X-ray diffraction measurement of total and partial static structure factors [7] arouse further attention to it.

$\text{Ag}_x\text{In}_{1-x}$  and  $\text{Ag}_x\text{Sn}_{1-x}$  liquid binary alloys are constituted from three different elemental systems Ag, In and Sn. These elements have completely filled d-bands. Nonetheless, their physical properties are significantly influenced by the d-band via sd (or sp-d) hybridization (sometimes referred to as sd mixing) [7,8]. The effect of sd-hybridization is also effective in the alloy state and, there are evidences that in some alloys this effect changes with relative alloy concentrations [9]. It is therefore important to take the hybridization effect into account for the study of both elemental metals and their alloys. In order to take this effect into account precisely any concrete theoretical expression has not been developed yet. So this effect is accounted for approximately by changing the relative occupancy of the s and d bands. In doing this there is no restriction as such to use suitable values for  $Z$  the effective s-electron occupancy number provided the self-consistent calculations of charge transfer support it. For example, Wills–Harrison [10] used  $Z = 1.5$  for all elements of the 3d, 4d and 5d series except for Au for which they

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used  $Z = 2$ . We should mention here that the metals studied in Ref. [10] involved elements with completely empty, partially and completely filled d-bands. Following the same line Bhuiyan et al. [11] used  $Z = 1.4$  for the liquid 3d transition metals. In the same spirit we take in the present work  $Z = 1.3, 1.5$  and  $1.7$  for Ag, In and Sn, respectively. We note here that the self-consistent calculations by Moriarty [12] shows that the value of  $Z$  lies in the range 1.1–1.8 for transition metals. The value of  $Z$  plays its important role through the interionic interaction [10,13]. So we require a model that can take into account both sp and d band effects adequately in the interionic interactions.

Bretonnet and Silbert (BS) have proposed a model [14] to describe interionic interactions, primarily, for liquid transition metals. This model treats sp and d bands separately within the well established pseudopotential formalism. The sp band is described via the empty core model; the d-band is derived from the d-band scattering phase shift by using an inverse scattering approach. The resulting model pseudopotential thus reduces to a simple local form which appears similar to that of the well-known Heine–Abernkov model [15]. The main difference between these two models is that the core term in the former one is derived from the scattering phase shift and is a function of distance, and in the latter one is a square well which is derived from the point of view of quantum defect method. The BS model is simple to handle numerically. Moreover, the local form permits one to extend this model to other liquid metals for which the effects of hybridization are significant. The BS model has already proved to be successful in describing some physical properties for less simple metals [11,16] and their alloys [5,17]. Note that the norm conserving non-local pseudopotentials are, in principle, to be preferred for accurate predictions. But there are evidences that local potentials describe physical properties, in some cases, even better [8] than the former ones.

So far several theories have been advanced to study the free energy and the energy of formation for liquid binary alloys. Among them: (i) the quasi-lattice theory [18]; (ii) the general microscopic theory (GMT) [19]; (iii) the computer simulation [20] and (iv) the empirical linear free energy theory [21] are commonly used. In the quasi-lattice theory the activity is expressed in terms of average interionic interaction energy and the formation of mixing via the Gibbs free energy. The energy of formation is then determined by fitting to the experimental data of the activity [22]. The linear free energy theory is an empirical one, and is applicable only when the solute concentration is very low [23]. The GMT is based on the electronic theory of metals, the static structure factor obtainable from the knowledge of interionic pair interaction through the statistical mechanics, and the perturbation or variational theory [19]. Each term in the GMT is clearly understandable from the physical point of view. Moreover, the GMT is relatively simple to handle numerically, and has proved to be successful for some liquid binary alloys [5].

For some binary alloys, the experimental values of the atomic volume,  $\Omega_{\text{Ex}}$ , differ from those of theoretical ones,  $\Omega (= x\Omega_1 + (1-x)\Omega_2)$ . The difference between these two values i.e.  $\Delta\Omega (= \Omega_{\text{Ex}} - \Omega)$  is known as the excess volume. For the alloys of our concern the excess volume is negative (see below). As the ionic number density per unit volume is inversely proportional to the atomic volume the experimental values of ionic number density is greater in this case than the theoretical values. As the ionic number density is involved in the theoretical calculations, the excess volume correction is therefore required for a quantitative study.

We note here that, the advent of sophisticated theories of metals for transition and less simple metals in the last two decades has opened a new window of interest to revisit the old approaches like the GMT for better predictions. The results of the present calculations justify this statement (see below).

The perturbation calculation requires such a reference system which can closely resemble the concerned real system. There are many theoretical and experimental evidences [24,25] that the hard sphere model can describe the structure of simple and less simple liquid metals and their binary alloys reasonably well. In particular, a recent work [17] showed nicely that the mixture of two hard spheres (HS) with different effective charges and diameters describes the structure of liquid  $\text{Ag}_x\text{In}_{1-x}$  alloys adequately. Prompted by the above results of success we employ the HS liquid as the reference system in the present work.

Finally, as far as we know, nobody before us theoretically studied the energy of formation for  $\text{Ag}_x\text{In}_{1-x}$  and  $\text{Ag}_x\text{Sn}_{1-x}$  liquid binary alloys by employing full potentials and as systematically as we have done in this work (see below).

The layout of this paper is following. Theories relevant to the present calculations are briefly described in Section 2. We present results of calculations, and some discussions on the results, in Section 3. Finally, in Section 4 we conclude this paper with some remarks that emerged from the results and discussions.

## 2. Theories

In order to calculate the energy of formation, the relevant theories, 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 per ion for an alloy may be written, in general, as

$$F' = F_{\text{Vol}} + F_{\text{eg}} + F_{\text{HS}} + F_{\text{Tail}}, \quad (1)$$

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