Full Length Article

Anomalous electronic behaviour of disordered alloy systems

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ABSTRACT

In the present work the concept of complex formation has been incorporated in the structure of well known Faber–Ziman formula for the purpose of studying the composition dependence of electrical resistivities of liquid alloy systems which possess anomalous nature and also exhibit large deviation from metallic behaviour around specific composition. Within the framework of complex formation model the thermodynamic properties of the systems have been calculated. The study reveals that the anomalous electronic behaviour of liquid Li–Pb, Na–Pb, Li–Sn and Na–Sn can be attributed to the preferential ordering of unlike atoms.

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1. Introduction

Liquid state mixture of two different metals may be considered to have structure in between the long range order characteristic of crystalline solids and total disorder characteristic of gases. These disorder systems can broadly be classified on the basis of their thermodynamic and electrical properties into two groups: symmetric and asymmetric. Asymmetry of alloy property curves as a result of anomalous mixing behaviour in the liquid state is usually attributed to the size effect, to the interaction between solute and solvent atoms or both and it is particularly pronounced for strongly interacting alloy systems, such as the Na-Pb [1], Ag-Hf [2], Al-Co [3], Al-Ni [4,5]. Phase diagrams of binary alloy systems, which have been studied in great detail experimentally [6] as well as theoretically [7] show that the liquid alloy systems which exhibit the associative tendency among the unlike constituent atoms are characterised by the presence of one or more intermetallic compounds in the solid state. The mixing properties of such molten alloy systems deviate from the regular solution behaviour and show a well-defined peak at one or more concentrations which lie in the vicinity of the stoichiometric compositions of the energetically favoured intermetallic compounds [1]. *The asymmetry around equiatomic composition is more evident for strongly interacting alloy systems mentioned above.* The work of Hansen [8] led Bhatia and his collaborators [9,10] to assume the existence of chemical complexes (associates) in the liquid state. The close similarity between the solid and liquid phase, at least near the melting point

of an alloy [11] has been later substantiated by neutron and X-ray diffraction experiments [12,13].

The complex forming alloy systems have been extensively studied both theoretically and experimentally and can be found in the literature under different names such as complex forming solution, compound forming solution or associated liquid solution.

Some liquid metal alloy systems, which form compounds in the solid states at one or more stoichiometric composition, exhibit anomalous behaviour in their thermodynamic properties, structural properties and electrical properties around some specific composition indicating pronounced deviation from ideal mixing [1]. These outstanding properties of binary liquid alloy systems with a strong nonideal mixing behaviour have been of long standing interest and it has to be admitted that the theoreticians have not been able to catch up with the experimentalists' rapid progress. However, in recent years, considerable progress [1–5,10,14–18] has been made in describing the anomalous behaviour of thermodynamic properties with the complex formation model initiated by Bhatia and his co-author [10,19]. However, their electrical and structural properties have been studied by only a few [20–22].

In the present work the concept of complex formation has been incorporated in the structure of well known Faber–Ziman formula for the purpose of studying the electrical resistivities of liquid alloy systems as a function of concentration which possess anomalous nature and also exhibit large deviation from metallic behaviour around specific composition. This has been successfully applied to determine the electrical resistivities of liquid Li–Pb, Li–Sn, Na–Pb and Na–Sn alloy systems at different compositions. Electronic density of states of liquid alloy systems considered for the study have been studied only at the composition of their maximum

resistivity to have an elementary idea about the behaviours of the alloy systems with respect to nearly free electron behaviour.

2. Computational detail

2.1. Complex formation model

Complex formation model [10,19,23–29] assumes the liquid binary alloy A–B as a ternary mixture consisting of free atoms A, free atoms B and their preferential association, referred as chemical complex $A_\mu B_\nu$.

Let us suppose that there are $n_A(= n_1 N)$ of free atoms A, $n_B(= n_2 N)$ of free atoms B and $n_m(= n_3 N)$ number of chemical complexes exist in the mixture. Then the total number of scattering points is

$$N_S = n_A + n_B + n_m = nN$$

where N is the total number of atom A and atom B i.e.,
$N = N_A + N_B$ and $n = n_1 + n_2 + n_3$ with

$$n_1 = 1 - C - \mu n_3$$
$$n_2 = C - \nu n_3$$

Here C is the concentration of the second component.

The free energy of mixing G_M of the mixture may be written as

$$G_M = -n_3 g + G^1$$

where g is the formation of energy of the complex and thus the first term $-n_3 g$ represents the lowering of the free energy due to the formation of the complex in the alloy. G^1 is the free energy of mixing of the ternary mixture A, B and $A_\mu B_\nu$. Since strong interactions are taken care of, via the formation of chemical complexes, the mixture can be treated as weakly interacting system. Hence for G^1, the conformal solution approximation [30] can be considered. This enables us to express G_M as

$$G_M = -n_3 g + RT \sum_{i=1}^{3} n_i (\ln n_i - \ln n) + \sum_{i\langle j} \sum \frac{n_i n_j}{n} W_{ij} \quad (1)$$

Here W_{ij} $(i,j = 1,2,3)$ are the interaction energies.

The equilibrium values of the chemical complex n_3 may be obtained through the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \quad (2)$$

$$\frac{n_1^\mu n_2^\nu}{n_3 n^{\mu+\nu-1}} = e^{-g/RT} e^Y \quad (3)$$

where,

$$Y = \frac{W_{12}}{RT} \left[(\mu + \nu - 1)\frac{n_1 n_2}{n^2} - \frac{\mu n_2}{n} - \frac{\nu n_1}{n}\right]$$
$$+ \frac{W_{13}}{RT} \left[(\mu + \nu - 1)\frac{n_1 n_3}{n^2} - \frac{\mu n_3}{n} + \frac{n_1}{n}\right]$$
$$+ \frac{W_{23}}{RT} \left[(\mu + \nu - 1)\frac{n_2 n_3}{n^2} - \frac{\nu n_3}{n} + \frac{n_2}{n}\right] \quad (4)$$

The equation can be solved numerically to obtain the equilibrium value of n_3.

The work has been initiated with the presumption that the chemical complex Li_4Pb exists in liquid Li–Pb, Li_4Sn in Li–Sn, Na_4Pb in Na–Pb and $NaSn/ Na_4Sn_3/ Na_3Sn$ in Na–Sn alloy systems. The interaction energies W_{ij} and g have been determined following the procedure suggested by Bhatia and Hargrove [10]. g has been taken nearly equal to $-(\mu + \nu)G_M$ as a starting point and then the interaction energies W_{12}, W_{13} and W_{23} have been adjusted to get the concentration dependent free energy of mixing G_M through

Eqs. (1) and (2). The process has been reported for different sets of energy parameters until a good fit for G_M is obtained. It may however be noted that once the energy parameters have been selected, they remain the same for all mixing.

The variations of computed values of free energy of mixing along with their experimental values and the equilibrium values n_3 of the complex as a function of composition of the constituent species of the alloy have been shown in Fig. 1 viz., 1(a), 1(b), 1 (c), 1(d) for Li–Pb, Li–Sn, Na–Pb, Na–Sn alloy systems respectively.

2.2. Structure factor

The partial and total structure factors of the liquid alloy systems in the whole composition range have been studied in the framework of hard sphere reference system [31] using the solution of the Percus–Yevick equation for m-component hard sphere mixture obtained by Hirioke [32] and later on described in detail by Hoshino [33].

Let us consider a ternary hard sphere mixture consisting of hard spheres of diameters σ_1, σ_2 and σ_3 corresponding to the free atoms A, free atoms B and the chemical complex $A_\mu B_\nu$ respectively. Let total number of hard sphere in volume V is N.

$$N = N_1 + N_2 + N_3 \quad (5)$$

Where N_1, N_2 and N_3 are the number of hard spheres corresponding to hard sphere diameters σ_1, σ_2 and σ_3 and their concentrations are given as,

$$X_1 = N_1/N = n_1/n; \quad X_2 = N_2/N = n_2/n; \quad X_3 = N_3/N = n_3/n \quad (6)$$

Here $n_1 = N_1/V; \quad n_2 = N_2/V$ and $n_3 = N_3/V \quad (7)$

The partial structure factors $S_{ij}(k)(i,j = 1,2,3)$ of this ternary system are known through the direct correlation function, $C_{ij}(r)$. This is obtained by solving the Percus–Yevick equation. Taking the symmetries $[S_{ij}(k) = S_{ji}(k) and C_{ij}(k) = C_{ji}(k)]$ into account for the ternary hard sphere mixture, the six independent partial structure factors are obtained which can be expressed as,

$$S_{11}(k) = \left[(1 - n_2 C_{22}(k))(1 - n_3 C_{33}(k)) - n_2 n_3 C_{23}^2(k)\right]/D(k)$$
$$S_{22}(k) = \left[(1 - n_1 C_{11}(k))(1 - n_3 C_{33}(k)) - n_1 n_3 C_{13}^2(k)\right]/D(k)$$
$$S_{33}(k) = \left[(1 - n_1 C_{11}(k))(1 - n_2 C_{22}(k)) - n_1 n_2 C_{12}^2(k)\right]/D(k)$$
$$S_{12}(k) = [(1 - n_3 C_{33}(k))\sqrt{n_1 n_2} C_{12}(k) + n_3 \sqrt{n_1 n_2} C_{13}(k)C_{23}(k)]/D(k)$$
$$S_{13}(k) = [(1 - n_2 C_{22}(k))\sqrt{n_1 n_3} C_{13}(k) + n_2 \sqrt{n_1 n_3} C_{12}(k)C_{23}(k)]/D(k)$$
$$S_{23}(k) = [(1 - n_1 C_{11}(k))\sqrt{n_2 n_3} C_{23}(k) + n_1 \sqrt{n_2 n_3} C_{12}(k)C_{13}(k)]/D(k)$$
$$(8)$$

The total structure factor have been obtained through the empirical relation,

$$S(k) = X_1 S_{11}(k) + X_2 S_{22}(k) + X_3 S_{33}(k) + 2(X_1 X_2)^{1/2} S_{12}(k)$$
$$+ 2(X_1 X_3)^{1/2} S_{13}(k) + 2(X_2 X_3)^{1/2} S_{23}(k) \quad (9)$$

The partial structure factors (PSFs) and the corresponding total structure factor of the individual system at equiatomic composition has been represented in Fig. 2(a) for Li-Pb, Fig. 2(b) for Li-Sn, Fig. 2 (c) for Na-Pb and Fig. 2(d) for Na-Sn alloy systems.

2.3. Electrical resistivity

Incorporating the complex formation model in the structure of [34] formula the electrical resistivity of complex forming binary liquid alloy may be written as

$$R = R_1 + R_2 \quad (10)$$