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Thermodynamical, electron and atomic transport properties of Na-Pb Alloy

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ABSTRACT

In the present paper the atomic and electron transport property of Na-Pb zintl alloy have been studied employing Harrison's first principle pseudopotential technique. The thermodynamical properties have also been calculated on the basis of compound formation employing Bhatia-Hargrove technique near the melting point. These techniques has been used to compute the thermodynamical mixing properties, partial and total structure factor, concentration – concentration fluctuation at long wavelength limit $S_{CC}(0)$ and chemical short range order parameter (CSRO) of the alloy. The results are in good agreement with experiment. Useful information has been interpreted regarding the nature of this alloy.

KEYWORDS

Electrical conductivity;
Thermodynamic properties;
Diffusion;
Structure.

INTRODUCTION

The liquid binary alloys and especially zintl alloys are subject of investigation, both experimentally and theoretically, due to their interesting physical properties and immense practical applications[1-6]. It has been well known that they show anomalous properties with respect to composition. A typical example is the liquid alkali-group IV alloy, for which a variety of properties suggest that compounds form at well defined compositions. However, in Na-Pb the small hump suggests the possible existence of an equiatomic compound besides the octet compound indicated by the peak. A simple explanation for the shift of the stoichiometry in liquid alkali-group IV alloys is provided by the stability rule proposed by Geertsma *et a1*[7] in terms of the so-called Zintl ions[8]. Zintl ions are referred to the ions which are isoelectronic to P or As atoms and hence tend to form tetrahedra like the tetrahedral P_4 and As_4 molecules in the gas phase. According to the works of Hoshino et al[9] and of Lai et al[10,11] the valence-electron charge density changes drastically in going from pure metals to an alloy. This redistribution of valence electrons has been shown by Lai et al[10] to be due to large electro negativity difference between components of the alloy. The transfer of valence electron charges from more electropositive ions to ions comparatively more electronegative has found to significantly affect the HS diameters. This leads, e.g., to a strong concentration dependence of the thermodynamic, electronic transport properties[6]. The electrical conduction theory in the liquid metal using pseudopotential concept provides an alluring field for investigating the electron transport properties of liquid metals and alloys as they are used in many fields of engineering and in metallurgical processes.

Similar fitting process and assumption have been made also by Hoshino and Young[12] in their theoretical study of the entropy of mixing for liquid Na-Pb. In contrast to the thermodynamic mixing properties, the theoretical interpretation of resistivity of Na-Pb alloy is even more qualitative. Matsunaga and Tamaki[13] have proposed the model of multicomponent scattering within a single conduction band. In this model three kinds of scattering centers, Na, Pb and Na Pb, are assumed to exist in the liquid state alloy.

In this paper, we present Harrison's first principle pseudopotential technique (HFPP) to study the atomic and electronic transport properties of Na-Pb alloy. Also, the Bhatia-Hargrove technique has been employed to study the thermodynamical properties of mixing of the system under study. This approach has recently been applied to study similar properties of various liquid alloys and has found to be quite successful[14-16]. The pre peak present in the partial structure factor of unlike atom pair signifies that there is a possibility of formation of compound in the system. Hence, it is proposed in this work to incorporate the concept of complex formation in the structure of Faber-Ziman's[17] formula as the most popular interpretation of anomalous thermodynamic data assumes the existence of chemical complexes (or associates) with finite time, although there is no direct evidence for it. However, an indication for such type of preferential association of the constituent species of the alloy is found in their phase diagram and also in their X-Ray and neutron diffraction pattern. The computations have been done for all the properties at 700 K as experimental data of thermodynamical properties are available for comparison[18].

FORMALISM

Thermodynamical properties

In complex formation, all mixed atoms are not in random arrangement. Some of them are randomly distributed while others coalesce into small groups bound by covalent bond. Hence liquid metal binary alloy becomes a ternary system consisting of free constituent ions of the component metals and chemical complex. Complex formation model[14-16,19-22] 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 $A_\mu B_\nu$ (A=Na, B=Pb, μ=4 and ν=1). The complex formation is calculated through the minimization of the Gibb's function G_M expressed as

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

Here W_{ij} $\left(i,\, j = 1,2,3\right)$ are the interaction energies, R is the molar gas constant and n is the total number of atoms in the case of compound formation.

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

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

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

where,

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

The equation can be solved numerically to obtain the equilibrium value of n_3. The work has been initiated considering the chemical complex Na_4Pb in Na-Pb alloy. The interaction energies W_{ij} and g have been computed on the basis of procedure suggested by Bhatia and Hargrove [19]. The value of g has been taken nearly equal to $-\left(\mu + \nu\right)G_M$ 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 equations (1) and (2). The process has been repeated 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. This gives the number of complexes n_3 with respect to concentrations at equilibrium and also the Gibb's function. The computed values have been shown in

Figure 1 along with the experimental values of Hultgren *et al.*[18]. Once the expression for G_M is obtained, other thermodynamic functions like heat of formation H_M and entropy of mixing S_M, which are related to G_M through standard thermodynamic relation follows readily as

$$\mathbf{H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{T,P,N}} \qquad \mathbf{(5)}$$

$$\mathbf{S_M = \left(\frac{H_M - G_M}{T}\right)} \qquad \mathbf{(6)}$$

The heat of mixing and entropy of mixing have been computed through equations (5) and (6) respectively, and are presented in Figure 2 along with their experimental values as obtained by Hultgren *et al.* [18].

Electrical resistivity

The results of electrical resistivities as function of composition of the constituent species of the alloy depend on the computed values of equilibrium values of the chemical complex (n_3), form factors ($w_{ij}(k,q)$) and partial structure factors ($S_{ii}(k)$ and $S_{ij}(k)$). Hence analysis of the results of electrical resistivities needs analysis of these parameters. The computation of electrical resistivity of ternary systems require three scattering potentials (form-factors) corresponding to two component metals and chemical complex and also six partial structure factors. The model parameters obtained by Ese and Reissland, 1973[23] as shown in TABLE 1 has been used to determine the form-factors.

The liquid electrical resistivity of binary alloys is computed through the well-known Faber–Ziman formalism. The common ingredient form factor $w(k,q)$ have been obtained through model potential represented by

$$W_R = -A \text{ for } r = r_m$$

$$= -\frac{Z}{r} \text{ for } r > r_m$$

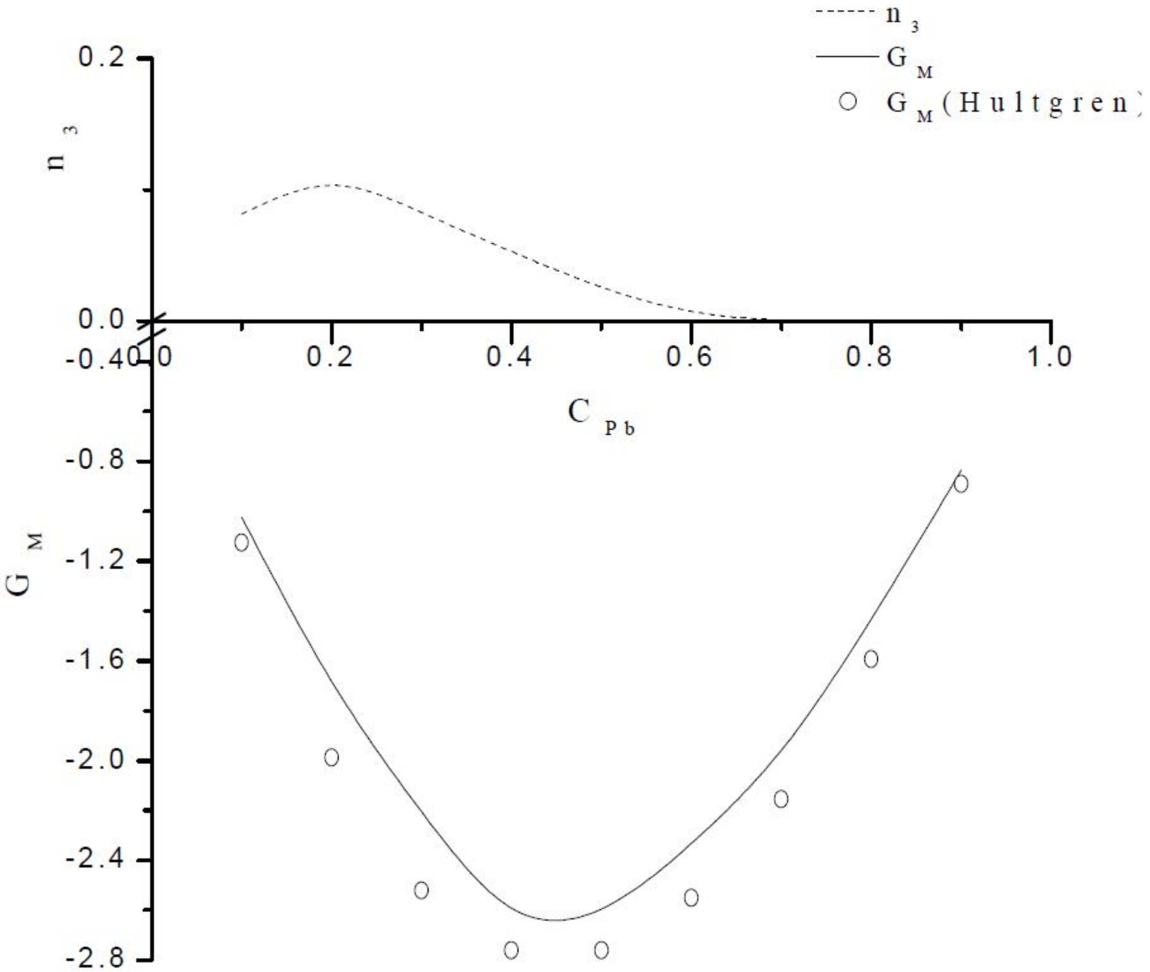

Figure 1 : The variation of Gibb's free energy of mixing as a function of composition

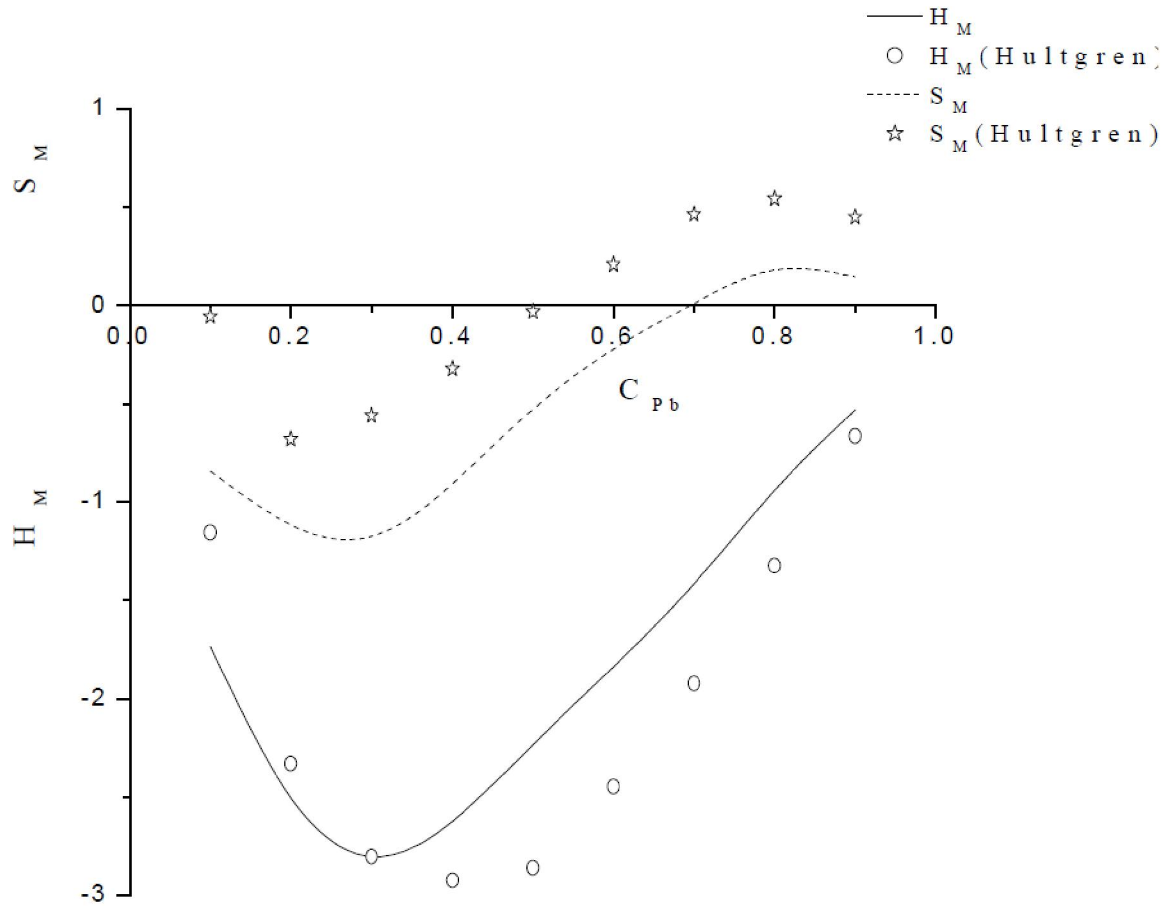

Figure 2 : The variation of heat of mixing and entropy of mixing and entropy of mixing as a function of composition

and the local unscreened form factor is given by

$$\mathbf{W^0(q)} = \left\{ -\left(\frac{4\pi \mathbf{Z}}{\Omega_0 \mathbf{q}^2}\right) \cos \mathbf{q r_m} \right\} - \left\{ -\left(\frac{4\pi \mathbf{Z}}{\Omega_0 \mathbf{q}^2}\right) \left(\sin \mathbf{q r_m} - \mathbf{q r_m} \cos \mathbf{q r_m}\right) \right\} \qquad \textbf{(7)}$$

where, r_m is the model radius, Z the valence, A the model parameter, Ω_0 the atomic volume and q the phonon wave vector. The model parameter is evaluated through the usual procedure of matching the logarithmic derivative of inner and outer wave functions. The Vasishtha–Singwi (V–S)[24] form of exchange-correlation has been used to obtain the screened local form factor given by

$$W(q) = \frac{W^0(q)}{\varepsilon^*(q)}$$

where $\varepsilon^*(q)$ is the modified Hartree dielectric function. The liquid electrical resistivity of the binary alloy is given by

$$\boldsymbol{\rho} = \left(\frac{\mathbf{3\pi}}{\hbar \mathbf{e}^2}\right)\left(\frac{\mathbf{\Omega}}{\mathbf{v_F^2}}\right)\left\langle \mathbf{F_1(q) + F_2(q)} \right\rangle \qquad \textbf{(8)}$$

where

$$\left\langle F_1(q) \right\rangle = 4\int_0^1 [c_1 w_1^2(\mathbf{k},\mathbf{q}) S_{11}(k) + c_2 w_2^2(\mathbf{k},\mathbf{q}) S_{22}(k)$$

$$+ 2(c_1 c_2)^{1/2} w_1(\mathbf{k},\mathbf{q}) w_2(\mathbf{k},\mathbf{q}) S_{12}(k)]\eta^3 d\eta$$

$$\left\langle F_2(q) \right\rangle = 4\int_0^1 [c_3 w_3^2(\mathbf{k},\mathbf{q}) S_{33}(k) +$$

$$2(c_2 c_3)^{1/2} w_2(\mathbf{k},\mathbf{q}) w_3(\mathbf{k},\mathbf{q}) S_{32}(k)$$

$$+ 2(c_1 c_3)^{1/2} w_1(\mathbf{k},\mathbf{q}) w_3(\mathbf{k},\mathbf{q}) S_{31}(k)]\eta^3 d\eta$$

where $\eta = q/2k_F$.

Here, *S(k)* and $w_i(k,q)$ with i = 1, 2, 3 respectively represent the partial structure factors and non-local screened form factors of the constituent elements and chemical complex.

The values of screened form factor $w_i(k,q)$ as a function of compositions have been obtained using the energy dependent non-local optimized model potential of Shaw[25] because it has proved very successful in the study of electronic transport properties of liquid metals. The screened non-local pseudo-potential matrix elements can be expressed as

$$w_i(k,q) = f_i(k,q) + \frac{4\pi}{\Omega q^2 \varepsilon^*(q)}[1 - G(q)]\rho_i + g_i(q)\left(1 - \frac{G(q)}{\varepsilon^*(q)}\right) \quad (9)$$

with

$$f_i(k,q) = -N\sum_{l=0}^{l_0}\left\langle k + q\left|\left(A_{il}(E) - \frac{Z_i}{r}\right)P_l\right|k\right\rangle$$

$$= -\frac{4\pi}{\Omega}\sum_{l=0}^{l_0}(2l+1)P_l(\mathrm{Cos}\theta)\int_0^{r_m}\left(A_{il} - \frac{Z_i}{r}\right)$$

$$\times j_l(|k+q|r) \times j_l(|k|)r^2 dr \quad (10)$$

$j_l(x)$ are spherical Bessel functions and $P_l(Cos\theta)$ are Legendre's polynomials, $g(q)$ is the non-local screening contribution given by

$$g_i(q) = \frac{4}{\pi^2 q^2 \varepsilon(q)}\int_{K \le K_F}\frac{f_i(k,q)}{K^2 - |k+q|^2}d^3k$$

$$\rho_i = \frac{4}{\pi}\sum_{l=0}^{l_0}(2l+1)\int_0^{K_F}k^2 dk\int_0^{r_m}j_l(Kr)\left(\frac{\delta A_{il}}{\delta E}\right)r^2 dr \quad (11)$$

where, *k* is the electron wavevector, ρ_i is the depletion hole which has been determined following the procedure of[25] and l_0 is the highest angular momentum to be modeled. For a given angular momentum, the energy dependent model parameters A_{il} have been determined by matching the logarithmic derivative of wavefunction at the boundary for different ionic term values which in turn yield crystal parameters at $E = E_F$.

The electrical resistivity has been calculated on the assumption that $2n_m$ valence electrons contribute to the formation of the chemical complex and therefore are localized in it. The number of conduction electrons n_c moving in the alloy volume is given by

$$n_C = [c_1 Z_1 + c_2 Z_2]N - 2n_m$$

and the mean number of valence electrons per atom is

$$Z_S = [c_1 Z_1 + c_2 Z_2] - \frac{2n_m}{N}$$

$$K_F = \left(\frac{3\pi^2 Z_S}{\Omega}\right)^{1/3}$$

Structure factor

The purpose of the present study of partial and total structure factors of liquid alloy in detail throughout the whole composition range is two fold: (a) to know whether the hard sphere model predicts the correct total structure factors which is essential to ascertain the correctness of the present approach and (b) to know to what extent the partial structure factors are suitable for predicting the correct electrical resistivity. The experimental data of partial and total structure factors of compound forming binary alloys are not available at different compositions; also they have insufficient accuracy. Thus one has to divulge into computational effort and this is achieved through the hard sphere reference system, obtaining the solutions of Percus–Yevik equation for m-component hard sphere mixture[26,27]. The total structure factor *S(k)* is given by

$$S(k) = c_1 S_{11}(k) + c_2 S_{22}(k) +$$

$$2(c_1 c_2)^{1/2} S_{12}(k)$$

$$+ 2(c_1 c_3)^{1/2} S_{13}(k) + 2(c_2 c_3)^{1/2} S_{23}(k) \quad (12)$$

where $S_{ii}(k)$ and $S_{ij}(k)$ are the partial structure factors, c_i's are the concentration fractions of the three scattering centers *A*, *B*, $A_\mu B_\nu$ (*A* = Na, *B* = Pb, $\mu = 4$ and $\nu = 1$). Here *k* is the wave vector.

These computations need two ingredients namely hard sphere diameters σ_i and packing fraction η related by

$$\eta = \pi(6\Omega)^{-1}\sum c_i \sigma_i^3$$

Here, c_i are the concentrations of the species and Ω is the volume of the alloy.

The hard sphere diameters σ_1 and σ_2 are calculated by matching the first peak of the structure factors of the constituent elements at their melting temperature. They have been assumed to be independent of temperature and σ_3 have been taken as 8.2 nm for Na-Pb alloy. The values of hard sphere diameter of Na-Pb alloy has been tabulated in TABLE 2. The number of complexes n_3 in conjunction with the hard sphere diameters are used to compute the partial and total structure factors.

TABLE 1 : Model crystal parameters* (a.u. = 2 ryd.) and their derivatives at Fermi energy

Metal	a_0	a_1	a_2	$\delta a_0/\delta E$	$\delta a_1/\delta E$	$\delta a_2/\delta E$
Na	0.312	0.357	-	-0.187	-0.117	-
Pb	1.93	2.0	1.38	-0.44	-0.20	0.28
			Complex**			
Na_4Pb	2.242	2.357	-	-0.34	-0.14	-

***Ese and Reissland (1973)**

TABLE 2 : Hard sphere diameters (a.u.) of Na and Pb in Na_4Pb alloys σ_3 = 8.2, Temp = 700 K

Conc. of Na C_{Na}	Volume Ω	σ_{Na}	σ_{Pb}
1.0	277.2	6.15	-
0.8	220.2	6.140	5.36
0.6	218.3	6.128	5.425
0.5	218.1	6.115	5.568
0.4	218.0	6.110	5.580
0.2	217.9	6.097	5.596
0.0	217.72	-	5.530

Diffusion

The available diffusion data in liquid alloys are divided into two groups: one is concerned with self-diffusion coefficient, used to describe diffusion of radioactive tracer atoms in liquids with uniform composition, and the other is due to interdiffusion coefficient which is called for in diffusion experiments associated with non-uniform composition. For a binary system of constant molar volume Darken, 1948[28] showed that the interdiffusion coefficient may be represented as

$$D_{12} = (c_2 D_1 + c_1 D_2)\left[1 + \frac{d \ln f_1}{d \ln c_1}\right] \quad (13)$$

where f_1 is the activity coefficient of 1, D_1 and D_2 are the self diffusion coefficients of the components 1 and 2. The variation in the term $(c_2 D_1 + c_1 D_2)$ accounts for two-thirds of the total variation of the interdiffusion coefficient with composition.

Concentration – Concentration Fluctuation, S_{CC} (0)

The stability and microscopic structures of binary alloys may be studied through the evaluation of Bhatia–Thornton partial structure factors for the long wavelength limit $q \to 0$. This has been termed as concentration–concentration structure factors $S_{CC}(k)$ related to Ashcroft–Langreth structure factors $S_{ij}(k)$ as

$$S_{CC}(k) = c_1 c_2 \left[c_2 S_{11}(k) + c_1 S_{22}(k) - 2(c_1 c_2)^{1/2} S_{12}(k)\right] \quad (14)$$

The ideal value $S_{CC}^{id}(0)$ is given by

$$S_{CC}^{id}(0) = c(1-c) = c_1 c_2 \quad (16)$$

and the actual $S_{cc}(0)$ is given by complex formation model as

$$S_{CC}(0) = \left[\sum_{i,j=1}^{3} \frac{n_j'^2}{n_i} - \frac{n'^2}{n} + \left(\frac{2n}{RT}\right) \sum \sum_{i<j} \left(\frac{n_i}{n}\right)' \left(\frac{n_j}{n}\right)' \frac{W_{ij}}{n^2}\right]^{-1}$$

where

$$i < j \quad (17)$$

where a prime denotes differentiation with respect to c_1. On the other hand, *Scc(0)* computed through the experimental Gibb's free energy of mixing are termed as experimental *Scc(0)*, obtained through

$$S_{CC}(0) = N k_B T \left(\frac{\partial^2 G_M}{\partial c^2}\right)^{-1}_{T,P,N} = (1-c) a_A \left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N}$$

$$= c a_B \left[\frac{\partial a_B}{\partial (1-c)}\right]^{-1}_{T,P,N} \quad (18)$$

where

$$a_A = a_0 + a_1 c + a_2 c^2 + ... + a_{10} c^{10}$$

$$a_B = b_0 + b_1 c + b_2 c^2 + ... + b_{10} c^{10}$$

Here, a_A and a_B are activity of the first and second constituent metals. At temperature above Debye temperature and in the long wavelength limit $S_{CC}(0)$ represents the mean square thermal fluctuations in the particle. The long wavelength limit ($S_{CC}(0)$) of the concentration–concentration structure factor[31] is of considerable importance[32,33] to study the nature of atomic order in binary liquid alloys. The basic advantage of *Scc(0)* is that one can determine it making use of the thermodynamic relations. The last two equalities of Eq. (18) can be used directly to compute $S_{CC}(0)$ from observed numerical data. This is usually known as experimental values of $S_{CC}(0)$. It is possible to use the variation of $S_{CC}(0)$ with concentration to understand the nature of atomic order in liquid alloys. Basically, the deviation of this quantity from its ideal values given by $S_{CC}^{id}(0) = c_1 c_2$, is significant in explaining the interaction between the components of the binary mixture. The basic inference is that $S_{CC}(0) < S_{CC}^{id}(0)$ implies a tendency for hetero-coordination (preference of unlike atoms to pair as nearest neighbours), while $S_{CC}(0) > S_{CC}^{id}(0)$ implies homocoordination (preference of like atoms as nearest neighbours). For a demixing system, $S_{CC}(0) >> S_{CC}^{id}(0)$. The experimental determination of $S_{CC}(0)$ from diffraction experiments is quite complicated; however, it can be calculated from the measured activity data.

Chemical short range order (CSRO) Parameter, ∝

The CSRO is yet another important parameter proposed by Warren[34] and Cowley[35]. Singh and his coworkers[29,30] have linked $S_{cc}(0)$ for $q \to 0$ to the CSRO parameter α through

$$(\mathbf{A},\mathbf{B})_{\mathbf{l,m,n}} = \mathbf{c}(\mathbf{1} - \boldsymbol{\alpha}_{\mathbf{l,m,n}}) \qquad \mathbf{(15)}$$

where *1, m, n* are the coordinates of the nearest neighbour of atom *A* or *B*. $(A,B)_{l,m,n}$ denotes the probability of finding A atom at the atomic site l, m, n as a nearest neighbour of a given *B* atom. In order to measure the degree of order in the liquid alloy, the Warren–Cowley short range order parameter[36,37] α can be computed. Experimentally, the value of α can be determined from the knowledge of the concentration–concentration structure factor and the number–number structure factors. However, in most diffraction experiments, these quantities are not measurable. On the other hand, α can be estimated from the knowledge of $S_{CC}(0)$[38]. Knowledge of α provides an immediate insight into the nature of the local arrangement of atoms in the mixture. $\alpha = 0$ corresponds to a random distribution, $\alpha < 0$ refers to unlike atoms pairing as nearest neighbour, whereas $\alpha > 0$ corresponds to like atoms pairing in the first coordination shell. From a simple probabilistic approach, one can show that the limiting values of α lie in the range

$$\frac{-c}{(1-c)} \le \alpha \le 1, \; c \le \frac{1}{2} \text{ and}$$

$$\frac{-(1-c)}{c} \ge \alpha \ge 1, \; c \ge \frac{1}{2}$$

For equiatomic composition the above relations simply reduces to

$$-1 \le \alpha \le +1$$

The minimum possible value of α is $\alpha^{\min} = -1$, which implies complete ordering of unlike atoms as nearest neighbour. On the other hand, the maximum value $\alpha^{\max} = +1$ implies total segregation leading to phase separation.

RESULTS AND DISCUSSION

Thermodynamic properties of mixing

The interaction energies obtained through the model are $W_{12} = -3.89$, $W_{13} = -2.8$, $W_{23} = -3.5$ and $g = 3.6$ at 700 K (in terms of RT). On experimental grounds a higher value of g > 3.5 suggests that Na-Pb is a strongly interacting system in the light of formation energy *g* and it comes in the category of the Hg–Na, Hg–K, Tl–Te, Mg–Bi, etc., for which the formation energies are much larger i.e., 8.294, 9.965, 10.84, 16.7 respectively in contrast to the light interacting systems like Mg–Sn, Ag–Al and Cu–Sn systems. Further, we observe that the all the interaction energies are repulsive in nature. This also supports the strongly interacting nature of Na-Pb alloy.

The variations of computed values of Gibb's function 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 Figure 1. The graph of G_M is in fairly good agreement with experiment. Also we observe that G_M is symmetrical for Na-Pb contrary to Al–Ca, Ca–Mg, Mg–Zn and Cu–Mg, etc.

A perusal of Figure 2 representing the heat of formation (H_M) and entropy of mixing (S_M) of Na-Pb alloy for various compositions at 700 K along with the experimental data of Hultgren *et al*. reveals that both heat of mixing and entropy of mixing are in good agreement with the experimental ones.

Electrical resistivity

The computed values of electrical resistivity have been shown in Figure 3. The electrical resistivity of the system is found to be asymmetric. No anomalous value is obtained at any concentration. The contributions from complex have been found quite asymmetric having a sharp peak.

Structure factor

In Figure 4 (a), the Partial Structure Factors (PSFs) of Na-Pb alloy has been drawn. In Figure 4 (b), the Total Structure Factor (TSF) of Na-Pb alloy is represented. It can be revealed from Figure 4 (a) that S_{ii} *(k)* remains positive throughout the range while S_{ij} *(k)* has both positive and negative values.

It is found in Figure 4 (b), that there is lateral shifting of main peak of the TSF towards higher k with the amount of doping of Pb atoms. This feature may be attributed to charge transfer taking place in the system. The transition from metallic to ionic regime is accompanied by a considerable volume contraction [39] due to shorter interatomic distances, which is reflected by the shift of the principal peak of S(k) and of the dispersion minimum to larger k. Formation of strong Na-Pb bonds also causes a shift of the dispersion, still dominated by the Na-Na correlations, towards higher frequencies.

It should be mentioned that, the TSF, S(k) shows the behaviour of random mixing without a sub-peak or asymmetry of the first peak and shows the behaviour of compound forming with a sub-peak below the first peak[40]. The partial structure factors of unlike atom pairs have maxima, which lies in between those of like pair of atoms in case of random mixing. On the other hand, in compound forming alloys the partial structure factor of

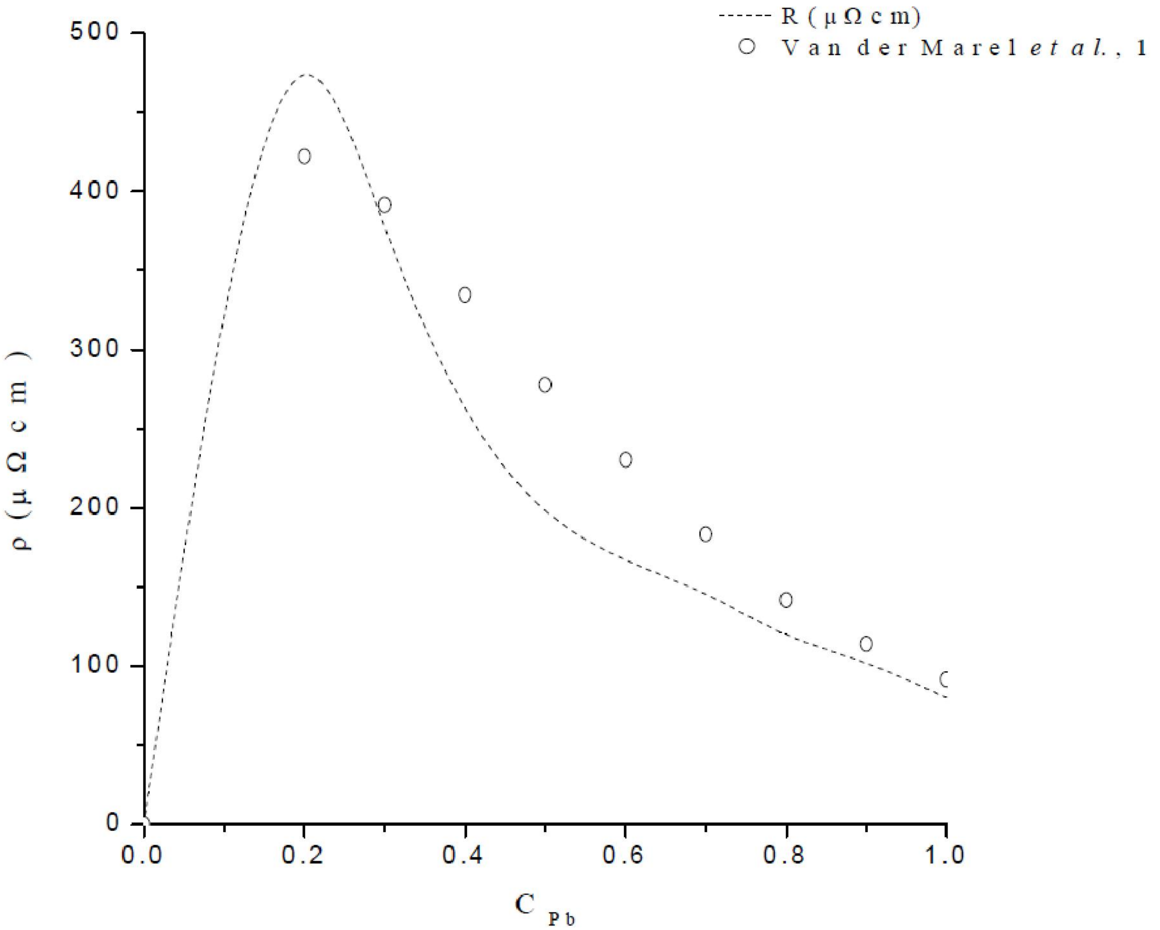

Figure 3 : Variation of resistivity with respect to concentration

unlike atom pairs have a very sharp peak with a sub-peak below the main peak which can also be seen in the figure. Various alloys also show their behaviour in between these two types. Negative peak in the lower region of k/k_F indicates preference for unlike nearest neighbours. The humps in the lower k regions are due to short-range order (SRO) with preference for unlike nearest neighbours[41]. Positive values of partial structure factors imply that the repulsive core part of the effective interionic potential is dominating whereas the negative values imply that the dominating part is attractive in nature.

Diffusion

There are a few systems for which an interdiffusion coefficient has been determined as a function of composition. Such calculations might be of interest for compound-forming systems, since the existence of ‘molecules’, even of a transient nature, would surely impede diffusion. It is found that as long as the term $\left(c_2D_1 + c_1D_2\right)$ varies monotonously with composition an alloy exhibiting a negative deviation from Raoult’s law should have a maximum in the relationship between diffusion coefficient and composition. Similarly, alloys with positive deviations from Raoult’s law can be expected to exhibit a minimum, while those with ideal behaviour should show monotonous concentration dependence. Figure 5 represents the composition dependence of interdiffusion coefficient of Na-Pb alloy. It is inferred from the figure that Na-Pb alloy shows negative deviation from Raoult’s law.

Concentration – Concentration Fluctuation and CSRO

The computed CSRO is presented in Figure 6 for perusal. From Figure 6, we observe that for Na-Pb we get $S_{CC}(0) \le S_{CC}^{id}(0)$ for all concentrations, while α is

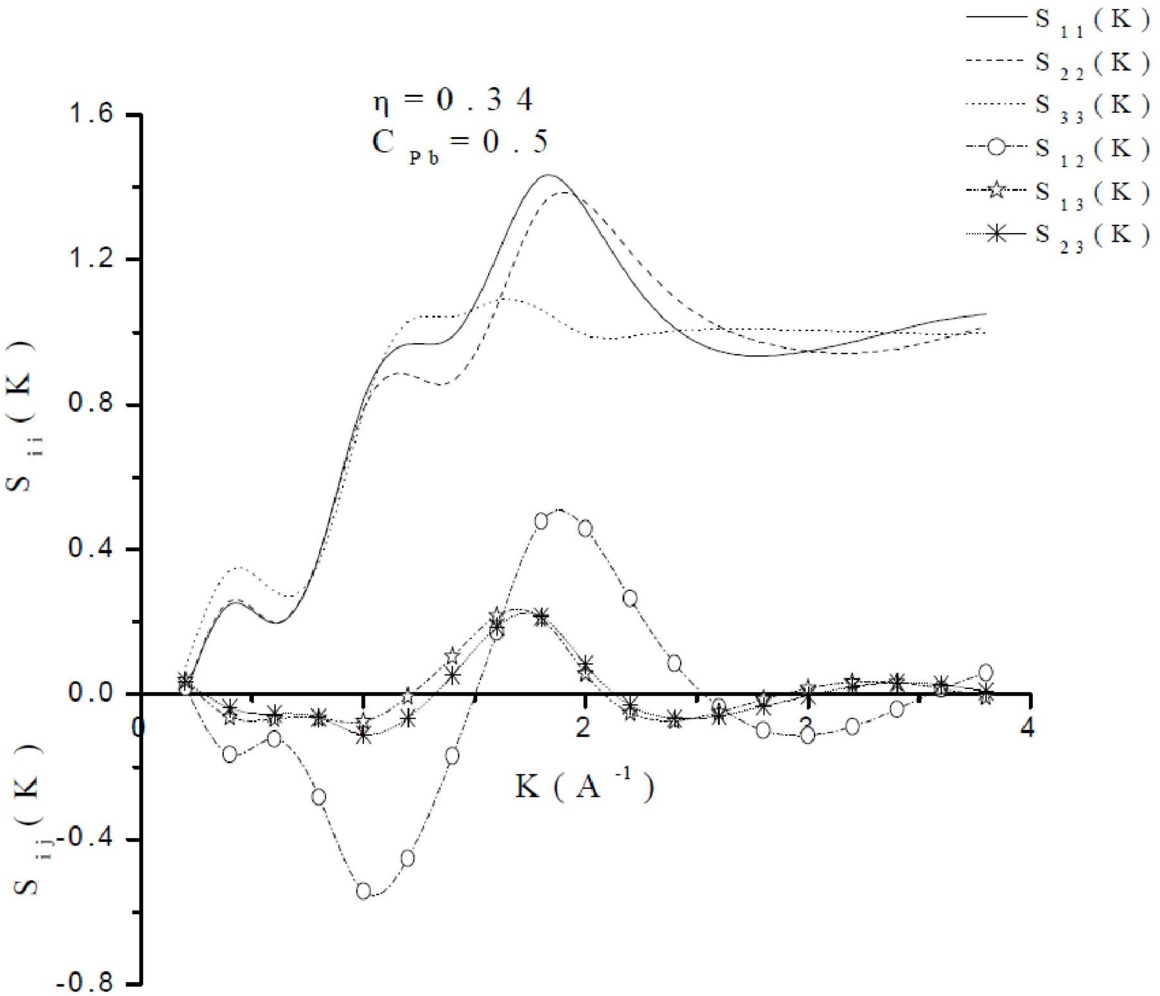

Figure 4 : Partial structure factors of liquid Na$_4$Pb alloy

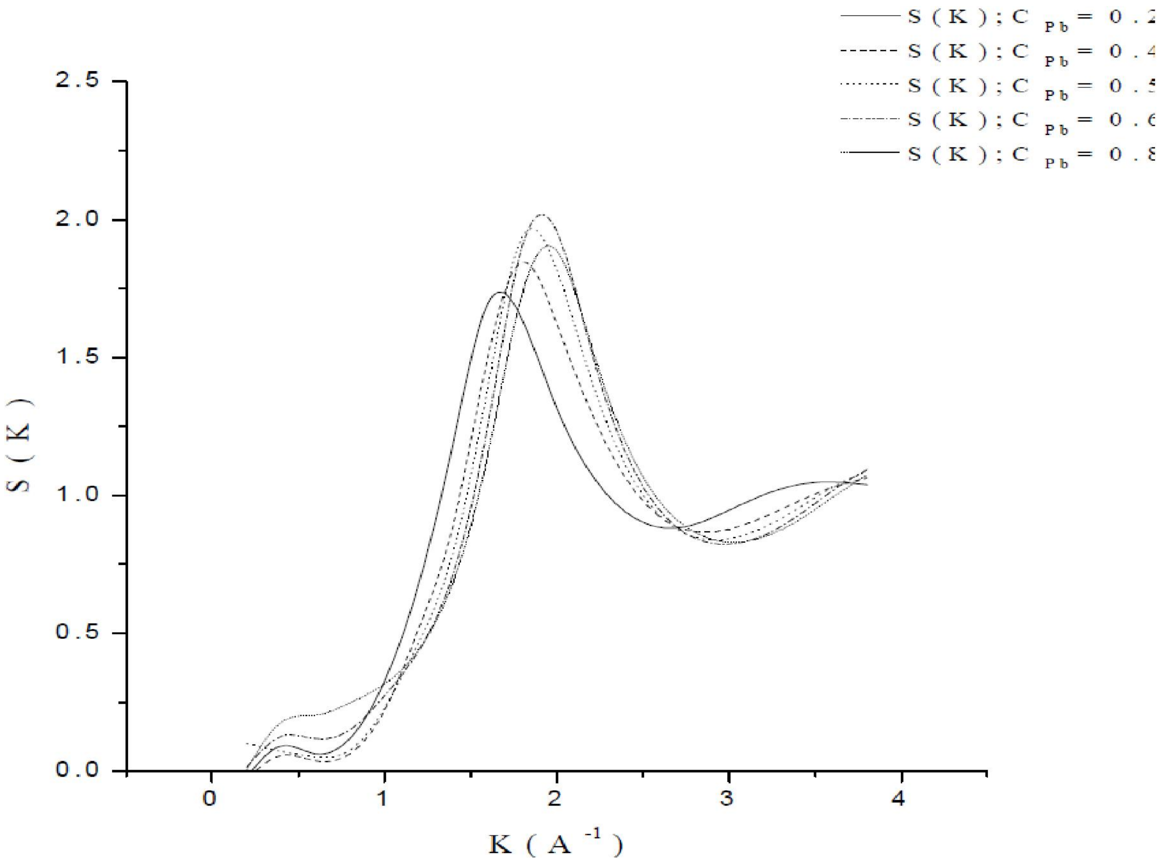

Figure 4b : Variation of total structure factor with respect to concentration

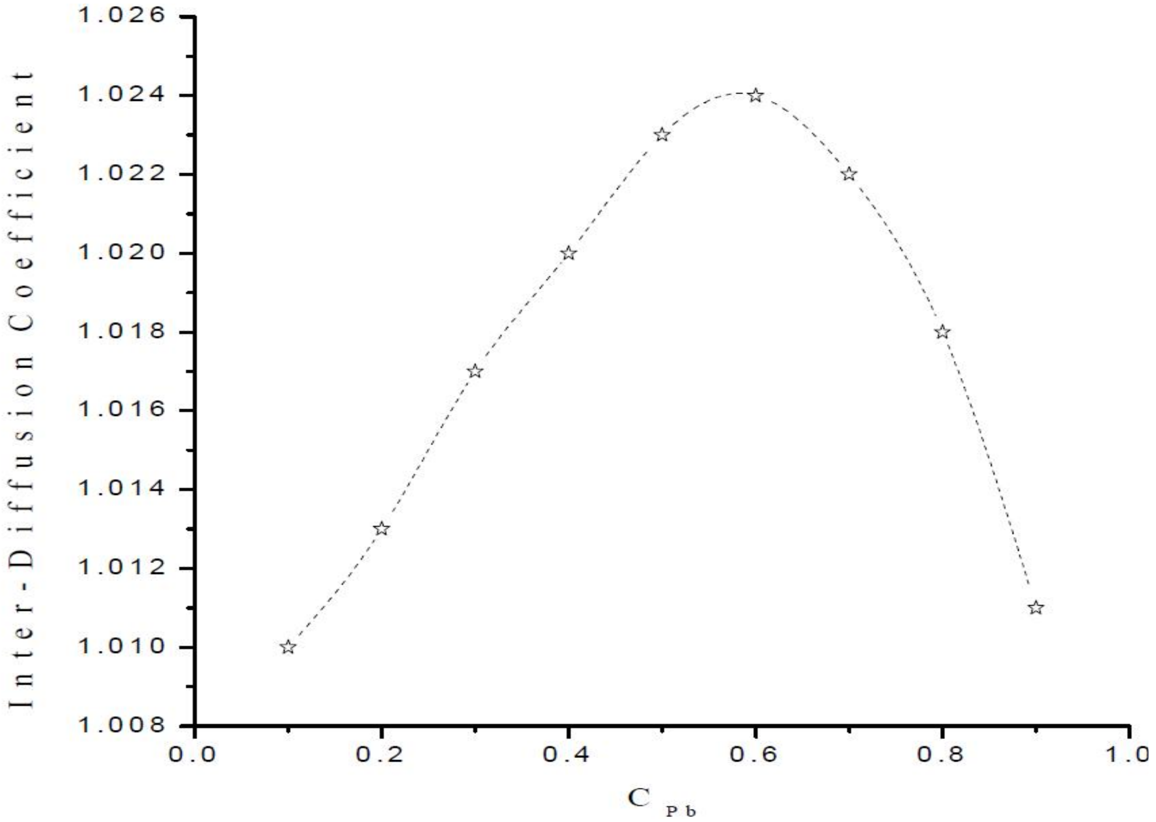

Figure 5 : Composition dependence of interdiffusion coefficient

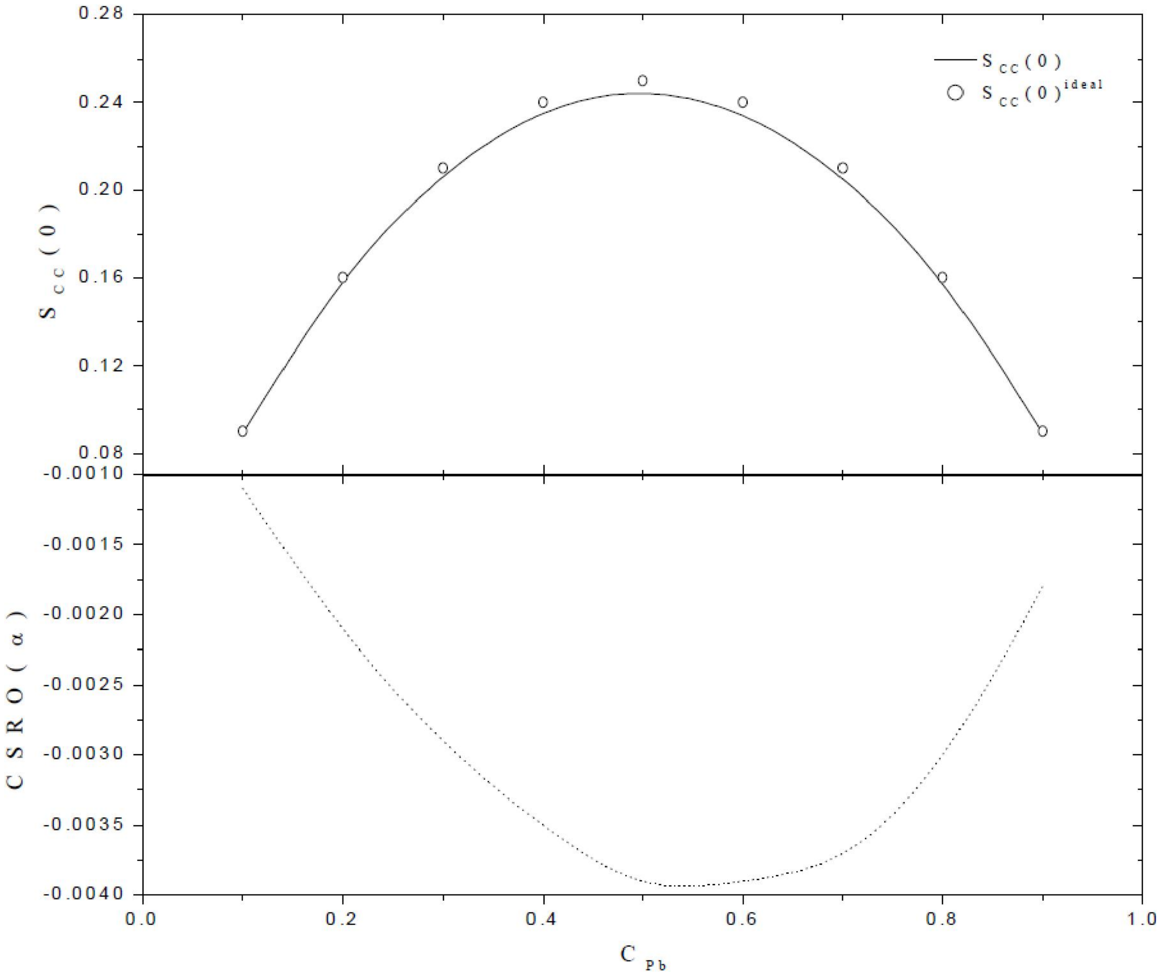

Figure 6 : Concentration dependence of S_{CC} (0) and CSRO

throughout negative. The theoretical and ideal data of $S_{cc}(0)$ are in good agreement.

CONCLUSIONS

a. The pre peaks in liquid alloys result from the formation of compounds or complexes. This is certainly suggestive for describing energetically favorable configuration of ions in liquid alloys.

b. The Faber-Ziman formula in conjunction with complex formation model (CFM) has been considered to determine the concentration dependent electrical resistivity of liquid Na-Pb alloy.

c. The electrical resistivity has been calculated on the assumption that $2n_m$ valence electrons contribute to the formation of the chemical complex and therefore localized in it.

d. Substantial effect of equilibrium values n_3 of the complex on the structure factors of liquid Na-Pb alloy has been found. The position of the peak values has been found shifted towards the longer wavelength side with the increase in the value of n_3.

e. The sub peak prior to first distinct peak in the PSF of like as well unlike atom pairs indicates the formation of compound in this system.

f. The charge transfer takes place in the system when the Pb is added to liquid Na as evident from Figure 4 (b).

g. The composition dependence of interdiffusion coefficient reveals that the alloy shows negative deviation from Raoult’s law.

h. The twin headed peak found in S_{33} (K) signifies the existence of some short-range order between like atoms.

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