

## Electrical resistivity of NaPb compound-forming liquid alloy using *ab initio* pseudopotentials

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**Abstract.** The study of electrical resistivity of compound-forming liquid alloy, NaPb, is presented as a function of concentration. Hard sphere diameters of Na and Pb are obtained through the interionic pair potentials evaluated using Troullier and Martins *ab initio* pseudopotential, which have been used to calculate the partial structure factors  $S(q)$ . Considering the liquid alloy to be a ternary mixture, Ziman formula, modified for complex formation has been used for calculating resistivity of binary liquid alloys. Form factors are calculated using *ab initio* pseudopotentials. The results suggest that Ziman formalism, when used with *ab initio* pseudopotentials, are quite successful in explaining the electrical resistivity data of compound-forming binary liquid alloys.

**Keywords.** *Ab initio*; resistivity; liquid alloys; binary.

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### 1. Introduction

Liquid metal alloys like NaPb which form compounds at one or more stoichiometric composition have been found to exhibit anomalous behavior in their thermodynamic, structural and transport properties. Entropy of mixing of NaPb exhibits positive values at both ends and negative values for intermediate concentrations [1]. Considerable success has been achieved to explain the anomalous thermodynamic properties of compound-forming alloys with the help of complex formation model proposed by Bhatia and Ratti [2]. Later, using hard sphere model, entropy of mixing of compound-forming alloys LiPb and NaPb has been explained by Hoshino and Young [3]. Though structural and thermodynamic properties of NaPb have been studied successfully by many [4–8], electrical resistivity of NaPb has been studied by only a few [9,10].

The most popular method to study the electrical resistivity of liquid metals and their alloys is the electrical conduction theory developed by Faber and Ziman [11] using the concept of model pseudopotential. This concept of pseudopotential for calculating various dynamic properties of metallic systems has been extremely

useful for the last three decades [12,13]. However, this approach has not been found adequate to explain anomalous electrical properties of many liquid alloys at a specific composition.

More recently, the construction of pseudopotentials has been shifted from model to *ab initio* construction of pseudopotentials. The problem with model pseudopotentials is their transferability, because, sometimes with change of environment, change of parameters are also required to get good agreement with experimental results. *Ab initio* pseudopotentials are free from this defect. Moreover, *ab initio* methods provide a lot of information about electronic, static and dynamic properties [14], which enables us to have a comparison with experimental results. Norm conserving pseudopotential concept allows improved calculations of atomic systems.

In order to explain the electrical resistivity of the alloy of Na and Pb, compound NaPb has been assumed at the stoichiometric concentration. In an earlier work [9,10] resistivity has been explained by assuming Na<sub>4</sub>Pb compound in NaPb alloy but recently [15] *ab initio* molecular dynamics has put the formation of compound Na<sub>4</sub>Pb in doubt. In §2 equations for calculating pair potentials and equations for the modified form of Ziman formula for calculating resistivity are given. In §3, the calculated hard sphere diameters and resistivities of NaPb alloy are given. Section 4 deals with the conclusion of the present work.

## 2. Theoretical formalism

An important application of pseudopotentials is the calculation of transport properties of disordered materials such as liquid or amorphous metals and alloys. Electrical resistivity of a binary liquid alloy has been explained in detail by Faber and Ziman. The essentials of the Faber–Ziman theory modified for a compound-forming binary liquid alloy are being given here. Further details can be found in [11,16]. Atomic units with  $\hbar = 1$ ,  $\hbar/(mc^2) = a_0 = 1$  and  $m = \frac{1}{2}$  are used throughout.

Complex formation model [17,18] has its basis on the fact that a typical binary liquid alloy forms a compound at one or more stoichiometric compositions and therefore behaves like a ternary mixture consisting of free atoms A, B and a chemical compound or pseudomolecule A<sub>α</sub>B<sub>β</sub> such that  $\alpha A + \beta B = A_\alpha B_\beta$ . There are  $n_A$  free atoms of A,  $n_B$  free atoms of B and  $n_m$  pseudomolecules in the alloy. The total number of scattering points are  $N_s = n_A + n_B + n_m = nN$ , where  $n = n_1 + n_2 + n_3$ ,  $n_1 = 1 - c - \alpha n_3$  and  $n_2 = c - \beta n_3$ . Here  $c$  is the concentration of the second component. The free energy of mixing  $G_M$  of the alloy may be written as  $G_M = -n_3g + G'$  where  $g$  is the formation energy of complex and  $-n_3g$  represents lowering of free energy due to the formation of the complex in the alloy. Here  $G'$  is the free energy of mixing of ternary alloy of fixed  $n_1, n_2$  and  $n_3$ . Since strong interaction energies are taken care of, through the formation of chemical compound, the alloy can be treated as a weakly interacting system. Here, for  $G'$ , conformal solution approximation [19] can be considered. So  $G_M$  can be expressed [20] as

$$G_M = -n_3g + RT \sum_{i=1}^3 n_i (\ln n_i - \ln n) + \sum_{i < j} \sum \frac{n_i n_j}{n} W_{ij},$$

where  $W_{ij}$  ( $i, j = 1, 2, 3$ ) are interaction energies. In order to calculate the interaction energies,  $W_{ij}$ s, compound-forming concentration  $c_c = (\alpha/(\alpha + \beta))$  was determined.  $c_c$  for NaPb alloy corresponding to the compound NaPb is 0.5. The whole concentration range is divided into two parts,  $0 < c < c_c$  and  $c_c < c < 1$ . Then at the stoichiometric composition  $c_c = (\alpha/(\alpha + \beta))$  and  $G_M = -n_3(g/RT)$  starting value for  $g/RT$  of  $k$ , is determined. Here  $n_3$  is given by  $n_3 = (c/\alpha)$ , for  $0 < c < c_c$  and  $n_3 = (1 - c)/\beta$  for  $c_c < c < 1$ . With this  $g/RT$  the expression for  $G_M$  for  $c < c_c$  contains the single unknown parameter  $W_{23}$  since  $n_1 \simeq 0$ . This value of  $W_{23}$  was determined from the observed data on  $G_M$  at an intermediate concentration between 0.1 and  $c_c$ . Similarly, a value of  $W_{13}$  is thus determined from the observed value of  $G_M$  at an intermediate concentration between  $c_c$  and 0.9. Now, by considering any intermediate concentration between 0.1 and  $c_c$  or  $c_c$  and 0.9 and using the above-calculated  $W_{23}$  and  $W_{13}$ , eq. (1) gives the value of  $W_{12}$ . The equilibrium values  $n_3$  of the compound are obtained through the condition  $(\delta G_M/\delta n_3)_{T,P,c} = 0$  which gives  $(n_1^\alpha n_2^\beta/n_3 n^{\alpha+\beta+1}) = e^{-g/RT} e^Y$  where

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

Liquid binary system with a compound requires six partial structure factors for the calculation of electrical resistivity. In the present work the partial structure factors  $S_{ij}$  ( $i, j = 1, 2, 3$ ) for ternary mixture have been calculated using Hoshino's expressions [21]. Here  $m$ -component hard sphere system using Hiroike's [22] solution of Percus–Yevic equation [23] have been used.

To calculate the partial structure factors for the ternary mixture three-component hard sphere mixture matrix is given by

$$S(k) = \begin{vmatrix} S_{11}(k) & S_{12}(k) & S_{13}(k) \\ S_{21}(k) & S_{22}(k) & S_{23}(k) \\ S_{31}(k) & S_{32}(k) & S_{33}(k) \end{vmatrix}. \quad (2)$$

For the  $m$ -component hard sphere mixture, model diameters are taken as  $\sigma_1 < \sigma_2 < \sigma_3, \dots, < \sigma_m$  and hard sphere ratio is given by  $\gamma_{ij} = (\sigma_i/\sigma_j)$ . The  $(2m - 1)$  parameters which describe the hard sphere system involve  $x_i = (n_i/n)$  where  $n = (N/V)$ ,  $n_i = (N_i/V)$  and  $\sum_{i=1}^m x_i = 1$  and packing fraction  $\eta_i = (\frac{\pi}{6})\eta_i\sigma_i^3$  satisfying  $\eta = \sum_{i=1}^m \eta_i$ . In order to calculate hard sphere diameters, interionic pair potential can be used by generalizing Harrison's [24] approach of pairwise potential between the metallic ions.

The pair potential has the familiar form of the screened Coulomb potential

$$V_{ij} = \frac{Z_i^* Z_j^*}{R} \left[ 1 - \frac{2}{\pi} \int_0^\infty F_{ij}^N(q) \frac{\sin(qR)}{q} dq \right], \quad (3)$$

where  $Z_i^*, Z_j^*$  [25–27] are effective valencies and  $F_{ij}^N(q)$  is a normalized energy wave number dependent characteristic that contains total band-structure effects in the

alloy using the self-consistent electron screening. In many cases, especially for non-local pseudopotentials, valence  $Z$  is replaced by effective valence  $Z^*$ . The effective valence charges  $Z_i^*$  and  $Z_j^*$  are given in the form  $Z_i^*Z_j^* = Z_iZ_j - \bar{Z}_i\bar{Z}_j$ , where  $Z$  is the true valence and  $\bar{Z}$  is the depletion hole charge that originates from orthogonality condition between valence and core electron wave functions.  $F_{ij}^N(q)$  is given by

$$F_{ij}^N(q) = -\left(\frac{q^2\Omega}{2\pi Z_i Z_j}\right)F_{ij}(q),$$

where, in the general case,  $F_{ij}(q)$  is given by

$$F_{ij}(q) = -\left(\frac{q^2\Omega}{8\pi}\right)\left[w_i(q)w_j(q)\frac{\epsilon^*(q)-1}{\epsilon^*(q)}\frac{1}{1-G(q)}\right]. \quad (5)$$

Here the quantities  $w_i(q), w_j(q)$  are Fourier transforms of self-consistent bare ion (unscreened) atomic pseudopotentials for the metallic component of the alloy, obtained by using generalized first principle pseudopotential theory. Here Troullier and Martins (TM) unscreened pseudopotentials have been used.  $G(q)$  is the exchange-correlation functional by Vashishta and Singwi [28].  $\epsilon^*(q)$  is the modified Hartree dielectric function. Here  $\Omega = \Omega_{\text{ideal}} = (1 - c_2)\Omega_1 + c_2\Omega_2$  where  $c_2$  is the concentration of second component in alloy and  $\Omega_1$  and  $\Omega_2$  are the atomic volumes of pure elements. In the present work, volume of alloy for NaPb has been taken from the work of Ruppertsberg and Speicher [29].

### 2.1 Electrical resistivity

Electrical resistivity of complex-forming liquid alloy using modified Faber-Ziman approach can be written as

$$R = R_1 + R_2.$$

Here  $R_1$  represents the scattering contribution from bare A and B ions whereas  $R_2$  represents the scattering contribution due to complex and can be expressed as

$$R_1 = \frac{3\pi}{\hbar^2 e^2} \frac{4\Omega}{V_F^2} \int_0^1 [x_1 v_1^2(q) S_{11}(q) + x_2 v_2^2(q) S_{22}(q) + 2\sqrt{x_1 x_2} v_1(q) v_2(q) S_{12}(q)] (q/2k_F)^3 d(q/2k_F) \quad (6)$$

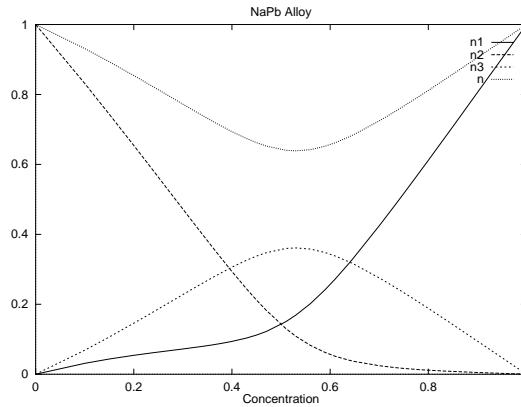
$$R_2 = \frac{3\pi}{\hbar^2 e^2} \frac{4\Omega}{V_F^2} \int_0^1 [x_3 v_3^2(q) S_{33}(q) + 2\sqrt{x_2 x_3} v_2(q) v_3(q) S_{32}(q) + 2\sqrt{x_1 x_3} v_1(q) v_3(q) S_{31}(q)] (q/2k_F)^3 d(q/2k_F), \quad (7)$$

where  $V_F = (\hbar k_F/m)$  is the Fermi velocity and  $k_F = (3\pi^2 Z_s)^{1/3}/\Omega$  is the Fermi wave vector.  $Z_s$  is the mean number of valence electrons per atom and is given by

$$Z_s = [(1 - c)Z_1 + cZ_2] - 2n_3.$$

$x_1, x_2, x_3$  are fractions of concentration of the elements and the complex in an alloy.  $v_1(q), v_2(q), v_3(q)$  are the respective non-local screened pseudopotentials.

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**Figure 1.** Concentration dependence of  $n_1, n_2, n_3$  and  $n$ .

### 2.2 Construction of *ab initio* pseudopotentials

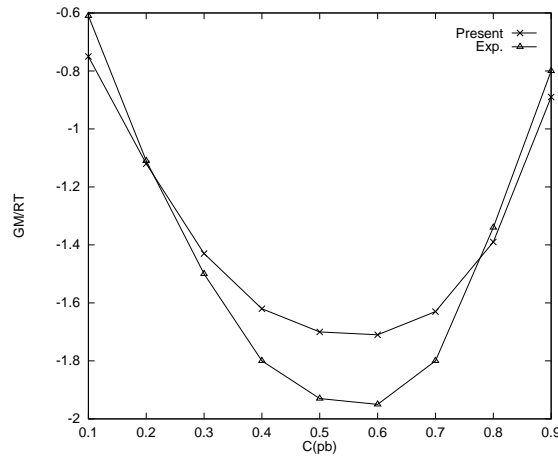
For the calculation of *ab initio* screened pseudopotentials, Troullier and Martins (TM) [30] method has been used because this method produces computationally efficient pseudopotentials with a plane-wave basis set. The problem of transferability as in traditionally used model pseudopotentials also does not exist. TM pseudopotentials have proved their applicability with the calculations of systems of a larger number of elements in the periodic table in contrast to other *ab initio* pseudopotentials like that of Bachelet, Hamann and Schluter [31]. In the present work fhi98PP code [32] to generate the TM *ab initio* pseudopotentials has been used. First *ab initio* pseudopotentials are constructed by all-electron calculation of free atom in a reference configuration and then the method of Troullier and Martins is used to construct the screened pseudopotential.

In the formulation of the present work one pseudopotential per atom has been calculated for both Na and Pb for  $l = 1$  component of angular momentum, because in each case best matching of eigenvalues and wave functions was obtained. This has been done to check the transferability.

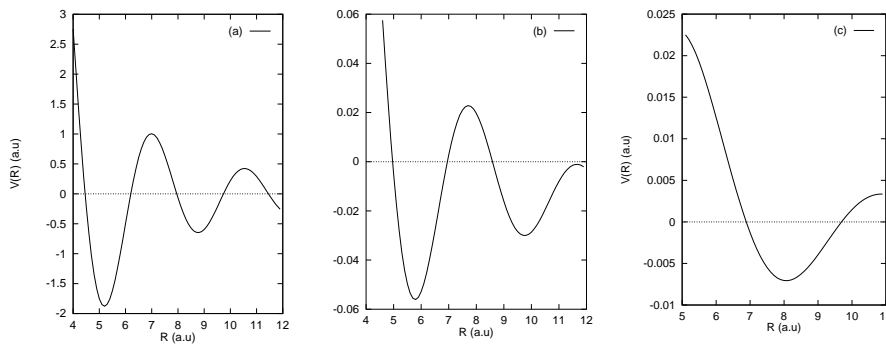
### 3. Results and discussion

Figure 1 shows the equilibrium values  $n_1, n_2, n_3$  for NaSn alloy. These values have been calculated using eq. (1).  $W_{ij}$  are the interaction energies to get good agreement with free energy of mixing  $G_M$ . Figure 2 shows that free energy of mixing for NaPb alloy are more or less in good agreement with the experimental results [4]. Here  $\alpha = \beta = 1$  has been chosen for compound NaPb.

The hard sphere diameters are determined using the relation  $V_{ij}(\sigma_i) = V_{\min} + \frac{3}{2}K_B T$  at temperature  $T = 700$  K for NaPb alloy. Here  $V_{\min}$  is the first minimum in the interionic pair potential. Pair potentials have been calculated through eq. (3) using *ab initio* pseudopotentials. Calculated values of hard sphere diameters



**Figure 2.** Free energy of mixing ( $G_M/RT$ ) vs. concentration for NaPb alloy. (\*) Present values and ( $\Delta$ ) experimental values [4].



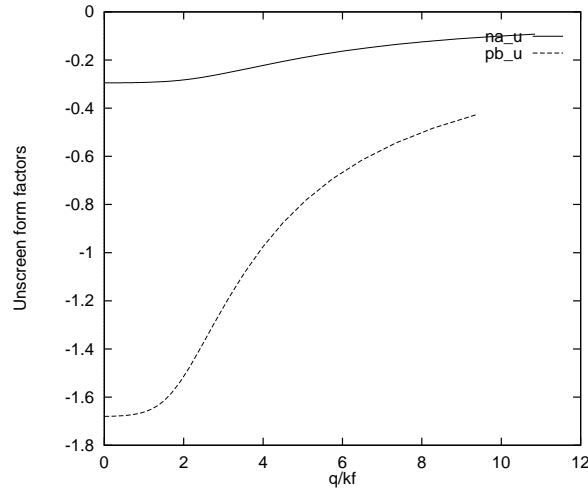
**Figure 3.** Pair potentials in (a) pure Na, (b) pure Pb and (c) NaPb alloy.

are given in table 1. Figure 3 shows the calculated pair potentials for NaPb alloy. Figure 3c shows the interionic pair potentials for  $\text{Na}_{0.5}\text{Sn}_{0.5}$ . Graphs show that the depths of potentials are decreasing for both Na and Pb in the alloy state, which indicates that effective interaction between alkali-alkali atoms decreases on alloying which is consistent with other work [7]. We define the effective valence in binary alloy to be  $[33]Z^* = x_1Z_1 + x_2Z_2$  where  $Z_1$  and  $Z_2$  are the true valence and  $x_1$  and  $x_2$  are the fractions of two elements in the alloy.

Figure 4 shows bare ion form factors for pure Na and Pb for the calculation of pair potentials. For the calculation of resistivity, Fourier transform of screened pseudopotentials used have been shown in figure 5. Here pseudopotential  $v_3$  for the complex has been considered as a disposable parameter and we assume that  $v_3(q) = \frac{v_1(q)+v_2(q)}{2}$  for NaPb compound which is virtual atomic approximation. Electronic configuration and pseudising core radii used to generate *ab initio* pseudopotentials for Na and Pb are given in table 2. In most cases atomic ground states work very well for the occupied atomic orbitals. But a specific way of writing

**Table 1.** Hard sphere diameters,  $Z_s$  and  $k_F$  for NaPb alloy (units in a.u.).

$C_{sn}$	$\sigma_{na}$	$\sigma_{Pb}$	$Z_s$	$k_F$
0.0	6.400	–	0.997	0.4882
0.1	6.390	5.570	1.30	0.5239
0.2	6.250	5.575	1.60	0.5665
0.3	6.247	5.579	1.90	0.6095
0.4	6.246	5.580	2.29	0.6589
0.5	6.245	5.860	2.50	0.6833
0.6	6.242	5.900	2.80	0.7163
0.7	6.240	5.980	3.10	0.7507
0.8	6.231	6.020	3.40	0.7847
0.9	6.220	6.180	3.70	0.8210
1.0	–	6.210	4.00	0.8674



**Figure 4.** Bare ion form factors.

**Table 2.** Electronic configuration and pseudocore radii for constructing *ab initio* pseudopotentials.

Metal	Electronic configuration	Core radii (a.u.)
Na	$3s^{1.0}3p^{0.25}3d^{0.25}$	$r_c(s, p, d) = (2.2, 2.2, 2.5)$
Pb	$6s^{2.0}6p^{2.0}6d^{0.0}5f^{0.0}$	$r_c(s, p, d, f) = (1.0, 1.0, 1.0, 1.0)$

the electronic configuration, resembling the solid state can be used, if it does not change the result much. As in the present work the electronic configuration of Na has been taken. The calculated values of electrical resistivity for NaPb alloy are

compared with experimental values in figure 6. Dependence of  $R$  on  $R_1$  and  $R_2$  is also shown in figure 6.

#### 4. Conclusion

In the present work, hard sphere diameters were calculated using *ab initio* pseudopotentials which in turn were used to calculate partial structure factors for the calcu-

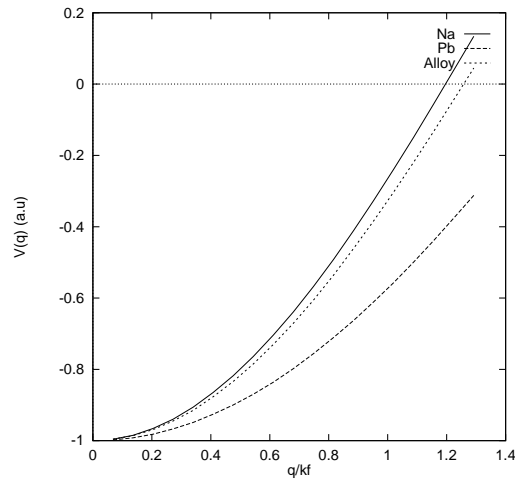


Figure 5. Fourier transform of screened form factors.

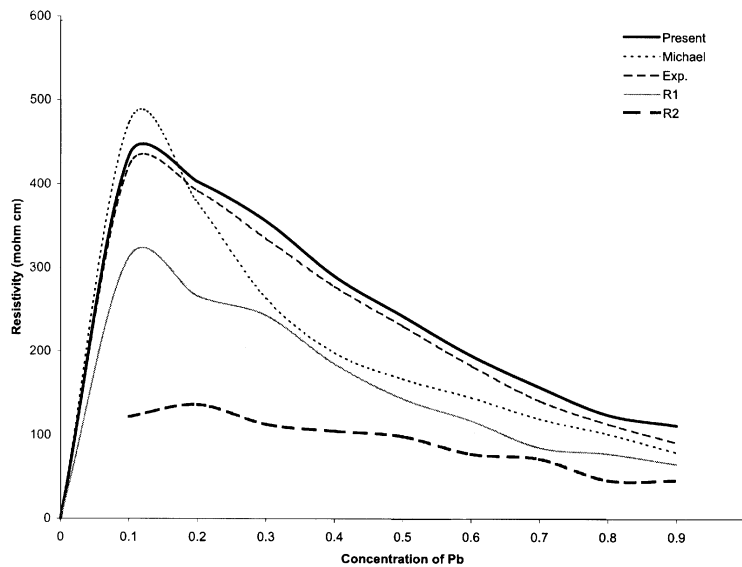


Figure 6. Concentration-dependent resistivity of NaPb alloy.



lation of electrical resistivity. The computed electrical resistivity of NaPb is given in figure 6 along with experimental results [34]. Electrical resistivity for NaPb are in excellent agreement with experimental results. It is found that the calculated electrical resistivity vary smoothly with the concentration of each constituent and well-defined ‘electrical resistivity surface’ pattern of continuity is followed. These results suggest that first principal approach for calculating pseudopotentials within the framework of Ziman formalism is quite good in explaining resistivity of complex-forming liquid alloys. It certainly shows that using screened *ab initio* pseudopotentials is superior to the earlier approach of using model pseudopotentials, which can be used for understanding other transport properties of liquid alloys having complex formation.

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