A Simultaneous Study of the Thermodynamic Property and Transport Coefficient of Na-based Liquid Alloys

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A first-principles nonlocal pseudopotential is applied to study the thermodynamic excess entropy of mixing and the electrical resistivity of Na-based liquid binary alloys. We show that both these properties can be studied simultaneously and self-consistently. For the two Na-based liquid alloys, the results obtained for the excess entropies of mixing are compared with each other in order to see the importance of various contributions and their physical significances. When compared with experimental data, we find that the input densities to the present calculation are crucial and must be highly reliable if an accurate excess entropy of mixing is to be obtained. The same input sources are then used to calculate the electrical resistivity for the Na-Pb system. It appears that the partial localisation of valence electrons on the more electronegative ions is the cause for the anomalies found in this liquid alloy system.

I. INTRODUCTION

Within the last three years, there have been a number of experiments reported for the liquid Na-Pb alloys. Among these the electrical resistivities have been measured independently by Mare1 et al. 1, Matsunaga and Tamaki 2, and Calaway and Saboungi 3, the thermodynamic properties by Tamaki et al. 4-5, and the magnetic susceptibilities by Matsunaga et al. 6. This liquid binary alloy has been extensively studied because all the above properties show the same anomalous feature at a same concentration. For example, the resistivity of liquid Na-Pb increases abruptly at the \( C_P \approx 0.25 \); the deviation of magnetic susceptibilities from linearity is maximum around \( C_P \approx 0.2 \) and the entropy of mixing shows a deep minimum at \( C_P \approx 0.22 \). In spite of these interesting anomalies, there are not many first-principles theories published in the literature. Hafner at al. 7 have advanced a phenomenological calculation for the entropy of mixing. Although the results obtained by them seem to predict quite well the overall structure, there is, however, an unsatisfactory feature found in the calculation. In their work in calculating the entropy of mixing, the pack-
ing fraction, \( \eta \), for an alloy is an input quantity. Instead of determining the \( \eta \) theoretically Hafner et al first fitted the packing densities for the pure metals to experimental entropies and then used them to obtain alloy packing fraction assuming that the hard sphere (HS) volumes remain unchanged. The latter assumption, in particular, is theoretically in doubt because according to the works of Hoshino et al \(^8\) and of Lai et al \(^9-10\) (hereafter refer to as I and II) 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 \(^9\) to be due to the electronegativity difference between components in an alloy. The transfer of valence-electron charges from more electropositive ions to ions comparatively more electronegative has found to significantly affect the HS diameters. For example, it is because of these subtle changes of HS diameters that lead us to account for such anomalous negative excess entropy of mixing for the liquid Na-Cs \(^9\). The electronegativity difference between Na and Pb is definitely much larger. Similar fitting process and assumption have been made also by Hoshino and Young \(^11\) 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 \(^2\) have proposed the model of multicomponent scattering within a single conduction band. In this model three kinds of scatterers, Na, Pb and Na, Pb, are assumed to exist in the liquid state alloy. The calculation of resistivity (denoted by \( \rho \) from hereon) then proceeds with the determination of mole fraction of Na, Pb using the thermodynamic mixing results measured by the same group. This variation of the mole fraction of Na, Pb vs. concentration is further fitted to experimental \( \rho \) to obtain relaxation times and hence the resistivity for the Na-Pb is calculated. As there is as yet no structural information available for this liquid binary alloy, the procedure described by Matsunaga and Tamaki is only speculative. On a somewhat general grounds, the resistivity of Na-Pb has been discussed theoretically by Calaway and Saboungi \(^3\). The line of argument used by the latter authors is based on the concept of electronic charge transfer and quite similar in spirit as the work to be presented below.

It is clear from the above discussion that there is need for more quantitative calculation to interpret such anomalies found in the Na-Pb system. In this paper, we present a quantitative and self-consistent calculation of the entropy of mixing and resistivity for the Na-Pb alloys. The method to be given below is the widely used variational thermodynamic approach. This approach has recently been applied \(^{10}\) to study similar properties for the Mg-based liquid alloys and has found to be quite successful. To compare the change in the results obtained, we have considered also liquid Na-K alloys at a temperature much higher than the liquidus. There are two further reasons that motivate us to study this alloy system. First, at a temperature \( T = 500^\circ\text{C} \), the excess entropy of mixing (denoted by \( S^e \) hereon) has been measured by Lantratov \(^{12}\) and found to be negative over the whole concentration region. This result is quite interesting for the \( S^e \) of Na-K alloys at \( T = 100^\circ\text{C} \) has been reported \(^{13}\) to be negative for \( 0 < C_K < 0.62 \) and becomes positive in the remaining concentration. Secondly, in view of the fact that almost all theoretical thermodynamic calculation of liquid binary alloys appeared in the literature are being carried out at or near liquidus temperature, it would be interesting to see how the features of mixing properties
change as temperature increases.

The presentation of the paper is as follows. In the next section, we discuss the results of $S^x$ for the Na-based liquid alloys. Tentative explanation for the variation of $S^x$ vs. concentration is given. The electrical resistivity calculation for the Na-Pb alloy is described in section III. There the modified Faber-Ziman theory is briefly mentioned. The results obtained for the resistivity are then compared with experiments. A conclusion that summarizes both these calculations is given in the same last section.

II. EXCESS ENTROPY OF MIXING

We follow I and write $S^x$ (in units of $Nk_B$) as

$$S^x = \Delta S^K + \Delta S^P + S^o$$  \hspace{1cm} (1)

Each of the terms on the rhs of eq. (1) has a physical interpretation and has been given in Umar et al.\textsuperscript{12}. $\Delta S^K$, the variation of Gibbs-

Na-

K\textsuperscript{2} and for the Na-Pb these are obtained from Hesson et al.\textsuperscript{15} upon considering the theoretical work of Bhatia and Singh.\textsuperscript{16} We now present and discuss the results.

We first depict in figs. 1a and 1b the various contributions to the excess entropy of

FIG. 1 Calculated values of the various contributions, $\Delta S_K$, $\Delta S_P$, and $S^o$, to the excess entropy of mixing for Na-K and Na-Pb liquid alloys. For the Na-K, $T = 500{\circ}C$ and for the Na-Pb, $T = 427{\circ}C$. 

mixing. Generally the $S^{ex}$ of Na-K liquid alloys is dominated by $\Delta S_{\Omega}$, although $S_{\Omega} + AS$, may contribute quite a significant amount. The Na-Pb alloys, on the other hand, have $S_{\Omega} \equiv 0$ for the entire concentration region. That $S_{\Omega} \equiv 0$ for the Na-Pb alloys is due to the fact that our variational calculations have yielded almost identical $\sigma_{Na}$ and $\sigma_{Pb}$ at each of the concentrations (see table 1). In particular, we note that the mean volume occupied

TABLE 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>$C_{pb}$</th>
<th>$\sigma_{Na}$</th>
<th>$\sigma_{Pb}$</th>
<th>$m^*_{c}(k_F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>5.956</td>
<td>5.776</td>
<td>1.002</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5.750</td>
<td>5.570</td>
<td>1.010</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>5.593</td>
<td>5.394</td>
<td>1.082</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5.251</td>
<td>5.252</td>
<td>1.012</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>5.111</td>
<td>5.111</td>
<td>1.120</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.017</td>
<td>5.018</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td>0.59</td>
<td>4.958</td>
<td>4.959</td>
<td>0.917</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>4.948</td>
<td>4.948</td>
<td>0.891</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>4.977</td>
<td>4.978</td>
<td>0.862</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>-</td>
<td>5.024</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.812</td>
</tr>
</tbody>
</table>

by a Pb ion (except for the $C_{pb} = 0.1$) does not change on alloying. Probably just because of this, the calculated $\sigma_{i}$ for the two components are almost similar. An immediate consequence of these changes in $\sigma_{i}$ is that the $S^{ex}$ of Na-Pb is not dominated by $\Delta S_{\Omega}$ (cf. fig. 1a for Na-K system) but in fact depends on the mutual cancellation between $AS_{\Omega}$ and $AS_{\Omega}$. When comparing the $\Delta S_{\Omega}$ for each of the Na-based alloys, it is found that $\Delta S_{\Omega}$ is significantly larger for the Na-Pb than for the Na-K alloys. Since $AS_{\Omega} = \ln (\Omega_1/\Omega_1\Omega_2^2)$, where $\Omega$ and $\Omega_1$ are respectively the atomic volumes of alloy and pure metals, we may attribute this large difference in $AS_{\Omega}$ to the considerably large volume of contraction for the Na-Pb system.

From the above qualitative analysis, it is thus apparent that we would expect the final $S^{ex}$ to be quite different in both these alloy systems. This is indeed true as can be seen from figures 2a and 2b. We observe further that our calculation for Na-K system has negative excess entropy of mixing over the whole concentration range (the $S^{ex}$ at $C_K = 0.7$ is probably due to error in experimental density). The experimental $S^{ex}$, however, predicts a loss in entropy throughout the entire concentration range for both Na-based alloys. It is interesting to note at this point that the present feature exhibited by Na-K alloys at 500°C is quite different from that occurred for the same system but at a lower temperature ($T = 100°C$) (cf. fig. 2a of I). Physically this corresponds to a further loss of entropy for the former system and can be traced to be connected with the increased volume of contraction ($A = 500°C, (AV%)_{max} = -3.3$ whereas at $T = 100°C, (AV%)_{max} = -1.5$) as the temperature of the system is elevated. Since the variation of packing density for the alloy crucially affects the contribution of $AS_{\Omega}$, we depict in fig. 3 our theoretical $\eta$. The positive (negative) deviation of $\eta$ (with respect to $\eta = C_{Na}\eta_{Na} + C_{Pb}\eta_{Pb}$) for the Na-Pb alloys accounts for the negative (positive) $AS_{\Omega}$ as has been previously justified by Hoshino(17) (see also discussion in I and II). By comparing the general structures and positions of minima obtained, noting that $S^{ex}$ is an extremely small and sensitive mixing quantity, and the fact that only experimental densities are used with no further adjustable parameter this level of agreement between theory and experiments may be considered as quite success-
FIG. 2 Calculated excess entropies of mixing for Na-K, denoted by \( \bullet \bullet \), and Na-Pb alloys, denoted by \( -- \), compared with experiments from (a) Hultgren et al.\(^{13}\) for Na-Pb denoted by \( - \), and (b) Lantratov\(^{12}\) for Na-K denoted by \( -- \).

As an application of the calculated \( \sigma_i \), we now apply them to the study of electrical resistivity for Na-Pb for which a number of recent experimental data are available for comparison.

FIG. 3 Packing density for Na-K and Na-Pb alloys. The coordinate axis on the LHS is for Na-K and the RHS is for Na-Pb.

III. ELECTRICAL RESISTIVITY

To calculate the resistivity for liquid binary alloys, the Faber-Ziman (FZ) theory has
frequently been used. Here we adopt the modified FZ theory which has previously been
derived by Wang et al \cite{18} in the Boltzmann-type of approach and recently been re-derived
by Itoh and Watabe \cite{19} within the Green function method. According to Wang et al the
electrical resistivity can be calculated to be

\[ \rho = \frac{\langle m^*(k_F) \rangle}{N_{k_F}} \times \]

\[ (3\pi \Omega / (4k_F^3)) \left( \int_0^{2k_F} dq \frac{q^2}{\langle k_F \rangle} \left[ \frac{W(r)}{W_0(r)} \right] \right) \]

where \( k_F \) is the Fermi wavevector, \( \langle m^*(k_F) \rangle \) is the full density-of-states effective mass (in
the usual FZ theory \( \langle m^*(k_F) \rangle \) is just the free electron mass), \( |N_{k_F}|^2 \) is the renormalisation
constant originated from the use of pseudowavefunction, \( \Omega \) is the volume of
the system, and finally, \( W(r) \) and \( W_0(r) \) are both the electron-ion pseudopotentials (assumed to
be weak) corresponding, respectively, to the dynamical and static ions configuration. In eq.
(2) \( \langle \cdots \rangle \) denotes an ensemble average over all the ionic configuration. Note that in
the present modified FZ theory, the pseudo-scattering matrix element is given by \( W(r) = W_0(r) \)
and hence requires a definite information about the liquid state \( \hat{c} \) crystal-like structure.
This is, unfortunately, a priori not known (readers interested should consult the work of
Wang et al for more details). The evaluation of the contribution from this term is not
necessary for the Na metal because the first reciprocal lattice vector is always less than
\( 2k_F \) and will not contribute to the resistivity. Hence

\[ \rho = \frac{\langle m^*(k_F) \rangle}{N_{k_F}} \times \rho_f \]

where \( \rho_f \) stands for the usual FZ-type theory (see Wang et al \cite{20-21} for example). For the Pb
metal such a contribution to the \( \rho \) from \( W_0(r) \) does not vanish and, in principle, must be
considered. The difficulty in calculating this term theoretically has therefore prompted us to
approximate \( \langle m^*(k_F) \rangle_{\text{Pb}} \) by the first order density-of-states effective mass (denoted
by \( \langle m^*(k_F) \rangle_{\text{Pb}} \) from hereon) because, if this is done, \( W_0(r) \) would be zero (see refs. 20 and 21
for a justification) for the Pb metal. Accordingly the resistivity for the alloy at any con-
ncentration would be

\[ \rho = \left[ \frac{m^*(k_F)}{N_{k_F}} \right]^2 \rho_f \]

in which \( m^*(k_F) \) is the density-of-states effective mass that lies between \( \langle m^*(k_F) \rangle_{\text{Na}} \)
and the first-order mass, \( m^*(k_F)_{\text{Pb}} \). We remark that the above equations for the resistivity
have been previously applied by Wang and Lai \cite{22} (to be referred to as III below) in their
study of \( \rho \) for Li-Pb liquid alloys.

Having written down the expressions for \( \rho \), the calculation can then be proceeded if(i)
the mean alloy atomic volumes, (ii) the \( \sigma_i \) and \( \eta_i \) to be used in the \( a_{ij}(q) \), and (iii) the ion-
electron pseudopotential are known. All these quantities have been employed in the
variational calculation of S\textsuperscript{2A} and for self-consistency exactly the same input sources are
used. As for the renormalisation factor, this has been obtained directly from the constructed pseudopotential. We are thus left with the determination of the density-of-states mass. Physically, \( m_\text{C}^*(k_F) \) is a first-order density-of-states mass plus higher order correction in which are included the partial localisation of valence-electron-charge-transfer effects. Theoretically, it is very difficult to calculate \( m_\text{C}^*(k_F) \) directly from first-principle because such a calculation would require a precise knowledge of an analogous \( \text{X} \text{crystal} \) structure for the metallic liquid. As a reasonable estimation, we follow II and III and obtain \( m_\text{C}^*(k_F) \) by considering the strength of the valence-electron charges partially localised on the electronegative ions. This phenomenon, called the valence-electron-charge-transfer, is found to be described quite well by a partial localisation function \( f(C) \). Mathematically, \( f(C) \), where \( C \) is the atomic concentration for the electronegative ions (for the alloy under consideration \( C = C_{\text{Pb}} \)), can be written

\[
f(C_{\text{Pb}}) = \frac{Z_{\text{Pb}}^\text{alloy}(k_F) - Z_{\text{Pb}}^\text{pure}}{(C_{\text{Na}}Z_{\text{Na}} + C_{\text{Pb}}Z_{\text{Pb}})}
\]

in which \( Z_{\text{Pb}} = Z - \rho_d \), is the effective valence charge with \( \rho_d \) the depletion charge density. Now eq. (5) represents fraction of a valence electron partially localised on the electronegative ions. Thus we see that by examining the change in \( f(C_{\text{Pb}}) \) vs. \( C_{\text{Pb}} \), we may deduce how \( m_\text{C}^*(k_F) \) varies with \( C_{\text{Pb}} \), because, physically, the larger the \( f(C_{\text{Pb}}) \), the heavier (larger) is the \( m_\text{C}^*(k_F) \). Therefore, for this purpose, we display in fig. 4 the concentration de-

![Fig. 4](image_url)

FIG. 4 Theoretical function \( f(C) \) (see text), denoted by \( \cdots \cdot \cdot \cdot \), and calculated electrical resistivities, denoted by \( \cdots \cdot \cdot \cdot \), for Na-Pb alloys. Experimental data are from (a) Matsunaga and Tamaki(2), denoted by \( \cdots \cdot \cdot \cdot \), and (b) Calaway and Saboungi(3), denoted by \( \cdots \cdot \cdot \cdot \).
This value for $m^*(k_F)$ can in turn be estimated as follows. First, we note that the band mass for solid Na metal has been calculated accurately by So et al.\(^{(23)}\) and is given by 1.046. At the temperature of interest here, it is reasonable to take $<m^*(k_F)> \equiv 1.005$ (cf. ref. 21 for Li-Na). For the alloy, the above consideration for $f(C)$ implies that $m^*_C(k_F)$ at $C_{PB} = <m^*(k_F)>_{Na}$ and $m^*_T(k_F)_{Pb}$. Furthermore, by taking into account effects such as volume contraction, electronegativity difference (compared with II and III), etc., we finally estimate $m^*_C(k_F)$ at $C_{PB} = 0.3$ to be 1.12. The $m^*_C(k_F)$ for the other concentrations are then determined by (i) assuming that eq. (4) with $m_f^*(k_F)$ works well for $0.4 < C_{PB} < 1$ (see discussion just above eq. (4) and also ref. 3) and (ii) observing that the contribution to $\rho$ from $\Gamma(r)$ becomes smaller and smaller as $C_{PB}$ approaches pure Na (see ref. 22, for example). Accordingly, the values of $m^*_C(k_F)$ are estimated and given in the same table 1. The results for the calculated $\rho$ using input data as described above are displayed in Fig. 4. For comparison, we present in the figure the experimental values of Calaway and Saboungi\(^{(3)}\) and Matsunaga and Tamaki\(^{(2)}\). There are two interesting points that merit emphasize.

In conclusion, we summarize the results found in this work:

(a) the $S^{ex}$ of Na-K and Na-Pb liquid alloys can be described by using a mixing of HS provided the HS diameters involved taking into account the electron-charge-transfer effects.

(b) the resistivity anomaly found in the liquid Na-Pb alloy can be physically attributed to the tendency of valence electrons partially localized on the more electronegative ions.

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REFERENCES