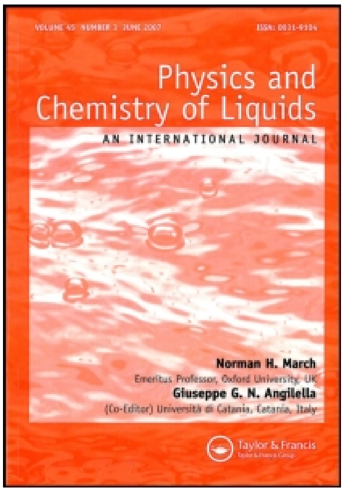

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S. Takeda[a]; S. Tamaki[b]; W. H. Young[cd]
[a] Department of Physics, College of General Education, Kyushu University, Fukuoka, Japan [b] Department of Physics, Faculty of Science, Niigata University, Niigata, Japan [c] School of Physics, University of East Anglia, Norwich, UK [d] Physics Department, College of Science, Sultan Qaboos University, Muscat, Oman

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A MODEL OF RESONANCE SCATTERING IN LIQUID Na–Pb ALLOYS

S. TAKEDA

Department of Physics, College of General Education, Kyushu University, Ropponmatsu, Fukuoka 810, Japan.

S. TAMAKI

Department of Physics, Faculty of Science, Niigata University, Niigata 950–21, Japan.

and

W. H. YOUNG*

School of Physics, University of East Anglia, Norwich, NR4 7TJ, UK.

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The curve of the electrical resistivity of liquid Na–Pb alloys has a large maximum around the composition of Na_4Pb corresponding to a minimum value of the concentration-concentration fluctuation in the long wavelength limit, $S_{cc}(0)$. The maximum in the resistivity curve is interpreted in terms of a resonance scattering of the conduction electrons by the short range ordered 'complex', based on the t-matrix formulation and with the help of thermodynamic data of these alloys.

1 INTRODUCTION

In recent years, the structural, thermodynamic and electronic properties of liquid Na–Me (Me; polyvalent metals) alloys have been studied (van der Lugt and Geertsma 1987, Tamaki 1987 and Young 1987) because of their interesting behaviours which are largely governed by the valence value of z of Me. In particular, if $z \geq 4$ these appear to be some sorts of "complex" formations or short range ordered atomic configurations, for which ideas beyond NFE theory are required.

In liquid Na–Pb alloys, it has been found that there is a stable short range order around the composition of Na_4Pb, which was directly and also indirectly recognised by several workers (Matsunaga *et al.* 1983a,b, van der Marel *et al.* 1982, and Calaway and Saboungi 1983). It is strongly suggested by the observation of the total structure factor (Takeda *et al.* 1987) that the liquid Na_4Pb is likely to be explained by the tetrahedral formation of Na atoms centered at Pb atoms and the local complex

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* Present address: Physics Department, College of Science, Sultan Qaboos University, PO Box 32486, Muscat, Oman.

formation model proposed by Hoshino and Young (1980) is suitable for this system as seen in Figure 1.

These facts encourage us to modelise a local formation of complex Na_4Pb or a local short range order corresponding to its complex, whatever it is either ionic or covalent. It may be hard to specify that this complex is extremely ionic or covalent. The above model, however, might be applicable for such a partially ionic and covalent system. With increasing temperature, some of these complexes are dissociated to form a mixture of Na, Pb and Na_4Pb complex. Under these situations, we will introduce the idea of resonance scattering for the resistivity of liquid Na–Pb alloys with the help of thermodynamic data measured by Matsunaga *et al.* (1983b).

2 THERMODYNAMIC MODEL OF LIQUID Na–Pb ALLOYS

If we assume the following chemical equation for liquid Na–Pb alloys,

$$c\mathrm{Na} + (1-c)\mathrm{Pb} \rightarrow (c-4c')\mathrm{Na} + (1-c-c')\mathrm{Pb} + c'\mathrm{Na_4Pb} \tag{1}$$

Corresponding to this equation, the total Gibbs free energy of the alloys can be written using the Flory approximation (Gray *et al.* 1980),

$$G = \sum c_i G_i^{(0)} + RT \sum^{3} c_i \ln \phi_i + \tfrac{1}{2} \sum_{i \neq j = 1}^{3}\sum c_i \phi_j \chi_{ij} \tag{2}$$

$$\phi_i = c_i v_i / V \quad V = \sum_{i=1}^{3} c_i v_i$$

$$c_1 = (c - 4c'), \quad c_2 = (1 - c - c'), \quad c_3 = c'$$

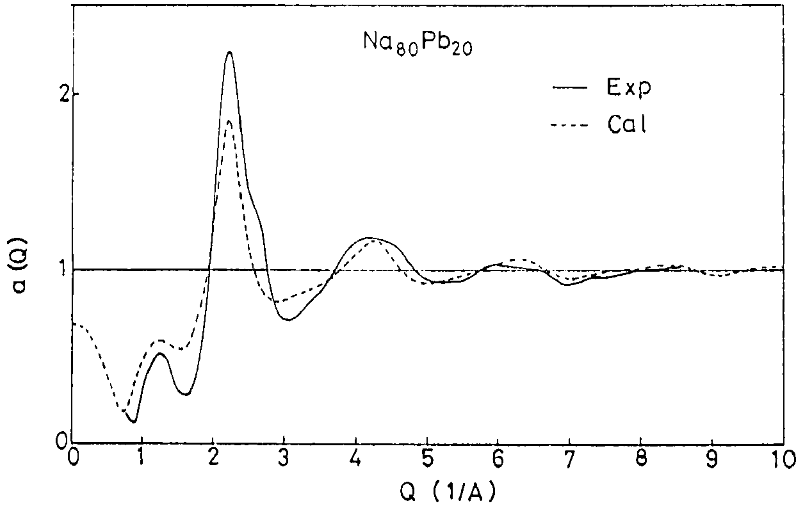

Figure 1 Solid line is observed total structure factor in liquid $Na_{80}Pb_{20}$ and small peak around $Q = 1.25A^{-1}$ suggests the existence of a chemical complex. Broken curve is calculated one based on the local formation of complex "Na_4Pb".

where v_i is the partial molar volume of species i ($1 = \mathrm{Na}$, $2 = \mathrm{Pb}$ and $3 = \mathrm{Na_4Pb}$). The first term on the right of Eq. (2) represents the contribution to the free energy due to the pure components,

$$\sum_{i=1}^{3} c_i G_i^{(0)} = cG_1^{(0)} + (1 - c)G_2^{(0)} - c'g \qquad (3)$$

The interchange energies represent the residual interaction between the species in the pseudobinary mixture. The Gibbs free energy of mixing ΔG is defined as follows,

$$\Delta G = G - cG_1^{(0)} - (1 - c)G_2^{(0)} \qquad (4)$$

Presumably the last term of Eq. (2) may be represented as the form of $c_3 W(c)$ because c_3 tends to be zero at both sides. Then we have

$$\Delta G = -c_3 g + RT \sum_{i}^{3} c_i \ln \phi_i + c_3 W(c) \qquad (5)$$

In liquid Na–Pb alloys, we could reproduce ΔG under the assumption that g is constant ($= 18.3$ kcal/mol) and $W(c)$ is varied with the change of concentration as seen in Figure 2. This figure indicates an interesting feature that the liquid alloys of $0.8 < c_{\mathrm{Na}} < 1$ are actually interpreted in terms of ideal solutions among the local clusters of $\mathrm{Na_4Pb}$, Pb and Na, because $W(c)$'s are almost zero in that region, and that the alloys of $0 < c_{\mathrm{Na}} < 0.8$ are exhibited in terms of regular solutions among the clusters and dissociated atoms. The reproducibility of ΔG is shown in Figure 3. The curves of c_i's for the entire concentration range are also calculated as shown in Figure 4.

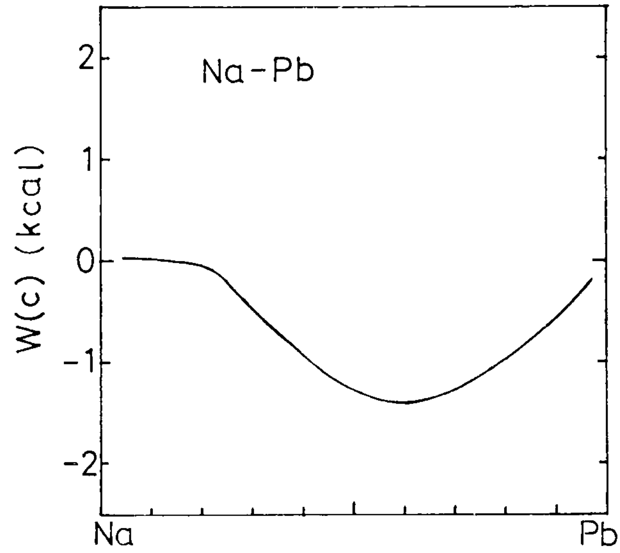

Figure 2 Concentration variation of the interchange energy in liquid Na–Pb alloys at 425°C.

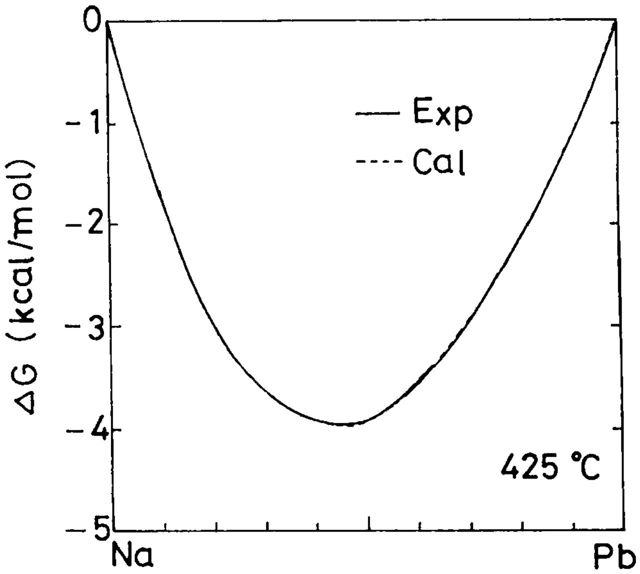

Figure 3 Comparison of calculated and experimental values of ΔG in liquid Na–Pb alloys at 425°C. Solid line is experimental values and dotted one is calculated one.

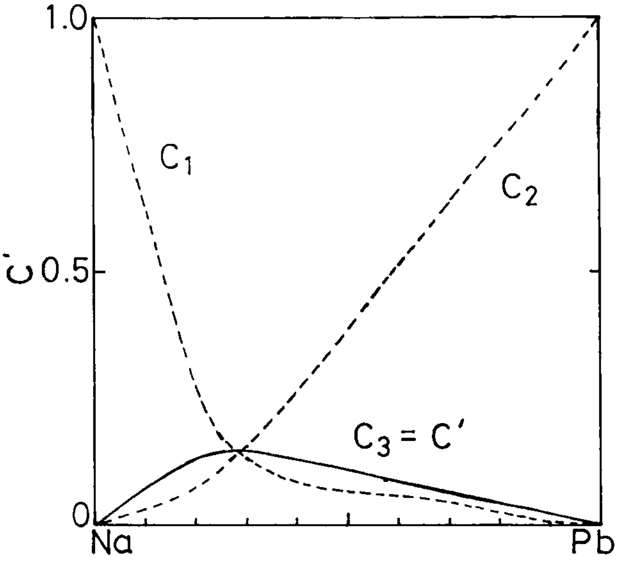

Figure 4 Curves of the atomic and complex fraction isotherm in liquid Na–Pb alloys at 425°C.

3 ELECTRONIC CONFIGURATION IN CONNECTION WITH THE THERMODYNAMIC MODEL

A simplified electronic configuration corresponding to above model might be stated as follows: The valence electrons of the dissociated or non-complex part of Na and Pb form a conduction band described by the NFE approximation. The Fermi energies under the NFE model are given by,

$$E_F = \frac{h'^2}{2m}\left[3\pi^2 \frac{NZ_{\mathrm{eff}}}{V}\right] \tag{6}$$

$$Z_{\mathrm{eff}} = (c - 4c')z_{\mathrm{Na}} + (1 - c - c')z_{\mathrm{Pb}}$$

which is shown in Figure 5.

The energy level of the bonding electrons forming a local complex, E_c, might be located near the Fermi level E_F of the conduction band. In other words, the electrons at the local complex resonate with the conduction electrons. The value of E_c, therefore, must be varied for all concentrations, because the value E_F is varied with the concentration. In what follows we will assume that $(E_F - E_C)$ is constant for all concentrations, for simplicity.

4 RESISTIVITY OF COMPLEX-FORMING LIQUID ALLOYS

There is an excellent article for the review of transport properties of liquid metals and alloys (van der Lugt and Geertsma 1987). The standard theory for the electrical

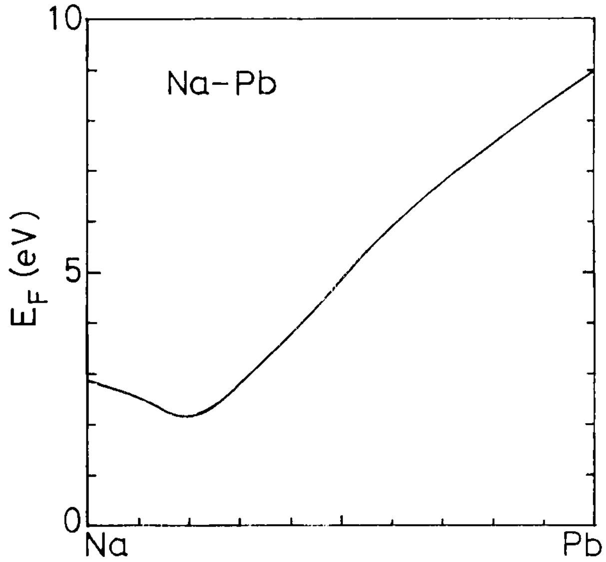

Figure 5 Concentration dependence of Fermi energy, E_F.

resistivity of liquid alloys were, however, proposed by Evans *et al.* (1971, 1972) using the t-matrix formulation. Let us apply the above theory to the present complex-forming system expressed by Eqs (1) and (6), then the electrical resistivity is,

$$\rho = \rho_1 + \rho_2 = A \int_0^{2k_F} |U(K)|^2 K^3 dK \tag{7}$$

$$|U(K)|^2 = T_1 + T_2$$

$$\begin{aligned} T_1 = {} & (c - 4c')|t_{\mathrm{Na}}|^2[(1 - c - c') + c' + (c - 4c')a_{\mathrm{Na-Na}}(K)] \\ & + (1 - c - c')|t_{\mathrm{Pb}}|^2[(c - 4c') + (1 - c - c')a_{\mathrm{Pb-Pb}}(K)] \\ & + (t_{\mathrm{Na}}t_{\mathrm{Pb}} + t_{\mathrm{Pb}}t_{\mathrm{Na}})[(c - 4c')(1 - c - c')a_{\mathrm{Na-Pb}}(K) \\ & - (c - 4c')(1 - c - c')] \end{aligned} \tag{8}$$

$$\begin{aligned} T_2 = {} & c'|t_c|^2[(1 - c - c') + (c - 4c') + c'a_{c-c}(K)] \\ & + c'(c - 4c')(t_{\mathrm{Na}}t_c^* + t_c t_{\mathrm{Na}}^*)[a_{\mathrm{Na}-c}(K)] \\ & + c'(1 - c - c')(t_{\mathrm{Pb}}t_c^* + t_c t_{\mathrm{Pb}}^*)[a_{\mathrm{Pb}-c}(K) - 1] \end{aligned} \tag{9}$$

where $A = (3\pi m/8e^2 hE_F)(V/Nk_F^4)$, k_F being the Fermi wave vector.

The term ρ_1 in Eq. (7) produced by T_1 is ascribed to the scattering of the conduction electrons due to dissociated atoms, and more or less, its value is deviated from the linearly interpolated values of the resistivities of pure elements Na and Pb.

In the present model, the scattering of the conduction electron for the complex resembles the resonance scattering to the virtual bound state of the 3d-transition solute in liquid metals (Tamaki 1968), because the conduction electrons in the present system resonate with the valence bonded electrons of the complex. This consideration allows us to assume that $|t_c|^2 \gg |t_{\mathrm{Na}}|^2$ and/or $|t_{\mathrm{Pb}}|^2$. Therefore the leading term in T_2 is the first one in Eq. (9).

The summation of the two other terms in T_2 is hereafter referred to as ΔT_2. And the resistivity ρ'_1 obtained from the value of $T_1 + \Delta T_2$ seems not to be very much deviated from the linearly interpolated resistivities of pure Na and Pb.

The partial structure factor between complexes $a_{cc}(K)$ is not known. However it may, more or less, oscillate around unity. Then we can approximate $c'a_{c-c} \simeq c'$ and the first term in T_2 is equal to as

$$c'|t_c|^2[1 - 4c'] \tag{10}$$

If the concentration c' is very small like a 3d-transition solute in metallic solvent, then it becomes exactly to the residual resistivity obtained by Friedel (1956).

Therefore the resistivity ρ'_2 produced by (10) is expressed in terms of the residual resistivity except for the factor $(1 - 4c')$ as follows,

$$\rho'_2 = \frac{4\pi h}{Z_{\mathrm{eff}} e^2 k_F} \frac{V}{N} c'(1 - 4c') \sum_{l=0}^{\infty} \sin^2(\eta_l - \eta_{l+1}) \tag{11}$$

where η_l is the phase shift of the electron wave scattered by the complex with the angular momentum l.

In the present case, it may be enough that all other phase shifts can be neglected except for η_0 and η_1 in the case that the valence orbitals in Na_4Pb form sp^3 hybridisation. Since the net charge of the local complex seems to be zero, the Friedel sum rule for η_0 and η_1 is written as follows,

$$\eta_0 + 3\eta_1 = 0 \tag{12}$$

Using this relation, ρ'_2 is rewritten in the following form,

$$\rho'_2 = \frac{4\pi hV}{Z_{\mathrm{eff}}e^2k_FN}c'(1-4c')F(x) \tag{13}$$

$$F(x) = x(19 - 80x + 128x^2 - 64x^3) \tag{14}$$

$$x = \sin^2 \eta_1$$

As described in the preceding section, the assumption g = constant for all concentration is valid to reproduce ΔG. This fact may correspond that the resonant energy value of the state E_c is almost constant for the whole concentration, although E_F varies with the concentration and has a minimum at the composition of Na_4Pb. On the other hand, it is well known that the resonance state at E_c is given by the following equation (e.g. see Harrison 1970)

$$\tan \eta_1(E_F) = \Gamma/2(E_c - E_F) \tag{15}$$

where Γ is the effective width of the virtual bound state. Then we have

$$\sin^2 \eta_1 = \frac{\Gamma^2}{4(E_F - E_c)^2 + \Gamma^2} \tag{16}$$

Putting Eq. (16) into (13) and (14), we have finally,

$$\rho'_2 = \frac{12\pi hV}{Z_{\mathrm{eff}}e^2k_FN}c'(1-4c')F\left[\frac{\Gamma^2}{4(E_F - E_c)^2 + \Gamma^2}\right] \tag{17}$$

5 CALCULATION OF RESONANCE SCATTERING

Based on the formulae mentioned above, the resonance scattering term ρ'_2 is actually calculated using the c's with a proper parameter E_c and Γ, as shown in Figure 6, where we take a combination values of $E_F - E_c = 0.44$ eV and $\Gamma = 1.15$ eV. By using these calculated values ρ'_2, we have estimated the resistivity isotherm and the results are shown in Figure 7 together with the observed one. The quantitative agreement between the theory and experiment for the entire concentrations is not excellent. However, the calculated curve is qualitatively close to the experimental one. If the contribution from $T_1 + \Delta T_2$ to the resistivity is not linear, then the trend of agreement between theory and experiment becomes more relevant.

Although the combination of $E_F - E_c$ and Γ is not unique, it is emphasised that the large deviation from a linearly interpolated value of resistivities of pure liquid

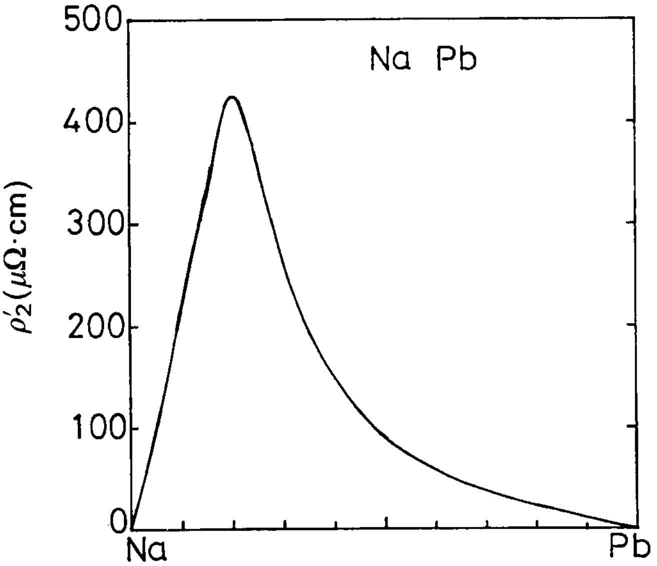

Figure 6 Curve of the calculated resistivity, ρ_2', by resonance scattering in liquid Na–Pb alloys.

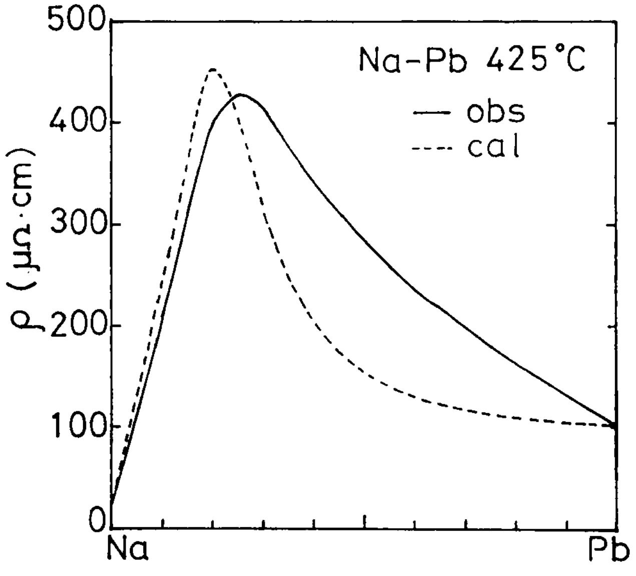

Figure 7 Solid curve is observed resistivity isotherm. Broken curve is the concentration variation of calculated one.

Na and Pb is qualitatively explained in terms of the resonance scattering model like the 3d-transition solutes in the liquid metals.

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