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STUDIES OF THERMODYNAMICAL AND ELECTRONIC TRANSPORT PROPERTIES OF Na–Sn ALLOY

The concept of complex formation has been incorporated in the structure of the Faber–Ziman formula for the purpose of studying the composition dependence of the electrical resistivities of Zintl alloys, which possess the anomalous nature and exhibit a large deviation from the metallic behavior around a specific composition.

Keywords: mixing, fluids, electronic transport, liquid alloys, thermodynamic properties.

1. Introduction

In view of the widespread practical applications, the physical properties of liquid binary alloys have attracted the attention of both theoreticians and experimentalists for past several decades [1–10]. A typical example is the liquid alkali–IV group element alloys, i.e., Zintl alloys, which are found to exhibit a quite peculiar crystal structure [11] and the anomalous behavior of structural properties, electronic structure, and thermodynamic properties. The calculations by Geertsma *et al.* [12] show that there is the non-clustered-to-clustered transition in Zintl alloys. Such transition is viable due to the size effect that may be supported by the fact that the asymmetric behavior of the alloy is usually attributed [13, 14] to the interaction between solute and solvent atoms or both. The role of alkali atoms is mainly to keep anions apart with the loss of the valence electron. The anions with valence electrons are responsible for the metallic-covalent part of the bonding, and the electrical conductivity is basically due to the electron hopping from one tetrahedron to another one. Thus, a low value of the anion–anion interaction between two adjacent clusters corresponds to a high resistivity, while a large anion–anion interaction within a cluster corresponds to a clustered configuration. As the size of alkali atoms increases, the anions are pushed so far apart that the anion–anion interaction between two adjacent clusters decreases considerably.

It is, therefore, more energetically favorable for the anions to group together, and the resistivity increases [15]. Such ionic compounds form the subject of the research interest that seeks to explain their valences in terms of the charge transfer. The variation of the alloy composition allows a change of the dominant type of interaction from metallic to ionic and to partly covalent due to the charge transfer. This leads, e.g., to a strong concentration dependence of the thermodynamic and electronic transport properties [16]. The electrical conduction theory in the liquid metal using the 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.

In the present communication, an attempt has been made to study the thermodynamical property. We will consider Gibbs' function based on the concept of the complex formation model (CFM) and the structure of Faber–Ziman's [17] formula as the most popular interpretation of anomalous thermodynamic data. We will assume the existence of chemical complexes (or associates) with finite lifetime, although there is no direct evidence for them. However, the indication for such type of preferential association of the constituent species of the alloy can be found in their phase diagrams and in X-ray and neutron diffraction patterns. The computations have been carried out for all the properties at 773 K based on the experimental data available for thermodynamical properties [18].

2. Theoretical Methodology

2.1. Thermodynamical properties

In the 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 bonds. Hence, the liquid metal binary alloy becomes a ternary system consisting of free constituent ions of the component metals and chemical complexes. The complex formation model [2, 13, 19–24] assumes the liquid binary alloy A – B as a ternary mixture consisting of free atoms A , free atoms B , and their preferential associates referred as chemical complexes $A_\mu B_\nu$.

Let us suppose that 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

$$N_S = n_A + n_B + n_m = nN, \quad (1)$$

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

$$n_1 = 1 - C - \mu n_3, \quad (2)$$

$$n_2 = C - \nu n_3 \quad (3)$$

where C is the concentration of the second component.

The free energy of the mixing G_M (Gibbs' energy or Gibbs' function) of the mixture may be written as $G_M = -n_3 g + G^1$,

$$(4)$$

where g is the formed complex energy. 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 [25] can be considered. This enables us to express G_M as

$$G_M = -n_3 g + RT \sum_{i=1}^3 n_i (\ln n_i - \ln n) + \sum_{i<j} \sum \frac{n_i n_j}{n} W_{ij}. \quad (5)$$

Here, W_{ij} ($i, j = 1, 2, 3$) 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

$$\left(\frac{\partial G_M}{\partial n_3} \right)_{T,P,C} = 0, \quad (6)$$

$$\frac{n_1^\mu n_2^\nu}{n_3^{n_1+n_2-1}} = e^{-g/RT} e^Y, \quad (7)$$

where

$$Y = \frac{W_{12}}{RT} \left[(\mu + \nu - 1) \frac{n_1 n_2}{n^2} - \frac{\mu n_2}{n} - \frac{\nu n_1}{n} \right] + \quad (8)$$

$$+ \frac{W_{13}}{RT} \left[(\mu + \nu - 1) \frac{n_1 n_3}{n^2} - \frac{\mu n_3}{n} + \frac{n_1}{n} \right] + \quad (9)$$

$$+ \frac{W_{23}}{RT} \left[(\mu + \nu - 1) \frac{n_2 n_3}{n^2} - \frac{\nu n_3}{n} + \frac{n_2}{n} \right]. \quad (10)$$

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 NaSn is formed in Na–Sn alloy. The interaction energies W_{ij} and g have been computed with the procedure suggested by Bhatia and Hargrove [19]. The value of g has been taken nearly equal to $-(\mu + \nu)G_M$ as a starting point. 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. [4] and [5]. 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.

2.2. Electronic transport properties

The computation of the electrical resistivity of ternary systems requires three scattering potentials (form-factors) corresponding to two-component metals and chemical complexes and six partial structure factors [2]. The model parameters obtained by Ese and Reissland, 1973 [26] shown in Table 1 have been used to determine the form-factors. Incorporating the CFM in the structure of the Faber–Ziman [17] formula, the electrical resistivity of the compound-forming binary alloy may be expressed as

$$R = R_1 + R_2, \quad (11)$$

where R_1 and R_2 represent, respectively, the contributions from the scattering by bare A and B ions

and from the chemical complex $A_\mu B_\nu$ which can be expressed as

$$R_1 = \frac{3\pi}{\hbar e^2} \frac{\Omega}{v_F^2} \langle F_1(q) \rangle, \quad (12)$$

$$R_2 = \frac{3\pi}{\hbar e^2} \frac{\Omega}{v_F^2} \langle F_2(q) \rangle, \quad (13)$$

where Ω is the volume of the alloy, v_F is the Fermi velocity,

$$\begin{aligned} \langle F_1(q) \rangle = & 4 \int_0^1 [x_1 w_1^2(\mathbf{k}, \mathbf{q}) S_{11}(K) + x_2 w_2^2(\mathbf{k}, \mathbf{q}) S_{22}(K) + \\ & + 2(x_1 x_2)^{1/2} w_1(\mathbf{k}, \mathbf{q}) w_2(\mathbf{k}, \mathbf{q}) S_{12}(K)] \eta^3 d\eta, \end{aligned} \quad (14)$$

$$\begin{aligned} \langle F_2(q) \rangle = & 4 \int_0^1 [x_3 w_3^2(\mathbf{k}, \mathbf{q}) S_{33}(K) + 2(x_2 x_3)^{1/2} w_2(\mathbf{k}, \mathbf{q}) \times \\ & \times w_3(\mathbf{k}, \mathbf{q}) S_{32}(K) + 2(x_1 x_3)^{1/2} \times \\ & \times w_1(\mathbf{k}, \mathbf{q}) w_3(\mathbf{k}, \mathbf{q}) S_{31}(K)] \eta^3 d\eta. \end{aligned} \quad (15)$$

Here, x_1 , x_2 , and x_3 are, respectively, the concentration fraction of three scattering centers A , B , and $A_\mu B_\nu$ which can further be expressed as

$$x_1 = \frac{n_A}{N_S}, \quad x_2 = \frac{n_B}{N_S} \quad \text{and} \quad x_3 = \frac{n_m}{N_S}. \quad (16)$$

The quantities $S(K)$ and $w(k, q)$ with subscripts 1, 2, 3 represent, respectively, the partial structure factors and non-local screened form-factors of the constituent elements and a chemical complex.

The values of the screened form-factor $w_i(k, q)$ as a function of the compositions have been obtained using the energy-dependent non-local optimized model potential of Shaw [27], because it has proved very successful in the study of electronic transport properties

Table 1. Model parameters (a.u. = 2 Ryd.) and their derivatives at the 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	-
Sn	1.831	2.052	1.795	-0.478	-0.246	0.183
Compound	a_0	a_1	a_2	$\delta a_0/\delta E$	$\delta a_1/\delta E$	$\delta a_2/\delta E$
NaSn	2.143	2.40	-	-0.38	-0.18	-

of liquid metals. The screened non-local pseudopotential matrix elements can be expressed as

$$\begin{aligned} w_i(k, q) = & f_i(K, q) + \frac{4\pi}{\Omega q^2 \varepsilon^*(q)} \times \\ & \times \left[1 - G(q) \rho_i + g_i(q) \left(1 - \frac{G(q)}{\varepsilon^*(q)} \right) \right], \end{aligned} \quad (17)$$

with

$$\begin{aligned} f_i(\mathbf{K}, \mathbf{q}) = & -N \sum_{l=0}^{l_0} \left\langle \mathbf{k} + \mathbf{q} \left| \left(A_{il}(E) - \frac{Z_i}{r} \right) P_l \right| \mathbf{k} \right\rangle = \\ = & -\frac{4\pi}{\Omega} \sum_{l=0}^{l_0} (2l+1) P_l(\cos \theta) \int_0^{r_m} \left(A_{il} - \frac{Z_i}{r} \right) \times \\ & \times j_l(|\mathbf{k} + \mathbf{q}|r) j_l(|\mathbf{k}|r) r^2 dr. \end{aligned} \quad (18)$$

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

$$g_i(q) = \frac{4}{\pi^2 q^2 \varepsilon^*(q)} \int_{K \leq K_F} \frac{f_i(K, q)}{K^2 - |K + q|^2} d^3 K, \quad (19)$$

$$\rho_i = \frac{4}{\pi} \sum_{l=0}^{l_0} (2l+1) \int_0^{K_F} K^2 dK \int_0^{r_m} j_l^2(Kr) \left(\frac{\delta A_{il}}{\delta E} \right) r^2 dr, \quad (20)$$

K is the electron wave vector, ρ_i is the depletion hole which has been determined following the Shaw procedure [27], 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 the wave function at the boundary for different ionic term values which yield, in turn, 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 is given by

$$n_C = [x_1 Z_1 + x_2 Z_2] N - 2n_m, \quad (21)$$

and the mean number of valence electrons per atom is

$$Z_S = [x_1 Z_1 + x_2 Z_2] - 2n_m/N, \quad (22)$$

$$K_F = \left(\frac{3\pi^2 Z_S}{\Omega} \right)^{1/3}. \quad (23)$$

The experimental data on the partial and total structure factors of compound-forming binary alloys are unavailable with respect to compositions; in addition, they have insufficient accuracy. Thus, one has to divulge into the computational effort, and this is achieved through the hard-sphere reference system, obtaining the solutions of Percus–Yevik equation for an m -component hard sphere mixture [28, 29]. The total structure factor $S(K)$ is given by

$$\begin{aligned}
 S(K) = & x_1 S_{11}(K) + x_2 S_{22}(K) + x_3 S_{33}(K) + \\
 & + 2(x_1 x_2)^{1/2} S_{12}(K) + 2(x_1 x_3)^{1/2} S_{13}(K) + \\
 & + 2(x_2 x_3)^{1/2} S_{23}(K), \quad (24)
 \end{aligned}$$

where $S_{ii}(K)$ and $S_{ij}(K)$ are the partial structure factors, cc_i 's are the concentration fractions of the three scattering centers $A, B, A_\mu B_\nu$ ($A = \text{Na}, B = \text{Sn}, \mu = 1$ and $\nu = 1$). Here, q is the wave vector.

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

$$\eta = \pi (6\Omega)^{-1} \sum x_i \sigma_i^3. \quad (25)$$

Here, x_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 the temperature and concentration, and σ_3 have been taken as 8.2 nm for Na–Sn alloy. The values of a hard sphere diameter of Na–Sn alloy have 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.

3. Results and Discussions

In the present work, the concept of CFM has been incorporated in the structure of the well-known Faber–Ziman formula for the purpose of studying the electrical resistivities of a Zintl alloy as a function of the composition which possess the anomalous nature close to the stoichiometric composition.

The Faber–Ziman formula which holds for the weak scattering might prove seriously inadequate for the purpose, because the mean free path of the conduction electrons is reduced to its minimum value, which is the atomic distance, at the composition close to

their resistivity maxima. However, one can think to investigate the applicability of the Faber–Ziman formula for the computations of the electrical resistivities of complex-forming liquid alloys with the presumption that the spin-orbit interaction, due to the close association of the constituent species of the alloy counterbalances the effect of a low mean free path.

3.1. Thermodynamic Properties

The phase diagram of liquid Na–Sn alloy shows several intermetallic compounds in the solid state. But there is an indication of peaks at Na_3Sn and NaSn . The neutron diffraction results for Na_4Sn_3 exhibit the most pronounced prepeak. In view of this, the work has been initiated in the case of Na–Sn alloy with the presumption that the chemical complexes NaSn coexist with free Na atoms and free Sn atoms in liquid Na–Sn alloys. The interaction energies obtained through the model are $W_{12} = -0.04$, $W_{13} = -0.56$, $W_{23} = -0.5$, and $g = 4.2$ at 773 K (in terms of RT). On experimental grounds, a higher value of $g > 3.5$ suggests that Na–Sn is a strongly interacting system in the light of the 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, and 16.7, respectively, in contrast to the light interacting systems like Mg–Sn, Ag–Al, and Cu–Sn. Further, we observe that all the interaction energies are repulsive in nature. This also supports the strongly interacting nature of Na–Sn alloy.

The variations of computed values of Gibbs' function along with their experimental values and the equilibrium values n_3 of the complex as a function of Gibbs' function composition of the constituent

Table 2. Hard sphere diameters (a.u.) of Na and Sn in Na–Sn alloys $\sigma_3 = 8.2$, $T = 773$ K

Conc. of Na C_{Na}	Volume Ω	σ_{Li}	σ_{Sn}
1.0	277.2	6.16	–
0.8	260.0	6.08	5.53
0.6	237.0	6.06	5.57
0.5	232.0	6.07	5.63
0.4	225.6	6.06	5.66
0.2	208.4	6.043	5.67
0.0	191.2	–	5.73

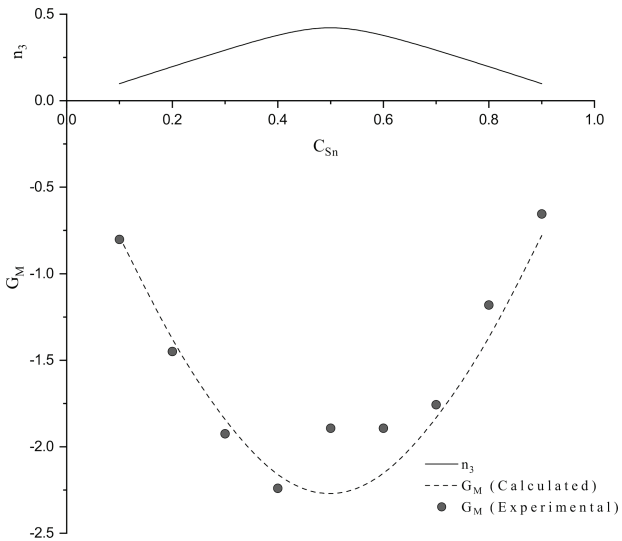


Fig. 1. Variation of Gibbs' function as a function of the composition at 773 K

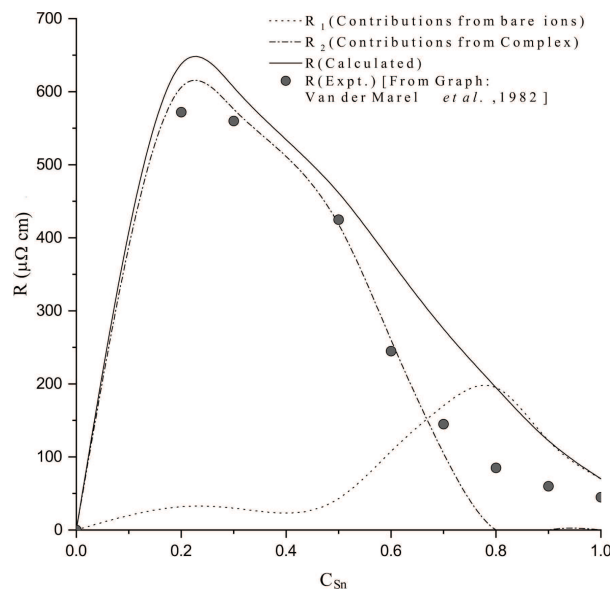


Fig. 2. Variation of the electrical resistivity of NaSn compound with respect to the concentration at 773 K

species of the alloy have been shown in Fig. 1. The Gibbs' function G_M shows a good agreement with experiment. We observe that G_M is symmetric for Na–Sn in contrary to systems Li–Sn, Al–Ca, Ca–Mg, Mg–Zn, Cu–Mg, and so on which possess the asymmetry.

3.2. Electronic Transport Properties

The computed values of the electrical resistivity of compound NaSn have been shown in Fig. 2. The elec-

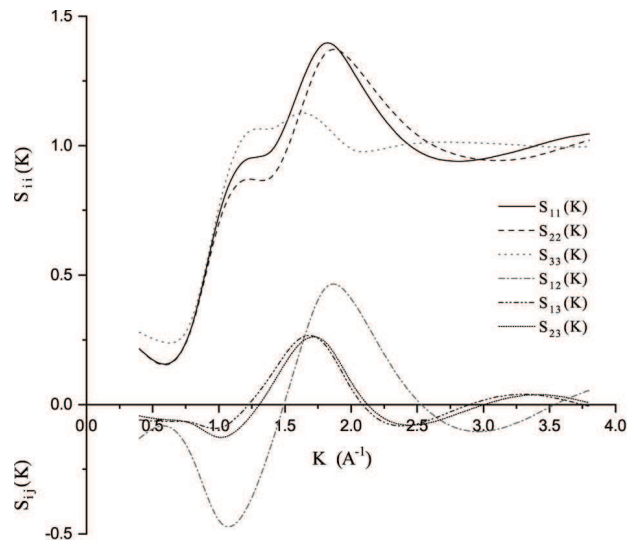


Fig. 3. Partial Structure factors of liquid NaSn compound of Na–Sn Alloy at 773 K

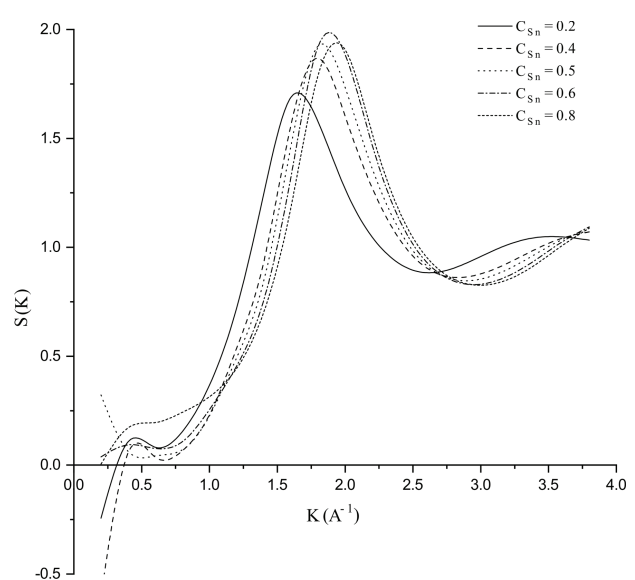


Fig. 4. Variation of the total structure factor with respect to the concentration of liquid NaSn compound of Na–Sn alloy at 773 K

trical resistivity of the system is found to be asymmetric. No anomalous value is obtained at any concentration. The contributions from complexes have been found quite asymmetric having a sharp peak. The calculated value has been compared with the result of Van der Marel *et al.* [30]. An excellent agreement is found between the calculated and experimental values. The scattering contributions R_1 from bare ions

and the scattering contributions R_2 from complexes have also been presented in the figure. The computed values of the electrical resistivities have been found in a close agreement with the experimental values.

The computed values of partial structure factors (PSF) of Na–Sn which have been considered as ternary systems using the determined hard sphere diameters (Table 2) and equilibrium values n_3 of the complex at the composition, where the electrical resistivities have been found maximum, have been shown in Fig. 3. The PSF of unlike species are oscillatory about zero in this system. The magnitude of peak values of $S_{11} = 1.3848$ have been found larger than that of $S_{22} = 1.2858$ and $S_{33} = 1.176$. The computed values of the total structure factors of liquid Na–Sn alloy are shown in Fig. 4. As a consequence of the large difference in electronegativities between the constituent elements, the alloy tends to have salt-like properties. Such ionic compounds form the subject of chemical studies that seek to explain their valences in terms of the charge transfer.

It is found in Fig. 4 that the main peak of the PSF is shifting toward higher K with the amount of doping of Sn atoms. This feature may be attributed to the charge transfer taking place in the system. The transition from the metallic to ionic regime is accompanied by a considerable volume contraction [31] due to shorter interatomic distances, which is reflected by a shift of the principal peak of $S(K)$ and of the dispersion minimum to larger K . The formation of strong Na–Sn bonds also causes a shift of the dispersion, still dominated by the Li–Li correlations, toward higher frequencies.

It should be mentioned that the PSF, $S(K)$, shows the behavior of a random mixing without a sub-peak or asymmetry of the first peak and shows the compound-forming behavior with a sub-peak below the first peak [32]. The partial structure factors of unlike atom pairs have maxima, which lie in between those of like pair of atoms in the case of random mixing. On the other hand, in compound-forming alloys, the partial structure factor of unlike atom pairs has 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 behavior in between these two types. The negative peak in the lower region of k/k_F indicates the preference for unlike nearest neighbors. The humps in the lower K regions are due to the short-range order (SRO) with the preference for

unlike nearest neighbors [33]. Positive values of the 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.

4. Conclusions

The hard sphere reference system can be used to predict the atomistic structure of complex-forming alloys using the Hiroike exact solution of the Percus–Yevick equation for the m -component mixture.

1. The Faber–Ziman formula in conjunction with the complex formation model (CFM) can be used in describing the electronic behavior of liquid alloys which possess anomalous nature.

2. 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.

3. Substantial effect of equilibrium values n_3 of the complex on the structure factors of liquid Na–Sn alloy has been found. The position of the peak values has been found shifted toward the longer wavelength side with an increase in the value of n_3 .

4. Scattering contributions to Ziman’s integrand from unlike scattering centers have been found oscillatory about zero, and their net effect seems to be negligible. Major scattering contributions to Ziman’s integrand come from the complex-complex structures. The scattering contributions from bare ions have been found nearly asymmetric.

5. The anomalous electronic behavior of liquid Na–Sn alloy occurs due to the preferential ordering of unlike atoms.

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

7. The shoulder at the high wave-vector side of the main peak reflects the short Sn–Sn distances characteristic of a tetrahedron. This shoulder may be interpreted as an evidence of the covalent bonding between some atoms in the liquid state.

8. The charge transfer takes place in the system, when Sn is added to the liquid Li.

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ВИВЧЕННЯ ТЕРМОДИНАМІЧНИХ ВЛАСТИВОСТЕЙ СПЛАВУ Na–Sn І ТРАНСПОРТУ ЕЛЕКТРОНІВ В НЬОМУ

Структуру формули Фабера–Зімана модифіковано із застосуванням поняття “утворення комплексу” з метою вивчення залежності електричного опору сплавів Цінтла від їх складу. Ці сплави аномальні, і поблизу певного значення відношення складових проявляють значне відхилення від поведінки металів.

Ключові слова: змішування, рідини, транспорт електронів, рідкі сплави, термодинамічні властивості.