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ANOMALIES IN NOBLE-METAL-BASED LIQUID ALLOYS

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Experimental data on liquid noble-metal-based alloys were analysed in terms of a pseudopotential approach. The anomalies in the heat of mixing, the electrical resistivity and the magnetic susceptibility were found to be reflected by the theory in a qualitative manner even if compound formation or short range order is not taken into account. The emphasis was placed on liquid Ag–In, but other examples of this particular class of alloys were also included in the discussion.

Keywords: Liquid alloys; Heat of mixing; Electrical resistivity; Magnetic susceptibility

INTRODUCTION

In the recent past, the non-simple behaviour of liquid metal mixtures has provoked a variety of experimental investigations and various theoretical attempts to understand the experimental findings. In particular, much effort has been devoted to the thermodynamic quantities, the electronic transport properties, and the structure of liquid systems with attractive interactions. The most pronounced features were the non-regular heat of mixing, the non-ideal entropy of mixing, marked deviations of the thermodynamic activity from Raoult's law, and unexpected variations of the electrical resistivity, the magnetic susceptibility and other physical quantities with composition and temperature. Semi-empirical interpretations have been given in terms of compound formation [1–5], charge transfer [6,7], or chemical short range order in the liquid [8,9]. Owing to the enormous output of experimental results it has become evident that ideal or regular systems are rather the exception than the rule. The question is whether such theoretical approaches are adequate for strongly interacting systems only, i.e. highly exothermic systems with asymmetric, triangular-shaped heat of mixing curves, extremely reduced or even negative entropies of mixing, drastic increases in the electric resistivities up to ionic or semiconducting behaviour, or the appearance of prepeaks

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or shoulders on the main peak of the structure factor [10]. Some of the most prominent examples are those of Au–Cs which is considered an ionic melt at the equiatomic composition [11,12], Mg–Bi which is a strongly interacting systems with semiconducting properties around Mg₂Bi [13], or alkaline-lead alloys being distinguished by the formation of polyanionic units like Pb₄⁴⁻ [14,15].

The whole class of weakly interacting systems, on the other hand, fails to give such clear evidences. Alloys of noble metals with polyvalent metals belong to this class of alloy systems. Apart from some exceptions they show rather small ($2\text{ kJ mol}^{-1} \geq H^m \geq -5\text{ kJ mol}^{-1}$) but asymmetric heats of mixing, anomalous variations in the entropy of mixing, maxima in the resistivity and more or less pronounced minima in the magnetic susceptibility. All in all, they display a non-simple behaviour although not as pronounced as in typical compound forming liquid alloys.

In a series of previous studies it was demonstrated that starting from the thermodynamic activity coefficients both the heat of mixing and the magnetic susceptibility in Au–In, Au–Ge, and Au–Sb can be interpreted by assuming the formation of compounds of the stoichiometry Au₃In, Au₄Ge and Au₅Sb [16–18]. Despite the obvious success of such a formal treatment it is questionable to assign these experimental findings strictly to the formation of compounds, chemical complexes or associations in the liquid. Even chemical short range order, although a reasonable assumption for the majority of the systems, is not always unambiguously indicated by the experiments.

In some more recent papers it could be shown that the trends in the magnetic susceptibility of noble metal – polyvalent metal systems are explainable on the basis of simple pseudopotential theory even if the influence of chemical interactions is completely ignored [19–21]. This article is designed to illustrate that the appearance of so-called anomalies in general can be understood without the pre-assumption of compound formation or chemical short range order. The system Ag–In was selected as typical representative, but others were also taken into consideration so as to draw the attention to the whole class of alloys.

RESULTS AND DISCUSSION

(a) Heat of Mixing

Various authors have studied the heat of mixing in liquid Ag–In alloys [22–24]. Results on the Ag-rich side are rather scarce but the position of the minimum around 40 at%In and the basic shape of the H^m vs composition curve is well established. The data points shown in Fig. 1 reflect the asymmetric form which is typical of the whole class of alloys. The results of Ag–Ge [25] and Ag–Sn [26] are also shown for comparison so as to emphasise the variability of the heat of mixing curves on polyvalent metal side. It seems that the underlying negative interactions ($H^m > 0$) present in all these systems are outweighed by positive interactions ($H^m < 0$) on the noble metal side which, in turn, are most pronounced at the composition where electron compounds are formed in the solid state [27]. Whether positive or negative interactions prevail on the polyvalent metal rich side varies from system to system. Obviously, Au–In is a system with positive interactions at all compositions while negative interactions dominate in Au–Ge.

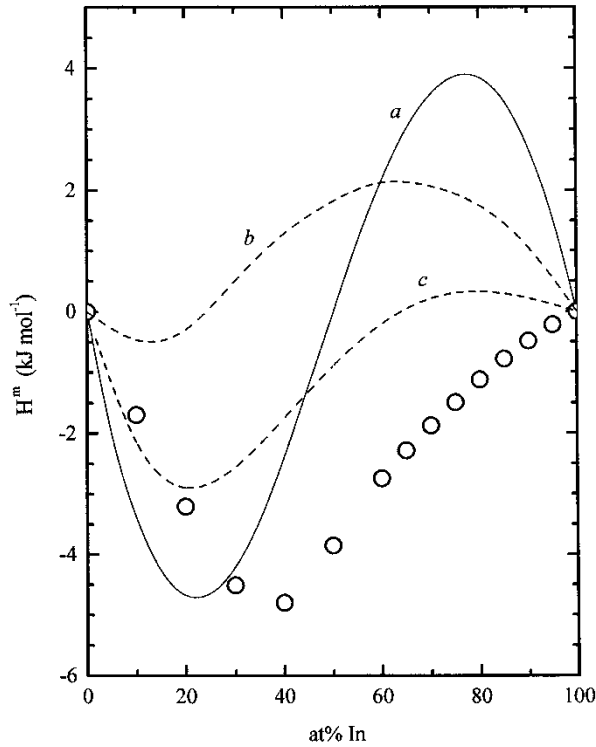


FIGURE 1 Heat of mixing in liquid Ag-based alloys: o Ag–In experimental at 1280 K [24]; *a* Ag–In calculated; *b* Ag–Ge experimental at 1250 K [25]; *c* Ag–Sn experimental at 1070 K [26].

The discussion of the thermodynamic properties was based on the theoretical treatment developed in terms of pseudopotential theory [28–30]. In the present article the convenient expressions formulated by Waseda and Jacob [31] and Bretonnet [32] have been applied. Accordingly, the free energy of an ion in a liquid binary system is composed of six different contributions

$$E_{\text{tot}} = E_{\text{es}} + E_{\text{eg}} + E_{\text{bs}} + E_{\text{H}} + E_{\text{cc}} + E_{\text{kin}} \quad (1)$$

which take account of the electrostatic energy of the ion in the electron gas, the interaction and correlation energy of the electron gas, the band structure energy, the Hartree energy, the energy of the core–core repulsion, and the kinetic energy of the ion. The electrostatic term is given by the relation

$$E_{\text{es}} = \frac{e^2}{\pi} \int_0^\infty dk [c_1 Z_1^2 (a_{11}(k) - 1) + c_2 Z_2^2 (a_{22}(k) - 1) + 2(c_1 c_2)^{1/2} Z_1 Z_2 a_{12}(k)] \quad (2)$$

c_1 and c_2 are the atomic fractions of the constituents, Z_1 and Z_2 are their formal valencies. k denotes the momentum transfer vector, and $a_{ij}(k)$ are the partial structure factors of the alloy.

The energy of the electron gas can be expressed in terms of the electron radius r_s

$$E_{\text{eg}} = \frac{Z}{2} \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s \right]. \quad (3)$$

The electron radius, in turn, is defined by the average valency of the atoms in the alloy ($Z = c_1 \cdot Z_1 + c_2 \cdot Z_2$) and the V , volume of the alloy as

$$r_s = \left(\frac{3}{4\pi Z} \cdot \frac{V}{N} \right)^{1/3}. \quad (4)$$

The calculation of the energy of the band structure is based on the structure factors $a_{ij}(k)$ and the pseudopotential form factors of the constituents, $w_1(k)$ and $w_2(k)$:

$$E_{\text{bs}} = \frac{1}{16\pi^3 e^2} \left(\frac{V}{N} \right)^2 \int_0^\infty dk k^4 [c_1 a_{11}(k) w_1^2(k) + c_2 a_{22}(k) w_2^2(k) + 2(c_1 c_2)^{1/2} a_{12}(k) w_1(k) w_2(k)] \cdot \frac{1 - \varepsilon(k)}{\varepsilon(k) \cdot [1 - G(k)]}. \quad (5)$$

The multiplicative factor at the end of Eq. (5) takes account of the screening effects. The Hartree energy, i.e. the long-wavelength component of the electron–electron, ion–ion and electron–ion interactions, was obtained from

$$E_{\text{H}} = Z \cdot \frac{N}{V} \lim_{k \rightarrow 0} \left[(c_1 w_1(k) + c_2 w_2(k)) \cdot \frac{V}{N} + \frac{4\pi Z e^2}{k^2} \right]. \quad (6)$$

The contribution of repulsive interactions between the atom cores to the total free energy is

$$E_{\text{cc}} = 2\pi \cdot \frac{N}{V} \int_0^\infty R^2 dR \cdot [c_1^2 \alpha_{11} u_{11}(R) g_{11}(R) + 2c_1 c_2 \alpha_{12} u_{12}(R) g_{12}(R) + c_2^2 \alpha_{22} u_{22}(R) g_{22}(R)]. \quad (7)$$

$u_{ij}(R)$ denotes the pairwise interaction potentials between the AA, BB and AB pairs, $g_{ij}(R)$ is the pair distribution function, and R is the radial distance.

The last term in Eq. (1) is kinetic energy of the ion given as $E_{\text{kin}} = 3kT/2$. For practical use the heat of mixing (i.e. the enthalpy of mixing) was identified with the change in internal energy of the system, i.e. $H^m \cong \Delta E = E_{\text{tot}} - c_1 E_1 - c_2 E_2$.

The calculations were based on the semi-empirical pseudopotential form factor of Borchs and DeGennaro [33] for silver and that of Bachelet *et al.* [34] for indium. Screening was accounted for by applying the conventional dielectric screening function $\varepsilon(k)$ and the correction for electron–electron interactions $G(k)$ as proposed by Vashista and Singwi [35].

The structure of the alloy was simulated by hard spheres which were assumed to interact via an additional square well potential [36,37]. The basic parameters

were the hard sphere diameters ($\sigma_1 = 5.03$ au, $\sigma_2 = 5.39$ au), the height ($\varepsilon_1/k_B = 240$ K, $\varepsilon_2/k_B = 90$ K), and the width of the square well ($A_1 = 2.15$, $A_2 = 2.25$). They were obtained by fitting the model to the experimental structure factors of the pure elements.

The repulsive energy was estimated by introducing Born–Mayer type potentials of the form $u(R) = \alpha \exp(-R/\lambda)$ into Eq. (7) and applying the values $\alpha_{11} = 1040.7$ au, $\alpha_{22} = 1102.6$ au, $\lambda_{11} = 0.5367$ au, $\lambda_{22} = 0.5364$ au [38]. The interaction potential between unlike pairs was taken as the root mean square of the like-neighbours interaction potentials.

Figure 1 shows how the calculations compare with the experimental results. As absolute values are considered it has to be emphasised that the calculated change in the internal energy due to alloying is only to about 1% of the total energy, therefore it is not surprising that the simplifications applied throughout the article have an essential impact on the absolute values. In particular, the volume of mixing is expected to have a drastic influence on the calculated heat of mixing. However, as the experimental volumes of mixing reported in the literature [39,40] are highly divergent, they have not been taken into account. The calculated curve shown in Fig. 1 refers to an ideal (i.e. additive) volume of mixing. The volumes of the pure elements were taken from the compilation of Crawley [41].

The model applied in this article is not capable to unambiguously predict the magnitude of the heat of mixing in liquid Ag–In, but it reflects at least in a qualitative manner its very particular variation with the composition in all noble-metal-based liquid alloys: negative heats of mixing on the noble metal side pointing to attractive interactions and the tendency to positive values on the polyvalent metal side hinting at negative interactions. The examples of Ag–Ge [25] and Ag–Sn [26] substantiate that despite the numerical disagreement the theory gives a first idea of the basic trends of these systems and reflects also some details of the phase diagram. It is a remarkable coincidence that stable electron compounds appear on the noble metal side of Ag–In and Ag–Sn, whereas for Ag–Ge where the repulsive interactions dominate ($H^m > 0$) only a metastable electron compound is reported [27].

(b) Electrical Resistivity

In a similar manner, the systems share also common features of the electrical resistivity. As has been shown by Busch and Güntherodt [42] the resistivities pass through maxima on the noble metal rich side accompanied by negative temperature coefficients in this particular range of composition. The typical example of Ag–In is shown in Fig. 2.

According to Faber and Ziman [43] the electrical resistivity of simple liquid metals can be expressed by an integral of the form

$$\rho = \frac{3\pi m^2 \Omega}{4e^2 \hbar^3 k_f^6} \cdot \int_0^{2k_f} a(k) \cdot w(k)^2 k^3 dk \quad (8)$$

which relates the resistivity to the structure factor $a(k)$ and the form factor of the model potential $w(k)$. k_f is the Fermi wave vector which is defined by the atomic volume Ω according to $k_f = (3\pi^2 Z/\Omega)^{1/3}$.

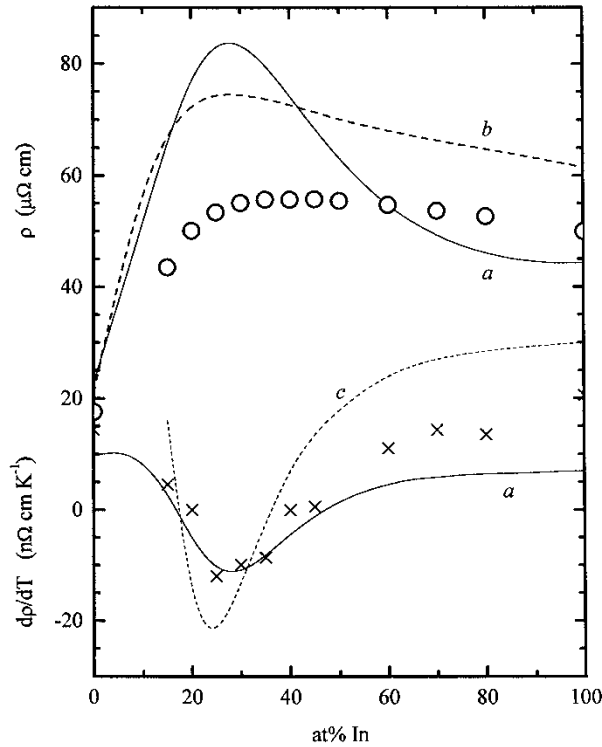


FIGURE 2 Electrical resistivity and temperature coefficient of the electrical resistivity in liquid noble-metal-based alloys: o, x Ag-In experimental at 1270 K [42]; a Ag-In calculated; b Cu-Sn experimental at 1070 K [42]; c Cu-Sb experimental [46].

Using the t -matrix formulation of the scattering problem [44] and extending the Ziman formula to the case of a two-component system the product $a(k) \cdot w(k)^2$ has to be substituted by

$$c_1^2 a_{11}(k) |t_1(k)|^2 + c_2^2 a_{22}(k) |t_2(k)|^2 + c_1 c_2 a_{12}(k) [t_1(k) t_2^*(k) + t_1^*(k) t_2(k)] + c_1 c_2 \{ |t_1(k)|^2 + |t_2(k)|^2 - 0.5 [t_1(k) t_2^*(k) + t_1^*(k) t_2(k)] \}. \quad (9)$$

The elements of the t -matrix, in turn, are determined by the phase shifts η_l of the individual partial waves according to

$$t(k) = \frac{2\pi \hbar^3}{m(2mE_f)^{1/2}} \cdot \frac{1}{\Omega} \sum_l (2l+1) \cdot \sin \eta_l \cdot \exp(i\eta_l) P_l(\cos \Theta). \quad (10)$$

E_f denotes the Fermi energy, l stands for the partial wave, and P_l are Legendre polynomials. In this article the evaluation was based on the phase shifts proposed by Waseda [45]: $\eta_0 = -0.201$, $\eta_1 = 0.004$ and $\eta_2 = 3.022$ for Ag, and $\eta_0 = 0.676$, $\eta_1 = 0.371$ and $\eta_2 = -0.005$ for In, respectively.

The resistivities were evaluated at 1270 K, and also at 1220 and 1320 K so as to have a measure of the temperature coefficient. As compared to the experimental results the theory predicts a more pronounced maximum, however, the principal shape of the resistivity curve is found to be roughly reproduced. The theoretical maximum is found to be closer to the noble metal side (30 at%In) but is still around the composition where the electron compounds appear in the phase diagram [27]. In excellent agreement with the experimental findings the temperature coefficients are expected to adopt negative values in this particular range of composition. The variation of the resistivity in liquid Cu–Sn [42] and that of the temperature coefficient in liquid Cu–Sb [46] are also included in Fig. 2 in order to emphasise the common features of the systems under investigation.

(c) Magnetic Susceptibility

It has been pointed out that the maxima in the resistivity are frequently accompanied by minima in the magnetic susceptibility [5,47,48]. This is apparent from Fig. 3 which shows the variation of the electronic susceptibility and its temperature coefficient with the composition in liquid Ag–In [20], Ag–Ge [21] and also that of Au–Ge [17]. By comparing Figs. 2 and 3 it becomes evident that both the maxima in the resistivity as well as the minima in the susceptibility appear at those compositions

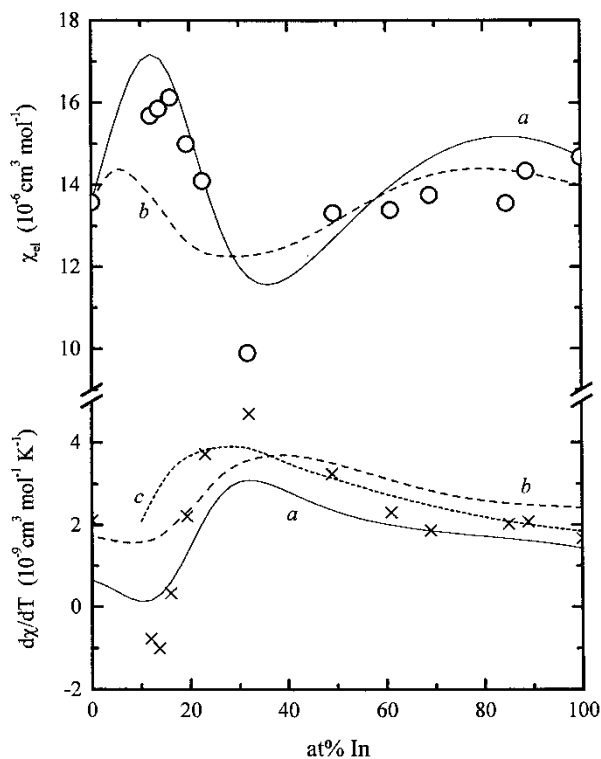


FIGURE 3 Electronic susceptibility and temperature coefficient of the magnetic susceptibility in liquid noble-metal-based alloys: o, × Ag–In experimental at the liquidus temperature [20]; a Ag–In calculated; b Ag–Ge experimental at 1280 K [21]; c Au–Ge experimental [17].

where electron compounds are formed in the solid state [27]. This coincidence at the specific electron concentration of $e/a \approx 1.6$ has been discussed in more details in a previous study on Au-based liquid alloys [19].

According to the theory, the total magnetic susceptibility of the alloy is the sum of the diamagnetic contribution of the ion cores χ_i and that of conduction electrons χ_{el} . Thus, provided the core susceptibilities are known, the electronic susceptibility can be deduced from the experimental susceptibility by

$$\chi_{el} = \chi_{tot} - \chi_i. \quad (11)$$

The susceptibility of the conduction electrons χ_{el} , in turn, is made up of a paramagnetic contribution χ_{spin} (spin susceptibility) and a diamagnetic contribution χ_{dia} . In the case of non-interacting particles the two terms sum up to the free electron susceptibility

$$\chi_{el}^{\circ} = \frac{2\mu_B^2 m_e N_A^{1/3}}{h^3 (3\pi^2)^{2/3}} \cdot V_m^{2/3} \cdot Z^{1/3} \quad (12)$$

which is primarily determined by the molar volume V_m and the formal valence Z . For the simple non-interacting case χ_{spin} and χ_{dia} can be written as $\chi_{spin}^{\circ} = 1.5\chi_{el}^{\circ}$ and $\chi_{dia}^{\circ} = -0.5\chi_{el}^{\circ}$, respectively. If interactions take place the individual contributions can be related to their free electron expressions as [49]

$$\chi_{spin} = \chi_{spin}^{\circ} \cdot (1 + \Delta_p) \cdot \delta_p^{ec} \quad (13)$$

$$\chi_{dia} = \chi_{dia}^{\circ} \cdot (1 + \Delta_d) \cdot \delta_d^{ec}. \quad (14)$$

The quantities Δ_p and Δ_d take account of the interaction between the ionic cores and the conduction electrons, while δ_p^{ec} and δ_d^{ec} refer to exchange and correlation effects between the electrons. Timbie and White [50] have proposed a theory to calculate Δ_p and Δ_d in liquid metals on the basis of a nearly-free-electron approximation. For pure elements their second-order perturbation theory with respect to the electron-ion potential yields

$$\Delta_i = -\frac{3 \cdot Z}{32 \cdot E_f^2} \cdot \int_0^{\infty} a(q) \cdot w^2(q) \cdot G_i(q) \cdot dq \quad (i = p, d). \quad (15)$$

Here, the momentum transfer vector k is expressed in units of the Fermi vector k_f i.e. $q = k/k_f$. The functions $G_p(q)$ and $G_d(q)$ are given as

$$G_p = 2q \cdot \ln \left| \frac{q+2}{q-2} \right| - \frac{8q^2}{q^2-4} \quad (16)$$

$$G_d = \frac{2}{q} \cdot (q^2 + 2) \cdot \ln \left| \frac{q+2}{q-2} \right| - \frac{8}{3} \cdot \frac{24 - 22q^2 + 3q^4}{(q^2 - 4)^2}. \quad (17)$$

In the case of a binary mixture, with the atomic fractions c_1 and c_2 , the product $a(q) \cdot w^2(q)$ stands for

$$a(q)w^2(q) = c_1w_1^2(q)a_{11}(q) + c_2w_2^2(q)a_{22}(q) + c_1c_2\{w_1^2(q) \cdot [1 - a_{11}(q)] + w_2^2(q) \cdot [1 - a_{22}(q)] - 2w_1(q)w_2(q) \cdot [1 - a_{12}(q)]\} \quad (18)$$

which now includes the partial structure factors $a_{ij}(q)$ and the pseudopotential form factors $w_i(q)$ of the constituents [49].

The interactions between the electrons (δ_p^{ec} and δ_d^{ec}) were accounted for by using the expressions put forward by Wilk *et al.* [51] and Kanazawa and Matsudaira [52].

The variations of the electronic part of the experimental susceptibility χ_{el} with the composition and that of the temperature coefficient are shown in Fig. 3 together with results obtained from the theory. As regards the reliability of the experimental values it has to be recalled that according to Eq. (1) χ_{el} always depends on the choice of the core susceptibilities χ_i . The literature data, on the other hand, are not very consistent [53–55]. In order to emphasize rather the shape of the curves than the absolute values the core susceptibilities were adjusted so as to fit the experimental electronic susceptibility of the pure elements to those obtained from theory: the values were $-37.62 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Ag^+ and $-22.84 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for In^{3+} . A detailed discussion of this particular subject has been given in a preceding paper on the magnetic anomalies of Ag-based liquid alloys [20,21].

It is apparent that the shape of the calculated curve is compatible with the experimental points. Even the maximum on the noble metal side – an experimental fact which has never been discussed – is found to be well reflected by the calculated curve. The temperature coefficient, on the other hand, displays a rather complex variation with composition which is not *a priori* understandable from the experimentalist's point of view. The marked feature is the minimum in the very vicinity of the noble metal followed by a flat maximum both occurring at those compositions where the extrema of the susceptibility occur. It is surprising that the calculations confirm all these hitherto unexplained details. The whole group of liquid noble metal – polyvalent metal alloys tends to exhibit these peculiar properties. Ag–Ge and Au–Ge are only two more typical examples [17,21].

CONCLUSIONS

The present calculations indicate that basically most of the exceptional features can be understood in terms of simple pseudopotential theory. It is apparent that the applied theory fails to give a satisfactory quantitative description of the experimental findings, however, the basic trends turn out to be reproduced. Whereas association models start out with the hypothesis of compound-formation at certain compositions, the models applied in this article are free from such pre-assumptions. The lack of better accordance is possibly due to the simplifications introduced into the models, but it cannot be denied that the exclusion of chemical short range order might be the major source of the divergency between theory and experiment. All in all, the considerations presented in this article are a further contribution to understand the anomalies in liquid noble-metal-based alloy systems.

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