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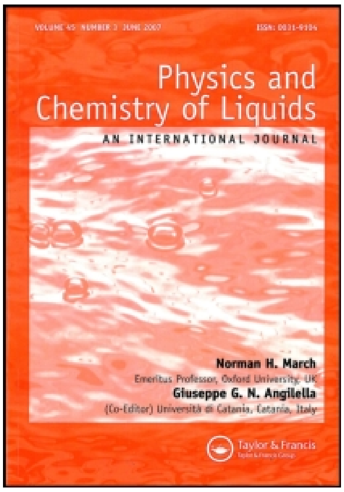

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MAGNETIC SUSCEPTIBILITIES OF LIQUID GOLD–ANTIMONY ALLOYS

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Magnetic measurements on liquid gold–antimony alloys are reported. The magnetic susceptibility varies in a non-uniform manner with the addition of antimony to gold. The electronic part of the susceptibility passes through a minimum located around 16 at%Sb, while, at the same composition, the temperature coefficient shows a local maximum. The results are analyzed within the context of "compound formation" and in terms of the valence electron concentration. The usefulness and the physical significance of the applied concepts are briefly discussed.

KEY WORDS: Electron concentration, compound formation.

1 INTRODUCTION

From a substantial body of earlier work it has become apparent, that ideal mixing behaviour is hardly ever observed in liquid alloys. The thermodynamic quantities, in general, show more or less marked deviations from a simple mixing behaviour which can be assigned to chemical interactions between unlike neighbours, to significant changes in the local structure of the liquid, or simply to a mismatch in the size of the constituents. The ability to form "compounds" might be understood as a direct reflection of extreme attractive interactions. Although the physical reality of such "compounds" seems not to be always clear, this conception yields at least a formal description of the local arrangement of the atoms, i.e. the chemical short range order in the liquid brought about by the attractive forces. The transport properties, on the other hand, reflect rather the electronic environment which might give rise to unexpected variations with composition. There are indeed many systems where the transport properties pass through minima or maxima at compositions different from those indicated by the thermodynamic quantities. In terms of "compound formation" this would imply the existence of two types of chemical "compounds" with different stoichiometries.

In two previous publications[1,2] the anomalous variation of the magnetic susceptibility with the composition of liquid Au–In and Au–Ge alloys has been explained, along

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[†] Dr. E. Wachtel passed away on November 14, 1989

with the thermodynamic functions of mixing, by assuming "compounds" of the stoichiometry AuIn and Au_3In, and AuGe and Au_4Ge, respectively. However, it has also been stressed that for the transport properties of noble metal based liquid alloys the concentration of valence electrons, i.e. the electron to atom ratio *e/a*, might be a crucial factor. The present paper is part of a systematic study on the interplay between the thermodynamic and the transport properties in alloys based on Au, with special emphasis on the influence of the increasing electron concentration in the series Au-In, Au-Ge and Au-Sb.

2 EXPERIMENTAL

Prior to the magnetic measurements, the alloys were prereacted by melting appropriate mixtures of the pure elements in sealed quartz ampoules using high purity gold sheet (4N, Ögussa, Austria) and antimony lumps (5N, Asarco, New York). After a homogenization period of 6 h at about 1400 K the alloys were cooled to ambient temperature, at a rate identical to that programmed during the magnetic measurements (5 K min^{-1}).

The magnetic susceptibilities of the samples were determined on a self-recording Faraday-type balance operating under inert atmosphere. Pure gold was measured in open alumina crucibles, whereas alloys with antimony had to be sealed in quartz vessels. The individual data points, recorded at a rate of 2–3 points min^{-1}, are represented in form of smooth curves. The average scattering is smaller than $5 \cdot 10^{-7} cm^3 mol^{-1}$, whereas the total accuracy of the reported susceptibilities amounts to about $\pm 1 \cdot 10^{-6} cm^3 mol^{-1}$.

3 RESULTS AND DISCUSSION

The discontinuities of the magnetic susceptibilities observed both on heating and cooling were found to be in good accordance with the phase transformations of the system[3]. Figure 1 shows the marked change of the susceptibility across the liquid–solid transition of the pure elements and their different ability of undercooling. It is furthermore a remarkable feature, that both the discontinuities and the temperature coefficients in the liquid state carry opposite signs.

Typical examples of the discontinuities observed in the alloys are given in Figure 2. They are either due to the initial precipitation of Au (22 at%Sb) or that of $AuSb_2$ (42 at%Sb), followed by the eutectic reaction between Au and $AuSb_2$ (up to about 66 at%Sb). Alloys with Sb-contents higher than 66 at%Sb show the typical discontinuities associated with the precipitation of Sb, followed by the abrupt change of opposite sign due to the peritectic formation of $AuSb_2$.

A summarized representation of the data obtained for the liquid state is given in Figure 3. Apart from some irregularities, the magnetic susceptibilities seem to vary smoothly from one element to the other, however, a more elaborate analysis of the data reveals that neither the susceptibiliy itself nor its temperature coefficient vary in a regular manner. The electronic part of the magnetic susceptibility X^e, deduced by subtracting the diamagnetic contributions X^{dia} of the individual ionic cores[4]

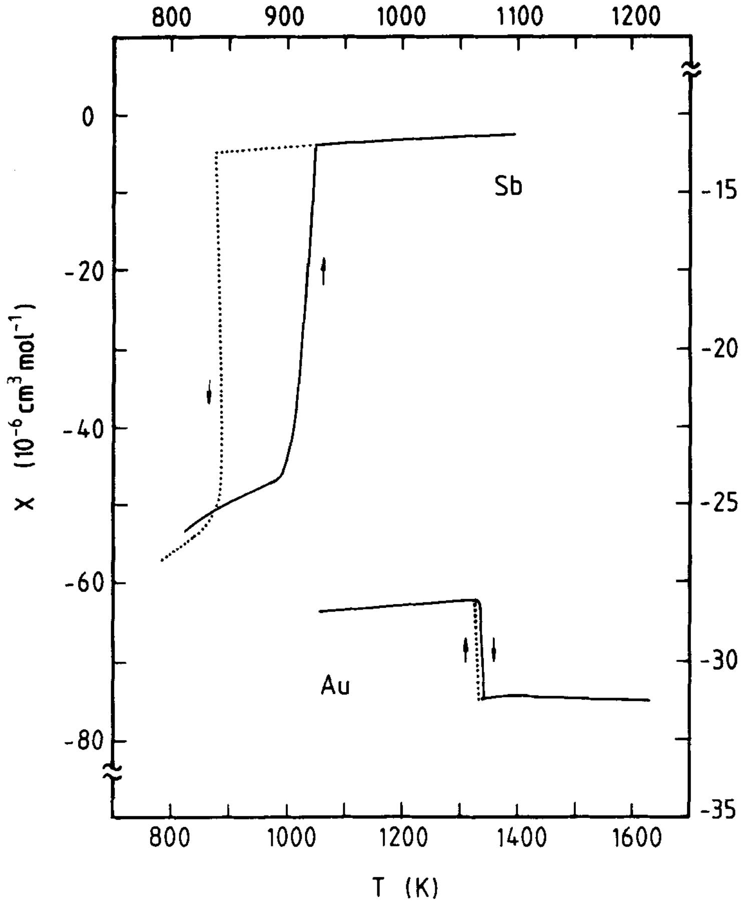

Figure 1 The magnetic susceptibility and the solid–liquid transition in Au and Sb (— heating,... cooling).

($-39.17 \cdot 10^{-6}$ cm^3 mol^{-1} for Au$^+$, and $-15.92 \cdot 10^{-6}$ cm^3 mol^{-1} for Sb^{5+}) from the experimental values, passes through a minimum around 16 at%Sb (Figure 4). There is some uncertainty imposed by the extrapolation of our data to the reference temperature of 873 K, but it is evident that the minimum deepens with decreasing temperature. Parallel to it, the temperature coefficient dX/dT tends to increase in a non-uniform way from Au to Sb, with a local maximum indicated at the same concentration (Figure 5).

The thermodynamic behaviour, on the other hand, points to a "critical" concentration different from that suggested by the magnetic susceptibility. The thermodynamic activities[5] show strong negative deviations from ideality, the enthalpies and the excess entropies of mixing are negative with highly asymmetric minima located around 25 at%Sb.

A similar behaviour has been observed in liquid Au–In and Au–Ge. The interpretation has been attempted in terms of "compounds" assuming the formation of AuIn and Au$_3$In, and AuGe and Au$_4$Ge, so as to explain the magnetic and the thermodynamic

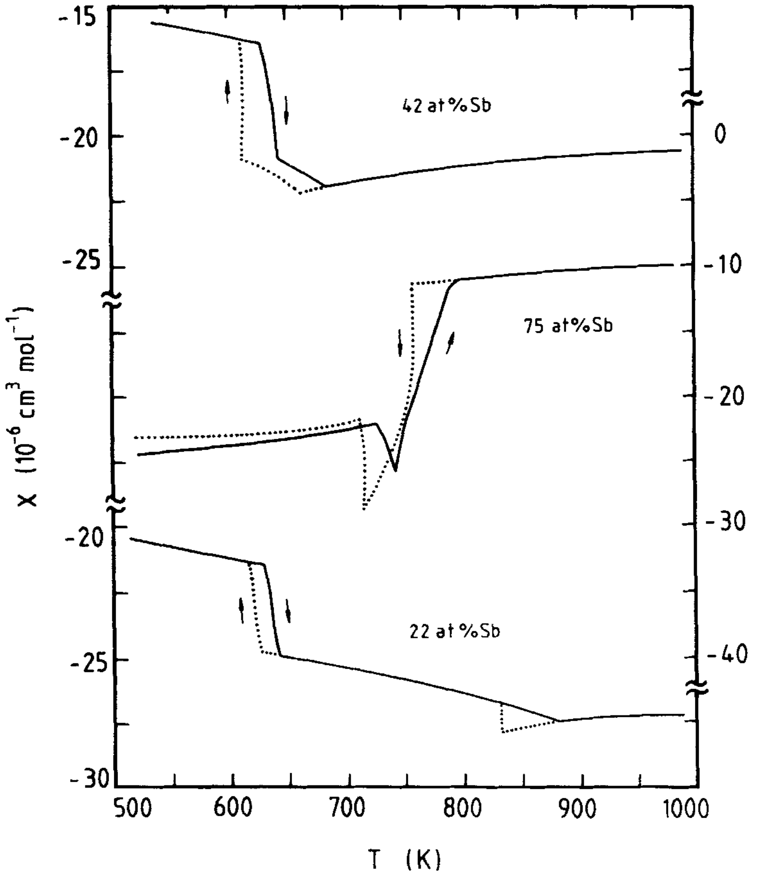

Figure 2 The magnetic susceptibility and the phase transformations in some typical Au–Sb alloys (— heating, ... cooling).

properties with the same set of model parameters[1,2]. The real existence of such "compounds" is certainly disputable, but in order to have a parallel description of the systems so far considered we applied the same procedure to Au–Sb assuming that

(a) the non-ideal behaviour of liquid Au–Sb is due to the hypothetical "compounds" AuSb and Au_5Sb

(b) the formation occurs according to mass action laws

(c) the respective equilibrium constants K_1 and K_2 are determined by fitting the Ideal Chemical Theory[6] to the experimental activity coefficients[5].

(d) the entropy of mixing is that of an assembly of hard spheres including a modified version of the configurational entropy[7,8]

(e) the magnetic susceptibility is free electron like with a modified free volume and reduced electron concentration[9].

The results of our calculations are summarized in Figure 6. The experimental activity coefficients[5] show a less structured variation than the curve fitted by $K_1 = 14$ and

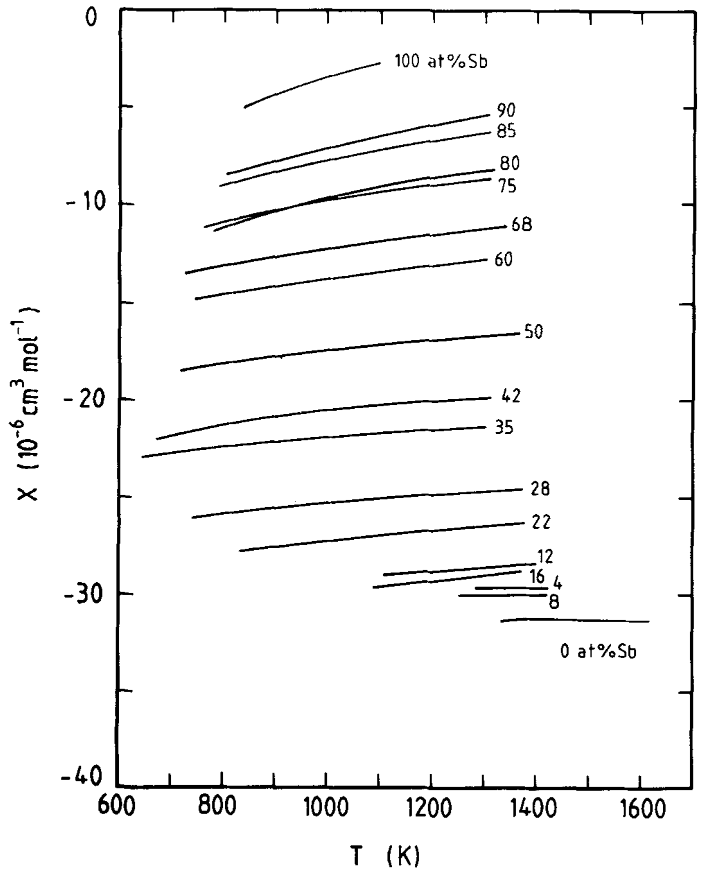

Figure 3 The magnetic susceptibility of liquid Au–Sb alloys as function of temperature and composition (— heating,... cooling).

$K_2 = 180$ (Figure 6a). The mole fractions of the formed "compounds" (Figure 6b) are of the same magnitude as those in Au–In and Au–Ge indicating a major part of the atoms to be involved in "compounds" formation[1,2]. The calculation of the entropies was based on the molar volumes of $11.29\,\text{cm}^3\,\text{mol}^{-1}$ and $20.86\,\text{cm}^3\,\text{mol}^{-1}$, the packing fractions of 0.448 and 0.338, and the hard sphere diameters of $2.53\cdot 10^{-8}\,\text{cm}$ and $2.75\cdot 10^{-8}\,\text{cm}$ for Au and Sb, respectively. There are some anomalies apparent around the equiatomic composition and on the Au-rich side, however, the experimental excess entropy of mixing[5] is found to be not correctly reproduced (Figure 6c).

The electronic susceptibility was deduced from the free electron formula which can be expressed in terms of the molar volume V_m and the average number of valence electrons per atom z according to

$$\chi^{eo} = \frac{2\cdot \mu_B^2 \cdot m_e N_A^{1/3}}{h^3\cdot (3\pi^2)^{2/3}} \cdot V_m^{2/3} \cdot z^{1/3} \qquad (1)$$

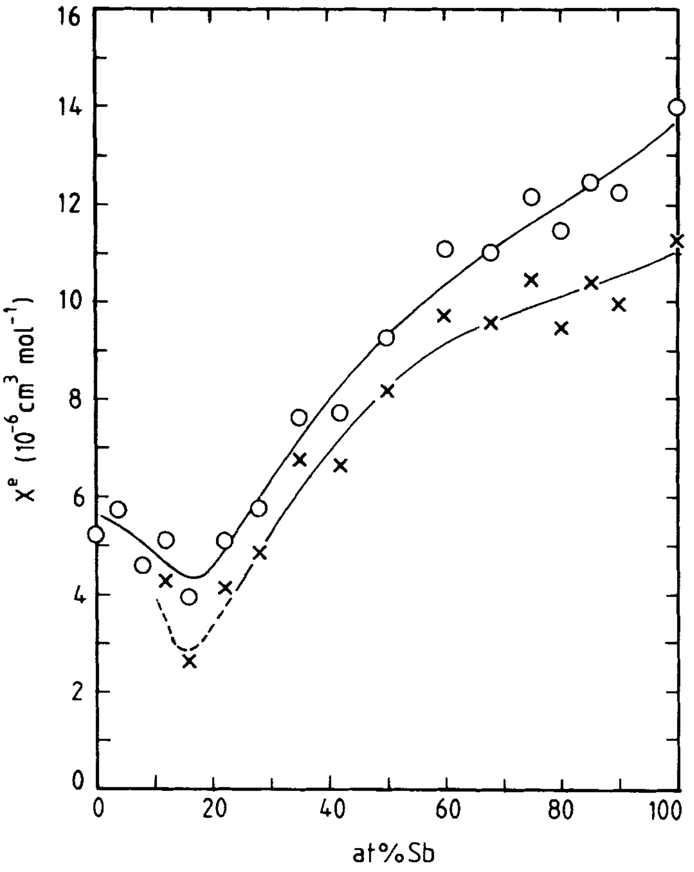

Figure 4 The electronic part of the magnetic susceptibility of liquid Au–Sb alloys as function of composition (× 873 K, ○ 1273 K).

Due to the formation of "compounds" the volume accessible to the conduction electrons and the average number of electrons is assumed to be decreased in amounts proportional to the fraction of the "compounds". The diamagnetic contribution of the cores to the total susceptibility is made up of four contributions, i.e. those of the free constituents and those of the "compounds" which are taken as adjustable parameters. The data points given in Figure 6d refer to the difference between the experimental values X^{exp} and those based on Eq. (1) associated with the appropriate adjustment of the diamagnetic contribution ($X^{\mathrm{o}} = X^{\mathrm{eo}} + X^{\mathrm{dia}}$). The solid line shown in the figure relates to core susceptibilities of $-48 \cdot 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for AuSb, and $-225 \cdot 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for $\mathrm{Au_5Sb}$, respectively. The agreement is acceptable, and the scattering is within the experimental accuracy.

Further details of the results on Au–In or Au–Ge and the applied formalism are given in our preceding papers[1,2], or the original articles[6–9]. As to the discrepancy between the calculated and the experimental entropies (Figure 6c) it has to be emphasized that the underlying expressions are free of adjustable parameters. Due to the lack

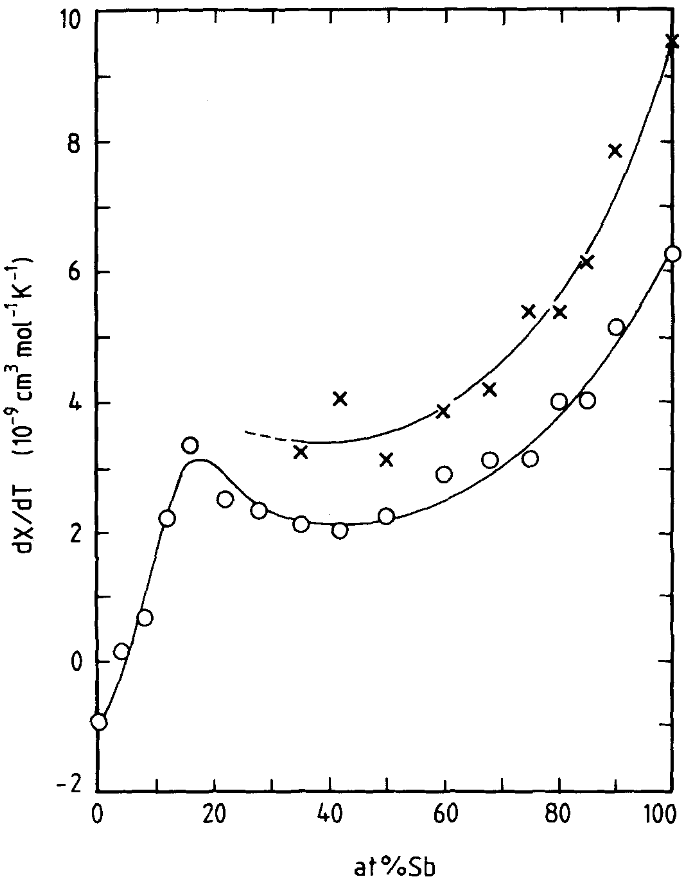

Figure 5 The temperature coefficient of the magnetic susceptibility as function of composition (× 873 K, ○ 1273 K).

of experimental data the volume of the alloys was assumed to be ideal. This is not very essential to the treatment of the magnetic data, but can be the decisive factor for the entropy of mixing which is highly sensitive to the volume of mixing. In order to illustrate this, we have estimated the volume of mixing V^{mix} from the statistical approach proposed by Okajima and Sakao[10]

$$V^{\text{mix}} = 8 \cdot V^{\text{mix}}_{0.5} \cdot x_{\text{Au}} \cdot x_{\text{Sb}} \cdot (1 - \alpha \cdot x_{\text{Sb}})/(2 - \alpha) \tag{2}$$

$V^{\text{mix}}_{0.5}$ denotes the volume of mixing at the equiatomic composition, and α is a constant independent of composition. If—by comparison with liquid Cu–Sb, Cu–Sn and Au–Sn—we consider $V^{\text{mix}}_{0.5}/V_{\text{ideal}} \approx -0.04$ and $\alpha \approx 1.4$ as best estimates for Au–Sb, we arrive at a much better reproduction of the experimental entropy values (Figure 6c). Obviously, there is a high degree of arbitrariness in estimating the volume of mixing in such a manner, however, the observed volume contraction of the rapidly quenched

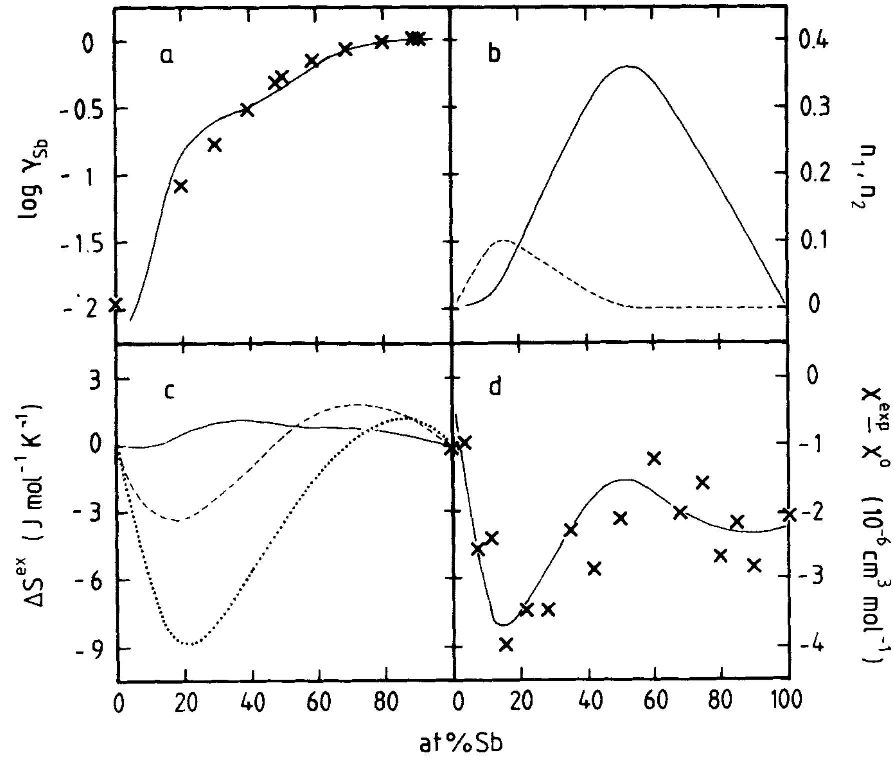

Figure 6 Theoretical representation of some experimental data on liquid Au-Sb alloys at 1273 K in terms of "compound" formation. a) The activity coefficient of Sb; × experimental[5]. — calculated; b) the mole fraction of xAuSb (—) and Au_5Sb (---); c) the excess entropy of mixing; .... experimental curve[5] fitted with $V^{mix} = 0$ (—), and $V^{mix} < 0$ (---); d) the deviation of the experimental susceptibility from the ideal behaviour; × experimental, — calculated.

metastable phases with respect to the equilibrium phases in Au–Sb seems to support the assumptions made above[11].

Considering the stoichiometries of the "compounds" (Au_3In, Au_4Ge, and Au_5Sb) there seems to be a systematic trend with the valency of the polyvalent element, but this is not necessarily a proof of the real existence of such "compounds". Instead of hypothesizing on the formation of Au_5Sb, in order to account for the minimum in the magnetic susceptibility around 16 at%Sb, we may focus on the electron concentration ($e/a \approx 1.6$) which should favour the formation of electron compounds. As a matter of fact, the hcp phase detected in splat cooled samples[3,11] is a metastable electron compound with $e/a \approx 1.5$.

The stability of such phases is due to the interaction between the Fermi surface and the Brillouin zone boundary, which implies that, in liquid and amorphous metals, such favourable electronic conditions occur if the diameter of the Fermi sphere coincides with the first peak of the structure factor, i.e. if $2k_f$ equals k_p. The strict calculation of the magnetic susceptibility involves suitable pseudopotentials and partial structure factors[12], but here we attempt a qualitative analysis in terms of the total structure factor. If we estimate k_f from the electron concentration per unit volume according to the expression $(3\pi^2 n)^{1/3}$ and if we assume k_P to decrease linearly from liquid Au ($2.66 \cdot 10^8\,\mathrm{cm}^{-1}$) to liquid Sb ($2.15 \cdot 10^8\,\mathrm{cm}^{-1}$), we expect the intersection to occur around 13 at%Sb. This would be sufficiently close to the critical concentration evidenced by the magnetic susceptibility (16 at%Sb) and the appearance of the hcp phase (15 at%Sb). In quench condensed amorphous films of Au–Sb the intersection of $2k_f$ and k_P was reported to occur around 20 at%Sb, suggesting the critical electron concentration ($e/a \approx 1.8$) to be increased with respect to liquid alloys[13].

In general, such an analysis in terms of k_f and k_P should also be applicable to other transport properties. In the past, this simple concept has been successfully applied to explain the maxima and the negative temperature coefficients of the electrical resistivity in certain composition ranges of noble metal based alloys[14]. In a recent paper[15], the experimental resistivity of liquid Au–Sb has been treated by using a quantitative theoretical treatment instead of simply comparing $2k_f$ to k_P. The integration of the Faber–Ziman formula–which also involves the partial structure factors in the integrand and the Fermi vector as integration limit—yielded a characteristic maximum of the resistivity and a minimum of the temperature coefficient around 15 at%Sb, in agreement with the critical concentration estimated by simply comparing k_f and k_P (13 at%Sb). The experimental resistivities differ in magnitude from those predicted by the theory, but they reflect the most remarkable details: a flat, though weakly pronounced maximum in the resistivity indicated at low temperatures on the Au-rich side, and a minimum in the temperature coefficient located at about 12 at%Sb. Thus, although the characteristic features seem to be less pronounced than expected, liquid Au–Sb seems to comply with the typical behaviour of alloys between noble-metals and polyvalent metals.

So far, the two limiting interpretations applied in this paper have proved their usefulness. Apparently, the concept of "compound formation" can be adapted so as to fit both the thermodynamic and the electronic behaviour, but it also necessitates a whole set of input parameters, some of them chosen in a more or less arbitrary manner. The interpretation in terms of the electronic environment, on the other hand, is based on one single parameter, i.e. the electron concentration applied either directly or by its impact on the value of k_f. It is apparent, that most of the electronic "anomalies" are well understood in terms of e/a, k_f, and k_P, without the necessity of introducing hypothetical "compounds". As to the thermodynamic behaviour of liquid alloys, the conception of "compounds" formation might still be a useful approach, but regarding the electronic behaviour the assumption of individual compounds in liquid alloys seems to be unnecessary.

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