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Magnetic susceptibilities of liquid gold–germanium alloys

P Terzieff†, K L Komarek† and E Wachtel‡§

† Institut für Anorganische Chemie, Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria

‡ Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestrasse 75, D-7000 Stuttgart 1, Federal Republic of Germany

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Abstract. The magnetic behaviour of liquid gold–germanium alloys has been characterized by susceptibility measurements performed from room temperature up to a maximum temperature of 1600 K with special emphasis on the liquid state. Throughout the range of composition the diamagnetic susceptibilities were found to decrease with the temperature except for the very gold-rich side where a tendency of opposite sign was indicated. The variation of the susceptibilities with alloy composition was non-ideal with a flat minimum located at about 18 at.% Ge. The interpretation was given in terms of ‘compound formation’ around the stoichiometric compositions AuGe and Au₄Ge. Alternatively, an interpretation based on a critical electron concentration was presented.

1. Introduction

During recent years the thermodynamic and electronic properties of liquid metals and alloys have attracted increasing attention. Meanwhile a strikingly high number of systems with a non-simple mixing behaviour is known. In contrast to an earlier understanding of the observed phenomena it has become evident that deviations from the ideal mixing behaviour are more the rule than the exception. In that sense, only a minority of binary or multi-component systems turn out to be ideal.

In a previous series of papers the present authors have attempted to explain both the thermodynamic and the magnetic properties of liquid Cd–Sb and Au–In alloys by one model based on the concept of compound formation [1–4]. Both systems exhibit an asymmetric heat of mixing versus composition curve and a moderately pronounced minimum in the magnetic susceptibility. Despite the fairly good description of the experimental results by the applied model, the formal character of the theoretical treatment had always been emphasized. Except for some very particular systems, there is in general no direct evidence for the occurrence of molecule-like associations in the melt.

In view of such fundamental questions and focusing on the magnetic susceptibility we decided to direct our attention, instead, to the electron concentration which is certainly one of the key factors for the transport properties. This and the following papers will concentrate on the systematic changes of the magnetic properties with the electron concentration in the series Au–In, Au–Ge and Au–Sb.

§ Dr E Wachtel passed away on November 14, 1989.

2. Experimental procedure

Samples of about 0.7 g were prepared by direct alloying of the elements using high-purity germanium bars (5N, Alfa-Ventron, USA) and gold sheet (4N, Ögussa, Austria) as starting materials. The mixtures were sealed under vacuum (quartz, 0.01 Pa) and subjected to a thermal treatment at about 1400 K. After a reaction period of about 16 h the homogenized alloys were cooled down to room temperature at a rate of 5 K min⁻¹ which was the same applied during the magnetic measurements.

The magnetic susceptibilities were determined in open alumina crucibles on a Faraday-type balance [5] kept under purified argon. The contributions of the thermocouple (Pt-Pt/Rh), the suspension rod, and the alumina crucible to the force exerted by the magnetic field as well as their variations with temperature were determined by separate measurements.

The temperature could be raised in a controlled manner up to 1400 K or, if necessary, even up to 1600 K. The data points taken with an average scanning rate of about 2 points min⁻¹ are represented in the figures by smooth curves. The scattering of the experimental points and the occasionally observed divergence between the heating and cooling curves—excepting the effect due to supercooling—were much better than 0.6 × 10⁻¹¹ m³ mol⁻¹. Concerning the total accuracy, the magnetic susceptibilities were estimated to be correct to within about 5%.

3. Results and discussion

The diversity in the discontinuity of the magnetic susceptibility across the solid–liquid transition of the pure elements reflects the difference in the behaviour of their valence electrons (figure 1). Pure Au, a typical metal both in the solid and the liquid state, shows only a small change of about 9% towards an increased diamagnetism in the liquid state. With a much more pronounced discontinuity of opposite sign (170%), pure Ge changes from a diamagnetic semiconducting solid to a paramagnetic metallic liquid. The experimentally observed magnetic susceptibility is the sum of the diamagnetic contribution of the ion cores (χ^{dia}) superimposed on the paramagnetic spin susceptibility of the electron gas. Taking the free-electron formalism as a first approximation, the spin part of the magnetic susceptibility (Pauli–Landau susceptibility) can be expressed in terms of the molar volume (V_m) and the number of valence electrons per atom (z).

$$\chi^0 = \chi^{\text{dia}} + 2 \left[\mu_0 \mu_B^2 m_e N_A^{1/3} / \hbar^2 (3\pi^2)^{2/3} \right] z^{1/3} V_m^{2/3}. \quad (1)$$

In evaluating (1) the diamagnetic core susceptibilities as well as the number of valence electrons were assumed to be additive throughout the range of composition. Regarding the uncertainty in the diamagnetic core susceptibilities given in the literature and excepting those elements with unfilled $d(1/N)$ or $f(1/N)$ shells this rather simple expression has proved to be applicable to a wide class of liquid metals and alloys.

Based on the molar volume of 11.39 cm³ mol⁻¹ [6] for liquid Au at the melting point, one obtains 7.9 × 10⁻¹¹ m³ mol⁻¹ for the spin part of the magnetic susceptibility. Together with the values calculated for the diamagnetic core of Au⁺ (−45.5 or −47.3 × 10⁻¹¹ m³ mol⁻¹ according to [7] and [8]) this gives values (−37.6 or

$-39.4 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$) which are in perfect agreement with our experimental value of $-39(\pm 2) \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$. Since the molar volume increases with the temperature, the susceptibility is also expected to increase continuously, but this is apparently not the case as already emphasized in a preceding paper [3]. Due to the lack of full reproducibility of the slight curvature above the melting point we took the linear high-temperature part as representative for liquid Au.

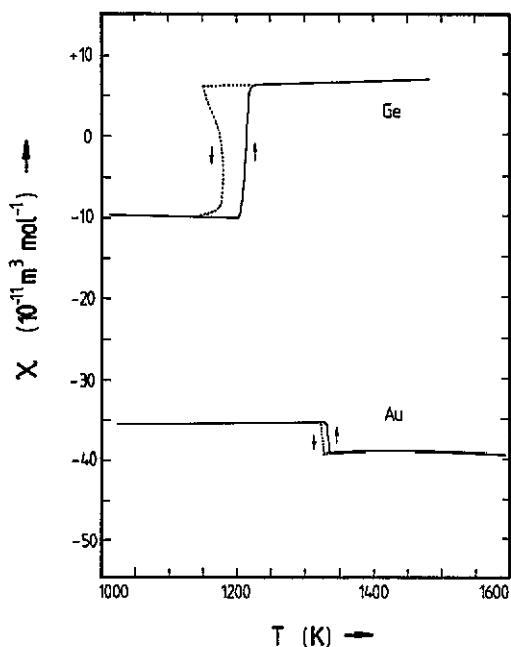


Figure 1. The magnetic susceptibility of Au and Ge at the solid-liquid transition (\uparrow heating, \downarrow cooling).

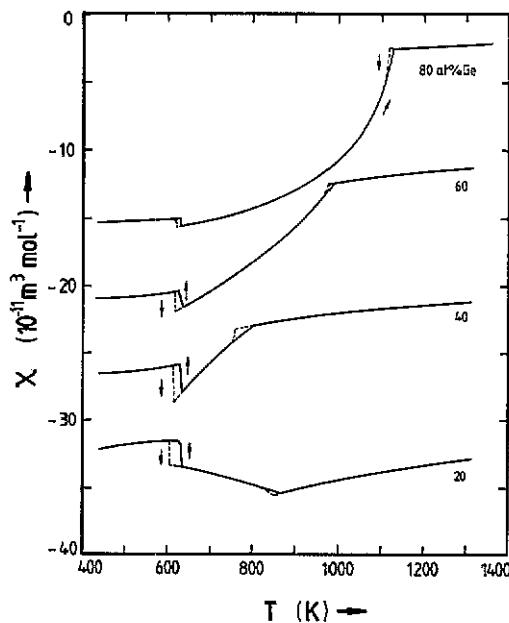


Figure 2. The magnetic susceptibility of some representative Au-Ge alloys as function of temperature (\uparrow heating, \downarrow cooling).

For liquid Ge with a molar volume of $13.22 \text{ cm}^3 \text{ mol}^{-1}$ [6] equation (1) yields $13.9 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ for the spin susceptibility at the melting point. Again, including contribution of the Ge^{4+} cores (-10.3 or $-8.8 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ according to [7] and [9]) this gives a total susceptibility of 3.6 and $5.1 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$, respectively. Our experimental value of $6.1 (\pm 0.3) \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ is somewhat higher but still in acceptable agreement. Furthermore, we find a similarly good accordance with our previous value of $5 (\pm 3) \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ determined under different experimental conditions [10] and one of about $5.7 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ estimated from the figure in [11]. The temperature dependence of the susceptibility of Ge correlates well with the variation of the molar volume with the temperature [6]. In contrast to pure liquid Au, the spin susceptibility of liquid Ge seems to be slightly enhanced. However, in view of the experimental accuracy and the uncertainty in the contributions of the diamagnetic cores, we neglected the effect of exchange enhancement.

Fourteen alloys of different composition have been investigated. The discontinuities observed at lower temperature are only a reflection of the binary phase diagram which shows a simple eutectic located at 28 at.% Ge and 634 K [12]. Some of the

susceptibility versus temperature curves are shown in figure 2 as representation of the whole series. They all have in common a sharp discontinuity at about 630 K due to the eutectic reaction which is accordingly most pronounced around the eutectic composition and disappears at the solubility limit of Ge in Au (≈ 3 at.% Ge) and of Au in Ge (≈ 0 at.% Au, figure 3).

The increase of the magnetic susceptibility with further increasing temperature on the Ge-rich side of the eutectic point arises from the progressive melting of Ge while the decrease on the Au-rich side is similarly due to the melting of Au (figure 2).

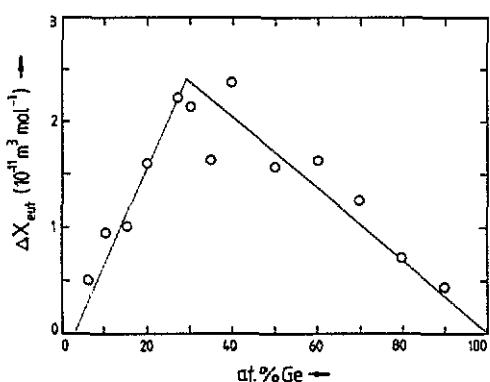


Figure 3. The discontinuity in the magnetic susceptibility of Au-Ge alloys due to the eutectic reaction (634 K).

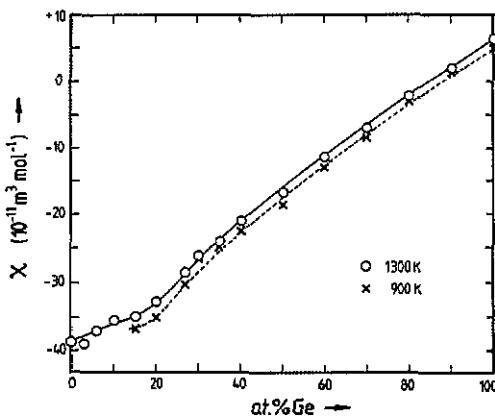


Figure 4. The magnetic susceptibility of liquid Au-Ge alloys as a function of composition.

The most interesting feature of this paper—the variation of the magnetic susceptibilities with composition—is illustrated in figure 4 for two different temperatures. Compared to the Au-In system where the magnetic susceptibility passed through a clear minimum at about 30 at.% In [3] we observed only a shallow dip located around 18 ± 1 at.% Ge in the case of Au-Ge. Vatolin and co-workers [13] have also reported such an anomaly, however, their extremely deep minimum around 25 at.% Ge is not compatible with the very small effect observed in our measurements.

This feature is better pronounced if the experimental values are compared with those emerging from (1) which represents the ideal case. On account of the smallness of the observed anomaly we tried to roughly estimate the influence of the volume effect on the magnetic susceptibility.

In the absence of experimental data and as a first approach, the volume of mixing is usually assumed to be additive, and in fact such an ideal behaviour has been reported [14]. However, this conflicts with the volume expansion of about 5% observed on solidification of the eutectic alloy [15]. Taking into account the thermal expansion of the elements (15×10^{-6} K⁻¹ for Au and 6.5×10^{-6} K⁻¹ for Ge, according to [16]) and correcting for the solubility of Ge in Au (≈ 3 at.%) with the help of the x-ray densities [17] we obtain $11.13 \text{ cm}^3 \text{ mol}^{-1}$ for the volume of the solid eutectic mixture and $10.60 \text{ cm}^3 \text{ mol}^{-1}$ for the eutectic melt. In spite of the large error introduced by the extrapolation of the elemental volumes down to the reference temperature of 634 K ($10.86 \text{ cm}^3 \text{ mol}^{-1}$ for liquid Au and $12.54 \text{ cm}^3 \text{ mol}^{-1}$ for liquid Ge [6]) we arrive at the excess volume of $-0.7 (\pm 0.3) \text{ cm}^3 \text{ mol}^{-1}$.

A volume change of such a magnitude would decrease the ideal spin susceptibility by about 4%. However, in view of the inconsistency with the results claimed by [14] we proceeded assuming the volume of mixing to be ideal, at least within $\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$.

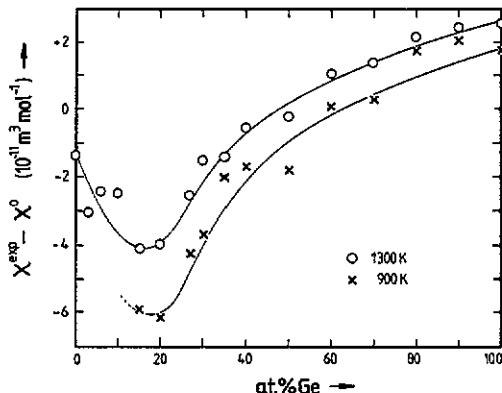


Figure 5. The deviation of the experimental magnetic susceptibility in liquid Au-Ge from the ideal mixing behaviour.

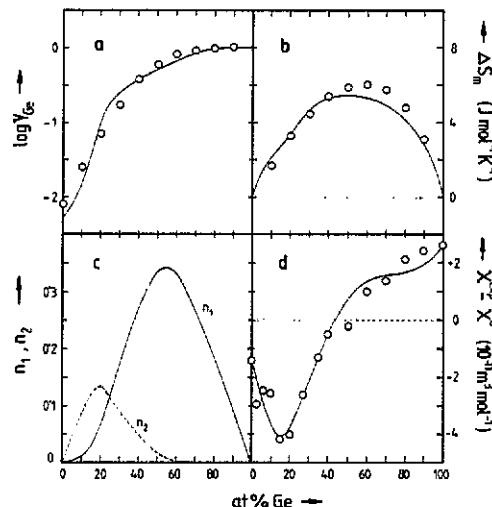


Figure 6. Theoretical representation of some properties of liquid Au-Ge at 1300 K. (a) activity coefficient of Ge [19]; (b) entropy of mixing [22]; (c) mole fraction of compounds; (d) departure of the magnetic susceptibility from the ideal behaviour.

Thus, we derived the ideal variation of the magnetic susceptibility with the composition from (1) by considering both the volume and the number of valence electrons to be additive. Figure 5 represents the difference between the experimental values and those calculated with (1) using the diamagnetic contributions given in [7]. Comparing this with figure 4, it becomes more obvious that the magnetic susceptibility varies anomalously with the composition as reflected by the characteristic minimum located around 18 at.% Ge. Moreover, it is remarkable that this minimum appears at a composition much closer on the Au-side than in the case of Au-In, where a similar but better pronounced minimum was located at about 30 at.% In [3]. In [3] the interpretation has been given in terms of 'compound formation' following a mass action law. Having assumed compounds of the stoichiometry AuIn and Au_3In , a parallel description of the thermodynamic and the magnetic properties could be presented. In order to offer a complete picture, we will apply the same formalism to the present system. Without outlining the theoretical backgrounds in too much detail, we will use the same notation as that adopted in the preceding papers [2-4].

The starting point of the treatment is to consider the stoichiometries of the compounds and the equilibrium constants which were determined by fitting the Ideal Chemical Theory proposed by Eckert and co-workers [18] to the experimental activity coefficients. The data reported by Hager *et al* [19] were converted to our reference temperature of 1300 K via the partial enthalpies of mixing also given in this paper. By analogy with Au-In, the fit shown in figure 6(a) refers to a mixture of two different compounds of the form AuGe and Au_4Ge with the equilibrium constants (K_1 , K_2)

Table 1. Model parameters for the thermodynamic and magnetic properties of liquid Au-Ge at 1300 K: the molar volumes (V_m), the equilibrium constants (K), the hard sphere diameters (σ), the packing fractions (η), and the diamagnetic core contributions (χ^{dia}).

	Au	Ge	AuGe	Au ₄ Ge
V_m (cm ³ mol ⁻¹)	11.363	13.335	—	—
K	—	—	14	180
σ (×10 ⁻⁸ cm)	2.523	2.417	3.448	4.604
η	0.446	0.334	—	—
χ^{dia} (×10 ⁻¹¹ m ³ mol ⁻¹)	-45.45	-10.23	-49.01	-214.9

listed in table 1.

The entropies of mixing were calculated with the hard-sphere expressions for a two-component system as practiced by Khanna *et al* [20], for example. For the configurational entropy we applied a modified version which takes account of the formation of two types of compounds [2, 21]. The essential parameters, the hard sphere diameters σ_{Au} and σ_{Ge} , were chosen so as to fit the entropies of the pure elements. As shown in figure 6(b) the calculations yielded a fairly good description of the experimental data which refer to 1423 K [22].

Since the extent of compound formation has already been determined in the course of our treatment (the mole fractions n_1 and n_2 are depicted in figure 6(c)) we may stress the fact that our version is free of adjustable parameters.

For a presentation of the magnetic susceptibility we applied the concept proposed by Takeuchi and co-workers [23] which can be understood as modification of (1). Due to the formation of chemical bonds the average number of free electrons is assumed to be reduced by amounts proportional to the mole fractions of the species and the number of electrons that make up the chemical bonds. Similarly, the volume accessible to the remaining part of the free electrons is diminished. Again, the reduction is considered to be proportional to the relative abundance and the volume blocked per particle; this volume was set equal to respective hard-sphere volumes. The diamagnetic part (χ^{dia}) of the susceptibility was split into four different contributions, each being made up of a particular value weighted with the respective mole fraction. The diamagnetic susceptibilities of the elements are taken from [7], those of the compounds (χ_1^{dia} and χ_2^{dia}) were treated as adjustable parameters. The very good fit shown in figure 6(d) was achieved with -49.0 and -214.9×10^{-11} m³ mol⁻¹, which are not very different from the additive values (-55.8 for AuGe and -192.1×10^{-11} m³ mol⁻¹ for Au₄Ge). The parameters used in our treatment including the packing fractions of the elements (η_1 , η_2) are summarized in table 1.

All in all, the applied formalism offers a very compact picture which covers both the magnetic and the thermodynamic properties of the system. However, judging by the magnetic properties alone, we see no direct reason to sustain the hypothesis of two different compounds, or of compounds at all.

As an alternative to the concept of chemical interactions being reflected in the thermodynamic properties one may also consider some other factors giving rise to the electronic anomalies. Therefore, as already emphasized in the introduction, we tend to focus our attention on the valence-electron density or the electron/atom ratio (e/a) which is more directly related to the magnetic susceptibility.

In fact, the coincidence of the minimum in the magnetic susceptibility with the

appearance of electron compounds in the system Au-In is presumably not fortuitous. Among the many phases reported for this system [12] our special attention goes to the high-temperature $\gamma(1/N)$ phase, an electron compound with an electron/atom ratio of 1.60 located at the composition where the susceptibility minimum occurs (30 at.%In). Since the valence-electron concentration per atom, e/a , is known to be directly related to the stability of the particular structure one may imagine some kind of special electronic configuration in the melt at about the same concentration. Therefore it is certainly not surprising to find the minimum of the magnetic susceptibility in Au-Ge at the concentration of 1.54 ± 0.08 electrons per atom (18 ± 1 at.% Ge) which is indeed very close to the value observed in Au-In (1.60). And once more, it cannot be fortuitous that the preferential formation of metastable β -AuGe, a HCP electron compound, occurs in just this very particular composition range of 16-25 at.% Ge covering an electron/atom ratio between 1.48 and 1.75 [12].

It has been pointed out that the coincidence of the first peak of the structure factor (k_p) with the diameter of the Fermi sphere ($2k_F$) designates a particular electronic situation [24]. Due to the lack of experimental values for these quantities at our reference temperature we approximated k_F by the free-electron expression $(3\pi^2 n)^{1/3}$ which relates k_F to the concentration of the conduction electrons per unit volume (n). The partial and the total structure factors of the alloys were calculated with the hard-sphere model [25] assuming the hard-sphere diameters to be independent of composition. The hard-sphere diameters of the constituents themselves were determined by adjusting the model to the experimental data given for the pure elements [26]. Placing our emphasis only on the position of the first peak we found the best reproduction with hard-sphere diameters of 2.58 and 2.52×10^{-8} cm and packing fractions of 0.46 and 0.34 (for Au and Ge, respectively). It is remarkable, that this set of parameters does not appreciably differ from the values applied for the treatment of the thermodynamic and the magnetic properties (see table 1).

Including the abovementioned uncertainty of the volume, we expect k_p , the position of the first peak of the total structure factor, and $2k_F$ to intersect somewhere between 15 and 19 at.% Ge which is indeed the position where we found our susceptibility minimum (18 ± 1 at.% Ge). The coincidence with the particular electron/atom ratio (e/a) and the appearance of metastable HCP β -AuGe has been pointed out above.

Waghorne and co-workers [15] observed the first diffraction peak at 2.73×10^8 cm $^{-1}$ (25 at.% Ge, 698 K), while Dutchak *et al.* [27] reported 2.75×10^8 cm $^{-1}$ for 27 at.% Ge and 633 K. In order to facilitate a comparison with their data we performed a calculation for the average temperature of 665 K which is also included in figure 7. The agreement with the experimental values of k_p is moderate but acceptable. However, the departure is not essential to the position of the intersection range between k_p and $2k_F$ which—extending now from 17 to 21 at.% Ge—is still within the region where the metastable $\beta(1/N)$ phase forms.

Thus, we have presented two distinctly different views of the phenomena frequently observed in liquid metals. The concept of compound formation seems to be applicable to the thermodynamic behaviour of the system with the option of being expandable to some other properties as well. For purely electronic properties, like the magnetic susceptibility, the more realistic picture in terms of valence-electron densities has to be given preference. Although crucial differences have become apparent we plan to substantiate our findings by systematically extending our considerations to other Au-based systems.

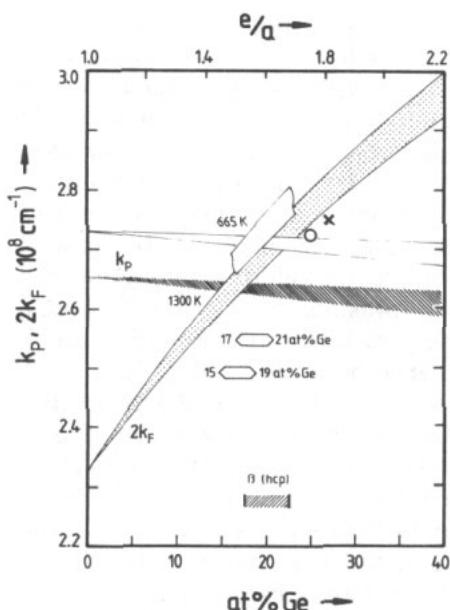


Figure 7. The Fermi vector k_F and the position of the first maximum of the total structure factor k_p in liquid Au-Ge as function of composition and electron concentration (x, experimental values [15, 27] respectively).

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