Magnetic susceptibility of liquid Ag-Ge, Ag-Sn and Ag-Pb

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Abstract

The electronic susceptibilities of liquid Ag–Ge, Ag–Sn and Ag–Pb alloys show the characteristic features of all liquid noble metal–polyvalent metal systems. Small additions of the alloying element (5–10 at.% Ge, Sn, Pb) give rise to an initial increase of the susceptibility whereas larger amounts of Ge and Sn (20–30 at.%) produce the minima typical of the whole class of alloys. In a complementary manner the temperature coefficients pass first through a pronounced minimum on the Ag-rich side followed by a drastic increase towards a maximum at higher concentrations of Ge, Sn or Pb. It is obvious that as in other noble metal–polyvalent metal systems the minima of the electronic susceptibility occur around the valence electron concentration of 1.6 electrons per atom.

Simple pseudopotential theory in the nearly free electron approach was used to discuss the unusual variation of the electronic susceptibility and its temperature coefficient with the composition of the alloys. As regards the composition dependence of the electronic susceptibility the theoretical predictions are more spectacular than actually observed, but at least for alloys with Ge and Sn the basic trends are found to be reproduced. The temperature coefficients, on the other hand, are found to be well explained for alloys with Sn and Pb and less for that with Ge. The reasons for the observed divergences are briefly discussed.

1. Introduction

The thermodynamic investigations of the past have revealed that liquid metal alloys hardly ever behave as ideal mixtures. Chemical interactions between the constituent atoms may give rise to chemical short-range order, or in the most prominent cases even to the formation of short-lived chemical complexes. It seemed plausible to assign all deviations from a simple mixing rule to such non-random mixing of the constituents. In some previous studies on gold-based liquid alloys it was attempted to describe the anomalies in thermodynamic and the magnetic properties with one single set of model parameters by assuming the formation

of chemical complexes of defined stoichiometry [1–3]. Concerning the composition where the anomalies occurred it became apparent that the magnetic anomalies did not match the thermodynamic anomalies. On account of this divergence two different types of chemical complex with different stoichiometries were assumed.

Meanwhile, it has become obvious that the magnetic anomalies, i.e. the minima in the electronic part of the magnetic susceptibility, occur at a critical valence electron concentration (electron to atom ratio) of $e/a \approx 1.6$ pointing to a purely electronic effect. Dupree and Sholl [4] demonstated that the pseudotential approach put forward by Timbie and White [5] was capable of explaining the observed susceptibility minima without the pre-assumption of chemical complexes. This could be verified for a series of Au-based liquid alloys [6]. In a recent paper, the consideration was successfully extended to liquid alloys of Ag with the trivalent main group elements Ga and In [7]. Apart from some divergence in the magnetic susceptibility, the calculated temperature coefficients—both the absolute values and in particular their peculiar variation with the composition—were found to be in good accordance with the experimental findings. This paper was designed to find out how far the magnetic properties of liquid Ag–Ge, Ag–Sn and Ag–Pb comply with the pseudopotential approach applied in the previous papers.

2. Method and theory

This paper is primarily concerned with the electronic part of the magnetic susceptibility and its temperature dependence. The total magnetic susceptibility χ_{tot} is, in general, assumed to be the sum of a temperature independent diamagnetic background χ_{ion} as represented by the ionic cores and an electronic contribution χ_{el} brought about by the conduction electrons. Experimentally, χ_{el} is obtained by subtracting the known core susceptibility from the measured susceptibility according to

$$\chi_{el} = \chi_{tot} - \chi_{ion}. \tag{1}$$

Since χ_{ion} is a temperature independent quantity, the temperature dependence of the total susceptibility is assigned to the electronic part χ_{el}. The electronic contribution, in turn, is made up of a paramagnetic term arising from the spin of the conduction electrons χ_p (Pauli spin susceptibility) and a diamagnetic contribution χ_d (Landau diamagnetism):

$$\chi_{el} = \chi_p + \chi_d. \tag{2}$$

For an assembly of non-interacting electrons and ions the electronic contributions sum up to the free electron susceptibility given as

$$\chi_{el}^0 = \frac{2\mu_B^2 m_e N_A^{1/3}}{h^3 (3\pi^2)^{2/3}} V_m^{2/3} Z^{1/3} \tag{3}$$

with χ_p^0 and χ_d^0 being related to χ_{el}^0 by $\chi_p^0 = 1.5\chi_{el}^0$ and $\chi_d^0 = -0.5\chi_{el}^0$, respectively. V_m denotes the molar volume of the alloy and Z is the averaged valence. In real systems, where interactions cannot be excluded, the individual contributions can be expressed as [4]

$$\chi_{p,d} = \chi_{p,d}^0 (1 + \Delta_{p,d}) \delta_{p,d}^{ec}. \tag{4}$$

Δ_p and Δ_d are the corrections due to the interaction between the ionic cores and the conduction electrons; δ_p^{ec} and δ_d^{ec} are those due electronic exchange and correlation. They were deduced from the formula given Wilk *et al* [8] and Kanazawa and Matsudaira [9]. The pseudopotential corrections Δ_p and Δ_d were obtained from the expression proposed by Timbie and White [5]:

$$\Delta_{p,d} = -\frac{3Z}{32E_f^2} \int_0^\infty a(q) v^2(q) G_{p,d}(q) \, dq. \tag{5}$$

The variable q is the momentum transfer vector k expressed in units of the Fermi vector k_f (i.e. $q = k/k_f$), Z denotes again the valency, E_f the Fermi energy, $a(q)$ the structure factor, $v(q)$ the pseudopotential form factor and $G_p(q)$ and $G_d(q)$ are universal functions of q. For binary mixtures the integrand has to be modified in terms of partial structure factors $a_{ij}(q)$ and the pseudopotential form factors $v_i(q)$ of the constituent elements.

Table 1. Hard sphere model parameters used to calculate the structure factors of pure liquid Ag, Ge, Sn and Pb: V_m molar volume, σ hard sphere diameter, ε/k_B height and A width of the repulsive square well.

	V_m (cm^3 mol^{-1})	σ (10^{-8} cm)	ε/k_B (K)	A
Ag	11.63	2.66	240	2.15
Ge	13.32	2.40	300	2.30
Sn	18.49	2.80	300	2.05
Pb	21.09	2.95	120	1.60

The calculation was performed (i) with the experimental structure factors listed by Waseda [10], and (ii) with those calculated for an assembly of hard spheres interacting via a repulsive square well potential [11, 12]. The model was adjusted to the experimental structure factors of the pure elements. The essential input parameters (molar volume V_m, hard sphere diameter σ, height ε/k_B and width A of the repulsive square well) are listed in table 1. Furthermore, the semi-empirical form factor proposed by Borchi and DeGennaro [13] was applied for Ag, while that of Heine and Abarenkov [14, 15] was used for the polyvalent elements. The volumes of the alloys were approximated by linear interpolation of the values given for the pure elements [16]. The details of the evaluation and the analytical expressions used to evaluate equations (4) and (5) are given in the in the original articles [4, 5, 8, 9] and the preceding papers on the particular subject [6, 7]. The original results, the experimental method and the construction details are given elsewhere [17–19]. Throughout the paper the general reference temperature was chosen to be 1283 K. As regards the significance of the experimental electronic susceptibility it has to be recalled that—in particular for Ag, but also for Pb—its contribution to the total susceptibility is rather small (cf table 2). Taking account of the differences in the literature data for the core susceptibilities ($\leqslant 3 \times 10^{-6}$ cm^3 mol^{-1}) and adding the experimental accuracy of at least $\pm 2 \times 10^{-6}$ cm^3 mol^{-1} the maximum incertainty of χ_{el} amounts to about $\pm 5 \times 10^{-6}$ cm^3 mol^{-1}. Thus, is is not surprising to find divergences of several units between theory and experiment. In order to achieve better comparison with the theory and to place the emphasis on the shape of the susceptibility–composition curve the core susceptibilities in all graphical illustrations (figures 1–3) were ajusted to fit the electronic susceptibilties of the pure elements to the calculated values. The temperature coefficients, in contrast, are independent of the choice of χ_{ion} and are thus of higher reliability. Their estimated accuracy is presumably better than $\pm 1 \times 10^{-9}$ cm^3 mol^{-1} K^{-1}.

3. Results and discussion

The variation of the electronic susceptibilty with the composition of the alloys is shown in figures 1–3. Although pronounced at a different extent, the observed shapes are typical of all liquid noble metal–polyvalent metal systems: a first maximum on the noble metal side (at 5–10 at.% Ge, Sn, Pb) followed by a subsequent minimum at higher concentration of the alloying element (≈ 25 at.% in Ag–Ge and Ag–Sn). In Ag–Pb the minimum is not reflected,

Table 2. Magnetic susceptibilities and temperature coefficients of liquid Ag, Ge, Sn and Pb at 1283 K: $\chi_{tot}^{(exp)}$ total susceptibility, χ_{ion} ion core contribution from [20], $\chi_{el}^{(exp)}$ experimental electronic susceptibility, χ_{el}^{0} free electron susceptibility, χ_{el} calculated electronic susceptibility; $d\chi/dT^{(exp)}$ experimental, $d\chi/dT$ calculated temperature coefficient.

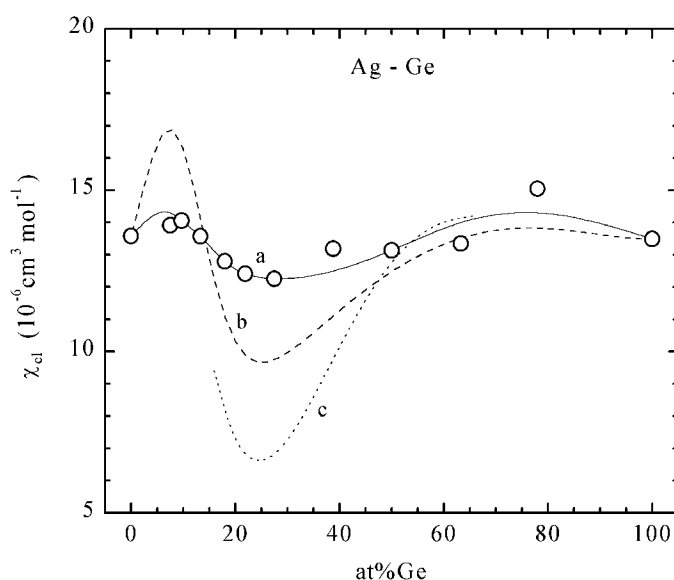|	$\chi_{tot}^{(exp)}$	χ_{ion}	$\chi_{el}^{(exp)}$	χ_{el}^{0}	χ_{el}	$d\chi/dT^{(exp)}$	$d\chi/dT$
	(10^{-6} emu mol^{-1})					(10^{-9} cm^3 mol^{-1} K^{-1})	
Ag	−24.39	−25.97	1.58	6.38	13.58	1.73[a]	0.65
Ge	6.45	−8.21	14.66	11.09	13.49	2.42	0.82[b]
Sn	−4.21	−17.61	13.40	13.80	17.16	2.03	1.23
Pb	−18.21	−26.80	8.59	15.06	19.19	3.28	1.66

[a] Averaged value.
[b] Taken from [2].

Figure 1. Composition dependence of the electronic susceptibility in liquid Ag–Ge alloys at 1283 K: a, experimental; b, calculated with model structure factors; c, calculated with experimental structure factors.

but the basic trend seems to be indicated. The resemblance to other Ag-based alloys and also Au-based alloys is obvious [6, 7].

The experimental points in figures 1–3 refer to the adjusted core susceptibilities of −37.97, −7.04, −21.37 and −37.40 × 10^{-6} cm^3 mol^{-1} for the ionic cores of Ag$^+$, Ge^{4+}, Sn^{4+} and Pb^{4+}, which deviate significantly from those given in the literature [20, 21]. This results from the divergence between the non-adjusted experimental and the calculated electronic susceptibilities. As a matter of fact, the electronic susceptibilites deduced with the help of the accepted literature data differ considerably from those actually shown in figures 1–3. Judged by the estimated experimental incertainty of ±5 × 10^{-6} cm^3 mol^{-1} the differences are small for Ge and Sn, but large for Ag and Pb. The obvious disagreement between the two sets of values is most probably due to the tentative choice of the form factor, which turned out to be one of the essential input parameters. However, as pointed out above, the dicussion will be continued with the adapted values and the emphasis will be
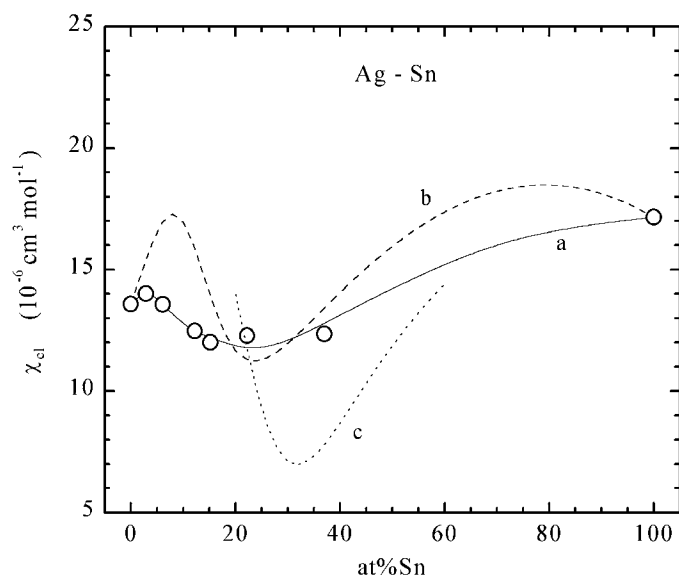
Figure 2. Composition dependence of the electronic susceptibility in liquid Ag–Sn alloys at 1283 K: a, experimental; b, calculated with model structure factors; c, calculated with experimental structure factors.
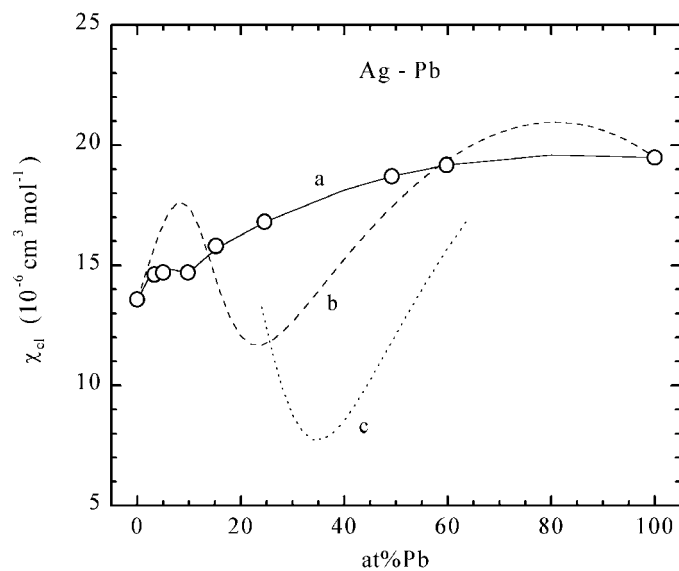

Figure 3. Composition dependence of the electronic susceptibility in liquid Ag–Pb alloys at 1283 K: a, experimental; b, calculated with model structure factors; c, calculated with experimental structure factors.

placed rather on trends than on absolute values. The numerical details are summarized in table 2.

The theoretical treatment yields the same principal shape of the susceptibility–composition curve for all systems (curves b in figures 1–3). It is evident that the theory overestimates

the extrema; however, the shapes of the curves are in fair agreement with the experimental trend observed in Ag–Ge and Ag–Sn. In Ag–Pb only the initial maximum is verified by a small hump on the Ag-rich side, but there is no experimental evidence of the predicted deep minimum. The application of experimental structure factors does not improve the divergencies between theory and experiment. On account of the experimental temperature range of the diffraction experiments the calculations were performed for temperatures 50 K above the liquidus temperature. The curves shown in figures 1–3 (curves c) were brought to the reference temperature of 1283 K with the help of the experimental temperature coefficients. The resulting minima are are even more pronounced than those obtained with the model structure factors (curves b). It is unclear whether this is due to the approximate character of the applied experimental structure factors (they are assumed to be independent of composition and representative of the range from 20 to 80 at.% Ag) or to the incorrect transformation of the susceptibilities from the liquidus temperature to the reference temperature (the susceptibility–temperature relationship was assumed to be linear).

By contrast, the temperature coefficients are found to be in much better accordance. They are independent of the chosen core susceptibilies and thus, on an absolute scale, even more significant. The marked decrease in the vicinity of Ag and the subsequent maximum at higher concentrations of polyvalent metal are evidently well reproduced by the theory (figures 4–6). Except for Ag–Ge where the experimental points are systematically shifted to higher values and higher concentrations of Ge, the divergencies are not far outside the experimental incertainty. A likewise satisfactory agreement using the same theoretical background was obtained for liquid Ag–Ga and Ag–In [7].
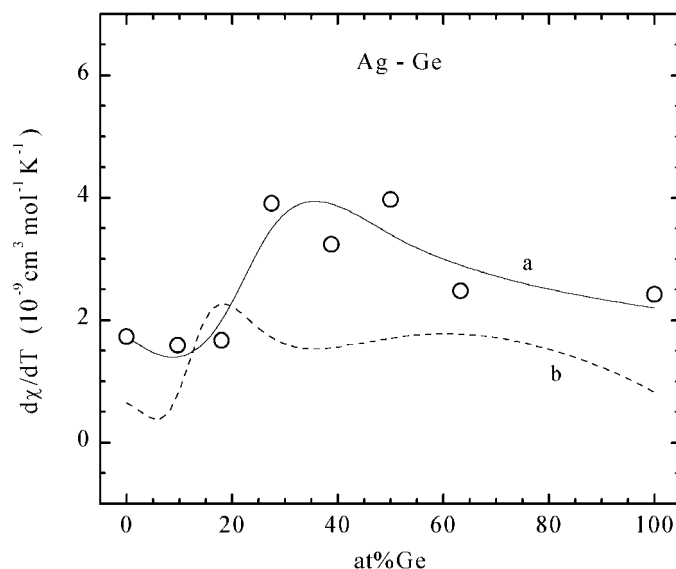

Figure 4. Temperature coefficient of the magnetic susceptibility in liquid Ag–Ge alloys: a, experimental; b, calculated.

In terms of the theory the observed departures from the free-electron values are accounted for by the corrections Δ_p, Δ_d, δ_p^{ec} and δ_d^{ec}. The values obtained for the pure elements are given in table 3. The enhancement of the para- and diamagnetic contribution due to electron–electron interactions is about the same for all elements ($\delta_p^{ec} \approx \delta_d^{ec} \approx 1.2$). The ion–electron interactions, on the other hand, have a marked influence on liquid Ag (i.e. the paramagnetic
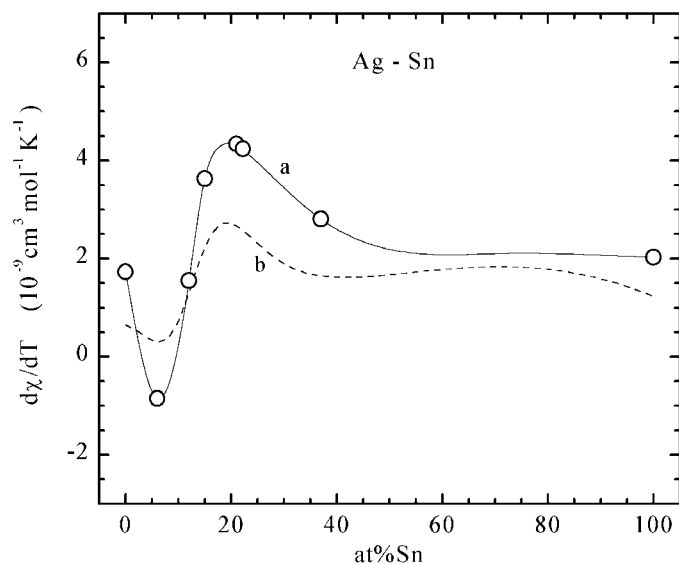
Figure 5. Temperature coefficient of the magnetic susceptibility in liquid Ag–Sn alloys: a, experimental; b, calculated.
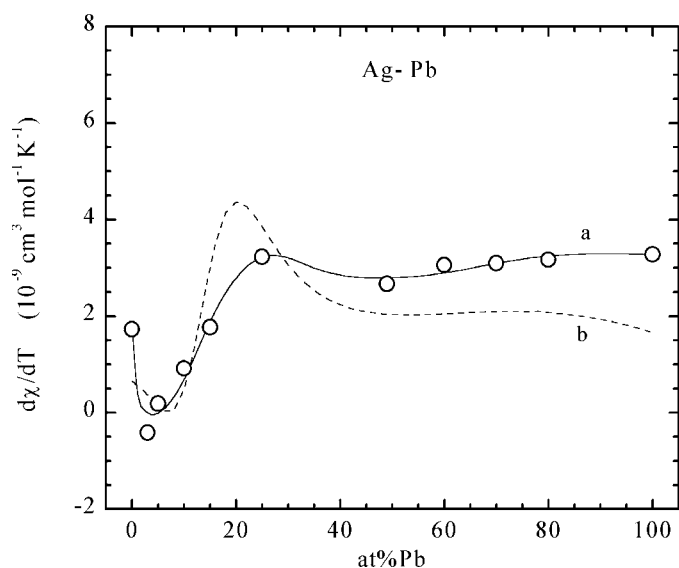

Figure 6. Temperature coefficient of the magnetic susceptibility in liquid Ag–Pb alloys: a, experimental; b, calculated.

term is enhanced by about 30%, and the diamagnetic term is decreased by 50%); their impact on Ge, Sn and Pb are small only.

According to the theoretical treatment used in this paper the pronounced deviations from a smooth free-electron-like behaviour in the alloys have to be assigned to the non-simple variation of the correction terms with the composition. δ_p^{ec} and δ_d^{ec} are found to vary in a smooth manner from one element to the other, thus giving rise to a uniform enhancement of

Table 3. Corrections to the free electron susceptibility in liquid Ag, Ge, Sn and Pb due to ion–electron interactions (Δ_p, Δ_d) and electronic exchange and correlation (δ_p^{ec}, Δ_d^{ec}).

	Δ_p	Δ_d	δ_p^{ec}	δ_d^{ec}
Ag	0.325	−0.490	1.23	1.23
Ge	−0.013	−0.029	1.19	1.13
Sn	−0.002	−0.031	1.20	1.15
Pb	0.002	−0.105	1.21	1.16
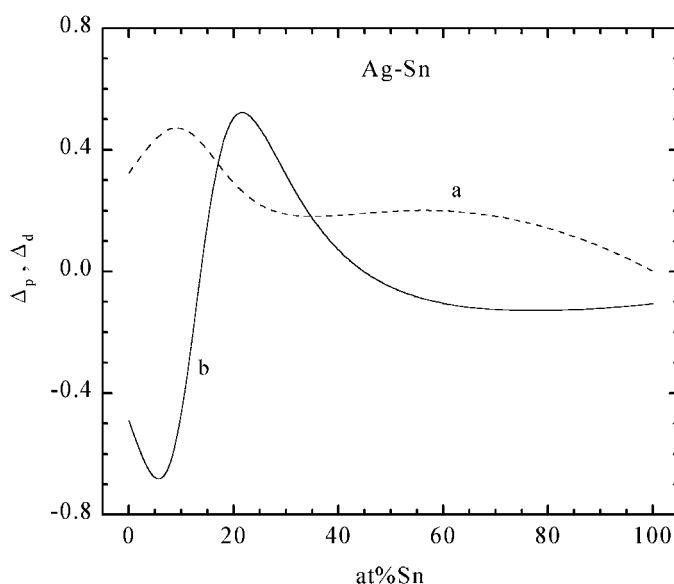
Figure 7. Pseudopotential corrections to the paramagnetic, a, and the diamagnetic part, b, of the electronic susceptibility in liquid Ag–Sn.

the susceptibility. The pseudopotential corrections Δ_p and Δ_d, on the other hand, show a rather spectacular variation with the composition. The example of Ag–Sn shown in figure 7 is typical for the whole series. Δ_p undergoes a further increase towards a flat maximum around 10 at.% of polyvalent metal giving rise to the maximum in the electronic susceptibility on the Ag-rich side. Δ_d passes first through a minimum at 10 at.% of the alloying element followed by a drastic increase to positive values with a maximum located around 22 at.%. This, in turn, increases the diamagnetic contribution and is thus responsible for the deep minimum of the total electronic susceptibility at higher concentrations of polyvalent metal. Based on the temperature coefficients (figures 4–6) the observed anomalies of the magnetic susceptibility are indicated to disappear with increasing temperature. Analogous findings were obtained for other Ag-based alloys [7].

Based on the careful analysis of Au-based liquid alloys it has been argued that the susceptibility minima are the reflection of the electronic stabilization of the liquid alloy at the specific electron concentration of $e/a \approx 1.6$. As a matter of fact, with the exception of Ag–Pb, throughout the series Ag–Ga, Ag–In, Ag–Ge and Ag–Sn electron compounds are known to be formed (including the metastable *cph* phase in Ag–Ge) in that particular range of composition [22]. Furthermore, it is remarkable that in all these systems the enthalpies of mixing follow an s-shaped curve with negative values on the Ag-rich side hinting at attractive

interactions between the constituent atoms. In Ag–Pb the heat of mixing is positive at all compositions indicating that the tendency of demixing prevails [23]. In fact, it has been suggested that the minima in the magnetic susceptibility are frequently the result of attractive chemical interactions in the liquid [24]. However, with regard to the present systems, it has to be emphasized that the theory applied in this paper yields such minima without the additional assumption of chemical short range order. The maximum on the noble metal side, on the other hand, seems to be a purely electronic effect.

4. Conclusion

Apart from some remaining divergences, the anomalous variation of the magnetic susceptibility and its temperature coefficient with the alloy composition in liquid Ag–Ge, Ag–Sn and Ag–Pb are well explained by the theoretical approach applied in this paper. The *a priori* assumption of compound like complexes in the liquid state seems not to be necessary to understand the basic trends of the systems. The theory suggests that the interactions between the conduction electrons and the ion cores are responsible for the unusual magnetic behaviour. A significant disagreement is indicated only for the system Ag–Pb, which fails to verify the predicted susceptibility minimum. It is unclear to what extent a non-random distribution of atoms (i.e. chemical short-range order) affects the calculations performed in this paper. Although the pseudopotential form factor of Ag is the most decisive input quantity, the preference of unlike neighbours (in compound forming systems) or that of like neighbours (in systems with demixing properties) might also have a strong influence.

Nevertheless, it should be emphasized that the treatment presented in this paper renders a fairly good qualitative picture of the experimental results without the presumed formation of chemical complexes or chemical short-range order. It is still moot to what extent the observed differences are due to the disregard of chemical short-range order, the simplifications made to evaluate the theoretical expressions or the theory itself.

References

[1] Terzieff P, Komarek K L and Wachtel E 1986 *J. Phys. F: Met. Phys.* **16** 1071
[2] Terzieff P, Komarek K L and Wachtel E 1992 *J. Phys.: Condens. Matter* **4** 1223
[3] Terzieff P, Komarek K L and Wachtel E 1994 *Phys. Chem. Liq.* **28** 145
[4] Dupree R and Sholl C A 1975 *Z. Phys.* B **20** 275
[5] Timbie J P and White R M 1970 *Phys. Rev.* B **1** 2409
[6] Terzieff P 1997 *Phys. Chem. Liq.* **36** 113
[7] Terzieff P and Tsuchiya Y 2000 *J. Phys. Soc. Japan* **69** 2629
[8] Wilk L, MacDonald A H and Vosko S H 1979 *Can. J. Phys.* **57** 1065
[9] Kanazawa H and Matsudaira N 1960 *Prog. Theor. Phys.* **23** 433
[10] Waseda Y 1980 *The Structure of Non-Crystalline Materials* (New York: McGraw-Hill)
[11] Silbert M and Young W H 1976 *Phys. Lett.* A **58** 469
[12] Gopala Rao R V and Ratna Das 1987 *Phys. Rev.* B **36** 6325
[13] Borchi E and DeGennaro S 1972 *Phys. Rev.* B **5** 4761
[14] Heine H A and Abarenkov I V 1964 *Phil. Mag.* **9** 451
[15] Harrison W A 1966 *Pseudopotentials in the Theory of Metals* (New York: Benjamin)
[16] Crawley A F 1974 *Int. Met. Rev.* **19** 32
[17] Arai Y 1997 *Thesis* Niigata University Graduate School of Science and Technology
[18] Arai Y, Shirakawa Y, Tamaki S and Azuma M 1995 *J. Phys. Soc. Japan* **64** 2594
[19] Arai Y, Shirakawa Y and Tamaki S J. 1994 *Phys. Soc. Japan* **63** 3815
[20] Hurd C M and Coodin P 1966 *J. Phys. Chem. Solids* **28** 523
[21] Selwood P 1956 *Magnetochemistry* (New York: Interscience)

[22] Massalski T B and Okamoto H 1987 *Phase Diagrams of Binary Gold Alloys* (Metals Park, OH: American Society of Metals)

[23] Hultgren 1973 *Selected Values of the Thermodynamic Properties of Binary Alloys* (Metals Park, OH: American Society of Metals)

[24] Sommer F 1982 *Z. Metallkde* **73** 77