

Magnetic susceptibility of liquid antimony-zinc alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 7563

(<http://iopscience.iop.org/0953-8984/5/41/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 01:59

Please note that [terms and conditions apply](#).

Magnetic susceptibility of liquid antimony–zinc alloys

P Terzieff[‡], K L Komarek[†] and K Hiebl[‡]

[†] Institute of Inorganic Chemistry, University of Vienna, Währingerstraße 42, A-1090 Wien, Austria

[‡] Institute of Physical Chemistry, University of Vienna, Währingerstraße 42, A-1090 Wien, Austria

Received 11 June 1993, in final form 30 July 1993

Abstract. Magnetic measurements on liquid Sb–Zn alloys around the composition of the intermediate phases SbZn, Sb₃Zn₄ and Zn₂Sb₃ are reported. The results give no clear evidence of an anomalous behaviour arising from the possible occurrence of association or chemical short-range order in the liquid state. The slightly increased temperature dependence of the magnetic susceptibility observed near the liquidus temperature seems to be that of a liquid semimetal. The deviations from the additive rule are very small and negative and tend to disappear with increasing temperature.

1. Introduction

The pronounced appearance of metastability in the Sb–Zn system has been the starting point for numerous investigations of the liquid state. It is well known that, by supercooling, the crystallization of the equilibrium phase SbZn can be suppressed, leaving stable Sb₃Zn₄ [1, 2]. There are strong indications that the preferential formation of Sb₃Zn₄ is related to a very special short-range order or even to the formation of chemical ‘complexes’ in the liquid, as evidenced by thermodynamic quantities [3, 4], electrical resistivity [5, 6] and mass density [7], and also by more recent theoretical considerations [8, 9]. In liquid Cd–Sb, our previous measurements yielded a small anomaly of the magnetic susceptibility centred around the composition of metastable Cd₄Sb₃ [10] which correlated well with the anomalies apparent in the thermodynamic properties [11–13], and the electrical resistivity of the system [5, 6]. Since both the thermodynamic behaviour [3] and, in particular, the electrical resistivity behaviour are much more pronounced in Sb–Zn than in Cd–Sb, we assumed this anomaly to be also magnetically better visible in Sb–Zn.

Such an anomalous magnetic behaviour has indeed been reported in the literature [14]. The present investigation was undertaken to confirm these previous results and to determine further details with emphasis on the particular composition range between 50 and 60 at.% Zn.

2. Experimental details

The alloys were prepared by direct reaction of the pure elements using high-purity (99.999%) antimony (Arsaco, New York) and high-purity (99.999%) zinc (Alfa-Ventron) as starting materials. Weighed amounts of the elements, sealed in quartz ampoules under a vacuum of 0.01 Pa, were subjected to a thermal treatment at about 1100 K. After a homogenization period of 10 h the samples were cooled to ambient temperature at a rate of 2 K min⁻¹. The

magnetic measurements were performed on a Faraday-type magnetic balance (Sus 10, Paar, Austria) in sealed quartz containers, applying different magnetic fields of 7.5, 9.9, 11.7 and 12.9 kOe. In general, the acquisition of the data occurred during the cooling period in order to extend the measurements into the supercooled region. The contributions from the individual quartz containers were assumed to be temperature independent. The variation in the magnetic susceptibilities with the field was non-systematic and almost negligible. The data presented throughout this paper refer to average values with a total experimental accuracy of better than $2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

3. Results and discussion

The composition of the alloys and their magnetic susceptibilities at 850, 970 and 1170 K are listed in table 1. A typical example of the observed susceptibility versus temperature curves is shown in figure 1, together with those of liquid Sb and Zn [15]. The pronounced discontinuity across the solid-liquid transition and the marked temperature dependence in both the solid and the liquid are similar to those of pure Sb and seem to be a typical feature of semimetals. Owing to the considerable degree of supercooling, the indicated transition temperatures are not those of the stable phase diagram [1].

Table 1. Magnetic susceptibility of liquid Sb-Zn alloys at 850, 970 and 1170 K.

Zn content (at.%)	Magnetic susceptibility ($10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)		
	850 K	970 K	1170 K
52.7	-4.35	-2.98	-2.21
53.5	-5.86	-4.26	-3.09
53.9	-7.06	-4.95	-3.15
55.5	-3.57	-1.88	-0.99
55.9	-4.72	-2.77	-1.51
56.9	-5.47	-3.44	-1.77
57.9	-3.96	-2.23	-0.69
58.8	-4.15	-2.22	-0.53
59.9	-2.98	-1.17	-0.68
60.8	-3.66	-1.74	-0.33

A summarized representation of the experimental data obtained for the liquid state is given in figure 2. All alloys of this very specific composition range exhibit the same non-linear, slightly increased temperature dependence of the magnetic susceptibility. This is remarkable, since neither liquid Zn nor liquid Sb exhibit such increased temperature coefficients. Liquid Zn shows a rather linear characteristic ($d\chi/dT \approx 0.4 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ [15]) whereas, for liquid Sb, $d\chi/dT$ increases from about $0.7 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ at 1170 K to about $1.3 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ at 850 K. In the high-temperature limit the average temperature coefficient of Sb-Zn alloys adopts the intermediate value of about $0.6 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ (at 1170 K), but at low temperatures ($2.2 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ at 850 K) it clearly exceeds the corresponding values for the pure elements (figure 3).

If the diamagnetic contribution χ_{dia} to the susceptibility is assumed to be constant and the electronic part χ_{el} to be well represented by the free-electron expression, the temperature

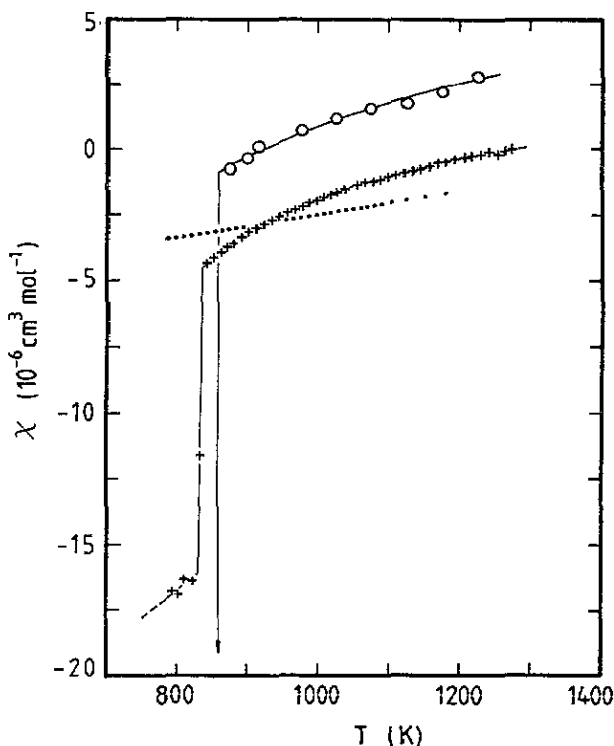


Figure 1. Temperature dependence of the magnetic susceptibility of liquid Sb (O), liquid Zn [15] (.....), and liquid and solid Sb-Zn 58.8 at.% Zn (+)

coefficient of the total susceptibility ($\chi = \chi_{\text{dia}} + \chi_{\text{el}}$) may be estimated from

$$d\chi_{\text{el}}/dT = -0.827 \times 10^{-6} z^{1/3} (A^{2/3} / \rho^{5/3}) (d\rho/dT) \quad (1)$$

which relates $d\chi_{\text{el}}/dT$ to the atomic mass A , the average valency z , the mass density ρ and its temperature derivative $d\rho/dT$. With an averaged density of about 6.2 g cm^{-3} , and a derivative of $4 \times 10^{-4} \text{ g cm}^{-3} \text{ K}^{-1}$ [7] we arrive at $d\chi_{\text{el}}/dT \simeq 5 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$. This is about one order of magnitude smaller than observed for liquid Zn, but nearly two orders of magnitude smaller than for liquid Sb-Zn and liquid Sb, which only emphasizes the semimetallic character of the materials under consideration.

Within our experimental accuracy, the magnetic susceptibilities seem to vary smoothly with composition. The deviations from the additive rule, $\chi - \chi_{\text{add}}$, are only very small; they are shown in figure 3 on an expanded scale and for two limiting temperatures. The values applied for the liquid elements at our reference temperatures (850 K and 1170 K) were $-1.1 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and $2.2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, respectively, for liquid Sb, and $-3.1 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and $-1.7 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, respectively, for liquid Zn [15]. Despite the high degree of scatter, our data seem to hint at negative deviations from the additive behaviour which tend to decrease with increasing temperature and Zn content. This implies a non-monotonic variation in the magnetic susceptibility over the entire range of compositions, presumably with a very flat minimum towards the antimony-rich side similar to that claimed by Endo [14] more on the zinc-rich side (about 62 at.% Zn). This is an

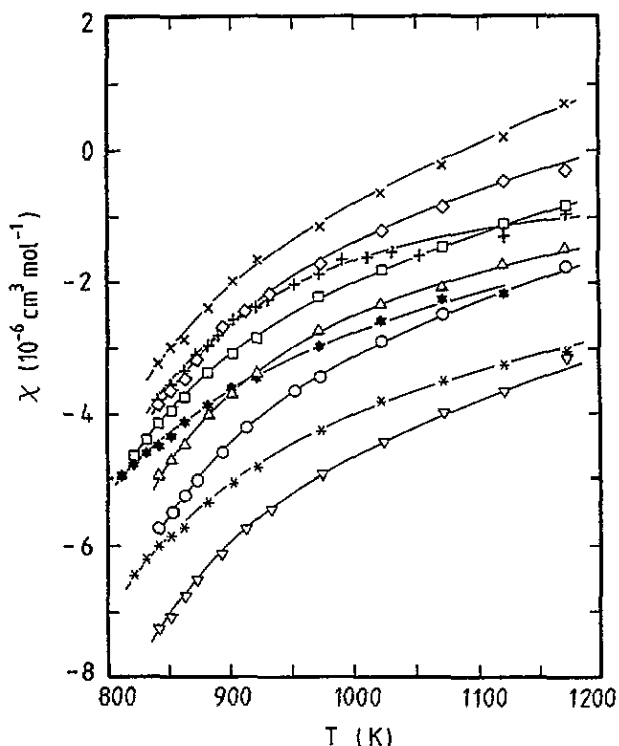


Figure 2. Temperature dependence of the magnetic susceptibility of liquid Sb-Zn alloys of different compositions: *, 52.7 at.% Zn; *, 53.5 at.% Zn; ▽, 53.9 at.% Zn; +, 55.5 at.% Zn; Δ, 55.9 at.% Zn; ○, 56.9 at.% Zn; □, 57.9 at.% Zn; ×, 59.9 at.% Zn; ◇, 60.8 at.% Zn.

interesting feature of the system; however, the present paper is primarily concerned with the more or less extremely pronounced anomalies reported around the critical concentration of 57 at.% Zn [4, 6].

Qualitatively, there is some agreement with the negative deviations observed by Endo [14], but—most possibly owing to the different position of the minimum—the trend with the composition is apparently not the same. To some extent, this divergence also reflects the limited experimental capability of determining the magnetic susceptibility of such nearly non-magnetic liquid alloys. On the other hand, it is worth noting that the weak anomaly indicated for Sb-Zn is about the same magnitude as that found for Cd-Sb [10].

The similarity between the behaviours of liquid Cd-Sb and liquid Sb-Zn has been well established. Thermodynamic investigations yielded deep depressions in the entropy of mixing, sharp minima in the enthalpy of mixing, and similarly pronounced shapes of the partial quantities around the stoichiometry Sb_3Me_4 [3, 11, 12]. The heat capacity measurements revealed positive, highly temperature-dependent deviations from the additive rule at about the same critical concentration [3, 12]. The electrical resistivities, although exhibiting a more complex behaviour for Cd-Sb, are also reported to pass through characteristic maxima [5, 6]. A semi-empirical and comprehensive interpretation of these liquid state phenomena has been given in terms of 'association' to larger chemical 'complexes' or some kind of chemical short-range order.

As regards the magnetic behaviour, the analogy between Sb-Zn and Cd-Sb seems to be self-evident; nevertheless for Sb-Zn our measurements failed to give clear experimental

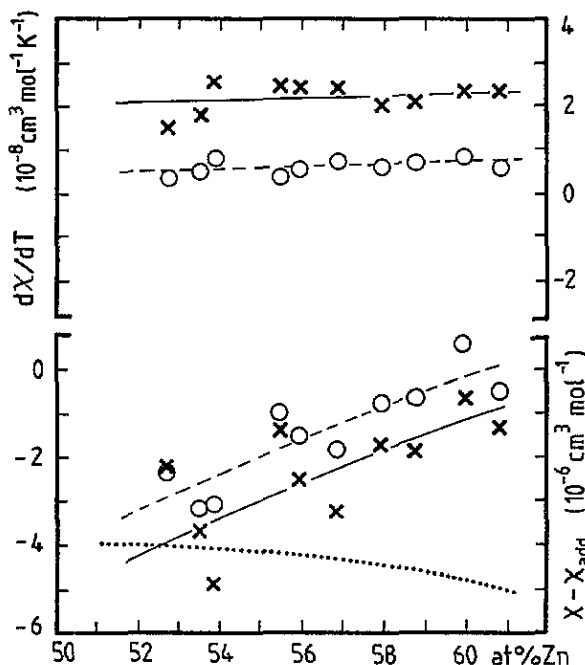


Figure 3. Temperature coefficients and deviations from the additive rule of the magnetic susceptibilities of liquid Sb–Zn alloys: \times , experimental data, this work, 850 K; \circ , experimental data, this work, 1170 K; \dots , data taken from [14].

proof of such an anomalous behaviour, at least not around the stoichiometry under discussion (Sb_3Zn_4 ; about 57 at.% Zn). At this point, it has to be emphasized that thermodynamic and electronic anomalies are not always correlated and may occur independently of one another at different compositions, as has been illustrated for liquid Au–In or Au–Ge [16, 17]. However, for Sb–Zn the extremely pronounced peak in the electrical resistivity suggested very particular electronic conditions around Sb_3Zn_4 . Thus it was surprising to find them not clearly reflected in the magnetic susceptibility. It is unclear to what extent the very small deviations from additivity and the non-linear temperature dependence of the magnetic susceptibility can be assigned to the occurrence of ordering or association processes in the liquid.

References

- [1] Hanson M and Anderko K 1958 *Constitution of Binary Alloys* (New York: McGraw-Hill)
- [2] Moffat W G 1984 *The Handbook of Binary Phase Diagrams* (New York: Genium)
- [3] Rubin I B, Komarek K L and Miller E 1974 *Z. Metallk.* **65** 191
- [4] Tsuchiya T and Kanai S 1993 *J. Non-Cryst. Solids* **156–8** 433
- [5] Bath A, Gasser J G and Kleim R 1982 *Phys. Lett.* **91A** 355
- [6] Mian M R, Mikula A and Komarek K L 1986 *Z. Metallk.* **77** 133
- [7] Dim L, Bath A, Gasser J G, Bretonnet J L and Kleim R 1981 *Phys. Lett.* **84A** 375
- [8] Gerling U and Predel B 1986 *Z. Metallk.* **77** 17
- [9] Gerling U, Lück R and Predel B 1986 *Z. Metallk.* **77** 80
- [10] Terzieff P, Komarek K L, Wachtel E and Predel B 1984 *J. Non-Cryst. Solids* **61–2** 1397
- [11] Geffken R, Komarek K L and Miller E 1967 *Trans. Metall. Soc. AIME* **239** 1151

- [12] Schick G and Komarek K L 1974 *Z. Metallk.* **77** 139
- [13] Terzieff P and Komarek K L 1985 *Z. Metallk.* **76** 397
- [14] Endo H 1927 *Sci. Rep. Res. Inst. Tohoku Univ.* **116** 201
- [15] Tsuchiya Y and Tamaki S 1974 *Phys. Chem. Liq.* **4** 157
- [16] Terzieff P, Komarek K L and Wachtel E 1986 *J. Phys. F: Met. Phys.* **16** 1071
- [17] Terzieff P, Komarek K L and Wachtel E 1986 *J. Phys.: Condens. Matter* **4** 1233