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Magnetic susceptibility and demixing in liquid Fe–Sn*

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Abstract

The magnetic behaviour of liquid iron–tin alloys has been determined by susceptibility measurements up to 1800 K. The magnetic moments of the iron atoms tend to decrease smoothly with progressive dilution ($4.4 \leqslant \mu_{\text{eff}} \leqslant 1.5$ μ_B), whereas the magnetic susceptibilities vary in a typical non-linear manner with the composition, indicating gradual changes in the magnetic environments. The data are tentatively analysed in terms of the phase diagram with special emphasis on the miscibility gap.

1. Introduction

The pronounced demixing behaviour of liquid Fe–Sn has been the subject of many preceding investigations. Although the existence of an extensive miscibility gap has been confirmed by various experimental techniques, its actual position in the equilibrium diagram is still not precisely known.

According to the more recent assessments of the phase diagram [1, 2], the region of immiscibility extends from about 30 to 70 at.% Sn at the monotectic temperature of 1400 K, with a critical temperature exceeding 1800 K. The theoretical treatment of the thermodynamic data in terms of the quasi-chemical approximation, on the other hand, indicated a more broadened and rather flat miscibility gap [3, 4].

The present study was aimed at (i) improving the information on the miscibility gap and (ii) determining the magnetic properties of the system with the help of high temperature susceptibility measurements.

2. Experimental details

The samples were prepared by direct alloying of the elemental sources (iron foil and tin rods with nominal purities of m4N8 and m5N+ respectively, Johnson–Matthey) sealed in quartz under a vacuum of about 0.01 Pa. Complete reaction was achieved by a single induction furnace melting followed by an equilibration period of about 15 h at 1450 K.

Magnetic measurements were performed on a Faraday-type balance kept under a protective argon atmosphere, applying a magnetic field of 18.6 kOe and typical heating and cooling rates of 5 K min^{-1}. The automatically recorded data are presented as smooth curves, the scattering of the experimental data being in general better than 1×10^{-6} cm^3 mol^{-1}.

3. Results and discussion

On account of the miscibility gap, a series of ten binary alloys have been prepared containing from 25 to 72 at.% Sn ($0.25 \leqslant x_{\text{Sn}} \leqslant 0.75$). The results of the magnetic measurements are summarized in Figs. 1 and 2. The magnetic susceptibility of elemental Fe exhibits the typical discontinuities associated with the melting point and the transition from the f.c.c. to the b.c.c. structure. Owing to the high degree of supercooling, the well-known Curie–Weiss-like behaviour of liquid Fe could be confirmed over a more extended temperature range. Pure Sn shows its typical diamagnetic, slightly temperature-dependent behaviour (Fig. 1).

In contrast with pure Fe, all alloys of Fe–Sn failed to give a similar linear relation between the inverse susceptibility χ^{-1} and the temperature T (Fig. 2). Although it would be plausible, this is apparently not induced by the demixing process, since even those alloys far outside the miscibility gap (25 or 72 at.% Sn) definitely show such a non-linear behaviour. The anomalies observed at temperatures below 1400 K, on the

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*Dedicated to Professor B. Predel on the occasion of his 65th birthday.

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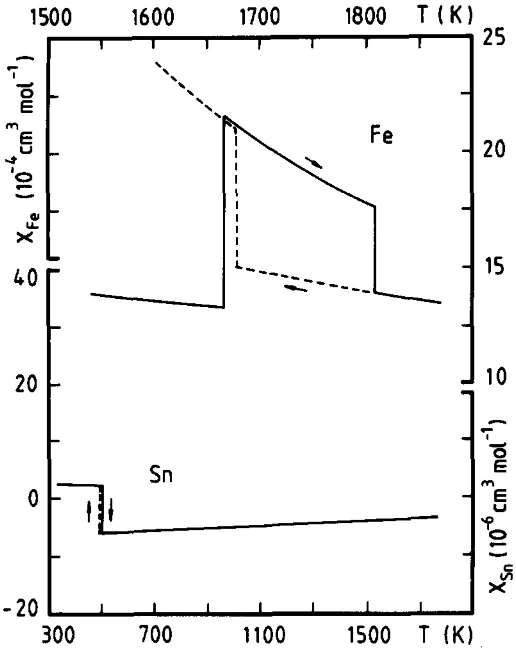

Fig. 1. Magnetic susceptibility of liquid Fe and liquid Sn as a function of temperature: ——, heating; – – –, cooling.

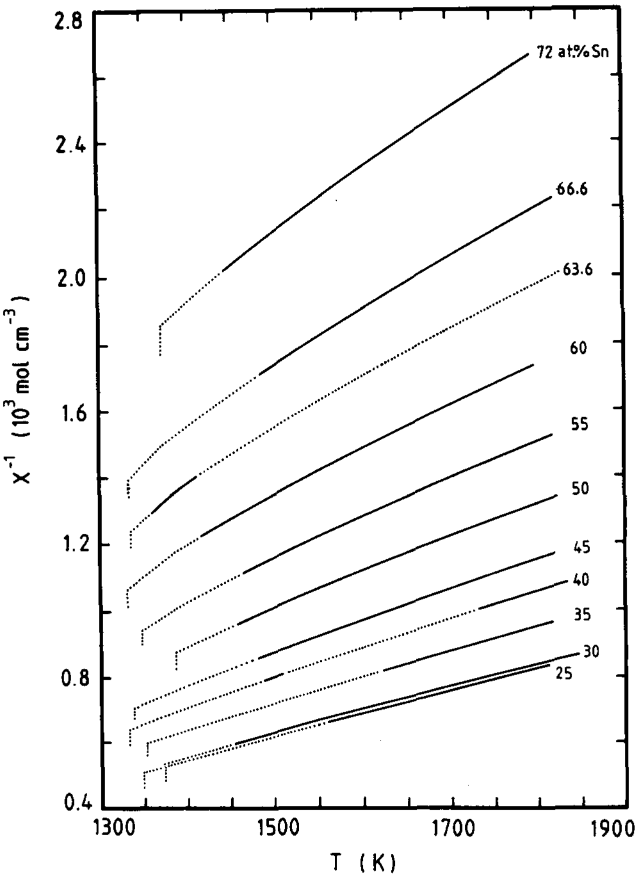

Fig. 2. Magnetic susceptibility of various liquid Fe–Sn alloys as a function of temperature: ——, heating; · · · · ·, cooling.

other hand, are directly related to the individual reactions of the separated liquid phases: the pronounced discontinuities are obviously due to the supercooled monotectic reaction of the Fe-rich liquid L_1 into α-Fe + L_2, whereas the additional breaks apparent at somewhat higher temperatures are presumably due to the equilibration reaction of the Sn-rich liquid L_2 into α-Fe + L_2.

In view of our high experimental accuracy, it was surprising not to find a clear indication of the miscibility gap. If, by simply ignoring the physical reality, *i.e.* assuming a single homogeneous melt, we split our experimental data into a constant term χ_0 and a Curie–Weiss term according to

$$\chi=\chi_0+\frac{C}{T-\theta_p} \tag{1}$$

we arrive at a perfectly linear relationship between $(\chi-\chi_0)^{-1}$ and T. The evaluation of the magnetic moments based on

$$\mu_{eff}=2.83\mu_B\left(\frac{C}{x_{Fe}}\right)^{1/2} \tag{2}$$

yielded a smooth variation with the composition which correlates well with the value for pure Fe and even with that reported for dilute alloys of Fe in liquid Sn, FeSn [5] (Fig. 3). The paramagnetic Curie temperature

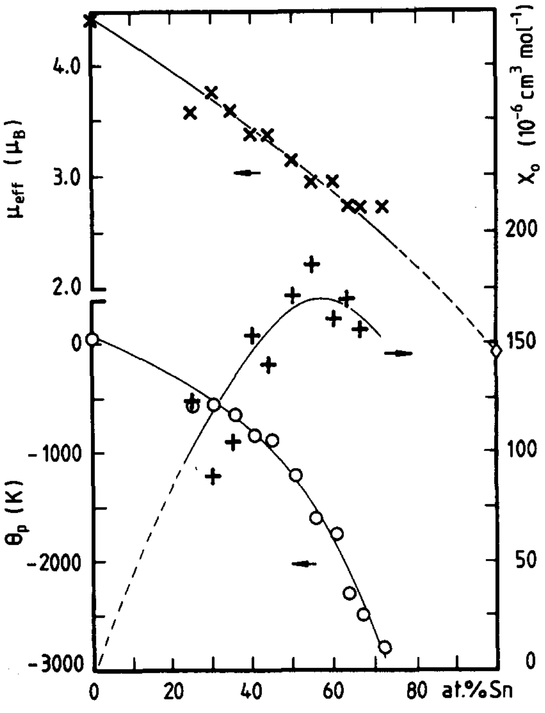

Fig. 3. Magnetic moment μ_{eff}, temperature-independent part of magnetic susceptibility χ_0, and paramagnetic Curie temperature θ_p in liquid Fe–Sn alloys as a function of composition: ×, +, ○, this work; ◇, taken from ref. 5.

θ_p was observed to vary in a similar smooth manner with the composition. The complete set of values deduced from eqns. (1) and (2) is given in Table 1 together with some other experimental data. Since in general most of the alloys refer to a mixture of two liquid phases, our values can only be of approximate character. It is also unclear whether the peculiar variation in the constant term χ_0 with the composition has a bearing on the miscibility gap or not.

The isothermal representation of the experimental data also fails to give a clear indication of the phase separation (Fig. 4). There are two possible reasons why the miscibility gap could not be detected. (i) If the magnetic susceptibility above the miscibility gap varies linearly with the molar fraction, the gap cannot be detected, since in the two-phase region the same dependence will be found. A similar conclusion also holds for the dependence on temperature. (ii) If the phase separation into two different melts has produced a strong geometrical separation under the influence of gravity [3], the mixing of the two liquids at temperatures above or outside the miscibility gap will be appreciably retarded. The linearity in the prospective miscibility gap has indeed been detected, but the deviation from linearity at the boundary of the two-phase region could not be determined owing to the first or second, or to both facts.

The apparently anomalous variation in the susceptibility with the composition as apparent from Fig. 4 is an inherent magnetic feature of the system rather than a reflection of the miscibility gap. In fact, similar shapes have been reported for the series Fe–Au, Fe–Zn, Fe–Ga and Fe–Ge [6]; one of them, the homologue Fe–Ge, has been added to Fig. 4. The limiting slopes on the Sn side are larger than those reported for dilute FeSn alloys [4, 6]. It seems that, magnetically, dilute alloys ($x_{Fe} \ll 1$) and also highly concentrated alloys of FeSn ($x_{Fe} \approx 1$) differ from those of intermediate composition. The magnetic moments presumably vary smoothly with the composition, so we may assign the difference directly to a gradual variation in the magnetic interactions between the Fe atoms, as expressed by the

TABLE 1. Experimental magnetic susceptibilities χ at 1400 and 1800 K, temperature independent contributions χ_0, magnetic moments μ_{eff} and paramagnetic Curie temperatures θ_p of liquid Fe–Sn alloys

Composition (at.% Sn)	Susceptibilities (10^{-3} cm^3 mol^{-1})			μ_{eff} (μ_B)	θ_p (K)
	$\chi_{1400\,K}$	$\chi_{1800\,K}$	χ_0		
0	1.818	1.402	–	4.40	52
25	1.825	1.227	0.122	3.57	−582
30.2	1.806	1.194	0.089	3.77	−547
35	1.569	1.046	0.105	3.60	−646
40	1.410	0.947	0.154	3.38	−840
44	1.289	0.869	0.140	3.38	−882
50	1.124	0.759	0.172	3.14	−1208
54.9	0.975	0.666	0.182	2.95	−1594
60.1	0.838	0.577	0.161	2.95	−1741
63.3	0.725	0.507	0.171	2.73	−2293
66.6	0.644	0.455	0.156	2.72	−2488
71.9	0.521	0.375	0.132	2.72	−2804
100	−0.004	−0.003	–	–	–

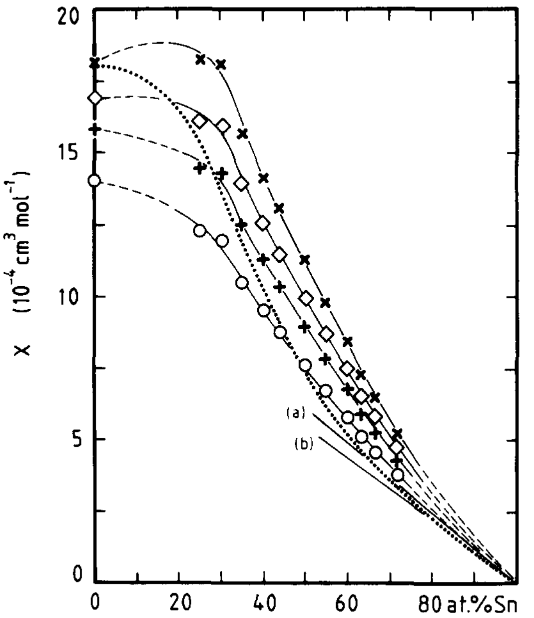

Fig. 4. Magnetic susceptibility of liquid Fe–Sn alloys as a function of composition: ×, ◇, +, ○, this work (1400, 1500, 1600, 1800 K); · · · · ·, data for Fe–Ge (1470 K [6]); (a), (b), data for dilute FeSn alloys (1600 K [5], 1000 K [7]).

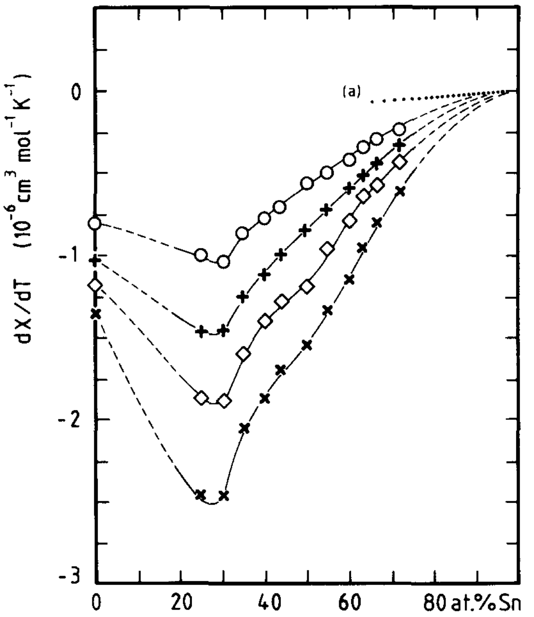

Fig. 5. Temperature coefficient of magnetic susceptibility in liquid Fe–Sn alloys as a function of composition: ×, ◇, +, ○, this work (1400, 1500, 1600, 1800 K); (a), dilute FeSn (1600 K [5]).

paramagnetic Curie temperature (Table 1). It is conceivable that the miscibility gap contributes to the complexity of the χ *vs.* T curves, but any assignment would be doubtful.

Such systematic changes are also apparent from the temperature dependence of the magnetic susceptibility and its variation with the composition (Fig. 5). We observe opposite trends in alloys rich in Fe and those of intermediate composition; again the limiting slope towards the Sn side diverges from that deduced for dilute alloys of Fe**Sn** [5].

The most characteristic feature is the deep minimum around 28 at.% Sn, which evidently coincides with the monotectic composition (32 and 30 at.% Sn according to the phase diagram [1, 2] and 26 at.% Sn for theoretical reasons [3]). The shallow dips superimposed on the ascending branches of the isotherms are most likely a manifestation of the miscibility gap. However, the effects are too small and thus inadequate for precisely locating the position of the miscibility gap.

In this context it is worth noting that the deviations from additivity, $\chi-\chi_{\mathrm{add}}$, pass through a cusp-like peak at the position of the monotectic composition (Fig. 6). Furthermore, it should be stressed that this "additional susceptibility" seems to be extremely temperature dependent. At present it is unknown whether this particular aspect is of purely magnetic, structural or thermodynamic, *i.e.* phase-diagram-related, origin.

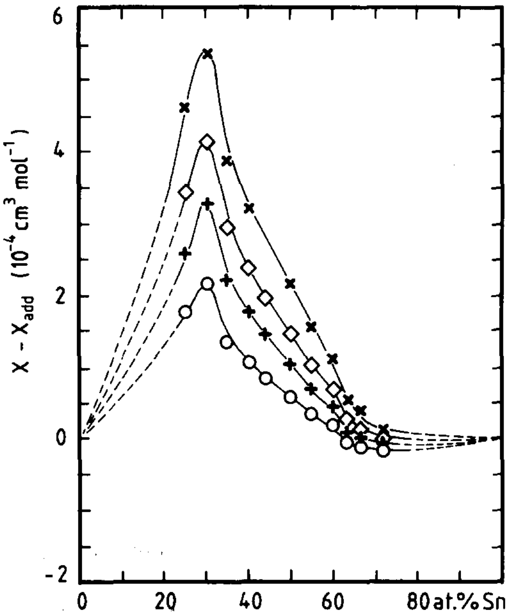

Fig. 6. Deviation of magnetic susceptibility from additive law in liquid Fe–Sn alloys as a function of composition at 1400 K (×), 1500 K (◇), 1600 K (+) and 1800 K (○).

4. Conclusions

The magnetic behaviour of liquid Fe–Sn is typical of the whole class of iron–polyvalent metal alloys. Although the relation between χ^{-1} and T is not strictly linear, the magnetic moments of the iron atoms are indicated to decrease smoothly with increasing dilution. The variation in magnetic susceptibilities with the composition shows a typical inflection-point-like behaviour. The marked deviations from additivity are most pronounced near the monotectic composition (28 at.% Sn) and extremely temperature dependent. At the same composition the temperature coefficient of the susceptibility passes through a deep minimum.

Owing to the smooth variation in the magnetic quantities around the equiatomic composition, the demixing reaction was found not to be clearly reflected by the magnetic measurements. Thus, on the basis of the magnetic data, the position of the miscibility gap in the equilibrium phase diagram could not be precisely located.

Acknowledgments

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