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The effect of the Ge content on the paramagnetic–antiferromagnetic transition in γ-Fe–Mn alloys

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Abstract. The temperature T dependence of magnetic susceptibility χ in the range 77–600 K and the Mössbauer absorption spectra at 310 K were measured for γ-Fe–30 at.% Mn alloys containing 2.01, 3.45, 5.63 and 8.73 at.% Ge. With increasing Ge content, the Néel temperature T_N decreases linearly while χ increases markedly and becomes temperature dependent above T_N, i.e. the Pauli paramagnetism of the alloys becomes a paramagnetism obeying the Curie–Weiss law. This behaviour of Fe–Mn–Ge is essentially similar to that of γ-Fe–Mn alloys containing Al or Si. The behaviour of the χ–T curves as well as the Mössbauer spectra results reveal that the increase in Ge content has led to a decrease in the itinerant character of 3d electrons in γ-Fe–Mn host alloys and to an increase in the localised net moment at the Fe atoms. These observations lead us to assume that alloying Fe–Mn with Ge alters the host density of states and consequently the Fermi level, which gives rise to a change in localised moment at Fe atoms. Finally, the Néel temperature of γ-Fe–Mn host alloys as a function of the average electron concentration has been discussed in brief.

1. Introduction

Previous investigations have reported the antiferromagnetism of γ-Fe–Mn alloys as well as the influence of the transition elements Ni, Co, Cr and V on the characteristics of the Néel transition of γ-Fe–Mn host alloys [1–5]. In the case of γ-Fe–Mn alloyed with non-transition elements, recent research by Zhang [4, 6–9] has shown that an increase in Al ($3s^23p^1$) or Si ($3s^23p^2$) content lowers the Néel temperature T_N and markedly increases the magnetic susceptibility χ, and the antiferromagnetic transition is accompanied by obviously anomalous changes in electric resistivity, elastic modulus and thermal expansion. These interesting phenomena reveal that the valence electrons of Al and Si probably interact with the outer-energy band of the host alloys, but it is as yet difficult to explain in detail how this occurs. Therefore we have extended our investigations to the addition of Ge ($4s^24p^2$) to gain a better understanding of the complex physical features of this system. To the best of our knowledge, the effect of Ge on the antiferromagnetic transition of γ-Fe–Mn has never been presented before.

In the field of magnetism, one of the interesting problems is the magnetic transition behaviour of antiferromagnetic alloys associated with the variation in average electronic concentration N (electron-to-atom ratio). The magnetic properties of dilute Cr alloys as a function of electron concentration have been studied in some investigations [10, 11],

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Table 1. Composition and phase structure of alloys tested.

Alloy	Composition (at.%)			Phase structure
	Mn	Ge	C	
1	31.52	—	0.20	γ
2	30.02	2.01	0.18	γ
3	29.87	3.45	0.14	γ
4	29.49	5.63	0.10	γ
5	28.11	8.73	0.08	γ + trace ε

and it has been found that solutes which are to the left of Cr in the periodic table diminish both the Néel temperature and the magnetic moment whereas those solutes which are to the right (except Fe, Co and Ni) increase these values. These features can be explained by the two-band model in [12], which was extended later in [13]. On the other hand, the effect of non-transition solutes such as Al, Si and Ge on the Néel transition of Cr alloys is more complicated than originally suspected; for example, Si [14] depresses T_N drastically, Ge (above 0.35 at.%) [15] increases T_N monotonically, while Al [16] affects T_N in a rather irregular way. Some recent investigation [17–19] display the existence of a magnetic triple point in Cr–Si and Cr–Ge alloys where the paramagnetic (P), incommensurate (I) and commensurate (C) phase boundaries meet. The above problems, as have been outlined, are still not sufficiently understood and are in contrast to each other. The antiferromagnetism of γ-Fe–Mn alloys at intermediate Mn concentrations is similar to that of Cr; however, the magnetic effects of Ge, Al or Si on this γ-Fe–Mn alloy are somewhat different from those on Cr host alloys. These matters are also discussed in the present paper.

2. Experimental procedure

γ-Fe–Mn–Ge alloys with a suitable amount of C added to stabilise the γ-phase were prepared from low-carbon pure Fe, electrolytic Mn and 99.999% pure Ge by induction furnace melting under an argon atmosphere at a pressure slightly above 760 mm Hg to protect the process of melting and casting from oxidation. The preparation details of raw specimens have been described elsewhere [6–9]. To avoid the disturbance of surface deformation, all specimens which are machine tooled were polished by electrolysis. The compositions and the crystal structures of the alloys tested were obtained by chemical analysis and x-ray diffraction respectively, the results of which are listed in table 1. Although the alloys show a variation in Mn content, the change in T_N associated with Mn content (28.1–31.5 at.%) is small [7, 20]. The magnetic susceptibility was measured with a model-300 magnetic balance. Mössbauer spectra measurements were carried out using a Mössbauer spectrograph (AST Ltd, USA) with a γ-radioactive source of ^{57}Co diffused in Pd. Foils about 25 μm in thickness which serve as the absorbers for Mössbauer spectra were obtained by mechanical working followed by an electropolishing operation. The Mössbauer experiment is done only at room temperature because of instrumental limitation.

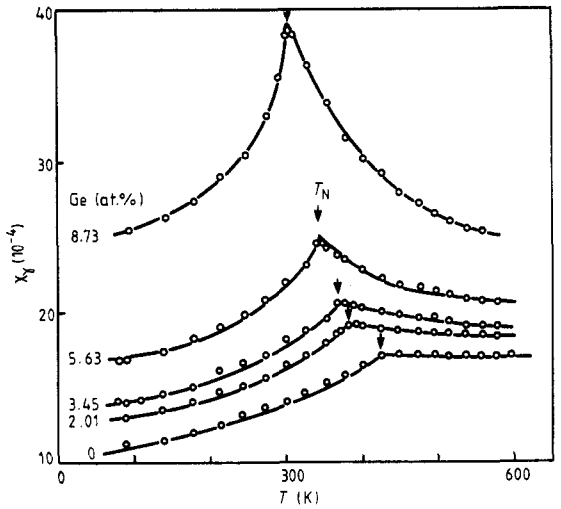

Figure 1. Effect of the Ge content on the temperature dependence of the volume magnetic susceptibility for γ-Fe–30 at.% Mn alloys (magnetic field intensity H = 4000 Oe).

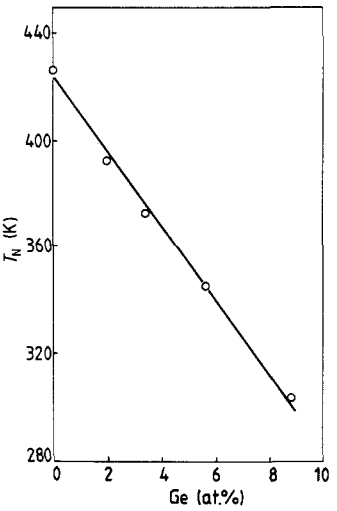

Figure 2. Relationship between the Ge content and Néel temperature.

3. Results and discussion

The effect of Ge on the temperature T dependence of magnetic susceptibility is given in figure 1. For $T > T_N$, the susceptibility of γ-Fe–30 at.% Mn alloy (alloy 1) is almost independent of temperature. This feature suggests an itinerant character of the 3d electrons and a very small or zero localised net moment in the host alloy. On the other hand, when γ-Fe–Mn is alloyed with Ge, the behaviour of the antiferromagnetic transition alters significantly. With increasing Ge content, T_N decreases nearly linearly (figure 2), the susceptibility increases rapidly and becomes temperature dependent, i.e. the Pauli paramagnetism above T_N of the alloys transfers progressively into a paramagnetic state obeying the Curie–Weiss law. Further a very sharp peak in χ is observed at the Néel point. These magnetic characteristics of the χ–T curves, which are similar to those of Fe–Mn–Al or Fe–Mn–Si alloys [4–9], reveal the existence of a localised moment in alloys containing Ge. However, since a Ge atom does not carry any magnetic moment, it may be interpreted that the outer-shell electrons of Ge overlap the d band of the matrix so as to induce or enhance the spin localisation at Fe sites. In order to obtain specific information concerning the effect of Ge content on the hyperfine field and iron atomic moment, Mössbauer measurements were carried out for γ-Fe–30 at.% Mn (0–8.7 at.%) Ge alloys. The shapes of the absorption spectra strongly suggest a hyperfine field distribution. The results of fitting the Mössbauer spectra evaluated by assuming a continuous hyperfine field distribution are shown in figure 3 and table 2. For the γ-Fe–30 at.% Mn alloy (alloy 1), our Mössbauer spectrum is similar to that of γ-Fe–Mn obtained in [1, 21]. With increasing Ge content, the width of the spectrum which is certainly a measure of the hyperfine field at the Fe nuclei decreases and the maximum of hyperfine field distribution $P(H)$ shifts towards low fields. The isomer shift increases towards the positive with increasing Ge content, and this probably reflects the change in 3d-electron band at Fe sites. Because of lack of Mössbauer spectra at different

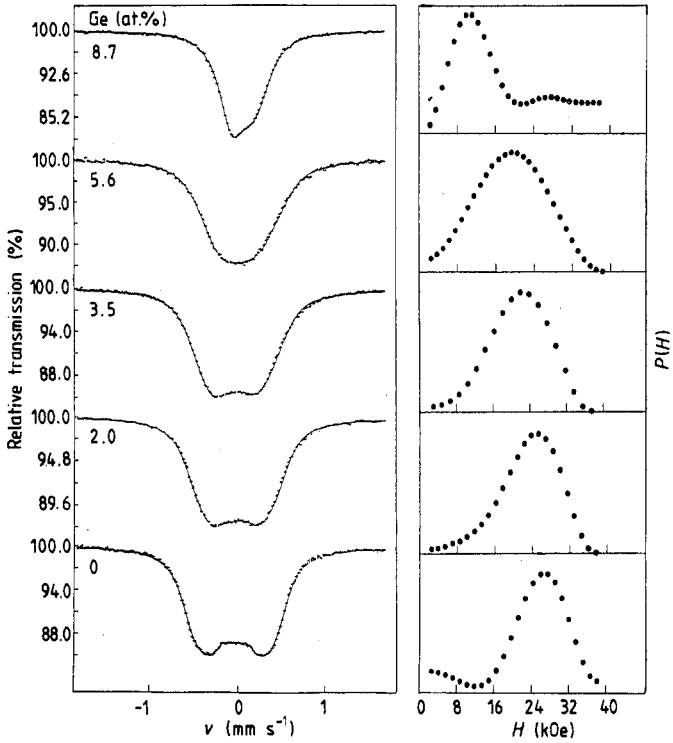

Figure 3. Mössbauer fitted spectra at room temperature and corresponding hyperfine field distributions $P(H)$ of γ-Fe–Mn alloys containing from 0 to 8.73 at.% Ge.

Table 2. Fitting results for the Mössbauer absorption spectra for experimental alloys, where H_i is the mean value of the hyperfine field.

Alloy	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	H_i (kOe)
1	−0.025	0	26.55
2	−0.01	0	24.14
3	−0.008	0	23.36
4	0.034	0	19.97
5	0.054	0	12.48

temperatures, it is impossible to distinguish the effect of the Ge content on the internal field from that of variations in T/T_N and to extrapolate the internal field $H_i(T)$ to $H_i(0\ K)$.

In the case of γ-Fe–Mn alloys with added Ni [2], Co [3], Cr [4], V [5], Cr and V have an electron-to-atom ratio N smaller than that of Fe–Mn, and it is suggested that the zero or small magnetic localised moment associated with their atoms only slightly affects χ and decreases T_N while, for Ni and Co with an N-value larger than that of Fe–Mn, it is suggested that the excess electrons localised at Ni or Co atom sites markedly increase χ but decrease T_N. Thus it can be seen that the Néel transition of these Fe–Mn-based alloys

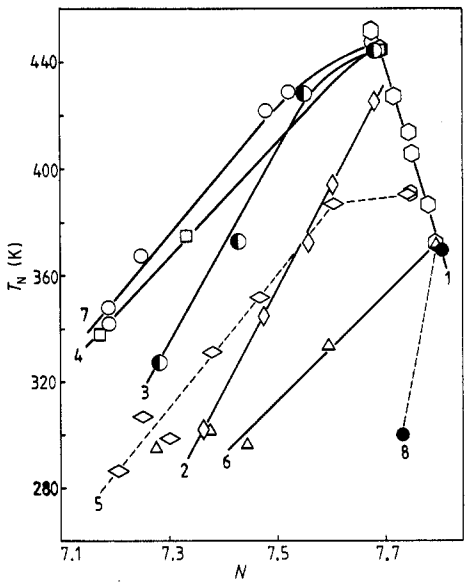

Figure 4. Néel temperature of γ-Fe–Mn host alloys as a function of mean concentration N of outer-shell electrons (electron-to-atom ratio): —○—, Fe–(19.7–31.7 at.%) Mn; —◇—, Fe–(28.1–31.5 at.%) Mn–(0–8.73 at.%) Ge; —◐—, Fe–(30.4–32.8 at.%) Mn–(0–8.71 at.%) Si; —□—, Fe–(27.7–31.7 at.%) Mn(0–8.7 at.%) Al; --◇--, Fe–(23.8–25.6 at.%) Mn–(0–9.8 at.%) Al; —△—, Fe–(19.2–22.7 at.%) Mn–(0–8.3 at.%) Al; —○—, Fe–Mn–Cr and Fe–Mn–Al–Cr; —●—, Fe–Mn–(0–1 at.%) V.

which have a localised magnetic moment cannot be explained by a rigid-band model. The T_N-values of several γ-Fe–Mn host alloys with additions of Al, Si, Ge, Cr and V as a function of mean electron concentration are summarised in figure 4. These curves are modified from the present work and [4–9, 22] and are obtained from susceptibility and resistivity measurements. For the solutes (up to 10 at.%) Al, Si and Ge dissolved in γ-Fe–Mn alloys, T_N decreases roughly linearly with decrease in mean electron concentration. This seems to imply a rigid-band model, but the physical features are rather different from those of 3d transition-metal solutes such as Cr or V. As regards this puzzling result, our previous papers [7–9] have suggested that the solutes Al, Si or Ge can induce or enhance the localised moment on the Fe atom sites as if the latter were a 'magnetic' solute interacting with the γ-Fe–Mn host alloys. Solutes Al, Si or Ge with an N-value ratio smaller than that of γ-Fe–Mn alloy do not, however, act as simple electron donors like others for which the N-value is larger than that of γ-Fe–Mn but probably acts as if they were a negative electron reservoir from which electrons are supplied to the magnetic bands of the host. In other words, it may be assumed that the valence electron band of the solute overlaps the d band of the matrix and this modifies the Fermi surface shape, the local net moment on Fe sites, the spin-density-wave (SDW) structure in the host and the antiferromagnetic energy gap below T_N. This explanation is also responsible for the obvious anomaly of such physical properties as resistivity and elastic modulus associated with the Néel transition and the ISDW-to-CSDW transformation in γ-Fe–Mn alloys containing Al [6–8], Si [9] or Ge (for which an investigation is already in progress). The rigid-band hypothesis overlooks the effect of solutes on the host band

structure; in effect, alloying alters the host density of states and consequently the Fermi surface. Therefore the non-transition elements Al, Si and Ge affect the electron band of γ-Fe–Mn alloys in a way which is different from that of Cr and V. Finally, it is important to note that the application of a simple rigid-band hypothesis should be restricted only to the dilute Cr alloys or γ-Fe–Mn alloys which suggest zero or a small magnetic net moment, and the antiferromagnetism is difficult to explain by this simple rigid-band approach when non-transition or ferromagnetic elements are alloyed to γ-Fe–Mn or dilute Cr alloys.

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References

[1] Endoh Y and Ishikawa Y 1971 *J. Phys. Soc. Japan* **30** 1614
[2] Shiga M 1967 *J. Phys. Soc. Japan* **22** 539
[3] Matsui M, Sato K and Adachi K 1973 *J. Phys. Soc. Japan* **35** 419
[4] Zhang Yansheng 1985 *Acta Metall. Sinica* **21** A295
[5] Zhu Naiping and Zhang Yansheng 1989 *Mater. Sci. Prog. (China)* **3** 147
[6] Zhang Yansheng 1984 *Acta Metall. Sinica* **20** A313
[7] Zhang Yansheng 1986 *Acta Metall. Sinica* **22** A470
[8] Zhang Yansheng 1987 *Acta Metall. Sinica* **23** A306
[9] Zhang Yansheng 1988 *J. Phys. F: Met. Phys.* **18** L229–235
[10] Koehler W C and Moon R M 1966 *Phys. Rev.* **151** 405
[11] Booth J G 1966 *J. Phys. Chem. Solids* **27** 1639
[12] Lomer W M 1964 *Proc. Phys. Soc.* **84** 327
[13] Fedders P A and Martin P C 1966 *Phys. Rev.* **143** 245
[14] Arajs S and Katzenmerer W E 1967 *J. Phys. Soc. Japan* **23** 932
[15] Arajs S, Aidun R and Moyer C A 1980 *Phys. Rev.* **22** 5366
[16] Yakhmi J, Gopalakrishnan I K, Lyer R M and Stanford J L 1987 *J. Phys. F: Met. Phys.* **17** L65
[17] Mizuki J, Copley J R D, Endoh Y and Ishikawa Y 1986 *J. Phys. F: Met. Phys.* **16** L195
[18] Alberts H L and Lourens J A J 1988 *J. Phys. F: Met. Phys.* **18** 123
[19] Van Rijn H J, Alberts H L and Lourens J A J 1987 *J. Phys. Chem. Solids* **48** 283
[20] Umebayashi H and Ishikawa Y 1966 *J. Phys. Soc. Japan* **21** 1281
[21] Ishikawa Y and Endoh Y 1967 *J. Phys. Soc. Japan* **23** 205
[22] Zhang Yansheng 1988 *Mater. Sci. Prog. (China)* **2** 56