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On the anomalies in some physical properties at the Néel transition of γ-Fe–Mn–Ge alloys

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Abstract. Measurements have been made of the electrical resistivity ρ, thermal expansivity $\Delta L/L$ and elastic modulus E of γ-Fe–Mn alloys containing 0–8.73 at.% Ge. Anomalies in ρ, $\Delta L/L$ and E are observed in the vicinity of the Néel temperature T_N for all these alloys. The effect of the Ge content on the anomalous behaviour of Fe–Mn alloy is essentially similar to those of the Al or Si content. The experimental results are qualitatively discussed on the basis of two postulates, i.e. firstly that the valence electron band of Ge overlaps the d band of the matrix so as to induce or enhance the localized moment on the Fe atom sites and secondly that the increase in the Ge content weakens the itinerant electron character of antiferromagnetic γ-Fe–Mn alloys.

1. Introduction

Recently, investigations [1–6] have been carried out on the antiferromagnetic transition of the γ-Fe–Mn matrix alloyed with non-transition elements Al, Si or Ge. The results indicated that an increase in Al, Si or Ge lowers the Néel temperature T_N, markedly increases the magnetic susceptibility χ and changes it to be temperature dependent above T_N. In addition, the Néel transition of γ-Fe–Mn alloys containing Al or Si is accompanied by an obviously anomalous change in such physical properties as electrical resistivity ρ, elastic modulus E and thermal expansivity $\Delta L/L$. These peculiar phenomena suggest that the magnetic character of γ-Fe–Mn-based alloys change from itinerant to localized and induce or enhance a localized net moment on Fe atoms as the concentration of these non-transition solutes are increased. Fairly recently, Zhang [6] has investigated the Néel transition of γ-Fe–Mn–Ge alloys by means of susceptibility and Mössbauer spectra measurements. As the study of anomalous changes in physical properties is of considerable value in exploring certain features of antiferromagnetic behaviour and in developing new functional alloys with a Fe–Mn host, we therefore made a detailed investigation of the effect of the Ge content on the temperature dependence of ρ, E and $\Delta L/L$ for γ-Fe–Mn alloys. To the best of our knowledge, the

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Table 1. Composition, phase structure and Néel temperature of alloys tested and mean electron concentration.

Alloy	Amount (at.%) Mn	Ge	C	Phase structure	Mean electron concentration e/a	Néel temperature (K)
1	31.52	—	0.20	γ	7.685	426
2	30.02	2.01	0.18	γ	7.605	393
3	29.87	3.45	0.14	γ	7.563	373
4	29.49	5.63	0.10	γ	7.479	345
5	28.11	8.73	0.08	γ + trace ε	7.369	303

anomaly in the physical properties for γ-Fe–Mn–Ge alloys has never been studied before.

2. Experimental procedure

The γ-Fe–30 at.% Mn-(0–8.73 at.%) Ge alloys listed in table 1 are the same as those used before [6]. The preparation details, purity characterization, phase structure and Néel temperature of the specimens are given in [6]. For measurements of the electrical resistivity, Young's modulus and the thermal expansion, samples 3 mm in diameter and 60 mm in length, samples 6 mm in diameter and 150 mm in length and samples 3 mm in diameter and 50 mm in length were prepared from the rod. The electrical resistivity measurements were made from liquid-nitrogen temperature to 490 K by the standard four-probe DC method. The voltage difference was measured using a 7081 model precision voltmeter with a sensitivity of 10^{-8} V, and the sample current was reversed for each reading in order to minimize the thermal EMF. Young's modulus was measured from 100 to 700 K by the sonic frequency resonance method with a microcomputer controlling a composite-oscillator system. The thermal expansion was measured from liquid-nitrogen temperature up to 700 K with a dilatometer by which the change in the length of specimens was detected using a mechanical micrometer with a sensitivity of 10^{-3} mm. The experimental errors in ρ, $\Delta L/L$ and E are estimated to be about $\pm 0.1\%$, $\pm 0.5\%$ and $\pm 3\%$, respectively. The large inaccuracy in the measurement of E arises mainly from the fluctuation of temperature along the length of specimens.

3. Results and discussion

As expected, an antiferromagnetic transition in an alloy is accompanied by an anomalous resistivity. The temperature dependence of electrical resistivity for the experimental alloys with different Ge contents is shown in figure 1. The observed resistivity $\rho_{am}(T)$ of antiferromagnetic Fe–Mn–Ge alloys can be viewed as a superimposition of ρ_r, $\rho_p(T)$ and $\rho_m(T)$, i.e.

$$\rho_{am}(T) = \rho_r + \rho_p(T) + \rho_m(T). \tag{1}$$

Here, ρ_r is the residual resistivity, $\rho_p(T)$ is the phonon contribution and $\rho_m(T)$ is the

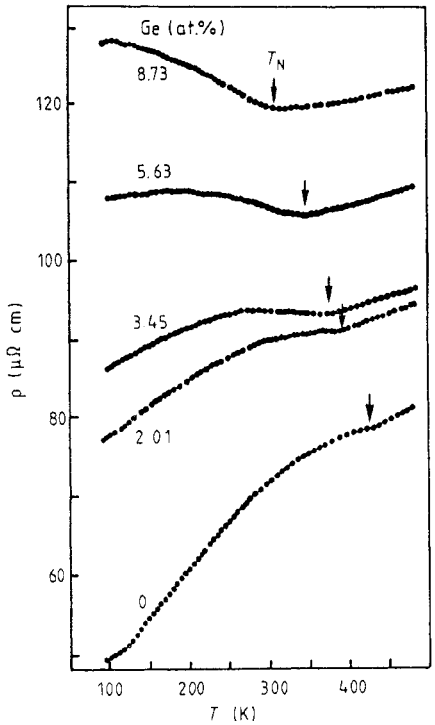

Figure 1. Effect of Ge content on the temperature dependence of electrical resistivity for Fe–30 at.% Mn alloys. The arrow indicates the Néel temperature determined by magnetic susceptibility measurements.

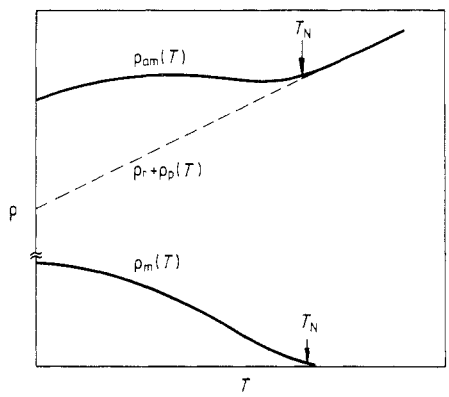

Figure 2. Schematic plot of relations between $\rho_{am}(T)$, $\rho_r + \rho_p(T)$ and $\rho_m(T)$.

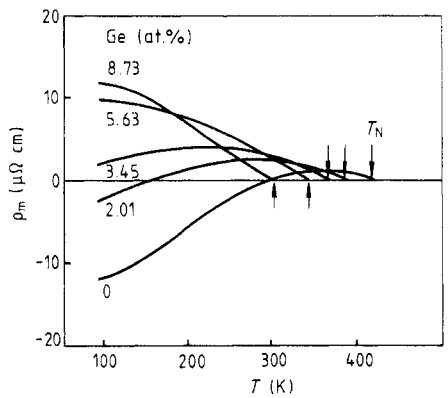

Figure 3. Effect of Ge content on the temperature dependence of the magnetic scattering resistivity ρ_m.

algebraic sum of antiferromagnetic ordered scattering and paramagnetic disordered scattering. The relations between $\rho_{am}(T)$, $\rho_r + \rho_p(T)$ and $\rho_m(T)$ are shown schematically in figure 2.

The anomaly in the resistivity below T_N for the sample without Ge (alloy 1) is similar to that for Cr, which was interpreted as due to the formation of an energy gap in some region of k-space below T_N. As the Ge content is increased, ρ_r increases markedly, T_N

decreases and the $\rho_{am}(T)$ anomaly becomes stronger. The effect of increasing residual resistivity in Fe–Mn is in the order Ge > Al > Si [2–5]. Above T_N, the resistivity for the Fe–30 at.% Mn alloy is linear with T_N, typical behaviour of resistivity due to electron–phonon scattering. On increasing the Ge content, however, the temperature dependence of the resistivity diverges from linearity at some point above T_N and results in a broadening of the range of anomaly; this feature probably arises because the paramagnetism of alloys above T_N changes progressively from Pauli paramagnetism to Curie–Weiss paramagnetism as a consequence of the localized net moment on the Fe atom sites. Below T_N, the derivative $d\rho/dT$ of the resistivity with respect to temperature shows a negative divergence and the ρ versus T curves of the alloy bend upwards with decreasing temperature. The temperature of the resistivity minimum and the magnitude of the increase in resistivity agree approximately with the T_N point and the peak value of susceptibility in the χ versus T curves reported elsewhere [6], respectively. With increasing Ge content in Fe–Mn alloys, the anomalous resistivity increases rapidly to present a negative temperature coefficient α. The magnetic contribution to electrical resistivity was evaluated from the observed resistivity as follows. The phonon part of resistivity obeys the Bloch–Grüneisen formula, however, in which the resistivity ρ_p decreases approximately linearly as the temperature falls inside the limits of about 500 K to above about 100 K. In a first approximation, extrapolate the linear part of the observed resistivity curves just above the T_N point; then, by subtracting the phonon contribution $\rho_p(T)$ and the residual resistivity ρ_r, thus obtained from the observed resistivity, we can get the temperature dependence of the magnetic contribution ρ_m of resistivity below the Néel temperature. Figure 3 shows the ρ_m versus T plots for each alloy. ρ_m increases with increasing Ge concentration. With decreasing temperature, the decrease in $\rho_p(T)$ is compensated by the increase in $\rho_m(T)$, i.e. $(1/\rho)(d\rho/dT) \simeq 0$, and then $(1/\rho)(d\rho/dT < 0$ when $|\Delta\rho_m(T)| > |\Delta\rho_p(T)|$. As the temperature is further decreased, the magnetization approaches saturation and the increase in resistivity due to the antiferromagnetic energy gap becomes constant gradually. Then $|\Delta\rho_m(T)|$ becomes smaller than $|\Delta\rho_p(T)|$, and the temperature coefficient $(1/\rho)(d\rho/dT)$ changes to positive again; hence some samples (alloys 3 and 4) show a broad maximum in the $\rho_{am}(T)$ curve. One of the present authors [3–5] has assumed that the origin of anomalous resistivity depends mainly on two factors: the truncation of the Fermi surface due to the antiferromagnetic energy gap and the magnetic scattering caused by the occurrence of a localized net moment on Fe atoms. In the case of concentrated alloys, it should be noted that alloy 5 with a high Ge content does not show a maximum and persists in having a negative temperature coefficient. A similar resistivity–temperature dependence has been observed in Fe–Mn host alloy with a high concentration of Al (more than 10 at.%) or Si (more than 9 at.%). This behaviour is probably due to the large amount of disorder caused by sufficient addition of these non-transition elements. Further work on these matters will be reported in forthcoming papers.

Figure 4 shows the results of linear thermal expansion measurements of the antiferromagnetic Fe–Mn–Ge alloys. As the polycrystalline specimens should be homogeneous after annealing, the observed linear expansivity $\Delta L/L$ is considered to be proportional to the volume expansivity $\Delta V/V$ of the specimen. As seen in figure 4, the thermal expansibility curves of these alloys indicate an anomalous volume expansion below the Néel temperature. In contrast to the anomaly of resistivity shown in figure 1, the additional volume expansion originating from the antiferromagnetic ordering decreases gradually with increasing Ge content. In association with the effect of Al, Si or Ge on the magnetic and resistive properties of Fe–Mn [3–6], it can be seen that the

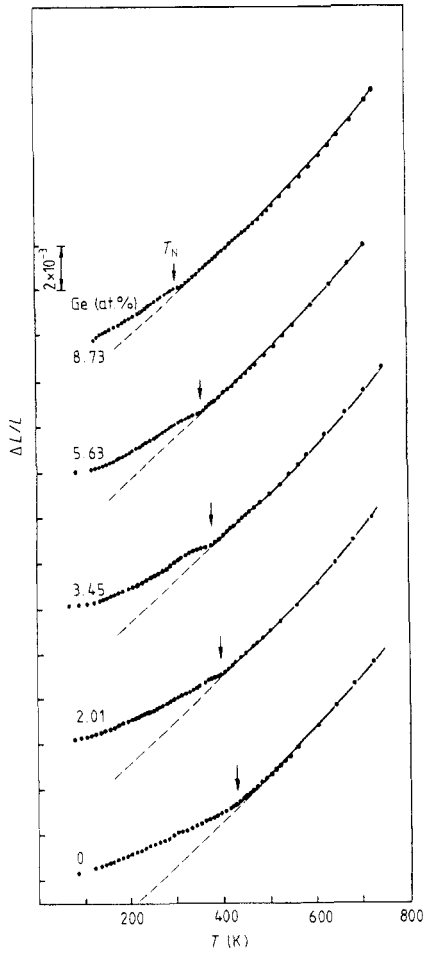

Figure 4. Effect of Ge content on the temperature dependence of the thermal expansion for Fe–30 at.% Mn alloys. The arrow indicates the same as in figure 1.

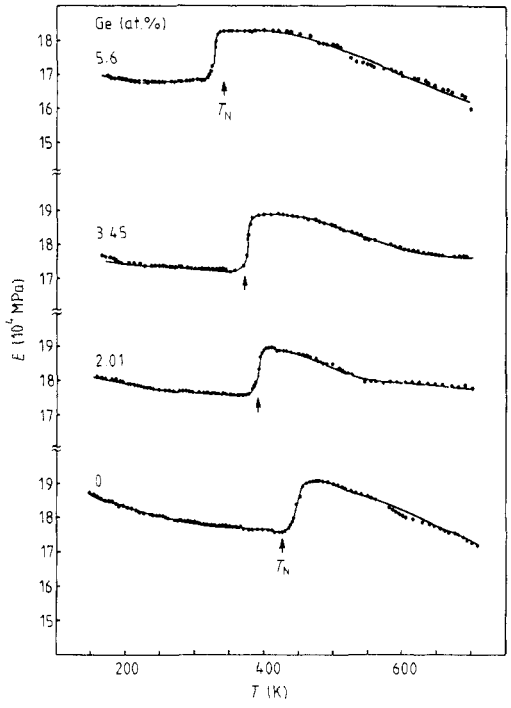

Figure 5. Temperature dependence of Young's modulus E for Fe–Mn–Ge alloys. The arrow indicates the same as in figure 1.

positive spontaneous volume magnetostriction $\omega_s(T)$ decreases with decrease in T_N in the same way as the change in electronic character of magnetism from itinerant to localized as the concentration of Ge is increased. However, in the case of Fe–Mn–Ge where localized magnetic moments on the Ge atoms are not expected, this may be interpreted as showing that the outer-shell electrons of Ge overlap the d band of the matrix so as to induce or enhance spin localization at Fe sites [6]. So far our information of the physical origin of such an anomalous expansion in antiferromagnetic alloys is still insufficient; it cannot be explained by the usual mechanism based on the volume dependence of exchange interaction nor by the Weiss theory, because these theories indicate volume expansion due to ferromagnetic ordering and volume contraction due to antiferromagnetic ordering. Katsuki and Terao [7] and Terao and Katsuki [8] have calculated the spontaneous volume magnetostriction of Fe–Ni alloys using the band

model and have obtained good agreement with the experiments. Applying the theory of the band width obtained in [7, 8] to the case of weak itinerant-electron ferromagnets and weak itinerant-electron antiferromagnets, Hayase *et al* [9] have assumed that the volume expansion due to antiferromagnetic ordering of the antiferromagnetic $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys originates in the volume dependence of the band energy. It is suggested that the large positive spontaneous volume magnetostriction $\omega_s(0)$ at 0 K of Invar alloys occurs when the positive contribution of the volume dependence of band energy is much larger than the negative contribution of the volume dependence of exchange energy. Hayase *et al* used the equation for the sublattice magnetization of weak itinerant-electron antiferromagnets given by Lidiard [10]; the spontaneous volume magnetostriction of weak itinerant electron antiferromagnets had been expressed as follows:

$$\omega_s(T) = \omega_s(0) - C\kappa M_s^2 T^2 / T_N^2 \tag{2}$$

where $\omega_s(0)$ is the spontaneous volume magnetostriction at 0 K, κ the compressibility and C the coupling constant between the volume strain and the sublattice magnetization M_s. Equation (2) holds in the temperature range $0 < T < T_N/2$ with regard to the antiferromagnetic Fe–Mn–Ni alloys. In the case of γ-Fe–Mn–Ge alloys, like the action of Al or Si, the itinerant-electron antiferromagnetism of Fe–Mn also decreased on increase in the Ge content and so we may suggest that these alloys are classified as weak itinerant-electron antiferromagnets. As shown in figure 4 and reported on our previous paper [6], with increasing Ge content, the Néel temperature T_N decreases, and the susceptibility χ increases and becomes temperature dependent; hence the spontaneous volume magnetostriction decreases gradually. The observed results for Fe–Mn–Ge are similar to those for $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys, but the physical features mentioned above are somewhat different from those of γ-Fe–Mn with dissolved Ni, for which the spin localizations exist at Ni atoms. Thus the decrease in $\omega_s(T)$ with increasing Ge concentration is qualitatively understandable from the theory of Katsuki and Terao and of Hayase *et al* and equation (2).

Some studies have been conducted on Young's modulus E in binary Fe–Mn alloys [11–13] and on the influence of the addition of ternary elements Cr, Al and Si [1, 2, 5]. The temperature dependence of E in the Fe–Mn–Ge alloy system is shown in figure 5. Each of the alloys shows an anomaly in the vicinity of the Néel temperature T_N due to the ΔE effect caused by the large spontaneous volume magnetostriction of antiferromagnetic ordering. When the Ge concentration is increased, the temperature coefficient $(1/E)(dE/dT)$, becomes smaller and the alloys show progressive Elinvar characteristics below T_N. The present specimens have a variation in Mn content. By referring the results of Bogachev *et al* [12]†, we can make a correction for the decrease in Mn content of our alloys; thus the corrected Ge concentration dependence of ΔE is shown in figure 6. In contrast to the anomaly of resistivity but similar to the anomaly of thermal expansion, the ΔE effect slightly reduces with increasing Ge content or decreasing electron concentration e/a. The origin of the anomalous E is about the same as that of the anomalous $\Delta L/L$ mentioned above, which may arise mainly from the large volume dependence of the band energy. It is interesting from the standpoint of weak itinerant-electron antiferromagnetism to discuss the relation between the distribution of valence electrons and the interatomic binding force in transition-element Fe–Mn host

† Bogachev *et al* examined the relation between the ΔE effect and the concentration of Mn in γ-Fe–(20–40 wt%) Mn alloys; the observed ΔE decreases by approximately 0.2×10^3 kg mm^{-1} for 1 wt% Mn.

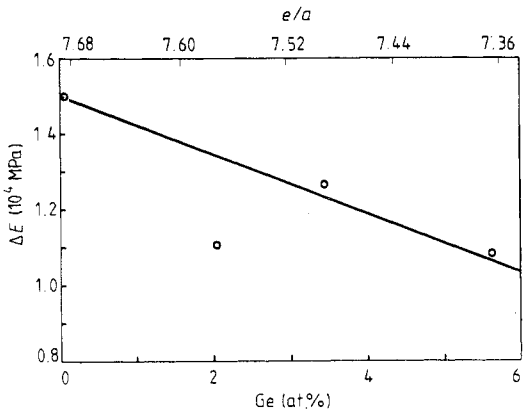

Figure 6. Effect of Ge content on the ΔE effect in Fe–Mn alloys.

alloyed with Ge, Al or Si. Theoretically, this may suggest that the electronic structure of itinerant electrons is reflected in the interatomic binding force through the anomalous distribution of valence electrons or in the peculiar Fermi surface, but it is at present not well understood.

In summary, alloying γ-Fe–Mn with different non-transition elements changes the electron-to-atom ratio and consequently the host density of states, which gives rise to considerable variations in its physical properties. The Néel transition in γ-Fe–Mn–Ge alloys is accompanied by an anomalous change in $\rho(T)$, $\Delta L/L(T)$ and $E(T)$. With increasing Ge content, the anomaly in the resistivity increases, while that in the thermal expansion and ΔE effect decreases, which may be interpreted by the assumption of decreasing itinerant character in Fe–Mn alloys. The effects of Ge on the behaviour of the Néel transition and the anomalous transport property of γ-Fe–Mn alloys are very similar to those of Al and Si. This is probably related to their similar outer-shell electrons.

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