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Kondo-like effect in antiferromagnetic γ-Fe–Mn–Ge alloys at low temperature

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Abstract. The temperature T dependence of the magnetic susceptibility χ and electrical resistivity ρ of γ-Fe–31 at.% Mn alloys containing 2–8.7 at.% Ge and 5.2 at.% Cr were measured in detail over the temperature range 5–500 K. The Néel transition of these alloys accompanied by an anomalous change in ρ has been observed at a temperature of 300–430 K. In lowering the temperature to about 5 K, no second resistivity anomaly for γ-Fe–31 at.% Mn or γ-Fe–31 at.% Mn–5.2 at.% Cr alloys was found, but a secondary resistivity minimum was observed below 50 K in the γ-Fe–31 at.% Mn–Ge alloys. The resistivity minimum temperature T_{min} increases in proportion to the Ge concentration, and the resistivity measured from T_{min} to about 5 K of the Fe–Mn–Ge alloys can be plotted as a linear function of log T, T^2 and $\sqrt{T}$. These results suggest that the resistivity minimum in antiferromagnetic γ-Fe–Mn–Ge alloys is due to a Kondo-like effect caused by localized magnetic moments on Fe atom sites which are induced or enhanced by the solution of Ge in γ-Fe–Mn alloys.

1. Introduction

The resistivity minimum phenomenon occurring in a dilute alloy of a transition elements in a simple metallic host has been called the Kondo [1] effect, and it is well established that the resistivity minimum is due to the spin-flip scattering of conduction electrons by localized magnetic moments on the magnetic impurities. For the antiferromagnetic incommensurate spin-density-wave (ISDW) state in Cr-based alloys, it has not been considered that the resistivity minimum is caused by the original Kondo effect, because the local moment on impurity atoms must be forced to order by the exchange field of the spin-density wave and the spin-flip scattering at low temperatures is suppressed. In some dilute chromium antiferromagnetic alloys, however, the resistivity minimum phenomenon at low temperatures has been found in Cr–Co [2, 3], Cr–Fe [4, 5], Cr–Si [6] and Cr–Ge [7] alloys. In the case of Cr–Co and Cr–Fe alloys, magnetic susceptibility measurements indicate that Co and Fe atoms form localized magnetic moments, and neutron diffraction studies show that the addition of a small amount of Co or Fe to Cr modifies the magnetic structure of Cr. The phase transition from the ISDW state to the commensurate spin-density-wave state occurs at the concentration of near 2 at.% Co [8] or about 2 at.% Fe [9, 10]. Therefore, it is considered that the Cr–Co and Cr–Fe alloys which have the spin-density wave state can show a resistivity minimum. These experimental results suggest that the resistivity minimum phenomenon in Cr–Co and Cr–Fe alloys is most appropriate for comparison with the Kondo effect in pure metal and alloys containing dilute magnetic solutes. However, the resistivity minimum in Cr–Ge and Cr–Si alloys cannot be understood, for it is difficult to associate the magnetic moments with either Si or Ge atoms. These interesting results have

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provoked a number of investigations on these two Cr-based alloys [11, 12]. Obviously, careful magnetic property studies are needed to elucidate the true origin of the electrical resistivity minimum in dilute Cr alloys or the γ-Fe–Mn host matrix. On the other hand, it is suggested that γ-Fe–Mn alloys with intermediate Mn contents (20–80 at.%) are also gap-type antiferromagnets similar to ISDW state chromium [13, 14], but it is very probable that a multiple-spin-density-wave state exists in γ-Fe–Mn. Therefore, it is expected that, when γ-Fe–Mn host alloys are alloyed with different elements, the interesting electrical and magnetic properties of the Kondo-like effect will occur, although reports of such studies are still few. The Néel transition and the Kondo-like effect of the γ-Fe–Mn alloys containing Al or Si have been studied by Zhang [15, 16], whose results indicate definitely that the $\rho(T)$ curves present clearly two resistivity minima, of which the high-temperature resistivity minimum is associated with the Néel transition while the low-temperature minimum corresponds to the Kondo-like effect. There have not been sufficient experimental data, however, to discuss the resistivity minimum phenomena in γ-Fe–Mn host alloys. Recently, Zhang [17, 18] has studied the Néel transition of γ-Fe–Mn–Ge alloys by means of susceptibility, Mössbauer spectra and physical properties measurements above 100 K. In order to understand this resistivity minimum phenomenon in the Fe–Mn host further, and to develop the new functional alloys with a Fe–Mn matrix, we have extended the measurement temperature range of magnetic susceptibilities and electrical resistivities down to about 5 K and prepared a γ-Fe–Mn alloy containing Cr for comparing the effect of the 3d-electron transition element Cr. To the best of our knowledge, the low-temperature resistivity minimum in γ-Fe–Mn–Ge alloys has never been reported before.

Table 1. Compositions and phase structures of alloys tested.

	Composition (at.%)						Néel
Alloy	Mn	Ge	Cr	C	Fe	Phase structure	temperature (K)
1	31.52	—	—	0.20	Balance	γ	426
2	31.01	—	5.22	0.16	Balance	γ	408
3	30.02	2.01	—	0.18	Balance	γ	393
4	29.87	3.45	—	0.14	Balance	γ	373
5	29.49	5.63	—	0.10	Balance	γ	345
6	28.11	8.73	—	0.08	Balance	γ + trace ϵ	303

2. Experimental procedure

The γ-Fe–Mn alloys containing 2.01, 3.45, 5.63 and 8.73 at.% Ge listed in table 1 are the same as those used before [17]. The preparation of samples was reported previously [15, 16]. The magnetic susceptibilities at temperatures from about 5 K to 300 K were measured with a magnetometer. The electrical resistivity was measured from liquid-helium temperature to 300 K by the conventional four-terminal DC method on samples 3 ± 0.01 mm in diameter and 62 mm in length. The voltage difference was measured using a precision digital voltmeter with a resolution of 5×10^{-8} V.

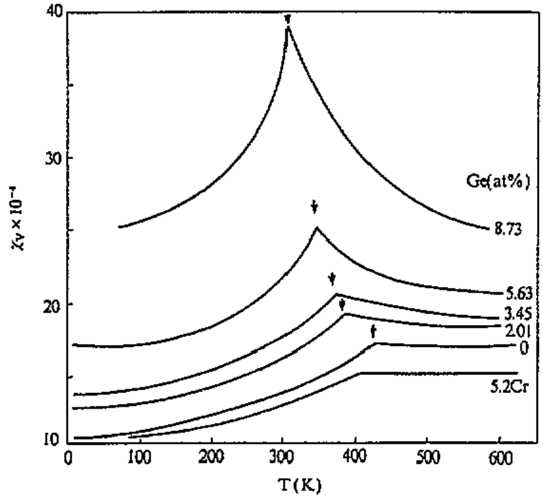

Figure 1. Effect of Ge or Cr content on the temperature dependence of the volume magnetic susceptibility χ_V and on the Néel temperature for Fe–30 at.% Mn alloys (magnetic field intensity $H = 4000$ Oe).

3. Results and discussion

Figures 1 and 2 show the temperature dependences of the magnetic susceptibility and the electrical resistivity for the Fe–30 at.% Mn alloys with different Ge contents and 5.2 at.% Cr. Some of the results in the temperature range 300–500 K have been reported previously [17, 18].

The arrows indicate the Néel temperature T_N determined from the susceptibility measurement. The behaviour of the χ–T and ρ–T curves for the γ-Fe–30 at.% Mn alloy indicate an itinerant character of 3d electrons and an absence of a localized net moment in this alloy. The susceptibility and resistivity of γ-Fe–Mn alloyed with 5.2 at.% Cr which also suggests zero or a very small magnetic moment has a temperature variation similar to that of γ-Fe–30 at.% Mn. On the other hand, alloying γ-Fe–Mn with Ge significantly alters the energy band structure and consequently the behaviour of the antiferromagnetic transition, which gives rise to considerable changes in its physical properties, such as the χ–T and ρ–T curves. With increasing Ge content, the Néel temperature T_N decreases linearly while the susceptibility χ increases markedly; for $T > T_N$, the magnetic state of the alloys transforms from Pauli paramagnetism to a paramagnetism obeying the Curie–Weiss law, and the anomalous resistivity increases rapidly to present a negative temperature coefficient below T_N. These features reveal the existence of a localized magnetic moment in Fe–Mn alloys adding Ge, but it is difficult to associate this directly with a localized moment on Ge atoms. However, it is well known that, in some cases, small changes in the chemical environment cause large changes in the magnetic behaviour of transition-metal ions in metallic systems. One could expect that large changes in the metallic host matrix cause extreme changes in the degree of localization of the electronic shells of transition-metal ions. It is also well known that the magnetic moment of the Fe atom depends strongly on its environment. In certain solvents, the Fe atoms possess a localized magnetic moment, whereas in others they do not. For example, Fe (less than 10 at.%) in γ-Mn has no localized moment [13] and it is possible that Fe in γ-Fe–Ir also has no moment. However,

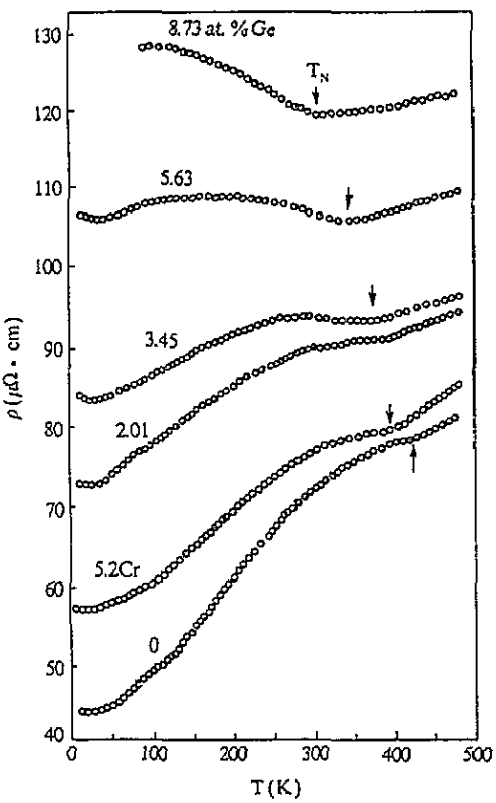

Figure 2. Effect of Ge or Cr content on the temperature dependence of the electrical resistivity *for Fe–30 at.% Mn alloys. The arrow indicates the* Néel temperature determined by magnetic susceptibility measurements.

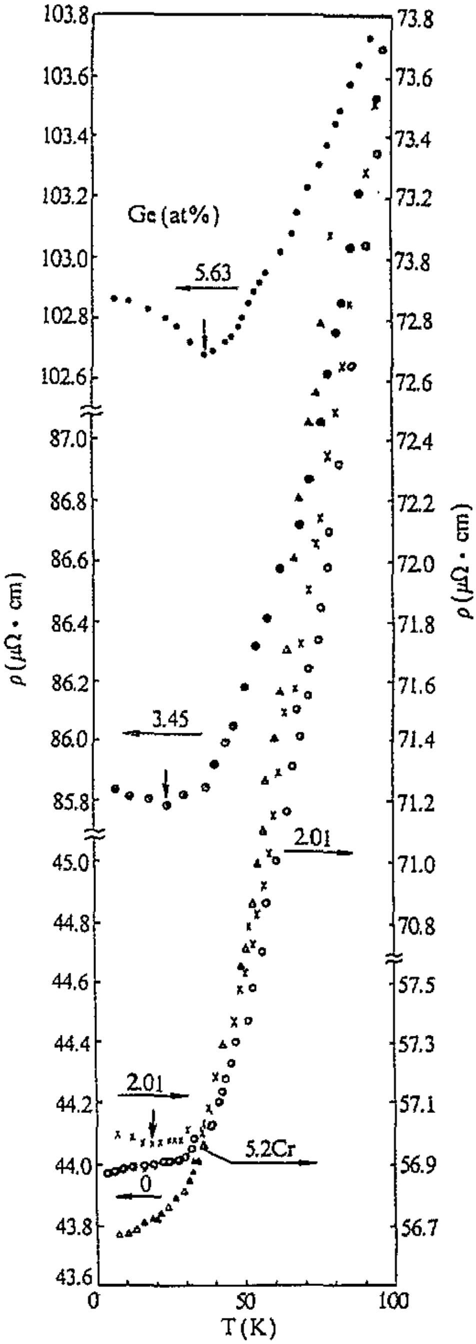

Figure 3. Resistivities of Fe–Mn, Fe–Mn–Ge and Fe–Mn–Cr alloys below 100 K. The arrows indicate *the temperature* T_{min} *at which the resistivity minimum* occurs.

on the addition of Pt, a localized moment develops on Fe ions, but the alloy still shows antiferromagnetic behaviour [19]. In the case of Fe–30 at.% Mn–Ge alloys, the solute Ge with an N-value (electron-to-atom ratio) smaller than that of γ-Fe–Mn alloy does not act as a simple electron donor like other elements for which the N-value is larger than that of γ-Fe–Mn alloy but probably acts as if it were a negative electron reservoir from which electrons are supplied to the magnetic band of the Fe–Mn host. Thus, it may be inferred that the valence electron band of Ge overlaps the d band of the matrix so as to induce or enhance the localized net moment on the Fe-atom sites.

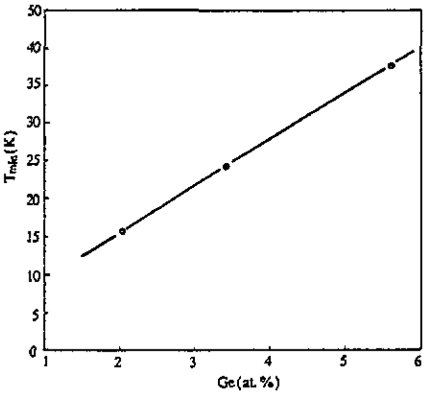

Figure 4. Temperature of the minimum T_{min} versus the concentration of Ge.

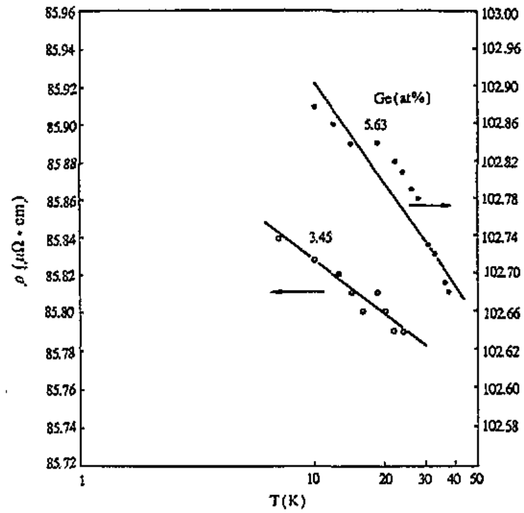

Figure 5. Resistivity against $\log T$ for the Fe–Mn–Ge alloy below T_{min}.

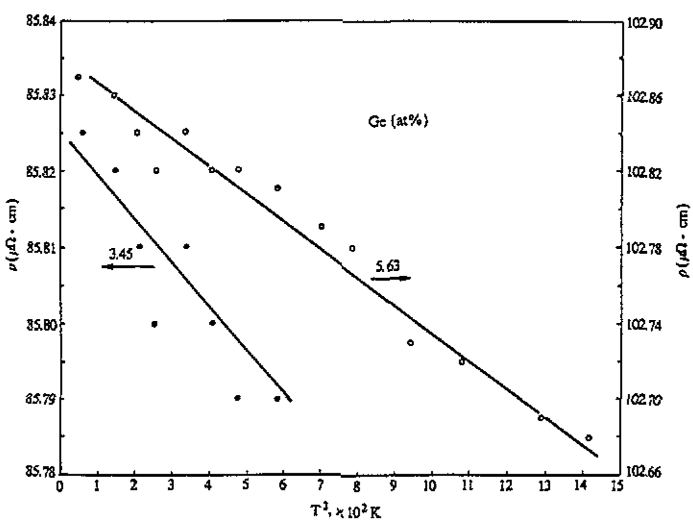

Figure 6. Resistivity as a function of T^2 for the Fe–Mn–Ge alloy below T_{min}.

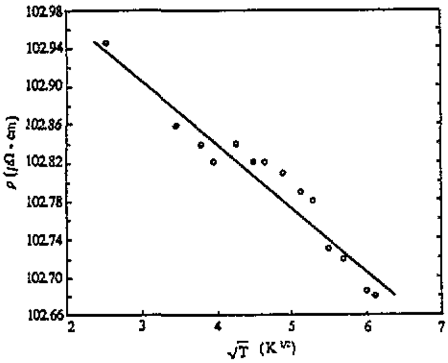

Figure 7. Resistivity versus $\sqrt{T}$ for the Fe–30 at.% Mn–5.6 at.% Ge alloy below T_{min}.

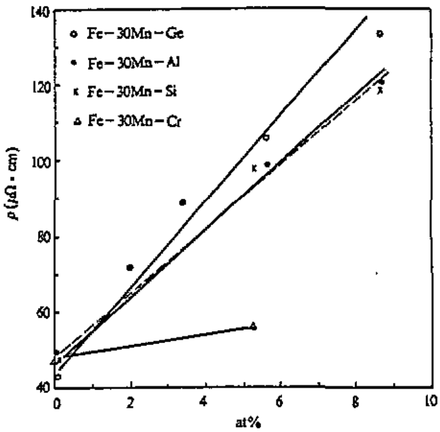

Figure 8. Effect of Ge, Al, Si and Cr contents on the residual resistivity of Fe–Mn-based alloys at about 5 K.

The detailed behaviours of the resistivities of various alloys below 100 K are shown in figure 3. The resistivity of γ-Fe–30 at.% Mn or γ-Fe–30 at.% Mn containing 5.2 at.% Cr does not indicate any anomaly within the experimental accuracy, but resistivity minima for 2.01 at.% Ge, 3.45 at.% Ge and 5.63 at.% Ge alloys are observed at about 16 K, 24 K and 38 K, respectively. As shown in figure 4, the resistivity minimum temperature T_{min} increases in proportion to the Ge concentration. The resistivity measured from T_{min} to 5 K for the alloys containing 3.45 and 5.63 at.% Ge are plotted as a linear function of log T in figure 5, T^2 in figure 6 and $\sqrt{T}$ in figure 7. The appearance of these experimental results is characteristic of the Kondo effect, but the low-temperature resistivity minimum in an antiferromagnetically ordered Fe–Mn matrix with dissolved concentrated non-transition elements Ge (Al or Si) is somewhat different from that in dilute alloys of a transition metal in a simple metallic host. Strictly speaking, the ordinary Kondo theory is not completely applicable to the case of γ-Fe–Mn–Ge alloys, so that the resistivity minimum at very low temperatures can be defined as the Kondo-like effect. However, the existence of a low-temperature resistivity minimum is now not satisfactorily understood on a theoretical basis. It is not clear why the resistivity minimum is observed only in Fe–Mn containing Ge, Al or Si and not in Fe–Mn or Fe–Mn–Cr alloys. The theoretical work by Kim [20] presents a possible mechanism for the resistivity minimum in dilute alloys in which the localized impurity states are non-magnetic, but the temperature dependences of the susceptibility indicate the existence of a localized magnetic moment in the Fe–Mn containing Ge (figure 1), Al or Si [15–17]; so the Kim thoery cannot satisfactorily explain the results. In the case of an antiferromagnetic Fe–Mn host, even if Fe–Mn–Ge can form localized magnetic moments, it is generally considered that the localized moments must be forced to be ordered and the spin-flip scattering at low temperatures is suppressed by the large exchange field of the spin-density wave. Apart from the classical materials, however, the resistance minimum has been observed in many other alloys such as dilute Cr alloys or Fe–Mn host alloys. Because the antiferromagnetic ordering of Fe–Mn is probably weakened by the adding of sufficient Ge [18], it is reasonable to suggest that the exchange field of the spin-density wave is not so strong as the spin-flip scattering of the conduction electrons and is suppressed completely. On the other hand, the feature of the electrical resistivity data which appears to be interesting from the viewpoint of the resistance minimum is the increase in the resistivity of Fe–Mn due to different dissolved elements. The composition dependence of the electrical resistivity of γ-Fe–Mn based alloys at about 5 K is shown in figure 8. It may be seen that the increase in the residual electrical resistivity of antiferromagnetic Fe–Mn due to 1 at.% Ge is about 12.5 $\mu\Omega$ cm which is of the order of that due to aluminium (8.8 $\mu\Omega$ cm) and silicon (8.9 $\mu\Omega$ cm). Electrical resistivity increases of the same order of magnitude are produced by nickel and cobalt which possess localized magnetic moments. The resistivity increases at about 5 K due to 1 at.% Cr which do not have magnetic moments in Fe–Mn are an order of magnitude smaller than those of Al, Si or Ge. The present results may indicate that a large increase in resistivity due to 1 at.% solute is capable of forming localized magnetic moments and then producing a low-temperature resistivity minimum. It should be remarked that a large increase in the residual electrical resistivity due to dilute (1 at.%) solutions of Fe in various 4d elements and alloys capable of producing localized magnetic moment has been predicted theoretically by Wolff [21]. Because of the difference between the outer-shell electrons in Fe and Ge atoms, it is also rather difficult to understand the resistivity minimum in Fe–Mn–Ge alloys by the Wolff model. In recent years, advances in the experimental and theoretical studies of concentrated Kondo systems (CKS) have explained the mechanism of the Kondo effect observed in some rare-earth intermetallic compounds such as $Ce_xLa_{1-x}Cu_2Si_2$, $Ce_xLa_{1-x}Al_3$, $Ce_{1-x}La_xNi_{0.8}Pt_{0.2}$, etc [22, 23]; however, it is suggested that the outer-shell electron of Ge, Al or Si ions in γ-Fe–Mn alloys are different from those of 4f, 3d and 4d ions in rare-earth compounds. At present, it is difficult to exlain clearly how the low-temperature resistivity minimum occurs in the γ-Fe–Mn alloys containing Ge, Al or Si by the CKS model. The effects of Ge on the behaviour of the Néel transition and the Kondo-like effect of γ-Fe–Mn alloys are very similar to those of Al and Si. This is probably related to their similar outer-shell electrons. The rigid-band hypothesis overlooks the effect of solutes on the host band structure and consequently the Fermi surface. Therefore, the magnetic and electrical behaviours of Fe–Mn-based alloys and Cr alloys with non-transition elements such as Ge, Si and Al are difficult to explain clearly by the simple rigid-band model or by the Kondo theory. Further research is necessary both experimentally and theoretically. Magnetoresistivity measurement, Mössbauer spectra and neutron diffraction should be helpful for exploring the physical features and thus in the development of a Kondo-like effect model.

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