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Resistivity of $RMn_{12-x}Fe_x$ alloys

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The electrical resistivity of $RMn_{12-x}Fe_x$ ($R=Er, Ho$) polycrystalline system with $x=0, 4, 5$, and 6 was measured over the temperature range of 4 to 300 K. The resistivity increases sharply near the Néel temperature T_N for $x=4, 5$, and 6 which, according to existing theories, can be ascribed to the formation of superzone gaps. Then, the resistivity increase should be proportional to the staggered magnetization m' below T_N , whereas we find experimentally that it is quadratic in m' . Thermal smearing of the gaps can lead to such a dependence. There is no evidence for superzone effects in $x=0$ compounds. A combination of spin disorder, phonon, and impurity scattering gives a good account for the experimental data. © 2001 American Institute of Physics.

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I. INTRODUCTION

Electrical transport is very sensitive to the electronic structure as well as to the magnetic nature of the materials studied. It is well established that the magnetic state of the inner $4f$ shell strongly affects the resistivity of rare-earth metals.¹ The anomalous behavior of the resistivity in rare-earth materials comes mainly from the s - f exchange interaction.^{2,3} Upon lowering the temperature, the resistivity drops abruptly at the Curie point in many ferromagnets as scattering by spin disorder decreases. On the other hand, in antiferromagnetic compounds, the resistivity often shows a sharp upturn at (below) the Néel temperature T_N . Carrier scattering by critical spin fluctuations near T_N can lead to such behavior.^{4,5} In addition, antiparallel alignment of spin can induce long period superlattices and, consequently, new electronic gaps. They reduce the effective number of conduction electrons giving rise to resistivity anomalies.⁶ Therefore, a study of electronic transport in magnetic materials is important for understanding their basic properties, and useful for future practical applications.

Rare-earth-transition-metal compounds of the $RMn_{12-x}Fe_x$ type (R =lanthanide series) crystallize in a body-centered tetragonal $ThMn_{12}$ type structure which has one R site and three nonequivalent Mn sites ($8i$, $8j$, and $8f$), each occupied by four transition-metal ions. They offer an interesting opportunity for magnetism studies in rare-earth intermetallics since their crystal structure is simpler than that of $R_2Fe_{14}B$ or R_2Fe_{17} . In addition, the magnetic interactions between Mn and Fe ions can be explored in a wide range of compositions. RMn_{12} compounds order antiferromagnetically at relatively low temperatures.⁷ Although RFe_{12} does not exist, solid solutions of the $RMn_{12-x}Fe_x$ type can be obtained for x up to 9 with $R=Er, Ho$. They have a complex

magnetic structure as shown by neutron diffraction and magnetization measurements performed on some of these alloys.⁸⁻¹⁰ Such a behavior arises from the competition between ferro- and antiferromagnetic interactions of $3d$ electrons (Fe and Mn ions) and a $3d$ - $4f$ exchange interaction. Furthermore, Fe atoms occupy preferably the $8f$ crystallographic sites, while Mn atoms show a strong tendency for $8i$ sites.⁸ A strong antiferromagnetic coupling between $3d$ ions leads to a noncollinear antiparallel arrangement of magnetic moments in the basal plane, with a propagation vector $[001]$. Along the c axis, a ferromagnetic component which can be attributed to R ions is found for some compositions. In addition, $3d$ ions in Fe rich alloys may contribute to the c -axis ferromagnetic moment. For $x \leq 5$, the substitution of Mn atoms by Fe atoms leads to an increase of the Néel temperature T_N which reaches a value of approximately 230 K for $x=5$.⁹ This rise is quite sharp for $x \leq 4$; T_N does not vary significantly with x over the values $x=4, 5$, and 6 . As shown by neutron scattering experiments, the magnetic structure of $RMn_{12-x}Fe_x$ varies strongly with the nature of the $3d$ -ions sublattice, from antiferromagnetic ordering in the basal plane for manganese-rich compounds to an almost ferrimagnetic ordering along the c axis for iron-rich systems. Interesting electronic transport properties are consequently expected in these alloys as the composition of the $3d$ -ions sublattice changes. However, only one study, to our knowledge, has been reported on electron transport properties of these systems.¹¹ It is a short report on the resistivity anomaly, observed at the Néel temperature in RMn_{12} compounds, that has been attributed to the formation of the antiferromagnetic band gap.

In this article, we report measurements of the resistivity in $RMn_{12-x}Fe_x$ ($R=Ho, Er$) polycrystalline samples with $x=0, 4, 5$, and 6 as a function of temperature in the range from 4 to 300 K. We choose these compositions for two reasons. First, neutron diffraction studies at various tempera-

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tures have been done for them.⁹ Second, for alloys with higher Fe content ($x > 6$), where the ferromagnetic coupling in the Fe sublattice becomes dominant, a different behavior is observed. This is however beyond the scope of the present article. The mixed intermetallic compounds with $x = 4, 5$, and 6 order antiferromagnetically at about 230 K and ferromagnetically below approximately 20 K, as obtained from neutron scattering studies.⁹ As the temperature decreases, the resistivity rises sharply, just below the Néel point, up to a maximum value at a lower temperature, and, for some compositions, drops at the Curie point. On the other hand, the resistivity of $x = 0$ compounds shows no apparent anomaly at $T = T_N$, which is about 80 K. It decreases monotonically with decreasing temperature. We use a simple model which, including spin disorder, phonon, and impurity scattering, accounts for the anomalous resistivities. In this model, a change in the Fermi surface brought about by the antiferromagnetic energy gaps is taken into account.

The experimental procedure is described in Sec. II. Results of resistivity measurements are reported and discussed in Sec. III. Average magnetic moments of the 3d ions and of ions on R sublattice, determined recently for these compounds,⁹ have been used in our numerical fitting. Conclusions are drawn in Sec. IV.

II. EXPERIMENT

The $RMn_{12-x}Fe_x$ compounds we studied were synthesized in a high frequency induction furnace under a purified argon atmosphere using the cool crucible method. We used an electrolytic iron (purity 4N); manganese and rare-earth elements were of purity 3N. The reacted materials were fused and subsequently cooled down five times to ensure a good homogeneity of compounds. The ingots obtained were checked by x-ray diffraction. In some samples with $x = 0$, small amounts of R_6Mn_{23} were detected.

The dc electrical resistivity measurements were performed with a six-probe method on bar shaped samples. The samples were spark cut from the bulk polycrystalline material and had typical dimensions of $1 \times 2 \times 10$ mm³. Before measurements were made, each sample was polished and checked for possible cracks. Platinum pressure contacts were applied to the samples. The mean relative error obtained for resistivity measurements is approximately 0.1%; absolute values were determined to within 5%.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show how the resistivity ρ of $RMn_{12-x}Fe_x$ ($R = \text{Ho, Er}$) varies with temperature in the range from 4 to 300 K, for some samples we studied. The resistivity of $ErMn_{12}$ and of $HoMn_{12}$ decreases with decreasing temperature, with a slight change of slope near the Néel point. This is more clearly seen in the plot of $d\rho/dT$ as a function of temperature shown in the upper inset of Fig. 1. Below approximately 50 K, ρ exhibits a T^2 behavior as expected for scattering of electrons by magnetic excitations.

The overall behavior of the resistivity in $x = 4, 5$, and 6 alloys (Fig. 2) is alike. At liquid helium temperatures, the measured resistivity tends to a constant value. It increases

FIG. 1. Resistivity data points versus temperature in $ErMn_{12}$ and $HoMn_{12}$ polycrystalline compounds. Only a small number of the data points are shown for the sake of clarity. The solid lines are numerical fittings to the resistivity. The upper inset shows $d\rho/dT$ versus temperature for the same samples. The temperature dependence of magnetic resistivity is exhibited in the lower inset.

with increasing temperature up to a maximum within the 120–160 K range. ρ decreases quite rapidly thereafter up to the Néel temperature, beyond which it starts to increase nearly linearly with temperature. For some compositions, the resistivity shows a maximum at or below 20 K. Such behavior is closely related to the magnetic order in the studied alloys. Critical spin fluctuations and/or superzone gap effects are important close to the ordering temperature and can be responsible for the observed anomalies. In addition, thermal fluctuations in spin systems contribute to the resistivity. Spin fluctuations are substantially reduced below T_N , and the relaxation time for conduction electrons increases as the temperature is lowered. Therefore, one expects a maximum in ρ below T_N . A drop in ρ below 20 K observed in $ErMn_{12-x}Fe_x$ for $x = 6$ and 5 and in $HoMn_{12-x}Fe_x$ for $x = 5$, is likely related to the ferromagnetic ordering of the rare-earth ions.

The resistivity may be expressed as $\rho = m/e^2 n_{\text{eff}}$ assuming that the scattering rate $1/\tau$ and the effective number of carriers n_{eff} may be separated.³ The total scattering rate can be written as

$$1/\tau = 1/\tau_0 + 1/\tau_{\text{ph}} + 1/\tau_{\text{mag}}, \quad (1)$$

where $1/\tau_0$ is the temperature independent scattering rate from impurities or defects, $1/\tau_{\text{ph}}$ arises from electron-phonon scattering, and $1/\tau_{\text{mag}}$ is the magnetic (spin) scattering rate.

FIG. 2. Resistivity data points versus temperature for some $RMn_{12-x}Fe_x$ alloys. Only a small number of the data points are shown for the sake of clarity. The inset shows the magnetic contribution obtained by subtracting the phonon and constant residual term from the total resistivity.

The phonon contribution is given by $1/\tau_{ph} = \alpha TG(\theta_D/T)$, where $G(\theta_D/T)$ is the Bloch–Grüneisen function and θ_D is the Debye temperature. The spin–disorder term can be approximated as $1/\tau_{mag} \propto (1 - m^2)$ where $m(T)$ is the normalized magnetization.^{2,3} At low temperatures, electrons scatter mainly against the spin waves. This is most clearly seen in $x=0$ samples, where $1/\tau_{mag} \propto T^2$ below 50 K.

Near the transition temperature T_N , critical spin fluctuations contribute to the scattering rate. Very close to T_N , a $1/\tau_{mag} \propto |\epsilon|^{1-\alpha}$ is expected for an antiferromagnet.⁴ Here, $\epsilon = (T - T_N)/T_N$ is the reduced temperature and the standard notation is used for critical components. For larger values of ϵ (but $|\epsilon| \leq 0.1$), $1/\tau_{mag} \propto |\epsilon|^{1/2}$.⁵ As the temperature decreases, the magnetic contribution to the total resistivity is expected to decrease as just discussed. Such a behavior is observed in $x=0$ alloys, as shown in the lower inset of Fig. 1. Here, we plot ρ'_{mag} , obtained by subtracting the phonon and constant impurity contribution from the total resistivity, versus temperature. On the other hand, the opposite dependence of ρ'_{mag} is encountered (if one assumes n_{eff} to be constant) for $x=4, 5$, and 6 alloys (see inset of Fig. 2). Therefore, it is clear that variations of n_{eff} , arising from superzone effects, are important in $x \neq 0$ alloys. In $RMn_{12-x}Fe_x$, they may be related to the preferential occupation of $8f$ sites by iron atoms, which show quite strong magnetocrystalline anisotropy along the c axis.⁹ Consequently, the magnetic ordering may be modified and new gaps in the conduction band may appear.

Miwa has pointed out that the ensuing energy gaps reduce the effective number of conduction electrons by a factor proportional to the gap energies.⁶ Similar results have been obtained by Elliot and Wedgwood in the case where the new

zone boundary touches the Fermi surface or splits it into two parts.¹² Furthermore, they found that the energy gaps of major importance are those that are proportional to oscillating magnetic moments. Thus, $n_{eff} = n_0(1 - \delta m')$, where $m'(T)$ is the normalized magnetization which gives rise to the formation of the energy gaps, and δ is a proportionality factor between the relative reduction of the carrier concentration and the magnetization.^{6,12} The electron–photon interaction may, however, smear the existing gaps and obliterate them, as in the effect of normal impurities in an excitonic insulator.¹³ Then, as suggested by Takada, n_{eff} should vary as the square of the order parameter, $n_{eff} \propto (1 - \delta m'^2)$.¹⁴

We explain our fitting procedure to the resistivity data presented next. Since ρ of $ErMn_{12}$ and $HoMn_{12}$ varies smoothly with temperature, we assume that there are no superzone gaps in these compounds. Their total resistivity is given by $\rho = \rho_0 + \rho_{ph} + \rho_{mag}$, where, as just noted, the subscripts 0, ph, and mag refer to residual, phonon, and magnetic resistivity, respectively. In $x \neq 0$ alloys, the variation of n_{eff} must be taken into account and $\rho = (\rho_0 + \rho_{ph} + \rho_{mag})/(1 - \delta m')$.^{6,12} However, we find that our fittings are not satisfactory with the $(1 - \delta m')$ reducing factor. Instead, it seems that the resistivity in all the concentrations we have studied does not vary as m' (staggered $3d$ -ions magnetization) but rather as m'^2 . This is shown in the upper left-hand side graph of Fig. 3 for the $ErMn_6Fe_6$ sample. The dashed line shows the best least-squares fit to the conductivity with a reducing factor of the form $(1 - \delta m')$ while the solid line exhibits the fitting for $(1 - \delta m'^2)$. A similar difference in the quality of fittings was found for other compositions. Consequently, we fit our resistivity data with m' squared in $x \neq 0$ alloys. We assume that m' is equal to the total $3d$ -electron moments in the basal plane. Its temperature variation is shown in Fig. 4 for a $ErMn_7Fe_5$ sample. Similar $m_T(T)$ dependences have been found for other compositions.⁹ We use these data, recently obtained by neutron diffraction studies, for magnetic moments of $3d$ and $4f$ ions in our calculations.

$\rho_{ph} = m/e^2 \tau_{ph} n_0$ and $\rho_{mag} = m/e^2 \tau_{mag} n_0$ where $1/\tau_{ph}$ and $1/\tau_{mag}$ have the functional form just described. We obtain the best fit with a $\theta_D = 400$ K for $x=0$ and $\theta_D = 300$ K for $x=4, 5$, and 6 (θ_D is approximately 400 K for $GdMn_{12}$).¹¹ We estimate α from the slope of ρ at high temperatures. Since both, localized $3d$ and $4f$ moments contribute to spin–disorder scattering, $\rho_{mag} = \beta(1 - m_T^2) + \beta'(1 - m_R^2)$, where m_T and m_R are transition-metal (staggered) and rare-earth sublattice magnetizations, respectively. The coefficients β and β' are related through the value of the resistivity at T_N . The magnon contribution to the scattering for an isotropic magnetic material can be written as $\rho_{mag} = \gamma T^2 \int_0^{4\hbar\omega_F/kT} x dx / [\exp(-x) + 1][\exp(x) - 1]$, where $\hbar\omega_F$ is the spin–wave energy corresponding to the Fermi wave vector, and k is the Boltzmann constant.^{1,15} Our fits are not very sensitive to the magnitude of $\hbar\omega_F$, as we apply the aforementioned expression for ρ_{mag} only at low temperatures. We use a value of 10 meV for it. The value of γ is chosen to fit the spin–disorder resistivity at 40 K.

Critical carrier scattering by spin fluctuations is taken into account only in pure compounds for $T \geq T_N$ since it improves significantly our fit to the experimental data in this

FIG. 3. Numerical fittings (solid lines) to the resistivity data in $RMn_{12-x}Fe_x$ alloys. Part (a) shows different fittings (dashed and solid line) to the $ErMn_6Fe_6$ resistivity. The values of T_N and T_C shown by arrows are from neutron scattering experiments.

temperature region. However, we find that $\rho_{\text{mag}} \propto |\epsilon|^{0.3}$ fits our data much better than $\rho_{\text{mag}} \propto |\epsilon|^{1/2}$ in the $0 \leq \epsilon \leq 0.4$ temperature range. Using the relations discussed, we are left with two adjustable parameters: β and ρ_0 for $x=0$ compounds and with one more parameter, δ , for $x \neq 0$ alloys. The results of our calculations are shown in Figs. 1 and 3 as the solid lines. The overall agreement is very satisfactory. Our fits reproduce all features of the experimental curves. The best least-squares fitting parameter values are given in Table I. We find that the amplitude of the s - $3d$ resistivity decreases with increasing x while the value of δ does not vary too

FIG. 4. The 3d magnetic moments in the basal plane for $ErMn_7Fe_5$ as a function of temperature (from Ref. 9). The 3d ions occupy 8f ($z=1/4, 3/4$), 8i ($z=0, 1/2$), and 8j ($z=0, 1/2$) positions.

much. On the other hand, the value of the residual resistivity increases appreciably with x , as expected for a mixed alloy in which $\rho_0(x) \propto x(12-x)$.¹⁶

The resistivity is also higher for $x=0$ compounds than for $x=4, 5$, and 6 alloys for $T \geq 150$ K. This may be attributed to a higher effective cross section for s - d spin scattering of Mn ions than of Fe ions (as seen from Table I). In addition, the s - d scattering of electrons by phonons, which is proportional to the density of states in the d bands, may contribute to it as well since the density of d states at the Fermi level is much higher for Mn than for Fe atoms.¹⁶

The reported results suggest that the conductivity of $RMn_{12-x}Fe_x$ ($x \neq 0$) antiferromagnetic systems is reduced by a factor which vanishes below T_N as the square of the staggered magnetization instead of linearly. A linear dependence of the conductivity on the magnetization (or on the superzone energy gap) in antiferromagnets has yet to be observed. For instance, normal Hall effect measurements seem to show that the effective number of conduction electrons does not vary linearly with the magnetization but as its square.¹⁷ Resistivity data obtained for thulium single crystals have also suggested below T_N an important reduction of the Fermi surface area which would be quadratic in the magnetization rather than linear.¹⁸ Such a variation of the Fermi surface has been suggested by Miwa.⁶ On the other hand, the thermal smearing of superzone gaps by electron-phonon interaction leads to the same effect.^{14,19} Therefore, our results are in line with these comments.

TABLE I. Values of fitting parameters β (the amplitude of s - $3d$ resistivity), ρ_0 , and δ for $RMn_{12-x}Fe_x$ ($R = \text{Er, Ho}$) alloys. The β and ρ_0 values are given in $\mu\Omega \text{ cm}$.

x	$\beta(R=\text{Er})$	$\beta(R=\text{Ho})$	$\rho_0(R=\text{Er})$	$\rho_0(R=\text{Ho})$	$\delta(R=\text{Er})$	$\delta(R=\text{Ho})$
0	100	98	20	11	0	0
4	40	48	80	67	0.35	0.45
5	35	35	83	70	0.37	0.43
6	34	23	85	87	0.36	0.30

IV. CONCLUDING REMARKS

We have measured the resistivity as a function of temperature in $RMn_{12-x}Fe_x$ antiferromagnetic compounds. The temperature-independent residual resistivity is quite small in $x=0$ samples, while it accounts for approximately 65% of the total resistivity in $x \neq 0$ samples. This is likely related to the disorder alloy scattering, in addition to a relatively high concentration of impurities and static lattice imperfections. Below the Néel temperature, electron scattering comes mainly from spin disorder. In $x=0$ compounds, spin-wave scattering dominates below about 50 K. This mechanism is not very important for $x \neq 0$ system, where electrons scatter mainly against disordered spins of the rare-earth ions in this temperature region. At higher temperatures ($T > T_N$), the magnetic resistivity saturates and the total resistivity increases linearly with temperature owing to phonon scattering. Antiferromagnetic ordering of transition-metal moments in $x \neq 0$ alloys leads to a rise in resistivity below the Néel temperature, which turns out to be quadratic in the staggered magnetization. This may be attributed to the thermal smearing of superzone gaps in the electronic density of states. Existing theories predict an increase in resistivity which is a linear function of the staggered magnetization. Therefore, a more careful examination of the effects which antiferromagnetic ordering has on conduction electrons may be needed. There is no evidence for superzone effects in $x=0$ compounds.

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