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ELECTRICAL RESISTIVITY OF THE PSEUDO-BINARY SYSTEM $Ce(Fe_{1-x}Al_x)_2$

by

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ABSTRACT

The electrical and magnetic properties of the Laves phase system $Ce(Fe_{1-x}Al_x)_2$ for $x \leq 0,20$ have been studied by means of electrical resistivity measurements from 1.5 to 300K. It is shown that the long range magnetic order of $CeFe_2$ is destroyed and that a spin glass phase leads to a minimum in the total resistivity with T_{2min} proportional to x. The freezing temperatures T_f are always smaller than T_{2min} and it appears a negative coefficient of the $AT^{3/2}$ dependence below T_f. The minimum in $d\rho/dT$ is well correlated with T_f.

Key-words: Metallic alloys; Magnetic properties; Electrical properties; Electrical resistivity; Spin glass.

INTRODUCTION

The pseudo-binary systems $M(Fe_{1-x}Al_x)_2$ with M=rare earth or 3d transition metal have their crystal structures and magnetic properties recently reviewed by Buschow (1974), Steiner (1979 and Hilscher (1982). Structural changes from C15 $MgCu_2$ to C14 MgZn type in the intermediate concentration range were observed for all these systems. A great variety of magnetic behavior is present in these series of intermetallic compounds. Breakdown of long range magnetic order in the disordered range takes place independently of the crystal structure changes. Remanence effects for M=Er, Tb, Dy and Ho (Steiner 1979) and irreversible effects for M=Y (Besnus et al. 1978) in magnetization was observed. A different but interesting system is Fe-Al with $[Fe_3Al]$ structure with 30 at % Al which becames ferromagnetic below 400K, and shows a mictomagnetic phase below 92K (Shull et al. 1976, Child 1981).

Little work has been done on pseudo-binary compounds, to our knowledge, using the electrical resistivity technique. Some results in $M(Fe_{1-x}Al_x)_2$ for M=Gd, Dy on the Al rich side, have been reported (Gratz et al. 1981).

In compounds that present magnetic irreversible effects, the majority of electrical measurements has been made on canonical spin-glasses binary alloys of noble metals with 3d transition metals (Ford et al. 1976). In previous papers we present results of electrical resistivity (Takeuchi et al. 1982) and magnetization (da Cunha et al. 1982) measurements for $Ce(Fe_{0.8}Al_{0.2})_2$. This compound does not shows a true long range magnetic order.

At low temperatures a peak in the static susceptibility with all characteristics of a spin-glass or mictomagnetic state was observed, whereas the resistivity behaves as $AT^{3/2}$ in this same range of temperature.

Now, in this work, we report resistivity experiments on $Ce(Fe_{1-x}Al_x)_2$ compounds for the iron rich side, $x \leq 0.20$, with the aim of studing the electrical and magnetic behavior due to the gradual substitution of Fe by Al in ferromagnetic $CeFe_2$. More specifically, we are interested in investigating the evolution in concentration of the ferromagnetic order and of the spin-glass or mictomagnetic state observed previously for x=0.20.

EXPERIMENTAL

Samples for x=0.02, x=0.035, x=0.07, x=0.10, x=0.125, x=0.15 were prepared. Casting in a cylinder form (1.5 mm diameter and 12 mm long) after remelting three or four times, was used for the sample preparation. Specimens were cut followed by annealing at 700ºC in argon atmosphere for one week. Weight losses were typically less than 1%. Quality and lattice parameter of all samples was observed from X-ray diffraction patterns at room temperature.

The electrical resistivity $\rho(T)$ was measured using a dc four-point method over the temperature range 1.5 - 300K using Ge and Pt as temperature sensors. Pressure contacts are used for voltage and In solder for current probes.

RESULTS

Powder X-ray diffraction of $Ce(Fe_{1-x}Al_x)_2$ for all samples

reveals the crystal structure of cubic $MgCu_2$ Laves phase with small amount of other phase for samples with higher Al concentration.

Lattice parameters a_o derived by least-square analysis of the Nelson-Riley function are presented in figure 1. If we extrapolate to Ce, from plots of a_o versus atomic number for the $R^{3+}Fe_2$ compounds (Burzo et al. 1971), the a_o of "$Ce^{3+}Fe_2$" would be of the order of 7.5 Å. In the same figure we trace the Vegard's law for tetra and trivalent Ce. We observe in our results a negative deviation from Vegard's law so, probably, the cerium ion persists tetravalent, as in $CeFe_2$, for the low Al concentration side of the series.

The temperature dependence of the total electrical resistivity over a temperature range 1.5 - 300K is shown in figure 2 where results for x=0 (Takeuchi et al. 1981) and x=0.20 (Takeuchi et al.1982) are included. No thermal hysteresis was observed and absolute error are estimated to be about 1% maximum. If we compare the curves of the ferromagnetic $CeFe_2$ and x=0.02 with those for the others concentrations we can at first observe the strong contrast of behavior mainly from T=0 just to intermediate temperatures. Also, the total variation that is of 116μΩcm for $CeFe_2$, is of 44μΩcm for x=0.035, and just only of 4.6μΩcm for x=0.20. We remark too that whereas the residual resistivity of $CeFe_2$ is 4.2μΩcm it reaches 146.3μΩcm for x=0.20.

As the temperature decreases from 300K, the resistivity for $x > 0.02$ drops until it attains a minimum at T_{1min} below which it increases to a broad maximum with further decrease of temperature. The derivative $d\rho/dT$, computed point by point in a three-point span to a third-order polinomial fit, is shown

also in fig. 2 for high temperatures. We can observe for $x \leq 0.035$ a broad maximum at a temperature T_d followed by a sharp maximum which is characteristic of a magnetic order-disorder transition. For $x \leq 0.07$ only a very spread maximum at T_d appears.

The low temperature (0 to 50K) total resistivity and $d\rho/dT$ are shown in fig. 3. For $x \geq 0.125$, a second minimum in the total resistivity appears at T_{2min} followed by a maximum before the resistivity drops to ρ_o (residual resistivity) whereas for $0.02 < x \leq 0.10$ this behavior is not so evident, the presence of a minimum in ρ been suggested by a minimum in $d\rho/dT$ rather than by $d\rho/dT=0$. Only for $x \geq 0.125$ negatives values of $d\rho/dT$ are present in the low temperature range. Values of T_{1min} and T_{2min} are listed in Table I.

DISCUSSION

I) High Temperatures

Curie temperatures (T_c) associated with the sharp maxima of $d\rho/dT$ for $x \leq 0.035$ are shown in figure 4. The concentration dependence is similar to that found in others $M(Fe,Al)_2$ (Hilscher 1982). For $x \geq 0.10$ we have only the broad maximum of $d\rho/dT$ at T_d and no transition to long range order was observed. These results are in agreement with magnetization measurements on the same samples (Franceschini et al.). In this way the determination of T_c for x=0.07 would be ambiguous because only one maximum is observed although his temperature is that of a T_c extrapolation as can be seen in figure 4 and also confirmed by magnetization measurements. As in $CeFe_2$ (Takeuchi et al.1981)and x=0.02 the maximum at T_d is a reflexe of the negative curvature

of the ρ versus T curve in this range of temperature and a theoretical explanation is not clear yet.

A plot of T_d and T_{1min} versus concentration is shown in figure 4 where we plot also ρ_o to see that the three parameters varies in the same way.

The minimum of ρ at T_{1min} can be explained in the following way. Starting from high temperature as the temperature is lowered the alloy tends to order magnetically (diminishing the magnetic resistivity), up to T_{1min}, where this process is inhibited by a new magnetic phase that introduce disorder and the resistivity increases, resulting in the appearence of a minimum in the ρ versus T curve. The degree of magnetic order that the alloys reaches depends on the concentration. In another way, the substitution of iron by aluminium undergoes a loss of long range magnetic order at low temperatures, (that begins to bring about for x=0.035) and, for higher Al concentrations, this range of the temperature extends to high temperatures until no long range order exists up to 300K. The contribution due to the phonon scattering obtained from the slope of the linear dependence of ρ at high temperatures is shown in table I as $(d\rho/dT)_{T>T_c}$. This contribution diminish roughly linear as the Al concentration increases.

Using Mathiessen's rule the spin disorder resistivity ρ'_{dis} was extracted from the extrapolation to T=0 of the linear dependence of the ρ at high temperatures and the results are in figure 4. We can observe that for $x \geq 0.07$ negative values appear. As we shall see in part II, at low temperatures, compounds with $x \geq 0.125$ exhibit a spin glass or mictomagnetic behavior. It is known (Mydosh et al. 1974) that scattering due to magnetic clus-

ters gives a contribution to the residual resistivity and this contribution must take place even for concentrations lower than x=0.125. Also effects of deviation from Mathiessen's rule may occurs.

A tentative estimate of the spin disorder resistivity has been made by using a simple extension of the expression for the effect of potential scattering on the spin disorder resistivity obtained by A. Troper et al. (1975). In our case, impurity potential acts at sites which do not coincide with spin scattering centers. The spin disorder resistivity may be written as:

$$\rho_{dis}(x) = \pi A(1-x)S_o(S_o+1)J_{eff}^2(x)\ \rho_s(E_F) \qquad (1)$$

where

$$A = \frac{3\ \Omega}{e^2 v_F^2 \rho_S(E_F)}$$

and

$$\left(\frac{J_{eff}}{J}\right)^2 \cong (1 + x\,\Delta)^2$$

Δ being a parameter to be fitted.

Using the experimental data for the concentrations x=0 and x=0.02 (ferromagnets) we have $\Delta = -11.3$. So we can write the expression (1) in terms of the spin disorder resistivity of the $CeFe_2$ ($\rho_{dis}(x=0)$),

$$\rho_{dis}(x) = (1-x)(1-11.3x)^2\rho_{dis}(0) \qquad (2)$$

The fitting obtained with this equation is shown in figure 4, for concentrations up to x=0.07. As expected, for $x > 0.02$ this gives values higher than ρ'_{dis}.

On the other hand the residual resistivity ρ_o, which contains two contributions, scattering by impurities and by clusters, was described with a polinomial expression that takes into account scattering by one site (term αx) and by two sites (term βx^2):

$$\rho_o(x) = 4.2 + \alpha x - \beta x^2 \qquad (3)$$

The better fit was obtained with $\alpha = 2067.8$ and $\beta = 5785.7$. Good agreement with the experimental results was attains. See figure 4.

Finally, if we subtract the spin disorder resistivity ρ'_{dis} from the calculated one, using equation (2) we obtain just the residual resistivity due to scattering by the clusters ($\rho_{o_{cl}}$). In figure 4 we plot $\rho_{o_{cl}}$ and also the $\rho_{imp} = \rho_o - \rho_{o_{cl}}$. We can observe that the effect of the residual resistivity due to the clusters becames important for $x > 0.02$, just where the ρ versus T curves begin to show the anomalous behavior. We remark that the expressions (1) and (3) are valid only for low concentrations. Results for $x > 0.05$ may be misleading.

II) Low Temperature

The low temperature variation of the total resistivity and $d\rho/dT$ for $x \geq 0.035$ are shown in figure 3. At first, we can observe the strong difference in behavior compared with that of the purely ferromagnetics alloys $CeFe_2$ or $x = 0.02$ where the electrical resistivity presents a initial behavior due to scattering by spin waves, proportional to T^2, with large coefficients of $1.2 \times 10^{-2} \mu\Omega cm/K^2$ (T^2 up to 32K) and $0.5 \times 10^{-2} \mu\Omega cm/K^2$ (T^2 up to 35K) respectively.

Low field magnetization measurements made in the samples x=0.20, 0.15, 0.125 (Franceschini et al.) have shown the existence of freezing, a spin glass or mictomagnetic state with freezing temperatures T_f characterized by a peak in the magnetic susceptibility with irreversible and remanent effects. The existence of this phase alters considerably the behavior of the ρ versus T curve in the range of temperature that these clusters are forming. The large residual resistivity with Fe substituted by Al is due in part to the disorder scattering from the randomly frozen spins and magnetic clusters.

In canonical spin glass systems (e.g. AuCr, AuFe, CuMn, etc) the variation of the electrical resistivity with the temperature, at low temperature, presents an initial behavior proportional to $T^{3/2}$, followed at higher temperatures by a broad maximum. Ford et al. (1976) have observed that this is a typical variation of ρ versus T in spin glass alloys. A theoretical description of the origin of the $AT^{3/2}$ behavior in ρ is given by Rivier et al. (1975) based in a spin diffusion model, where the appearance of the negative coefficient A in the $T^{3/2}$ term is explained. But this theory is unable to describe systems where the impurity introduces very strong potential.

Comparing the experimental results obtained in electrical resistivity with others technics, for example, magnetization or Mössbauer effect, the temperature of the maxima in $d\rho/dT$ is often associated with the freezing temperature of the spin glass phase determined by these technics. Recent results of electrical resistivity experiments in the system PtMn seem to lead to the conclusion that not only the maximum in $d\rho/dT$ corresponds to spin glass freezing temperature but the minimum in ρ too (Sarkissian et al. 1974). Also, a negative $T^{3/2}$ behavior below about

$(1/2)T_{min}$ and T_f at smaller temperatures than the minimum was observed.

As we can observe in figures 3 and 5, the results present by our concentrated system are similar to the PtMn ones. For $x \geq 0.125$, below the temperature where $d\rho/dT$ passes by a minumum, the resistivity behaves as $AT^{3/2}$, with A negative, followed by a minimum at a higher temperature. So we associate T_f with the temperature of the minimum of $d\rho/dT$ and this results agree with the T_f determined by magnetization measurements. We observe that in the range $x \geq 0.125$, where typical spin glass behavior appears in magnetic measurements, we have negative values of $d\rho/dT$. For lower concentrations of Al, $0.02 < x \leq 0.10$, $d\rho/dT$ has only positive values and also with a minimum. If we continue to associate a freezing temperature to the minimum in $d\rho/dT$ the variation of T_f with concentration gives as shown in figure 4.

For concentrations $x \leq 0.10$ the preliminary measurements in magnetization are not enough to characterize a well definite magnetic freezing temperature, so we believe that the association of the freezing temperatures given by magnetic and resistivity experiments in this range of concentration, must wait for confirmation. The coefficients of the $AT^{3/2}$ term are listed in Table I. These values are of the same magnitude of the canonicals spin glass (Ford et al. 1976).

In general if we regard the data of resistivity measurements in spin glass systems where a minimum appears, as e.g. PtMn (Sarkissian et al. 1974 , Kästner et al. 1978), RhFe (Murani et al. 1970) we can say that the freezing temperatures as determined from magnetic measurements, may fall in this minimum,

after or before, it depends on the concentration. This dependence is related to the range of temperature where superposing effects like Kondo, spin-glass and phonon scattering are dominant. We can argue in a simple way, at least for the iron concentrated alloys, that as temperature increases from T=0 to T_f the rate of the spin correlation length to the mean free path ξ/λ decreases and after T_f the phonon scattering dominates.

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REFERENCES

- Besnus M.J., Bauer P. and Genin J.M. 1978 J.Phys.F: Met.Phys. 8 191.
- Burzo E., Angew Z. 1971 Physik 32 127.
- Buschow K.H. 1977 Rep. Prog. Phys. 40.
- Child H.R. 1981 J. Appl. Phys. 52 1732.
- da Cunha S.F., Franceschini D.F., Senoussi S. and Takeuchi A.Y. 1982 J. Phys. F: Met. Phys. 12 3083
- Dwight A.E. Privated Communication.
- Ford P.J., Mydosh J.A. 1976 Phys. Rev. B 14 2057.
- Franceschini D.F. and da Cunha S.F. to be published.
- Gratz E., Grossinger R., Oesterreicher H. and Paker F.T. 1981 Phys. Rev. B 23 2542.
- Hilscher G. 1982 J. Magn. Magn. Mat. 27 1.
- Kästner J., Wassermann E.F., Matho K. and Tholence J.L. 1978 J. Phys. F: Met. Phys. 8 103.
- Murani A.P. and Coles B.R. 1970 J. Phys. C 2 5159.
- Mydosh J.A., Ford P.J., Kawatra M.P. and Whall T.E. 1974 Phys. Rev. B 10 2845.
- Rivier N. and Adkins K. 1975 J. Phys. F: Met. Phys. 5 1745.
- Sarkissian B.V.B. and Taylor R.H. 1974 J. Phys. F: Met. Phys. 4 L243.
- Shull R.D., Okamoto H. and Beck P.A. 1976 Solid State Commun. 20 863.
- Steiner W. 1979 J. Magn. Magn. Mat. 27 1.
- Takeuchi A.Y. and da Cunha S.F. 1981 J. Phys. F: Met. Phys. 11 L241.
- Takeuchi A.Y. and da Cunha S.F. 1982 J. Magn. Magn. Mat. 30 135.
- Troper A. and Gomes A.A. 1975 Phys. Stat. Sol. (b) 68 99.

CAPTIONS

Fig. 1 - Lattice parameter of $Ce(Fe_{1-x}Al_x)_2$ as a function of concentration at room temperature (●). Dwight (Δ). "$Ce^{3+}Fe_2$ (▲).

Fig. 2 - Total electrical resistivity as a function temperature. The full curves represent $d\rho/dT$ in arbitrary units.

Fig. 3 - Low temperature ρ versus T curves and $d\rho/dT$ in arbitrary units.

Fig. 4 - Variation of T_c, T_d, T_{1min}, T_f and residual and magnetic resistivities in function of concentration x.

Fig. 5 - Low temperature resistivity plotted against $T^{3/2}$ for some concentrations.

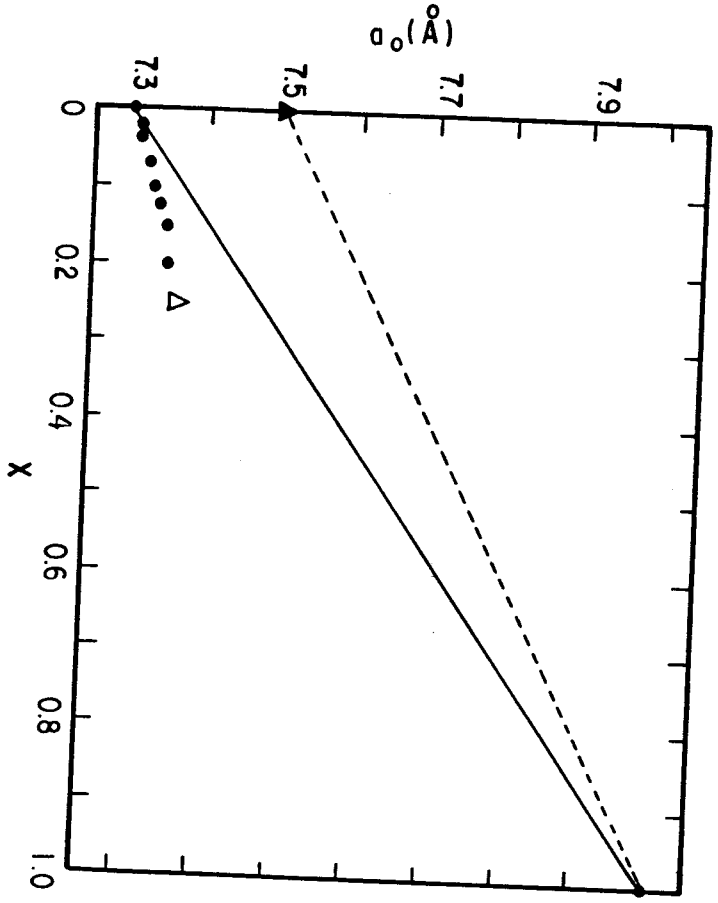

Fig. 1

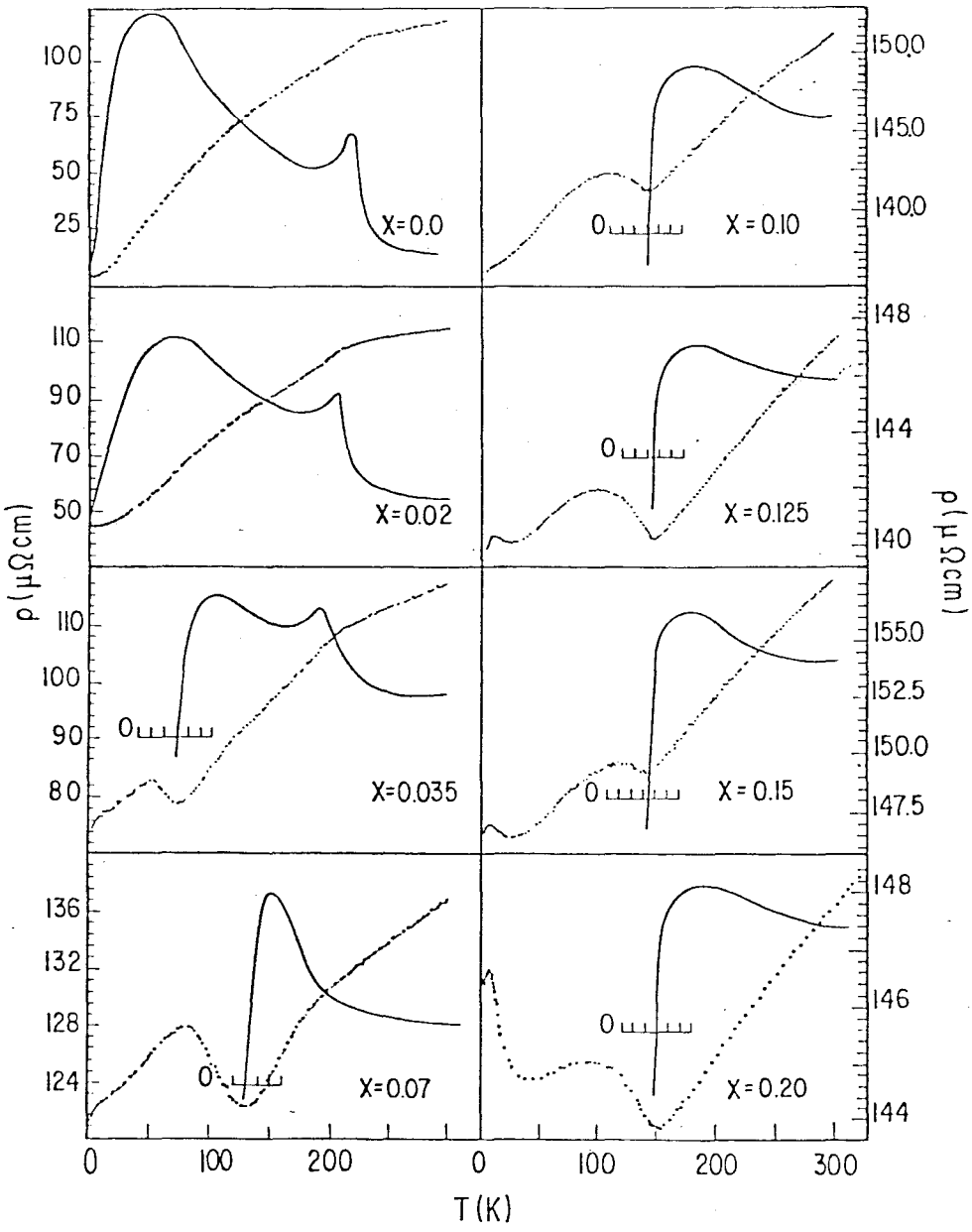

Fig. 2

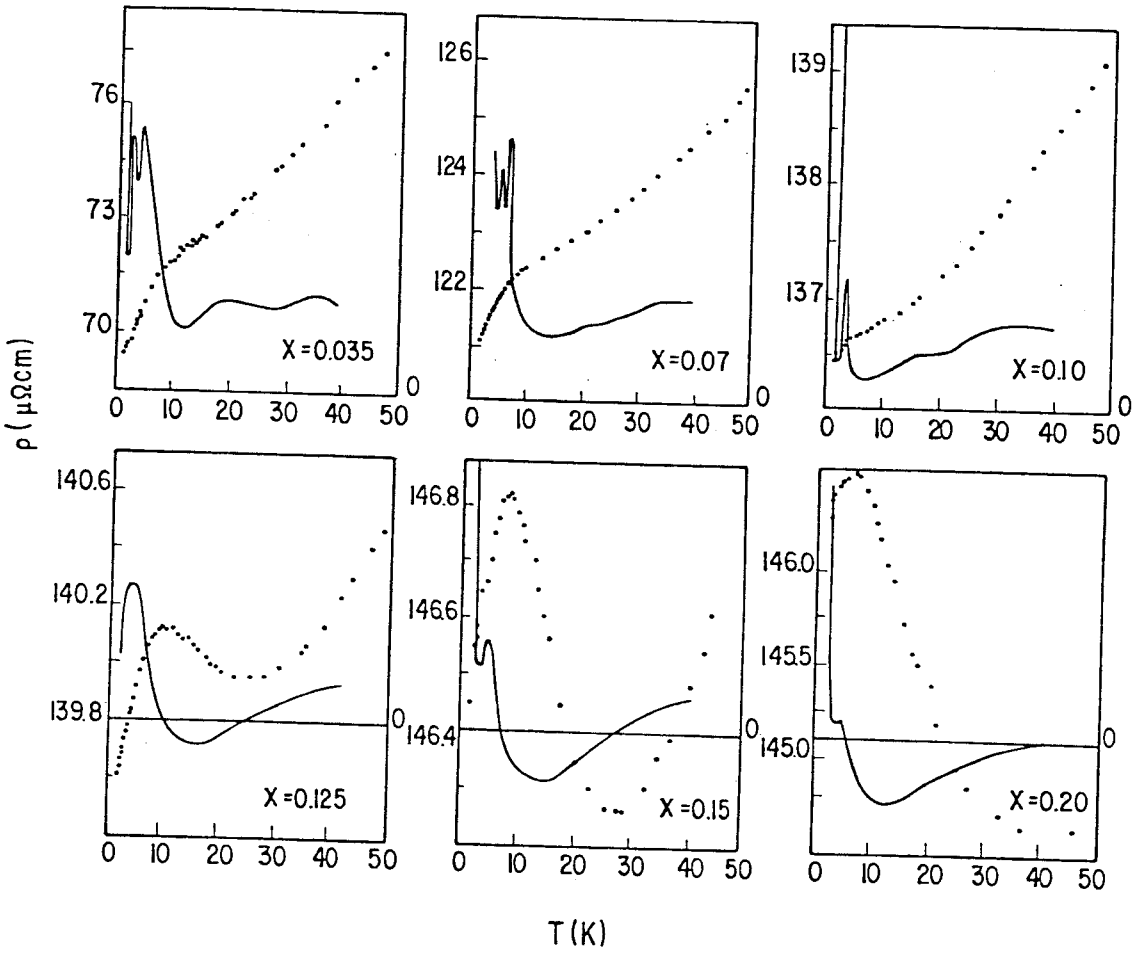
ρ (μΩcm)
76
73
70
X=0.035
0
0 10 20 30 40 50
126
124
122
X=0.07
139
138
137
X=0.10
140.6
140.2
139.8
X=0.125
146.8
146.6
146.4
X=0.15
146.0
145.5
145.0
X=0.20
T(K)

Fig. 3

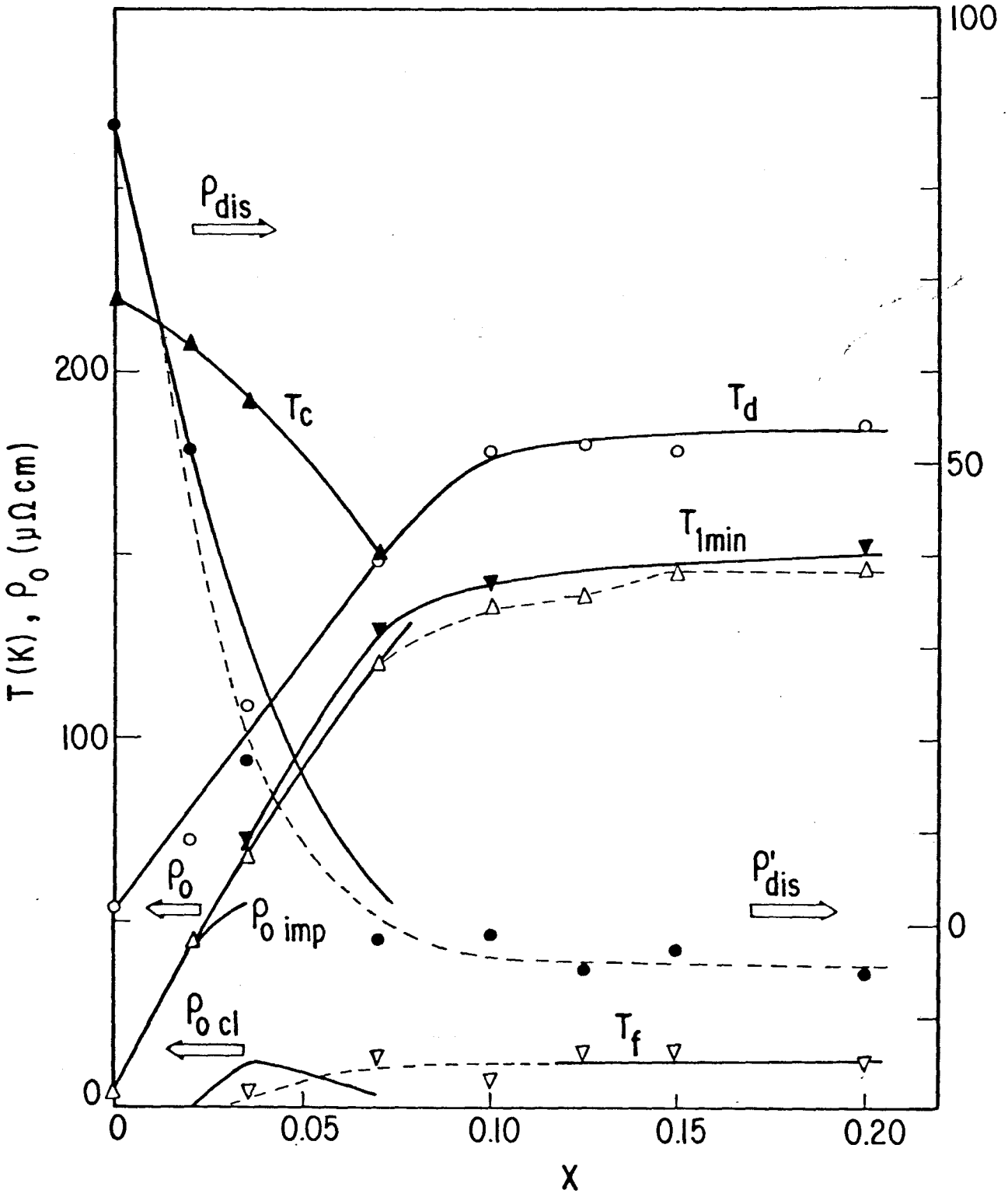
100
50
0
200
100
0
0
0.05
0.10
0.15
0.20
X
T (K), ρ0 (μΩcm)
ρ (μΩcm)
ρdis
Tc
Td
T1min
ρ0
ρ0 imp
ρ0 cl
ρ'dis
Tf

Fig. 4

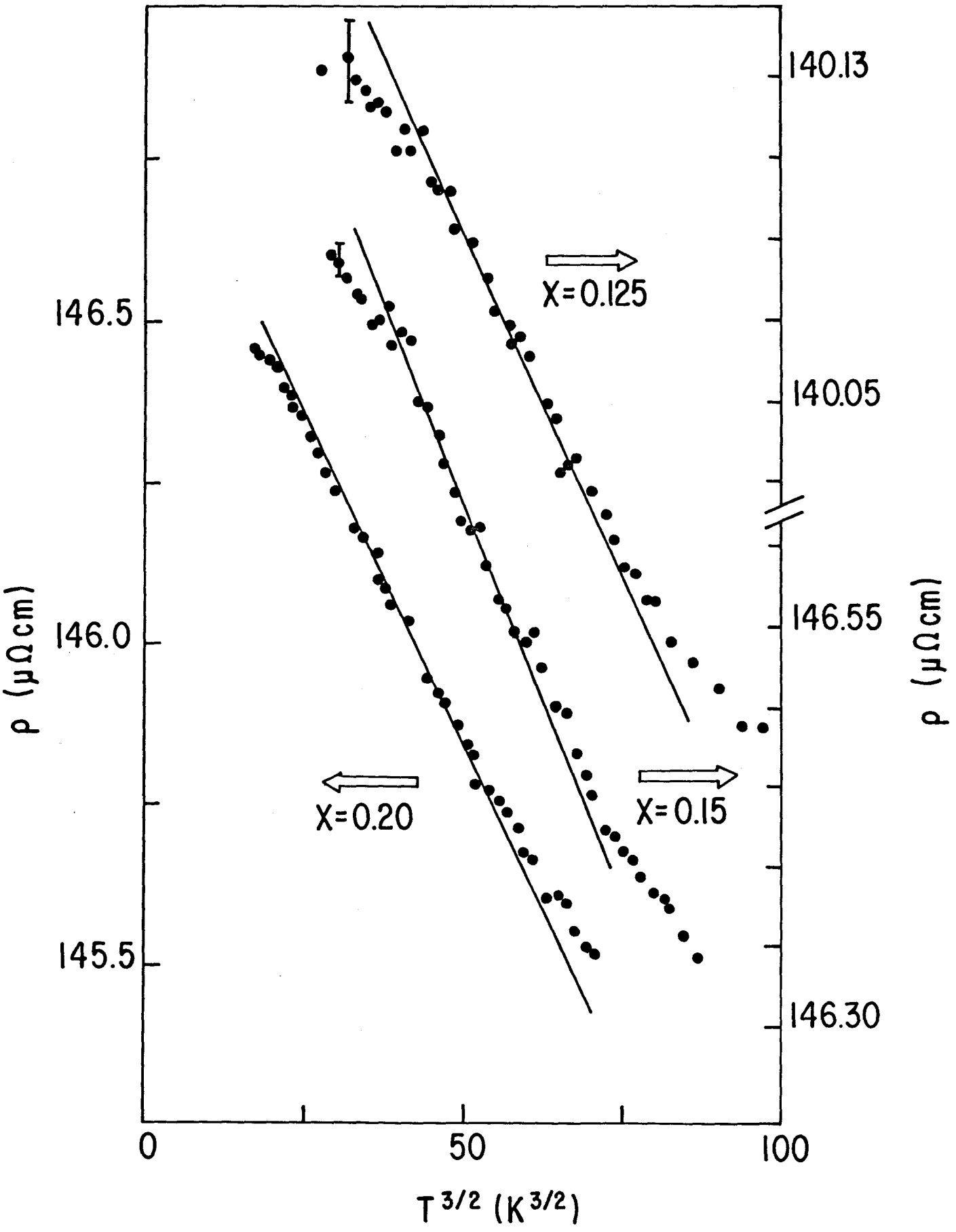
140.13
146.5
140.05
X=0.125
146.0
146.55
ρ (μΩcm)
ρ (μΩcm)
X=0.20
X=0.15
145.5
146.30
0
50
100
T 3/2 (K 3/2)

Fig. 5

TABLE I

x	0	0.02	0.035	0.07	0.10	0.125	0.15	0.20
T_{1min} (K)	-	-	72.0	130.0	143.0	144.5	143.0	152.0
T_{2min} (K)	-	-	-	-	-	24.5	27.5	42
$(d\rho/dT)_{T > T_c}$ $x10^{-2}$ $\mu\Omega cm/K$	9.0	6.4	8.0	5.5	5.3	4.1	4.8	2.2
A $n\Omega cm/K^{3/2}$	-	-				-3.4	-9.9	-20.7