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MAGNETIC PROPERTIES OF $Ce(Fe_{1-x}Al_x)_2$ (Al-RICH SIDE)

by

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ABSTRACT

Magnetic properties of the Laves phase system $Ce(Fe_{1-x}Al_x)_2$ were investigated by means of magnetization and electrical resistivity measurements for $0.60 \leq x < 0.90$. X-ray powder diffratograms reveal that at least up to 40% of iron in $CeAl_2$ (x=0.60) the samples are single-phase. A magnetic phase diagram is proposed where, in this range of concentration, the system changes from a ferromagnetic to a quasi ferrimagnetic phase around x=0.80. At low temperatures the mixed phase character was indicated by spin-glass behaviour, walls pinning of ferromagnetic domains and frustration.

Key-words: $Ce(Fe_{1-x}A\ell_x)_2$; Magnetism - phase diagram; Electrical resistivity; Spin-glass.

INTRODUCTION

The pseudo-binary intermetallic compounds $R(Fe,Al)_2$ (R=Rare Earth or Y, Zr) have been extensively investigated in recent years [1-4]. The gradual substitution of Fe by non magnetic elements like Al allows the observation of changes in magnetic properties as a function of concentration.

The measurements performed in these systems show that distinct behaviours are found in the Al-rich side as compared to the Fe-rich side. For the Fe-rich side one has:
i) For the general case (any R), decrease of the Curie temperature T_C and increase of the saturation magnetization with increasing Al concentration; ii) Critical values of the stoichiometry z in the systems $R(Fe,Al)_{2-z}$ can imply in different crystal structure and/or different magnetic properties; iii) occurrence of reentrant spin glass behaviour in the system $Y(Fe,Al)_2$ at low temperatures; iv) Ferrimagnetic behaviour originating from the antiparallel coupling between heavy rare earth moments and Fe moments. For the Al-rich side one has: i) comparatively lower T_c and higher saturation magnetization; ii) Initial decrease followed by an increase in the critical temperature T_c with the Fe concentration. The initial decrease is less pronounced than that in the Fe-rich side; iii) Fe usually exhibits a magnetic moment; this was verified in $Y(Fe,Al)_2$ by Mössbauer measurements [5]; iv) As compared to the Fe-rich side, the magnetic behaviour shows more delicate aspects. In previous papers of A.Y.Takeuchi et al.[6] and D.F.Franceschini et al. [7], measurements of electrical resistivity and magnetization were reported for the system $Ce(Fe,Al)_2$ in the Fe-rich side. The low T_c (230 K) found in the ferromagnetic $CeFe_2$ as compared to other

RFe_2 is attributed to the abnormal behaviour of the Ce ion: charge transfer from the A site to the d-band of iron at the B site of the AB_2 compound. In this system, the normal decrease of the T_c with the substitution by Al is followed by the occurrence of spin-canted coupling or "antiferromagnetic component" of the iron moments at low temperatures. The existence of the spin-canted phase in this concentration range was later discussed by S.F. da Cunha et al [8] in terms of competing exchange and anisotropy.

On the other hand, $CeAl_2$ exhibits a quite distinct behaviour as compared to $CeFe_2$. Peculiarities like the Kondo effect at a temperature near 6K and modulated antiferromagnetic structure (MAS) at low temperatures [9] make this system very interesting. Differently from the other side (x=0) of the system $Ce(Fe_{1-x}Al_x)_2$ the Ce ion in $CeAl_2$ shows a +3 configuration and is antiferromagnetically coupled, with a T_N=3.8K. This kind of magnetic ordering is rather unique in the sense that all Al-rich $R(Fe,Al)_2$ R with moment, are ferromagnetic. This suggest that the unstable rare earth 5d electrons strongly interact with the conduction electrons thus modifying the magnetic coupling. The investigation of these two opposite processes in the system $Ce(Fe_{1-x}Al)_2$ and the study the effect of Fe substitution for Al in the Kondo effect, in the magnetic phases, valence changes and also cristalographic phase changes, are some of the motivations of this study.

In an earlier work A.Y.Takeuchi et al.[10] studied the Al-rich side with Al substituted by Fe up to 10% in $CeAl_2$. Electrical resistivity and magnetization measurements revealed that changes in the electronic density allow a decrease of T_N and an increase of the Kondo effect and of the residual resistivity. In this paper we report results for Al concentrations from x = 0.60 to x = 0.88.

EXPERIMENTAL

The $Ce(Fe_{1-x}Al_x)_2$ compounds were prepared by arc-melting in purified argon atmosphere stoichiometric amounts of Ce, Fe and Al. The samples were annealed at 800°C for one week. Phase homogeneity was checked by X-ray powder diffractometry using CuK_α radiation. The magnetization measurements of bulk samples were performed in a vibrating sample magnetometer in static fields up to 13 kOe in the temperature range of 2-300K. Some measurements at 4.2K were carried out in fields up to 80kOe. The electrical resistivity measurements were made by the d.c. four probe technique in the same temperature range. Ingots ($2x2x10mm^3$) with indium solder for current contacts and pressure assembly for potential contacts were used. The temperature was munitored with Ge and Pt sensors in the resistivity measurements and GaAsAl in the magnetization measurements.

RESULTS AND DISCUSSION

Powdered samples analyzed by X-ray diffraction present a single cubic $MgCu_2$ structure. The lattice parameters deduced using Nelson-Riley extrapolation are shown in fig.1. Clear deviations from Vegard's law (dotted line) can be observed in both end concentrations. Note in the figure the appearance of a mixed phase around 15% Al, independently of the preparation techniques, annealing procedures, etc. In the intermediate concentration range we tried to prepare some samples, but without success.

The question of how to attribute the valence to Ce in this system is very delicate. Note that in one end ($CeFe_2$), Ce is almost tetravalent and in the other one ($CeAl_2$) is trivalent, and that

the deviations from Vegard's law are negative and positive respectively. The estimate of the valence by using only the lattice parameter results is controversial and requires a deeper discussion. In the present work the use of X-ray diffraction is limited to the quality control of the sample and to obtain the lattice parameters.

Experimental results will be presented and discussed for $0.60 \leq x < 0.90$, but before that we would like recall some results for $0.90 \leq x \leq 1.0$ [10]. The substitution by Fe in $CeAl_2$ induces an increase of the residual resistivity and of the magnetic susceptibility (M_g/H). The Kondo effect and the antiferromagnetic structure, with T_N decreasing with x, are also preserved. A transition at high temperatures however, appears for $x < 0.95$.

$0.80 \leq x < 0.90$

The temperature dependence of the magnetic susceptibility $\chi_g = M_g/H$ (Fig. 2) in a magnetic field of 0.1kOe presents in this range of concentration, a broad maximum at intermediate temperatures and increases with increasing Fe concentration. The zero field cooling (ZFC) measurements and thermoremanent effects for field cooling (FC) can be observed. Hysteresis loops at 5K for ZFC samples (Fig. 3) are of S-type with coercitive field H_c decreasing with decreasing Al concentration up to x=0.80 where H_c is practically indetectable. For FC measurements up to 13kOe no difference from that of ZFC was observed, for all concentrations.

At temperatures above 150K magnetization drops (Fig. 2) indicating a transition at a critical temperature T_c to a paramagnetic phase. A broadening of this transition, particularly for higher Al concentrations, is observed even at low applied field. This fact indicates that the exchange integral J of the 4f moments of Ce

is weak. As the coupling between these moments is through the RKKY interaction, the reduction of J can be due to the perturbation of the conduction electrons caused by the substitution by Fe. This initial perturbation decreases with increasing Fe concentration.

The field dependence of the magnetization up to 13kOe for various temperatures shown in fig. 4 is in agreement with the χ_g versus T curves. Above T_c a paramagnetic behaviour is observed and below T_c the curves M_g versus H bend but do not show sign of saturation for any concentration. We have also made experiments of M_g versus H at 4.2 for fields up to 80kOe and no saturation was observed [11].

The variation of T_c with Al concentration obtained by extrapolation of M_g^2 versus T to $M_g = 0$ shows that the effect of the substitution of Al by Fe for $x < 0.90$ is an initial increase of T_c up to $x = 0.86$; beyond this point T_c increases slowly.

The $1/\chi_g$ versus T curves gives positive paramagnetic temperatures in this range of concentration, between 172K ($x = 0.88$) to 245K ($x = 0.80$) that allow us to infer, supposing no ordering of the Fe moments, a ferromagnetic coupling of the Ce moments.

The temperature dependence of the total electrical resistivity over the temperature range of 2 - 300K is shown in fig. 5. We have presented these curves in several figures with different resistivity scales since the variation of the total resistivity is very different for each concentration. The absolute error was estimated to be about 1% maximum and no thermal hysteresis was observed. At low temperatures the resistivity increases with decreasing temperatures giving rise to a minimum which is pre-

sented in fig. 6. The variation of the temperature of these minima T_{min} with Al concentration is inserted in the same figure.

In the curves ρ versus T we do not observe any anomaly at temperatures where the magnetization shows a paramagnetic transition. On the other hand the minima at low temperatures are a remaining Kondo effect of the range of concentration $0.90 \leq x \leq 1.0$, as checked by plots of ρ versus ℓn T.

It is interesting at this point to remark that the sample x = 0.86 that presents the lowest value of χ_g and of effective moment $\mu_{eff} = 1.33\mu_B$/form), presents at the same time the highest value of T_{min} (Fig. 6). As T_{min} is directly related to the Kondo temperature and the magnetic interaction and Kondo effect are competitive processes, these results are totally coherent. Therefore at low temperatures the Kondo effect persists up to x = 0.86; from that point the magnetic order begins to takes place and T_{min} or T_K decreases.

The strong increase of the residual resistivity $\rho_0 [\rho(T = 2K)]$ with concentration can be observed in fig. 7 where results of the Fe-rich side [6] are included.

The positive paramagnetic temperatures and the values of magnetic effective moments indicate that the Ce moment persists with addition of Fe, with a weak ferromagnetic Ce-Ce coupling assisted by the m_d moment of the Fe.

Although the characterization of a reentrant spin glass phase [12] is not always obvious the characteristics of the χ_g versus T with thermomagnetic irreversible effects suggest that this is the case here.

b) $0.60 \leq x < 0.80$.

The temperature dependence of the susceptibility in this range of concentration presents a well pronounced maximum (T_{max}) at low temperatures that increases and shifts to lower temperature when the Fe concentration increases (Fig.2). At intermediate temperatures the value of χ_g decreases with increasing Fe concentration and, at higher temperatures, a second transition occurs which width increases with the addition of Fe up to x=0.65; at this concentration it becomes increasingly difficult to determine a critical temperature.

At low temperatures the irreversible susceptibility component χ_{IR} is strongly time dependent, and therefore affected by the time scale of measurements. Although similar behaviour was observed in the previous range, these effects are more striking here. Also, measurements in higher magnetic applied field on the sample x=0.60 (Fig.8) show that a broader peak with lower intensity was obtained and that T_{max} shifts to lower temperatures. These behaviours suggest a possible reentrant spin glass phase.

Afterwards, hysteresis loops were obtained for $T < T_{max}$ with applied fields up to 13kOe (Fig.3) and no displaced loops for field cooling experiments were observed. However, a loop at T=4.2K for x=0.70 performed with FC of 1.25 kOe (Fig.9) has a spin-glass--like form similar to that of $Y(FeCo)_2$ [13]. In this same sample the variation of the thermoremanent magnetization (TRM) with time (fig.9) does not depend as -lnt, but this fact is not decisive since several different dependences were proposed, for example that of Chamberlin et al. [14].

It is known that the experimental characterization of a spin glass is not easy, the loss of magnetization at low temperature with irreversible effects can be, for example, related to a spin-canted phase or an antiferromagnetic phase. However, the existen

ce of a canted phase in this range of concentration can be discarded as M_g in the M_g versus H curves always increases for decreasing temperatures and that the electrical resistivity do not show an additional scattering due to the magnetic moments disorder [8]. The high values of the susceptibility suggest the coexistence of a possible ferromagnetic coupling between some Fe moments; this coexistence is in agreement with the observed gradual increase of χ_g with Fe concentration.

The hysteresis loops in this concentration range (Fig.3) present interesting features, different from the previous one. The virgin curve have a positive initial curvature, the remanent magnetization is bigger and, more important, the width of the loop increases with Fe concentration from zero ($x = 0.80$) up to 4kOe ($x = 0.60$). These behaviours are attributed to the presence of ferromagnetism in this concentration range.

The field dependence of the magnetization (fig. 4) also presents a distinct behaviour mainly at low fields where a positive curvature becomes more marked with increasing Fe concentration, a fact that can be related to the existence of Bloch walls.

At intermediate temperatures ($\sim$100-200K) below the transition to a paramagnetic phase, the value of the magnetic susceptibility decreases with increasing iron concentration. On the other hand the field dependence of the magnetization in this range of temperatures (Fig. 4) presents non linear curves. These results indicate that the magnetic phase in this concentration and temperature range is composed of a ferromagnetic ordering of the Ce moments with antiparallel coupling with some Fe moments, that is, a quasi-ferrimagnetic phase.

The electrical resistivity as a function of temperature for

x=0.65 and x=0.60 (fig. 5) presents an "anomaly" in place of the minimum of the previous concentrations and below this temperature the resistivity drops, indicating some magnetic order in the system. Observe, however, that for x=0.65 the residual resistivity has the highest value of the series, ρ_o= 175.2 μΩ cm. Also in this range of concentration no anomaly was observed at the high temperature transition.

CONCLUSION

The results of X-ray diffraction show that the pure cubic C15 structure of the end compound persists up to 40% at of Fe in the Al-rich side. In this side of the series line intensities gradually decrease with increasing Fe concentration indicating the probable proximity of the solubility limit of the cubic phase C15.

The substitution of Al by Fe is not a simple dilution process. A large change of the density of states with a high value of the residual resistivity and enormous changes of the complex magnetic structure of the $CeAl_2$ is observed. The paramagnetic temperatures change from negative to positive values around x=0.90, the coupling of the Ce moments changing from antiferromagnetic ($T_N < 2K$) to weak ferromagnetic for $x < 0.90$.

The weak ferromagnetism of Ce persists for $0.60 \leq x < 0.80$ but the Ce moments couple with some Fe moments giving rise to a quasi-ferrimagnetic phase.

In addition to the differences above described in the discussion between the two ranges of concentration, as for example, the behaviour of the coercitive field at low temperatures as a function of the concentration, we have observed that the irreversible

susceptibility component, defined as $\Delta\chi = \chi_R - \chi_{IR}$, as a function of temperature is much higher of $x \leq 0.80$ than for $x > 0.80$, suggesting two different origins for this remanent magnetization. So, at low temperatures if for $x > 0.80$ we had a reentrant spin glass-like behaviour, for $x < 0.80$ it is more probable that iron ferromagnetism mixed with pinning of domain walls and "frustration" take place. Moreover, the critical high temperature T_c changes abruptely for $x > 0.80$ whereas for $x < 0.80$ we observe a fairly constant value.

We propose a preliminary magnetic phase diagram for $Ce(Fe_{1-x}Al_x)_2$ (fig. 10) including the Fe-rich side [7]. The dashed line separates roughly the two magnetic regions. It is worthwhile further investigations to define with precision the threshold of the various magnetic phases of this complex diagram.

CAPTIONS

Fig. 1 Concentration dependence of the lattice parameter for $Ce(Fe_{1-x}Al_x)_2$ and crystallographic structure including the Fe-rich side (▨) mixed phase.

Fig. 2 Temperature dependence of the magnetic susceptibility $\chi_g = M_g/H$. (a) $0.80 < x < 0.9$ (b) $x \leq 0.80$. For each concentration, at low temperatures the down curve corresponds to the ZFC experiment.

Fig. 3 Hysteresis loops at 5K and ZFC samples for various concentrations.

Fig. 4 Field dependence of the isothermal magnetization for various temperatures and concentrations.

Fig. 5 Temperature dependence of the total electrical resistivity for various concentrations.

Fig. 6 Low temperature dependence of the total electrical resistivity. Insert: concentration dependence of T_{min}.

Fig. 7 Concentration dependence of the residual resistivity.

Fig. 8 Temperature dependence of $\chi_g = M_g/H$ for x=0.60 and applied field of 1kOe and 0.1kOe. Open symbols are FC and full symbols are ZFC experiments.

Fig. 9 ZFC Hysteresis loop (a) and time dependence (b) of the remanent magnetization at 4.2K and at applied field of 3,5kOe for x = 0.70.

Fig.10 Proposed magnetic phase diagram for $Ce(Fe_{1-x}Al_x)_2$ including the Fe-rich side [7].

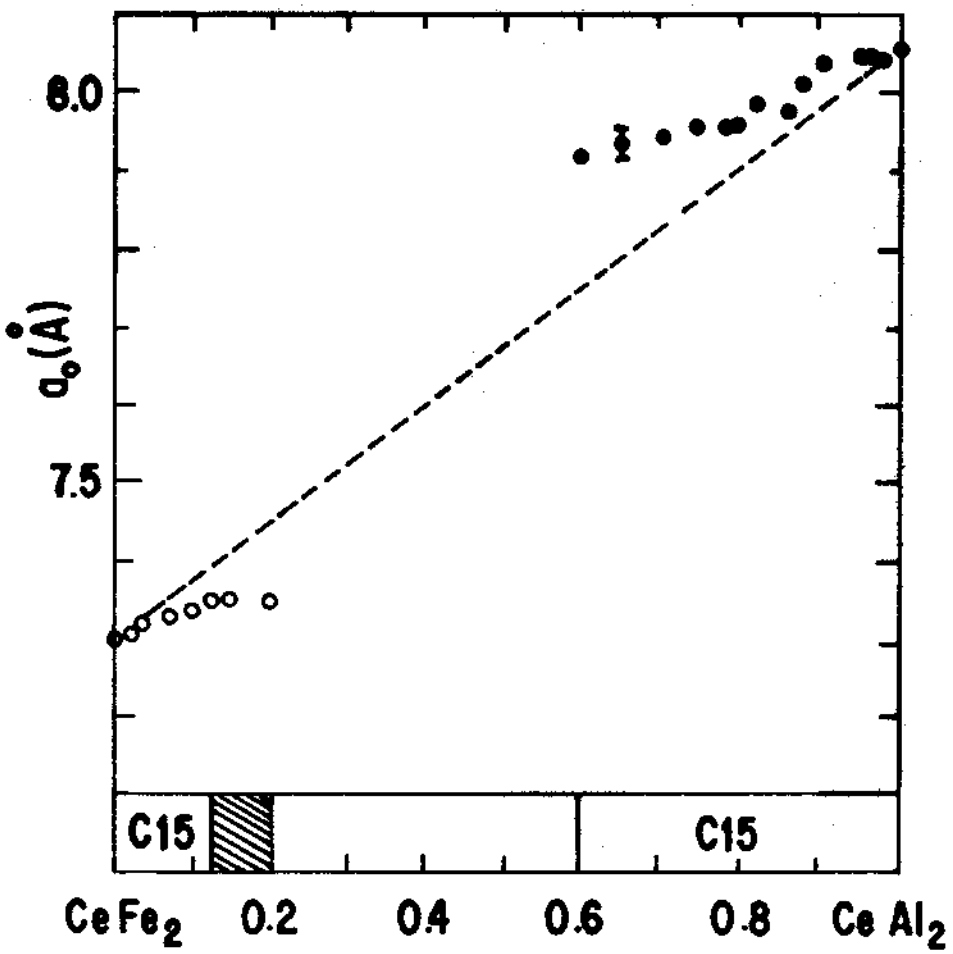


Fig. 1

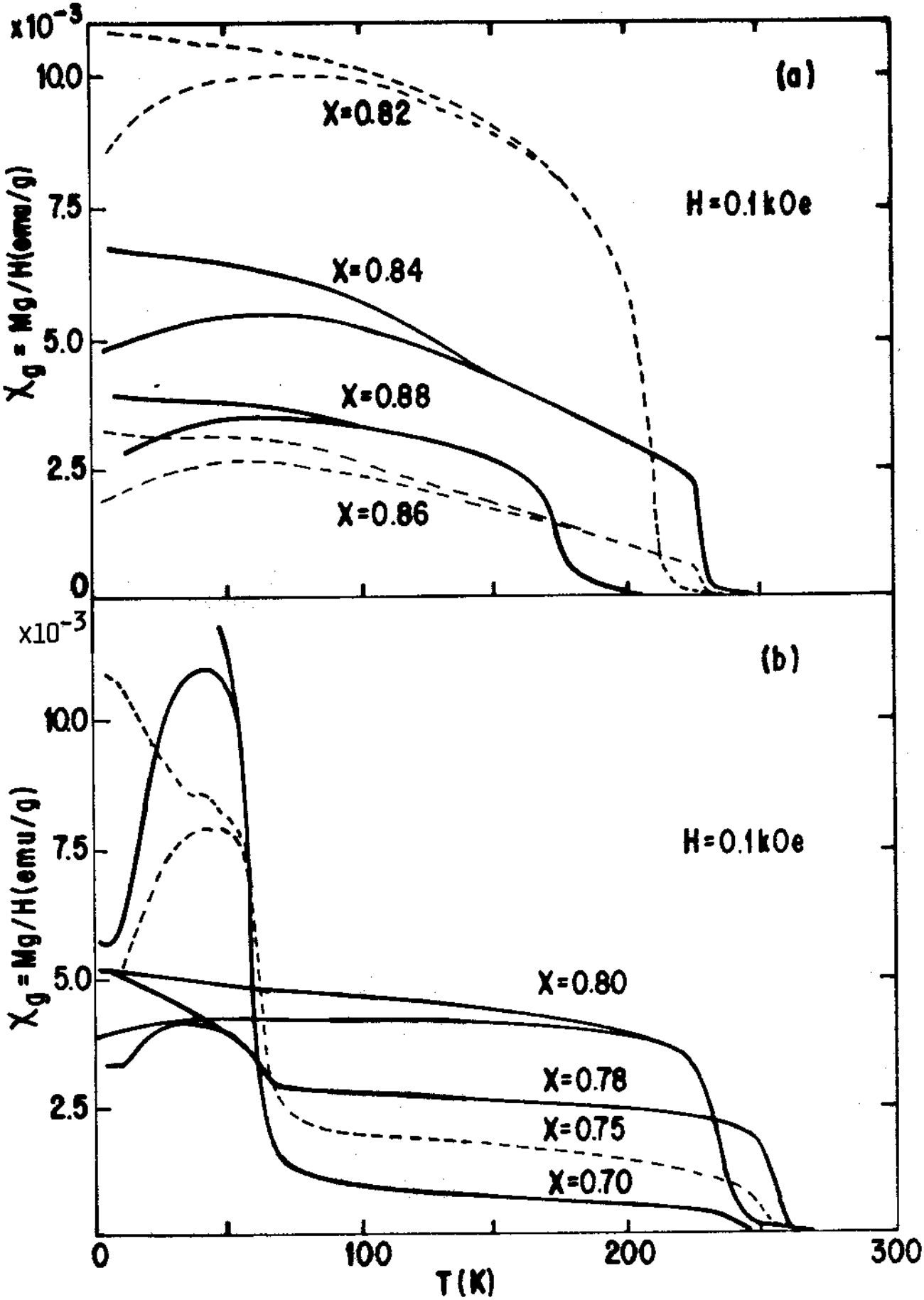

x10⁻³
10.0
7.5
5.0
2.5
0
χg = Mg/H(emu/g)
(a)
X=0.82
H=0.1kOe
X=0.84
X=0.88
X=0.86
x10⁻³
10.0
7.5
5.0
2.5
χg = Mg/H(emu/g)
(b)
H=0.1kOe
X=0.80
X=0.78
X=0.75
X=0.70
0
100
200
300
T(K)

Fig. 2

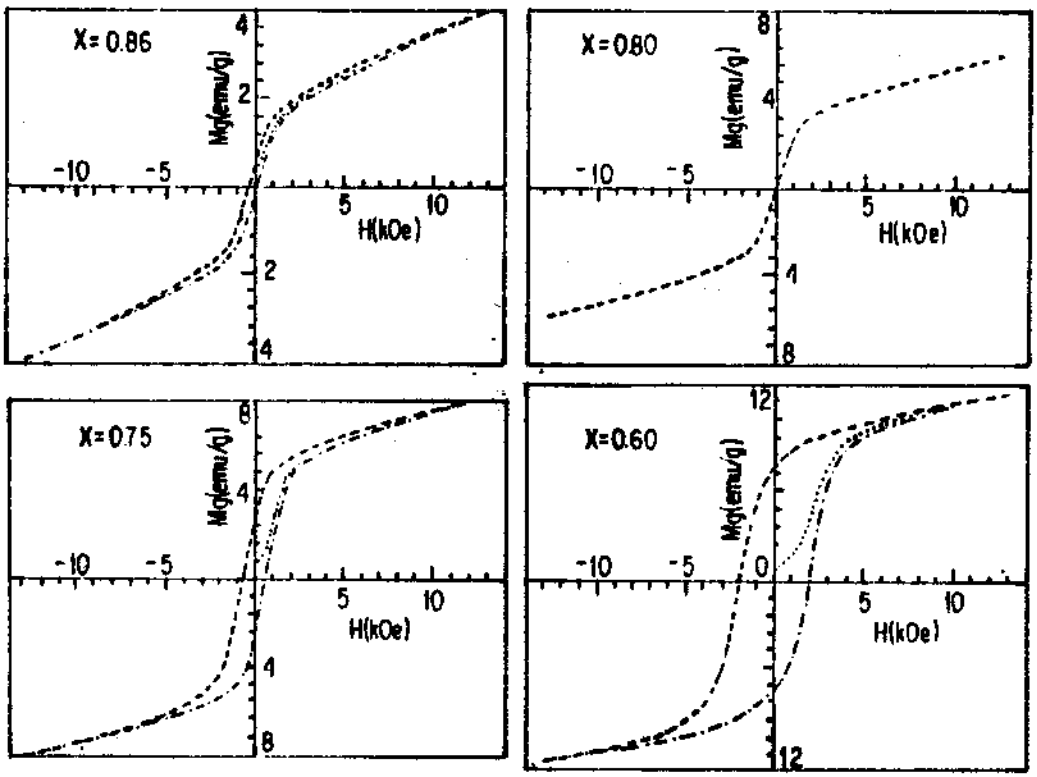

X= 0.86
Mg(emu/g)
H(kOe)
X=0.80
Mg(emu/g)
H(kOe)
X=0.75
Mg(emu/g)
H(kOe)
X=0.60
Mg(emu/g)
H(kOe)

Fig. 3

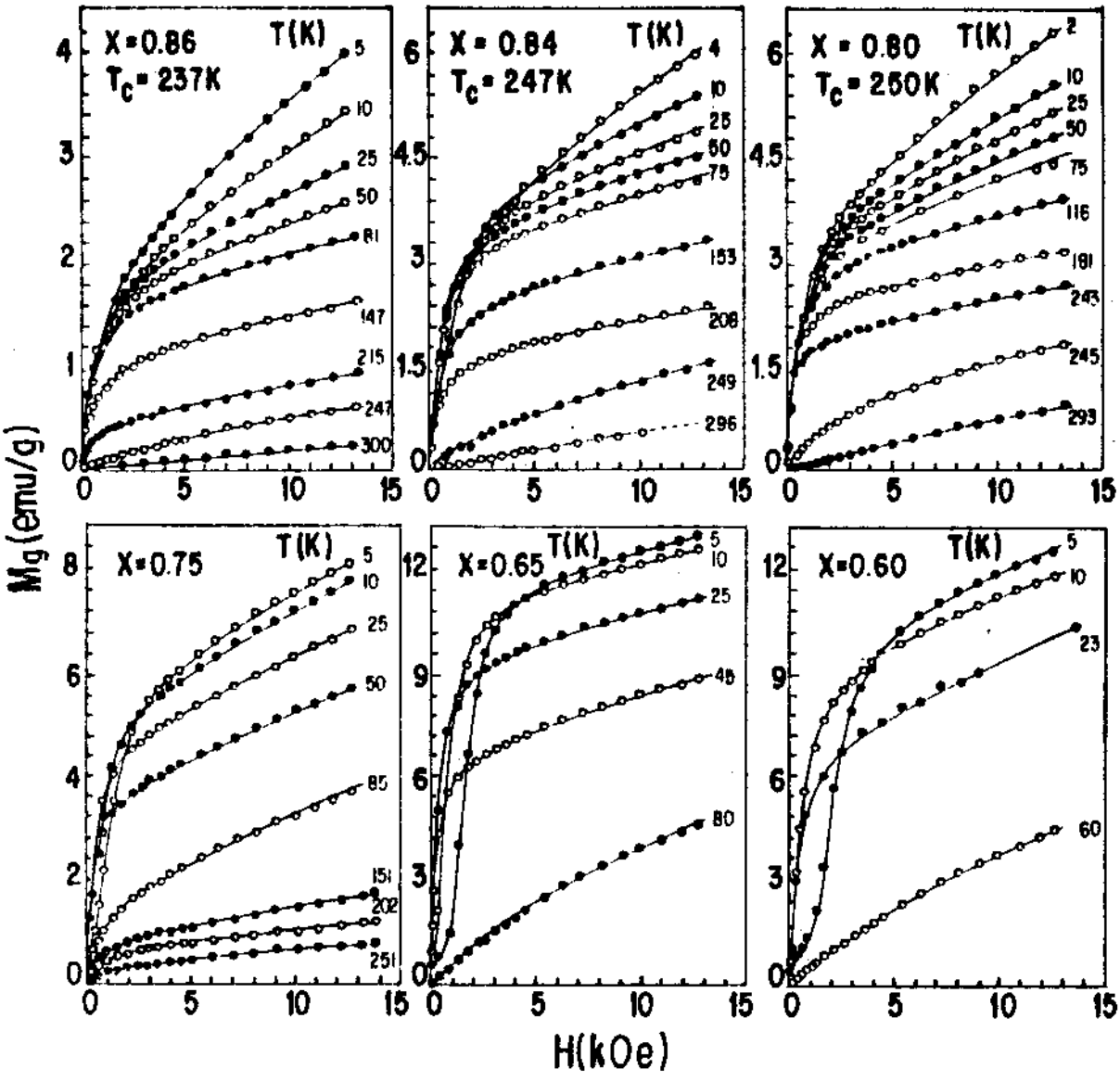

X=0.86
T(K)
T_c = 237K
5
10
25
50
81
147
215
247
300
X = 0.84
T_c = 247K
4
10
25
50
78
153
208
249
296
X = 0.80
T_c = 250K
2
10
25
50
75
116
181
245
293
X=0.75
5
10
25
50
85
151
202
251
X=0.65
5
10
25
46
80
X=0.60
5
10
23
60
Mg(emu/g)
H(kOe)

Fig. 4

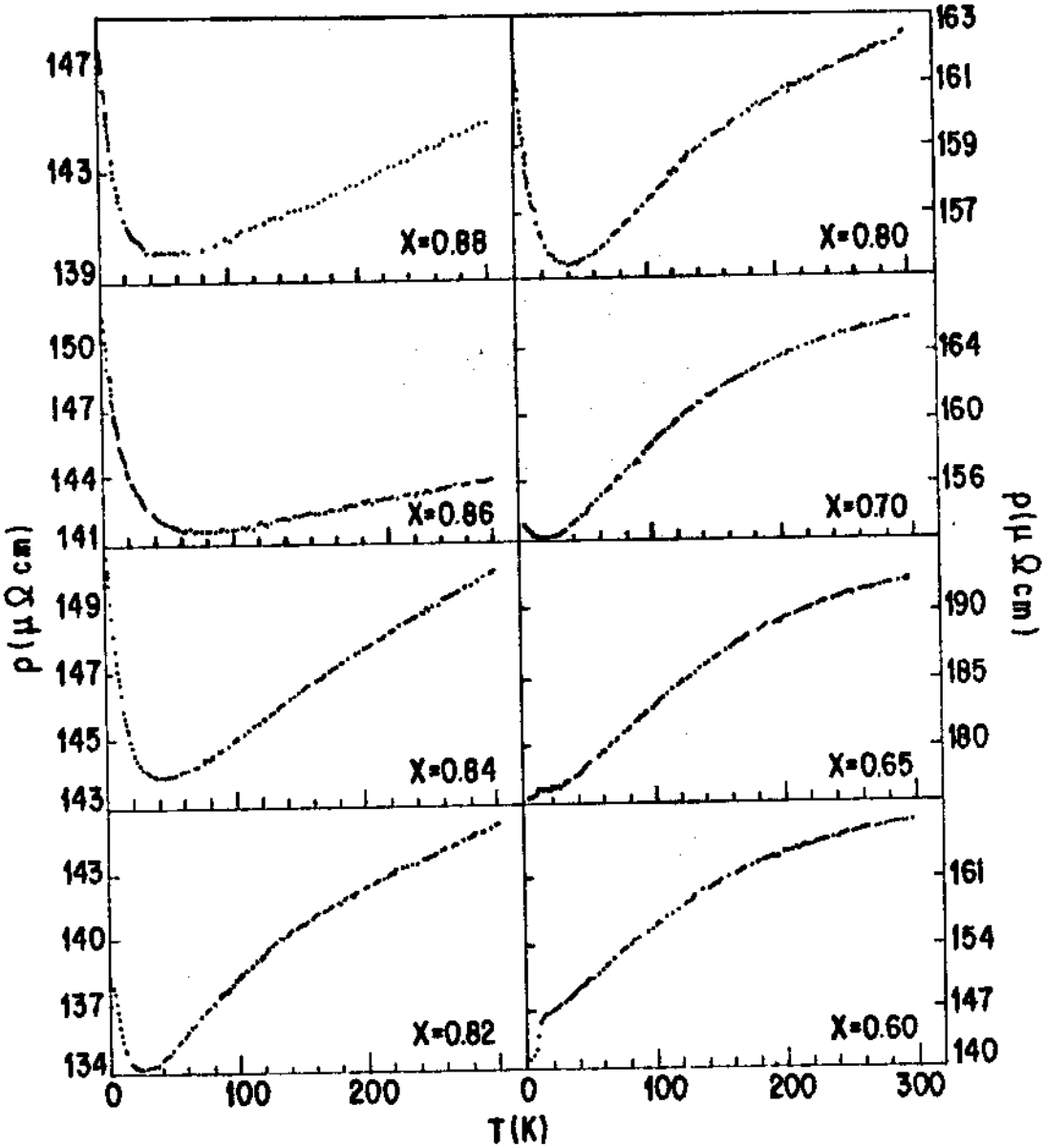


Fig. 5

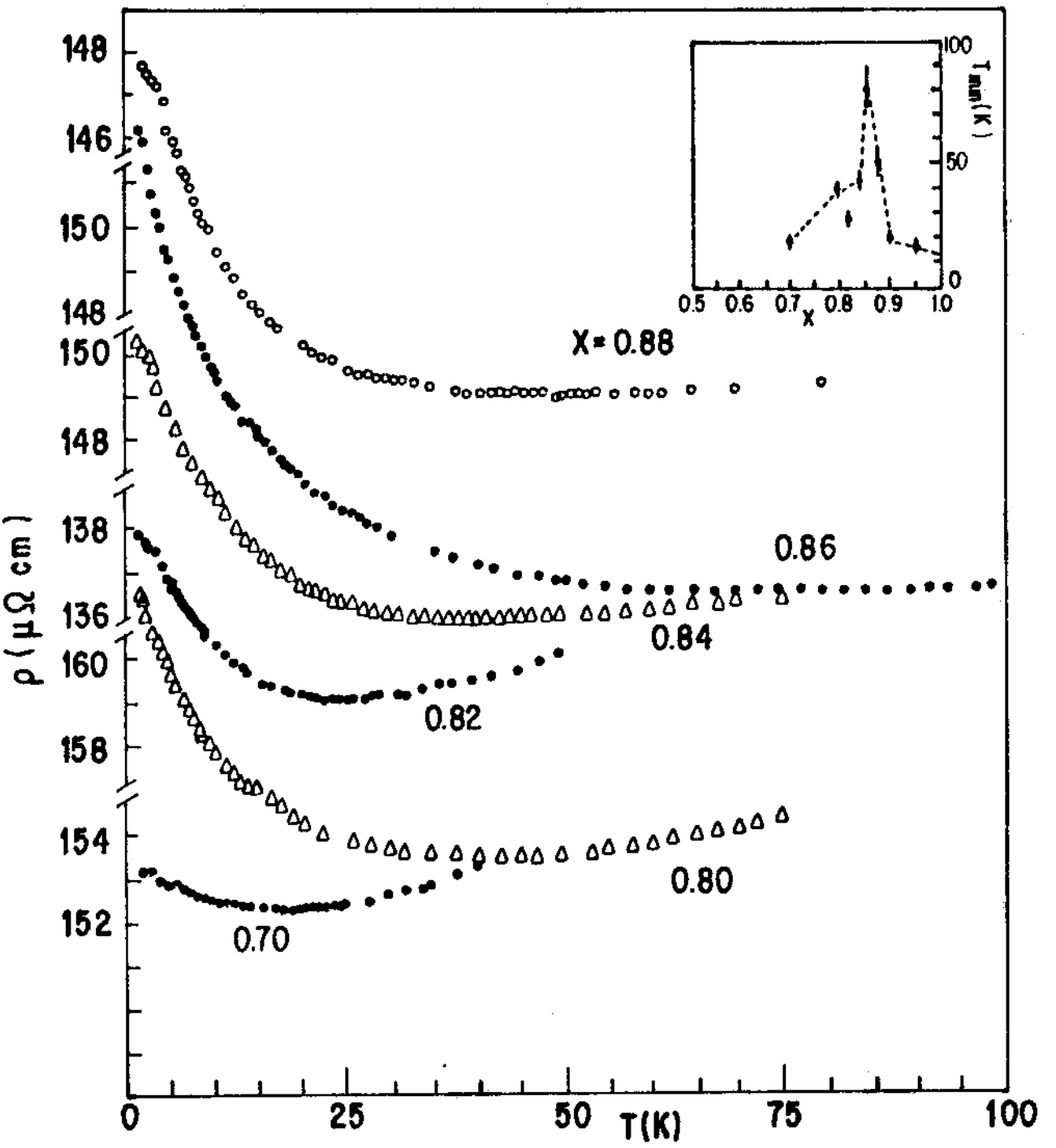
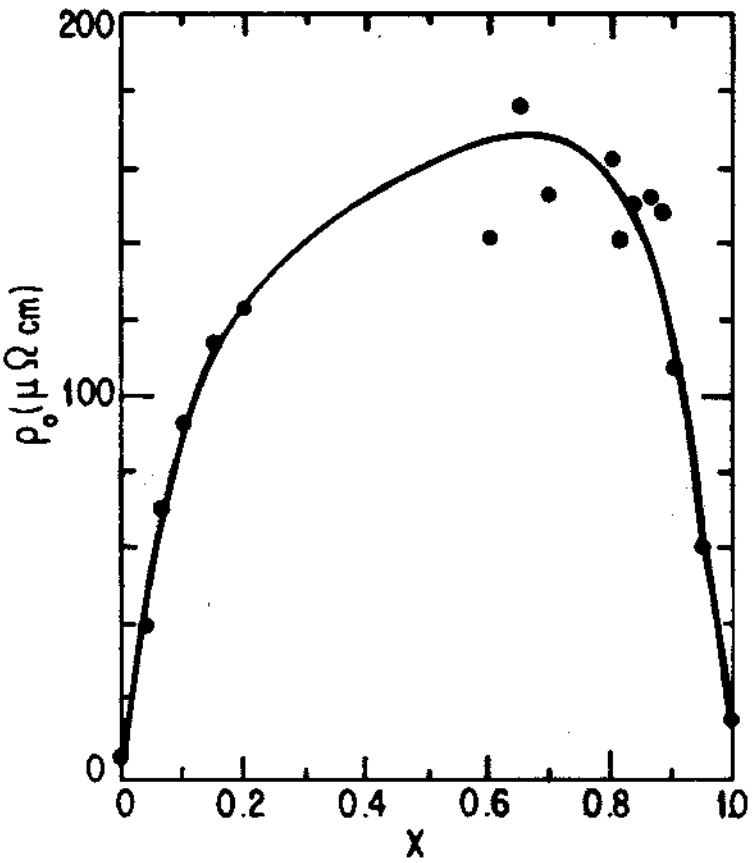

148
146
150
148
150
148
138
136
160
158
154
152
ρ (μΩ cm)
X = 0.88
0.86
0.84
0.82
0.80
0.70
0
25
50
75
100
T(K)
100
50
0
T_min (K)
0.5
0.6
0.7
0.8
0.9
1.0
X

Fig. 6



Fig, 7

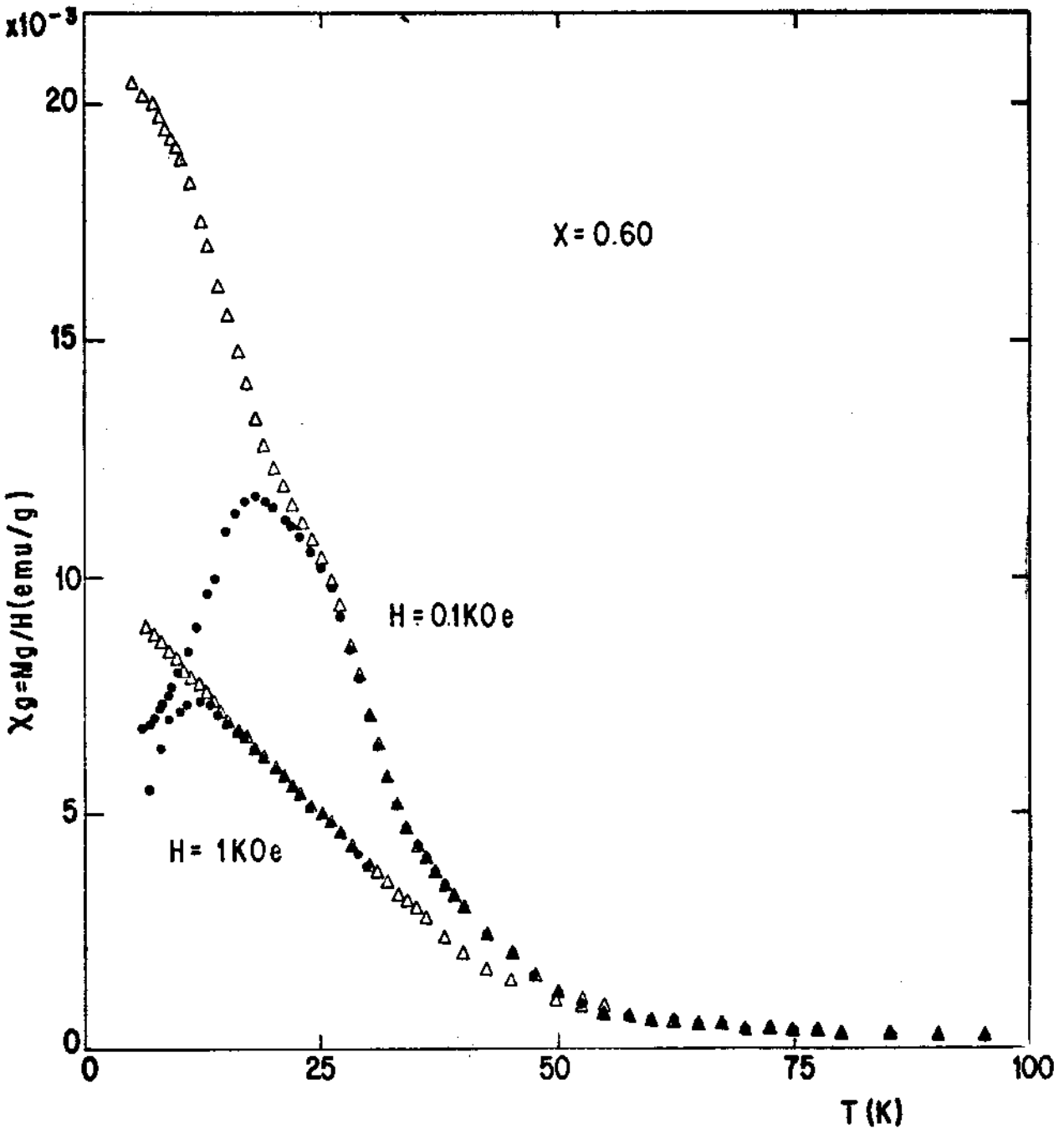
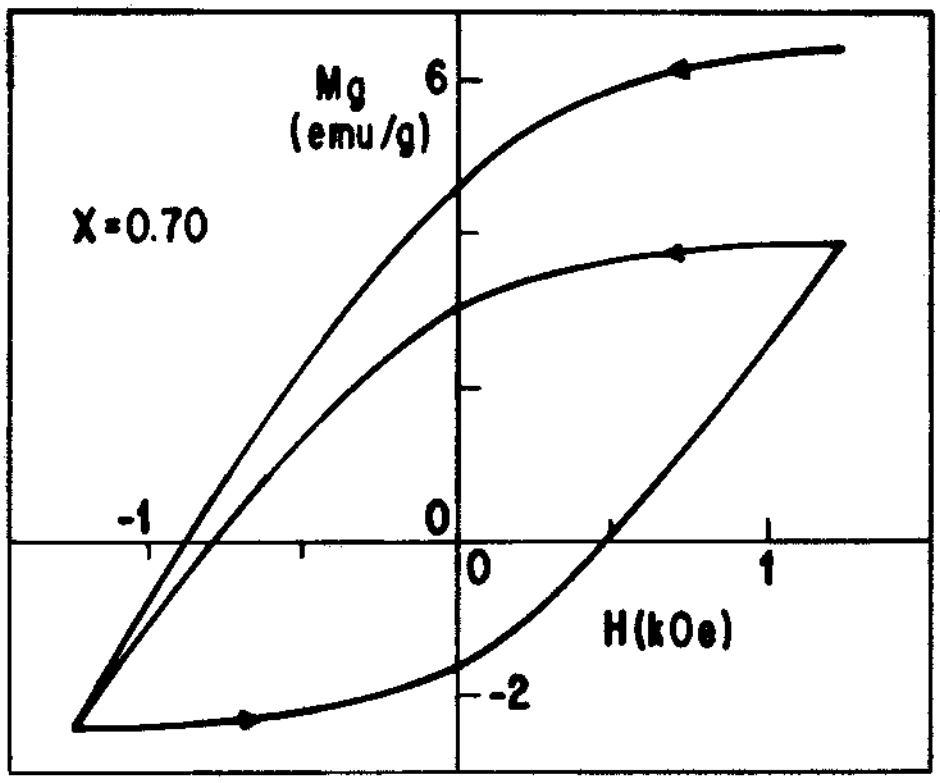


Fig. 8



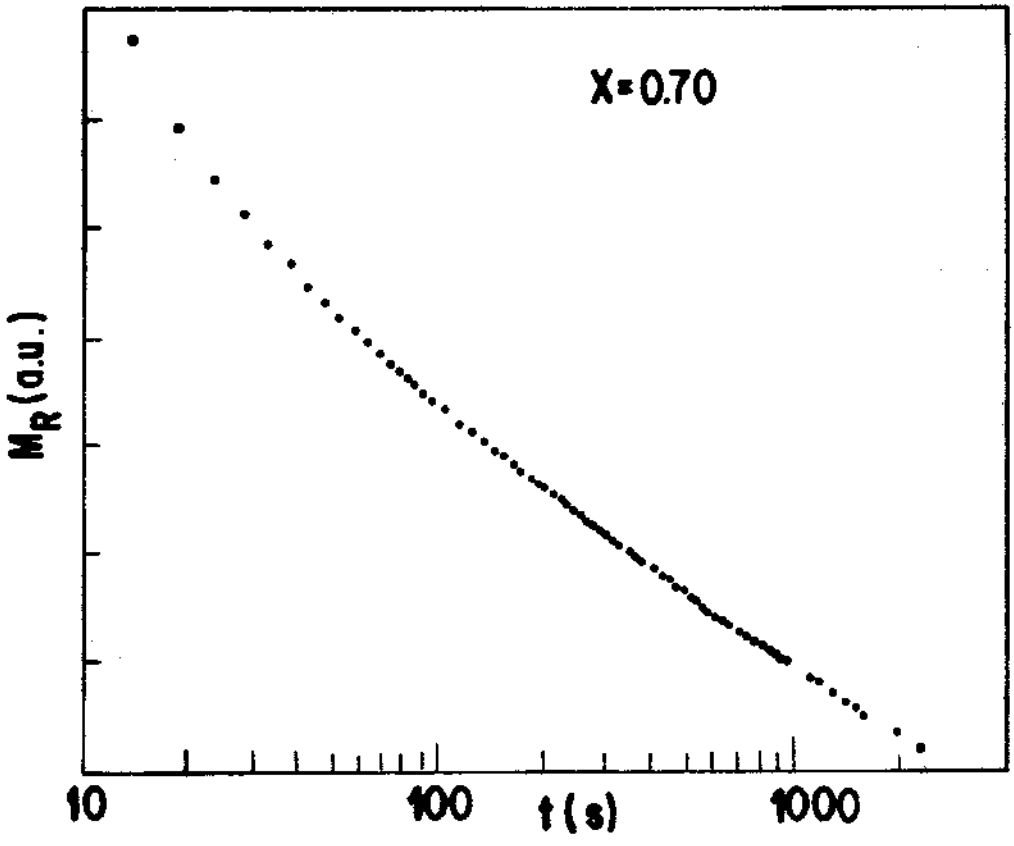


Fig. 9

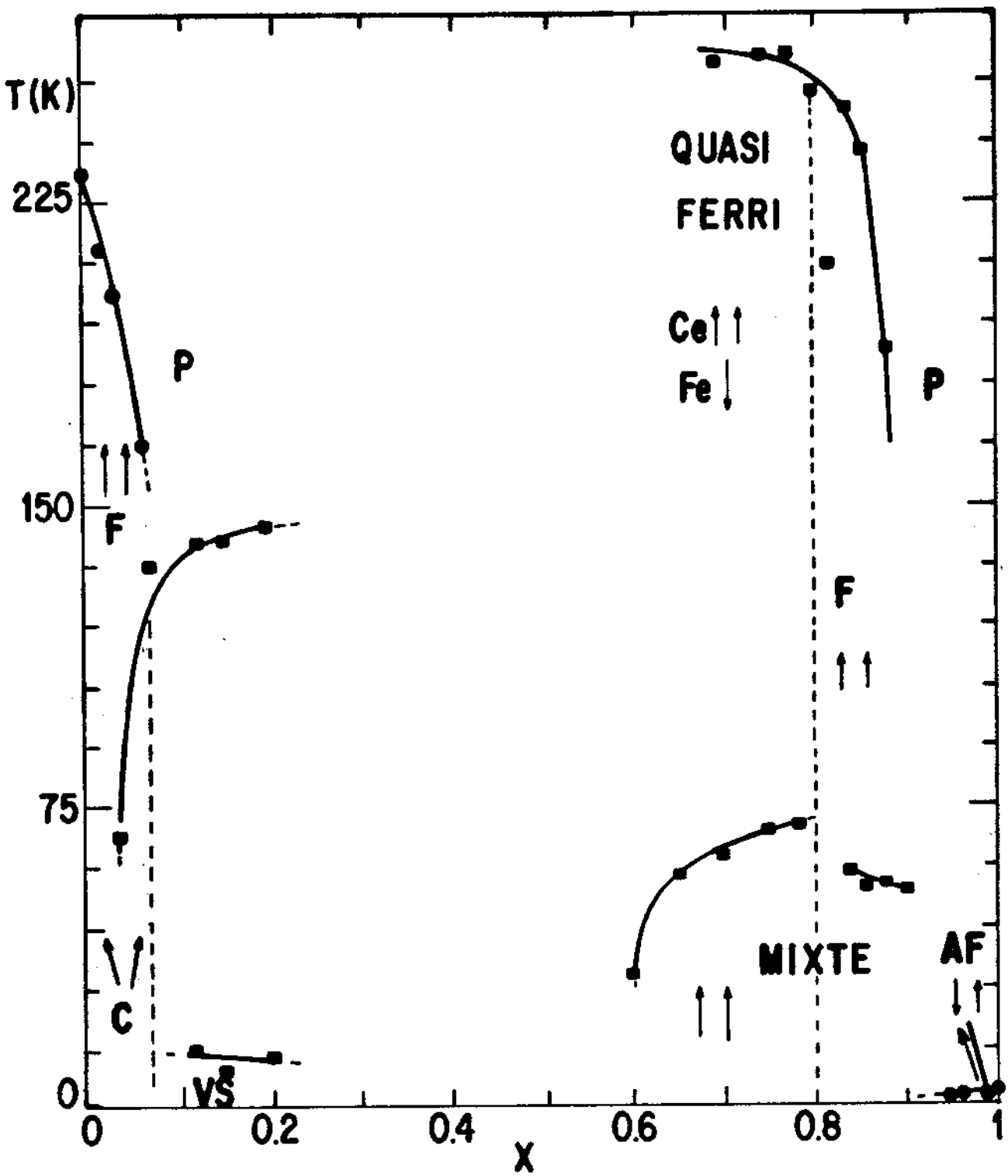

T(K)
225
150
75
0
0
0.2
0.4
0.6
0.8
1
X
P
F
C
VS
QUASI
FERRI
Ce
Fe
P
F
MIXTE
AF

Fig. 10

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