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EFFECTS OF Al SUBSTITUTION BY Fe IN $CeAl_2$

by

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ABSTRACT

Magnetization and electrical resistivity measurements of the $CeAl_2$ with Al substitution by Fe up to 10%at Fe show that the competition between the increasing Kondo effect and the antiferromagnetism persists. Change of the electronic density is followed by a decreasing Neel temperature and an increasing residual electrical resistivity. The probable appearance of ferromagnetism of the Ce moments, at intermediate temperature range, is discussed. The small decrease of the lattice parameter with Fe concentration or the magnetic behaviour do not show evidence of valence changes in the Ce ion.

Key-words: $Ce(Fe,Al)_2$; Magnetization; Electrical resistivity; Kondo effect; Spin-glass-like; Laves phase.

1 INTRODUCTION

The magnetic concentrated Kondo system (CKS) $CeAl_2$ presents a variety of anomalous and interesting behaviours, attributed to the reasonable degree of delocalization of the 4f cerium electrons. The modulated antiferromagnetic structure (MAS) [1] for example, results from the competition between Kondo effect ($T_K \cong 7K$) and RKKY interaction ($T_N \cong 3.8K$). Studies performed in this system reveal that the application of an external pressure ($P \gtrsim 65$ kbar) in the nearly trivalent Ce-ions, cause a transition into a volume - collapsed state, suggesting intermediate valence (IV) of the Ce ions [2]. A similar transition can be induced by the simulation of pressure, (lattice or chemical pressure) by alloying $CeAl_2$ (lattice parameter $a_o = 8.06Å$) with an isostructural compound RAl_2 with smaller a_o.

On the other hand studies performed in the compound $CeFe_2$ ($a_o = 7.3Å$) [3] have indicated that the ferromagnetic ordering (T_C=230 K) in this compound is due to the Fe moments inferring no moment or a 4^+ IV-state for the Ce ions. Recent L_{III} experimental results give a value of +3.3 to the Ce ions valence in $CeFe_2$. The excepcional low both a_o and T_C, as compared with others RFe_2, were attributed to the IV-state of the Ce ions. Therefore, we expected that the pseudo-binary system $Ce(Fe_{1-x}Al_x)_2$ allow us to study many interesting magnetic properties. In the Fe-rich side, the decrease of T_C with Al concentration is followed by the occurrence of a new magnetic phase [3,4] which magnetic ordering nature is controversial [5-7].

In a previous work, Takeuchi and da Cunha [8] show that for $x < 0.90$ the system changes from a ferromagnetic to a quasi-ferrimagnetic phase around $x = 0.80$ (20%at Fe). At low temperatures the mixed phase character was indicated by spin-glass behaviour, frustration and wall pinning of ferromagnetic domains.

The purpose of this work is to investigate the magnetic behaviour of the intermetallic compound $CeAl_2$ ($x = 1.00$) with the Al substitution by Fe down to $x = 0.90$ (10%at Fe), from magnetization, electrical resistivity and lattice parameters results. It is interesting to follow the influence of the substitution of Al by Fe on the magnetic interaction between the 4f electron of the Ce ions and the conduction electrons.

2 EXPERIMENTAL

Polycrystalline samples of $LaAl_2$ and of the pseudo-binary intermetallic system $Ce(Fe_{1-x}Al_x)_2$ between $x = 1.00$ and $x = 0.90$ were prepared from stoichiometric amounts of the elements by arc-melting under an argon atmosphere and subsequently annealing for one week at a temperature of 800°C. X-ray powder patterns using CuKα radiation show that this system crystalizes in the cubic $MgCu_2$ type of structure. The lattice parameters a_0, derived by least square analysis using Nelson-Riley's extrapolation, for the various alloy compositions,is given in table 1. We can observe that the values of a_0 are very close to that of the end compound $CeAl_2$. These results show that the pressure effect of the Fe for $x \geq 0.90$ (10%at Fe) in this system is very weak, so no changes due to the variation of the volume available for the conduction electrons take place in the density of states.

The electrical resistivity was measured by the standard DC four probe technique, in casted ingots ($\sim 2 \times 2 \times 10 mm^3$) over a temperature range between 2 and 300 K. The temperature was measured with Ge and Pt thermometers, attached to the sample holder. The magnetization measurements were performed between 2 and 300 K using a PAR vibrating sample magnetometer, in magnetic fields up to 13kOe. The temperature for the magnetic measurements was monitored using a GaAsAl thermometer.

3 RESULTS AND DISCUSSION

The experimental results of the total electrical resistivity $\rho(T)$ of the system $Ce(Fe_{1-x}Al_x)_2$ for $x = 1.0$, 0.95 and 0.90 are shown in the fig. 1. According to these experimental data, we can observe that the main features present in $CeAl_2$ (i.e. maximum and minimum), due to the Kondo effect, magnetic ordering and Fermi liquid behaviour, persist down to $x = 0.90$ (10%at Fe). The substitution of Al by Fe yield an increase in the temperature T_{min} (whereas T_{max} has a constant value of 6 ± 1K) and also a remarkable effect in the residual resistivity ρ_0. As the magnetic resistivity behaves as $- \ln T$ in this range of temperature, we can relate T_{min} with T_K which increases with increasing Fe concentration.

The magnetic contribution ρ_m to the electrical resistivity of this system as a function of ln T (fig. 2) was obtained by subtracting the phonon contribution $\rho_{ph}(T)$ from the measured resistivity shown in fig. 1, using the non-magnetic isostructural reference compound $LaAl_2$. These curves present a maximum at a temperature of 4K due to the magnetic ordering, followed by a minimum (Kondo effect) around 15K and a broad maximum around 100K and decrease logarithmically as T goes up to 300K. Excepting the low temperature regime ($T < 5K$), these results agree with the theoretical description of the combined Kondo effect crystalline field, previously deduced and applied to $CeAl_2$ [9] that is, lnT behaviour of the magnetic resistivity $\rho_m(T)$ for $k_BT > \Delta$ and $k_BT << \Delta$ (Δ= splitting of the crystalline field). In these curves we note that the broad maximum associated to Δ decreases in intensity and is shifted towards lower temperatures with increasing Fe concentration, indicating the approximation of the exited Γ_8 to the fundamental Γ_7 level.

The temperature dependence of the magnetic susceptibility χ_g (=M_g/H) for $x = 0.90$ and $x = 0.92$ in a static magnetic field of 0.1 and/or 1kOe is shown in fig. 3. The detailed behaviour of χ_g at low temperatures for some concentrations is given in fig. 4. We can observe that the antiferromagnetic ordering temperature T_N has a gradual decrease with the addition of Fe. A simple extrapolation indicates that towards $x = 0.80$, $T_N \rightarrow 0$. However, as the antiferromagnetic ordering temperature decreases a gradual appearance of a new magnetic phase takes place as shown by the sudden drop in the $\chi_g(T)$ curves at higher temperatures T_C. These curves, for $x \leq 0.92$, present distinct behaviour for the zero-field-cooled (ZFC) and the field-cooled (FC) samples for temperatures lower than the high temperature transition T_C. Moreover, the maximum found at intermediate temperature becames rounded with higher applied fields. The isotherms $M_g(H)$ in this range of temperature (fig. 5) present curved but without any trace of saturation for applied field up to 13kOe. We can also observe in fig. 5 that for $x = 0.90$ at low temperature a metamagnetic-like transition or wall pinning is evidenced for magnetic fields about 3kOe.

From the experimental results of the lattice parameters a_o (Ta ble 1), we can conclude that the variation of the volume available for the conduction electrons with the substitution of Fe at the Al sites is pratically null for $x \geq 0.90$. Therefore, the decreasing of the Neel temperature T_N cannot be explained by the pressure arguments (see Introduction). As the magnetic behaviour of the Kondo system, at low temperatures on the basis of the Kondo lattice model, results of the competition between the Kondo effect and RKKY interaction, and both depends on $|J\rho(E_F)|$ (J = exchange interaction, and $\rho(E_F)$ density of states at Fermi level), exponentially and quadratically respectivelly, in our case we infer that the decreasing of T_N is associated with the increase of the $\rho(E_F)$. In the CKS like $CeAl_2$, the increase of the density of state, supposing J constant, favours a non-magnetic singlet ground state, with a consequent increase of Kondo temperature T_K. We can guess that the increase of density of states $\rho(E_F)$ in the system $Ce(Fe,Al)_2$, come from the great difference between the substituted metal Al(sp) to the Fe(3d). The observed abnormal residual resistivity ρ_0 and the increase of the temperature of the minimum (T_{min}) with Fe concentration are coherent with this assumption.

The magnetic transition (T_C) that appear for $x \leq 0.92$ at a higher temperatures in the χ_g versus T curves is not very clear. In general, a magnetic transition is accompained by an anomally in resistivity (ρ) or in the derivative $d\rho/dT$. Clearly, the electrical resistivity data present qualitativelly the same behaviour of $CeAl_2$ as trivalente Ce ions, crystalline field, Kondo effect, etc. Moreover, the effective paramagnetic moments obtained from the linear part of the reciprocal susceptibility are those of a trivalente Ce ion (as for $x = 0.90$ where $\mu_{ef} = 2.53\,\mu_B$/form), in agreement with the lattice parameters results a_0. On the other hand, studies performed in the

AB_2 compounds with $MgCu_2$-type structure indicated that the magnetic percolation limite for the B-sites, localize in more higher Fe concentration that the present study. From the above observations we can infer that the most probable arrangement of the magnetic moments in this range of temperature is a parallel coupling of the 3^+ Ce-ions, assisted by the m_d moment of the Fe. Coherent with this assumption, the paramagnetic temperatures θp change from negative values ($\theta p = -33K$) for the antiferromagnetic compound $CeAl_2$ to positive ($\theta p = +40K$) for $x = 0.90$. The appearance of the Fe moments (not ordered) in this concentration range is not unique. For example, Mössbauer results performed in $Y(Fe_{0.30}Al_{0.70})_2$ reveals that magnetic Fe moments exist for this concentration [10].

Summarizing our present experimental study, we can say that the substitution of Fe at the Al site in $CeAl_2$ trend to yield a non-magnetic ground state. In addition, a new magnetic transition appear for $x \lesseqgtr 0.92$ at intermediate temperatures with some typical spin-glass-like behaviour. The nature of this magnetic ordering is not very clear and seem to be related to a tendency of ferromagnetic ordering of the Ce moments. The existence of the spurious crystalline ferromagnetic phase can be discarded as the Curie temperature (T_C) in the Fe-rich side, is relatively higher than this one. The magnetic irreversibility observed for $x \lessgtr 0.92$ is a beginning of the magnetic characteristics of the system with higher Fe concentrations [8] as spin-glass-like behaviour and pinning of magnetic domain walls. To know the reason why any effect was detected in the ρ vs. T curves at the higher temperature transitions and further informations about this system will require the extending of our studies with other experimental techniques.

FIGURE CAPTIONS

Fig. 1 - Electrical resistivity as a function of the temperature for $x = 1.00$, $x = 0.95$ e $x = 0.90$.

Fig. 2 - Magnetic resistivity as a function of the temperature.

Fig. 3 - Magnetic susceptibility as a function of temperature for ZFC e FC samples and/or different applied fields.

Fig. 4 - Low temperature dependence of the magnetic susceptibility. In the insert, the concentration dependence of the Neel temperature T_N.

Fig. 5 - Isothermal magnetization as a function of the magnetic field for various temperatures and $x = 1.00$, $x = 0.95$, $x = 0.92$ and $x = 0.90$.

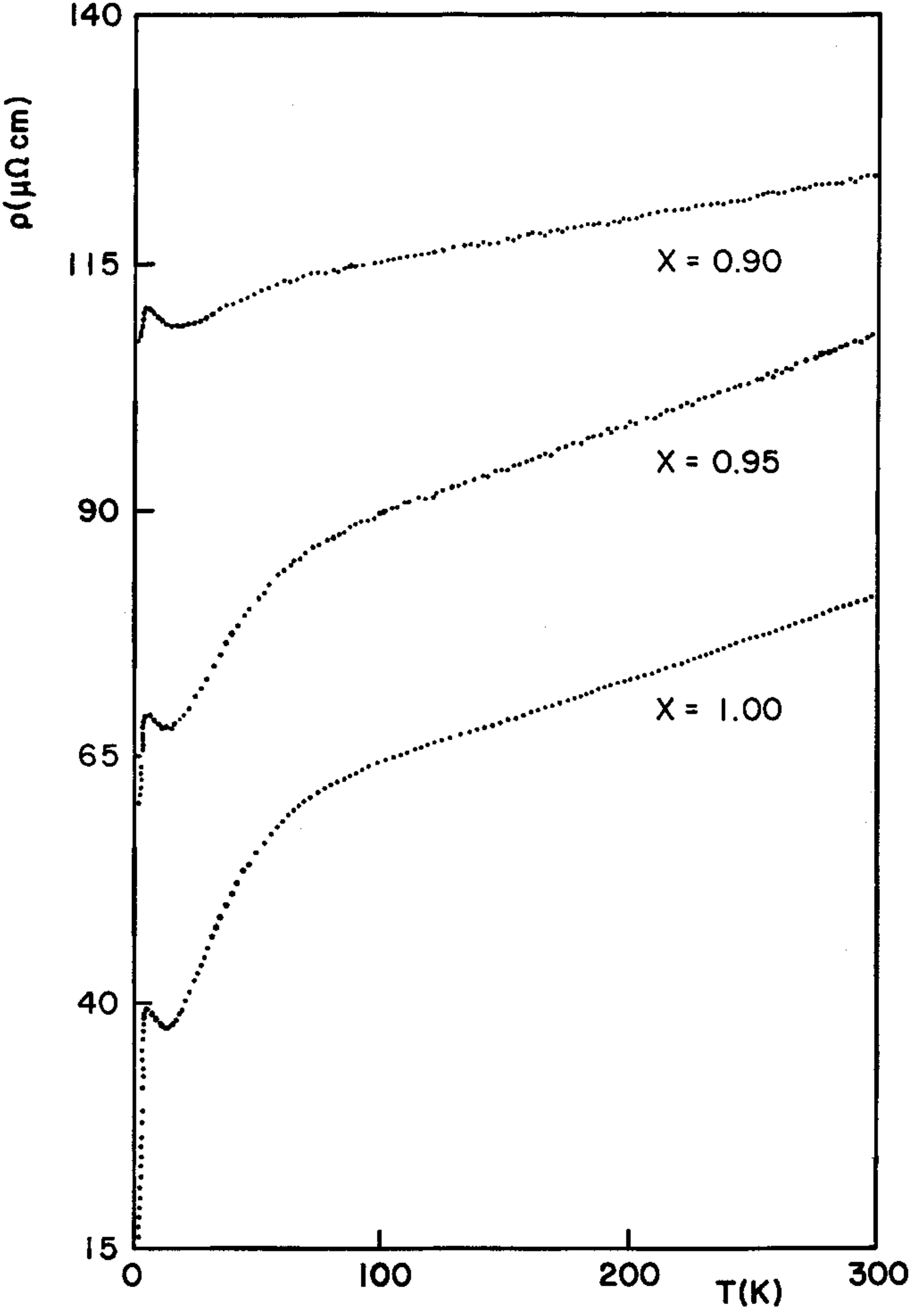

Fig. 1

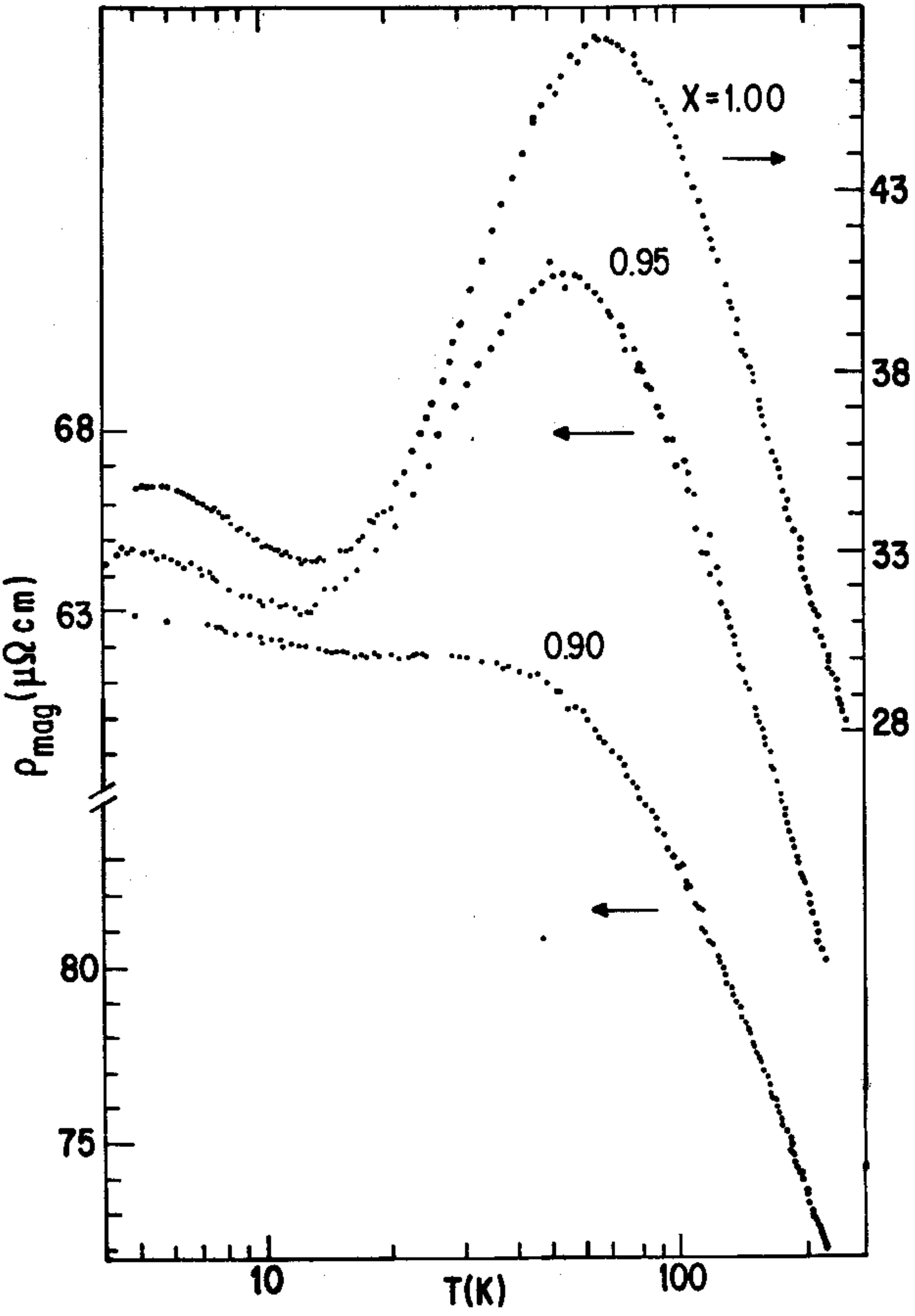

Fig. 2

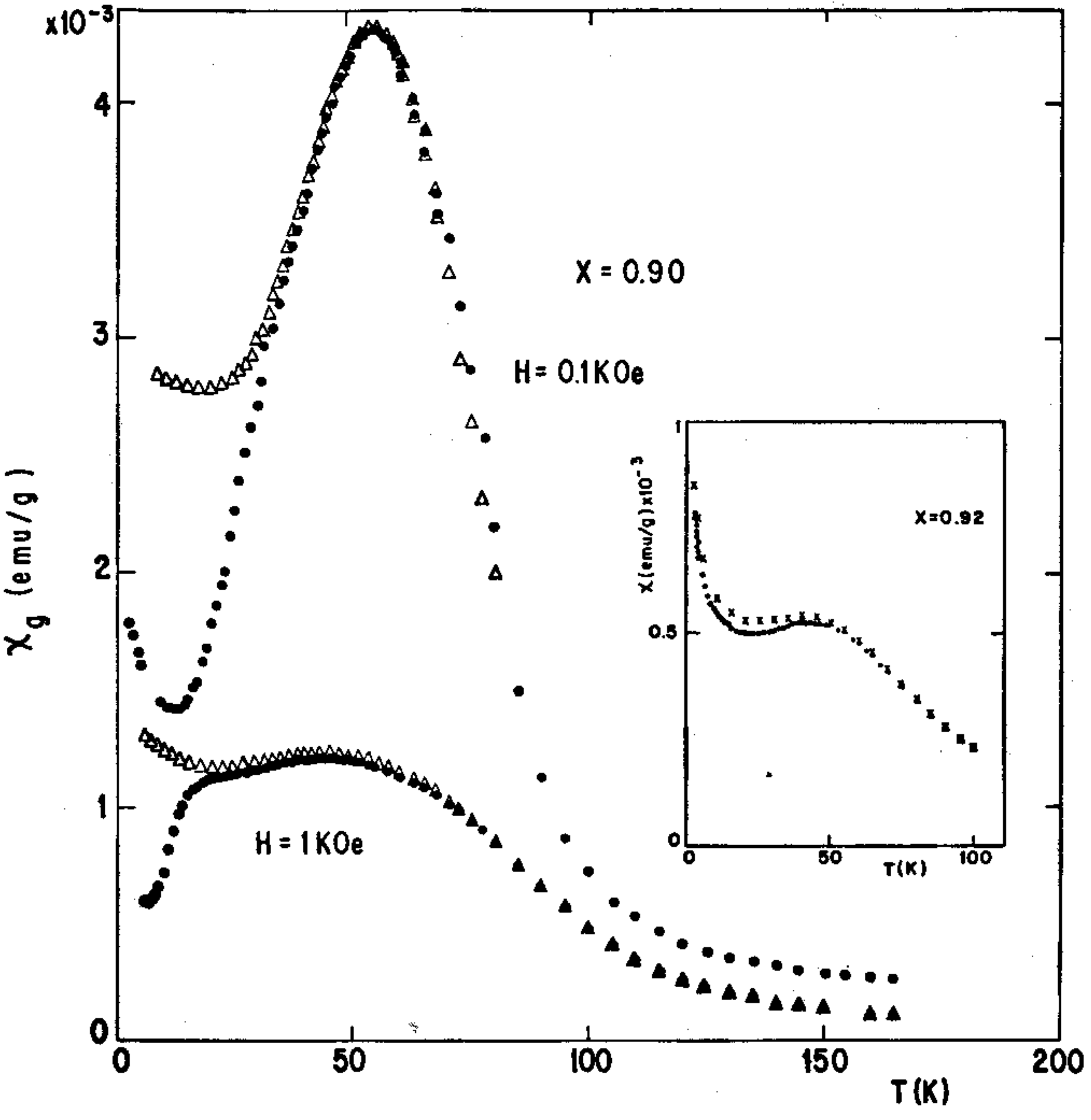
x10⁻³
4
3
2
1
0
χ_g (emu/g)
X = 0.90
H = 0.1KOe
H = 1KOe
0
50
100
150
200
T(K)
X(emu/g)x10⁻³
X=0.92
1
0.5
0
0
50
100
T(K)

Fig. 3

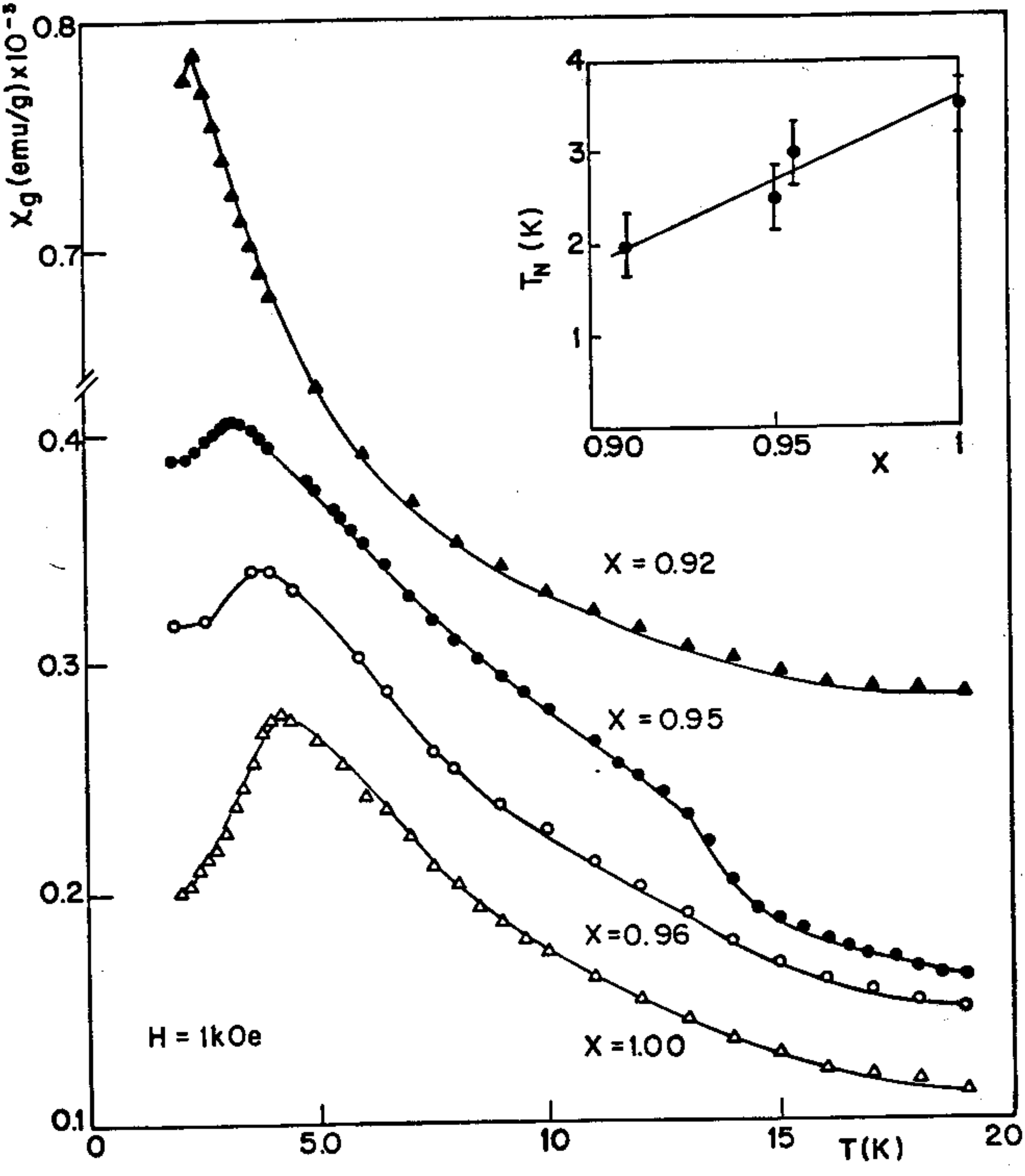
χ_g (emu/g) x 10^{-3}
0.8
0.7
0.4
0.3
0.2
0.1
0
5.0
10
15
20
T(K)
X = 0.92
X = 0.95
X = 0.96
X = 1.00
H = 1kOe
T_N (K)
4
3
2
1
0.90
0.95
1
X

Fig. 4

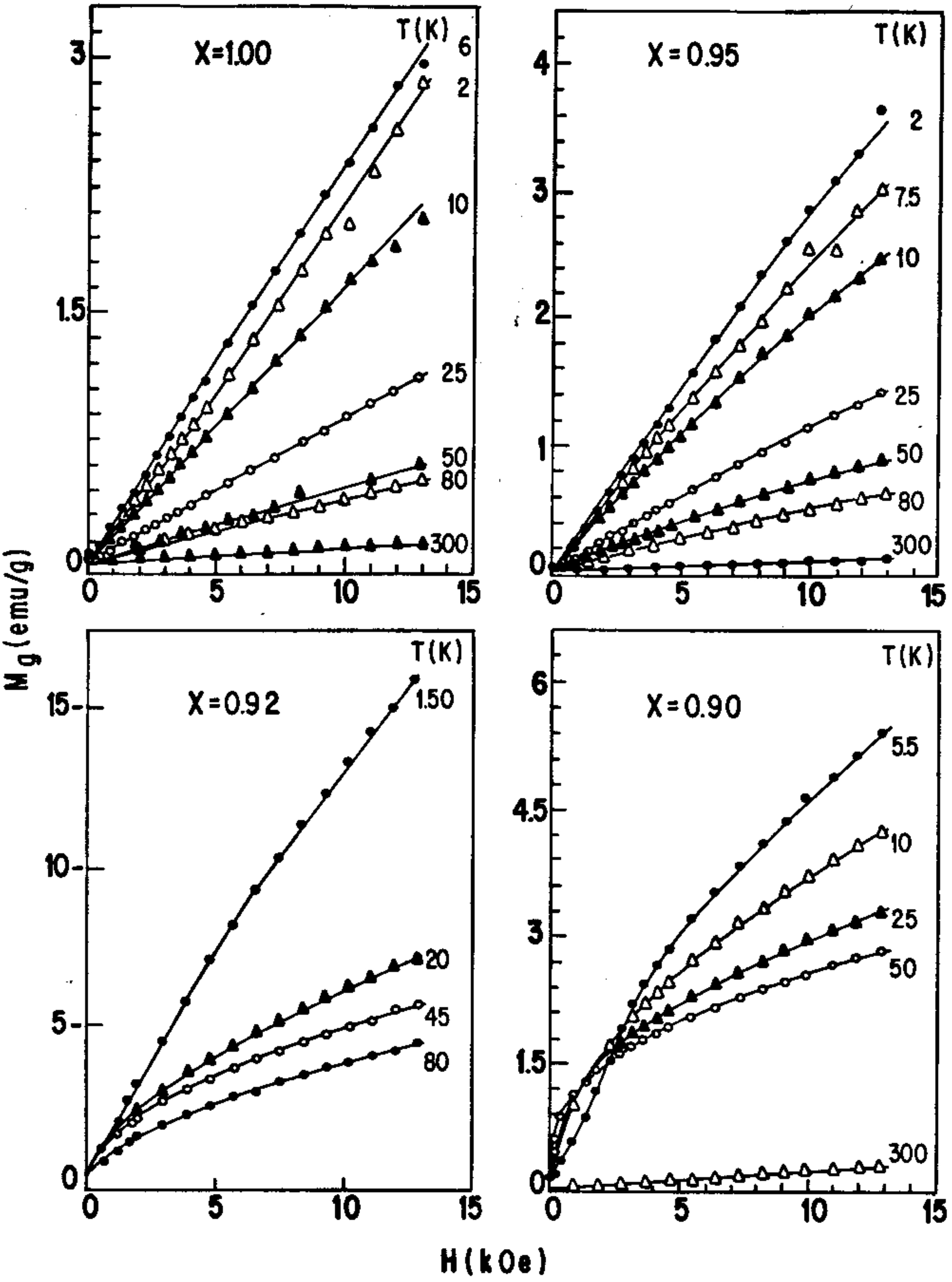
X=1.00
T(K)
6
2
10
25
50
80
300
3
1.5
0
X=0.95
T(K)
2
7.5
10
25
50
80
300
4
3
2
1
0
X=0.92
T(K)
1.50
20
45
80
15
10
5
0
X=0.90
T(K)
5.5
10
25
50
300
6
4.5
3
1.5
0
0
5
10
15
M_g (emu/g)
H(kOe)

Fig. 5

TABLE 1

x	a_o (Å)	T_N (K)	$\chi_g(T_N)$ (10^{-3} emu/g)
1.00	8.064 ± 0.006	3.5	0.28
0.96	8.055 ± 0.005	3.0	0.34
0.95	8.055 ± 0.005	2.5	0.4
0.92	8.050 ± 0.005	2.3	0.8
0.90	8.043 ± 0.007	<2	>1

T_N (T of $(d\chi/dT)_{max}$)

χ_g (T_N, H = 1kOe)

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