CBPF-NF-016/91

MAGNETIC PROPERTIES OF THE PSEUDO-BINARY INTERMETALLIC COMPOUNDS: $Hf(Fe_{1-x}Al_x)_2$

by

L.C. SAMPAIO and S.F. da CUNHA

Centro Brasileiro de Pesquisas Físicas - CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290 - Rio de Janeiro, RJ - Brasil

Abstract

From magnetization measurements in policrystalline $Hf(Fe_{1-x}Al_x)_2$ samples,it was observed that the magnetization is not saturated even at high fields (70 kOe). It is suggested that in $Hf(Fe_{1-x}Al_x)_2$, a high anisotropy energy and consequently narrow domain walls exist. Magnetization vs. temperature curves present a different behaviour if the sample is cooled with field (FC) or without (ZFC) field. This difference is applied field dependent and is a maximum in the range $0.45 < x < 0.50$. The ZFC curve is irreversible with temperature while FC is reversible. In the intermediate concentration range, the coercive field decreases rapidly with temperature. These behaviour can be explained by domain wall pinning and not by spin or cluster glass effects. In the magnetic phase diagram, (T_C vs x) two different slopes were found and T_C vanishes at $x = 0.63$, approximately. To compare the $Hf(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$ results, we performed the same measurements on a $Zr(Fe_{0.68}Al_{0.32})_2$ sample and found a similar irreversibility of ZFC magnetization which has not been detected in the literature.

Key-words: Magnetism of intermetallics; $Hf(Fe, Al)_2$; Wall motion; Time effects in magnetization; Magnetization irreversibility; Laves phase.

1- Introduction

Much work has been done in the systems $Y(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$ and very interesting magnetic properties have been observed. For instance, in $Y(Fe_{1-x}Al_x)_2$ there is a freezing phenomena which are characteristic of a cluster glass behaviour in Fe-rich side ($0.1 < x < 0.35$), so in the magnetization versus temperature measurements, the zero field cooling (ZFC) and field cooling (FC) curves are different [1,5]. On the other hand, in $Zr(Fe_{1-x}Al_x)_2$ no freezing phenomenon was observed [1,4]. In $Hf(Fe_{1-x}Al_x)_2$, the ZFC and FC curves are also different but this fact is related to another phenomenon. We have already discussed the system $Hf(Fe_{1-x}Al_x)_2$ in the intermediate concentration range in another paper to $Hf(Fe_{0.5}Al_{0.5})_2$ (6). It has been observed in $Hf(Fe_{0.5}Al_{0.5})_2$ through magnetization versus applied magnetic field measurements that the magnetization is not saturated, even in high fields (70 kOe); these measurements have suggested us that the anisotropy energy is high.

Systems with high anisotropy energy have narrow domain walls ($\delta \propto \sqrt{J/K}$, where J and K are the exchange and anisotropy constants, respectively) and in this case there is an energy difference when the center of the wall is just at an atomic plane or just between two planes (7). This energy difference ΔE is periodic with the period D (interplanar distance) and is powerful dependent with the domain wall

width δ, by $\Delta E \propto e^{-\pi(\delta/D)}$ (8). ΔE hinders the wall motion and gives rise to an intrinsic domain wall pinning. Another contribution to the domain wall pinning is the extrinsic pinning which is attributed to the impurities and to all kinds of defects. As these contributions are independent, the coercive field can be written as the sum of both contributions (9):

$$H_C(T) = H_{C,int}(T) + H_{C,ext}(T). \quad (1)$$

Therefore, systems like $Dy(Fe_{1-x}Al_x)_2$ (10), $(Dy_xY_{1-x})Al_2$ (11), $(Dy_xY_{1-x})Fe_2$ (12) and $(Tb_xGd_{1-x})Al_2$ (13) with very narrow domain walls have their magnetic properties strongly influenced by the intrinsic domain wall pinning.

In order to better understand the role of Zr and Hf isoelectronics metals in the systems $A(Fe_{1-x}Al_x)_2$, we have studied the magnetic properties of the $Hf(Fe_{1-x}Al_x)_2$ by magnetization measurements. We have compared the results of the $Hf(Fe_{1-x}Al_x)_2$ with the $A(Fe_{1-x}Al_x)_2$ (A = Y, Zr) [1,5]. For a brief comparison, we also have made magnetization measurements in $Zr(Fe_{0.68}Al_{0.32})_2$ and we have found a difference between ZFC and FC curves, which has not been observed in literature [1,4].

2 - Experimental

Polycrystalline $Hf(Fe_{1-x}Al_x)_2$ samples were prepared in an arc-melting furnace under a purified argon atmosphere in stoichiometric proportions. Hf, Fe and Al metals have the

purity (Johnson Matthey Chemicals LTD), 99.9%, 99.999% and 99.999%, respectively. $HfFe_2$ has an admixture of phases, cubic C-15 and hexagonal C-14, although the cubic phase is predominant (14). This admixture of phases remains up to x = 0.15. In order to stabilize a single phase in the range x = 0 and 0.15, we have made an annealing (800 ^{o}C, 1 week) but it was not successful. For x = 0.08, approximately, the cubic phase is almost stabilized (fig 1). However, in the range between x = 0.15 and 1.00 the hexagonal phase is stabilized, with or without annealing. The single phase was verified by x-ray diffractogram at room temperature. The lattice parameters a and c were obtained by extrapolation of the Nelson-Riley function and they increase linearly with x in good agreement with Vegard's law (15).

The magnetization measurements were made using a PAR vibrating sample magnetometer. The Curie temperature was obtained by extrapolation of the M^2 vs T to M^2 = 0 with low applied field (60 Oe) and saturation magnetic moment was obtained also by extrapolation of the M vs. 1/H to 1/H = 0 on fields up to 70 kOe.

3 - Results and Discussion

Magnetization versus temperature and applied magnetic field measurements have been made for compositions $0.15 \le x \le$

1.00 and ac susceptibility for x = 0.40 and 0.50.

Magnetization versus applied magnetic field measurements at several temperatures are shown in fig. 2. The samples were always cooled without applied field. At low temperatures, after a critical field H_p (propagation field say, a field after which the wall can move), we have observed a faster increase of the magnetization. In high fields, the magnetization increases slowly and it is not saturated even at 70 kOe, indicating a high anisotropy energy and consequently narrow domain walls. These effects are more pronounced in $0.40 \leq x \leq 0.55$. The origin of the anisotropy energy can be related to magnetocrystalline field due to the lower symmetry of the hexagonal C - 14 structure.

In the hysteresis loops, we observe a time effect in the demagnetizing region which has been attributed to the appearance of the wall deformation. See ref. (6). Due to the time effect, the coercive field is defined as the field necessary to annul the magnetization in the hysteresis loop measured with the rate of 54 Oe/s and the maximum field of 13 kOe. In fig. 3, we show the temperature dependence of the coercive field H_c for samples in the range $0.30 \leq x \leq 0.55$. For x = 0.30, there is a slow decrease of H_c while in x = 0.55 the coercive field decreases rapidly. According to eq. 1, we can qualitatively identify for x = 0.30 both

contributions; the intrinsic term at low temperature and the extrinsic term at higher temperatures. For higher Al concentration, the intrinsic contribution becomes more important, and for $x = 0.50$ and $x = 0.55$ it is dominant. The intrinsic contribution was fitted by an exponential function.

Magnetization versus temperature measurements are shown in fig 4 for $0.30 \leq x \leq 0.55$. The samples were cooled with (FC) and without (ZFC) applied magnetic field. At low temperatures in the ZFC curve, the magnetization is constant up to a characteristic temperature T_D. Above T_D the magnetization increases and decreases near $T_C/2$. On the other hand, the FC curve is always decreasing from low temperatures.

ZFC curve is irreversible with the temperature while FC curve is reversible (fig 5). When the ZFC curve is interrupted and the sample is cooled from any temperature bellow T_C, the magnetization increases and assumes different values. It is interesting to remark that the irreversibility behaviour in the ZFC curve occurs nearly up to T_C and as an example, for $x = 0.15$ the irreversibility exists even up to high temperatures, say 355 K. In $Y(Fe_{1-x}Al_x)_2$ contrary this cluster glass behaviour exists and the irreversibility remains only up to the freezing temperature T_f. This temperature is a maximum for $x = 0.20$ where $T_f = 50$ K,

approximately. The irreversibility in $Hf(Fe_{1-x}Al_x)_2$ remains almost up to T_C, say temperatures higher than in $Y(Fe_{1-x}Al_x)_2$. This fact is important and distinguishes these two systems.

To understand the irreversibility behaviour in $Hf(Fe_{1-x}Al_x)_2$, we consider the domain wall pinning by the Pierls potentials (intrinsic to narrow walls) and by all kinds of defects. In the ZFC curve at low temperatures, when the temperature increases the walls absorb thermal energy and at $T > T_D$ it can move, changing the domain configuration and the total magnetization. Inside the domains, there is another contribution which is the spontaneous magnetization. Therefore, when the sample is cooled from $T < T_C$ in the ZFC state, the domain configuration remains unchanged; only the temperature dependence of the spontaneous magnetization exists which is reversible (Fig. 5).

We have observed that the difference of magnetization in the FC and ZFC curves depends on the magnetic field applied.We defined the susceptibility difference at 4.2 K as $\Delta \equiv (M/H)_{FC}(4.2$ K$) - (M/H)_{ZFC}(4.2$ K$)$, and we found an exponential decrease with the applied field. This is shown in the fig. 6 for $x = 0.45$. In $Hf(Fe_{1-x}Al_x)_2$ compounds, it is important to measure the magnetization at low fields where pinning effects are more pronounced. Δ attains almost negligible values at 1000 Oe.

The coercive field H_C and Δ exhibit a similar Al concentration dependence with a maximum in the range $0.45 <$ $x < 0.50$ (fig. 7). This behaviour can, in principle, be envisaged as a result of a maximum inhomogeneities of exchange and anisotropy energies in the intermediate concentration region (16) and/or metallurgical heterogeneities.

The concentration dependence of the Curie temperature T_C and the saturation magnetization M_S are very similar. Both, decrease linearly with x and have two different slopes (fig. 8 and tab. 1) in the same regions. T_C vanishes at $x =$ 0.63, approximately.

From band calculations, some papers report a calculated magnetic moment at A site in AFe_2, where A = Y, Zr and Hf (17,18) and found an anti parallel moment. This moment is induced by hybridization of the 3d states on Fe atoms and the 4d or 5d states on A atoms and for $HfFe_2$ they found -0.43 u /at(18). Recently, from polarized neutron experiments, C. Ritter found $m_Y = -0.67$ μ_B and $m_{Fe} = 1.77$ μ_B (19). As there is a dilution of the Fe moment we suppose, to a first approximation that, if there is a magnetic moment on Hf atoms it is negligible and we attributed whole magnetic moment to Fe.

According to Grössinger and Hilscher [1,4], in

$Zr(Fe_{1-x}Al_x)_2$ no freezing effect was observed (For fields larger than 500 Oe). As Hf is tetravalent like Zr and also has in the Laves phase AFe_2 (A = Zr, Hf) almost the same d_{A-A} distances (20), we suggest a similar behaviour for the systems $Hf(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$. In their magnetic phase diagrams, we observe almost the same slopes in the first Al-concentration range as is illustrated in the table 1. We prepared a stoichiometric sample $Zr(Fe_{0.68}Al_{0.32})_2$, just in the range where the maximum of the magneto crystalline anisotropy occurs (3). At low fields a different behaviour in ZFC and FC curves was observed (see fig. 9) as in $Hf(Fe_{1-x}Al_x)_2$ (x > 0.15). The T_C obtained is 148 K which is in agreement to Grössinger, 146 K (2). In fig. 6 we have shown that Δ ($\Delta \equiv (M/H)_{FC}$(4.2 K) $-$ $(M/H)_{ZFC}$(4.2 K)) for $Hf(Fe_{0.55}Al_{0.45})_2$ has an exponential field decay and it is important to measure the magnetization versus temperature curves at low fields. The failure to detect difference between ZFC and FC by the other authors may be due to a rather high external applied field to measure the magnetization. Therefore, in $Zr(Fe_{1-x}Al_x)_2$ can exists, as in $Hf(Fe_{1-x}Al_x)_2$, the domain wall pinning effect.

4. Conclusion

Hf$(Fe_{1-x}Al_x)_2$ has an admixture of phases, cubic C-15 and hexagonal C-14 in the range 0 < x < 0.15, whereas in 0.15 < x < 1.00 the hexagonal phase is stabilized. For x = 0.08, approximately, the cubic phase is almost stabilized. There is no saturation of the magnetization even in high fields

(70kOe). Therefore, we suggest that a high anisotropy energy exists in $Hf(Fe_{1-x}Al_x)_2$. Consequently, the domain walls are narrow and they are pinned by Pierls potentials and all types of impurities and defects. The different behaviour in the ZFC and FC curves and the presence of the propagation field at low temperatures in the magnetization versus applied field are explained by domain wall pinning rather than by cluster glass effects which appear in $Y(Fe_{1-x}Al_x)_2$. The pronounced exponential decay of the coercive field in the intermediate concentration range $(0.40 < x < 0.55)$ indicates that the intrinsic domain wall pinning appears as the predominant contribution. The two slopes in the magnetic phase diagram may be due to the faster decrease of the anisotropy than the magnetization as x approaches x_c, which is also observed in the Zr system.

Figure Captions

Table 1- dM_S/dx and dT_C/dx for $Hf(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$.

Figure 1- Structural phase diagram for $Hf(Fe_{1-x}Al_x)_2$.

Figure 2- Magnetization vs. applied magnetic field at several temperatures.

Figure 3- Temperature dependence of the coercive field for $0.30 \leq x \leq 0.55$.

Figure 4- M/H vs. temperature in the range $0.30 \leq x \leq 0.55$, $H_{ap} = 60$ Oe.

Figure 5- M/H vs. temperature for $x = 0.45$, $H_{ap} = 60$ Oe.

Figure 6- Exponential field dependence of the $\Delta \equiv (M/H)_{FC}(4.2$ K) $- (M/H)_{ZFC}(4.2$ K).

Figure 7- Al-concentration dependence of the Δ (a) and of the coercive field H_C (b).

Figure 8- Al-concentration dependence of the T_C and M_{Fe}.

Figure 9- M/H vs. temperature for $Zr(Fe_{0.68}Al_{0.32})_2$, $H_{ap} = 60$ Oe.

Table 1

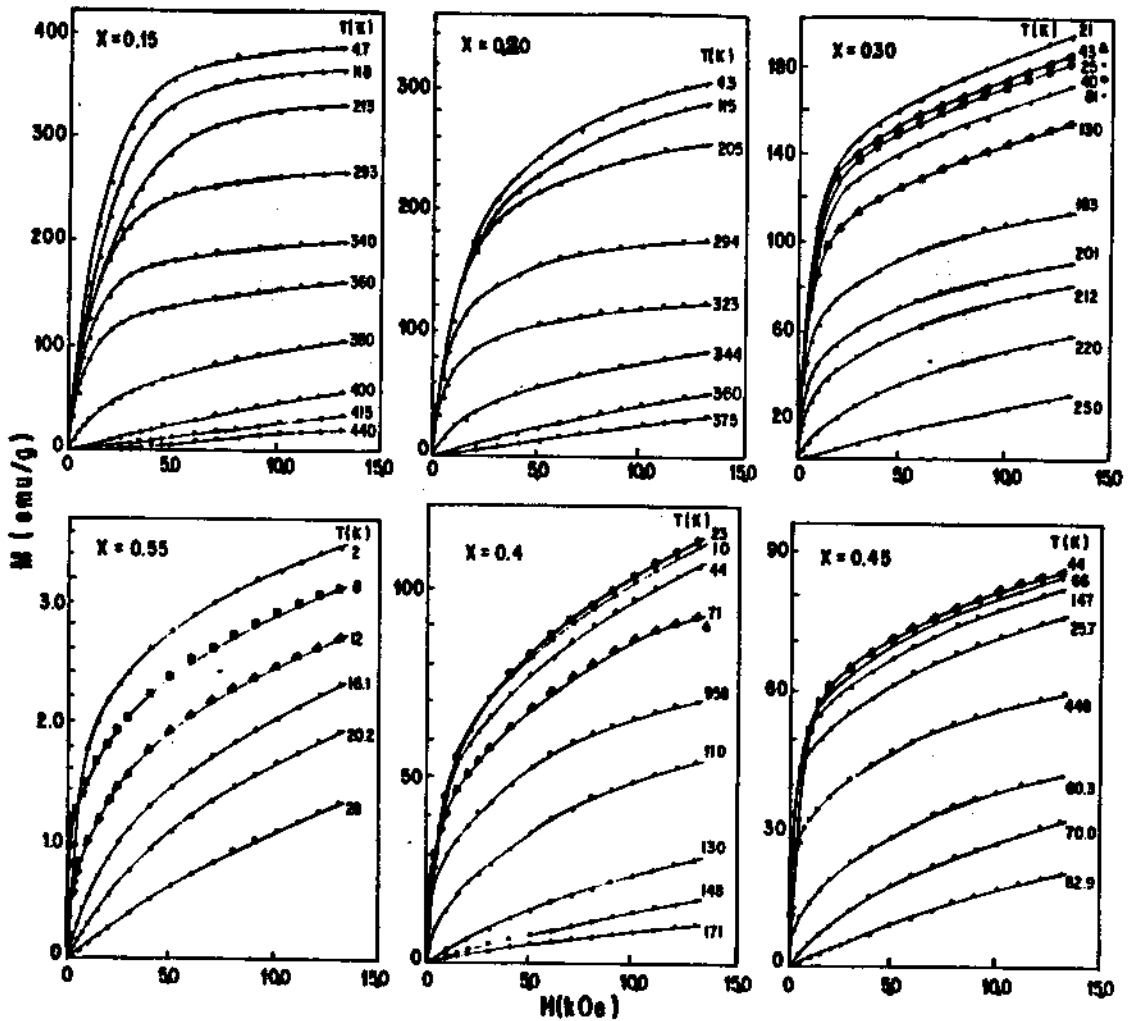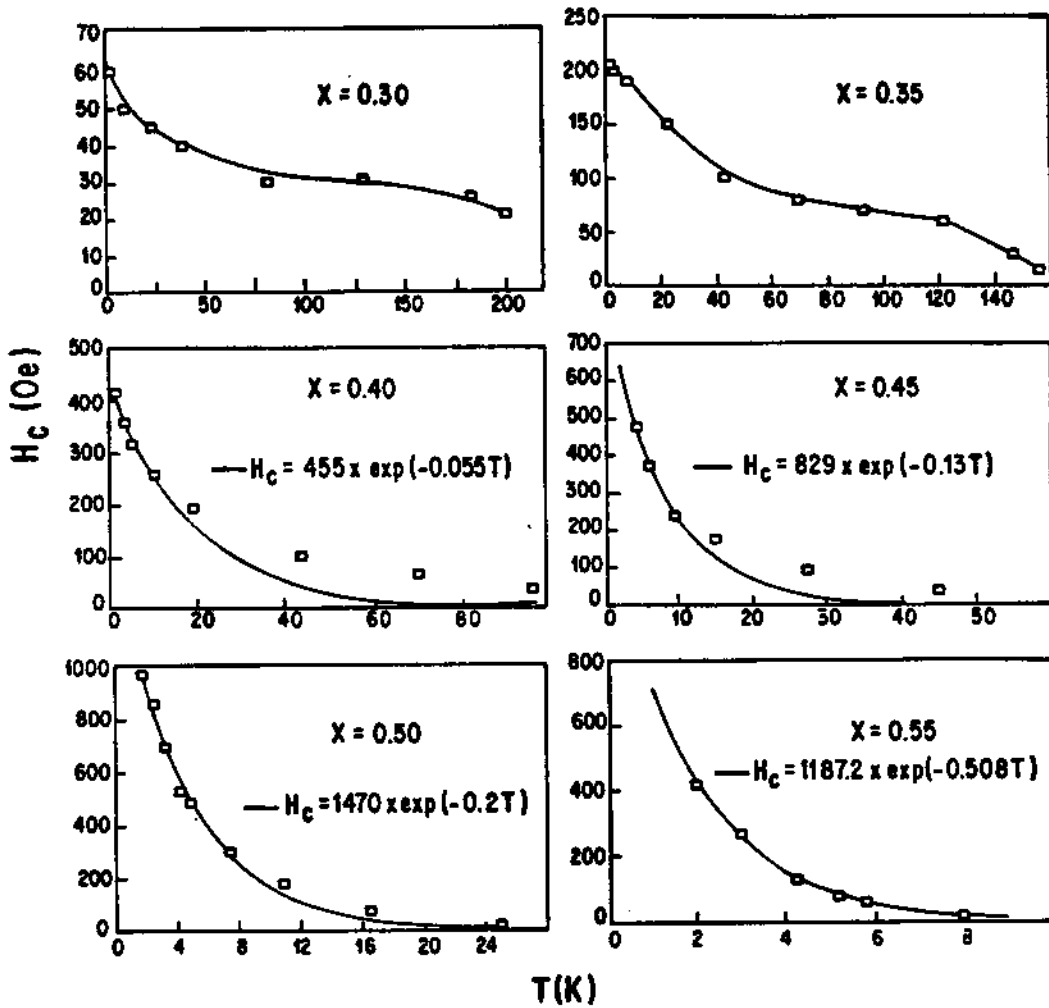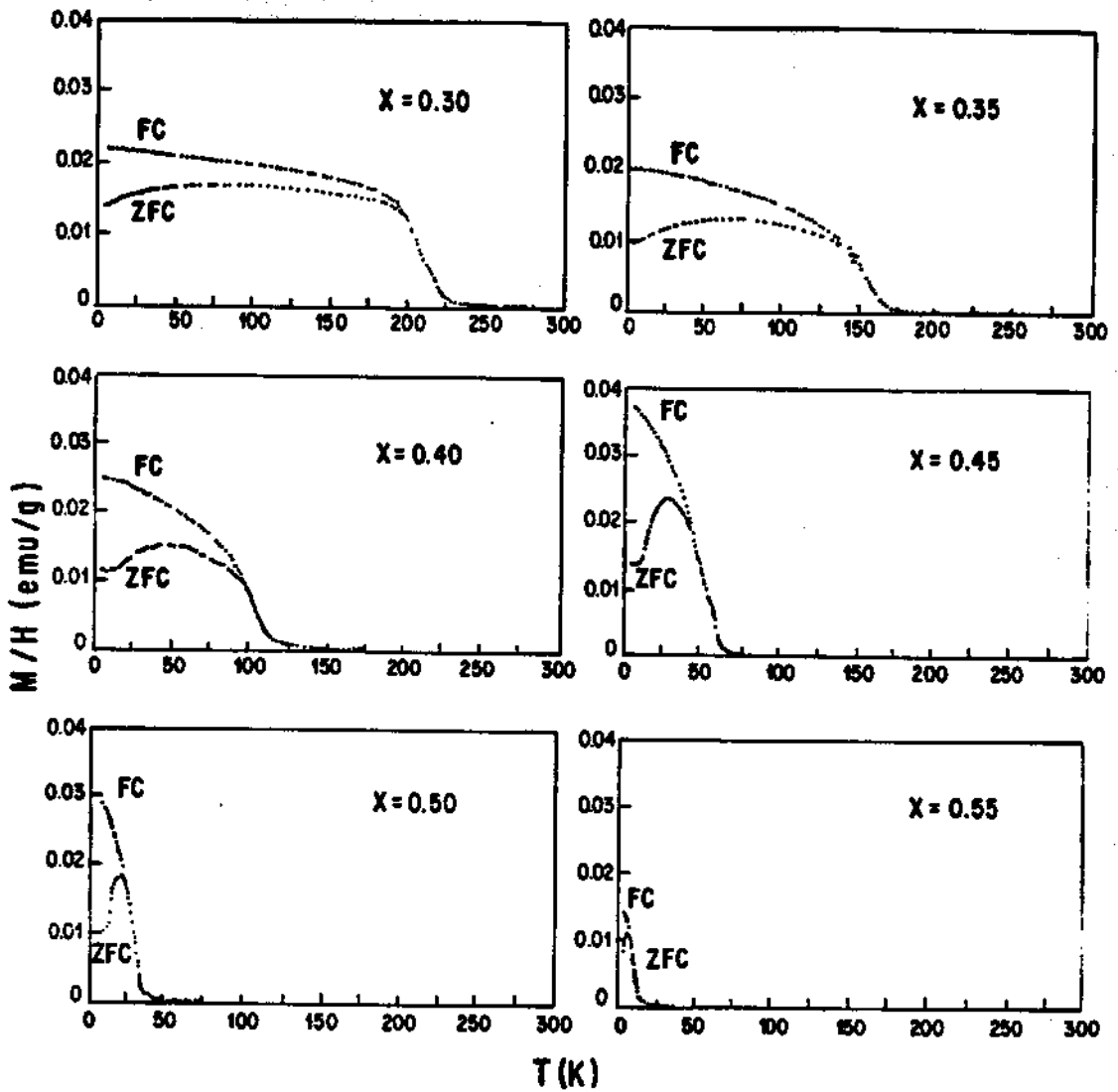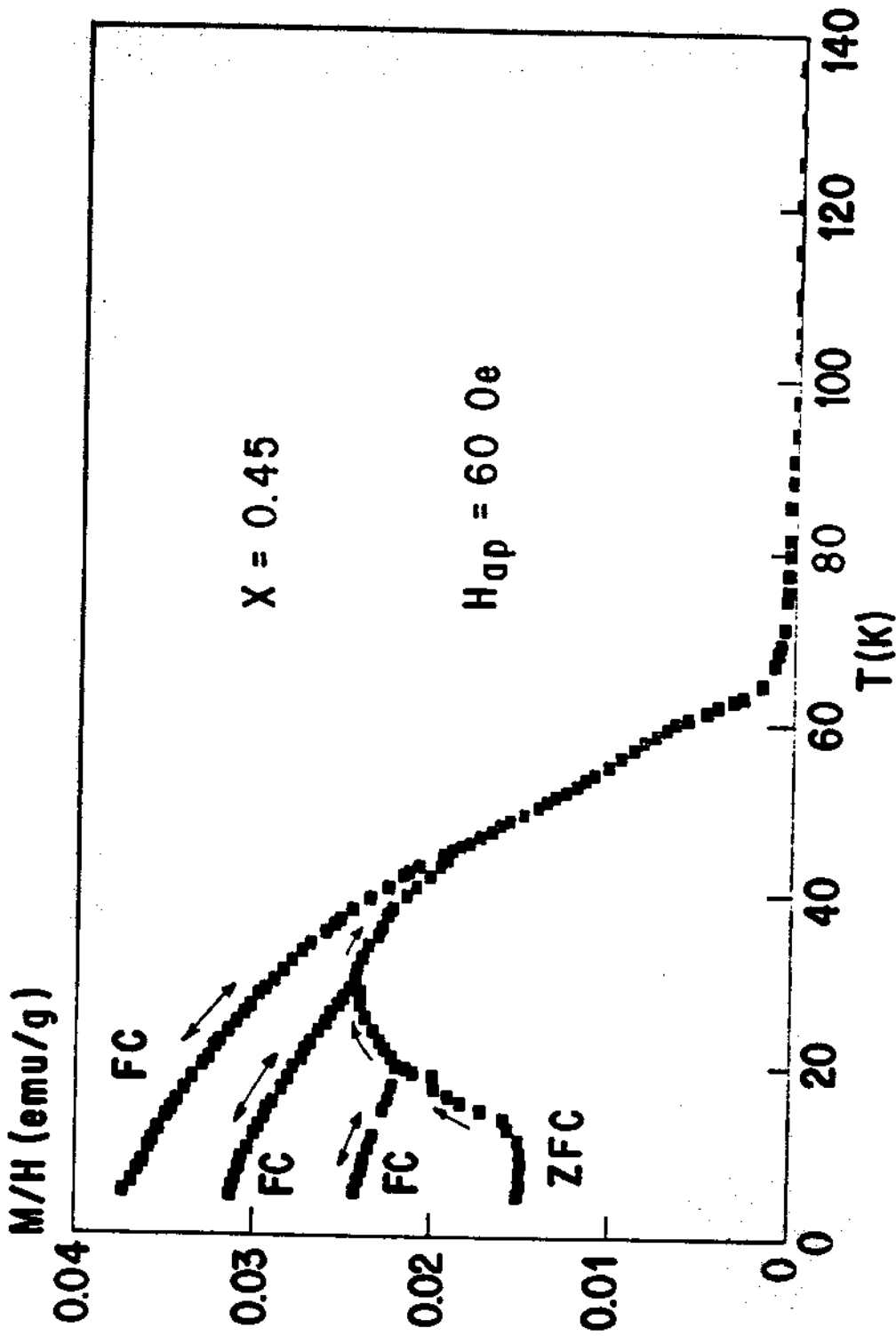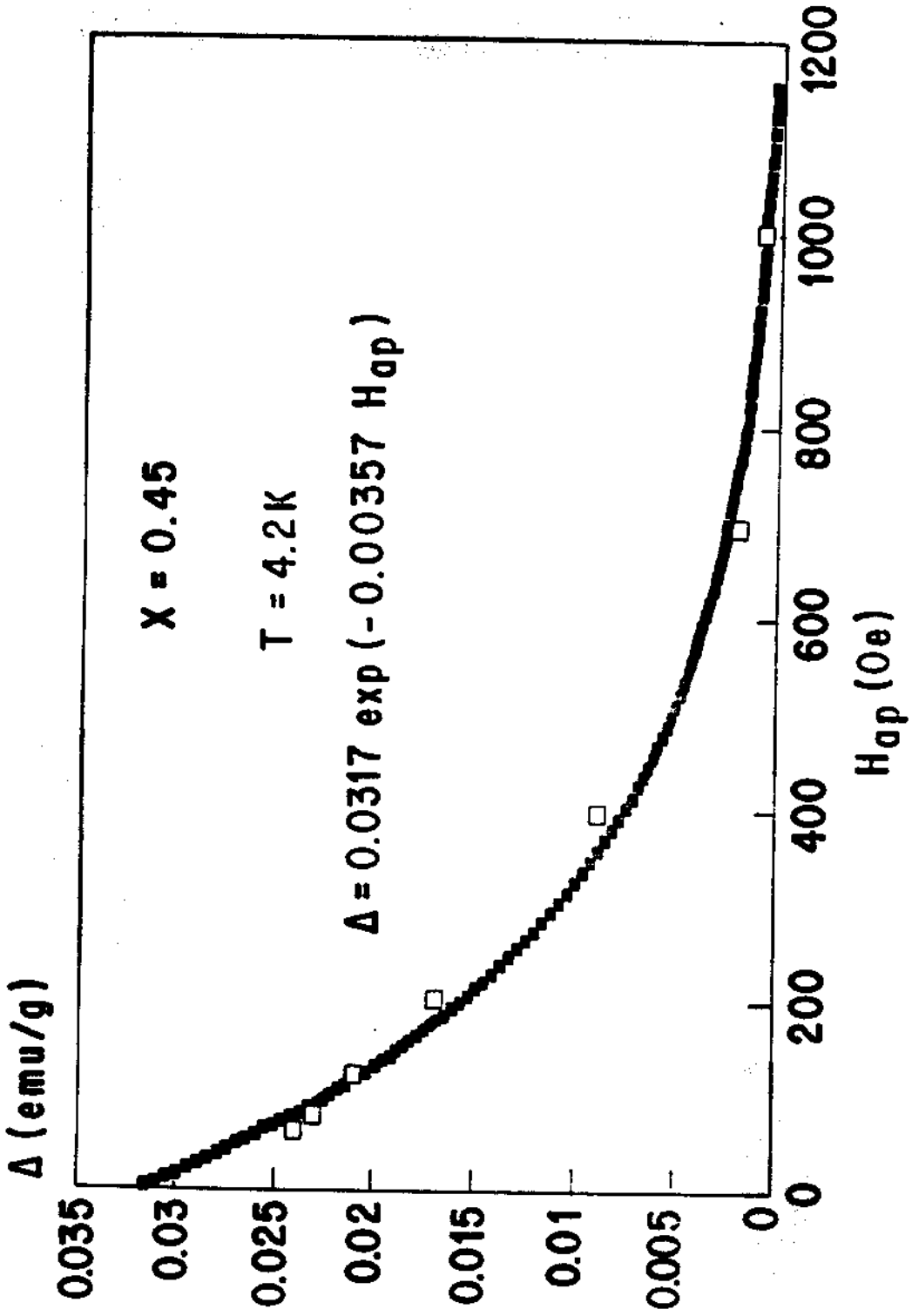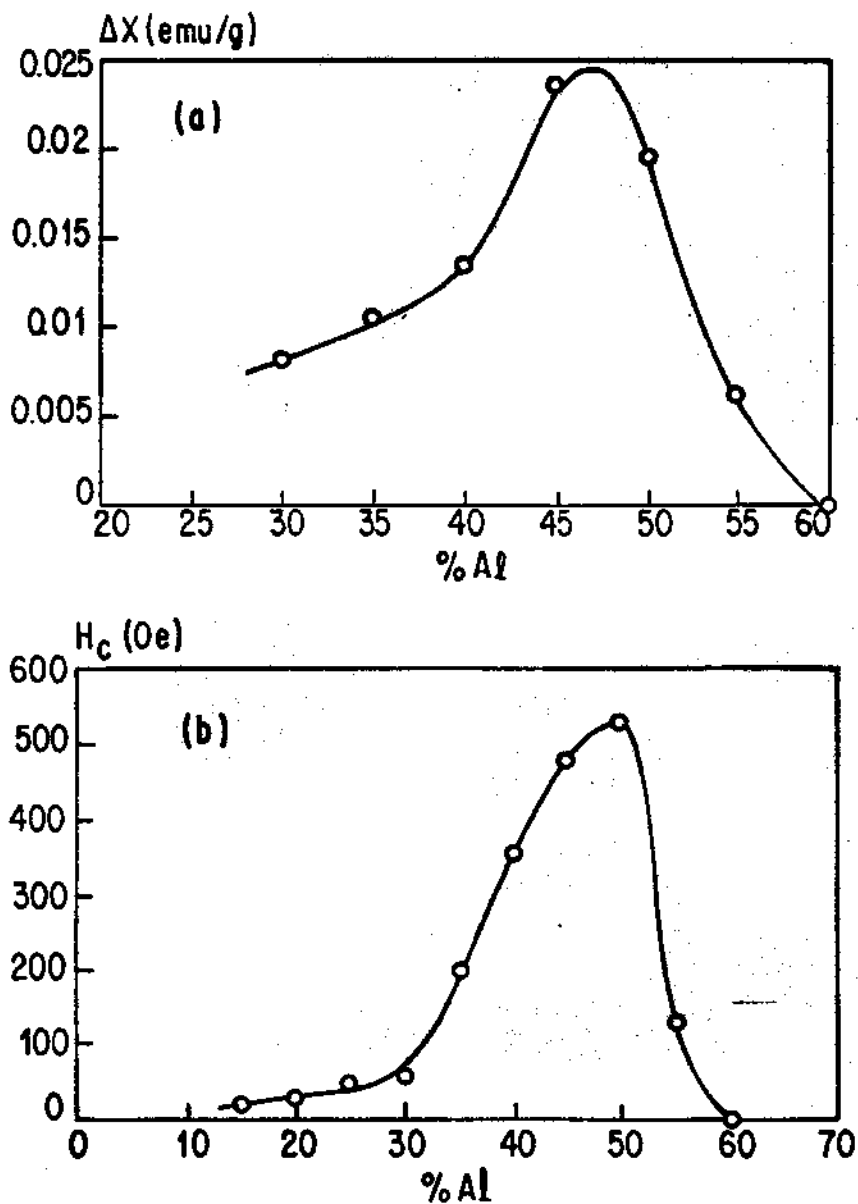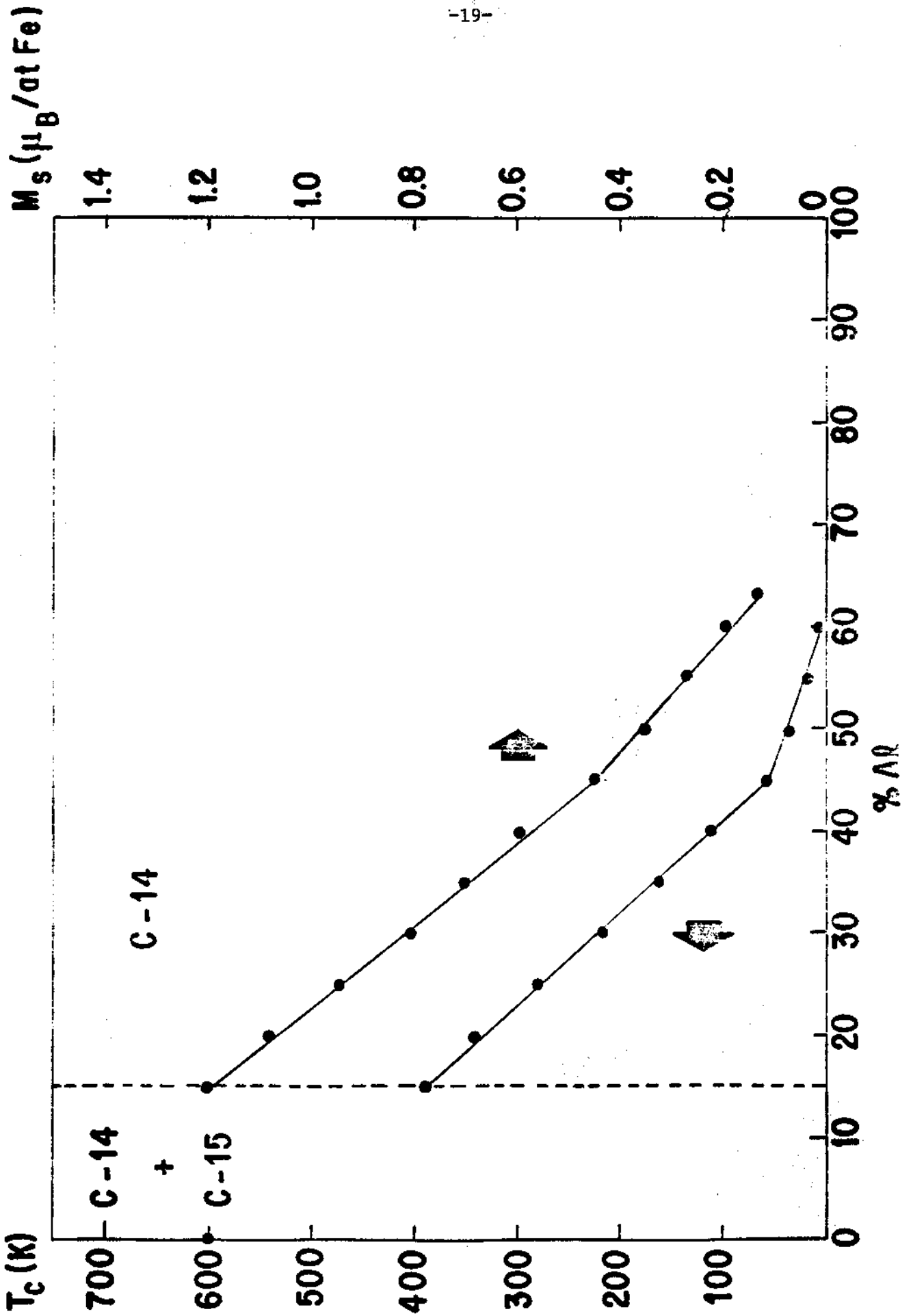|	$\dfrac{dM_S}{dx}(\mu_{B/Fe}$ at %Al$)$	$\dfrac{dT_C}{dx}(K_{/at}$ %Al$)$
Hf$(Fe_{1-x}Al_x)_2$		
I 0,15 < x < 0,45	− 0,0258	− 11,3
II 0,45 < x < 0,63	− 0,0169	− 3,5
Zr$(Fe_{1-x}Al_x)_2$ (ref.3)		
I 0,26 < x < 0,40	− 0,0264	− 11,4
II 0,40 < x < 0,55	− 0,022	− 4,6
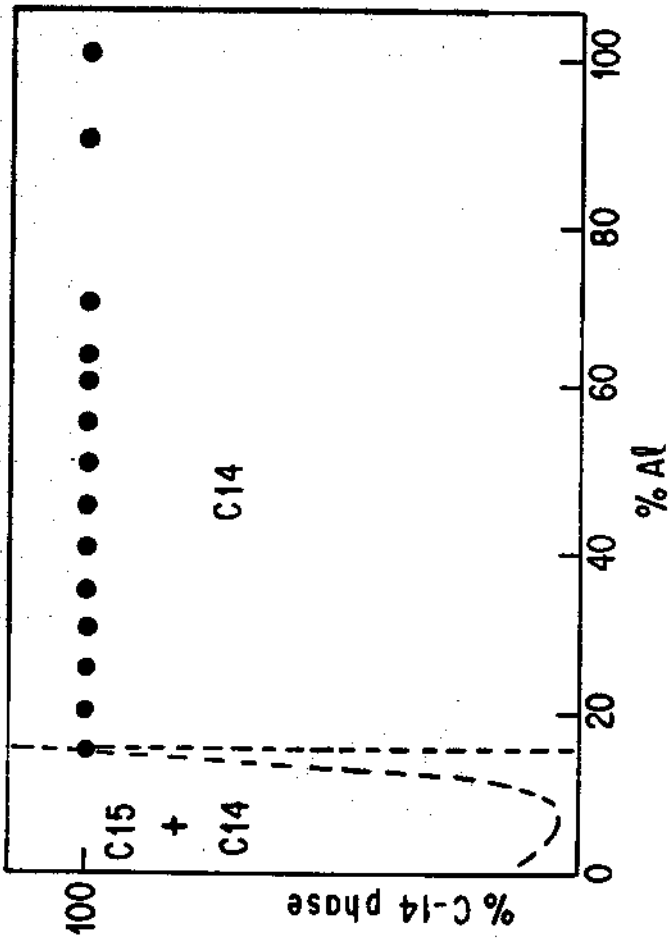
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8
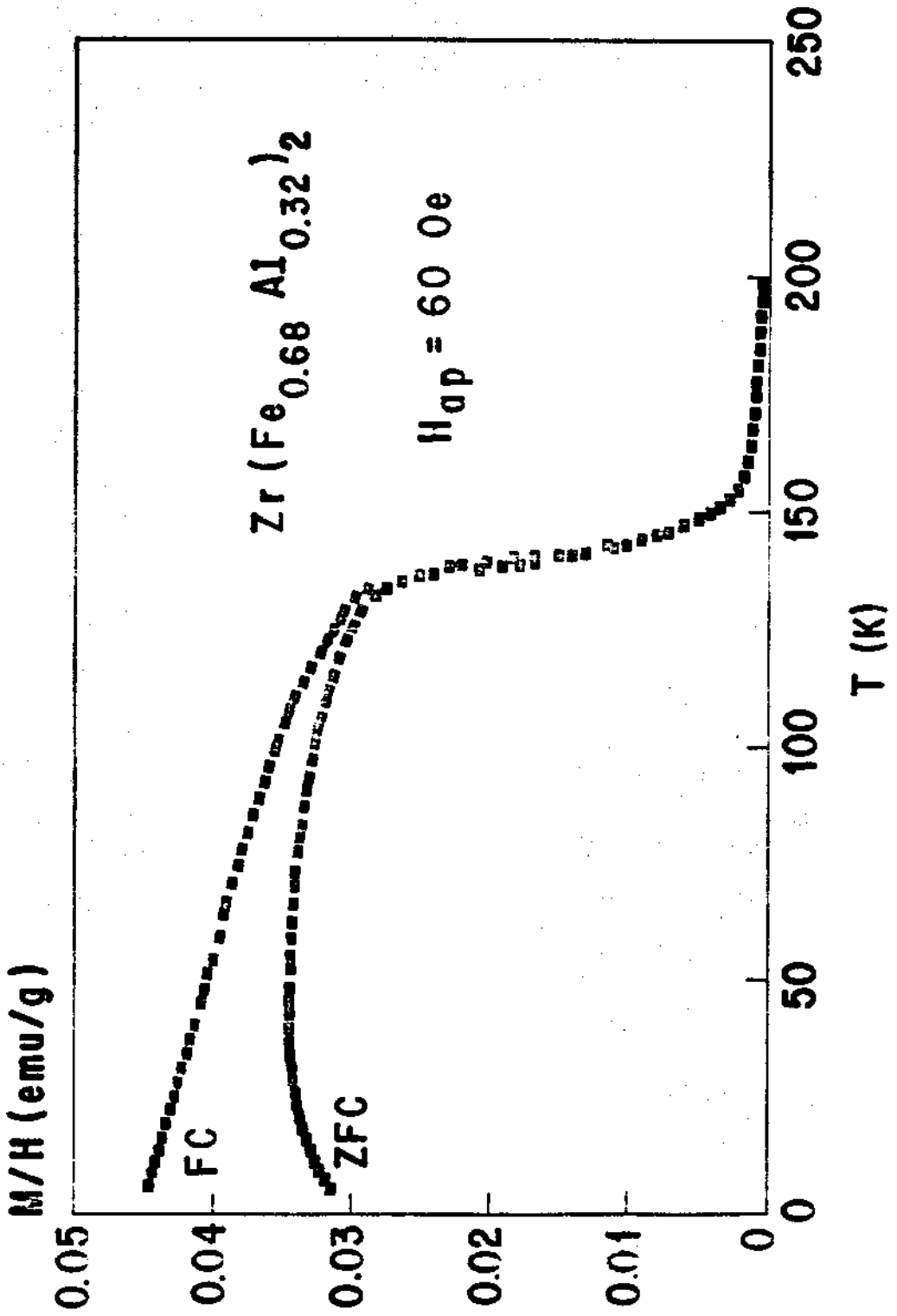
Fig. 9

References

[1] G. Hilscher, R. Grössinger, V. Sechovsky and P. Nozar

J. Phys. F : Met. Phys. 12 (1982) 1209-26

[2] G. Hilscher, R. Grössinger

J. Magn. Magn. Mat. 15 - 18 (1980) 1189

[3] R. Grössinger.G. Hilscher, and G. Wiesinger

J. Magn. Magn. Mat. 23 (1981) 47

[4] G. Hilscher

J. Magn. Magn. Mat. 27 (1982) 1

[5] S. F. da Cunha, G. P. Souza and A. Y. Takeuchi

J. Magn. Magn. Mat. 73 (1988) 355

[6] L. C. Sampaio and S. F. da Cunha

J. Magn. Magn. Mat. 88 (1990) 151

[7] J. J. Van Den Broek and H. Zijlstra

IEEE Trans. Magnetics - 7, 226 (1971)

[8] H. R. Hilzinger and H. Kronmüller

phys. stat. sol. (b) 54, 593 (1972)

phys. stat. sol. (b) 59, 71 (1973)

[9] R. Kütterer, H. R. Hilsinger and H. Kronmüller

J. Magn. Magn. Mat. 4 (1977) 1

[10] V. Sima, R. Grössinger, V. Sechovsky, and H. Sassik

J. Phys. F. : Met. Phys. 14 (1984) 981-1004

[11] J. I. Arnaudas, A. Del. Moral and J. S. Abell

J. Magn. Magn. Mat. 61 (1986) 370

[12] K. M. B. Alves, N. Alves, L. C. Sampaio and S. F. da
     Cunha and A. P. Guimaraes

     J. Appl. Phys. 67 (9), 5867

[13] J. I. Arnaudas, A. Del. Moral, P. A. Algarabel and J. S.
     Abell

     J. Magn. Magn. Mat. 61 (1986) 381

[14] F. P. Livi

     Solid State Comm. 22 (1977) 107

[15] L. C. Sampaio

     Thesis - CBPF/CNPq (1990)

[16] D. J. Craik and E. Hill

     Phys. Letters 48A, 3 (1974) 157

     D. J. Craik, E. Hill and A. J. Harrison

     IEEE Trans. on Magn, Magn-11, 55 (1975)

[17] P. Mohn and K. Schwarz

     Physica 130B (1985) 26-28

[18] H. Yamada and M. Shimizu

     J. Phys. F : Met. Phys. 16 (1986) 1039-1050

[19] C. Ritter

     J. Phys.: Condens. Matter 1 (1989) 2765

[20] K. Kai and T. Nakamichi

     J. Phys. Soc. Japan 30 (1971) 1755