

MAGNETIC CHARACTER OF SOME
RARE-EARTH SOLID SOLUTION ALLOYS

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by

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TO MY PARENTS

ABSTRACT

The magnetic character of some rare-earth solid solution alloys have been studied by electrical resistivity, low-field susceptibility and higher fields susceptibility measurements.

The four-probe potentiometric technique and the mutual inductance method were used for the resistance and low-field susceptibility measurements, respectively. The latter has constituted a very sensitive way of investigating magnetic phase diagrams. A Faraday susceptibility balance apparatus using an electromagnet, was modified in order to employ a superconducting solenoid magnet, providing fields up to 5 Tesla.

A number of *Pr-Y* alloys have been investigated. These alloys go through the structure sequence *dhcp*→*Sm*-type→*hcp* by adding *Y* into *Pr*. Susceptibility measurements show clearly that *Y* perturbs the singlet character of *Pr* and magnetic ordering takes place. The effects of field cooling and the behaviour of the resistivity have been used to provide evidence for the nature of the magnetic ordering. In the alloys with *hcp* structure, long range magnetic ordering seems to occur; and, a correlation between the de Gennes factor $\xi = x(g_J - 1)^2 J(J+1)$ and the temperature of the peak susceptibility is found, x being the concentration of *Pr* in *Y*.

Characteristics of spin glass freezing are observed in alloys with *dhcp* and *Sm*-type structures. For the *Pr*-50% *Y* alloy, in the *Sm*-type structure, remanent magnetization appears after cooling in a magnetic field. The crystalline sequence was drawn with help of susceptibility measurements and X-ray diffraction patterns.

Alloys of *Pr* with low and moderate *Sm* concentration have also been studied. Some of these alloys show a rather sharp peak in the low-field susceptibility measurements, in contrast with the smooth behaviour of the resistivity measurements. Tentative explanations are given.

So far, there is little information in the literature about dilute *Sm*-rare earth alloys. Attempts to understand the magnetic character of *Sm* alloys, with *Pr*, *Nd* and *Gd* as solutes, have been made. For these three kinds of alloys, susceptibility measurements manifest very different behaviour. In *Sm*-2%, 5%, 10% *Gd* alloys, a sharp peak in low-field susceptibility is observed. Magnetization measurements were also made on *Sm-Nd* and *Sm-Gd*.

A computing program using cubic spline function has been used to evaluate the temperature derivative of the resistivity.

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INTRODUCTION

There has been great interest in the peculiar magnetic properties displayed by the rare earth metals and their alloys. Extensive studies have been performed on *hcp*-heavy rare earth alloys. However, little is known about the magnetic structures and ordering temperatures in light rare earth alloys in the *dhcp* or *Sm*-type structures. There has been a comprehensive study of *Y*-heavy rare earth alloys, while only *Y-Nd* alloys, in the *hcp* structure have been investigated (except for some neutron diffraction work of *Y-Pr*). Studies of *Y-Pr* and *Y-Sm* are clearly needed. It is also interesting to observe the magnetic properties in alloys where *Pr* is the *hcp* host, since its singlet ground state character requires a finite concentration of magnetic solute before long-range ordering is obtained.

In this work a systematic study of the magnetic and structural properties of the *Pr-Y* system in the *dhcp*, *Sm*-type and *hcp* structures is carried out. Preliminary investigations have been made on some *Pr-Sm* alloys in the *dhcp* structure, which were complicated by the presence of *fcc-Pr* structure.

Little work has been performed in alloys with *Sm*, because of its complicated structural behaviour. Within the *hcp* structure, only *Gd-Sm* and *Tb-Sm* alloys have been investigated. For alloys in the *Sm*-type structure the appropriate non-magnetic host would be a *La-Y* alloy in the *Sm*-type structure, but careful metallurgical work would be needed. It is of interest to study

the changes in magnetic ordering within the Sm -type structure in both Sm -light rare earth and Sm -heavy rare earth alloys, although the extent of the phase may be rather limited. In this work some Sm based alloys are studied, where Gd is taken as the heavy rare earth solute, and Pr (non-Kramer's ion) and Nd (Kramer's ion) as the light rare earth solutes.

CHAPTER 1

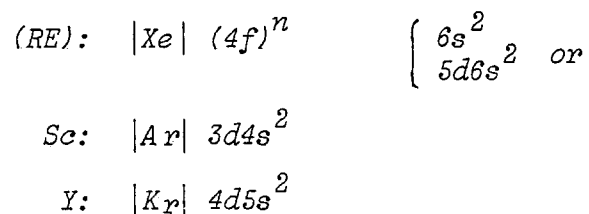
1. Rare earth elements and their alloys

This chapter will give a general account of some of the physical properties of the rare earth elements, which comprise the elements from *La* to *Lu* in the periodic table, and are characterized by the gradual filling of the *4f* shell. In discussing the rare-earths, we must also include the non-magnetic elements *Sc* and *Y*; their ionic and structural behaviour has made them ideal diluents.

In the Table 1.1 we summarise some of the properties that we will make reference to many times throughout this thesis.

1.1 Ionic properties

The electrons in the rare-earths elements are in the inert gas Xenon structure, except for the *4f* electrons and the *6s*² or *5d6s*² electrons. Similarly, for *Sc* and *Y*, but with no *4f* electrons; their deeper closed shells are in the Argon and Krypton structures respectively, plus one *d*-electron and two *s*-electrons. Hence, their electronic configurations may be written as follows:



In metals and compounds, they are usually triply ionized (see Table 1.1) and the *4f* electrons of the rare-earths ions, which

TABLE 1.1

Ionic and structural properties of the rare earth elements

Z	Element	R^{3+} $4f^n$	Ground State	S	L	J	g_J	$(g_J - 1)^2 J(J+1)$	p^2	p_{exp}^2
21	Sc	0	$1S_0$	0	0	0	0	0	0	0
39	Y	0	$1S_0$	0	0	0	0	0	0	0
57	La	0	$1S_0$	0	0	0	0	0	0	0
58	Ce	1	$2F_{5/2}$	1/2	3	5/2	6/7	0.18	6.43	6
59	Pr	2	$3H_4$	1	5	4	4/5	0.80	12.8	12
60	Nd	3	$4I_{9/2}$	3/2	6	9/2	8/11	1.84	13.1	12
61	Pm	4	$5I_4$	2	6	4	3/5	3.20	7.2	-
62	Sm	5	$6H_{5/2}$	5/2	5	5/2	2/7	4.46	0.71(2.5)	2.4
63	Eu	6	$7F_0$	3	3	0	0	0	0(12)	12.6
64	Gd	7	$8S_{7/2}$	7/2	0	7/2	2	15.75	63	63
65	Tb	8	$7F_6$	3	3	6	3/2	10.50	94.5	92
66	Dy	9	$6H_{15/2}$	5/2	5	15/2	4/3	7.08	113	110
67	Ho	10	$5I_8$	2	6	8	5/4	4.50	112	110
68	Er	11	$4I_{15/2}$	3/2	6	15/2	6/5	2.55	92	90
69	Tm	12	$3H_6$	1	5	6	7/6	1.17	57	52
70	Yb	13	$2F_{7/2}$	1/2	3	7/2	8/7	0.32	20.6	19
71	Lu	14	$1S_0$	0	0	0	0	0	0	0

cont...

Element	Struc. 25°C	a(Å)	c(Å)	c/a*
Sc	hcp	3.309	5.268	1.592
Y	hcp	3.650	5.741	1.573
La	dhcp	3.772	12.144	1.610
Ce	fcc	5.16		
Pr	dhcp	3.672	11.833	1.611
Nd	dhcp	3.659	11.799	1.612
Pm	-	-	-	-
Sm	rhomb	3.626	26.18	1.605
Eu	bcc	4.580		
Gd	hcp	3.634	5.781	1.591
Tb	hcp	3.604	5.698	1.581
Dy	hcp	3.593	5.655	1.574
Ho	hcp	3.578	5.626	1.572
Er	hcp	3.560	5.595	1.572
Tm	hcp	3.537	5.558	1.571
Yb	fcc	5.483		
Lu	hcp	3.505	5.553	1.584

* In case of dhcp and Sm structures c/2a and c/4.5a is given

determine the electronic states of interest, are shielded from their surroundings by the $5s$ and $5p$ electrons.

Fig. 1.1 shows the radial charge density for the $4f, 5s$, $5p$ and $6s$ electrons of Gd^{3+} which clearly demonstrates that the $4f$ electrons are deep inside the ion. Therefore, the magnetic moments are highly localized and the influence of the neighbours will not be through the direct overlapping of their charge density, but through other interactions; predominantly the indirect-type exchange interaction and the crystal-field interactions.

The ground states of the rare-earths are determined by Hund's rules. The spin and orbital angular momentum of the individual $4f$ electrons combine to give maximum total spin S and maximum orbital angular momentum L , for that S (see Table 1.1). Furthermore, the spin-orbit interaction for the $4f$ electrons is larger than other interactions. This makes J a good quantum number. For the light rare-earths, L and S combine to give $J = L - S$ and for the heavy rare-earths $J = L + S$ (see Table 1.1)

Paramagnetism of free ions

The magnetic moment of an ion in a state defined by J_i is given by $g_{J_i} \mu_B J_i$, where g_{J_i} is the Landé factor and μ_B is the Bohr magneton. The presence of a magnetic field along z -axis lifts the $(2J_i + 1)$ degeneracy of this level. Using the Maxwell-Boltzman statistics, the susceptibility of N ions can be calculated from

$$\chi = - \frac{N}{H} \frac{\sum_i \frac{\partial E_i}{\partial H} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \quad \dots (1.1)$$

where E_i is the magnetic energy of the particular i^{th} state

$$E_i = \langle -g_i \mu_B J_{iz} H \rangle \quad \dots (1.2)$$

and the brackets represent the mean value.

For most of the rare-earths, the energy difference between the ground state and any excited state is greater than kT at room temperature. The probability of an ion of being in an excited state is negligible. Hence, in first approximation

$$E_J = \langle J M_J | -g_J \mu_B J_z H | J M_J \rangle \quad \dots (1.3)$$

where J defines the ground state with M_J splittings.

Substituting (1.3) in (1.1), it is found that the paramagnetic susceptibility is

$$\chi = \frac{N g_J^2 \mu_B^2 J(J+1)}{3kT} = \frac{N \mu_B^2 p^2}{3k_B T} \quad \dots (1.4)$$

$$p^2 \equiv g_J^2 J(J+1) \quad \dots (1.5)$$

a result in accord with the Curie law describing the experimentally observed dependence on $1/T$.

Observing Table 1.1, we can see that p deduced from experiments shows very good agreement with p calculated from expression (1.5).

The only exceptions are Sm^{3+} and Eu^{2+} where higher energy levels contribute to χ and a second order approximation must be used. The magnetic energy of the ion to the order H^2 is

$$E_H = -\mu_{zi}H - \sum_n \frac{2|\mu_{ni}|^2 H^2}{E_n - E_i} \quad .. (1.6)$$

where

$$\mu_{ni} \equiv \langle J_n M_{J_n} | g_{J_i} \mu_B J_z | J_i M_{J_i} \rangle \quad .. (1.7)$$

The second term in (1.6) accounts for the admixture of different J states induced by the magnetic field. Replacing (1.6) into (1.1), gives a complicated temperature dependence expression for the susceptibility and we shall not give details, but quote the result deduced by Van-Vleck (1932),

$$\chi = N \frac{\sum_J \left[g_J^2 \mu_B^2 J(J+1)/3kT + \alpha_J \right] (2J+1) e^{-E_J/kT}}{\sum_J (2J+1) e^{-E_J/kT}} \quad .. (1.8)$$

where α_J is the Van-Vleck temperature-independent term. This result agrees with the experimental susceptibilities for Sm^{3+} and Eu^{2+} , see Table 1.1.

1.2 Structural behaviour in metals and alloys

The crystalline structures of all the elements (except Eu) are of close-packed nature, and may be described in terms of stacking sequences involving three types of layer. Fig. 1.2 shows the four structures observed in the metals, with the three different close-packed layers defined as A , B and C .

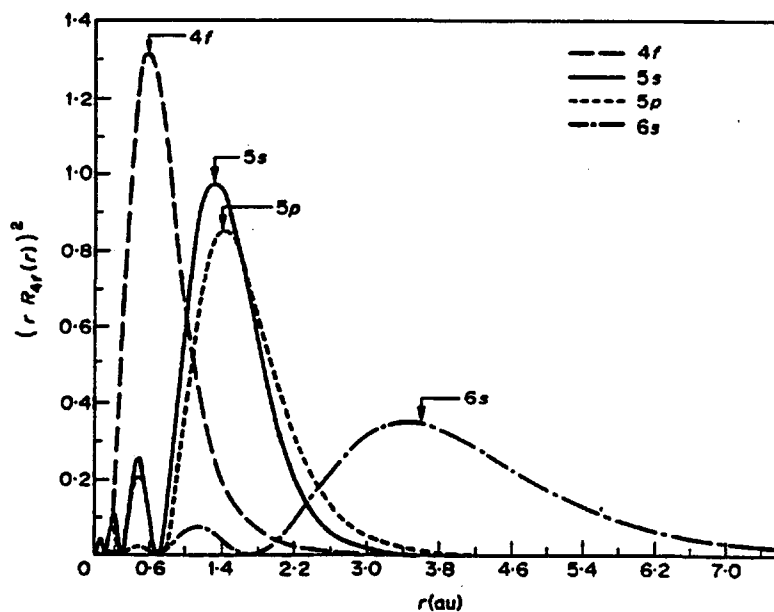


Fig.1.1: The radial charge densities for the 4f, 5s, 5p and 6s electrons of Gd^{3+} (after Freeman and Watson 1962).

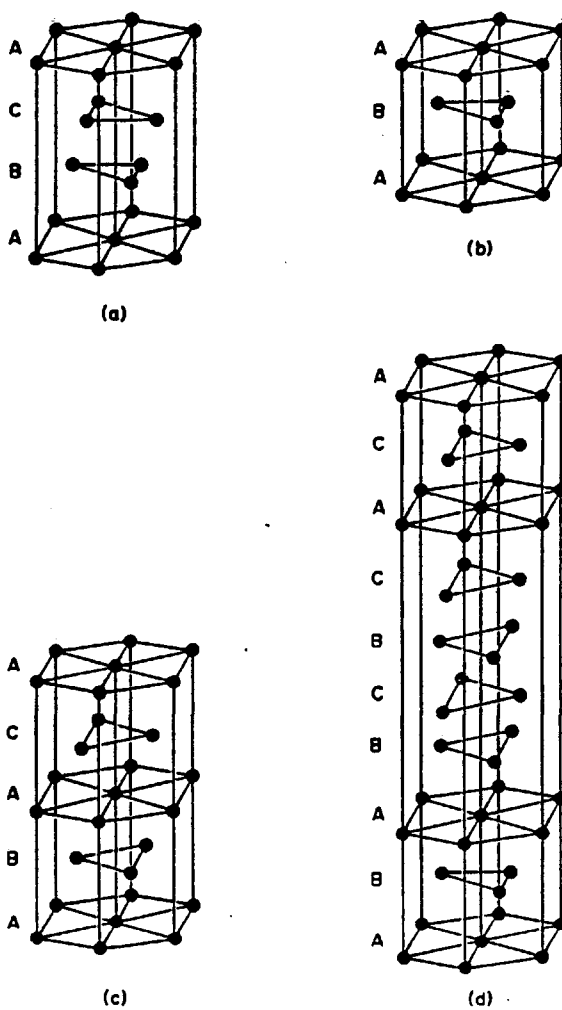


Fig.1.2: The four close-packed structures observed for the rare earth metals: (a) fcc (b) hcp (c) dhcp (d) Sm-type.

At room temperatures, heavy rare-earths, excepting *Yb*, together with *Y* and *Sc*, have the hexagonal close-packed structure with a c/a ratio smaller than the ideal value of 1.633. On the other hand, light rare-earths such as *La, Pr, Nd* have the double-hexagonal close-packed structure. However, they can also exist in the face-centered cubic form with the same atomic volume. For example *fcc-La* is stable from 310°C to 861°C and *fcc* forms of *Pr, Nd* are metastable structures that can be made by quenching from high temperatures.

Sm has a rhombohedral structure which is peculiar to this element and it is usually described in terms of a non-primitive hexagonal unit cell with a c -axis four and a half times that of the *hcp* structure, Fig. 1.2d.

Ce crystallizes in the *fcc* structure at room temperature, but it is more complex and may exist in several allotropic forms. *Eu* and *Yb* are atypical members of the series. They are divalent in the metallic state and consequently their ionic diameters are greater than the rest of the series. *Eu* crystallizes in the body-centered structure and *Yb* in the *fcc* form found in *La*. A review of the structural properties of rare-earth metals is given by Taylor and Darby 1972.

In Table 1:1 are quoted the c/a ratios for the room temperature structures.

One of the most remarkable features in the structural behaviour of the rare-earths metals is that the sequence $hcp \rightarrow \textit{Sm-type} \rightarrow dhcp \rightarrow fcc$, which is observed throughout the series for decreasing atomic number, is

also observed as a function of pressure and alloying. High-pressure experiments, Klement and Jayaraman 1967, have suggested that a trivalent-rare-earth metal under pressure undergoes a similar structure sequence. Some attempts have been made in order to explain it, in terms of the participation of the f electrons, Gschneidner and Valletta 1968. On the other hand, Duthie and Pettifor 1977, have correlated this change with the d -band occupancy through the d -band energy contribution to the total energy. Recent measurements of Vohra et al 1981 have confirmed this experimentally, with the observations of Sm -type and $dhcp$ structures when Y , in which no f electrons are present, but with a d electron, is stressed under very high pressures.

By alloying a light rare-earth with a heavy one, intermediate structures between the components are obtained. Fig. 1.3 shows a typical phase-diagram of a L - H rare-earth system exhibiting the already known structural sequence $hcp \rightarrow Sm\text{-type} \rightarrow dhcp \rightarrow fcc$, Spedding et al 1962. The Sm -type phase exists over a relatively narrow composition and, for a given light solvent, it shifts progressively to higher concentrations with increasing atomic number of the heavy solute. In a similar way, for a given heavy solvent, it shifts to lower concentrations with increasing atomic number of the light solute, Beaudry et al 1965, Harris et al 1966.

Y has been recognized as effectively a heavy rare-earth. Spedding et al. 1962 have found a similar phase diagram to that of Fig. 1.3 for the La - Y system and also have given the different compositions of the light rare-earths in which the Sm -type form is found to be stable, in various Y alloys.

As has already been mentioned the structures differ only in the stacking sequence of the atomic layers. The stackings $ABAB...$

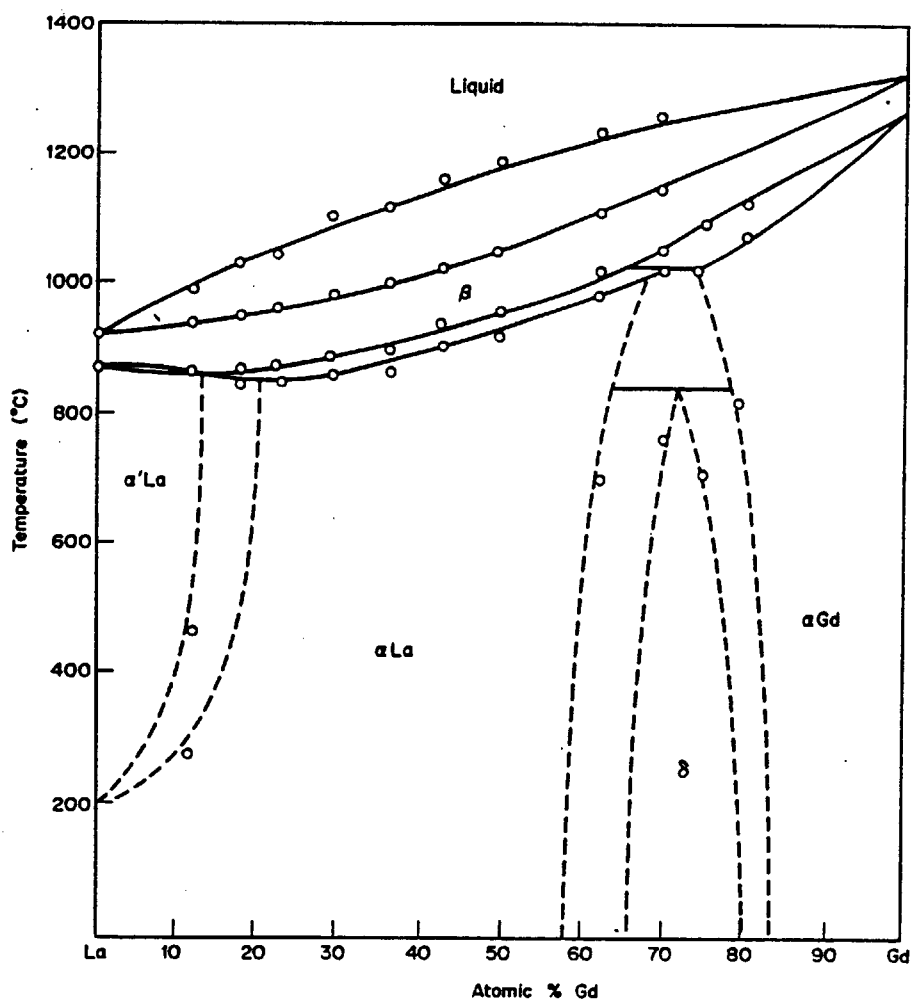


Fig.1.3: The phase diagram of the La-Gd system showing the structural sequence hcp→Sm-type→dhcp→fcc with increasing La content (after Spedding et al. 1962).

and $ABCABC\dots$ correspond to the hcp and fcc structures, while Sm -type and $dhcp$ structures have more complicated sequences. These are $ABACABAC\dots$ for $dhcp$ and $ABABCBCAC\dots$ for Sm -type, see Fig. 1.2. In the Sm -type and $dhcp$ structures, there are some lattice sites with approximate local cubic (c) symmetry and other sites with hexagonal (h) local symmetry. The sequence of structures may then be visualized as:

$hhh\dots$	$hhchhc\dots$	$hchc\dots$	$ccc\dots$
(hcp)	(Sm -type)	($dhcp$)	(fcc)

This fact is of significance in the consideration of the magnetic properties in the metals and alloys.

1.3 Magnetism in metals

As has been said already, when rare-earths atoms are brought together to form a metal, the $4f$ electrons remain closely bound inside outer closed shells and the wave functions on neighbouring ions overlap only negligibly. Therefore, the diverse magnetic properties exhibited throughout the series can not be explained with the direct overlapping between $4f$ electrons on different sites. However, they do interact, but the coupling between $4f$ orbitals is indirect, involving the polarization of the conduction electrons.

1.3.1 The indirect exchange interaction

Exchange arises as a consequence of the Coulomb electrostatic interaction between electrons and the Pauli exclusion principle.

The exchange interaction between a conduction electron of

spin $\bar{s}$ at position $\bar{r}$, and a $4f$ spin $\bar{S}$ at position $\bar{R}$ is given by the Heisenberg Hamiltonian,

$$\mathcal{H}_{sf} = - j_{sf} (\bar{r} - \bar{R}) \bar{S} \cdot \bar{s} \quad \dots (1.9)$$

known as sf interaction.

If $j(\bar{r}-\bar{R})$, the exchange integral, is negative the local moment $\bar{S}$ will prefer conduction electrons with antiparallel spin $\bar{s}$ and will keep apart those with parallel spin $\bar{s}$. Consequently, the conduction electron gas will be polarized. Zener 1951 was the first to suggest an exchange coupling between the conduction electrons and the inner d electrons in order to explain the tendency for ferromagnetic alignment in some transition metals. Later on Ruderman and Kittel 1954 explained how the conduction electrons can be polarized in dealing with nuclear magnetic moments in metals. Subsequently, Kasuya 1956 and Yosida 1957 extended and adapted the theory for sf and sd interactions.

By means of the $\mathcal{H}_{sf}$ interaction, ions interact with each other and the ultimate result is the indirect exchange interaction which also has the Heisenberg form,

$$\mathcal{H}_{ff} = - \sum_{i,j}' \mathcal{J}(\bar{R}_i - \bar{R}_j) \bar{S}_i \cdot \bar{S}_j \quad \dots (1.10)$$

where $\mathcal{J}(\bar{R}_i - \bar{R}_j)$, the exchange integral, can be written in the Fourier transform as

$$\mathcal{J}(\bar{q}) = \sum_{i,j}' \mathcal{J}(\bar{R}_i - \bar{R}_j) e^{i\bar{q} \cdot (\bar{R}_i - \bar{R}_j)} \quad \dots (1.11)$$

and in terms of the sf exchange as

$$\mathcal{J}(\vec{q}) = \sum_q j_{sf}^2(\vec{q}) \chi(\vec{q}) e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} \quad \dots (1.12)$$

$\chi(\vec{q})$ is the generalized susceptibility.

Using the *RKKY* (Ruderman-Kittel-Kasuya-Yosida) approximation, in which $j_{sf}(q) = j_0$, it can be shown that, Kittel 1968,

$$\mathcal{J}(\vec{R}_i - \vec{R}_j) = \frac{9\pi}{2\Omega^2} \frac{z^2 j_0^2}{E_F} f(2K_F |\vec{R}_i - \vec{R}_j|) \quad \dots (1.13)$$

where

$$f(x) = \frac{\sin x - x \cos x}{x^4} \quad \dots (1.14)$$

is of long-range and oscillatory nature, dying out as $\cos(2K_F r)/r^3$ at large r . The exchange interaction is always between the spins $\vec{S}$. However, the total angular momentum $\vec{J}$ specifies the state of a rare-earth ion; the exchange interaction can then be expressed as

$$\mathcal{H}_{ff} = - \sum_{i,j} (g_J - 1)^2 \mathcal{J}(\vec{R}_i - \vec{R}_j) \vec{J}_i \cdot \vec{J}_j \quad \dots (1.15)$$

by replacing $\vec{S}$ for $(g_J - 1)\vec{J}$, the projection of $\vec{S}$ onto $\vec{J}$. The factor $(g_J - 1)$ (See Table 1.1) is negative for the light elements and positive for the heavy ones.

The exchange energy is proportional to $(g_J - 1)^2 J(J + 1)$, which is called the de Gennes factor G . Values of this factor are quoted in Table 1.1 for all the elements. Heavy rare-earths have relatively higher exchange energies than the light rare-earths and this confirms the strong magnetic ordering observed for the second half of the series. The elements from *Tb* to *Tm* first undergo an

antiferromagnetic phase transition at a defined temperature T_N . Followed by a second transition from antiferromagnetism to ferromagnetism at a lower temperature T_C . Values of T_N and T_C are given in Table 1.2. Gd is found to be ferromagnetic from 293 K down to absolute zero.

The Hamiltonian $\mathcal{H}_{ff}$ may be used within the molecular field theory to obtain the paramagnetic Curie temperature θ_p :

$$k\theta_p = \frac{3\pi Z^2 j_O (g-1)^2 J(J+1)}{\Omega^2 E_F} \sum_{i,j}' f(2K_F |\bar{R}_i - \bar{R}_j|) \quad .. (1.16)$$

Thus, θ_p is found to be proportional to the de Gennes factor G . Expression (1.16) is reasonably followed by the heavy-rare metals (See Taylor and Darby 1972) and also accounts for the Curie temperature for some alloys and compounds.

The *Néel* temperatures of the heavy-rare earth metals are also dependent on the de Gennes factor in the form $G^{2/3}$. Weinstein et al (1963) and Child et al 1965 have studied some alloys of Y-substituted heavy-rare earths and found that T_N is correlated with the de Gennes factor $\xi = x(g-1)^2 J(J+1)$ where x is the atomic concentration of the rare-earth. Provided that x is not too small T_N is proportional to $\xi^{2/3}$.

Moreover, recent work of Pelzl et al 1977 taken together with Child et al 1965, Nagasawa and Sugawara 1967, Sarkissian and Coles 1976, shows that for $\xi > 1$, the *Néel* temperatures in $(HRE)_x Y_{1-x}$ alloys, display the previous $\xi^{2/3}$ dependence while in the range $0.1 < \xi < 1$, there is a deviation from this law and suggests a variation more likely as $\xi^{1.2}$.

TABLE 1.2

Values of Néel and Curie temperatures for the heavy
rare-earth metals

	$T_N(K)$	$T_c(K)$
Gd	-	293.2
Tb	229	221
Dy	178.5	85
Ho	132	20(1)
Er	85	19.6
Tm	58	25(2)

(1) ferromagnetic component along c-axis

(2) ferrimagnetic

Attention will be focused on this fact, later on in the thesis.

Finally, it is interesting to point out that for Sc substitution alloys the behaviour is different than for the Y alloys. The results on heavy rare-earth- Sc alloys deviate drastically from the $\xi^{2/3}$ dependence, Abbundi et al 1978.

1.3.2 Crystal Fields

So far the interaction which tends to align the $4f$ moments relative to each other, in a specific orientation has been discussed. However, the highly anisotropic $4f$ orbitals are subject to an ionic electric field that tends to align the moments along preferential crystallographic directions.

Suppose that the electrical potential $V(\vec{r})$ is produced by charges which are outside the ion. Then $V(\vec{r})$ satisfies Poisson's equation and may be expanded in terms of the spherical harmonics:

$$V(\vec{r}) = \sum_{l,m} A_l^m r^l Y_l^m(\vec{r}) \quad \dots (1.17)$$

where,

$$A_l^m = \sum_j \frac{4\pi}{(2l+1)} \frac{z_j}{R_j^{l+1}} (-1)^m Y_l^m(\vec{R}_j) \quad \dots (1.18)$$

In the notation of operator equivalents (Stevens K.W.H. (1952) the crystal field Hamiltonian may be described as

$$\mathcal{H}_{cf} = \sum_{l,m} B_l^m O_l^m(\vec{J}_i) \quad \dots (1.19)$$

where B_L^m is related to the crystal field parameter A_L^m , and $O_L^m(\vec{J})$ is the operator equivalent of spherical harmonics represented in terms of J_x , J_y and J_z .

For sites with hexagonal symmetry only B_2^O , B_4^O , B_6^O and B_6^6 are non zero. For cubic sites in the double hexagonal and *Sm* structures, taking into account the non idea c/a ratio, B_4^3 and B_6^3 are also non zero. For really cubic symmetry B_2^O is equal to zero.

For heavy rare-earth metals, the exchange interaction dominates the magnetic properties and the crystal fields give rise to a magnetic anisotropy. Neutron diffraction measurements have been made on single crystals of these metals, and have revealed a number of different magnetic structures, Koehler W.C. 1972, such as the basal-plane ferromagnet, the helix, the cone and the longitudinal wave structure.

All these structures may be explained in terms of the indirect exchange interaction which produces long-range periodic ordering together with the crystal fields which force the moments to align along the basal plane or the c -axis depending on the forms of B_L^m given in equation (1.19).

In the case of light rare-earth metals, crystal-field effects are comparable to exchange effects and sometimes they prevail over the exchange interactions, not allowing the magnetic moments to order at all, as in *Pr*.

Also, due to the existence of two kinds of sites with different local symmetry, the explanation of the magnetism in light-rare-earths becomes more complicated than in the heavy ones. Details

of the magnetic properties of *Pr*, *Sm* and *Nd* will be discussed in subsequent chapters.

1.4 Electrical resistivity

Rare earth metals and alloys exhibit distinctive electrical resistivity properties. This is due to the particular exchange interaction between the conduction electrons and the localized *4f* electrons, together with the rather anisotropic Fermi surfaces and the complex magnetic structures.

The resistivity may be due to different scattering processes with the conduction electrons. If these scattering mechanisms operate independently, the total resistivity at any temperature is given by the sum of the various contributions (Mattheissen's rule),

$$\rho(T) = \rho_{\text{residual}} + \rho_{\text{phonon}}(T) + \rho_{\text{magnetic}}(T)$$

where ρ_{residual} arises from crystalline imperfections of the lattice, $\rho_{\text{phonon}}(T)$ originates from lattice vibrations, and $\rho_{\text{magnetic}}(T)$ arises from disorder of the spin system.

At temperatures above ordering $\rho_{\text{phonon}} \propto T$, while at low temperatures the phonon resistivity may have a higher power law dependence on T . In the paramagnetic state the spin disorder resistivity is found to be independent of the temperature, Kasuya 1956 and de Gennes and Friedel 1958, and proportional to the de Gennes factor, de Gennes 1962. This may be derived experimentally from the difference between the low temperature residual resistivity and the intercept on the resistivity axis of the extrapolated high

temperature phonon scattering contribution. There is a good correlation between the observed values of ρ_{magnetic} and the spin dependent de Gennes factor, for the heavy rare-earth metals. At and below ordering temperature the spin disorder resistivity is not so simple, and depends on the type of magnetic ordering present. For an isotropic ferromagnet the scattering of conduction electrons by spin waves leads to a contribution at low temperatures proportional to T^2 (Mannari 1959). Then Mackintosh 1963 predicted an exponential factor in the magnetic resistivity for an anisotropic ferromagnetic rare earth,

$$\rho_{\text{magnetic}} \propto T^2 \exp(-\Delta/KT) \quad \dots (1.20)$$

where the anisotropic energy Δ is the minimum energy required to excite a spin wave.

Additionally, the abrupt change in the resistivity at the Néel point has been explained in terms of the appearance of magnetic superzone boundaries within the Brillouin zone (Mackintosh 1962). When the antiferromagnetic ordering takes place, introduces new periodicities into the lattice which produce an additional "magnetic" Brillouin zone. These intersect and deform the free-electron Fermi surface giving rise to a decrease in the effective number of electrons for conductivity and an increase in the resistivity at T_N . Once the transition from antiferro- to ferromagnetic ordering occurs (elements from Tb to Tm), the resistivity falls off rapidly due to the disappearance of these periodic structures.

Coles 1958 suggested that for a binary alloy (containing localized spin moments) the resistivity becomes,

$$\rho = (\rho_{\Delta} + \rho_s + \rho_T)F$$

where ρ_{Δ} , ρ_s , ρ_T are perturbations due to the atomic disorder, the spin disorder and the thermal disorder, respectively, and F depends upon the conduction electron configuration. The factor F , and hence the resistivity, will be different for an ordered or a disordered state of the alloy.

Elliott and Wedgwood 1963 have successfully explained the anomalous resistivities of the heavy rare earth metals using a simple theory which includes the spin disorder scattering, and the changes of the Fermi surface by the superzone boundaries.

1.5 Spin glasses

In view of the relatively new concept of spin glass (Coles 1972), this is an opportunity to give a summary of some of the relevant work being done on metallic systems, and specially those on rare-earth alloys.

A spin glass has been defined as a random, magnetic system characterized by a random freezing of the moments without long-range order at a well defined freezing temperature T_g . The conventional spin glasses are the diluted alloys of CuMn and AuFe alloys, systems formed by a good magnetic element and a non-magnetic one. However, many types of metallic and non-metallic system (intermetallic

compounds, amorphous, insulators, etc.) have magnetic properties characteristic of spin glasses. Sometimes, the words "micromagnetism" or "cluster glasses", in higher concentration alloys, are used to describe spin glass behaviour.

The spin glass system has distinctive magnetic and transport properties. A sharp peak is observed in the low-field a.c. susceptibility at the temperature T_g , Cannella and Mydosh 1972, which is rounded off and reduced by the application of a small d.c. field (few hundred Oe). However, no Bragg reflections appear in neutron diffraction measurements, which indicates absence of long range order. Also the magnetic contribution to the specific heat, exhibits no sharp anomaly at T_g , but a broad maximum well above T_g . Perhaps the more characteristic properties are the remanent magnetizations. The thermo-remanent magnetization is obtained after cooling in a field from temperatures well above T_g , and decreases with T when it is measured in zero field. The isothermal magnetization can be obtained when a small field is first applied and subsequently removed at the same temperature, well below T_g . The zero field-cooled dc susceptibility is similar to the ac susceptibility cusp, provided that the dc field is not too high, for finite time measurements.

Experiments on the dc susceptibility of CuMn (1 to 6 at % Mn) (Morgownik and Mydosh 1981) above T_g indicated a Curie-Weiss law at temperatures much higher than T_g , with a paramagnetic Curie temperature which is a linear function of the concentration. On approaching T_g there are deviations which increase with decreasing temperature. Furthermore, hysteresis experiments in some dilute alloys show shifted loops with sharp reversals of the magnetization, well below T_g . "Square" hysteresis loops have been observed in

CuMn and AgMn alloys, Monod et al 1979, Préjean et al 1980. Also Préjean et al 1980 found that the addition of non-magnetic impurities (Au, Pt) with strong spin-orbit coupling in CuMn alloys, sharply increases the anisotropy field which maintains the remanent magnetization in the direction of the initial applied field. On the other hand, impurities without spin-orbit coupling (Al) had practically no effect. The ac-susceptibility, the temperature T_g and the value of the remanent magnetization are not modified by these impurities.

The electrical resistivity of the spin glasses may have different dependences with temperature for different systems. Ford and Mydosh 1976 found that the magnetic resistivity ρ_m of several *3d* alloys, has a $T^{3/2}$ dependence below T_g . At much lower temperatures, a T^2 dependence has been obtained by Laborde et al 1973. Around T_g , ρ_m increases roughly linearly with T , and at much higher temperatures reaches a maximum, followed by a continuous fall-off. The maximum tends to disappear as the concentration of the solute increases. (In other spin glasses ρ_m saturates at about T_g). In addition, $d\rho_m/dT$ develops a maximum at a temperature T_m which in general has no definite relation with T_g , unlike long-range ordered substances where the maximum characterizes the Curie or Néel temperature. Sometimes a minimum in the resistivity is observed, Sarkissian and Taylor 1974. They found a resistance minimum for alloys of Pt-Mn up to 11%Mn, and a $T^{3/2}$ dependence of the resistivity below the minimum temperature.

Attempts to understand such a great corpus of experiments have been made by many authors, and a very brief account will be given here. Good review articles are given by Blandin 1978 and Fischer 1982.

The spin glass properties previously summarized, depend upon the concentration of the magnetic atoms. This indicates that these properties are due to interaction between impurities. The interactions between the magnetically randomly distributed impurities are mainly indirectly via the *RKKY* exchange. This is certainly valid for rare earth spin glass alloys; for *3d* metallic glasses, direct exchange interaction might also need to be considered.

The question that many authors have tried to answer is whether the spin glass state corresponds to a true phase transition or not. A model that explained some of the fundamental properties of spin glass was based on a classical Heisenberg picture within the mean field approximation. The random distribution of impurities over all lattice sites (random site distribution) has been replaced by a random bond distribution P_{ij} between nearest neighbours with spin $\vec{S}_i$ on all lattice sites. A new phase was considered to occur, with no conventional ferro- or antiferromagnetic ordering, but characterized by an "order" parameter $q = \langle \overline{S}_i \rangle^2$, where the inner brackets mean thermal average and the outer ones mean spatial average. Improvement of this model was made considering an Ising picture with infinite range interactions. A given spin interacts with all other spins with the same distribution $P(J_{ij})$. Both theories predict a phase transition in the susceptibility with non-zero q for $T < T_g$ and zero for $T > T_g$. A model based on the existence of two-level systems attempted to interpret the remanence and hysteresis properties. This consists of atomic configurations with two adjacent energy minima between which tunneling or thermal hopping takes place. Another model which tries to unify the mean field theories with the two-level systems, includes the Onsager theory. In this case, the Weiss field

acting on a given spin is considered to be the sum of the field produced by all spins in the absence of the spin in question, plus the Onsager reaction field, i.e. the field due to the polarization, by the spin, of its neighbours. This theory explains hysteresis effects and has led to similar results to those of mean field theories.

On the other hand, some authors predict no phase transition. They argue that the characteristic peak in the susceptibility is a non-equilibrium phenomenon, resulting from the finite observation times used for the evaluation of the susceptibility, and this viewpoint implies that the Curie law holds for all temperatures.

Rivier and Adkins 1975 have explained the $T^{3/2}$ resistance behaviour in terms of long wave length excitations which are diffusive in character, with a damping constant Λ . The conduction electrons are scattered locally by the diffusion modes giving a resistivity at low temperature of the form $\rho \sim C \left(\frac{T}{\Lambda}\right)^{3/2}$

Spin glass in rare-earth alloys

Sarkissian 1975, 1977 and Sarkissian and Coles 1976 have observed spin glass-type behaviour in alloys of Gd , Tb , Dy in Sc and Y below a certain well defined critical concentration, above which long-range helical ordering is manifest. All alloys exhibit a maximum in the dc susceptibility measurements and show remanent magnetization. The Curie law is obeyed at high temperatures, but there are deviations when approaching ordering temperature. The resistivity ρ follows the general pattern for a spin glass, with the

temperature of the maximum (generally broad) in $d\rho/dT$ about the value of temperature defined by the susceptibility peak. The sharpness of the peak observed in the ac susceptibility, characteristic of the $3d$ -spin glasses, is also found in $Sc-Gd$ alloys. The peak is gradually smeared out by an applied magnetic field. However, a rather rounded peak is observed in $Sc-Tb$ alloys, which on the contrary, becomes sharper with applied magnetic fields, Sarkissian 1977.

Ferrick et al 1982 measured dc susceptibility on a $Sc-25\% Dy$ alloy, in a number of applied fields, and found similar behaviour to that of $Sc-Tb$ spin glass alloys.

It is interesting to draw attention to the fact that $Sc_{1-x} RE_x$ systems require large rare-earth concentrations, $15\% < x < 39$, for the onset of long-range magnetic ordering to occur, in contrast with $Y_{1-x} RE_x$ alloys, where a minimum of $x \sim 2.5\%$ is required to observe helical ordering. This is due to the strong d -character of Yttrium metal which induces exchange enhancement. Below these critical concentrations, spin glass ordering takes place.

Bennett and Coles 1977 studied alloys of $(La, Gd) Al_2$ and observed spin glass behaviour, in both dc susceptibility and resistivity measurements, for alloys of up to 9% Gd substitution. The dc susceptibility shows a sharp peak in applied fields of $5 Oe$.

Bruss et al 1979 found typical spin glass properties in the ac susceptibility, the low field magnetization and neutron diffraction measurements performed on $Y_{1-x} Er_x Al_2$ alloys with $10\% < x < 40\%$. The ac susceptibility peak is smeared out by the application of small dc fields. Early neutron diffraction and susceptibility measurements

made by Finnemore et al 1968, suggest spin glass behaviour in the more dilute alloys in the $\underline{La-Gd}$ and $\underline{La-Tb}$ systems. They found a broad neutron diffraction maximum in $\underline{La-Tb}$ alloys with 10 and 20% solute. For $\underline{La-Gd}$ alloys, the sharp peak in the dc susceptibility was smeared out and suppressed by a small external magnetic field.

Ping and Coles 1982 studied alloys of $U_{1-x} Gd_x Al_2$ and found field-cooling effects in the susceptibility peak, and resistivity minimum similar to that of $\underline{Pt-Mn}$ alloys, for concentrations $10\% < x < 30\%$, which suggest spin glass formation.

Crystal-field effects are important in rare-earth metals. Hence, a theory to account for the spin glass behaviour must include them. Sarkissian 1977 has suggested that single-ion anisotropy is responsible for the rounded peaks seen in $\underline{Sc-Tb}$, $\underline{Sc-Dy}$ alloys, where spin-orbit couplings are strong. When weak anisotropy is present, rather sharp peaks are found, as is the case for Gd , which is an S -solute. Theoretical support for this statement is given by Ghatak 1976 who has investigated the effect of uniaxial anisotropy on the spin glass susceptibility properties. He found that the parallel susceptibility exhibits a sharp cusp, while the perpendicular susceptibility shows a rounded maximum, when the anisotropy is comparable or greater than the exchange field.

Some Pr -heavy rare-earth alloys also show spin glass-type freezing and will be discussed later in Chapter 3. In such systems the host is non-magnetic in the special sense that the exchange interaction between the magnetic ions is insufficient to induce the magnetic ordering.

CHAPTER 2

2. Experimental techniques and sample preparation

In the following Chapter, the experimental techniques employed in the present work will be described. The electrical resistivity and the ac-susceptibility apparatus will be described only briefly as they have already been discussed in detail elsewhere. A more extended description will be given for the low and high field susceptibility equipment in which a Faraday-type force balance is used, and which has been significantly modified in the present work.

2.1 Electrical Resistivity apparatus

The electrical resistance measurements are performed using the conventional four-probe dc potentiometric method. Specimen temperature may be varied between $1.6K$ to $300K$ by using the double dewar technique.

The current is supplied through a Tinsley dc current stabiliser Type 5753 which supplies currents from 100 mA to $2A$ stabilized to within a few parts in 10^6 . Samples are connected in series with each other and with a $0.01\ \Omega$ manganin standard resistor Type RS2, which is maintained at room temperature. Voltages across the samples and standard resistor are measured on a thermo-electric potentiometer of Diesselhorst pattern in conjunction with a Tinsley Photocell Galvanometer Amplifier Type 5214 and a secondary galvanometer, both used as null indicators. Thermal emf can be avoided by reversing the current flowing through the samples. This is done by an oil filled

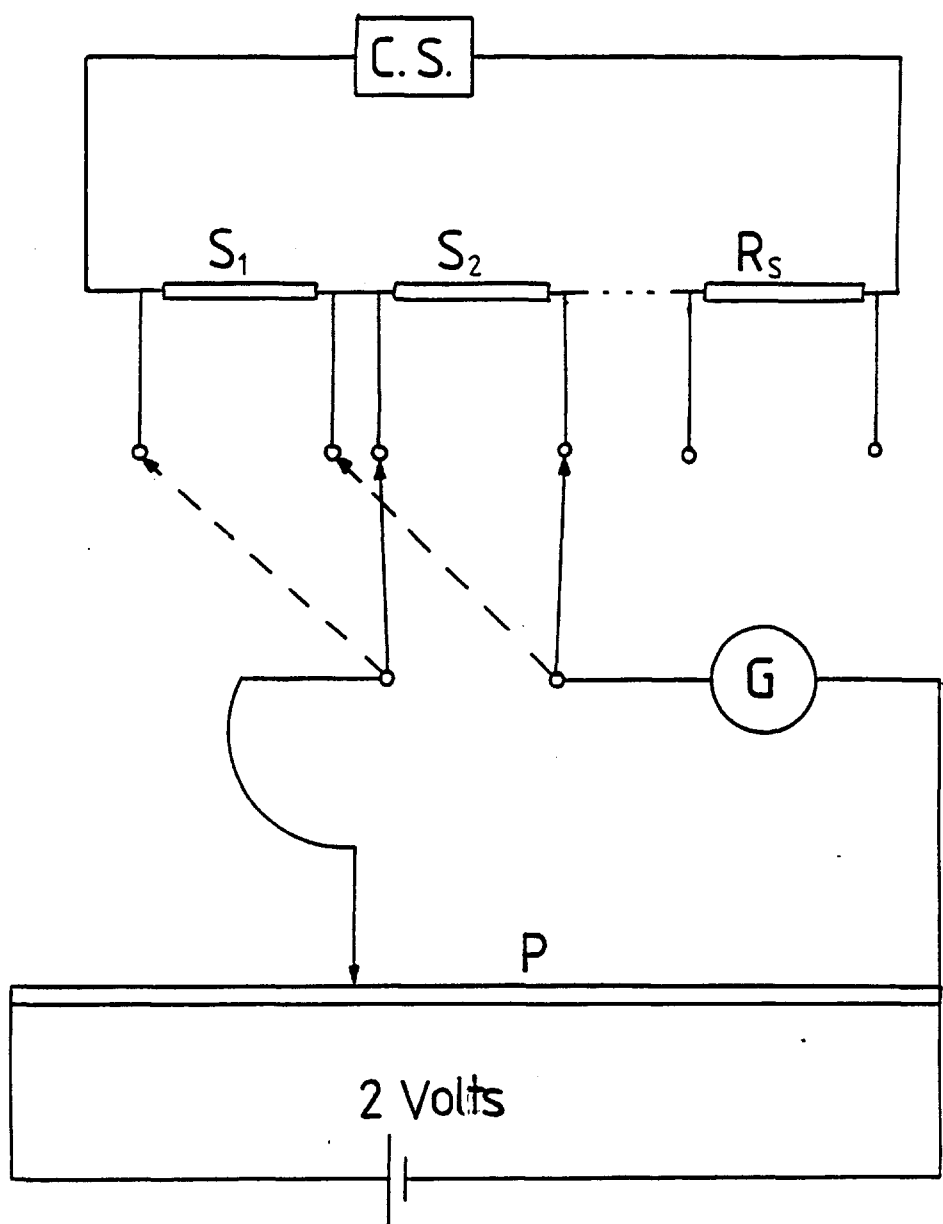


Fig.2.1: Schematic diagram for the electrical circuit of the resistivity apparatus; C.S.: current stabiliser; $S_1, S_2 \dots$: samples; R_s : standard resistor; G: galvanometers; P: thermo-electric potentiometer.

thermo-electric free Tinsley switch Type 4092. Fig. 2.1 shows a schematic diagram for the electrical circuit.

In order to hold the samples, four platinum leads (two as potential leads and two as current leads) are spot-welded to each of them, and then the leads are soldered to the holder. The samples are placed in a symmetrical manner around a cylindrical araldite block, and surrounded by a copper can to ensure a continuous slow warming-up. The current was set as small as possible ($\sim 150\text{ mA}$) in order to avoid Joule heating effects.

Various thermometers are employed. Temperatures below 4.2K are determined from the helium vapour pressure. An Allen Bradley carbon resistor ($47\ \Omega$ at 300K) is used for measuring temperatures between 4.2K and 17K together with a $\text{Au-0.03\%Fe}$ vs Chromel thermocouple, which is also utilized up to 50K . For measuring above 30K up to room temperature, there is a Pt-wire thermometer. A silicon diode (1S922) thermometer, calibrated for the whole range, was also attached to the sample holder, in order to have quick information of the temperature. A detailed account of the apparatus in earlier forms is found in Bellau's and Sarkissian's thesis.

2.2 Magnetic ac-Susceptibility apparatus

The mutual inductance method is used for the magnetic ac-susceptibility measurements, by means of an ac-Hartshorn-bridge (Maxwell 1965 and Anderson et al 1970). The sample temperature is varied from 1.5K to 300K , using the double dewar technique, as in the resistivity equipment.

The apparatus consists of:

- 1) co-axial primary and secondary coils made of copper wire and placed inside the helium dewar. The secondary coil is composed of two sections, upper and lower, with the windings in opposite directions in order to approximate to null induced signal for empty coils. The sample is located in the upper section and its exact position is that where the induced signal is maximum at a given temperature. Details of the construction of the co-axial coils are given in Sharif's thesis.
- 2) a variable mutual inductance (Tinsley 4229) together with a ratio transformer (Sullivan F9100) coupled to the secondary circuit, and connected in opposition with the coils in order to get the balance condition.
- 3) an ac-signal source connected to the primary circuit which is given by an Ortec Brookdeal 9472 oscillator. The field amplitudes may vary from $\sim 10^{-2} G$ to a few G . The frequency was maintained at $\sim 240 \text{ Hz}$ for all measurements.
- 4) a null detector system which itself consists of a Brookdeal Low Noise Amplifier type 450 and a Brookdeal Ortholoc 9502 two-phase lock-in analyser; in the latter the in-phase (inductive) and the quadrature components of the induced signal (resistive) are detected simultaneously. See the schematic diagram in Fig. 2.2.

The measurements are made by bringing the bridge to a balance condition, where the quadrature signal is annulled by the Ortholoc phase-shift control and the in-phase signal is annulled by means of the variable mutual inductance and the ratio transformer. Then, under this condition, the sample susceptibility is proportional to the difference of the mutual inductance when the sample is placed into the

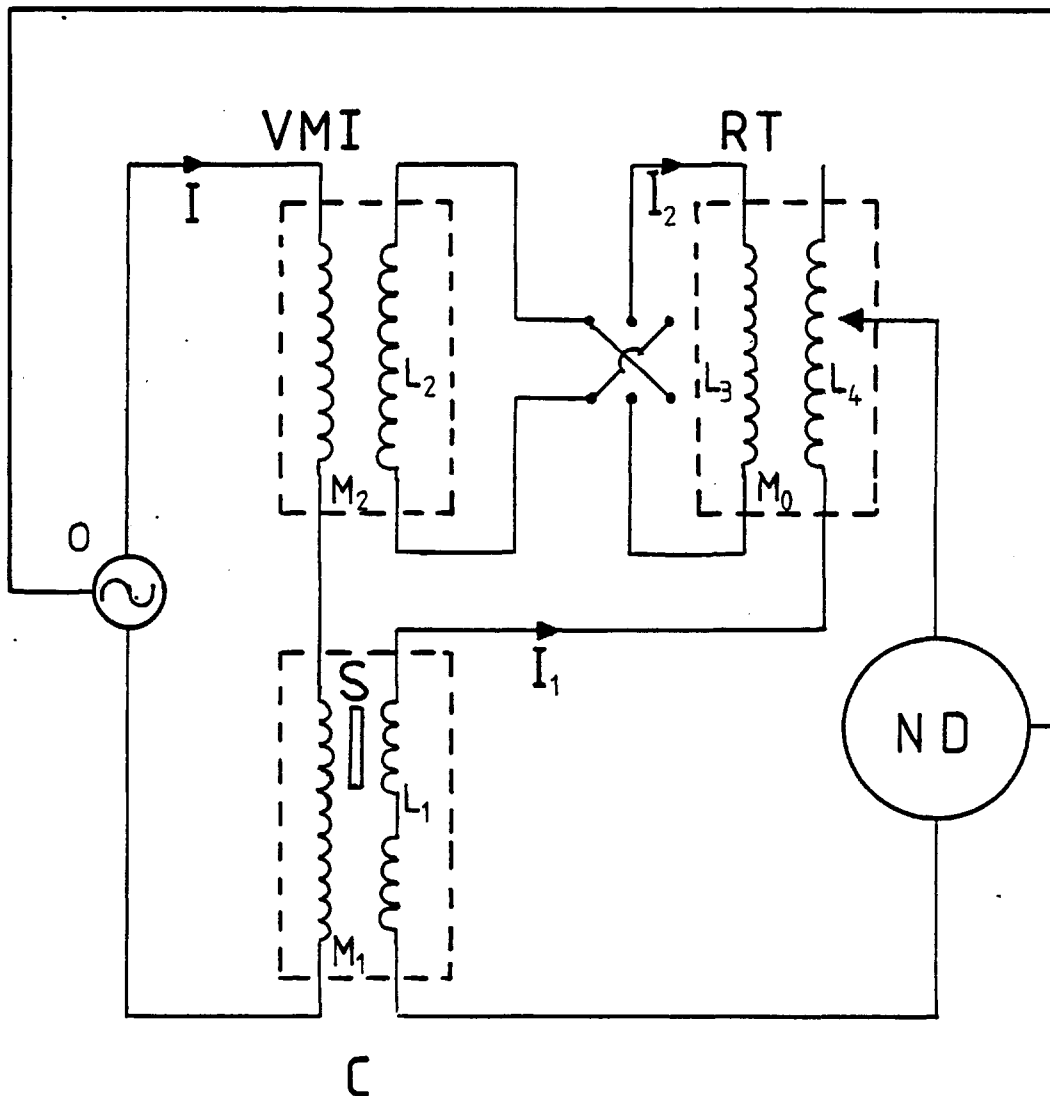


Fig.2.2: Schematic diagram for the electrical circuit of the magnetic ac-susceptibility apparatus; C: primary and secondary coils; S: sample; VMI: variable mutual inductance; O: oscillator; ND: null detector, RT: ratio transformer

secondary less the mutual inductance for empty coils.

Electrical circuit

In the following calculations, the inductances have been considered ideal, and any resistive part as zero.

From the circuit of Fig. 2.2, we get the following two Kirchhoff equations:

$$M_O I_1 + (L_2 + L_3) I_2 = -M_2 I \quad \dots (2.1)$$

$$(L_1 + L_4) I_1 + M_O I_2 = -M_1 I$$

where L and M denote self-inductance and mutual inductance respectively.

$$\text{Then } I_1 = \frac{M_1 (L_2 + L_3) - M_O M_2}{M_O^2 - (L_1 + L_4) (L_2 + L_3)} I \quad \dots (2.2)$$

For the balance condition $I_1 = 0$. This means that for empty coils we have,

$$M_1 (L_2 + L_3) - M_O M_2 = 0$$

$$\text{or } M_1 = \frac{M_O M_2}{L_2 + L_3} \quad \dots (2.3)$$

When the sample is inserted in the coils, the mutual inductance of the coils changes from M_1 to $M_1(1 + \chi)$, where χ

is the volumen susceptibility of the sample.

Then,

$$\chi = \frac{1}{M_1(L_2 + L_3)} [(M_O M_2)_{in} - (M_O M_2)_{out}] \quad \dots (2.4)$$

or $\chi = K [(M_O M_2)_{in} - (M_O M_2)_{out}] \quad \dots (2.5)$

where M_O and M_2 are the values given by the ratio transformer and the variable mutual inductance respectively. K is a geometrical factor which can be determined experimentally.

The mass susceptibility will be:

$$\chi_m = \frac{VK}{m} [(M_O M_2)_{in} - (M_O M_2)_{out}] \quad \dots (2.6)$$

where V and m are the volumen and mass of the sample respectively. V should remain constant for all samples.

Calibration

Pure manganese was used to calibrate the bridge. The calibration factor K was checked by measuring the diamagnetic susceptibility for lead and niobium at $4.2K$, when both are in the superconducting state.

Thermometry

A diode type 1S922 is used to measure the range of temperature from $4.2K$ to $300 K$. The circuit diagram is shown in Fig. 2.3. The

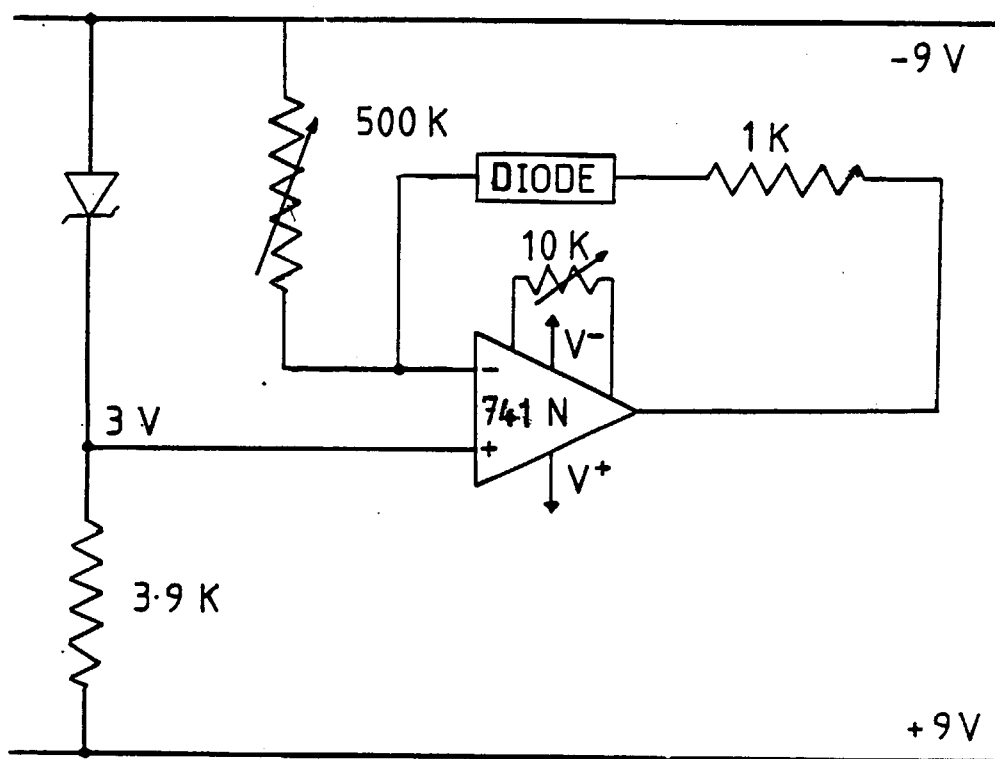


Fig.2.3: Circuit diagram for the diode thermometer.

diode was calibrated against a Germanium thermometer for the range between 4.2 K and 20 K and against a platinum resistor for the remaining range. Temperatures below 4.2K are determined from the helium vapour pressure by means of a manostat.

2.3 Faraday Susceptibility Balance Apparatus

Magnetic susceptibility in higher fields were made in a Faraday balance constructed by Male (1976), in which fields up to 8.5 KG were given by an electromagnet. Modifications have been made in order to use a superconducting solenoid magnet providing high fields (up to 50 KG). Furthermore, the solenoid has the advantage that field and field gradient can be separately varied and hence zero field magnetization can be performed.

The force method

The force acting on a sample with uniform magnetization $\bar{M}$ situated in a non-uniform magnetic field $\bar{H}$ is given by

$$\bar{F} = - m \bar{M} \cdot \nabla \bar{H} \quad \dots (2.7)$$

where m is the mass of the specimen.

If the magnetic field is produced by an electromagnet with truncated poles as shown in Fig. 2.4, the force in the z -direction will be,

$$F_z = m \chi_m H_y \frac{dH_y}{dz} \quad \dots (2.8)$$

where χ_m is the mass susceptibility. The field is along the y -axis and it has been assumed that only the gradient along the z -axis is of importance. The factor $K \equiv H_y dH_y/dz$ is determined experimentally using a standard sample.

When the field is provided by a solenoid, the direction of the magnetization $\bar{M}$ of the sample coincides with the direction of the field $\bar{H}$ and with the axis along which the force is measured. However, because the field is uniform, one needs an auxiliary field to provide a constant value of dH_z^0/dz in the region where the sample is located. This is done by Helmholtz coils antiparallel wound. (See the schematic diagram of Fig. 2.5). Then the force is given by

$$F_z = m M_z \frac{dH_z^0}{dz} \quad \dots (2.9)$$

$$\text{or} \quad F_z = m \chi_m H \frac{dH_z^0}{dz} \quad \dots (2.10)$$

The magnetic field

The electromagnet. This was a Newport type A with truncated conical poles, and the current was provided by an Irvin type C298 2 KW Magnet power supply. Measuring the field along the z -axis by a Hall probe gaussmeter, the position A (See Fig. 2.4) of maximum $K \equiv H_y dH_y/dz$ is found to be 3 mm above the edge of the poles. A plot of H_y^2 vs z shows that K does not change appreciably in a region of ± 5 mm along A. The calibration was made at room temperature and 77 K using high purity Tantalum.

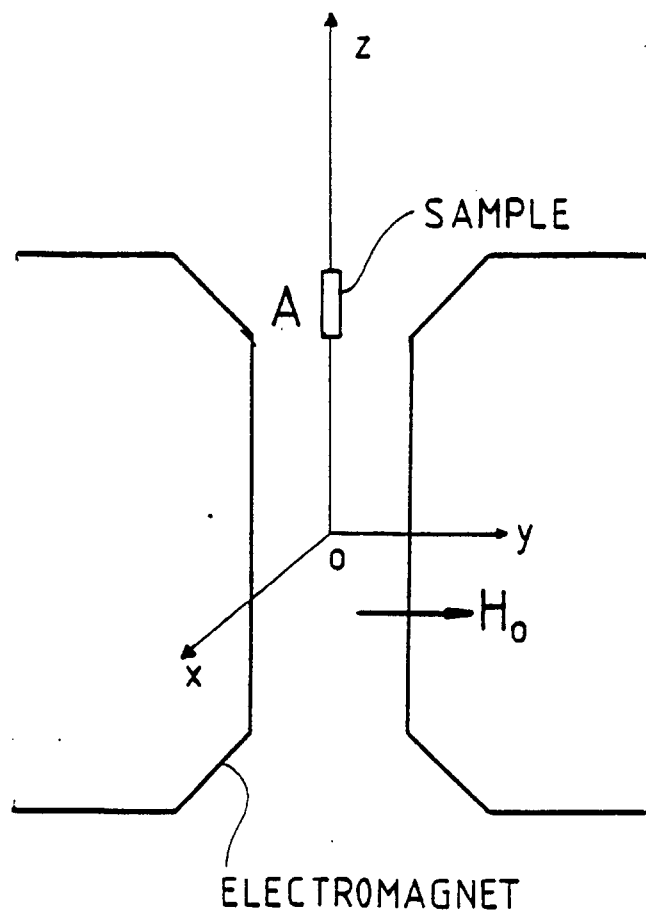


Fig.2.4: Position of the sample in the electromagnet poles.

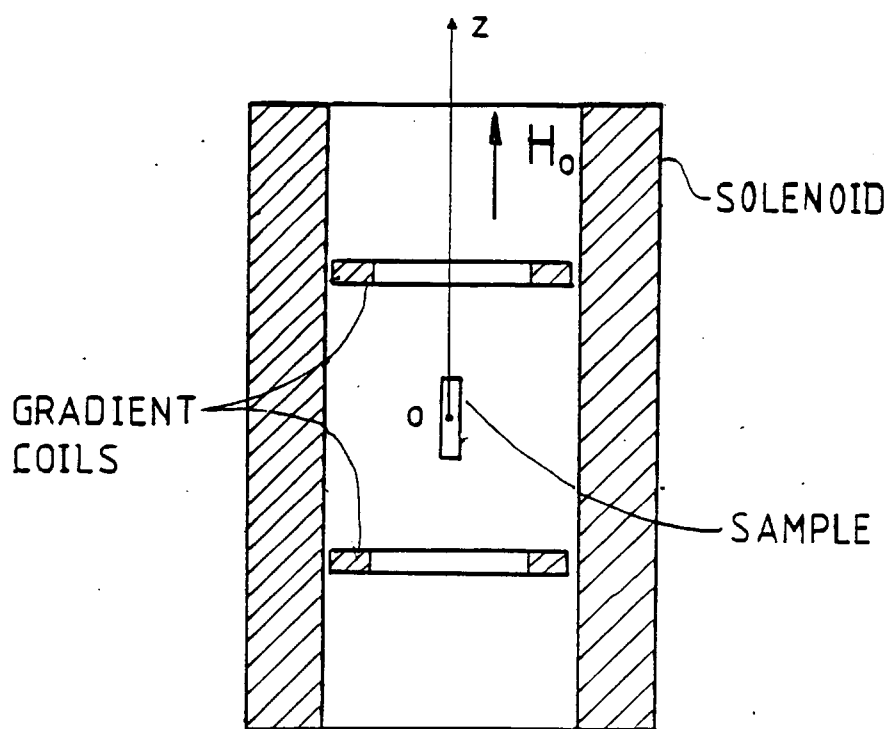


Fig.2.5: Position of the sample in the solenoid set-up.

The superconducting solenoid magnet. This is a Q1511, 5 Tesla Magnet supplied by Oxford Inst. It has a homogeneity of 0.1% over 10 mm δv and a variation of 1.3 in 10^5 over 10 mm length. The current field is 7.128 Amp/Tesla. A Sol 60/5 Coutant Power Supply together with a 100 Amp Magnet Controller provides the current.

The field gradient coils were a Helmholtz pair connected antiparallel, constructed by the author. A computing program following the method given by Zijlstra (1967), was used to find out the best coil dimension which gives a constant gradient over a maximum distance (10 mm) around the origin. The coils were wound on a tufnel form, each coil having ~ 1000 turns of superconducting wire. The current was given by an Apt Regulator power supply TCU 0550. High purity Tantalum was used for calibration, giving $dH_z^0/dz = 22.6 \text{ G/cm per } 100 \text{ mA}$. The sample was located at the centre of the gradient coils and solenoid with a precision of 0.5 mm. In order to avoid any undesirable force due to gradients in the main field, a correction procedure was performed. This procedure was to take the effective force as the subtraction of the force with the gradient coils switched off from the force with the coils switched on, whilst keeping the main field constant, Stewart 1975.

The microbalance and suspension assembly

The apparent increase in mass $W = F_z/g$ (g is the gravity acceleration) due to the field, is measured by a microbalance LM600 Beckman-Riic which has a resolution of $1\mu \text{ gr}$. The sample is suspended freely and vertically inside a stainless steel tube. The microbalance is located on a platform free of vibration, inside a chamber connected to the suspension tube.

For measurements with the electromagnet, a vertical suspension made of quartz was used, with one piece of constantan as a upper hook and one piece of high purity aluminium as lower hook. Aluminium wire was glued to the sample in order to fix it to the suspension and for the purpose of avoiding lateral movements, a counter-weight made of gold was suspended under the sample in the position of zero field gradient of the electromagnet. See Fig. 2.6a. When the same suspension system was used with the solenoid set-up the gold counter-weight was consequently located in a region where the main field is non-uniform, and hence it produced an undesirable force. The gold counter-weight was removed and the suspension was changed. The new suspension was made partly in quartz and partly in aluminium (99.99% purity) rod, as is illustrated in Fig. 2.6b.

Cryogenics and thermometry

The double dewar technique was used with the electromagnet set-up. Details are given by Male (1976).

For the superconducting magnetometer, the rig becomes more complicated and three dewars are needed. Fig. 2.7 shows the schematic diagram of the cryostat. The suspension tube T is located in the dewar D_1 which has a narrow tail in order to position the field gradient coils G and the superconducting solenoid magnet M , which are immersed in the helium dewar D_2 . The outside dewar D_3 is for liquid nitrogen.

Two thermometers are affixed (with Ge varnish) to the suspension tube, as near as possible to the position of the sample S . (See Fig. 2.7): a carbon $47\ \Omega$ Allen-Bradley resistor for the 4.2 to $18\ K$ range, calibrated against a Germanium thermometer; and a

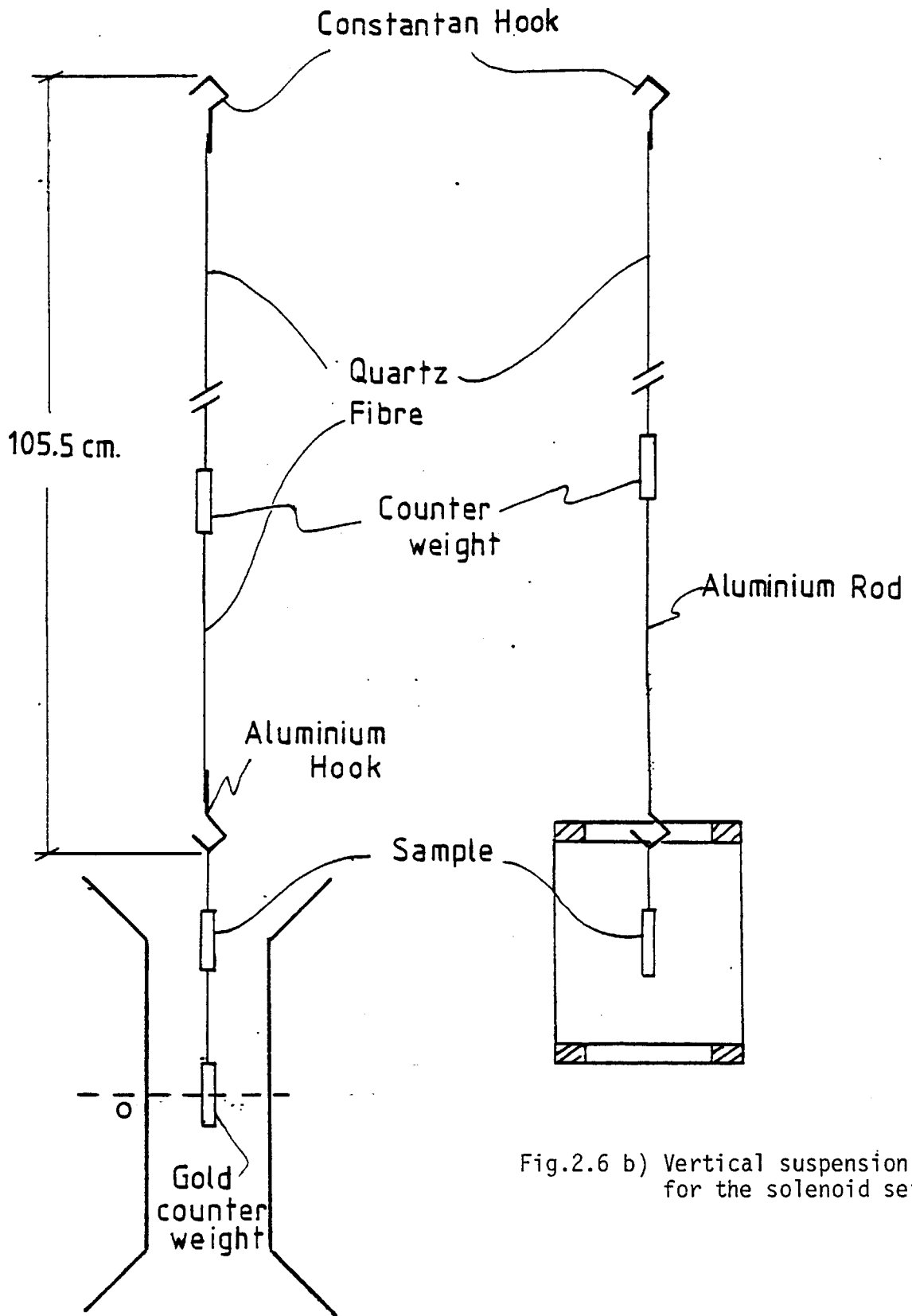


Fig.2.6 b) Vertical suspension for the solenoid set-up.

Fig.2.6 a) Vertical suspension for the electromagnet set-up.

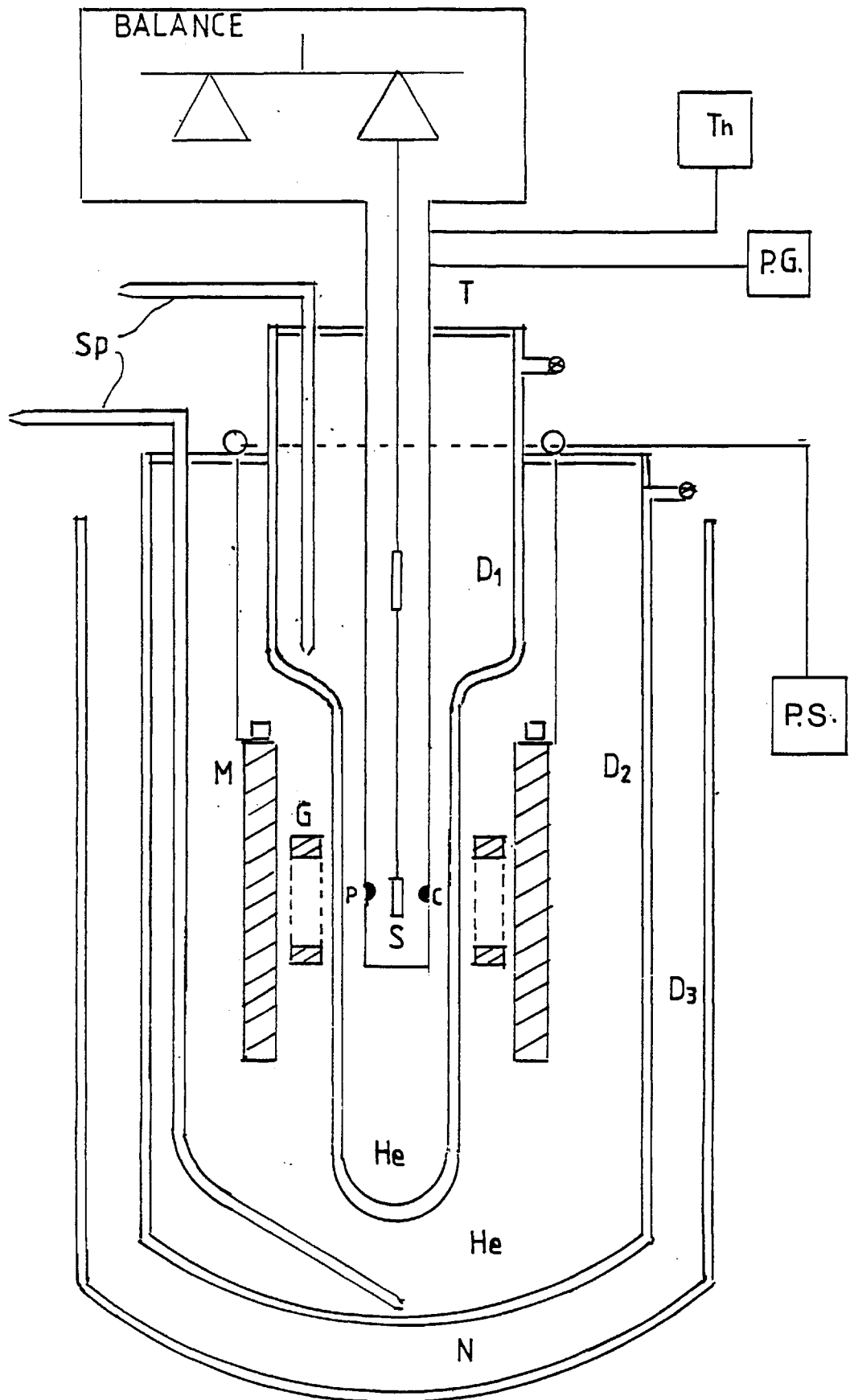


Fig. 2.7: Schematic diagram of the cryostat for the Faraday Susceptibility Balance apparatus. T: suspension tube; D: dewars; S: sample; G: gradient coils; M: solenoid; Sp: siphons; P and C: platinum and carbon thermometers; P.S.: power supply for the solenoid; P.G.: power supply for the gradient coils; Th: power supply for the thermometers.

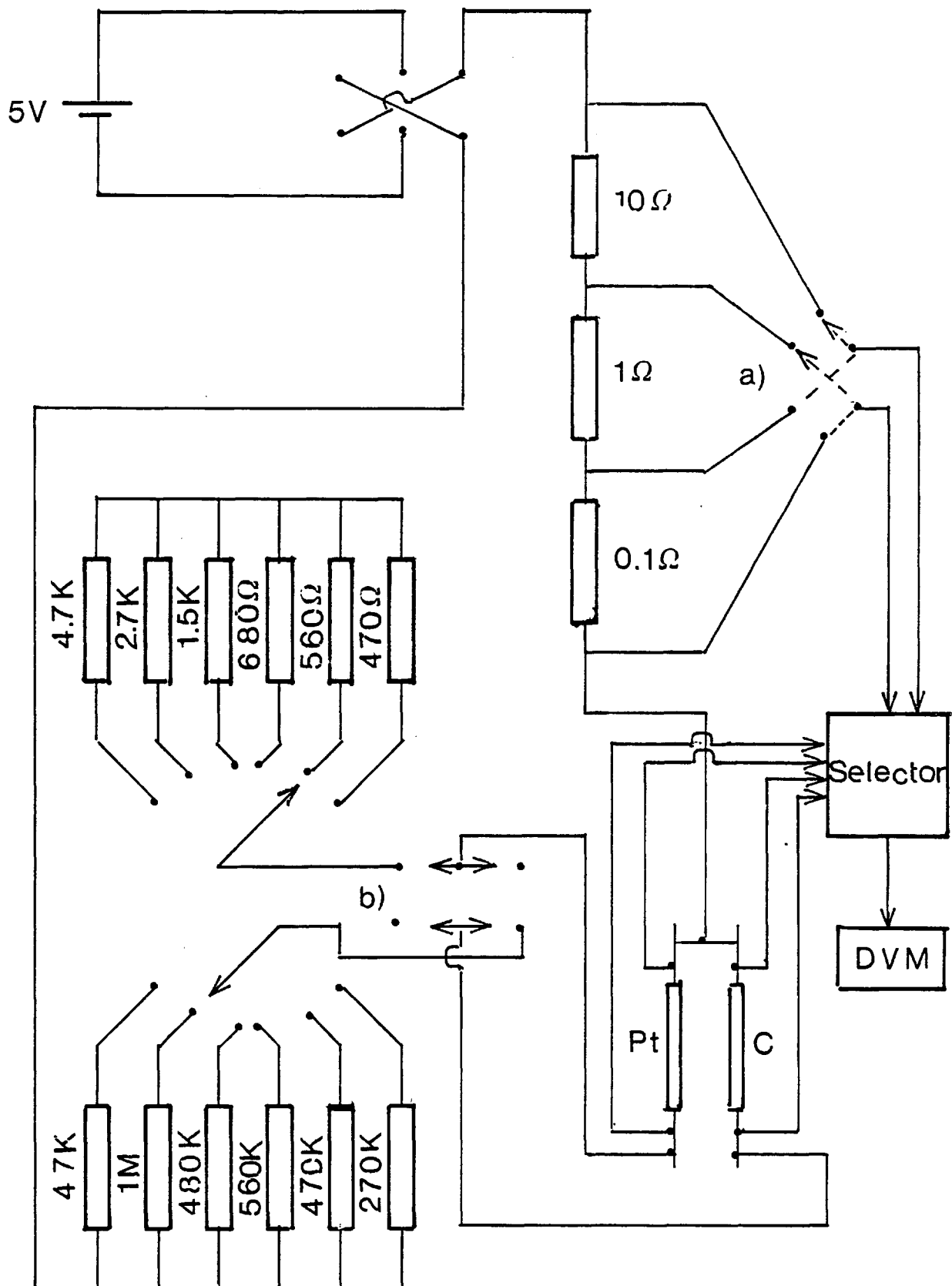


Fig. 2.8: Circuit diagram for the thermometers.
Pt and C: platinum and carbon thermometers;
a) Standard resistors; b) current selector.

platinum resistor for 18 K to 300 K range, calibrated using the α -function technique. Both thermometers used the same circuitry, Fig. 2.8. Temperatures below 4.2 K are known from the helium vapour pressure.

2.4 Sample preparation

The raw materials, with an estimated purity of 99.9%, were provided by Rare Earth Products. In general, less than 0.1% of other rare earth metallic impurities and approximately 0.02% of base metal impurities is expected. For the specific batch of *Pr* used in making the *Pr - Y* alloys, the amount of rare earth impurities were below the limits of detection by the method employed (X-ray fluorescence spectrometry), $< 200 \text{ ppm}$.

The alloys were prepared from the pure metals in an Argon-arc furnace with a suction-casting device, designed by Stone 1977. The required quantities of raw material for making an alloy, were carefully weighed and placed together on the water-cooled copper hearth of the arc-furnace. The chamber was flushed twice with argon and finally re-filled with argon to a pressure of 30 cm Hg below atmospheric. A titanium getter placed in the copper hearth was made molten for about one minute in order to check that the argon atmosphere was clean. Then, the metals were melted to a button, and turned over and re-melted several times to ensure homogeneity. All the samples, except pure *Sm**, were sucked down into a copper mould, and rods of cross section between 2 to 5 mm² and of length 20 to 40 mm were obtained in order to use them for the resistivity measurements. Pieces of $\sim 1 \text{ cm}$ length sectioned from the samples were used for the

* It proved impossible to suck down pure *Sm* into the mould, and compositions rich in *Sm* proved difficult to cast.

susceptibility measurements.

For heat treatment, the samples were sealed into quartz envelopes at a pressure of 10^{-5} Torr. The different heat treatments given to the alloys are specified in the relevant chapters.

The crystalline structures of the *Pr-Y* alloys were checked by X-ray using a Guinier camera with a wavelength of *Cu K α* ($\lambda = 1.542\text{\AA}$). The mass absorption coefficients for these elements are quite high, consequently, long exposure times were required.

CHAPTER 3

3. Magnetic ordering in the *dhcp*, *Sm* and *hcp* structures of the *Pr-Y* system

During the past fifteen years, there has been a considerable effort aimed at an understanding of the magnetic properties of *Praseodymium* and its alloys. This Chapter will be concerned with the magnetic character observed in a number of *Pr-Y* alloys. These are of interest because *Pr*-ions may experience different environments, corresponding to the sequence of crystal phases *dhcp*→*Sm*-type→*hcp* by adding *Y*, without the complications of producing this sequence by addition to *Pr*, of moment-bearing heavy rare-earths.

Before discussing the *Pr-Y* alloys, an account of the most relevant studies on *Pr* metal and its alloys will be given.

3.1 Magnetic properties of *dhcp* and *fcc Pr*.

As has been mentioned before, crystal-field effects in *Pr*, are large compared with exchange interactions. Bleaney, 1963 was the first to point out the importance of the crystal field in its magnetic properties. For many years experimental studies of *dhcp Pr* have been carried out to see whether it orders magnetically or not. The heat capacity, measured by Parkinson et al., 1951, displays a very large anomaly which is attributed to the crystal-field splittings of the *4f* electronic state. The susceptibility measurement made by Lock, 1957, indicates that *Pr* obeys the Curie law above 100 K, with an effective atomic moment of $3.56 \mu_B$ (compared with $3.58 \mu_B$ for the free ion) and remains constant at a value of $1.55 \cdot 10^{-3} \text{ emu/gr}$, from 4K down to 1.3K - behaviour associated with Van-Vleck type susceptibility (see Chapter 1).

On the basis of these experiments, and taking the exchange interactions between ions by the molecular field theory into account, Bleaney concluded that the ground states of Pr^{3+} atoms on both hexagonal and cubic sites are singlets. (This can occur only for non-Kramer's ions, i.e. ions with an even number of f electrons.) In a singlet state, the ionic moment is quenched and therefore there is no magnetic ordering down to absolute zero temperature, unless the exchange is strong enough to induce magnetism through the polarization of the singlet states, Cooper, 1967.

Soon after, Cable et al., 1964, performed neutron diffraction measurements on a polycrystalline sample. At 1.4K they obtained neutron diffraction patterns with reflections additional to those attributable to nuclear reflections, and claimed to have found antiferromagnetic ordering in Pr , with a Néel temperature of 25K. However, Arajs and Dunmyre, 1967, found no anomalous behaviour in both resistivity and susceptibility measurements on a polycrystalline sample, in the temperature range between 15K and 90K. Furthermore, measurements of susceptibility carried out by Johansson et al. 1970, 1971, in a single crystal of Pr showed no signs of spontaneous magnetic ordering down to 2K. The reciprocal susceptibility (see Fig.3.1) in both [110] and [001] direction follows a Curie-Weiss law, with effective moments of $3.54 \mu_B$ and $3.59 \mu_B$ respectively. The susceptibility is found to be very anisotropic with $\chi^{\perp} \gg \chi^{\parallel}$, and while $\chi^{\perp}$ shows the Van-Vleck behaviour at low temperatures, $\chi^{\parallel}$ displays first a maximum around 30K and then a minimum near 10K. Rainford, 1972, has interpreted the maximum as due to effects of depopulation of the excited states as the temperature is lowered, and suggests that the minimum is not a real effect and may be due to the presence of small grains in the crystal, with an unfavourable orientation, giving some

perpendicular susceptibility. More recent measurements of susceptibility made by Sakamoto et al. 1976, also on a single crystal, show good agreement with the measurements of Johansson et al. (see Fig.3.1). The maximum of χ'' was reproduced but not the minimum. Sakamoto et al. attributed the minimum in Johansson measurements, to the presence of *fcc Pr*, which exhibits a ferromagnetic Curie-point at about 9K.

McEwen et al. 1973, also have investigated the magnetization at very high fields (up to 37T) of a single crystal of *Pr* (see Fig. 3.2). The magnetization at 4.2K shows a large anisotropy and a tendency towards saturation at high fields. However, the induced magnetic moment is still far away from the free-ion value of $3.2 \mu_B/\text{atom}$, even for fields of 35T. The abrupt increase observed for fields applied in the $[001]$ direction is ascribed to the mixing of low-lying crystal field levels into the singlet ground state (Touborg et al. 1978).

3.1.1 Singlet ground state magnetism

Consider a system in which the crystal-field splitting is formed by a singlet-ground state $|g\rangle$ and a first excited state $|e\rangle$, with energy splitting Δ . In the presence of a magnetic field H along z -axis and in the absence of exchange, the total Hamiltonian is

$$\mathcal{H} = \sum_i V_{C,i} - g_J \mu_B H \sum_i J_{iz} \quad (3.1)$$

where the first term is the crystal-field and the second, the Zeeman term.

The applied field induces admixture of the two states and a Van-Vleck type temperature-independent susceptibility is obtained. Using (1.1) and assuming for simplicity that the excited state is

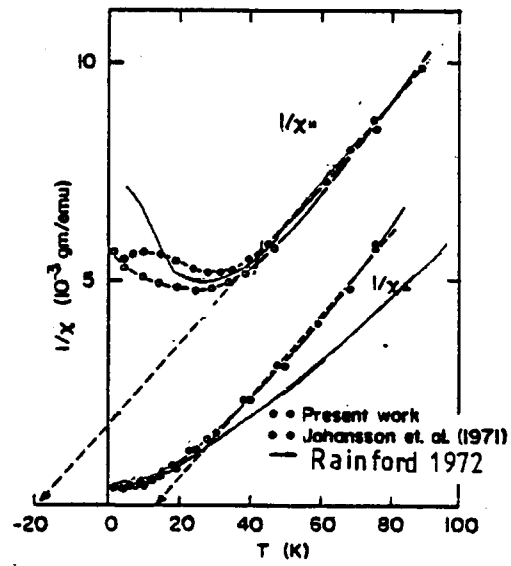


Fig.3.1: Reciprocal of the magnetic susceptibility for the C-axis and basal plane of a single crystal of Pr (after Sakamoto, 1976).

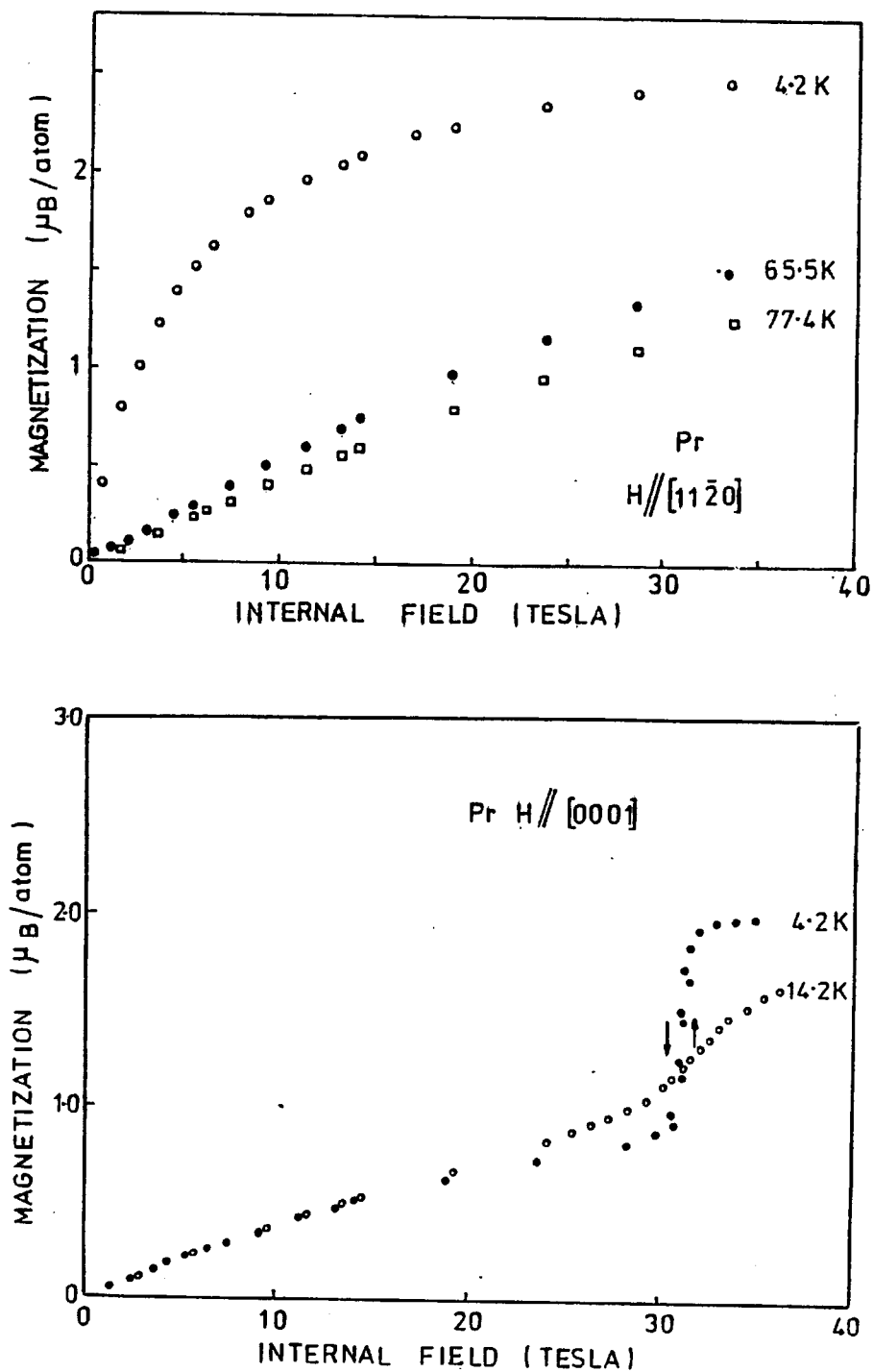


Fig.3.2: The high field magnetization of Pr as a function of internal field along $[11\bar{2}0]$ and $[0001]$ directions (after McEwen et al. 1973).

also a singlet, the susceptibility per ion is found to be

$$\chi_{CF} = 2g^2 \mu_B^2 \frac{|\langle e | J_z | g \rangle|^2}{\Delta} \tanh \left(\frac{\Delta}{2kT} \right) \quad (3.2)$$

where first order perturbation theory was used in order to get the perturbed states. As discussed by Bleaney, 1963, the effect of the exchange can be included within the molecular-field approximation. In this case the Hamiltonian is

$$\mathcal{H} = \sum_i V_{C_i} - \sum_{i,j} J_{ij} \bar{J}_i \cdot \bar{J}_j - g_J \mu_B \sum_i J_{iz} \quad (3.3)$$

$$\text{or } \mathcal{H} = \sum_i V_{C_i} - H_{MF} \sum_i J_{iz}$$

where

$H_{MF} = H + 2J(Q) \langle J \rangle$. In a similar way, the molecular-field induces a magnetic moment in the singlet ground state. Then the inverse of susceptibility per ion is given by

$$\frac{1}{\chi} = \frac{1}{\chi_{CF}} - \frac{2J(Q)}{g^2 \mu_B^2} \quad (3.4)$$

and, replacing χ_{CF} , we reach the following expression

$$\frac{1}{\chi} = \frac{\Delta}{2g^2 \mu_B^2 \alpha^2} \left(\frac{1}{\tanh(\Delta/2kT)} - \frac{4J(Q) \alpha^2}{\Delta} \right) \quad (3.5)$$

$$\alpha \equiv |\langle e | J_z | g \rangle|$$

where it can be seen that the effect of the exchange on $1/\chi$ is to shift the curve of $1/\chi$ vs T rigidly downward for ferromagnetic exchange, or upward for antiferromagnetic exchange, Cooper, B.R. 1972. Furthermore, the ratio of exchange to crystal field ($\eta \equiv 4J(Q) \alpha^2 / \Delta$)

gives the threshold value of exchange for magnetic ordering. This implies that the system remains a Van-Vleck paramagnet down to absolute zero temperature, unless $\eta \geq 1$, Trammell, 1963.

3.1.2 Crystal-field splittings of Pr

Rainford, 1972, found that, although the ground states in both type of site were singlets, the level scheme proposed by Bleaney, 1963, predicts the wrong sign for the magnetic anisotropy. Using the updated experimental data, Rainford estimated a new set of crystal-field and molecular field parameters, which accounts better for the experimental results. He used the following crystal-field for the hexagonal and cubic sites

$$V_C(h) = B_2^1(h)O_2^0 + B_4^1(h)O_4^0 + B_6^1(h) \left\{ O_6^0 + \frac{77}{8} O_6^6 \right\} \quad (3.6)$$

$$V_C(c) = B_2^1(c) O_2^0 + B_4^1(c) \left\{ O_4^0 + 20\sqrt{2} O_4^3 \right\} + B_6^1(c) \left\{ O_6^0 - (35/\sqrt{8}) O_6^3 + \frac{77}{8} O_6^6 \right\} \quad (3.7)$$

where the non-ideal c/a ratio has been considered (see Chapter 1). The crystal-field parameters needed to give an overall agreement with the experimental data were

$$B_2^1(c) = 0, \quad B_2^1(h) = 4.92K, \quad B_4^1(c) = B_4^1(h) = 0.0232K, \\ B_6^1(c) = B_6^1(h) = 9.84 \times 10^{-4} K \quad (3.8)$$

Because χ'' is scarcely different from zero and much smaller than χ' , see Fig.3.1, the ground state at the hexagonal sites must be the state $|0\rangle$, the excited state is the doublet $|\pm 1\rangle$. Rainford also predicts a singlet ground state Γ_1 and a triplet Γ_4 as first excited state at

the cubic sites. The crystal-field parameters also gave the following energy splitting

$$\Delta_h = 28 K \quad \text{and} \quad \Delta_c = 88 K \quad (3.9)$$

which are in good agreement with the experimental values

$$\Delta_h = 25 K \quad \text{and} \quad \Delta_c = 92 K \quad (3.10)$$

In Fig.3.1 the solid lines are obtained with the crystal-field parameters in Eq.(3.8) by fitting two molecular-field parameters, Rainford, 1972. As may be seen, at low temperatures there is a very good agreement with the susceptibility measurements. However, the minimum in the perpendicular susceptibility cannot be accounted for, and may not be a real effect, as has been discussed earlier. The preliminary crystal-field energy level found by Rainford are shown in Fig.3.3.

3.1.3 Magnetic excitations and dispersion relations in *Pr*.

The elementary magnetic excitations in *Pr* are the magnetic excitons, which correspond to linear combinations of excitations from the ground state to excited states on the hexagonal and cubic sites. The study of these excitations shows that the isotropic exchange form used to consider the coupling between ions is a simplified one, and reveals that anisotropic exchange is of considerable importance, Jensen, 1977.

Preliminary magnetic excitation studies were made by Rainford and Houmann, 1971, using neutron diffraction scattering measurements on a single crystal of *Pr*. (They reported $\Delta_h = 2.14 \text{ meV}$ or $25 K$.)

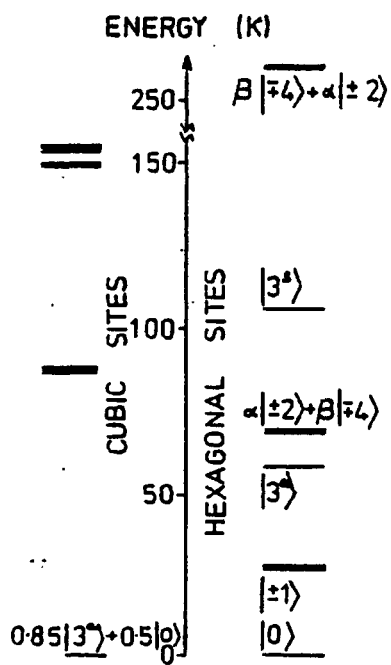


Fig.3.3: Preliminary crystal field energy levels (after Rainford, 1972).

A more extensive investigation has been made by Houmann et al. 1975, 1979.

Houmann et al. 1975, used the two-ion exchange coupling, given by Lindgard and Houmann, 1971, in order to study the splittings in the energies of the modes propagating on the hexagonal sites. They found clear evidence for a strong anisotropy in the exchange, but no indications of magnetic ordering above 0.4 K, although the exchange is approximately 90% of the critical value necessary for inducing an antiferromagnetic state. In Figs. 3.4a and 3.4b are shown the dispersion relations at 6.4 K for the magnetic excitations propagating on the hexagonal and cubic sites, respectively. In Fig. 3.4c is shown the Brillouin zone for the *dhcp* structure. Houmann et al. 1979 have analysed these experiments on the basis of the hybrid molecular-field random-phase approximation (Cooper 1972, Buyers et al. 1975). Houmann et al. 1979, have included in their theory the effect of all $(2J + 1) = 9$ crystal-field levels and the magnetoelastic coupling. The single-ion Hamiltonian used for the hexagonal ions was similar to that of Eq.(3.3), including the magnetoelastic term B_{22} (Jensen, 1979)

$$\mathcal{H}_0 = V_C(n) - \frac{3}{16} \frac{B_{22}}{c_j} \langle O_2^2 \rangle O_2^2 - g_J \mu_B \bar{H}_{MF} \cdot \bar{J} \quad (3.11)$$

The two-ion Hamiltonian took the following form

$$\mathcal{H}_{ff} = \sum_{i>j} J(ij) (\bar{J}_i - \langle \bar{J}_i \rangle) \cdot (\bar{J}_j - \langle \bar{J}_j \rangle) + \frac{1}{2} \sum_{i>j} \left[\chi(\bar{r}_i - \bar{r}_j) J_i^+ J_j^+ + \chi^*(\bar{r}_i - \bar{r}_j) J_i^- J_j^- \right] \quad (3.12)$$

where the normal Heisenberg coupling and the anisotropic exchange coupling were considered. When the wave vector $\bar{q}$ is along the

b -axis (see Fig.3.4 c), the excitons propagating on the hexagonal sites are pure x - and y -modes, and because the hexagonal lattice has two ions per unit cell, they are split into two branches (acoustic and optical branches), see Fig.3.4 a. The dispersion relations are

$$\begin{aligned}\epsilon_x^2(\bar{q}) &= \Delta_h \left[\Delta_h - 2M^2 \left(\mathcal{J}(\bar{q}) - \mathcal{K}(\bar{q}) \pm |\mathcal{J}'(\bar{q}) - \mathcal{K}'(\bar{q})| \right) \right] \\ \epsilon_y^2(\bar{q}) &= \Delta_h \left[\Delta_h - 2M^2 \left(\mathcal{J}(\bar{q}) + \mathcal{K}(\bar{q}) \pm |\mathcal{J}'(\bar{q}) + \mathcal{K}'(\bar{q})| \right) \right]\end{aligned}\quad (3.13)$$

where $M^2 = J(J+1)/2$. $\mathcal{J}(\bar{q})$ and $\mathcal{J}'(\bar{q})$ are the Fourier transforms of the Heisenberg coupling within and between the two hexagonal sublattices, and the equivalents for the anisotropic coupling are $\mathcal{K}(\bar{q})$ and $\mathcal{K}'(\bar{q})$. The dispersion relations of Fig.3.4 show four branches in the basal plane and only two branches in the c -axis. This implies that the double degeneracy of the x - y modes is lifted by anisotropic exchange, but when $\bar{q}$ is parallel to the c -axis, the excitons are degenerate. In the latter case the anisotropic coupling parameters K in Eq.(3.13) are zero. It is of interest to notice that the coupling between hexagonal ions is largest for $q \sim 0.25 \text{ \AA}^{-1}$ along ΓM , and η does not exceed 0.92-0.95.. This is the so-called incipient magnetic soft mode, i.e., the mode which corresponds in wave-vector and polarization with the magnetic structure formed when the system is forced to order.

The dispersion relations for the excitons propagating on the cubic sites are shown in Fig. 3.4. The significant difference from the case of the hexagonal sites is that the anisotropic coupling K , seems to be unimportant for these excitons. The magnetic coupling between ions in both hexagonal and cubic sites has been considered negligible, Jensen, 1976. Table 3.1 shows the wave-functions and relative energies of the crystal-field levels for the hexagonal sites calculated by Houmann et

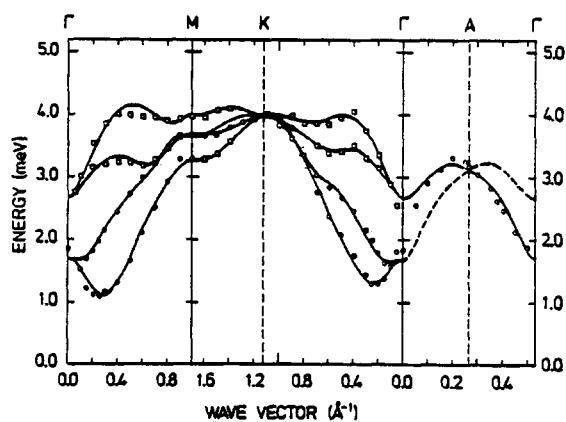


Fig.3.4 a) Dispersion relations for the magnetic excitations propagating on the hexagonal sites in Pr at 6.4K (after Houmann et al. 1979).

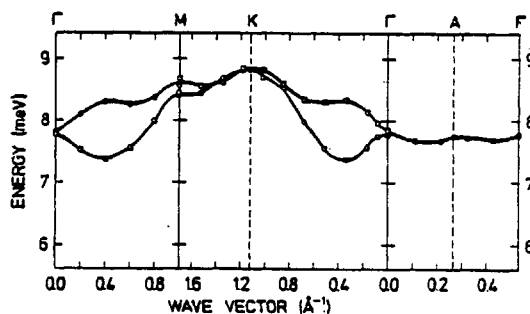


Fig.3.4 b) Dispersion relations for the magnetic excitations propagating on the cubic sites in Pr at 6.4K (after Houmann et al. 1979).

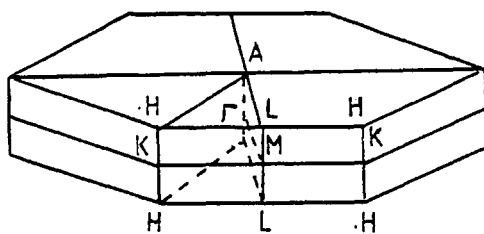


Fig.3.4 c) Brillouin zone for the dhcp structure.

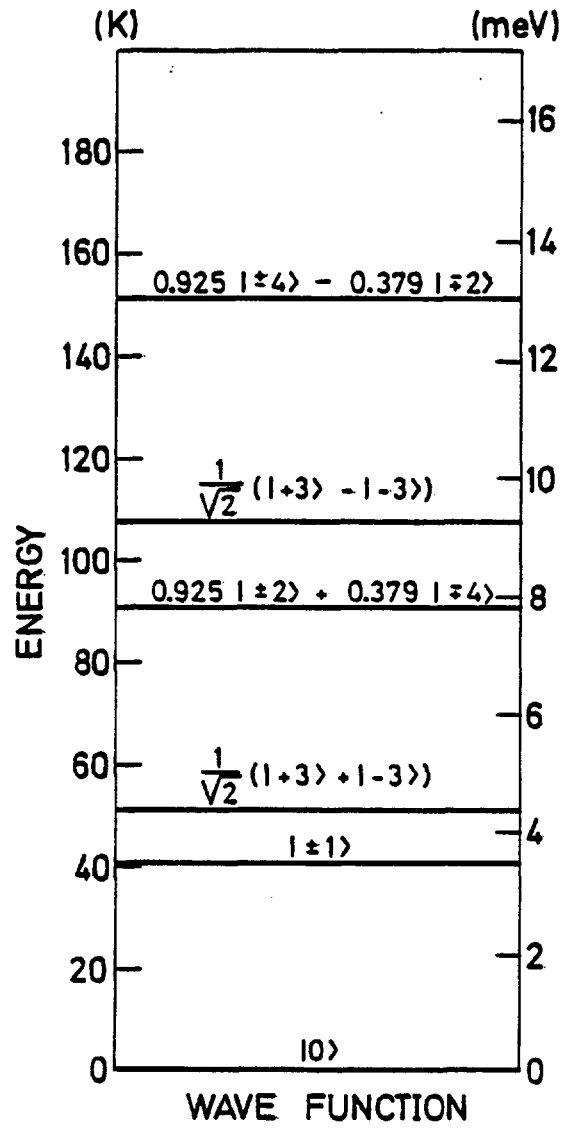


Table 3.1: Wave functions and relative energies of the crystal-field levels for the hexagonal sites in Pr (after Houmann et al. 1979).

al. 1979. They found the energy splittings for both sites to be

$$\Delta_h = 3.52 \text{ meV} = 40K \quad \text{and} \quad \Delta_c = 8.3 \text{ meV} = 96K \quad (3.14)$$

3.1.4 Electron-nuclear magnetism

So far, the interaction between the electronic spins and nuclei has not been included. However, Murao, 1971, has made clear the importance of the hyperfine interaction in considering singlet ground state systems, especially when the threshold value $2 \alpha^2 T(Q)/\Delta$ is near unity. In this case the Hamiltonian may be written as

$$\mathcal{H} = V_C - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j - \sum_i A \vec{I}_i \cdot \vec{S}_i \quad (3.15)$$

where the last term is the hyperfine interaction between the electronic spins $\vec{S}_i$ and the nuclear spins $\vec{I}_i$. In the molecular-field approximation it becomes

$$\mathcal{H} = V_C - \sum_i \left[2 \sum_j J_{ij} \langle \vec{S}_j \rangle + A \vec{I}_i \right] \cdot \vec{S}_i \quad (3.16)$$

This means that at low temperatures a weak magnetic ordering will develop via nuclear spin polarization, even at values of $2 \alpha^2 T(Q)/\Delta$ below unity. For ^{141}Pr the ordering will occur between 10 and 100 mK, with a saturation moment of the order of $0.1 \mu_B/\text{atom}$, McEwen and Stirling, 1981.

Lindelof et al. 1975, measured the heat capacity on a single crystal of Pr , which was known not to order above 1.8K. They found a sharp increase (λ -type anomaly) in the nuclear specific heat which they ascribed to a co-operative magnetic ordering of the hexagonal-site nuclei at 25-30 mK. This electronic ordering is associated with the hyperfine interaction discussed by Murao.

Hauschultz et al. 1978, measured the electrical resistance along the c -axis of a single crystal, from 20 mK to 5K. Below 0.5K they observed an increase in the resistance which was also associated with the nuclear co-operative anomaly below 30 mK.

McEwen et al. 1981, using thermal neutron scattering techniques, have observed an elastic peak with wave vector

$$Q_2 = 0.13 \tau_{100} \quad (q \sim 0.25 \text{ \AA}^{-1})$$

for temperatures below 1K. This peak was ascribed to the appearance of long-range magnetic ordering (anti-ferromagnetic phase) in Pr, consistent with Murao's theory, although the transition temperature is higher than the predicted temperature.

3.1.5 Magnetic ordering in Pr induced by uniaxial stress

The application of a uniaxial stress along the a -axis removes the two-fold degeneracy of the excited states on the hexagonal sites and consequently reduces the separation between the ground and first excited states. The threshold value will increase and hence magnetic ordering will appear at higher temperatures.

McEwen et al. 1978, 1981, have examined the dispersion relations for magnetic excitons propagating on the hexagonal sites when uniaxial stress is applied along the $[1\bar{2}10]$ direction, see Fig. 3.4c. At 5K they observed that the optic mode propagating along ΓM , see Fig. 3.4a, has a considerably lower energy at a pressure of 800 bars. This decrease is more pronounced where the ordering wave vector is $q \sim 0.25 \text{ \AA}^{-1}$. It is expected that when this mode goes to zero, under a suitable pressure, an anti-ferromagnetic structure will be observed.

3.1.6 Magnetic ordering in *fcc-Pr*

Bucher et al. 1969, have investigated a polycrystalline sample of *fcc-Pr*. Their magnetization measurements revealed a ferromagnetic ordering below 8.7 K. Low-field susceptibility shows a sharp peak at T_C , but no specific heat anomaly could be detected. Observations of Birgeneau et al. 1972, in neutron diffraction studies made using material from the same source, were contradictory. They obtained indications of a magnetic transition at 20 K, but no anomaly around 8.7 K. As yet, there is no satisfactory explanation for this peculiar behaviour.

3.1.7 Conclusion

The singlet-ground state, close to the threshold value for magnetic ordering, makes *dhcp Pr* unique amongst the rare-earth elements.

It is clear that *dhcp Pr* single crystal does not order above 1 K, but it does develop long-range order in the range of mK via hyperfine interaction. Magnetic ordering at higher temperatures may be induced by uniaxial stress.

However, *Pr* continues to pose unresolved questions. Neutron diffraction measurements, McEwen and Stirling, 1981, Burke et al. 1981, Bjerrum Møller et al. 1982, have shown a broad elastic scattering peak (central peak) below 10 K, which at first they thought not to be a true physical property of pure *Pr*. Now the central peak appears to be related to strong magnetic fluctuations. It seems that in *Pr* there is, simultaneously, a very strong tendency towards magnetic order and a great ambiguity in the ordering wave vector, Bjerrum Møller et al. 1982.

3.2 Magnetism in Pr-rare earth alloys

A number of investigations on alloys of various rare earth metals in *Pr* made by Sarkissian, 1977b, 1978a, 1978b, led him to suppose that the kind of magnetic ordering which appears in the more dilute alloys of *Pr-RE*, depends on whether the added solute is a light or heavy metal. The addition of small amounts of *Nd* ($\sim 2.5\%$) to *Pr*, induces long-range anti-ferromagnetism, Lebech et al. 1975, and Sarkissian, 1977b. On the other hand, there is absence of long-range magnetic ordering in *hcp Pr-Gd* alloys, even at high solute concentration ($\sim 20\%$ *Gd*) Sarkissian, 1978a. The magnetism found in this latter case, is the spin glass-type magnetic freezing, already discussed in Chapter 1. It was suggested that the suppression of long-range order to give spin glass freezing, may be associated with the difference in spin-orbit character of host and solute. The factor $(g_J - 1)J$ has opposite sign for light and heavy elements. This results in a magnetic structure where the magnetic moments are randomly parallel or antiparallel, even in the case that *sf* interaction is such that it aligns all the spins of host and solute parallel to each other.

3.2.1 Pr-light rare earth alloys

Neutron diffraction measurements, Lebech et al. 1975, made on single crystals of *Pr* 3%, 5.5%, 26.3% *Nd*, exhibited anti-ferromagnetic ordering on the hexagonal sites, below 6.3K, 6.5K and 11.4K respectively. No evidence of ordering could be found on the cubic sites.

High-field magnetization measurements up to 37T, McEwen et al. 1973, showed that the abrupt increase observed in the magnetization of pure *Pr* at high field (see Fig. 3.2) is still found in the alloy system (up to 26% *Nd*). This indicates that the crystal-field at the *Pr* sites is not drastically altered by the addition of *Nd*.

Sarkissian, 1977b, has found a sharp peak in *dc*-susceptibility (~ 5 Oe) measurements on various *Pr-Nd* alloys. The peak disappears as the field is increased and ferromagnetic saturation behaviour is reached at higher field (~ 500 Oe). The resistivity presents anomalies associated with anti-ferromagnetic ordering.

Pr-Ce alloys have been studied by electrical resistivity and *ac, dc* susceptibility measurements, Sarkissian 1979. A Kondo-like resistance minimum has been observed for alloys with concentrations up to 20% Ce. There is no clear evidence whether spin glass or anti-ferromagnetic ordering develops for alloys with concentrations between 20% to 40% Ce, but anti-ferromagnetism is found for a *Pr-42% Ce* alloy.

Preliminary low-field magnetization experiments on dilute Pr-Sm alloys, Sarkissian 1978a, have shown magnetic characteristics associated with long-range order. This will be discussed again. Götz et al. 1979, have studied dilute alloys of Pr-Eu, with concentrations of solute between 0.5% to 6%, by Mössbauer spectroscopy and magnetization measurements. They found that there is no indication of magnetic ordering from the magnetization experiments, but magnetic hyperfine splittings below a critical temperature are found. These may correspond to an antiferro or spin glass magnetic phase.

3.2.2 Pr-heavy rare earth alloys

Chatterjee et al. 1971, have measured neutron diffraction and magnetization on several samples of Pr-Tb. They observed deviations from Curie-Weiss behaviour at low temperatures for 10, 20% Tb alloys. The *Pr-30% Tb* alloy exhibited a broad maximum in the magnetization, at around 20K and no Bragg reflections in the diffraction pattern.

Sarkissian 1977b, performed similar measurements to that of Pr-Nd on several alloys of Pr-Tb (0.5-20% Tb). The magnetization-temperature experiments show a peak, for solute concentrations higher than 3% Tb. However, the resistivity does not show any anomalous behaviour associated with long-range order. He ascribed these features to spin glass-type ordering.

Tissot and Blaise, 1970, made magnetization measurements in a number of Pr-Gd alloys, covering the whole range of concentrations. They could not find any magnetic ordering for concentrations of Gd up to 46%. In contrast, Sarkissian 1978a, found spin glass behaviour for alloys with concentrations between 5% to 20% Gd. He observed the characteristic sharp peak in the *ac* susceptibility and field cooling effects in *dc*-susceptibility. Furthermore, resistivity measurements did not show the distinctive changes which occur when anti-ferromagnetic ordering is present. This is due to the absence of superzone boundary effects when spin-glass is manifest. The contradictory result of Tissot and Blaise is attributed to the use of high magnetic fields which cause smearing in the susceptibility peak. This reflects the importance of the use of low-field susceptibility in dealing with spin glass, in order not to misjudge the experimental results.

Susceptibility and resistivity measurements on *dhcp* Pr-Tm alloys showed no signs of magnetic ordering, Sarkissian 1979. This is because both *Pr* and *Tm* have singlet ground states, and large concentrations of solute may be needed to produce any magnetic state.

3.3 Praseodymium-Yttrium alloys

The main interest in studying the $Pr-Y$ system is to observe how magnetism develops in these alloys when the local crystallographic environment of the Pr -atoms is changed by the successive stabilization of the d_{hcp} , Sm -type and hcp structures.

As has been mentioned in Chapter 1, Y behaves much as a heavy rare earth in its ionic and structural properties. In addition, Y is a strong d -like element which induces exchange enhancement. Alloys of $Y-HRE$ exhibit long-range order, even at low concentration of solute, followed by the appearance of spin glass freezing at a lower concentration of heavy rare earth. This behaviour is in sharp contrast to that of $Sc-HRE$, in which large amounts of solute are needed in order to obtain any magnetic ordering.

So far, little work has been done in alloys of Y -light rare earth. Resistivity measurements on $Y-Ce$ alloys have been done by Hill et al 1969. They observed a Kondo resistance minimum for the hcp alloys up to 44% Ce . For the d_{hcp} alloys, antiferromagnetic ordering was found. However, Ce is not a very representative light rare earth element because its f electron occupies a virtual bond state rather than a true bond (Coqblin and Blandin 1968), typical of other rare earths. This produces a Kondo-like effect.

As a matter of comparison it is more interesting to consider the $Nd-Y$ system, (Sharif and Coles 1978), which involves a light rare earth similar to Pr . Both the Pr and Nd stable crystal structures are d_{hcp} and both present a fcc metastable structure which has been revealed to be ferromagnetic, Bucher et al 1969. Crystal field effects in Pr and Nd are of considerable importance compared with

their weak exchange interaction, see Table 1.1. Moreover, some workers (McEwen et al 1981) attribute to *Pr* (at low temperatures) and dilute alloys of *Pr-Nd*, magnetic structures similar to that of pure *Nd*. However, unlike *Pr*, *Nd* (Kramers-ion) has proved to have very complicated magnetic phases, still not well understood. Many magnetic transitions have been observed in a single crystal of *Nd*, Lebech 1981, Forgan, 1979; the main ones occur at ~ 20 K and ~ 7.5 K. Hexagonal and cubic sites order magnetically in both transitions.

Alloys of *Nd-Y* in the *dhcp* structure exhibit two magnetic transitions like those of pure *Nd*. The metastable ferromagnetic *fcc* is present in the as-cast alloys, but can be easily removed by annealing. The magnetism in alloys with *Sm*-type structure is not yet clear. It is suggested that the strong susceptibility peak observed in these alloys marks the onset of hysteretic magnetic ordering. Alloys of *Nd-Y* in the *hcp* structure show a single antiferromagnetic transition for concentrations between 12% to 50% *Nd*. The rather interesting result is that for 50% *Nd* alloy, the Néel temperature is 40 K, far higher than the highest ordering temperature of pure *dhcp Nd* and the Curie temperature (~ 29 K) of *fcc Nd*. It is not until concentrations of *Nd* of the order 20% that the Néel temperature goes down to ~ 20 K. Below 12% *Nd* spin-glass magnetic freezing appears.

3.3.1 X-ray analysis of the samples

The alloys were prepared as described in the section 2.4, and proved to be easy to cast into the mould. The loss of material was less than 0.1%. hence no further analysis was made and the nominal concentration was taken as the true concentration. The samples were annealed for homogenization (of structure) at 500°C for seven days and air cooled. X-ray diffraction using a Guinier camera was made

on the annealed samples, and in order to determine the crystal structures and crystal parameters, the following procedure was employed: - measurement of the line positions X of each diffraction pattern on the film, by means of a micrometer. Four different samples were registered simultaneously on one piece of film. For each pattern, the θ angles and therefore the spacing d of the reflecting planes causing each line were calculated from the line positions.

- indexing of the pattern by the graphical method for powder hexagonal systems. An assumption is first made as to which of the three crystal systems (*hep*, *Sm*-type or *dhep*) the unknown structure belongs to. Then the correct Miller indices are assigned to each reflection. A Bunn chart was constructed from numerical data given in International Tables for X-ray Crystallography Vol II. This chart consists of a network of curves, one for each value of hkl , where values of $1/d^2$ are plotted against c/a ratios. (For *dhep* and *Sm*-type structure, the parameter c is considered as twice or 4.5 times, respectively, that of the *hep* structure). The observed values of d for a given pattern are marked on a strip of paper and then placed on the chart and moved vertically and horizontally until each mark coincides with a line of the chart. In this way, c/a ratios for each sample were obtained and each line of the pattern indexed. This method also reveals easily the presence of two-phases in the alloy. Fig. 3.5a shows the c/a ratios as a function of Y concentration.

- calculation of a and c for each line, using the c/a ratio obtained from the chart and the different d_{hkl} values. For a specific alloy, the a and c values were taken as the average of the values calculated for each line. Figs 3.5b and 3.5c show a and c values as a function of Y concentration.

The atomic volume was calculated from

$$V_{at} = \frac{\sqrt{3}}{4} a^2 c$$

considering two atoms per unit cell for the hexagonal structure. In Fig. 3.5d are shown the V_{at} values as a function of concentration. The results exhibited in Fig 3.5a show that the correlation between the c/a ratio and the type of structure is rather smooth. However, in the $dhcp$ region the c/a ratio does not change much (around 15% of the total change) compared with the change which occurs in the $dhcp$ region (around 56%). In the Sm -type region c/a values are smaller than the c/a of pure Sm metal. The parameter c follows quite the same variation, with respect to the structures, as the c/a ratio. For alloys in the Sm -type structure, the c values vary around the value of pure Sm (that is $5.829\overset{0}{\text{\AA}}$); this value lies between the c values of the alloy constituents. In contrast, the parameter a varies more drastically when the structure changes from hcp to Sm -type form. The a value increases rapidly in the hcp structure and then drops down when the Sm -type structure becomes stable; then increases steadily until it reaches the $dhcp$ form where a does not vary much. It is interesting to point out that for pure Sm the a value ($3.628\overset{0}{\text{\AA}}$) is smaller than the a values of the both alloy constituents. In Fig 3.5b are also shown two small strips (between pairs of dashed lines), which represent the two-phase regions. The samples 37.5% and 55% Y are two-phase alloys and Fig 3.5a exhibits the a value of each alloy for both type of structures. Coles 1980 has suggested that in the boundaries of the Sm -type structure, there is a high density of stacking faults. This formation may explain the small value of a in these regions.

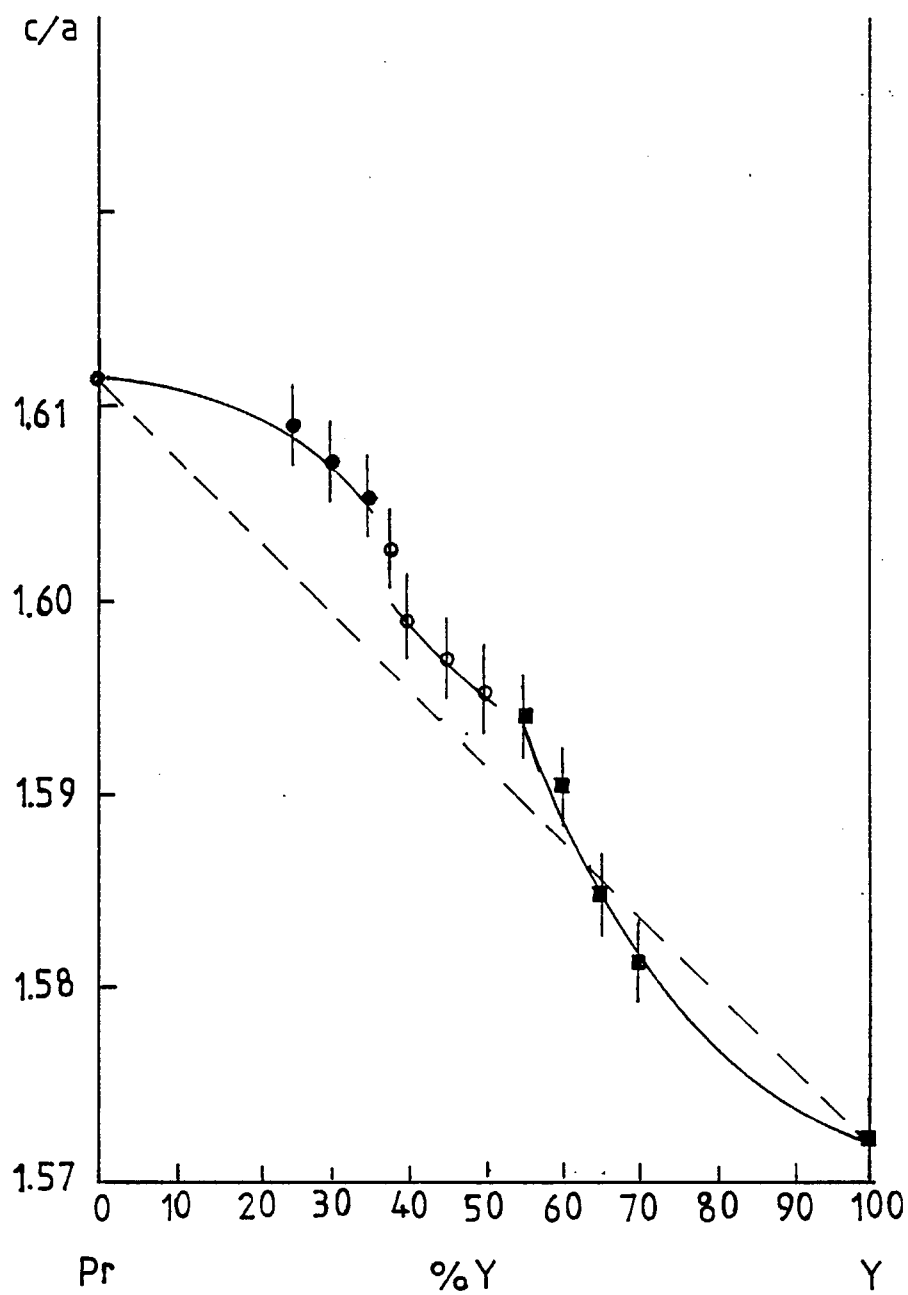


Fig.3.5 a) c/a ratios of the Pr-Y alloys as a function of Y concentration.

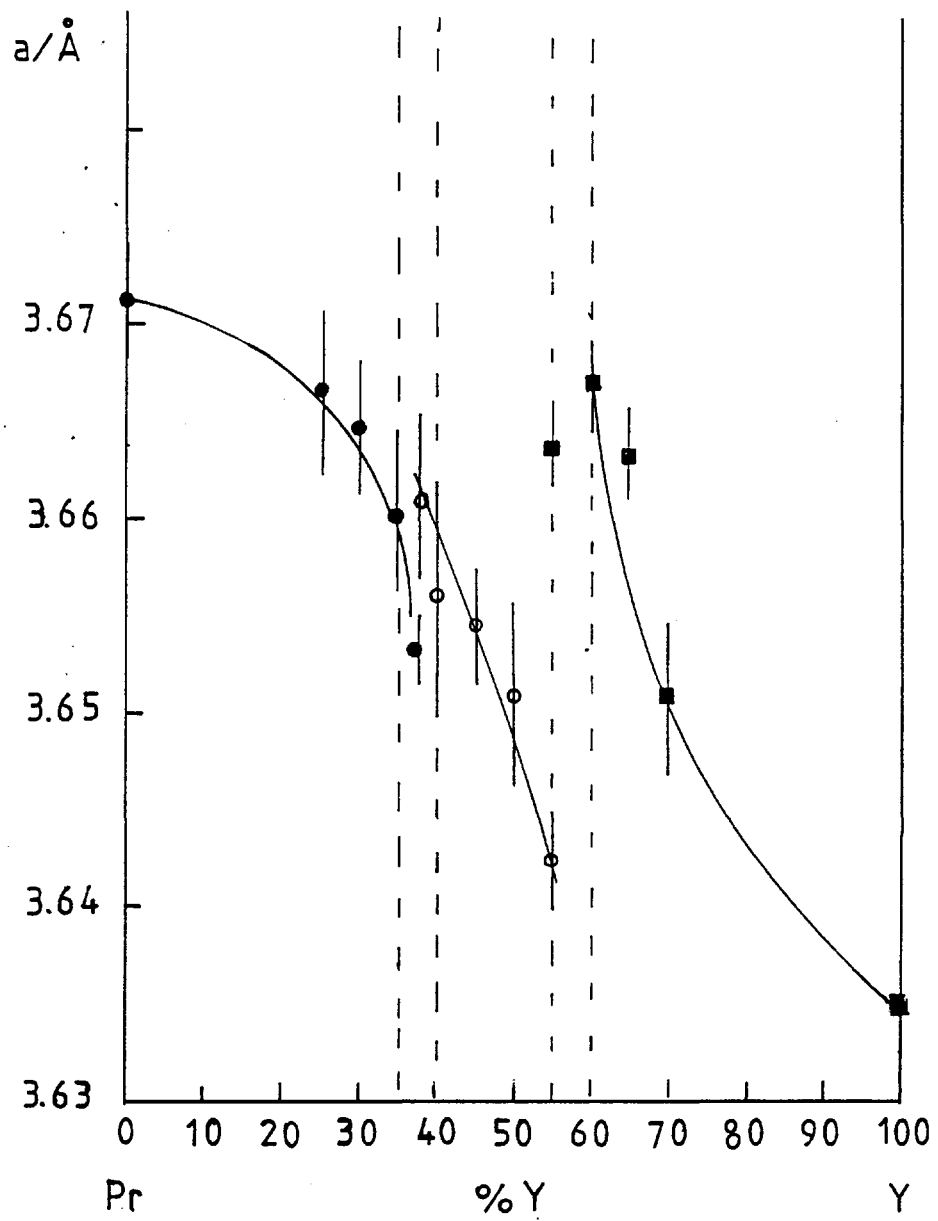


Fig.3.5 b) a values of Pr-Y alloys as a function of Y concentration.

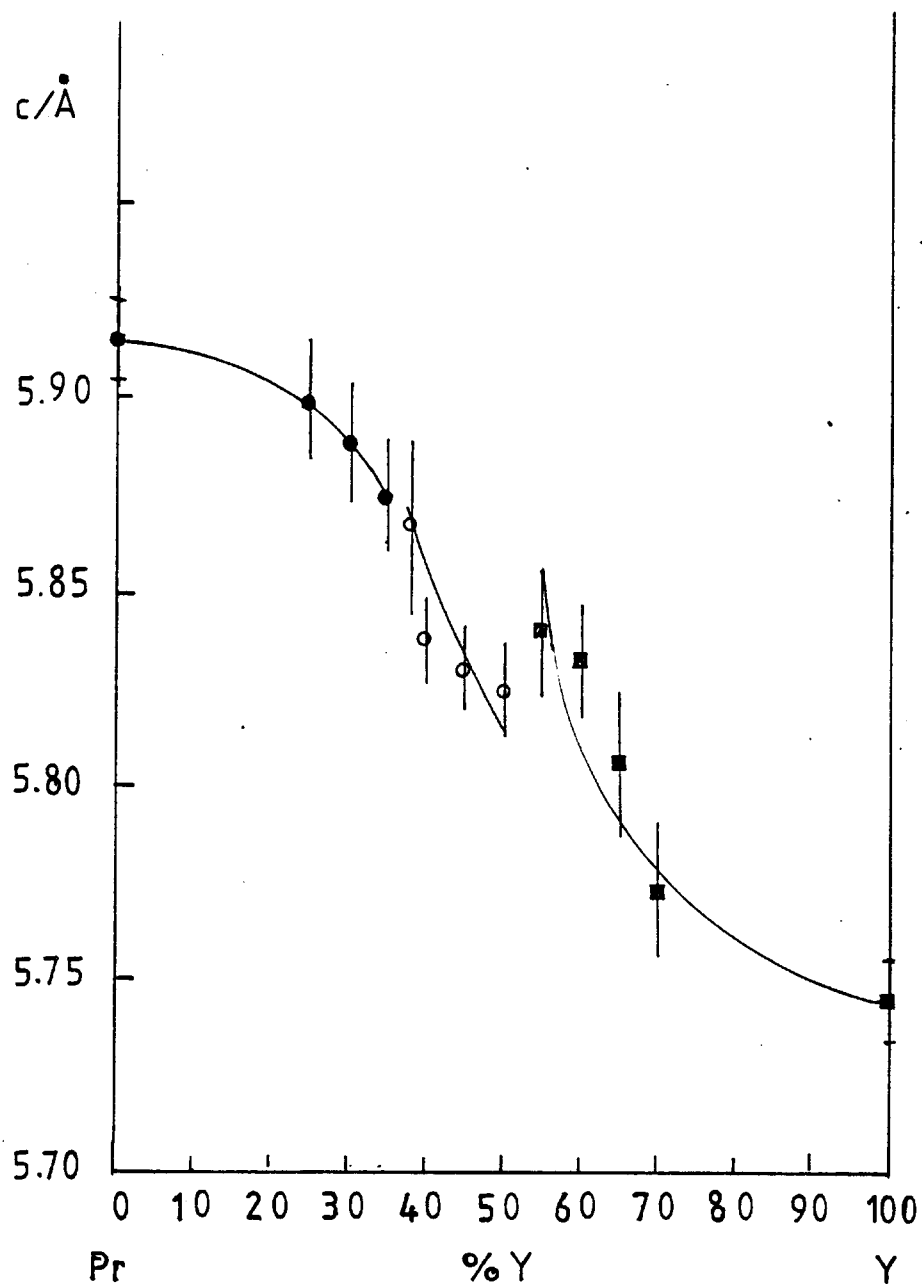


Fig.3.5 c) c values of the Pr-Y alloys as a function of Y concentration.

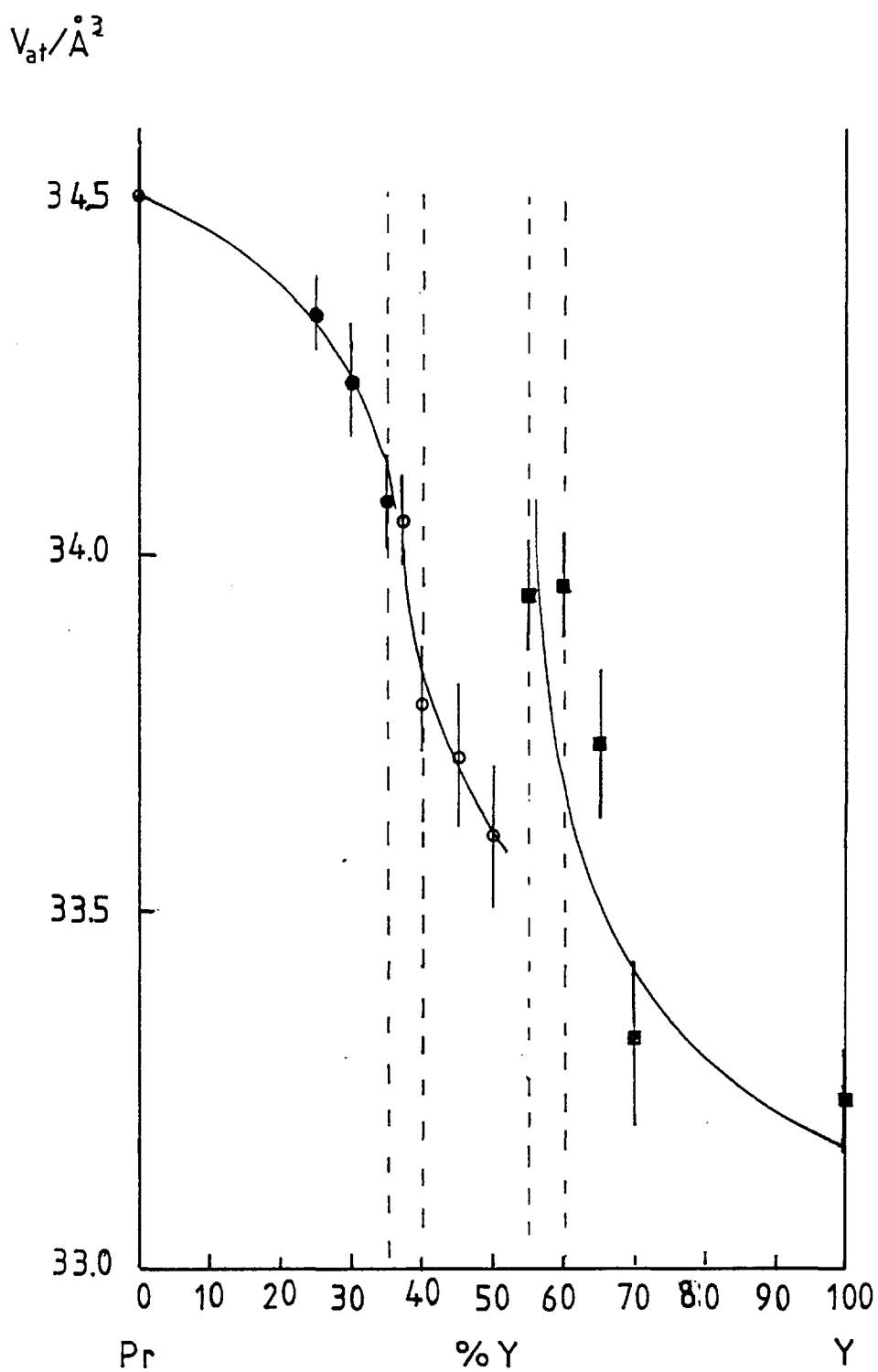


Fig.3.5 d) Atomic volume of the Pr-Y alloys as a function of Y concentration.

So far, no phase diagram of the *Pr-Y* system has been reported in the literature. Spedding et al 1962 verified the existence of *Sm*-type structure in this system for the *Pr*-50.3% *Y* alloy, a value of concentration which coincides with the present work. Also, Harris et al 1966 have analysed by X-ray a number of alloys in which the different structures occur. Their results differ from those quoted in this work; nevertheless qualitative agreement is observed. They have reported 40% *Y* concentration for the alloy which presents the *Sm*-type structure, but *hcp* structure for the alloy with 50% *Y* concentration. This discrepancy could be attributed to the different heat treatment used.

3.3.2 Results

The ac-susceptibility of pure *dhcp Pr* is shown in Fig 3.6. It exhibits the characteristics of a singlet ground state Van-Vleck paramagnet, although there is a small decrease below ~ 4 K, also observed in the χ'' (see Fig 3.1). This effect has been ascribed to the depopulation of the low lying $| \pm 1 \rangle$ doublet state as the temperature is lowered. The inverse of the susceptibility, Fig 3.7, obeys the Curie-Weiss law above ~ 100 K, with an effective moment of 3.62 ± 0.05 and a paramagnetic temperature θ of $+ 2.8 \pm 1$ K. Below 100 K the susceptibility deviates from the Curie-Weiss law towards higher values of susceptibility. It is of interest to notice that Johansson et al 1970, 1971 found a paramagnetic temperature of $+ 12.2$ K and $- 20$ K for the inverse of susceptibility in the $[110]$ and $[001]$ directions, respectively.

Upon diluting *Pr* with *Y*, the character of the susceptibility changes. Fig 3.6 shows the low-temperature susceptibility (scaled to their maximum value) for pure *Pr*, *Pr*-25% *Y* and *Pr*-30% *Y* (all three

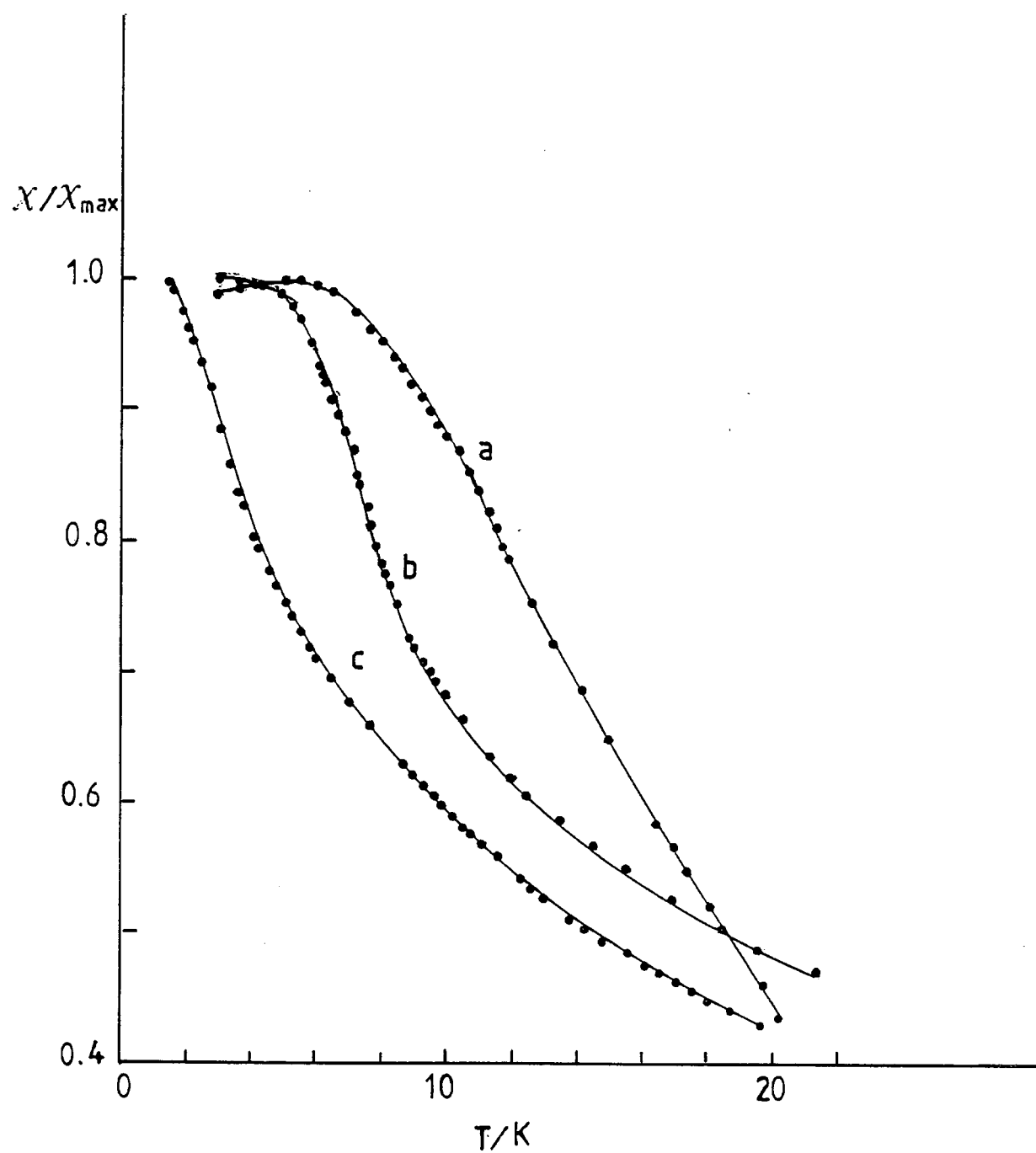


Fig. 3.6: Ac-susceptibilities (scaled to their maximum value) of a) pure dhcp Pr, b) Pr-25%Y and c) Pr-30%Y alloys.

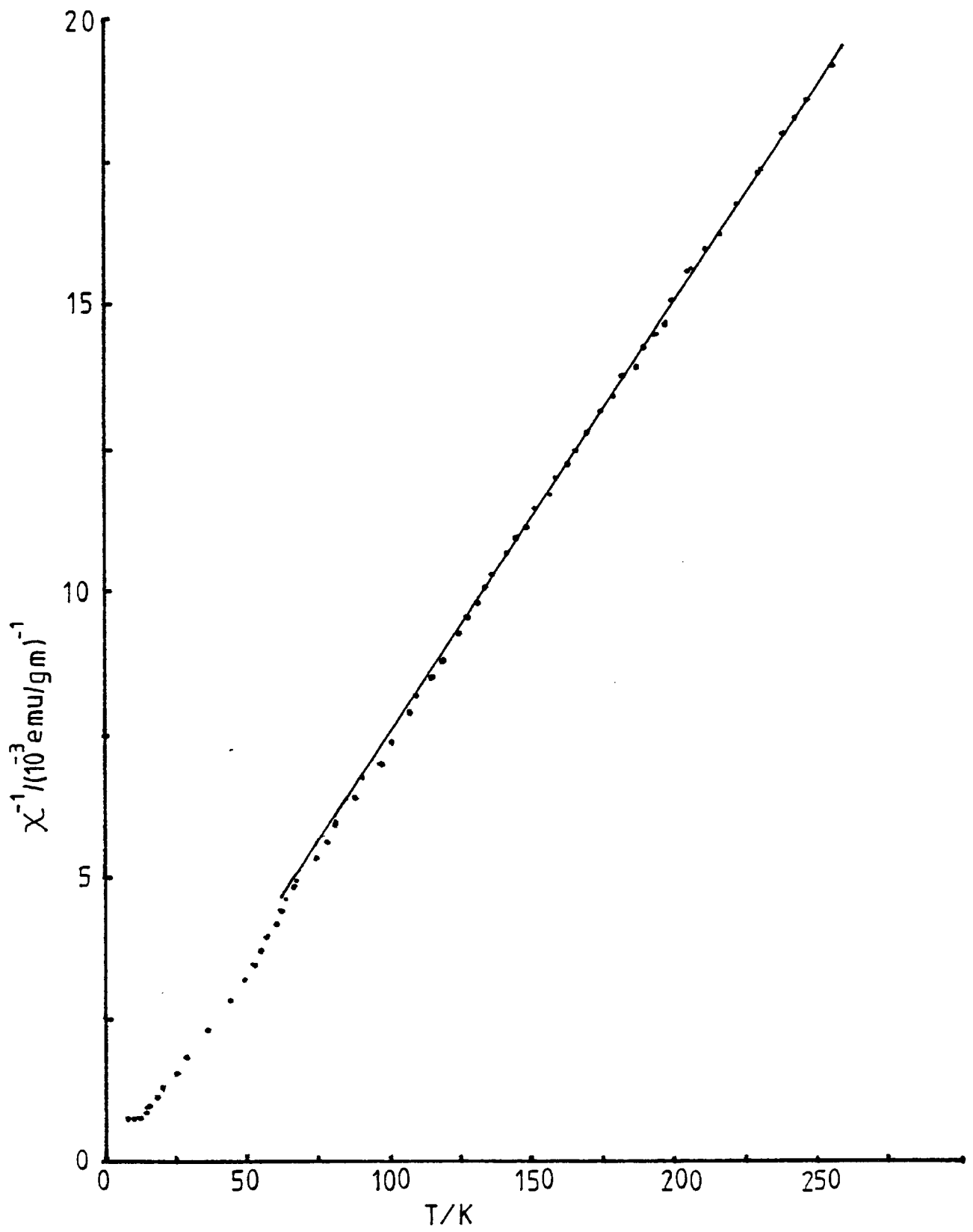


Fig. 3.7: Inverse of susceptibility as a function of temperature for dhcp Pr.

belong to the *dhcp* structure). The *Pr*-25% *Y* alloy does not order above 1.5 K and the *Pr*-30% *Y* seems to have a rounded maximum at about 1.5 K.

The ac-susceptibility of a number of alloys of *Pr*-*Y* are shown in Figs 3.8 and 3.9 for the as-cast and annealed samples, respectively. A clear dependence of the maximum-temperature (T_{max}) as a function of *Y* concentration is observed. (The proper concentration to each alloy is specified in the Figs.) The as-cast alloys may contain more than one phase, especially at or near the *Sm*-type structure, due to the quench from high temperatures when the alloy is made. The extraneous phase was removed by heat treatment and the corresponding structure for the annealed samples was discussed in the previous subsection. For all samples, the maximum of the susceptibility is rather rounded. Fig 3.10 shows the peak-susceptibility value of the annealed alloys as a function of *Y* concentration. The *Pr*-50% *Y* alloy exhibits the highest value.

The peak-temperature dependence with *Y* concentration is exhibited in Fig 3.11 for the as-cast and annealed alloys. It can be seen that, for a given alloy between 30 to 50% *Y*, the T_{max} shifted to a quite lower value of temperature after the sample was annealed, which indicates a mixture of phases in the as-cast alloys. This fact may also give account for the high values of the maximum-susceptibility found in the 35, 40 and 45% *Y* alloys. For a given alloy between 55 and 75% *Y*, there was, instead, only a small shift towards higher temperatures, after the sample was annealed. This suggests the presence of *Sm*-type structure in the alloy. Surprisingly, the *Pr*-80% *Y* alloy exhibited a maximum at around 10 K, which proved to be difficult to remove it (see Fig 3.9) using the same heat treatment. It is not clear why this should be the case. The *Pr*-90% *Y* alloy does

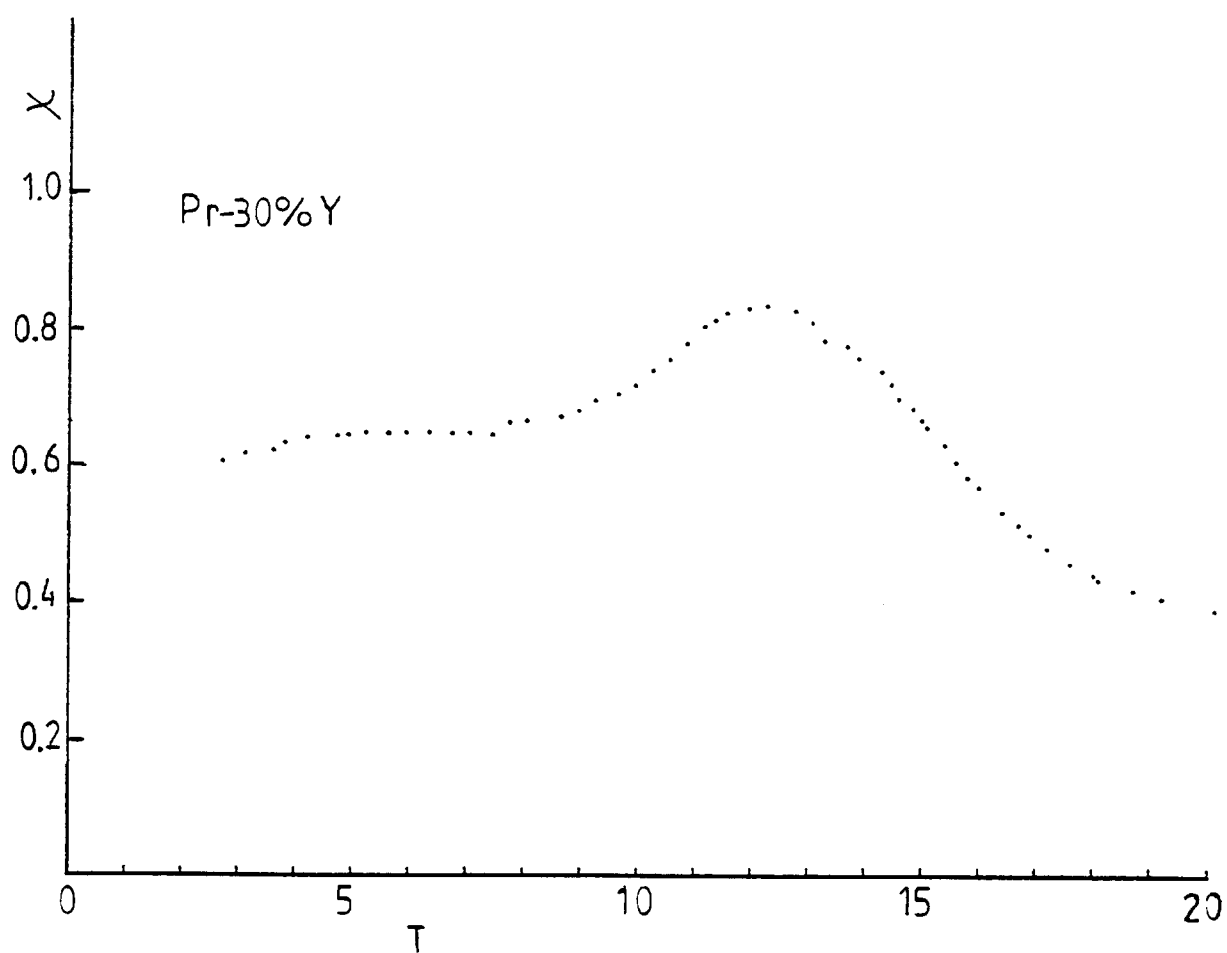
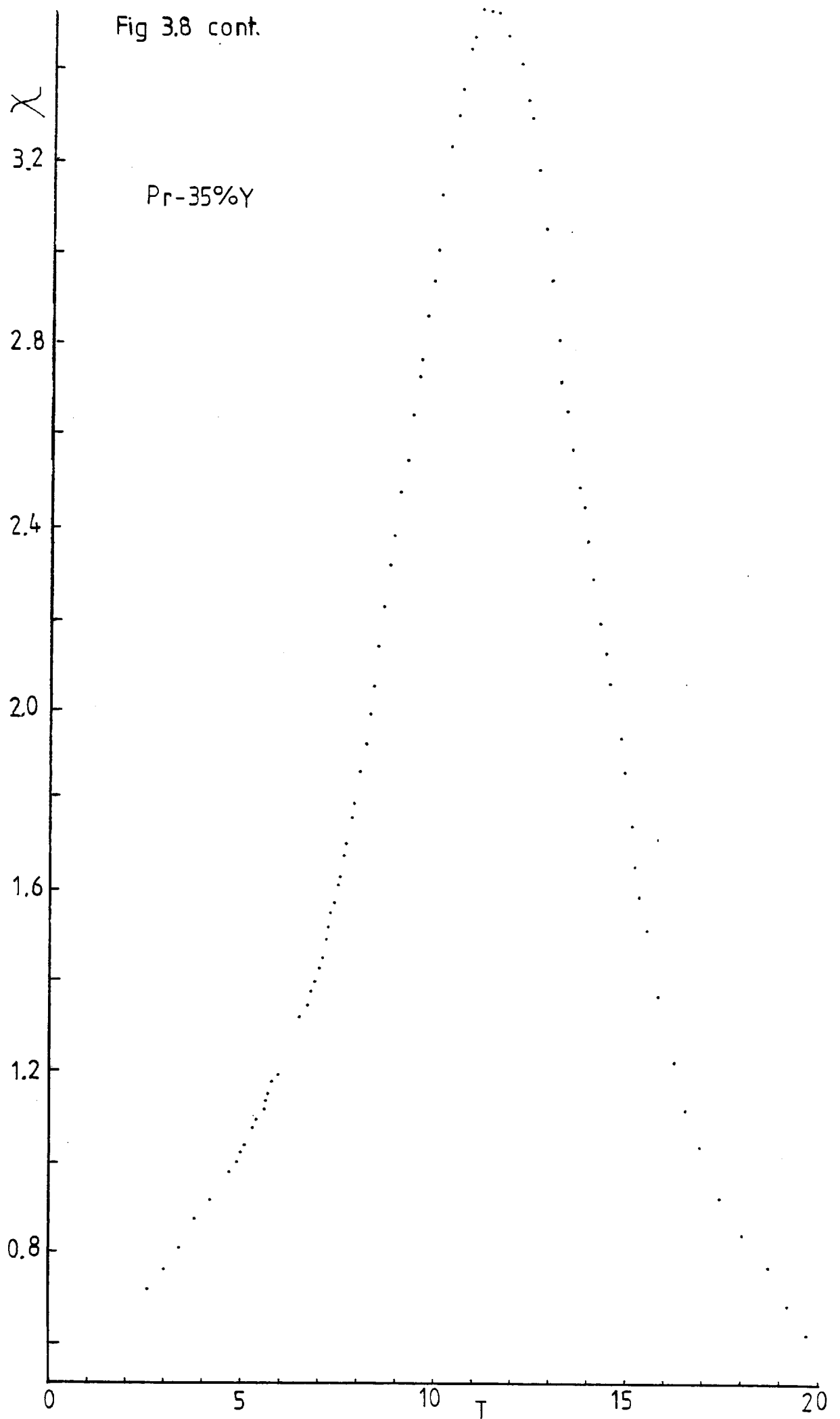


Fig 3.8: Ac-susceptibility for the as-cast Pr-Y alloys.

units: T in K
χ in 10⁻³ emu/gm



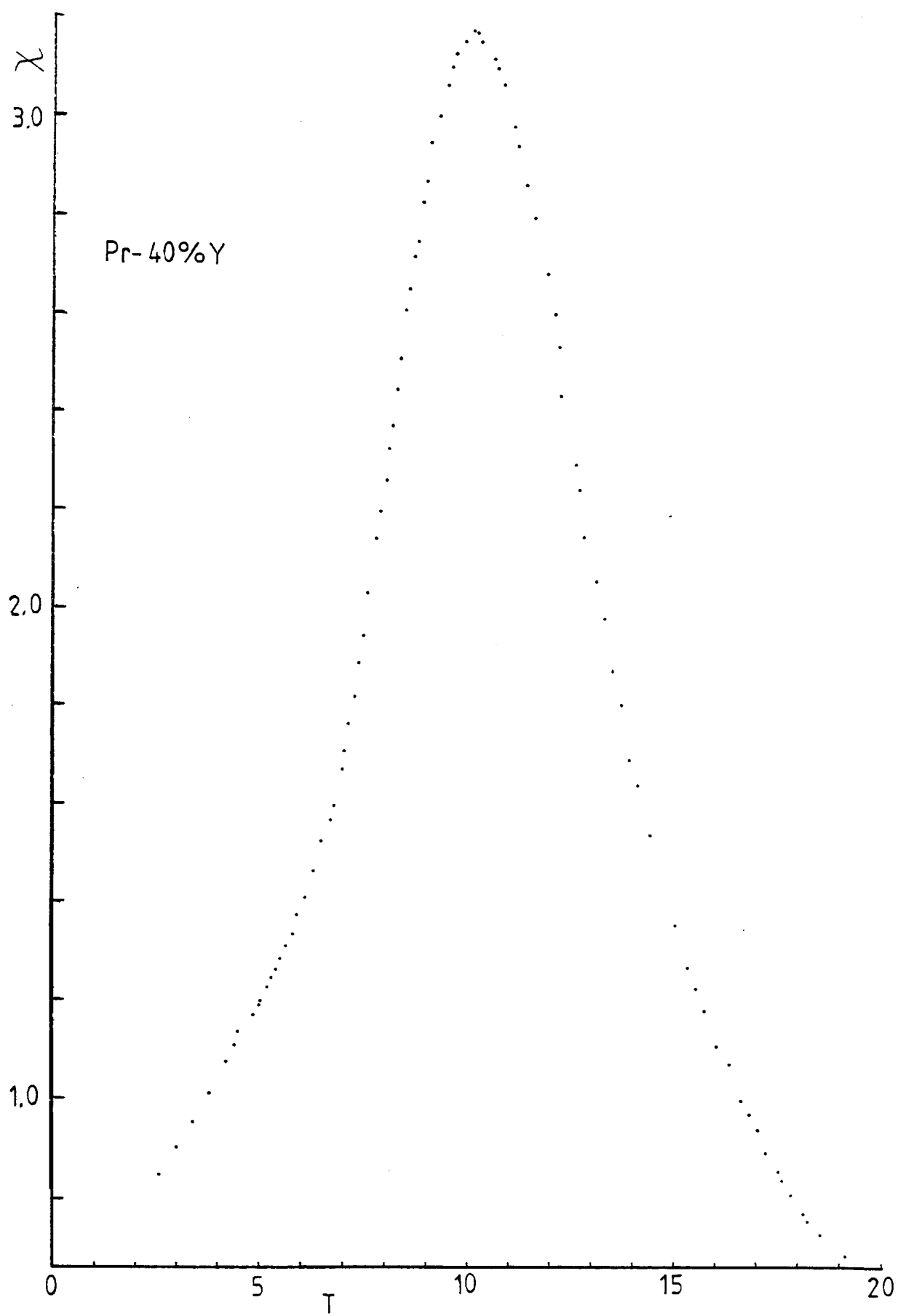


Fig 3.8 cont

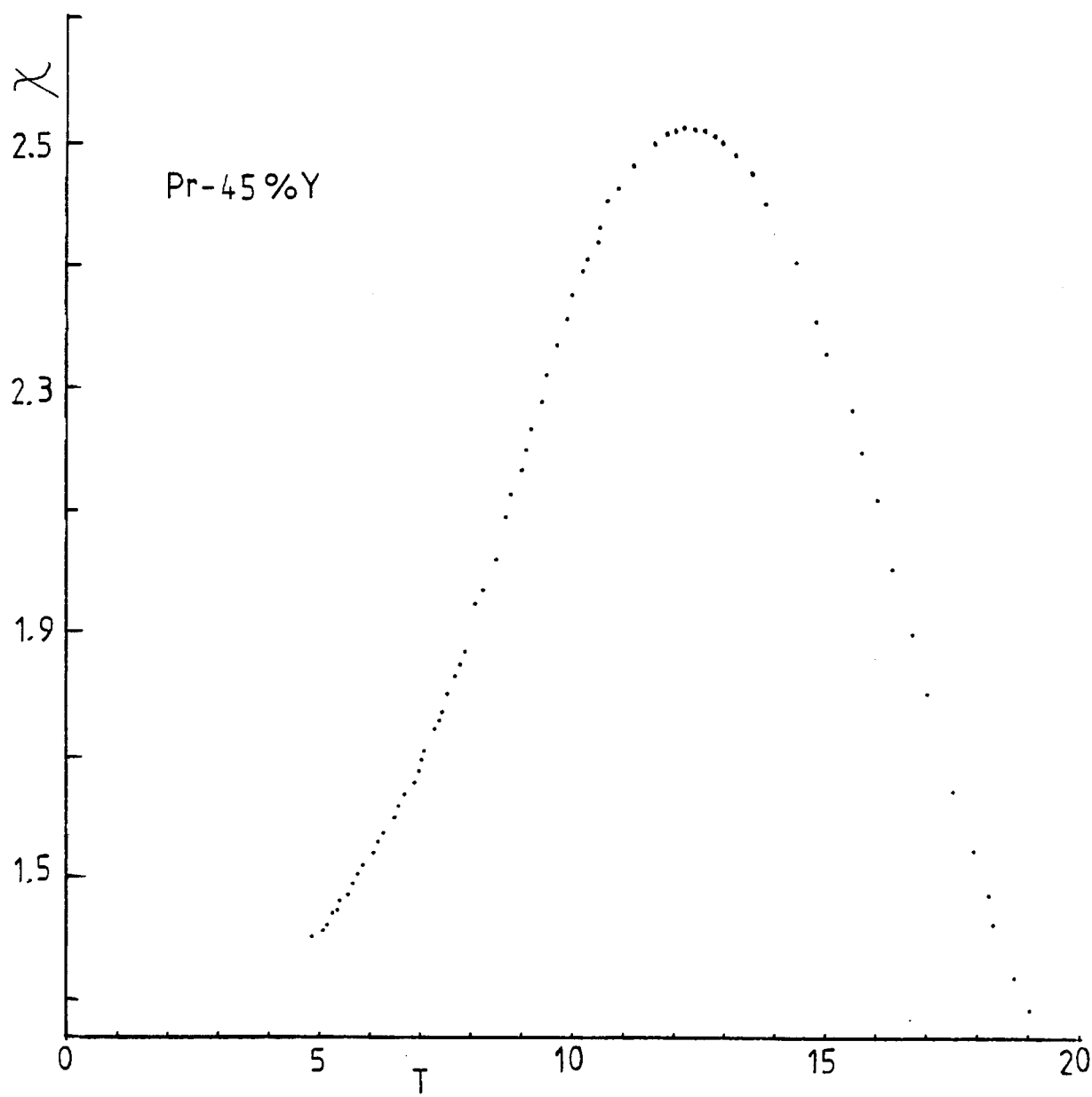


Fig 3.8 cont

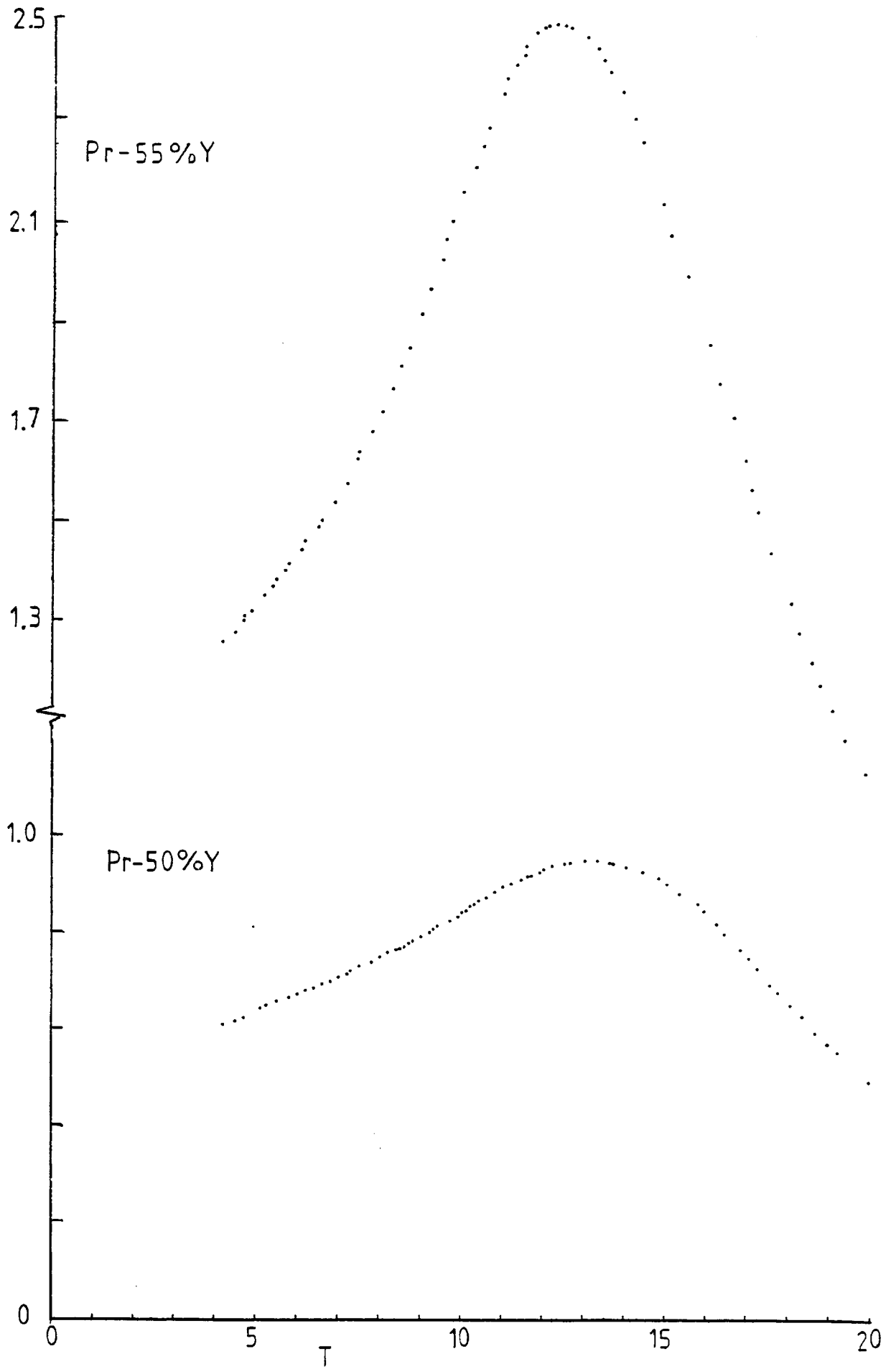


Fig 3.8 cont

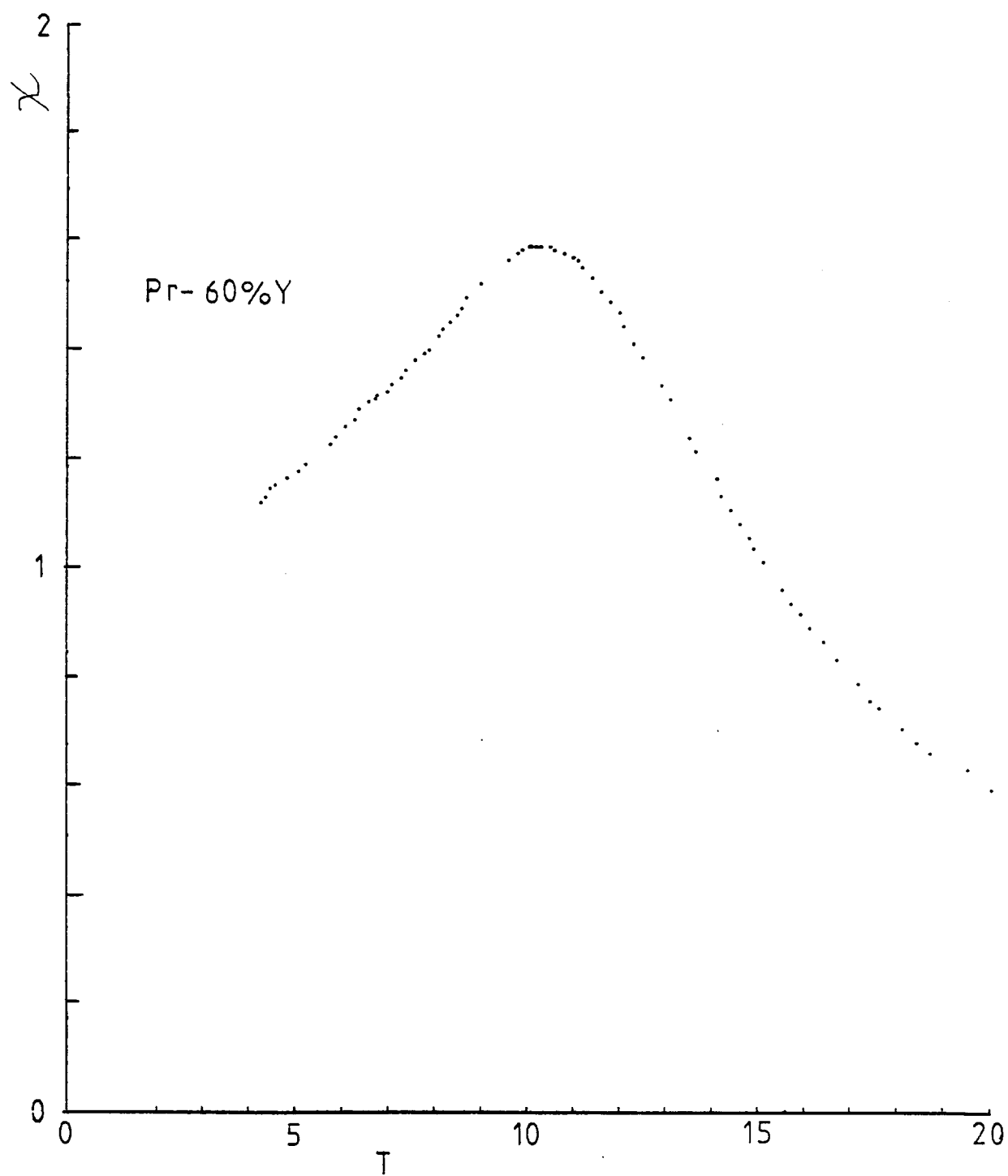


Fig 3.8 cont

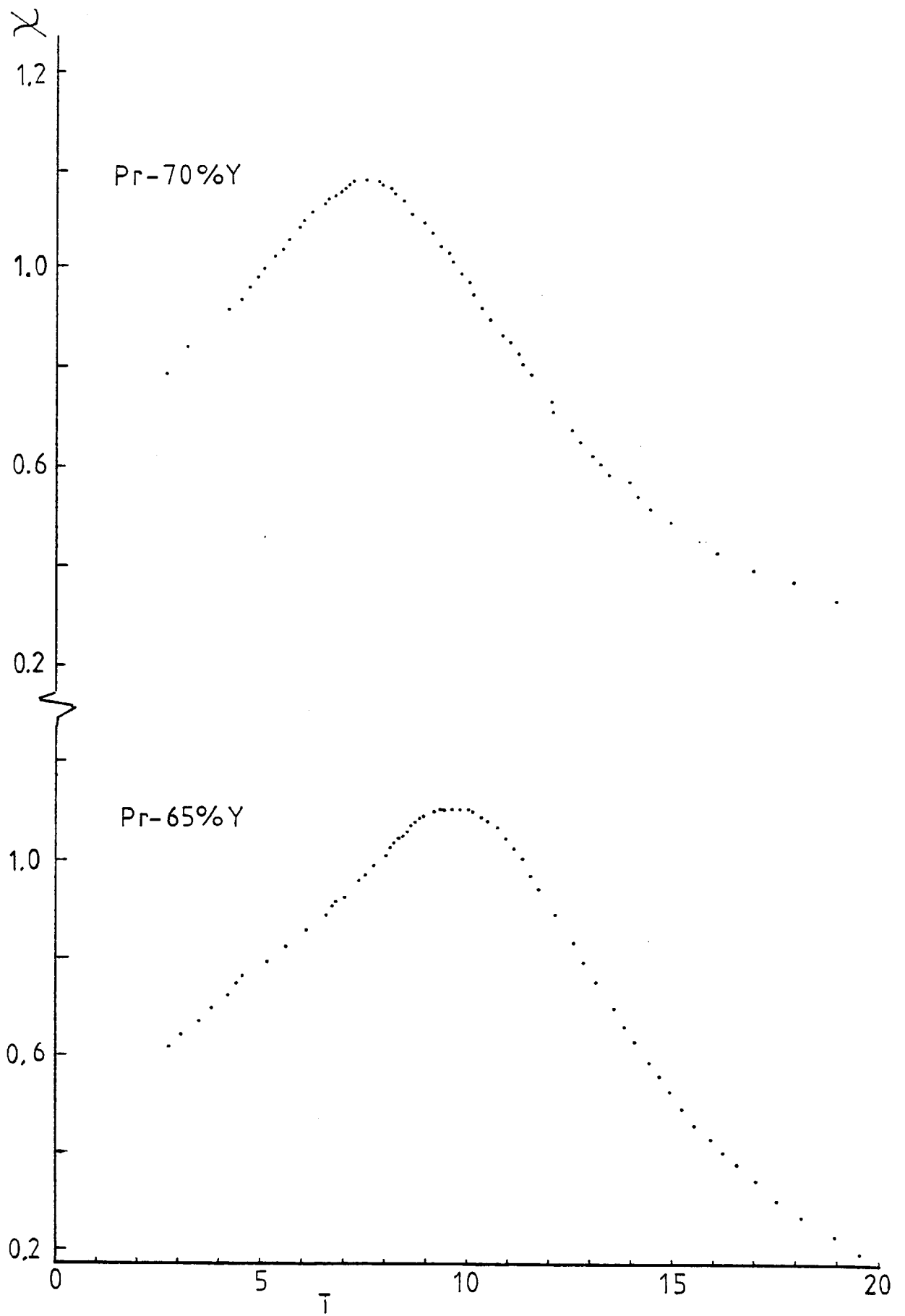


Fig 3.8 cont

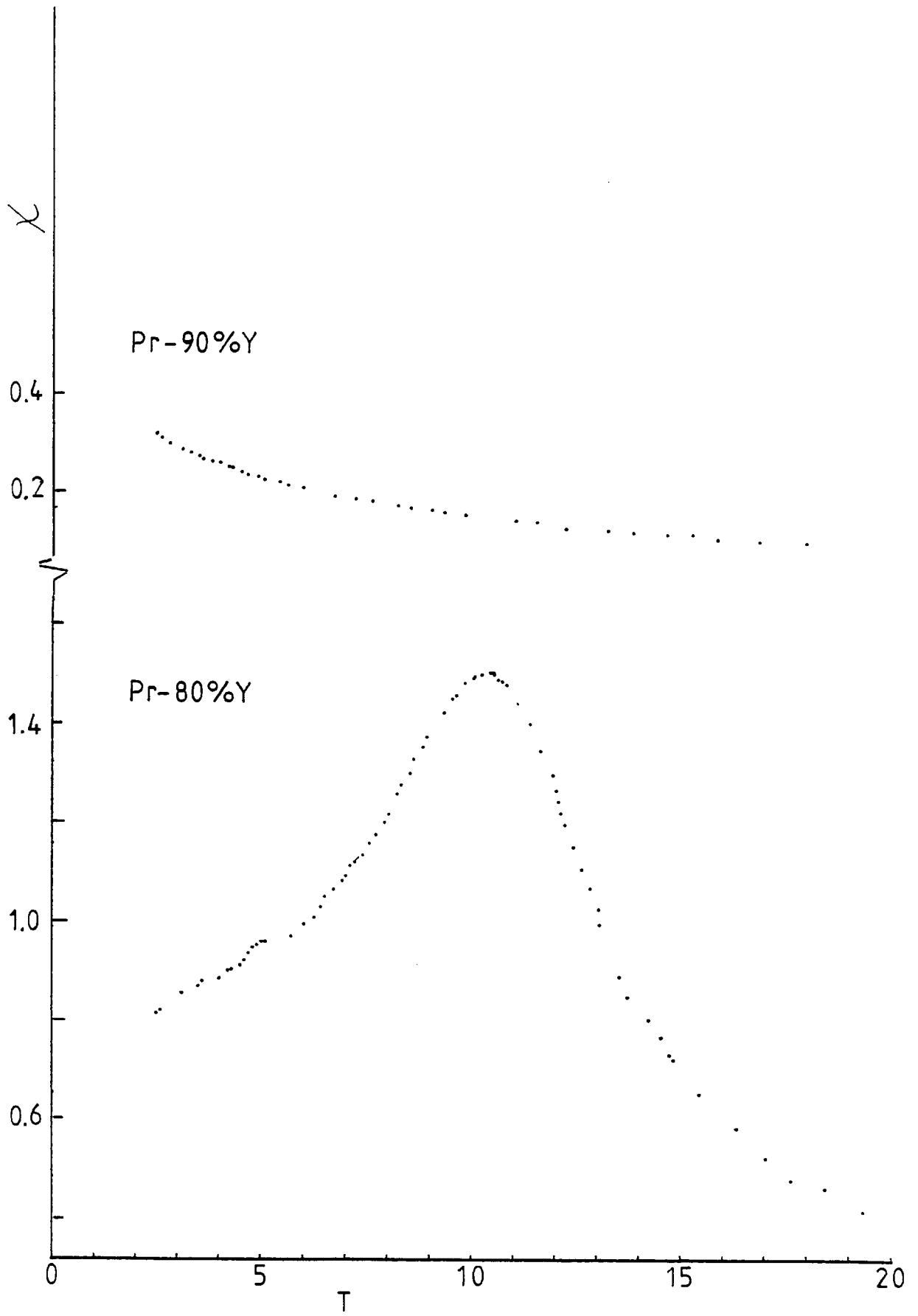


Fig 3.8 cont

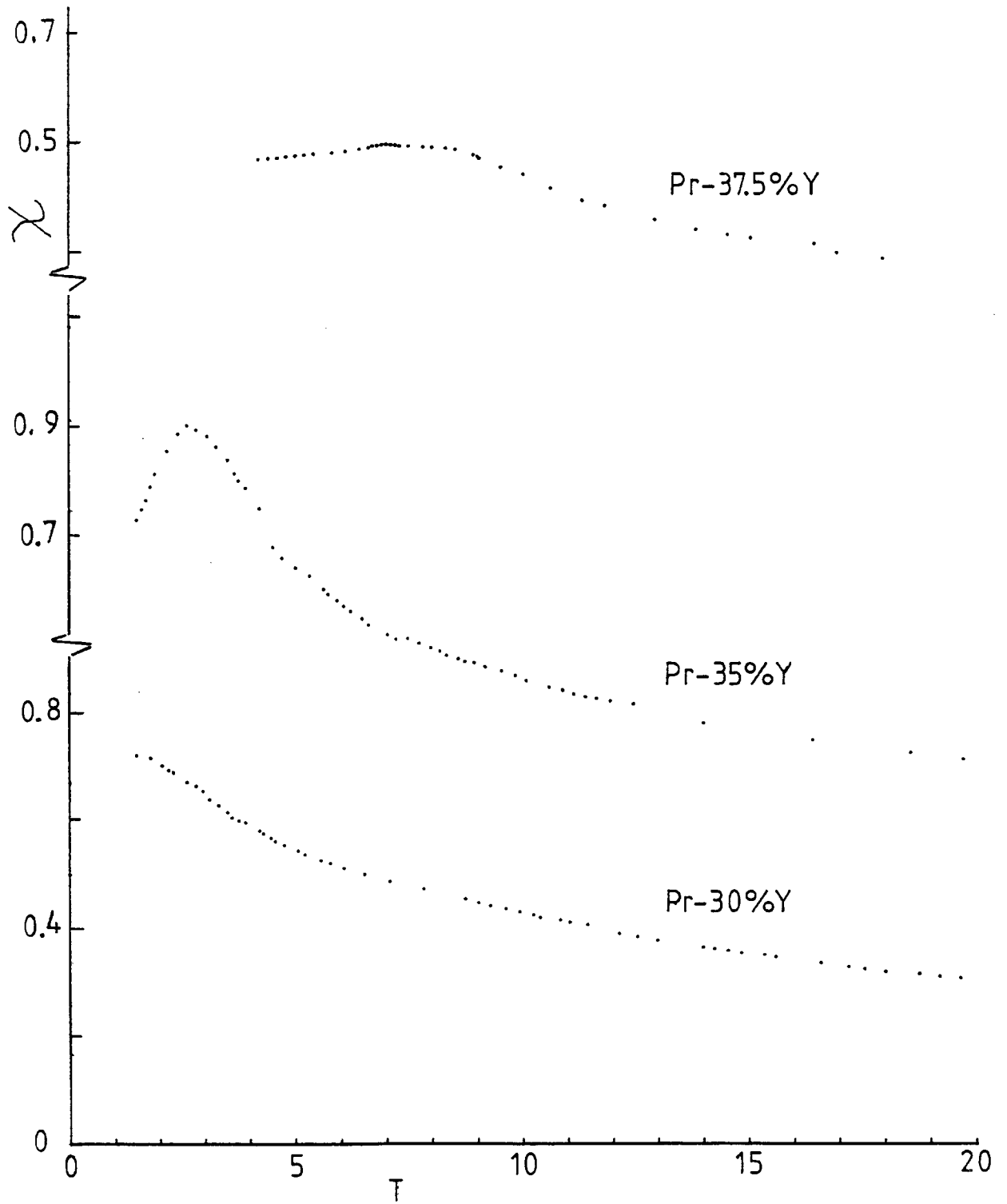


Fig. 3.9: Ac-susceptibility for the annealed Pr- γ alloys.
units: T in K
 χ in 10^{-3} emu/gm

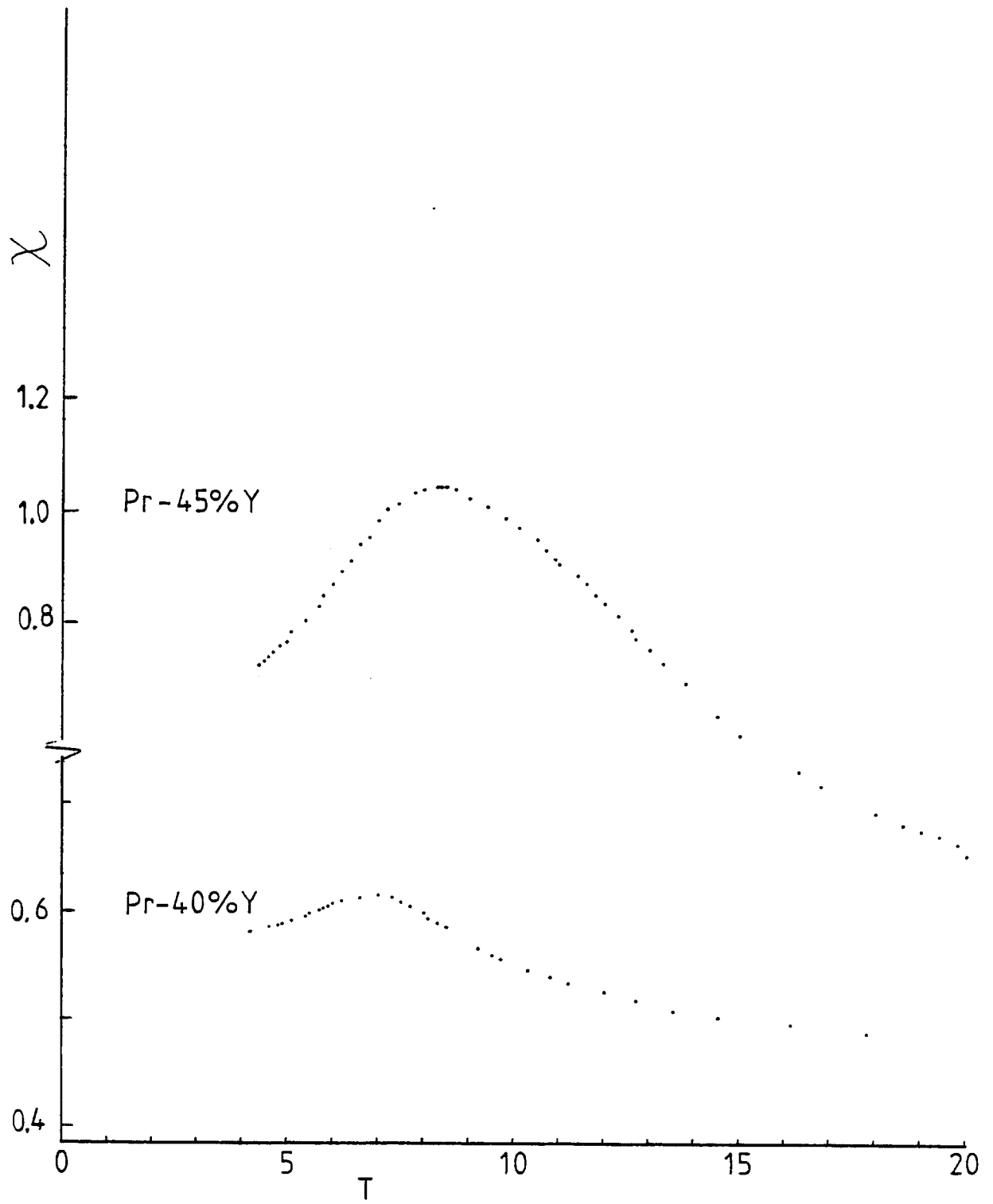


Fig 3.9 cont

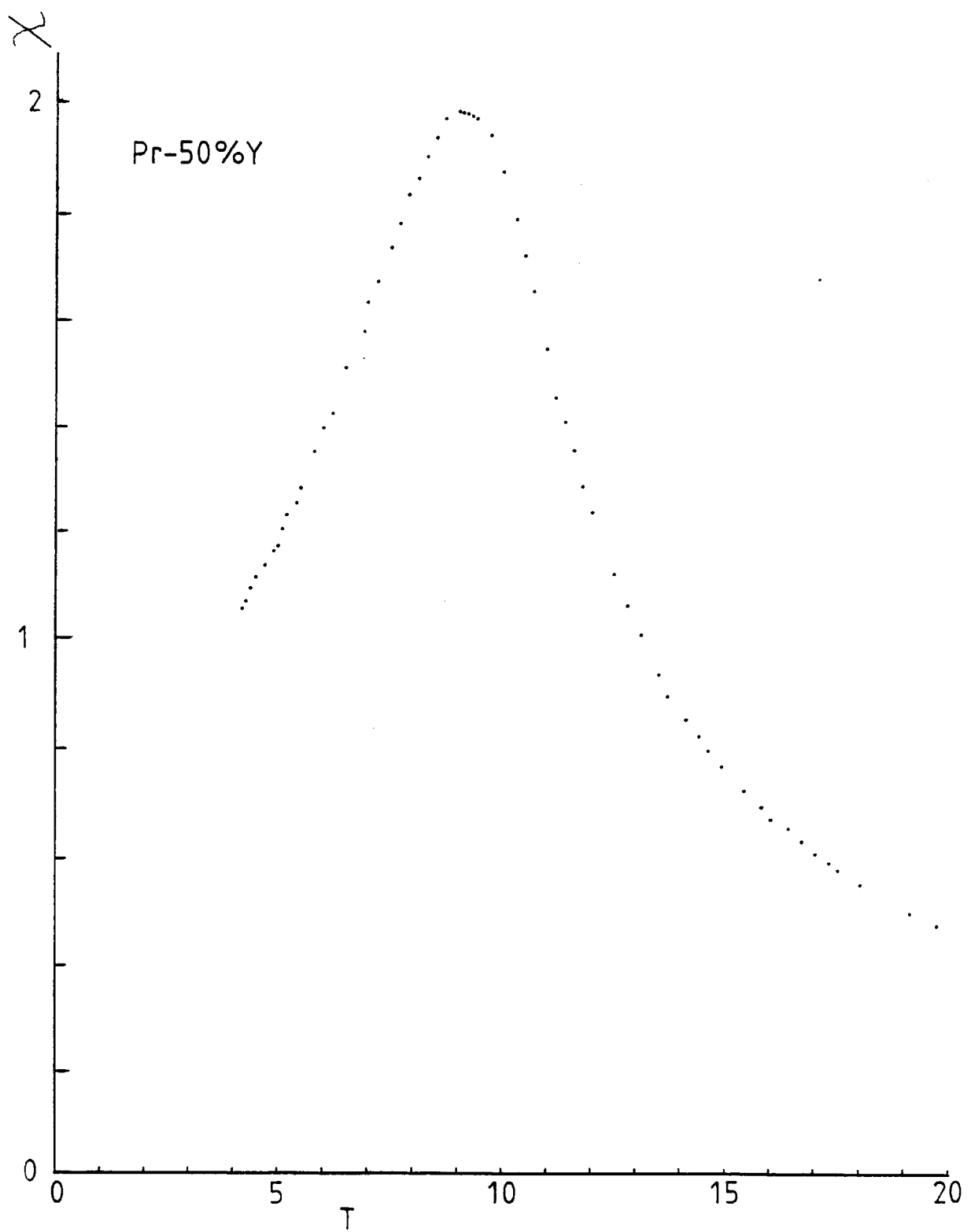


Fig 3.9 cont

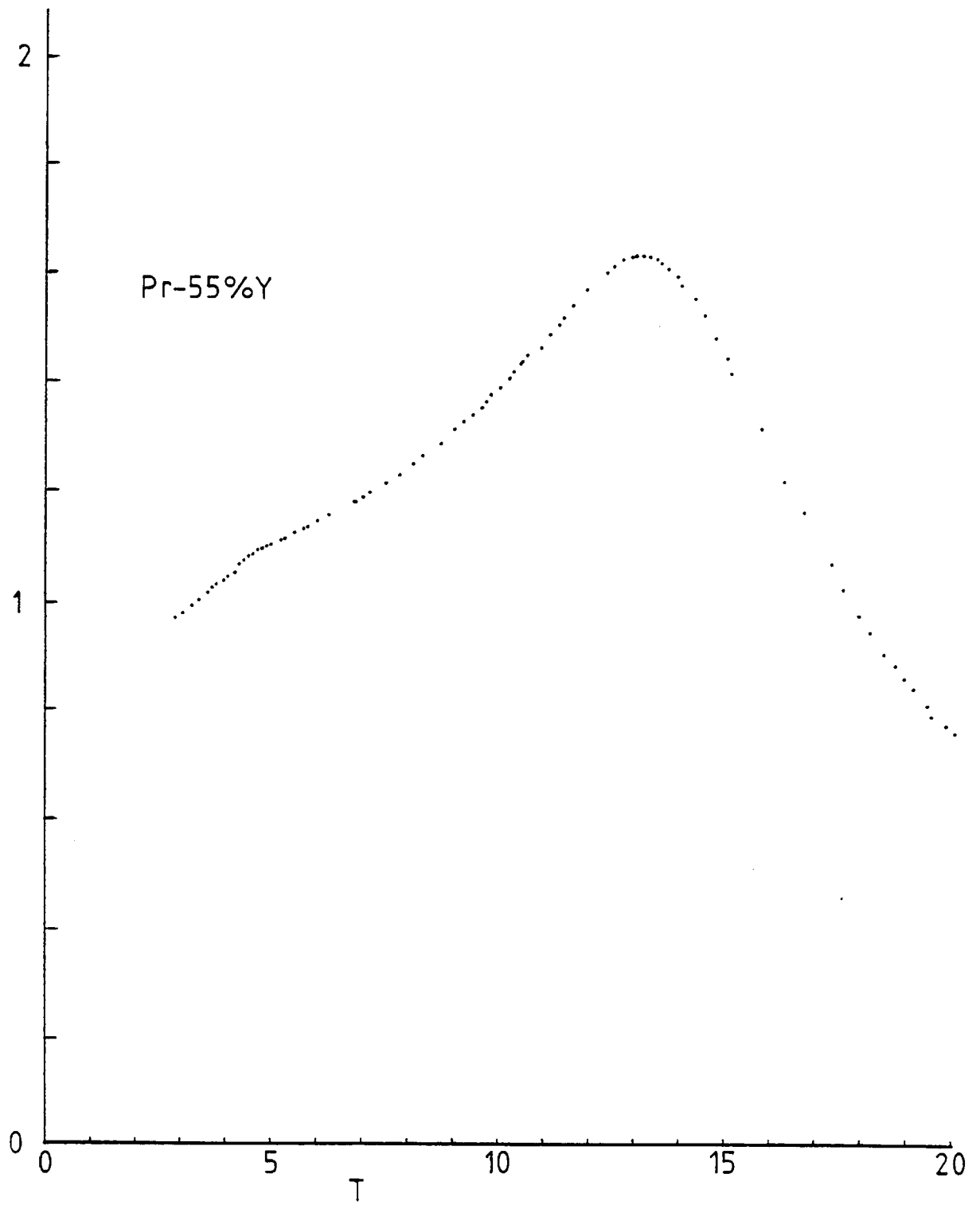


Fig 3.9 cont

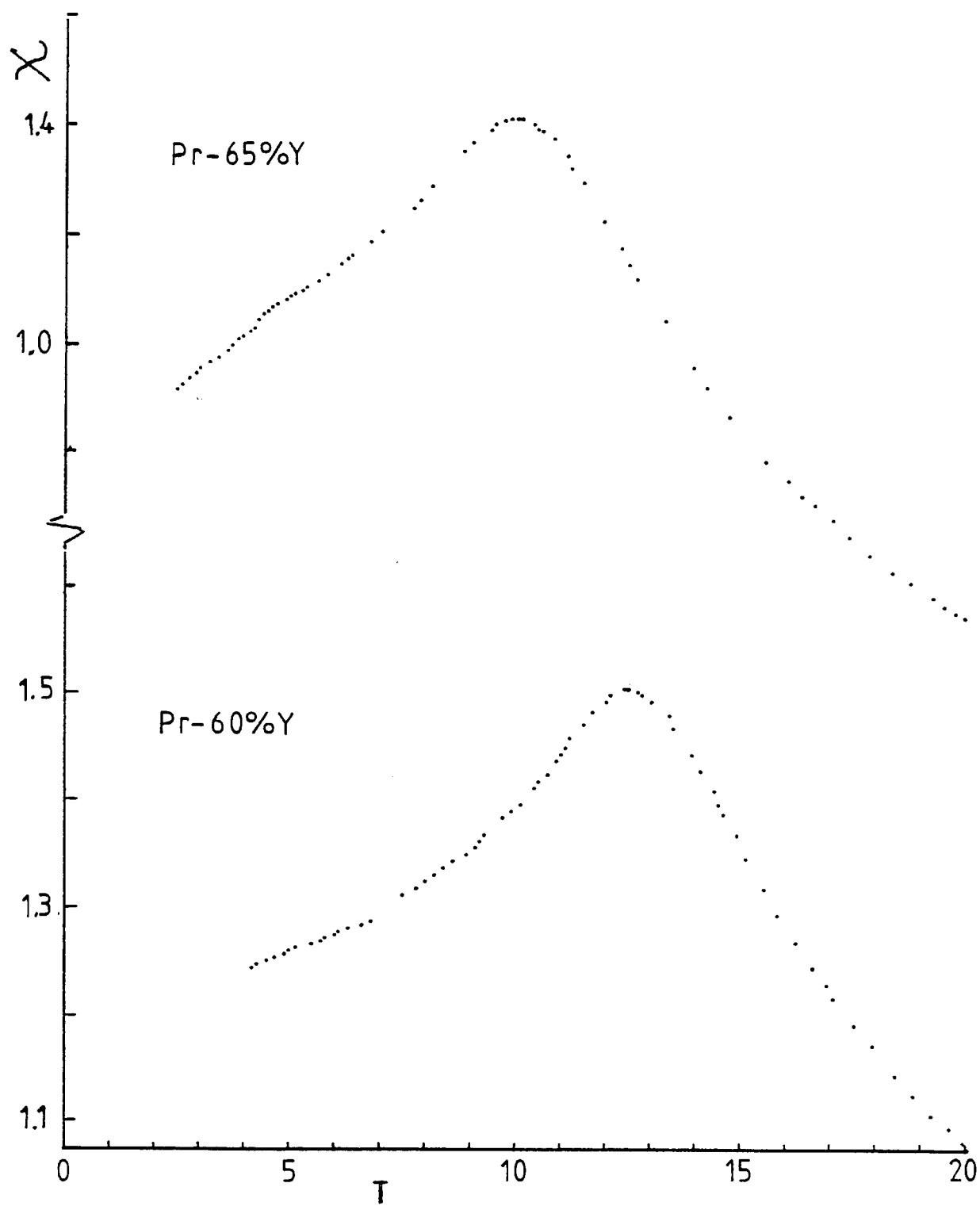


Fig 3.9 cont

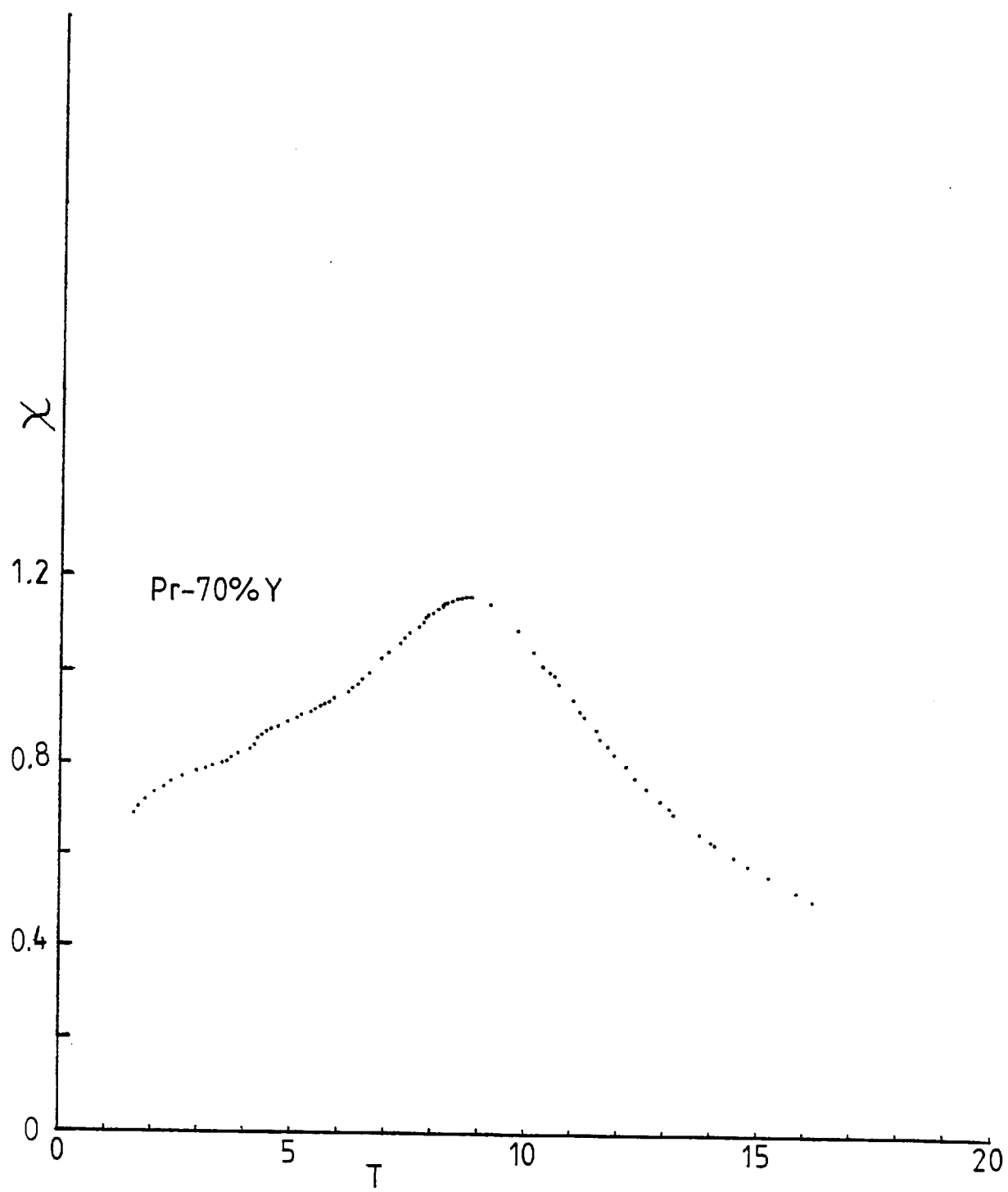


Fig 3.9 cont

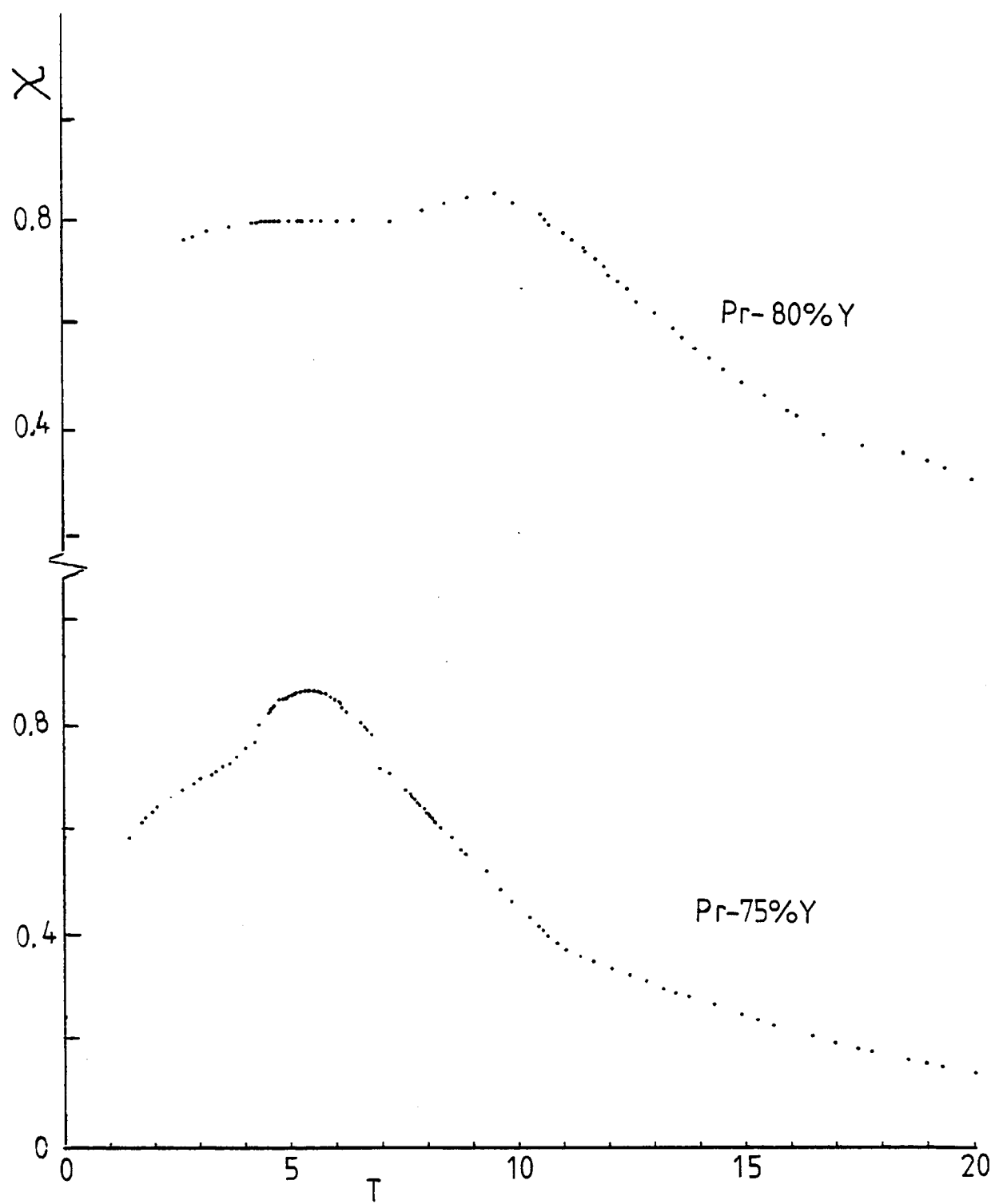


Fig 3.9 cont

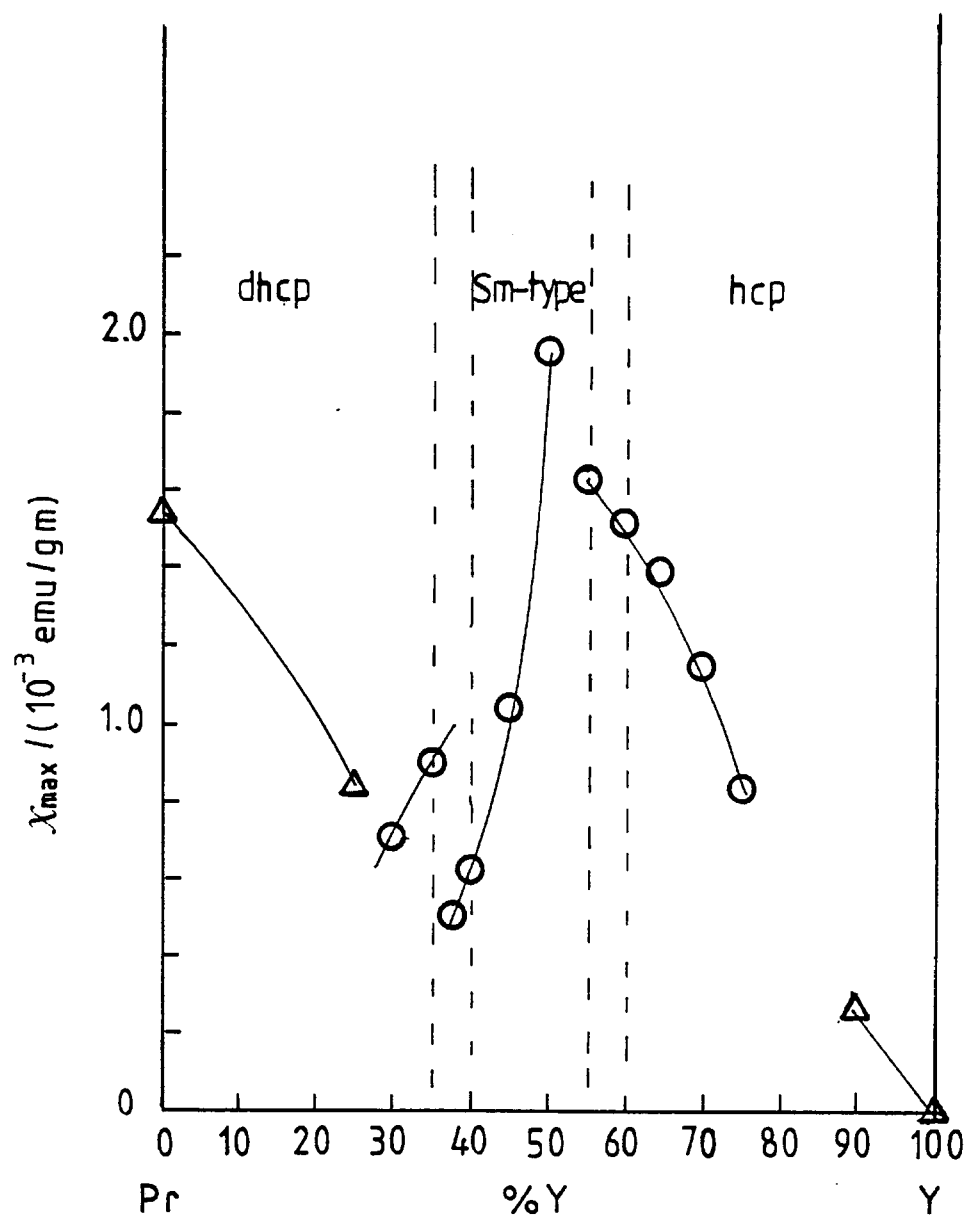


Fig.3.10: Peak-susceptibility values of the annealed Pr-Y alloys as a function of Y concentration. Δ : maximum of the susceptibility at 4.2K.

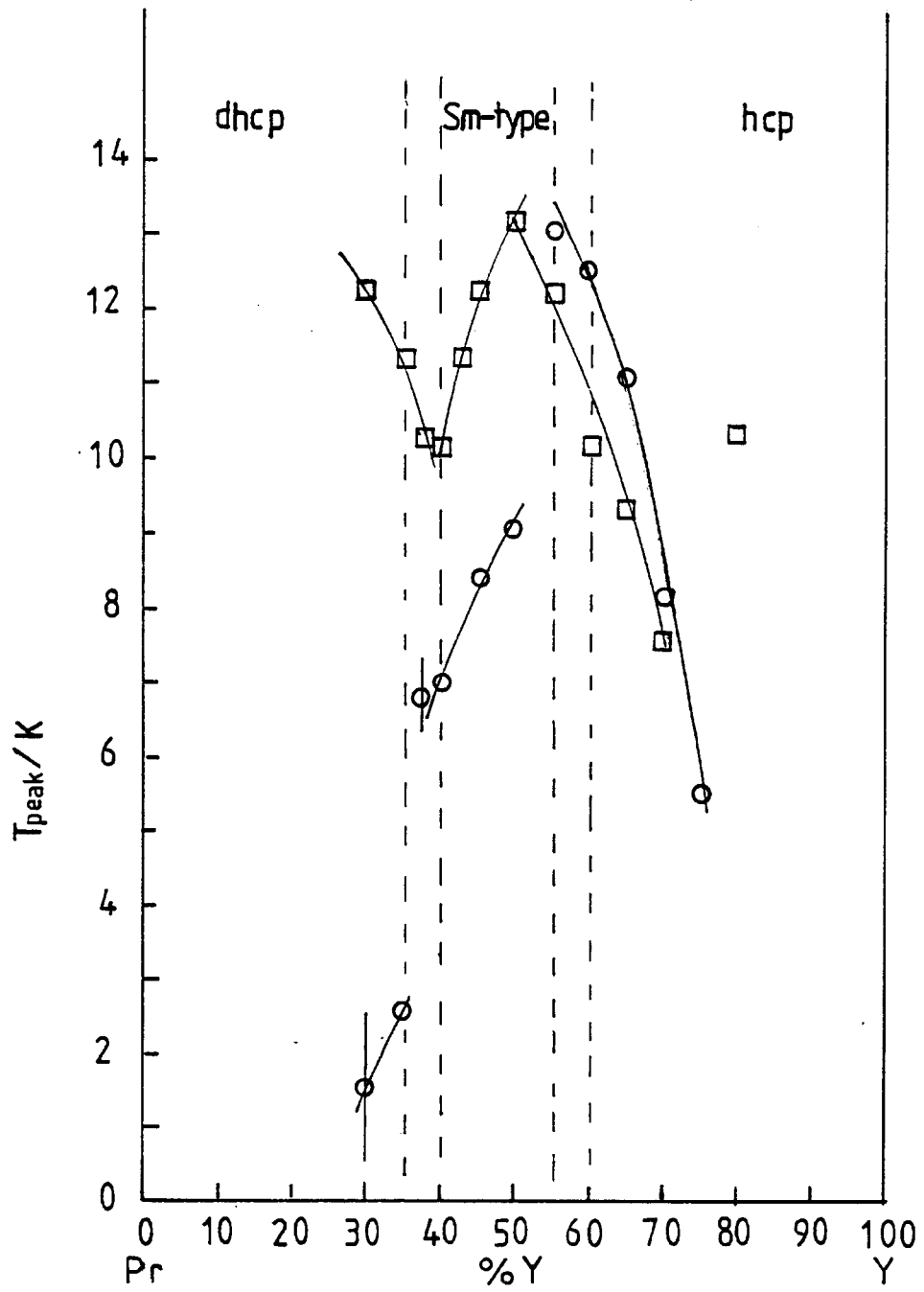
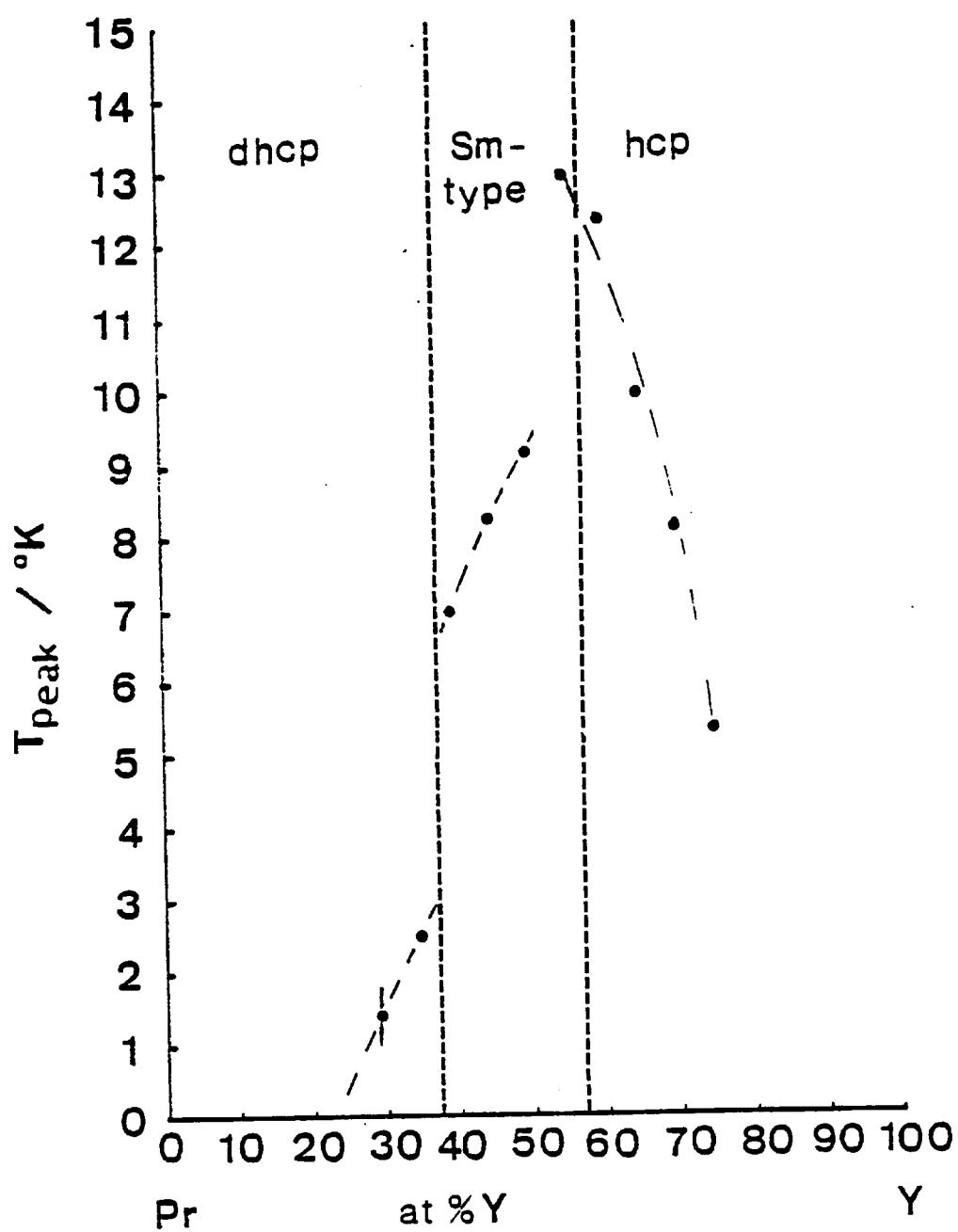


Fig.3.11: Peak-temperature as a function of Y concentration for the as-cast ($\square$) and annealed ($\circ$) alloys.



annealed alloys

Fig 3.11 cont

not order above 1.5 K and has a low value of susceptibility at 4.2 K, see Figs 3.8 and 3.10.

The inverse of susceptibility for the 10, 50 and 60% *Y*, plotted in Fig 3.12 follows a Curie-Weiss law, and in Table 3.2 are quoted the values of the effective moments and the paramagnetic temperatures together with those for pure *Pr*.

Observing again the dependence of T_{max} of the annealed alloys as a function of concentration, it is interesting to remark that in the range 30-50% *Y* (*dhcp* and *Sm*-type structures) the maximum shifts towards higher temperatures while the *Pr* content is decreasing. It reaches the highest value of temperature for the 50% *Y* alloy. On the contrary, in the *hcp* region, the maximum shifts to lower temperatures with decreasing *Pr* content, as expected.

In ac-susceptibility measurements, one may easily detect magnetic ordering, but it is difficult to answer unambiguously the question as to whether or not these susceptibility maxima correspond to the onset of long-range order. Electrical resistivity and dc-susceptibility experiments have been performed on samples chosen from each type of structure, in order to throw light on the previous results.

In Fig 3.13 are plotted the reduced susceptibility (M/H) as a function of temperature, of the 35% *Y*(*dhcp*), 50% *Y*(*Sm*-type) and 60-70 % *Y*(*hcp*) alloys, when cooled in an applied magnetic field from high temperatures. The χ ac data are also plotted for comparison. The experiments were performed on the Faraday balance (see Chapter 2) in the following manner: the sample was first cooled in zero field (without nulling the earth's field) and the susceptibility (M/H) measured in a certain applied magnetic field which is specified in

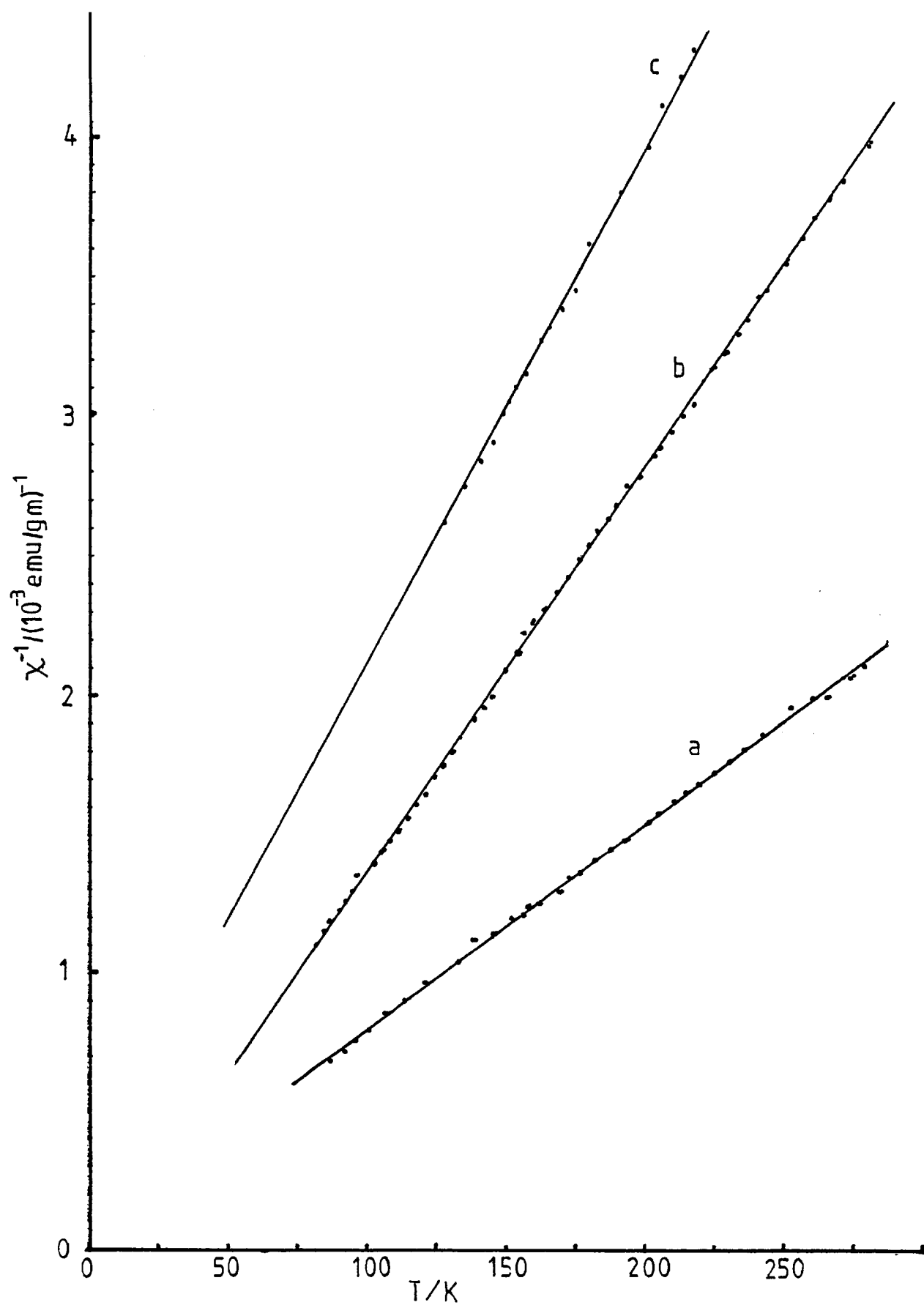


Fig.3.12: Inverse of susceptibility as a function of temperature for the a) 10%Y, b) 50%Y and c) 60%Y alloys.

%Y	p	θ
10	3.62 ± 0.05	$+ 2.8 \pm 1$
50	3.87 ± 0.05	$- 8.6 \pm 1$
60	3.72 ± 0.05	$+ 7.1 \pm 1$
Pr	3.90 ± 0.05	-13.7 ± 1

TABLE 3.2 Effective magneton number p
and paramagnetic temperature θ
of some Pr-Y alloys.

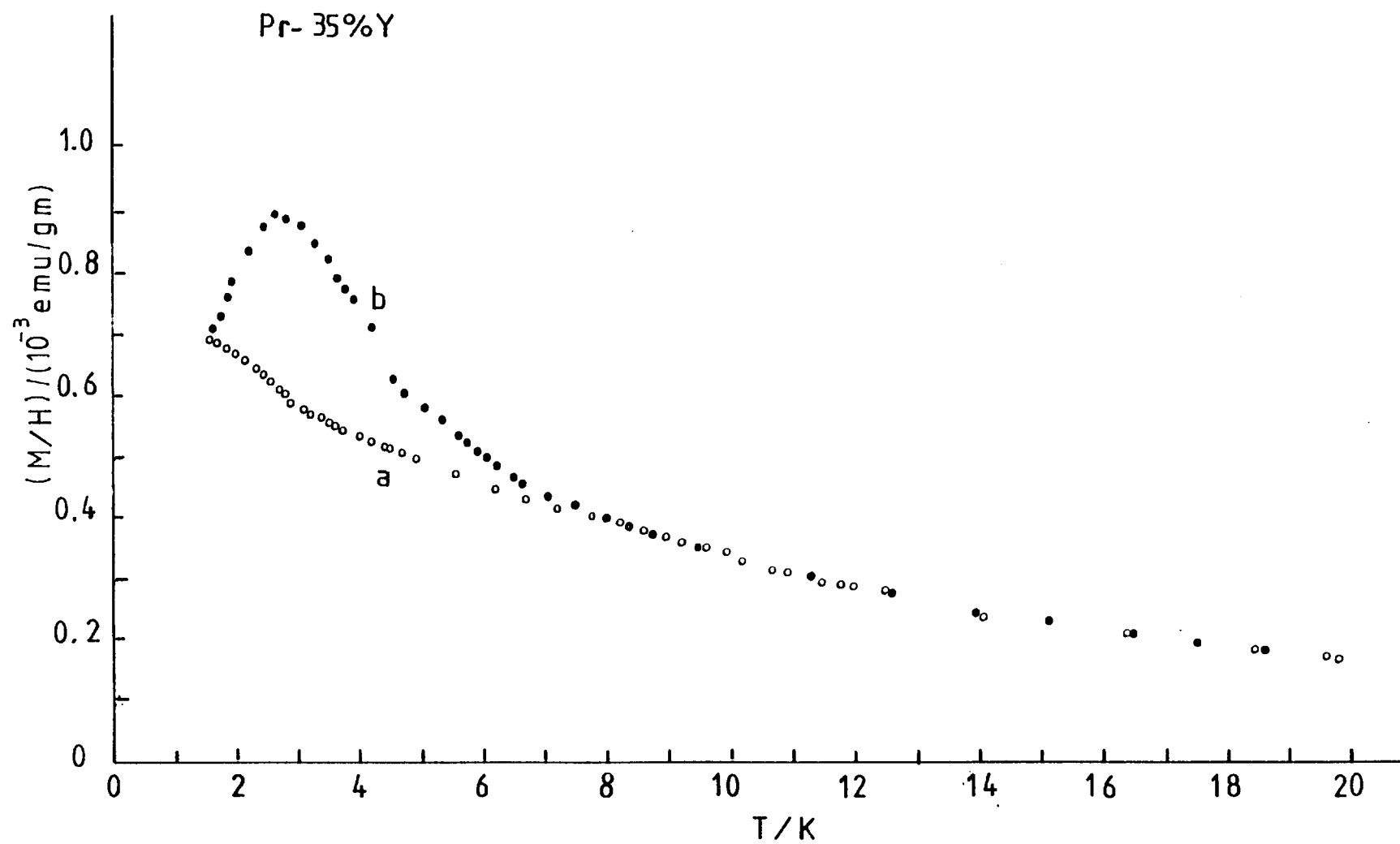


Fig.3.13: a) Dc-susceptibility as a function of temperature for the 35%Y alloy. a) sample cooled in 350 Oe; b) ac-susceptibility for comparison.

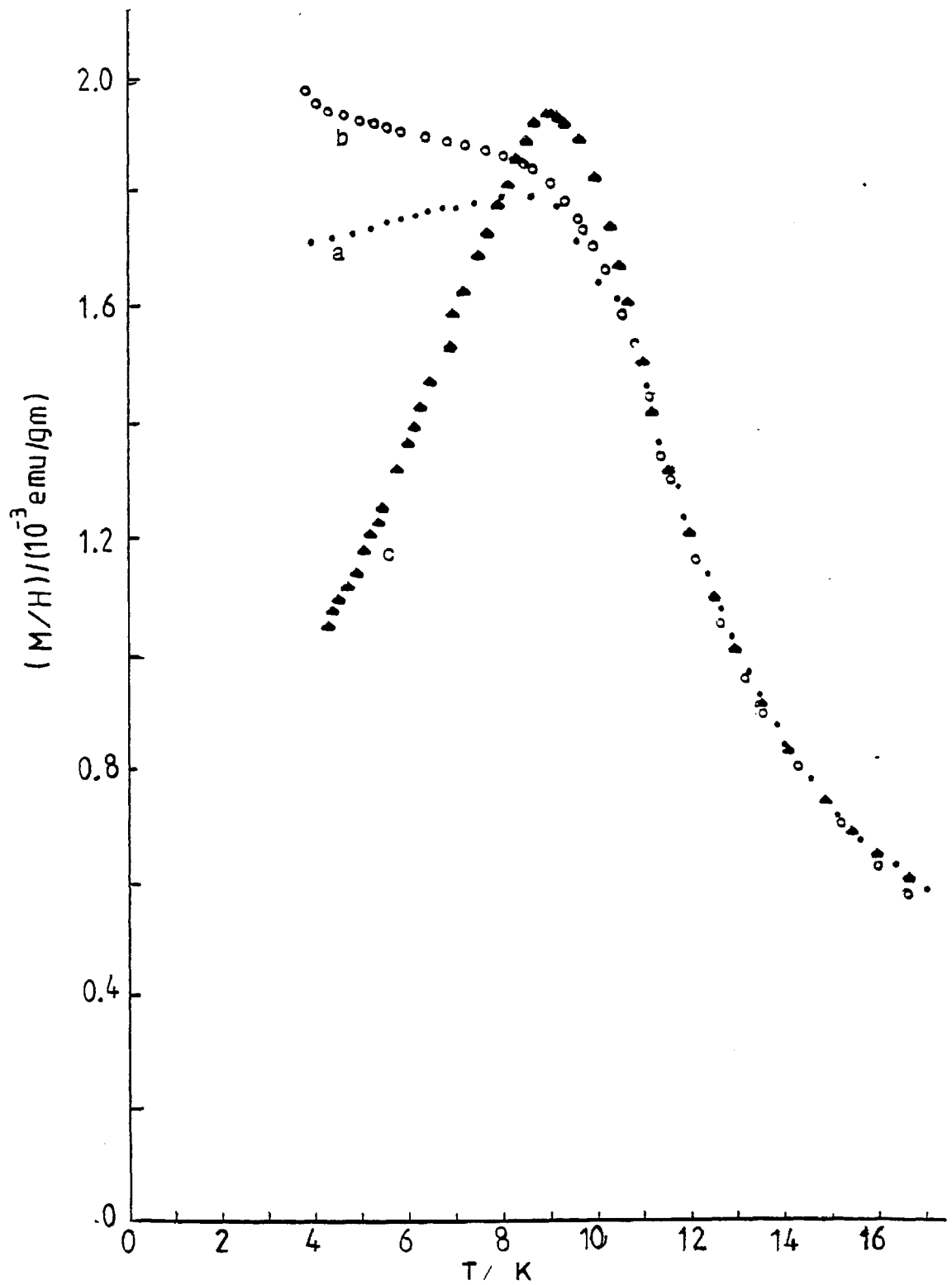


Fig.3.13: b) Dc-susceptibility as a function of temperature for the 50%Y alloy. a) sample cooled in zero field and measured in a field of 160 Oe; b) sample cooled in 160 Oe; and c) ac-susceptibility for comparison.

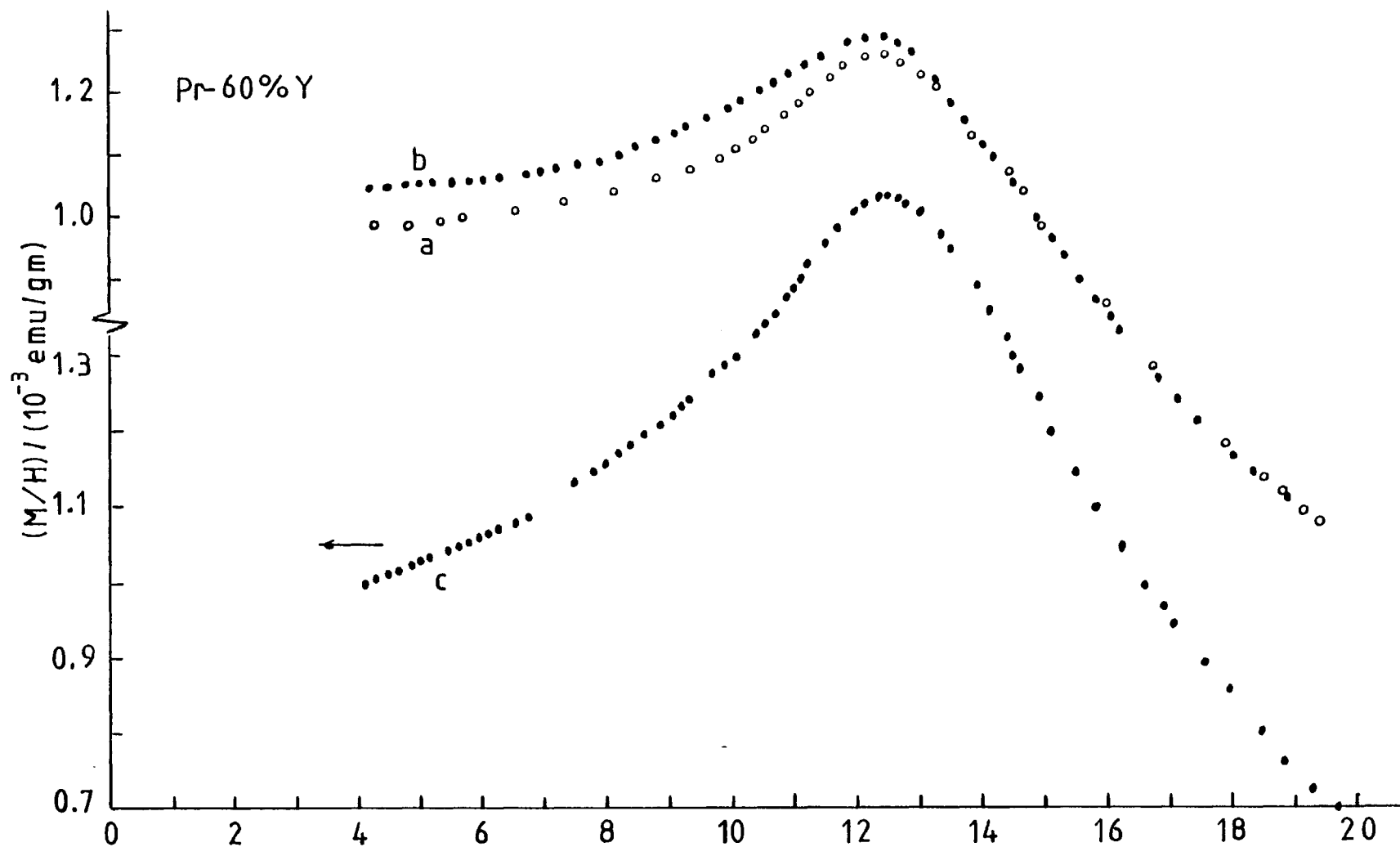


Fig.3.13: c) Dc-susceptibility as a function of temperature for the 60%Y alloy. a) sample cooled in zero field and measured in 350 Oe; b) sample cooled in 350 Oe; and c) ac-susceptibility for comparison.

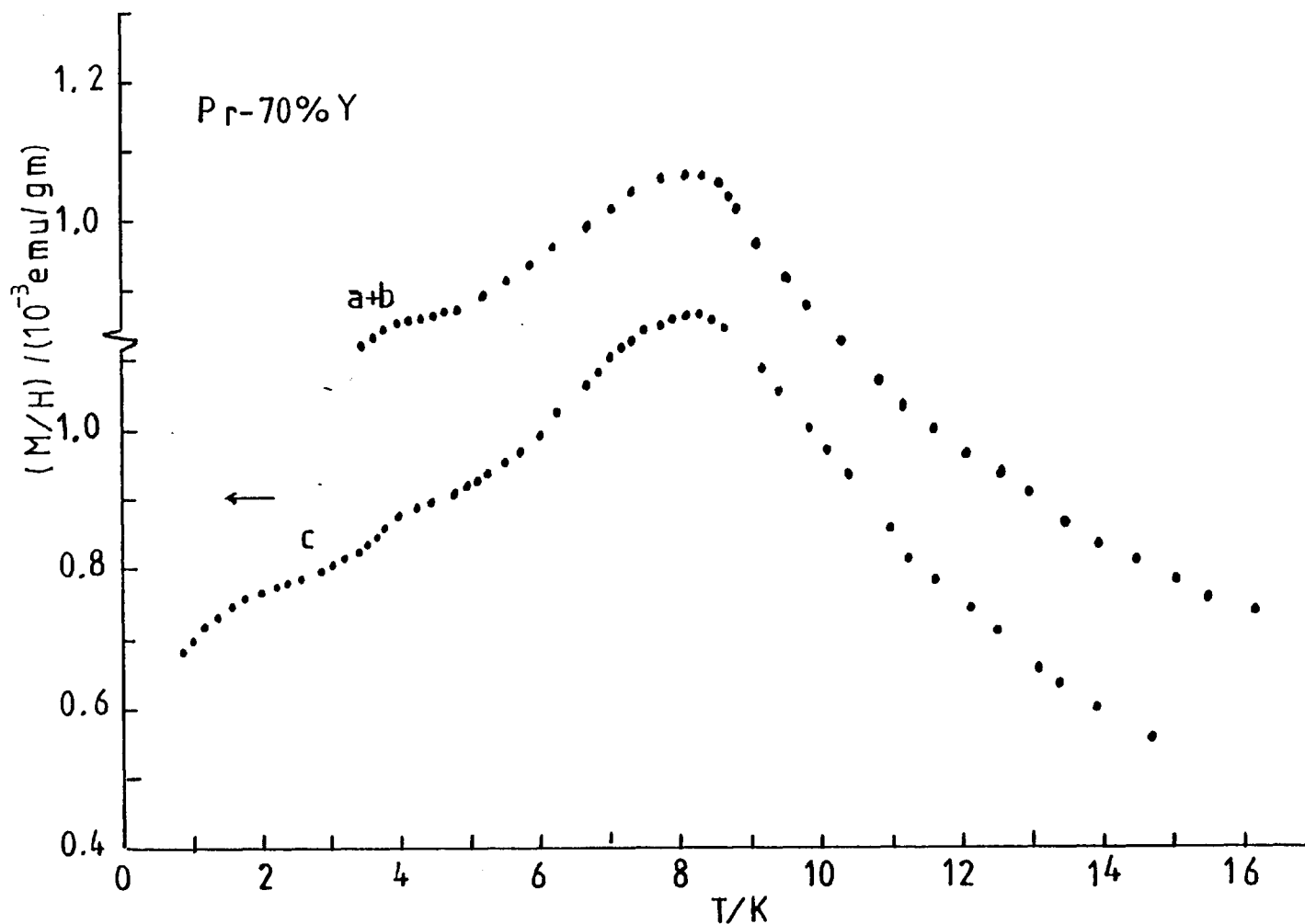


Fig.3.13: d) Dc-susceptibility as a function of temperature for the 70%Y alloy. a) sample cooled in zero field and measured in 870 Oe; b) sample cooled in a field (see text); and c) ac-susceptibility for comparison.

the Fig. Then, the sample temperature is brought to a much higher value than the ordering temperature, cooled in an applied field and the susceptibility (M/H) measured in the same applied field; the latter was maintained during the experiment.

The appearance of remanent magnetization was observed for *Pr*-35% *Y*(*dhcp*) when cooled in a field of 350 *Oe*. There was a complete suppression of the χ_{ac} peak and it may be noticed that the magnetization increases more rapidly below the ordering temperature, with a shape of the curve that suggests the presence of a ferromagnetic component. Remanent magnetization was also found for *Pr*-50% *Y* alloy when cooled in a field of 160 *Oe* and 350 *Oe*; the smearing of the peak-susceptibility when cooled in zero field and measured in a relatively high field was observed. When the temperature was maintained at a fixed value (1.5 K for 35% *Y* and 4.2 K for 50% *Y*), there was a time dependent effect (which decreases with time) after the field was turned off.

The case of the *Pr*-60% *Y*(*hcp*) alloy is different from the previous ones, since only a small remanence was found when cooled in a field of 350 *Oe* (see Fig 3.13); the peak was less pronounced as compared with the χ_{ac} when cooled in zero field. For *Pr*-70% *Y*(*hcp*), no remanent magnetization or field cooling effects could be detected, even after cooling in a much higher field (5 K *Oe*). There was not an appreciable smearing of the peak when compared with the χ_{ac} measurement.

In Fig 3.14 are shown the electrical resistivity, $\rho(T)$, experimental data and fitted curves, and its derivatives with respect to temperature, $d\rho(T)/dT$, for 40-45-50-60-70% *Y* alloys, from 2 to 25 K. The fitted curve and its derivative for each alloy, were calculated

at the ICCU using the E02BCF computer program, which evaluates a weighted least-squares approximation to the given experimental data by a cubic spline; see Appendix 2 for details. One can observe that the behaviour of the resistivity for 60-70% $Y(hcp)$ alloys, although less pronounced, resembles that of the antiferromagnetic $Pr-Nd$ alloys, Sarkissian 1977b, 1978a. These changes in the resistivity are clearly displayed in $d\rho/dT$, where a minimum and a maximum are obtained near the peak-susceptibility: see Table 3.3. For the other three alloys, no drastic changes are observed and the derivatives are similar to that of pure Pr .

The resistivity data were further analysed by fitting them to the expression

$$\Delta\rho \equiv \rho - \rho_0 = AT^n$$

where ρ_0 was taken as the extrapolated value at $T = 0$. The resistivity of Y below ~ 8 K is almost independent of the temperature and $\Delta\rho_Y$ is very small compared with $\Delta\rho_{alloy}$. Hence, in good approximation $\Delta\rho_{alloy}$ is considered to give the magnetic resistivity of the alloys at these low temperatures. Above 8 K, because phonon scattering becomes significant (the Debye temperature is relatively low for these elements) and Matthiessen's rule is not well obeyed, it is not straight-forward to obtain the magnetic resistivity. In Fig 3.15 is shown a log-log plot of $\Delta\rho_{alloy}$ vs T , for the 40-45-50-60-70% Y alloys. The resistivity was found to be proportional to $T^{3/2}$ for all alloys. This is nicely confirmed in Fig 3.16, where a plot of $\Delta\rho$ vs $T^{3/2}$ is shown. Above 10 K, a clear deviation from this law is observed. The resistivity of pure Pr is also plotted for comparison and one can see a completely different behaviour at low temperatures; $\Delta\rho_{Pr}$ varies rapidly with increasing temperature.

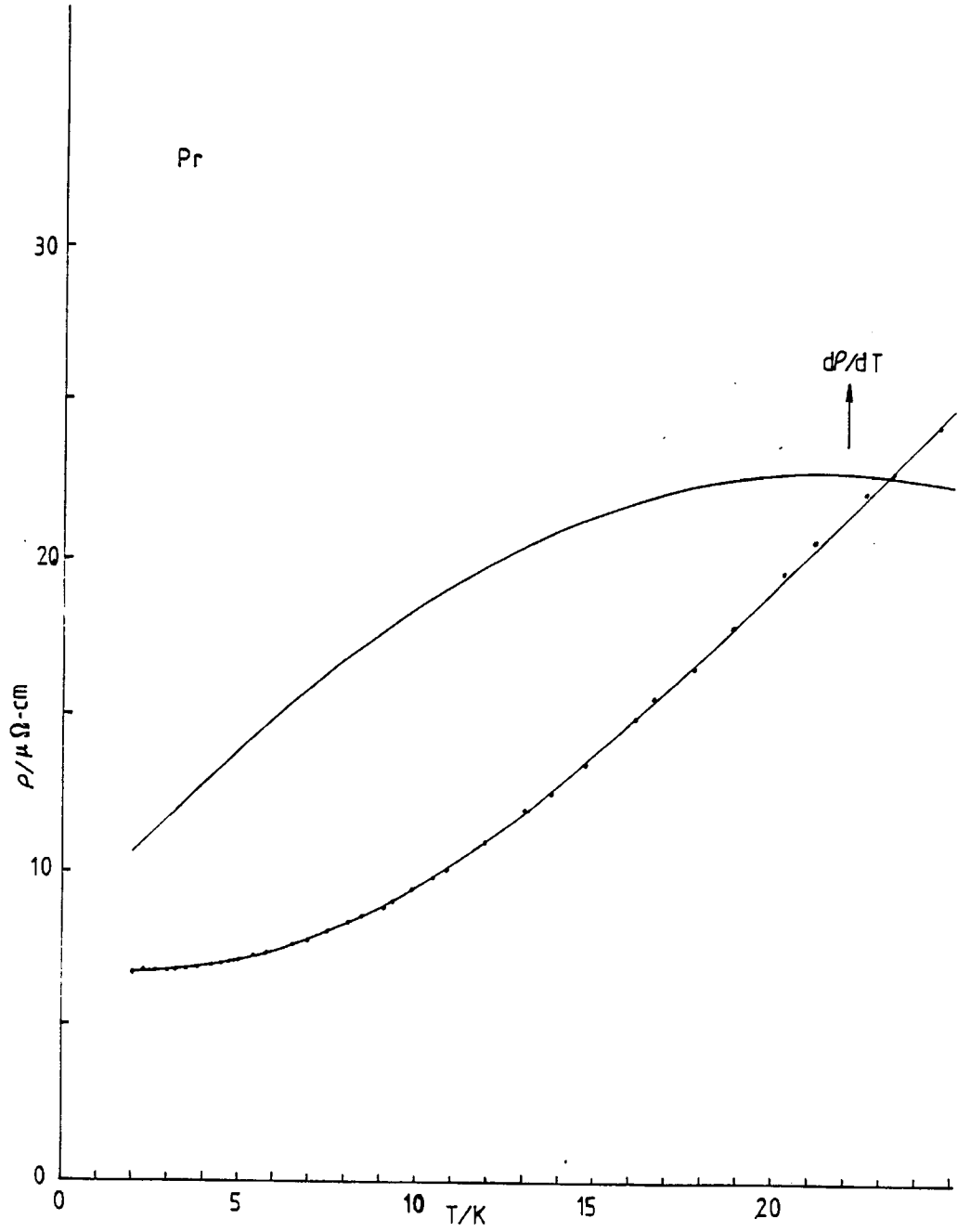


Fig.3.14: Electrical resistivity, $\rho(T)$, and its derivative $d\rho(T)/dT$, for the 40-45-50-60-70%Y alloys and Pr.

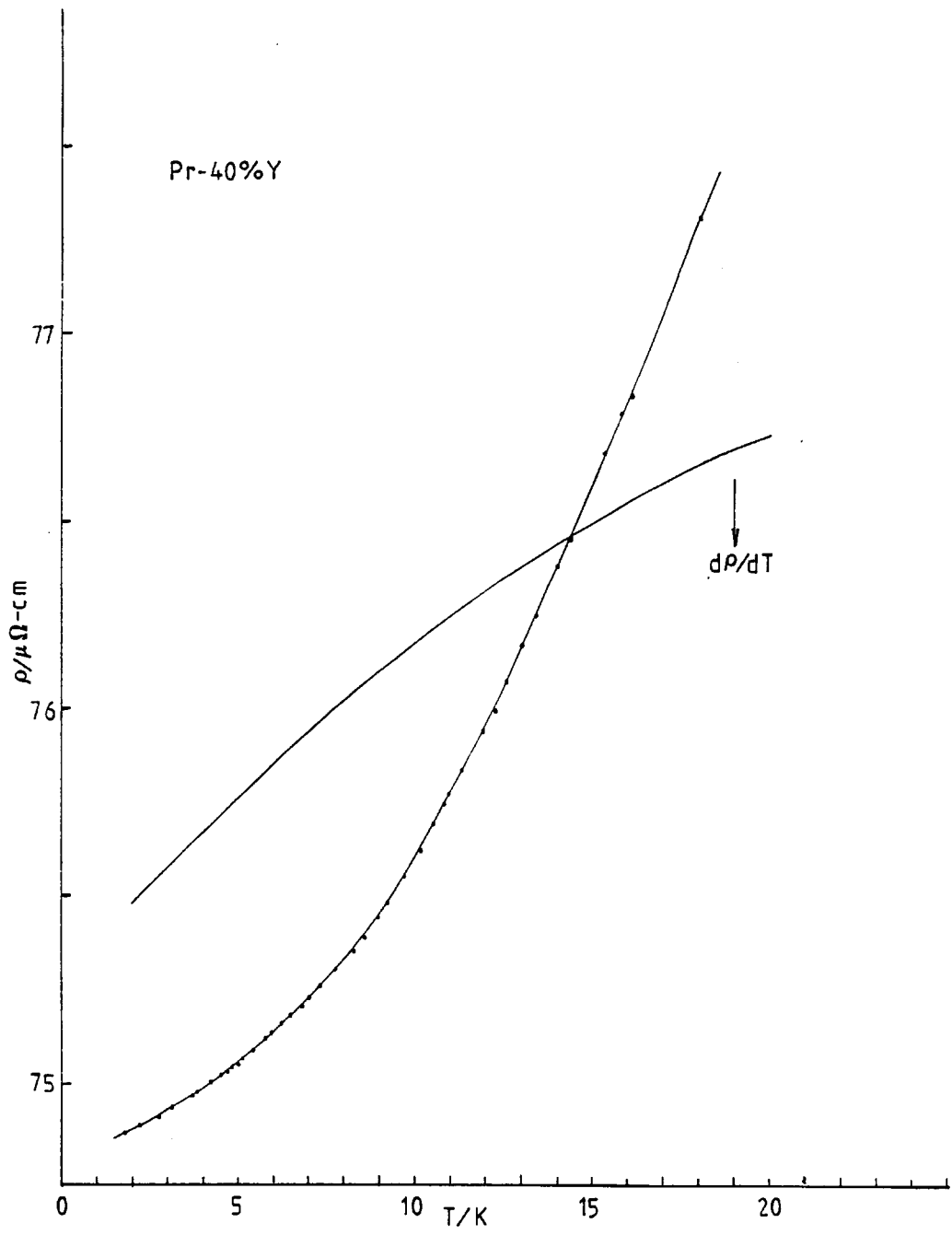


Fig 3.14 cont

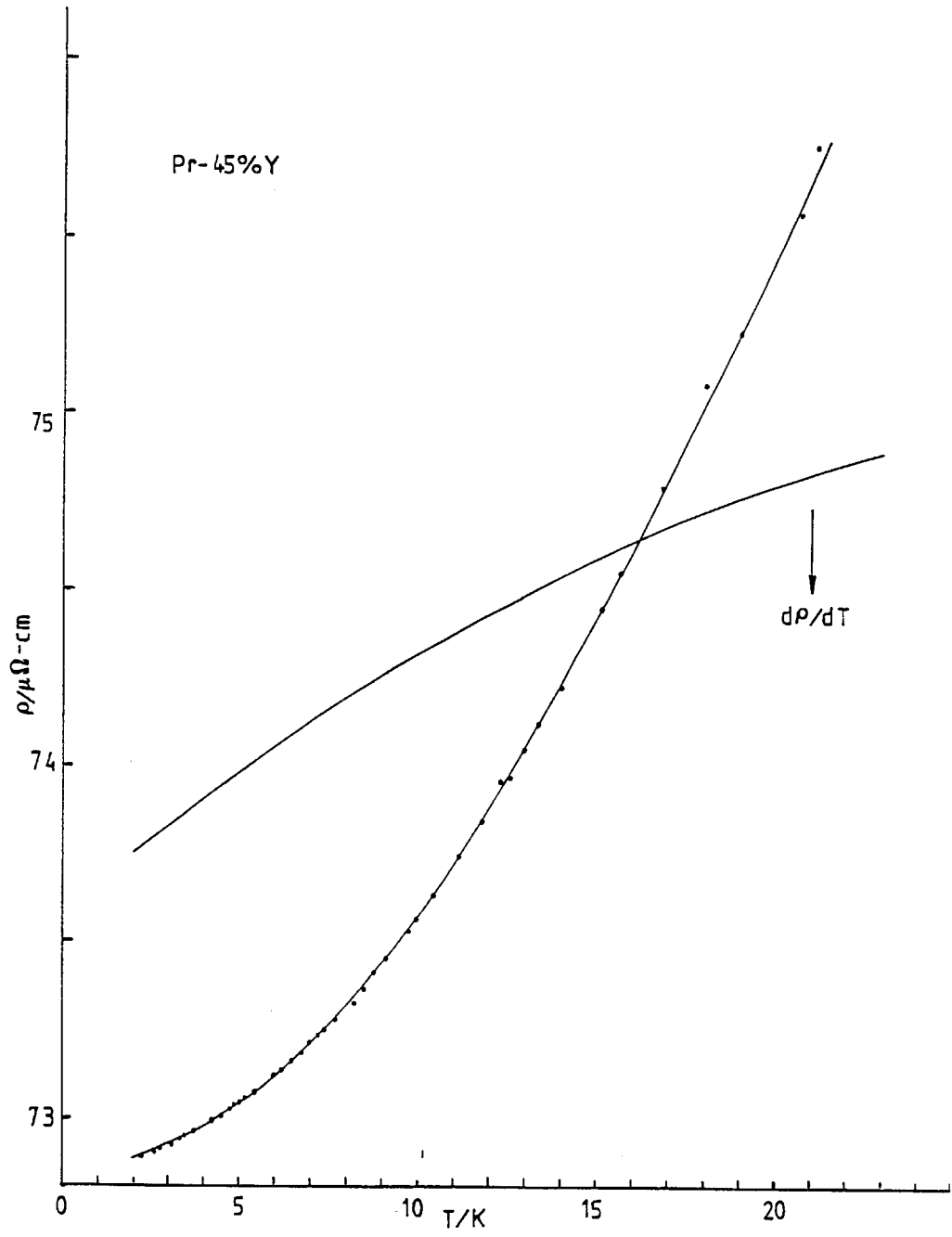


Fig 3.14 cont

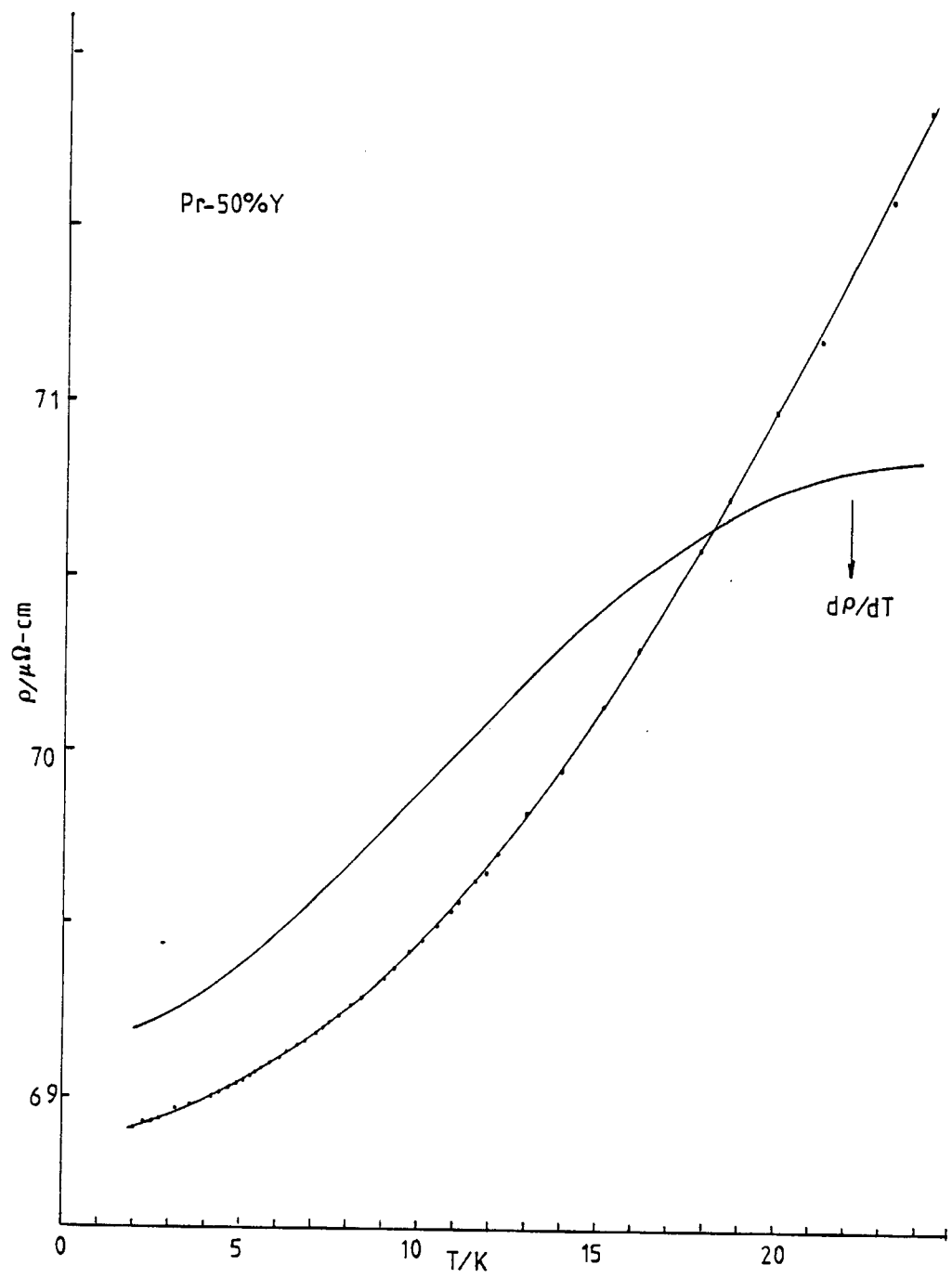


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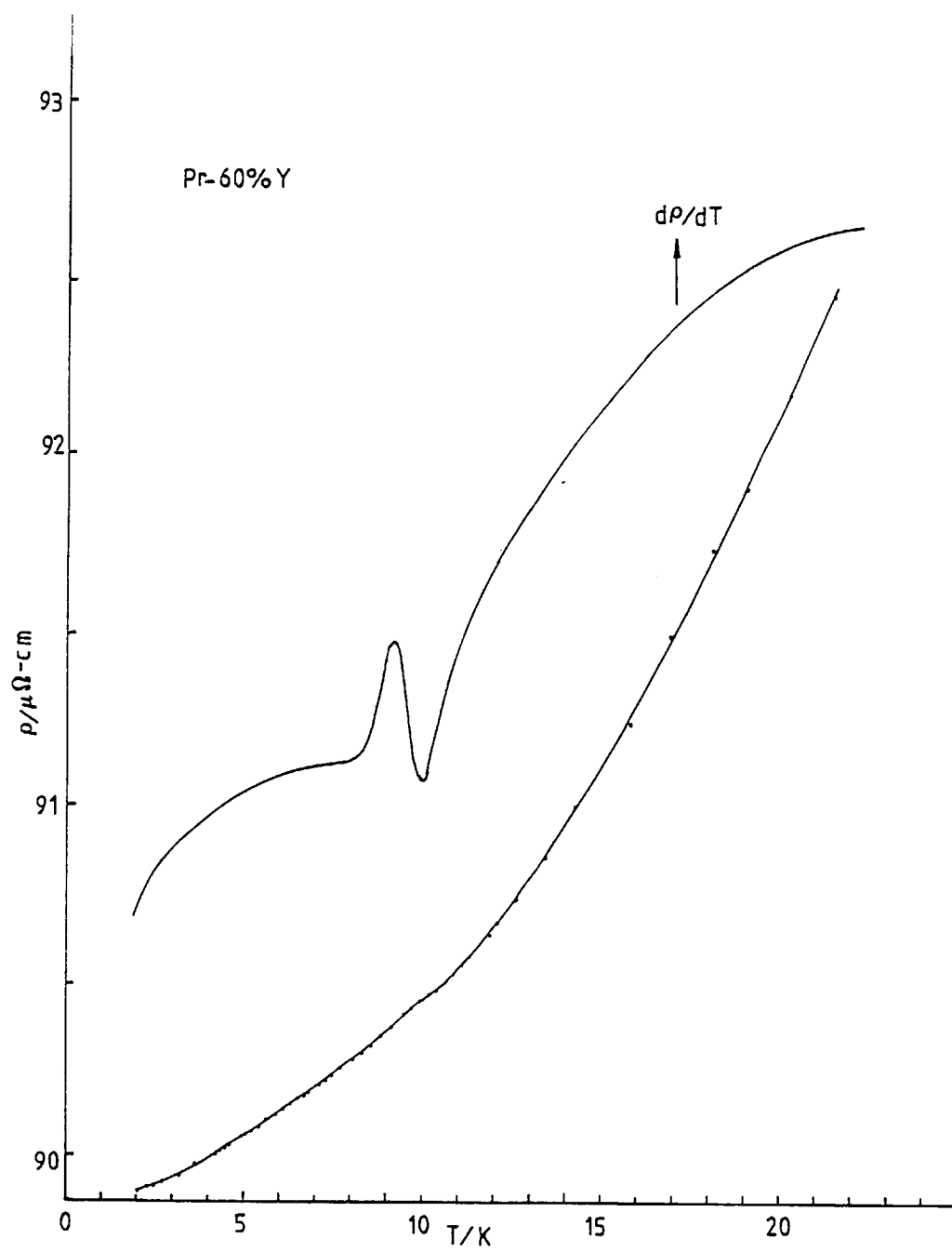


Fig 3.14 cont

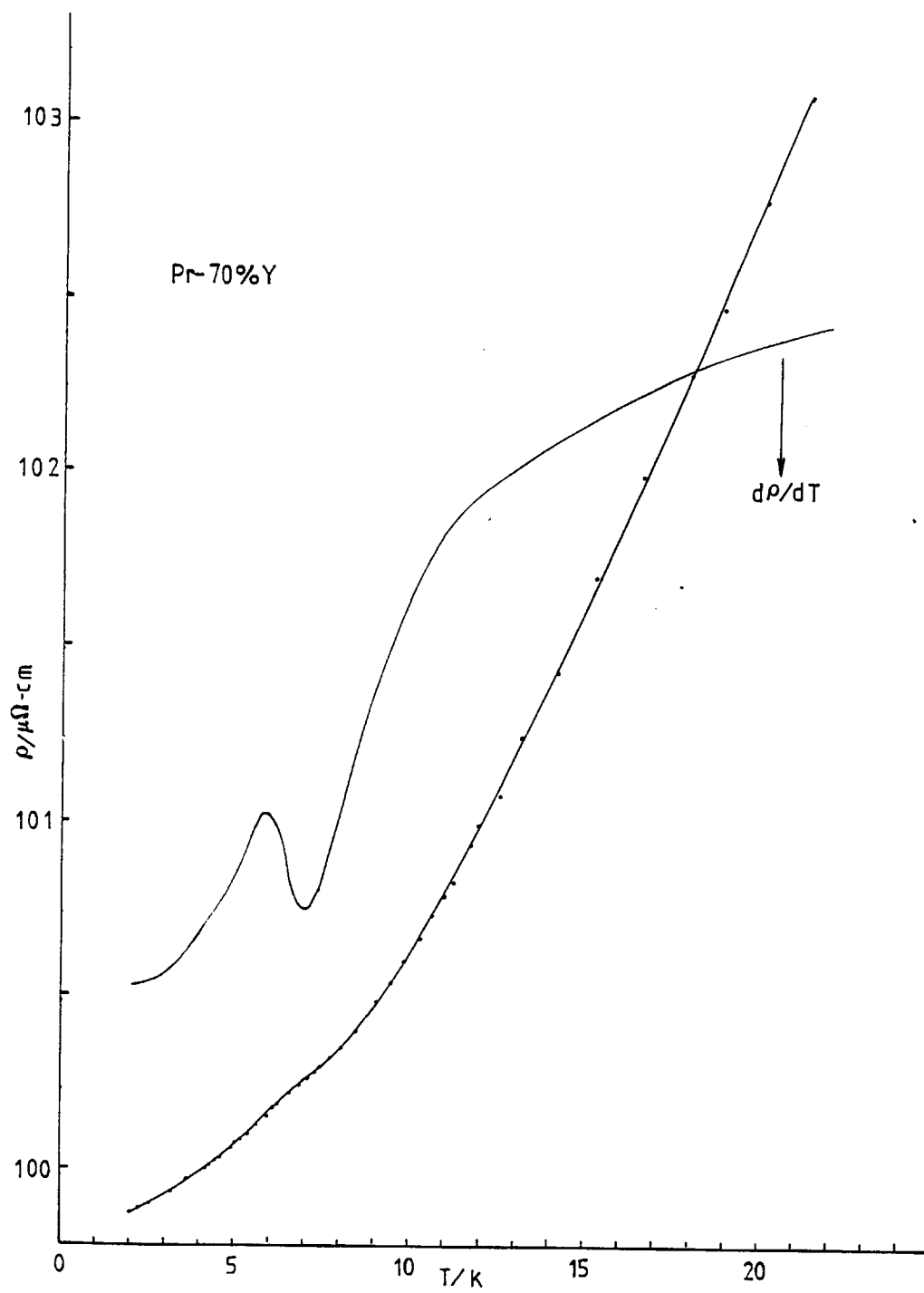


Fig 3.14 cont

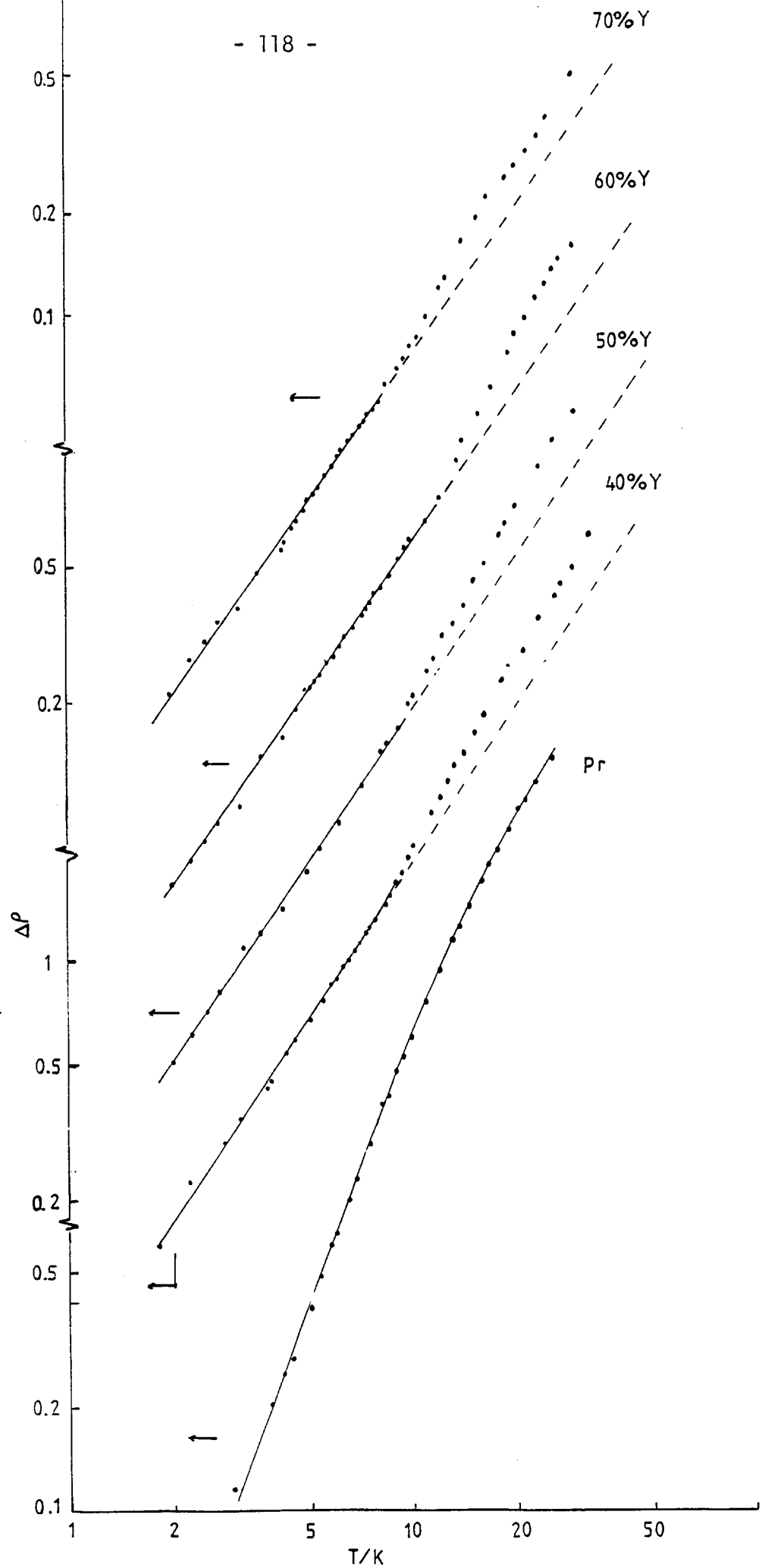


Fig.3.15: Log-log plot of Δp_{alloy} vs T , for the 40-50-60-70% alloys, and pure dhcp Pr for comparison.

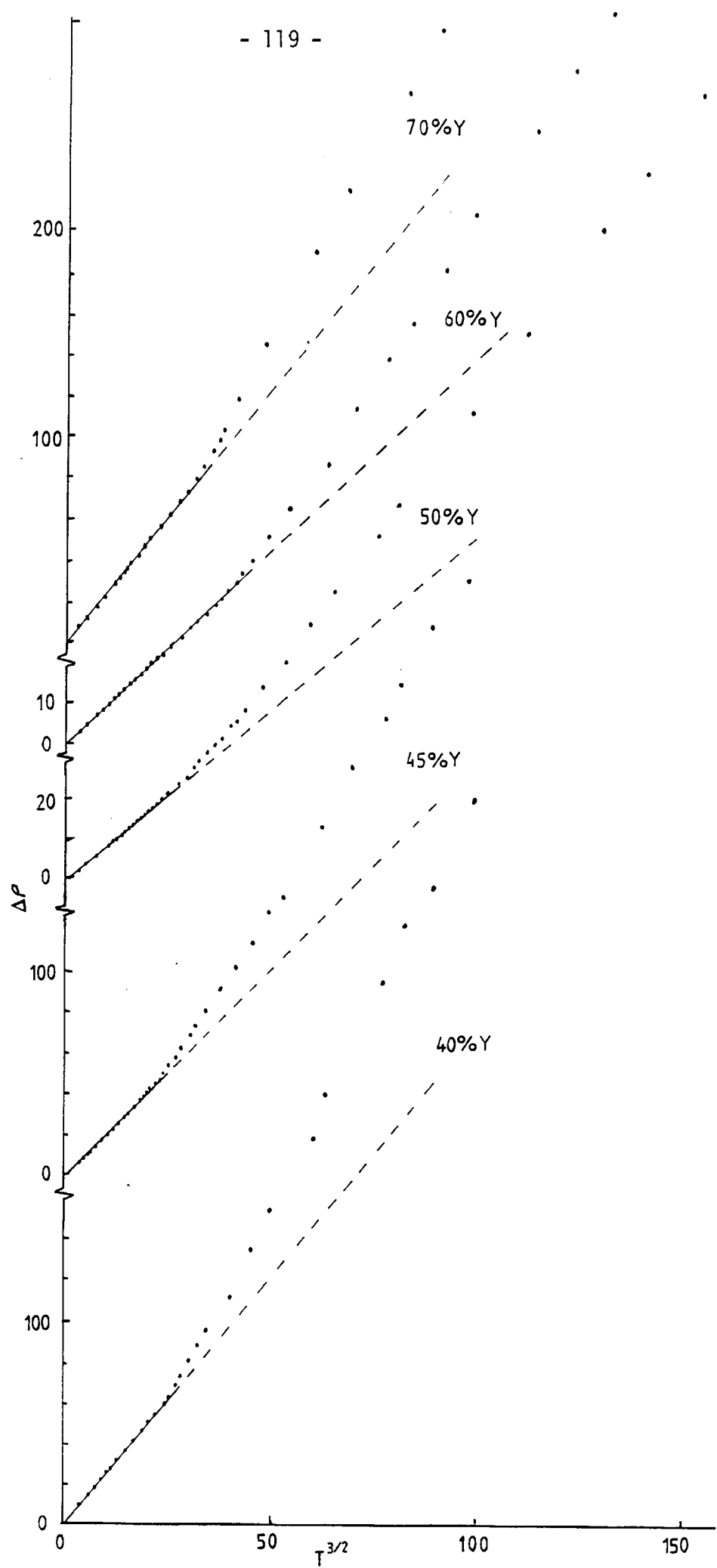


Fig.3.16: Δp vs $T^{3/2}$ for the 40-45-50-60-70%Y alloys.

Below ~ 8 K, the curves exhibited in Fig 3.16 were fitted to a straight line and values of the coefficient A calculated. These values are quoted in Table 3.3, together with the values of the resistivity at 4.2 K; see Fig 3.17. The error in the electrical resistance measurements is less than 0.01%; however, there is an overall error of $\sim 5\%$ in the values of ρ and A due to the inaccuracy in the determination of the dimensions of the samples.

3.3.3 Discussion

On the basis of these experiments, it is clear that the rather well isolated singlet character of pure Pr , which prevents zero field ordering above 1 K, is disturbed in the alloys with Y . In order to understand the magnetic behaviour of the Pr - Y system, attention must certainly be focussed upon the exchange and crystal-field interactions.

The ac-susceptibility measurements show clearly variations associated with changes of crystal structure. Remarkable agreement is found between the crystalline sequences deduced from X-ray analysis, Fig. 3.5, and the behaviour observed in the susceptibility measurements, Fig 3.11, for the as-cast and annealed samples.

The Curie-Weiss law is obeyed above 100 K as in pure Pr . The deviation from this law is due to crystal field effects. The paramagnetic Curie temperatures quoted in Table 3.2, suggest ferromagnetic-type exchange coupling for Sm -type alloys and antiferromagnetic coupling for hcp alloys.

The magnetic behaviour of the Pr - Y system will be discussed in terms of three regions of concentration, characterized by their crystalline structure.

TABLE 3.3 Experimental values of some parameters
of *Pr*-*Y* alloys. See text.

%Y	$\chi_{\max}^{\text{ac}}$ (a)	$T_{\max}^{\text{ac}}$ /K	T_1 (c)	T_2 (c)	$\rho_{4.2}$ (d)	A (e)
25	0.83(b)	-				
30	0.71	~1.5				
35	0.90	2.6				
37.5	0.50	6.9				
40	0.62	7.0			75	2.4
45	1.04	8.4			73	2.2
50	1.96	9.0			69	1.8
55	1.62	13.1				
60	1.51	12.5	9.2	10.0	90	1.9
65	1.39	10.0				
70	1.16	8.2	5.8	7.0	100	2.6
75	0.84	5.4				
90	0.25(b)	-				
<i>Pr</i>	1.50(b)	-				

17

(a) 10^{-3} emu/gr, $\pm 5\%$ error

(b) at 4.2 K

(c) maximum and minimum temperatures in $d\rho/dT$, K

(d) $\mu\Omega$ - cm

(e) 10^{-8} $\mu\Omega$ - cm $K^{-1.5}$

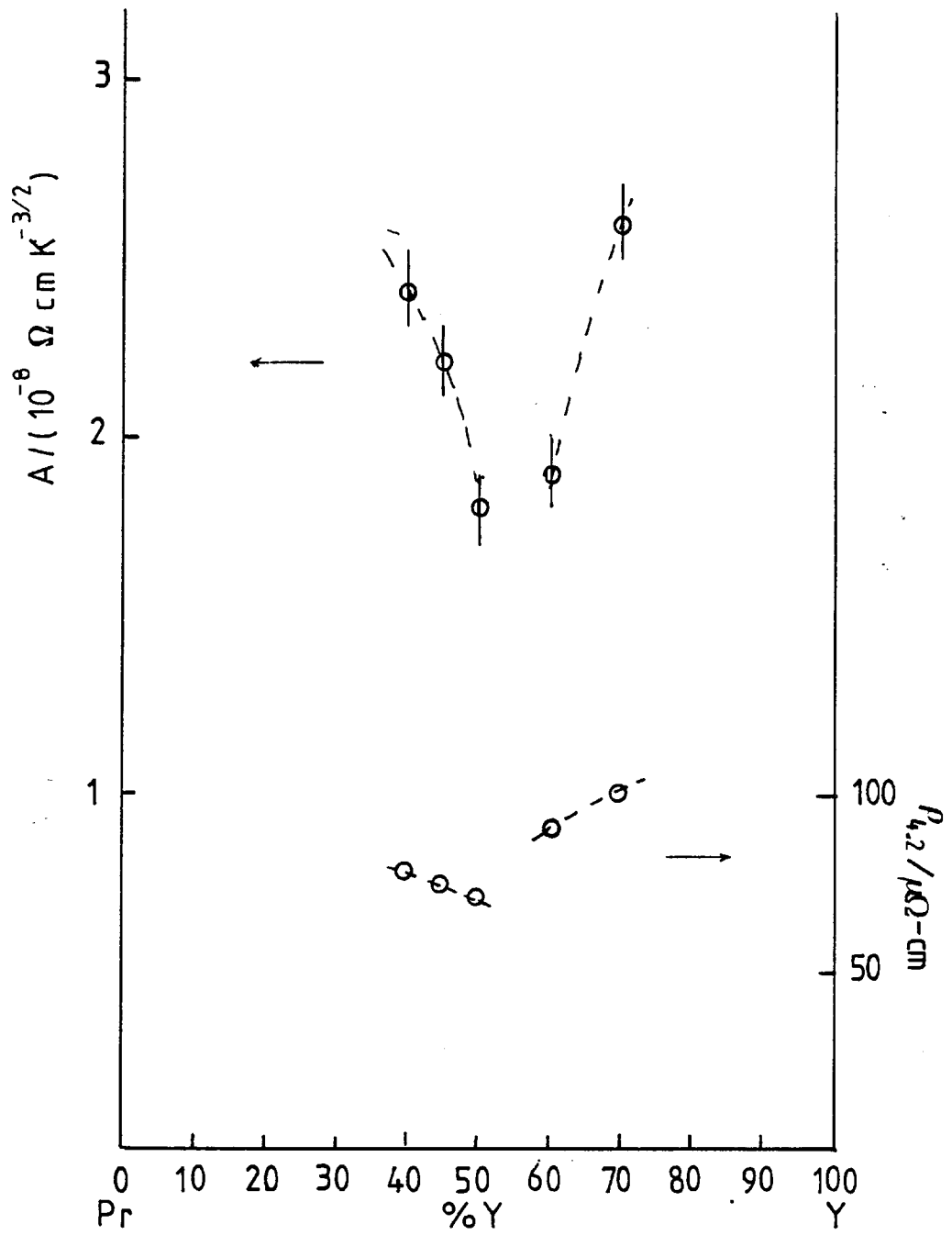


Fig.3.17: Values of the coefficient A and resistivity at 4.2K as a function of Y concentration.

Alloys with the *dhcp* structure

Alloys with concentrations smaller than $\sim 25\%$ *Y* do not order above 1.5 K, but magnetic ordering is found for 30-35% *Y* alloys. Two things must be remarked: first, all these alloys have the same structure as pure *Pr*, and secondly, magnetic ordering appears gradually with decreasing *Pr* content. This suggests that the crystal field is strongly modified.

By observing Fig 3.5 it may be noticed that the crystalline parameters a and c change only slightly for concentrations up to 25% *Y* and more rapidly for higher concentrations of *Y*. This may imply that the magnetic ordering obtained in alloys with the *dhcp* structure is induced by stress which could remove the degeneracy of the first excited state and increase the threshold value n , as happens when an uniaxial pressure is applied along the *a*-direction; see section 3.1.5. The gradual increase of ordering, despite decreasing *Pr* content, is consistent with the progressive stress produced by the addition of *Y*.

It is interesting to estimate the parameter α , in the case of the experiment performed by McEwen et al 1978; in this case, an uniaxial pressure of 800 bars (7.5 was the Néel temperature obtained) was applied on a single crystal of *Pr*. From the bulk modulus

$$B = -V \frac{dP}{dV}$$

where V is the volume and P the pressure, the parameter α is found to be $3.667\text{\AA}$, assuming that c does not change. McEwen et al have also shown that the transition is of antiferromagnetic origin. It should be expected that antiferromagnetism will also appear in *dhcp Pr-Y*

alloys, but it seems that this is not the case. As has been seen before, (a) a peak in the ac-susceptibility measurement and (b) remanent magnetization in the dc-susceptibility are observed for the *Pr*-35% *Y* alloy. This behaviour has some of the characteristics of spin glass freezing in rare earth alloys. However, the reduced magnetization (M/H) behaves more like that of a ferromagnet; see Fig 3.13a.

One interesting point that was not possible to answer, is whether magnetic ordering below 1.5 K will appear for alloys with small concentrations of *Y* or not. Most probably, there is a critical concentration of *Y*, higher than 25% *Y*, in which *Pr* is induced to order magnetically.

Alloys with the *Sm*-type structure

Alloys in the *Sm*-type structure exhibit a rounded peak in the ac-susceptibility measurements, which shifts towards high temperatures when *Pr* content is decreasing. The dc-susceptibility measurements for the *Pr*-50% *Y*, show the smearing of the peak due to a relatively high applied magnetic field and the appearance of remanent magnetization when cooled in a field; similar effects have been observed in *Pr-Gd* and *Pr-Tb* alloys, Sarkissian 1978. The resistivity measurements for 40-45-50% *Y* alloys show a $AT^{3/2}$ dependence at low temperatures, where the coefficient A decreases with decreasing *Pr* concentration; see Fig 3.17. All these effects are characteristics of spin glass freezing ordering. The sharp peak normally observed in ac-susceptibility of 3d spin glass systems and 4f spin glass with weak anisotropy, is not obtained for these alloys. This is attributed to the single-ion anisotropy present in the rare earth metals, and especially in *Pr*; see section 1.5

The ordering temperature is surprisingly high ($\sim 8, 9$ K) if one takes into account the low concentration of *Pr*. As only hexagonal sites order magnetically, this is consistent with the fact that in the *Sm*-type structure there are $\frac{2}{3}$ of the lattice sites with hexagonal symmetry, and $\frac{1}{3}$ with local cubic symmetry, in contrast with the *dhcp* structure; see section 1.2. Then, it is clear that the exchange interaction overcomes the effects of crystal-field, but it is not easy to find an explanation for the fact that there is an increase of ordering temperature and of peak-susceptibility, see Fig 3.10, when *Pr* content is decreasing. The distortions suffered by the unit cell because of the drastic decrease of the crystalline parameters a and c with the addition of *Y*, may provide an answer to this puzzling behaviour. Jensen 1979 has pointed out the importance of the magnetoelastic effects. The contribution of the hexagonal sites to these effects are relatively strong, while contributions of the cubic sites are small. The magnetoelastic term in eq. 3.11 shows that γ strain, which describes distortions of the hexagonal symmetry of the basal plane, are the important ones.

Alloys with the *hcp* structure

In the more concentrated *hcp* alloys, it seems that long-range magnetic ordering takes place, as in *hcp Nd-Y* alloys where a single antiferromagnetic peak has been seen.

No remanent magnetization or field cooling effects were detected in the *Pr*-70% *Y* alloy. However, remanent magnetization when cooled in a magnetic field, and smearing of the peak, when measured in a relatively high field were observed in the *Pr*-60% *Y* alloy. These effects were much less pronounced than for the *Pr*-50% *Y*

(*Sm*-type) alloy, which may suggest that the sample was not completely homogeneous.

The resistivity measurements in both alloys show changes associated with periodic antiferromagnetic ordering, see section 1.4. The derivative $d\rho/dT$ exhibited a minimum near the ac-susceptibility peak as obtained in the *Pr-Nd* alloys, Sarkissian 1977. At low temperatures, the resistivity follows a $AT^{3/2}$ dependence where A has a higher value for the *Pr*-70% *Y* alloy.

McEwen and Stirling 1979* have investigated by neutron diffraction, single crystals of *Pr-Y* alloys. For 90% *Y* they found weakly dispersed excitations ascribed to transitions between the ground and excited states. For *Pr*-80% *Y* weak magnetic satellites were detected below 6 K. These results are consistent with the present work, in the sense that long-range ordering appears in *hcp* alloys of *Pr-Y*, provided that the *Pr* concentration is large enough.

Touborg et al 1978 have investigated the crystal fields in dilute alloys of *Pr* in *Y* and *Lu*. They determine the energy splittings at zero field and as a function of field for ions on the hexagonal sites of *Pr*, from susceptibility measurements, and neglecting the exchange interaction. The parallel and perpendicular inverse susceptibility of a single crystal of *Pr*-98.75% *Y* is shown in Fig. 3.20. This is similar to that for pure *Pr*, see Fig 3.1. They found that the energy splitting between the states $|0\rangle$ and $|\pm 1\rangle$ is about 2.84 meV (33 K) at zero field, which is lower than the one calculated by Houmann et al 1979, see (3.14). In the latest neutron scattering experiments reported by Houmann et al 1975 it was

* Unpublished result.

3.19 meV (37 K).

In the indirect exchange interaction, a conduction electron interacts successively with the localized moments, tending to align them in a particular orientation relative to each other. If the conduction electron polarized by a given *Pr* ion loses its "information" before it goes on the next *Pr* ion, the exchange interaction will be reduced in strength. The preference for spin glass freezing in the *Sm*-type alloys, in contrast with the long-range order in the *hcp* alloys, may be associated in terms of how many *Pr* ions contribute to the *sf* interaction as they enter the cubic and hexagonal sites in the various stacking sequences.

Competition between the exchange interaction and the crystal field effects has the interesting consequence that the correlation between the de Gennes factor $\xi = x(g_J - 1)^2 J(J + 1)$ (x is the concentration of rare earth) and the ordering temperature, is analogous to that of *Nd-Y hcp* alloys.

It was indicated by Nagasawa and Sugawara 1967 and Pelzl et al 1977 that the ordering temperature deviates from $\xi^{2/3}$ dependence below $\xi = 1$, see Fig 3.18. The values of the de Gennes factor G for pure metals are quoted in Table 1.1. For pure *Pr*, $G = 0.80$.

Separately in Fig 3.19 are plotted the data for *Pr-Y* alloys together with the data for *Nd-Y* (Sharif and Coles 1978), *Tb-Y*, *Gd-Y* (Sarkissian 1976) corresponding to long-range and spin glass magnetic ordering. Below $\xi = 1$, there is a clear deviation from $\xi^{2/3}$, which occurs for both types of magnetic ordering. There is no explanation for this behaviour.

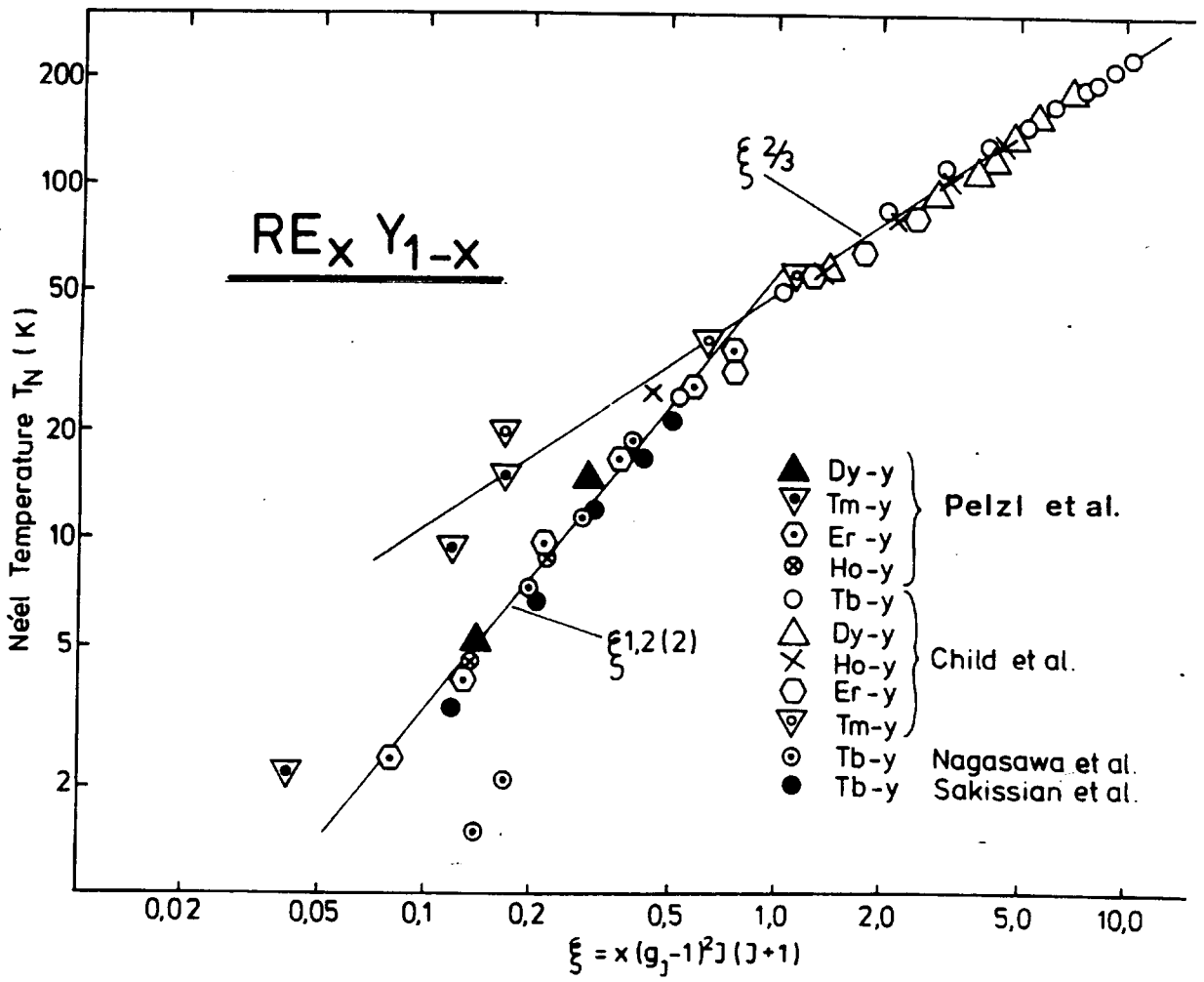


Fig.3.18: Log-Log plot of the ordering temperatures of the $(RE)_x Y_{1-x}$ alloys vs the de Gennes Factor ξ .

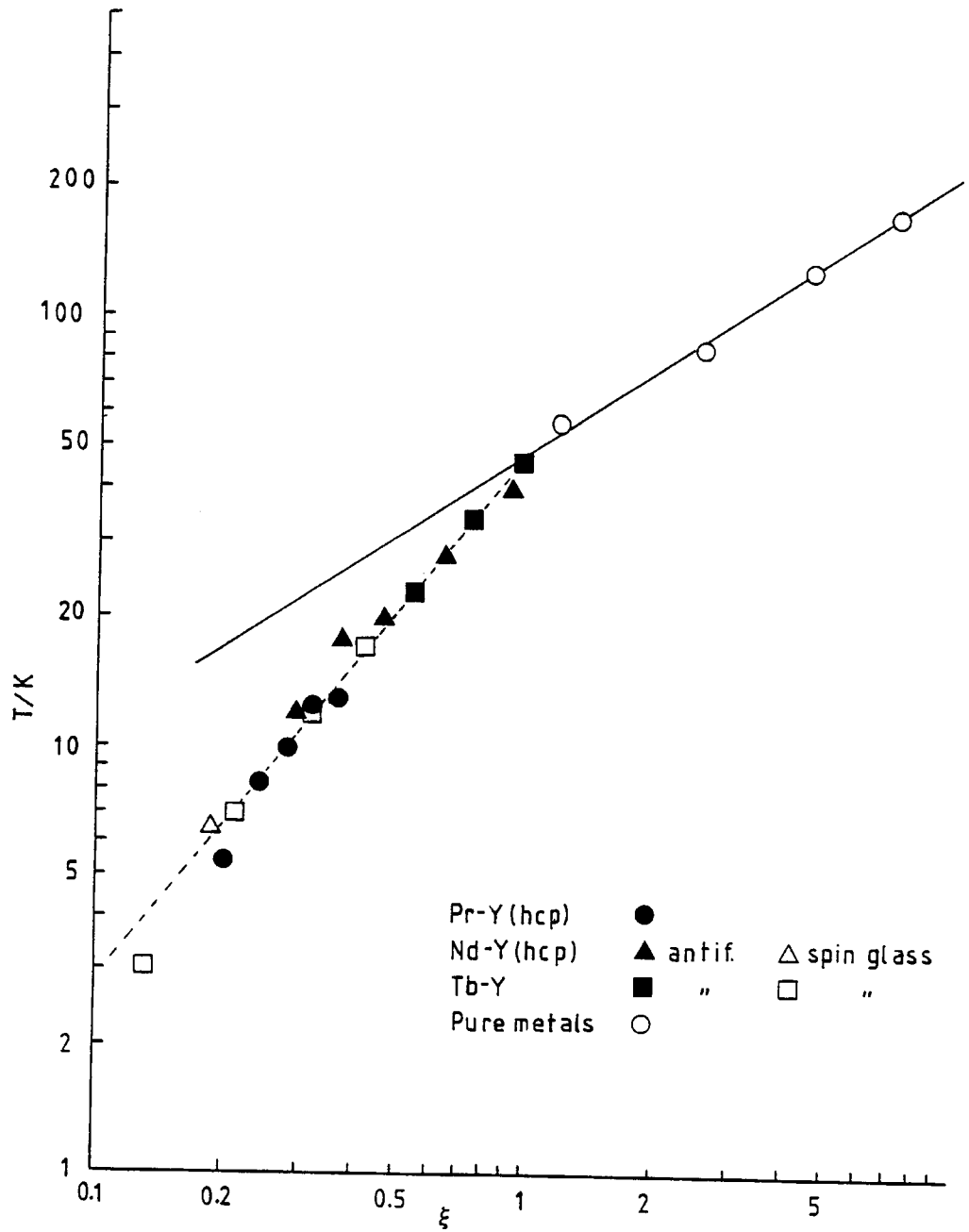


Fig.3.19: Log-Log plot of the ordering temperatures for Pr-Y, Nd-Y, Tb-Y and Gd-Y alloys, vs the de Gennes factor ξ .

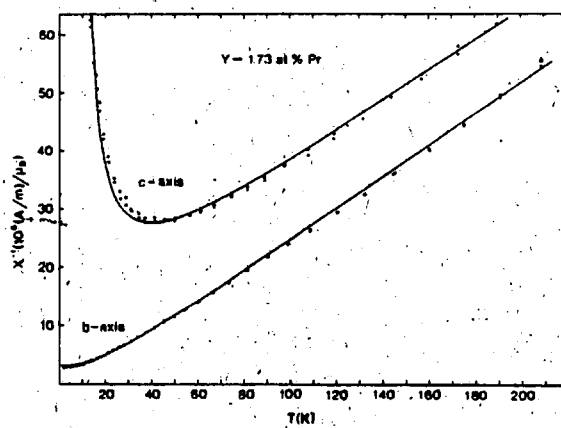


Fig.3.20: Parallel and perpendicular inverse susceptibility of a single crystal of Pr-98.75%Y.

3.3.4 Conclusion

Magnetic ordering can be induced in *Pr* when *Pr*-atoms experience different crystallographic environments (*dhcp* $\rightarrow$ *Sm*-type $\rightarrow$ *hcp*) due to the addition of *Y*.

Susceptibility peaks have been observed for all three phases but the magnitudes and concentration dependences of the peak temperatures are distinctly different.

Long-range order seems to occur in the more concentrated alloys in the *hcp* structure, whereas for *Sm*-type alloys, the competition between exchange and crystal-field interactions has the striking result that the magnetic behaviour has the characteristics of spin glass. In the *dhcp* alloys, *Y* perturbs the singlet ground state, but its magnetic character is not clear.

A correlation between the de Gennes factor ξ and the ordering temperature has been found for the *hcp* alloys. The behaviour observed in *Nd-Y* and *Pr-Y* alloys, suggest that the hexagonal structure favours the onset of magnetic ordering.

As has been seen before, the magnetic properties of pure *Pr* are still not completely understood. Certainly, it is not the intention in this work to attempt to answer all the peculiar features found in these alloys, but rather to throw light on the behaviour of *Pr* metal and *Pr-Y* alloys. Unresolved questions will be properly answered when more detailed neutron diffraction experiments are performed on these alloys. Also, quantitative studies will be possible when single crystals are available.

CHAPTER 4

4. Magnetic character of some *Sm* alloys

So far, little work has been done on binary alloys of *Sm* with other rare earths metals, and particularly on alloys within the *Sm* crystallographic structure. It is of interest to study the changes in the magnetic ordering in both *Sm*-light rare earth and *Sm*-heavy rare earths alloys, although the extent of the *Sm* phase may be rather limited. This chapter will be concerned with some *Sm* based alloys. *Gd*(*S*-state), *Nd*(Kramers ion) and *Pr*(non-Kramers ion) have been selected as the rare earth solute.

First, a summary of the most important studies on *Sm* will be given.

4.1 Magnetic properties of *Sm* metal

Samarium exhibits unusual structural behaviour and distinctive magnetic properties. The crystal structure can be visualized in terms of a nine-layer stacking sequence, in which $\frac{2}{3}$ of the atomic sites have approximate local hexagonal symmetry and $\frac{1}{3}$ approximate local cubic symmetry; see section 1.2. The ionic moment is exceptionally low ($\frac{5}{7} \mu_B$) compared with the ionic moments of the other elements in the series. In addition, admixture of the excited state $J = \frac{7}{2}$ multiplet into the ground state $J = \frac{5}{2}$ multiplet, affects the paramagnetic susceptibility and the usual Curie law is not obeyed; see section 1.1.

4.1.1 Magnetic structure

The magnetic structure as determined by Koehler and Moon 1972 has been generally accepted. They performed neutron diffraction measurements on a single crystal of *Sm*, and found that its magnetic behaviour may be described in terms of independent contributions from the two crystallographic sites.

The moments on the hexagonal sites order antiferromagnetically below 106 K. The spins are parallel to the $\bar{c}$ -axis with two ferromagnetic layers pointing along the plus c direction and, for the next two layers, along the minus c direction. The magnetic sequence becomes a plane of ferromagnetic layers $0++0--0++...$ along the $\bar{c}$ -axis, in which 0 signifies disordered moments on the cubic-site planes; Fig. 4.1a. This structure gives zero exchange field on the cubic sites.

Below 13.8 K, the moments on the cubic sites become independently ordered antiferromagnetically. The spins are also parallel to the $\bar{c}$ -axis, but the ferromagnetic layers are parallel to the $(10\bar{1}1)$ planes with a $++--++--...$ sequence, see Fig. 4.1b.

Koehler and Moon observed a very small net moment per atom ($\sim 0.1 \mu_B$) which was attributed to a large polarization of the conduction electrons parallel to the ionic spin.

4.1.2 Some physical properties

Arajs and Dunmyre 1966 have measured the electrical resistivity and magnetic susceptibility of a polycrystalline sample of *Sm*. The resistivity data exhibits two clear anomalies at 12 K and 106 K, and ρ is almost linear with temperature below 300 K. The magnetic susceptibility shows a very sharp peak at 14 K and only a small maximum at 108 K; above this latter temperature, the susceptibility decreases slowly and the well known Curie-Weiss law is not obeyed.

Jennings et al 1959 have measured the specific heat of a *Sm* polycrystalline sample. They found a small peak at 14 K and a much higher and broader peak at 106 K.

McEwen et al 1974 have performed low-field susceptibility and high field (up to 38T) magnetization measurements on *Sm* single crystals. At 4.2 K, the basal plane magnetization increases linearly with field. The perpendicular magnetization rises smoothly, up to ~ 23 T, where an abrupt increase occurs; see Fig. 4.2. This sudden increase does not happen for temperatures above 14 K, and thus is supposed to come from the rotation of the moments on the cubic sites when the Zeeman energy is greater than the anisotropy energy. At 20.4 K, the perpendicular magnetization is found to be linear with field; see Fig. 4.2. These results are in agreement with the behaviour of an antiferromagnet, the a and c axis being the easy and hard directions of magnetization, respectively. At 30T, the moment was about $0.1 \mu_B/\text{atom}$, a value in accordance with the nuclear

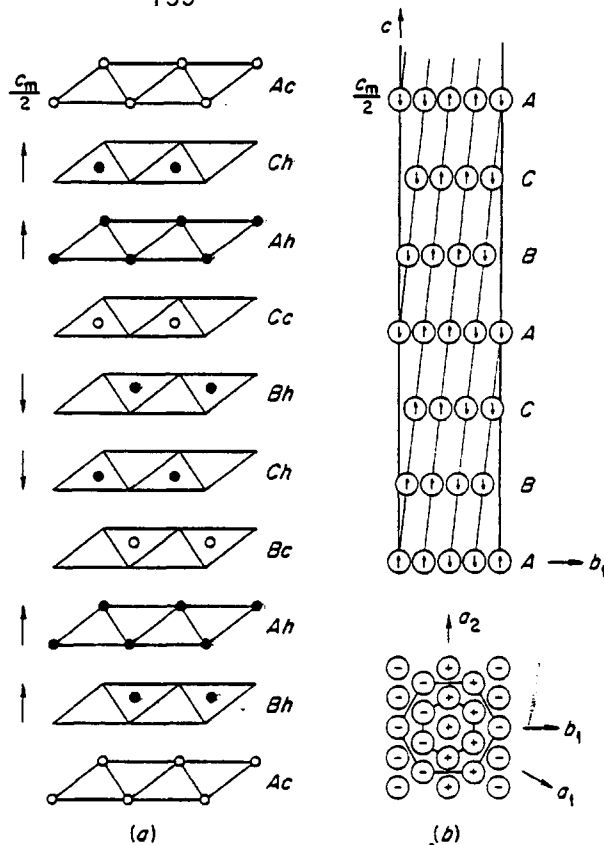


Fig.4.1: (a) High-temperature magnetic structure of Sm, involving only the hexagonal-site ions.
(b) Low-temperature magnetic structure of Sm, involving only cubic-site ions (after Koehler and Moon).

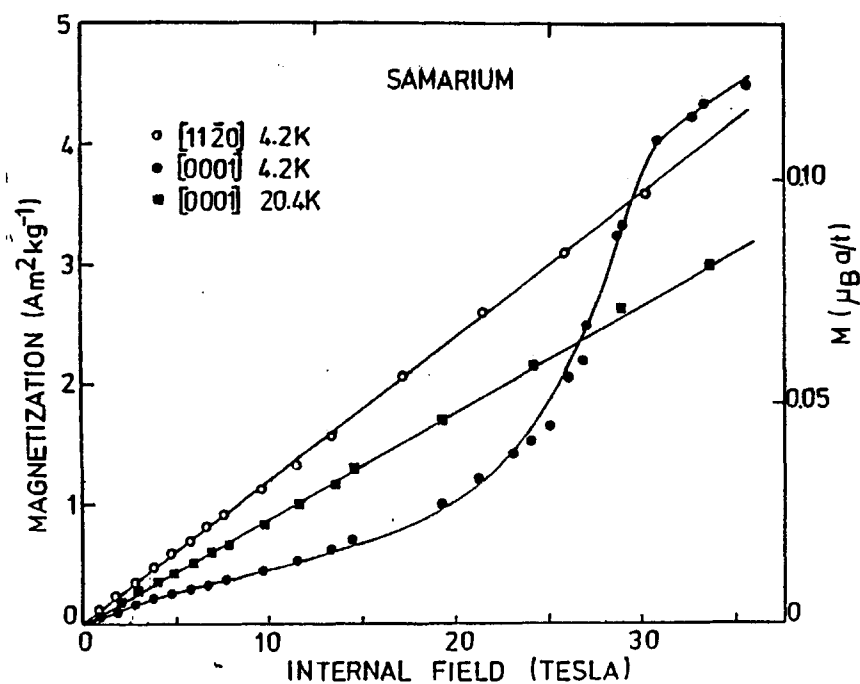


Fig.4.2: High field magnetization of Sm at temperatures above and below $T_{NC} = 14\text{K}$ (after McEwen et al. 1974).

diffraction results of Koehler and Moon. The parallel susceptibility exhibits two clear anomalies at 14 K and 106 K, but the perpendicular susceptibility only shows a small maximum at 14 K.

4.1.3 Crystal-field splittings

Until now, there has been no definite knowledge of the energy splittings of Sm metal. However, some attempts have been made in order to observe the effects of the crystal field and exchange interaction on the ground state multiplet of the free-ion ${}^6H_{5/2}$.

Moon and Koehler 1973 calculated approximate ground states for the cubic and hexagonal sites. They considered a Hamiltonian with a crystal-field term (for hexagonal or cubic symmetry), and with an exchange term in the molecular field approximation. For the hexagonal sites the ground state was found to be $|{}^5/2, {}^5/2\rangle$, but the large exchange induces a slight admixture of the excited state multiplet $J = 7/2$. Then, the approximate ground state is,

$$|g_H\rangle = 0.996|{}^5/2, {}^5/2\rangle - 0.084|{}^7/2, {}^5/2\rangle$$

The saturation moment for this state is $0.57 \mu_B/\text{atom}$. For the cubic sites, they estimated a ground state of the form,

$$|g_C\rangle = 0.952|{}^5/2, {}^5/2\rangle + 0.306|{}^5/2, -1/2\rangle$$

where only the multiplet $J = 5/2$ was taken into account. The

moment is found to be $0.634 \mu_B/\text{atom}$. However de Wijn et al 1974 deduced that the quartet Γ_8 as ground state, gives a better fitting to the data. An ideal cubic crystal field lifts the sixfold degenerate multiplet $J = 5/2$, leaving a quartet Γ_8 (two of the states are a mixture of $|5/2, 3/2\rangle$ and $|5/2, -5/2\rangle$, and the other two are a mixture of $|5/2, 5/2\rangle$ and $|5/2, -3/2\rangle$) and a doublet $\Gamma_7(|5/2, \pm 1/2\rangle)$. The exchange interaction on the cubic sites is expected to be negligible.

4.1.4 Phase transformations

Jayaraman and Sherwood 1964 investigated the effects of high pressure on the structural and magnetic behaviour of *Sm* metal. They found a phase transformation to *dhcp* structure at ~ 40 kbar and 300°C . For this phase, the Néel temperature occurring at 14 K shifted to 27 K. This is consistent with the fact that there are more cubic sites in the *dhcp* structure. They did not observe any anomaly in the susceptibility around 106 K for the normal form of *Sm*, but a kink around 110 K was obtained for the *dhcp* phase.

There is another phase transformation to the *hcp* structure at normal pressure and $\sim 600^\circ\text{C}$, Mardon and Koch 1970, Coles 1981. McEwen and Touborg 1976 observed an anomaly in the susceptibility at about this high temperature, which was attributed to this crystal transformation.

4.2 Experimental review of *Sm* alloys

Fujimori et al 1974 investigated the magnetic ordering

in some $Gd-Sm$ alloys, with Gd concentrations greater than 75%. The magnetization vs temperature curves in fields of 30 kOe show similar behaviour to that of pure Gd . The ferromagnetic Curie temperature varies from 293 K, for pure Gd , to 250 K, for 25% Sm , and is proportional to the de Gennes factor $\{\sum c_i (g_i - 1)^2 J_i (J_i + 1)\}^{2/3}$, where c_i is the concentration of each element. In the hcp structure, the magnetic moment of Sm^{3+} is found to be $0.9 \mu_B/\text{atom}$. Also the Sm magnetic moments are aligned ferrimagnetically with the Gd magnetic moments. This means that there is a parallel alignment between the spin moments but an antiparallel alignment between the total angular moments. Aaraj et al 1974 measured the electrical resistivity in some $Gd-Sm$ alloys up to 35% Sm . They found similar results to those quoted previously by Fujimori et al 1974.

Eguchi et al 1981 performed magnetization measurements at 4.2 K on several single crystals of $Gd-Sm$ up to 30% Sm . The $\bar{c}$ -axis is the easy direction of magnetization, and the magnetic moment decreases linearly with Sm concentration. They found that the single-ion and two-ion anisotropy is responsible for the high magnetocrystalline anisotropy along the $\bar{c}$ -axis.

Yao et al 1980 have measured the electrical resistivity of $Sm-3\%$ Dy between 15 and 300 K. They found that the Néel temperature of Sm corresponding to the transition for the hexagonal sites, dropped to 103 K. Note that Dy metal has a transition at 180 K from a paramagnetic state to a spiral antiferromagnetic structure, and becomes ferromagnet below 85 K.

Caton et al 1982 have investigated the magnetic behaviour of several *hcp Dy-Sm* alloys, by electrical resistivity and low and high field susceptibility measurements. The ferromagnetic Curie temperature of *Dy* was not lowered by the addition of *Sm*, up to 80% *Sm*. On the other hand, the anti-ferromagnetic Néel temperature of *Dy* decreased steadily up to 150 K for 40% *Sm*. They found that the sample containing 80% *Sm* had a mixture of *hcp* and *Sm* structures, although it was not clear where the polymorphic transition occurred.

Okamoto et al 1980 measured the magnetic susceptibility on various single crystals of *Tb-Sm* alloys. *Tb* metal has a spiral antiferromagnetic structure, similar to *Dy*, from 229 K down to 219 K, and then transforms to a basal ferromagnet. Alloys with concentrations less than 10% *Sm* show two transitions like pure *Tb*, and the difference between both transition temperatures decreases with increasing *Sm* concentration. In alloys from 10% up to 50% *Sm*, the antiferromagnetic structure disappears and ferromagnetism takes its place. The Curie temperature decreases linearly with increasing *Sm* concentration. In the *Sm*-rich alloys, the first transition of *Sm* corresponding to the hexagonal sites increased steadily with decreasing *Sm* content. For 80% *Sm* alloy, the second transition increased abruptly to ~ 90 K.

Touborg et al 1978 made preliminary measurements of susceptibility on a single crystal of $\underline{Y}$ -3% *Sm*. The susceptibility was found to be almost temperature independent in the range

20-280 K. This is a rather surprising result because Sm^{3+} is a Kramers-ion. One would expect a constant susceptibility at low temperatures only in the case of a singlet ground state.

Achiwa and Kawano 1973, 1980 performed neutron diffraction on single crystals of *Tb*-light rare earth alloys in the *Sm*-type structure. For *Tb*-20% *La*, *Tb*-20% *Pr* and *Tb*-25% *Nd* alloys, they found the same magnetic structure corresponding to the high temperature ordering of pure *Sm*. For the *Tb-La* alloy, the second magnetic transition was not observed. On the other hand, the *Tb-Pr* and *Tb-Nd* alloys undergo a martensitic transformation from *Sm*-type to *hcp* crystalline forms, below 30 K. In the *hcp* form, the alloys have a ferromagnetic structure similar to that of pure *Tb*. The Néel and Curie temperature for the two crystalline structures are given below,

	<i>Sm</i> -type T_N/K	<i>hcp</i> T_C/K
<i>Tb</i> -20% <i>La</i>	124	-
<i>Tb</i> -20% <i>Pr</i>	130.5	163.5
<i>Tb</i> -25% <i>Nd</i>	129	180

The reverse phase transformation happens above the Curie temperature. It seems that *hh* and *hch* sequences of packed layers favour parallel and antiparallel arrangement of the magnetic moments at the hexagonal sites respectively. The moments at the cubic sites remain disordered.

4.3 Sm-rare earth alloys

4.3.1 Metallurgy

The alloys were prepared as described in section 2.4. Pure *Sm* proved impossible to suck down into the mould. The pieces of *Sm* used in the experiments were cut from the raw material with a spark erosion machine. The alloys proved difficult to cast and several attempts were made in order to obtain suitable samples for the resistance measurements. The loss of material was between 1 to 2%, mainly due, it is thought, to the high vapour pressure of *Sm*. It is interesting to observe how different are the values of the vapour pressure for the elements used in this work, given at the melting point,

<i>Sm</i> :	1.2	mm Hg
<i>Pr</i> :	10^{-7}	" "
<i>Nd</i> :	10^{-5}	" "
<i>Gd</i> :	10^{-4}	" "

Thus, it is reasonable to suppose that only *Sm* is the lost material and the concentrations can be re-estimated:

<i>Sm</i> alloy	Nominal %	Estimated %
<i>Pr</i>	{ 5	{ 5.08
	(10	(10.34
<i>Nd</i>	5	5.04
<i>Gd</i>	{ 2	{ 2.03
	{ 5	{ 5.14
	(10	(10.23

As yet, no phase diagram for the *Sm-Pr* system has been reported in the literature. For the *Sm-Gd* and *Sm-Nd*, only a schematic phase diagram is reported (Moffatt W.G., The Handbook of Binary Phase Diagrams); see Fig. 4.3. In the *Sm-Gd* alloys, a gradual transition from *Sm*-type to *hcp* structure is reported, although the region in which it occurs is not indicated. The *Sm-Nd* phase diagram shows that the *Sm*-type structure is stable up to 10% *Sm* concentration. Unfortunately, no X-ray measurements could be performed on our samples, in order to know the structure, because all the elements have a high mass absorption coefficient for the $K\alpha_{Cu}$ wavelength; and the $K\alpha_{Mo}$ wavelength, for which the mass absorption coefficient is very low, was not available. At first it was assumed that the alloys were structurally homogeneous, and no heat treatment was done. However, it will be apparent from the susceptibility measurements, that some of the alloys contained two phases.

The details will be explained later, for the respective samples. Also, because of the high vapour pressure of *Sm*, it was found difficult to do heat treatments on the samples, but nevertheless two of them were annealed at 500°C, and the loss of material was not very significant.

4.3.2 Samarium - Results and discussion

The magnetic susceptibility of polycrystalline *Sm* exhibits a sharp peak at ~ 14 K and a small peak at ~ 106 K (see Fig. 4.4) similar to that quoted by Araj and Dunmyre 1966. The applied magnetic field was 1.5 kOe. On the other hand,

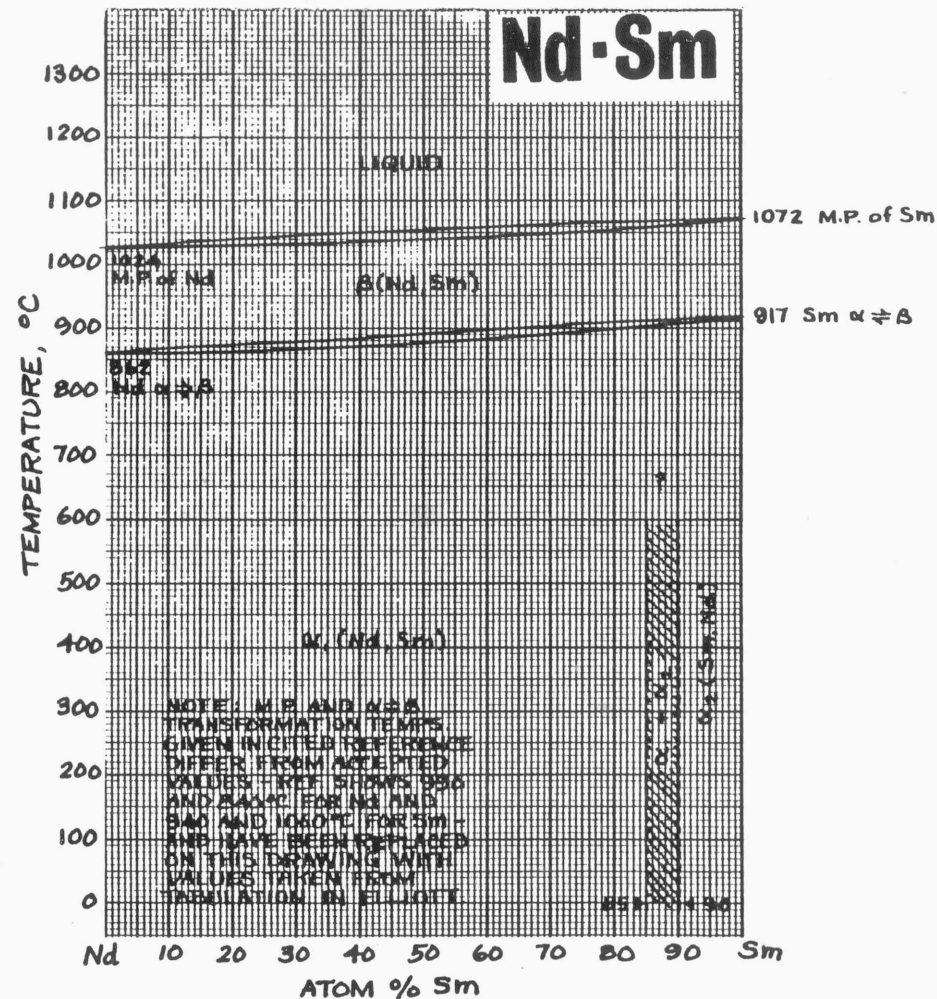
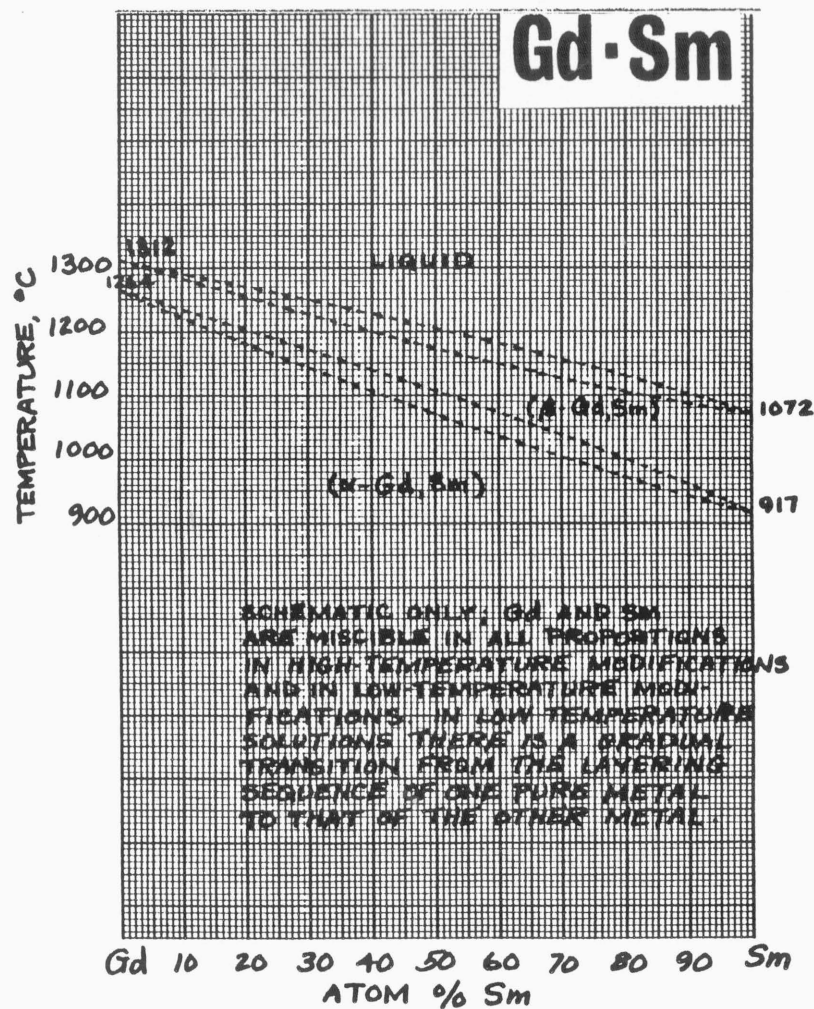


Fig.4.3: Phase diagram of Sm-Gd and Sm-Nd systems.

it was difficult (sometimes impossible) to perform ac-susceptibility measurements on pure Sm and alloys rich in Sm , because the apparatus is not sensitive enough to measure with any accuracy such low values of susceptibility ($\sim 10^{-5}$ emu/gr). The experimental data of ac-susceptibility was only obtained for the temperature range 4–30 K, and has been represented by a dashed line in the Fig. 4.4, together with the dc-measurements for comparison. It is remarkable that the low field susceptibility drops very sharply below the transition temperature down to 4.2 K, while the high field susceptibility remains constant below ~ 8 K. This may be evidence for an irreversible susceptibility. Fig. 4.5 exhibits the electrical resistivity ρ and its derivative, with respect to the temperature, $d\rho/dT$. (As has been mentioned in Chapter 3, the derivatives are calculated using the E02 BCF computer program at the ICCG, see Appendix 2 for details). In a first attempt to fit the resistivity data, the derivative $d\rho/dT$ exhibited a sharp peak at ~ 12 K (see Fig. 4.5a) a result which agrees with that of Arajs and Dunmyre 1966, but disagrees with the Néel temperature obtained from susceptibility measurements. A second attempt was made which gave a better fitting to the data. The derivative shows a maximum at ~ 12 K and a minimum at ~ 14.2 K (see Fig. 4.5b). This suggests that the resistivity may display behaviour similar to that of D_y near the antiferromagnetic transition, Boys and Legvold 1968. The c -axis resistivity of D_y shows a very marked hump with a minimum in $d\rho/dT$ at T_N , while the basal plane resistivity curve does not possess this hump. Moreover, in the case of some ferromagnet materials (see Sousa et al 1979), a sharp peak in $d\rho/dT$ is found at T_c . This is ascribed to the

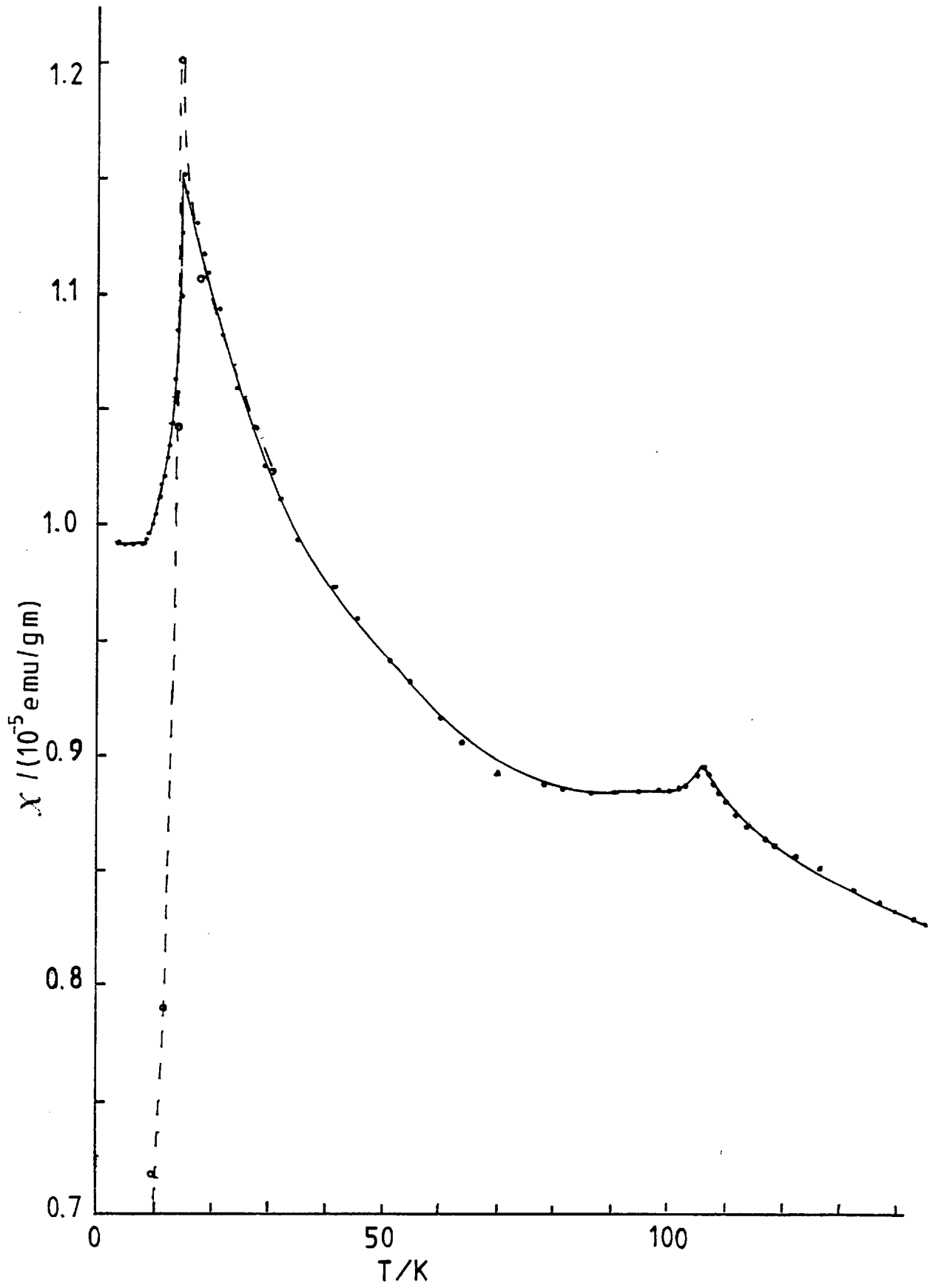


Fig.4.4: (●) Dc and (○) ac-susceptibility as a function of temperature of Sm.

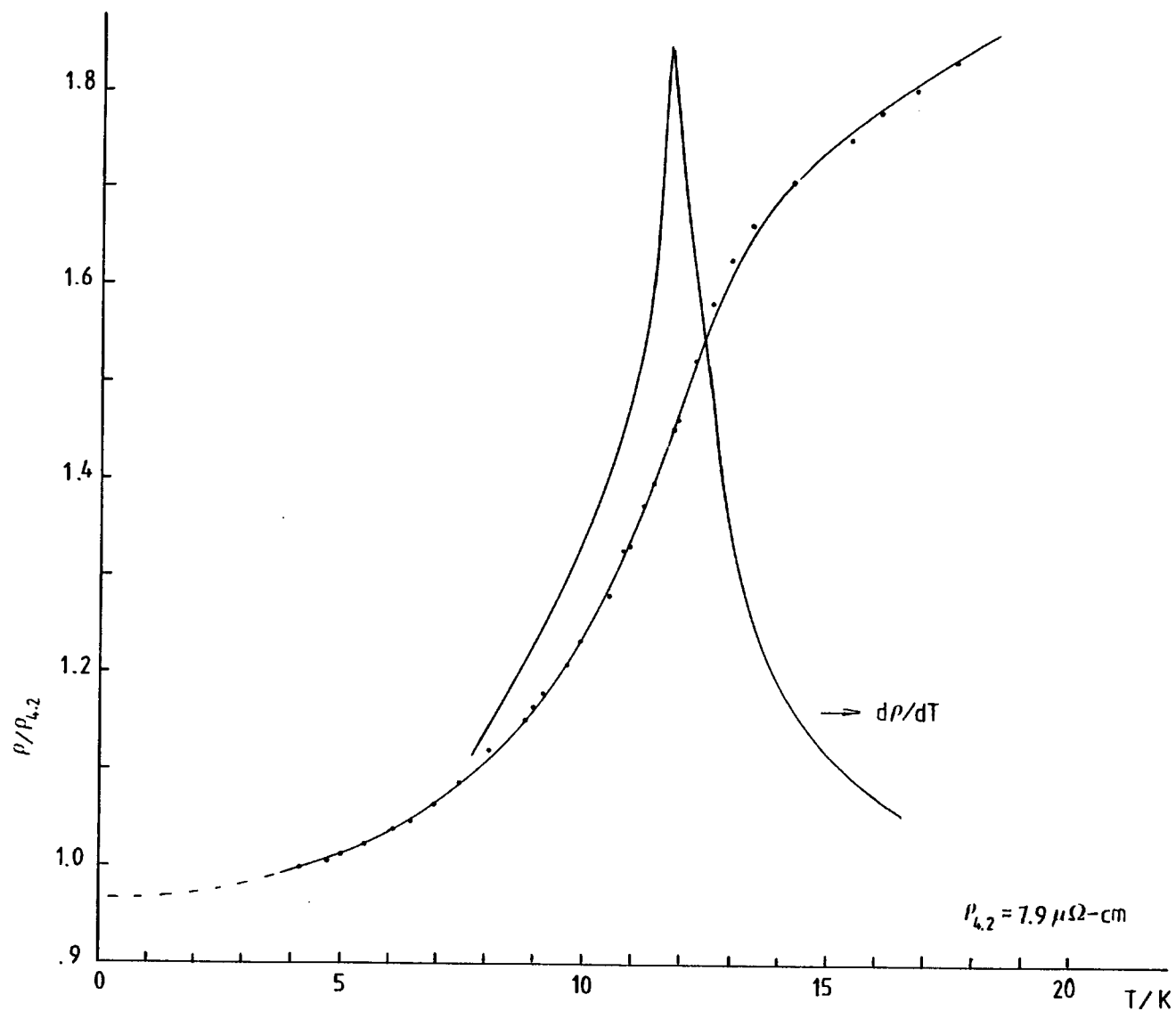


Fig.4.5: a) Electrical resistivity ρ and $d\rho/dT$ of Sm showing the low temperature transition. First fitting.

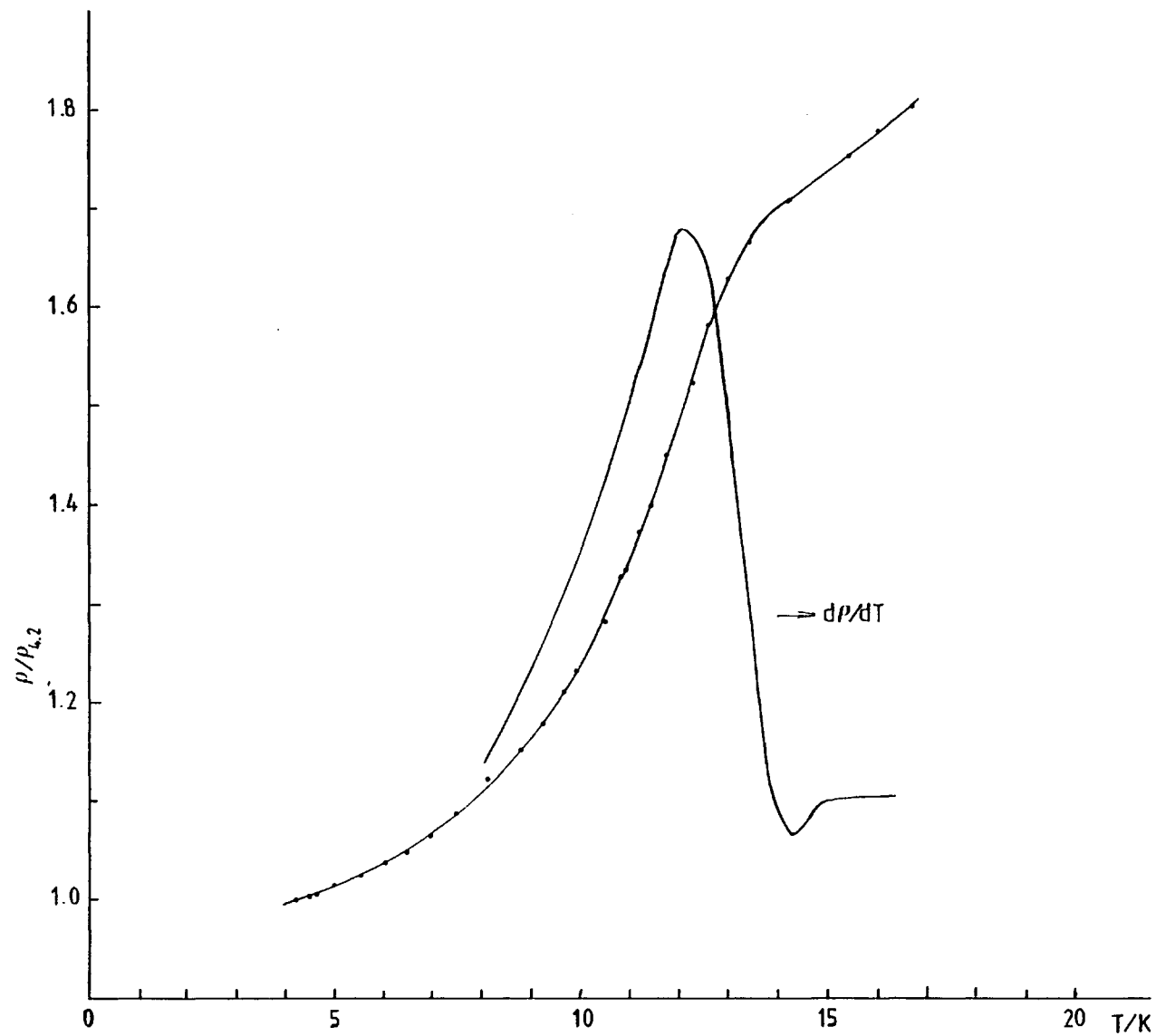


Fig.4.5: b) Electrical resistivity ρ and $d\rho/dT$ of Sm showing the low temperature transition. Second fitting.

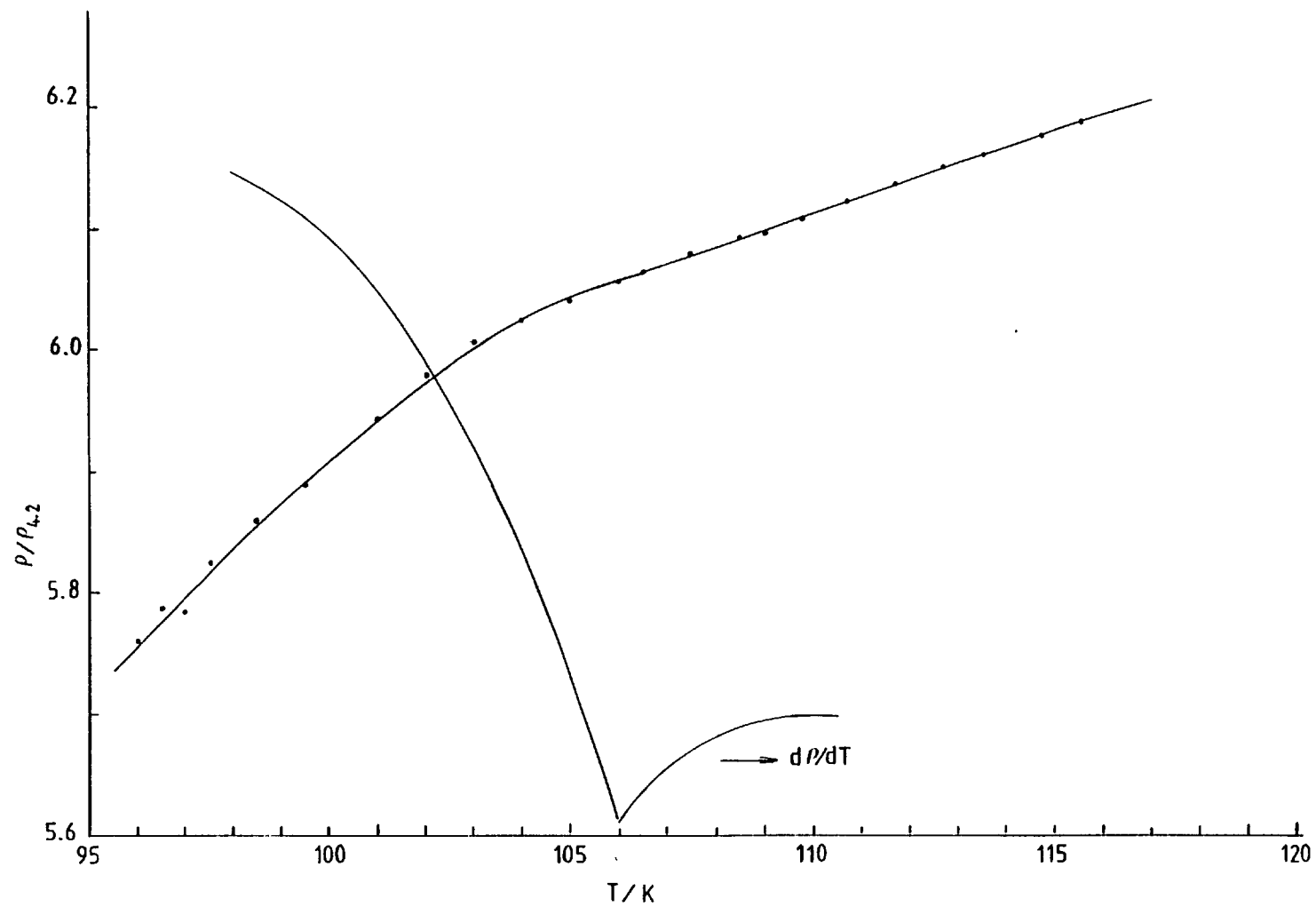


Fig.4.5: c) ρ and $d\rho/dT$ of Sm showing the high temperature transition.

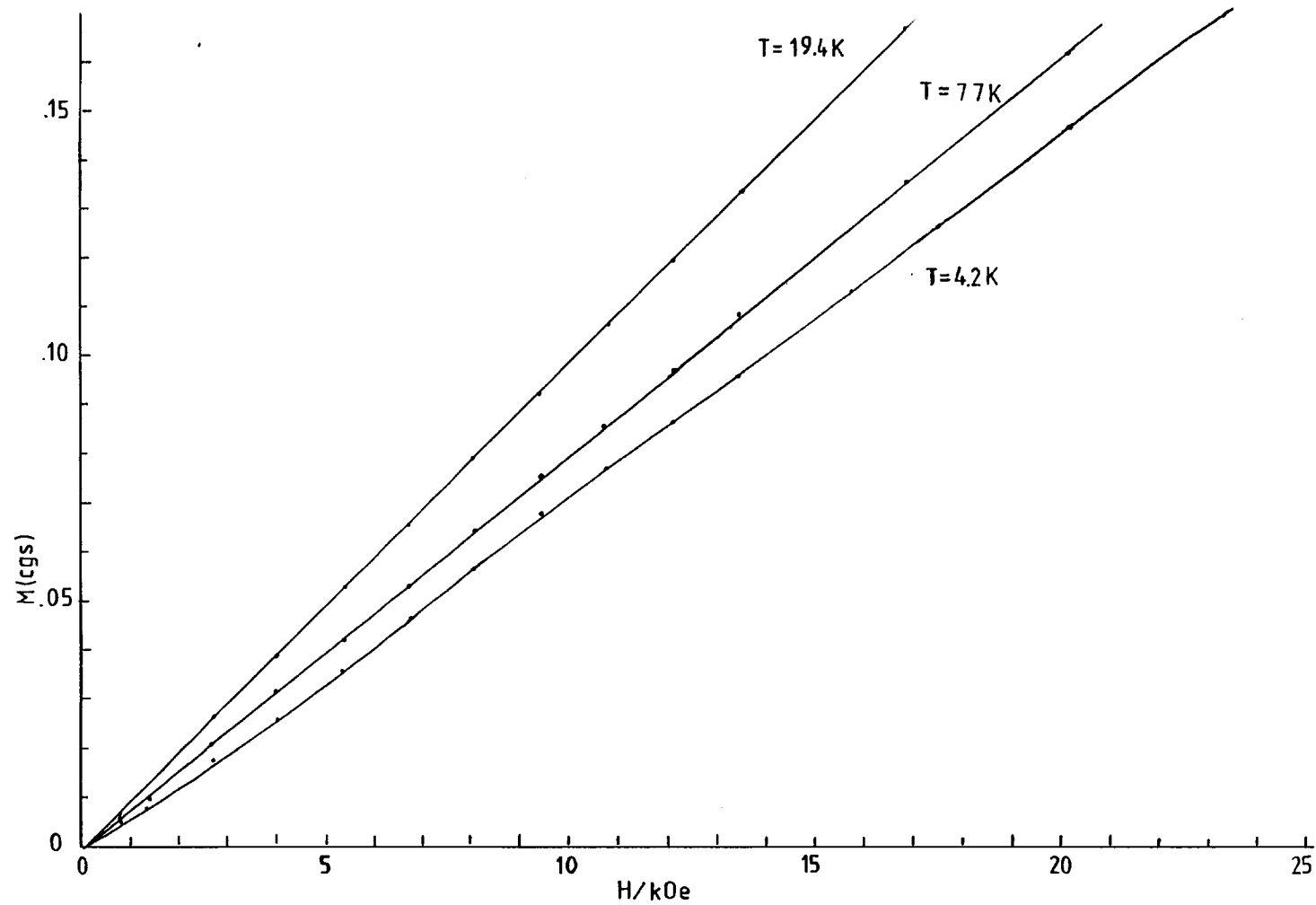


Fig.4.6: Magnetization vs applied field for Sm.

effects of critical fluctuations, and gives different contributions to the resistivity along the c - or b -axis. For an antiferromagnet similar behaviour can be expected. In a polycrystalline sample, the resistivity will depend upon the preferred orientation of the specimen. Krithivas and Meaden (1975) have observed a sharp peak in $d\rho/dT$ near 14 K, in a polycrystalline sample of Sm . They ascribed this peak to critical effects (Fisher and Langer-behaviour). A resistivity measurement on a single crystal of Sm is needed to clarify this matter. Fig. 4.5c shows the high temperature anomaly, which agrees with the susceptibility measurements.

The magnetization measurements up to fields of ~ 20 kOe are shown in Fig. 4.6. At 20 K and 77 K, the magnetization increases linearly with field. At 4.2 K, the behaviour of the magnetization suggests that there is a small field-induced admixture of the crystal field levels. This effect is ascribed only to the cubic sites because it does not occur above 14 K. No hysteretic effects were observed.

4.3.3 $Sm-Pr$ and $Sm-Nd$ alloys in the Sm -type structure.

Results and discussion

The magnetic susceptibility of $Sm-5\%$, 10% as-cast alloys are shown in Fig. 4.7. The susceptibility of $Sm-5\%$ Pr alloy in an applied field of 1.5 kOe, exhibits a sharp peak at ~ 12 K, not as sharp as that for pure Sm , and a kink at around 100 K. Instead, the susceptibility of $Sm-10\%$ Pr alloy in an applied field of 400 Oe, increases smoothly down to 70 K, then rises more rapidly and flattens out at low temperatures, without the

appearance of any peak. The values of susceptibility increase with increasing *Pr* content, as expected. No ac-susceptibility measurements were performed on these alloys.

The electrical resistivity measurements show also interesting results. For *Sm-5% Pr*, two sharp anomalies are clearly observed: one at around 8.4 K and the other at ~ 100.5 K. The detailed variation of ρ and $d\rho/dT$ at and in the vicinity of these temperatures is shown in Fig. 4.8. The data corresponding to the lower transition could only be fitted to give a maximum in $d\rho/dT$ at a temperature well below the susceptibility peak temperature. The reasons for this peculiar behaviour have been discussed in the previous section. For *Sm-10% Pr*, a smooth anomaly is observed at high temperatures, but not at low; see Fig. 4.9.

This magnetic behaviour suggests that the alloys may have the same magnetic structure as observed in pure *Sm*. Notice that neutron diffraction revealed this particular magnetic structure for a *Tb-Pr* alloy in the *Sm*-type form, as has been already mentioned. The decrease of Néel temperature with increasing *Pr* content is expected because of the small exchange contribution of *Pr*.

The magnetic behaviour exhibited by the as-cast *Sm-5% Nd* alloy proved difficult to interpret. The susceptibility was found to depend upon the value of the applied field and on whether the sample was cooled in a field or not. Some of the measurements were performed in a field produced by an electromagnet

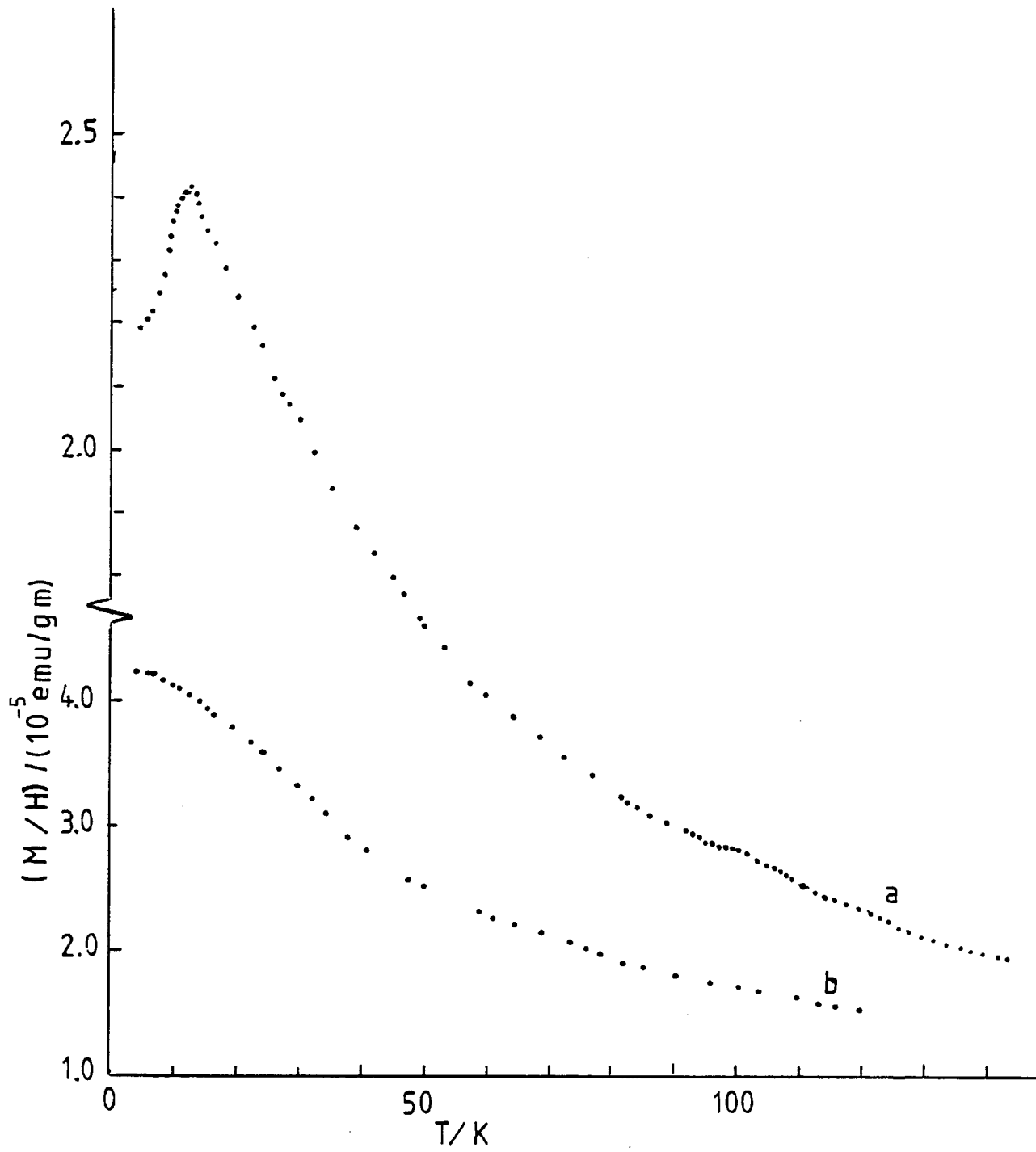


Fig.4.7: Dc-susceptibility as a function of temperature for
a) Sm-5%Pr and b) Sm-10%Pr alloys.

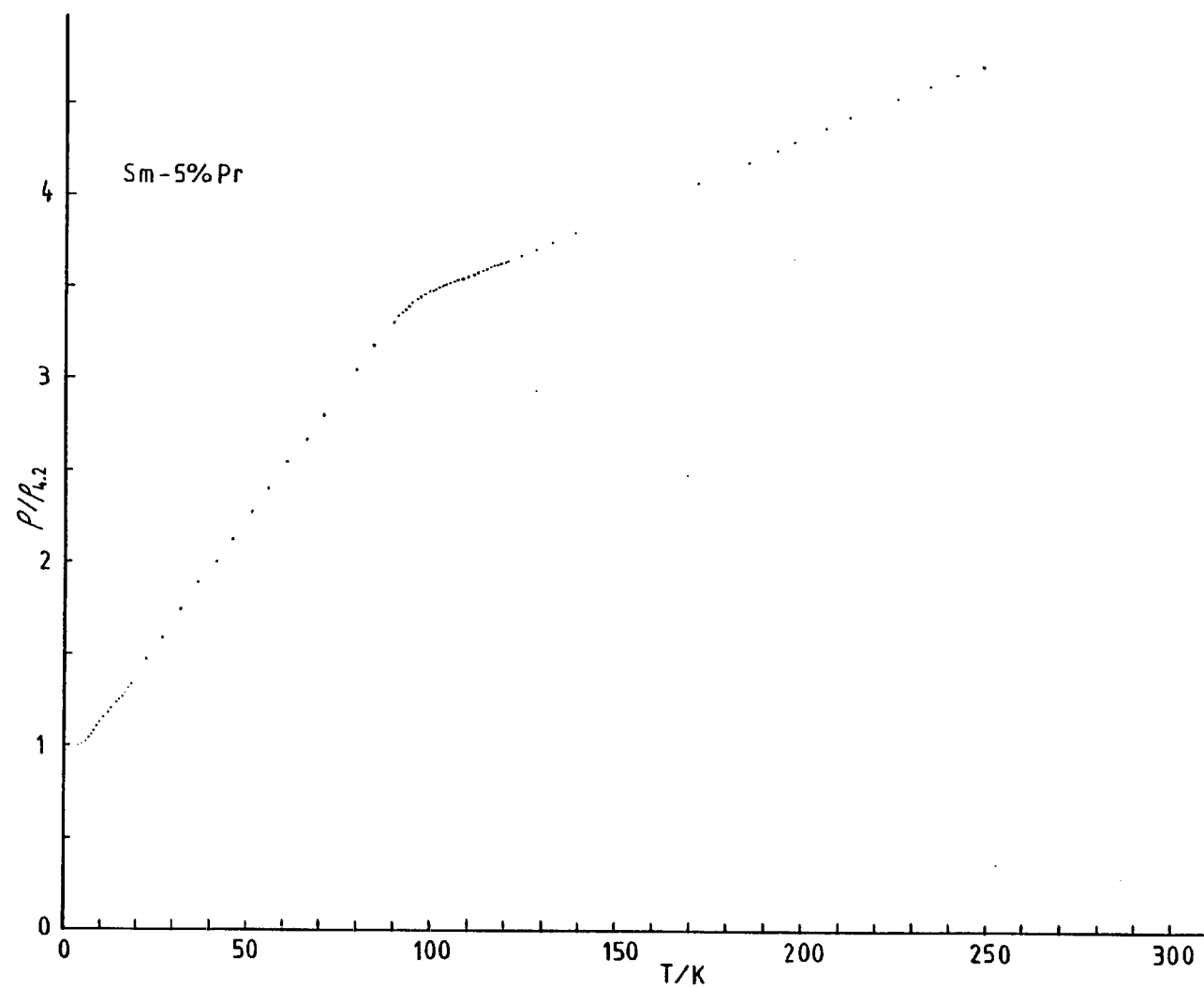


Fig.4.8: Electrical resistivity ρ and $d\rho/dT$ for the Sm-5%Pr alloy.

cont.

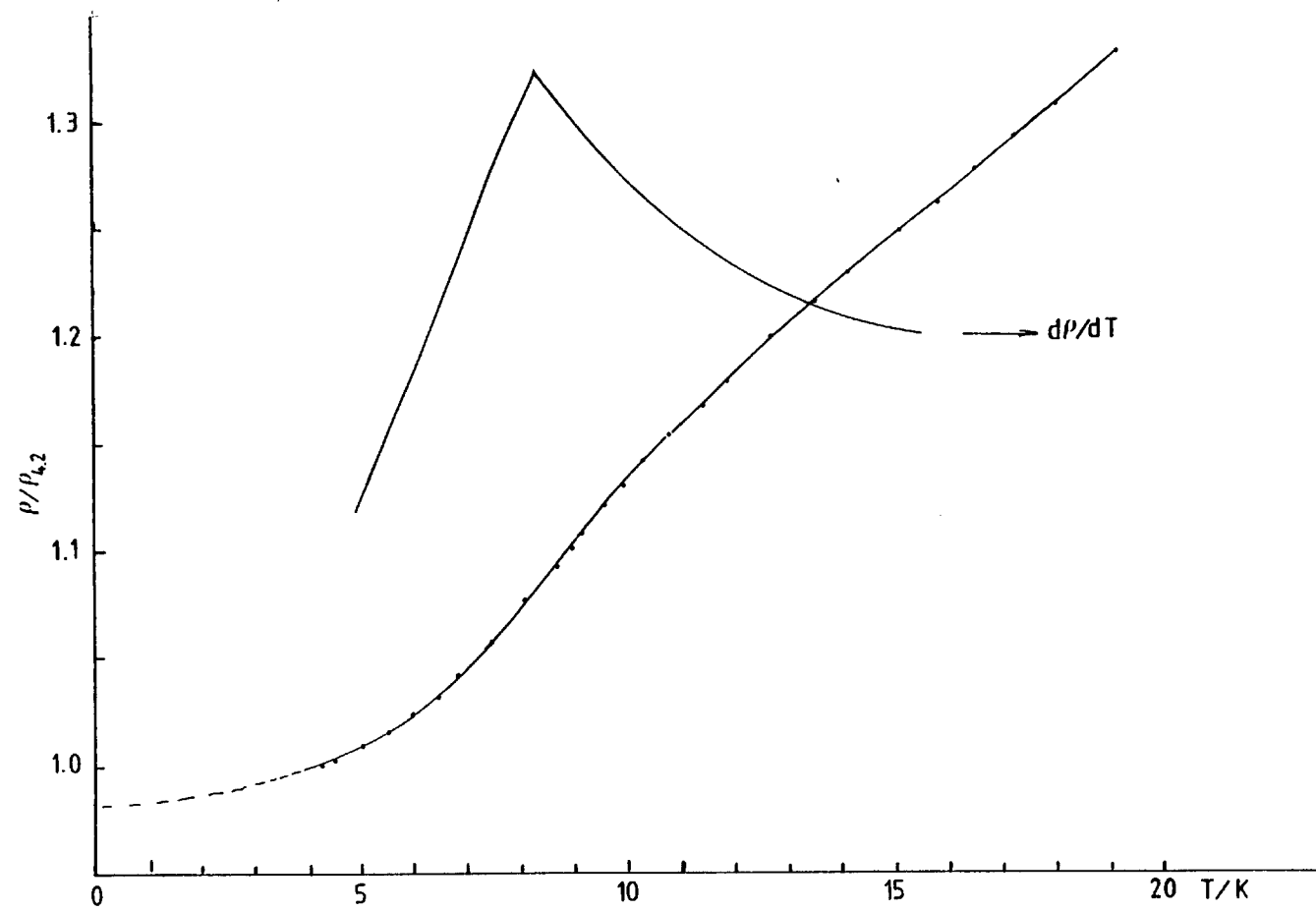


Fig 4.8 cont

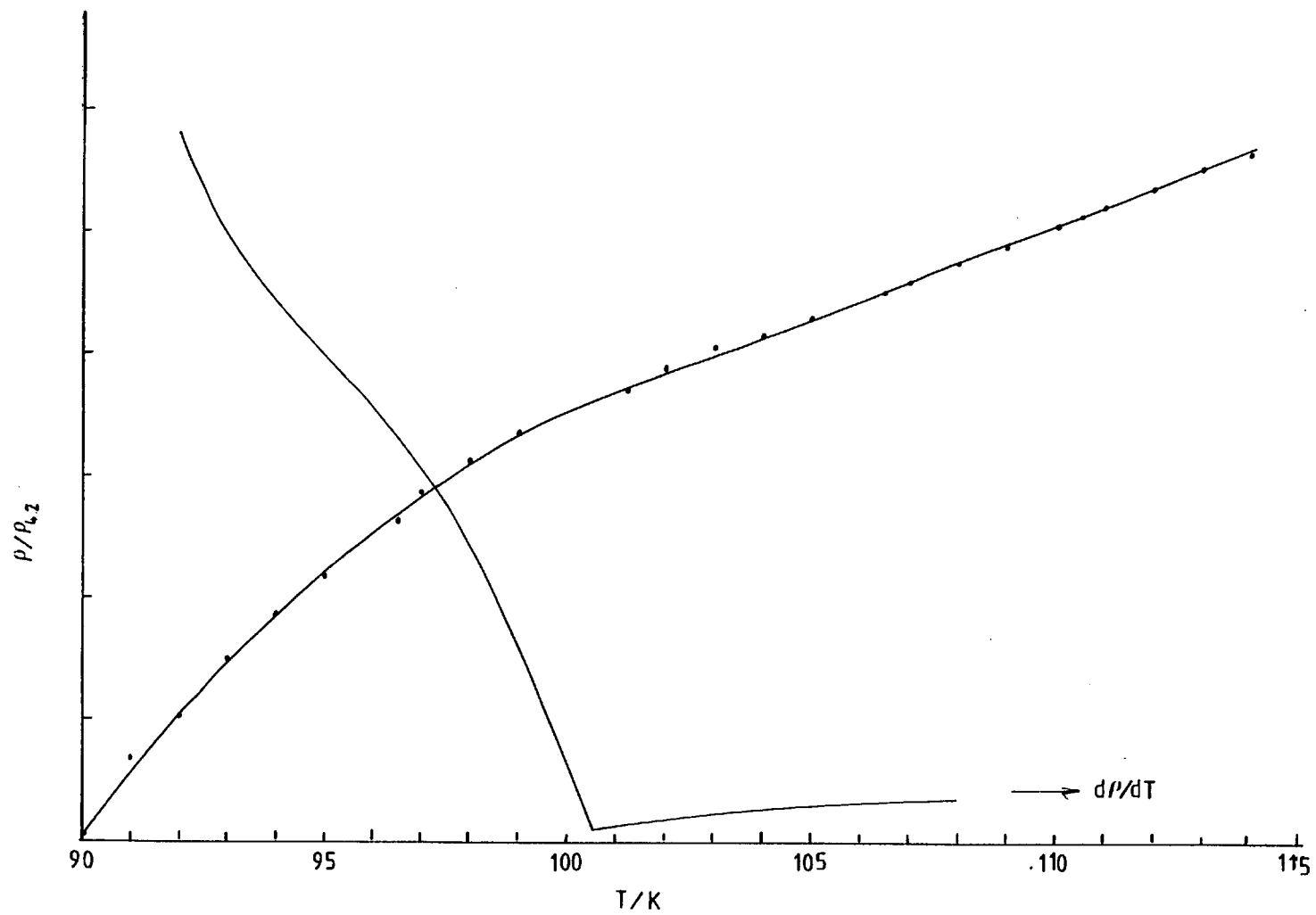


Fig 4.8 cont

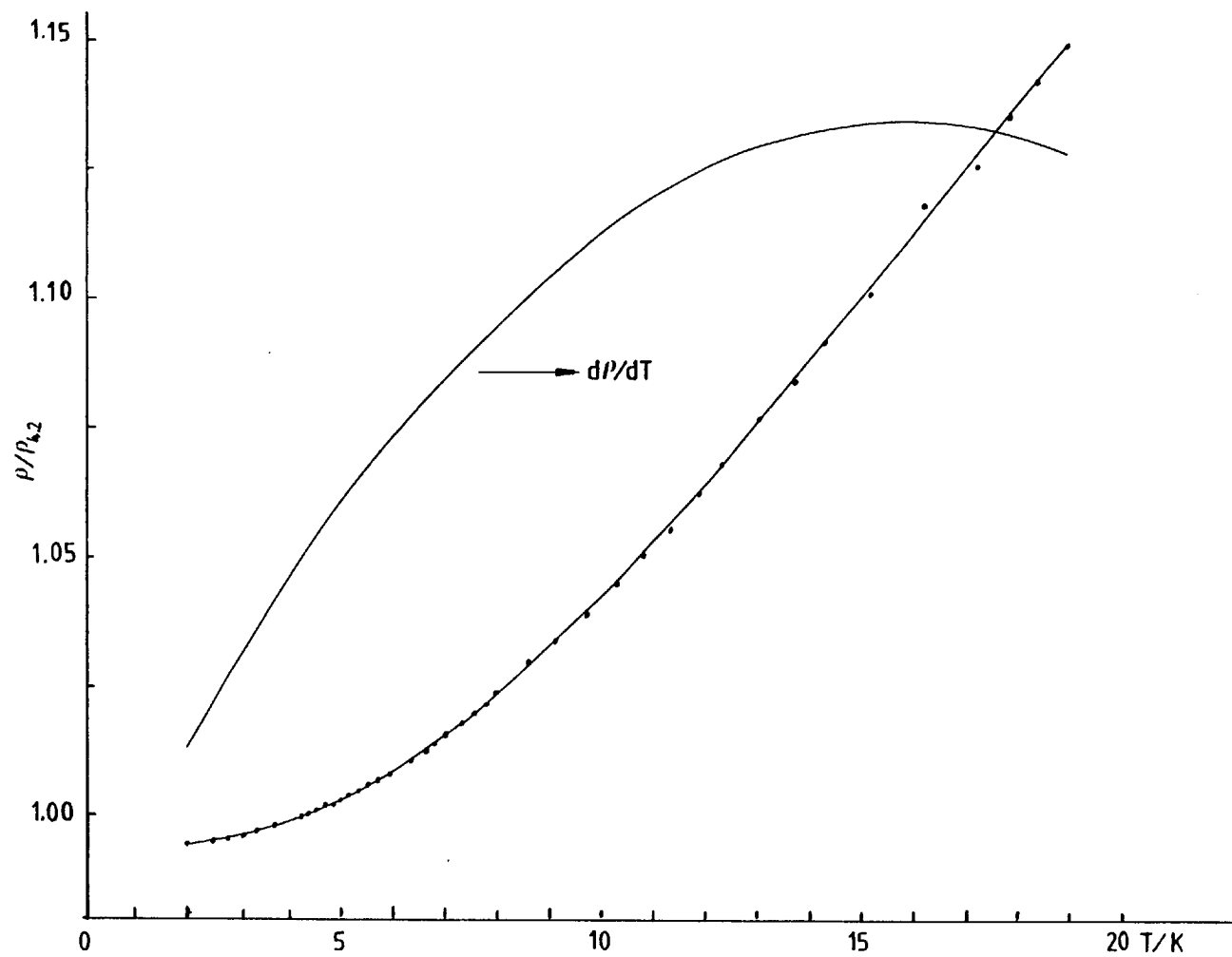


Fig.4.9: Electrical resistivity ρ and $d\rho/dT$ for the Sm-10%Pr alloy.

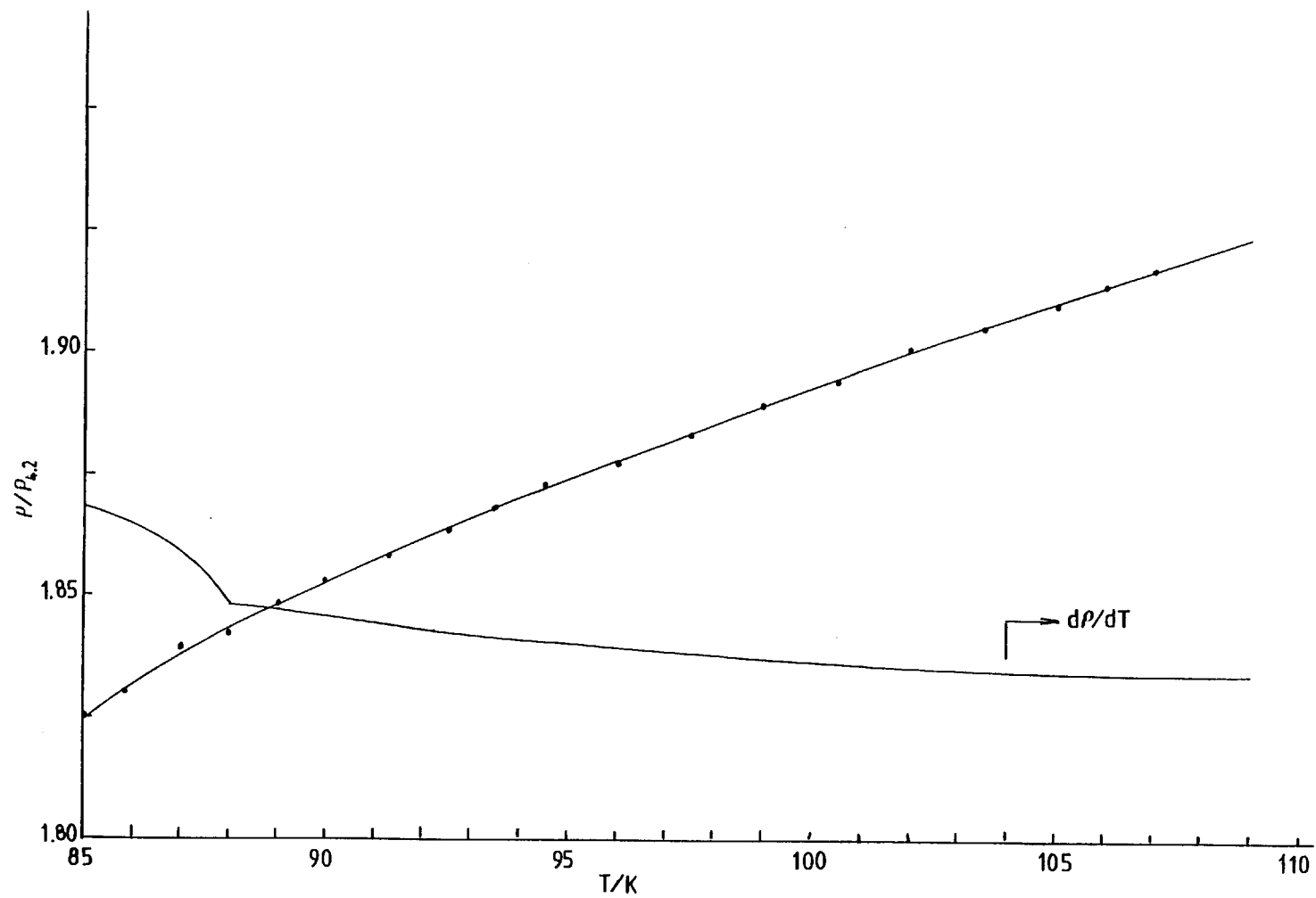


Fig 4.9 cont

and some in a field produced by a solenoid (see Chapter 2 for details).

In Fig. 4.10 is shown the susceptibility (M/H) as a function of temperature when measured in two fields using the electromagnet. For the curve a), the sample was cooled in zero field down to 4.2 K and (M/H) measured in a field of 660 Oe on warming. (For the remainder of the Chapter, "zero field" means with earth's magnetic field only). For the curve b), the sample was cooled in zero field down to 77 K and (M/H) measured in a field of 1.5 kOe. In the latter case it was not possible to measure at low temperatures because of the high signal produced by this relatively high field. The ac-susceptibility shows a kink at around 92 K, and then rises steadily as the temperature increases, see Fig. 4.11. It is interesting to notice that at low temperatures, the magnitude of the ac-susceptibility is much lower than the dc-susceptibility, while at temperatures near the kink, both susceptibilities are of comparable magnitude. A similar behaviour was found in the susceptibility of pure *Sm* below 14 K. In the neighbourhood of 100 K, the dc-susceptibility was re-measured with the solenoid set-up; see Fig. 4.12. For a) and b) curves, the sample was cooled in zero field and in 400 Oe down to 77 K, respectively, and the magnetization vs temperature measured in zero field and in 400 Oe. Remanent magnetization was only observed in b). The sample was again cooled down to 77 K, but in a higher field of 10 kOe and magnetization vs field measured; see Fig. 4.13. No hysteresis effect was found. The magnetization was linear with field and a small remanent

magnetization was detected. Such peculiar behaviour is not well understood at present, and may involve (in this as-cast specimen) the presence of two crystallographic phases or segregation. Strong dependence on the applied field has been seen in the heat capacity measurements of pure *Nd*, Forgan et al 1979. Thermal history and hysteretic effects are of considerable importance in *Nd*, and there is not a complete understanding of its magnetic nature.

The behaviour observed in the inset of Fig. 4.10 may be due to a non-homogeneous specimen or to internal stress. Thus, an annealing for one week at 500°C was performed on the sample to see the effects. The dc-susceptibility when cooled in zero field and in 400 Oe was found to be the same; see Fig. 4.14. The susceptibility shows a kink at around 92 K, then increases more rapidly and at 10 K becomes constant, behaviour which is very similar to the ac-susceptibility measurement of the as-cast alloy. At each of several fixed temperatures, the magnetization was measured in 400 Oe and in zero field. This magnetization difference is plotted in Fig. 4.15. It suggests the presence of a ferromagnetic component. The electrical resistivity of the as-cast sample is shown in Fig. 4.16. At low temperatures, $d\rho/dT$ exhibits a maximum at ~ 8.2 K and a minimum at ~ 9.2 K, similar to that observed in pure *Sm*. This is consistent with the susceptibility measurements. At high temperatures there is an anomaly at around 100 K, although $d\rho/dT$ has not a well defined minimum.

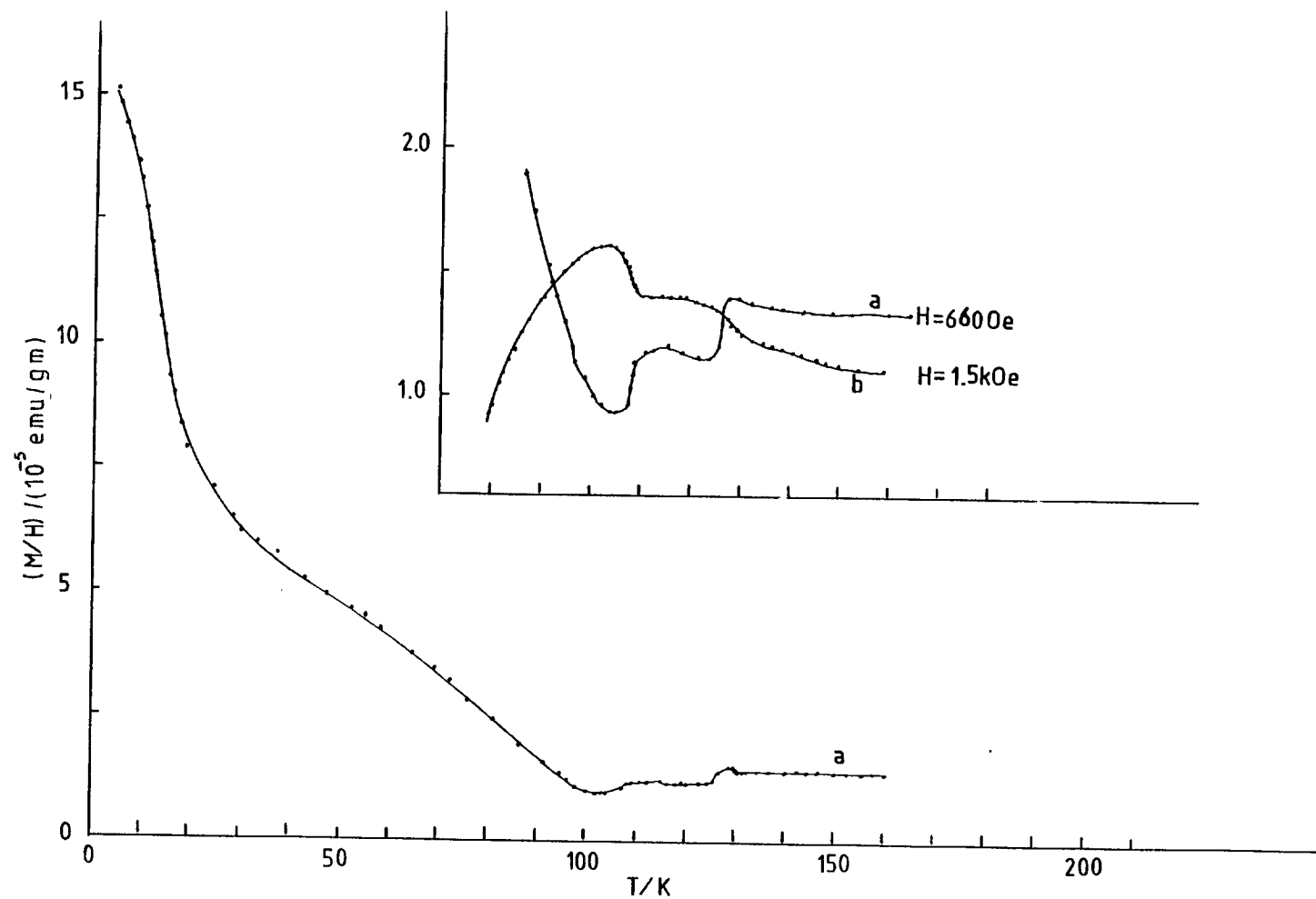


Fig.4.10: Dc-susceptibility as a function of temperature for the Sm-5%Nd as-cast alloy. See text.

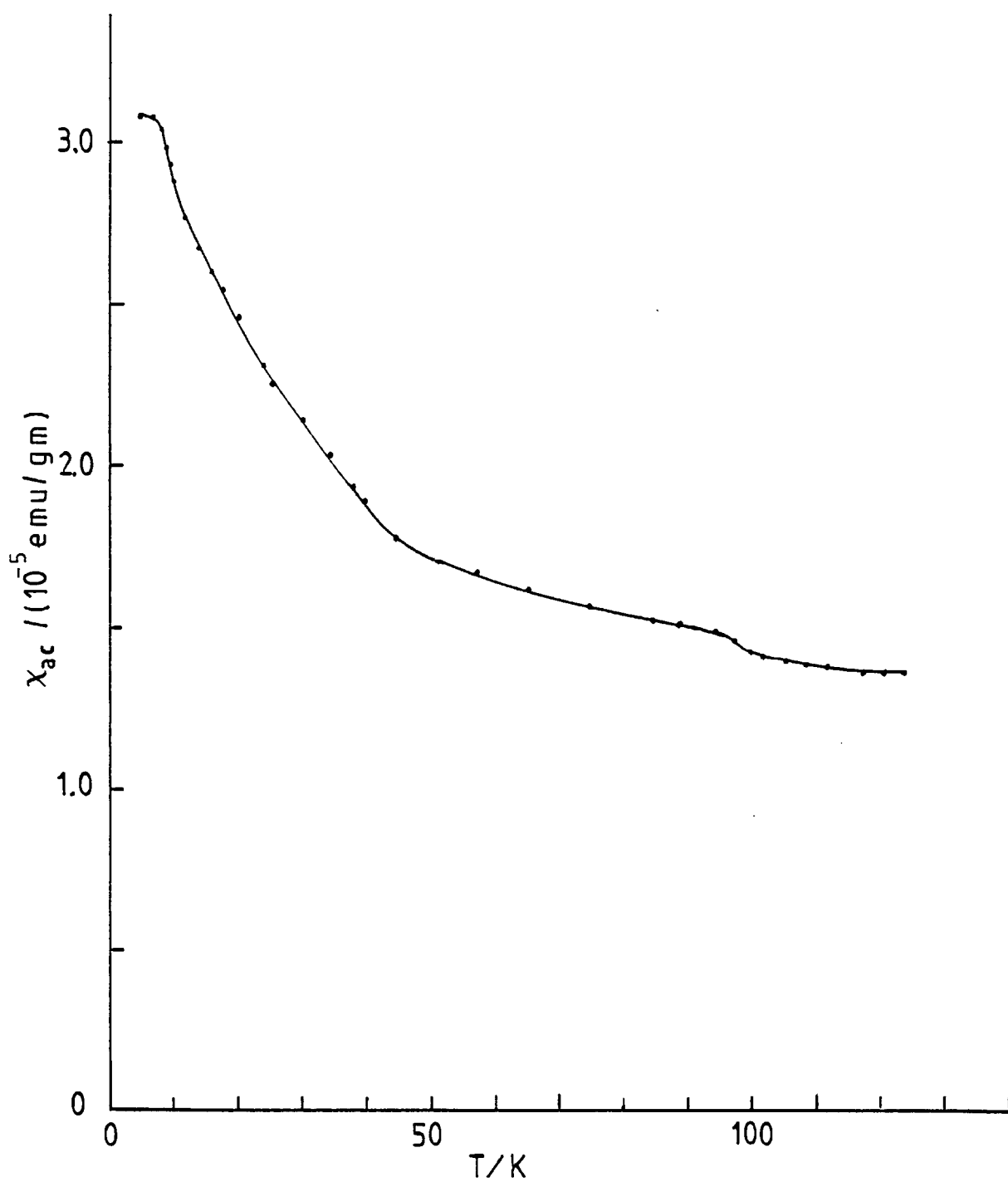


Fig.4.11: Ac-susceptibility as a function of temperature for the Sm-5% Nd as-cast alloy.

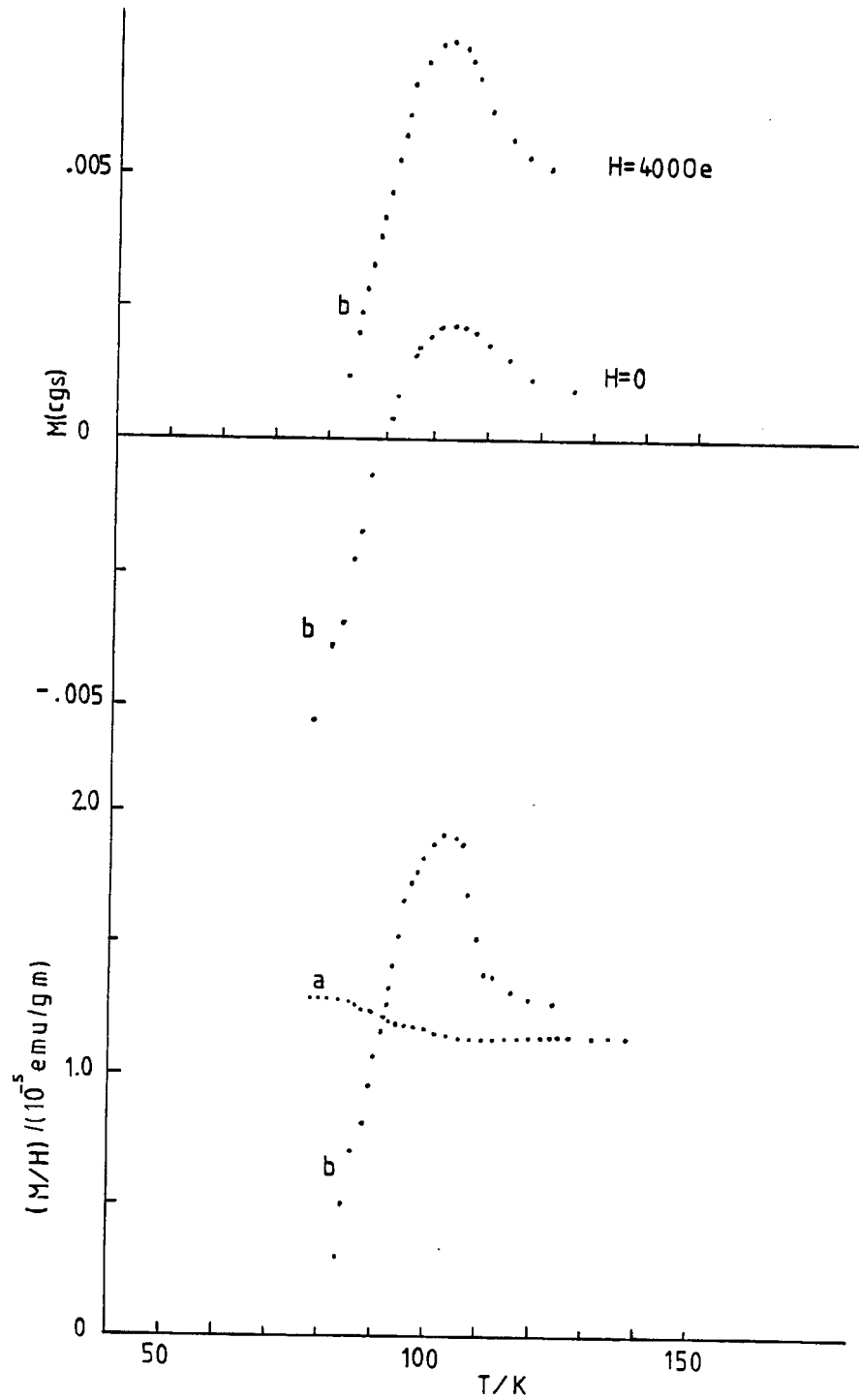


Fig.4.12: Dc-susceptibility in the neighbourhood of 100K for the Sm-5% Nd as-cast alloy. See text.

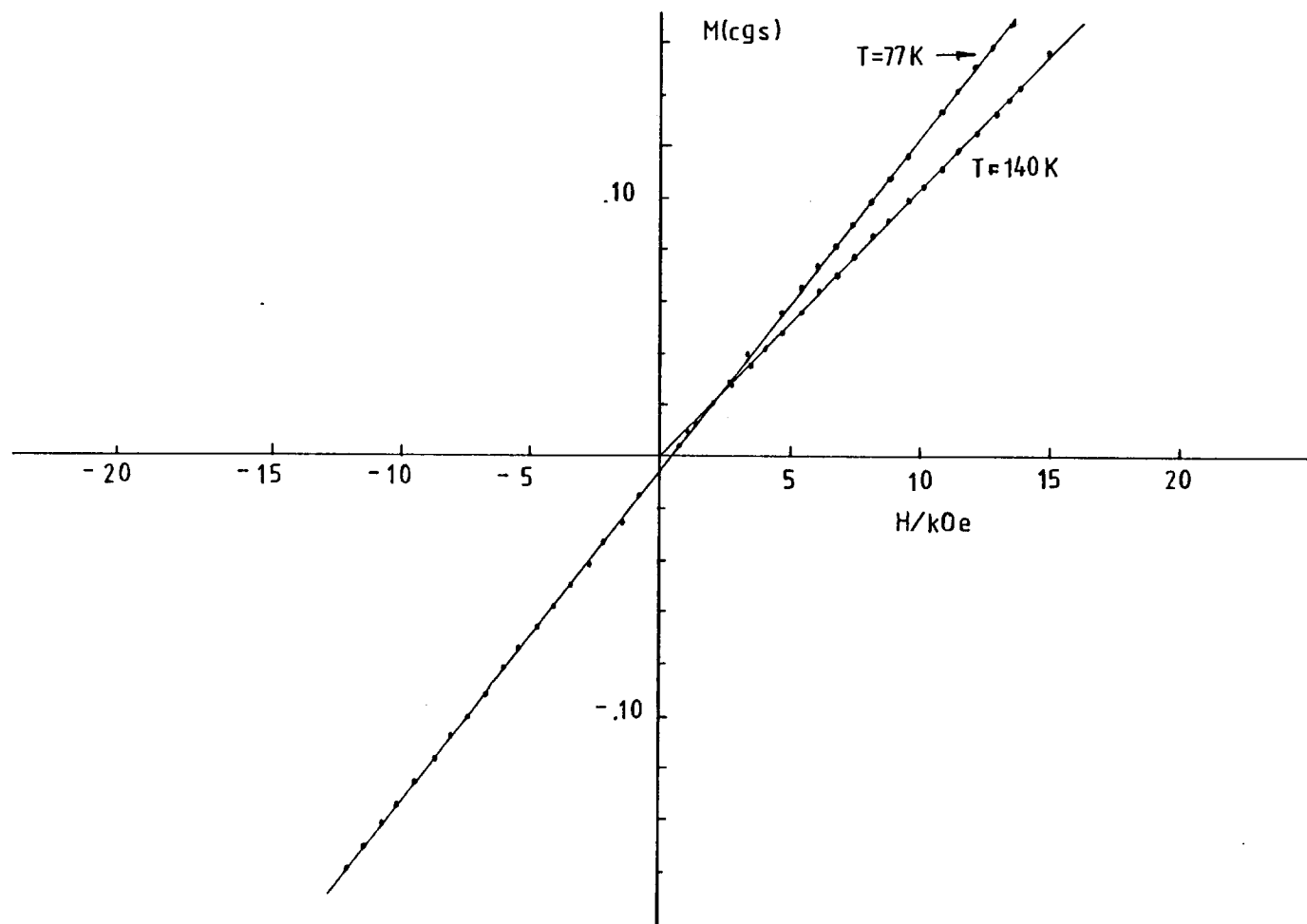


Fig.4.13: Magnetization vs applied field for Sm-5% Nd as-cast alloy.

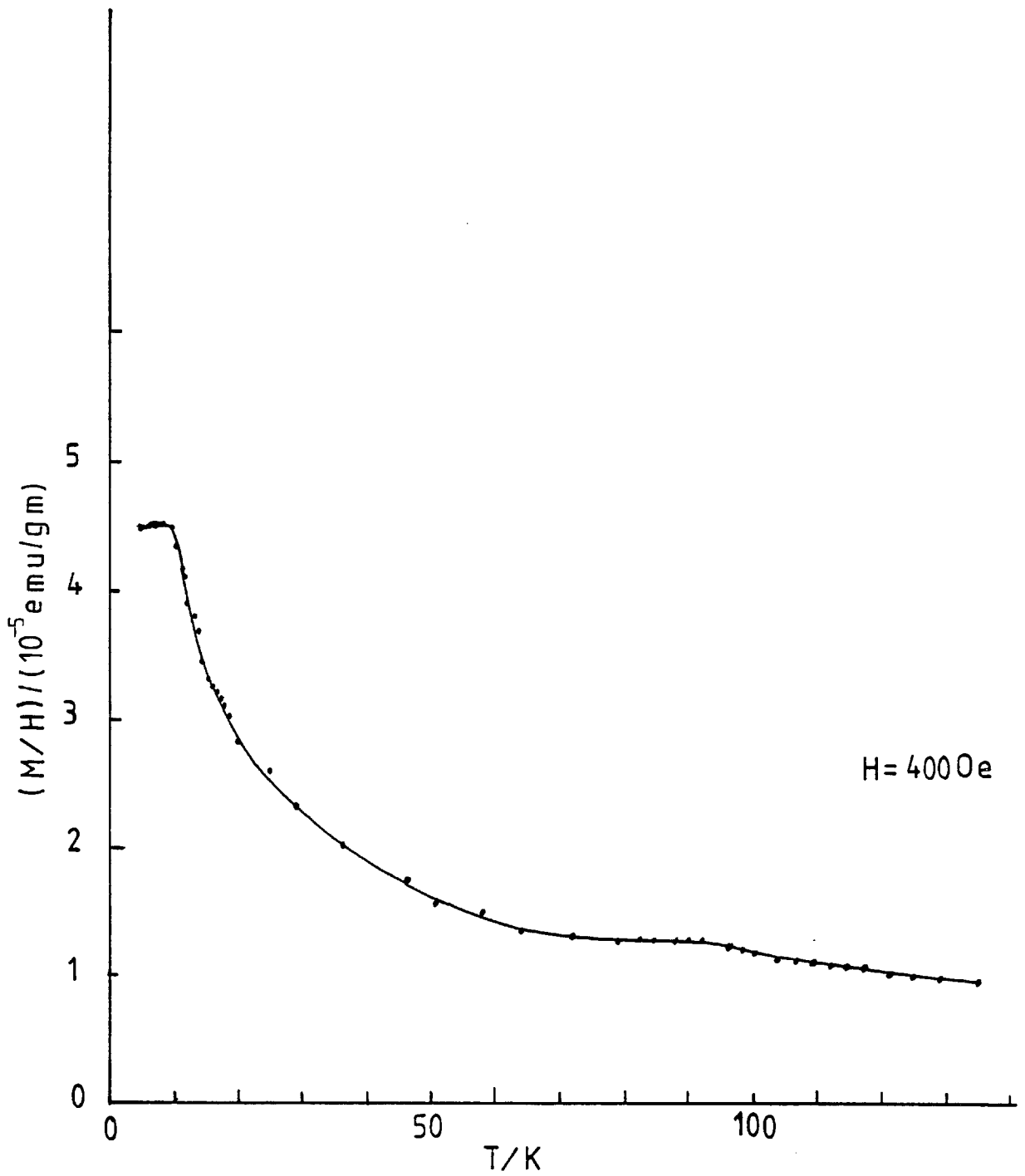


Fig.4.14: Dc-susceptibility as a function of temperature for the Sm-5% Nd annealed alloy.

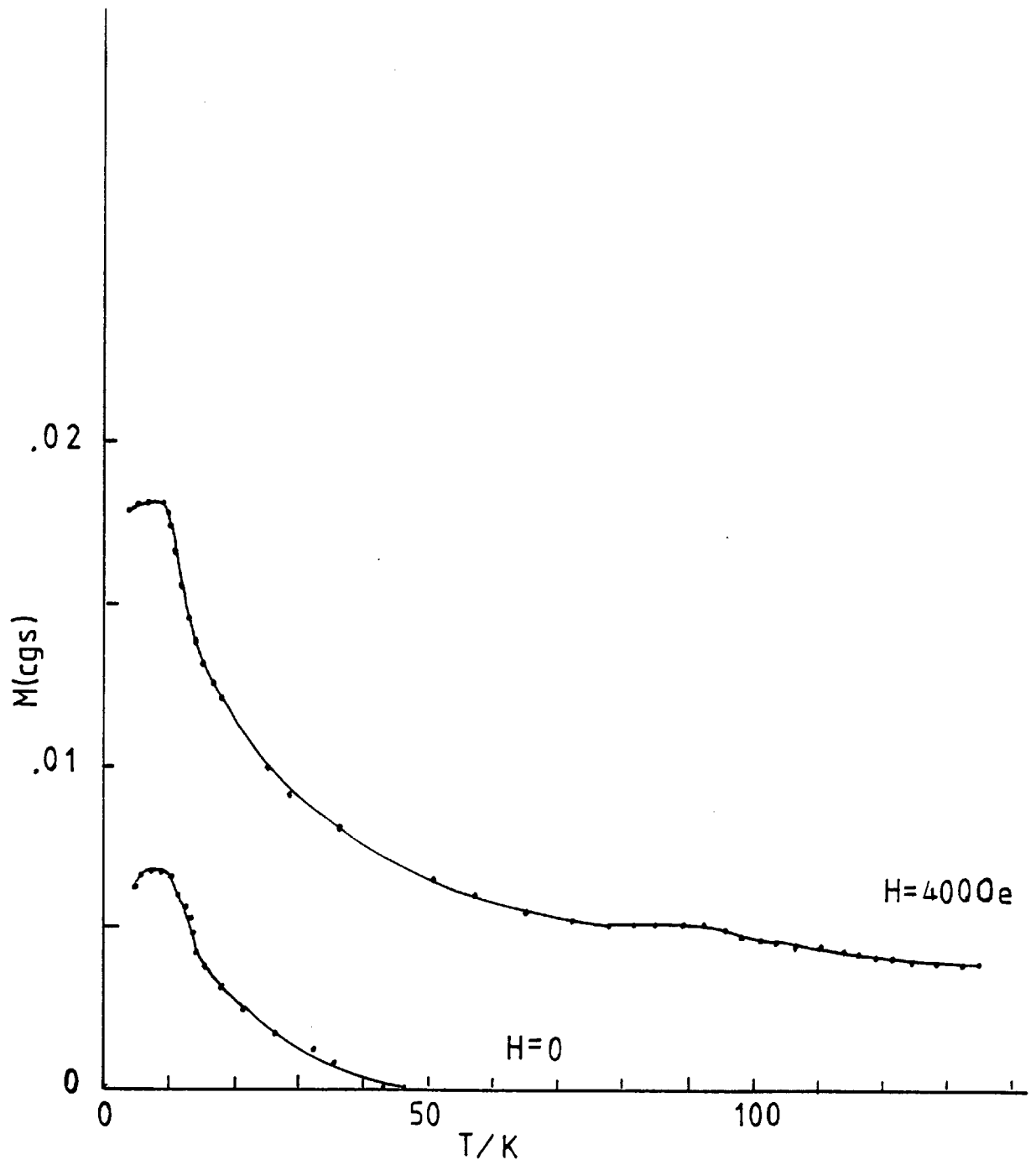


Fig.4.15: Magnetization as a function of temperature for the Sm-5% Nd annealed alloy. See text.

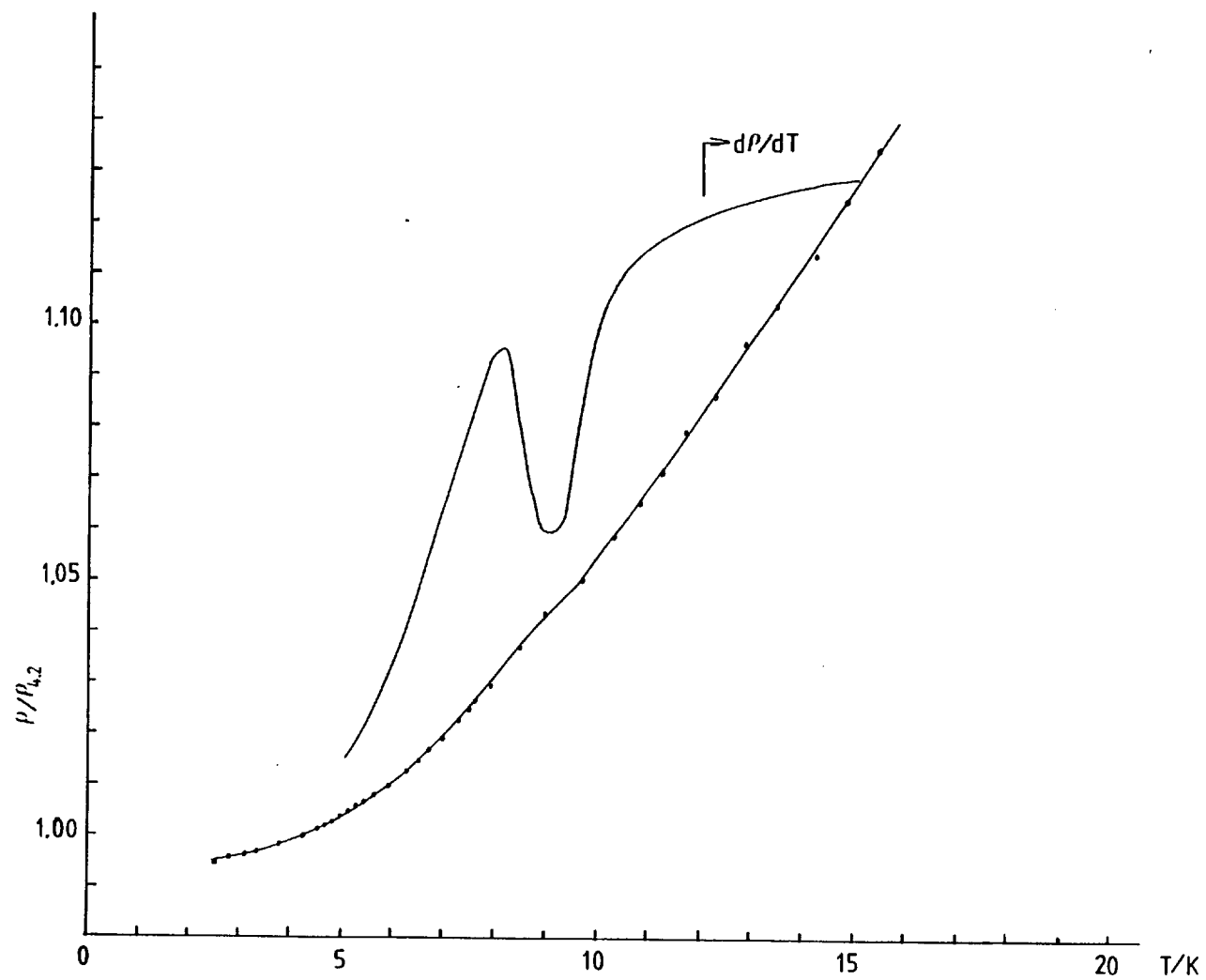


Fig.4.16: Electrical resistivity ρ and $d\rho/dT$ for the Sm-5% Nd as-cast alloy.

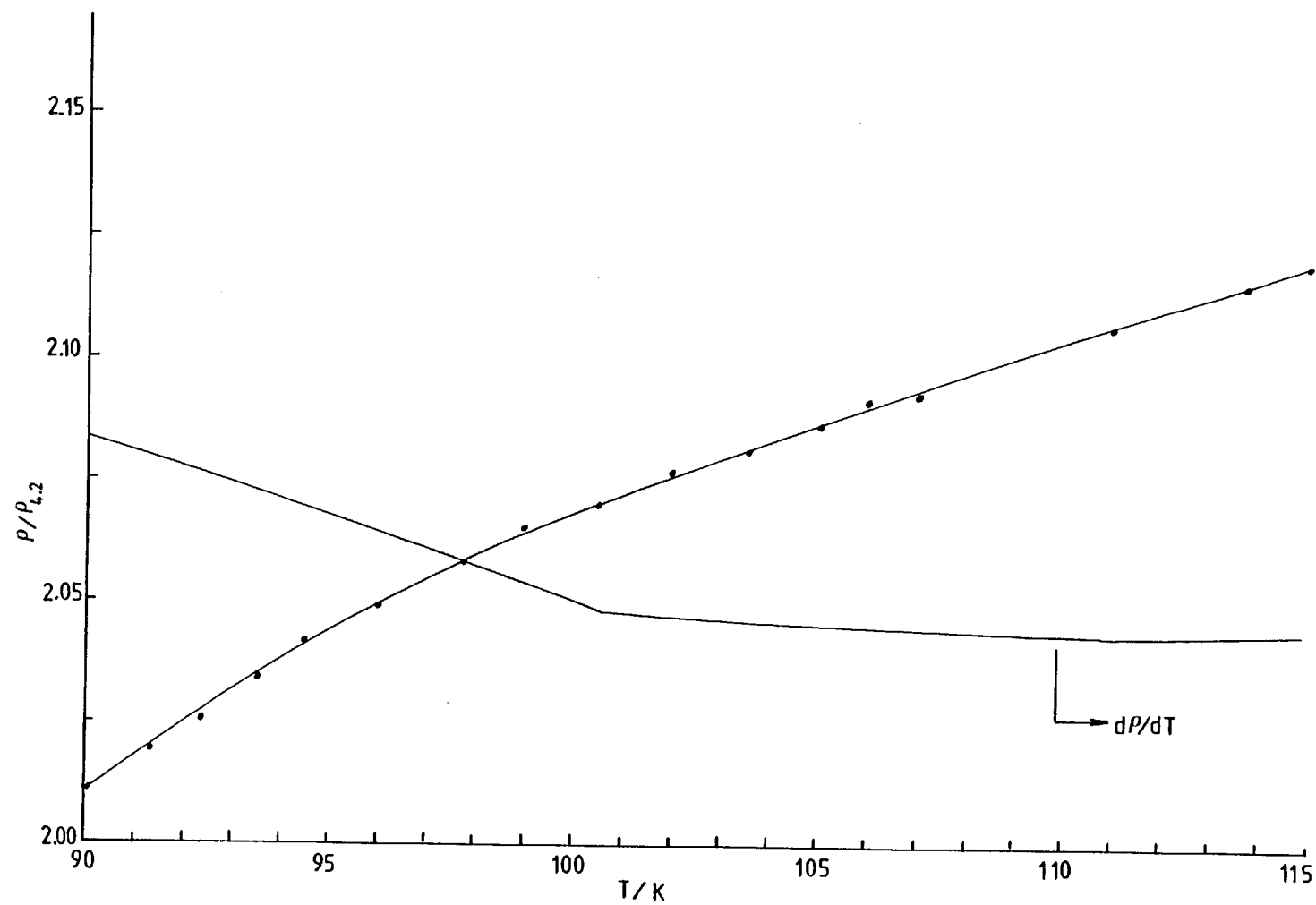


Fig 4.16 cont

From these results it is apparent that the two anomalies observed in pure *Sm*, are still present in the *Sm*-5% *Nd* alloy, but the high temperature transition does not show up despite the addition of atoms with high values of ionic moments. The magnetic dependence is a particular characteristic of *Nd*. This kind of dependence is not found in *Sm* nor in *Sm-Pr* alloys. It would seem that as-cast *Sm-Nd* contained some *dhcp* structure or inhomogeneities which were removed by annealing.

4.3.4 *Sm-Gd* alloys in the *Sm*-type structure.

Results and discussion

At first, the dc-susceptibility measurements were rather confusing. The results exhibited peculiar magnetic hysteresis effects, strong thermal hysteresis and a high dependence on the field. These effects were difficult to interpret because they were performed in the electromagnet set-up. Consequently, the new solenoid set-up was more adequate and some results were better understood. However, there are some points that need to be studied in more detail.

The ac-susceptibility for the *Sm-Gd* alloys is shown in Fig. 4.17. This measurement turned out to be difficult to perform on these alloys, partly because of not enough sensitivity of the apparatus, and partly because of the big temperature gradient on the specimen at high temperatures. All samples exhibited a rather sharp peak at 111, 113 and 115.5 K for the 2, 5 and 10% *Gd* as-cast alloys, respectively. The lower value

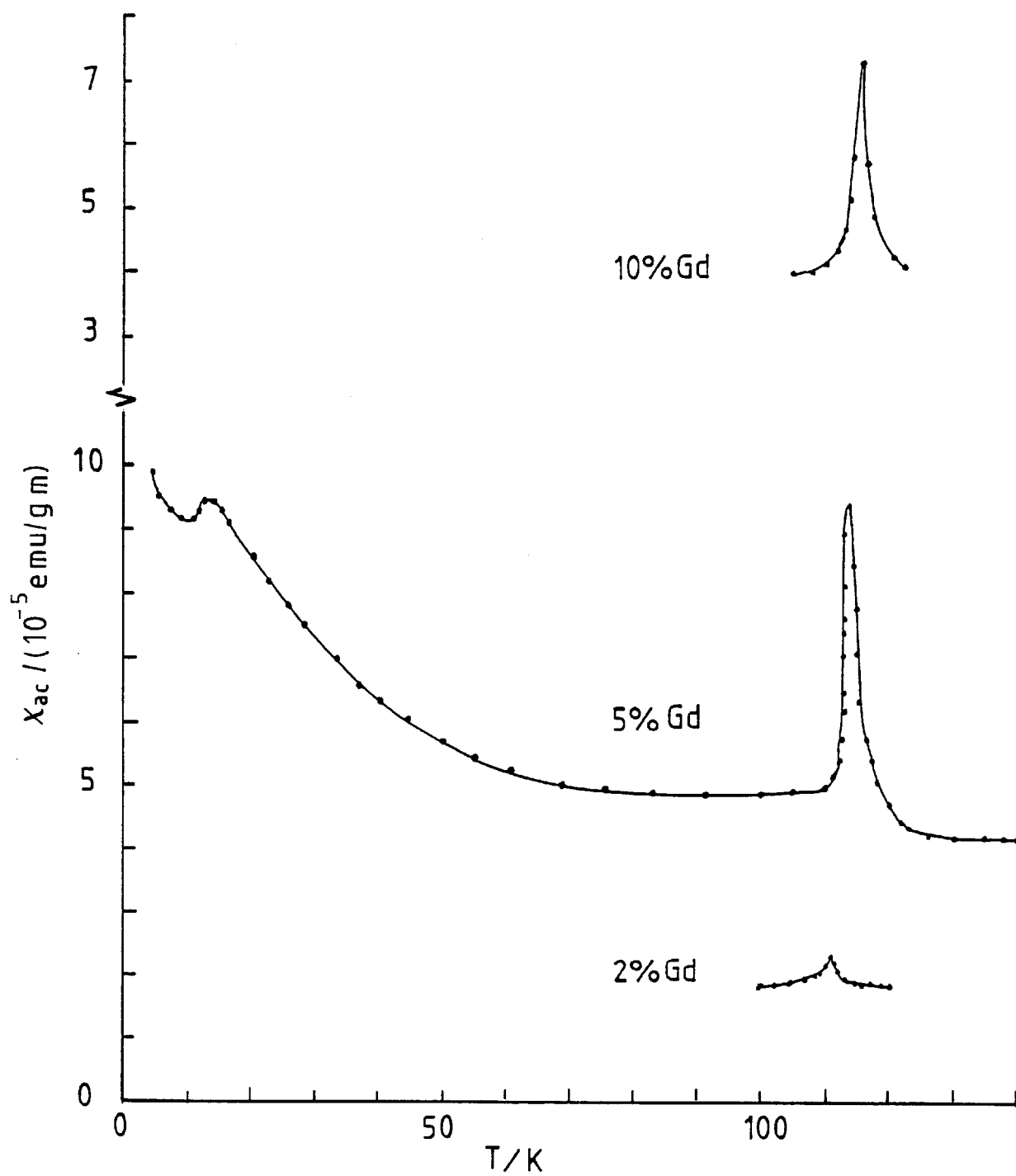


Fig.4.17: Ac-susceptibility for the Sm-2, 5 and 10% Gd as-cast alloys as a function of temperature.

of susceptibility observed for the 10% *Gd* alloy with respect to the 5% *Gd* alloy, may be due to the large temperature gradient found for this sample. If a superimposed dc field of 160 Oe is applied, the sharp peak is completely suppressed. At low temperatures, a rounded maximum is found for *Sm*-5% *Gd* alloy. (The other two samples were not measured). The fact that susceptibility increases below 10 K is not understood.

The resistivity measurements and its derivative with respect to the temperature are shown in Fig. 4.18. Sharp changes in the slope are observed at 111 and 112.5 K for 2 and 5% *Gd* as-cast alloys, respectively. These results are in very good agreement with the ac-susceptibility measurements. For the 10% *Gd* as-cast alloy, a good fitting to the data points was not possible; see Fig. 4.18. At around 14 K, a very broad maximum in $d\rho/dT$ is found for all three alloys.

In Fig. 4.19 are shown the magnetization vs field curves for the 5% *Gd* as-cast alloy, when measured in different states of the sample. The curve a) was determined at 142 K, the paramagnetic region. In curves b) and c), the sample was cooled down to 77 K in + 2 kOe and -2 kOe, respectively. This procedure gave an unexpected behaviour: a displaced cycle without hysteresis. The sample was then cooled in a higher field (10 kOe), and in a smaller field (400 Oe). Similar properties were observed. However, a smaller remanent magnetization was obtained when cooled in zero field, curve d). The curve e) was measured at 4.2 K after cooling the sample in the remanent field of the solenoid.

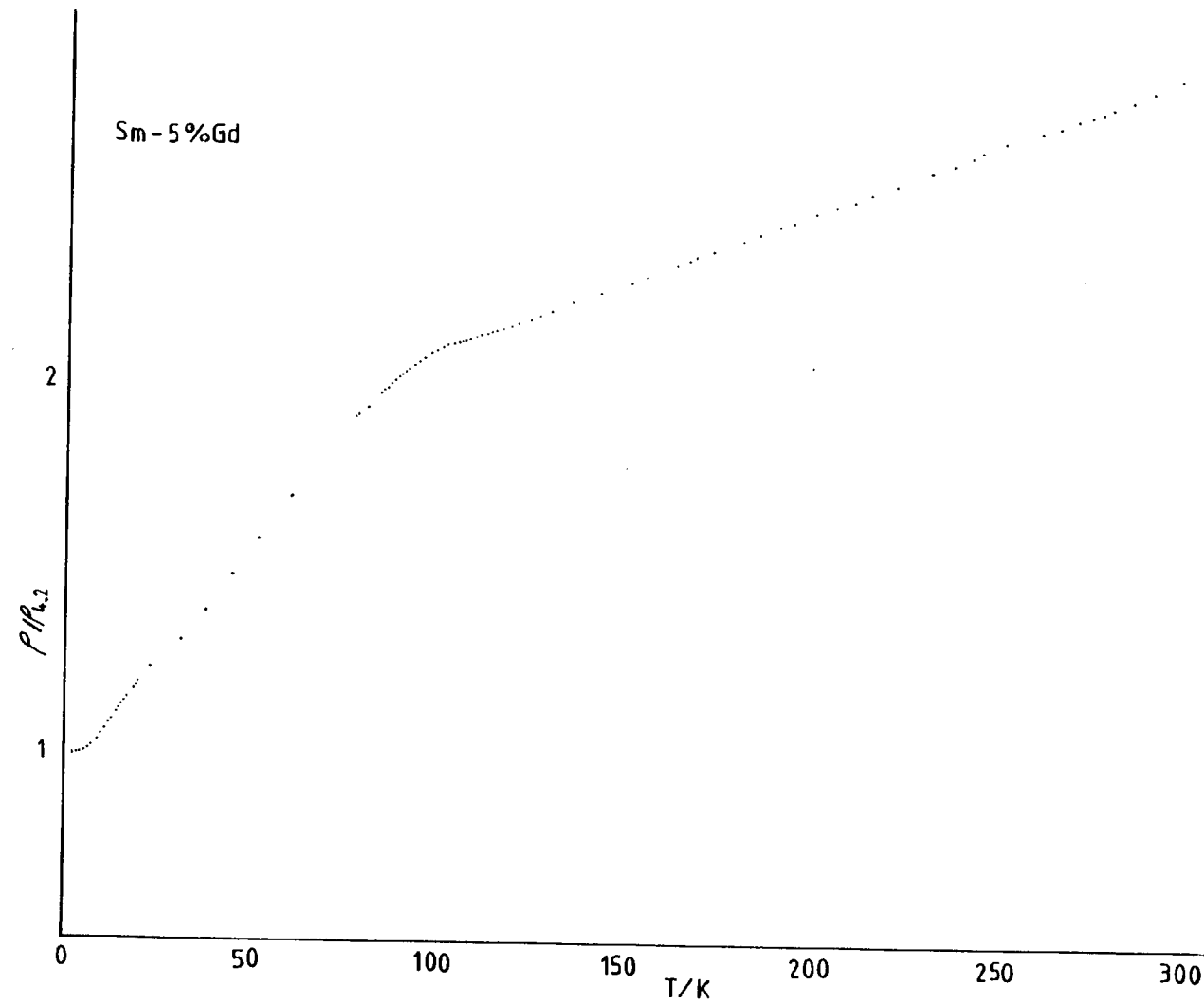


Fig.4.18: Electrical resistivity ρ and $d\rho/dT$ for the Sm-2, 5 and 10% Gd as-cast alloys.

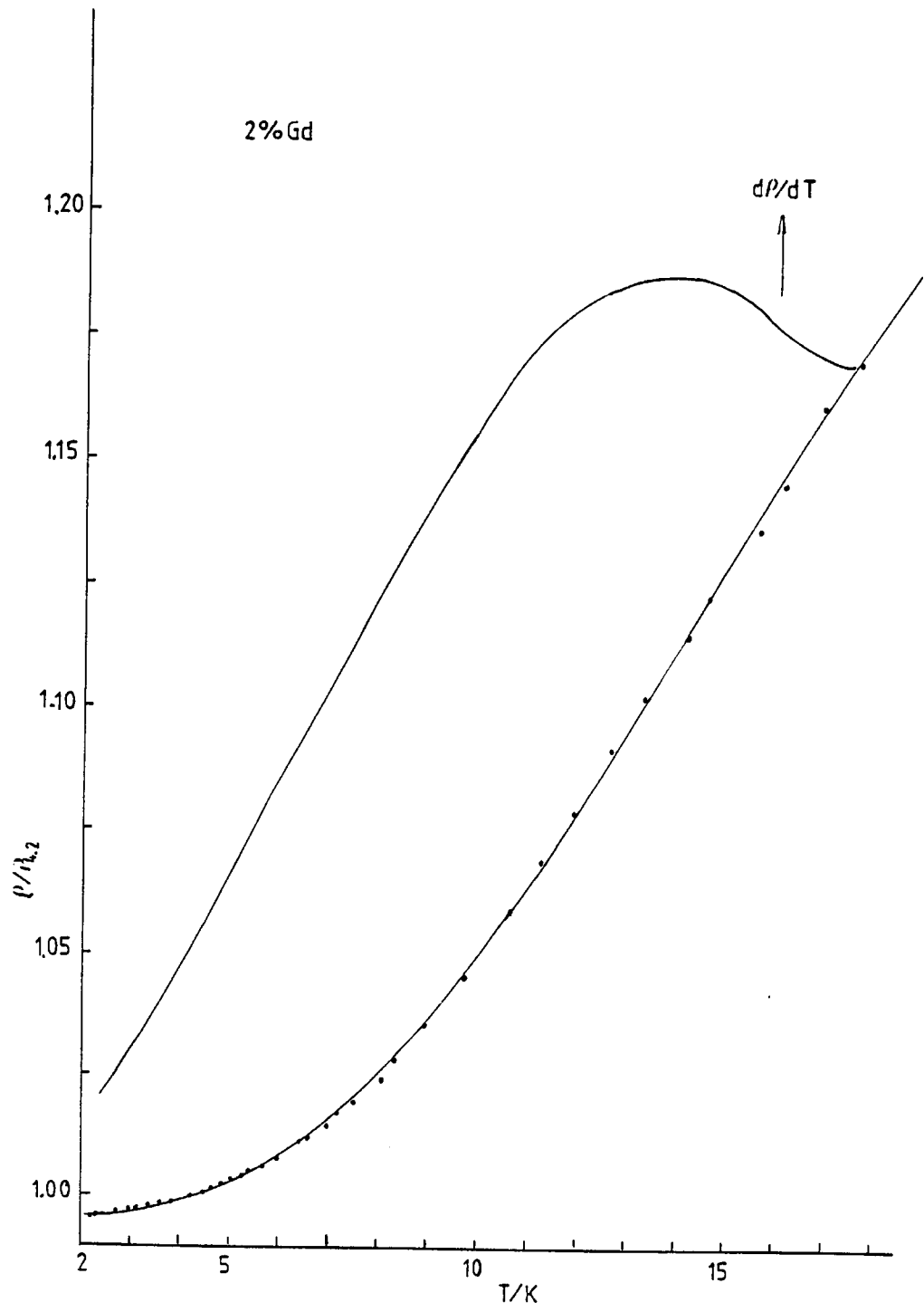


Fig 4.18 cont

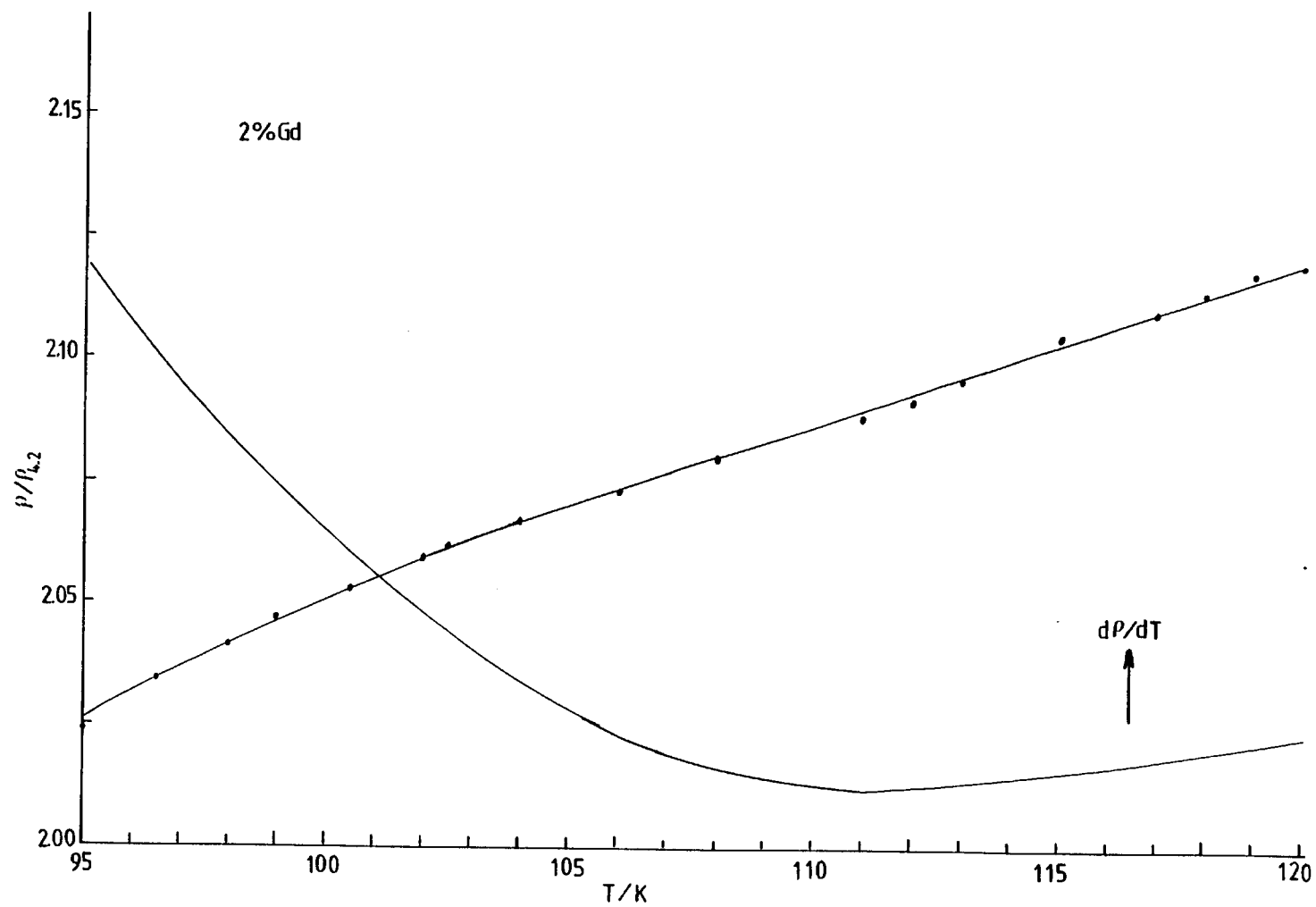


Fig 4.18 cont

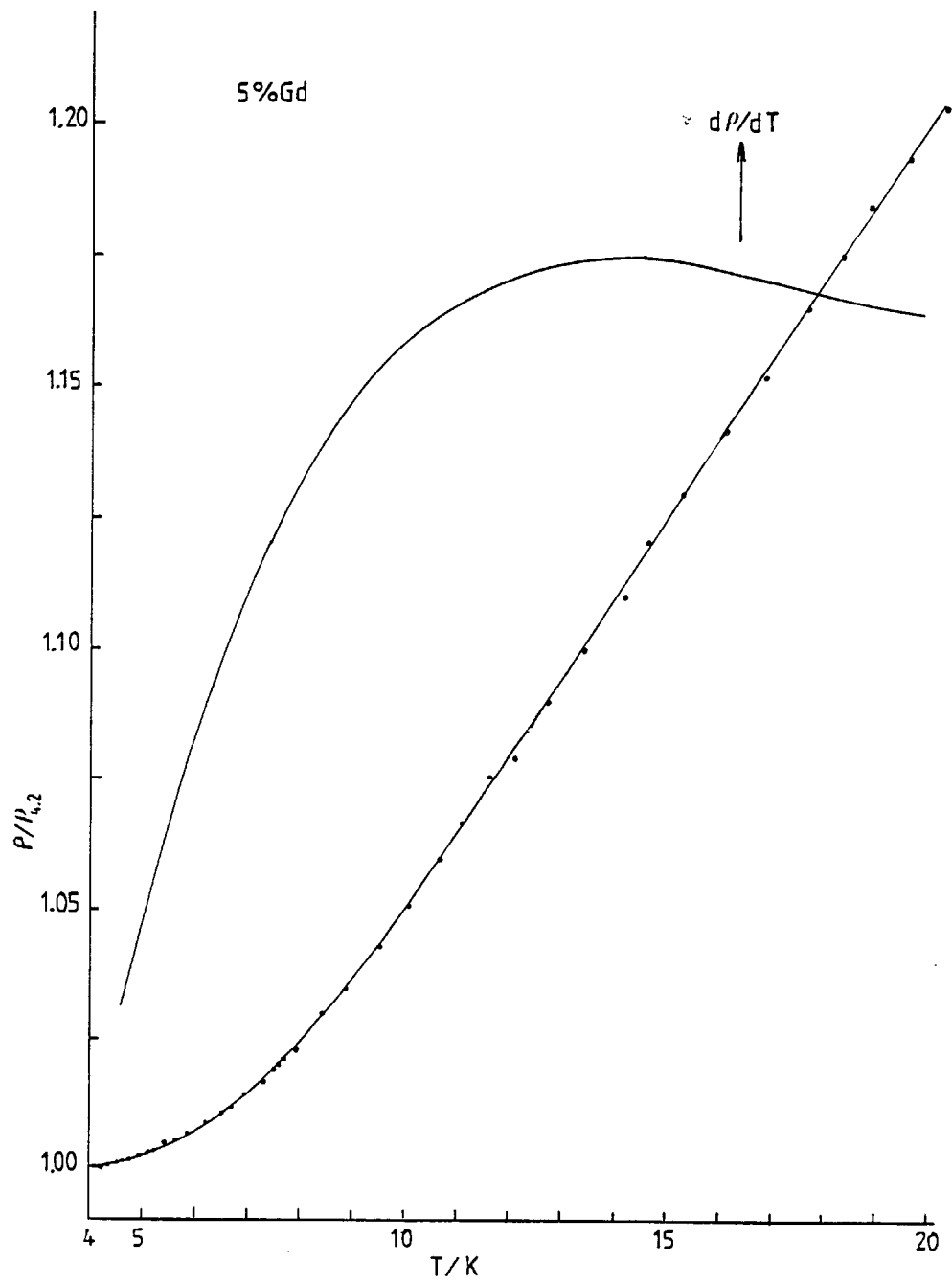


Fig 4.18 cont

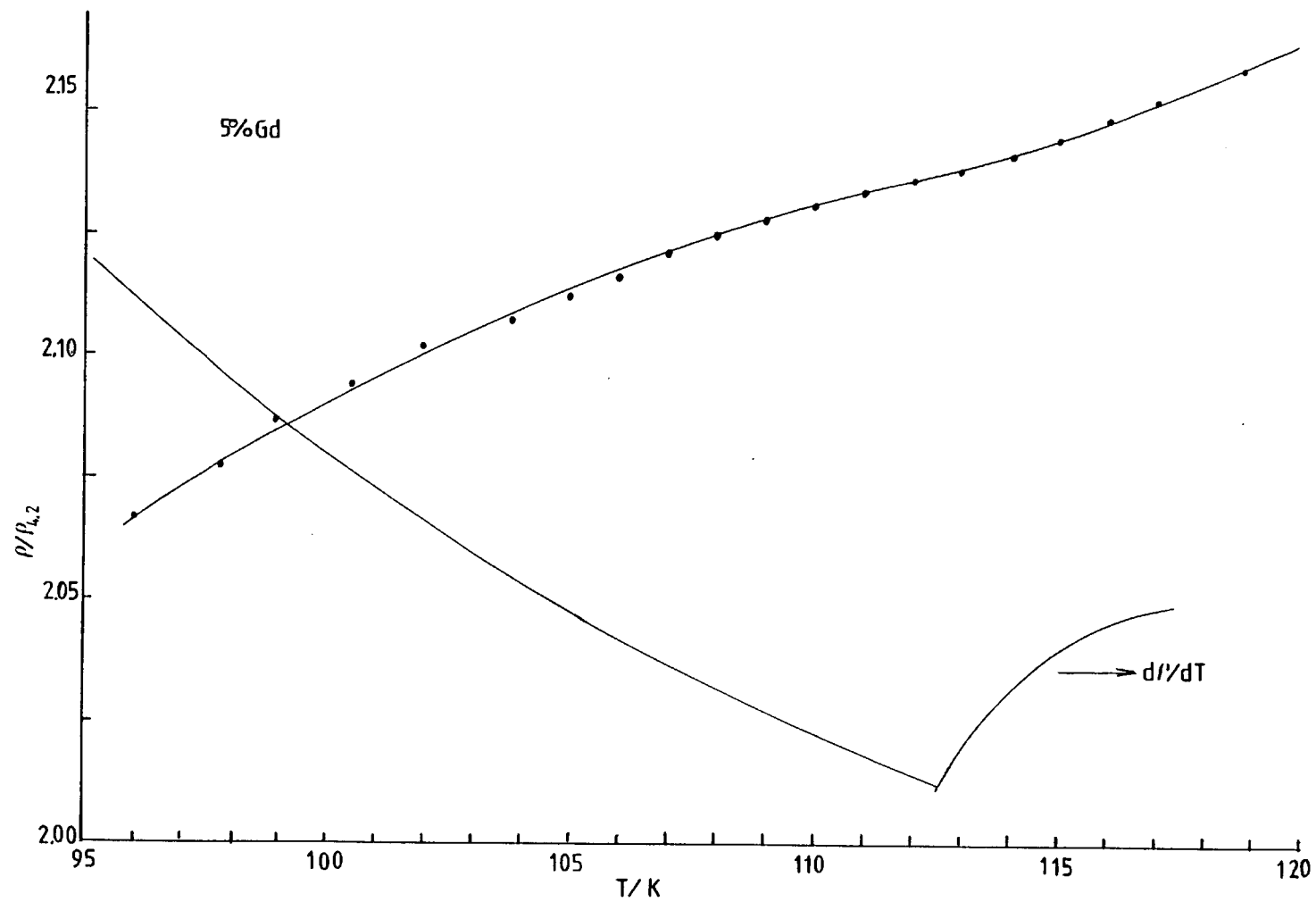


Fig 4.18 cont

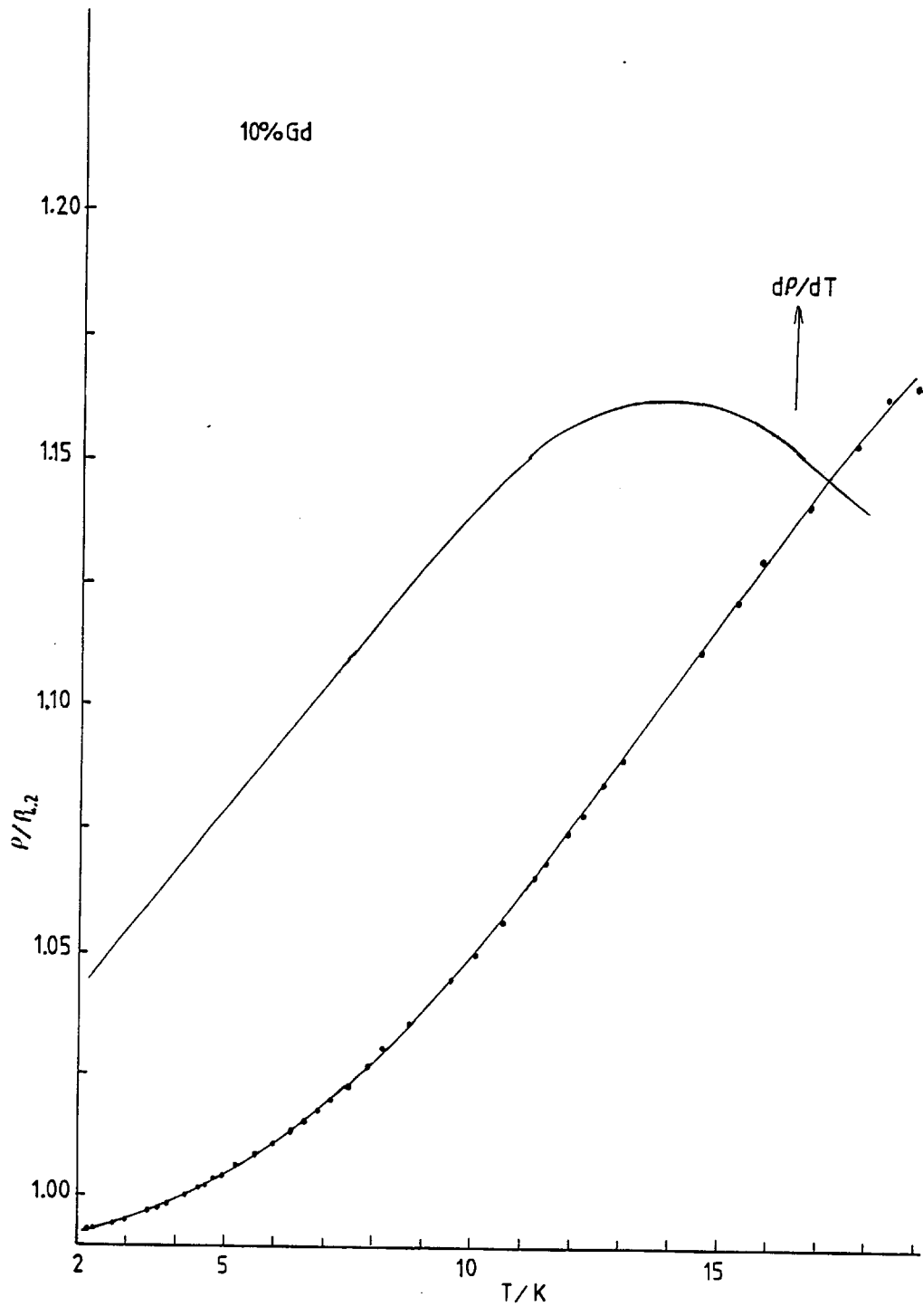


Fig 4.18 cont

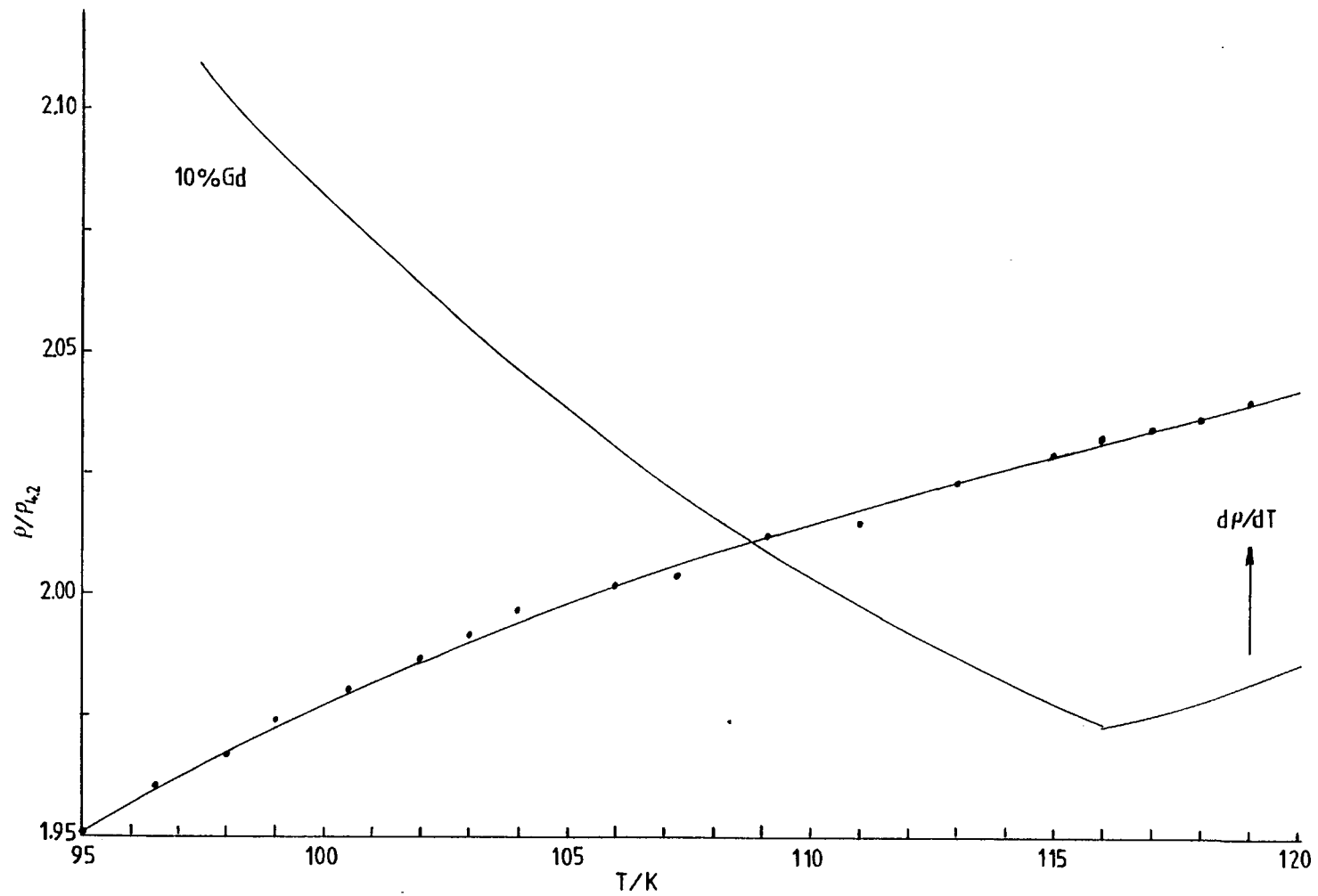


Fig 4.18 cont

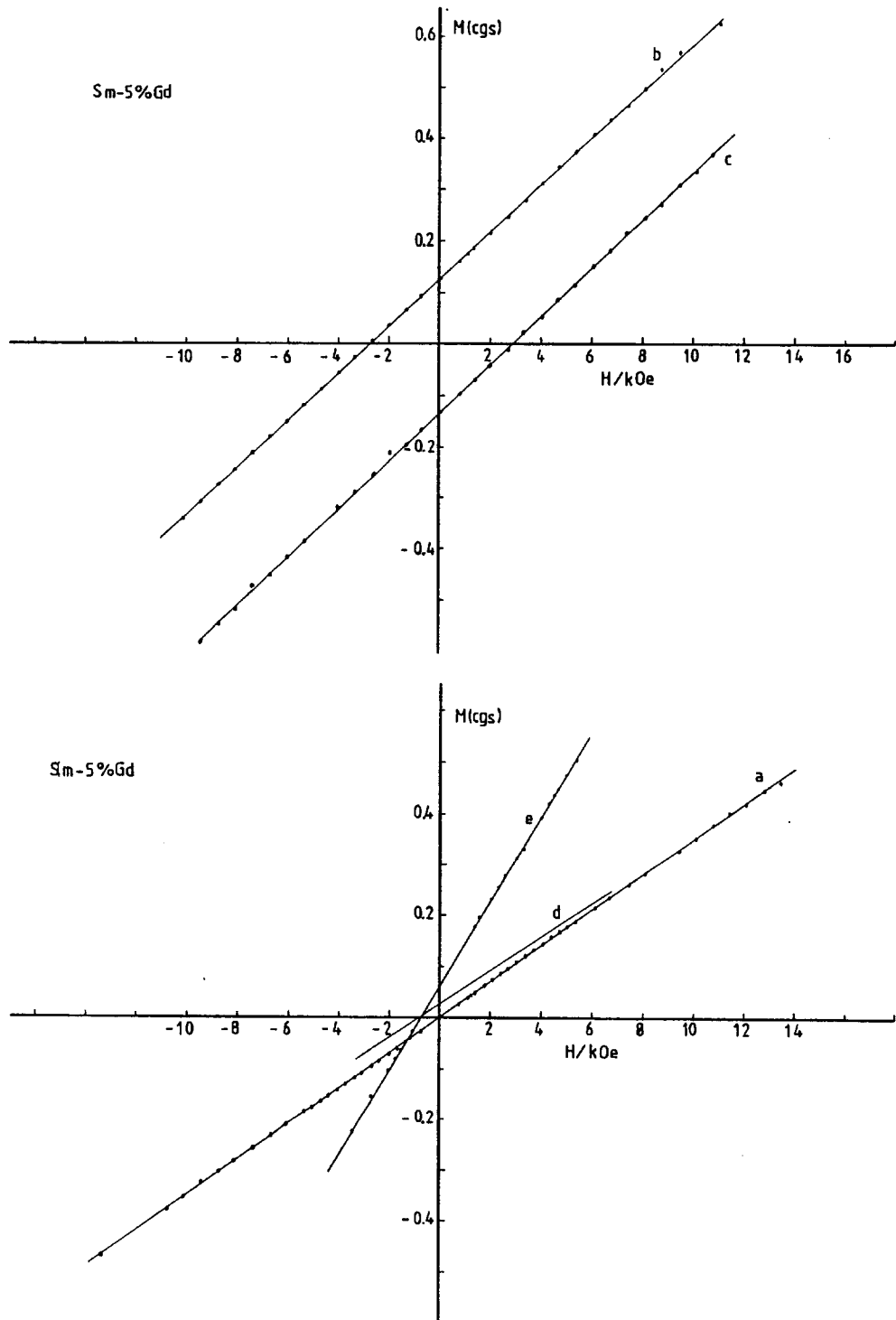


Fig.4.19: Magnetization vs applied field for the Sm-5% Gd as-cast alloy.

Magnetization vs field measurements were also made on the *Sm-2% Gd* alloy. Similar behaviour was observed, see Fig. 4.20. A displaced cycle without hysteresis can be observed in curves b) and c), when the sample was cooled in +2 kOe and -2 kOe. Fig. 4.21 shows a hysteresis loop obtained after cooling the sample in zero field down to ~ 100 K. This strongly suggests a ferromagnetic component.

In order to understand more the nature of these results, magnetization vs temperature measurements were performed. Fig. 4.22 shows (M/H) vs T for the *Sm-5% Gd* as-cast alloy when the sample was cooled down to 4.2 in the remanent field of the solenoid and the magnetization measured in 750 Oe. At around 130 K, another step down was obtained, which immediately suggested that the sample had two structural phases. This fact was in disagreement with the microprobe report, Monk 1981, which indicated no signs of second phase. Nevertheless, it has to be taken into account that small amounts of ferromagnetic materials are more easily detected with magnetization or susceptibility measurements than with X-ray or microprobe and optical analysis.

The dc-measurements were studied in more detail. Fig. 4.23 shows the magnetization vs temperature when the *Sm-5% Gd* alloy was cooled in 400 Oe down to 77 K, and the magnetization measured in 400 Oe and in zero field. Two steps down show up. Afterwards, the sample was cooled in zero field and (M/H) measured in 400 Oe. Two sharp peaks were clearly observed, see Fig. 4.24a): one at ~ 112.5 K and another at ~ 136 K. The first peak is consistent

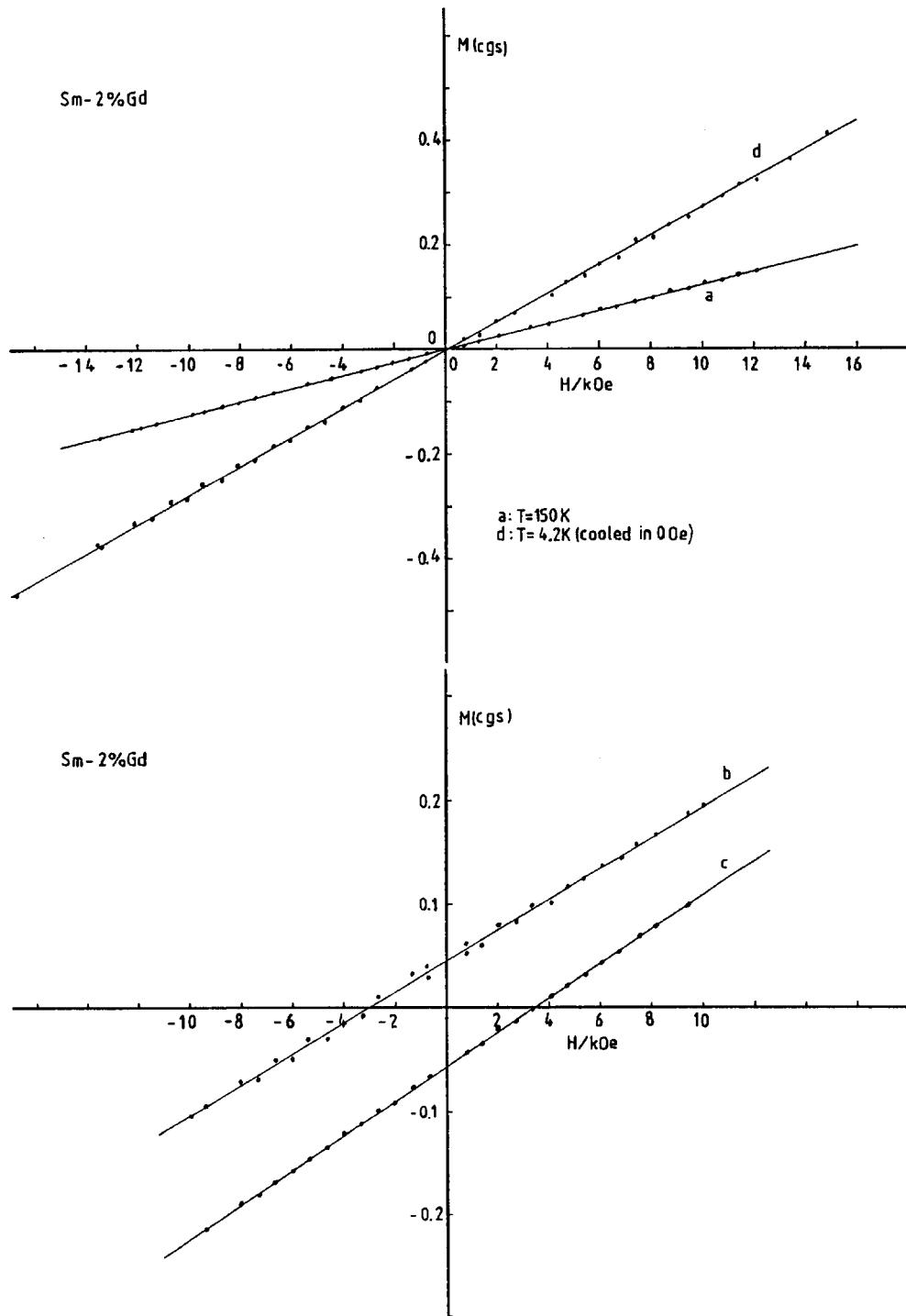


Fig.4.20: Magnetization vs applied field for the Sm-2% Gd as-cast alloy.

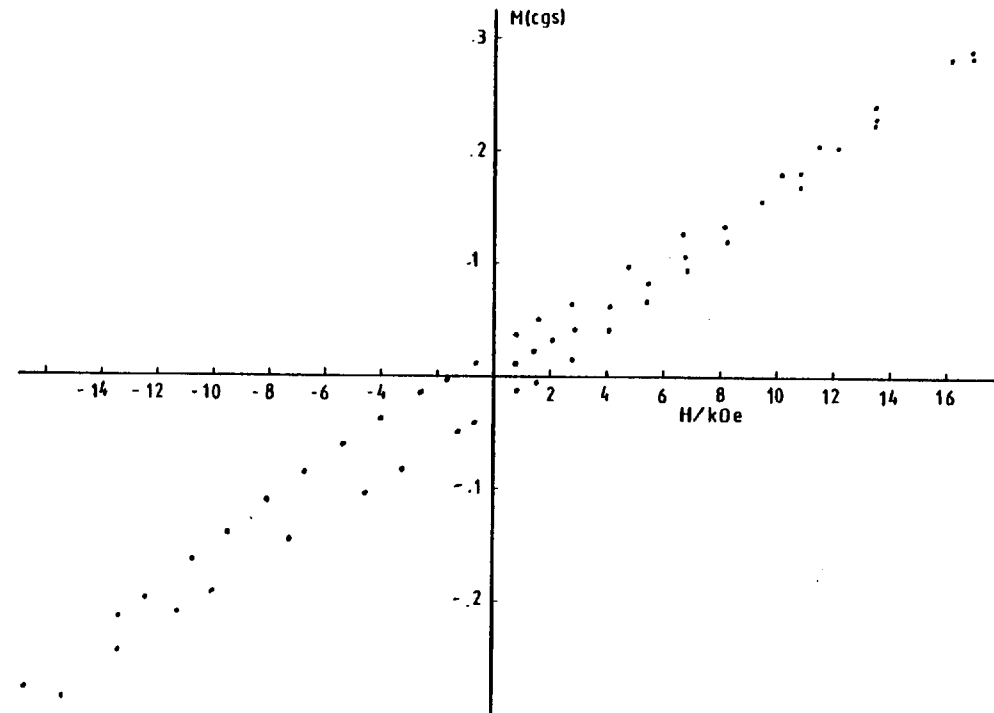


Fig.4.21: Magnetization vs applied field for the Sm-2% Gd as-cast alloy, after cooling the sample in zero field.

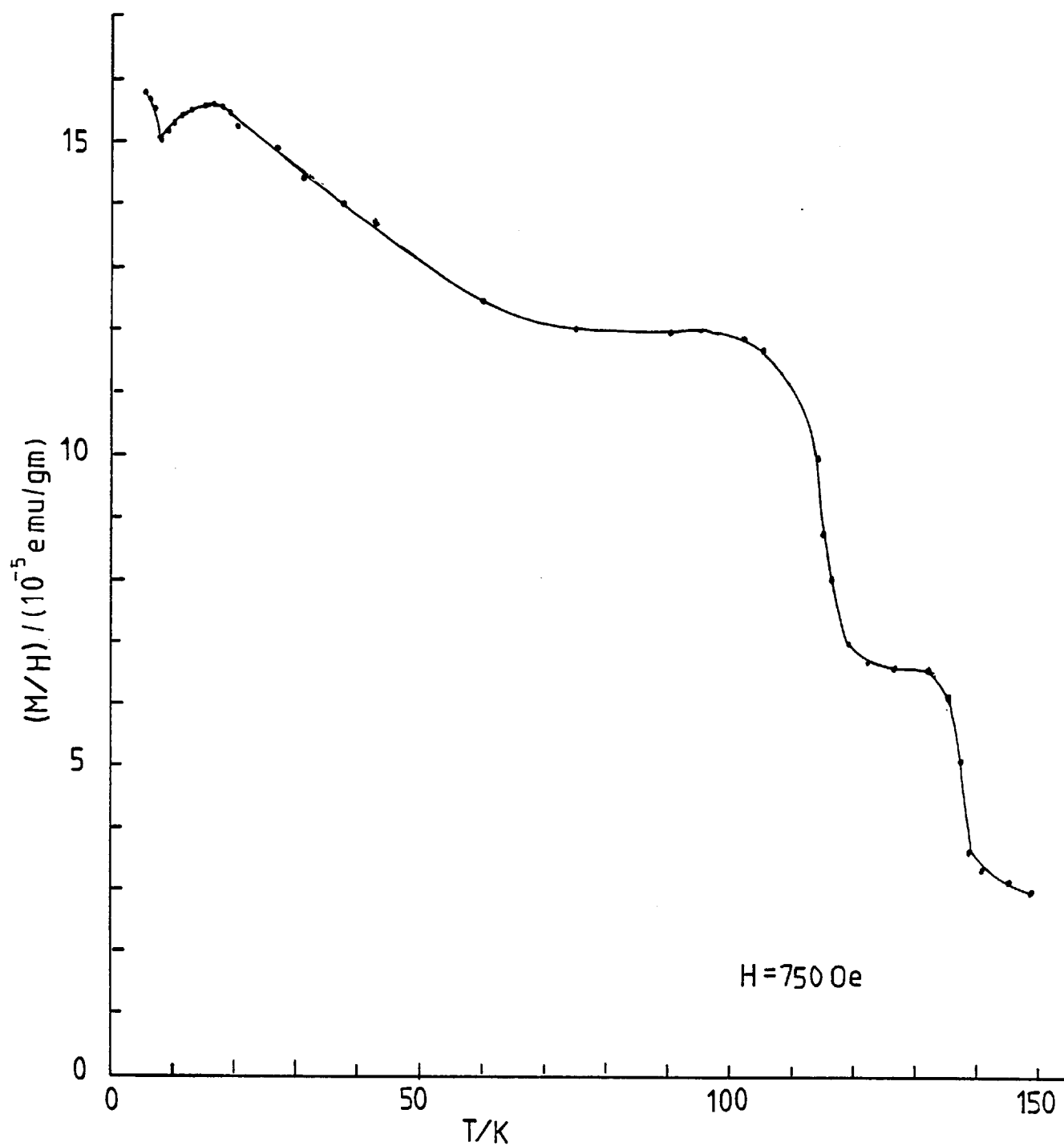


Fig.4.22: Dc-susceptibility as a function of temperature for the Sm-5% Gd as-cast alloy. See text.

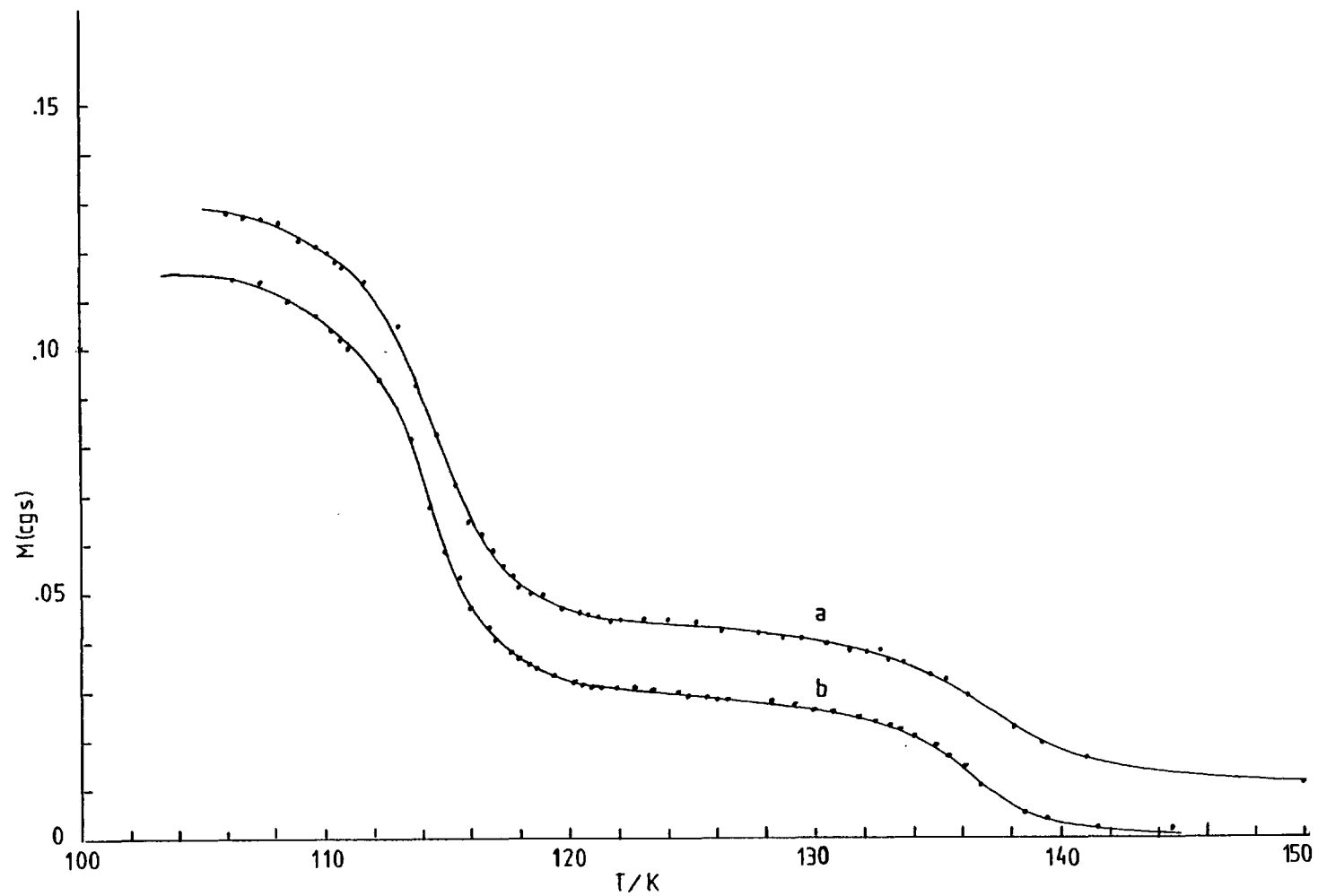


Fig.4.23: Magnetization as a function of temperature when the Sm-5% Gd as-cast alloy was cooled in 400 Oe down to 77K; and the M measured in a) 400 Oe, and in b) zero field.

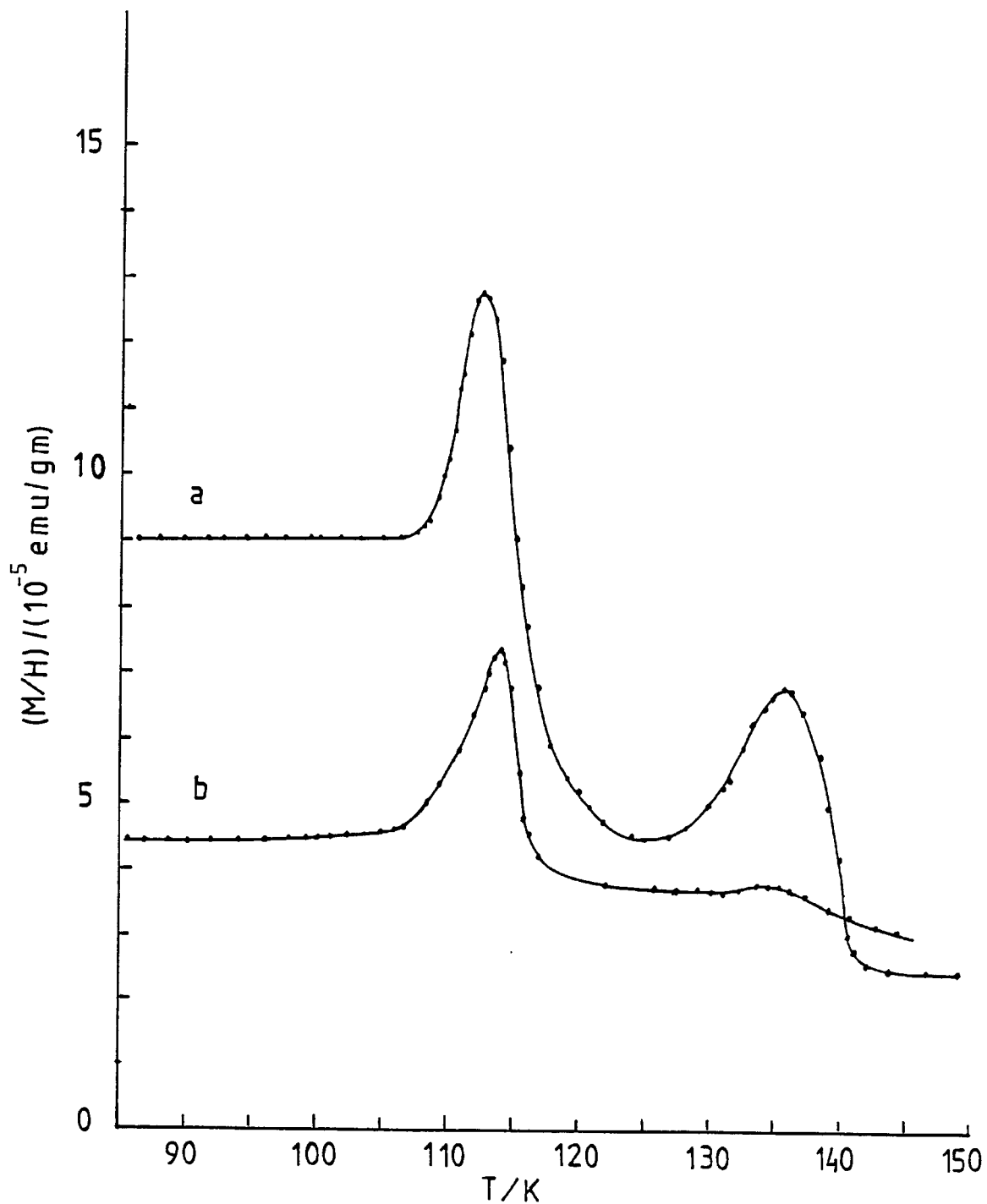


Fig.4.24: Dc-susceptibility when cooled in zero field for the Sm-5% Gd; a) as-cast, and b) annealed alloy.

with the ac-susceptibility and resistivity measurements and is ascribed to the high temperature transition of the *Sm*-type structure alloy. The second peak may be ascribed to the ferromagnetic transition of the *hcp* structure. To prove this statement, the sample was annealed for one week at 500°C in order to remove the second phase. The loss of material was less than 2% and the concentration was re-estimated as 5.6% *Gd*. Fig. 4.24b) shows the magnetization vs temperature for the annealed sample when cooled in zero field. The first peak shifted in temperature to 114 K, but the shape remains unchanged. The second peak was greatly reduced. Fig. 4.25 shows (M/H) vs T for the complete range of temperatures. Notice that this result coincides remarkably well with that of the ac-susceptibility, Fig. 4.17, with the difference that the low temperature transition is much sharper for the annealed alloy. One more comment is about the impossibility of seeing the second peak in the χ_{ac} . As has been said before, these measurements were difficult to perform due to a big gradient temperature on the sample, at high temperatures. In addition, the peak was very sharp and the signal very small, which greatly reduced the probabilities of obtaining the transition.

Fig. 4.26 shows the high temperature peak in more detail. The sample was cooled in zero field down to 77 K, and the magnetization measured in 400 Oe and in zero field. Similar behaviour is found after cooling the sample in a field of 400 Oe, but a larger remanent magnetization is obtained. Fig. 4.27 a and b shows the magnetization vs field for the as-cast and annealed sample, respectively. The effects of displaced cycles

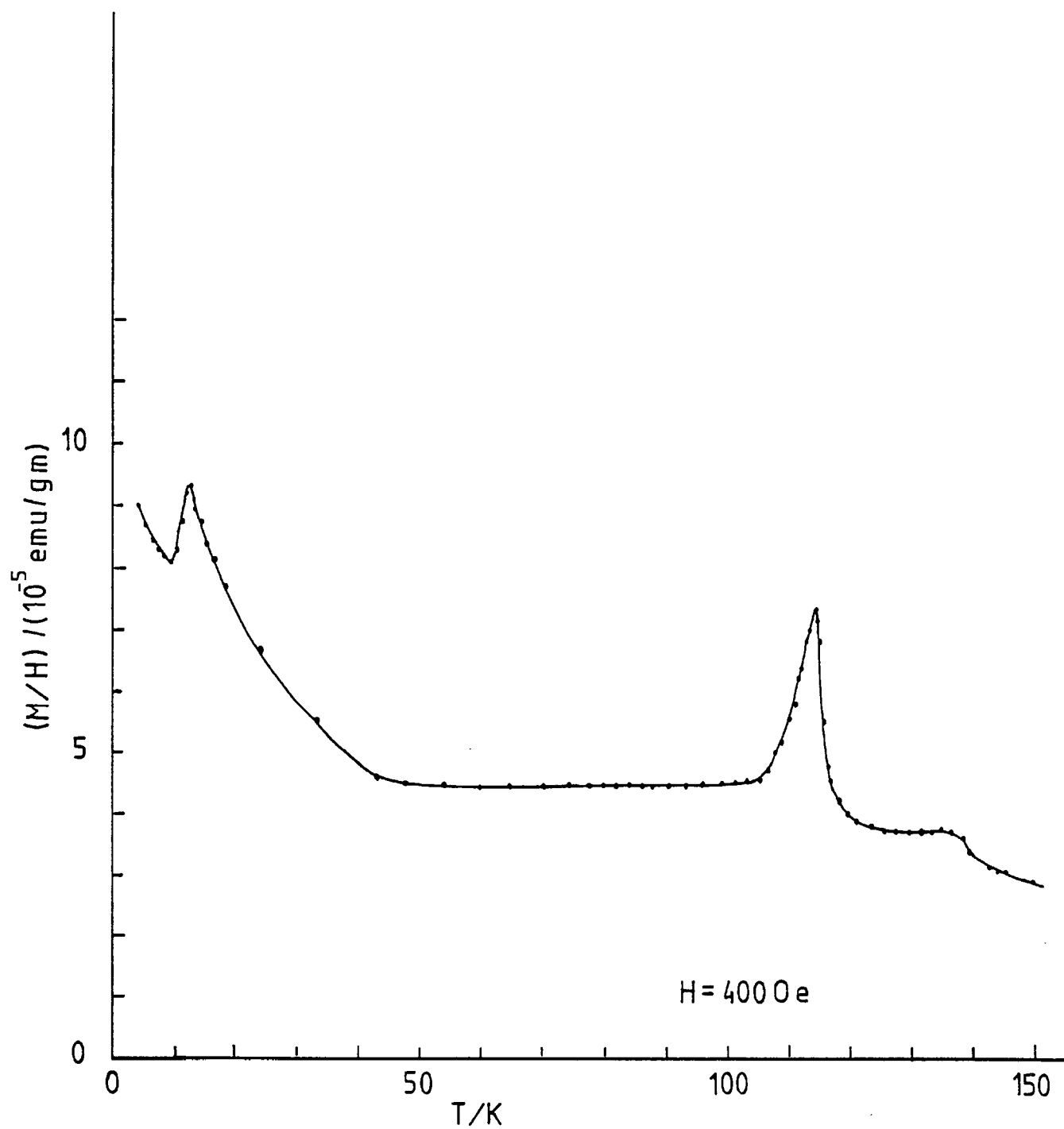


Fig.4.25: Dc-susceptibility as a function of temperature for the Sm-5% Gd annealed alloy.

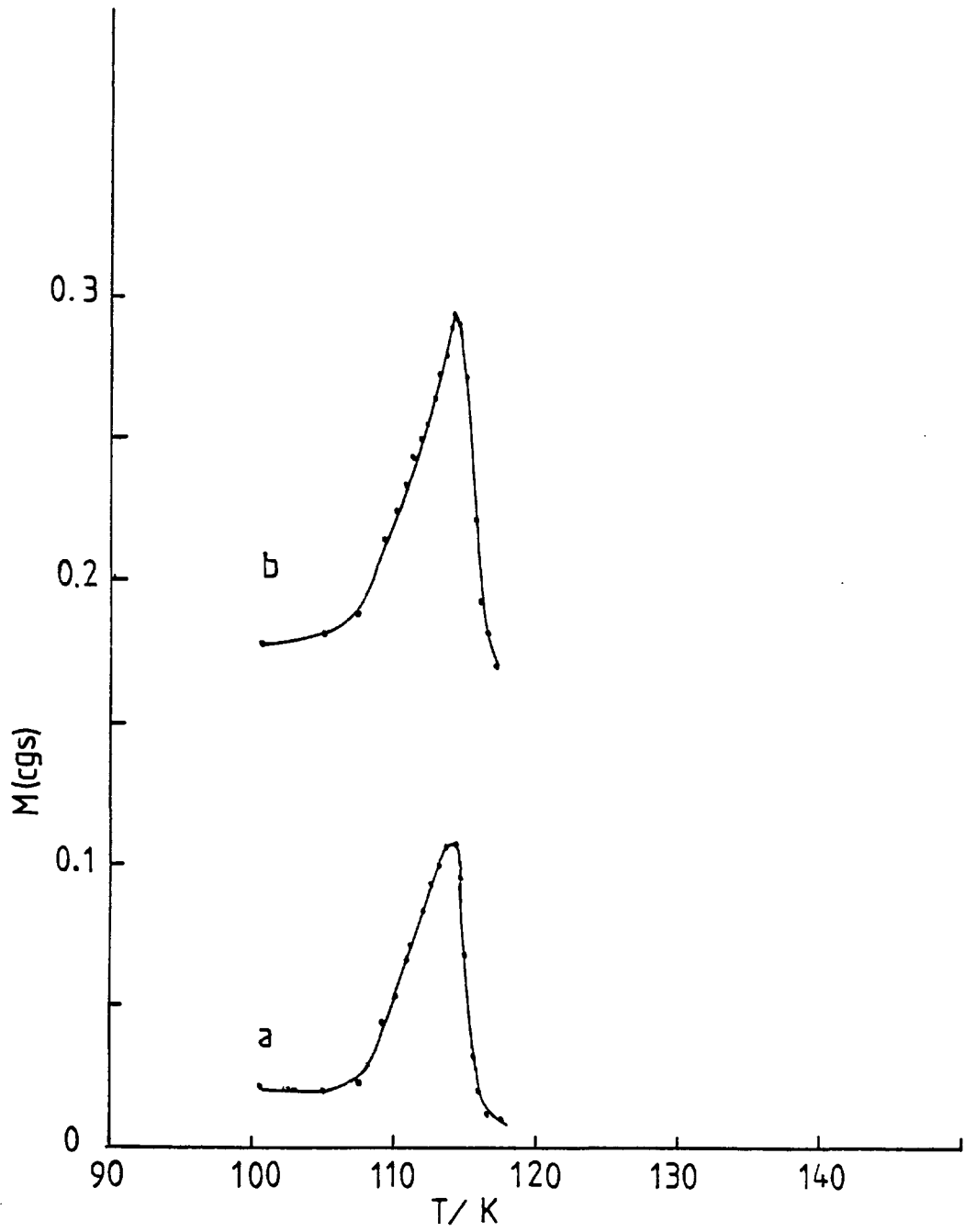


Fig.4.26: Magnetization vs temperature in the neighbourhood of 110K for the Sm-5% Gd annealed alloy when cooled in zero field and measured in a) zero field, and b) 400 Oe.

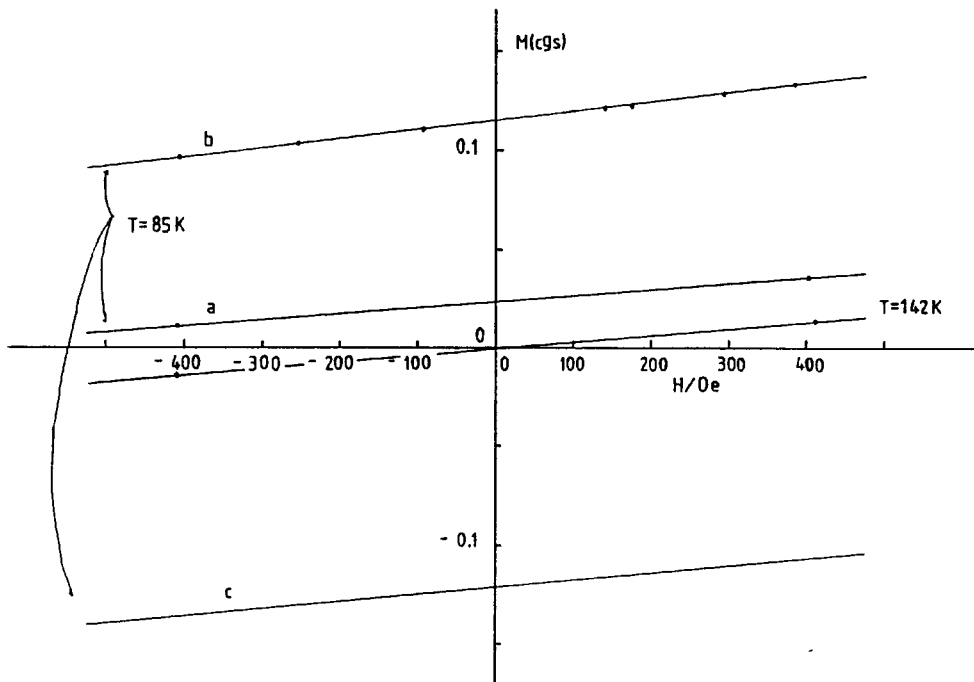


Fig.4.27: a) Magnetization vs field (at low fields) for the Sm-5% Gd as-cast alloy.

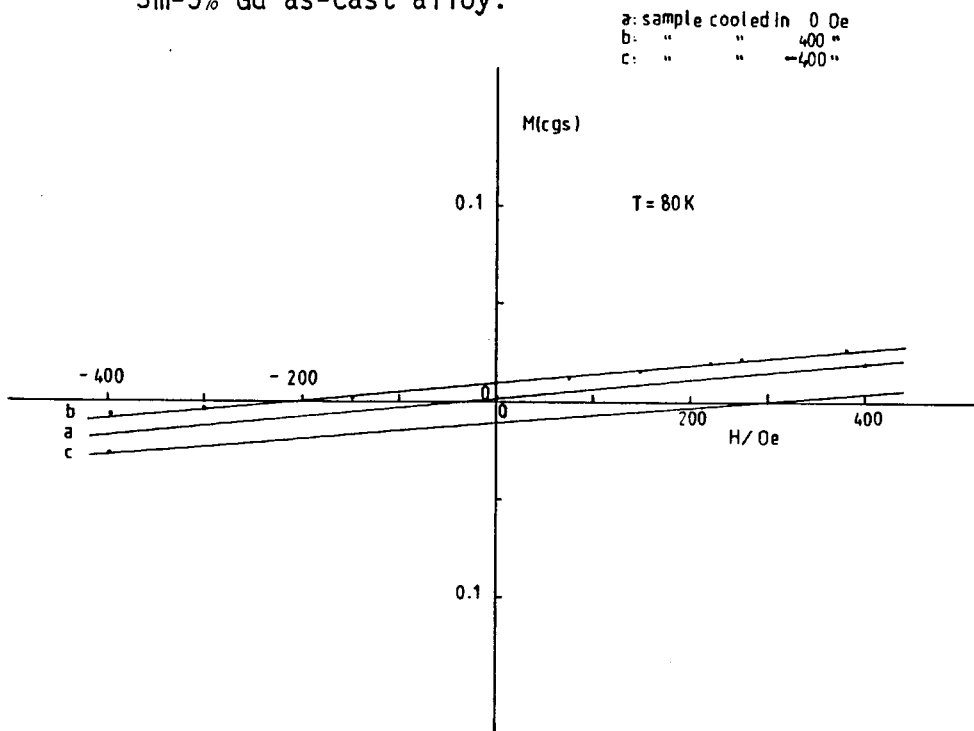


Fig.4.27: b) Magnetization vs field (at low fields) for the Sm-5% Gd annealed alloy.

were much smaller for the annealed sample, which suggests that the phenomena was due to the presence of two phases in the specimen.

For the as-cast *Sm*-2% *Gd* alloy, analogous results were found. Fig. 4.28 shows the dc-susceptibility when cooled in zero field down to 4.2 K and measured in 870 Oe. Fig. 4.29 exhibits the dc-susceptibility when cooled in zero field down to 77 K and measured in 400 Oe. This clearly displays two peaks: one at 111 K and the other at ~ 132 K. The first peak coincides with the ac-susceptibility and resistivity measurements, and is ascribed to a magnetic transition in the *Sm*-type structure alloy. The second peak is ascribed to the ferromagnetic transition in the *hcp* structure, as happens in the *Sm*-5% *Gd*.

4.3.5 Conclusion

The magnetic properties of *Sm* are distinctly and differently perturbed by the addition of a light rare earth, such as *Pr* and *Nd*, and a heavy rare earth, such as *Gd*.

The transition temperatures for the resistivity and the susceptibility measurements are summarized in Table 4.1. Both agree with each other reasonably well. Notice that for the low temperature magnetic ordering, the resistivity exhibits a sharp transition only for pure *Sm*, *Sm*-5% *Pr* and *Sm*-5% *Nd*. For the *Sm*-10% *Pr*, the transition does not occur. Fig. 4.30 shows the preliminary magnetic phase diagrams for the *Sm-Pr* and *Sm-Nd* systems.

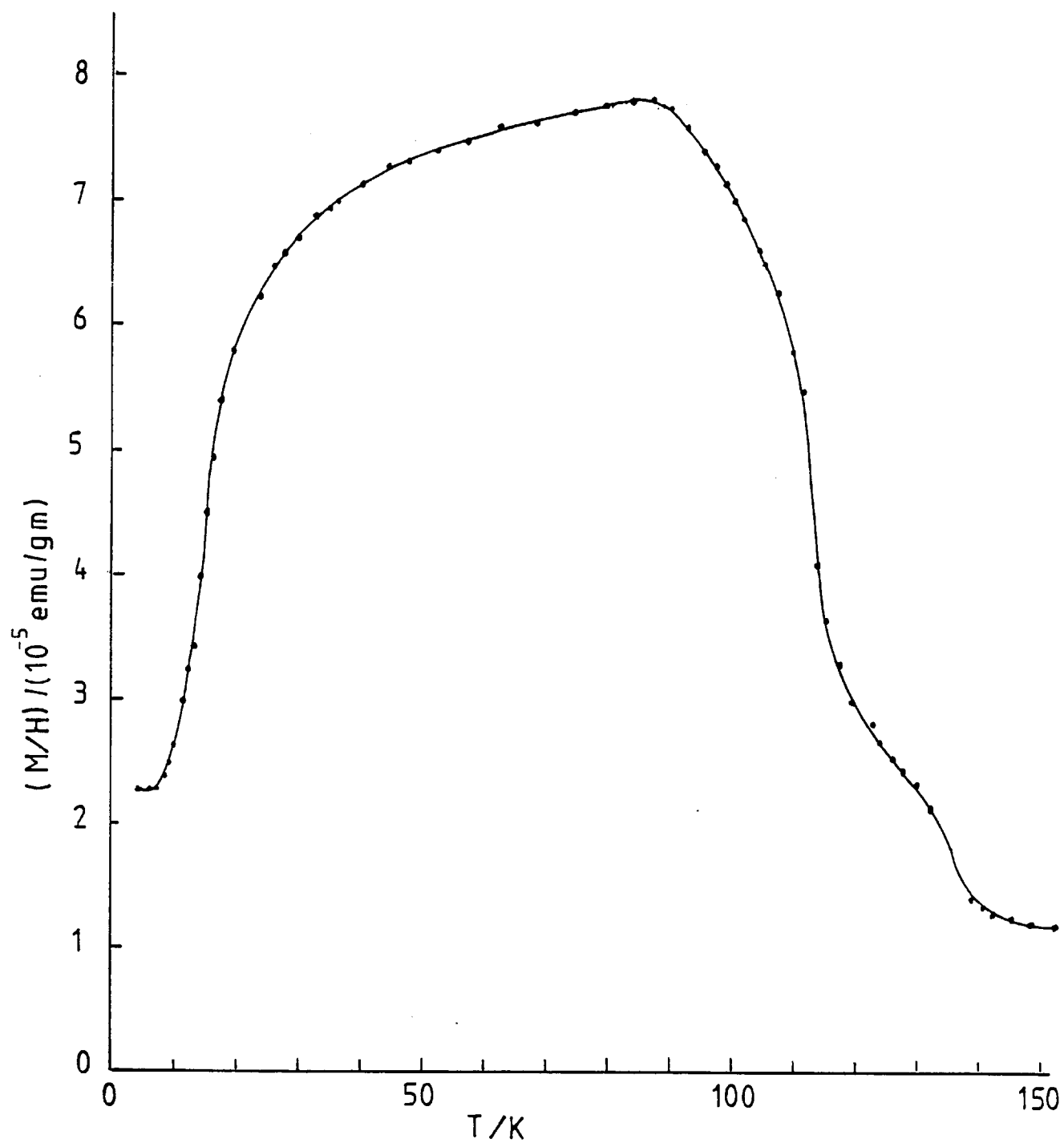


Fig.4.28: Dc-susceptibility for the Sm-2% Gd as-cast alloy when cooled in zero field down to 4.2K and measured in 870 Oe.

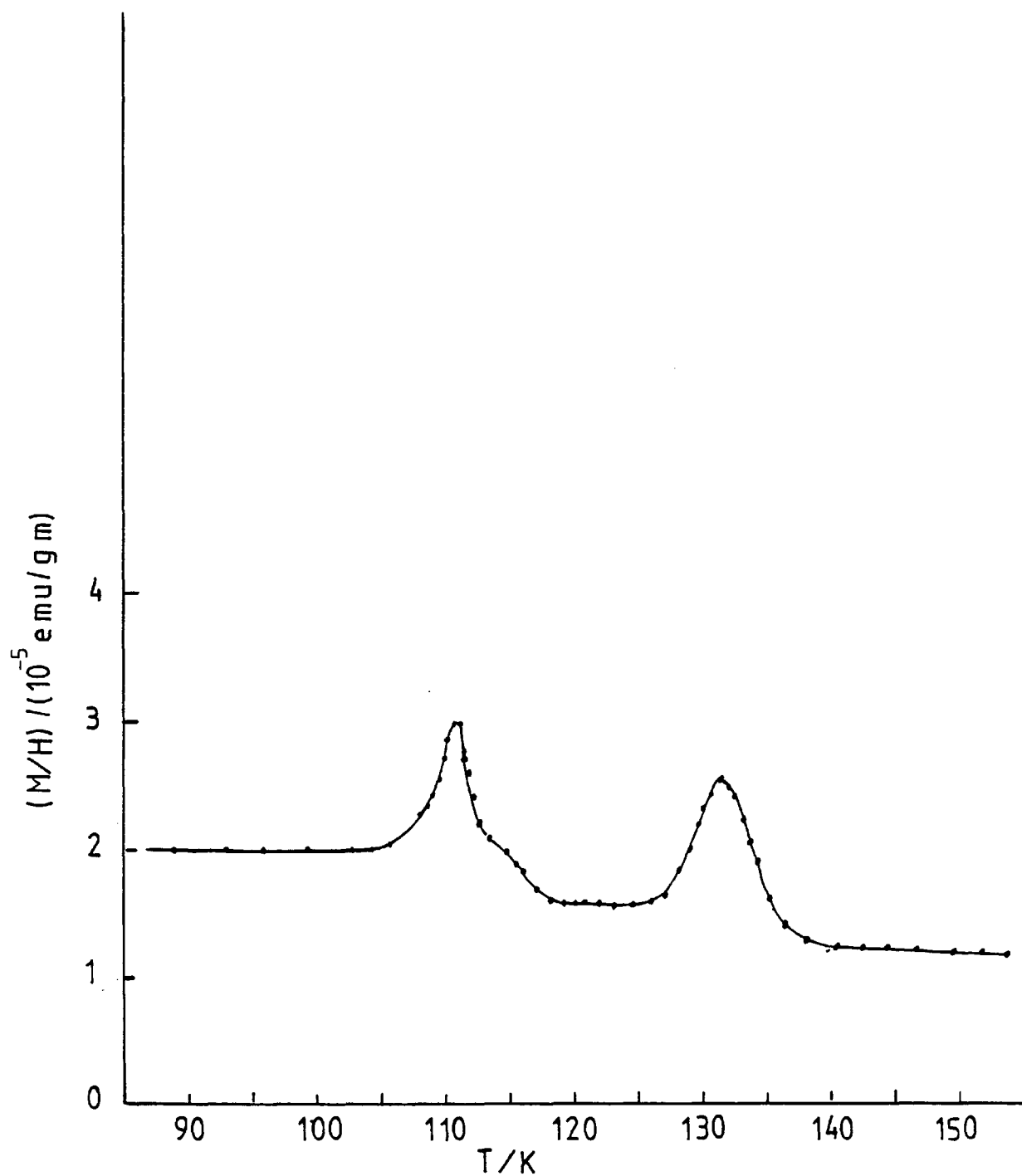


Fig.4.29: Dc-susceptibility for the Sm-2% Gd as-cast alloy when cooled in zero field down to 77K and measured in 400 Oe.

It is rather surprising and not easy to understand why none of the two transitions becomes enhanced by the addition of Nd , although the magnetization is very much increased.

Fig. 4.31 shows the preliminary magnetic phase diagram for the $Sm-Gd$ system. Results for the Gd -rich concentration alloys have been taken from Eguchi et al 1981. The upper temperature transition T_1 is slightly raised, but the low temperature transition T_2 is slightly lowered with the addition of Gd . This is in contrast with $Sm-Tb$ alloys, Okamoto et al 1980, where T_2 shifts to quite high temperatures with increasing Tb concentration. For a $Sm-21\%$ Tb alloy, T_2 was found to be 95 K. On the other hand, the shift of the temperature T_1 is similar for both systems. The most remarkable feature is the sharpness of the high temperature susceptibility peak observed in the $Sm-Gd$ alloys. This peculiar behaviour was not found in the Sm -light rare earth alloys, and has not been observed in the $Sm-Tb$ alloys. Also, it would seem that the extent of the Sm structure in these systems is very limited indeed.

One of the main interests when dealing with these alloy systems, is to determine the direction in which the magnetic moments order, and thus to determine whether the alloy displays ferromagnetism or a more complicated magnetic ordering. This becomes difficult without the help of neutron diffraction experiments, but some considerations can be put forward.

It has already been seen in Chapter 1 that the exchange interaction aligns the 4f moments relative to each other, and the

TABLE 4.1: Resistivity and susceptibility transition temperatures of pure *Sm* and some *Sm* alloys

	ρ		χ	
	T_1/K	T_2/K	T_1/K	T_2/K
<i>Sm</i>	12.0(a) 14.2(b)	106	14.0	106
5% <i>Pr</i> (as-cast)	8.4(a) ? (b)	100.5	12.0	100
10% <i>Pr</i> (as-cast)	?	?		
5% <i>Nd</i> (as-cast)	8.2(a) 9.2(b)	?	7.5	92(c)
5% <i>Nd</i> (annealed)	*	*	9±1	92±2
2% <i>Gd</i> (as-cast)	13.9(a)	111	*	111 133(d)
5% <i>Gd</i> (as-cast)	14.2(a)	112	13	113 135(d)
10% <i>Gd</i> (as-cast)	13.8(a)	111 ?	*	116
5% <i>Gd</i> (annealed)	*	*	13	114

(a) Maximum in $d\rho/dT$

(b) Minimum in $d\rho/dT$

(c) ac-susceptibility

(d) Due to *hcp* structure

* not measured

Estimated error $(T_1 = \pm 0.3 \text{ K})$
 $(T_2 = \pm 0.5 \text{ K})$

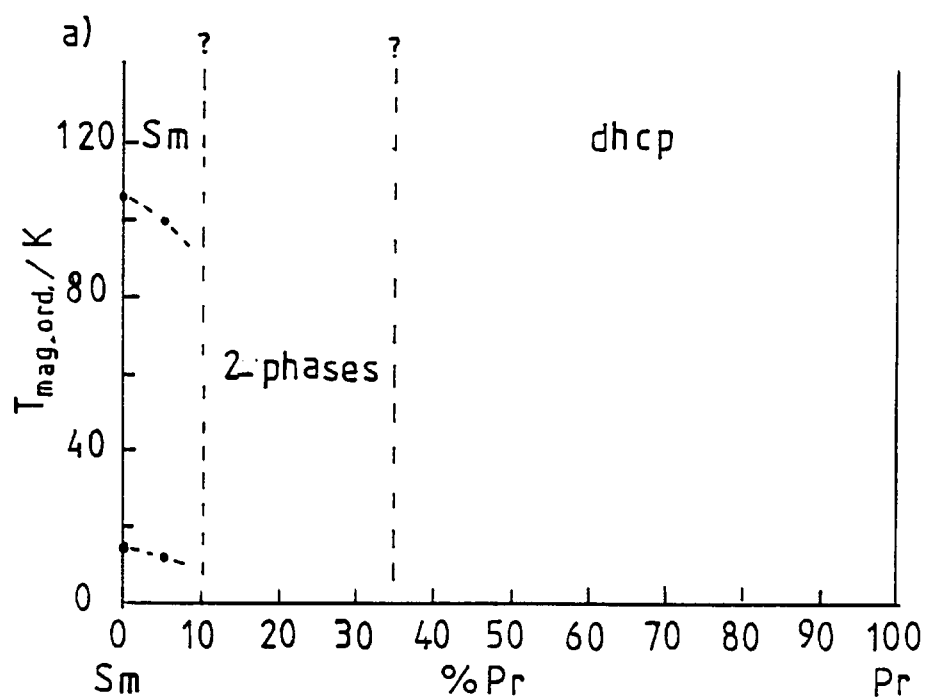
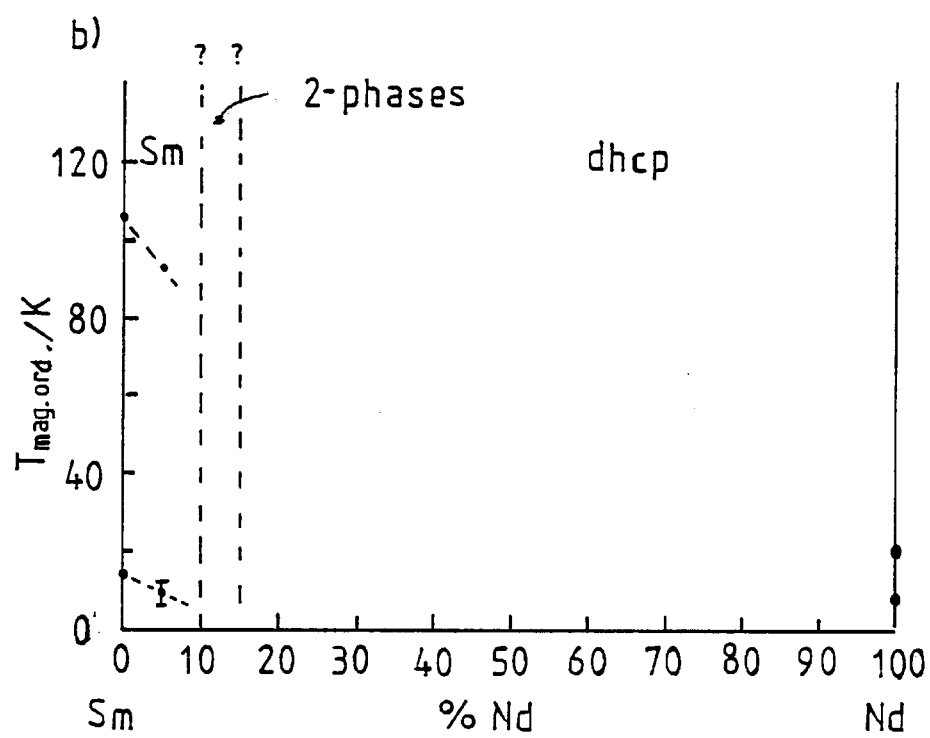


Fig.4.30: Preliminary magnetic phase diagrams for a) Sm-Pr and b) Sm-Nd systems.

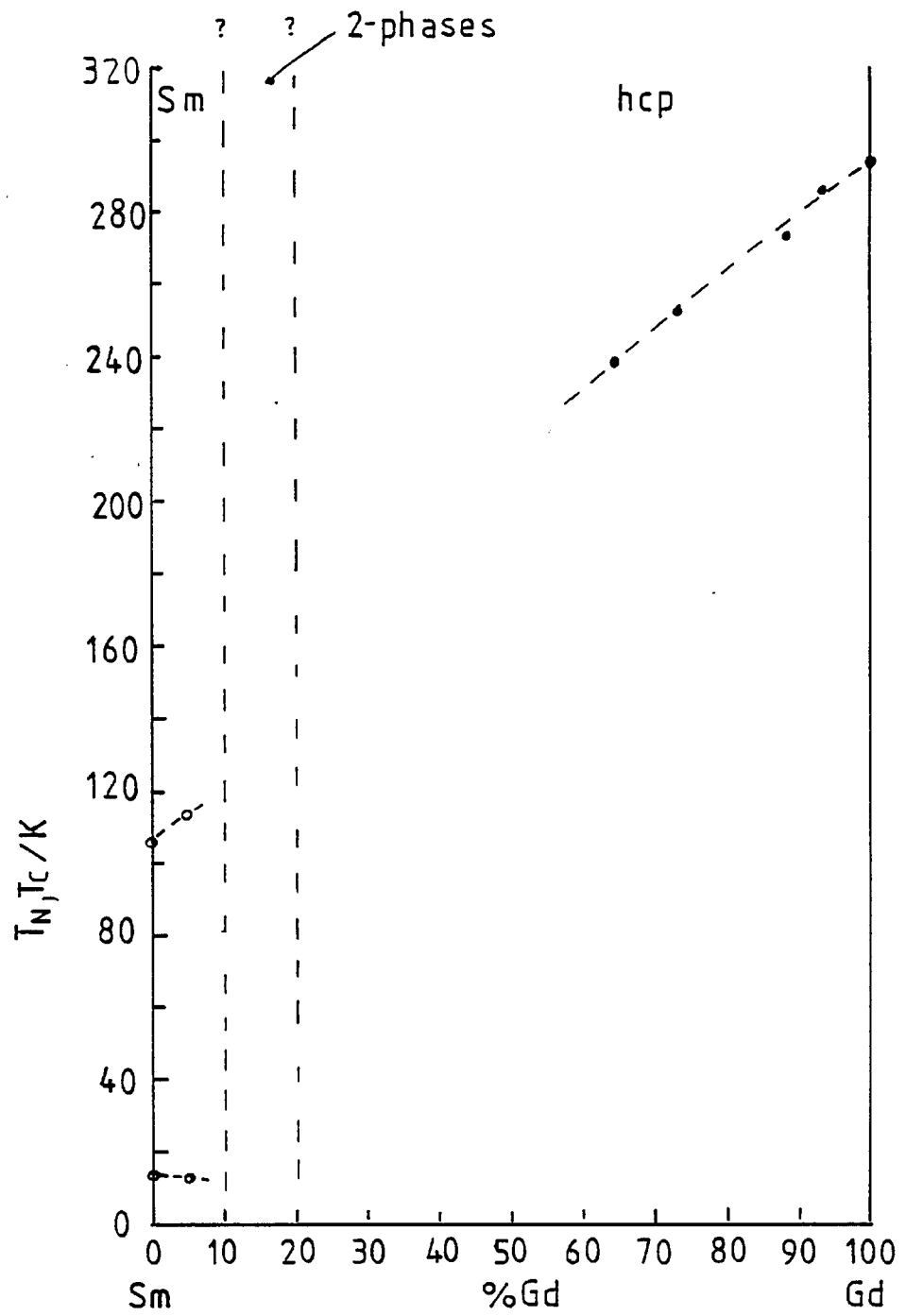


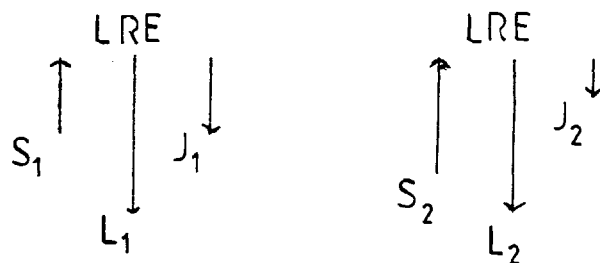
Fig.4.31: Preliminary magnetic phase diagram for the Sm-Gd system.
• Eguchi et al. 1981
o Present work.

crystal field interaction tends to align the moments along particular crystallographic directions. In rare earths, the single-ion anisotropy (crystal field) and the two-ion anisotropy (exchange anisotropy) are responsible for the direction in which the moments order. In recent years these effects have become a topic of interest, Jensen 1977, both experimentally and theoretically. In Chapter 3, the importance of single and two-ion anisotropy in the magnetism of *Pr* was discussed. Jensen pointed out these effects in *Tb* and *Er*. On the other hand the orbital moment of *Gd* is zero and anisotropic effects should not be very important. However, Chikazumi et al 1971 have observed that small amounts of an anisotropic rare earth into *Gd*, changes its anisotropy dramatically, and because *Gd* has the maximum spin value $S = 7/2$, the exchange is strong enough to rotate the impurity moment in the crystal.

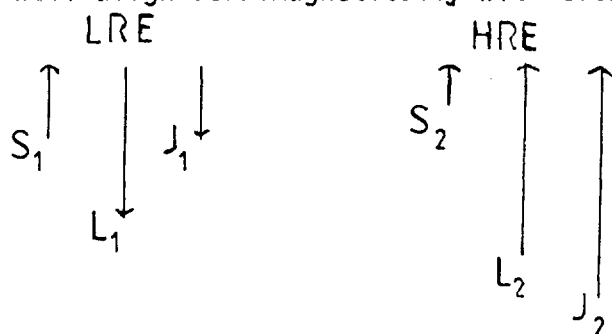
There are two interesting works to comment on in this context. One of them Achiwa and Kawano 1973, 1980, has already been mentioned. They have observed the same magnetic structure as in pure *Sm* for the *Tb-Pr* and *Tb-Nd* alloys when the alloys possessed the *Sm*-type crystal structure. This suggests that two-ion anisotropy is as important as single-ion anisotropy. On the other hand, Hansen and Lebech 1976 observed by neutron diffraction measurements, an inhomogeneous magnetic structure in the *Tb*-65% *Tm* alloy. The spins associated with the *Tb* ions were lying in the basal plane, while the spins associated with the *Tm* ions were along the *c*-axis. This means that the anisotropy is caused mainly by the crystal field. Thus, the anisotropy effects

in alloys may depend upon the crystalline structure formed and the elements involved.

Assuming that only isotropic exchange interactions are present, the magnetic moments of a light-light rare earth alloy will couple ferromagnetically,



In the case of a light-heavy rare earth alloy, the magnetic moments will align ferrimagnetically with each other,



When the atoms are brought together to form the alloy, the crystal field and anisotropic exchange will determine the direction of the moments to order. Specifically for the alloys concerned in this work, anisotropy will play an important role.

It seems probable that *Sm-Pr* alloys within the *Sm*-type structure will have the same magnetic structure as pure *Sm*. Due to the low exchange interaction of pure *Pr*, the drop in the ordering temperature is expected. However it is not clear whether the *Pr* magnetic moments order or not.

In pure *Sm*, the cubic sites remain disordered above 14 K. It has to be pointed out that the magnetic structure of *Sm* has the characteristic feature that produces an exchange interaction which exactly vanishes at the cubic sites. This is because of crystallographic and magnetic symmetry considerations. However, this is no longer true in the *Sm* alloys. This may be the reason why there is not a well defined low temperature transition in *Sm-Nd* alloys. Further experimental studies are required in order to understand the magnetic behaviour of *Sm-Nd* alloys within the *Sm*-type structure, although the extent of the phase is quite limited. The *Sm-Gd* alloys exhibited the most striking results among the alloys studied in this section. The well defined transition at high temperatures indicates a strong coupling between *Sm* and *Gd* magnetic moments which produces a ferrimagnetic structure. The interesting displaced cycles observed in the magnetization measurements are due, it is thought, to the presence of two phases in the specimen. As can be seen in Fig. 4.27, the remanent magnetization was very much reduced after removing the second phase by annealing the specimen. Displaced hysteresis loops have been observed in many alloys when cooled in an applied magnetic field. This was explained in terms of a magnetic interaction between antiferro- and ferromagnetic phases and between ferri- and ferromagnetic phases, see Jacobs and Bean 1963. Recent works have shown that *CuMn* alloys in the spin glass state exhibit displaced hysteresis loops, and anisotropy is responsible for these effects. Levy and Morgan-Pond 1982 have explained this anisotropy in terms of interactions arising from spin-orbit scattering by the magnetic impurities themselves. Detailed neutron diffraction measurements are clearly needed in order to understand the anisotropy in rare earths alloys.

CHAPTER 5

5. Magnetic character of some $Pr-Sm$ alloys in the $dhcp$ structure

The magnetic ordering which appears in Pr with the addition of another rare earth, has already been discussed in Chapter 3. The character of this magnetic ordering depends upon whether the added rare earth is light or heavy. Long-range antiferromagnetism has been observed in $dhcp$ $Pr-Nd$ alloys at solute concentrations greater than about 3% (McEwen et al 1975), but spin glass type-freezing seems to occur in $Pr-Gd$ alloys; see section 3.2. Certainly, one should expect that the singlet character of Pr will be disturbed in the alloys with Sm . Preliminary dc-susceptibility measurements (in 15 Oe) on $Pr-Sm$ as-cast alloys with concentrations of 5, 10, 20% Sm , exhibited sharp peaks at 3.5, 5 and 8.5 K, respectively (Sarkissian 1978*). These results were associated with long-range periodic antiferromagnetism. In this Chapter, electrical resistivity and ac-susceptibility measurements of some $Pr-Sm$ alloys will be reported.

5.1 In search of antiferromagnetism in $Pr-5\%$ Sm .

Metastable fcc phase

The ac-susceptibility measurements of the $Pr-5\%$ Sm as-cast alloy exhibited a rounded maximum at ~ 4.2 K and a sharp peak at 8 K; see Fig. 5.1a. This rather striking result led us to suppose that the sharp peak was due to the presence of $fcc-Pr$ in the specimen.

* unpublished result

As has been mentioned before, the *fcc* structure of *Pr* and *Nd* may be obtained by quenching from high temperatures, and both proved to be ferromagnetic in character, Bucher et al 1969. They reported a Curie temperature of 8.7 K for *Pr* and 29 K for *Nd*. It is interesting to notice that this structural phase has been retained in *Nd* and *Nd-Y* as-cast specimens, Sharif and Coles 1978. In *Nd*, it was easily removed after heat treatment, but in the alloys persisted even after long periods of annealing.

The *Pr-5% Sm* sample was annealed several times at a temperature of 600°C in order to completely remove the phase, but it continued to appear even after 54 days of annealing (it shifted down to 6.7 K); see Fig. 5.1. It should be pointed out that small amounts of ferromagnetic materials can be easily detected with the ac-susceptibility measurements. This behaviour is in contrast with that of the *Pr-Y* alloys, in which a short heat treatment was enough to remove a second phase present and to stabilize the equilibrium structure.

The rounded maximum appeared to be stable after the heat treatment and was ascribed to a magnetic transition in the *dhcp* phase of the alloy. It shifted towards a lower temperature (3.5 K), but its shape remained unchanged. The electrical resistivity measurements of the as-cast alloy is shown in Fig. 5.2. The temperature-dependence of the resistivity characteristic of an antiferromagnetic long-range magnetic ordering, as in *Pr-Nd* alloys (Sarkissian 1977b) was not found. These results clearly indicated that the singlet ground state

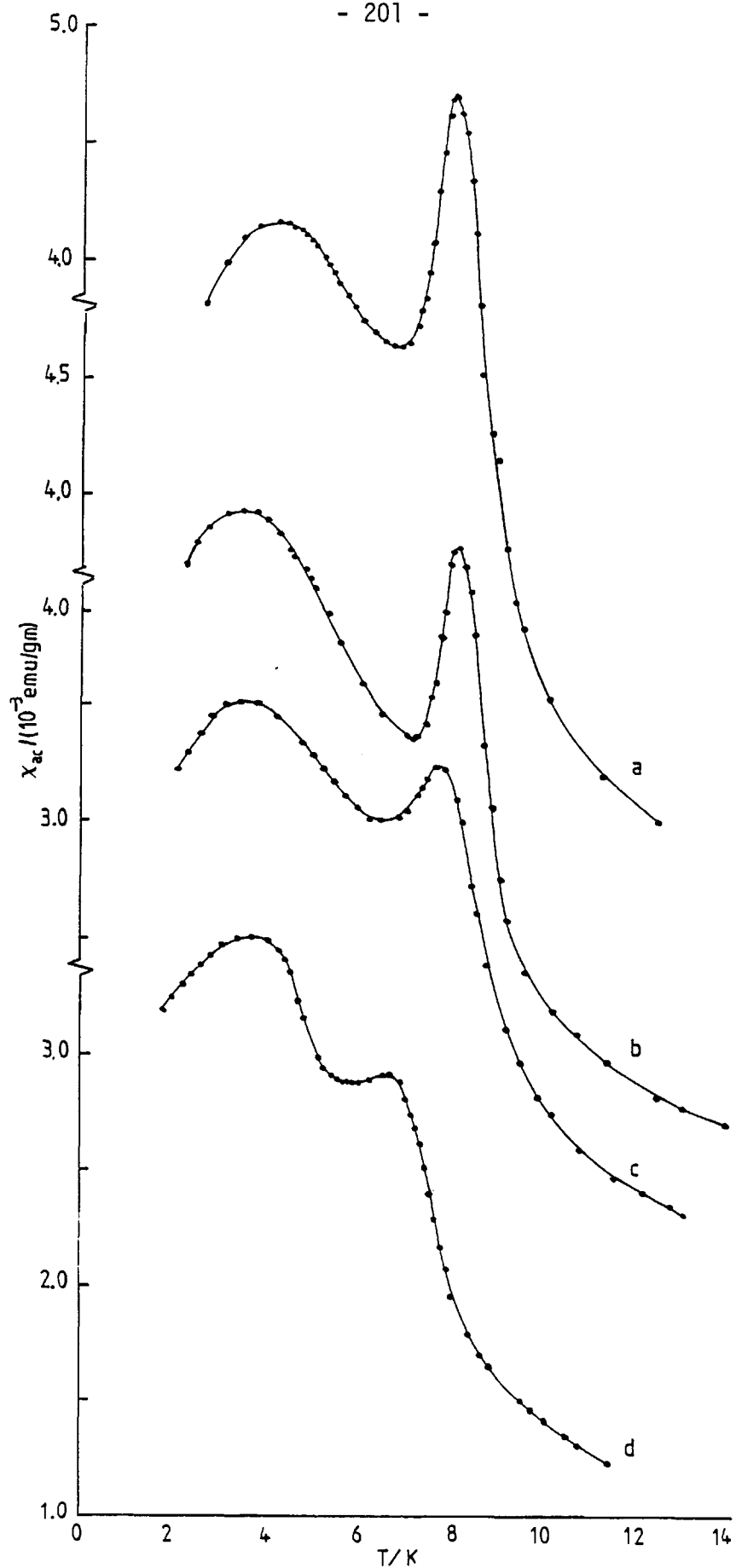


Fig.5.1: Ac-susceptibility as a function of temperature for the Pr-5% SM alloy. a) as-cast; b) after 3 days, c) after 24 days, and d) after 54 days of annealing.

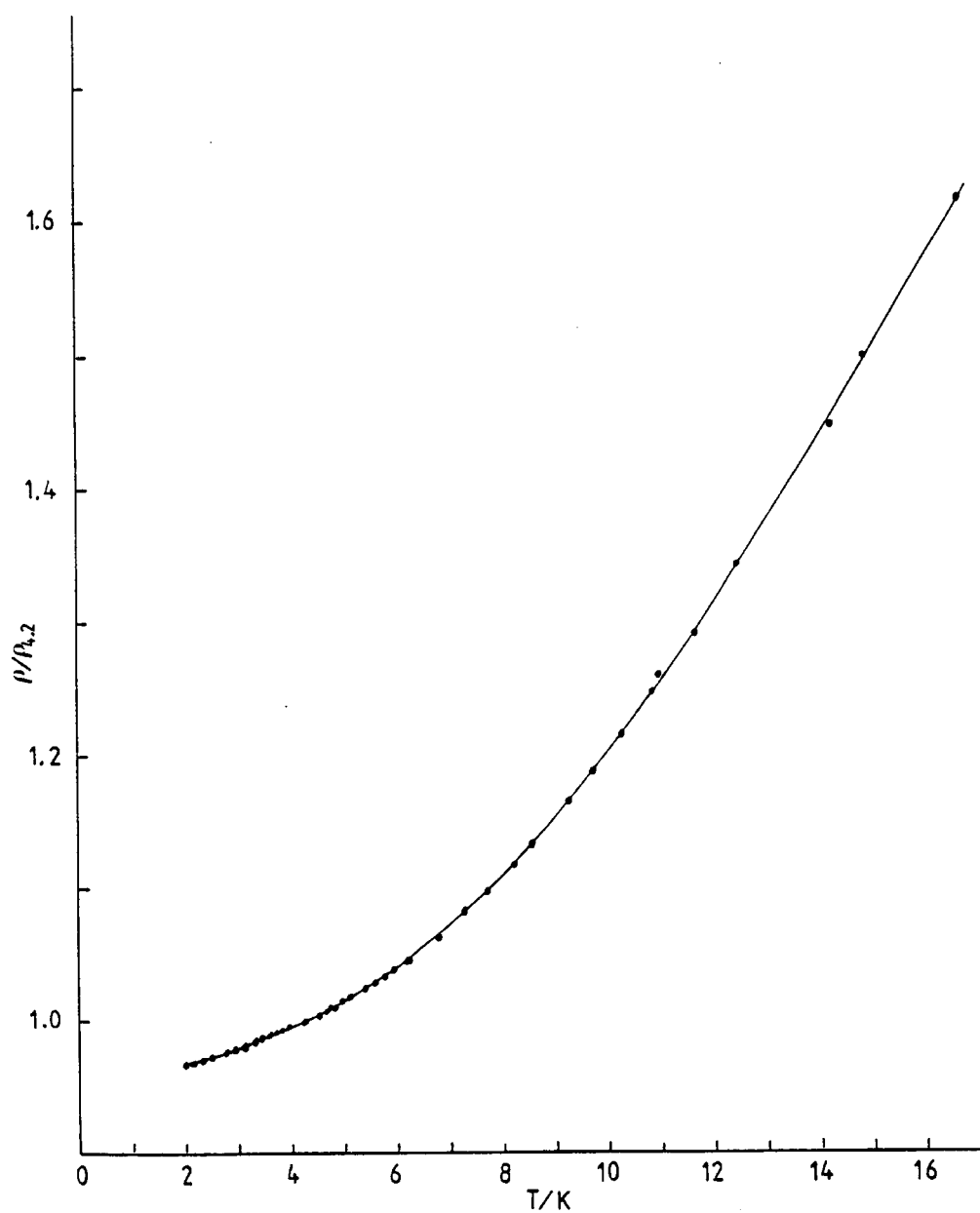


Fig.5.2: Electrical resistivity of the Sm-5% Pr as-cast alloy.

of pure *Pr* is perturbed by the presence of *Sm*. However, the origin of the magnetic ordering remains uncertain.

5.2 *Pr*-10% *Sm* and *Pr*-20% *Sm* alloys

Results and discussion

The ac-susceptibility measurement of the *Pr*-10% *Sm* as-cast alloy exhibited a sharp peak at 4 K (see Fig. 5.3), which suggested long-range antiferromagnetic ordering. However the electrical resistivity measurement could not confirm this assumption; see Fig. 5.4.

The experimental results for the *Pr*-20% *Sm* as-cast alloy are shown in Fig. 5.5 and 5.6. Unexpectedly, two rounded maxima were observed in the susceptibility: one at ~ 4.5 K and another at ~ 11.5 K; see Fig. 5.5a. Another specimen was prepared and a similar result was found; see Fig. 5.5b. This behaviour is not easy to understand. In this range of composition one should expect to produce an homogeneous sample. The resistivity measurement shown in Fig. 5.6, does not manifest clearly a long-range ordering, although some small anomaly seems to exist near 5 K.

5.3 Conclusion

Evidence for the presence of the ferromagnetic *fcc* structure of *Pr* has been obtained. This metastable structure proved difficult to remove from the *Pr*-5% *Sm* alloy. It is not clear whether some of the *fcc* structure is present in as-cast alloys of *Pr*-10% and 20% *Sm*.

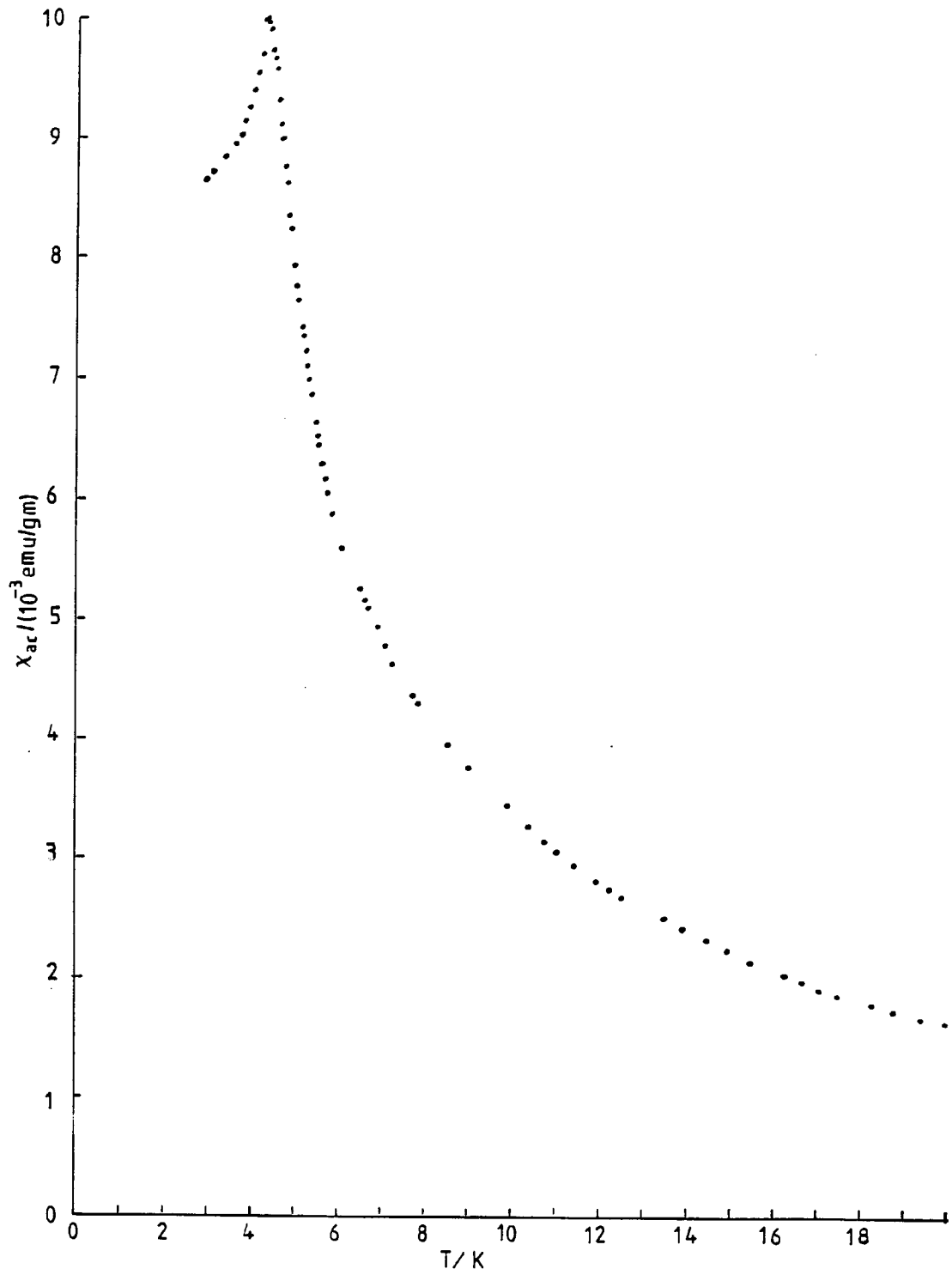


Fig.5.3: Ac-susceptibility as a function of temperature for the Pr-10% Sm as-cast alloy.

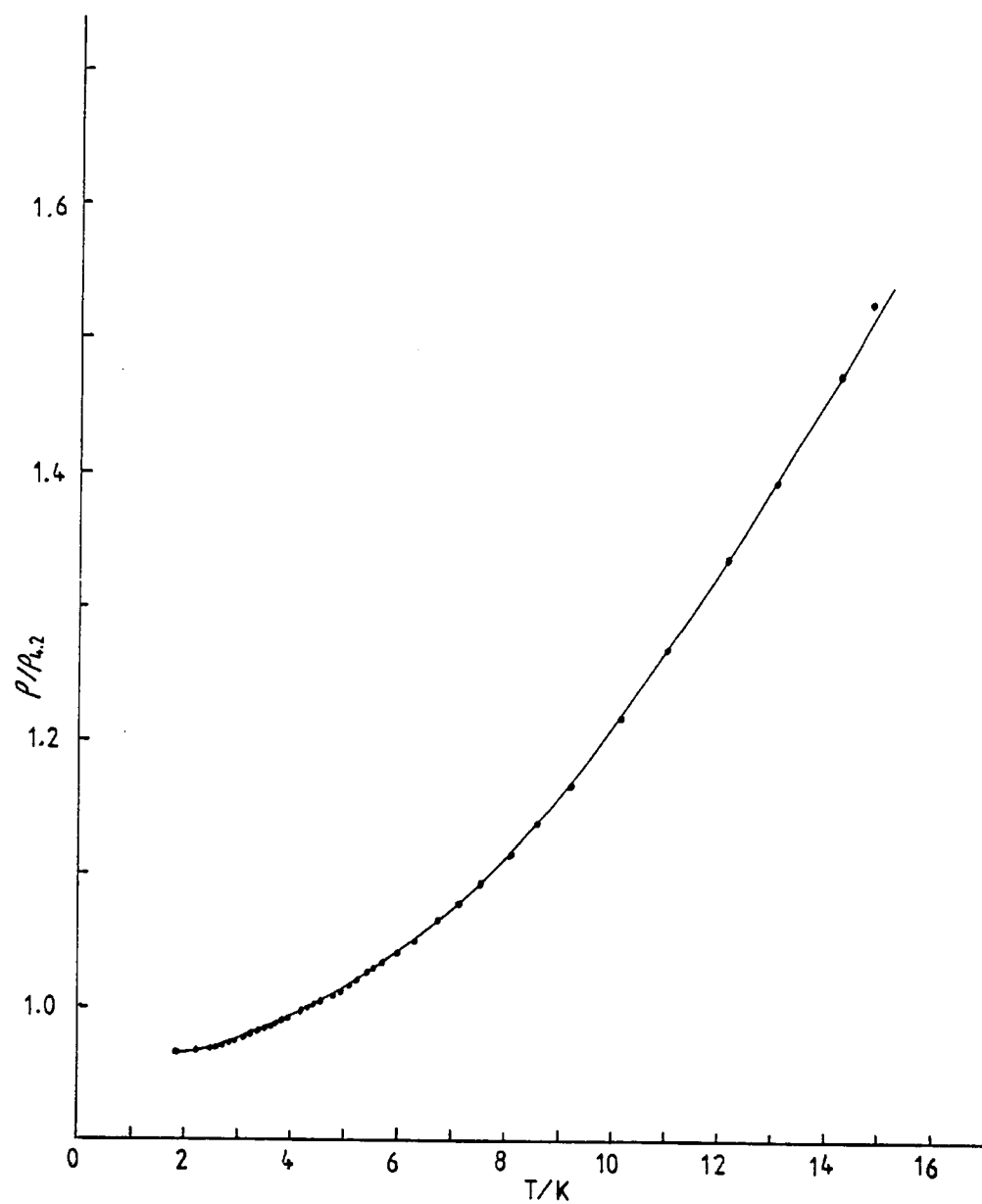


Fig.5.4: Electrical resistivity for the Pr-10% Sm as-cast alloy.

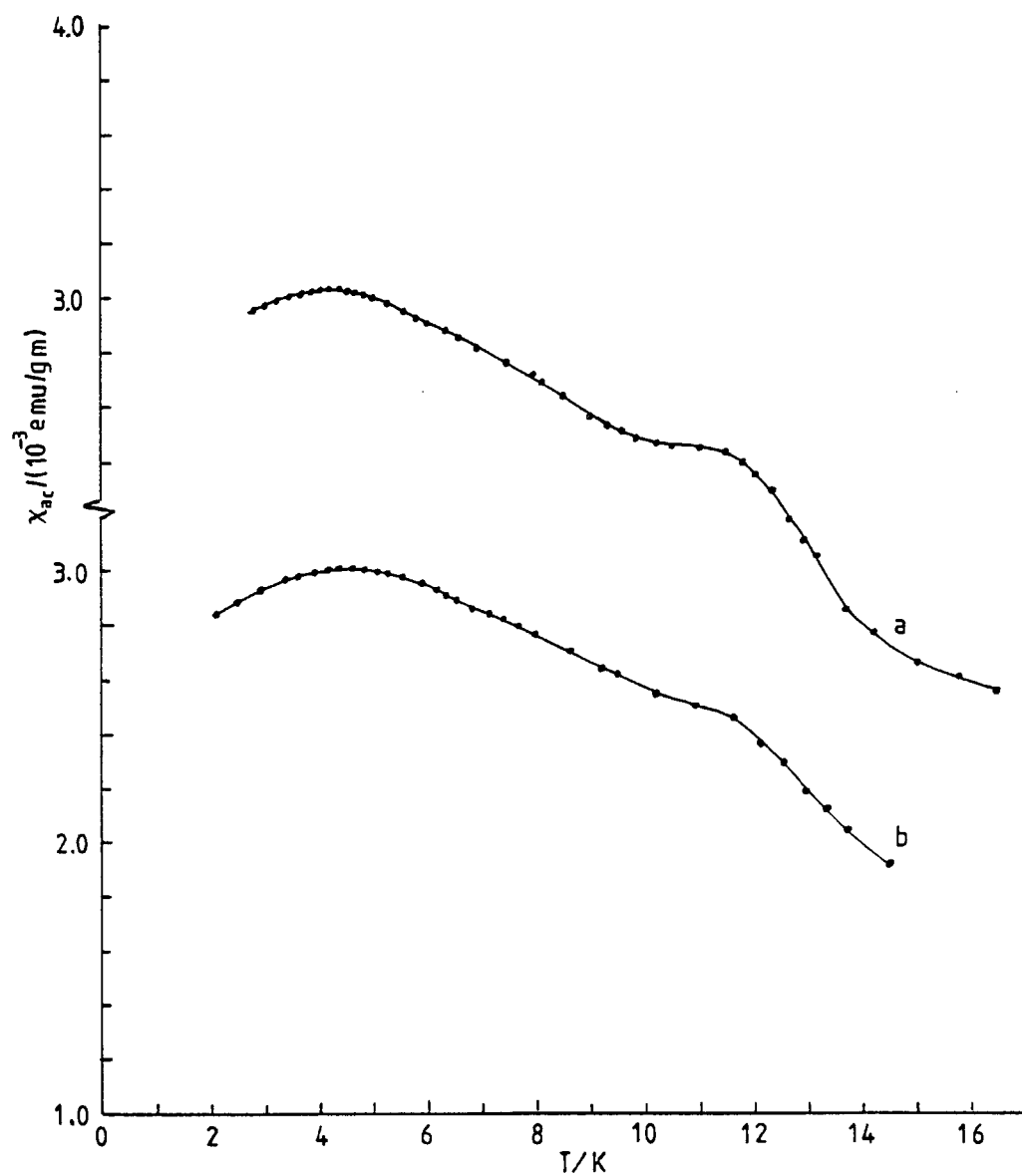


Fig.5.5: Ac-susceptibility as a function of temperature for the Pr-20% Sm as-cast alloy. See text.

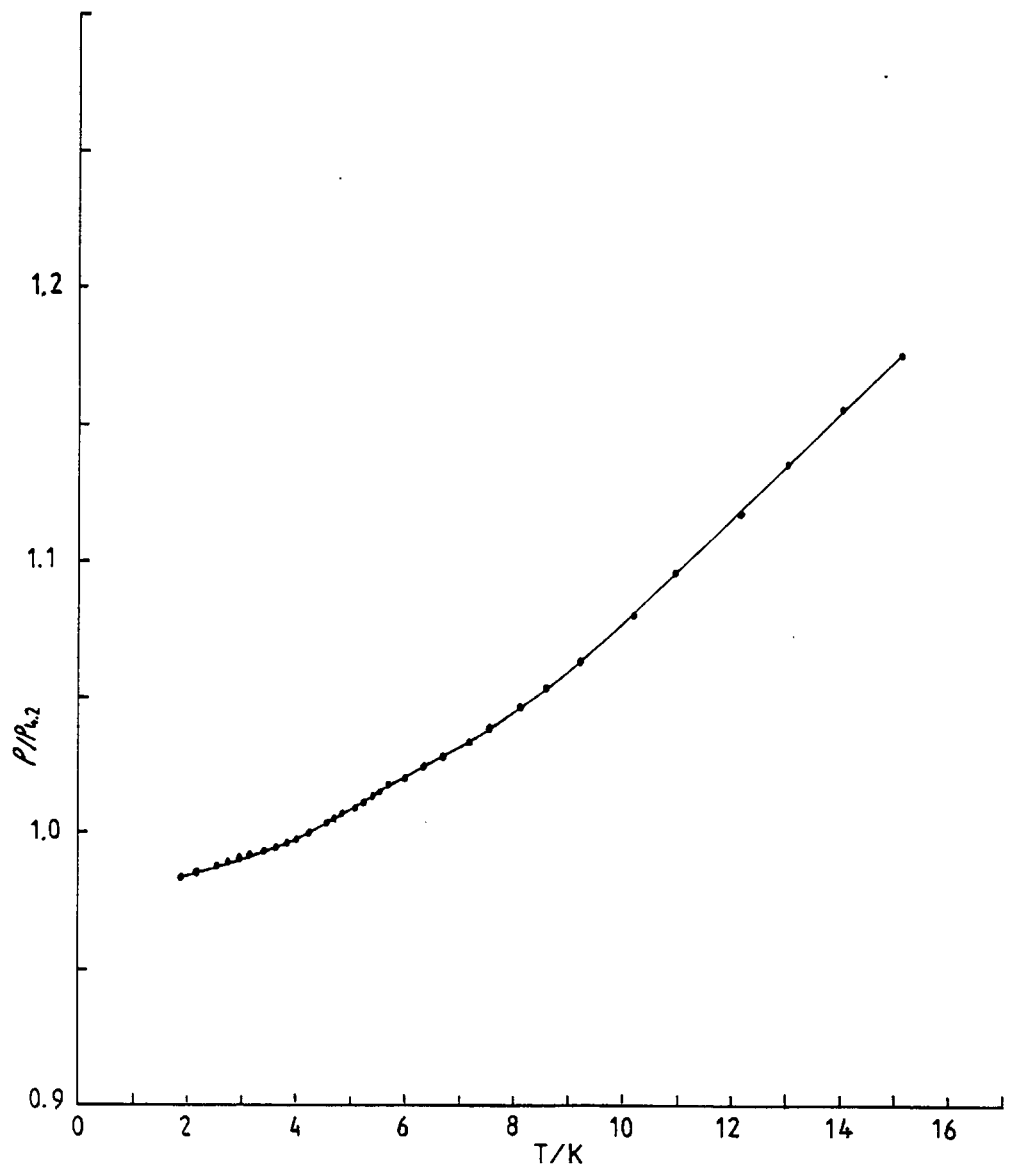


Fig.5.6: Electrical resistivity for the Pr-20% Sm as-cast alloy.

Fig. 5.5 gives a slight indication of an extra phase in the latter. It seems that careful preparation and structural analysis of the samples will need to be performed before drawing any conclusion from these experiments.

The ac-susceptibility measurements of the 5% and 10% alloys are in relative agreement with the dc-susceptibility measurements of Sarkissian 1978. On the other hand, the sharp peak observed at 8.5 K in his *Pr*-20% *Sm* alloy was not obtained in our specimen. Probably the peak is due to the presence of *fcc* structure in his sample.

The effects of changes in the structural environment on the magnetic behaviour of *Pr* and *Nd* atoms are rather similar, although *Pr* possesses a singlet character in both the cubic and hexagonal sites of the *dhcp* phase. For both, the *hcp* structure gives higher ordering temperatures than either *dhcp* or *Sm*-type structures (e.g. *Pr*-Y and *Nd*-Y alloys); it even exceeds the Curie temperature of the *fcc* forms of the pure metals. Furthermore, the fact that crystallographic sites with local cubic environment in *dhcp* *Pr* remain magnetically disordered, while cubic sites in *fcc*-*Pr* ordered ferromagnetically, is rather interesting. It seems clear that effects of the crystal structure on the conduction band play an important part and that one cannot argue simply from the proportion of cubic and hexagonal sites. How many layers of cubic sites are needed in order to induce long-range ferromagnetic order? What are the effects of alloying *Pr* with elements with strong magnetism, as *Sm*, on the cubic sites of the *dhcp* structure? One might expect two

transitions in such alloys, as one finds in $Pr-Nd$ (Bhoghosian and Coles, private communication). In the Pr -rich $Pr-Nd$ alloys a ferromagnetic component to the magnetization appears below the lower transition (Bhoghosian and Coles, also McEwen et al 1975). In $dhcp$ $Pr-Sm$ alloys it may therefore not be surprising to find a tendency towards ferromagnetic ordering, where cubic sites are involved.

APPENDIX 1

Magnetic ac-susceptibility of some intermetallic compounds

$PrAl_2$ compound

All rare earths combine with aluminium to produce $RAAl_2$ compound, and its crystalline structure is the cubic Laves phase structure. There have been extensive studies on the magnetic properties of these compounds by means of magnetization, heat capacity measurements and neutron diffraction techniques; see Wallace 1973 for a review. All $RAAl_2$ compounds (except *Ce* and *Eu*) have exhibited ferromagnetic ordering.

Heat capacity measurements of $PrAl_2$ and $NdAl_2$ are very similar; they do not show the simple λ -type behaviour, but a pronounced shoulder, Dennadas et al 1971 ($PrAl_2$ at 34 K and $NdAl_2$ at 65 K). The ac-susceptibility measurement of $PrAl_2$ is reported in Fig. A1. A very sharp peak characteristic of ferromagnetic ordering, is observed at 34 K. It may be noticed that this peak is found to be asymmetric, as the heat capacity measurements show. A superimposed dc-field of 32 Oe reduces the peak, but not drastically.

$PrNi_5$ and $NdNi_5$ Compounds

The crystalline structure of the RNi_5 compounds is the hexagonal type $CaCu_5$. Nesbit et al established that with $R = Pr, Sm$ and Yb the compounds remained paramagnetic down to 1.4 K, whereas with $R = Gd$ to Er ferromagnetic ordering occurred at temperatures between 10 and 25 K. For $NdNi_5$, magnetic

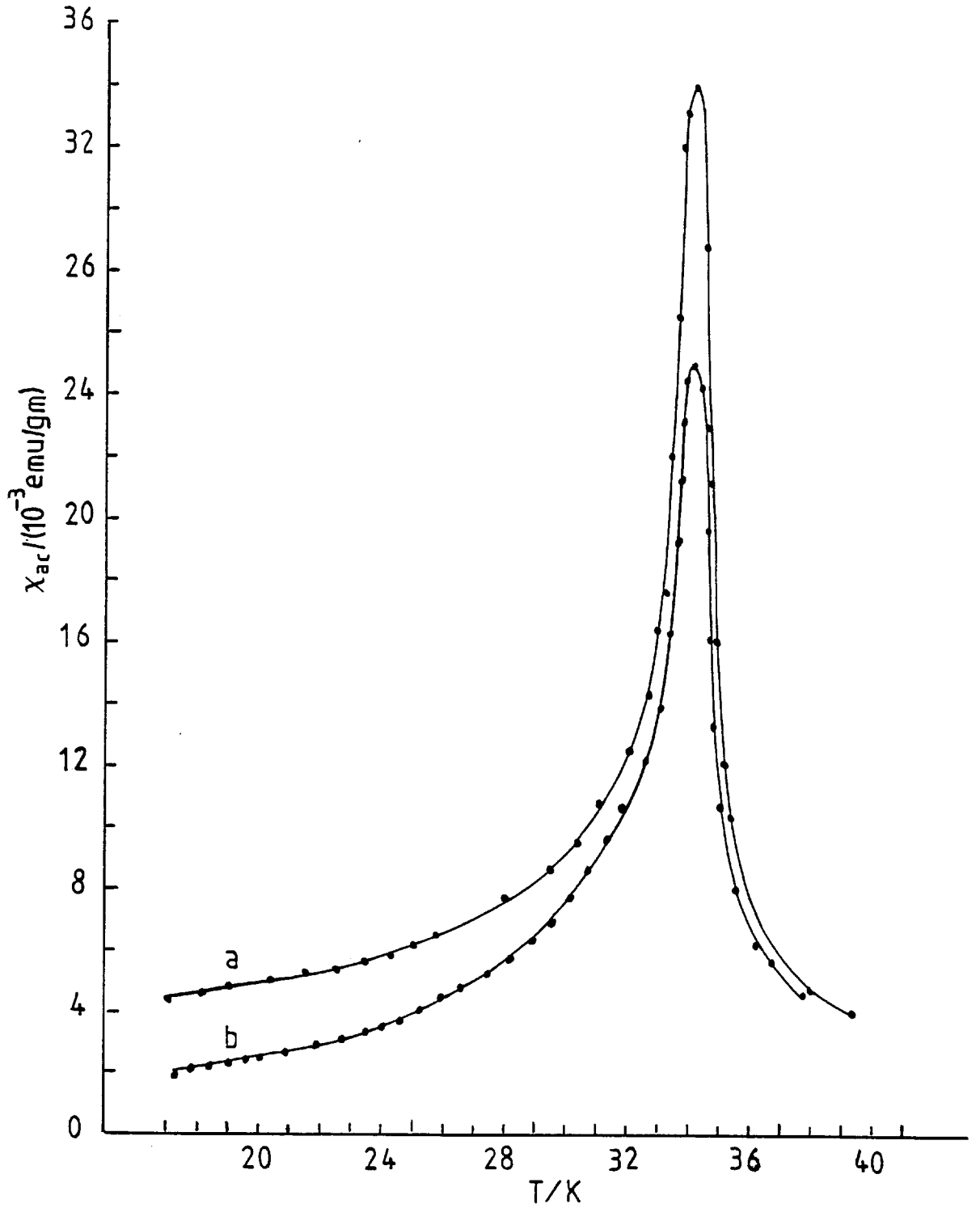


Fig.A1: Ac-susceptibility for the Pr Al_2 compound a) in zero field; and b) in a superimposed field of 32 Oe.

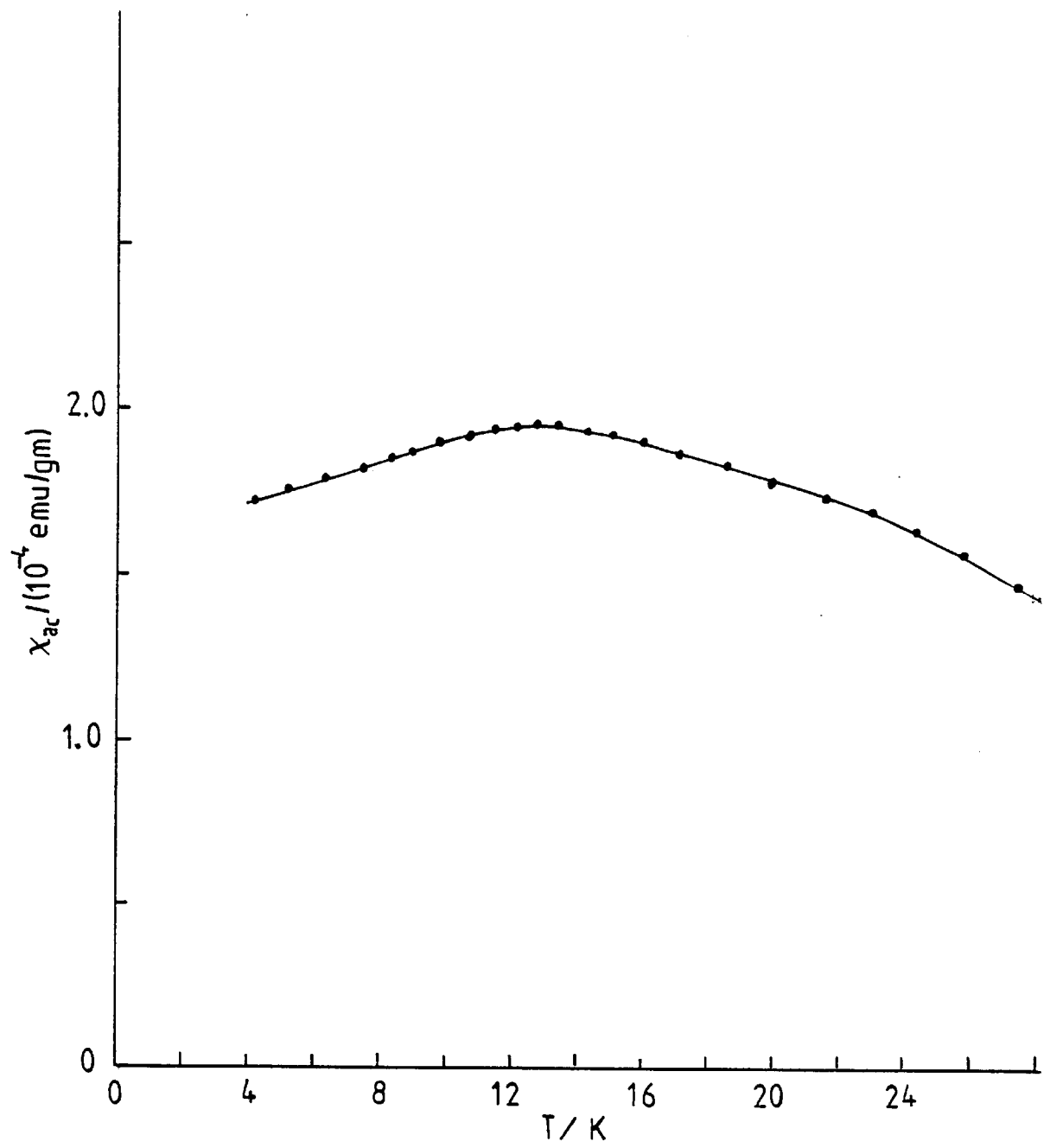


Fig.A2: Ac-susceptibility for the PrNi_5 compound.

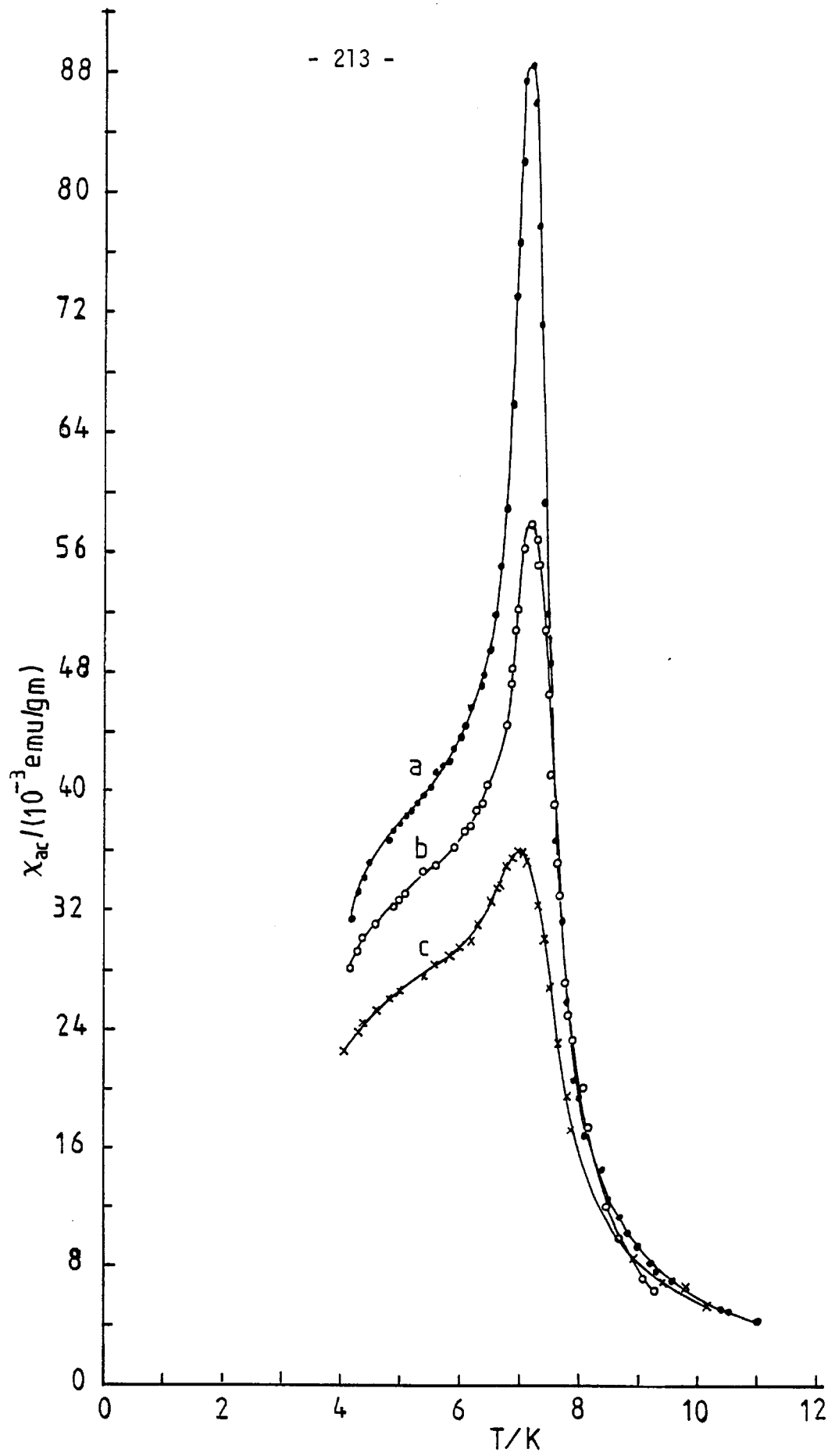


Fig.A3: Ac-susceptibility for the NdNi_5 compound a) in zero field; and b) in a superimposed field of 32 Oe; c) in a superimposed field of 160 Oe.

measurements at 20 kOe give a Curie temperature at 13 K. In contrast, the heat capacity (in zero field) exhibits a λ -type transition at 6.4 K. For $PrNi_5$, dc-susceptibility measurements show a rounded maximum at ~ 13 K, but heat capacity measurements failed to show a λ -type anomaly near 13 K, indicating that the susceptibility maximum does not correspond to a Néel point; see Wallace 1973. (Ni atoms seem to remain magnetically disordered).

The ac-susceptibility measurements of $PrNi_5$ and $NdNi_5$ compounds are reported in Figs. A2 and A3, respectively. $PrNi_5$ shows a rounded maximum at ~ 12.5 K, which suggests only a slight perturbation of the singlet character of Pr in the compound. In contrast $NdNi_5$ shows a very sharp peak at 7.1 K, which is greatly reduced by a superimposed dc-field of 160 Oe. This result coincides with the heat capacity measurement.

Conclusion

These compounds show nicely the effects of the crystal structure on the magnetic properties of Pr and Nd atoms. $PrAl_2$ and $NdAl_2$ manifest rather high ordering temperatures in the *fcc* matrix. The hexagonal $PrNi_5$ shows weak magnetism in contrast with the ferromagnetic behaviour of $NdNi_5$.

APPENDIX 2

Fitting of data points by a cubic spline

The E02 BCF computing program at the ICCC (Imperial College Computing Centre) was used in order to fit the data points of the electrical resistivity measurements. This program evaluates a weighted least-squares approximation to an arbitrary set of data points by a cubic spline and its first three derivatives; see Cox 1974.

A cubic spline consists of a set of cubic polynomial arcs joined end to end with continuity in value and in first and second derivative at each join (or knot). This degree of continuity is sufficient for most practical purposes. The positions of the knots are at the choice of the user. The curve-fitting process will consist of choosing the positions of a small number of knots, deriving the corresponding spline by means of the computing program, and testing it graphically against the data. Then increasing the number of knots in regions where the fit is inadequate and testing again. Too many knots can produce unwanted fluctuations. In general, more knots are needed where the behaviour of the curve is changing rapidly, and fewer where it is changing slowly. The exact positioning of the knots is not critical.

This program is very useful in applications which require the continuity to be less than the full continuity provided by the cubic spline. A discontinuous slope at some point, can be

obtained by placing three coincident knots at the given point. Similarly, a discontinuity in the second derivative at any point can be achieved, while maintaining continuity of slope, by placing two knots at the point.

For each set of data, knot positions were chosen initially in regions where the function or its derivatives change more rapidly than elsewhere. In all cases an attempt was made to improve the first fit by using more knots. Then, if the fitted curve was not good enough, additional knots were inserted in regions where the fit was inadequate. The chosen approximation was the one which was smooth and had residuals approaching the accuracy of the data.

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MAGNETIC ORDERING IN THE dhcp, Sm AND hcp STRUCTURES OF THE Pr-Y ALLOYS

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Measurements of electrical resistivity, low field ac susceptibility and higher field susceptibility have been used to study magnetic ordering in the Pr-Y system, and the magnetic behaviour has been correlated with X-ray diffraction indications of crystal structure. Susceptibility peaks have been observed for all three phases but the magnitudes and concentration dependences of the peak temperatures are distinctly different. In the phase with the Sm structure the peak temperature increases with decreasing Pr content. The effects of field cooling and the behaviour of the resistivity have been used to provide evidence about the character of the magnetic ordering.

1. Introduction

In the past fifteen years there has been a considerable effort [1-3] aimed at a better understanding of the magnetic properties of praseodymium, and its alloys. It is clear now that dhcp Pr has a singlet ground state and magnetic ordering occurs only if the exchange interaction exceeds a certain critical value [1]. It has been suggested that the kind of magnetic ordering [4] which appears in Pr-rare earth alloys depends on whether the added rare earth is light or heavy. dhcp Pr-Nd alloys exhibit long range order whereas dhcp Pr-Gd, Pr-Tb alloys behave as spin glasses. However, these alloys are complicated by the presence of both $J = L - S$ and $J = L + S$ moments and are not very suitable for studies of the effects on Pr of the changing crystalline structure at higher alloy concentrations.

It is of interest to study Pr-Y alloys because in these we may let Pr-atoms experience different environments corresponding to the sequence of crystal phases dhcp $\rightarrow$ Sm-type $\rightarrow$ hcp by adding Y, without the complications of producing this sequence by addition of moment bearing heavy rare-earths. As shown by previous work on Nd-Y [5], ac susceptibility measurements constitute a

convenient and sensitive way of exploring magnetic phase diagrams; and these have been supplemented by dc susceptibility and resistance measurements.

2. Methods and materials

Samples were prepared from pure metals (provided by Rare Earth Products) in an arc furnace, and annealed at 500°C for one week. Conventional potentiometric methods were used for resistivity measurements and the mutual inductance method for ac susceptibility measurements at a frequency of 240 Hz. The higher field susceptibility measurements were performed with a Faraday-type force balance using fields up to 330 Oe from an electromagnet; a few measurements were also made with this balance using a superconducting solenoid at up to 10 kOe.

3. Experimental results

At low temperature pure dhcp Pr shows the characteristics of a singlet ground state Van-Vleck paramagnet. Upon dilution with Y, the character of the susceptibility changes. For a 30% Y alloy, the data suggest that there would be a rounded maximum at about 1.5 K. Fig.1 shows a clear

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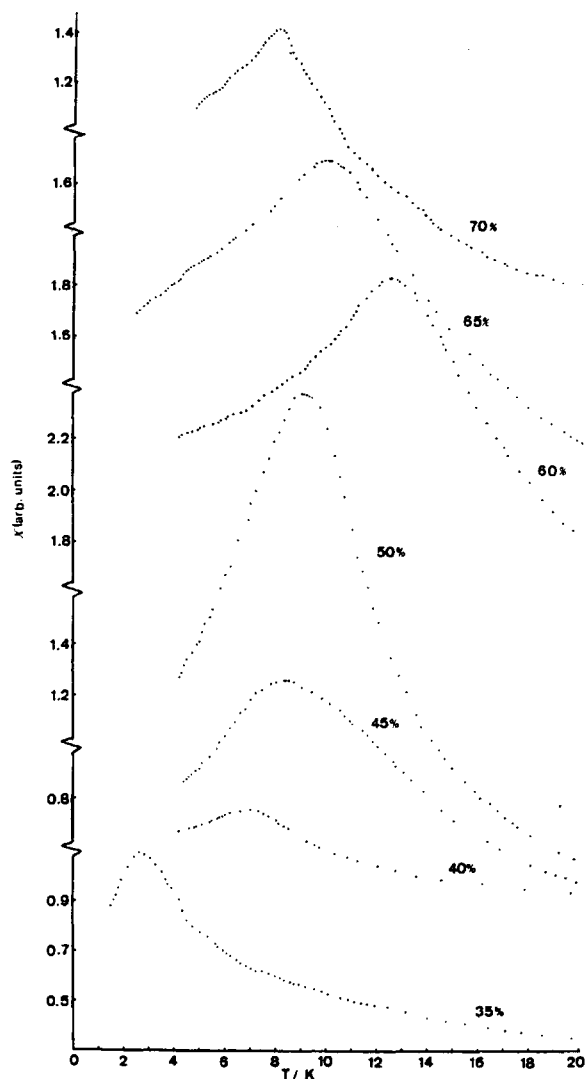


Fig. 1. Ac susceptibility plotted against temperature for alloys in the concentration range 35–70% Y. The vertical scale is the same (with shifted zero) for all curves.

dependence of a peak temperature in χ measurements as a function of Y concentration, and it is interesting to remark that in the range 35–50% Y, the peak shifts towards higher temperatures while the Pr content is decreasing. Comparison of the concentration dependence of the susceptibility peak temperatures in both as-cast and annealed samples, together with X-ray diffraction patterns, indicates ranges of composition (in annealed al-

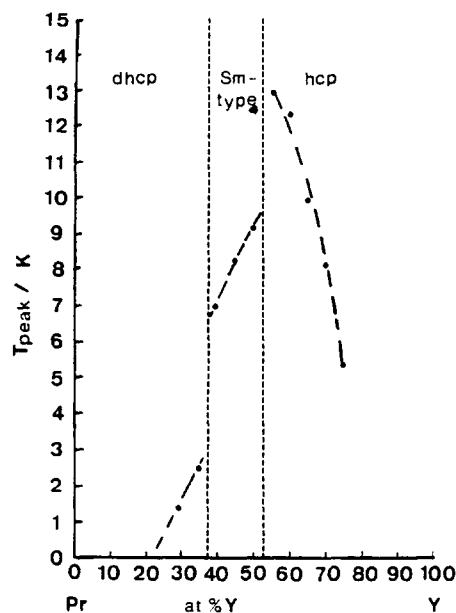


Fig. 2. Temperatures of susceptibility maxima in Pr-Y annealed alloys as a function of Y concentration.

loys) for the dhcp, Sm-type and hcp crystalline structure shown in fig. 2. Intervening two-phase regions, which should occur if normal phase equilibrium character exists, are not shown in this figure.

The important question of whether these peaks correspond to the onset of long-range order is not easy to answer unambiguously. Resistance curves (see fig. 3) do not, except perhaps in the 70% Y alloy, exhibit clearly anomalous behaviour near the peak temperature, whereas well-defined anomalies indicative of long-range antiferromagnetism have been found in Pr-Nd alloys [4,6], rather like those found in Y-Gd, Y-Tb alloys, where helical ordering takes over from spin glass behaviour with increasing solute content.

Fig. 4 shows the dc susceptibility measurements for the Pr-50% Y alloy, which we believe to be in the Sm-type structure, together with the ac susceptibility curve. The smearing of the χ peak due to relatively higher magnetic fields and the appearance of remanent magnetization when cooled

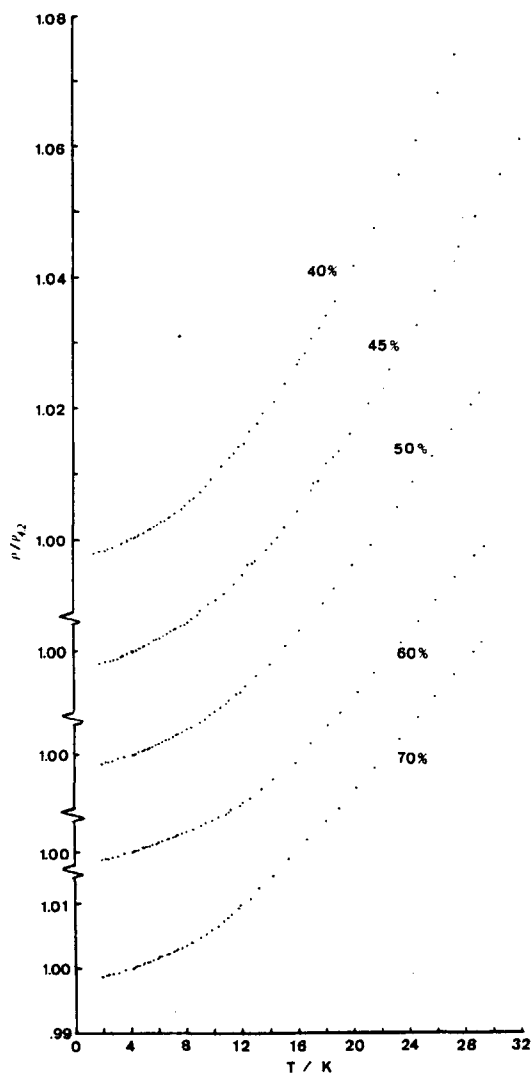


Fig. 3. Resistivity, normalized to resistivity at 4.2 K, plotted against temperature for alloys in the concentration range 40–70% Y. The vertical scale is the same (with shifted zero) for all curves.

in a magnetic field are characteristics of spin-glass freezing ordering. These effects also have been seen in Pr-Gd and Pr-Tb alloys.

However, we could not detect remanent magnetization or field cooling effects in the Pr-70% Y alloy, which is in the hcp structure, even after cooling it from high temperatures in a much higher field (5 kOe). Detailed investigations have not yet been carried out into the magnetic freezing character of the dhcp alloys.

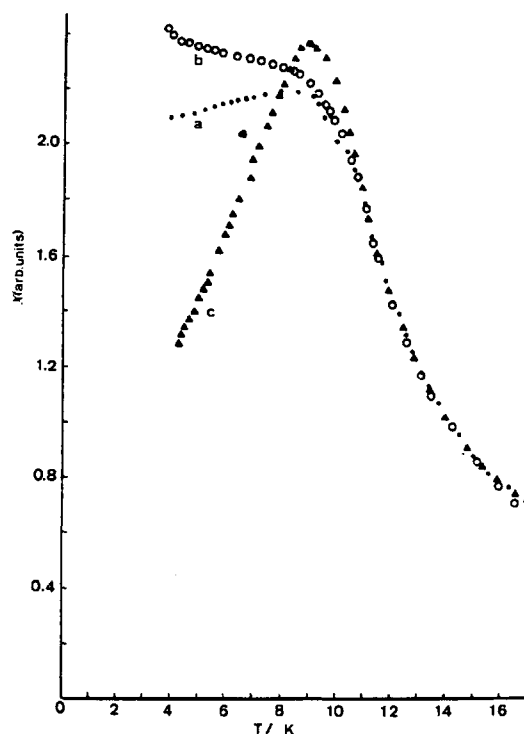


Fig. 4. DC susceptibility measurements plotted against temperature for the 50% Y alloy. (a) sample cooled in zero field; (b) sample cooled in a field of 160 Oe; and (c) ac susceptibility for comparison.

4. Discussion

It is interesting that χ measurements show clearly variations associated with changes of crystal structure, and help us to draw the crystalline sequence, already seen in fig. 2.

It is clear that the rather well isolated singlet character of pure Pr, which prevents zero field ordering above 1 K, is disturbed in the alloys with Y. In the more concentrated alloys in the hcp phase, it seems that long-range magnetic ordering takes place, as in hcp Nd-Y alloys where a single antiferromagnetic peak has been seen. The corresponding temperature increases rather rapidly with Pr concentration. It is interesting to note that the maximum value (~ 13 K at 60% Y) is lower than the maximum value in Nd-60% Y (~ 30 K) in about the ratio of the corresponding values of the quantity $(g_J - 1)^2 J(J + 1)$ which enters the

RKKY coupling interaction. This then suggests that the exchange interaction dominates the crystal field effects.

In the Sm structure phase the competition between exchange and crystal field effects has the rather striking result that the magnetic freezing has the characteristics of a spin glass instead of those of a long-range antiferromagnet. To understand these results, we need to consider the role played by the Y atoms as they enter the cubic and hexagonal sites of the various stacking sequences in the different crystalline structures, but we are not yet able to reach any firm conclusions.

In the dhcp structure alloying with Y clearly

perturbs the singlet ground state of Pr enough to lead to some type of magnetic freezing but its character is not yet clear.

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