

This thesis is dedicated to the memory of Caluste Gulbenkian.

STUDIES OF THE ONSET OF MAGNETIC ORDER IN
SOLID SOLUTION ALLOYS

Thesis submitted for the Degree of Doctor of Philosophy
in the University of London

by

Boghos Valodia Boghos SARKISSIAN

Physics Department
Imperial College of Science and Technology
London S.W.7

August 1975

Abstract

Magnetic phase diagrams of some solid solution alloy systems have been studied by electrical resistivity and magnetic susceptibility measurements. The resistance measurements were made using standard potentiometric techniques, and magnetization measurements by the force method using a high sensitivity Faraday apparatus.

The systems investigated were Pt-Mn, (Pt-Pd)-Mn, Ru-Fe, dilute Mo-Fe, Sc-rare earth and Y-rare earth (RE:Gd:Tb:Dy) solid solution alloys.

For the dilute Pt-Mn alloys the electrical resistivity due to Mn solute displays a positive logarithmic temperature dependence. However, interactions between the solute atoms result in a spin freezing (spin glass) which is indicated by a minimum in the resistivity vs. temperature curve. The temperature at which the minimum appears increases linearly with the Mn concentration; for alloys > 11 at% Mn the character of the resistivity undergoes further changes because of atomic short range order in this system.

(Pt-Pd)-Mn as a ternary alloy system has been studied to examine the effect of the local environment on the Mn solute by varying both (Pt-Pd) concentration as a host and Mn concentration as a solute. Addition of Pt to Pd seems more likely to depress the strong exchange enhancement of the Pd.

The iso-electronic alloy system Ru-Fe has been investigated for h.c.p alloys with Fe concentrations up to 70%. A T^2 temperature dependent contribution to the resistivity due to Fe solute has been found, the coefficient of which increases with Fe concentration up to a critical concentration at about 50 at% Fe, after which it falls steadily. Because of the similarity of this behaviour to that in the Pd-Ni, Rh-Co, Rh-Fe and Pt-Ni alloy systems we ascribe this to magnetic ordering.

Low temperature resistivity measurements on dilute Mo-Fe alloys show that

there is a gradual transition to a low temperature non-magnetic state. Application of l.s.f. theory to our results indicates a characteristic temperature T_{sf} of $1.5 \pm 0.2^\circ \text{K}$.

The Sc-RE and Y-RE solid solution alloys are of special interest as long-range helical magnetic ordering has been reported in these systems. The exact behaviour is unclear at low solute concentrations. New electrical resistivity and magnetic susceptibility measurements have been obtained and careful analysis of these data yields values for the critical concentrations for helical ordering which are in agreement with values obtained from other types of measurements, in particular with neutron diffraction data. Below these critical concentrations helical ordering does not exist and the magnetic character is that of a "spin glass" as in Cu-Mn and Au-Fe alloys. For non S-state solutes the behaviour at low concentrations will be complicated by crystal field effects. For the dilute Gd alloys the possibility of higher order magnetic scattering effects has been considered.

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ACKNOWLEDGMENTS

To my supervisor, Professor B.R. Coles, I would like to express my sincere gratitude for the interest, encouragement and personal guidance which he has shown through the course of this work. I am also greatly indebted to Dr. A.D. Caplin for advice concerning the dilution refrigerator and the microbalance.

I am grateful to Dr. H.E.N. Stone for his considerable help in the metallurgical aspects of this work and for careful reading of the manuscript.

I wish to thank Dr. N. Rivier and Dr. D. Sherrington for many valuable and stimulating discussions during this work. I am grateful to Dr. B. Southern for useful discussions and also for the theoretical calculations on the resistivities of dilute Sc-rare earths and Y-rare earths alloys.

In particular I should like to extend my thanks to Drs. B. Rainford, D. Griffiths, R.H. Taylor and C. Guy for helpful discussions and the latter for his help in using the V.S.M apparatus.

I am grateful to Dr. R.L. Rusby of the National Physics Laboratory for allowing me to use his He^3 resistance apparatus and Dr. Vaccarone for great help with the dilution refrigerator.

I am particularly indebted to L.K. Nicholson and M.H. Bennett for careful reading of the manuscript. I wish to thank Mr. Pon Wei Hou and Mr. S. Male for allowing me to quote their unpublished results and also Dr. A. Murani and Dr. A. Tari for useful discussions at the beginning of this work. I am also indebted to the whole of the Solid State group for their help and valuable discussions.

My particular thanks to Miss D. Eastwood for her efficient typing of the manuscript. I wish also to express my deepest gratitude to Miss M. Sarkissian for her help and encouragement throughout this work.

Finally, I wish to express my deepest gratitude to the Calouste Gulbenkian Foundation, Lisbon, for providing the financial support for this work and I respectfully dedicate this thesis to the memory of Calouste Gulbenkian.

INTRODUCTION

The main object of this work has been to further the understanding of the magnetic behaviour of what is called "magnetic glass or spin glass" alloys. The approach to this problem was made by dissolving well defined magnetic atoms in a non-magnetic host matrix. Within this limitation we have chosen the type of alloys where the presence of the solute element gives local moment effects even in very low solute concentrations and with significant interactions between potentially moment-bearing atoms or ions such as (a) 3d, e.g. Mn in Pt and Pd, (b) 4f, e.g. Gd, Tb, Dy in Y and Sc. By increasing the concentration of the dissolved magnetic impurities (where there is an extended range of solubility of the impurity), the indirect and (sometimes) direct interaction between impurities leads to various types of magnetic ordering; by such a study of ordering the magnetic phase diagrams of these systems and the properties associated with critical concentrations from one magnetic state to another may be studied.

Electrical resistivity measurements provide a good indication of the different sorts of magnetic ordering and the mechanisms involved in the interaction between these magnetic impurities both in the dilute and concentrated limits. Magnetic measurements also provide the detailed study of the magnetism. Both these measurements were involved in the study of the magnetic properties of these alloys.

In Chapters I and II, we summarize some of the theoretical aspects of the problem of "the local magnetic moment formation" and the "magnetic order" in alloys. In Chapter III we describe some of the experimental techniques which have been used in the experiments and the preparation of the alloys.

In Chapter IV, we present experimental results with discussions of the magnetic behaviour of Mn solute in the d-type hosts. In the first part we deal with

the Pt-Mn alloy system, which until now has been the subject of few investigations. Spin glass behaviour is characterized by a minimum in a plot of resistivity versus temperature. In the second part we show the effect of the electronic environment on the behaviour of this minimum by the use of a ternary (Pt-Pd)-Mn alloy. It is hoped that our measurements will lead to further understanding of this minimum where it is observed in other spin glasses.

In view of the rather confusing results of various types of measurements on the c.p.h (isoelectric) Ru-Fe alloy system, electrical sensitivity measurements have been made to study the magnetic ordering, since this method proved to be a very useful probe in other isoelectric systems; this is given in the first part of Chapter V. In contrast to the situation in the Ru-Fe system, iron dissolved in Mo carries a local moment although both are d-type, and therefore we have studied the low temperature magnetic behaviour of the latter by electrical resistivity measurements; this is given in the second part of this Chapter.

Finally, in Chapter VI, we present the magnetic properties of some solid solutions of some heavy rare-earths (Gd:Tb:Dy) in Sc and Y, where it is shown that there is a critical concentration for the long range antiferromagnetic helical ordering region. The theories developed for the rare-earth metals might apply to them. Below this critical region, the spin glass character provided by these rare-earth magnetic ions, in the absence of the crystal field effects, is also understandable in terms of the promising current concept of spin glass theories. We will also show the effects of the crystalline electric fields on the magnetic properties of these alloy systems.

CHAPTER I

Formation of local magnetic moments in metalsIntroduction

Considerable attention has been directed towards an understanding of the local magnetic moment formation problem in alloys, in which the impurity atom may retain its magnetic moment (1) (2). Associated with such local moments is the well known resistance minimum phenomenon.

Kondo (10) successfully explained the peculiar behaviour observed in the transport properties of many alloy systems. But his theory produced a divergence in the scattering amplitude of a conduction electron interacting with a localized magnetic moment via the s-d interaction. This was subjected to more exact many body calculations which have had some success in removing it, and have been described as a formation of a "singlet bound state" between the impurity spin and a compensating cloud of conduction electrons (4) (5) (32) (33) (34) (37) (45).

The Kondo divergence was successfully removed by the spin fluctuation theory (52) (53) (57) (59) (60) in which the low temperature non-magnetic behaviour is seen as truly characteristic of the impurities, while the high temperature paramagnetism gives a Curie-like behaviour to the susceptibility. This theory appears to give correct expression for most of the observed physical properties.

In this chapter, we will summarize some of these theoretical concepts which were involved in the fundamental problem of localized magnetic states in alloys.

1.1. Friedel-Anderson model and Hartree-Fock approximation (H-F)

When an atom with a partially filled shell is dissolved in a metallic host its energy levels in general stay within the conduction electron band, because the latter is so broad, as is pointed out by Friedel (1). The impurity state is not truly localized and it will be able to leak out into the conduction band state having the

same energy; this has been called the "virtual bound state" (VBS) which has an energy width Δ . In many cases a localized resonance state will occur in which the average number of $\underline{d}$ or $\underline{f}$ electrons localized at the impurity site with spin up $\langle n_{\underline{d} \text{ or } \underline{f}}^{\uparrow} \rangle$ is not equivalent to that of those with spin down $\langle n_{\underline{d} \text{ or } \underline{f}}^{\downarrow} \rangle$. Then a net localized moment will survive on the impurity cell, i.e. the exchange and correlation effects will split the VBS. If n is the number of electrons and ΔE is the gain in energy when an electron of spin up goes to a spin down state then a net localized moment will exist under the condition $n \Delta E > \Delta$. Friedel suggested that the scattering must be consistent with the overall electrical neutrality of the conductor, and derived the total screening charge Z arising from the perturbation due to placing a 3d atom in a non-magnetic host metal, related to the phase shift η_{l0} and the partial wave component of the free conduction electron state, as :

$$Z = \frac{2}{\pi} \sum (2l+1) \eta_{l0}(E_F) \quad 1.1.1.$$

$\eta_{l0}(E_F)$ being the phase shift at the Fermi level. The residual resistivity ρ_0 for a concentration X of impurities is :

$$\rho_0 = \frac{4\pi X}{P K_F} \sum l \sin^2(\eta_{l0} - \eta_{l-10}) E_F$$

where P is the valency of the host, K_F its Fermi wave vector, and $(2l+1)$ is the degeneracy of the state. This expression is strictly valid only for free electrons in a spherical potential. Completely neglecting the contribution of the other phase shifts except the resonance terms, then :

$$\rho_0 = \frac{4\pi X}{P K_F} (2l+1) (\sin^2 \eta_l + \sin^2 \eta_{l+1}) E_F$$

For the transition metal impurities, $l = 2$ ($2l+1 = 5$)⁺ and in terms of the

⁺ neglecting the crystal field splitting effect on five-fold degenerate d-electron state

average number of d - electrons, the residual resistivity can be written as :

$$\rho_o = \frac{4\pi\chi}{P K_F} 5 \left(\sin^2 \left(\frac{\pi \langle n_{d\uparrow} \rangle}{5} \right) + \sin^2 \left(\frac{\pi \langle n_{d\downarrow} \rangle}{5} \right) \right) \quad 1.1.2$$

This equation which predicts a residual resistivity should exhibit a double peak with a minimum in the middle, the two peaks are related to the virtual states with up and down spins crossing the Fermi level as the d levels get filled. The experimental results for alloys of 3d - impurities in Cu verify these conclusions quantitatively.

For non-magnetic impurities :

$$\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = N_d/2$$

and

$$\rho_o = \frac{4\pi\chi}{P K_F} 10 \sin^2 \left(\frac{\pi N_d}{10} \right) \quad 1.1.3$$

The residual resistivities given by equation (1.1.3) increases as one goes across the 3d series, and then decreases as the d level gets filled. This is observed experimentally in alloys of 3d - impurities in Al.

To put these ideas on a more quantitative basis, Anderson (2) and Wolff (3) described the theoretical concept of magnetic moment formation in alloys. They both used the VBS concept to explain the moment formation on Fe group ions in non-magnetic metals. Anderson assumed that the d - state of the Fe impurity is a localized d - orbital level in a sea of free electrons representing the conduction band of the host. The physical concept in Anderson's model is that the tendency towards magnetism naturally arises from the electron-electron Coulomb repulsion U between two electrons localized on the impurity atom.

Anderson used the Hamiltonian in the form

$$H = H_s + H_d + H_{sd} \quad 1.1.4$$

where H_s is the unperturbed conduction electron Hamiltonian of the host metal, H_d is the Hamiltonian of the isolated impurity cell, and H_{sd} is the s-d mixing interaction. Anderson assumed that the moment on the d-shell is given by the spin of localized electrons, and the orbital angular momentum is ignored. Within the H-F approximation, the density of state of the localized electrons is given by

$$n_{d\sigma}(\epsilon) = \frac{1}{\pi} \frac{\Delta}{(\epsilon - E_{d\sigma})^2 + \Delta^2} \quad 1.1.5$$

where $E_{d\sigma} = E + U \langle n_{d\sigma} \rangle \quad 1.1.7$

In the absence of crystal field effects, a factor $(2l+1)$ arises due to orbital degeneracy (Klein and Heeger (4)). σ is the spin of the d-state and $\Delta(\epsilon)$ is the half width of the virtual level which is given by :

$$\Delta(\epsilon) = \pi \bar{Y}^2 \rho_s(\epsilon) \quad 1.1.6$$

where $\rho_s(\epsilon)$ is the density of states of the conduction electrons at the Fermi surface. The number of electrons with spin orientation σ is given by :

$$\langle n_{d\sigma} \rangle = \frac{2l+1}{\pi} \cot^{-1} \left(\frac{E_{d\sigma} - E_F}{\Delta(E_F)} \right) \quad 1.1.7$$

Anderson introduces the dimensionless parameter $Y = U/\Delta$, the ratio of Coulomb integral to the width of virtual state. If Y is large a self-consistency argument yields a magnetic state; small Y corresponds to a non-magnetic state.

It is clear that the condition for the virtual level to possess a moment is determined by its position and width in comparison with the Coulomb energy. If it lies close to the Fermi level and is narrow relative to U it will be split by the Coulomb interaction and thus polarize, otherwise it remains unmagnetized,

i.e. the condition for localized moment formation depends on the position and width of the V.B. level which is proportional to the density of states.

Wolff approaches the problem as scattering of host band electrons from the impurity potential in which the scattering amplitude may show a resonance corresponding to the V.B. level of the impurity. He showed that the localized moment formation essentially arises from the electron-electron exchange potential at the impurity site. Hence, the basic mechanism in the Anderson and Wolff approaches is the same, the latter being more appropriate for d-impurities in d-hosts. (See the discussion by Rivier and Zitkova (6) of Rh-alloy data (7)).

For large values of Δ , equation (1.1.7) has a solution given by $\langle n_d^\uparrow \rangle = \langle n_d^\downarrow \rangle$, i.e. the impurity is non-magnetic [(4) (5)]. An Anderson model for $(2l+1)$ degenerate localized impurity orbitals (discussed by Anderson (2) and more fully by Heeger (4) (5)) gives a condition for the presence of a magnetic moment:

$$(U + 4J) \rho_{d\sigma}(E_F) = 1 \quad 1.1.8$$

where $\rho_{d\sigma}(E_F)$ is the added density of states per unit orbital. $(U+4J)$ is the parameter (for $l=2$) which determines whether or not the final state is magnetic. U and J are the Coulomb and exchange integrals respectively, between two electrons localized on impurity atoms in the metal. Hence the condition for the occurrence of magnetism is given in terms of Δ by

$$(U + 4J)/\pi\Delta = 1 \quad 1.1.9$$

The charge neutrality in the Anderson model has been discussed in (4) (5) and is consistent with the Friedel sum rule. Hence the number of localized electrons in the orbitally degenerate case ($l=2$) is found to be:

$$Z = 5 \sum_{\sigma} N_{\sigma} \quad 1.1.10$$

where N_{σ} is the total occupation number common to each of the virtual levels of a given spin σ .

1.2. Modification of the Hartree-Fock result by correlation

Schrieffer and Mattis (8) discussed the importance of the correlation energy in determining the ground state of the metal with an impurity atom. They showed that the hypothetical single d-orbital impurity is always magnetic if Coulomb repulsion is sufficiently strong because the interacting localized electrons change to an odd number of electrons having total spin of $\frac{1}{2}$, i.e. in the limit $U/\Delta \gg 1$, the spin up and spin down electrons become strongly correlated to avoid simultaneous occupancy of the localized levels. On the other hand they showed that, in the limit of a small fraction of an electron or hole on the impurity on average, the ground state exhibits no localized moment, because correlation effects beyond the Hartree-Fock approximation suppresses the moment formation. In addition they found that the ground state exhibits localized moments even in the low-density limit, provided that there are degenerate orbitals to be occupied (showing the importance of orbital degeneracy in magnetism).

In their calculation they expressed the effective Coulomb potential as :

$$U_{eff} = U \left[\left(1 + U/\pi\epsilon_d \right) \tan^{-1}(\epsilon_d/\Delta) \right]^{-1} \quad 1.2.1$$

where ϵ_d is the d-state resonance energy and Δ the VBS width.

Since

$$U_{eff} \rightarrow \tan^{-1}(\epsilon_d/\Delta)/\pi\epsilon_d \quad \text{as} \quad U \rightarrow \infty$$

and $\tan^{-1}(\epsilon_d/\Delta)/\pi\epsilon_d < \Delta$, then it is clear that very large U_{eff} is impossible. Even if it was possible for $U \rightarrow \infty$ no localized moment would occur.

A complete discussion by Schrieffer and Mattis for the suppression of moment

formation in the sense of the Anderson H-F approximation model is given in (9). By including correlation effects, they showed that in the low density limit the localized moment formation does not exist regardless of the value of U .

It is clear then that the H-F approximation is good only in the non-magnetic region, i.e. in the limit $U/\Delta < 1$. In the opposite limit, i.e. for $U/\Delta \gg 1$ the theory should start in an alternative manner since the H-F treatment overestimates the tendency towards magnetism. The large Coulomb interaction discourages the simultaneous occupation of the state by two electrons and it tends to keep, for example, the spin up on the impurity cell while the spin down electron is in the conduction band or vice-versa. Such on-off hopping suggests a non-degenerate ground state singlet which is non-magnetic [see (8) (5)]. Clearly the H-F approximation has limitations in the problem of the formation of moments in metals.

1.3 Resistance Minimum - Kondo effect

Kondo (10) was the first to show that the scattering of conduction electrons from a well defined localized impurity spin with a negative sign of the exchange interaction leads to a resistance minimum. This resistance minimum occurs whenever the impurity atom is magnetic, and it has been noted that this effect does not arise from the impurity-impurity interaction. Experimental evidence for this is the weak concentration dependence of the temperature of the minimum.

Sarachik (11) showed a strong connection between the appearance of the resistance minimum and existence of the temperature dependent susceptibility [(12) (13)]. Several good experimental reviews exist [(14) (15) (16)].

Kondo used the s-d exchange model with the assumption that the interaction of a moment of spin S with the conduction electron of spin s is

represented by a term in the Hamiltonian :

$$H = -JS.s \quad 1.3.1$$

where J is the strength of the exchange interaction. In terms of conduction electron creation and annihilation operators, the above equation can be written as:

$$H = -(1/2N) \sum_{kk'} [S_z (c_{k\uparrow} c_{k'\uparrow} - c_{k\downarrow} c_{k'\downarrow}) + (S_+ c_{k\downarrow} c_{k'\uparrow} + S_- c_{k\uparrow} c_{k'\downarrow})] \quad 1.3.2$$

where k, k' are the initial and final momenta of the scattered electrons, $S_{\pm}$ are raising and lowering operators for the components S , N is the number of impurity atoms in the crystal, and $J_{kk'} = J = \text{constant}$ for isotropic zero range δ -function potential (4). The transition probability of scattering a conduction electron from state k to k' via s-d interaction, using the first Born approximation is given by:

$$W_{kk'} = \frac{2\pi}{\hbar} (J/2N)^2 S_z^2 \delta(E_k - E_{k'})$$

with scattering amplitude $t_{kk'}^1 = -(J/2N) \delta_z$ which leads to a contribution to the resistivity given by [(17) (18)]:

$$\rho_m = \frac{2\pi N(0)/m}{2N\alpha\hbar} J^2 S(S+1) \quad 1.3.3$$

where $N(0)$ is the density of states of width $2D$.

By going beyond the first Born approximation in perturbation theory, Kondo showed that the spin contribution to electrical resistivity is of the form :

$$\rho_{spin} = c \rho_m \left(1 + 4JN(0) \log_e (K_B T/D) \right) \quad 1.3.4$$

where c is the concentration of the impurity, ρ_m is the first Born scattering term (equation 1.3.3). Thus if $J < 0$, i.e. antiferromagnetic coupling, ρ_{spin} represents a contribution to the resistivity which increases logarithmically as the temperature is decreased. By adding the lattice resistivity to the spin scattering

term one obtains a resistance minimum as a function of the temperature.

ρ_{spin} begins to diverge, as $T \rightarrow 0$, and dominates the impurity resistivity below a characteristic temperature called Kondo temperature (T_K), given by

$$KT_K = D e^{-N/IJN(0)} \quad 1.3.5$$

This is physically unacceptable because the resistivity must saturate at the unitarity limit. For 3d-transition impurities, this term is given by (19)

$$\rho_u = n_i \left(\frac{m}{X_e 2h \rho} \right) 2S \quad 1.3.6$$

and for free electron gas

$$\rho_u = 3.8 (2S) \mu\Omega \text{ cm/a\%}.$$

where S is the impurity spin, ρ is the host metal density, m is the electronic mass, n_i is the number of impurities and X is the electronic concentration.

This saturation behaviour was first seen in Cu-Fe (20) and Cu-Cr (21).

Experimentally, a variety of systems shows a logarithmic increase in resistivity with decreasing temperature.

The Kondo divergence appears in a variety of physical properties; we will consider magnetic susceptibility and specific heat. Thermo-electric power is considered in (22).

Magnetic susceptibility

Yosida and Okiji (23) have calculated the spin polarization of the conduction electrons due to the s-d exchange interaction and the magnitude of the localized spin by perturbation theory up to the fourth order in J , the exchange integral. They found that :

$$\sigma = \rho J / 2N$$

and

$$\langle S_z \rangle = \frac{g \mu_B S(S+1)H}{3kT} \left[1 + \frac{(JP)^2 \log_e(k_B T/D)}{1 - JP \log(k_B T/D)} \right]$$

and hence the magnetic susceptibility (4)

$$\chi(T) \approx \frac{g^2 \mu_B^2 S(S+1)}{3KT} \left[1 - \frac{J\rho}{1 - J\rho \log(K_B T/D)} \right] \quad 1.3.7$$

where ρ is the host density of states per atom and σ is the spin polarization of the conduction electrons. For the ferromagnetic interaction, $J > 0$, no singularity in the magnetic susceptibility is found in the whole temperature region, while for $J < 0$ (antiferromagnetic interaction) logarithmic divergence appears as the temperature is lowered to T_K . Scalapino (24) found that the magnetic susceptibility determined from s-d exchange interaction follows a Curie law behaviour at high temperature, and is given by :

$$\chi(T) = \chi_p + \frac{\mu_B^2}{KT} \left[1 + \frac{N(0)J}{1 - N(0)J \log(K_B T/D)} \right] \quad 1.3.8$$

where χ_p is the temperature independent conduction band contribution to the susceptibility. Equation (1.3.8) diverges at temperatures less than the Kondo temperature; at high temperatures, i.e. $T \gg T_K$ it reduces to

$$\chi(T) = \chi_p + \frac{\mu_B^2}{KT} \quad 1.3.9$$

which is simple Curie law behaviour. As extensions to these theories Miwa (25) used the same sort of perturbation theory and Giovannini et al (26) calculated the susceptibility for general values of the magnetic field. They showed that the high field magnetization at low temperature i.e. ($g \mu_B H \gg K T$) is given by :

$$M/H = \frac{g^2 \mu_B^2 S(S+1)}{3KT} H \left[1 + \frac{J\rho}{1 - J\rho \log(g \mu_B H/D)} \right] \quad 1.3.10$$

This equation becomes singular for the value of magnetic field:

$H_c = \frac{D}{2 \mu_B} e^{-1/N(0)J}$. The singularity is similar to the low field susceptibility except that it depends on $g \mu_B H$ instead of KT (i.e. the field rather than the temperature). However for intermediate values of $g \mu_B H$ there is different behaviour for different values of the temperature.

We can conclude from this that a high temperature Curie-Weiss law is consistent with the Kondo effect and the non-degenerate Anderson model for localized moments.

Specific heat

The study of the perturbation expansion of the free energy in zero external magnetic field has been done by Kondo (27). For $T > T_K$, he obtained the entropy change due to s-d interaction as :

$$\Delta S(T) = K \log_e (2s+1) + \frac{8/3 \pi^2 s(s+1) (J\rho)^3 K}{[1 - 2J\rho \log_e (K\beta T/D)]^3} \quad 1.3.11$$

where the first term, $K \log (2s+1)$, is temperature independent and is the entropy due to the $(2s+1)$ degree of freedom of the local spin. The second term is temperature dependent. For $J < 0$ it represents a decrease of the entropy, even at $T > T_K$, has a value less than the "free spin" value which is in quantitative agreement with Franks et al (28) data, while it diverges at a temperature $T_K = \frac{D}{K} e^{-1/N(0)J}$. For $J > 0$ the entropy is positive at all temperatures. The excess specific heat (4) is then given by :

$$\Delta C(T) = \pi^2 s(s+1) (J\rho)^4 K_\beta [1 - 4|J|\rho \log_e T] \quad 1.3.12$$

which implies that ΔC falls off logarithmically with increasing temperature.

1.4. The ground state of the magnetic impurity and $T < T_K$

We have shown that the Kondo divergence appears in a variety of physical properties, so the s-d model is limited to the logarithmic accuracy (29) (30) (31). A large theoretical activity has been based on Kondo divergency, and at this point we will refer to a few of the points that emerge.

Nagaoka (32) (33) showed that the divergence of the perturbation theory breaks down below a critical temperature near the Fermi surface. This is due to the formation of a quasi-bound state between the conduction electron spin and the localized moment spin, i.e. as the temperature becomes lower a quasi-bound state around the localized moment appears gradually below T_K . He also showed that at $T=0$ the electron scattering cross-section attains a maximum value of $4\pi/K_F^2$ for $l=0$. Hamann (34) used the same approach as Nagaoka and found that the electrical resistivity was of the form :

$$\Delta\rho = \frac{2\pi c}{ne^2 K_F} \left[1 - \log_e(T/T_K) \right] \left[\log_e^2(T/T_K) + S(S+1)\pi^2 \right]^{-1} \quad 1.4.1$$

when $T=T_K$, the resistivity temperature curve has an inflection point. In Hamann theory there is no place for a quasi-bound state at $T < T_K$. His calculations show that non-interacting impurities give no contribution to the specific heat, and the effective local moment entering the magnetic susceptibility is found to be cancelled at $T=0$ for spin $\frac{1}{2}$.

Suhl (35) and Abrikosov (36) discussed the Kondo divergency, and the two models have been shown to be closely related to that of Nagaoka (32) (37). Suhl and Wong (38) showed the important role of the influence of ordinary potential scattering from the impurity on the properties of the quasi-bound state. It has also been shown (26) (39) that the quasi-bound state can be broken up by applying a magnetic field greater than $H_c = \frac{KT_K}{\mu_B}$. The quasi-bound state is described as a polarization cloud built up in the conduction electron gas, tending to reduce the effective magnitude of the spin.

Mattis (40) proved that for antiferromagnetic coupling ($J < 0$) and impurity spin $\frac{1}{2}$, the ground state is a singlet. Zittartz (41) (42) used Nagoaka's equation to calculate the thermodynamic properties at $T < T_K$. They obtained the low temperature specific heat as:

$$\Delta C(T) = K_B \pi^2 S(S+1) / \log^4(T/T_K) \quad 1.4.2$$

Hence in the limit $T \rightarrow 0$, ΔC goes to zero asymptotically as $(\log T)^{-4}$.

Yosida (43) used the exchange model in a simple variational calculation to demonstrate that an impurity moment with spin $\frac{1}{2}$ plus the conduction electrons form a ground state singlet; whereas Heeger and Jensen (44) investigated such a ground state singlet by means of a many body variational calculation for ($J < 0$) s-d exchange interaction. Ishii and Yosida (45) obtained a constant zero-temperature susceptibility for a singlet bound state in the form $\chi \sim \mu_B^2 / K T_K$ where is the singlet ground state energy for $J < 0$ in the s-d exchange interaction. Ishii (46) showed that the behaviour of the singlet ground state energy in the applied magnetic field (H) is of the form:

$$\epsilon = \left((K T_K + \mu_B^2 H^2) \right)^{1/2} \quad 1.4.3$$

This equation represents the ground state energy for a state of lower energy than the free Fermi sea plus local spin energy. Kondo (47) expanded these theories to show that the usual susceptibility obtained at $T = 0$ in the singlet calculation (45) (46) can also be a property of the non-singlet model. In discussing the possibility of a singlet ground state Heeger (4) emphasized certain analogies with the superconducting ground state. He suggested that one can regard the Kondo divergence as the effect of an indirect electron-electron interaction via impurity spin, as follows. Electron 1 is

scattered by the impurity causing its spin to flip over. The scattering of electron 2, then depends on the fact that the previous scattering had taken place, i.e. the electrons interact indirectly. Such an excitation (indirect electron-electron interaction via intermediate local moment) leads to the onset of a many body condensed state for the impurity-conduction electron system below T_K . Heeger argued that evidence for the existence of this condensed state as $T \rightarrow 0$ is the resistivity of Cu-Fe, Au-V and Cu-Cr alloys.

1.5. The relation between the Anderson model and the exchange (Kondo) model

As mentioned earlier, the H-F self-consistent field approach is limited to arrange $U/\Delta < 1$ i.e. in the non-magnetic limit is a good approximation. In the magnetic region, $U/\Delta \gg 1$, Anderson and Clogston (48) argued that the V.B. level for spin up ($\uparrow$) is filled and below the Fermi energy, and for spin down ($\downarrow$) is empty and above the Fermi energy. Under these conditions, by lowering the energy of spin down ($\downarrow$) conduction electrons, using 2nd order perturbation theory, such that the spin down ($\downarrow$) has hopped on to the impurity cell at the same time as the spin ($\uparrow$), the energy shift was calculated to be:

$$V\epsilon_d = - V^2/U \quad \text{1.5.1}$$

This gives a negative conduction electron polarization, i.e. such mixing interaction lead to an anti-ferromagnetic interaction between the localized impurity and the conduction electron spin.

Schrieffer and Wolff (49) used a cononical transformation of the Anderson Hamiltonian in the limit $U/\Delta \gg 1$ to show that the relation between the Anderson model and the Kondo model can be expressed as:

$$J = \frac{2 |V_{kd}|^2 U}{\epsilon_d(\epsilon_d + U)} \quad \text{1.5.2}$$

Since $\epsilon_d < 0$ the coupling constant is negative, i.e. antiferromagnetic.

Schrieffer (50) showed that small changes in J may shift the Kondo temperature T_K so that alloys like Cu-Co and Au-Co, which have been considered to be non-magnetic on the Anderson H-F approximation characteristically have high T_K and large exchange coupling; alloys which look magnetic characteristically have low T_K with low exchange coupling and narrow (VBS) compared to the Coulomb interaction U . The appearance, and the disappearance of the local moments on a transition metal impurity in ternary alloys $[(13) (14) (15)]$ as the electron concentration of the matrix is varied, may be explained by the variation of T_K with the exchange coupling constant J - Schrieffer carried out a similar transformation in the case of an impurity with several d-orbitals. The relation between the two models is then expressed by :

$$J_m = - \frac{V_{km} V_{km}^*}{\epsilon_m(\epsilon_m + U)} \frac{1}{2S} = \frac{-|V|^2 U}{\epsilon_m(\epsilon_m + U)} \frac{1}{2S} \quad 1.5.2$$

where m is the quantum number of a singly occupied orbital, given by $m_1, m_2, \dots, m_{2l+1}$, and S is the spin of an isolated atom (given by Hunds rule).

In the absence of admixture, $J_m \rightarrow 0$

Schrieffer argued that a 3d-series impurity in an Al host, has very high T_K . The Schrieffer-Wolff transformation is carried out in the limit $U/\pi\Delta \gg 1$, i.e. the impurity spin must be well defined. Thus one has to expect an infinite Coulomb interaction energy U (see ref. (4) page 303) which causes difficulties. A second problem is that one still has to consider the divergence and ground state of the system, because the above transformation is related to the many body Hamiltonian, and

$$\log_e KT/\theta \rightarrow \infty \quad \text{as the temperature is lowered.}$$

1.6. Localized spin fluctuation (l.s.f.)

Friedel-Anderson theory predicts a sharp and unphysical boundary between the magnetic and non-magnetic ground states of the system, and is only

useful in the local moment formation problem when the system is far from the H-F instability. Experimentally a smooth boundary between the two regions has been observed (51). Hence one must expect that the existence of a moment is a time dependent. This consideration (dynamics) has been omitted in H-F theory.

Rivier and Zuckerman (52) (53) pointed out that localized spin fluctuation concepts (l.s.f.) are important for a temperature $T \ll T_K$. This overcomes the sharp and unphysical boundary between magnetic and non-magnetic states. They argued that l.s.f. is a multiple scattering, of the localized electron-hole pairs, i.e. repeated scattering between d-electrons of spin ($\uparrow$) occupying localized states of energy E at the impurity site, and corresponding holes with energy $E+U > E_F$ with a life time τ_{sf} given by $\tau_{sf} \gg (k_B T)^{-1}$. The dynamic susceptibility $\chi_d(\omega)$ is shown to be the form

$$\chi_d(\omega) = \frac{\chi_o(\omega)}{1 - U \chi_o(\omega)} \quad 1.6.1$$

where $\chi_o(\omega)$ is the local susceptibility in the absence of enhancement effects, which arise in the presence of Coulomb interaction between electrons. This exchange enhancement of the spin susceptibility was first discussed by Stoner (54) and was generalized to obtain the theory of paramagnon effects in metals with strongly enhanced susceptibility (55) (56).

Rivier (57) showed that equation (1.6.1) can be written as:

$$\chi_d(\omega) = \frac{1}{\pi} \frac{U^2}{\left(1/\tau_{sf}\right)^2 + \omega^2} \quad 1.6.2$$

where

$$1/\tau_{sf} = \frac{1 - U \rho_d}{\pi \rho_d}$$

and

$$\rho_d = \Delta \left(\pi \left(E_d^2 + \Delta^2 \right) \right)^{-1} \quad (\text{see equation 1.1.6})$$

It is clear that for $1/\tau_{sf} \ll 1$, one gets a sharper peak in $\chi_d(\omega)$ i.e. the

magnetization remains for a longer time. The mean spin fluctuation frequency $1/\tau_{sf}$ as a function of $\pi \Delta/U$ for the case of (VBI) at the Fermi energy is shown in Fig. 1.1.

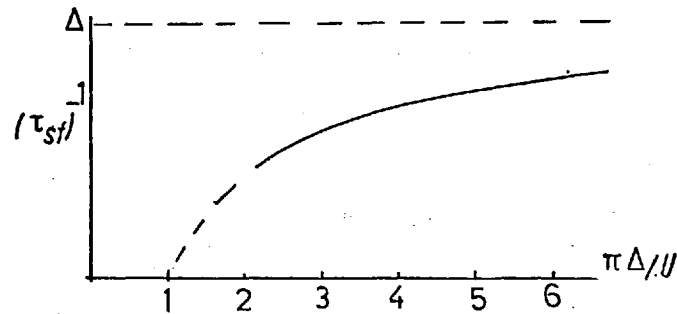


Fig. 1.1

It is clear from the curve, as $1/\tau_{sf} \rightarrow 0$ i.e. $\tau_{sf} \rightarrow \infty$, for $U/\pi\Delta < 1$ (in the H-F limit). Hence τ_{sf} is of order of Δ in the non-magnetic limit and increases as U/Δ increases and deviation occurs near the H-F instability condition.

Rivier and Zuckerman argued that the impurity appears experimentally to be magnetic only if the life time of the spin fluctuation, τ_{sf} , is long compared to the thermal fluctuation time, on the other hand if ;

$$K_B T \gg (\tau_{sf})^{-1}$$

the alloy has non-magnetic properties leading to a spin compensated state

(Nagaoka condensation which is based on a different approach, analogous to

I.s.f.). At high temperature i.e. $\tau_{sf} \gg (K_B T)^{-1}$ the spins appear to be long

lived and the moment will be established, since the spin fluctuations are slower

than the thermal fluctuations, and the system appears to be magnetic (Kondo type)

with a Kondo temperature obtained from spin fluctuation theory as:

$$K T_K^{sf} = (\tau_{sf})^{-1} \quad 1.6.3$$

From this the resistivity has been obtained in the form :

$$\rho = \rho_0 \left[1 - \left(T/T_K^{sf} \right)^2 \right] \quad 1.6.4$$

Before this theory was postulated, Caplin and Rizzuto (58) found that

the low temperature resistivity of Al-Mn and Al-Cr could be described by equation (1.7.8) with $T_K^{sf} \sim 530^\circ \text{K}$ for Al-Mn and $T_K^{sf} \sim 1200^\circ \text{K}$ for Al-Cr, which are in reasonable agreement with Rivier and Zuckerman's theory.

Rivier and Zlatić (59) have developed a universal curve for the resistivity behaviour in l.s.f. . In the case of Al-Mn the scattering leads to a finite resistivity at $T=0$; the temperature dependent resistivity initially decreases as $(1-AT^2)$, then as $(1-BT)$ and finally follows the logarithmic behaviour given by $(-c \log_e T)$. They also argued (60) that the l.s.f. mechanism in Rh-Fe and Al-Mn alloys is the same. In Rh-Fe the l.s.f. occurs in the d-band and the scattering of conduction electrons increases as l.s.f. excitations increase, while in Al-Mn the l.s.f. occur in a virtual bound state, but a conduction electron must first occupy the extra d-orbital before l.s.f. scattering can take place. In the case of Al-Mn and related alloys the phase shift is $\pi/2$, and the effect of the l.s.f. can only be to decrease the resistivity from its lower temperature resonance scattering value. The sign of the temperature dependence of the resistivity of Al-Mn is the opposite of that of Rh-Fe. A quite different mechanism from l.s.f. or paramagnons is introduced in the theory of nearly ferromagnetic metals and will be discussed in the next section.

1.7. Exchange enhanced Metals

The static susceptibility of pd is anomalously large, and it has been established it is strongly enhanced by short range intra-atomic Coulomb interaction between d-electrons. The exchange enhanced Pauli spin susceptibility was first discussed by Stoner (54) (61). The H-F theory indicates that the static susceptibility of the metal is larger than the Pauli free electron susceptibility by a factor $\left(1 - U_0 N(0)\right)^{-1}$, where $N(0)$ is the density of states at the Fermi

level and U_0 the intra-atomic Coulomb interaction between two electrons in the same impurity cell. The Stoner approach was extended [(55) (56)] to obtain the threshold instability of the ferromagnetic state, where the strong intra-atomic Coulomb interaction in the d-band leads to low-frequency fluctuations and large amplitude local fluctuations in the spin density of the d-electrons.

The consequences of the local perturbation in exchange enhanced metals has been connected with the problem of moment formation by Lederer and Mills (62), who discussed the effect of local spin fluctuations on the electrical resistivity of pd and pd-Ni alloys. They showed that the scattering of electrons by spin fluctuation gives a contribution to the electrical resistivity which is proportional to T^2 . At low temperatures the phonon resistivity is negligible, so one observes a very large spin fluctuation contribution of the form AT^2 [(63) (64)]. To describe the electrical resistivity of Pd-Ni and related alloys Lederer and Mills have taken into account only the change in the strength of intra-atomic Coulomb repulsion of the impurity (Ni in this case) and the system is described by the Hamiltonian :

$$H = T + U_0 \sum_i n_{i\uparrow} n_{i\downarrow} + \delta U n_0 \uparrow n_0 \downarrow \quad 1.7.1$$

where $n_{i\sigma}$ is the number operator for the creation and annihilation of electrons, T is the kinetic energy of the electrons and δU is the change in the intra-atomic Coulomb energy upon alloying the host with the impurity. They assumed a uniform host exchange enhancement locally at the impurity cell which increases the Coulomb interaction δU . The potential scattering effects are not included so that the model is applicable only to isoelectric systems like Pd-Ni, Pt-Ni, Rh-Co, Rh-Fe, Ru-Fe, Os-Fe etc. The local increase of the intra-atomic Coulomb potential enhances the susceptibility of the alloy around the impurity.

This was found to be of the form :

$$\Delta\chi(r, \omega) = \frac{\delta U \overline{\chi}_o(\omega)}{1 - \delta U \overline{\chi}_o(0, \omega)} \quad 1.7.2$$

where $\overline{\chi}_o(\omega) = \sum \chi_o(r, \omega)$ is the total host susceptibility and

$\chi_o(r, \omega)$ is the exchange enhanced r-dependent susceptibility function

which describes the response of the system at r to a perturbation at the origin. The fluctuations of the magnetization have locally a larger amplitude at low frequencies than in Pd which explains the increase in the T^2 coefficient, A, in Pd-Ni alloys and also the increase in the susceptibility of Pd upon alloying it with Ni. From equation (1.7.2) the spectral density $A(r, \omega)$ is given by :

$$A(r, \omega) = 2\text{Im} \chi(r, \omega) + 2c\delta U \left(\frac{\chi^2(r, \omega)}{1 - \delta U \chi(\omega)} \right) \quad 1.7.3$$

where the 2nd term is the spectral density of localized spin fluctuations due to impurities. Consequently Lederer and Mills found that

$$\chi^{-1} d\chi/dC = \delta U \overline{\chi}_s \alpha \quad 1.7.4$$

where $\alpha = (1 - \delta U \overline{\chi}_s)^{-1}$ and $\overline{\chi}_s$ is the static susceptibility of the host. They showed that when the local enhancement is large, i.e. $\alpha \gg 1$, $\chi^{-1} d\chi/dC$ is large. In the dilute Pd-Ni alloys $\chi^{-1} d\chi/dC \simeq 100$ from the data of Shattiel et al (65) and for Pt-Ni alloys $\chi^{-1} d\chi/dC \simeq 10-12$. Hence the difference between these two systems is due to the large value of $\overline{\chi}_s$ produced by a strong exchange enhancement of the Pd-host (66).

Extending Lederer's and Mills' calculations to high temperatures, Kaiser and Doniach (67) obtained a universal curve for the spin fluctuation resistivity in which the temperature dependence changes gradually from T^2 to T at a temperature of order $\frac{1}{4}$ the spin fluctuation temperature, T_{sf} . At high temperature the model predicts a significant decrease with temperature in the local exchange enhancement,

leading to a reduction of the scattering below the T low. They showed that the spin fluctuation temperature, T_{sf} , corresponds to the peak in the spectral density, $A(r, \omega)$, (see Lederer and Mills). Thus the transition from the T^2 to T behaviour in the resistivity produces direct measurements of $k_B T_{sf}$ which is the energy of the peak in the localized spin fluctuation excitation spectrum: Kaiser and Doniach obtained T_{sf} from resistivity data on dilute Ir-Fe and Rh-Fe alloys.

The analogy between the exchange enhanced and the local moment formation theory leads to an argument that is not one of moment formation approach but a gradual tendency towards the ferromagnetic instability. Hence one expects (see ref. (56)) that dX/dC decreases in magnitude when $T \gtrsim T_{sf}$.

1.8. Local moment formation in rare-earth metals and crystal field effects

1.8a Local moment formation

The discussion of local moment formation earlier is not directly applicable to the rare-earth ions. The unfilled 4f-shell has an average radius of roughly $0.4 \text{ \AA}$ and lies well within the 5s and 5p shells, so that the overlap between neighbouring 4f states is negligible, and the structure of the moment in the magnetic state is well defined. Thus the question of the Kondo effect for the rare-earth impurities in metals is quite interesting.

As mentioned earlier, the condition for the VB level to carry a moment is that it should lie close to the Fermi level. Band theory calculation for rare-earth metals have shown that the 4f state lies either well below or well above the Fermi energy, for example for Gd^{+++} (68) the 4f state is about 11 eV below Fermi energy. For Yb, however, there is some evidence that the full level is not far below the Fermi level (69), thus the local moment formation of rare-earth impurities in metals has received little attention.

Some experimental evidence, however, suggests that rare-earth shells demagnetize because of the near instability of a particular valence state [(70) (71) (72)], and fall into the (VBS) category. Hence an antiferromagnetic s-f exchange interaction leads to Kondo effects. The valence instabilities of 4f ions may appear at the beginning (Ce^{+++}), in the middle (Sm^{+++} , Eu^{+++}) and at the end (Tm^{++} Yb^{++}) of the Lanthanide series. YCe alloys show resistance minimum anomalies (73) with spin fluctuations resistivity $\rho = \rho_0(1 - (T/T_{sf})^2)$ on the non-magnetic side, $T < T_{sf}$. LaCe alloys (74) show $\log T$ behaviour in the resistivity in the magnetic region, $T > T_{sf}$. Yb shows Kondo effects when diluted in Au-Ag alloys (75) and Au -alloys (76). In other rare-earths, the direct ferromagnetic s-f exchange interaction leads to an increase in the gradient of the resistivity temperature curve (77).

1.8b Crystal field effects

As discussed earlier, Anderson, in his treatment of the localized magnetic state, pointed out that the orbital angular momentum of the d-state is quenched as a result of its interaction with the band electrons, so that only the spin angular momentum contributes to the moment. Yosida et al (78) showed that the crystal field splitting is less than the V.B. level; and Yafet [(79) (80)] has estimated the crystalline field splittings of various 3d-impurities in noble metals and finds them to be quite small.

The 4f-electrons behave like free ions, the ground state being given by Hund's rule. Hence the spin-orbital coupling is relatively strong. This couples the angular momenta $\vec{L}$ and $\vec{S}$ to give the total angular momentum, $\vec{J}$, and is larger than other interactions. Thus $\vec{J}$ is a good quantum number and only the lowest $\vec{J}$ multiplet is normally populated at room temperature. The effect of the crystal field is to lift the $(2J+1)$ degeneracy of the level and it splits by typically the order 100°K . The magnetic properties of the ion are given in terms of N non-

interacting ions and for the ground state multiplet the susceptibility is given by the Curie law :

$$\chi = \frac{N \mu_B^2 g^2 J(J+1)}{3 K T} \quad 1.8.1$$

If the next excited multiplet is of low energy, the crystal field modifies the free ion susceptibility, by a constant temperature independent term at low temperature is given by Van-Vleck (81).

The possible origin of the crystal field in the rare-earth salts is thought to be the electrostatic field. In the metals there is the further theoretical complication due to the screening of the electrostatic field by the conduction electrons.

A general treatment of the crystal field is that the symmetry of the array of charges around an ion produces an electrostatic field with potential energy given by :

$$V(\vec{r}) = \sum \frac{e Z}{|\vec{r} - \vec{R}|} \quad 1.8.2$$

for 4f-electrons where the overlap between the neighbouring ions is negligible.

Hence $V(r)$ is a solution of Laplace's equation and in terms of spherical harmonics it has the form :

$$V(r) = \sum_l \sum_{m=-l}^{m=+l} A_l^m r^l Y_l^m(r) \quad 1.8.3$$

For a point charge model A_l^m can be written :

$$A_l^m = \sum_j \left[\frac{4\pi}{2l+1} \right] Z_j / R_j^{l+1} \frac{1}{l!} Y_l^{-m}(\hat{R}_j) \quad 1.8.4$$

Thus it is necessary to calculate the matrix elements of the interaction, which are in the form $\langle 4f \rangle \sum V_l(r) |4f \rangle$ where the average of

$\sum V_l(r) = V_l^m$ is taken over the electrostatic states. The matrix elements for $l > 6$ will be zero. Using operator equivalents computational methods, one can evaluate the matrix of V_l^m between the states $|J, M_J\rangle$. This was originally introduced by Stevens (82), and obtained by substituting J_x, J_y, J_z for X, Y, Z . Some operators and their equivalents are given by $[(83) (84) (85)]$.

In terms of operator equivalent notation, the crystal field Hamiltonian has been written :

$$H_{cf} = \sum_{l,m} A_l^m \langle r^l \rangle O_l^m = \sum_{l,m} B_l^m O_l^m \quad 1.8.5$$

where B_l^m 's are related to the crystal field parameters,

For hexagonal crystal field symmetry :

$$H_{cf}^h = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 \quad 1.8.6$$

The B_2^0 term vanishes in the nearest neighbour point charge model, for c/a ratio equal to the ideal value for the hexagonally closed-packed (h.c.p.) lattice.

For cubic field symmetry :

$$H_{cf}^c = B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 + 21O_6^4) \quad 1.8.7$$

The splittings and degeneracies of the various levels and the lowest energy level structure are related to the angular momentum J , whether it has half integral ground states like Ce^{+++} or full J ground states like Pr^{+++} . Kramer's theorem (86) states that, for rare earths with half integral states, their energy levels in the absence of an external field will have an even-fold degeneracy, if the Hamiltonian which characterises the system is invariant under time reversal.

The effect of the external magnetic field H on the crystal field level is

to interact with the magnetic moments of the 4f-electrons to lift any remaining degeneracy in the level structure. So one has to take into account the interaction term given by $g \mu_B \vec{J} \cdot \vec{H}$

Several experimental techniques have been used to obtain information about crystal field effects. Inelastic neutron scattering measurements of the magnon dispersion relations give the most detailed information. Susceptibility, high field magnetization, Mossbauer and E.P.R. measurements can be understood and give details of crystal field effects.

Williams and Hirst (87) have measured the susceptibility of the dilute alloys of Ag and Au with heavy rare-earth impurities, and deduced that the fourth and sixth order crystal field parameters, B_4^0 B_6^0 have magnitudes too large to agree with the point charge model.

1.9. Effect of the crystal field on s-f exchange interaction Kondo effect

Elliott (88) applied spherical charge scattering to the case of one 4f-electron or hole to calculate the form of interaction between 4f-electrons (which are tightly bound to each atom) and the conduction electrons, using the conventional spin-spin s-f exchange Hamiltonian

$$-2J_{ex} \cdot s \cdot S_{4f} \quad 1.9.1$$

where J_{ex} is the interaction constant. Coqblin and Schrieffer (89) treated the inter-band mixing* between the conduction electrons and localized electrons. They started with the Anderson Hamiltonian for a state with total angular momentum J, it was then written in the form :

$$H = \sum_{k,\sigma} \epsilon_k n_{k\sigma} - \sum_{\substack{KK' \\ \sigma\sigma'}} J c_{K'\sigma'}^\dagger c_{K\sigma} + \left(c_\sigma^\dagger c_{\sigma'} - \delta_{\sigma\sigma'} \frac{1}{2} J + 1 \sum_{\sigma''} n_{\sigma''} \right) \quad 1.9.2$$

* In the case of a $4f^1$ electron or hole like Ce^{+++} Yb^{+++} . The $4f^n$ configuration ($n > 1$) has been treated in a different way by (90)

where ϵ_K is the energy of a conduction electron of wave number k , $c_{k\sigma}$ are the conduction electron creation operators in a state of wave vector k and spin σ and c_0 are the 4f electrons (holes) operator in a state of total angular momentum J with component σ .

Fulde and Peschel (91) calculated the electronic self energy of the conduction electrons, in the presence of crystalline field split impurities, for the case of two singlets. They showed that in the case of a non-magnetic ground state singlet well isolated from higher levels, the inelastic scattering will be small.

Hirst (92) calculated the resistivity due to s-f interaction in the dilute rare-earth alloys, using the interaction Hamiltonian in the form :

$$H_{sf} = V_c - 2(\lambda - 1) J_{ex} \cdot J_s \quad 1.9.3$$

where V_c is the spin independent Coulomb scattering term. The expression for the resistivity is obtained in the form :

$$\rho = CR (\lambda - 1)^2 \sum_{ij} e^{\delta_{ij}/KT} \frac{\delta_{ij}/KT}{e^{\delta_{ij}/KT} - 1} \frac{1}{2} \sum_i |\langle ij | \vec{J} \cdot \vec{S} | ij \rangle|^2 \quad 1.9.4$$

where

$$R = \frac{m^*}{2 N_v e^2} \frac{2\pi}{\hbar} N_E^1 (2 J_{ex})^2 \quad 1.9.5$$

m^* is the effective mass of the conduction electrons, N_v is the atomic density of the lattice in cm^{-3} , c is the concentration of the impurity and δ_{ij} is the energy difference of the core states. If $KT \gg \delta_{ij}$ then:

$$\rho = C_R (\lambda - 1)^2 J(J+1) / 4 \quad 1.9.6$$

Murani (93) fitted the resistivity data of dilute Au-Ho, Au-Dy alloys to the Hirst theoretical calculation by using level schemes obtained from the susceptibility results.

Coqblin (94) pointed out that the expression $-2J_{ex}(\lambda - 1) \vec{J} \cdot \vec{s}$ leads to confusing results in the case of Ce alloys which are the only ones that show a resistivity minimum. He also showed that the Coqblin-Schrieffer Hamiltonian⁺ (equation 1.9.2) is the best starting point for alloys like YCe which show the Kondo effect with crystalline field effects.

Maranzana (95) has treated the influence of the crystal field on the Kondo effect for the case of the CeAl_3 compound (96). He began with the Kondo Hamiltonian and found that the effect of the crystal field is to modify the Kondo minimum and cause a broad resonance peak in the resistivity-temperature curve at energies comparable to the crystal field splitting energies. Soda (97) used the Coqblin-Schrieffer Hamiltonian within the framework of the Nagaoka theory to calculate the effect of the crystalline field of the host on the s-f interaction. He argued that for small splitting, the resulting integral equation shows the Kondo effect with a Kondo temperature smaller than for no splitting; for a ground state doublet, the high levels produce a high Kondo temperature, while for ground state singlet no Kondo anomaly could be found. Blume et al (98) showed that for a particular case of anisotropic s-d exchange interaction, the partition function

⁺ since it takes into account combined spin and orbital exchange scattering.

for inelastic conduction electron scattering from a non-magnetic two level

impurity is equivalent to that of the Kondo problem. They showed that $J_{ex} = 2\delta$

where J_{ex} is the s-d exchange interaction with longitudinal exchange given

by $\frac{1}{2} J_{ex}^z \rho_z \sigma_z / N$ and transfer exchange given by $\frac{1}{2} J_{ex}^{\perp} (\rho_+ \sigma_- + \rho_- \sigma_+) / N$

ρ is the conduction electron spin density, σ is the impurity Pauli spin matrix and 2δ is impurity excitation energy.

CHAPTER II

Interaction between localized moments – onset of the magnetic order

Introduction

The theoretical concept which had evolved for describing the formation of magnetic moments in very dilute magnetic alloys neglects interactions between impurities, and it has recently been recognised that the impurity-impurity interaction exists even for very dilute random alloys. This leads to long-range oscillation spin polarization as the result of s-d or s-f exchange interactions between localized impurity spins and conduction electron spins. At low enough temperatures internal effective fields, which give rise to the interactions, lead to a certain type of magnetic ordering. In the absence of the onset of long range order the interactions modify the single impurity properties and there is considerable evidence of competition between simple magnetic ordering and the Kondo effect. Such a long range interaction suppresses the logarithmic divergence and can give rise to a resistance maximum or minimum. For high concentrations a direct interaction between neighbour impurities might be involved, to give short-range magnetic order.

From the time of the first suggestion that indirect magnetic coupling via the conduction electrons might be responsible for magnetic ordering in some metals long range ferromagnetic coupling has been observed in several dilute solid-solution alloys of the ferromagnetic transition elements in Pd and Pt. There has been considerable interest in the intrinsic magnetic properties of such systems, in which the magnetic impurities are relatively far apart.

The evidence for the localization of magnetic moments and for anomalous magnetic ordering in dilute solid solutions of Mn in Cu (117) focused interest on

these and related alloy systems in concentration ranges higher than those for which the idealized single impurity effect is observed. The name "spin glass" has been used to describe alloys having these magnetic properties (118)

11.1 Long range interaction between localized moments

Zener (99) showed that interaction between s and d electrons gives rise to a ferromagnetic alignment of the localized d-electron moments. In Zener's s-d interaction model, using 1st order perturbation theory, the exchange interaction is written as :

$$H = - J \vec{S} \cdot \vec{s} \quad 11.1.1$$

where S represents the localized d-spins, s represents spin of the conduction electrons and J is the exchange coupling constant.

Physically, the s-f interaction model is more appropriate for rare-earth metals and alloys where the magnetic moments are well characterized by the 4f-electrons.

Zener showed that a localized magnetic moment $\langle S_{nz} \rangle$ induces a uniform spin polarization $\langle S(r) \rangle$ in the conduction electron's states, this is given by

$$S(r) = J \rho \sum \langle S_{nz} \rangle \quad 11.1.2$$

where ρ is the density of state per atom per spin. Second order perturbation calculations in the s-d model have been done by Kasuya (100), Yosida (101), Ruderman and Kittel (102), who showed that the magnitude of the interaction is a function of distance between localized spins and is given by

$$J(|R_n - R_m|) = -2 \left(\frac{J^2}{N} \right) \left[\frac{P(\epsilon_F)}{4} \right] \sum H(q) e^{i \vec{q} \cdot \vec{R}}$$

where

$$H(q) = 1 + \left[\frac{4K_F^2 - q^2}{4K_F q} \right] \log \left[\frac{q + 2K_F}{q - 2K_F} \right]$$

These are called the Linhard functions. The final form $J(R) = J(R)$ (see ref. 27) is given by

$$J(R) = 6\pi z J^2 \rho \left[\cos^2 K_F R / (2 K_F R)^3 - \sin^2 K_F R / (2 K_F R)^4 \right] \quad \text{II.1.3}$$

where zN is the total number of conduction electrons, K_F is the electronic wave vector at the Fermi surface. Thus the interaction decreases as $1/R^3$ for large R , and the period is given by $(2 K_F)^{-1}$. This type of interaction has become known as the RKKY - interaction.

II.2 The spatial distribution of the screening charge

We have seen that perturbation calculations on s-d or s-f exchange Hamiltonian lead to a spin polarization $S(r)$ which is proportional to $\cos(2K_F \vec{r}/R^3)$ around the local moment. Blandin (103) showed that the effective interaction between impurities is given by

$$2 \propto E_F / \pi \cos 2K_F \vec{R} / (K_F R)^3 \vec{S}_1 \cdot \vec{S}_2 \quad \text{II.2.1}$$

where $\alpha = \eta_{\downarrow} / \epsilon_F + \pi - \eta_{\uparrow} / \epsilon_F$. Friedel's (1) spatial distribution of the excess charge $\Delta \rho(R)$ for large R exhibits long-range oscillations in terms of the phase shift η_l and electronic spin σ . this is given by :

$$\Delta \rho_{\sigma} = -K_F^3 / 4\pi^2 \sum_l (-1)^l / (2l+1) \sin \eta_{l\sigma} \cos(2K_F R + \eta_{l\sigma} / K_F R) \quad \text{II.2.2}$$

Equation (II.1.2) has been used to explain the NMR properties in Cu-Mn alloys.

Caroli et al (104) (105) discussed the magnetic coupling between impurities due to spin polarization, in the case of Cu-Mn alloys (where the VBS width $\Delta \gg TK_B \gg K_B T_K$). Within the effective exchange interaction energy $E_{int}(R) = -J(R) \vec{S}_1 \cdot \vec{S}_2$ it was found that for large values of R and degenerate d-orbitals the above relation may be written in the form

$$E_{int}(R) \approx E_F / 2\pi \sum_{\sigma\sigma'} \frac{(2l+1) \sin \eta_{l\sigma} \sin \eta_{l\sigma'}}{\sigma\sigma'} \cos(2K_F R + \delta_{l\sigma} + \delta_{l\sigma'}) \vec{S}_1 \cdot \vec{S}_2 \quad \text{III.2.3}$$

where $J(R)$

$$= \alpha \cos(12K_F R + \psi) / (K_F R)^3$$

α, ψ are constants depending on the phase shift $\eta_{l\sigma}$. The Caroli interaction provides a more effective coupling between the VBS than direct exchange when the separation between magnetic impurities is not sufficiently close for direct coupling.

II.3 Interactions between nearest neighbour atoms

The effect of the local influence of one impurity on another has been discussed by Alexander and Anderson (106) who calculated the interaction between two similar, closely situated non-degenerate magnetic impurities in a non-magnetic host. Within the H-F approximation, and applying Anderson Hamiltonian as in the single impurity case described earlier (see section I.1), U is the Coulomb repulsion between two electrons in a localized state and

$$V_{12} = \int \varphi_1^*(r) \varphi_2(r) H_d dr = V_{21}^*$$

is the transfer integral between the two d-states (i.e. direct coupling). The indirect interaction of the d-state with the band is given by

$$H_{sd} = \sum_{iK,\sigma} \left(V_{Ki} c_{K\sigma}^* a_i + V_{iK} a_i^* c_{K\sigma} \right) \quad \text{II.3.1}$$

Alexander and Anderson showed that the sign of the effective interaction between the moments depends on the VBS. If the VBS is symmetrical about the Fermi level, then the interaction is anti-ferromagnetic, however if one of the VBS levels is closer to the Fermi surface than the other, the interaction is ferromagnetic. They

argued that the anti-ferromagnetic effect required low density of the Fermi level because it is a kinetic exchange effect, i.e. it constitutes a gain in energy by virtual transfer of electrons from a full spin down level on the atom, to an empty spin down level, or vice versa.

Moriya (107) extended this theory to include the case of a pair of different atoms and showed that atoms with half filled d-shells always couple with each other antiferromagnetically regardless of the magnitude of their atomic magnetic moments. The change of the magnetic moment and the number of d-electrons due to d-d admixture is large only when the moment is small, this is true for non-degenerate and degenerate d-orbitals. In the degenerate case, for a fixed value of $U+4J$ the change in moments depends on J . The J -dependence is large when the VB levels are located asymmetrically about the Fermi surface, and the localized moment is small. Moriya also argued that the polarization of a non-magnetic atom when dissolved in a magnetic metal is due to the covalent admixture with neighbouring magnetic atoms.

II.4 Effective internal field-effect of the interactions on "Kondo" anomalies

For systems with interaction effects, such as dilute random alloys, Klein-Braut-Marshall (108) assumed the existence of indirect "Ising model" type interactions via the conduction electrons between the magnetic impurities. They defined the function $P(H)$ as the probability distribution of the effective field as seen by an impurity atom at a given origin. With two particle correlation approximations $\langle U_i \cdot U_j \rangle$ taken into account, they found the impurities to be strongly correlated with the moments at the origin. The impurities are concentrated within a critical radius of the origin given by

$$R_c = 0.5c^{-\frac{1}{3}} d$$

where d is the lattice constant and c is the fractional concentration. Impurities located outside R_c are uncorrelated and approximately randomly orientated, this implies that the field at the origin is the sum of two independent contributions with different probability distributions. The calculations of K-B-M lead to the idea that the solid is made up of small clusters of impurities (with an average of 3.3 impurities per cluster for Cu-Mn including the spin at the origin) which interact with each other via the RKKY potential. At low temperatures the impurities are strongly correlated with the spin at the origin within the cluster, and the effective spin per particle is less than the free ion spin. At high temperatures the cluster correlation decreases, which decreases the susceptibility and the internal structure of the cluster breaks up increasing the effective moment per impurity.

Liu (109) extended further the effective field distribution theory, the main difference between his theory and the K-B-M theory is that in the latter case it was concluded that the field distribution shifts to a higher value as the temperature increases, whereas in Liu's theory the most probable field becomes lower as the temperature increases. Both these theories assume that the local impurity moment obeys a Brillouin law, and examine the response of the bare local impurity moments to the effective fields to find the contribution to the specific heat. Both theories have some success in explaining experimental observations in Cu-Mn, Au-Fe, Ag-Mn and Cu-Co alloys.

Two magnetic impurities can couple at low temperatures to form a "correlated" pair due to interacting impurity spins. Beal-Monod (110) and Matho and Beal-Monod (111) calculated the Kondo type resistivity due to scattering of the conduction electrons by a pair of interacting magnetic impurities. The exchange energy for this process is given by

$$-W \vec{S}_1 \cdot \vec{S}_2$$

where $\vec{S}_1, \vec{S}_2$ represent the impurity spins. They deduced the spin part of the resistivity as :

$$R_s = R_u \left(\frac{\pi \epsilon}{2} \right)^2 \frac{S_{\text{eff}}^2}{\beta W} \begin{cases} 1 + \gamma \log T/T_0 + \gamma \log (T^2 + W^2)/T_0^{1/2} & W > 0 \text{ (F)} \\ 1 + 2\gamma \log (T^2 + W^2)/T_0^{1/2} & W < 0 \text{ (AF)} \end{cases}$$

where $\beta = (KT)^{-1}$, R_u is the unitarity limit of the resistivity per scattering wave. At low temperature for ferromagnetic (F) coupling they found that half of the Kondo divergence flattens off to a constant value, whereas for antiferromagnetic coupling (AF) no divergence was found at all. This is due to the shifting of the Kondo anomaly away from the Fermi surface. The major modification to the Kondo expression is through the effective spin amplitude, S_{eff}^2 such that

$$S_{\text{eff}}^2 / S(S+1) \rightarrow (S + 1/2) / (S + 1) \quad \beta W \rightarrow \infty \quad (\text{F coupling})$$

$$\rightarrow 1 \quad W \rightarrow 0 \quad (\text{no coupling})$$

$$\rightarrow 0 \quad -\beta W \rightarrow \infty \quad (\text{A.F. coupling})$$

The effective Kondo temperature for a pair, T_K , for both F and A.F. coupling was found to be lower than T_{K0} (Kondo temperature for isolated impurity), also for A.F. coupling with $W \geq KT_{K0}, T_K = 0$, i.e. the resistivity no longer diverges at $T=0$.

Matho-Beal-Mondo extended their approach to dilute random alloys, taking account of the coupling between pairs of interacting impurities. The total resistivity of a given random dilute alloy is described as the sum of contributions due to "isolated" and "coupled" impurity atoms. This resistivity which is found to be temperature and concentration dependent is given by :

$$\rho(c, T) - CR_v = NCR_o \left[1 - N_s(T)C/2 \right] \quad \text{II.4.1}$$

where R_0 is the isolated spin resistivity (Kondo resistivity) and $N_s(T) = 2W / KT$ is defined as the number of sites (super-thermal or impurity sites) having mean occupation given by $\bar{n}$, $N_s(T)$ shows that the coupling depends on temperature and breaks up when the temperature exceeds the coupling energy W . From the equation (II.4.1) it may be seen that at a given temperature the resistivity deviates from the ideal single impurity form $\log T$ temperature dependence, and becomes proportional to c^{-2} .

Experimentally, the absolute slope of the $\log T$ term decreases, when the impurity concentration increases (goes as c^{-1} at large c) whereas the slope of $\rho(T)/c$ against $\log T$ is concentration independent for isolated impurities. A maximum appears in $\rho(T)$ vs. T curve at a temperature which is proportional to the concentration, c , and below this temperature the resistivity decreases linearly with temperature [see ref. (16)]. Matho and Beal-Mondo were able to obtain a reasonable fit to the experimental data for ($C < 2000$ ppm) for Au-Mn, Cu-Mn, Ag-Mn, etc.

In alloys where no resistivity maximum appears at finite impurity concentration, there is a suppression of the Kondo slope at a certain temperature T (interaction temperature) which depends linearly on the impurity concentration. Star and Nieuwenhuys (112) showed that even for $cdT/dc \ll T_K$, the impurity-impurity interactions are still reflected in the resistivity. Star (113) has given an empirical rule that the concentration of the dilute alloys should be lower than T_K/T_F to be free of interaction effects (T_F is the Fermi Temperature). Suhl (114) attempted to explain the anomalous concentration dependence in the residual resistivity of Cu per unit concentration of magnetic impurity (115) (116) in terms of interactions between randomly distributed spins. He showed that there is a critical concentration, $c_{critical}$, below which the logarithmic behaviour diverges; this is given by :

$$c_{crit.} = K E_F / A J^2 S(S+1) \cdot T_K$$

where A is a constant of order unity, J is the exchange coupling constant, E_F is the Fermi energy, S is the impurity spin. The Kondo temperature is replaced by an effective temperature T_{eff} which is given by

$$\left(k_B T_{eff} \right)^2 = \left(k_B T_K \right)^2 + \left(CA J^2 S(S+1) / E_F \right)^2 \quad 11.4.2$$

where $AJ^2 S(S+1) / E_F$ is the width of the probability distribution of the random internal effective field.

11.5 Spin Glasses

The discovery of the unusual magnetic behaviour of Cu-Mn (117) alloys gave rise to considerable interest in "more concentrated" magnetic alloys where the concentration of localized magnetic impurities is larger than the well studied Kondo non interacting limit. The impurities in this new class of magnetic materials are randomly distributed at substitutional sites in the crystalline non-magnetic host. The name "spin glass" (118) is now used to describe such systems. The random distribution of impurities means that the interactions are random and thus no long-range order exists. The moments are frozen in random orientations as a result of the RKKY interaction between them.

Spin glasses exhibit unusual magnetic and transport properties. The initial static susceptibility has a broad maximum when measured at 1 KOe after cooling the sample to low temperature in zero field. On application of an external magnetic field thermal remanent moments are induced (i.e. the magnetization increases); this magnetization decays with time and temperature when the field is removed (117). Recently Cannella and Mydosh (119) discovered a cusp in low frequency a.c. susceptibility as a function of temperature for Au-Fe and Cu-Mn alloys in zero field at a temperature where the maximum in the static susceptibility is observed.

Above this temperature the susceptibility follows Curie-Weiss behaviour and sometimes superparamagnetic contributions are observed as a result of the strong d-d overlaps interaction which increases with increasing concentration. This is because for concentrations greater than a few % of solute there will be local regions where nearest neighbour atoms are grouped in clusters; such regions should then be treated as superparamagnetic clusters. There are however no basic changes in the properties of the alloy system, so that it may still be described as a spin glass (120) (121) or a "cluster glass".

The specific heat has a broad maximum at a temperature not necessarily equal to the maximum in the susceptibility. The low temperature specific heat is linear and concentration independent (122). This indicates that the entropy of a system with a bounded energy spectrum has been frozen in below the spin glass temperature (123).

The electrical resistivity of spin glasses increases monotonically as $T^{3/2}$ (124) (125) (126) at low temperatures and goes through an inflexion point, flattening out to reach the spin disorder limit at high temperatures. Definite correlation is observed between the "freezing" or ordering temperature and the temperature at which the maximum in $d\rho/dT$ occurs. In contrast to the behaviour of most spin glass alloys in which the resistivity increases monotonically with temperature, a minimum in resistivity (127) (128) has been observed in a number of spin glasses *. The temperature of the minimum increases with increasing concentration of solute as does the spin freezing temperature, but this temperature is not necessarily equal to the temperature of the maximum in susceptibility.

Rivier and Adkins (129) recently proposed a spin diffusion theory to describe the elementary excitation in spin glasses. These excitations are diffusion modes and

* The magnetic properties possess spin glass characteristics.

statistically independent and random. Any spin flip excitation on an impurity site is unable to propagate like a magnon (spin wave) but is damped with some diffusion constant Λ . The conduction electrons are scattered locally by such diffusion modes and this leads to a resistivity at low temperature of the form :

$$\rho \propto c \Lambda^{-3/2} T^{3/2} \quad \text{II.5.1}$$

i.e. the low temperature $T^{3/2}$ law follows from the nature of the elementary spin diffusion excitations in spin glasses.

Rivier (130) gave a theoretical justification for the origin of the minimum in spin glasses, on the same basis as the theory of Adkins and Rivier. He showed that the condition for a resistivity minimum to occur is $|V|/\Gamma > 1$ where V is the electrostatic potential due to the difference in the core charge of the host metal and the impurity atom; and Γ is the band width of the host. The conduction electrons are scattered by the elementary excitations of the spin glass and by an electrostatic potential $|V|$. At low temperature the resistivity has the form

$$\rho \propto c \left[1 - \text{const.} (T/\Lambda)^{3/2} \right] \quad \text{II.5.2}$$

where c is the concentration of the impurity. As $T_{\min.} \propto \Lambda(c)$ and $\Lambda \propto c^{4/5}$ then

$$\rho_0 - \rho_{\min.} \propto c \quad \text{II.5.3}$$

where ρ_0 is the resistivity at $T = 0$ and $\rho_{\min.}$ is the resistivity at $T = T_{\min.}$

Adkins and Rivier (131) showed that the generalized local molecular field theories account for the cusp in the magnetic susceptibility of a spin glass by defining a spin distribution $P(H)$ similar to that given by Klein-Brout-Marshall (108)

as discussed earlier. Other theories of the susceptibility cusp are currently a subject of mixed study.

11.6 Magnetic order in rare-earth metals and alloys

The magnetism in the rare-earth metals and their alloys can be described in terms of localised tripositive ions embedded in a sea of conduction electrons, with moments corresponding to the unfilled 4f-shell (given by Hunds rule). The difference in magnetic properties arises from the difference in the angular momentum state of the 4f shell. Different forms of ordered spin structure have been observed at both low and high temperature ranges.

The direct overlap between 4f-orbitals (ion cores) on neighbouring ions is negligible and the interaction between the ion cores then arises indirectly through the polarization of the conduction electrons. Such an interaction is often oscillatory and is long-range. This gives rise to a variety of periodic spin structure for rare-earth metals and alloys.

The equilibrium magnetic ordering can be described through phenomenological theory (132). The Hamiltonian for the system is the sum of exchange and anisotropy terms

$$H = H_{\text{iso. ex.}} + H_{\text{an.}} \quad 11.6.1$$

where

$$H_{\text{iso. ex.}} = - \sum_{i \neq j} J(R_i - R_j) S_i \cdot S_j \quad 11.6.2$$

where S_i and S_j are the spins at the lattice sites i , j , and $J(R_i - R_j)$ represent the exchange coupling between spins. The second term is given by

$$H_{\text{an.}} = H_{\text{an. ex.}} + H_{\text{cf.}} + H_{\text{ms.}} \quad 11.6.3$$

and depends on the orbital contribution to the ionic moments. $H_{\text{an. ex.}}$ is the anisotropy exchange resulting from non-sphericity of a 4f wave function at finite radius. H_{sf} is the anisotropy energy of the unstrained crystal lattice. H_{ms} is due to the magnetostriction effects of single ion and double ion contributions, which arise from modulation by the strain of the crystal field and anisotropic exchange interaction.

Simple helical spin ordering at $T = 0$ has been discussed by Nagamiya (133) in great detail. It was shown that for a general elliptic helical ordering of spins written in terms of components as :

$$\begin{aligned} S_{nX} &= A \cos (Q \cdot R_n + \alpha) \\ S_{nY} &= B \cos (Q \cdot R_n + \beta) \\ S_{nZ} &= C \cos (Q \cdot R_n + \gamma) \end{aligned} \quad \text{II.6.4}$$

where Q is the wave vector of the helical spin structure, and $(A, B, C, \alpha, \beta, \gamma)$ are arbitrary constants. Nagamiya pointed out that the magnetic periodicity is incommensurate with the lattice periodicity since the magnitude of the wave vector Q is determined by the exchange coefficient.

Nagamiya calculated the Neel temperature within the Weiss molecular field theory in the form

$$T_N = S(S+1) / 3K \quad 2 J(Q) \quad \text{II.6.5}$$

where $J(Q)$ is the exchange coupling between two spins, for maximum and positive $J(Q)$; the magnetisation M is given by

$$M = B_S [2J(Q) / S^2] M / K T \quad \text{II.6.6}$$

where B_S is the Brillouin function.

At high temperatures (above Neel temperature) $Q = 0$, then

$$M = \left[\frac{S(S+1)}{3KT} \right] \left[\lambda \mu_B H S + 2J(Q) \right] S^2 M \quad \text{II.6.7}$$

where λ is the spectroscopic splitting factor, $\mu_B = 2\hbar/2mc$ is the Bohr magneton, and H is the external field. The volume susceptibility then closely approximates to the Curie-Weiss law :

$$\chi = \frac{(\lambda \mu_B)^2 S(S+1)}{3K(T-\theta)} \quad \text{II.6.8}$$

with the paramagnetic Curie - temperature

$$\theta = 2 \left[\frac{S(S+1)}{3K} \right] J(Q) \quad \text{II.6.9}$$

Nagamiya considered an anisotropy energy with uniaxial symmetry giving rise to an easy axis of spin orientation. The simplest form of anisotropy energy ($W(S_Z)$) originates from one atom (a single ion) in the crystalline electric field along the z-axis and has been written in the form

$$W(S_Z) = D \left[S_Z^2 - \frac{1}{3} S(S+1) \right] \quad \text{II.6.10}$$

when $S = \frac{1}{2}$, $W(S_Z) \rightarrow 0$.

Within the Weiss molecular field approximation, for the longitudinal component, the Neel temperature for $J(Q)$ maximum was found to be :

$$KT_N = 2J(Q) \left[\frac{T_r S_z^2 e^{-W(S_Z)/KT_N}}{T_r e^{-W(S_Z)/KT_N}} \right] \quad \text{II.6.11}$$

This equation shows the effect of the anisotropy on the ordering temperature. The anisotropy hence may suppress or enhance the magnetic ordering temperature,

depending on the sign of the anisotropy and its strength relative to that of the exchange term, it also depends on the total angular momentum J (whether it is half or full integral). This work has been reviewed by Elliott (134), Kasuya (135) and Cooper (136).

If the ion has orbital angular momentum, then the state of the rare earth ion is specified by its total angular momentum J . It can be argued that it is the component of S along J that matters in the conduction electrons core exchange interaction (137) (138), in which case the spin may be replaced by :

$$S = (\lambda - 1) J$$

where λ is the Landé factor. The factor $(\lambda - 1)$ is negative for the light series and positive for the heavy series. Thus equation (II.6.2) can be written in the form :

$$H_{iso. ex.} = - \sum_{i \neq j} (\lambda - 1)^2 J_i \cdot J_j \quad \text{II.6.12}$$

The expression $(\lambda - 1)^2 J(J + 1)$ occurs in many of the discussions of rare-earth metals and alloys, and is often referred to as the de Gennes parameter.

II.7 Magnetic superzone energy gaps - contribution to resistivity anomalies

When a helical spin magnetic order sets in, the conduction electrons see a new periodic exchange potential with a periodicity which is different from that of the crystal lattice. Consequently, the structure of the conduction band will be changed, new boundaries of energy discontinuity in reciprocal space will be introduced which are known as superzone boundaries. Using a free electron model and the molecular field approximation, Miwa (139) showed that the magnitude of the energy gap for sinusoidal oscillation with amplitude $S_Z(T)$ along the c-axis is given (like E_r) by

$$\Delta(g \pm Q) = J(g \pm Q) S_Z(T) F(G) \quad \text{II.7.1}$$

$F(G)$ is the structure factor (summed over n atomic sites in a unit cell in real space), G is the reciprocal lattice vector. For certain values of G , $F(G) = 0$ and associated gaps vanish.

The effect of the gap is to reduce the effective number of electrons for conductivity in a direction perpendicular to the plane of the gap. Mackintosh (140) and Miwa (139) have discussed the effect of such new boundaries on resistivity anomalies observed for the rare-earth below the ordering temperature. Elliott and Wedgwood (141) used a simple theory, which includes spin disorder scattering and the effect of the gaps on a spheroidal Fermi surface, in order to calculate the anomalous resistivities of heavy rare-earth metals (for single crystals). They showed that the electrical resistivity along the hexagonal z-axis will have a maximum below the ordering temperature given by

$$\rho_z = \frac{\alpha + \beta T + \gamma(1 - 1/2 M^2 - \dot{M}^2)}{1 - \Gamma(M^2 + \dot{M}^2)} \quad \text{II.7.2}$$

where α , β , γ are adjustable parameters, M , $\dot{M}$ are the magnetization in

the axial and basal plane directions respectively, and

$$\Gamma = (3\pi J_{sf} J) / 4 E_F K_F \sum l_i \quad 11.7.3$$

where J_{sf} is the effective exchange interaction between the conduction electrons and the ion with angular momentum J , and l_i represents the position of the magnetic superzone planes and is given by

$$l_i = \frac{1}{2}(G \pm Q)$$

Hence the resistivity of alloys can sometimes indicate the character of the magnetic ordering.

11.8 Spin wave gap

At low temperatures great information will be obtained from the dispersion relations of the spin wave excitations. Niira (142) derived an expression for the temperature dependence of the departure of the magnetization from the saturation value at 0°K for ferromagnetic crystals

$$M(T) - M(0) = A T^{3/2} e^{-\Delta/KT} \quad 11.8.1$$

where A is a constant which depends upon the magnetic properties of the crystal, Δ is the anisotropy energy gap which represents the minimum energy required to excite a spin wave. Experimentally the value found for the spin wave gap $\Delta/K = 20^\circ\text{K}$ for Tb and Dy which is in accord with direct observation by inelastic neutron scattering experiments.

The anisotropy gap also manifests itself at low temperatures in other properties, such as specific heat, resistivity. Mannari (143) has calculated that a spin wave energy proportional to q^2 (q being the spin wave vector) will lead to a resistivity proportional to T^2 for ferromagnets and T^4 for antiferromagnets. Mackintosh (144) showed that for anisotropic ferromagnets the resistivity may be written as

$$\rho_m = C T^2 e^{-\Delta/KT} \quad 11.8.2$$

where C is a constant. For magnetically ordered spiral spin structures as in Ho, Er where the resistivity is proportional to the T^4 , again an activation energy will be introduced by the anisotropy and the resistivity will be modified to

$$\rho_m = C T^4 e^{-\Delta/KT} \quad 11.8.3$$

Experimentally there is little evidence to support this relation.

11.9 Induced moment systems and the singlet ground state

The crystal field acts as a perturbation upon the ordered state and modifies the magnetic behaviour of rare earth ions. For materials for which the exchange and crystal field energies are comparable, the relative strength determines whether the ground state is magnetic or not.

In non-interacting systems where the ground state is a singlet, the effect of the applied field is to induce Van Vleck susceptibility. Within the molecular field approximation Bleaney (145) pointed out that the effect of the exchange is to polarize the ground state singlet (i.e. non-Kramers state) wave function when the lowest crystal field level is a non-magnetic singlet and the first excited state is also a singlet. The resulting inverse susceptibility is given by

$$(\chi)^{-1} = (\chi_{cf})^{-1} - A \quad 11.9.1$$

where χ_{cf} is the susceptibility of the non-interacting ion due to crystal field effects, and A is the molecular field constant. The effect of the exchange is to shift the inverse susceptibility curve vertically upwards for antiferromagnetic exchange, and downwards for ferromagnetic exchange. Bleaney showed that, at 0°K , there is a threshold value for A for the magnetic ordering.

The induced moment system has been treated also by collective excitation theory by Trammell (146), Cooper (147) and Wang and Cooper (148). Fulde and

Peschel (91) discussed the effect of the conduction electrons which mediate the interaction between the magnetic ions.

CHAPTER III

Apparatus and experimental methods

Introduction

The electrical resistivity measurements on alloys from a series of systems reported in this work were made in a cryostat originally constructed by Bellau (149), but subsequently rebuilt with some modification by Tari (150). The magnetic measurements were made with high sensitivity Faraday microbalance apparatus ($\pm 1 \mu\text{g}$ force and maximum field of 50KG) described in detail by Bell (151). The magnetic measurements on a Pt 15% Mn sample have been done with a vibrating sample magnetometer (VSM) originally built by Murani (152).

Low temperature resistivity measurements of some Pt-Mn (0.5% and 3% Mn) alloys and dilute Mo-Fe alloys have been done in $\text{He}^3\text{-He}^4$ dilution refrigerator constructed by Oxford Instrument Company. Temperatures of down to 0.03°K were obtainable. Resistivity measurements below 1.5°K on Pt 0.09% Mn, Pt 0.3% Mn and Pt-1% Mn have been done in a He^3 cryostat (153) at NPL.

No descriptions will be given of the Faraday apparatus and VSM as these have already been described in detail by ref. (151) (152).

The dilution refrigerator will be described only briefly since it does not contribute to the major part of this work. Electrical resistivity apparatus will be described briefly also; minor modifications have been made since the beginning of this work.

III.1 Electrical resistivity apparatus

III.1.1 The Cryostat

The cryostat consists of a two concentric double glass tubes arrangement (Fig. III.1a) with an isothermal sample chamber which is capable of housing up to four samples. The samples are positioned in a symmetrical fashion around a

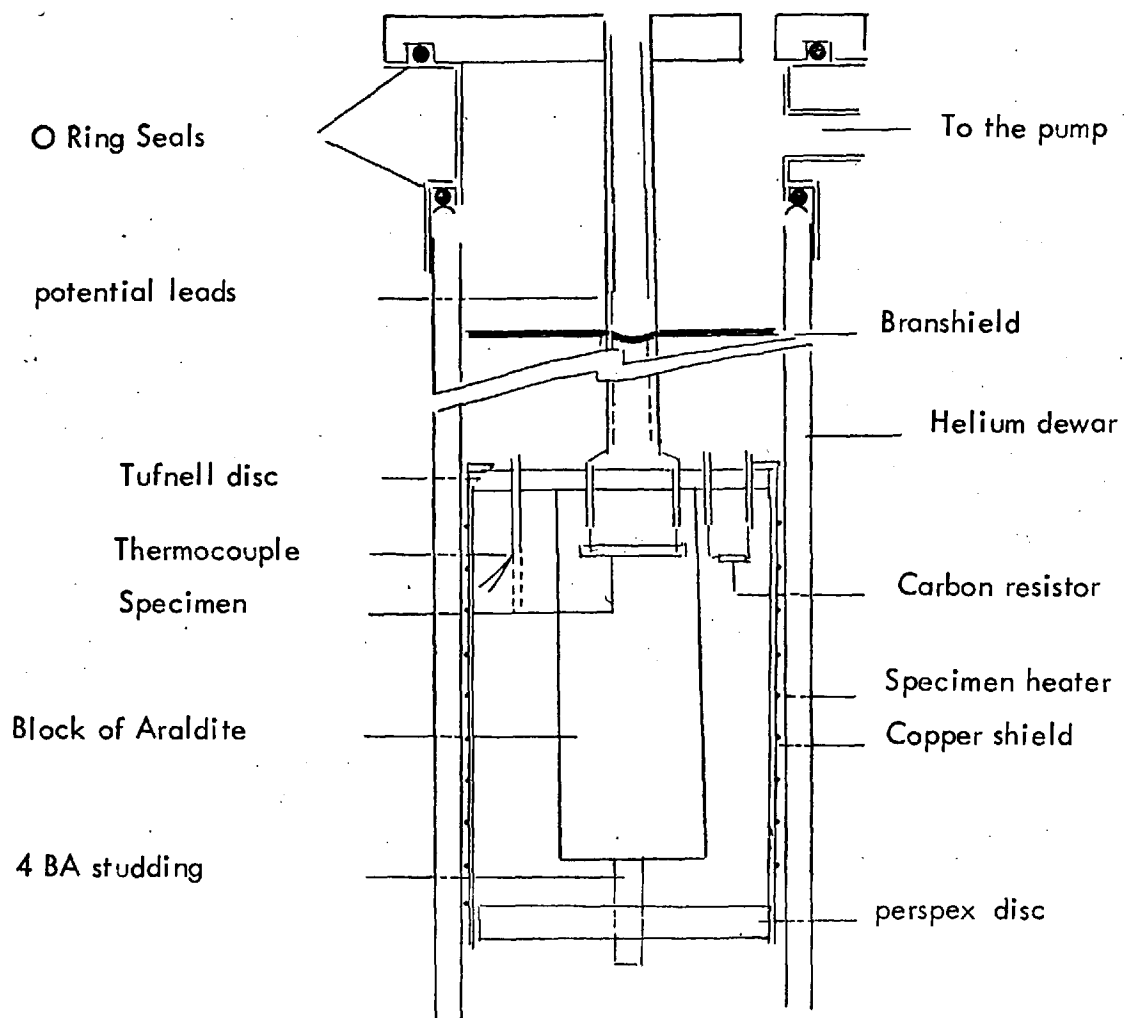
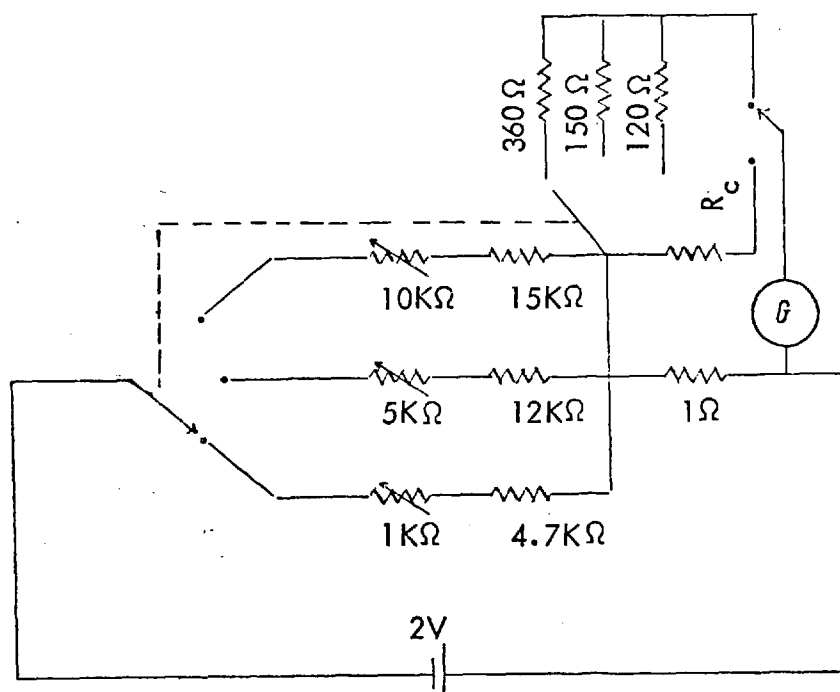


Fig. III.1a. The cryostat (after ref. 150)

Fig. III.1b Diagram of the Carbon Thermometer Circuit



cylindrical block of araldite which ensures a steady warm up due to its high specific heat at low temperatures. A copper can with a wall thickness of about 0.05" surrounds the samples and slides on a tufnel disc, onto which the specimen holder is attached. The lower end of the copper can is closed with a perspex disc with a hole to let helium gas into the specimen chamber during the warm-up. This arrangement is suspended from the top plate by a German silver tube; insulated constantan wire of 36 S.W.G. is wound uniformly along the copper case and used as the specimen heater.

The potential leads are 40 S.W.G. enamel coated copper wires, the current leads consist of seven single eureka wires of 26 S.W.G. A wire wound resistor $100\ \Omega$ is used as a bath heater. All the leads are brought down through the main supporting tube. A brass shield of circular form is fixed onto the supporting tube, which acts as a radiation shield.

The samples were connected in series with an external standard manganin resistance of $0.01\ \Omega$ which was maintained at constant room temperature. An external brass plate on the top of the cryostat contained insulated copper-pins at which all the potential, current and thermometer leads were connected to the external electric circuit. All the joins were made by low thermal solder to reduce the effect of thermal e.m.f. in these leads.

III.1.2 Thermometry

Temperatures below 4.2°K were determined from the helium vapour pressure (read from a mercury manometer) or from a carbon resistor (Allen Bradley). Below 2.3°K an oil manometer was used.

A carbon resistance thermometer was used from 4.2°K to 17°K simultaneously with a gold 0.03% iron versus chromel thermo couple. Above these temperatures the same thermocouple and a Pt-wire thermometer were used up to room temperature.

Temperatures were determined from the vapour pressure using the 1958 He⁴ temperature scale, with an accuracy better than 10mK.

III.1.2a The carbon resistance thermometer

Because of its high sensitivity, and its excellent reproducibility on cycling between He⁴ temperature and room temperature, an Allen Bradley carbon resistance thermometer (nom 47 Ω at 300°K) was used in the temperature range 1.5°K to 17°K.

The circuit used to provide currents to the carbon thermometer is shown in Fig.

III.1b. The circuit is constructed in such a way that the range of temperature from 1.5°K to 17°K is divided into three to obtain better sensitivity. The temperature is obtained from the deflection of the galvanometer calibrated in terms of resistance by replacing the carbon resistor with a resistance box.

The thermometer was calibrated against the He⁴ vapour pressures, by using the resistance temperature relationship.

$$\log R + C / \log R = A + B / T$$

A, B and C are parameters determined from the calibration

III.1.2b The thermocouple

A Au-0.03% Fe - chromel thermocouple is very stable and retains a thermoelectric power in excess of 10 $\mu\text{V}/^\circ\text{K}$. The reference junction of the thermocouple was immersed in LHe⁴ at the bottom of the inner dewar, and the other junction fixed to a copper bar at a position which was thermally equivalent to those of the samples.

The thermo-electric powers were read directly by using a Keithley nanovoltmeter as a D.C. amplifier having a noise level less than 0.1 μV the output being displaced on a DVM. The temperatures have been deduced using data given by Berman et al (154).

III.1.2c Pt resistance thermometer

Pt thermometers are very stable and quite sensitive above 30°K. High purity Pt-wire of resistance ratio ~ 700 was employed as a thermometer to determine the temperature range 30°K to room temperature. A four-terminal potentiometric method was used to determine the resistance of the thermometer which was connected in series with the samples.

The resistance-temperature calibration of the thermometer was made by measuring its resistance at 4.20K and at the ice point, and using the tabulated values of the function

$$Z = [R(T) - R(4.2)] / [R(273) - R(4.2)]$$

given by White (155). The agreement between the Pt thermometer and Au-Fe vs. chromel thermocouple above 30°K was better than 0.2°K.

III.1.3 Electrical circuit

The measurements were made by the standard four probe d.c. potentiometric technique. A Tinsley photo cell galvanometer amplifier and a secondary galvanometer with a thermal-free Tinsley potentiometer of Diesselhorst pattern were employed to measure the potential across the samples. The galvanometers were used mainly as null indicators but the lowest decade of the potentiometer is of 0.1 μ V steps and by adjusting the galvo-amplifier sensitivity until the galvanometer spot could be made to deflect 10 mm from the balance position upon turning a potentiometer dial by 0.1 μ V, one could then measure to 10 nV.

The current circuit consists of the Tinsley D.C. current stabilizer type 5753 and was designed to supply a sample current (constant current source) from 100 mA to 2A, stabilized to within a few parts in 10^6 .

A feedback arrangement was used to stabilize the current; this was done by connecting the potential drop across a 0.5 Ω standard resistance in opposition to

the reference voltage provided by a Mallory cell source. Different currents were selected by dividing the voltage of the 1.35V Mallory cell by means of 10K Ω Helipot.

In order to obtain thermal-free potentials across the samples, two measurements were made with current flowing in the forward and reverse directions. This has been done by an oil filled type 4092 thermo-electric free Tinsley switch. The e.m.f's in the potentiometric circuit are eliminated by the Diesselhorst design.

III.1.4 Experimental procedure

After each sample had been mounted by soldering it in its position in the sample chamber, the electrical circuit and the thermometry were checked and room temperature resistance measurements were done.

For high temperature measurements (below room temperature to the nitrogen point) the inner dewar was pumped before cooling, and an atmosphere of He gas introduced to the dewar by connecting it to a helium return line. The temperature was lowered by adding a small quantity of liquid nitrogen to the outer dewar. Stabilization of the temperature was maintained by pumping on the interspace of the inner dewar. The temperature was then reduced further by adding more liquid nitrogen.

For the helium run, it is necessary to flush out the interspace several times by using a rotary pump. Following this the nitrogen dewar was topped up with liquid nitrogen.

After cooling the cryostat to about 77°K, the temperature could be checked by the Pt thermometer, and liquid He⁴ was transferred then using standard syphon technique.

Measurements at the helium boiling point were made, the return line was isolated from the inner dewar, and the temperature was lowered by pumping on He⁴ using a rubber diaphragm type manostat. After the measurements were made to the

lowest temperature 1.5 K, the pump was shut off and the bath heater was used to go to 4.2 K.

The bath heater was afterwards used to boil off helium until the level was below the specimen chamber. Measurements were then taken by the warming up procedure, using the specimen heater.

III.2 The He^3 - He^4 dilution refrigerator

The dilution refrigerator was designed and constructed by the Oxford Instrument Company, to achieve high circulation rates and powerful refrigeration. The lowest temperature reached was $\sim 0.03^\circ\text{K}$, with a cooling power of ~ 128 erg/sec at 0.08°K .

As the construction was not part of this work, it will not be described in detail except for the sample holder and the method used to mount the specimens.

The dilution unit of this refrigerator consists of a sintered copper condenser with a main impedance to develop an osmotic pressure difference to drive the He^3 flow. A hot tube still to distil concentrated He^3 from the dilute superfluid solution, one continuous type heat exchanger connected in series with a several step type heat exchanger to increase cooling power of the refrigerator and finally a mixing chamber of stainless steel type, where phase separation between dilute and concentrated phase occurs and cooling is achieved. Scientific and technical features of dilution refrigerations are discussed in detail by Wheatley et al (156) (157).

III.2.1 Sample holder and specimen mounting

The sample holder is made of a high conductivity copper plate of $R_{300}/R_4 \sim 300$, after it was machined to a regular rectangular plate (Fig. III.2a). The top of the copper plate is hard soldered to the OFHC Cu female, the whole arrangement is then secured to a high conductivity copper screw heated at the bottom of the mixing chamber. Apiezon "N" grease is used to increase the thermal contact.

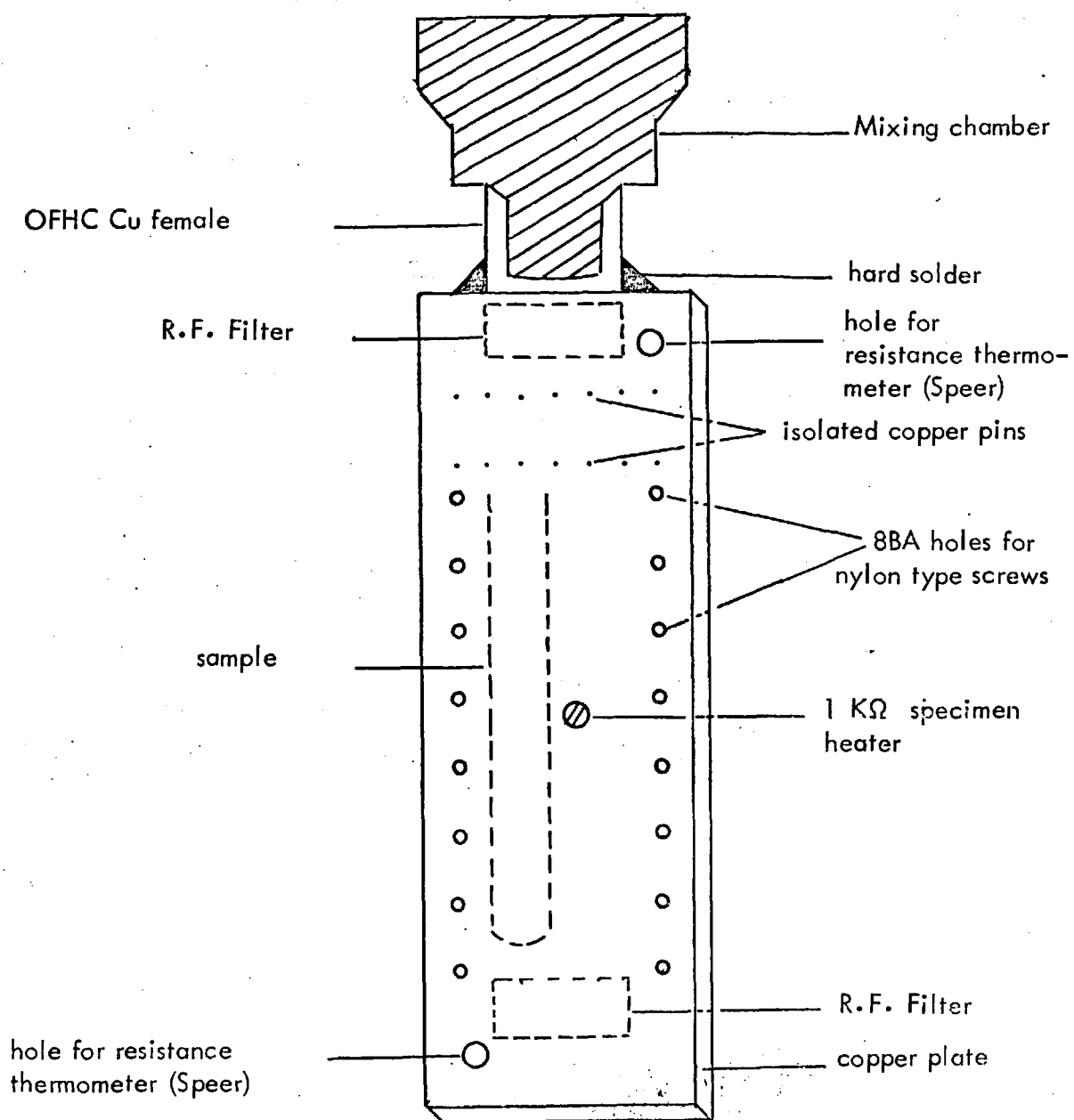


Fig. III.2a sample holder

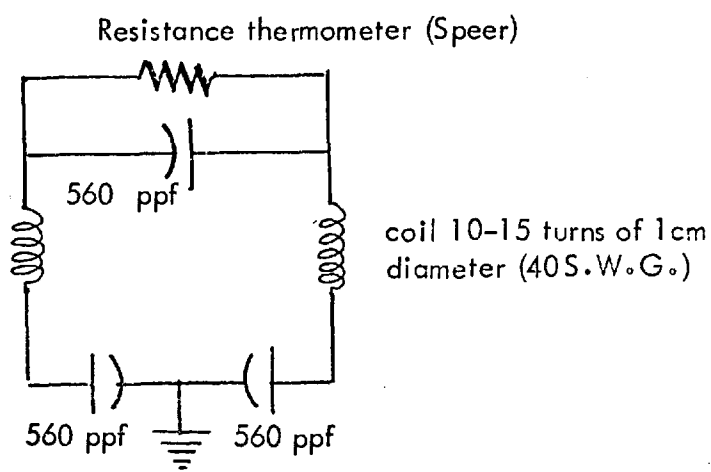


Fig. III.2b R.F. filter

Holes are drilled into the sample holder to accommodate cylindrical type resistance thermometers; Apiezon "N" grease is used to increase the thermal contact between the thermometers and the sample holder, 8BA holes are drilled for nylon type screws and thin isolated copper sheets are used to press the samples against the sample holder to increase the thermal contact.

Isolated copper pins were fixed on the top of both sides of the sample holder for the potential current and thermometer leads.

R.f. filters (Fig. III.2b) are fixed on the sample holder and along the whole dilution unit, in order to ground r.f. which becomes a serious heat source at low temperature. Manganin wire of $1\text{ K}\Omega$ resistance wound outside a Cu capsule and hard soldered to the sample holder serve as specimen heater.

Electrical leads of copper are admitted to the working space by tubes and are vacuum sealed at room temperature. On entering the low temperature enclosure, the wires are bound at the 1.2°K pot by winding them around this pot. A copper pin board was used as electrical connector for these leads.

Thin superconducting Niomax wires (0.05mm) are used to join the potential, current and thermometry leads to the pin board. All wires were covered by P.T.F.E. sleeving in order that the heat conducted to the mixing chamber should not be excessive. The thermal anchoring of the wires is completed by binding and varnishing them on different heat exchangers and interconnecting tubes, before connections are made to the thermometers or the samples.

A coil of 40 S.W.G. copper wire with 2800 turns wound on the tail of a 1.2°K pot shielder (which is a brass isothermal shield consisting of a can screwed to the 1.2°K pot) has been used as a primary coil for mutual inductance

measurement of superconducting samples.

A solenoid to supply 740 Oe/Amp was made by winding a solenoid of 12000 turns to the tail of the inner vacuum chamber (IVC) which is a brass vacuum can and is bolted to the flange with an Indium "O" ring seal; the interior is pumped by a leak detector model 8A to a pressure less than 10^{-6} torr to isolate the dilution unit from the LHe⁴ dewar. The whole enclosure is immersed in a reservoir of liquid helium, which in turn is separated from the outer vacuum chamber (OVC) by nitrogen shielding, the LN₂ jacket sitting above the whole arrangement.

The thermal gradient in the sample holder (the temperature difference between the top and the bottom of the copper plate) was found to be less than 1 mK at 0.03°K. The thermal resistance (contact resistance) at the screwed-joint to the mixing chamber was determined to be less than 2×10^{-5} K sec/erg at 100 mK.

Resistance thermometers (Speer carbon resistors of 220Ω , $\frac{1}{2}$ mW) were used to measure the temperature. These thermometers were located on the still, heat exchangers, mixing chambers, and there were two thermometers also, one at the top and the other at the bottom of the sample holder. One of the latter thermometers was calibrated by Oxford Instrument Company. The resistances of these thermometers were measured by an a.c. resistance bridge (Oxford Instrument Company) with very low power dissipation 10^{-12} W. The resistance measurements were made by standard four terminal d.c. potentiometric methods, by passing a standard current through the sample, which is in series connection with a standard resistance. In all cases long wires from the specimens were used. Current leads of 40 S.W.G. copper were soldered at both ends of the sample; these wires were coated by ordinary solder after stripping the insulation. This

procedure reduces the heating effect upon becoming superconducting leads at low temperatures. 0.15 mm Pt wires were spot-welded to provide potential leads.

To ensure good thermal contact with the thermometry, the samples were pressed against the sample holder by insulated thin sheets of Cu with Apiezon "N" grease after electrical insulation had been made with the sample holder using cigarette paper and G.E. varnish. After allowing the G.E. varnish to dry (normally 24 hours) the earthing between the samples and sample holder was checked.

Superconducting transition temperature measurements were also made, by measuring the mutual inductance as a function of temperature. Cylindrical form samples were used, and a coil of 40 S.W.G. copper wire with ~ 3000 turns was wound on each sample, which formed a secondary coil connected to one arm of the mutual inductance bridge; the second arm is connected to the primary coil which is wound on the tail of the 1.2°K pot shielder. Thermal contact was ensured by pressing each end of the sample between the small pieces of pure Cu and in turn fixing to the sample holder by G.E. varnish and Apiezon "N" grease.

The mutual inductance was measured by an a.c. mutual inductance bridge at 70HZ, built by Oxford Instrument Company. The induced eddy currents effect in the sample holder and the mixing chamber were found to be serious below $\sim 0.3^{\circ}\text{K}$. This was overcome by reducing the sensitivity of the bridge by an external series resistor to the bridge. The effect of the vertical component of the earth's field was eliminated by measuring the critical field of the samples for normal and reverse directions of the solenoid current. No compensation of the horizontal component was made.

III.2.2 Operation of the dilution refrigerator

After cooling the cryostat to liquid helium temperature (this takes about 24 hours) and pumping away the exchange gas from (IVC) to a pressure less than 10^{-6} torr, the measurements of resistance and mutual inductance may be made.

The 1.2°K pot is filled with liquid helium by opening a needle valve under the partial vacuum space with the needle valve closed, the temperature of the 1.2°K pot is reduced by pumping on the liquid helium to 1.2°K and so the temperature of the 1.2°K Shilder is also reduced to 1.2°K .

The helium mixture was then condensed at 1.2°K and slowly passed through the main impedance constriction to cool the dilution unit below 4.2°K . During this process the thermometers were watched and the effect of cooling is observed. When the condensation of the mixture was completed, further cooling was achieved by turning on the still power to obtain the desired He^3 circulation rate.

The dilution unit was then cooled down steadily to its final low temperature $\sim 0.03^{\circ}\text{K}$ at which the phase boundary was forced in to the mixing chamber.

This procedure takes about eight hours. The cooling power of the refrigerator was found to be reproducible upon changing the heat input to the sample holder. No further cooling was obtained when the inlet valve to the condenser was closed and the valve to the storage volume opened (i.e. on single cycle operation).

The measurements of the resistance were made by warm up procedure; this has been done by turning on sample power and waiting for equilibrium to be established for short thermal transients.

The measurements of the mutual inductance were made during the cooling down process as this was sufficiently slow for these measurements.

The calibration of the thermometers was also checked against the critical fields of well-annealed specimens of high purity Zn, Pb and Cd. No appreciable difference was observed between the thermometers, the specimen and that of the mixing chamber upon increasing or decreasing the heat input to the sample holder. Although the temperature resolution was better than 1 mk, the calibration was only accurate to 10 mk. The Joule heating effect was checked by changing the current through the samples, until no variation was found in the resistivity of the sample, due to this effect.

III.3 Sample preparation

Raw materials were as follows:-

Materials	Supplier	Estimated Purity %
Pt	J.M.	99.99
Pd	J.M.	99.99
Mn	K.L.	99.995
Ru	J.M.	99.99
Fe	K.L.	99.999
Y	R.E.P.	99.9
Sc	R.E.P.	99.99
Gd	R.E.P.	99.9
Dy	R.E.P.	99.9
Tb	R.E.P.	99.9

J.M. = Johnson Matthey Ltd.

K.L. = Koch-Light Ltd.

R.E.P. = Rare earth Products Ltd.

All the samples in this work were prepared in an argon arc furnace, as described by Stone (158). The procedure as follows: after careful weighing the required quantities of the pure materials were grouped together on the water cooled copper hearth (care was taken with handling). In an atmosphere of argon at pressure of 30 mmHg, the materials were then arc melted to button form and were turned and re-melted several times to ensure homogeneity.

Most of the alloys (except Pt-Mn and Pd-Pt-Mn alloys) were sucked down in to a uniform cylindrical shape using a mould with a cylindrical cavity, ranging in diameter between 1.6 to 2.3 mm and 2 to 3 cm long *. In the case of Pt-Mn

* The geometrical factor for the conversion from the resistance to specific resistivity was measured to better than one per cent; a micrometer and travelling microscope were employed for the diameter and length measurements respectively.

and Pt-Pd-Mn alloys, the melted ingots were then drawn into wires using non-ferrous tools, uniform samples of 1mm in diameter and 3-4 cm long. Thinner wires 20-30 cm long were drawn for the dilution refrigerator and He^3 resistance measurements.

Different heat treatments have been given for the different systems, as follows:

a) Pt-Mn and (Pt-Pd)-Mn alloys

A short anneal (about half an hour) in a vacuum of 10^{-5} Torr at 750°C was given for each sample, except for those with high concentration of Mn in Pt; other heat treatments were also given for the latter type of alloys (see the discussion on Pt-Mn alloy). This short anneal was intended to reduce the risk of Mn depletion from the surface of the wires.

b) Ru-Fe alloys

For alloys containing 10-45% Fe no heat treatment was given for the cast samples; alloys with 50-70% Fe were homogenised in vacuum at 1100°C for 24 hours and water quenched.

c) Y-RE and Sc-RE alloys

For all alloys (dilute and concentrated), no heat treatments were given to the cast samples, in order to avoid possible reaction with quartz envelopes.

CHAPTER IV

Experimental results and discussion of Pt-Mn and (Pt-Pd)-Mn alloy systems

IV.1 Pt-Mn alloy system

Introduction

Considerable interest has been shown in the magnetic properties of Mn solute in Pd metal, where the addition of Mn to Pd leads to a rather complicated magnetic phase diagram (159) (160). The initial ferromagnetic behaviour gives way on raising the Mn concentration to spin glass behaviour, as Mn-Mn nearest neighbour anti-ferromagnetic coupling becomes important. Platinum alloys are expected to have similar magnetic properties. In order to study the magnetic properties of the Pt-Mn alloy system, the electrical resistivity of solid solution Pt-Mn alloys both in the dilute limit (down to 0.09% Mn) and more concentrated limit (to 21% Mn) have been measured.

Previous investigations include the specific heat study of Nieuwenhuys et al (161), who concluded that there was a well-defined moment on the Mn atoms at fairly low concentration ($< 1\%$ Mn) and that the ordering may be spin glass like. Specific heat measurements by Sacli et al (162) on alloys $\leq 1.35\%$ Mn showed anomalies similar to Nieuwenhuys et al specific heat data with an increase in transition temperature as a function of Mn concentration. Early thermo-electric power measurements by MacDonald et al (163) on dilute Pt-Mn alloys, showed a negative gain in the thermoelectric power due to Mn solute. No other measurements beyond these have been reported.

In the following we present electrical resistivity measurements which clearly suggest that Pt-Mn alloys form "Coles type" alloys*, and in contrast to Pd-Mn alloys no ferromagnetism has been observed; instead they show spin glass behaviour down to the lowest concentration studied. This is indicated by the impurity resistivity which decreases with temperature and is followed by a broad resistance minimum.

* a term used by Rivier and Zlatić for systems like Pd-Ni and Rh-Fe

Above about 11% Mn, the magnetic state is modified by short range atomic order and the character of the resistivity is quite sensitive to annealing temperature.

Magnetization data for the alloy 15% Mn will also be reported.

IV.1.1 Results *

Fig. (IV.1) shows a plot of the resistivity at 4.2 K as a function of concentration of Mn, Fig. (IV.1a) shows our lower concentration $\leq 0.5\%$ Mn alloys; the linearity of the curve (up to 11% Mn) is confirmed by the nominal and analysed concentration of Mn. $\rho_{4.2}$ reaches a maximum of $\approx 40 \mu\Omega \text{ cm.}$ at about 12% Mn. As C is further increased $\rho_{4.2}$ levels off and is sensitive to annealing temperature as discussed later.

(a) Alloys with concentration $\leq 0.5\%$ Mn

Plots of incremental resistivity per atomic per cent ($\Delta\rho/C = [\rho_{\text{alloy}} - \rho_{\text{Pt}}(T)]/C$) against temperature for alloys $\leq 0.5\%$ Mn are shown in Fig. (IV.2). Data in the temperature range $1.5^\circ\text{K} - 10^\circ\text{K}$ has been taken using a He^4 cryostat, for 0.09% Mn and 0.3% Mn alloys, the low temperature measurements ($0.6^\circ\text{K} - 1.5^\circ\text{K}$) have been done in a He^3 cryostat (153). Measurements on the 0.5% Mn alloys were performed down to about 30 mK (dotted line) using a $\text{He}^3 - \text{He}^4$ dilution refrigerator. A plot of incremental resistivity ($\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{Pt}}(T)$) against temperature for the 0.5% Mn alloy is shown in Fig. (IV.7c). Data below 1.2°K is that taken using the dilution refrigerator, a clear minimum at $0.45 \pm 0.1^\circ\text{K}$ is observed with positive temperature coefficient above $T_{\text{min.}}$

The incremental resistivity per atomic per cent against $\log_e T$ plots for the same $\leq 0.5\%$ Mn alloys are shown in Fig. (IV.3). It is clear that the logarithmic behaviour is not obeyed over the whole temperature range. Values for the coefficient of $\log_e T$ are listed in the Table (IV.1).

* All compositions are given in atomic per cent.

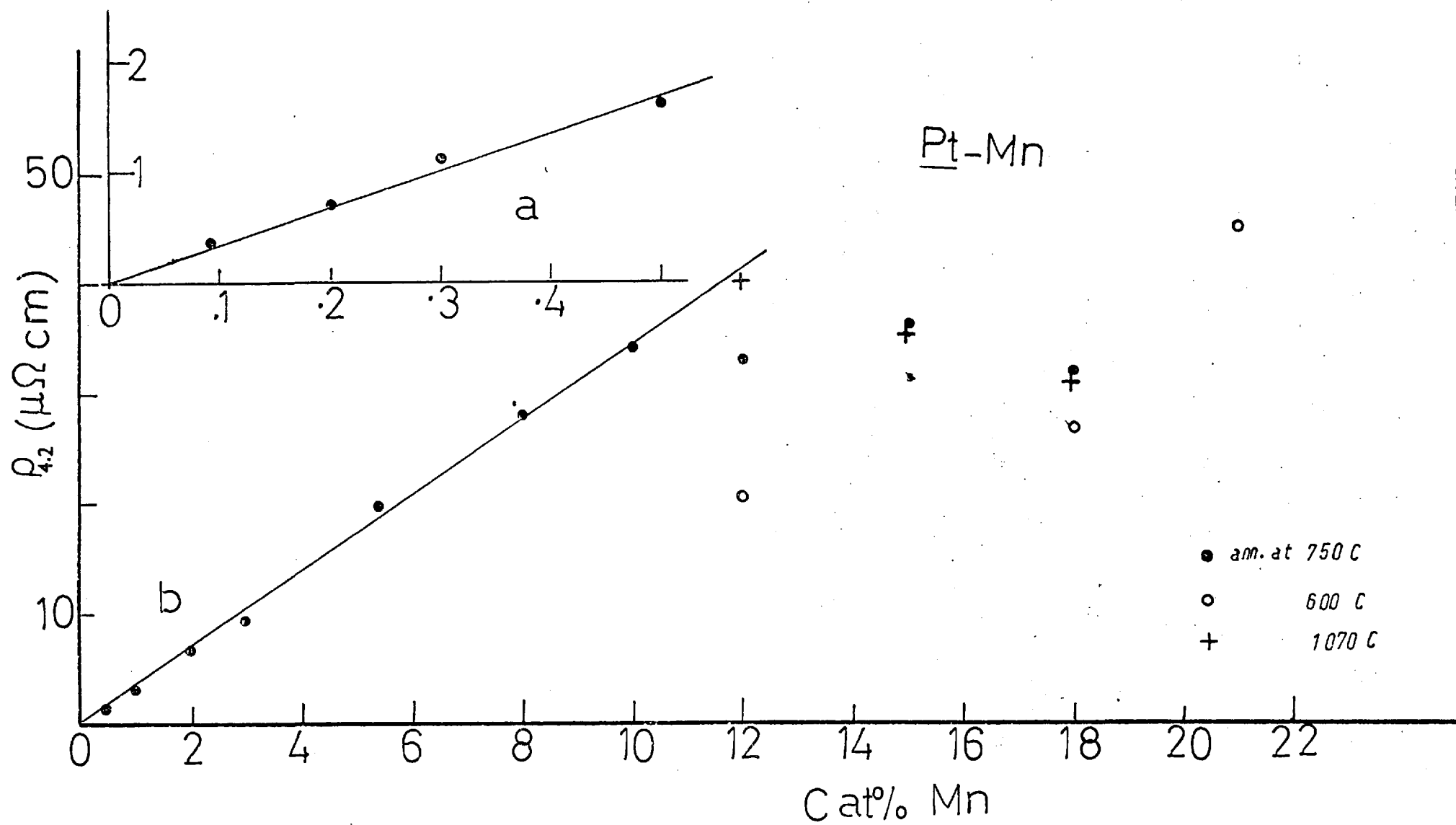


Fig IV.1

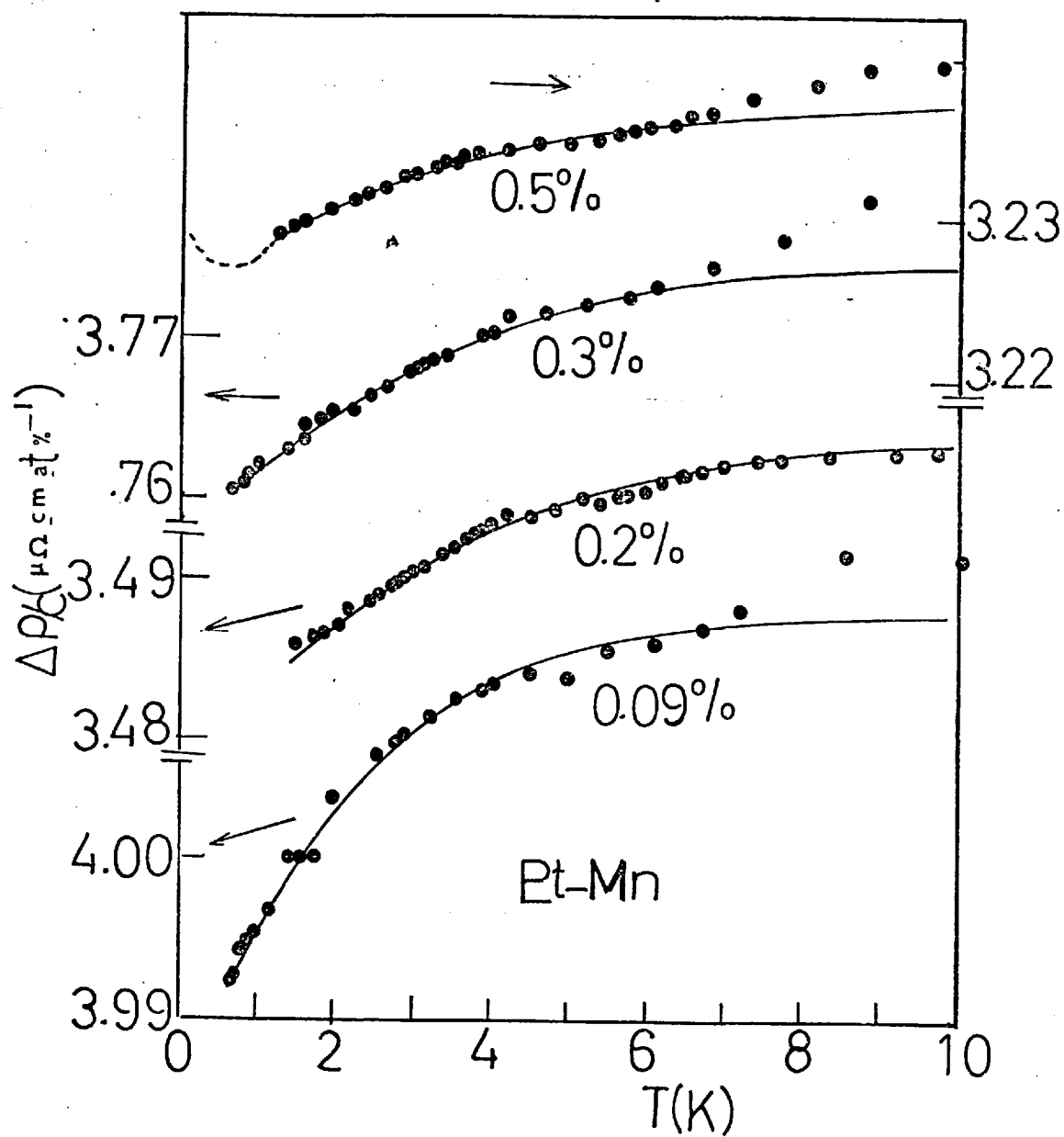


Fig IV.2

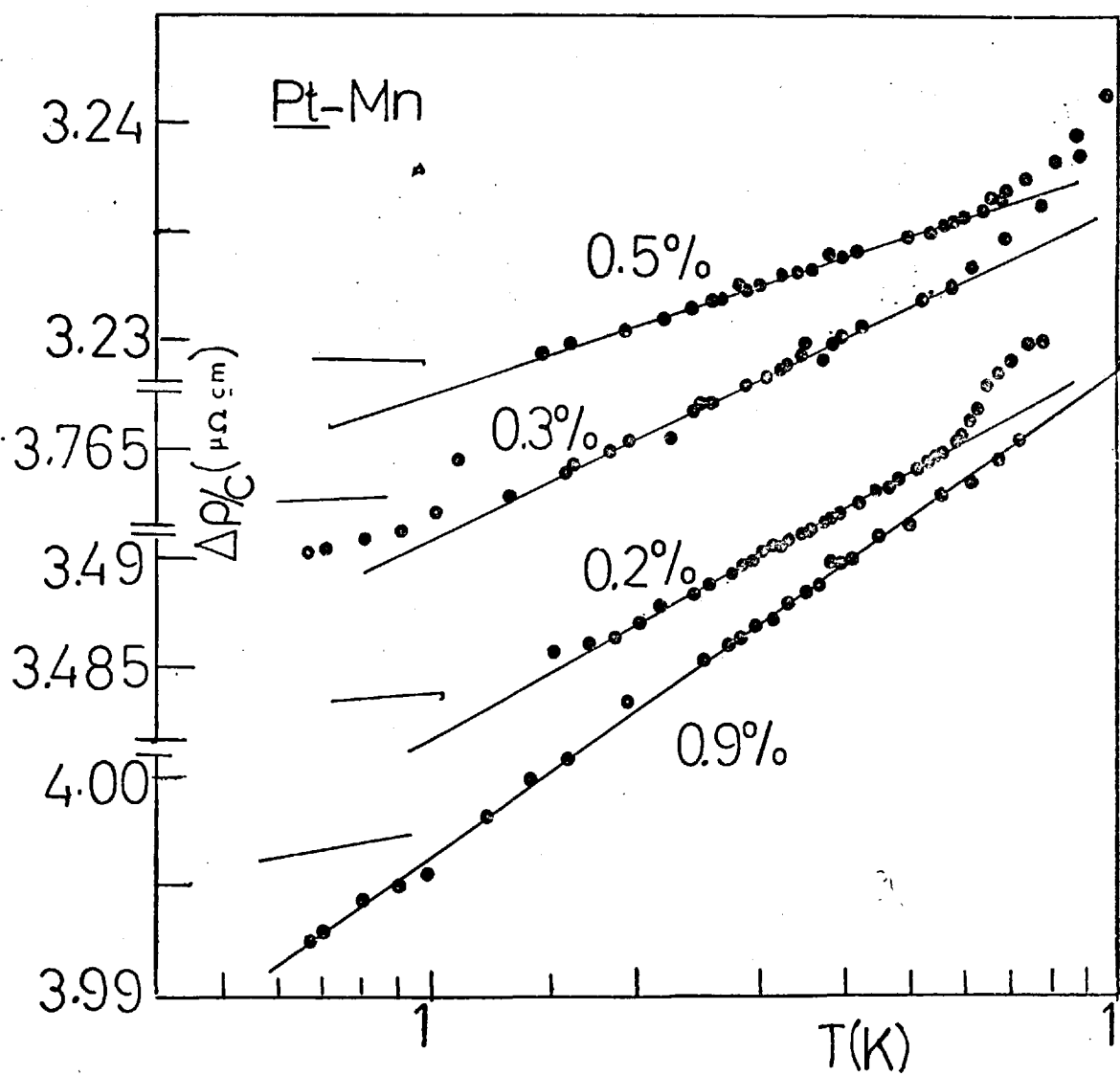


Fig IV. 3

(b) Alloys with concentration $1 \leq C \leq 12\% \text{ Mn}$

The incremental resistivity ($\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{Pt}}(T)$) against temperature for alloys in the concentration range $1 \leq C \leq 12\% \text{ Mn}$ are shown in Fig. (IV.4). Data for the 1% Mn alloy between 1.5 °K - 0.6 °K having been taken in He³ cryostat. The most notable feature is the resistance minimum with T_{min} , increasing with increasing the concentration. The highest curve (12% Mn) shows data for the alloy annealed at 1070°C for 4 hr and quenched (see the discussion).

Plots of $\Delta\rho$ against $T^{3/2}$ for the alloys $5.4 \leq 11\% \text{ Mn}$ are shown in Fig. (IV.5), where near $\frac{1}{2}T_{\text{min}}$. The resistivity falls approximately as $(1 - T^{3/2})$. Values of $(T_2 - T_{\text{min}})$ for increasing concentrations of the alloys listed in table (IV.2) are plotted in Fig. (IV.6).

The incremental resistivity of the sample Pt - 3% Mn measured down to 40m°K in the dilution refrigerator is shown in Fig. (IV.7a). The high temperature data (1.5 °K - 12 °K) from the He⁴ cryostat, in Fig. (IV.7b) shows the same data plotted against $T^{3/2}$. The bars indicate the error in the measured resistance.

(c) Alloys with concentration $12 \leq C \leq 21\% \text{ Mn}$

Plots of incremental resistivity ($\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{Pt}}(T)$) against temperature for alloys of 12%, 15% and 18% Mn for different annealing temperatures are shown in Fig. (IV.8). The curves, a, b, c represent the alloy 12% Mn annealed at 600° C for 24 hr and cooled in air, (b) annealed at 750 °C for $\frac{1}{2}$ hr and quenched in water, (c) annealed at 1070° C for 4 hr and quenched in water. Curves (d), (e) are those of 15% Mn alloys annealed at 750 °C for $\frac{1}{2}$ hr and 1070 °C for 4hr respectively and then water quenched. Curves (f), (g) represent the 18% Mn alloys annealed at 750° C for $\frac{1}{2}$ hr and 1070°C for 4hr respectively and quenched. The arrows indicate the maximum in the slope given by $d\Delta\rho/dT$ and the dashed line for the alloy 15% Mn indicates the maximum in the magnetization vs. temperature curve.

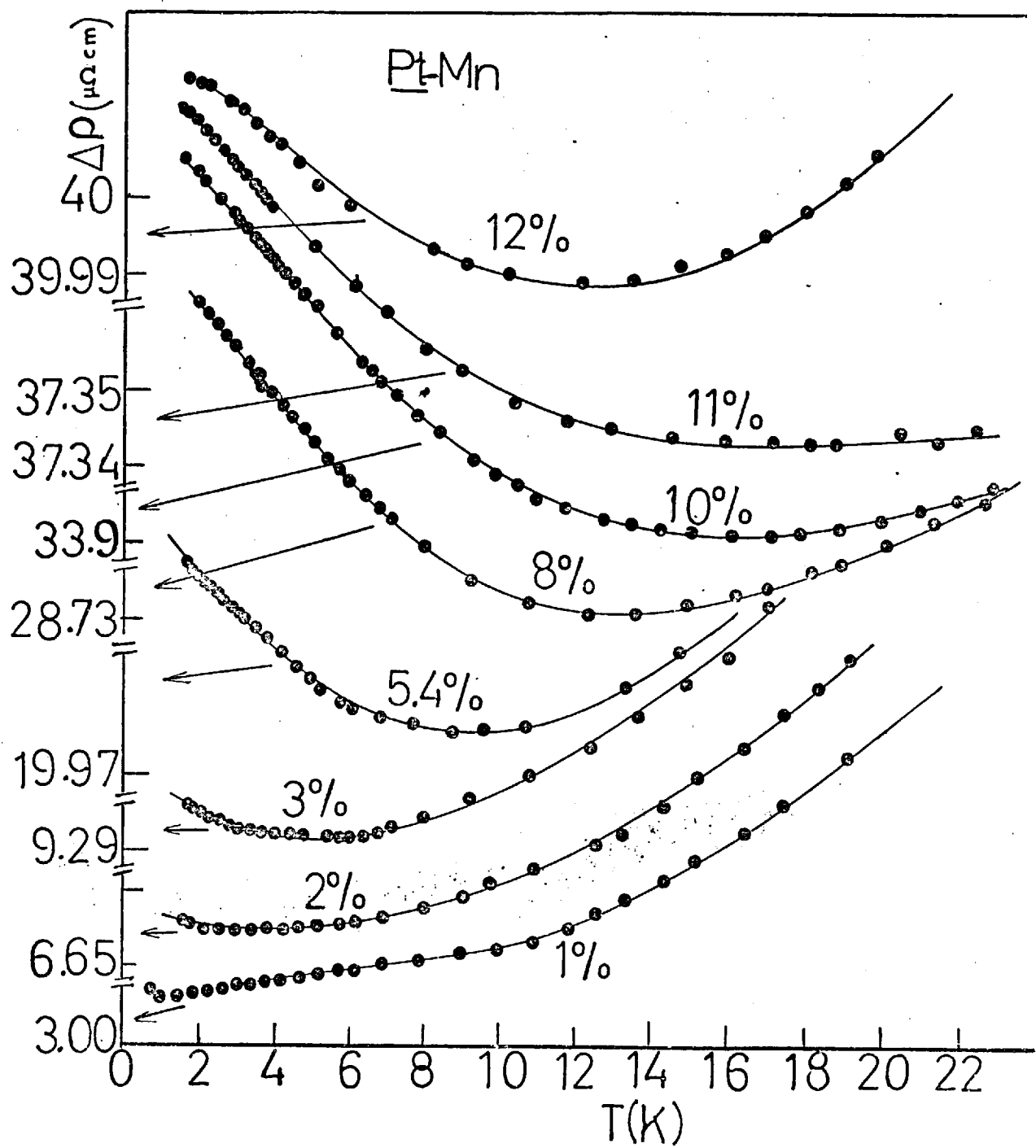


Fig IV.4

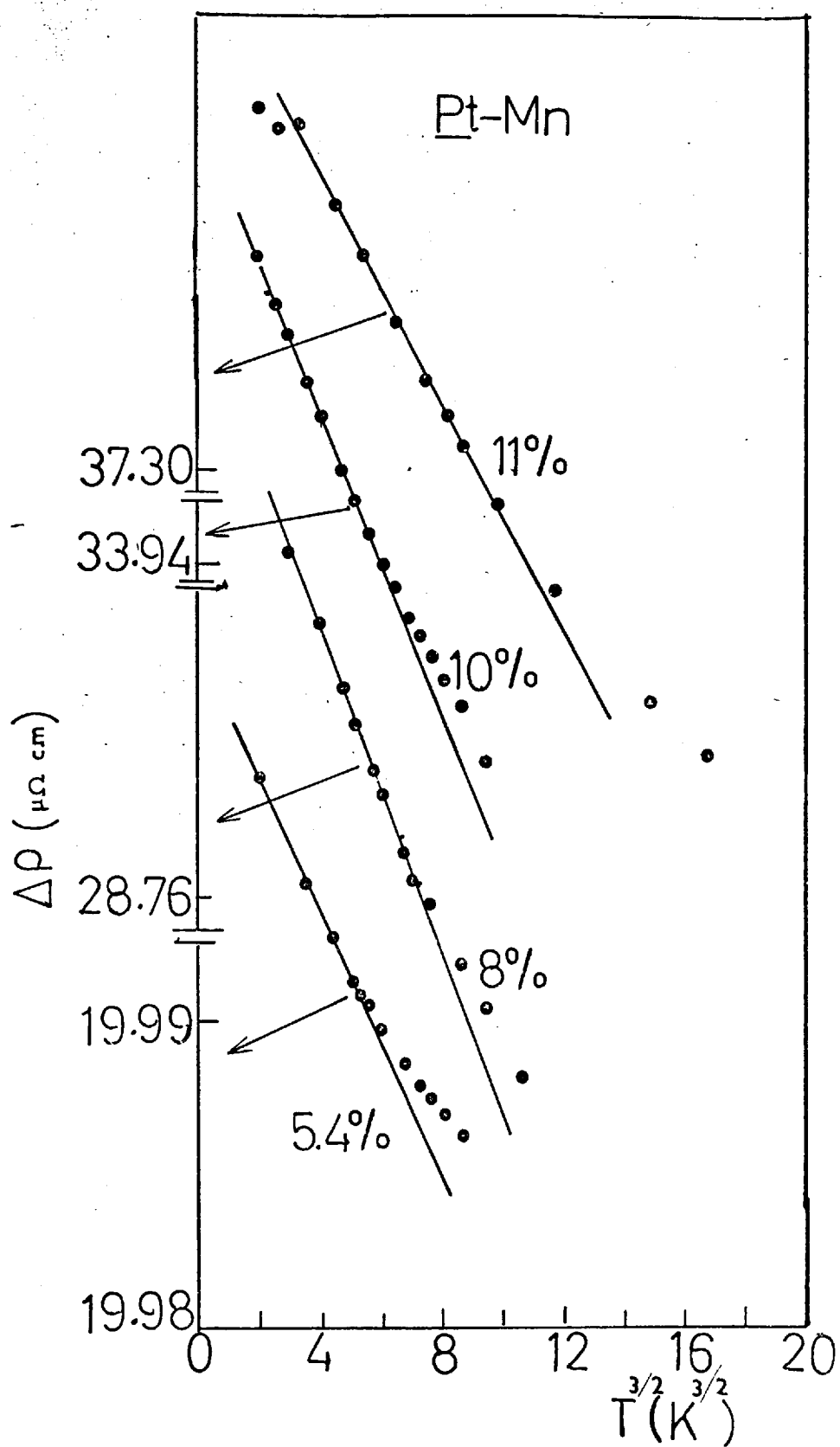


Fig IV. 5

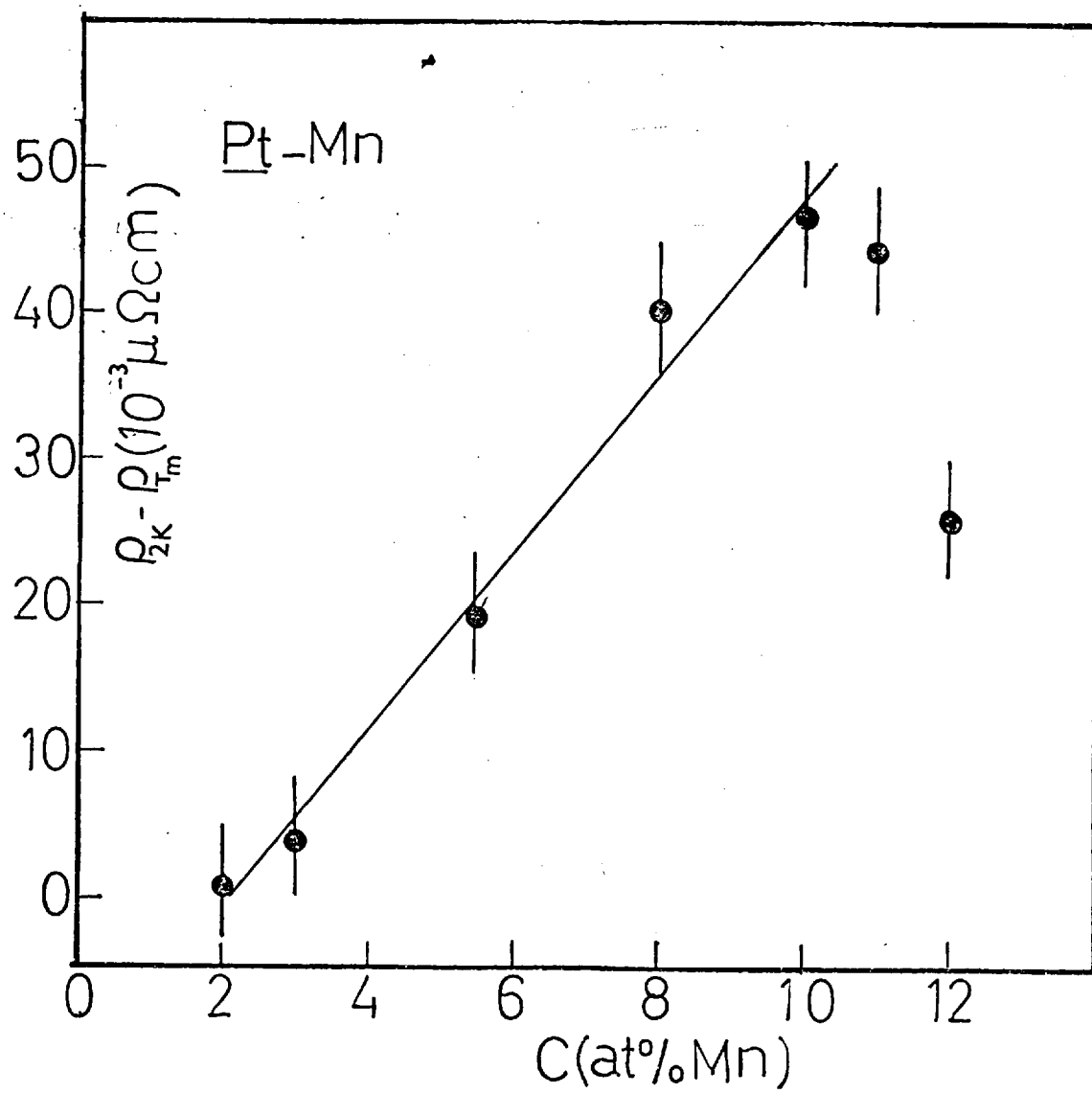


Fig IV.6

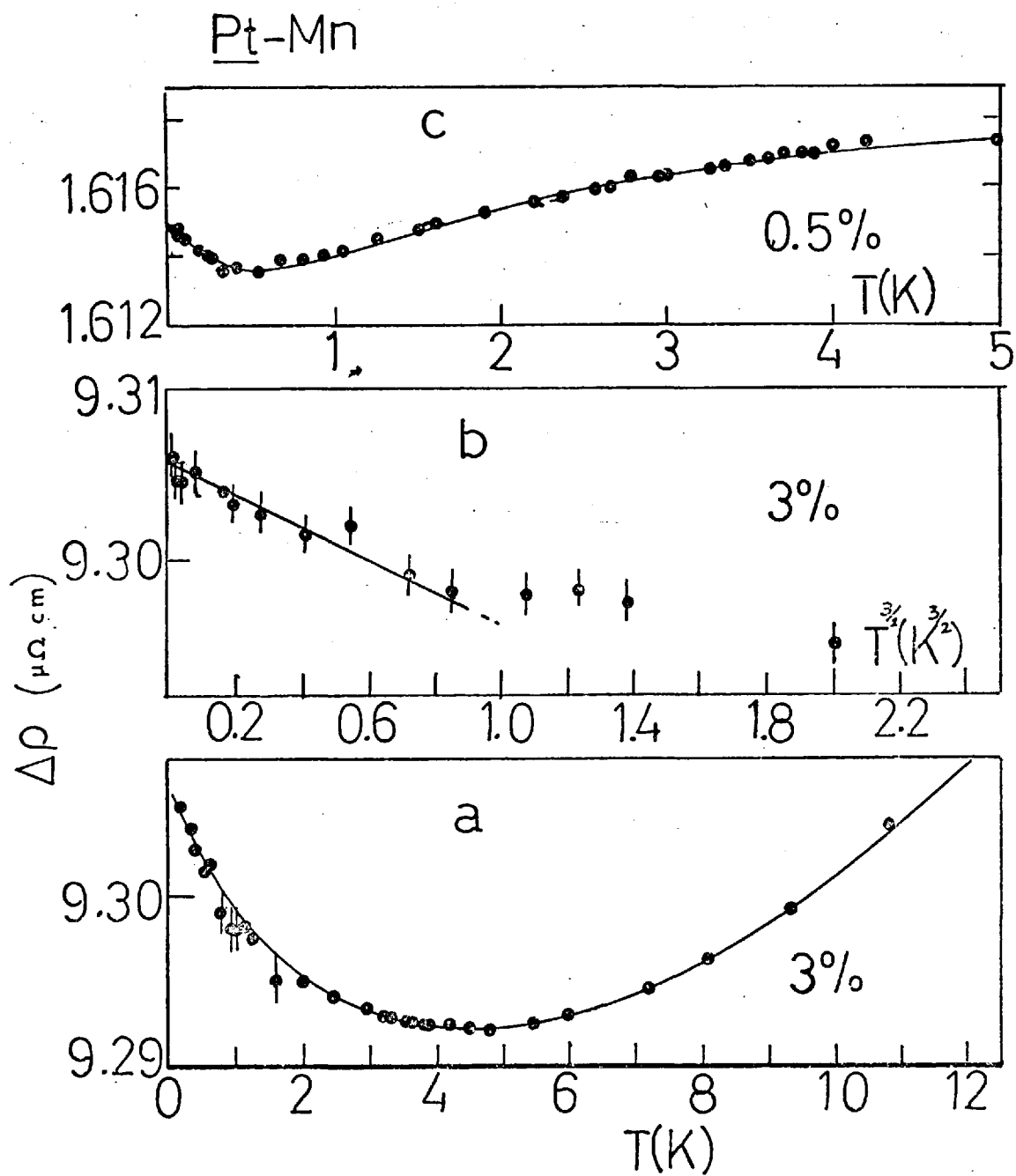


Fig IV. 7

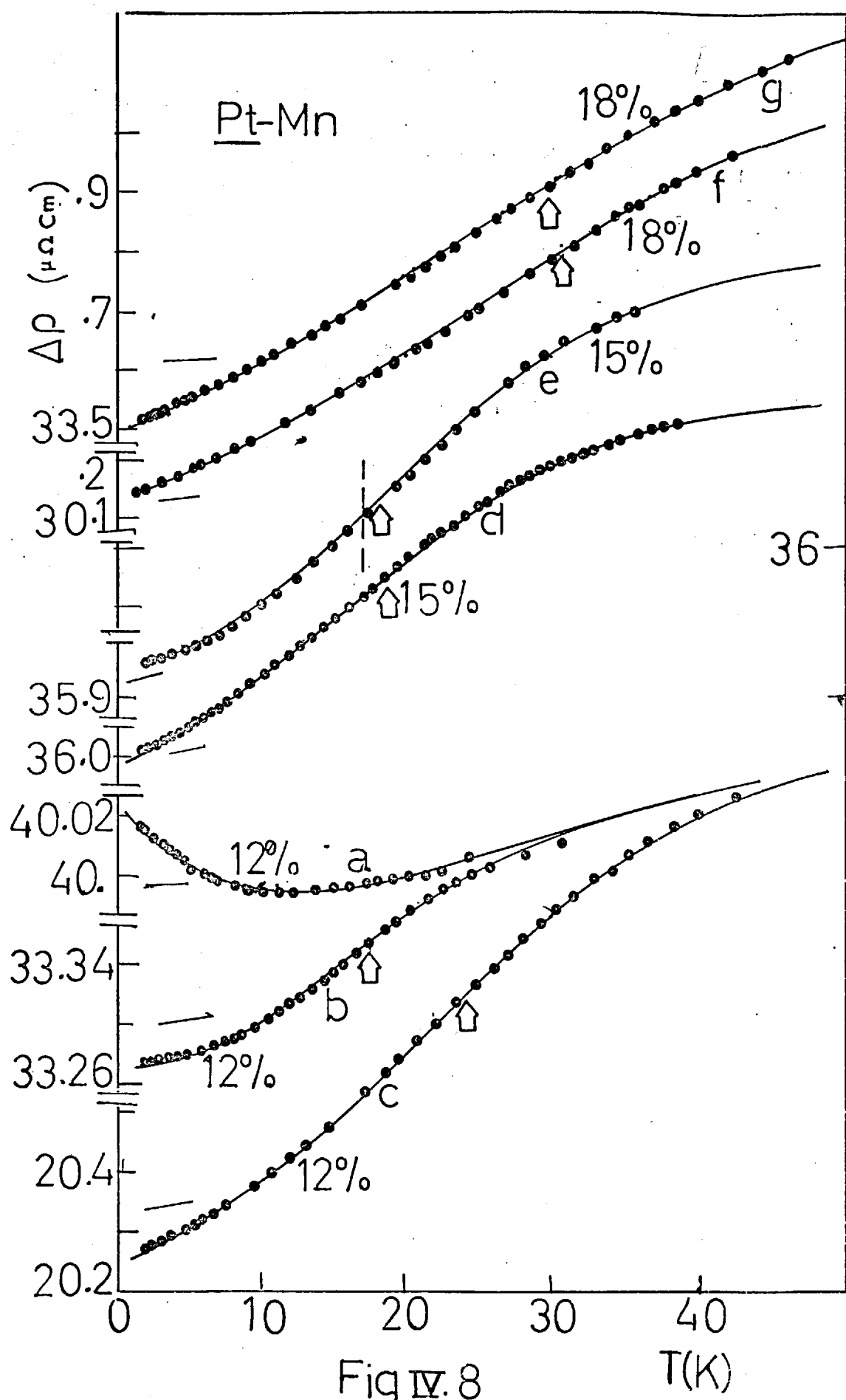


Fig. (IV.9) shows the incremental resistivity $\Delta \rho$ against $T^{3/2}$ for the alloys 15% and 18% Mn annealed at different temperatures. The best fit to the data was obtained with the simple expression $\Delta \rho = \rho_0 + AT^{3/2}$, the range of this $T^{3/2}$ fit to the data being different for different annealing temperatures. The deviation from straight line behaviour indicates a slower than $T^{3/2}$ variation, tending towards a linear dependence at higher temperatures.

Fig. (IV.10a) shows the isothermal magnetization of Pt-15% Mn alloy (arbitrary units) as a function of the field H at 4.2 K after cooling in zero external field. The alloy was quenched from 1070° C after annealing for 4 hr. Note the increase of the magnetization upon reversing the external field H and also the isothermal remanent magnetization (OA) after complete cycling.

The magnetization (in arbitrary units) measured in a field of 0.5kG vs. temperature, for the same sample is shown in Fig. (IV.10b) after cooling the sample to 4.2°K in zero field. A broad maximum at about 17°K was observed, which is characteristic of the behaviour in spin glass systems.

Fig. (IV.11a) shows the magnetization (in arbitrary units) vs. the applied field at 4.2°K for the same 15% Mn alloy. The sample was then cooled in a field of 8kG, (OA) represents the resulting remanent magnetization (field cooling effect). (OB) represents the isothermal remanent magnetization plus the magnetization due to (OA).

The temperature variation of remanent magnetization for the same sample in stage OB is shown in Fig. (IV.11b); note that the remanent magnetization disappears at about 24°K, this behaviour is similar to that of spin glass materials.

Fig. (IV.12) shows the incremental resistivity ($\Delta \rho = \rho_{\text{alloy}} - \rho_{\text{Pt}}(T)$) vs. temperature plot for the alloys 18% and 21% Mn. Both alloys were annealed at 600° C and cooled in air. At low temperatures curvature towards a higher

Fig IV.9

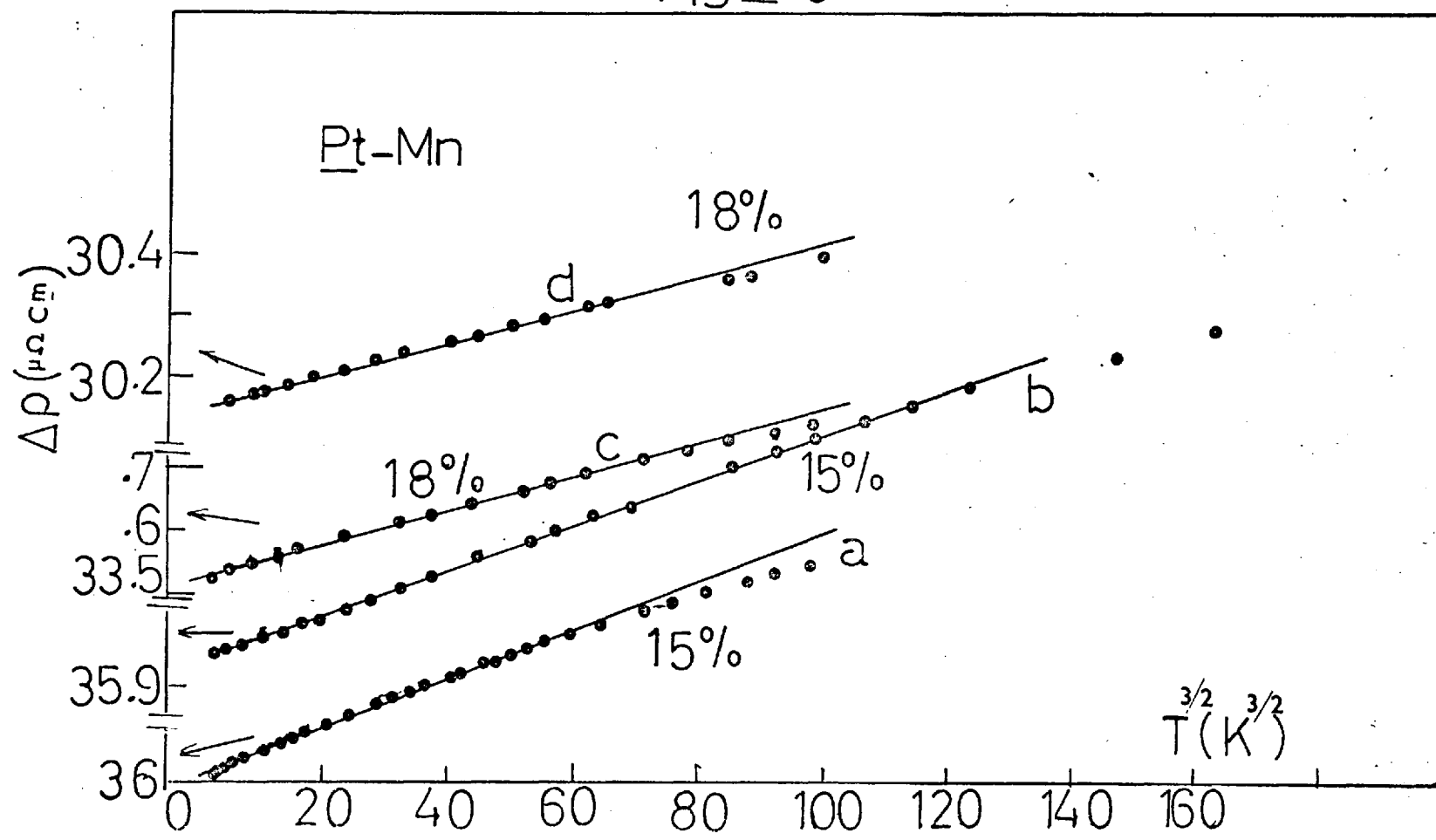


Fig IV.10
Pt 15%Mn

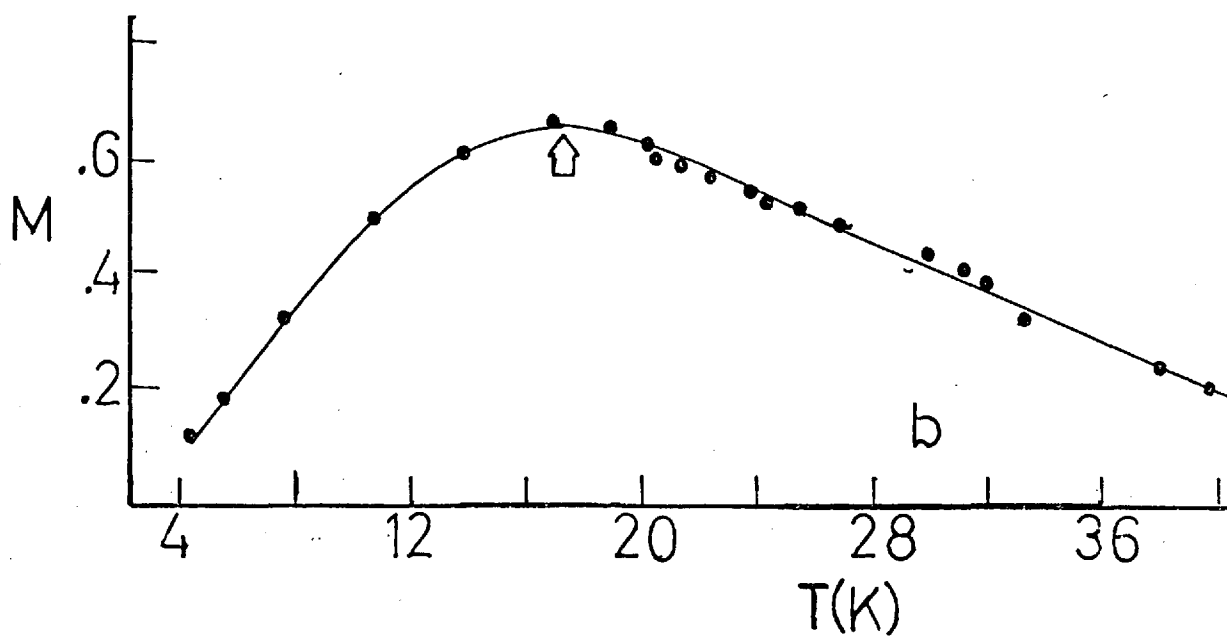
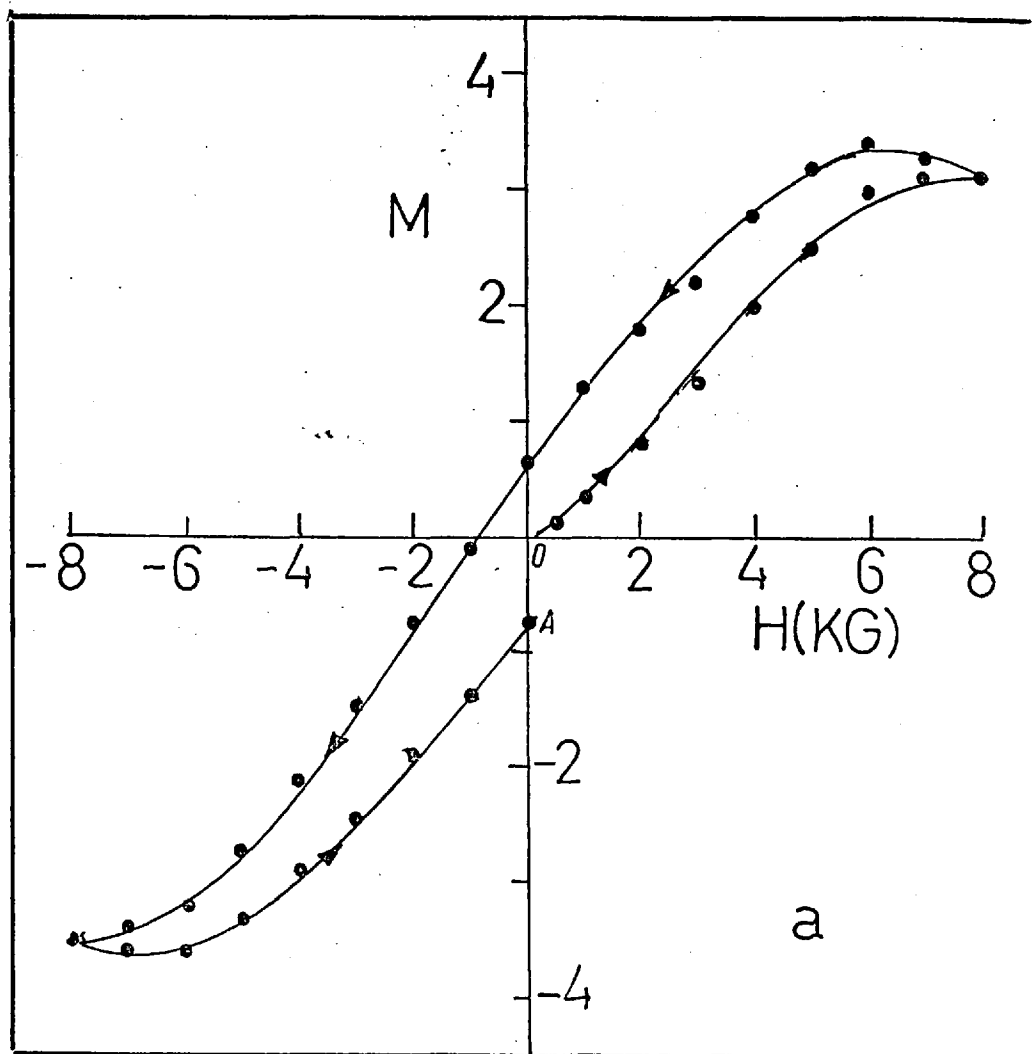
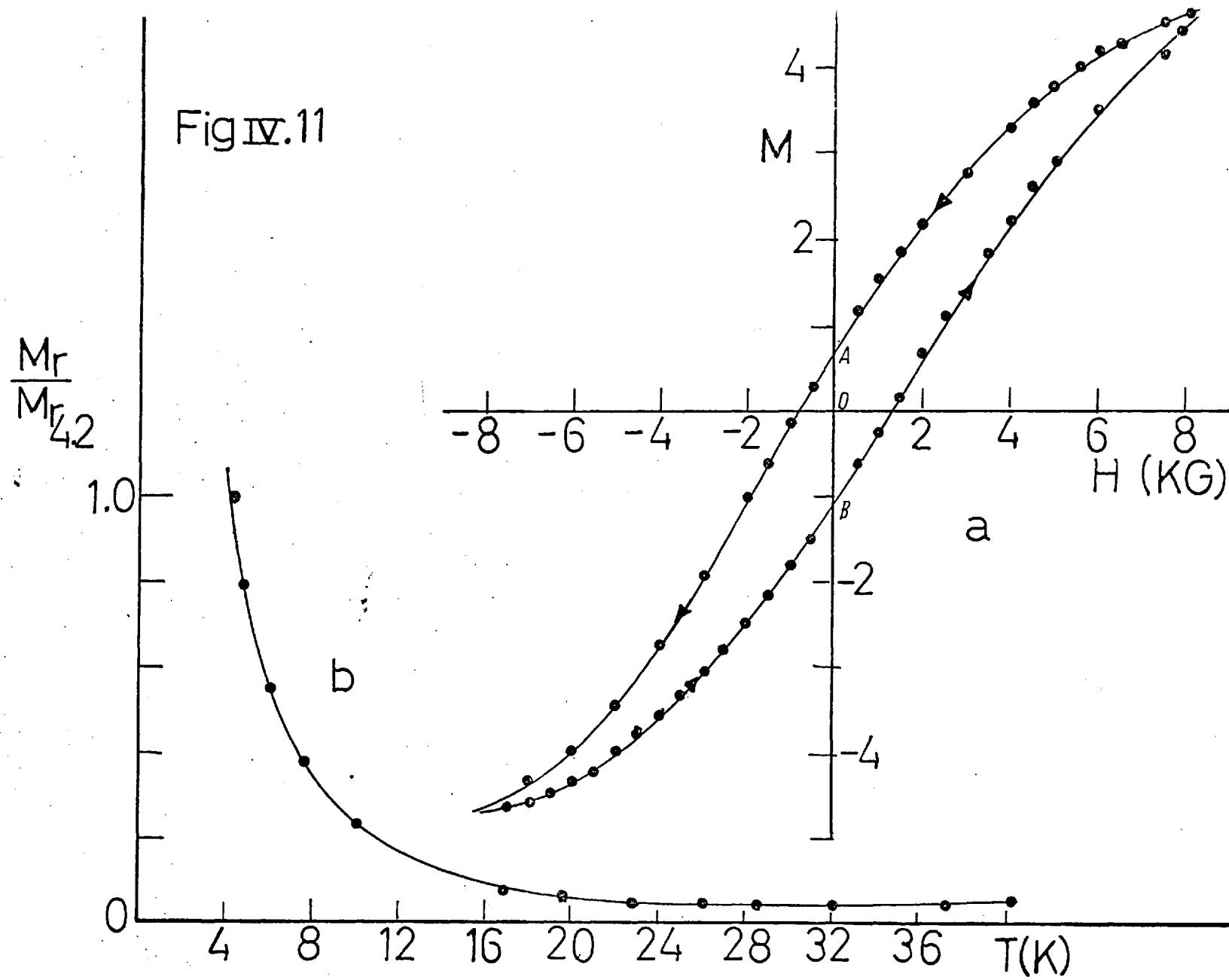


Fig IV.11



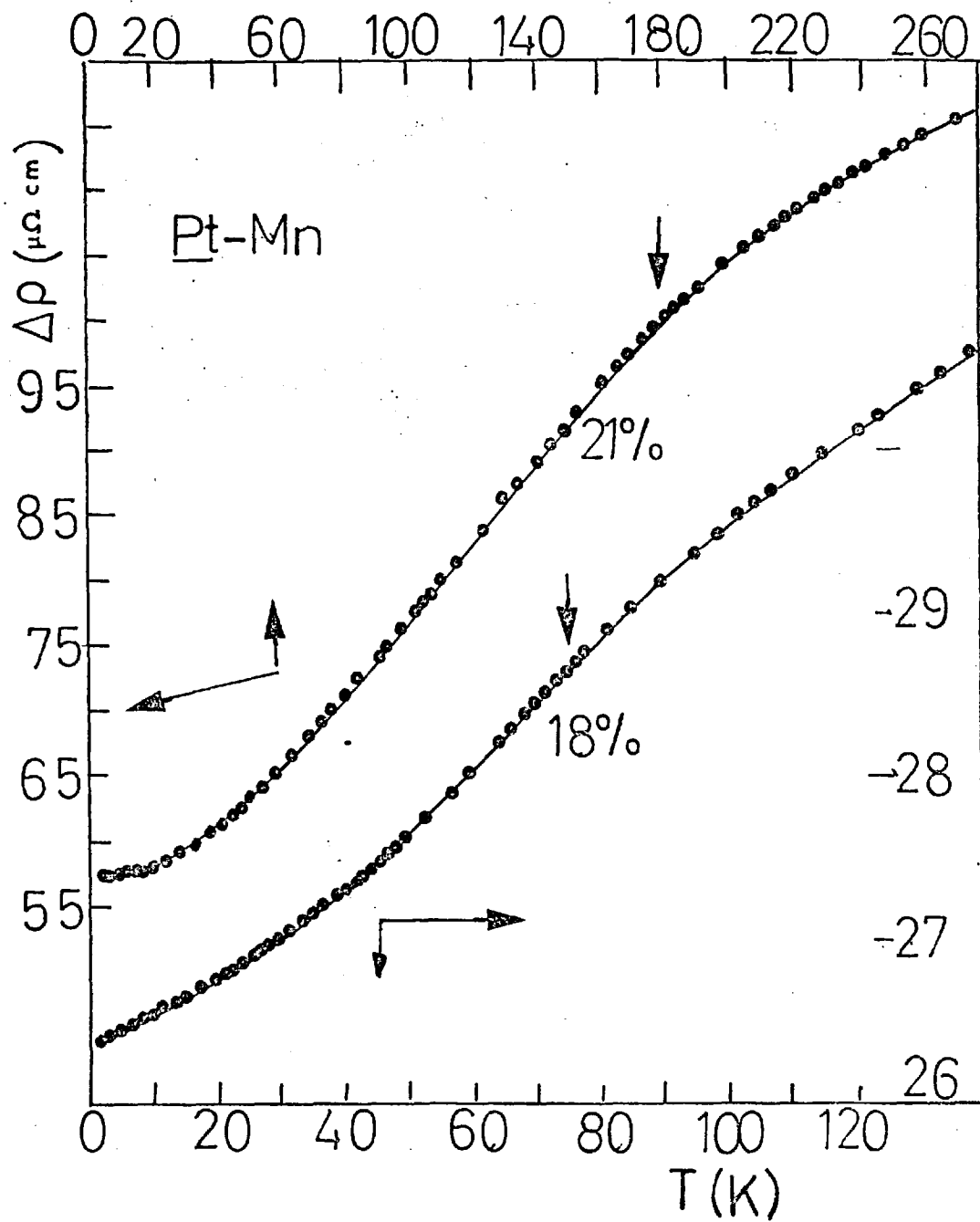
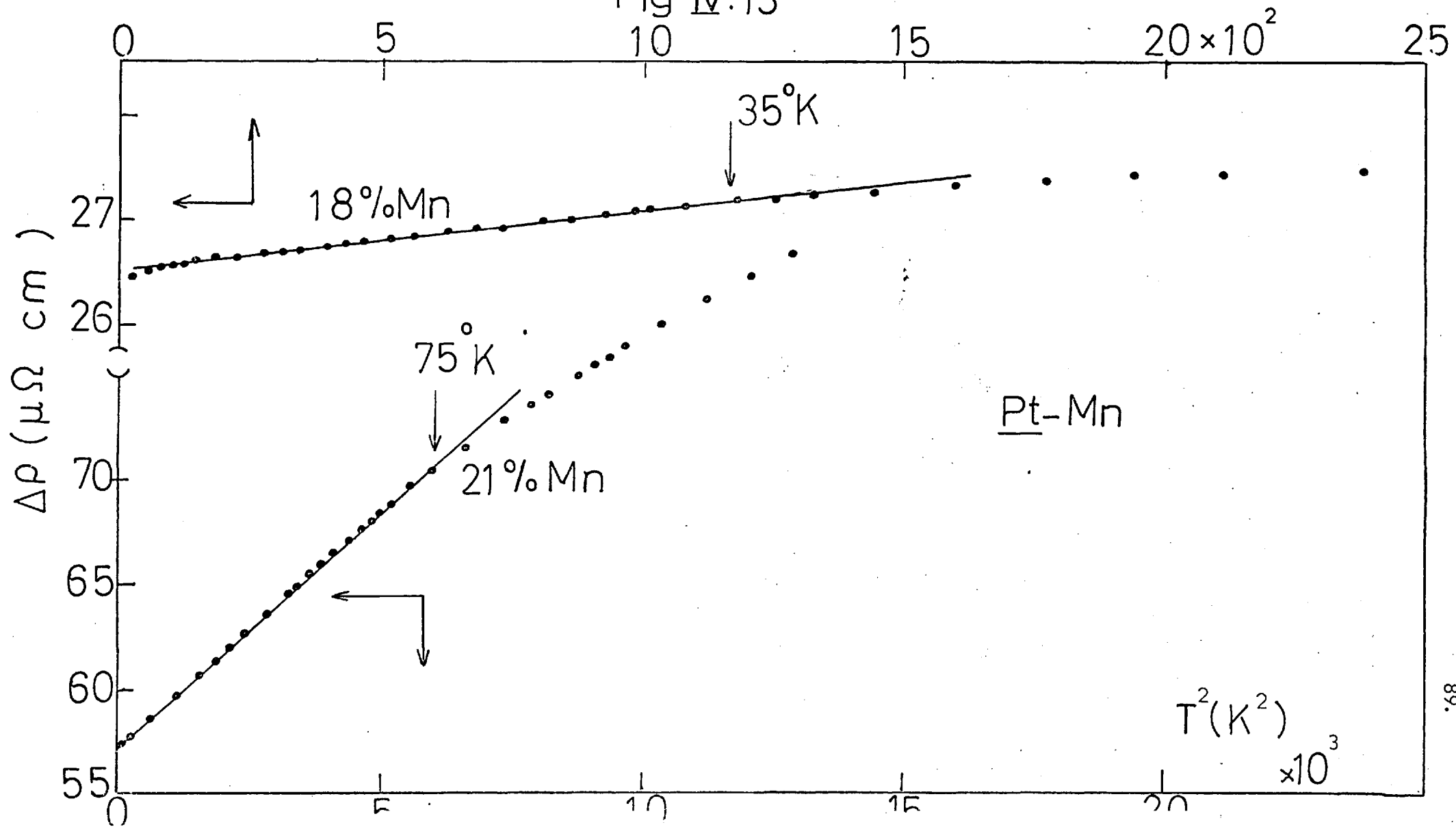


Fig IV.12

Fig IV.13



power in T (stronger than $T^{3/2}$) is found. The best fit to this data was found to be $\Delta \rho \propto T^2$ (see Fig. IV.13). This dependence is attributed to ferromagnetic contributions from short range atomic order in disorder $\text{Pt}_3 \text{Mn}$.

IV.1.2 Discussion

(a) Alloys $\leq 0.5\% \text{ Mn}$

The electrical resistivity of systems with local moments can have a temperature dependent contribution. We have already discussed the problem of local moment formation and its effect on electrical resistivity in Chapter I. Examination of Fig. IV.2, where the incremental resistivity $\Delta \rho(T)$ decreases rapidly with decreasing temperature suggests a logarithmic variation. Consequently, the incremental resistivity $\Delta \rho(T)$ plotted against $\log_e T$ in Fig. IV.3, where there exists a well-defined logarithmic region in the 0.09% alloy, and to a progressively lesser extent in the other alloys containing up to 0.5% Mn, the region of logarithmic character is shifted to higher temperature as the concentration of the Mn solute is increased. Above about 8°K deviation from log behaviour presumably arises from deviations from Matthiessens rule, although these deviations seem rather low in view of the fairly high Debye temperature of pure Pt ($\sim 230^\circ \text{K}$). However, we note that similar effects in dilute Pt-Fe alloys (164) have also been observed at $\sim 8^\circ \text{K}$ and attributed to deviations from Matthiessens rule. Because of this deviation the analysis of the data is limited to temperatures below 8°K .

Values for the coefficient (A) of $\log T$ with increasing concentration are estimated and listed in table (IV.1). These indicate a non-linearity in the concentration dependence of the spin resistivity as a result of correlation

C% Mn	A/C $\mu \Omega$ cm/at % $^{\circ}$ K
0.09	3.12 ± 0.005
0.2	2.40 ± 0.005
0.3	2.12 ± 0.005
0.5	1.45 ± 0.005

Table IV.1

between Mn solute atoms. This is consistent with the decrease of the log T range with increasing concentration as shown in Fig. (IV.2).

It is clear that the Pt-Mn system forms Coles type alloys since a positive temperature coefficient has been observed (59) (60). In view of searching for a T^2 behaviour as observed for several Coles alloys e.g. Rh-Fe (126), and to study the ground state of the 0.09% Mn alloy, measurements have been performed on 0.09% and 0.3% Mn alloys in the He³ temperature range. No T^2 or linear T behaviour, as characteristically seen in localized spin fluctuation systems, has been observed. The Pt-0.09% Mn sample shows no deviation from a logarithmic behaviour down to the lowest temperature studied. For the 0.2%, 0.3% and 0.5% Mn alloys at low temperatures the experimental points deviate from a logarithmic temperature dependence because of the long-range oscillatory type RKKY interactions. Consequently the 0.5% Mn sample was measured in the He³ - He⁴ dilution refrigerator down to 30 mK Fig. IV.2 dotted line, see also Fig. (IV.7c). A clear resistance minimum at $0.45 \pm 0.1^{\circ}$ K has been observed which substantiates the earlier measurements of Hansen and de Pater (private communication, see also Nieuwenhuys et al who found a resistance minimum in a nominal Pt-0.1% Mn alloy at 0.36° K.

From the above analysis of the measurements interesting features emerge; there is clear evidence of a resistance minimum in the low concentration alloys at the lowest

temperatures, and above the temperature of this minimum there exists a well-defined logarithmic region. Magnetic susceptibility measurements made in this laboratory by Hou, on the alloy Pt-0.09% Mn, who concluded that there exists a well-defined moment on the Mn atom, and that the paramagnetic Curie temperature is almost zero, are consistent with specific heat data by Nieuwenhuys et al (161) and Sacli et al (162). The thermoelectric power of dilute Pt-Mn alloy measured by MacDonald et al (163) exhibits a negative peak of approximately $0.5 \mu\text{V/K}$ which suggests that Mn possesses a magnetized virtual bound state in Pt.

Unfortunately no direct theoretical treatment exists which might account quantitatively for the electrical resistivity of dilute Pt-Mn alloys which have been investigated. We note however that no electrical resistivity or other microscopic measurements have been done on more dilute Pt-Mn alloys and it would be interesting to see the disappearance of the Mn solute interaction effects (which are responsible for the resistivity minimum) and possibly to observe single impurity effects.

As we mentioned, the electrical resistivity due to Mn solute in 0.09% alloy displays a logarithmic temperature dependence down to 0.6°K and from the non-linearity in the slope of $\log T$ with the concentration in more concentrated alloys indicates that the characteristic temperature is very low. This is presumably comparable to Au-Fe (165) or Au-Mn (166) alloys, where the Kondo temperature is very low and the effect of correlations between Fe solute or Mn solute atoms are observable down to very dilute concentrations and very low temperature (167).

The origin of the positive temperature coefficient in the electrical resistivity of Rh-Fe and related alloys has been discussed by several authors (10) (59) (60) (67) (168) and we have discussed the possibly related theoretical concept in Chapter I. Perhaps the most satisfactory model which accounts for the T^2 dependence and the positive logarithmic temperature dependence is the localized spin fluctuation theory

(59) (60) (67).

Loram et al (164) have suggested a simple phenomenological theory to calculate the positive logarithmic temperature dependence in Pt-Fe alloys in which the scattering takes place from a system of fluctuating moments which are related to the electron phase shifts by the Friedel sum rule. On this model a positive temperature coefficient is predicted for $|Z| < 5/2$ in agreement with the experimental data for Pd and Pt containing Ni, Co, Fe and a negative temperature coefficient for Cr and Mn which is not in agreement with the present investigation.

Comparison of the most dilute (0.09%) alloy with the Rivier and Zlatić (RZ) theory (59) (60) which it will be seen is far from dilute in this context, since no T^2 behaviour nor a linear in T behaviour has been observed, except for a $\log T$ region, which is the predicted behaviour above the spin fluctuation temperature (T_{sf}). The difficulty in attaining unitarity limit may be ascribed to the breakdown of Matthiessens rule. Hence RZ theory might be valid in very low concentration where one expects single impurity effects to be seen.

From the parallelism between "Kondo" alloys and "Coles" alloys (59) (60), it is of interest to compare the dilute Pt-Mn alloy with dilute Au-Mn (166) or Au-Fe (167) alloys in which, as the temperature increases, the effect of the superposition of a rising resistivity due to spin glass (spin freezing) behaviour on the falling Kondo resistivity leads to a maximum, by contrast to the decreasing resistivities like Pt-Mn in which competition against the spin freezing leads to a resistance minimum.

An attempt was made to explain the present resistivity data by the Beal-Monod and Matho model (see Chapter II, section II.4) for coupled pairs of impurity spins under the influence of their RKKY interaction, resulting in a deviation from the ideal single impurity resistivity, which progressively becomes larger and passes through a maximum. However, regarding extensions to this internal field distribution approximation, one is unable to explain the resistance minimum for more concentrated

Pt-Mn alloys, where clear evidence of "spin glass" character is confirmed by susceptibility, resistivity and specific heat measurement.

(b) Alloys with concentration $1 \leq C \leq 12\% \text{ Mn}$

We have seen that even in the dilute limit the resistivity contribution per Mn concentration shows concentration dependent effects. It follows that there is a tendency towards the onset of magnetic order due to the stabilization of the moment on the Mn atoms. This is indicated by a resistance minimum in 0.5% alloy and by a maximum in specific heat at about 0.4 K for 0.26% alloy (162). This suggests that as the concentration is further increased the temperature of the minimum in resistivity should increase because the strength of the interaction energy increases between the Mn solute atoms. The strong resistance minimum observed for the 2% alloy in He⁴ temperature range and minimum for the 1% alloy in He³ temperature range, is shown in Fig. (IV.4).

Fig. IV.4 shows a plot of incremental resistivity for alloys $1 \leq C \leq 12\% \text{ Mn}$ and the most notable feature of these plots is the strong resistance minimum, the temperature of which increases linearly as a function of concentration. Murani and Coles (127) reported that Rh-Fe alloy systems in the concentration range 3-15% Fe show resistance minima which are similar to those found in Pt-Mn alloy systems. They attributed this to spin glass type magnetic ordering similar to that in Cu-Mn and Au-Fe alloys in which the susceptibility shows a round maximum and other characteristics of the "spin glass" materials (see Chapter II, section II.5). Similar resistivity minima have been reported in Pt-Co alloys (128).

The behaviour of the resistivity as a function of temperature below the temperature of the minima for 5, 4, 11% Mn alloys is shown in Fig. (IV.5) (see also Fig. (IV.7a, b) for the alloy 3% where the low temperature data performed in the dilution refrigerator) below about $\frac{1}{2} T_{\min}$ the resistivity falls approximately as $(1 - T^{3/2})$ showing a temperature dependence related to that of the canonical spin glasses such as Cu-Mn and Au-Fe.

Magnetic susceptibility measurements made by Hou (private communication) on alloys containing 5.4, 8, 11, 12% Mn in Pt (on the same samples as used for resistivity data) show broad susceptibility maxima at 7, 12, 18, 20°K respectively and all of these show a frozen component of the magnetization when the alloys are cooled in an applied field. The temperature of these maxima agree fairly well with the characteristic temperatures obtained from the resistivity which is consistent with the magnetization measurements of Star on Pt - 1.64% Mn alloy (see ref. (161)) who observed a magnetic order similar to Au-Fe and Cu-Mn alloys. In view of these measurements we are led to the conclusion that both the minimum (as in Rh-Fe) and maximum in $d\Delta\rho/dT$ (124) (125) signify spin glass ordering in these alloys, and that $T^{3/2}$ behaviour arises from the dynamics of spin glass materials. It will also be of interest to see whether Pt-Mn alloys manifest the sharp cusps in differential zero field susceptibility-temperature curves as is observed in well established spin glass materials.

We have seen that the temperature dependence of the electrical resistivity of the spin glass materials is simply $T^{3/2}$, but one might also get a $T^{3/2}$ behaviour in ferromagnetic alloys (169) (170). A possible origin of the $T^{3/2}$ dependence in spin glasses has been proposed on spin diffusion theory by Rivier and Adkins (see Chapter II, section II.5) and the condition for spin glass resistivity minimum has recently been given by Rivier (130). A comparison of our results with theory may now be made. A tendency towards the $T^{3/2}$ dependence is apparent in the incremental resistivities of alloy $3 \leq C \leq 11\%$ Mn down to about $\frac{1}{2}T_{\min}$. For the 3% alloy where low temperature measurements were made using the dilution refrigerator, we see that within the limits of experimental error, the $T^{3/2}$ behaviour is seen to extend to $\sim 0.8^\circ\text{K}$. To examine the relation given by

$$\rho_0 - \rho_{\min} \propto C$$

(see equation II.5.3), data for the resistivity increment $(\rho_2 - \rho_{min})$ has been deduced for alloys $2 \leq C \leq 11\% \text{ Mn}$, these values which are listed in table (IV.2)

C% Mn	$\rho_2 - \rho_{min} \text{ n}\Omega \text{ cm}$
2	0.5
3	3.25
5.4	19
8	40
10	46.5
11	44
12	26

Table IV.2

have been plotted in Fig. IV.6 against the Mn concentration, and show a linear behaviour up to 10% Mn. The reduction in the resistivity $(\rho_2 - \rho_{min})$ from this behaviour for the alloys 11%, 12% Mn is a real effect and is connected to the change in character of the resistivity at $\sim 11\% \text{ Mn}$ which is due to the importance of atomic short range order in this system. This will be further discussed in the next section. So the evidence for the equation (II.5.3) to be obeyed is restricted to up to 10% Mn. This comparison suggests that the general form of the calculated resistivity is correct and the present investigation is consistent with Rivier and Adkins theory. For the 12% alloy we found that the character of the resistivity undergoes a further change, instead of a resistance minimum it changes to a behaviour similar to that of spin glasses and is quite sensitive to the annealing temperature. Probable causes of this effect will be discussed later in connection with the more concentrated alloys.

(c) Alloys with concentration $12 \leq C \leq 21\% \text{ Mn}$

The magnetic state of a certain type of alloy depends very sensitively on the degree of atomic order, and it is known that the atomic order-disorder effect

manifests itself in associated electrical and magnetic properties of these materials. Atomic ordering takes place in Pt-Mn alloys near the composition Pt_3Mn which is ferromagnetic (171) with a Curie temperature above room temperature. This enabled us to recognize clearly the change in the resistance character at $\sim 11\%$ Mn, and the influence of the heat treatment on the behaviour of the resistivity.

Fig. (IV.8) shows alloys of 12%, 15%, 18% Mn annealed at different temperatures. The 12% alloy, when annealed at 1070°C for 4 hr and very rapidly quenched, gave a resistance minimum, but with the temperature of the minimum shifted to lower temperature (by ~ 8 K) then would be suggested for a 12% alloy (see Fig. IV.4) and also Fig. (IV.8)). Fig. IV.8b shows a 12% alloy annealed at 750°C for $\frac{1}{2}$ hr and quenched; considerable changes in the character of the resistivity are seen, from a minimum to a resistivity which increases monotonically with temperature, having a maximum in the slope $d\Delta\rho/dT$ at about 18 K. Fig. (IV.8c) shows the same alloy annealed at 600°C for 24 hr and then cooled in air, the maximum in the slope of the resistivity is found to be at about 23 K. The difference between curve b and c is that the low temperature resistivity for curve c has a larger slope than that of b, which indicates that the tendency towards a minimum is still relevant. These variations in the character of the resistivity and the freezing temperature with decreasing annealing temperature seem to point strongly to a progressive increase of short-range atomic order in the alloy. Short range atomic order would also explain the reductions in the residual resistivities (at $T = 0$) for concentrated ($>11\%$ Mn) alloys, since in the randomly aligned systems an additional contribution to the residual resistivity comes from the high proportion of the moments which are frozen into a spin glass state.

For more concentrated alloys, 15%, 18%Mn, the resistivity vs. temperatures for

different annealing temperatures are shown in Fig. (IV.8, d, e, f, g). No considerable differences have been observed in the character of the resistivity or in the maximum in the slope $d\Delta\rho/dT$, except that the low temperature data ($\sim 5^\circ\text{K}$) for 15% alloy annealed at 1070°C for 4 hr and quenched have smaller slopes than that of the same alloys when annealed at 750°C for $\frac{1}{2}$ hr. This is attributed to the same reason mentioned earlier. From the above description it follows that even with high temperature treatment we are unable to produce a resistance minimum in 15% alloy and that the competition between well randomized spin glass and short-range atomic order effects leads to a resistivity which increases monotonically with the temperature to produce a spin glass state. The behaviour of the resistivity as a function of the temperature is found to be simply $T^{3/2}$ as shown in Fig. (IV.9). It follows that the alloys are still in the spin glass state and this is confirmed by the magnetization data performed on 15% Mn alloy in V.S.M. apparatus for the alloy annealed at 1070°C for 4 hr and then quenched. The magnetization vs. temperature curve Fig. (IV.10b) shows a broad susceptibility maximum at about 17 K, which is a feature of spin glass behaviour, and an induced remanent magnetization (Fig. (IV.11b) and also (IV.10a)) which disappears around 24°K , similar to that found in many spin glasses.

The character of the magnetization isotherm at a temperature (4.2°K) below the onset of spin glass freezing temperature in 15% alloy is shown in Fig. (IV.10a) after cooling the sample in zero field. This strongly resembles that behaviour observed in normal spin glasses with induced isothermal remanence and with slow saturation at high fields. However, there is a very important fact in that the magnetization in the reversed sections of the cycle at first increases before coming down; the effect is also observable when the sample is cooled in an applied field (8KG) Fig. (IV.11a).

This effect can probably be attributed to what is called an "Exchange -

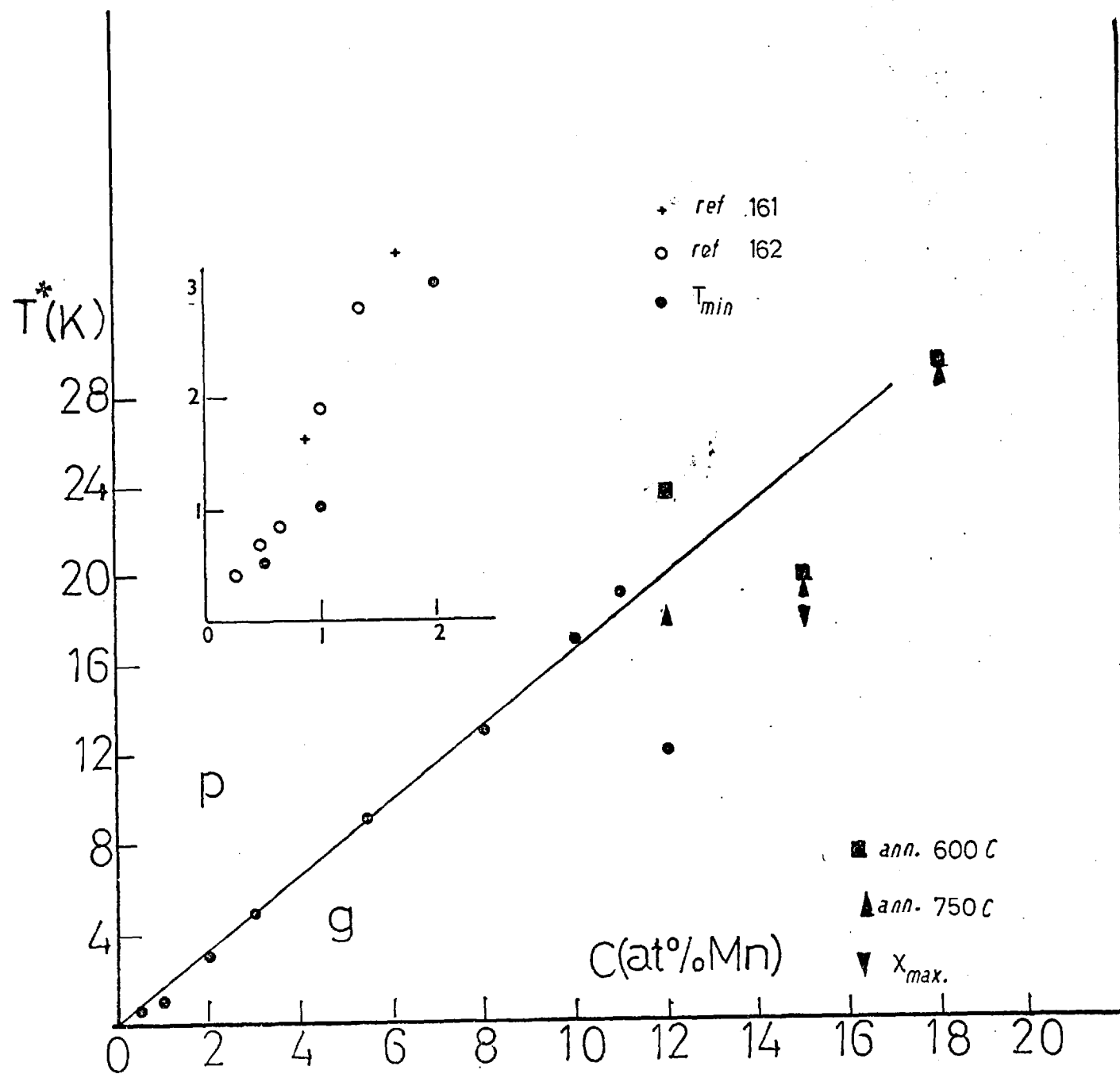
anisotropy effect" (172), which is an exchange coupling between antiferromagnetic Mn-Mn nearest neighbours asserting themselves against the ferromagnetic coupling of Mn-Pt atom neighbours (short range atomic order); this causes a parallel alignment for some of the atomic moments, thus increasing the net magnetization of the sample.

The maximum in the magnetization vs. temperature curve for the 15% alloy is at 17°K which is lower than expected from the low concentration trend. This might be related again to the effect of competition between different types of interaction preventing the occurrence of the susceptibility maximum at the expected temperature.

Incremental resistivity data for the 18%, 21% Mn alloy is shown in Fig. (IV.12). Both alloys were annealed at 600°C for 24 hr and cooled in air. The important respect in which the resistivity of 18% alloy differs from those discussed above is that the temperature dependence of the electrical resistivity seems to be T^2 rather than $T^{3/2}$ (as shown in Fig. IV.13) with a maximum in the slope much higher in temperature ($\sim 70^\circ\text{K}$). Similar temperature dependence for the electrical resistivity is found for the 21% alloy with a maximum in the slope at a temperature $\sim 180^\circ\text{K}$. These alloys (presumably) can be called inhomogeneous ferromagnetic (as one expects, low temperature annealing gives rise to ferromagnetism with the growth of atomically ordered regions); however, this ferromagnetism can be eliminated by high temperature annealing, when the destruction of short range order restores Mn-Mn nearest neighbour couplings which oppose ferromagnetism (for fuller discussion see (159)). It is indeed a complicated regime which depends strongly on the heat treatment which gives rise to widely varying short range atomic order, and the magnetic ordering becomes more and more complicated.

For these alloys of more than $\sim 11\%$ Mn the competing interactions and short range atomic ordering make detailed interpretations difficult without other types of measurement.

Fig IV.14



Conclusion

In the course of the present investigation, Mn dissolved in Pt falls into the "good moment" category, with very low spin fluctuation temperatures, comparable (presumably) with Au-Fe or Au-Mn alloys. The Pt-Mn system forms Coles type alloys and the resistivity in the extremely dilute limit might be described by the Rivier and Zlatic theory.

The Pt-Mn alloy system behaves quite differently from its Pd or Rh based counterparts. The alloys show neither a T^2 region nor linear in T regime, nor a region of ferromagnetism. Instead they show behaviour, even at the lowest concentration studied, attributable to spin glass behaviour, apart from some modification resulting from short range atomic ordering, which progressively increases with increasing Mn concentration and decreasing temperature of annealing.

The magnetic phase diagram for the Pt-Mn alloy system is shown in Fig. (IV.14) where we have summarized all the transition temperatures ($T_{\min}$, $d\Delta\rho/dT$, $T_{\max}$). Data for specific heat maxima reported by Nieuwenhuys et al (161) and Sacli et al (162) is also included.

It is perhaps important here to mention that below the spin fluctuation temperature, the temperature of the resistance minimum (or specific heat maximum) for more dilute alloys probably will be lower than would be expected by extrapolation from higher concentration data because of the weakening correlation between Mn - solute atoms which are responsible for the resistance minimum.

IV.2 (Pt-Pd) - Mn ternary alloy system

Introduction

The unexpected magnetic character of Mn as solute in Pt, as compared to in its counterpart Pd, has focussed our interest on the study of the effect of varying the local

environment around the Mn solute by varying the (Pt-Pd) composition. One might thus get a better understanding of the spin glass resistivity minimum as noted in Pt-Mn alloys. The solid solution of Mn in palladium has been the subject of considerable interest. Resistivity measurements by Williams and Loram (169) and Sarachick and Shattiel (173), susceptibility measurements by Rault and Burger (174) and specific heat measurements by Boerstol (175) indicate ferromagnetism for low Mn concentrations ($C < 3\% \text{ Mn}$) due to a long-range host polarization. Specific heat measurements on more concentrated Pd-Mn alloys are given by Zweers et al (160). Neutron diffuse scattering measurements by Ahmed and Hicks (176) on 10% Mn alloy indicate that the Mn moments are frozen to a sort of spin glass character. Coles et al (159) discussed the details of different types of interaction between Mn solute in Pd at large Mn concentration, where the initial ferromagnetism gives way to spin glass behaviour at around 5% Mn.

In this section we report the electrical resistivity measurements on some (Pt-Pd)-Mn alloys a ternary system made by varying the relative (Pt-Pd) composition and the Mn solute concentration. Unfortunately no detailed conclusions can be drawn from these resistivity measurements. However the addition of Pt to Pd seems to depress the strong exchange enhancement of the Pd metal.

IV.2.1 Results

The resistivity of each alloy was measured with and without Mn, and the temperature dependent part of resistivity $\Delta \rho(T)$ (incremental resistivity) due to Mn solute has been determined and according to Matthiessen's rule :

$$\Delta \rho(T) = \rho_{\text{alloy}}^{\text{Mn}}(T) - \rho_{\text{alloy}}(T)$$

where $\rho_{\text{alloy}}^{\text{Mn}}(T)$ refers to resistivities of an alloy with Mn, $\rho_{\text{alloy}}(T)$ to resistivities of an alloy without Mn of the same Pd/Pt ratio.

Fig IV.15

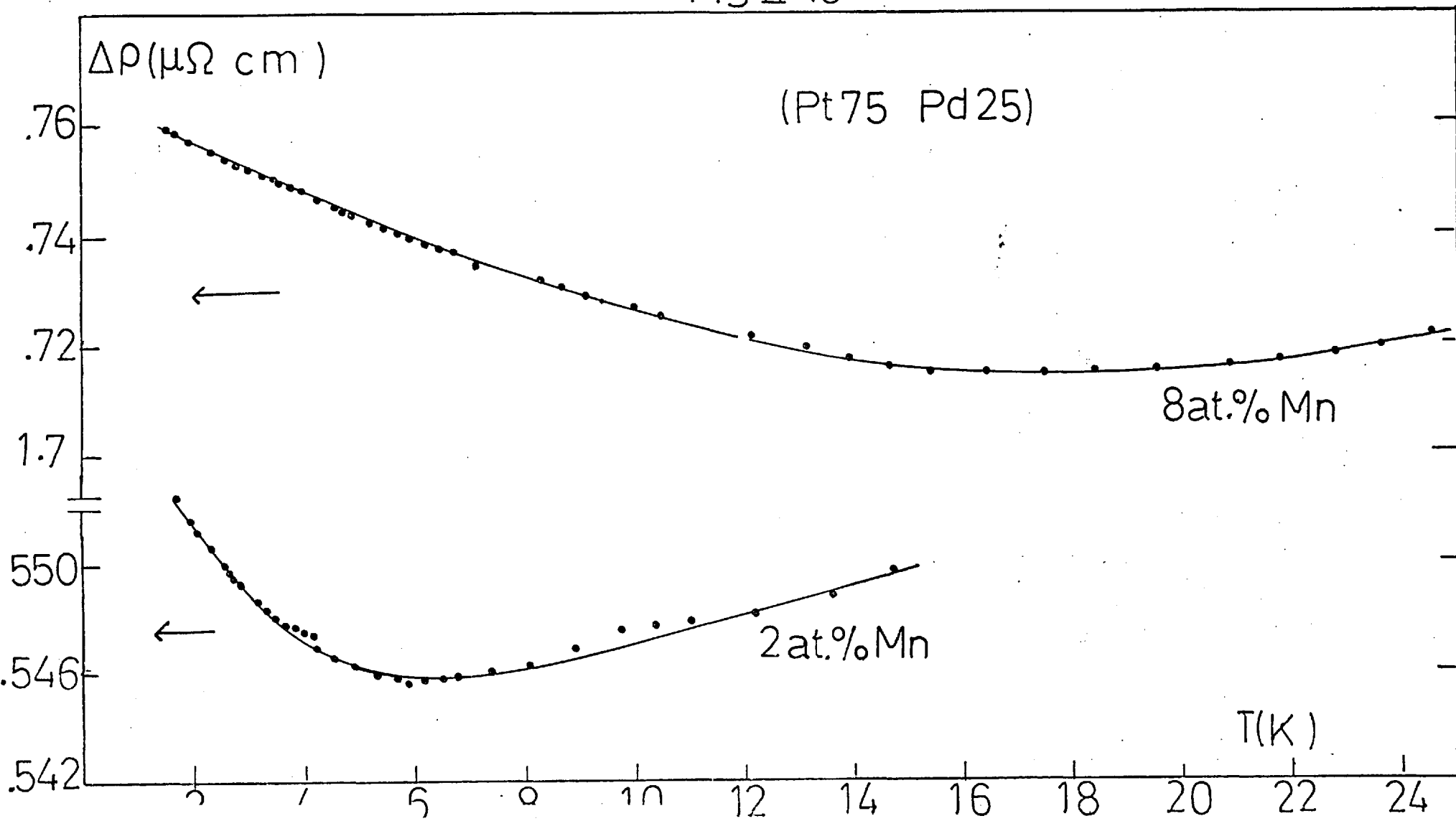
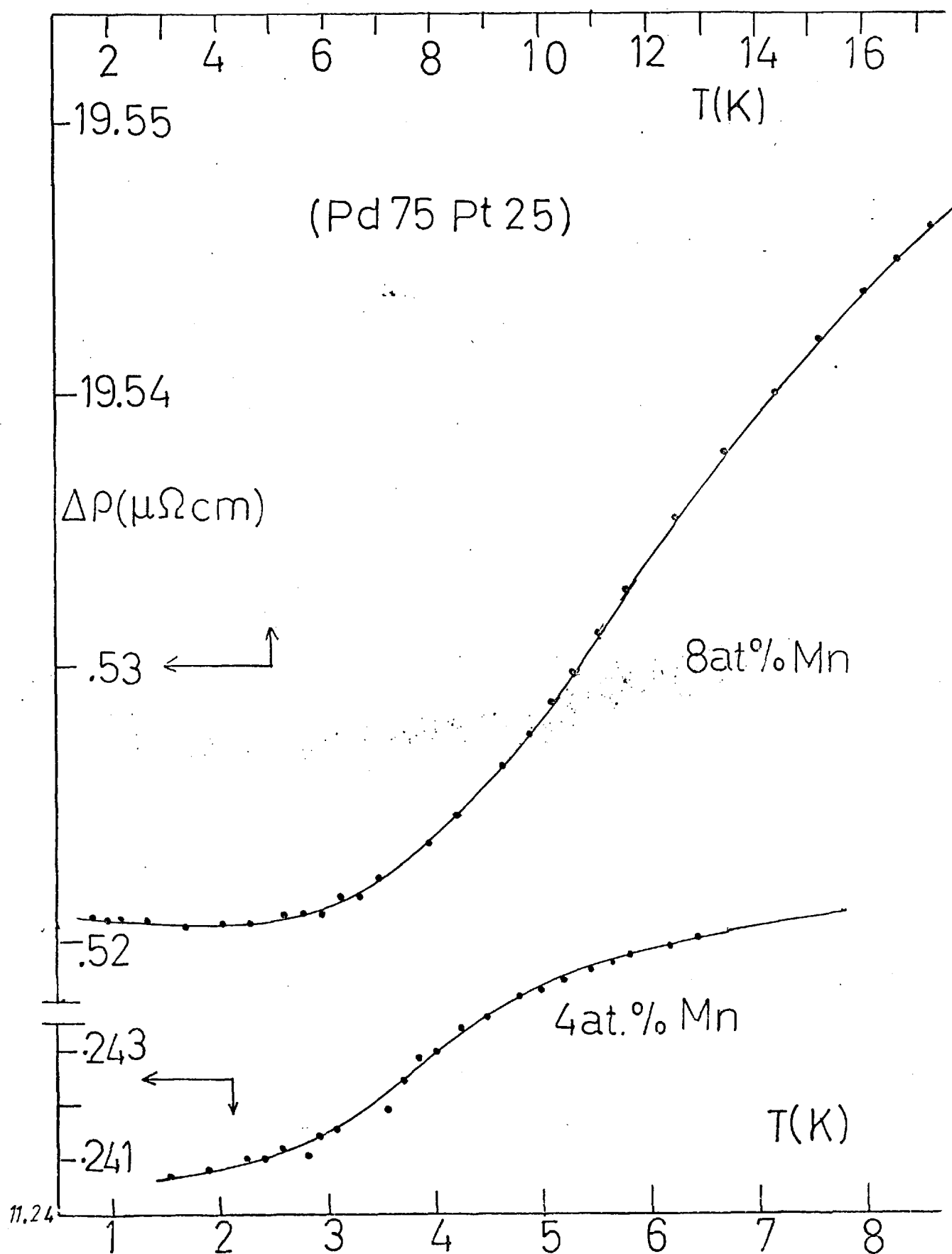
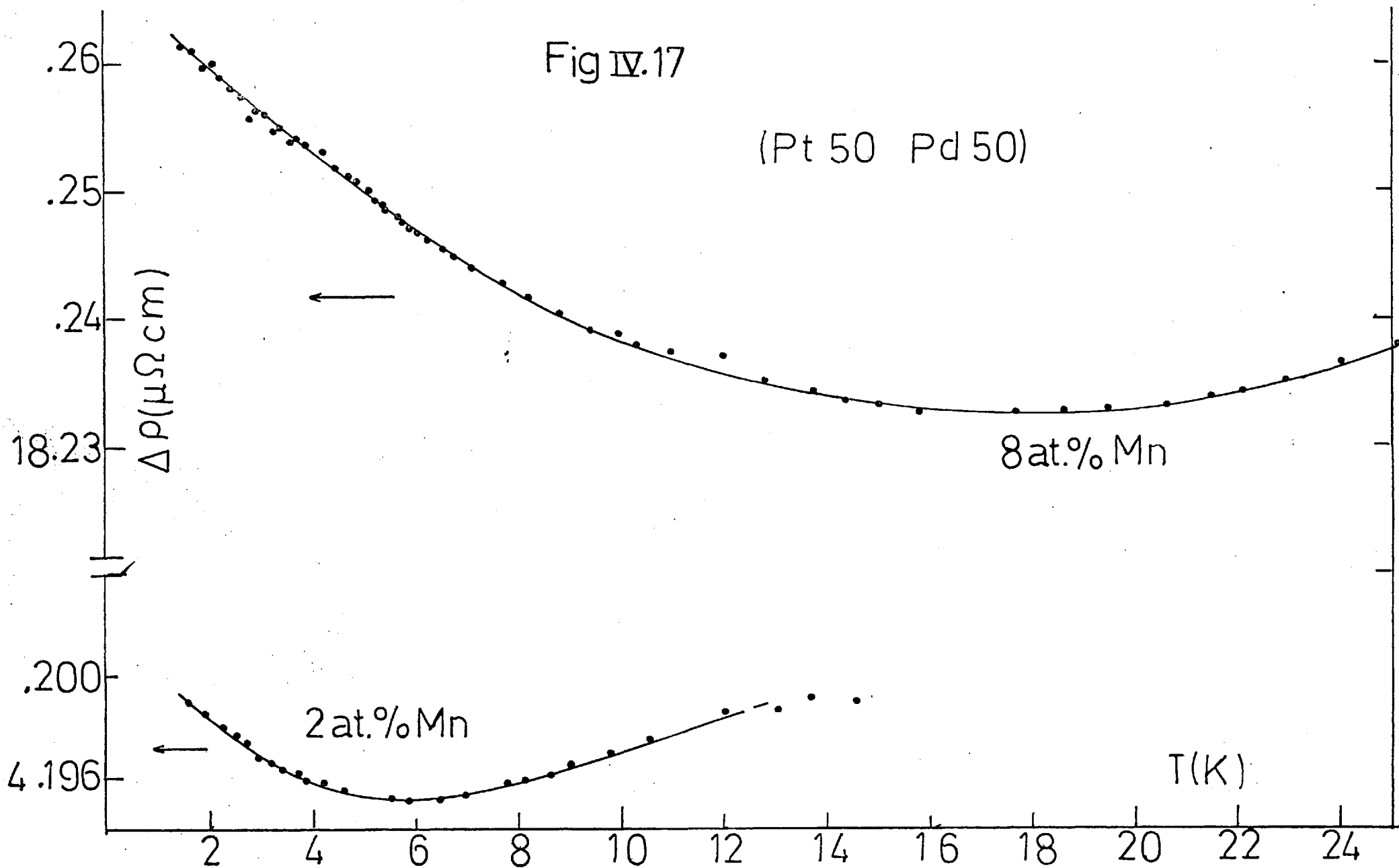


Fig IV.16





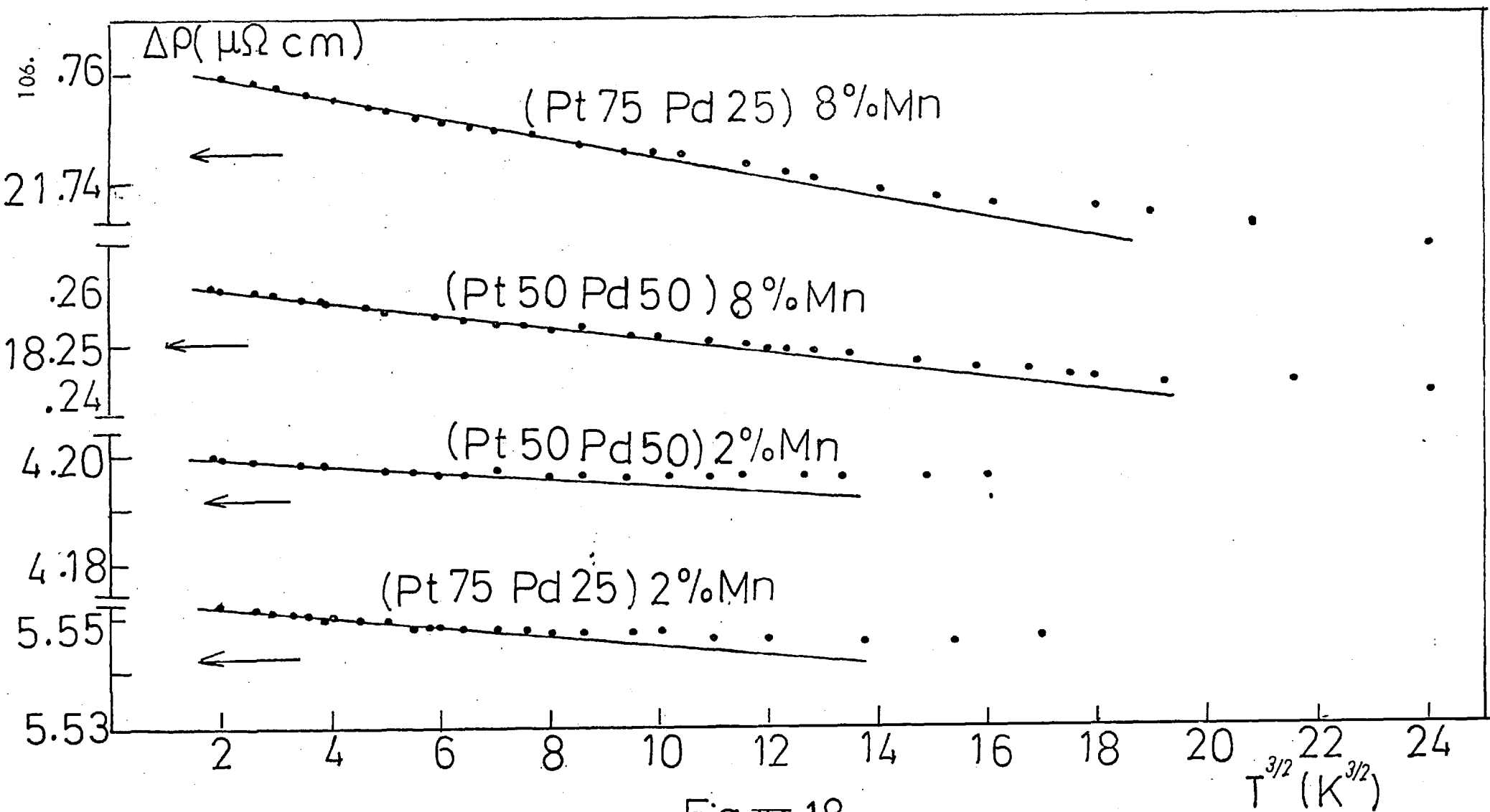


Fig IV.18

Fig IV. 19

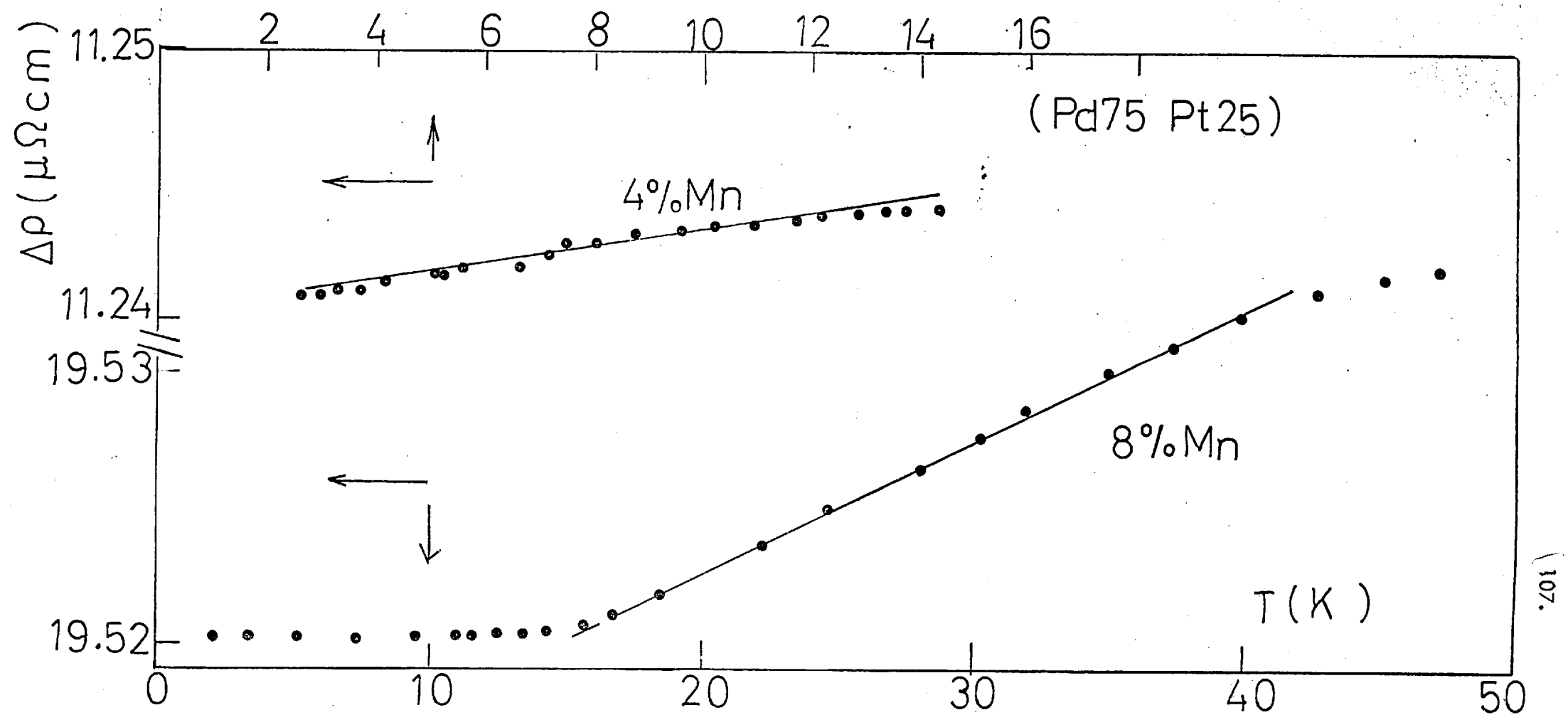


Fig. (IV.15) shows the incremental resistivity of 2% and 8% Mn solute in (Pt75-Pd25) * alloys. There is clear evidence of the resistivity minimum for these alloys at 6°K for 2% Mn alloy and at 18°K for 8% Mn alloy. Comparison of these data with Pt-Mn alloys of the same Mn concentration indicates an increase in the temperature of the resistivity minimum, as it was observed at 3°K and 12°K for 2% and 8% Mn alloys respectively in the absence of Pd.

The incremental resistivity at 4% and 8% Mn in (Pt75-Pt25) alloys is shown in Fig. (IV.16). No spin glass resistivity minimum is observed; however, the character of the resistivity is similar to that of Cu-Mn or Au-Fe alloys and also similar to the behaviour of the Mn resistivity in Pd-Mn and Pt-Mn alloys for concentration $\geq 5\%$ Mn and 12% Mn respectively.

Fig. (IV.17) shows the incremental resistivity of 2% and 8% Mn in (Pt50-Pd50) alloys. A spin glass resistivity minimum is also observed at 6°K for 2% Mn alloy and 18°K for 8% Mn alloy.

The temperature dependence of the resistivity of alloys which show spin glass resistivity minima is plotted against $T^{3/2}$ in Fig. (IV.18). It seems that the range of this $T^{3/2}$ temperature dependence increases with increasing Mn concentration. For Pd-rich alloys where the incremental resistivity increases monotonically, the resistivity increases initially faster than T and slower than the T^2 behaviour - probably a $T^{3/2}$ dependence, Fig. (IV.19); however it is difficult from the data alone to distinguish whether this $T^{3/2}$ behaviour is of physical significance, or whether a more complicated dependence may be used to interpret these data.

IV.2.2 Discussion

The addition of Pd to Pt increases the temperature of the minimum in the resistivity due to the Mn solute (Fig. IV.2) and (Fig. IV.15). If the temperature

* All the compositions are given in atomic per cent.

of the resistivity minimum is a measure of the interaction energy between the Mn-solute moments, then addition of Pd to Pt increases this interaction energy, possibly increasing the conduction band - polarization of the host.

The suppression of the ferromagnetism in the alloy with 4% Mn in a (Pd75-Pt25) alloy (where inhomogeneous ferromagnetism is observed for the same concentration of Mn in Pd (150) (159), suggests a lessening in the long-range Pd d-band polarization which yields the ferromagnetism. This seems consistent with Williams work (177) on Pd-Pt alloy, where he observed a strong depression in the room temperature susceptibility upon addition of 1% Pt to Pd. The character of the resistivity of 4% Mn and 8% Mn in (Pd75 - Pt25) alloys is different from that of Pd-Mn alloys in the spin glass region, where no well defined $T^{3/2}$ behaviour is observed. This is possibly attributed to the effect of Pt atoms which surround the Mn solute, and contribute to a spin glass minimum; hence one would expect modified solute resistivity. However, the monotonic increase in the solute resistivity is the general feature of these alloys.

For alloys where $Pt/Pd = 1$, the resistivity of the Mn gives a minimum of spin glass character, but the temperature of the minimum in the resistivity which is due to Mn is not greatly enhanced over that of Mn in Pt-rich alloys as one would expect. It should be remembered however that the spin glass alloys of the Pd-Mn system do not show a resistivity minimum. A more detailed discussion is not justified since the moment distribution of Mn solute and the polarization cloud around these atoms are not obtainable from these resistivity measurements.

Study of neutron scattering experiments will give direct information on the distribution of the polarization cloud around the Mn atoms, and the role of the local environment effect on the Mn moments. However, the details of the magnetic scattering

expected for magnetically frozen (disordered) systems are hard to estimate.

The variation in the magnitude of the moment with the relative composition of (Pt-Pd) by magnetization measurements will also be of interest. Whatever the details of such measurements may be, the Pt seems likely to depress strongly the well known exchange enhancement of the Pd, and hence suppress the long-range ferromagnetism.

The failure to observe ESR resonance in (Pt 10 - Pd 90) 2% Mn alloy (S. Male, private communication) is probably related to the depression of the exchange enhancement of the Pd upon alloying with Pt. This may be also connected with (a) a general failure to observe ESR resonance in a Pt 2% Mn alloy (R.H. Taylor, private communication) and (b) observation of a resonance in Pd where enhancement is strong (159).

A varying type of interaction would exist for Mn atoms, depending upon the local environment. Our measurements, which show a minimum and monotonic increase (with absence of any sharp change in the slope) in the resistivity depending on the relative concentration of (Pt-Pd), suggest that Mn moments are frozen into "spin glass" magnetic behaviour. The $T^{3/2}$ low temperature dependence and resistivity minimum are probably understandable in terms of Rivier and Adkins theory (129) (130), who have proposed a spin diffusion theory (see Chapter II, section II.5 and also the discussion given on Pt-Mn alloys). The residual resistivity at 4.2° K is larger in Pt-rich alloys than in Pd-rich alloys; the latter is smaller than that in alloys where (Pt-Pd) contents are equal; these values for 8% Mn are approximately 21.75, 19.52, 18.25 $\mu\Omega$ cm respectively. This is probably due to a higher proportion of frozen moments which contribute extra residual resistivity as compared to Pd-rich alloys, or else it may be due to the extra scattering from the electrostatic potential from the difference in the core charge of the host (Pt-Pd) and the Mn, which is the condition for the spin glass resistivity minimum, see ref. (130).

From the discussion given above, and also the discussion given on Pt-Mn alloys, the point which we can make is that the temperature of the resistance minimum is not always a measure of the "spin freezing" temperature of a magnetically frozen system; since it is the result of competition between more than one type of interaction.

Perhaps it is worth mentioning at this stage the possible reason for the absence of the ferromagnetism in solid solutions of Mn in Pt. We believe it is connected with the absence of the polarization cloud * around Mn atoms (where ferromagnetism arises from the long-range host polarization upon adding 3d-solute to Pd and Pt) where the RKKY type oscillations between Mn solute atoms lead to spin glass (spin freezing) ground state; on the other hand, with increasing Mn concentration, antiferromagnetic Mn-Mn nearest neighbour interaction becomes significant.

Our understanding of these results is still insufficient to provide any detailed explanations, in view of the absence of any other measurements; however, we have suggested some tentative explanation of our results.

* No significant enhancement in the effective moment of Mn (free ion) was found (Hou, private communication).

CHAPTER V

Results and discussions of c.p.h. Ru-Fe solid solutions and dilute Mo-Fe alloys

V.1 C.p.h. Ru-Fe alloys

Introduction

Extensive work on the magnetic properties of isoelectric Pd-Ni alloys has been done, where ferromagnetism sets in rapidly with increasing nickel concentration. But little attention has been paid to the Ru-Fe isoelectric system, although this should be of particular interest since the close-packed hexagonal solid solution extends (178) to more than 70% Fe, and its investigation should provide some information about the magnetic character of Fe in a c.p.h. structure to be compared with ferromagnetism of b.c.c Fe and the antiferromagnetism of f.c.c Fe.

From the magnetic susceptibility data (179) (180), electrical resistivity measurements (181) (182) and superconducting behaviour in the dilute Fe in Ru alloys revealed the solute as non-magnetic but with local enhancement effects as in the dilute alloy problem. Kao and Williams (182) estimate a local spin fluctuation (l.s.f) temperature of $\sim 700^\circ\text{K}$ from the observed T^2 behaviour in the electrical resistivity.

Claus (183) found a large peak in the coefficient of the linear term in the specific heat measurements in the Ru-Fe alloys in the c.p.h. phase at $\sim 59\%$ Fe. This is reminiscent of the peak near the critical composition for ferromagnetism in b.c.c V-Fe, but as the author points out no marked change in the nearly temperature independent susceptibility is found anywhere in the c.p.h. Ru-Fe phase. The only extensive investigations of iron-rich but c.p.h. Ru-Fe alloys are those of Ohno (184). He came to the conclusion that such alloys are antiferromagnetic but the susceptibility, Mossbauer effect, thermoelectric power, and neutron scattering data could not confirm the magnetic order and were not straightforward in their character and interpretation. We have therefore examined the system by resistivity measurements using an analysis of the data that has proved helpful for Pd-Ni (185), Rh-Co (186) and Rh-Fe (126)

systems in indicating the composition at which magnetic ordering sets in with increasing 3d-solute concentration.

V.1.1 Results and discussion

The resistivity at 4.2 K is shown for our alloys as a function of composition in Fig. (V.1). The more rapid increase above $\sim 50\%$ Fe is rather surprising, although such effects have been observed in other transition metal alloys; their occurrence in an isoelectric system is suggestive in itself of some changes in magnetic character.

The electrical resistivity as a function of temperature for the alloys concentration range $10 \leq C \leq 70\%$ Fe is shown in Fig. (V.2). The low-temperature behaviour for the alloys is shown in Fig. (V.3) and Fig. (V.4), where we show ρ vs T^2 . The best fit to the data was obtained with the expression

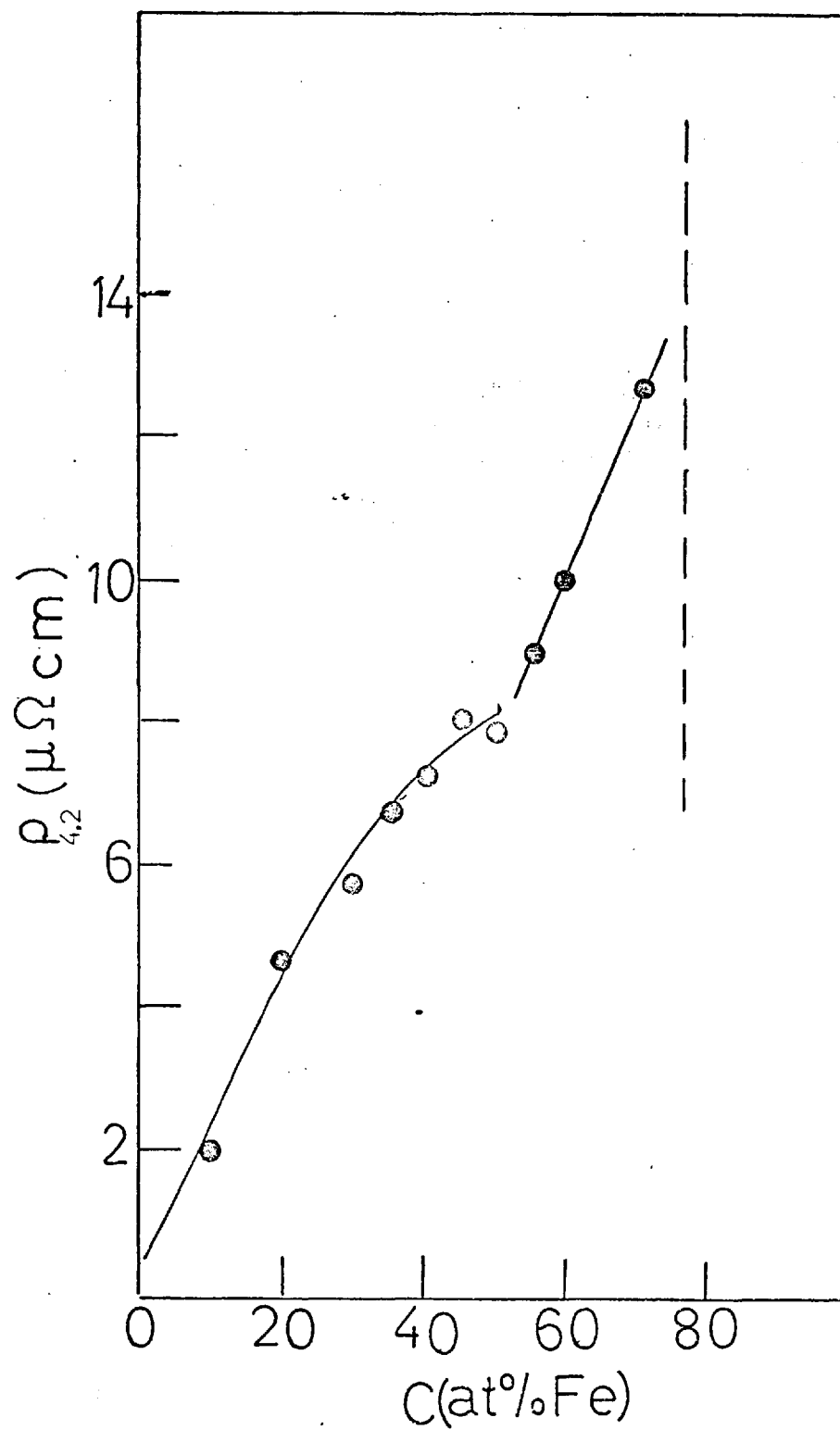
$$\rho = \rho_0 + AT^2$$

The range of this T^2 fit decreases with increasing concentration, while its coefficient increases reaching a maximum at critical composition for ordering and then decreases.

According to localized spin fluctuation theory by Rivier and Zlatic (59) (60), the observed T^2 behaviour is a sort of enhanced electron-electron scattering. For more concentrated alloys of this type this is a matter on which there is less agreement. At one extreme the T_{sf} value can be treated as depending on the average exchange enhancement in the alloy and falling to zero at the composition where (in a CPA-type of analysis (187)) long range magnetic order to be expected; at another the criterion for solute magnetization is expressed in terms of a required number of solute atom nearest neighbours (cf Perrier and Tholence (188)).

However, there will exist at low temperature a solute concentration above which some type of magnetic order is to be found and above which spin fluctuation (or spin waves) are progressively more difficult to excite as the temperature characteristic of the ordering increases. Thus the temperature-dependent spin fluctuation scattering

Fig V. 1



Resistivity at 4.2° K of c.p. hex. solid solutions of Fe in Ru. The broken vertical line indicates the approximate limit of this phase.

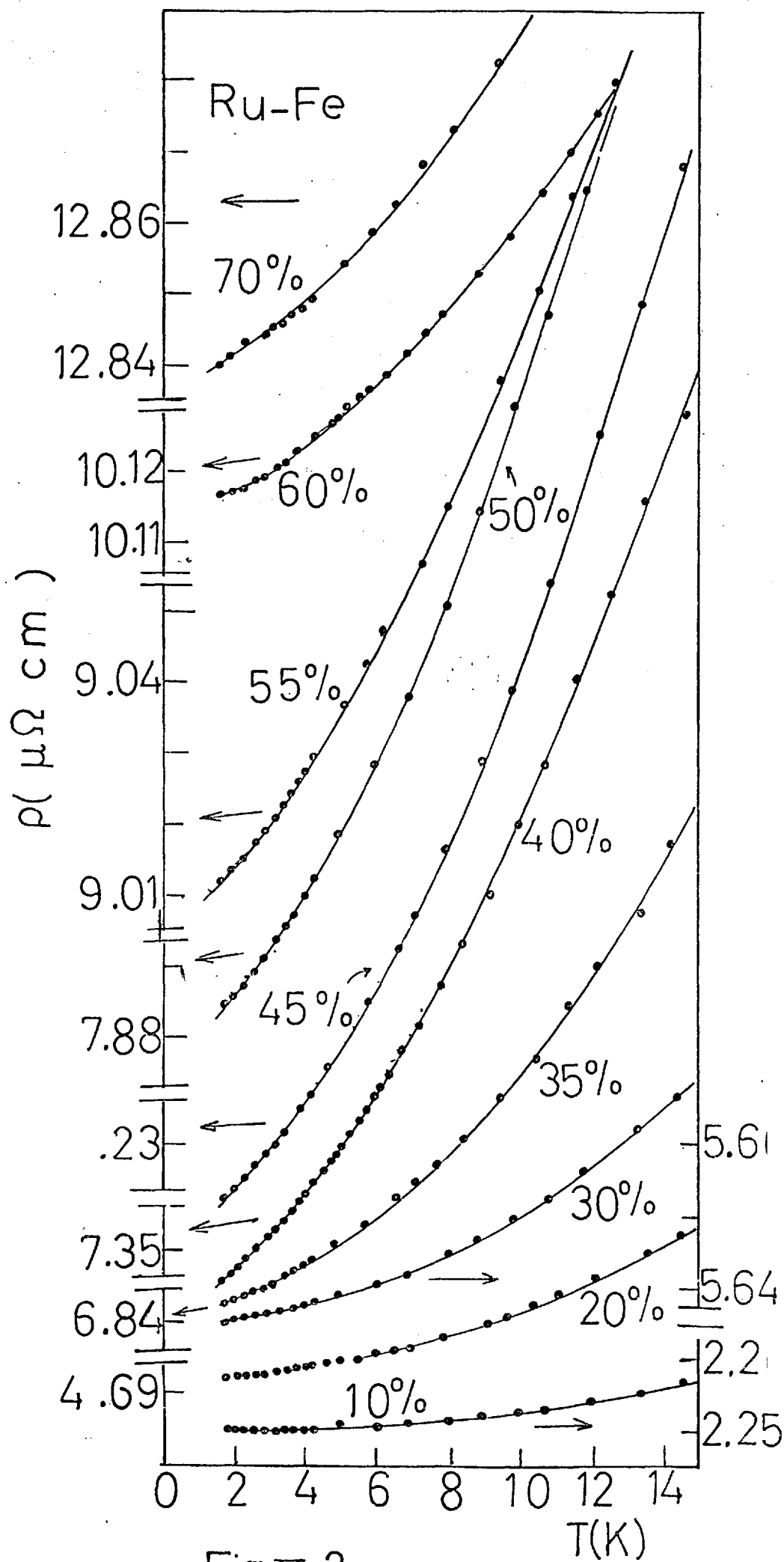


Fig V. 2

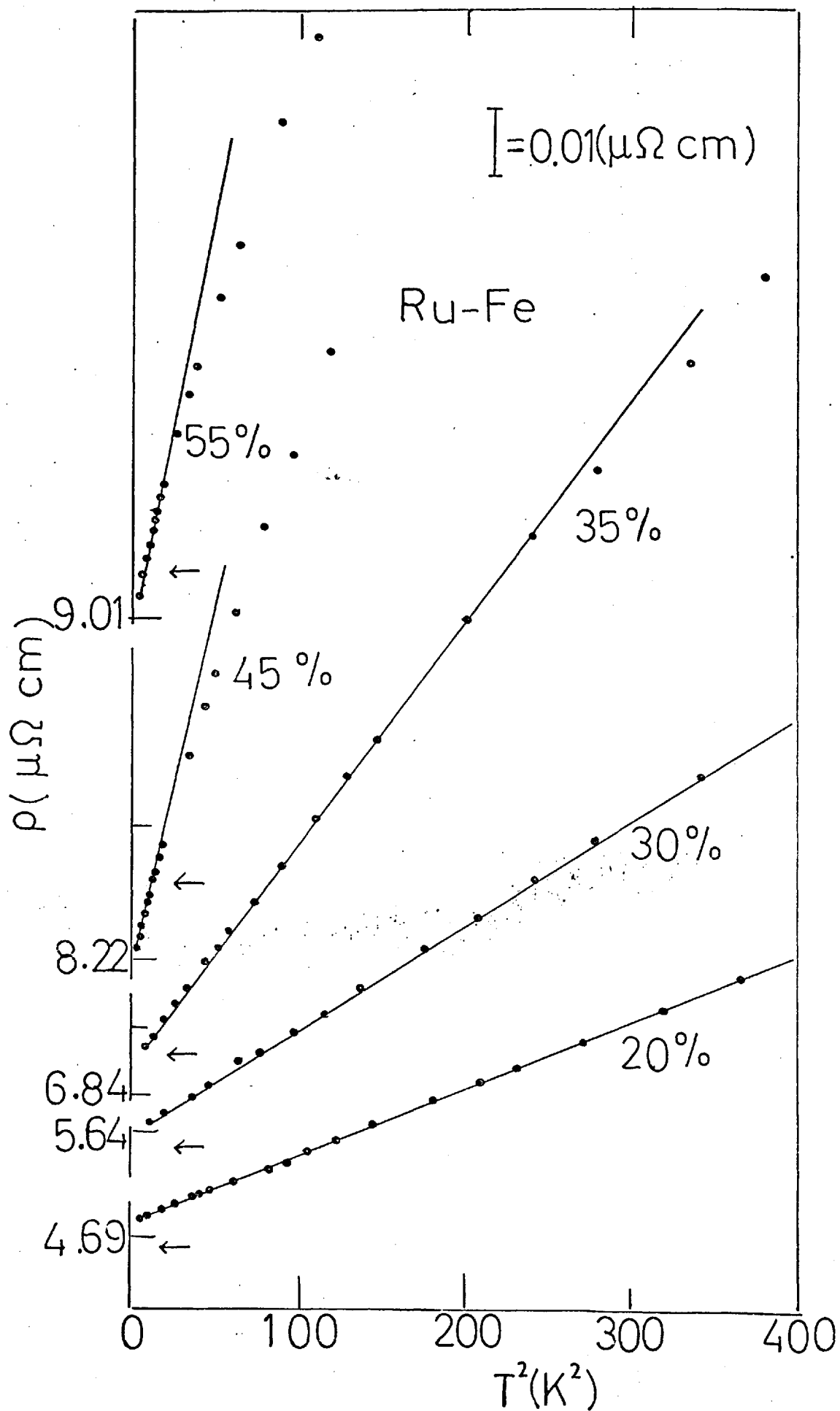


Fig V. 3

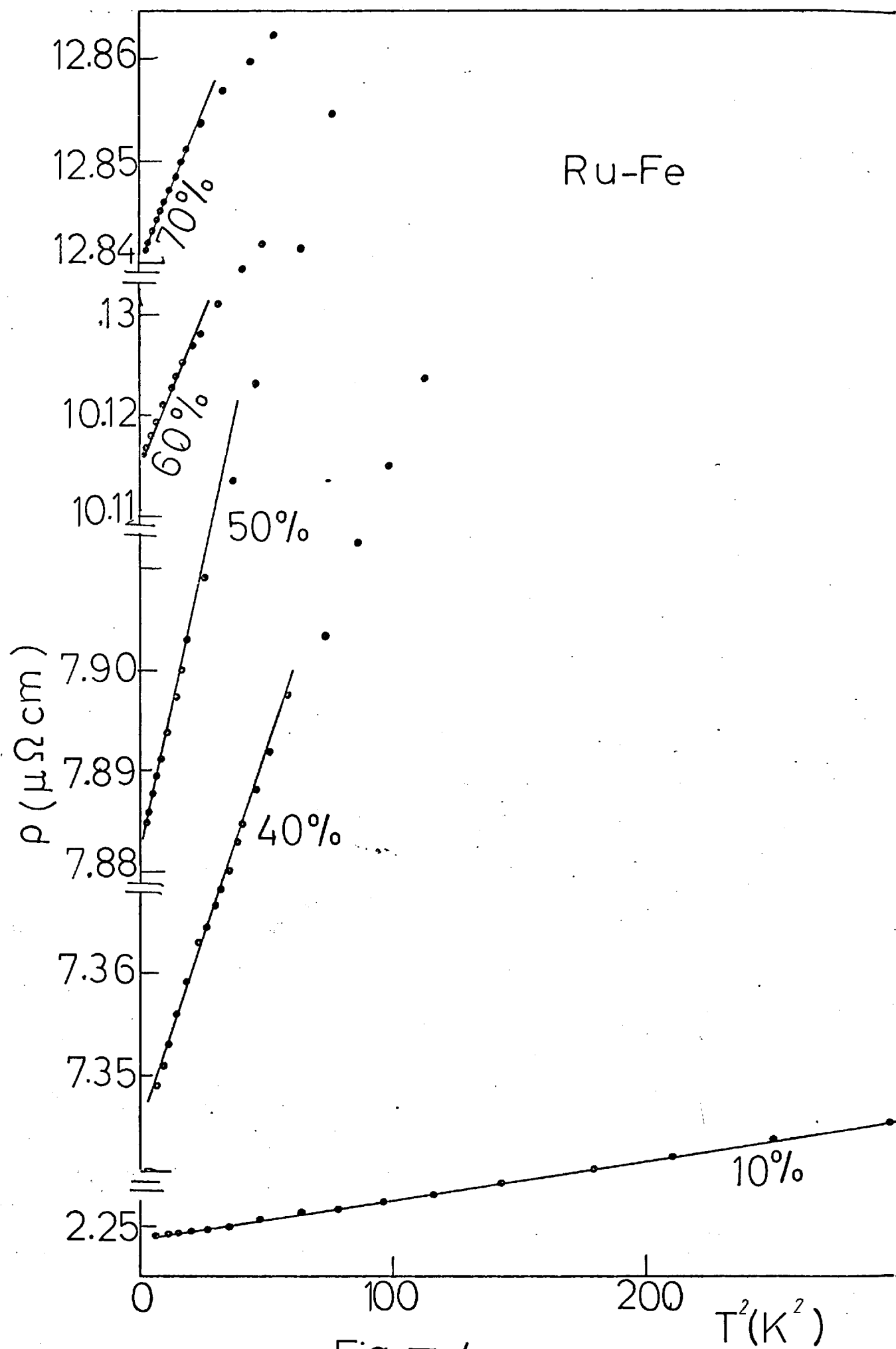


Fig V.4

term in electrical resistance will, as a function of solute concentration increases at first linearly then more rapidly, reach a maximum at critical concentration for the magnetic ordering and then decreases. This behaviour has been observed in a number of alloy systems like Pd-Ni (185), Rh-Co (186) and Rh-Fe (126).

In the Pd-Ni and Rh-Co systems the spin-fluctuation scattering in the low temperature range was found to deviate from a simple AT^2 form near the critical composition for magnetic order. Hence a plot of $\frac{\rho}{T_1} - \frac{\rho}{T_2}$ was a more honest presentation of the data than of A , with T_1 and T_2 not greater than 4.2°K where the phonon scattering term ($\sim 10^{10}$ ohm cm for Rh and Ru) is negligible and the resistivity is mainly due to the magnetic origin. This was essential for Rh-Fe where Rusby (126) showed that a T^2 behaviour only existed, even for very dilute alloys, below 2°K . In the Ru-Fe system because of the large value of T_{sf} (126) in the dilute limit a T^2 regime can be clearly identified for most of the alloys, Fig. (V.3) and Fig. (V.4). We have therefore plotted the coefficient of this term and the value of $\frac{\rho}{4} - \frac{\rho}{2}$ as a function of composition in Fig. V.5. (Values of the coefficient A and that of $\frac{\rho}{4} - \frac{\rho}{2}$ are listed in Table (V.1).

The peaks are extremely pronounced and of a transition to a magnetically ordered (or frozen) state at $50 \pm 2\%$ Fe, in agreement with the work of Ohno (184). The maximum magnitude of the spin fluctuation resistivity at 4.2°K is about 20×10^{-9} ohm cm which may be compared to $\sim 10 \times 10^{-9}$ ohm cm for Pd-Ni (185), $\sim 70 \times 10^{-9}$ ohm cm for Rh-Co (186), $\sim 200 \times 10^{-9}$ ohm cm for Rh-Fe (126) and $\sim 300 \times 10^{-9}$ for Ni₃ Gd (189).

However, the difficulty in interpreting the character of the magnetically ordered state in these iron-rich c.p.h Ru-Fe alloys comes from our magnetic susceptibility measurements on the 55% Fe alloy; the susceptibility has almost temperature independent behaviour with perhaps a slight decrease ($\sim 4\%$) below about 20°K , Fig. IV.6, and

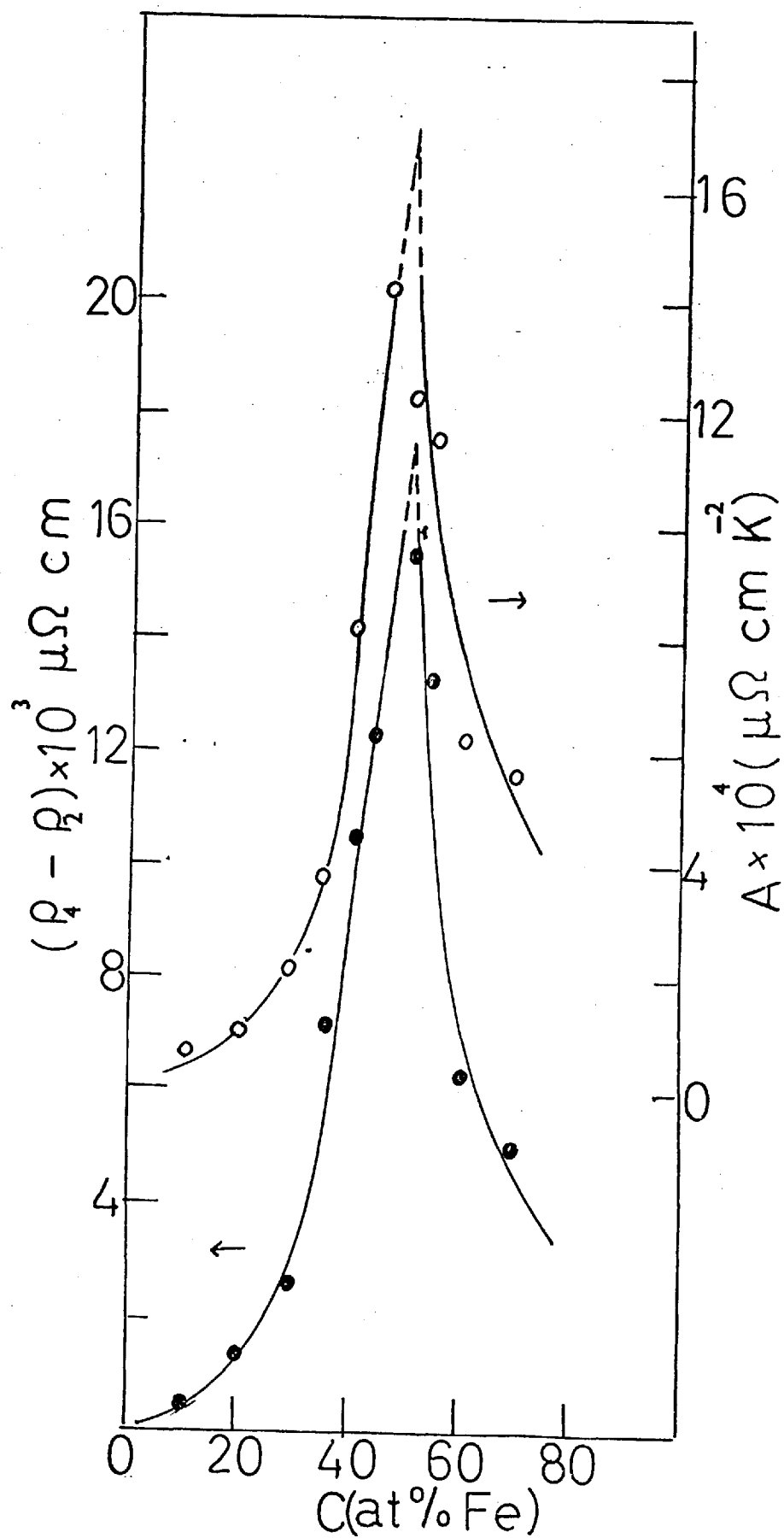


Fig V. 5

C% Fe	$(\rho_4 - \rho_2) \times 10^{-9} \Omega$	$A \times 10^{-4} \mu\Omega cm K^{-2}$
10	0.5	0.7
20	1.4	1.0
30	2.5	2.1
35	7.2	3.8
40	10.5	8.2
45	12.3	14.3
50	15.5	12.3
55	13.3	11.7
60	6.2	6.2
70	5	5.6

Table V.1

the magnetization of this alloy increases linearly with the applied field, Fig. (V.7). These observations rule out ferromagnetism. But the absence of any sharp maximum in $\chi(T)$, and any magnetic superzone boundaries effects in the resistivity, that we find in Y-Gd alloys (see the results in Chapter VI) and are well-known in Cr metal, suggests that the type of the magnetic order is unlikely to be an incommensurate antiferromagnetic.

In principle, we are probably left with a choice between a spin-glass type of spin freezing or an itinerant antiferromagnetism with a large concentration of non-magnetic Ru atoms substituted at random on both (all) sublattices. The first would correspond to what happens in Rh-Fe alloys with 3-15% Fe (126) (127), the latter to say Mo-Cr alloys with ~ 10 -20% Mo. The Mo-Cr system should provide a better basis of comparison since the specific heat behaviour found in Ru-Fe by Claus (183) is in fact very like that seen in Mo-Cr (190) alloys near the critical concentration ($\sim 75\%$ Cr) for the onset of itinerant (but commensurate) antiferromagnetism. No

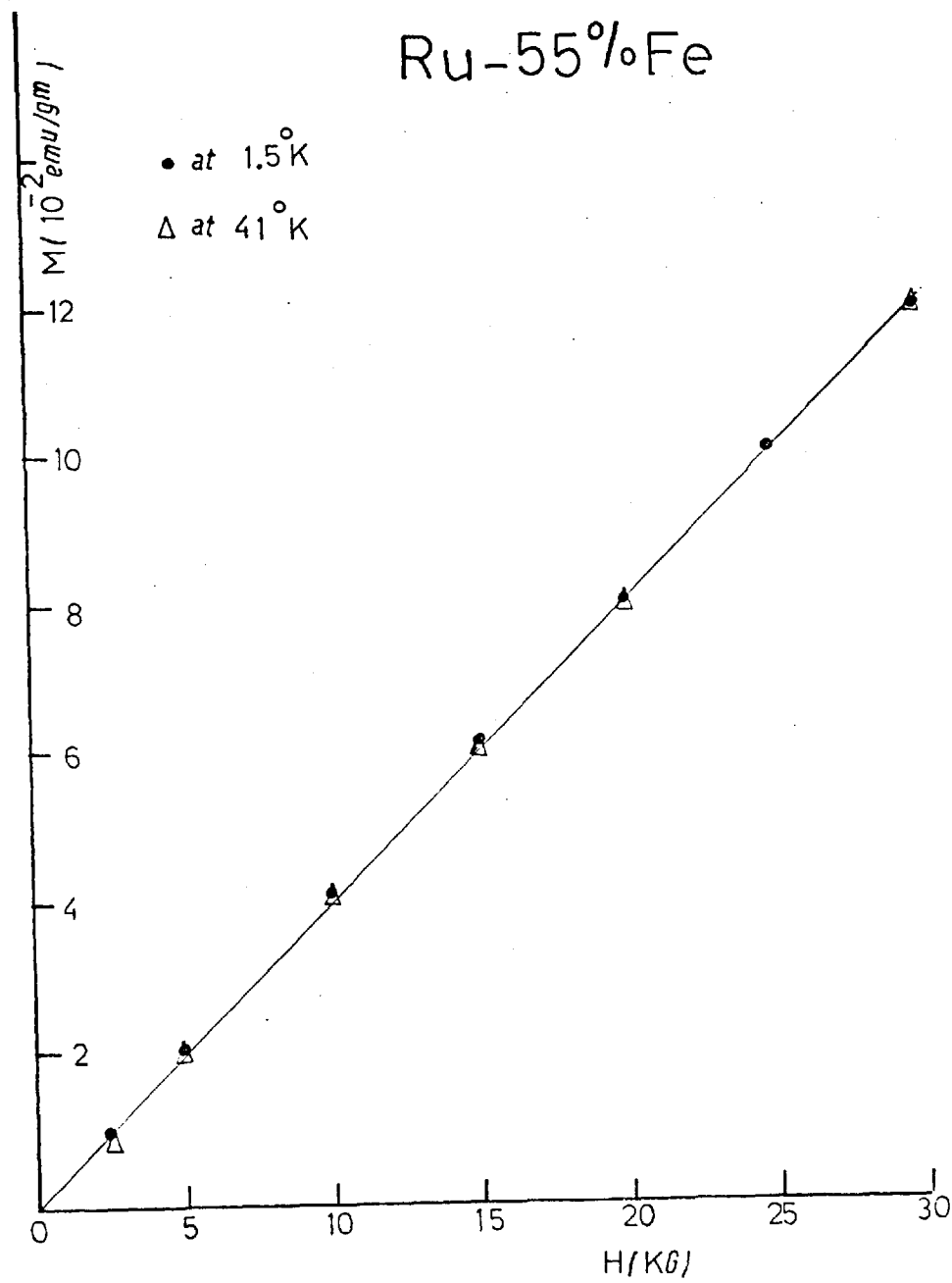


Fig. 7.

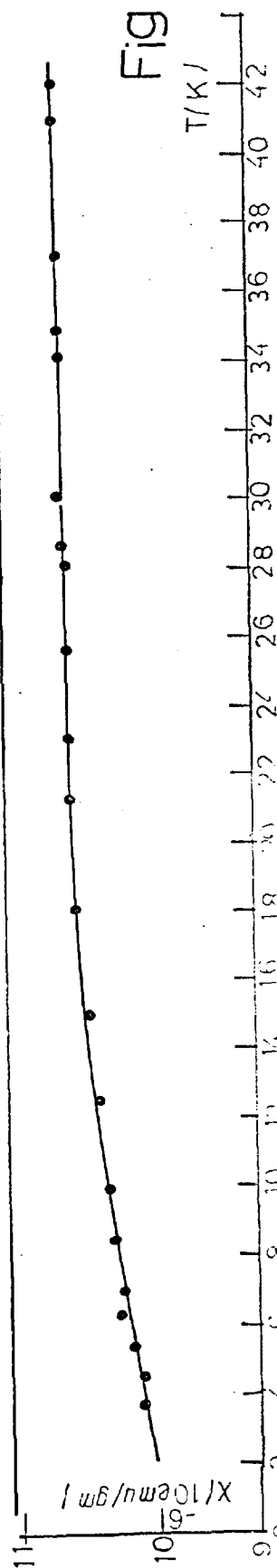


Fig. 6

detailed resistivity data of the sort we need seem to be available for Mo-Cr alloy. Therefore an itinerant antiferromagnetic ordering is what we believe happens in h.c.p. Ru-Fe alloys since, at the concentration of Fe involved, a simple spin glass of good local moments seems unlikely.

Comparison of our results with those from measurements (184) of Mossbauer effect and neutron scattering in Ru-Fe is not easy although we seem to be in reasonable agreement about the critical concentration. At present we feel that our resistivity data are the strongest evidence for the onset of some type of magnetic order in this system.

V.2 Dilute Mo-Fe alloys

Introduction

The iron solute resistivity in Mo-Fe was found by Coles (181) to have a resistance minimum (Kondo effect) character in the dilute limit ($C < 0.02\%$ Fe) and then the onset of long range interactions between impurities suppress this contribution giving rise to a maximum for a concentration $\sim 0.65\%$ Fe. Maley and Taylor (191) fit the low temperature Mossbauer effect data to localized spin fluctuation theory and estimated $T_{sf} \sim 1^\circ \text{K}$. Claus (192) showed from the susceptibility and specific heat measurements that the iron atom carries a magnetic moment of $3 \mu_B$ and from low temperature Curie-Weiss fit to the susceptibility data estimated the Kondo temperature $\sim 1.3^\circ \text{K}$, in good agreement with the value estimated by Maley and Taylor.

Effects of Fe impurities on the superconducting transition temperature T_c of Mo have been studied by Takayanagi et al (193) where it is shown that the addition of Fe strongly depresses the T_c temperature. Sugawara et al (194) resistance measurements in the dilute Mo-Fe alloys indicated that the iron impurity displays a logarithmic variation in the He⁴ temperature range.

It is interesting, then, to study the magnetic character of Mo-Fe alloys at low

temperature by resistance measurements. In this section we present the resistivity of the two dilute samples with concentration ~ 100 ppm (at) Fe and ~ 250 ppm (at) Fe. These measurements have been made in the dilution refrigerator down to about 40 m K. Non-magnetic behaviour is seen to characterize the impurity resistivity at low temperature based upon the localized spin fluctuation theory predicted by Rivier and Zlatic (59) (60).

V.2.1 Results and discussion

The two samples were obtained from KOCH-LIGHT and JOHNSON MATTHEY. The first was in the form of a thin wire of diameter (0.25 mm) and of length 20 cm, and the second was a strip of ~ 0.5 mm width cut from a sheet of thickness 0.1 mm. The spectroscopic analyses accompanying the samples gave the concentration as 250 ppm (at) Fe and 100 ppm (at) Fe respectively (with less than 5 ppm Mn). This was confirmed by independent spectroscopic analyses and by the Kondo slope compared with data from ref (194).

The effect of heating in the samples was checked by changing the current through the samples and no variation was found in the resistivity of the samples due to this effect. The measurements and mounting of the samples are described in Chapter III. A constant magnetic field of 110 Oe kept the 100 ppm sample normal, however no superconducting transition was observed in 250 ppm sample down to 40 mK. The high residual resistivities of these samples attributed to the non-magnetic impurities and also to the non-annealed samples.

The dilution refrigerator data $\leq 1.2^\circ\text{K}$ are connected with the results in the helium vapour pressure range (taken in He^4 resistivity cryostat). These are plotted against $\log T$ in Fig. (V.8); deviations from the logarithmic behaviour are evident in both alloys at 1°K for the 100 ppm sample and 0.4°K for 250 ppm sample. The results below these temperatures are plotted against T and T^2 in Fig. (V.9) and Fig. (V.10).

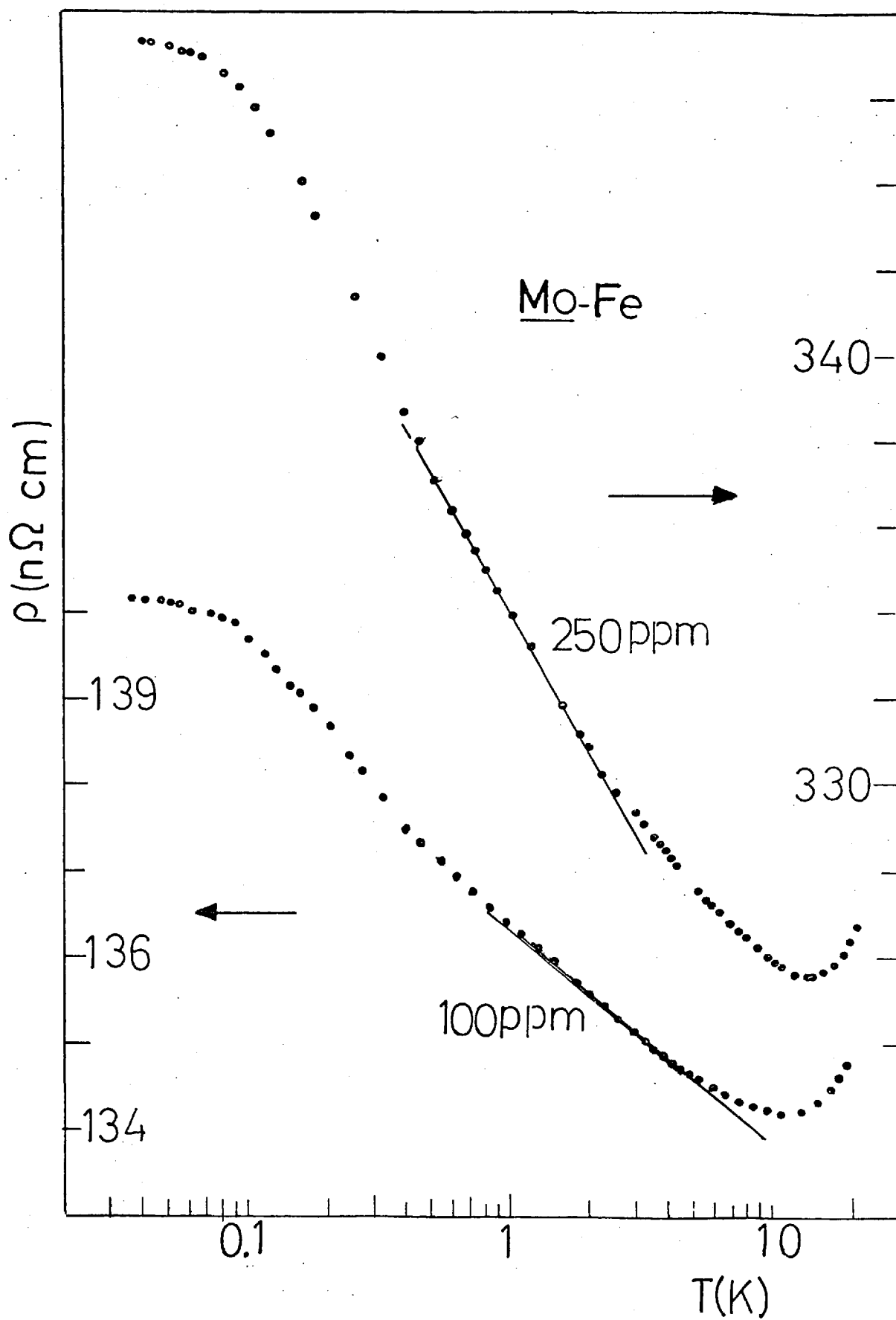
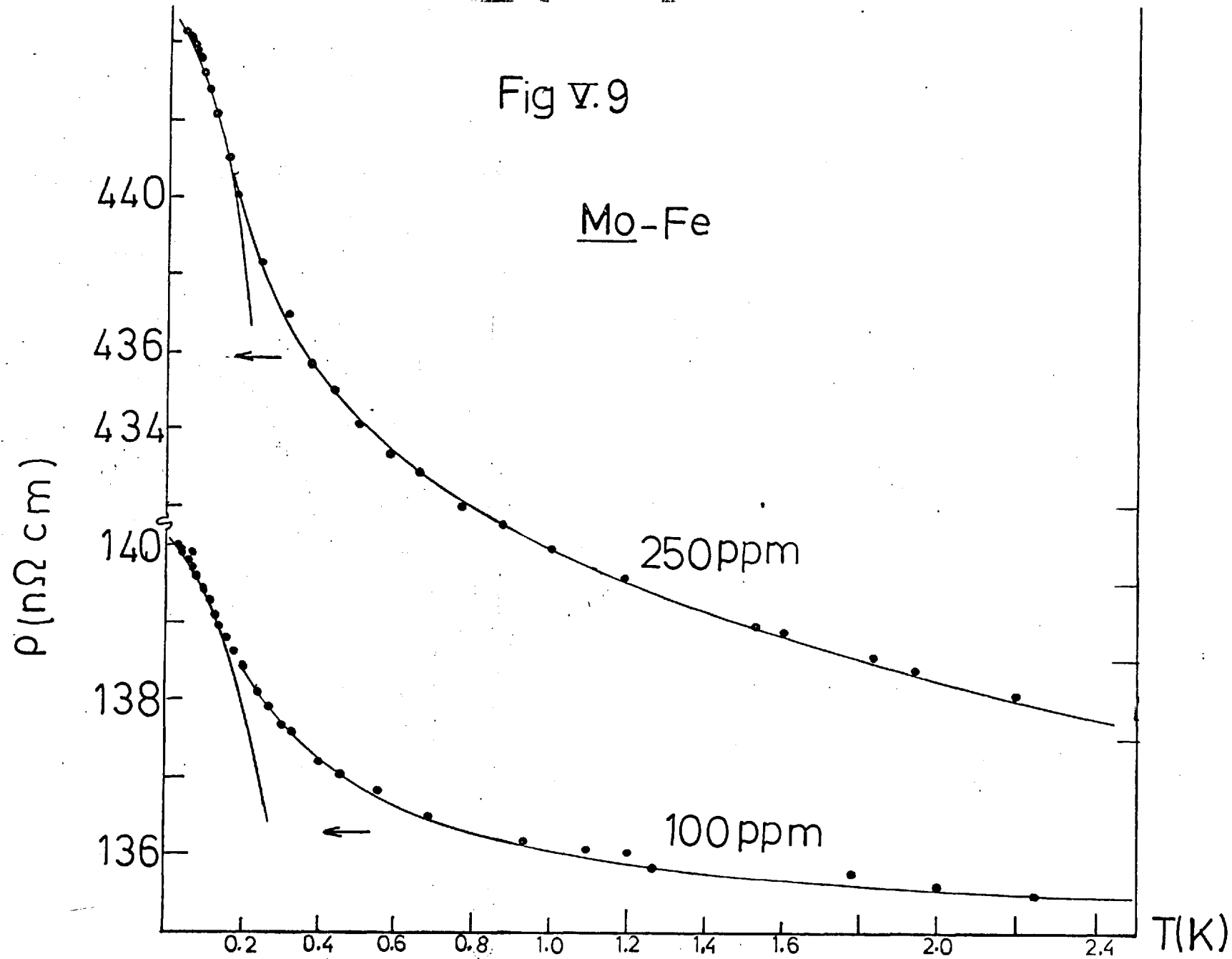


Fig V.8



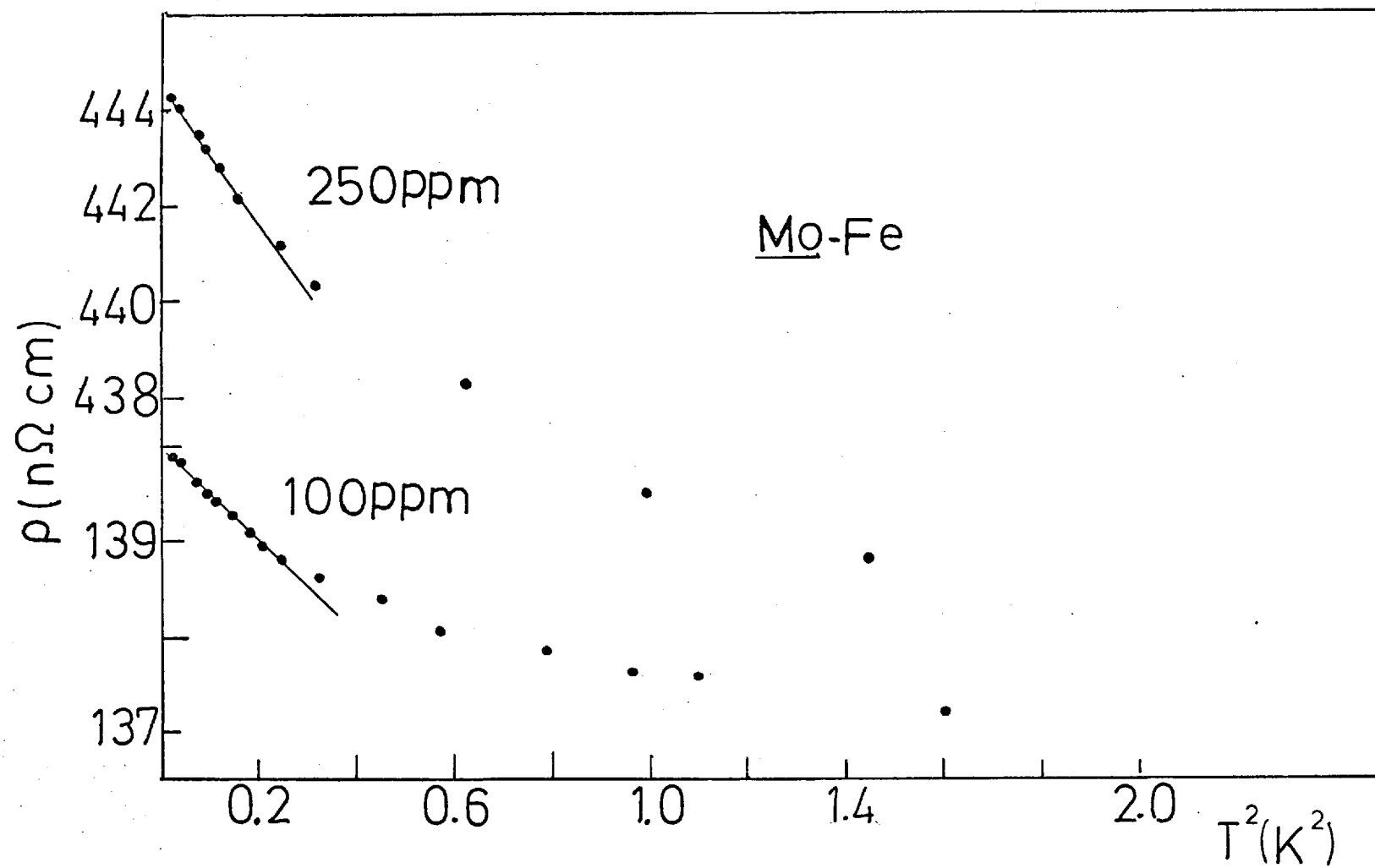


Fig V.10

From the latter it may be seen a T^2 law is obeyed below about 0.2°K for the 100 ppm sample and 0.14°K for the 250 ppm sample. This temperature behaviour may be convincingly suggested by observing also a linear plot of the data. It is evident also that there is a change from the T^2 to a linear region, which appears as an inflection in the region 0.2°K to 1°K for 100 ppm sample and 0.14°K to 0.4°K for 250 ppm sample. The variation in the results from one sample to the other indicates the effect of the interactions between impurities; this is also indicative by variation of T_{sf} temperature with Fe concentration.

It is clear from Fig. (V.8) that the observed logarithmic regions of these alloys are only extended in relatively short range and evidently reduced in the more concentrated sample by the effect of interaction. In this temperature range, however, the resistivity of pure Mo makes a significant contribution in such dilute alloys, and should be subtracted from the alloy resistivity. Unfortunately, the resistivity of pure Mo could not be measured because no high purity Mo is available now, and no data extending below 20°K have been reported in the literature. Therefore from the present data the range of the logarithmic region is difficult to identify. However, a well defined logarithmic variation in this system is confirmed from the data of ref (194), where the logarithmic region extends down to $\sim 10^\circ\text{K}$.

The most satisfactory explanation for the data presented on Mo-Fe alloys is the localized spin fluctuation theory predicted by Rivier and Zlatic described in Chapter I, section I.7. A stringent comparison of the theory with experiment can be made from the resistivity as a function of the temperature. At the lowest temperature T^2 behaviour ($1-AT^2$) is found, although the range of this behaviour is relatively short range $0.04 - 0.2^\circ\text{K}$. At higher temperatures a linear region is predicted by the theory, and this appears to be observed for Mo-Fe alloys, followed by an inflection region towards the logarithmic variation. This region is observable at a lower temperature for the 250 ppm alloy than that for the 100 ppm sample and the range of this

behaviour is extended in high temperature for the latter. This fact is attributed to the interaction effects between iron impurities. However, conclusive results may possibly be obtained if different concentrations were to be measured.

According to Rivier and Zlatic's theory, T_{sf} determines the temperature at which the low temperature logarithmic law gives way to the linear law; the values of T_{sf} for the present alloys were roughly estimated to be below 1 °K for the 100 ppm alloy and 0.5 °K for the 250 ppm alloy. However, because of the interaction effects, these values cannot be taken as the characteristic temperature of these alloys. The equation 1.6.4

$$\rho = \rho_0 \left(1 - (T/T_{sf})^2 \right)$$

is valid for $T < T_{sf}$. We have fitted the data to the region which displays T^2 behaviour to the above equation; the spin fluctuation temperatures obtained were $T_{sf} = 1.5 \pm 0.2$ °K for 100 ppm sample and 1.1 ± 0.2 °K for 250 ppm sample. These values are in agreement with the previous estimate of Maley and Taylor (191), and in better agreement with the T_{sf} obtained from susceptibility measurements by Claus (192).

The present resistivity data on Mo-Fe alloys have shown that there is a gradual transition to a low temperature non-magnetic state. This has been interpreted as low-temperature deviation from the logarithmic behaviour observed in the high temperature region. Application of l.s.f. theory to our results indicates a characteristic temperature $T_{sf} = 1.5 \pm 0.2$ K, provided that the alloy is sufficiently dilute. In practice it is necessary to reduce the concentration, to observe the interaction-free resistivity.

CHAPTER VI

Results and discussions : Sc-RE and Y-RE solid solutions (RE:Gd:Tb:Dy) *

Introduction

A number of solid solution alloys of heavy rare-earth metals in Yttrium and Scandium are known to give long range magnetic ordering. Paramagnetic-helical antiferromagnetic transitions have been reported for Y-Tb (195), Y-Gd (196) (197) and Y-Dy (198) alloys. For Y-Tb alloys Nagasawa and Sugawara (199) reported an effective moment per Tb atom larger than the magnetic moment ($9.72 \mu_B$) of the Tb^{+++} ion, and the Néel temperature vanishes at low concentration ($\sim 1\%$ Tb). Maxima in susceptibility have been reported for alloys Y 1% Gd and Y 1% Dy (197) at about 3.4 K and 1.34 K respectively.

Neutron diffraction measurements on Gd-Sc by Child and Cable (196) and Tb-Sc (200) by Child and Koehler show that the helical phase does not exist for less than about 25% Gd or Tb. The Néel temperature for Sc-Gd alloys vanishes at a concentration of $\sim 15\%$ Gd down to 4.2 K (201).

Spedding et al (202) have measured the magnetic susceptibility of dilute Sc-Gd alloys; a negative paramagnetic Curie temperature has been reported with effective moments greatly enhanced over the free ion value, such enhancements to the effective moments have also been reported by Wohlleben (203).

The data of Sugawara and Soga (204) on 0.5% Tb in Y suggests small crystal field splitting, such that several sublevels of ground state of the Tb ion are populated at helium temperature.

Resistivity measurements on dilute La, Y, and Sc-RE alloys have been made by Sugawara and collaborators (74); their results show the occurrence of many common features in these systems, with differences associated with the character of the

* Part of this work was reported at the 1975 Solid State Physics Conference at Manchester.

4f-solute including the moments, crystal field effects, the instability of the 4f electrons etc. Specific heat measurements on a series of Y-Gd (205) alloys have shown that there is a maximum associated with the magnetic ordering; a statistical model was used to explain many aspects of their results.

Thus it seems that although helical ordering is found down to quite low concentrations of magnetic element in some of these alloys (neutron results are available down to 5%Tb in Y-Tb) there is strong evidence for a critical concentration below which a helix is not formed in the Sc - alloys and the exact behaviour is unclear at low solute concentrations for the Y alloys. However even if helical ordering is not found in dilute alloys solute-solute interactions via conduction electrons must still exist. Measurements have therefore been carried out of the electrical and magnetic properties in the hope of elucidating the character of the magnetic phase diagrams. Where the coupling is weak (at low concentrations) the behaviour will be complicated for non S-state solutes by crystal field effects. These have been considered in detail by Hog and Touborg (206) (207) for very dilute single crystals. For Gd alloys it will be seen that the possibility of higher order magnetic scattering effects must be considered.

The object of our studies in these systems (Sc-RE, Y-RE) is determining whether one can use the electrical resistivity (or combination of electrical resistivity and magnetic susceptibility) to distinguish helical ordering from other types of low temperature spin freezing such as the spin glass. It turned out that this was possible since (as in the resistivity of Dy along c-axis or in the resistivity of polycrystalline Cr) the onset of long range spin density wave type antiferromagnetism is accompanied by the magnetic-superzones-induced resistivity hump, with a minimum in resistivity at Néel temperature. It has therefore been possible to map out tentative magnetic phase diagrams that show the temperature and type of spin freezing in the various

systems. In the spin glass regions the "glass" temperature is defined more easily by the susceptibility than by the resistivity.

In the following sections we will present the results and discussions in the following pattern:-

VI.1 Experimental results

VI.1.1 The concentrated alloys

- (a) Sc-Gd alloys
- (b) Y-Gd alloys
- (c) Sc-Tb alloys
- (d) Y-Tb alloys
- (e) Sc-Dy and Y-Dy alloys

VI.1.2 The dilute alloys

- (a) S-state impurities (Gd^{+++}) in Sc
- (b) Non S-state impurities (Tb^{+++} , Dy^{+++}) in Sc
- (c) S-state impurities (Gd^{+++}) in Y
- (d) Non S-state impurities (Tb^{+++} , Dy^{+++}) in Y

VI.2 Discussion

VI.2.1 The concentrated alloys

- (a) Sc-Gd and Y-Gd alloy systems
- (b) Sc-Tb and Y-Tb alloy systems
- (c) Sc-Dy and Y-Dy alloy systems

VI.2.2 The dilute alloys

- (a) Non S-state impurities (Tb^{+++} , Dy^{+++}) in Y and Sc
- (b) S-state impurities (Gd^{+++}) in Y and Sc

VI.3 Summary

VI.1 Experimental results

In this work, we have measured the resistivity of our Sc and Y as a function of the temperature; the resistivity ratio, equal to the resistivity at room temperature divided by the resistivity at 4.2 K, for Sc and Y was found to be ~ 20 and ~ 25 respectively, whereas Colvin and Araj (208) quote 5 for Sc, Alstad et al (209) and Araj et al (210) quote 25 for Y.

The resistivity of Sc and Y below ~ 7 K was found to be almost temperature independent and at low temperature the subtraction of pure Sc and Y from the alloy resistivity gives the magnetic or spin resistivity. However, above 8 K, where phonon scattering becomes significant and because Matthiessen's rule is not well obeyed, for the dilute alloys such a way of obtaining the magnetic resistivity becomes increasingly uncertain. In more concentrated alloys, however, the essential features of the resistivity behaviour are maintained, particularly below the magnetic ordering temperature when the resistivity of the host is subtracted from that of the alloy. The residual resistivity of these alloys was found to increase linearly with concentration at the low concentration region, and slower than linear on the high concentration side for Y-RE alloys, Fig. VI.1. A sharp increase seems to occur for Sc-RE alloys at a concentration comparable to critical concentration for helical magnetic ordering, Fig. VI.2 (see below). However, the residual resistivities data are rather scattered in some alloys. This is partly accounted for by the effect of dislocations or defects in the unannealed samples; possible gaseous contamination during the preparation might also account for the latter.

The magnetic measurements were made on cylindrical samples (the same samples were used for the resistivity measurements) 4-5 mm long and 2-2.3 mm in diameter using the Faraday microbalance (151). No demagnetization correction to the effective field within the sample has been made, since no low field measurements have been made. (The demagnetization correction is not negligible for samples with large magnetization in very low field measurements). The general features of the curves will not be affected by ignoring this effect.

All the concentrations are nominal and given in atomic per cent.

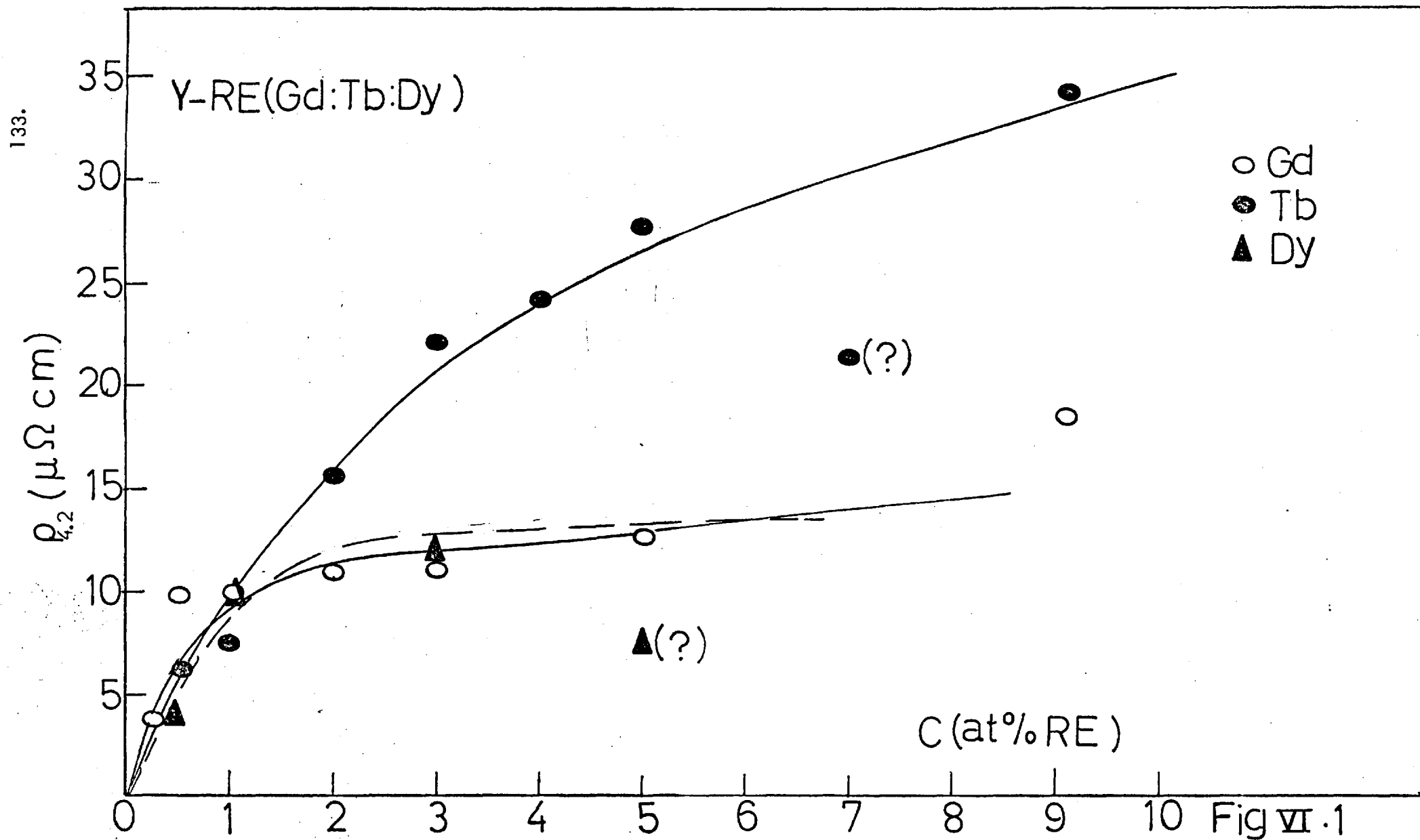
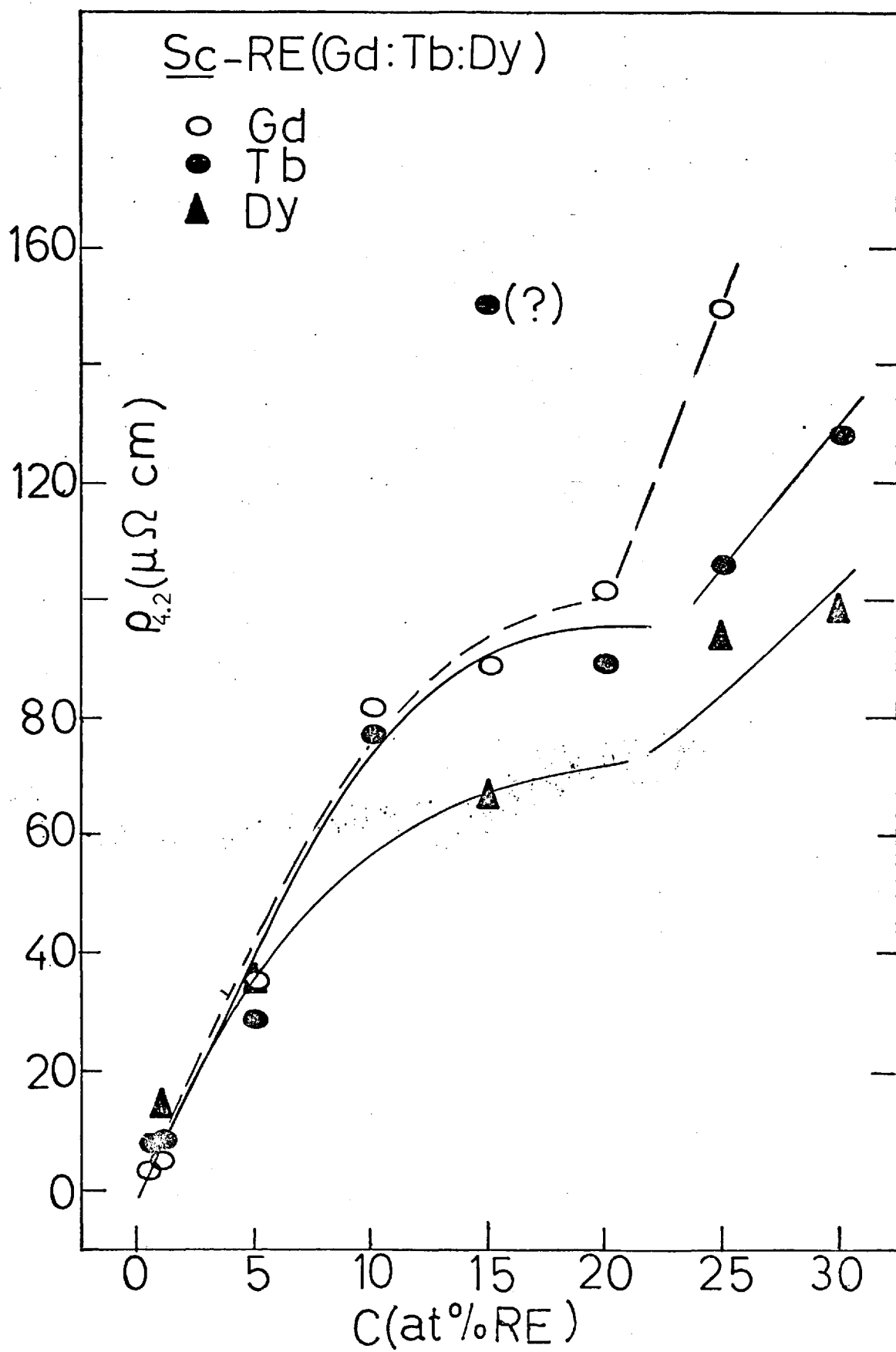


Fig VI. 2



VI.1.1 The concentrated alloys

(a) Sc-Gd alloys

Figure VI.3 shows the full temperature dependence of the incremental resistivity $\Delta \rho(\rho(T) - \rho(T)_{Sc})$ for 5%, 10%, 15%, 20% and 25% Gd alloys. In alloys with $\leq 20\%$ Gd the behaviour is quite different from that of 25% Gd alloy and similar to normal spin glass materials. The low temperature behaviour for 25% Gd alloy is deduced from the log-log plot of $\Delta \rho(T) - \Delta \rho(1.5)$ vs. the temperature (Fig. VI.4a). The effect of the magnetic ordering in this alloy is clearly indicated by the anomalous resistivity hump. The low temperature initial resistivity behaviour for $\leq 20\%$ Gd alloys is shown in Fig. VI.5 where we show $\Delta \rho$ vs. $T^{3/2}$ down to the lowest temperatures; the best fit to our data was obtained with the expression $\Delta \rho = \Delta \rho_0 + \beta T^{3/2}$. It is clear that the range of this $T^{3/2}$ fit increases with increasing concentration, the deviation of data points from this behaviour indicates a slower than $T^{3/2}$ variation (presumably) tending towards a T dependence, which can be seen more clearly from Fig. VI.3, given by a maximum in the slope of $\Delta \rho(T)$. The coefficient β of the $T^{3/2}$ dependence was found to decrease slowly with concentration, and a plot of $\log \beta$ vs. $\log c$ for alloys $\leq 20\%$ Gd is shown in Fig. VI.6, where a straight line can be drawn indicative of a linear proportionality; a power law such as $c^{-0.7 \pm 0.1}$ would be the best fit to the observed data.

The behaviour of the magnetic susceptibility vs. temperature curve is given in Fig. VI.7, where we show the susceptibility $(\chi_{\text{alloy}} - \chi_{Sc})$ against T measured in a field of (~ 0.5 KG). A Curie-Weiss plot $(\chi_{\text{alloy}} - \chi_{Sc})^{-1}$ vs. T is typical of many such alloys (Fig. VI.8); a large enhancement in effective moments per Gd atom has been observed in these with paramagnetic Curie temperature as listed in table VI.1

Magnetization-field isothermals for these alloys are shown in Fig. VI.9 and 10 which are the plots of reduced magnetization M/M_s vs. H/T , where the full line is the Brillouin curve for $J = 7/2$. High temperature (40.5 K) magnetization-field isothermals for the alloys 10% and 15% Gd are also shown in Fig. VI.11. The temperature variation

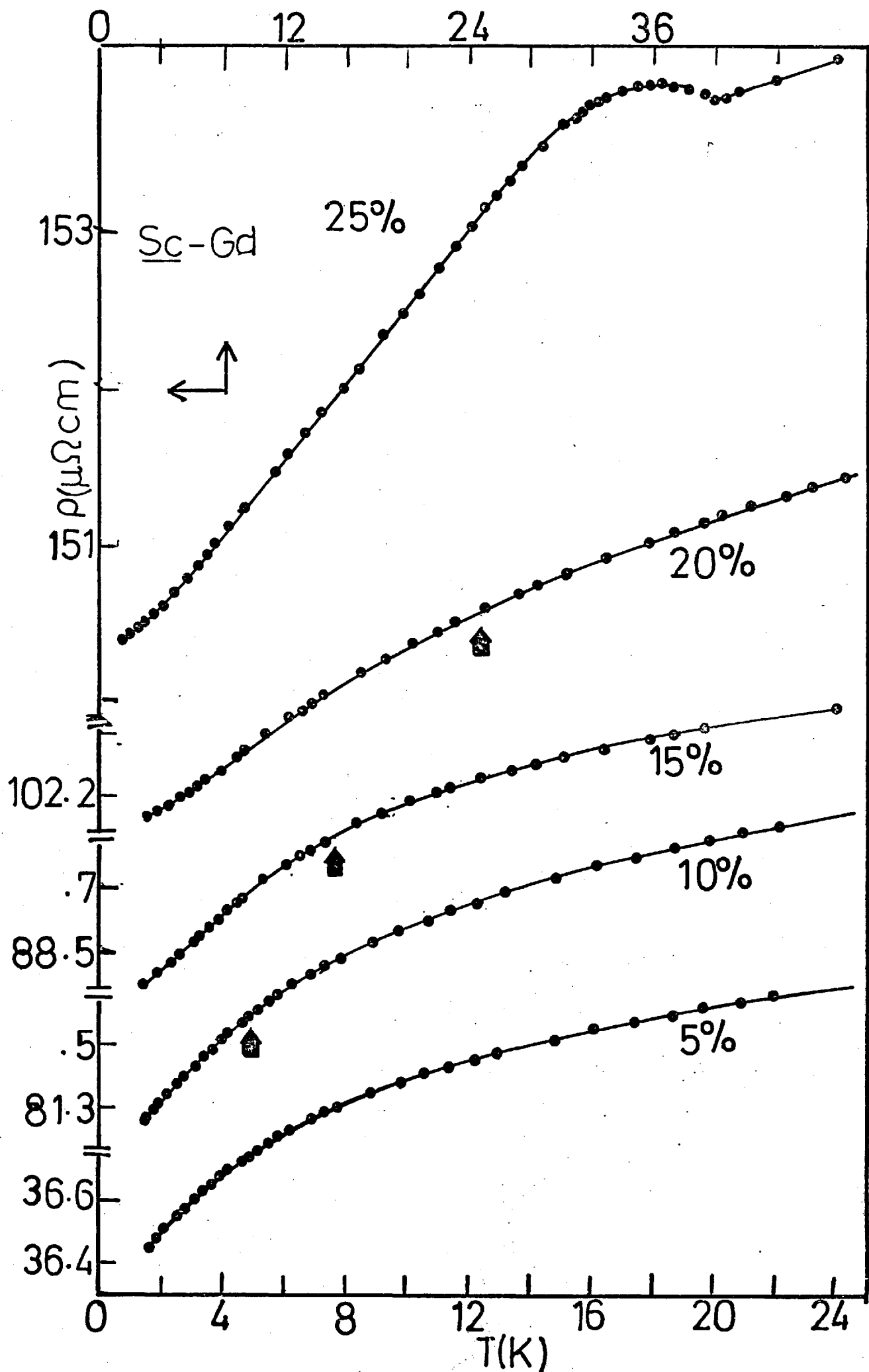


Fig VI. 3

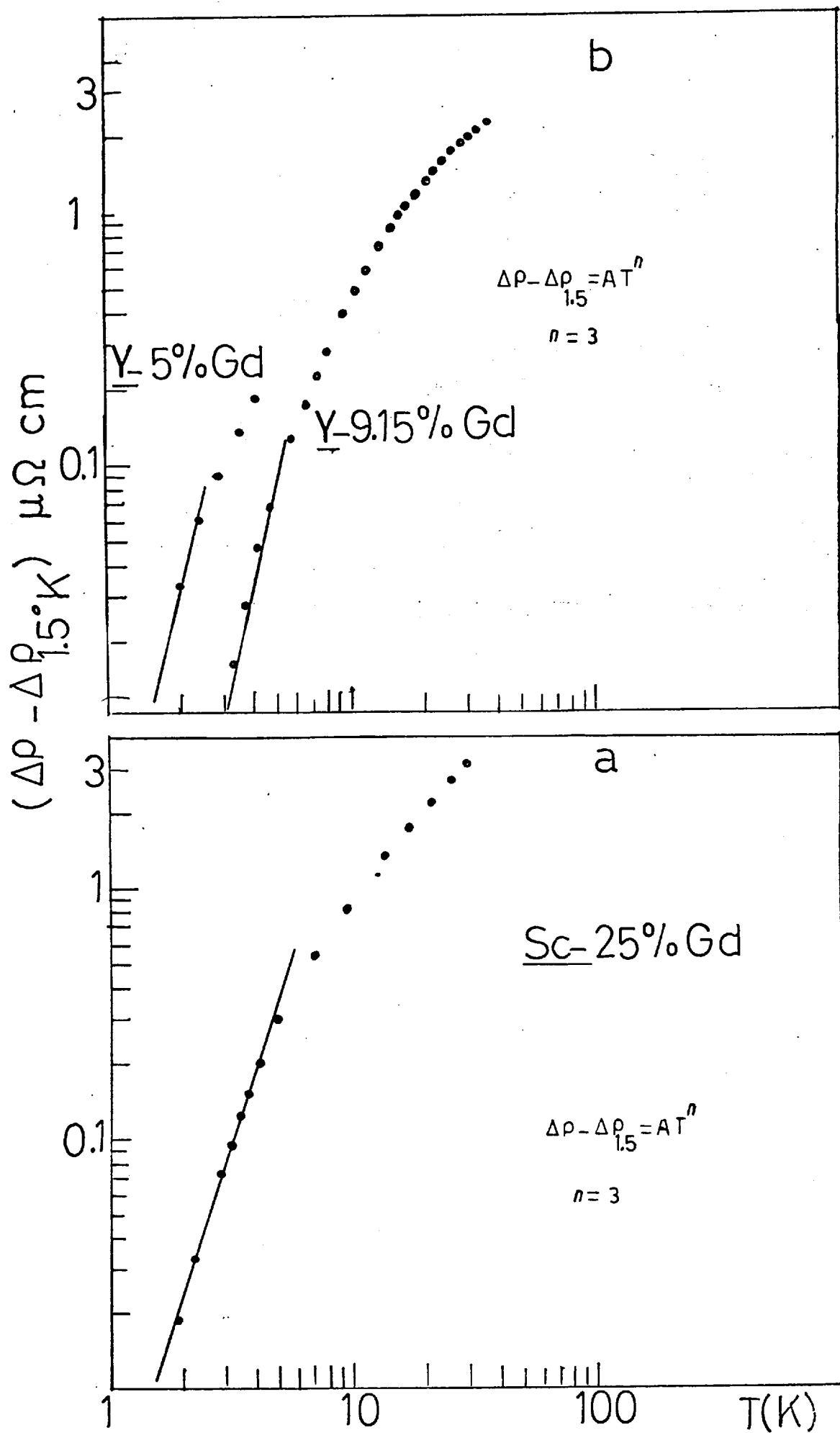


Fig. 4

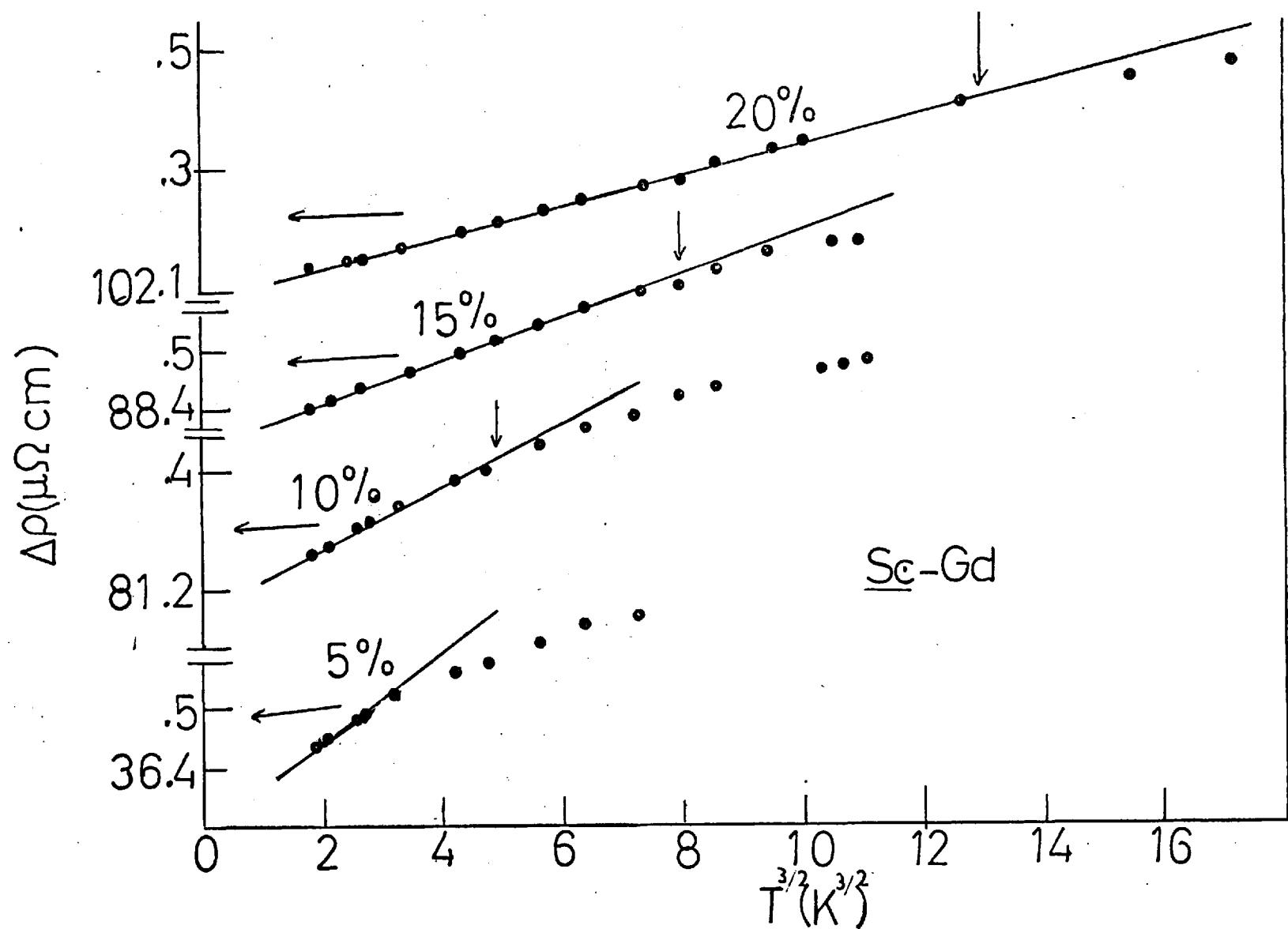


Fig VI. 5

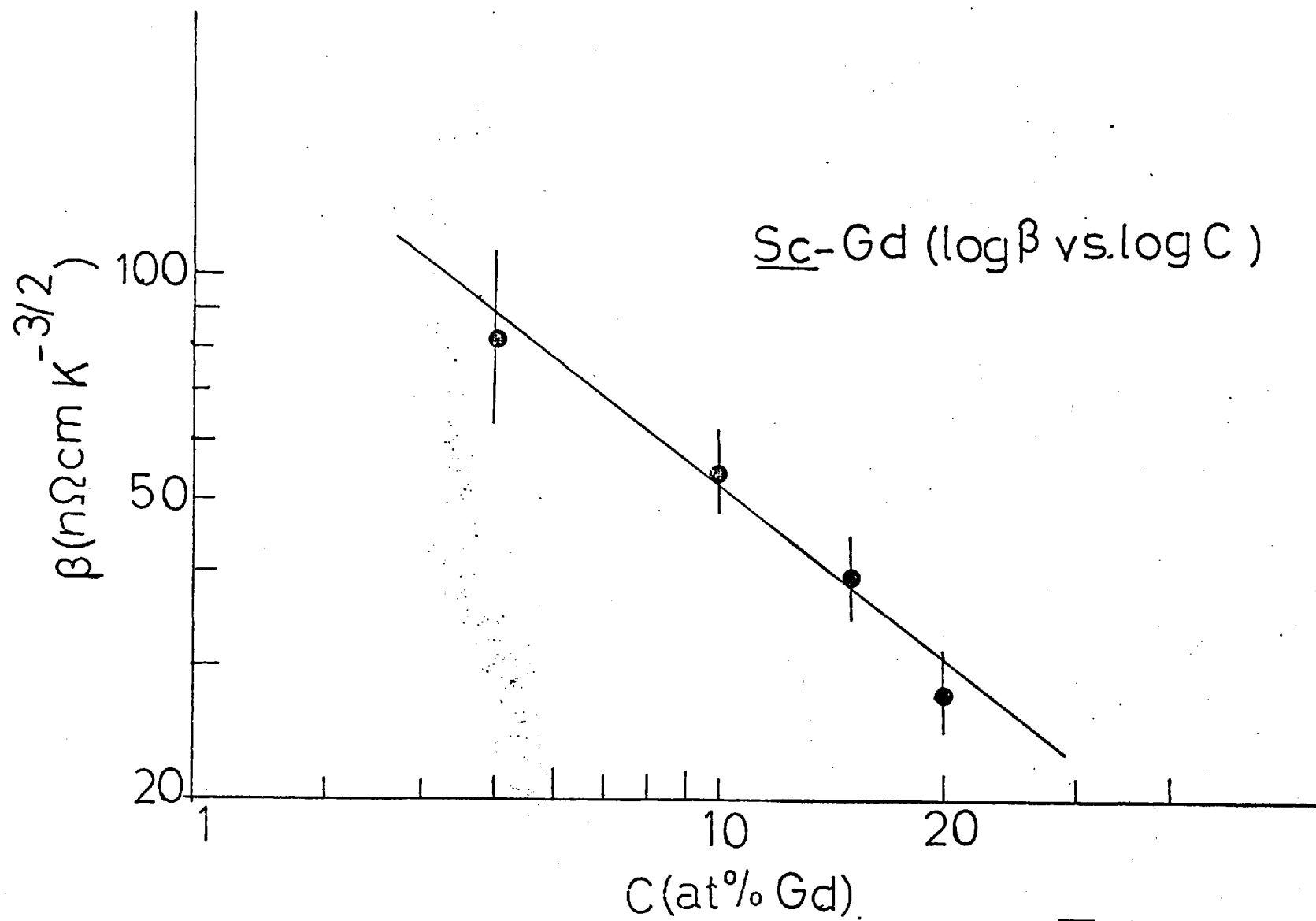


Fig VI.6

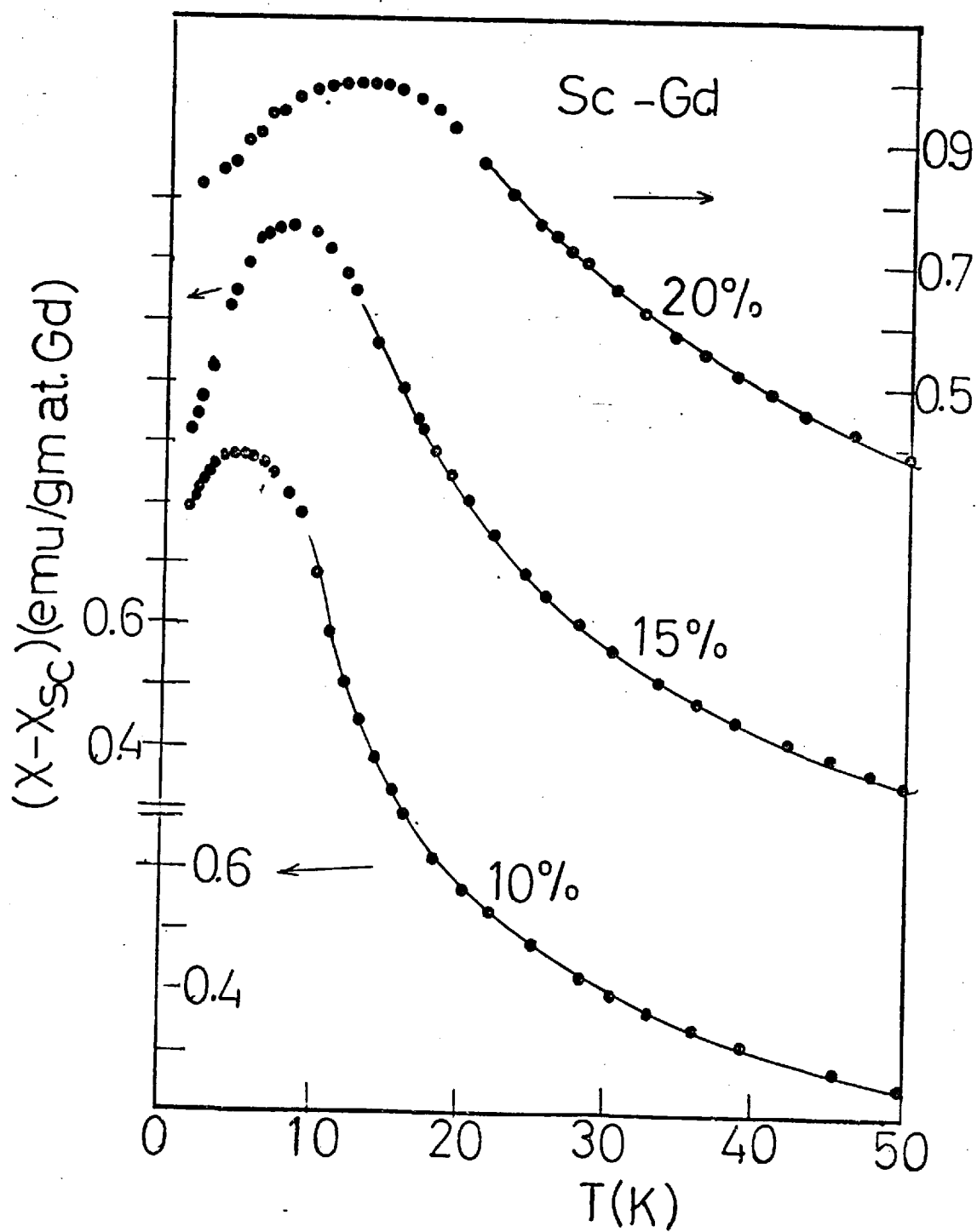


Fig VI. 7

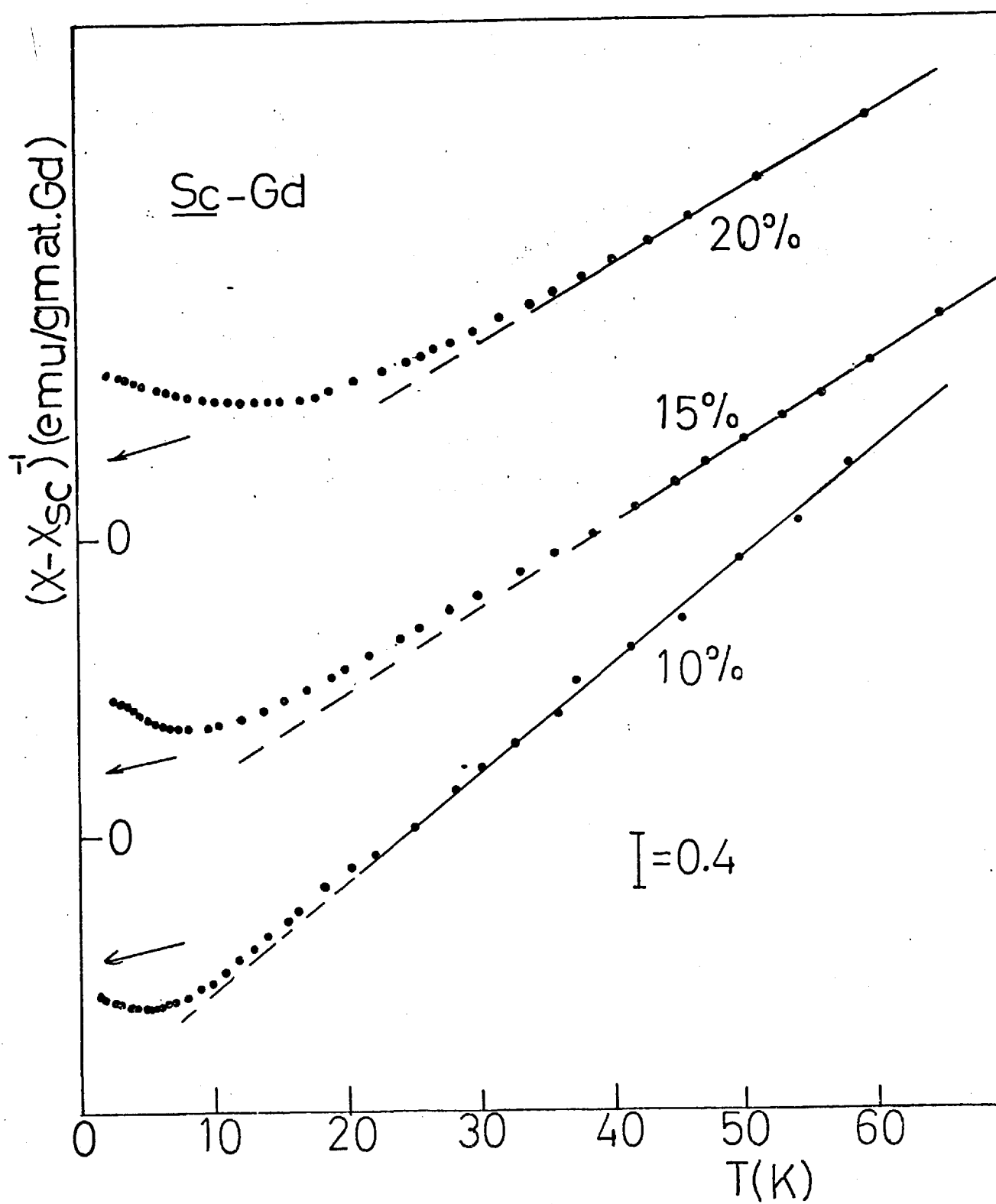


Fig VI.8

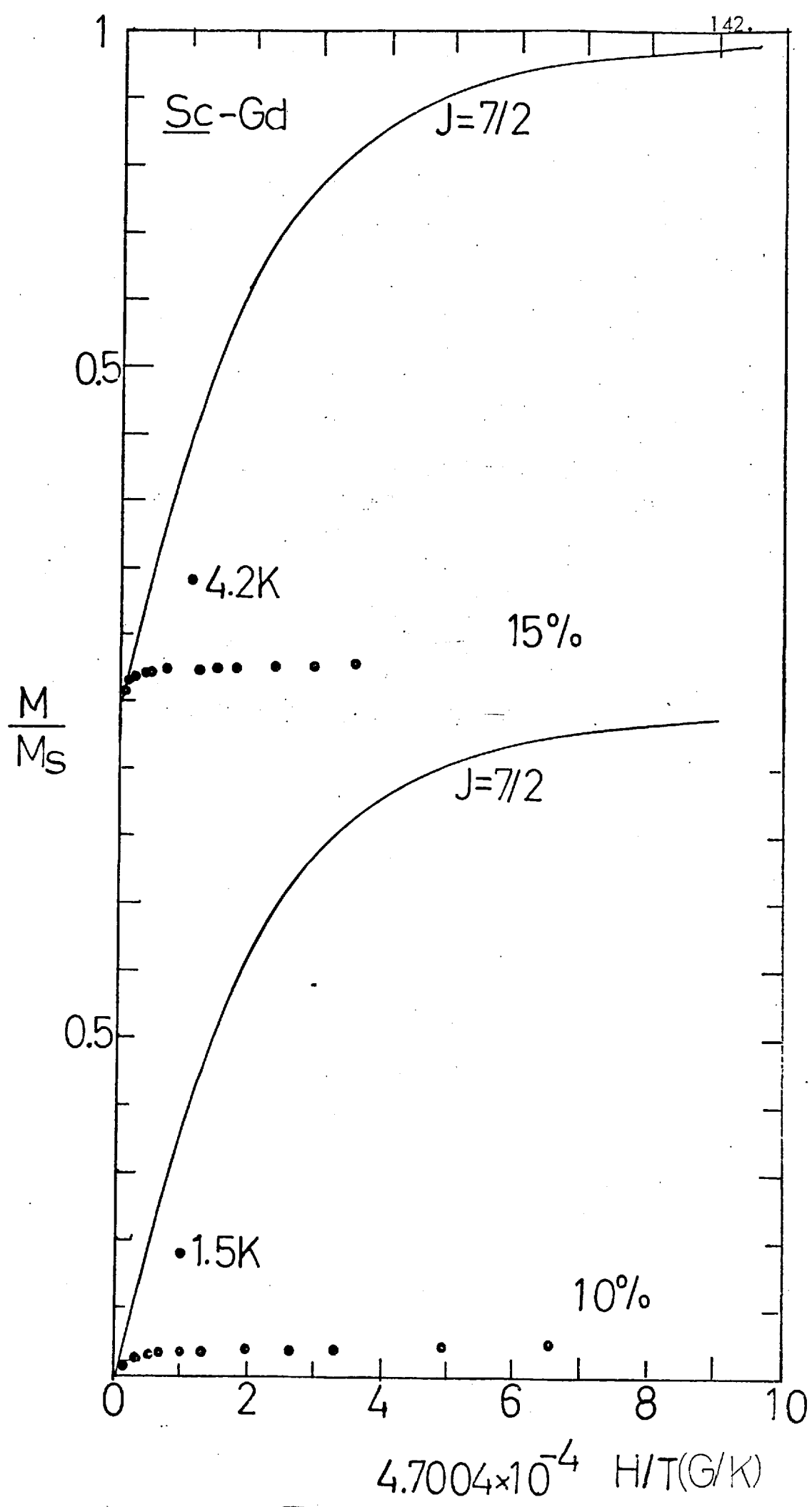


Fig VI. 9

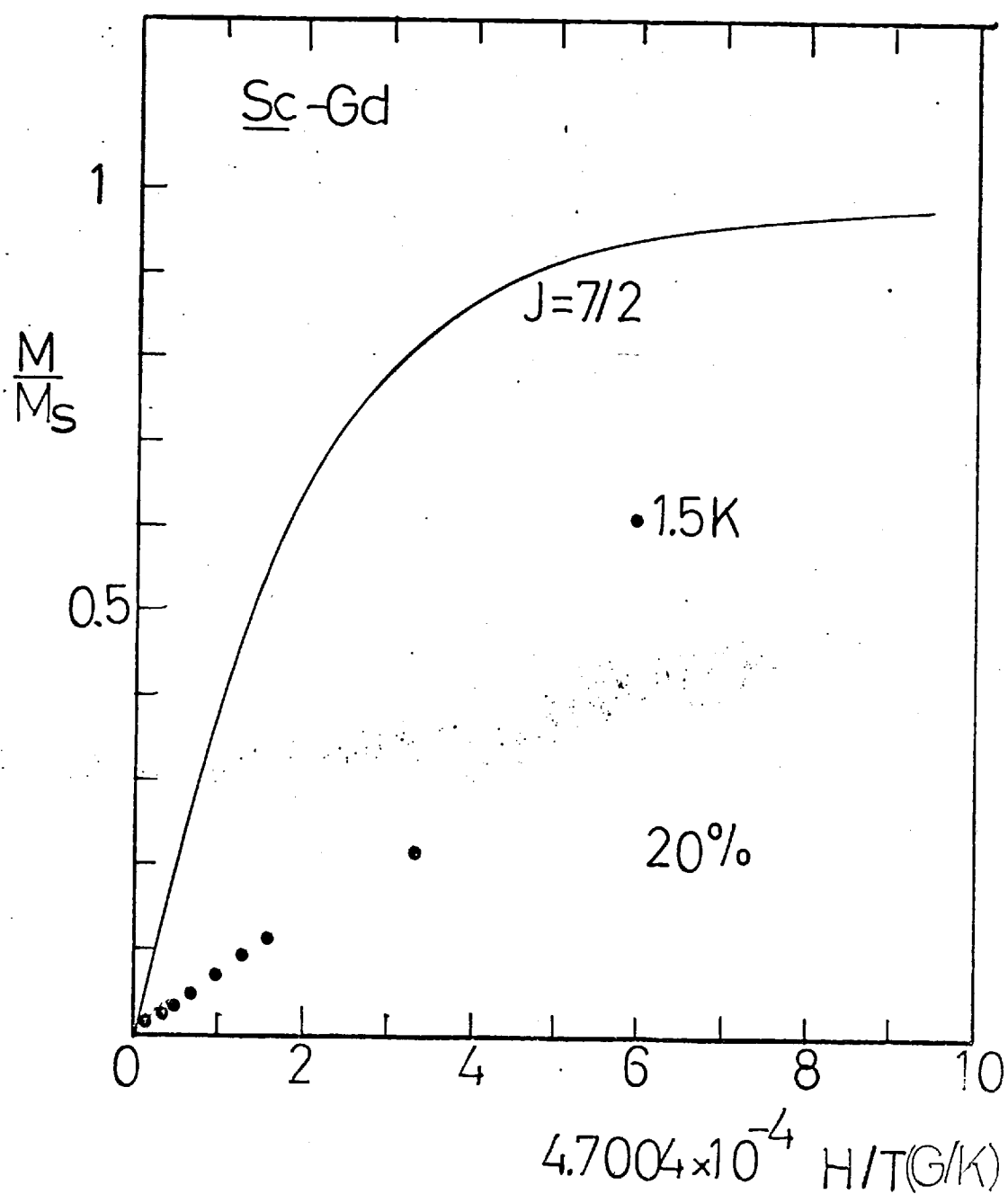


Fig VI · 10

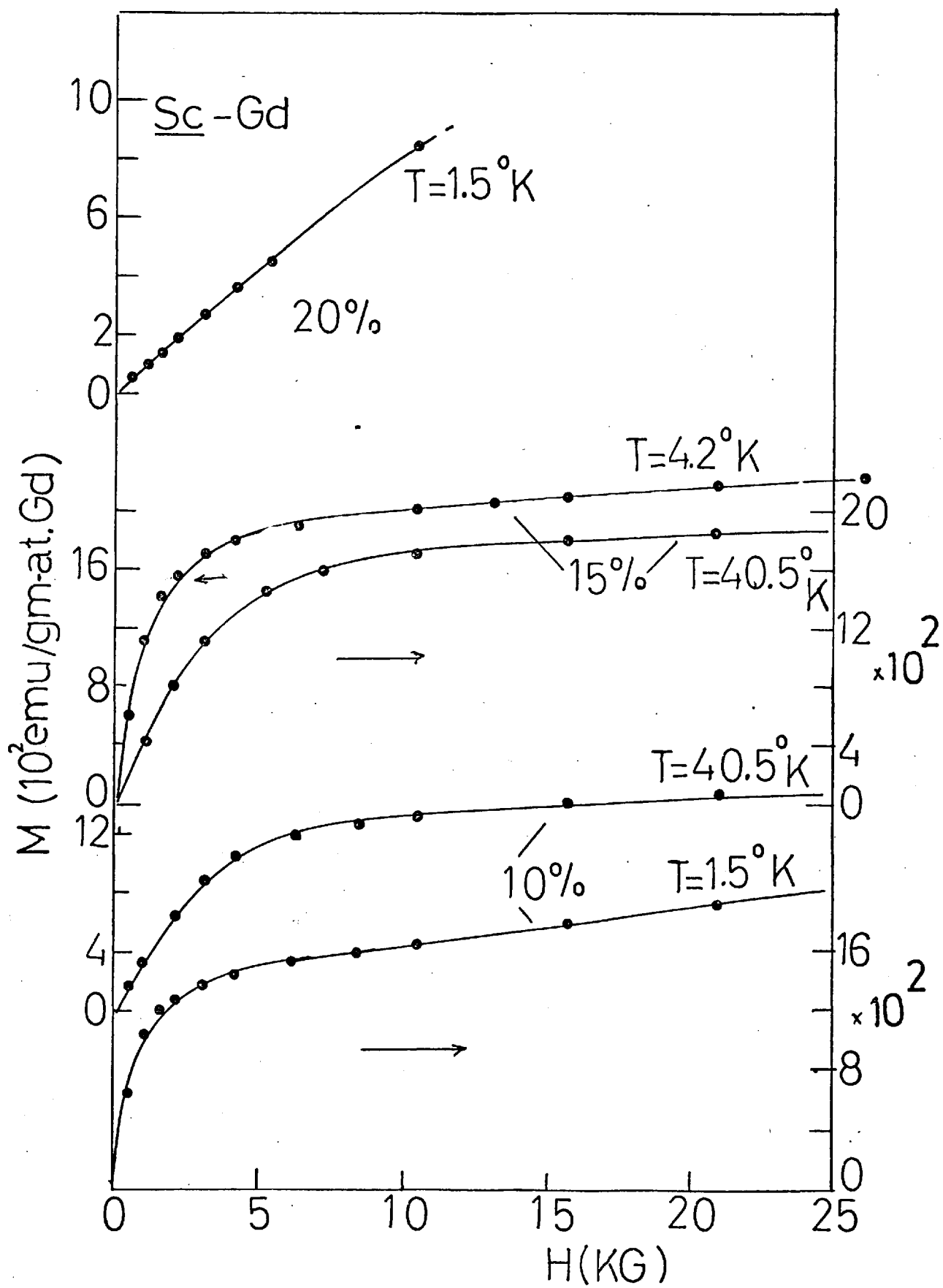


Fig VI .11

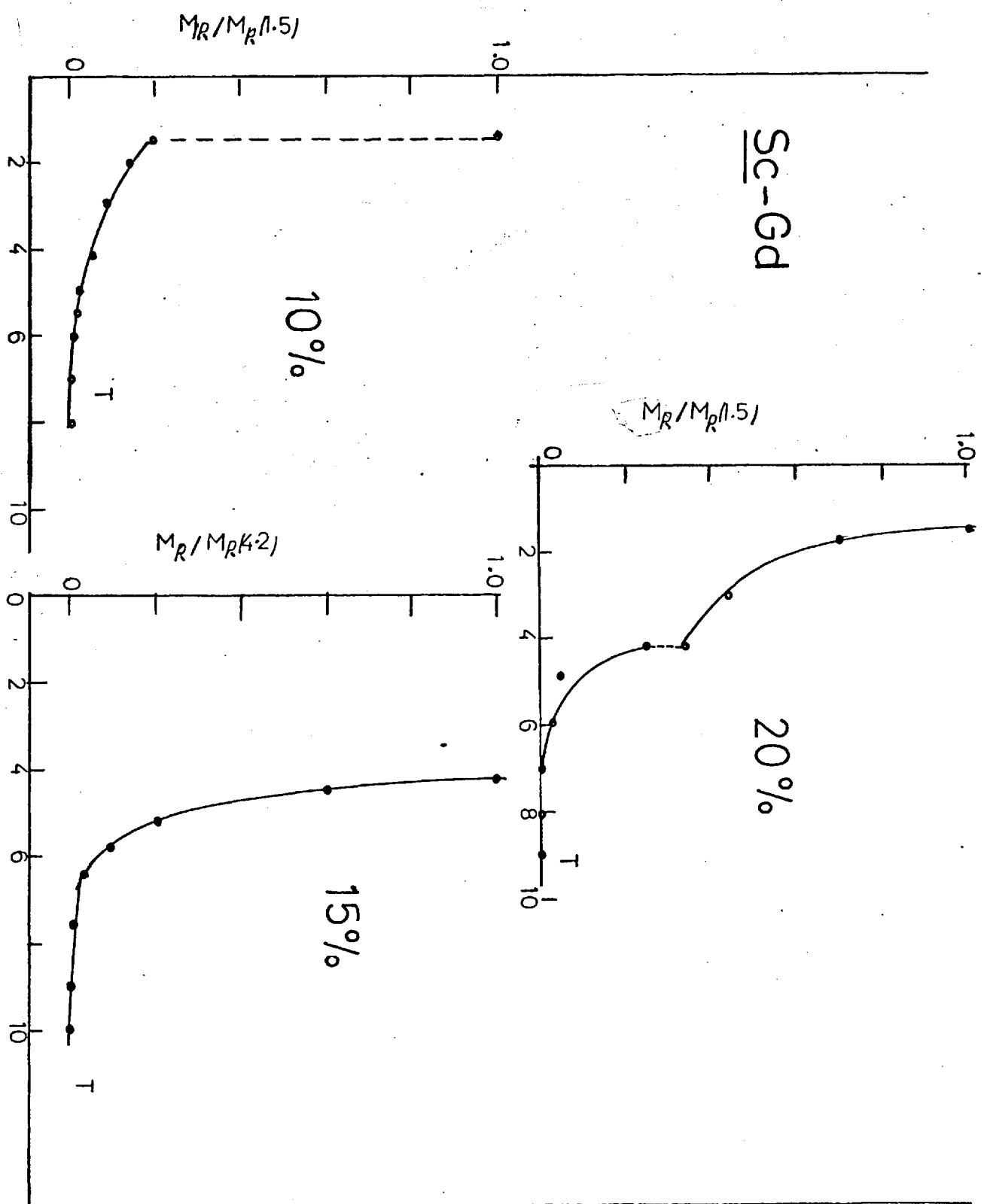


Fig VI.12

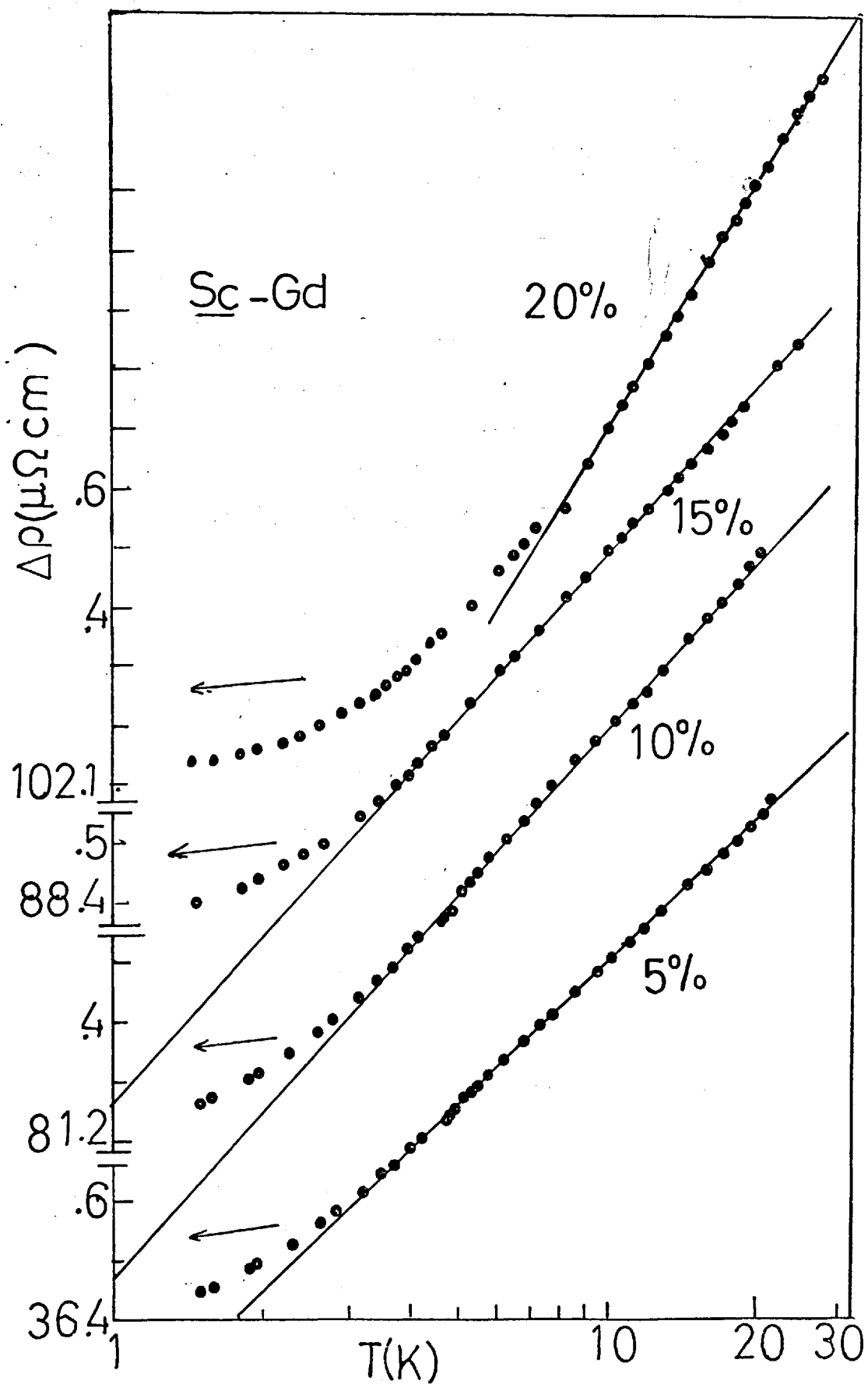


Fig VI. 13

of remanent magnetization for alloys $\leq 20\%$ Gd is shown in Fig. VI.12. This magnetization is induced after reducing the external field to zero, from its original value, and disappears at about the spin freezing temperatures and decays roughly exponentially. The dashed line indicates the decay in this magnetization with the time for a fixed temperature.

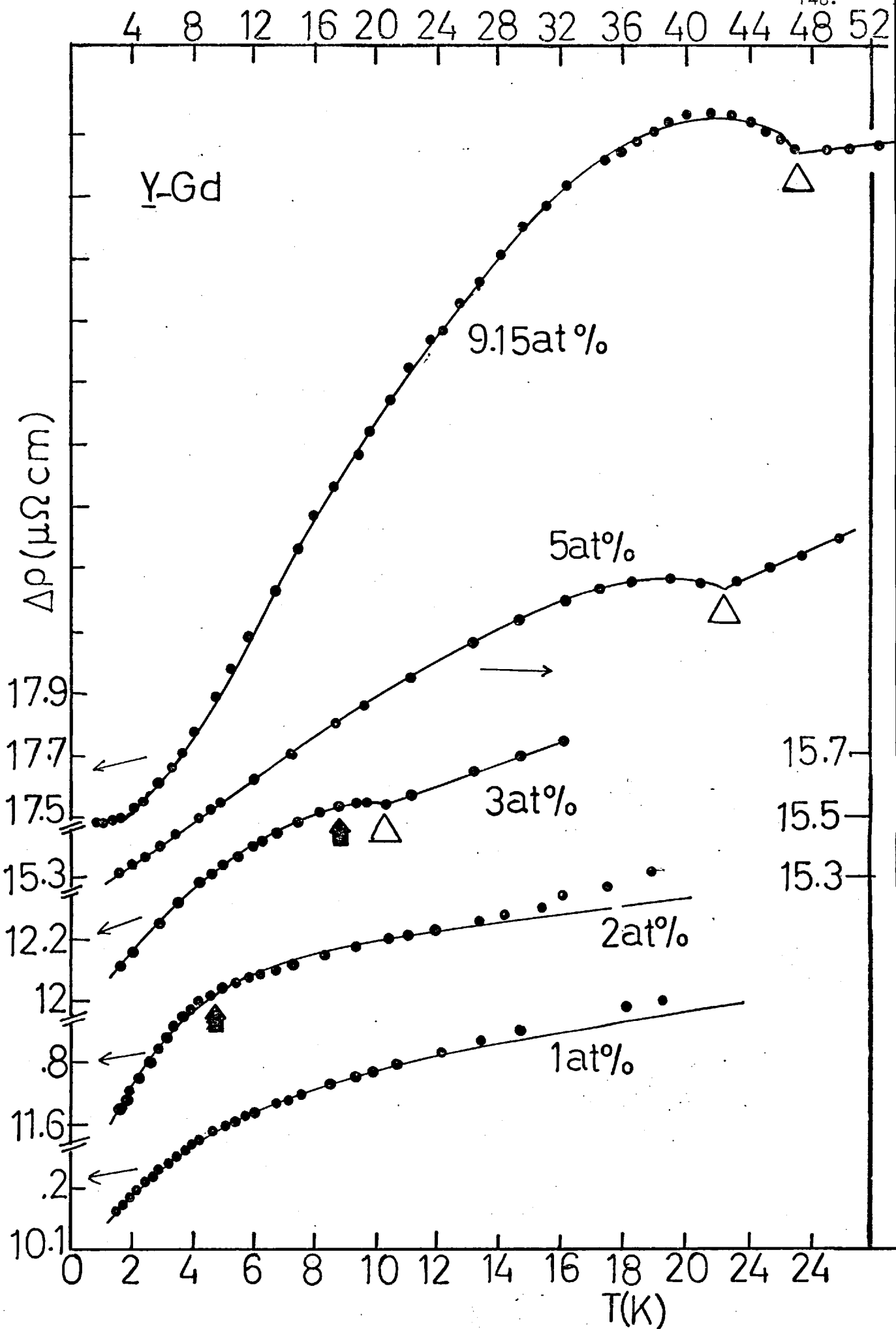
For alloys $\leq 20\%$ Gd we observed that $\Delta\rho$ at high temperatures is increasing much more slowly. In an attempt to fit this behaviour to a power law, a best fit to the data was obtained with the expression $\Delta\rho = \Delta\rho_0 + A \log T$, (see Fig. VI.13) with a positive coefficient of the logarithmic term which varies non-linearly with the Gd concentration (table VI.1).

(b) Y-Gd alloys

In Y-Gd alloys, the incremental resistivity $\Delta\rho (\rho_{\text{alloy}} - \rho_Y)$ has been plotted in Fig. VI.14, for the alloys 1%, 2%, 3%, 5%, and 9.2% Gd. Alloys with concentration $\leq 2\%$ Gd have similar features to Sc-Gd alloys in the range $c \leq 20\%$ Gd, the resistivity behaviour at low temperature for the alloy 2% might be $T^{3/2}$ while for the 1% alloy $T^{3/2}$ behaviour is not observable, because of the low ordering temperature ($< 1.5^\circ\text{K}$). The high temperature behaviour for $\Delta\rho(T)$ can again be expressed by

$$\Delta\rho = \Delta\rho_0 + A \log T$$

and is shown in Fig. VI.15, where the 0.5% Gd alloy is also included for comparison. The magnetic susceptibility measurements for alloys 1%, 2%, 3% is shown in Fig. VI.16, where no magnetic order in 1% Gd in the measured temperature range is observed; a broad maximum in 2% alloy was noted which is quite different from the sharp



Solid arrows indicate the temperature of the maximum in the susceptibility vs temperature curve, triangles indicate the Neel temperatures.

Fig VI.14

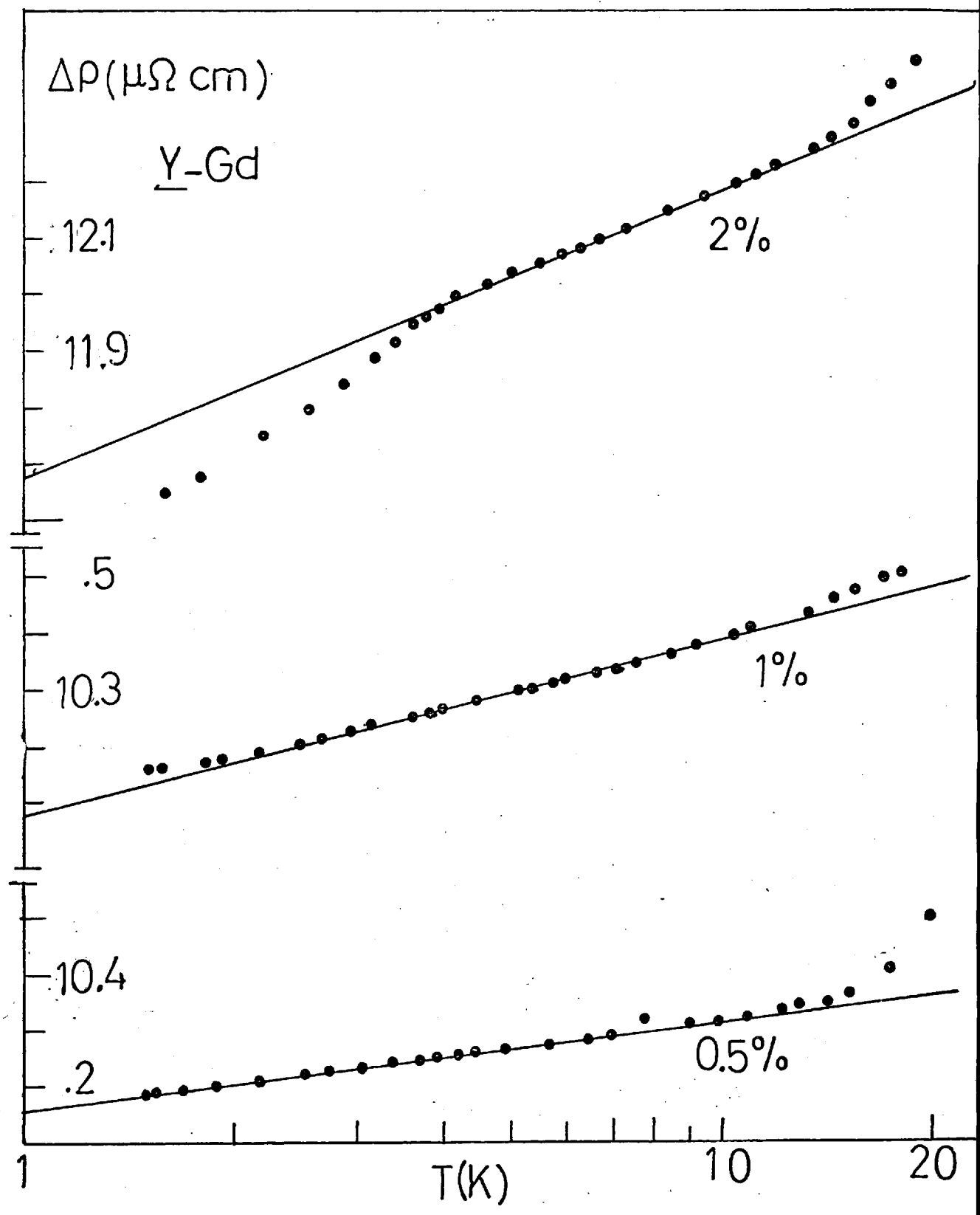


Fig VI.15

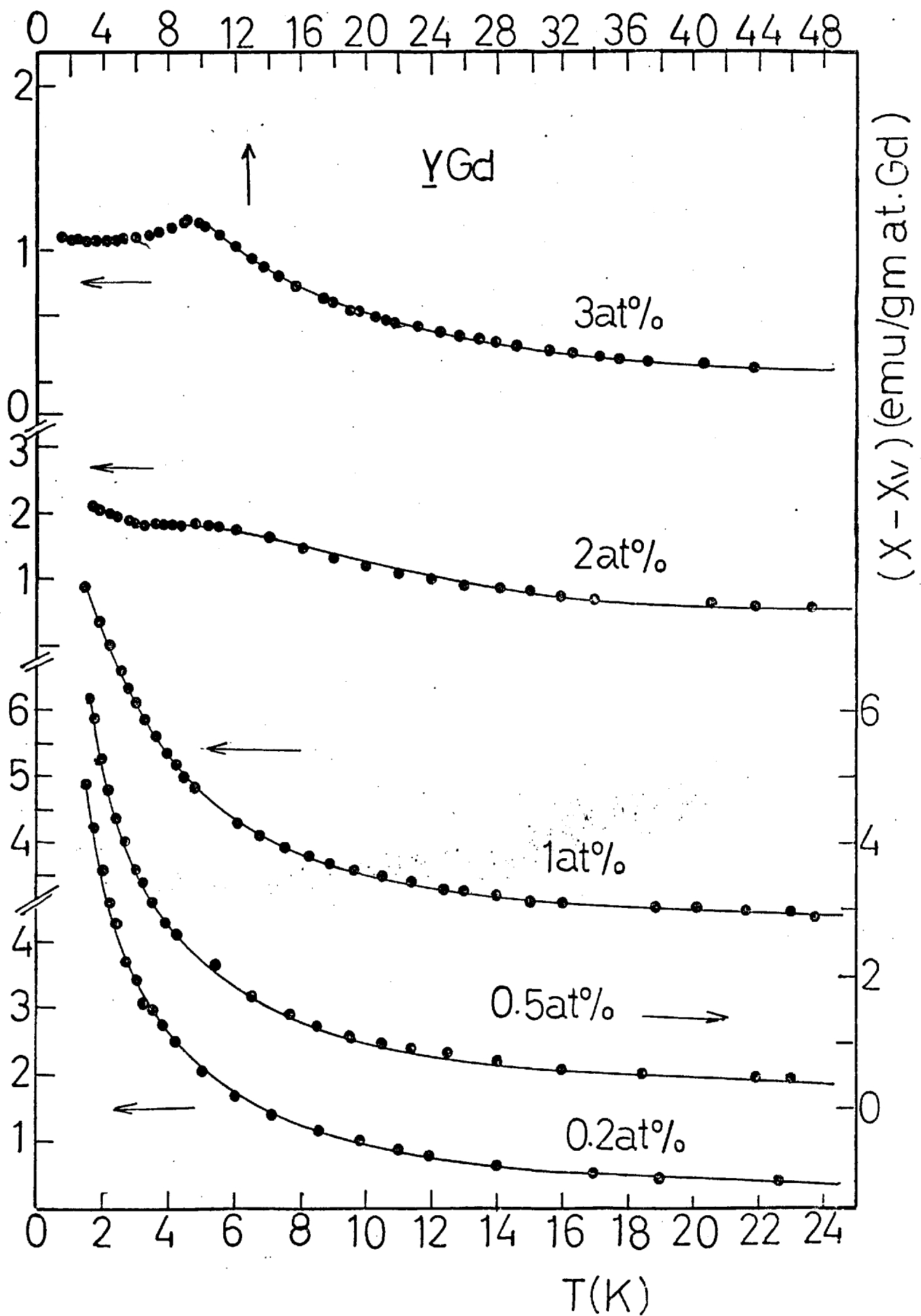


Fig VI .16

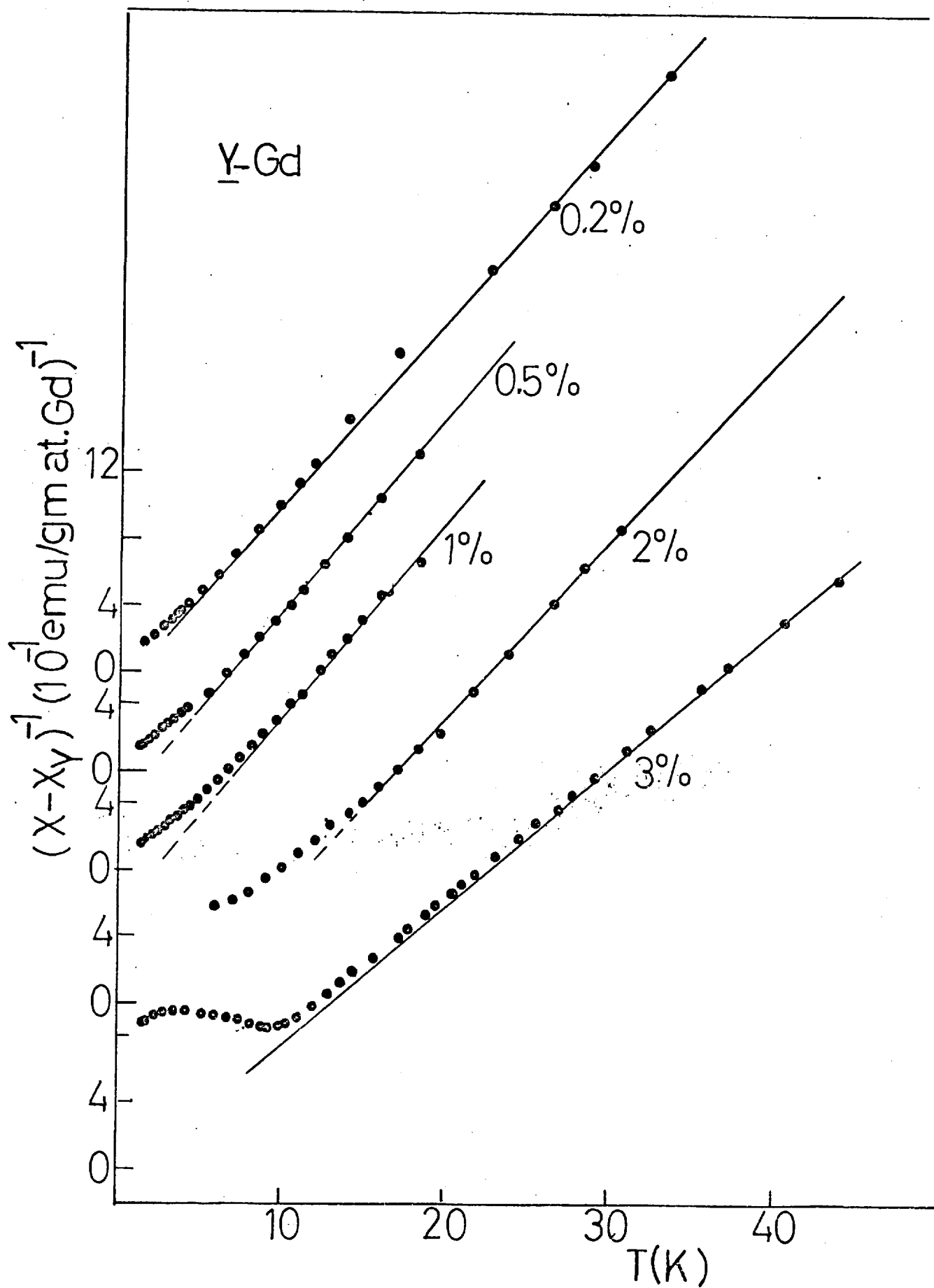


Fig VI.17

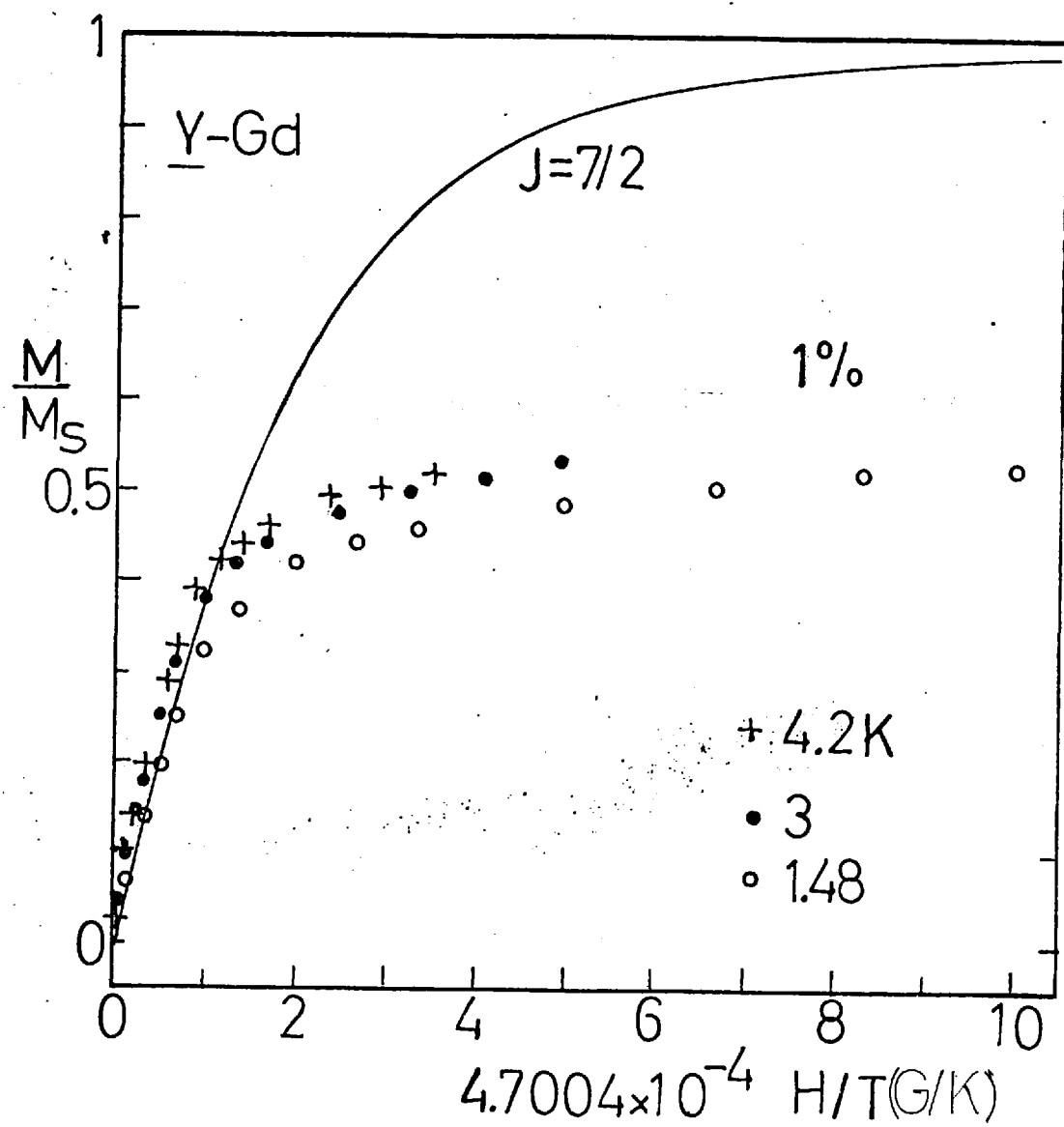


Fig VI.18

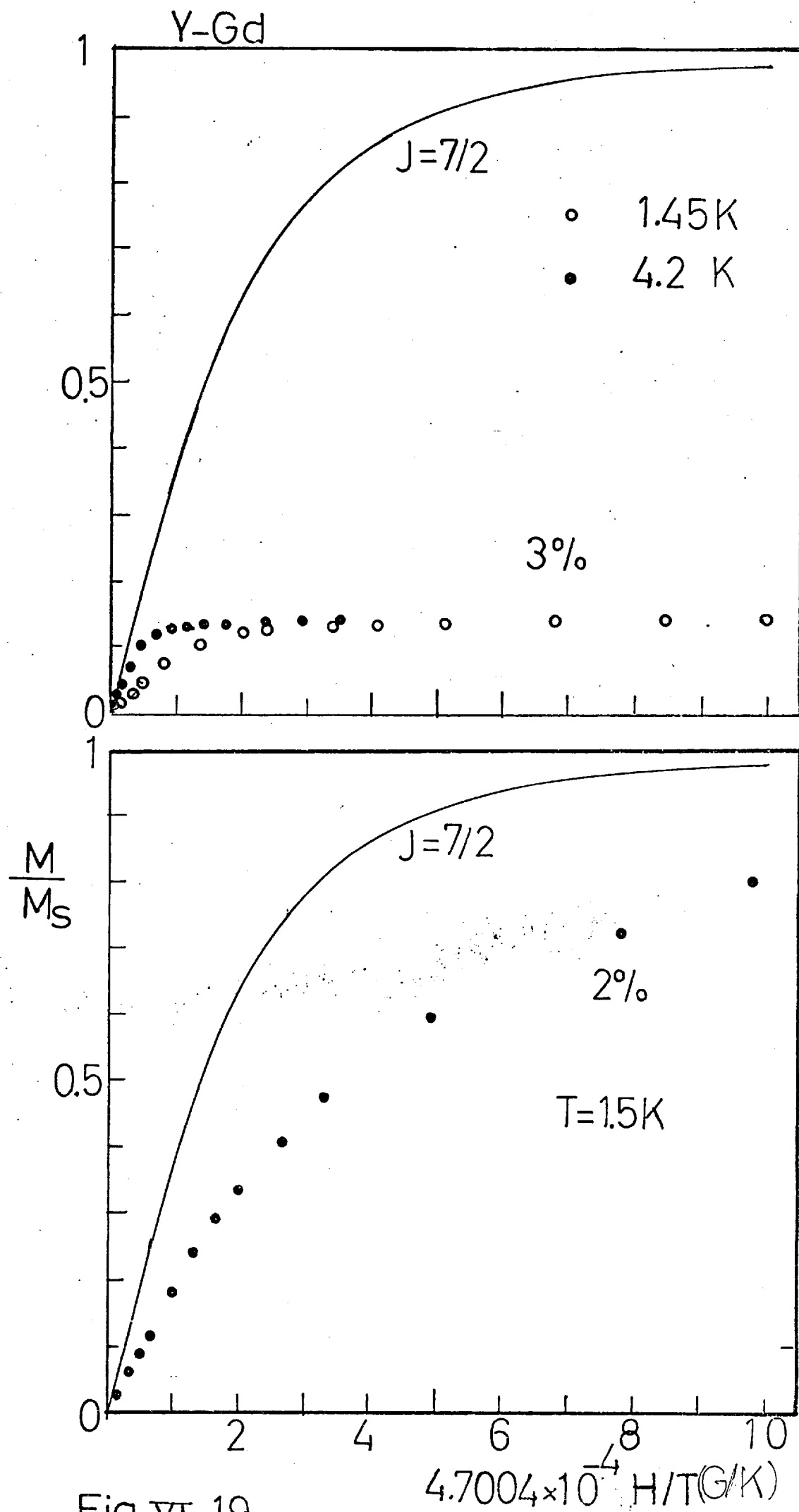


Fig VI.19

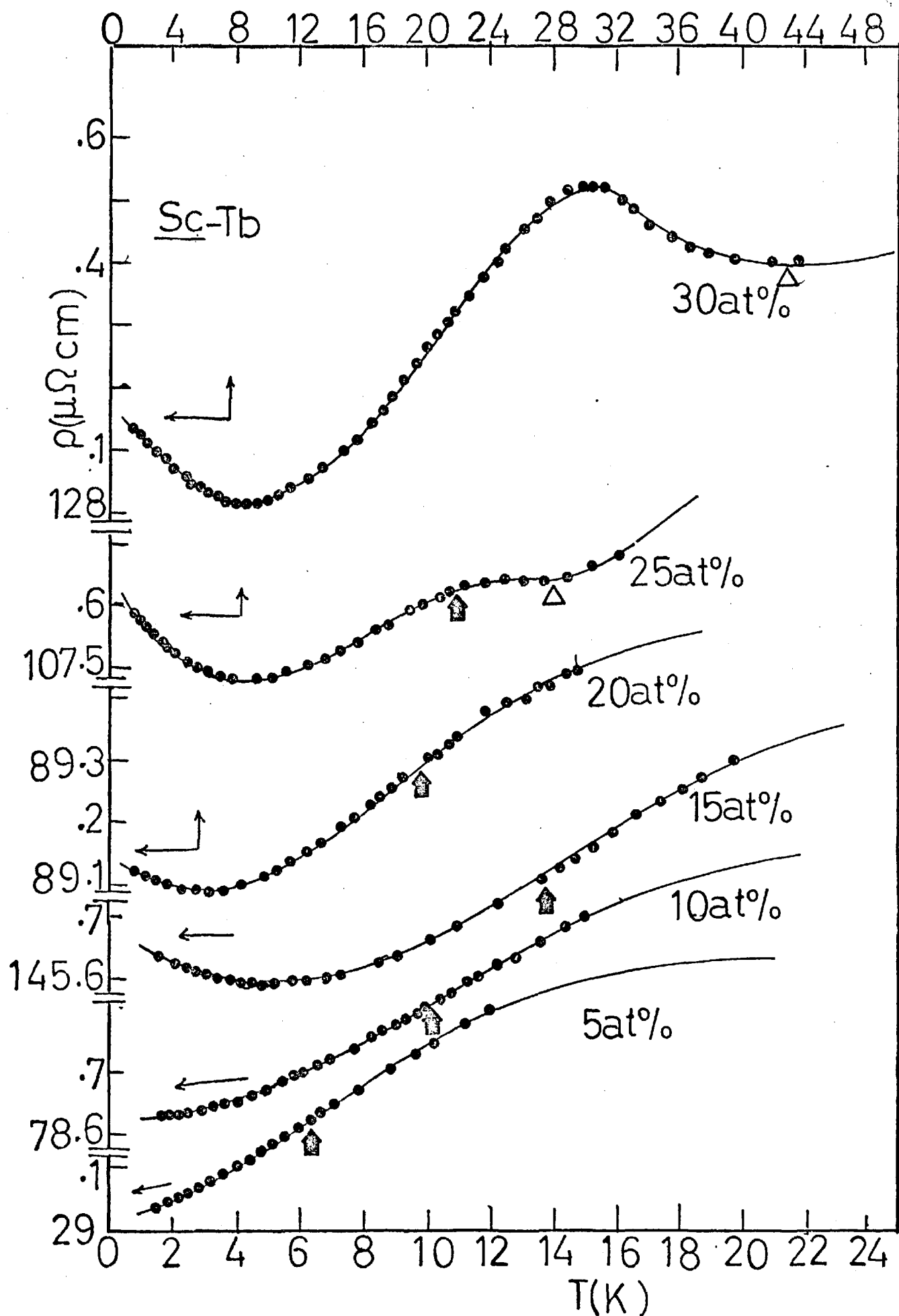
susceptibility maximum observed in the 3% Gd alloy, where it undergoes antiferromagnetic helical ordering transition. This is confirmed with the magnetic superzone effect observed in the resistivity measurement at the same temperature similar anomalies in the resistivity are observed for 5% and 9.2% Gd alloys (see Fig. VI.14). The low temperature behaviour for the alloys 5% and 9.2% Gd deduced from the log-log plot $(\Delta\rho(T) - \Delta\rho(15))$ vs. the temperature is shown in Fig. VI.4b.

Paramagnetic Curie temperatures and effective moment per Gd are deduced and listed in Table VI.2. The Curie-Weiss plots for these alloys are shown in Fig. VI.17. Reduced magnetization (M/M_s) as a function of applied field divided by temperature for the 1% Gd alloy up to (~ 30 KG) and below 4.2°K is shown in Fig. VI.18, corresponding plots for 2% Gd alloy (up to ~ 30 KG) and 3% Gd alloy (up to 30 KG) are shown in Fig. VI.19. A Brillouin curve for $J = 7/2$ is shown by the full line. At low and high fields, significant deviations are apparent in both glass and helical regions.

(c) Sc-Tb alloys

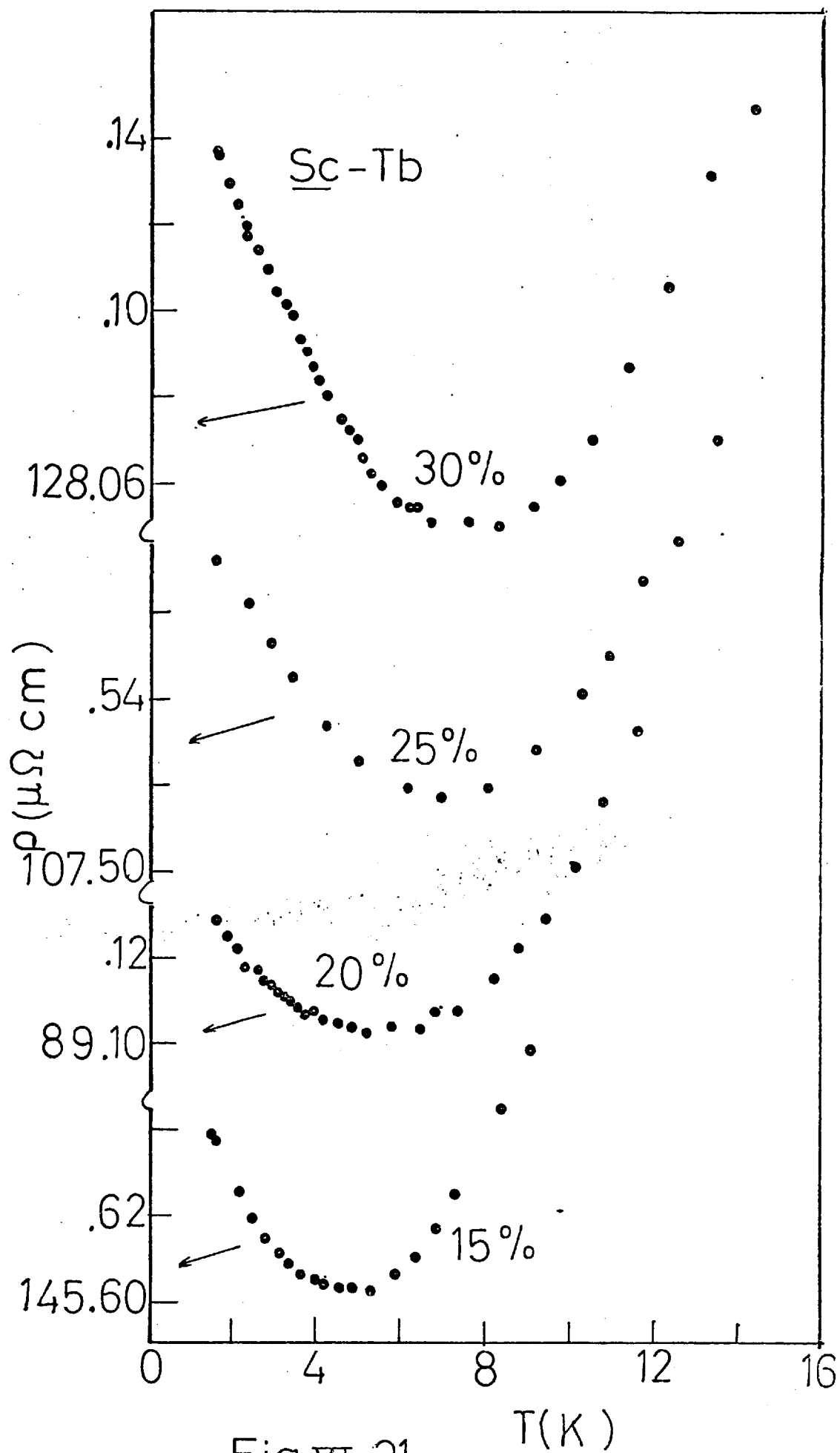
Results for the incremental resistivity $\Delta\rho(\rho_{\text{alloy}}(T) - \rho_{\text{Sc}}(T))$ vs. the temperature T for alloys containing 5%, 10%, 15%, 20%, 25% and 30% Tb are shown in Fig. VI.20. Careful examination of the present results enable the following comments to be made :

- (1) At lower temperatures alloys with $\geq 15\%$ Tb have a clear resistance minimum. The temperature of this minimum T_{min} increases linearly with Tb concentration (Fig. VI.21). A tendency towards a minimum in 5% and 10% alloys is also observable in the low temperature resistivity.
- (2) Alloys with concentration $\leq 20\%$ Tb, the character of the resistivity above



Solid arrows indicate the temperature of the maximum in the susceptibility vs temperature curve, triangles indicate the Neel temperatures.

Fig VI.20



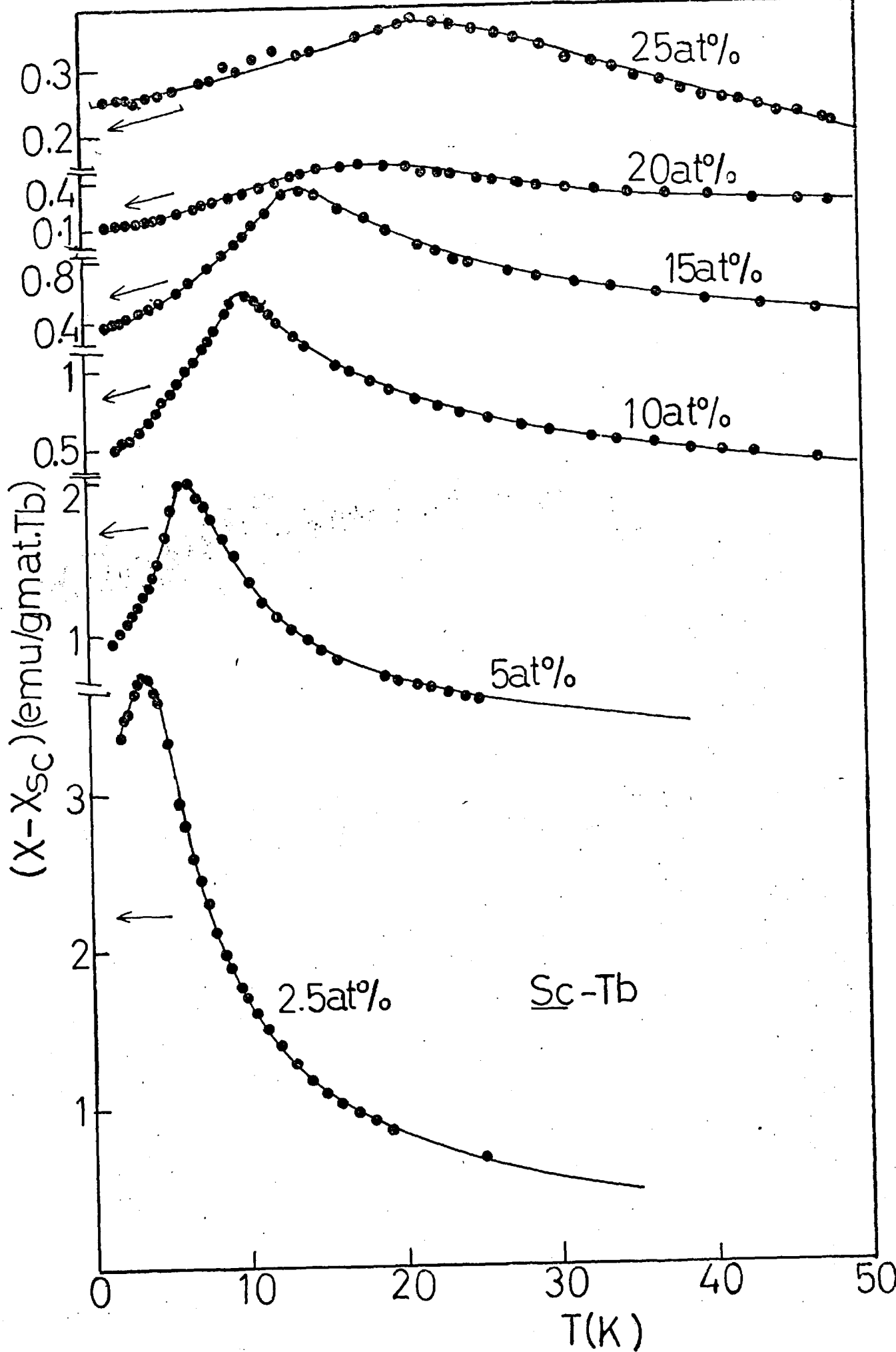


Fig VI.22

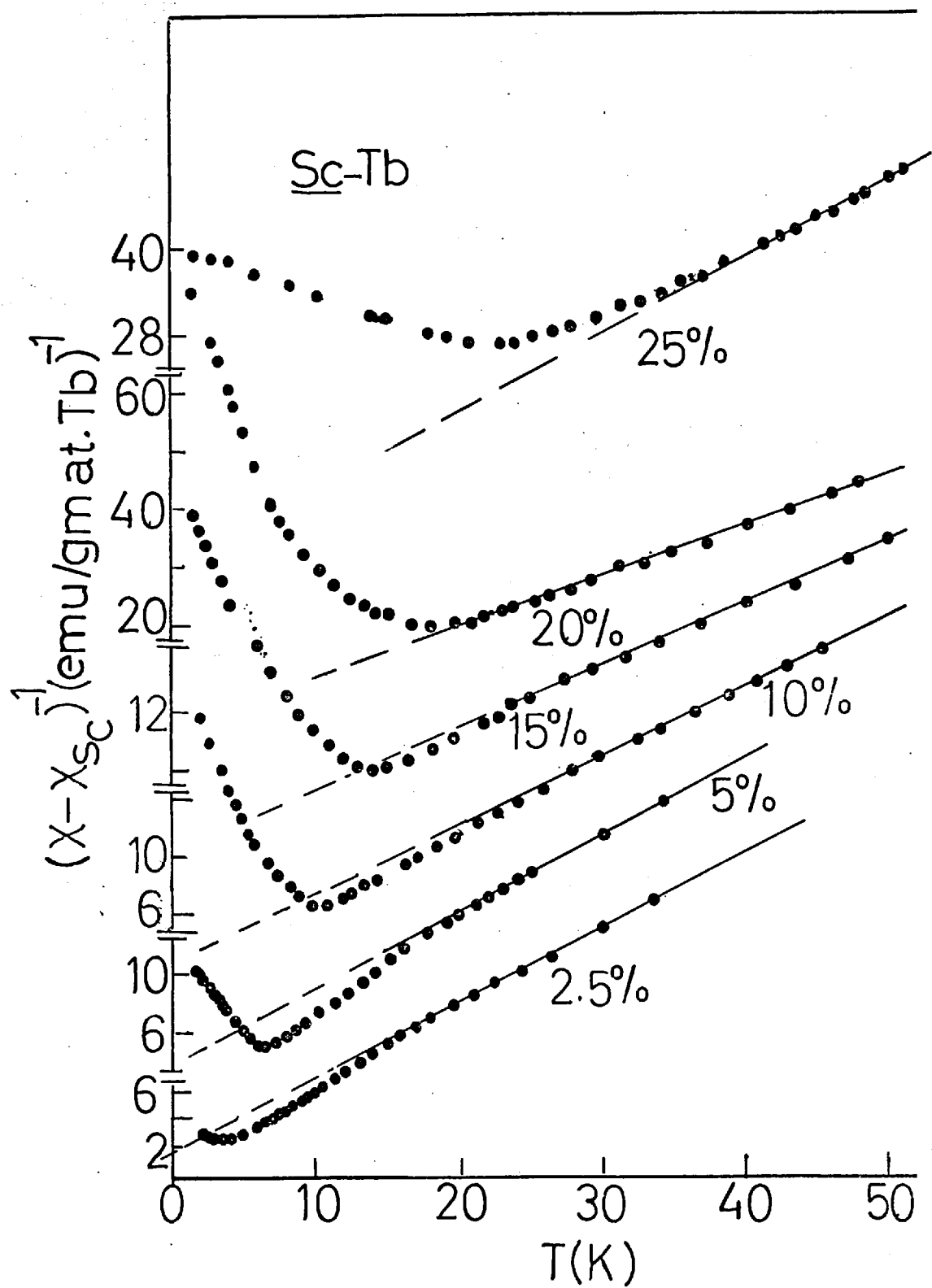


Fig VI-23

the resistance minimum is spin glass like with spin freezing temperature given by the maximum in the slope, i.e. by $d\Delta\rho/dT^*$. This is also confirmed by our magnetic susceptibility measurements (Fig. VI.22), where we show the susceptibility of 2.5%, 5%, 10%, 15%, 20% and 25% Tb alloys plotted against the temperature, the maximum in the susceptibility being in agreement with that given by the maximum in the slope of the resistivity ($d\Delta\rho/dT$).

(3) Alloys with concentration 25% and 30% Tb. The helical antiferromagnetic ordering is clearly indicated by magnetic superzone effects.

(4) A strong anisotropy effect was observed in the susceptibility of these alloys (which is more clearly indicated in the Curie-Weiss plot, Fig. VI.23) which increases with increasing Tb concentration; this might be related to the observed resistance minimum.

(5) At high temperature the susceptibility approaches a Curie-Weiss law behaviour, with an effective moment larger than the free Tb⁺⁺⁺ ion value (Table VI.3). At temperatures above the susceptibility maximum (minimum in Curie-Weiss plot), some dilute alloys show marked deviations from the Curie-Weiss law. This effect could be attributed to the crystal field splittings. For more concentrated alloys this effect is not observable, where the exchange interaction becomes much larger than the crystal field effects. The straight line drawn through the Curie-Weiss plot through the higher temperature points gives a negative intercept for the low Tb concentration side and a positive intercept for the high Tb concentration. These and other parameters are listed in Table VI.3.

(6) Magnetization vs. field isotherms of these alloys are shown in Fig. VI.24, where clear evidence of both magnetic order effects and "mixing" induced by the application of the magnetic field are observed; the associated effects of this can clearly be seen at higher fields. Fig. VI.25 and 26 show the temperature variation of reduced

* See Chapter II section II. 5.

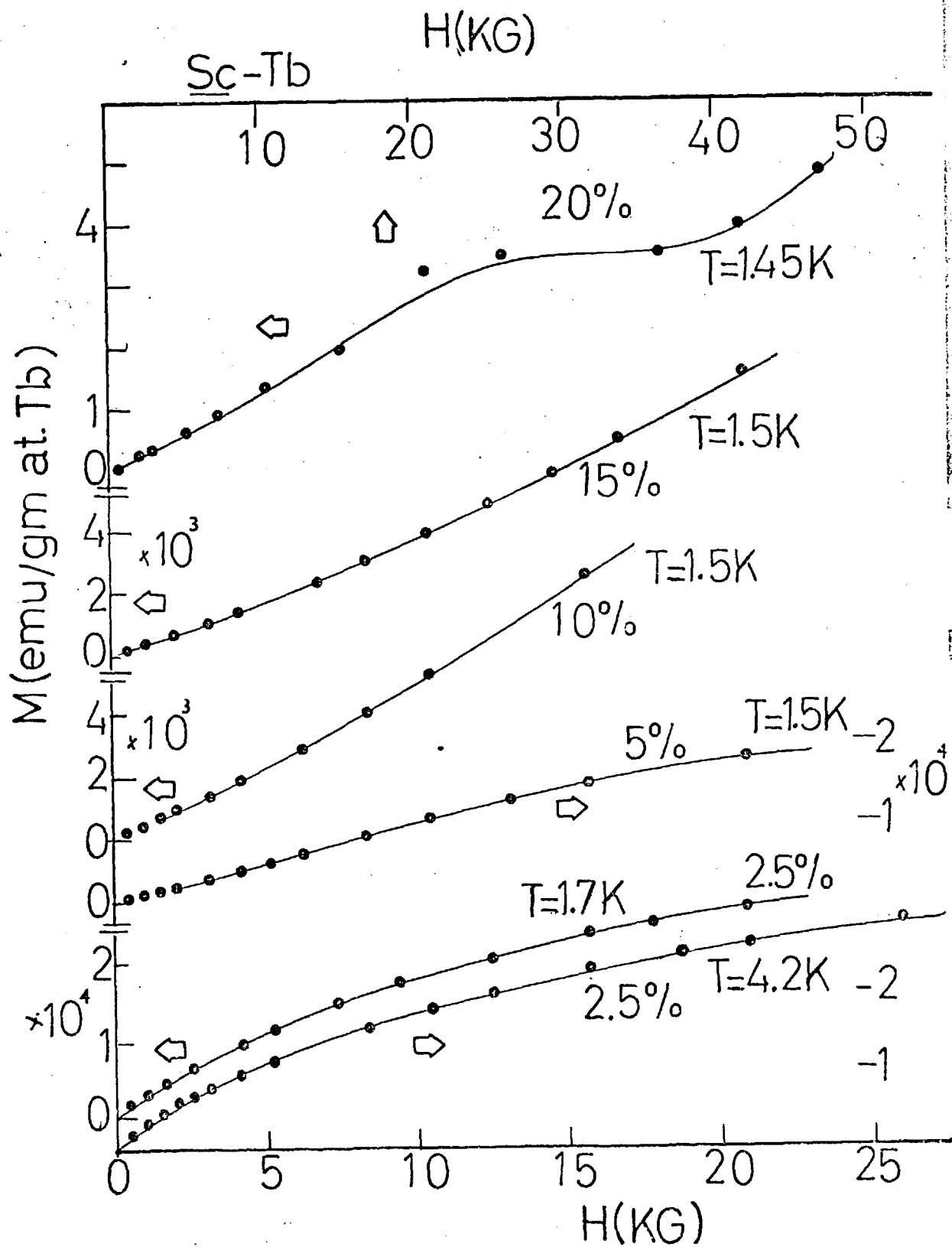


Fig VI · 24

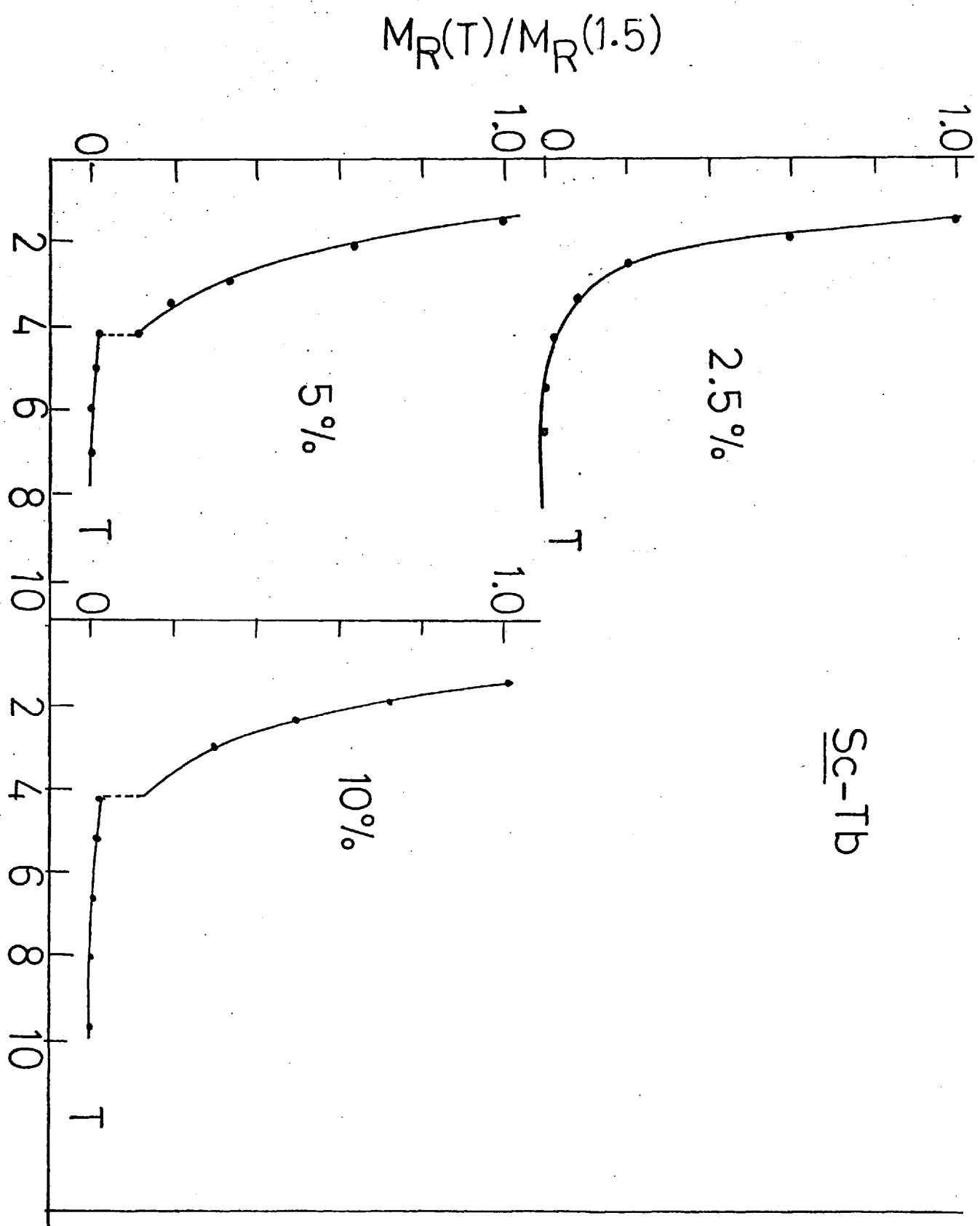
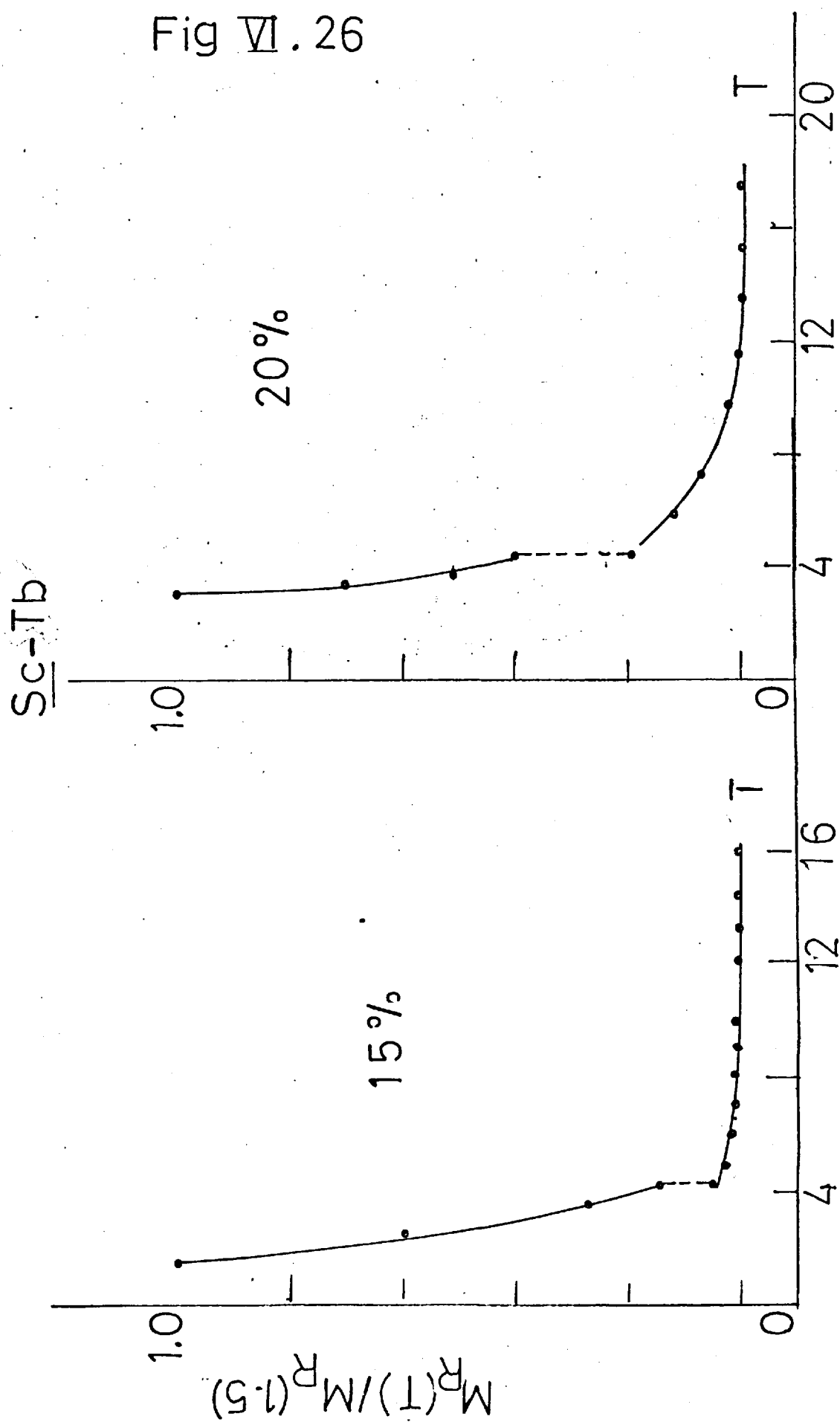


Fig VI. 25

Fig VI. 26



remanent magnetization ($M_{rem}(T)/M_{rem}(1.5)$) for alloys in the range $c \leq 20\%$ Tb. This magnetization was induced as described before.

(d) Y-Tb alloys

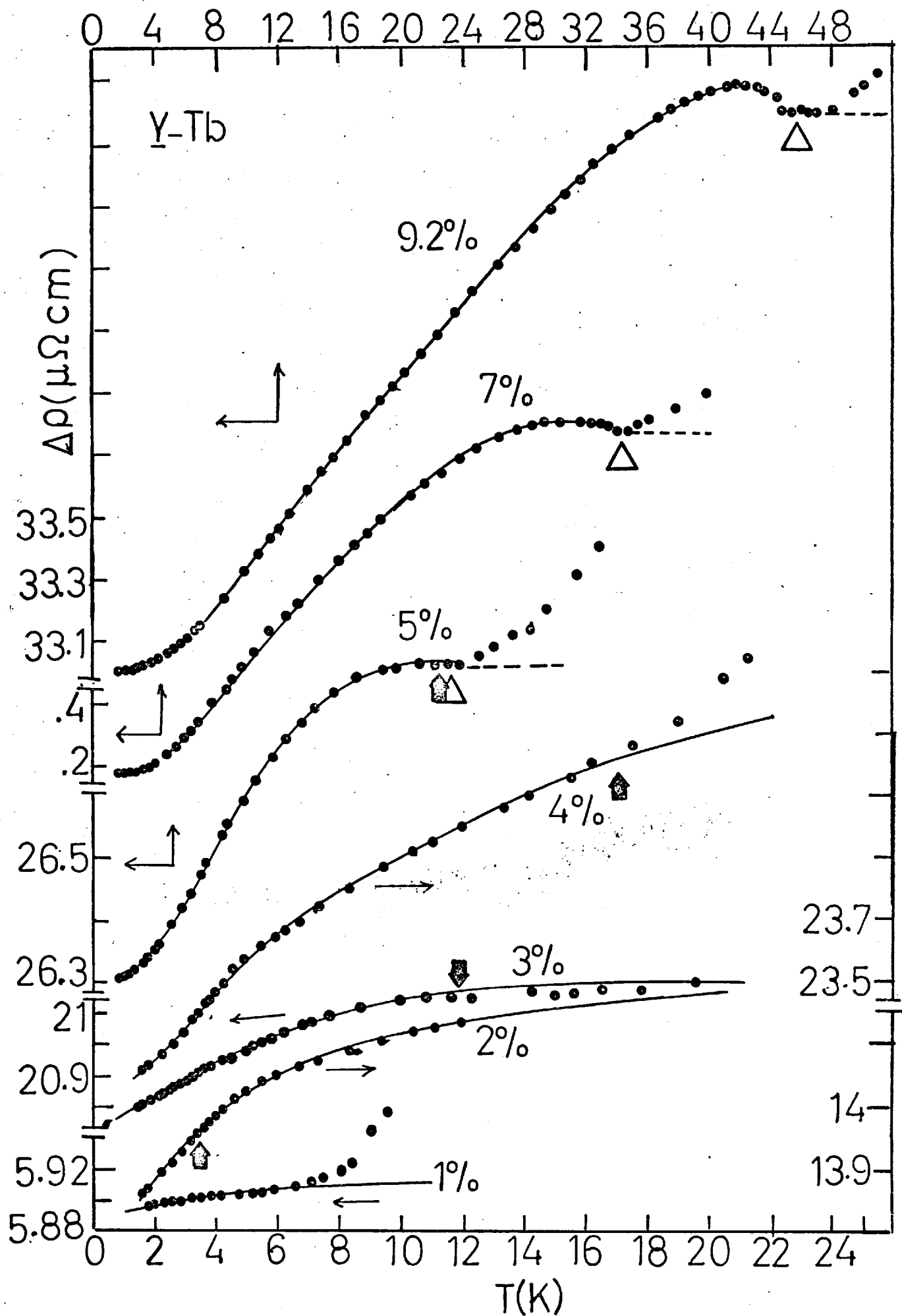
Incremental resistivity $\Delta\rho(\rho_{alloy} - \rho_Y)$ vs. temperature for 1%, 2%, 3%, 4%, 5%, 7% and 9.2% Tb alloys are shown in Fig. VI.27. Alloys with concentration $\geq 5\%$ Tb show the magnetic superzone effects. For alloys with lower concentration of Tb, the dependence $\Delta\rho(T)$ is similar to spin glass materials and quite different from the more concentrated alloys. However, the behaviour of the spin resistivity is different from the simple type of spin glasses because of the effects of the crystalline electric field. No resistance minimum at low temperature was observed in this case.

The magnetic susceptibility vs. temperature plot is shown in Fig. VI.28, where a broad maximum in susceptibility at freezing temperature is observed. At high temperatures the alloys obey a Curie-Weiss law with $(\chi_{alloy} - \chi_Y)^{-1}$ linear in the temperature T (Fig. VI.29); the paramagnetic Curie temperature is positive for all Tb concentrations and increases with Tb concentration. The effective moment per Tb ion as determined from paramagnetic Curie-constant is larger than the free (Tb^{+++}) ion value. These with other parameters are listed in Table VI.4.

Magnetization vs. field isotherms in high magnetic fields are shown in Fig. VI.30, where the effects of magnetic ordering and level crossing are clearly observable. The temperature dependence of the remanent magnetization for alloys $\leq 5\%$ Tb is shown in Fig. VI.31.

(e) Sc-Dy and Y-Dy alloys

Experimental results for incremental resistivity $\Delta\rho(\rho_{alloy}(T) - \rho_{Sc}(T))$ for Sc-Dy alloys are shown in Fig. VI.32 for the alloys 5%, 15%, 25% and 30% Dy. A well defined onset of magnetic order is observed similar to that in other Sc-RE and Y-RE alloys in the 25% and 30% Dy alloys indicating a helical state.



Solid arrows indicate the temperature of the maximum in the susceptibility vs temperature curve, triangles indicate the Neel temperatures.

Fig VI. 27

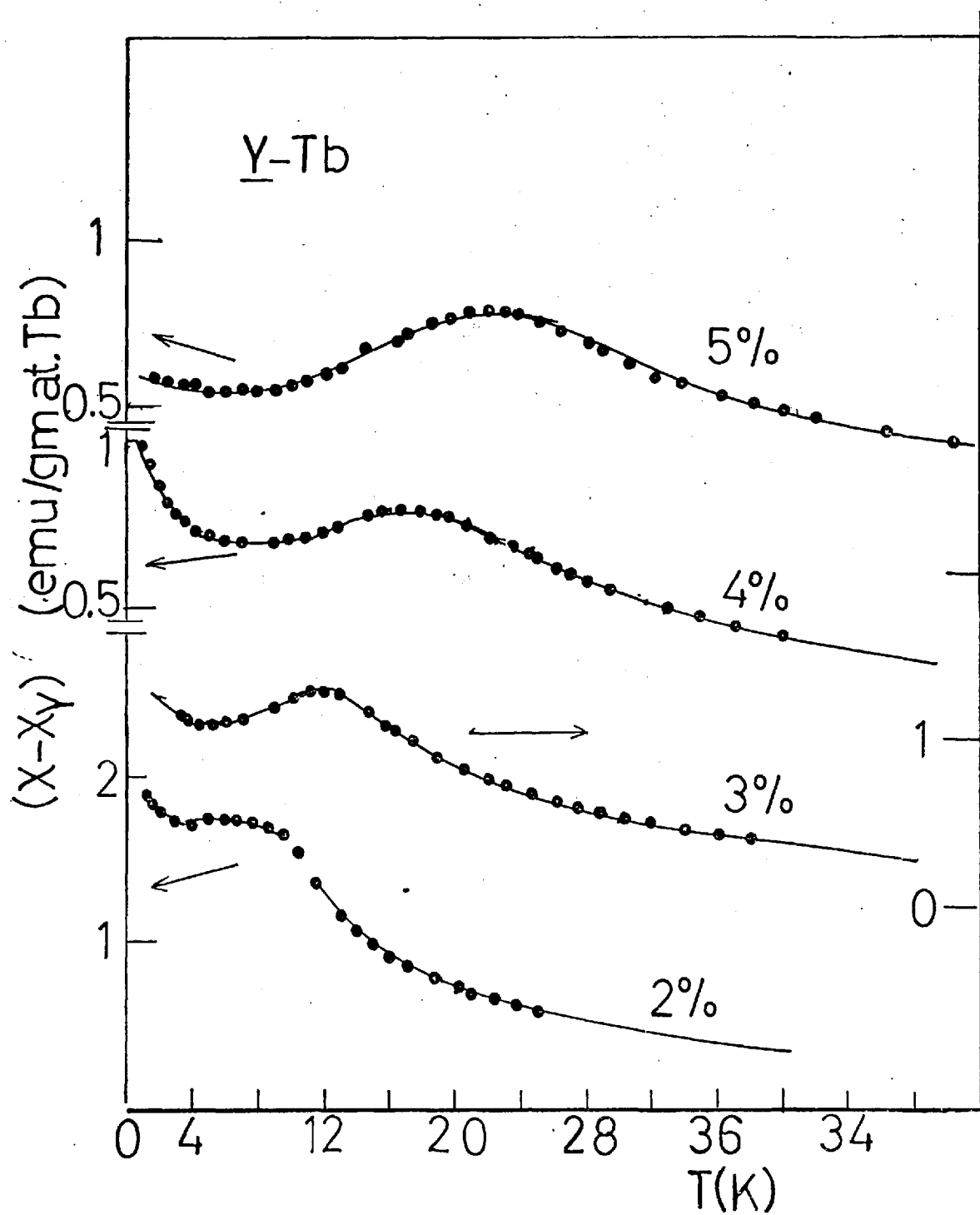


Fig VI, 28

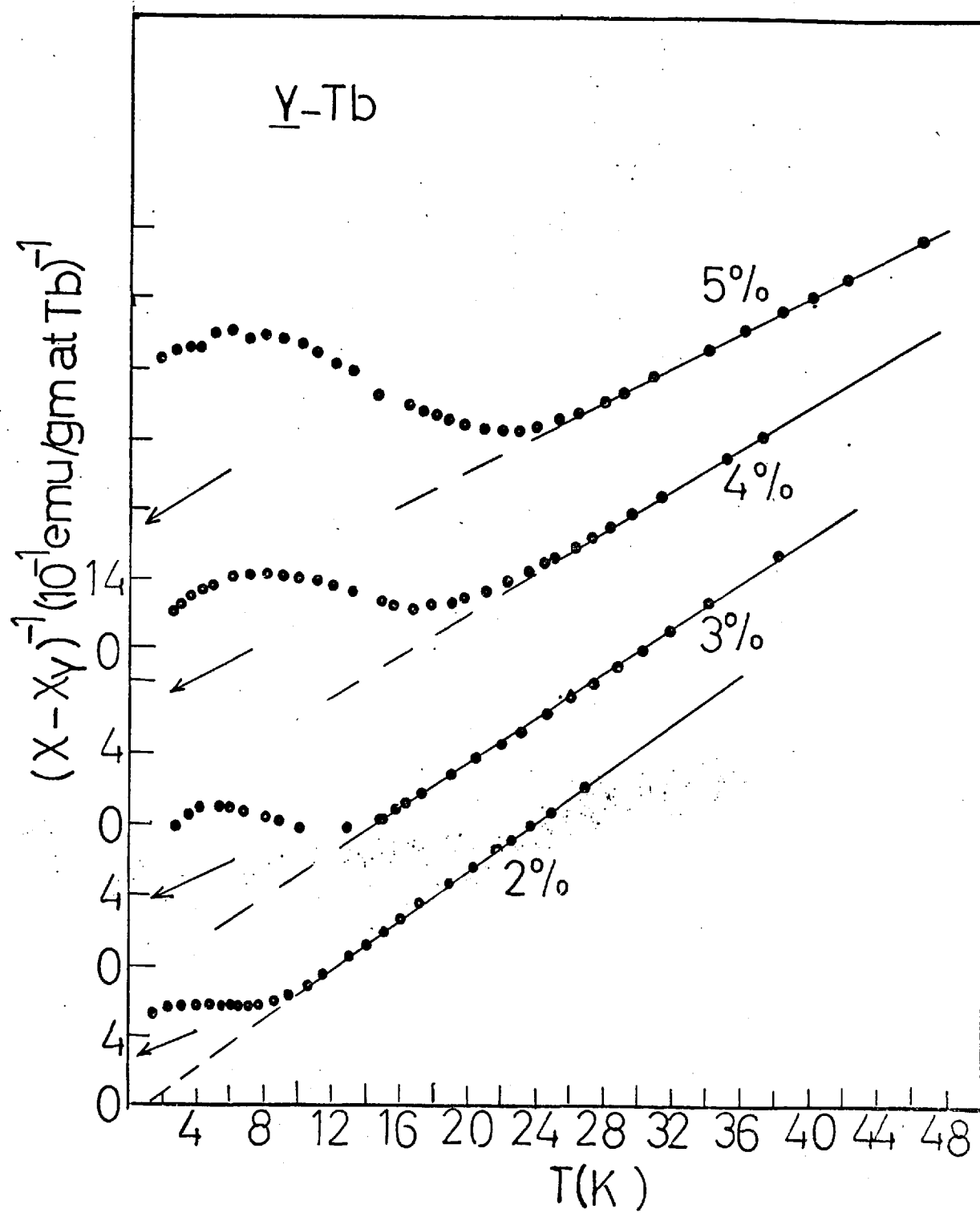


Fig VI. 29

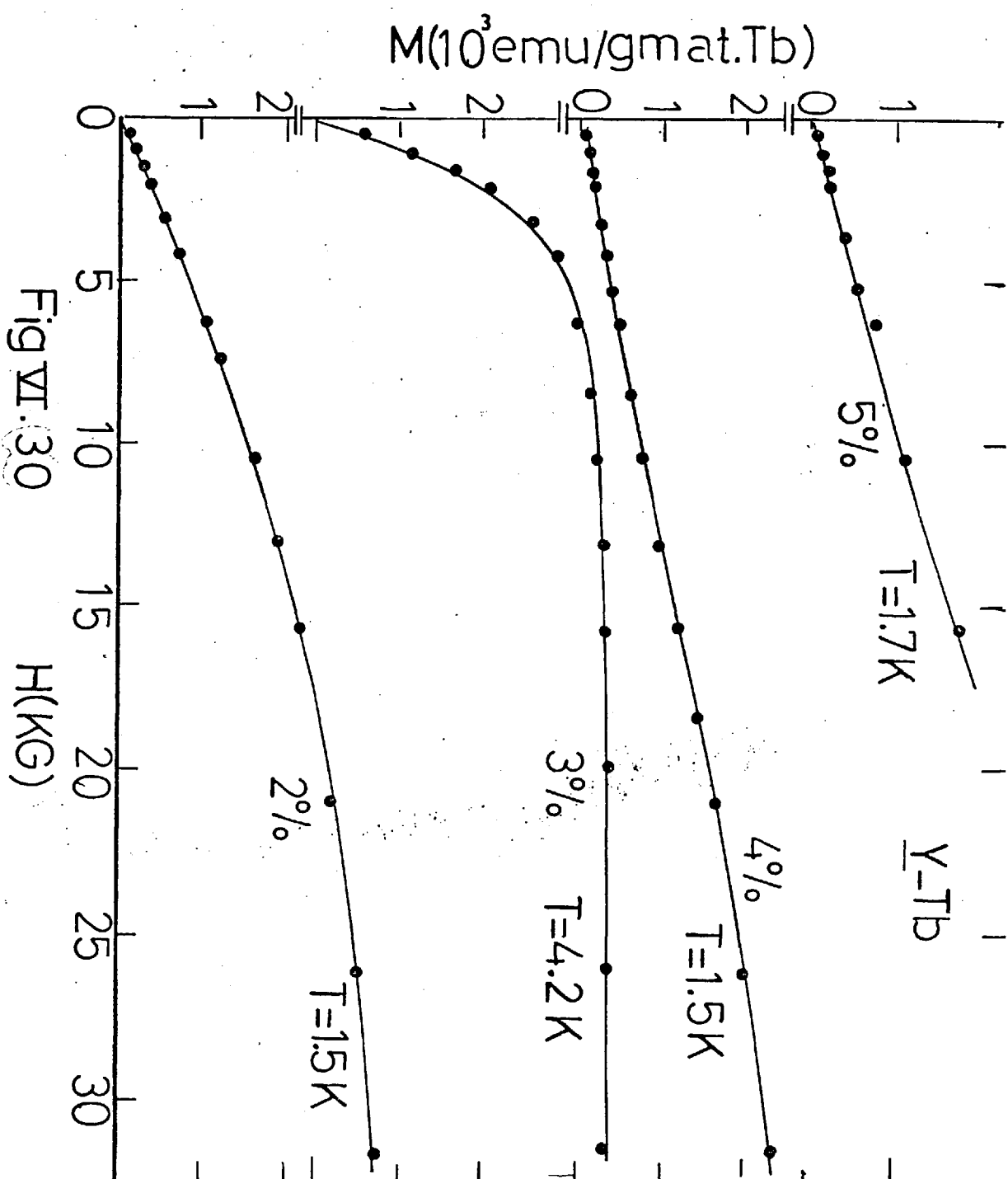


Fig VI.30

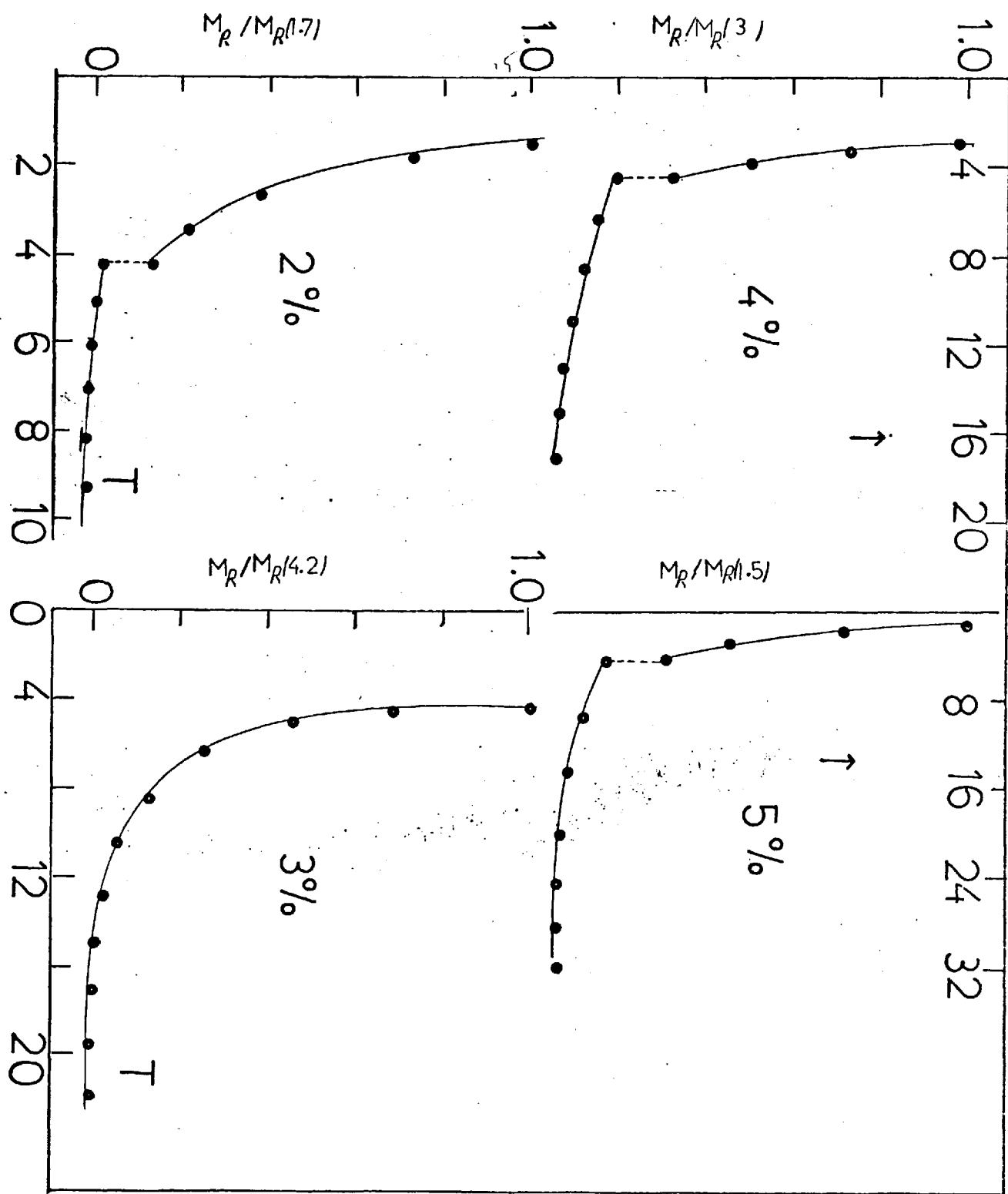
$\bar{Y}-Tb$ 

Fig VI.31

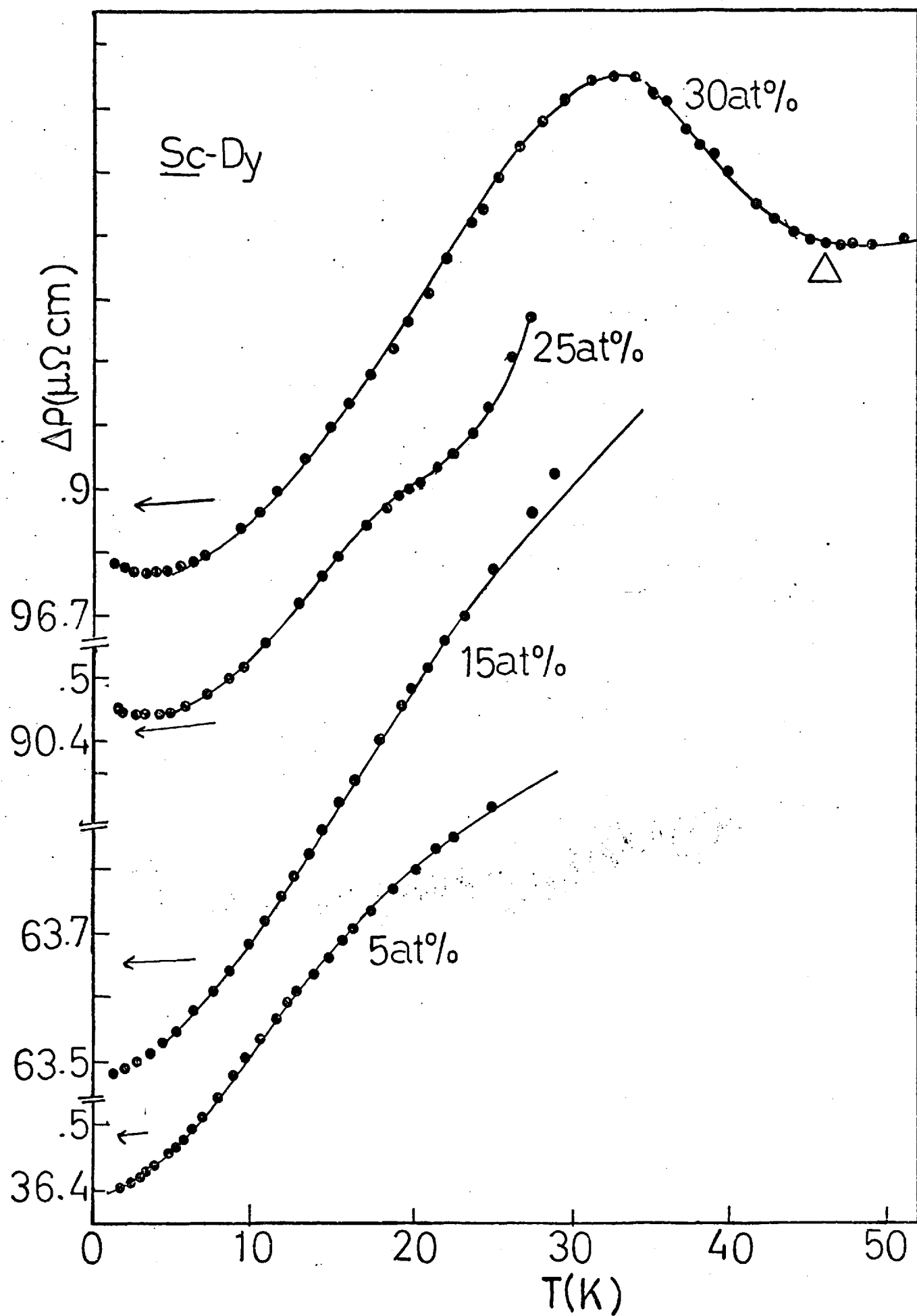


Fig VI · 32

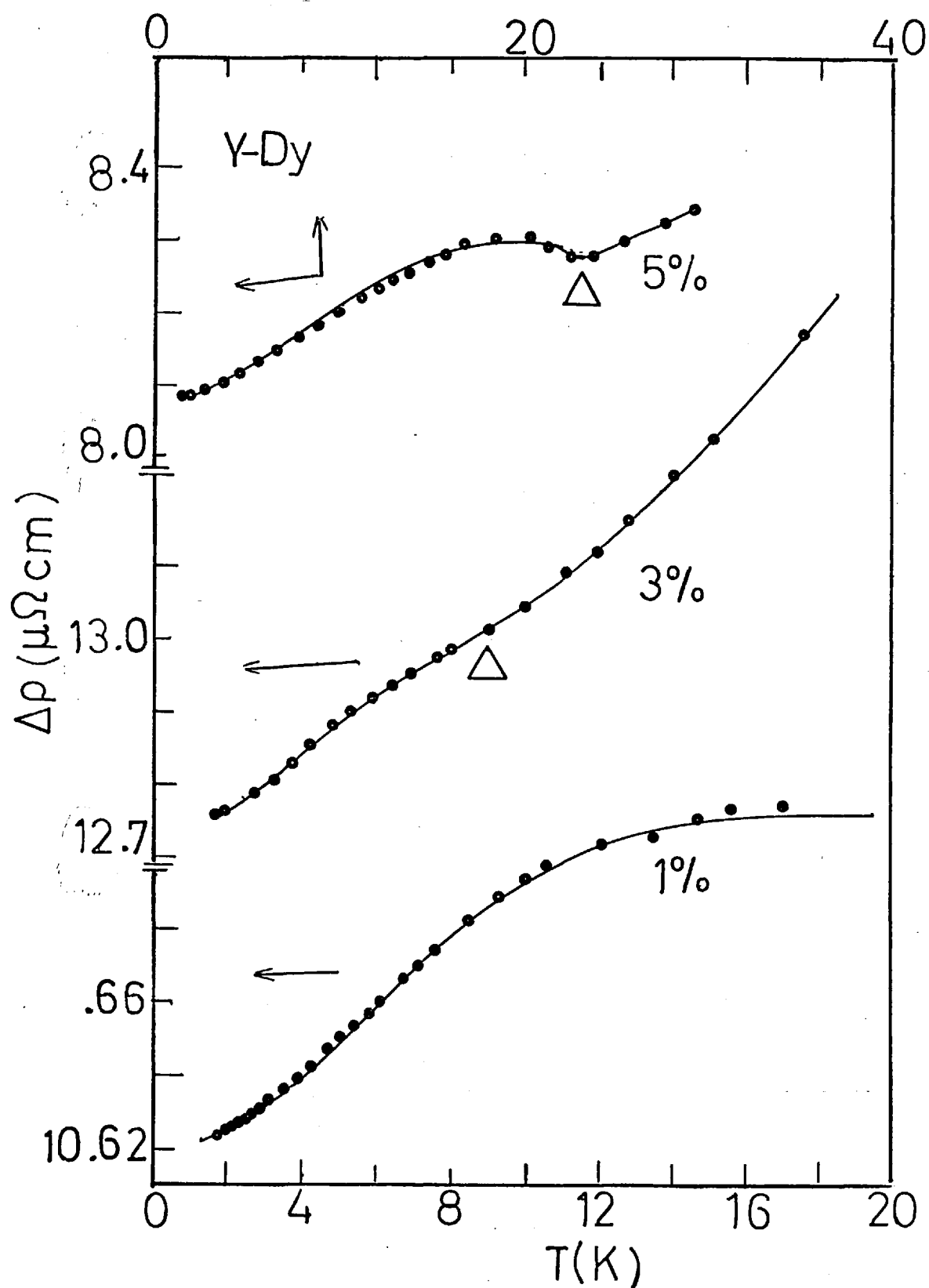


Fig VI.33

Fig VI.34

171.

$(X - X_{Sc}) (\text{emu/gm-at.Gd})$

Sc-5at%Dy

0

4

8

12

16

20

24

28

32

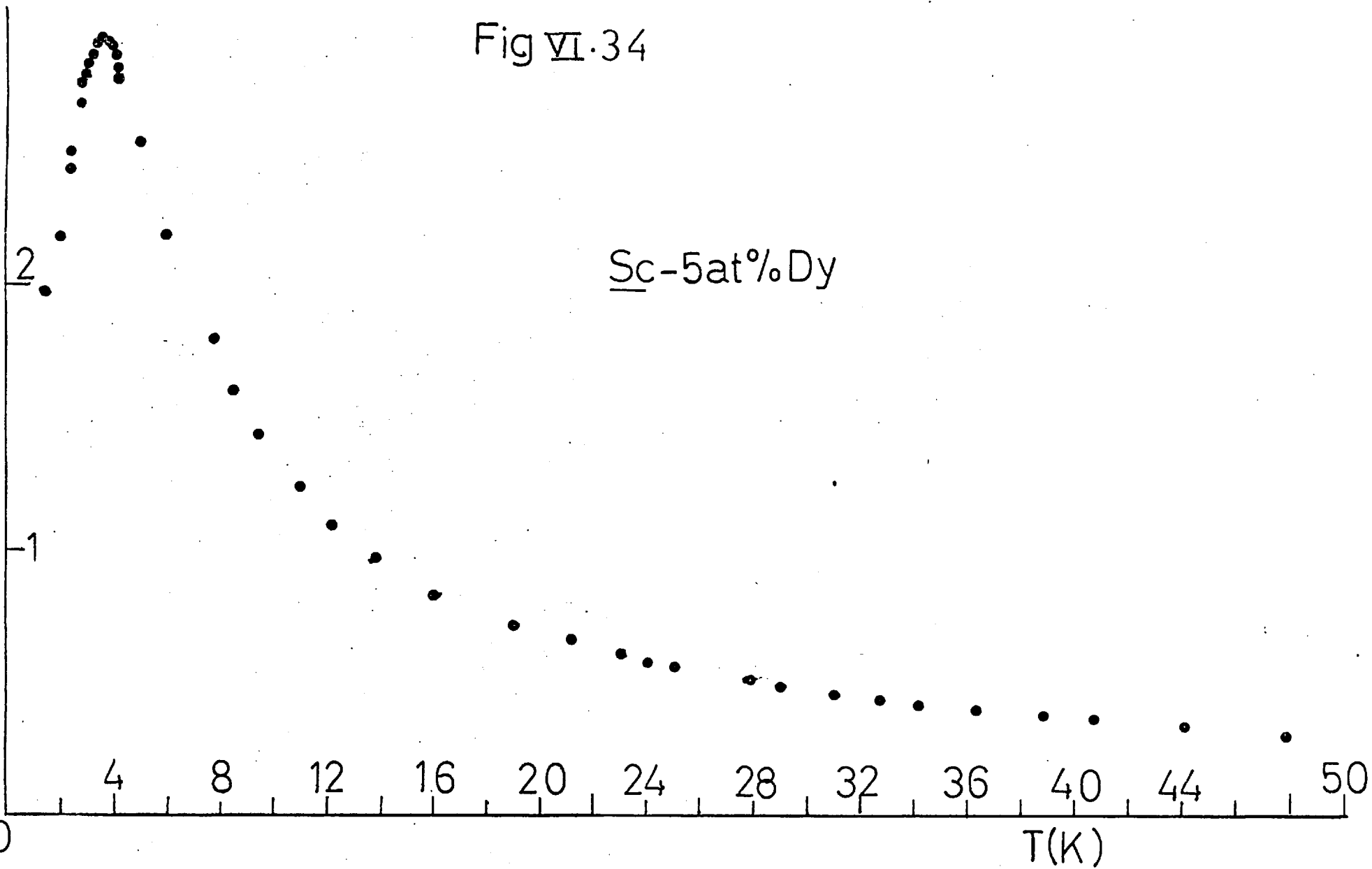
36

40

44

50

T(K)



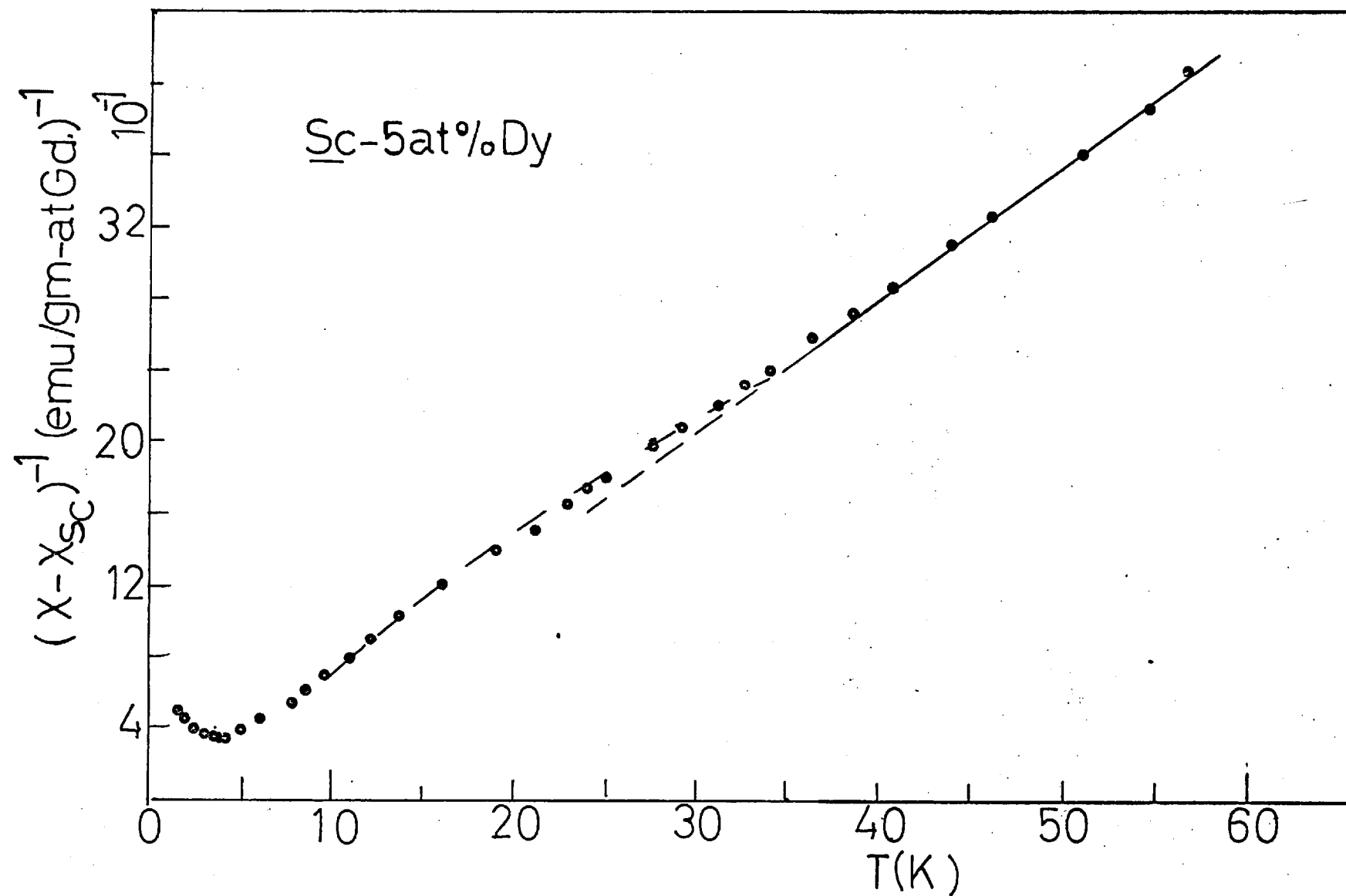


Fig VI. 35

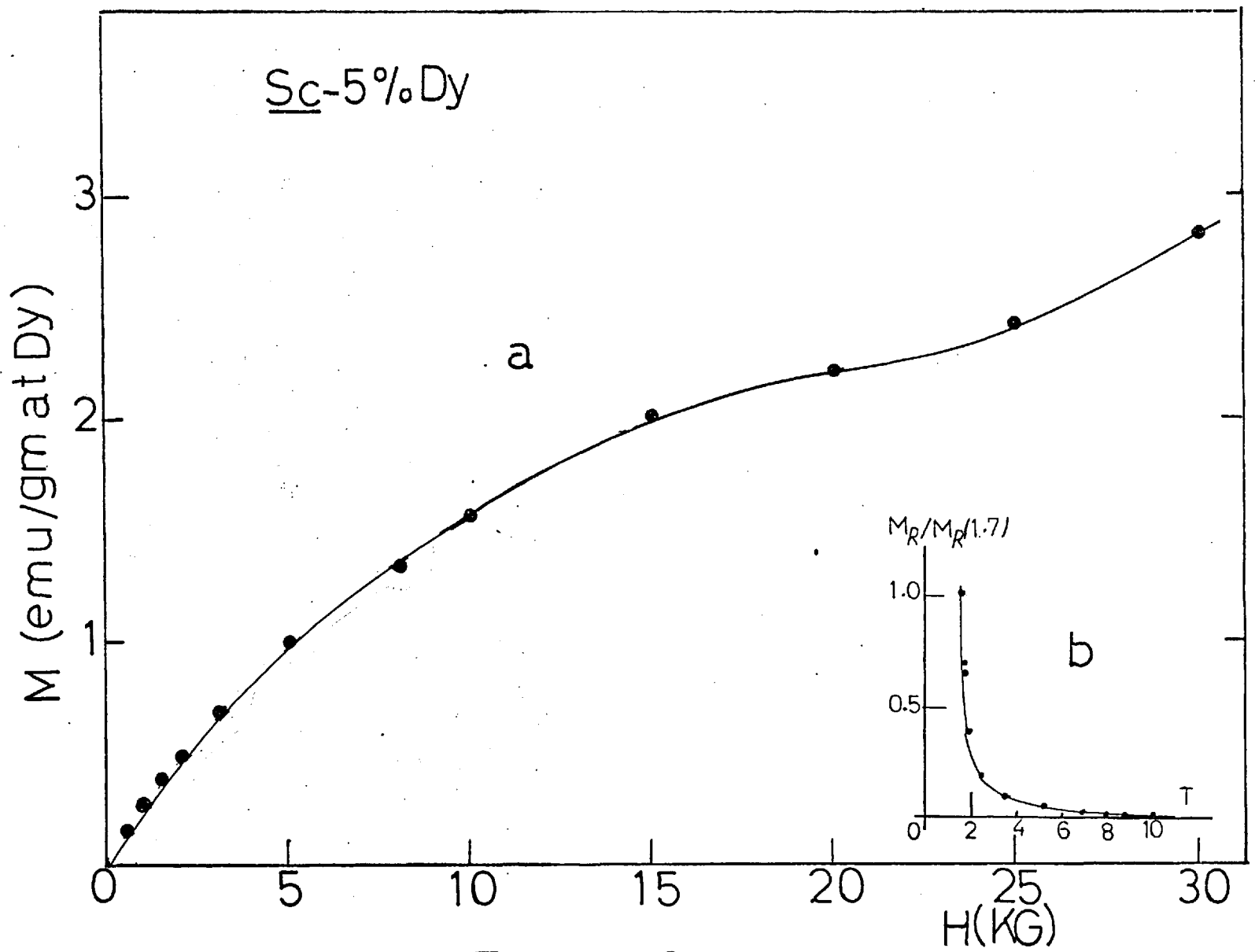


Fig VI.36

For the alloys 5% and 15% Dy quite different behaviour in $\Delta \rho(T)$ is noted, the behaviour being similar to spin glass materials. The corresponding plots for Y-Dy alloys are shown in Fig. VI.33. for the 1%, 3% and 5% Dy alloys. In alloys 3% and 5% Dy again effects of magnetic superzone are observable; the alloy 1% Dy shows behaviour similar to Sc-Dy alloys in the concentration range $c \leq 25\%$ Dy.

The initial susceptibility measurements on 5% Dy alloy show a maximum at about 3°K with the characteristics of spin glass materials (Fig. VI.34). At high temperatures the susceptibility becomes Curie-Weiss like (Fig. VI.35). As the temperature is lowered deviations from this behaviour are indicated by a hump which is related to crystal field splitting effects, followed by a minimum in the Curie-Weiss plot (maximum in susceptibility) due to magnetic ordering. The high field isothermal magnetization curves for this alloy are shown in Fig. VI.36a; Fig. VI.36b shows the temperature variation of the induced remanent magnetization for the same alloy.

VI.1.2. The dilute alloys

(a) S-state impurities (Gd^{+++}) in Sc

Excess resistivity per atomic per cent $\Delta\rho/c[\rho_{\text{alloy}}(T) - \rho_{\text{Sc}}(T) - \rho_{\text{alloy}}(1.5\text{K})]/c$ is plotted against the temperature T in Fig. (VI.37. Below about 10°K the temperature dependence is dominated by Gd impurity scattering and varies logarithmically with temperature, Fig. VI.38. The impurity resistivity below $\sim 10\text{ K}$ can be represented by the function

$$\Delta\rho/c = \Delta\rho_0 + A/c \log T$$

with the slope of the $\log T$ term increasing with Gd concentration (Table VI.7), the result demonstrating conclusively that the temperature dependence is partly a result of interaction between magnetic Gd impurities - the alloys are too concentrated for the isolated impurity effect to be observed in its simplest form.

(b) Non S-state (Tb^{+++} , Dy^{+++}) in Sc

Fig. VI.39 shows the low temperature excess resistivity $[\rho_{\text{alloy}}(T) - \rho_{\text{Sc}}(T) - \rho_{\text{alloy}}(1.5\text{K})]/c$ plotted against temperature for the alloys 0.2%, 0.5% and 1% Tb and corresponding curves for Dy impurity is shown in Fig. VI.40 for concentrations 0.2%, 0.5% and 1% Dy.

For the case of Tb alloys, a striking decrease in the resistivity with decreasing temperature is observed; a similar low temperature resistance anomaly for the case of Dy alloys has been observed. Such behaviour can not be described by a logarithmic function, consequently an attempt has been made to fit the observed behaviour of the resistivity to the crystal field splitting of the degenerate ground state for the rare-earth ion. I am very grateful to Dr. B. Southern for making the theoretical calculations of the resistivity, and also of the crystal field energy levels using the parameters of Hog and Touborg.

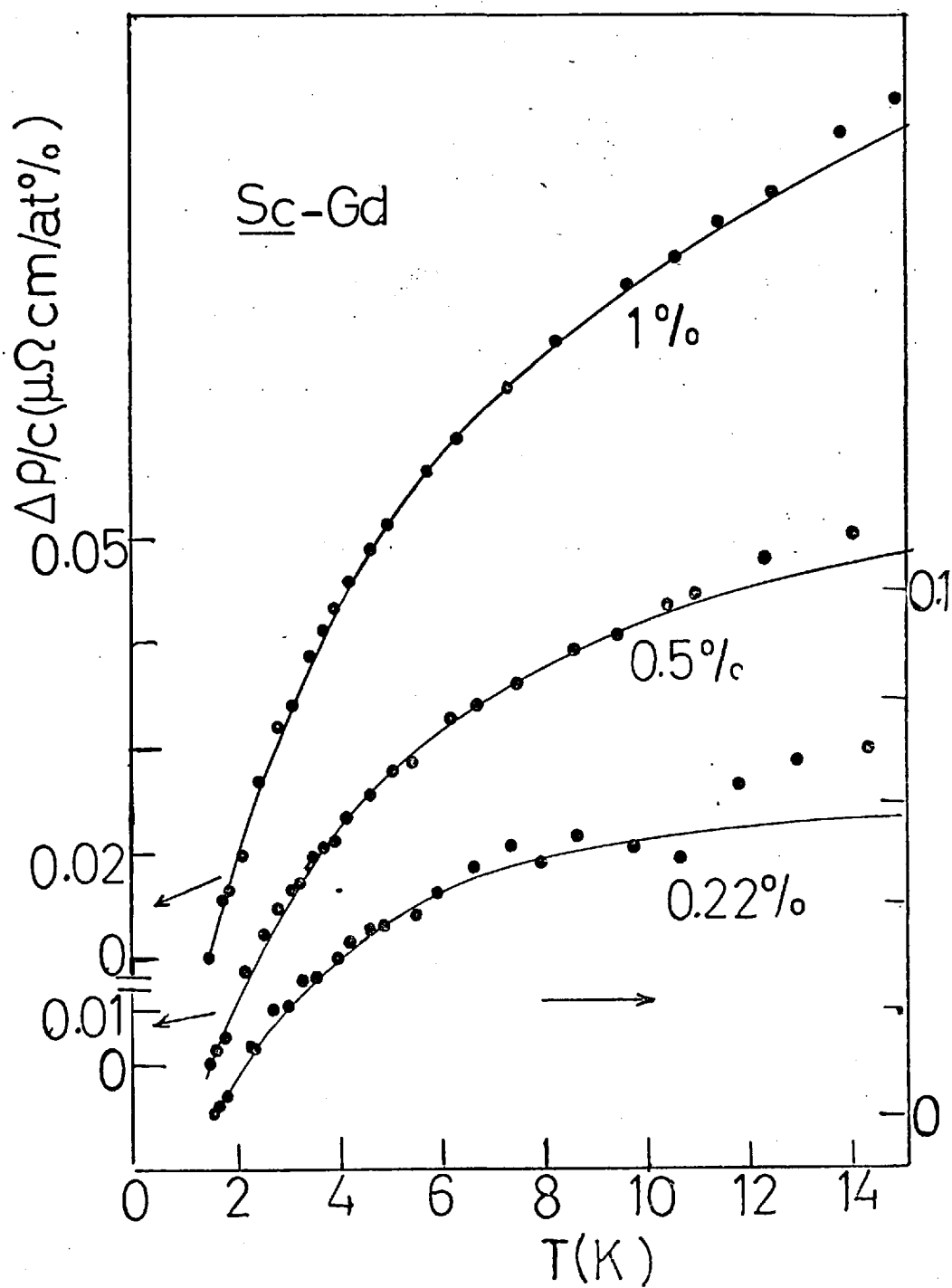
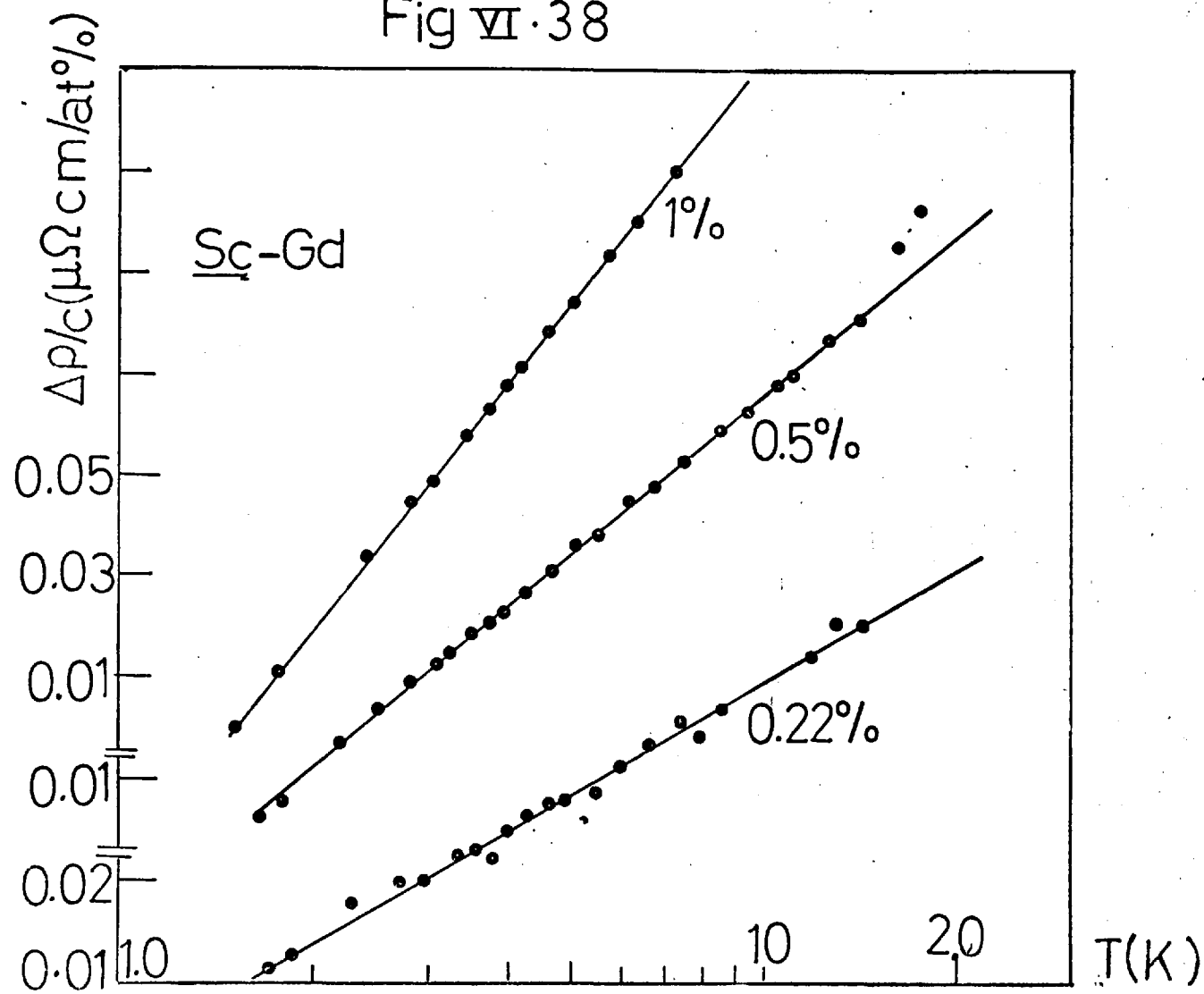


Fig VI.37

Fig VI.38



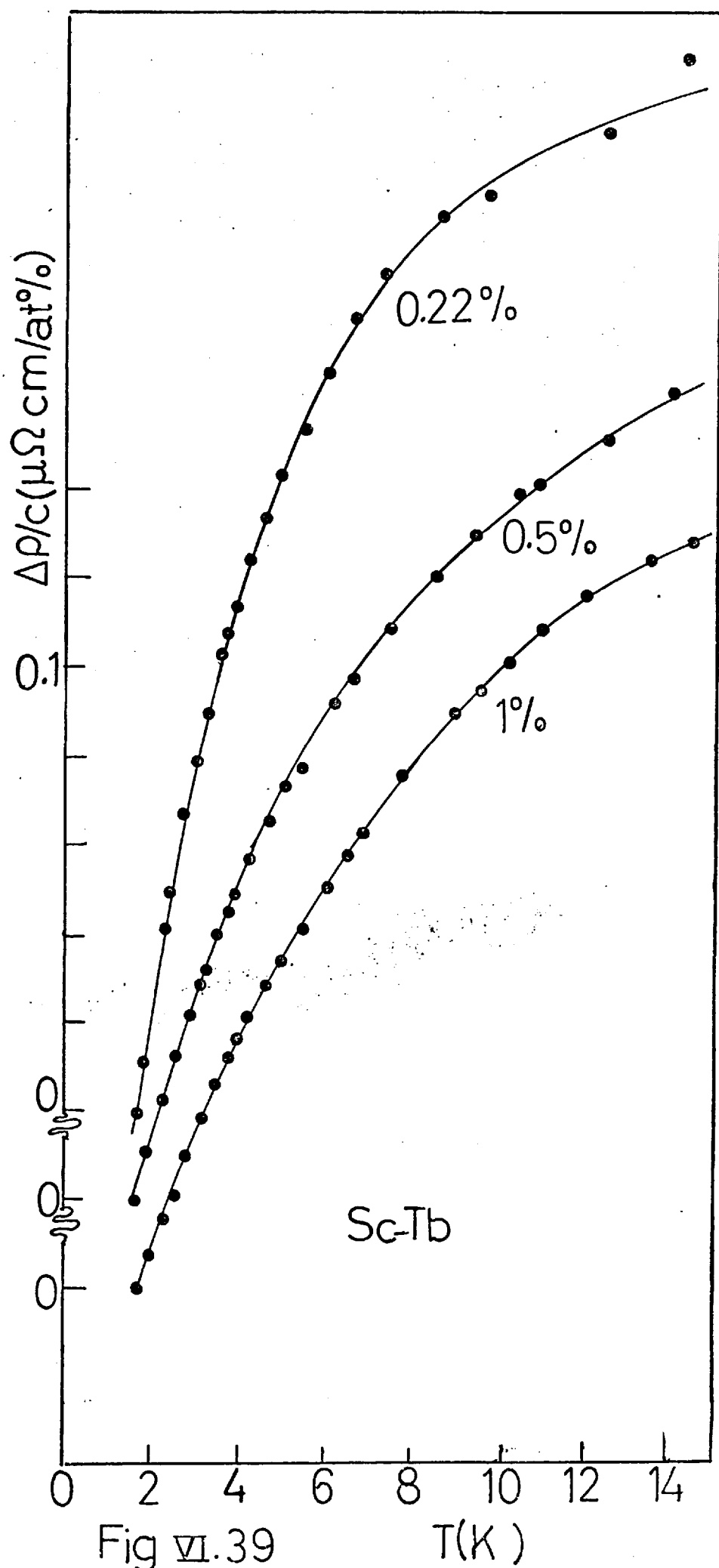


Fig VI.39

T(K)

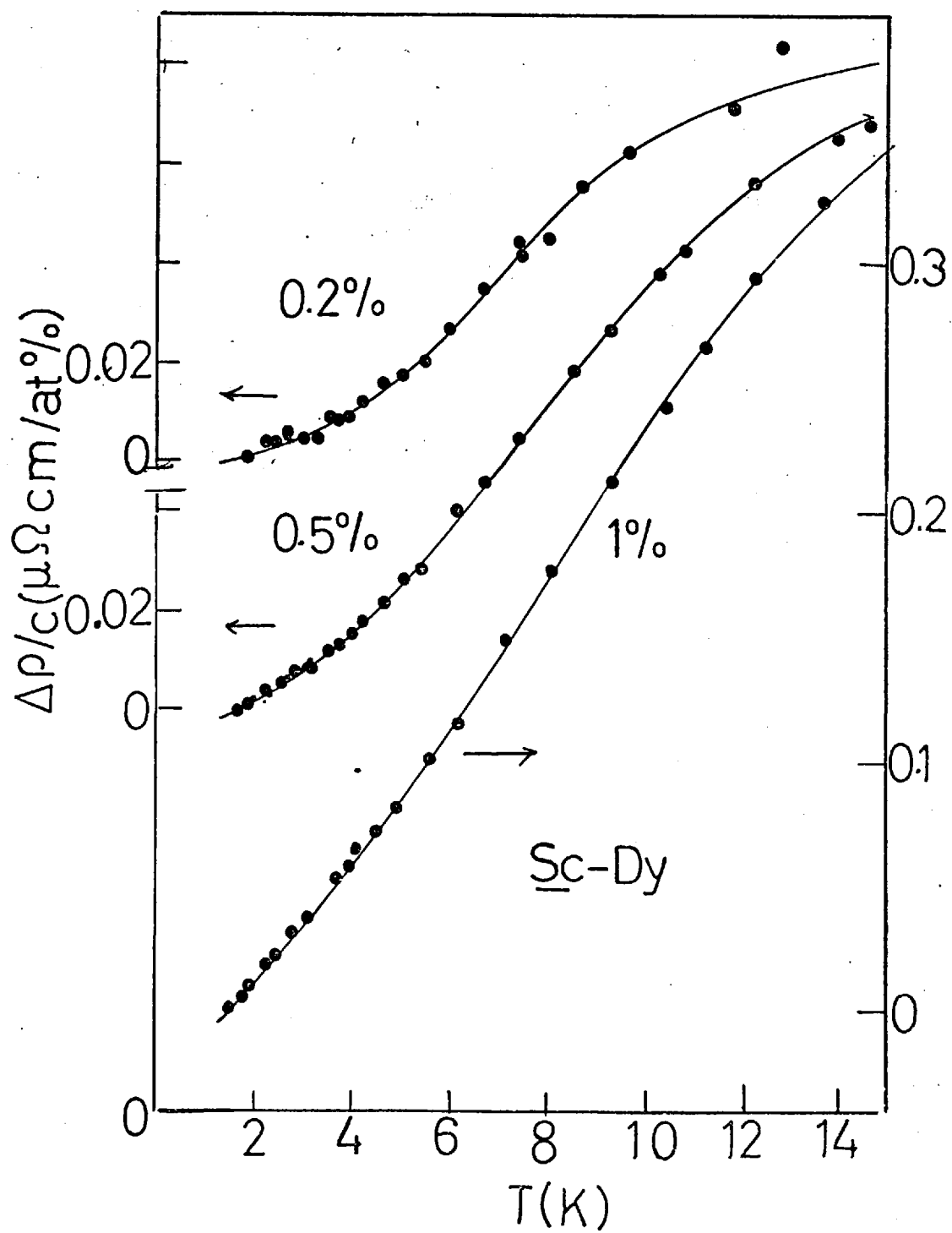


Fig VI.40

Crystal field (hexagonal) parameters B_{20} , B_{40} , B_{60} and B_{66} obtained by Hog and Touborg (206) from the magnetization measurements on the dilute single crystals and are, for Tb: 30.7×10^{-2} K, 18.9×10^{-4} K, -6.2×10^{-6} K, and 125×10^{-6} , and for Dy: 8.6×10^{-2} K, -19.6×10^{-4} K, 28.6×10^{-6} K and -266×10^{-6} K. A calculation of the resistivity due to s-f interactions in dilute alloys of the rare-earths has been given by Hirst (92) (see Chapter I, section 1.9) Using these parameters and Hirst's expression for the resistivity (equation 1.9.4), a computer program has been written to diagonalize the $(2J+1)(2J+1)$ crystal field matrix for a given constant (single) J, ($J = 6$ for Tb⁺⁺⁺ and $J = 7/2$ for Dy⁺⁺⁺) manifold and the temperature dependent magnetic resistivity calculated. It is found to be in reasonably good agreement with the observed results (Fig. VI.41 and 42) which show the plot of magnetic resistivity divided by the magnetic resistivity at $T \rightarrow \infty$ (spin disorder resistivity (18) vs. the temperature.

The fits of the measured electrical resistivity data to the theoretical curve have been made as follows.

a) For the case of Tb⁺⁺⁺ ion

By comparing the relation

$$\left(\frac{\Delta \rho(T=2K) - \rho_0}{\Delta \rho(T \rightarrow \infty) - \rho_0} \right)_{Exp} = \left(\frac{\rho_{mag}(T=2K)}{\rho_{mag}(T \rightarrow \infty)} \right)_{Exp} = \left(\frac{\rho_{mag}(T=2K)}{\rho_{mag}(T \rightarrow \infty)} \right)_{Theo.} \quad VI.1$$

where $\Delta \rho(T=2K) = \rho_{alloy}(T=2K) - \rho_{sc}(T=2K)$, ρ_0 is the residual resistivity and

$$\Delta \rho(T \rightarrow \infty) = \rho_{alloy}(T=300K) - \rho_{sc}(T=300K)$$

Hence ρ_0 has been found and subtracted from each data point.

b) For the case of the Dy⁺⁺⁺ ion

The resistivity of the alloy is expressed as:

$$\rho(T) = \rho_{ph}(T) + \rho_{ar} + \rho_{ir} + \rho_m(T) \quad VI.2$$

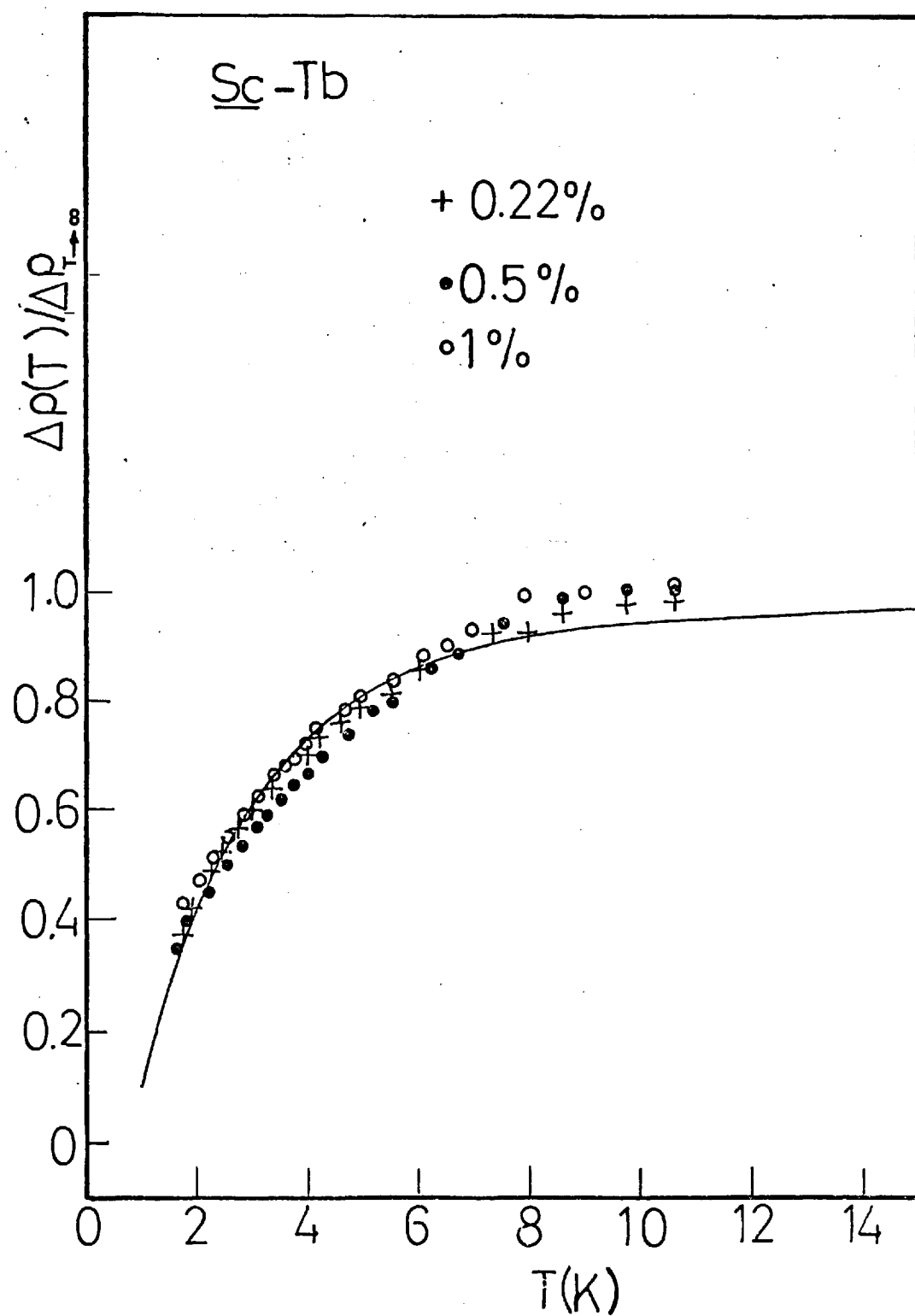
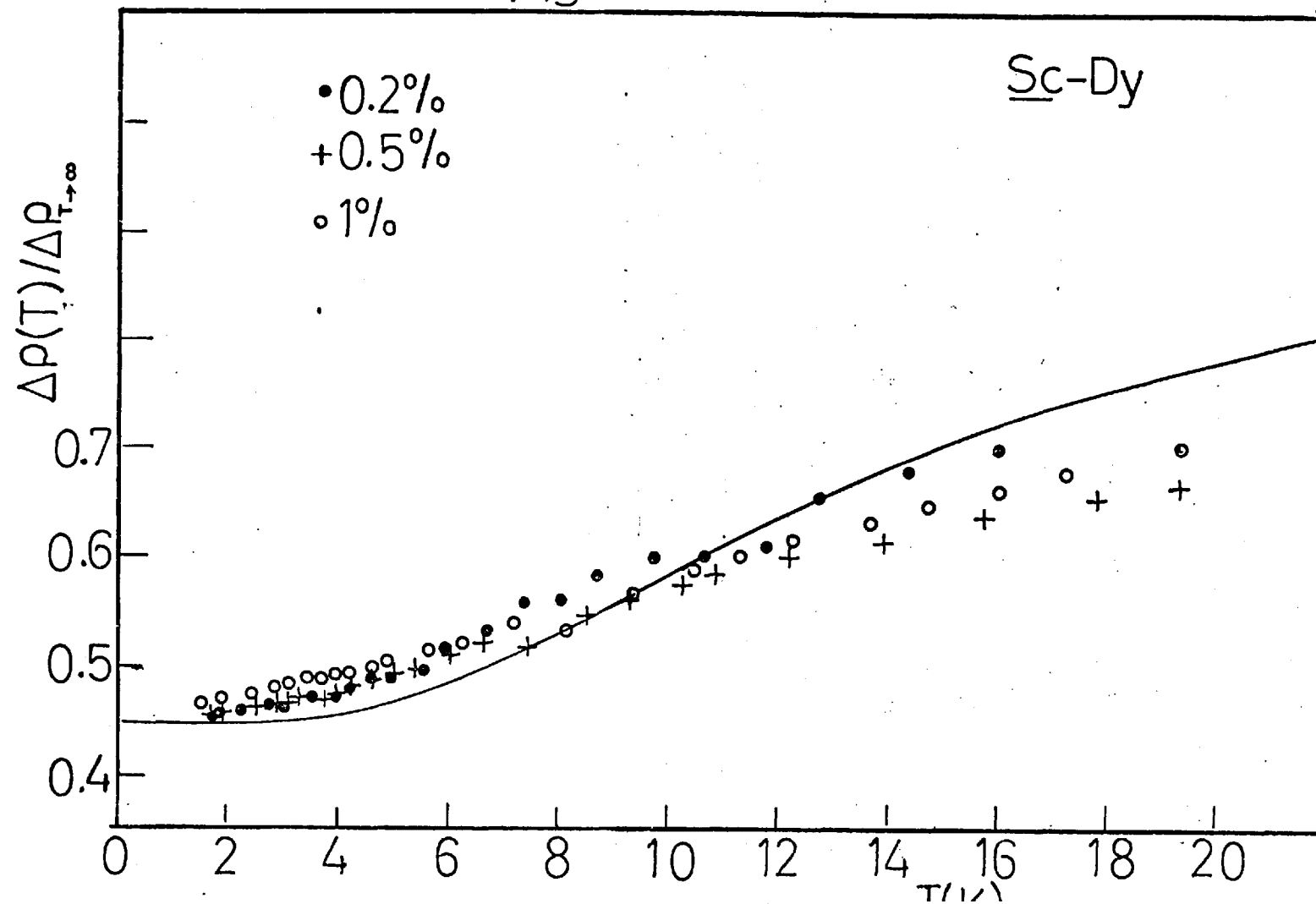


Fig VI.41

Fig VI.42



where $\rho_{ph}(T)$ is the phonon resistivity, ρ_{ar} , ρ_{ir} are the atomic disorder resistivity and the impurity resistivity respectively, $\rho_m(T)$ is the magnetic resistivity.

At $T = 0$,

$$\rho(T \rightarrow 0) = (\rho_{ar} + \rho_{ir}) + \rho_m(T \rightarrow 0) \quad \text{VI.3}$$

and at $T \rightarrow \infty$

$$\rho(T \rightarrow \infty) = (\rho_{ar} + \rho_{ir}) + \rho_m(T \rightarrow \infty) \quad \text{VI.4}$$

where $\rho(T \rightarrow \infty) \equiv \rho_{\text{alloy}}(T=300) - \rho_{ph}(T)$

Using the relation:

$$\left(\frac{\rho(T \rightarrow 0) - (\rho_{ar} + \rho_{ir})}{\rho(T \rightarrow \infty) - (\rho_{ar} + \rho_{ir})} \right)_{Exp.} = \left(\frac{\rho_{mgs}}{\rho_m(T \rightarrow \infty)} \right)_{Theo.} \quad \text{VI.5}$$

where ρ_{mgs} is the ground state magnetic resistivity, and $(\rho_m(T \rightarrow \infty))$

is the magnetic resistivity for full J value. From the extrapolations of the $\rho-T$ curve to $T = 0$, $\rho(T \rightarrow 0)$ is found, and by comparison of these relations, $(\rho_{ar} + \rho_{ir})$

$\rho_m(T \rightarrow 0)$ and $\rho_m(T \rightarrow \infty)$ have been deduced. Hence

$$\frac{\rho(T) - \rho_{ph}(T) - (\rho_{ar} + \rho_{ir})}{\rho_m(T \rightarrow \infty)} = \frac{\rho_m(T)}{\rho_m(T \rightarrow \infty)}$$

plotted as a function of the temperature. For the case of Tb^{+++} the deviation from the theoretical line above 7°K may be attributed to the break down of Matthiessen's rule, and also to the difficulty in finding the spin disorder resistivity $(\rho_m(T \rightarrow \infty))$. For Dy alloys the high temperature deviation of the data points, might also be attributed to these facts.

The energy levels for Tb and Dy ions are shown in Fig.VI.43 (see also ref.

(206). In the case of Tb^{+++} , the ground state is a non-magnetic singlet with a doublet only about 3.86 K higher; a third singlet is 7.5 K above the ground state, the next energy levels are a doublet and another doublet separated by ~ 12 K and then a singlet separated by ~ 15 K. Other energy levels are more than 40 K higher.

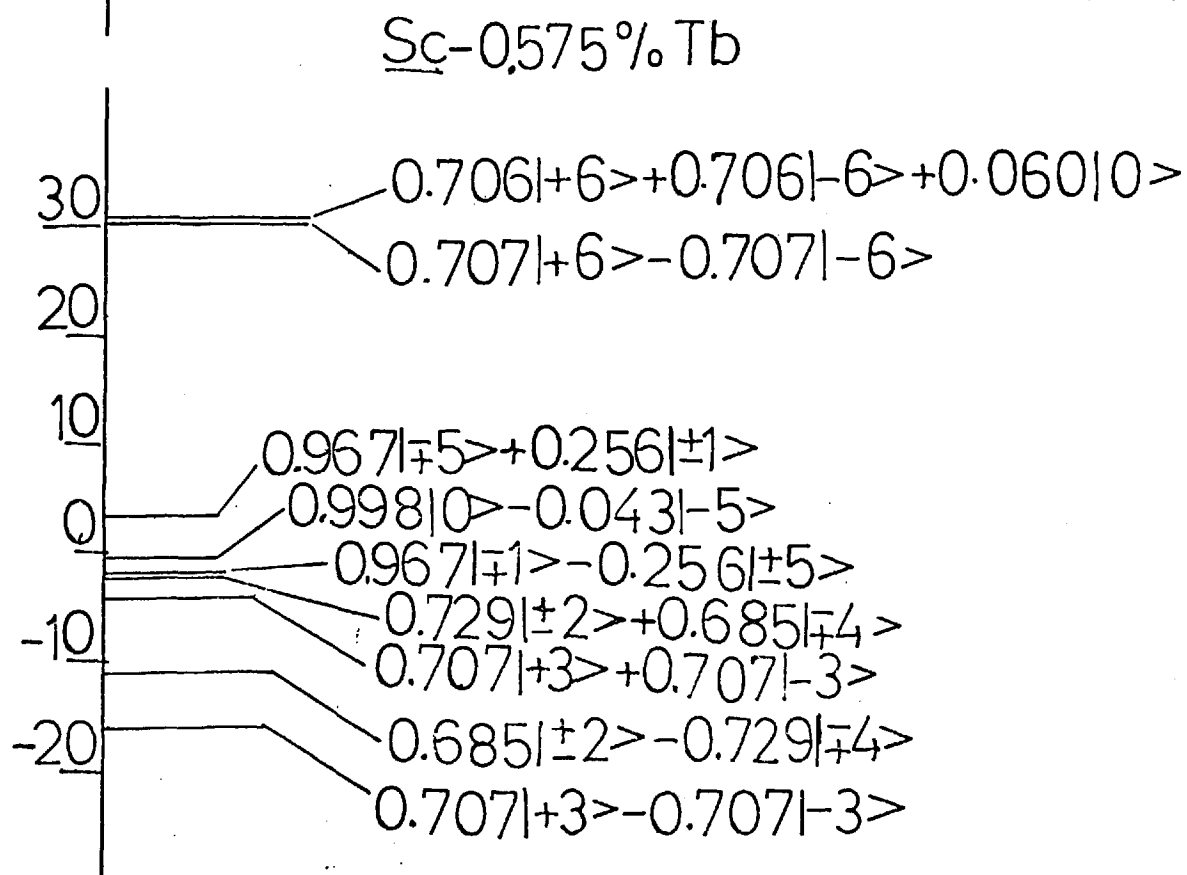
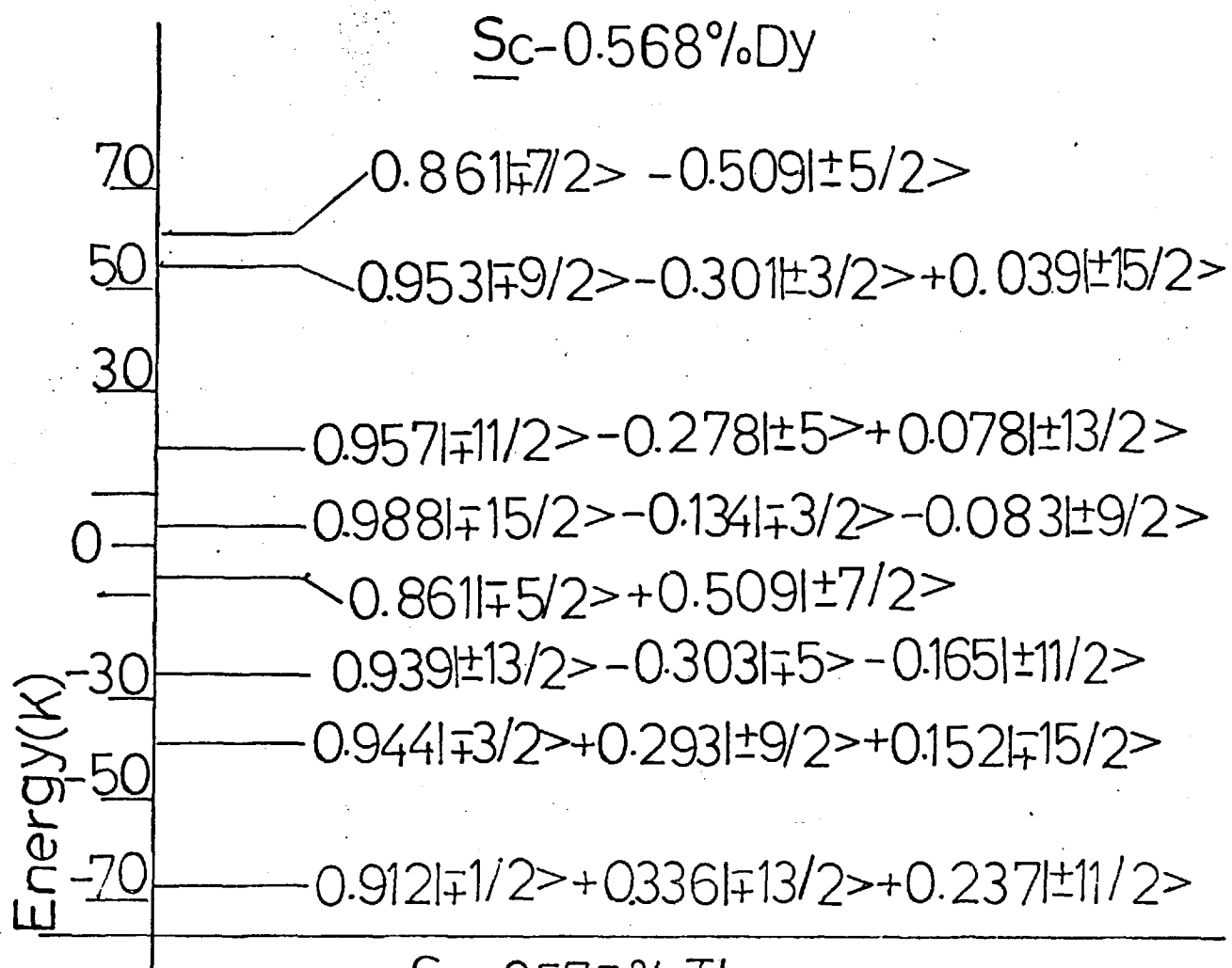


Fig VI.43

The crystal field split energy levels scheme for Dy shows a ground state doublet to be $|\pm 1/2\rangle$ with small admixture of $|\pm 3/2\rangle$ and $|\pm 11/2\rangle$ with energy 67.943°K separated by another doublet with energy 28.6°K above it, and a second doublet with energy $\sim 42^\circ\text{K}$ higher. Other energy levels are also doublets.

(c) S-state impurities (Gd^{+++}) in Y

Fig. VI.44 shows the excess resistivity per atomic per cent $(\rho_{\text{alloy}}(T) - \rho_Y(T) - \rho_{\text{alloy}}(1.5))/c$ vs. the temperature T . The low temperature decrease in the resistance below about 6 K for 0.2% alloy is similar to the Sc-Gd alloys but the temperature dependent behaviour strongly deviates from logarithmic function, as is shown in Fig. VI.45. The 0.5% Gd alloy is also plotted on the logarithmic scale.

The field dependences of the magnetization of the 0.2% and 0.5% Gd alloys at different temperatures ≤ 4.2 K are shown in Fig. VI.46 with maximum fields of 30 KG and 12KG for 0.2% and 0.5% Gd alloys respectively, the full curve is the Brillouin curve for $J = 7/2$. A plot of the initial susceptibility (at 1 KG field) $\Delta X (X_{\text{alloy}} - X_Y)$ against T is shown in Fig. VI.16 for the alloys with 0.2% and 0.5% Gd. The Curie-Weiss plot for these alloys is given in Fig. VI.17, which shows a positive paramagnetic Curie temperature and effective moments larger than the free (Gd^{+++}) ion value (Table VI.8).

(d) Non S-state impurities (Tb^{+++} Dy^{+++}) in Y

Fig. VI.47 shows excess resistivity per atomic per cent $(\rho_{\text{alloy}} - \rho_Y - \rho_{\text{alloy}}(1.5))/c$ vs. temperature for 0.2% and 0.5% Tb alloys. Fig. VI.48 shows the same plot for 0.2% and 0.5% Dy alloys. The low temperature decrease in resistivity with decreasing temperature is also fitted to the theoretical curve calculated from the crystal field parameters of Hog and Touborg (207), as described earlier (Fig. VI.49

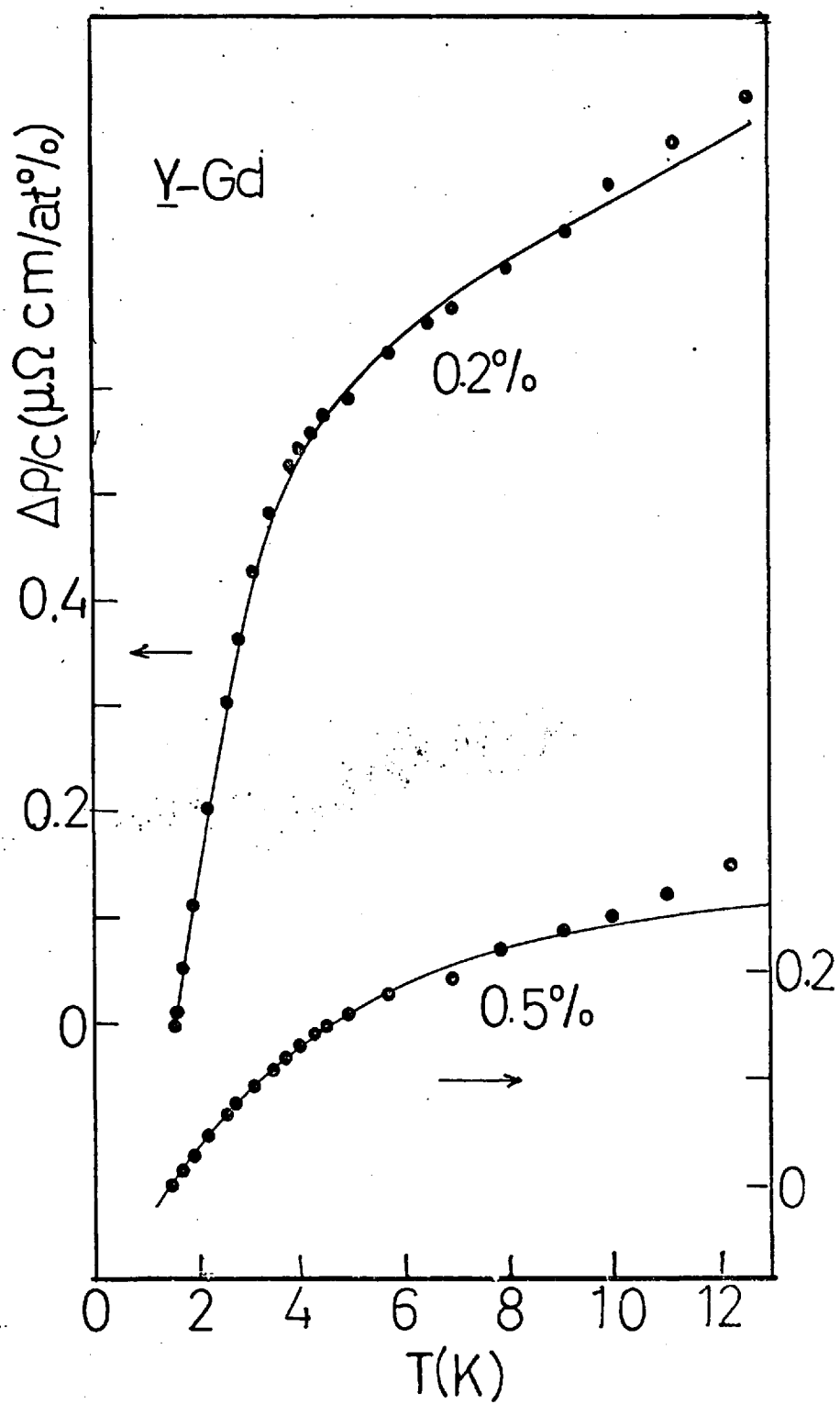


Fig VI 44

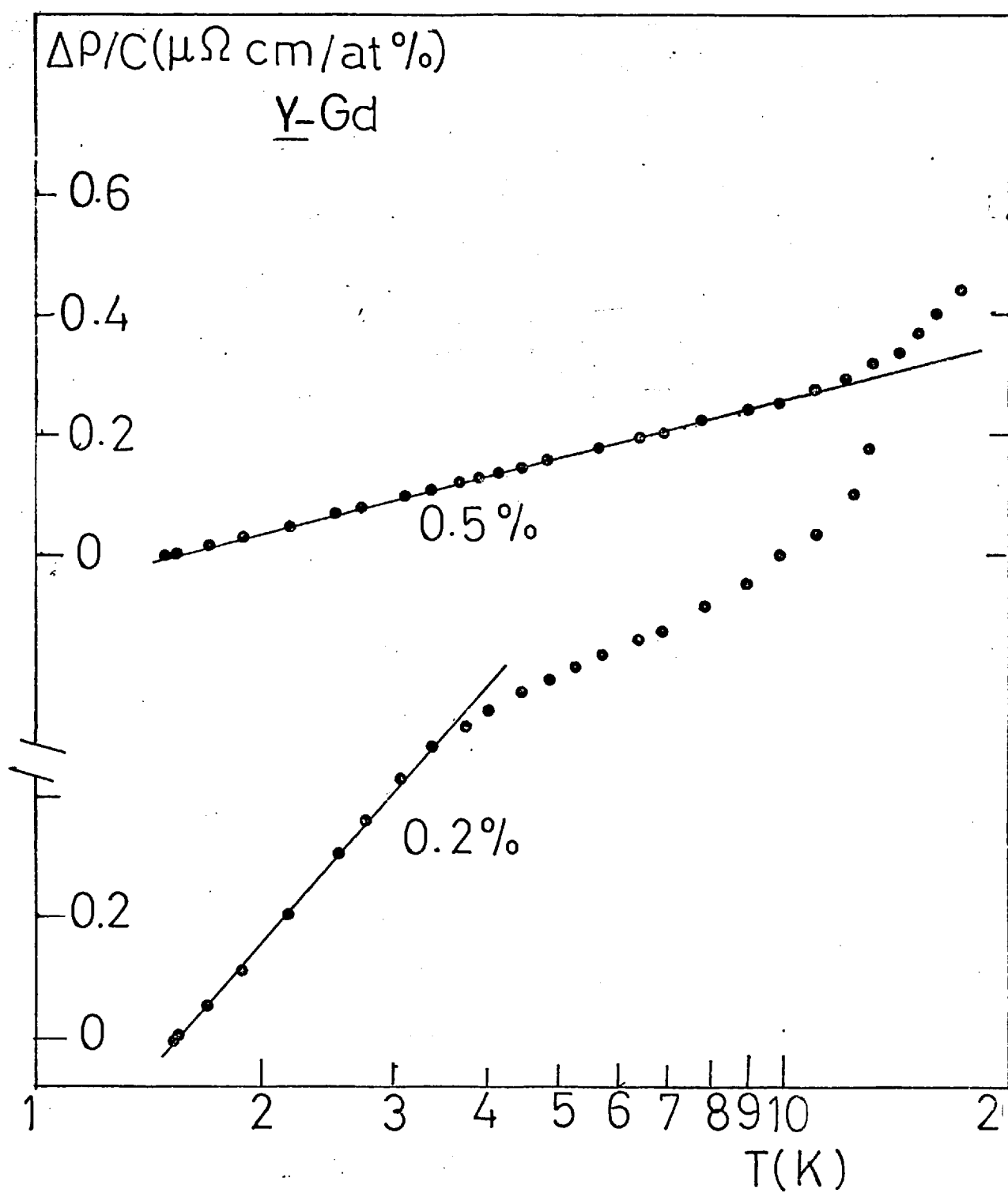
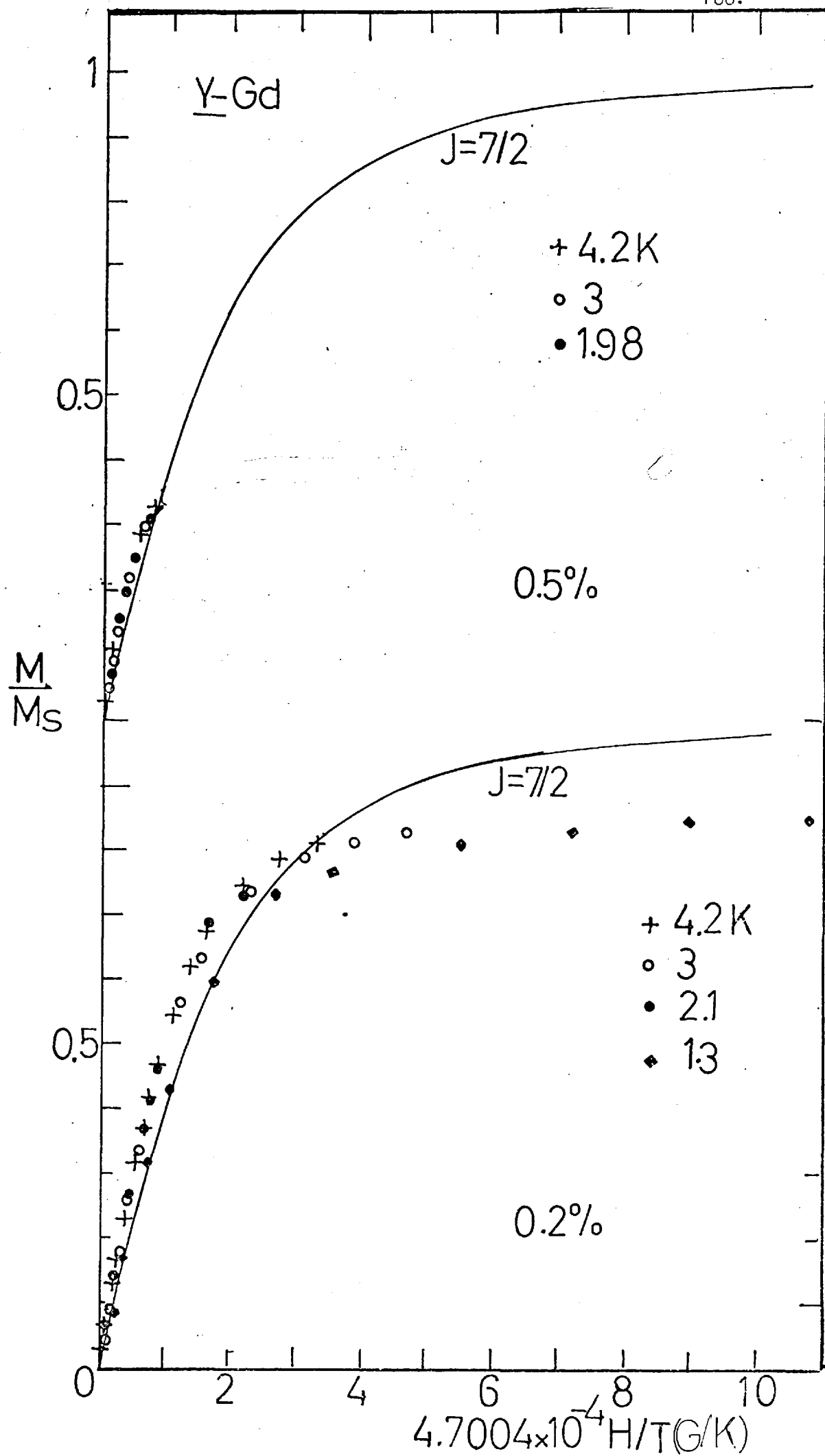


Fig VI·45



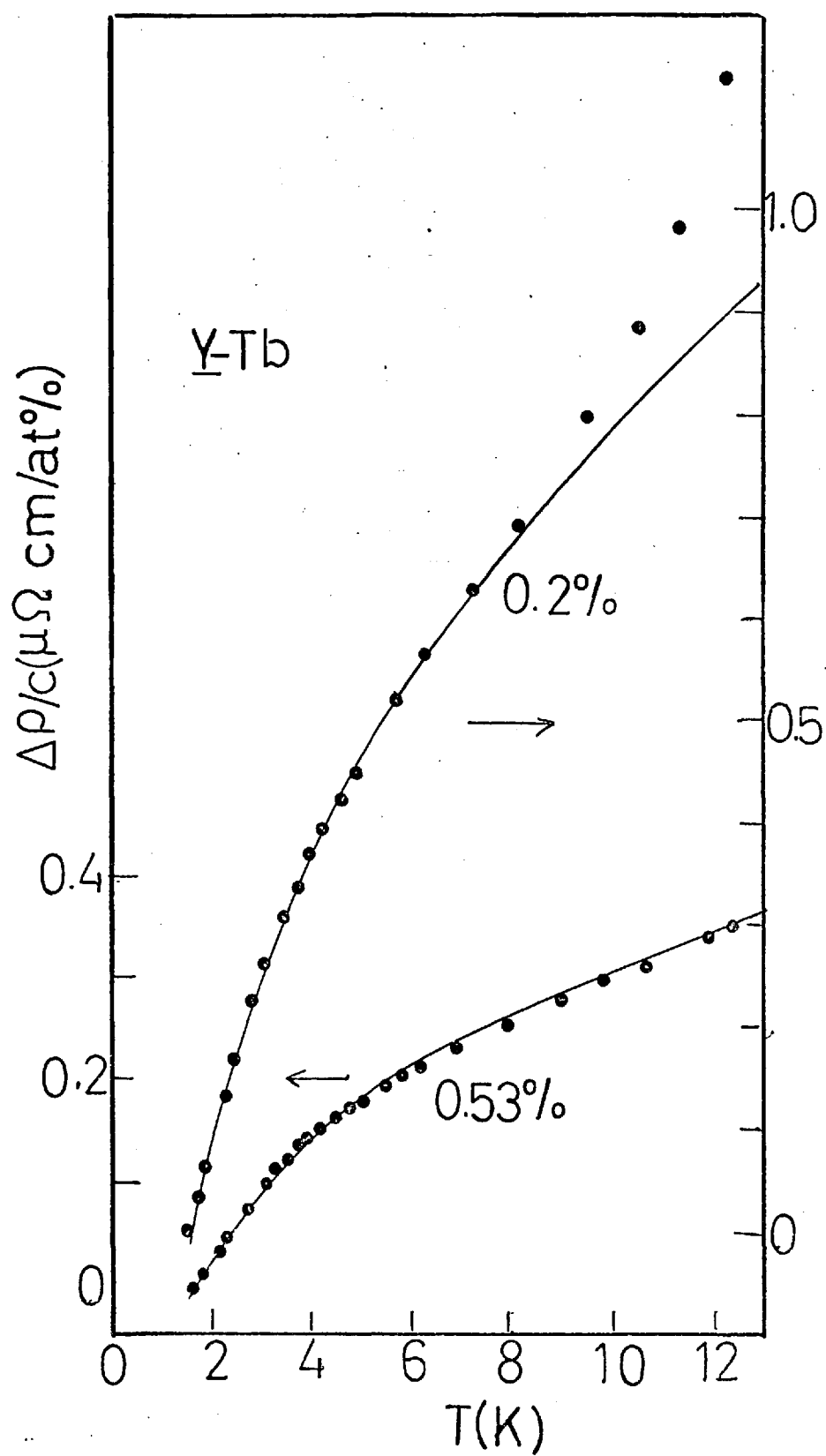
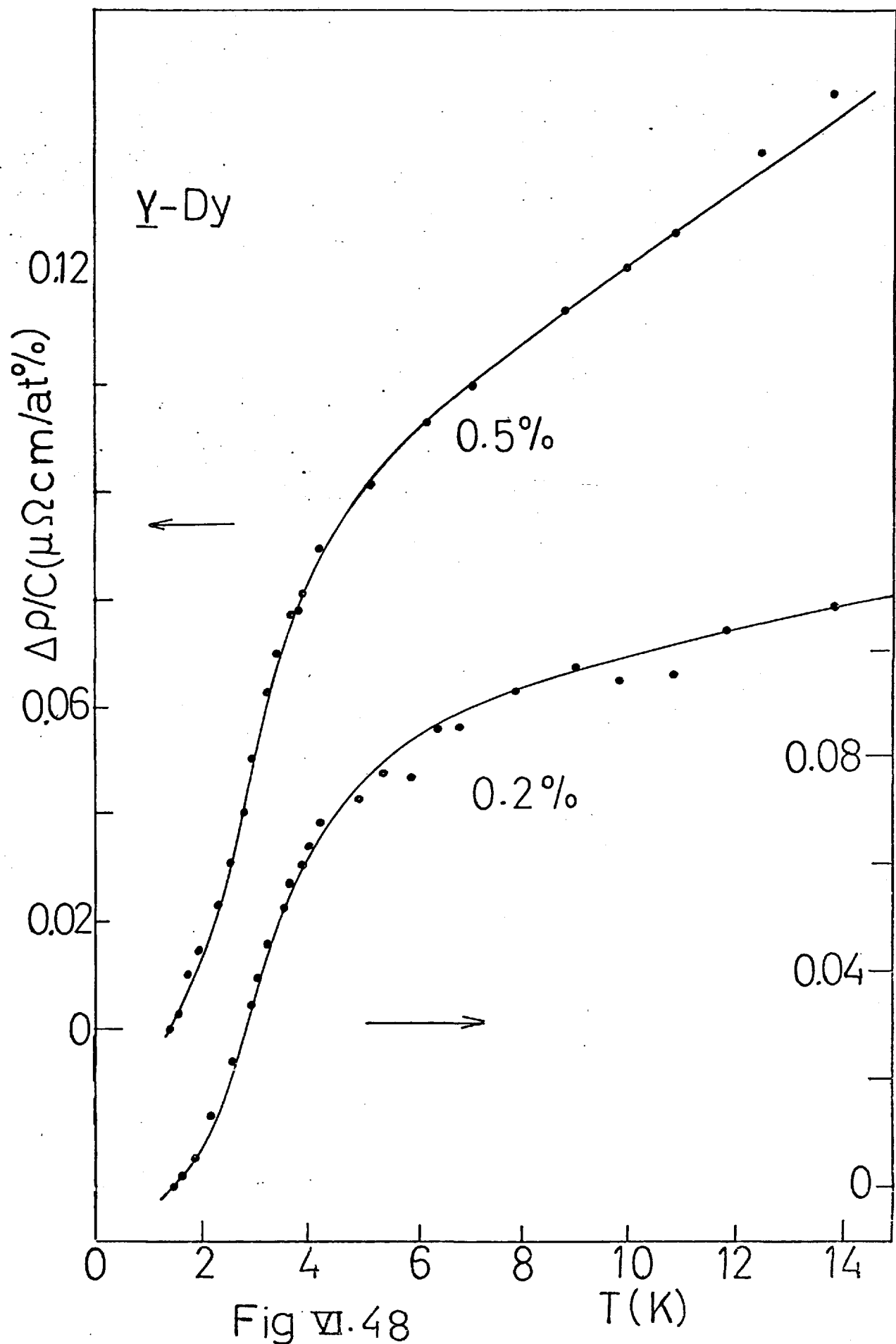


Fig VI.47



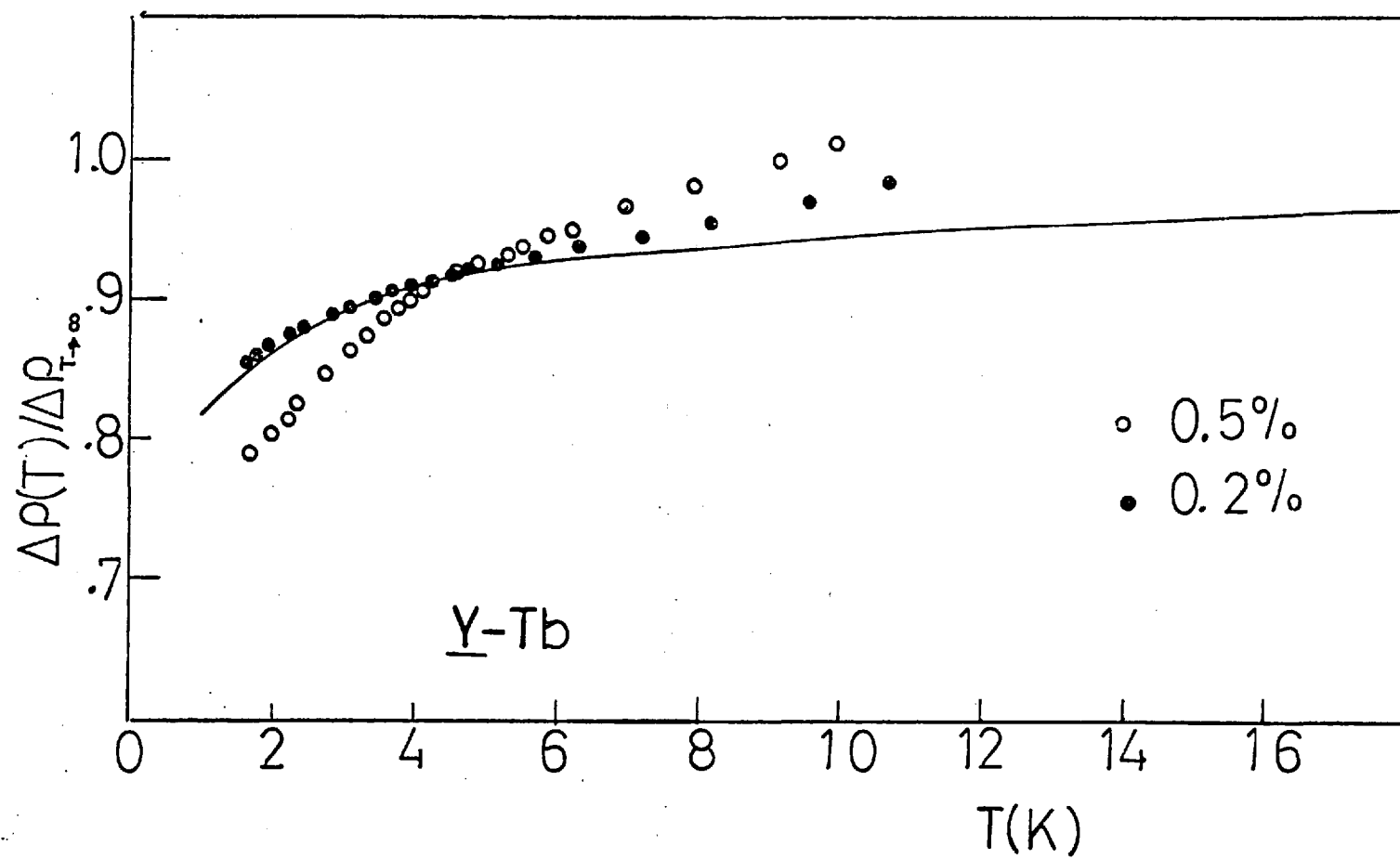


Fig VI.49

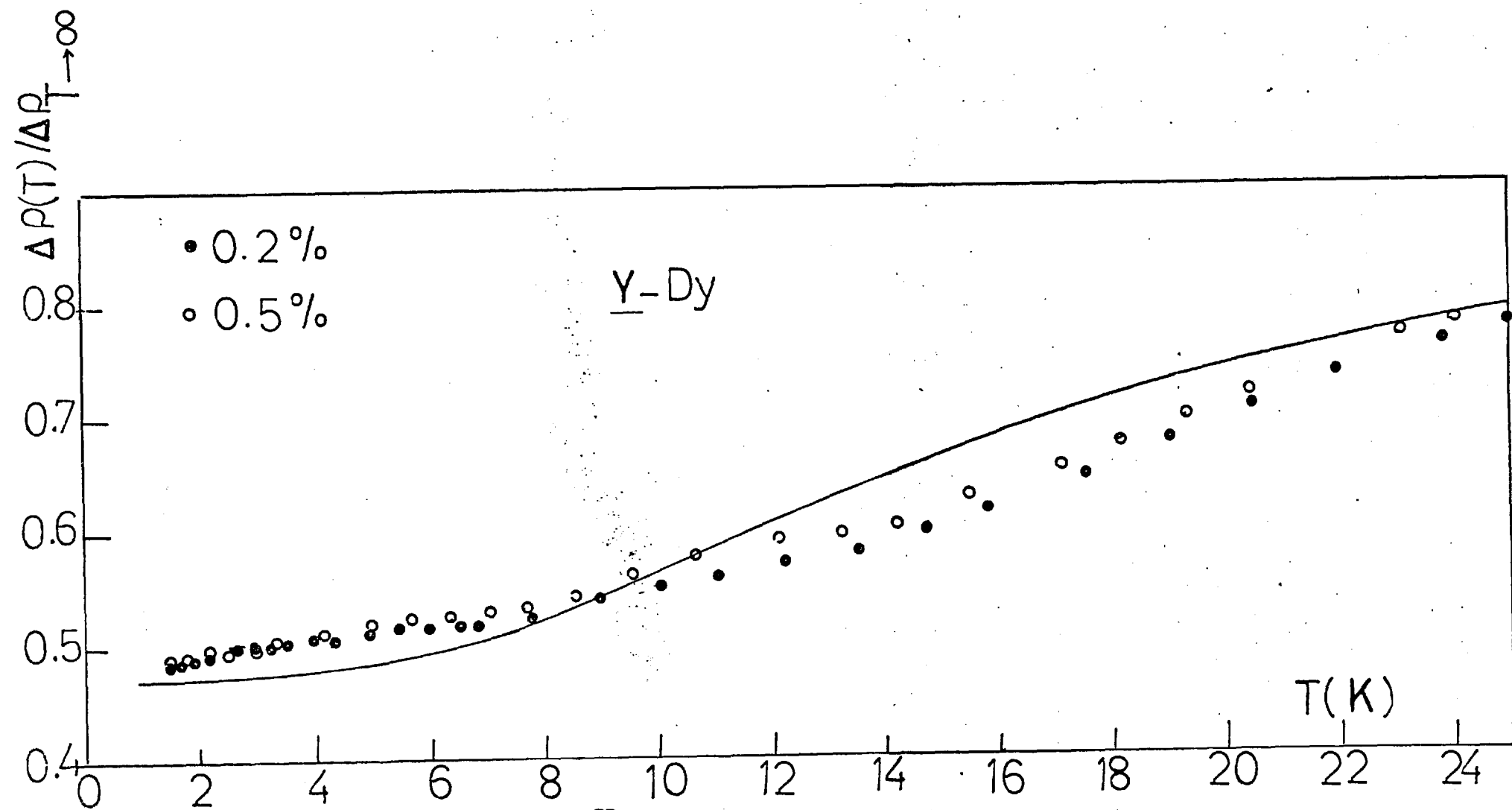


Fig VI.50

and 50) with crystal field parameters given, for Tb: 0.945K , $0.589 \times 10^{-3}\text{K}$, $-0.145 \times 10^{-4}\text{K}$, and $0.100 \times 10^{-3}\text{K}$, and for Dy: 0.321K , $-0.293 \times 10^{-2}\text{K}$, $0.418 \times 10^{-4}\text{K}$, and $-0.333 \times 10^{-3}\text{K}$. Low temperature deviation for Tb and Dy alloys from the theoretical curve is indicative of interaction effects; the high temperature deviation is again attributed to the breakdown of Matthiessen's rule. The energy levels of Tb and Dy ions dissolved in Y are shown in Fig. VI.51. The ground state of Tb is highly degenerate and is not singlet (accidentally); the state $|\mp 1\rangle$ predominates with small admixture of the $|\pm 5\rangle$ state. The first excited state is a singlet with $|0\rangle$ and lies about 0.1 K higher, the third state is dominated by $|\mp 2\rangle$ doublet with energy $\sim 2\text{ K}$ higher than the ground state; the fourth and fifth states are singlets and separated by $\sim 10\text{ K}$ and $\sim 15\text{ K}$ from the ground state. Other states are doublets and lie at higher energies.

In Dy the ground state is a Kramers doublet, the $|\mp 1/2\rangle$ predominates with small admixture of $|\mp 13/2\rangle$ and $|\pm 11/2\rangle$. The first excited state is again a doublet with energy of $\sim 40\text{ K}$ higher than the ground state and by $|\mp 3/2\rangle$ predomination; the third level is a doublet separated by $\sim 95\text{ K}$ from the lowest state. Other states are at high energy separation from the ground state.

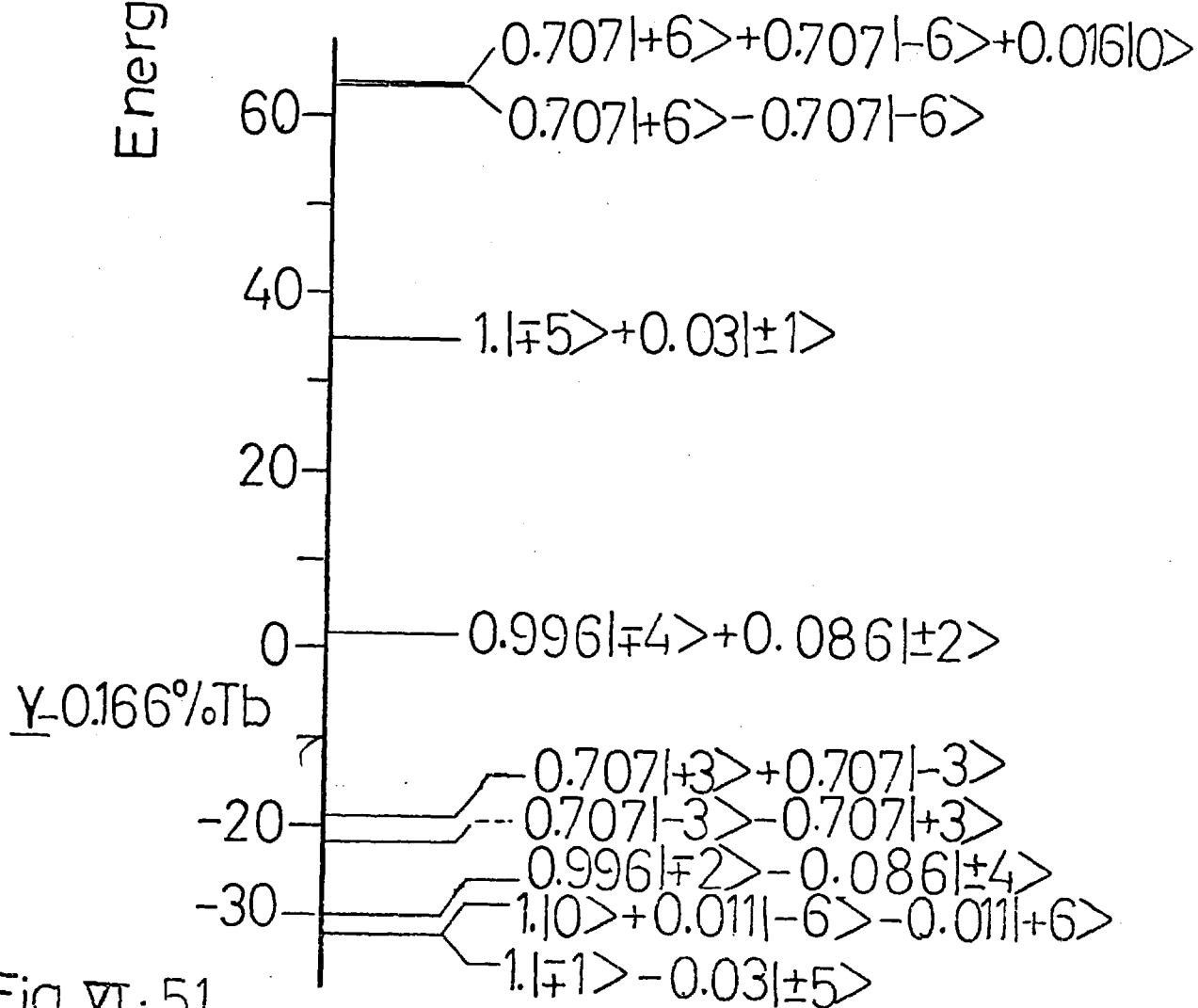
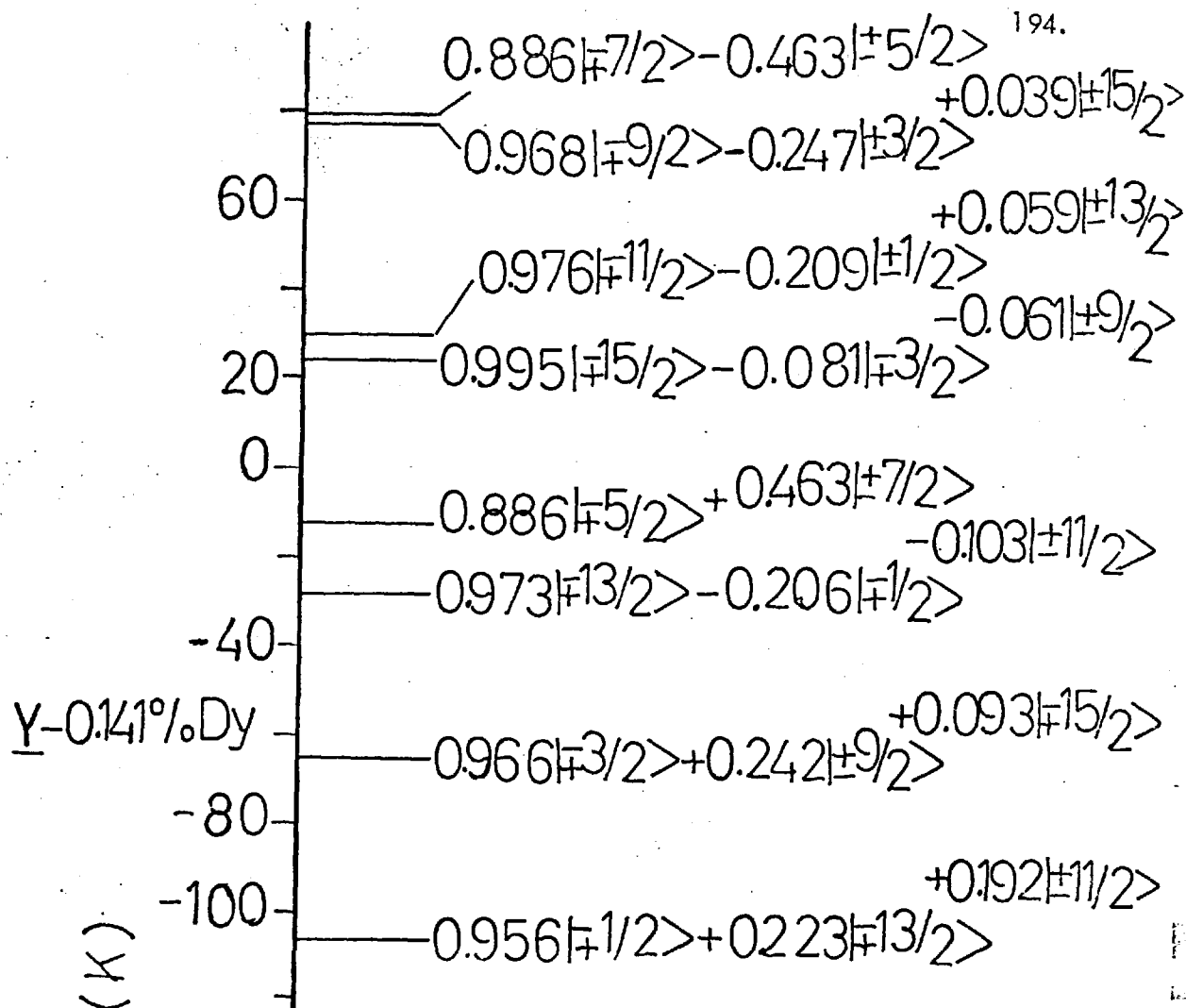


Fig VI. 51

VI.2 Discussion

To elucidate the magnetic phase diagrams of these alloy systems, we start the discussion with the concentrated alloys. In alloys in which the spins freeze in spin glass like manner, a maximum in the temperature derivative of the electrical resistivity at the spin freezing temperature generally will appear, and usually tends to be rather broad. We have referred to this by the expression, "maximum in $d\rho/dT$ " (see also Chapter II, section II.5).

VI.2.1 The concentrated alloys

(a) Sc-Gd and Y-Gd alloy systems

Our results show some rather general similarities between these two systems, so we will discuss them together. From the behaviour of the incremental resistivity of these alloys (Fig. VI.3 and 14) we can simply distinguish the type of the magnetic ordering; a progressive change in the character of the resistivities is observable as the concentration of Gd increases. We have called the state of alloys with $c \leq 20\%$ Gd in Sc and $\leq 2\%$ Gd in Y by the generic term "magnetic glass or spin glass", using our interpretation of the term originated by Coles (118).

Starting with the lower concentration spin glass region, the initial temperature dependence of $\Delta\rho(T)$ for Sc-alloys may be fitted to a simple $T^{3/2}$ power law (Fig. VI.5). However, in Y-alloys the 2% Gd alloy but not a 1% alloy or 0.5% alloy shows a $T^{3/2}$ behaviour, and this is due to their low ordering temperatures ($< 1.5^\circ\text{K}$). As the temperature is increased, $\Delta\rho(T)$ deviates directly towards a linear dependence. The temperature range of the fit to this $T^{3/2}$ dependence slowly increases with Gd concentration, the coefficient of this behaviour, β , decreasing with concentration, and varying as $c^{-0.7 \pm 0.1}$, Fig. VI.6. These initial dependences of the resistivity on temperature can be related to the scattering of conduction electrons by localized damped spin wave excitation proposed by Rivier and Adkins for spin glass theory, who showed the initial temperature

dependence of the resistivity increases as $T^{3/2}$. However, the theory does have difficulty in accounting for the coefficient of this $T^{3/2}$ behaviour, where a $c^{-0.2}$ power law is predicted by the theory (129).

The spin glass magnetic behaviour of these systems is also evident in the initial susceptibility measurements, Fig. VI.7 for Sc-Gd, Fig. VI.16 for Y 2% Gd where we observed broad maxima characteristic of the spin glass systems. Results for Sc-Gd are in strong disagreement with Nigh et al (201) magnetic measurements where no maximum in the susceptibility is observed for less than 25% Gd alloy. The spin freezing temperatures are taken to be the temperatures of the susceptibility maxima (T_m) where T_m is slightly higher than the temperature given by the maximum in $d\Delta\rho/dT$ (Fig. VI.3 and 14, the arrows indicate the temperatures of the susceptibility maxima).

The susceptibility of these alloys obeyed a Curie-Weiss law at high temperature, and above the temperatures of the susceptibility maximum there are deviations from the Curie-Weiss law, which start at well above the temperature of the maximum in susceptibility, we believe they are due to the effects of short range magnetic order. This effect is detectable in the high temperature (40.5°K) magnetization-field isotherm (Fig. VI.11) for the Sc-Gd alloy (10% Gd and 15% Gd) where the low temperature and the high temperature curvature observed are due to strong exchange interactions between Gd atoms above the spin glass ordering. S. Male (private communications) has observed the presence of short range magnetic order at high temperature in the ESR spectra of Sc-15% Gd and Y-2% Gd alloys*. The

* The ESR measurements performed on the same samples were used for the resistivity and magnetization measurements.

effective magnetic moments per Gd atom are always larger than the free ion value (table VI. 1 and 2) in these systems and increase towards the high Gd concentration side; this also might be indicative of the effects of short range magnetic order above their spin freezing temperature.

Additional confirmation for this view comes from our resistivity measurements, where we observed that $\Delta\rho(T)$ above the glass temperature is increasing much more slowly than before. A best fit to these data was obtained with the expression $\Delta\rho/c = \Delta\rho_0 + A/c \log T$ (Fig. VI.13 and Fig. VI.15), but apparently the coefficient of this logarithmic behaviour A is not linear with Gd concentration (see Table VI.1 and Table VI.2), we attribute this effect to the scattering of conduction electrons by interacting Gd impurities, indirectly via the RKKY at larger distances, so that the interacting Gd moments (possibly) start to form pairs, triplets ... (short range magnetic ordering).

The character of the magnetization isotherm at a temperature below the spin glass on set temperatures in these alloy systems (Fig. VI. 9 and 10 for Sc-Gd and Fig. VI.18 and 19 for Y-Gd alloys) strongly resembles the behaviour observed in normal spin glasses. In Sc-Gd alloys a strong time dependence in the response to a magnetic field, and a remanent magnetization (which decays with time and disappears a little above the spin glass temperature) have been found (Fig. VI.12). No appreciable isothermal remanent magnetization was found for $\leq 1\%$ Y-Gd alloys down to the lowest temperatures. This is attributed to very low spin freezing temperatures ($< 1.5^\circ\text{K}$) as may be expected from the extrapolation from the high concentrated alloys. However, the Y-2% Gd alloy shows such an effect where the spin freezing temperature is about 4.7°K .

As the content of Gd in the Sc and Y increased above about 20% and 2% respectively, large changes in $\Delta\rho(T)$ were observed for 25% Gd in Sc and 3%,

c%	$A/c \mu\Omega \text{ cm/at } \% ^\circ\text{K}$	$T_o ^\circ\text{K}$	$\beta_n \Omega \text{ cm/K}^{3/2}$	$T_m \text{ K}$	U_{eff}	$\vartheta ^\circ\text{K}$	$ \vartheta /T^*$
5	1.54	2.5	78.0				
10	0.91	4.0	54.5	4.6	9.688	-1.6	0.347
15	0.613	5.0	38.3	8.0	11.328	+2.8	0.350
20	0.67	7.0	27.2	13	11.827	+5.8	0.446
25		40*					

Table VI.1 (Results for Sc-Gd alloys)

T_o = spin freezing temperature from the maximum in the slope of resistivity vs. temperature curve.

* = The Neel temperature from the sharp increase in the resistivity with decreasing temperature.

T_m = spin freezing temperature from the maximum in the susceptibility vs. temperature curve.

T^* = Magnetic transition temperature (T_m or Neel temperature).

c%	$A/c \mu\Omega \text{ cm/at } \% ^\circ\text{K}$	$T_o ^\circ\text{K}$	$T_N ^\circ\text{K}$	$T_m ^\circ\text{K}$	U_{eff}	$\vartheta ^\circ\text{K}$	$ \vartheta /T^*$
1	0.31	<1.5			8.162	+2.5	
2	0.255	3		4.7	8.656	+7.6	1.617
3			10	9.0	9.755	+1.2	0.133
5			21				
9.15			47				

Table VI.2 (Results for Y-Gd alloys)

T_o = spin freezing temperature from the maximum in the slope of the resistivity vs. temperature curve.

T_N = Neel temperature from the sharp increase in the resistivity with decreasing temperature.

T_m = Magnetic transition temperature from the maximum in the susceptibility vs. temperature curve.

T^* = Magnetic transition temperature (T_N or T_m)

5% and 9.15% Gd in Y, representing a strong magnetic scattering. There is a drop in $\Delta\rho/c$ with c which we attribute to the ordering becoming more and more long-range helical antiferromagnetic. This is apparent in Fig. VI. 3 and 14 where there are well defined magnetic ordering temperatures below which the resistivity increase develops a "hump" in the resistivity vs. temperature curve; this is a manifestation of the magnetic superzones boundaries created by an antiferromagnetic super lattice (see Chapter II section II.7.)

The initial temperature dependence of the resistivity (below about 5°K) for these alloys was found to be proportional to T^3 with an accuracy of about $\pm 5\%$ in the exponent, Fig. VI. 4 a and 4b, which is quite different from the $T^{3/2}$ behaviour found in low concentration-spin glasses, suggesting a contribution other than that due to damped spin waves mentioned earlier. This rapidly changing resistivity at low temperatures comes from electron magnon scattering, which is not extended to wide temperature intervals, but below the Neel (T_N) temperature indicates that the magnetic ordering is of an incommensurate helical antiferromagnetic type modified by magnetic superzones.

The sharp maximum in the initial susceptibility of the Y-3% Gd alloy at 9°K is quite different from those with broad maximum in the spin glass region; this is a good indication of helical magnetic order and consistent with the magnetic superzone effect observed in the resistivity of the same sample. The magnetization vs. field isotherm for this alloy is also different from those normal to spin glass materials, since no time dependent response to the field or isothermal remanent magnetization is observed.

It is clear that the initial susceptibility of Y-Gd alloys below T_N or T_{glass} appears to be increased, suggesting that there may be some uncoupled Gd-moments which follow Curie-Weiss law with decreasing temperature. Alternatively, there may be present some oxide impurities, such as Gd_2O_3 which has a Neel temperature

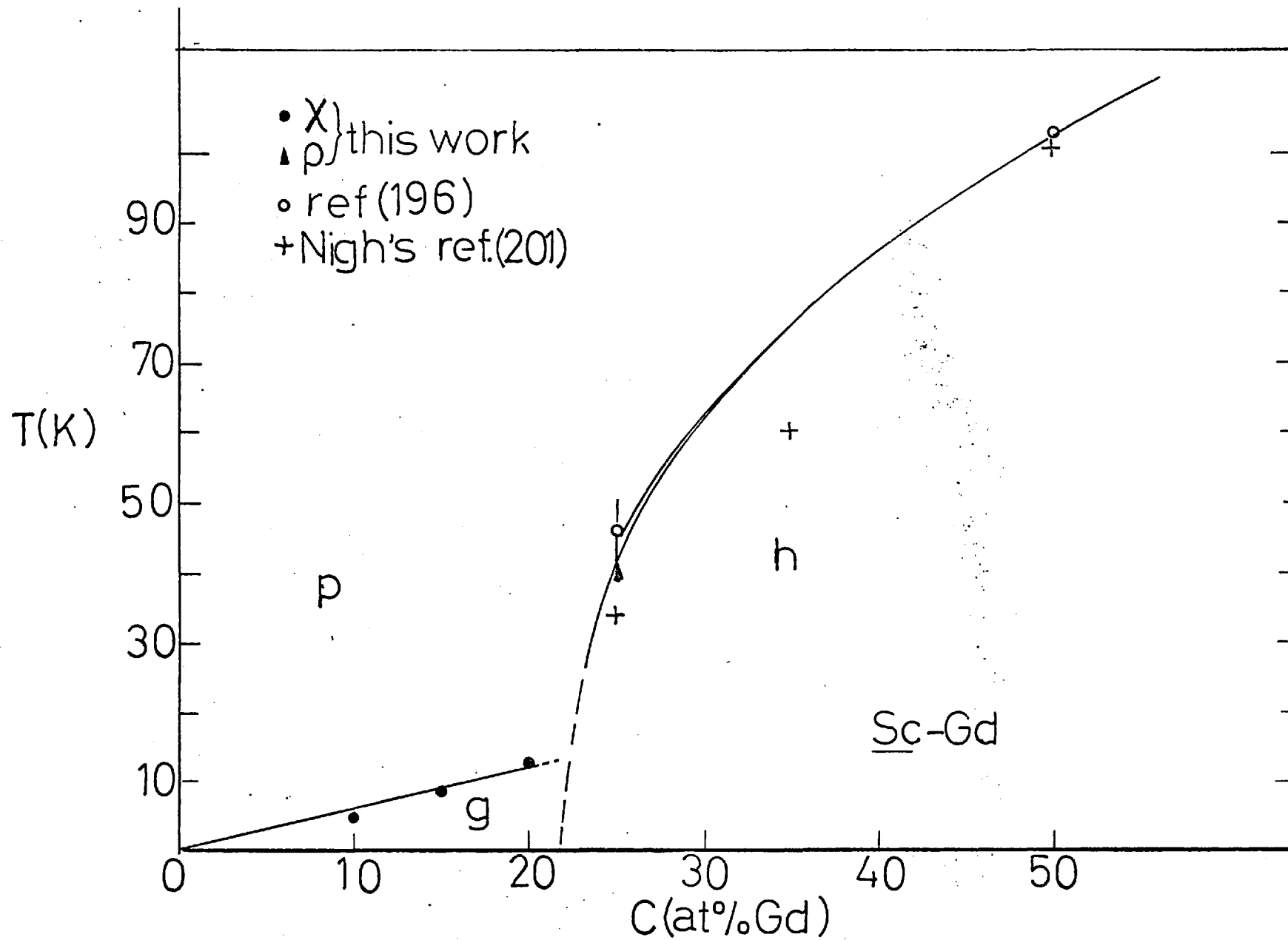


Fig VI.52

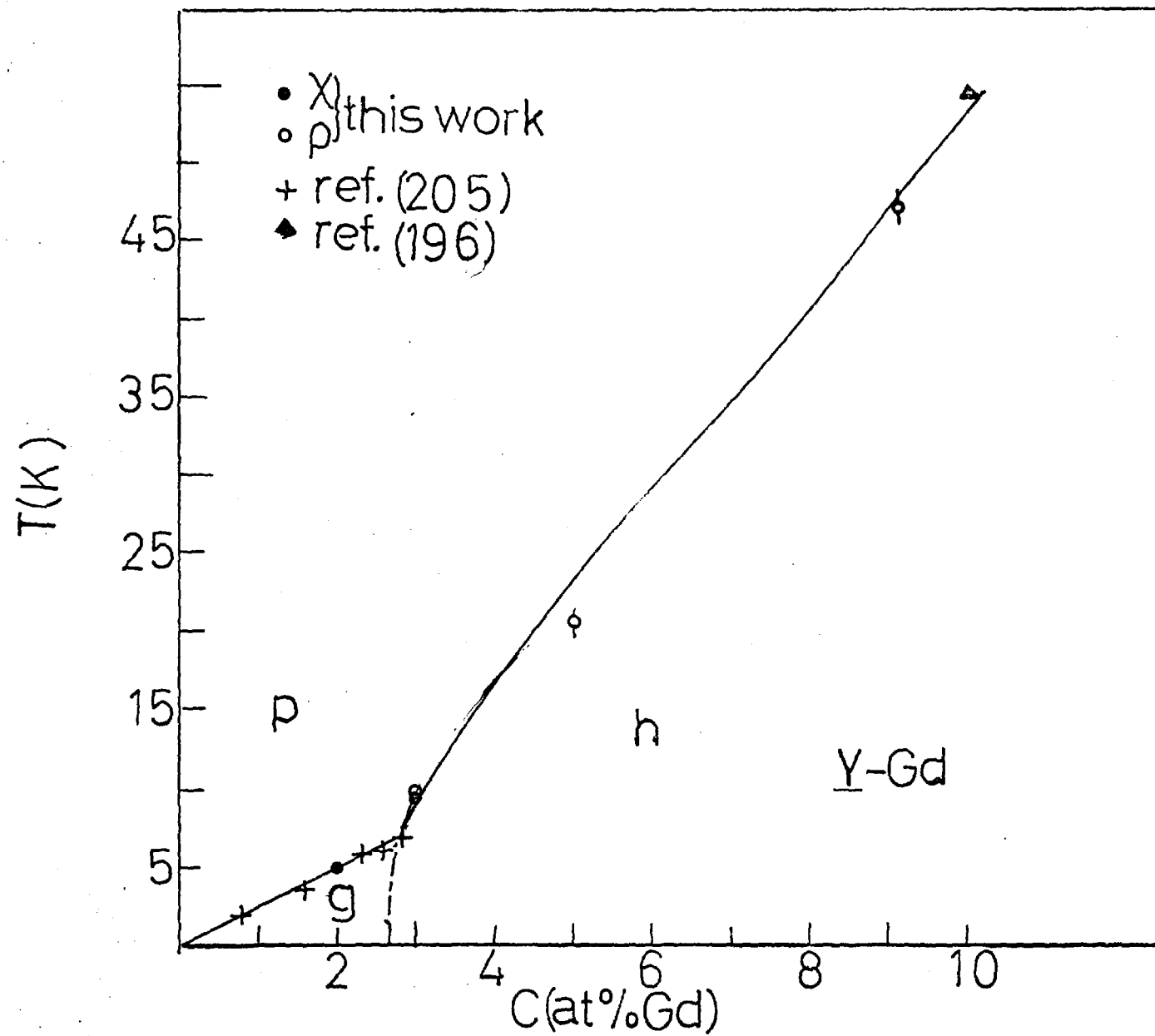


Fig VI.53

of 1.5K. Such oxides are known to have a strong effect on the specific heat of Gd(211).

Our results are confirmed by neutron diffraction measurements by Child and Cable (196) who found no helical magnetic ordering for alloys with $< 25\%$ Gd in Sc, while 10% Gd in Y gave helical ordering with transition temperature about 59°K. Our results are also in agreement with specific heat measurements on Y-Gd alloys by Bonnerot et al (205) who found the ordering temperature given by the maximum in specific heat varies linearly with Gd concentration.

The magnetic phase diagrams for Sc-Gd and Y-Gd alloys are shown in Fig. VI.52 and 53, which include data from our own resistivity and magnetization measurements and the neutron diffraction results of Child and Cable (196) as well as the specific heat maxima observed by Bonnerot et al (205).

Special interest can be attached to the fairly sharp changes in character above about 3% Gd in Y and 20% Gd in Sc. The dashed line is an extrapolation drawn so as to give the critical concentration for long range helical order within experimental error. We thus expect that 22% Gd in Sc and 2.8% Gd in Y should exhibit long range helical order. The last value is consistent with recent theoretical calculations by Southern and Sherrington (212) who used a spin-wave stability condition to determine a critical concentration for the onset of helical order in Y-Gd alloys.

(b) Sc-Tb and Y-Tb alloy systems

Because of crystal field splitting the results of these systems can not simply be due to spin effects only, and one would expect complicated and varied behaviour. The initial susceptibility of these alloys is shown in Fig. VI.22 and 28; the maximum in the susceptibility is interpreted as being due to the magnetically ordered alloys and does seem to be a sign of magnetic ordering down to the lowest concentrations. A Sc-2.5% Tb alloy orders at 3°K, and preliminary magnetization measurements made in Y-1.25% Tb alloy recently showed susceptibility peak due to magnetic order at

about 3 K, the latter in contrast to Nagasawa and Sugawara's (199) susceptibility measurements where no maximum was observed for about 1% Tb alloy. The most notable characteristic of the magnetic behaviour in Sc-Tb alloys below the ordering temperature is that there appears to be large anisotropy, and the maximum in the susceptibility is sharper than for the normal spin glass materials (compare it with Sc-Gd alloys). We believe these are related to the crystalline electric field effects. In Y-Tb alloys, the susceptibility shows a rounded maximum, and below the maximum appears to increase with decreasing temperature analogous to Y-Gd alloys, and thus we attribute to the same reason discussed earlier.

However, many of the essential features of the spin glass behaviour are manifest in these systems in the concentration range $\leq 20\%$ for Sc-Tb alloys and $< 5\%$ for Y-Tb alloys, below T_{glass} the effect of an applied field is to produce large remanent magnetization, time dependent response to the applied field, and large induced isothermal remanent magnetization upon cycling the sample in magnetic field (Fig. VI. 25, 26, 31).

At high temperatures the alloys obey a Curie-Weiss law. Above the spin glass temperatures, there are deviations from this behaviour, which start at temperatures well above this temperature (most observable in dilute Tb side in Sc-Tb alloy) and they are due to the crystal field effects. The paramagnetic Curie temperature Θ (table VI.3) is negative for low Tb concentrations in Sc-Tb alloys and becomes positive as the magnetic glass type ordering becomes opposed by the long range helical ordering with the positive Θ nature required. In Y-Tb alloys Θ is always positive (table VI.4) and increases with increasing Tb concentration. Since, however, crystal field effects may give a pseudo-paramagnetic Curie temperature of several degrees, we attributed this fluctuation in Θ to this effect.

c% Tb	$T_o^{\circ}\text{K}$	$T_N^{\circ}\text{K}$	$T_m^{\circ}\text{K}$	$U_{\text{eff}}(\mu\beta)$	$\vartheta^{\circ}\text{K}$	$ \vartheta /T^*$	$T_{\text{min}}^{\circ}\text{K}$
2.5			3.5	11.846	-0.6	0.17	
5.0	7.0		6.5	11.657	-3.2	0.49	
10.0	11.0		10.6	13.411	-3.4	0.32	
15.0	15.0		14.0	13.411	-4.4	0.31	3.7
20.0	18.0		18.0	13.354	-2.0	0.11	5.5
25.0		26 ± 2	21.5	13.350	+2.0	0.09	7
30.0		42 ± 2					8.2

Table VI.3 (Results for Sc-Tb alloy)

c% Tb	$T_o^{\circ}\text{K}$	$T_N^{\circ}\text{K}$	$T_m^{\circ}\text{K}$	$U_{\text{eff}}(\mu\beta)$	$\vartheta^{\circ}\text{K}$	$ \vartheta /T^*$
1	1.5					
1.25			3			
2	3		7	10.623	+1.0	0.09
3	4		12	10.828	+3.6	0.33
4	4.5		17	10.950	+4.0	0.36
5		23 ± 1	22	11.960	+4.0	0.18
7		34 ± 1				
9.2		46 ± 1				

Table VI. 4 (Results for Y-Tb alloys)

T_o = spin freezing temperature from the maximum in the slope of resistivity vs. temperature curve.

T_N = Neel temperature from the sharp increase in the resistivity with decreasing temperature.

T_m = magnetic transition temperature (T_{glass} T_N) from the maximum in the susceptibility vs. temperature curve.

T^* = magnetic transition temperature (T_m , T_N).

The paramagnetic moments of these alloys are greater than the free ion values. This enhanced effective moment can be attributed to the polarization of the conduction electrons parallel to the Tb impurities.

Magnetization vs. field isothermals for these alloys are shown in Fig. VI.24 and 30, where clear evidence of both magnetic order and "mixing" by the application of a magnetic field are observed; the associated effects of this can clearly be seen at higher fields. The effects of the magnetic order are larger at low fields indicated by the low field curvature, and the upward curvature at high fields is attributed to the crossing of the excited states through the ground state.

Further evidence for the magnetic character of these alloys is provided by the behaviour of the incremental resistivity vs. the temperature. In alloys $\geq 25\%$ Tb in Sc and $\geq 5\%$ Tb in Y, it is clear that a well-defined magnetic state of the helical antiferromagnetic order is observable by the magnetic superzone effects. These effects do not seem to be present in the lower Tb concentration side, where $\Delta\rho(T)$ behaviour is similar to the resistivity of spin glass materials. However, is affected by the crystal field splitting effect. In Y-Tb alloys the spin disorder resistivity should be that characterized by its lowest J level, an inelastic scattering to a level $1/2^\circ$ K may be expected to be small above LHe⁴ temperature, as is indicated by the resistivity data in the dilute limit.

However, in Sc-Tb alloys the situation is more complicated as is indicated by the resistance minimum at low temperature, which increases with Tb concentration. It is clear that this minimum is not the magnetic ordering temperature, neither in the spin glass region $\leq 20\%$ Tb or in the helical region. The spin freezing temperature is given by both maxima in the slope of the resistivity vs. temperature curve (well above the temperature of the minimum) and by the maximum in the susceptibility vs. temperature. The Neel temperature also lies well above the temperature of this

resistance minimum. This rather complicated effect may be related to the crystal field mixing the excited states levels into the ground state. Below the ordering temperature the situation is more complicated as the exchange field (increasing with Tb concentration) will mix a temperature dependent amount of the several excited states into the ground state level (see Fig. VI.43). This is possible in this case since the energy separation between these states is not large. Then the Tb ions appear to line up with respect to some sort of local molecular field to give a state with the full Tb moment randomly oriented and freeze out upon decreasing the temperature; and give rise to an additional scattering to the conduction electrons which led to the observed resistance minimum, probably analogous to the resistance minimum in Pt-Mn, Rh-Fe or Pt-Co alloys discussed earlier.

These results can not be related to any existing theories of elementary excitations of ordered states; in the glass regime possibly there will be a combination of ordinary spin waves (induced moment) and Rivier and Adkins damped spin waves excitations. The simple molecular field theory of helical ordering is clearly inadequate to describe these effects.

It should be emphasized that the magnitude of the ordering temperature in the spin glass region may not be deduced from the maximum in the slope of incremental resistivity as no simple spin glass behaviour is observed. However, these temperatures are consistent with the temperatures which were determined from the maximum in the susceptibility.

The Y-5% Tb alloy shows the characteristic spin glass effect in the magnetization measurements, a round maximum in susceptibility, response to cooling in field, thermoremanent magnetization etc. However, the resistivity exhibits the character

of the helical antiferromagnetic order, although both the resistivity and magnetic measurements have been done on the same sample. However, we attributed this discrepancy to the concentration fluctuation along the sample, hence one would expect a sharp change in the character from spin glass to helical order in Y-Tb alloys at about 5% Tb.

In the Sc-25% Tb alloy both resistivity and susceptibility measurements confirm the long range helical order. However, there is a difference in the Neel temperature deduced from both measurements; this is attributed probably to the deviations from Matthiessen's rule, and the latter reason also prevented analysis of the data above the Neel temperature in helical ordered alloys. Effects of the breakdown of Matthiessen's rule are also observable in the Y-Tb alloys above the spin freezing temperatures.

In Fig. VI.54 and 55, we have plotted the magnetic phase diagram for Sc-Tb and Y-Tb alloy systems respectively. The figures include data from our own resistivity and magnetization measurements, the neutron diffraction data (201) (195) and Nagasawa and Sugawara's (199) susceptibility data. It can be seen that the critical concentration for long range helical antiferromagnetic order is given by about 22.5% and about 5% for Sc-Tb and Y-Tb alloy systems respectively.

From a comparison of the phase diagrams of these systems with those for the Sc-Gd and Y-Gd alloys, the following conclusions can be drawn:

1. T_N for Sc-Gd and Sc-Tb scales with a simple de Gennes factor $(\lambda - 1)^2 J(J+1)$ and also with the effective spin factor $c (\lambda - 1)^2 J(J+1)$ in the long range helical antiferromagnetic region, and the same is true for Y-Gd and Y-Tb alloys.
2. The spin glass "spin freezing" temperatures for Sc-Gd and Sc-Tb alloys do not scale with the simple de Gennes or the effective spin factor with which this might be expected to be consistent if the crystal field effects were negligible; that is

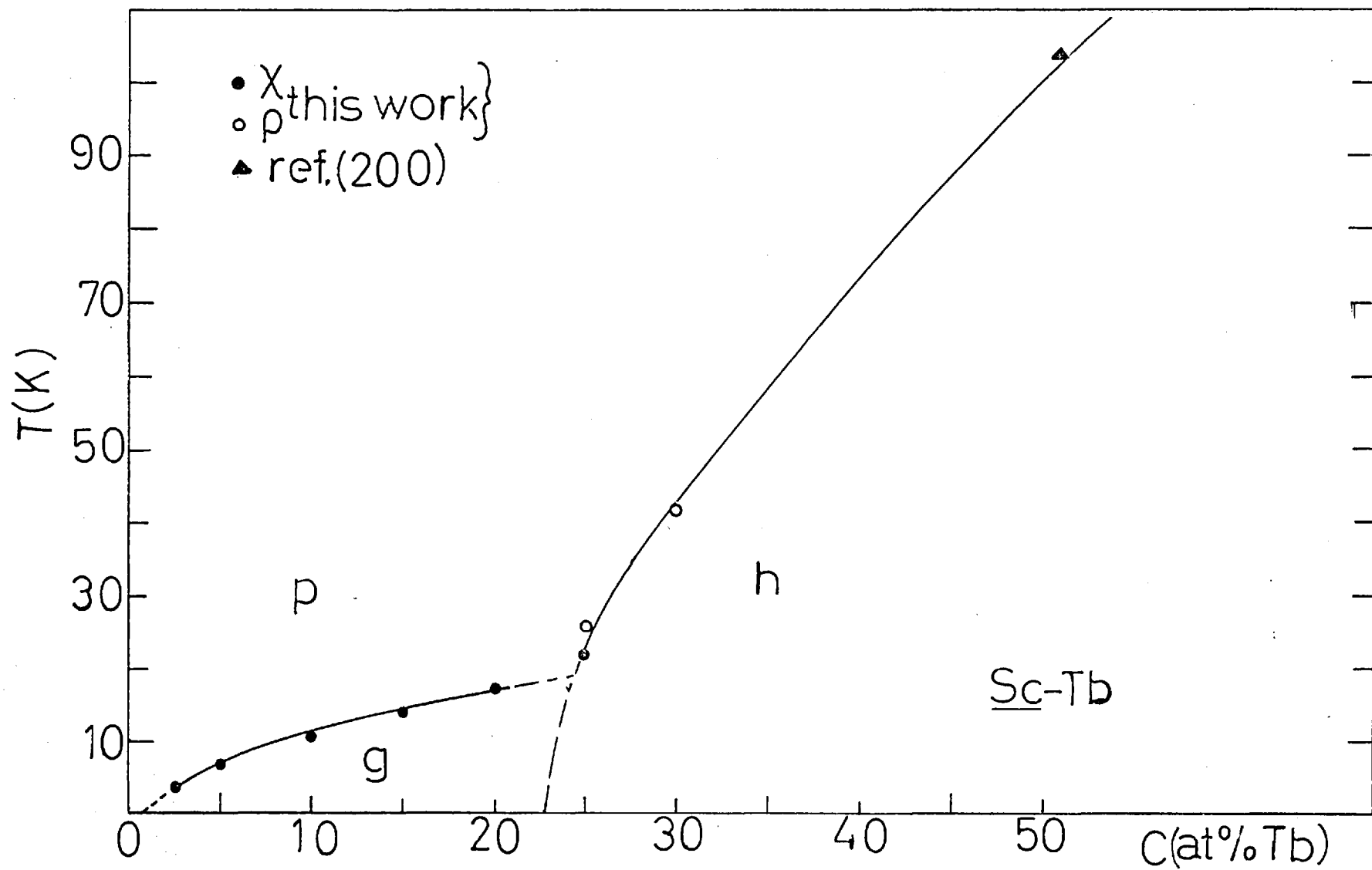


Fig VI. 54

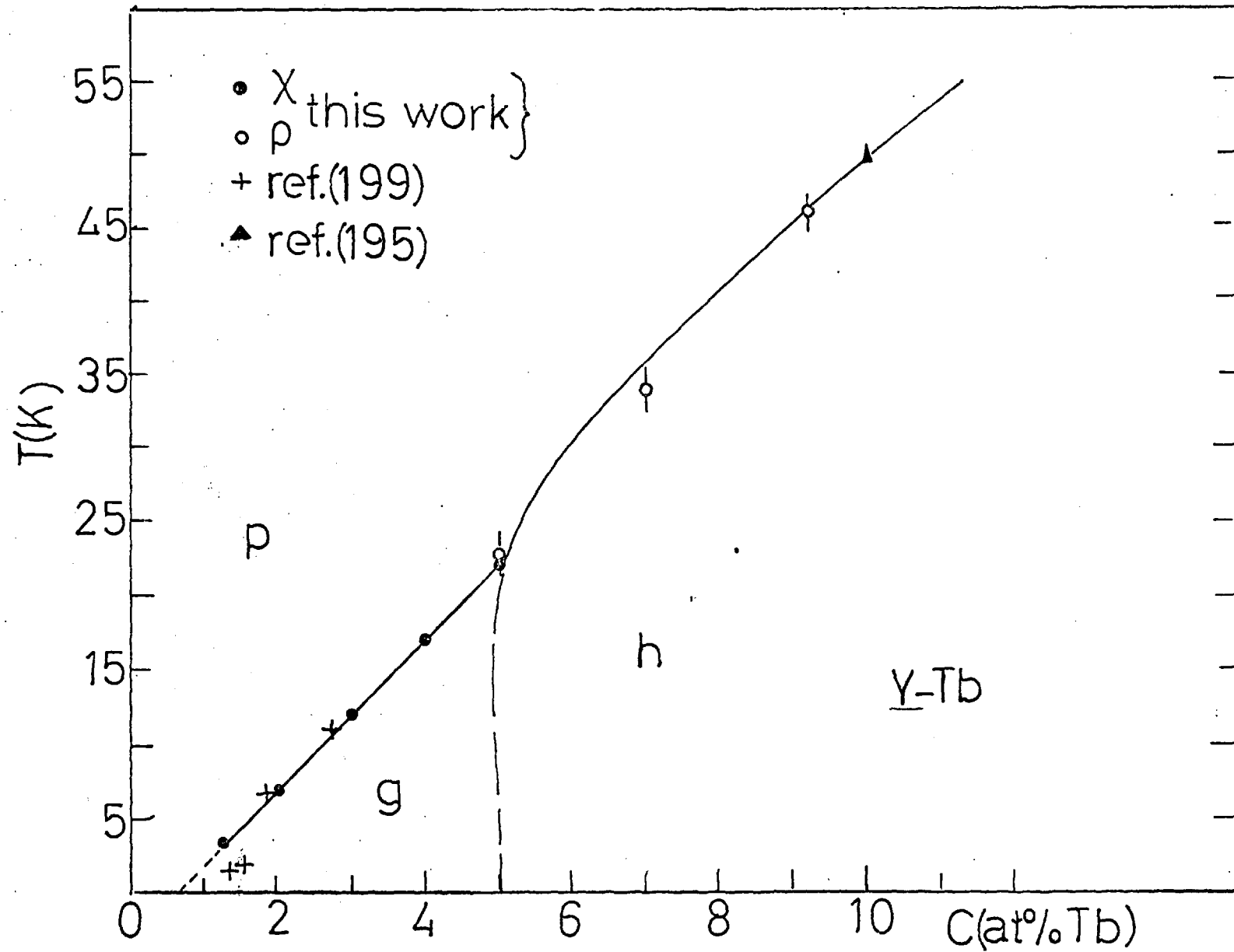


Fig VI.55

$T_{\text{glass}}^{\text{Tb}} > T_{\text{glass}}^{\text{Gd}}$. The same is true for Y-Gd and Y-Tb alloys.

The strength of the magnetic interactions, as judged by the characteristic temperatures (ordering temperatures), is weaker in the spin glass region for the Gd alloys than in the Tb alloys, suggesting a contribution other than the exchange interaction responsible for this high temperature ordering in non-S-state ion systems. We have seen in Chapter II section II.6 that crystal field effects are a perturbation upon the exchange ordered states and so produce anisotropy terms which are functions of ($|J_X\rangle$, $|J_Y\rangle$, $|J_Z\rangle$). For a positive anisotropy energy less than the exchange energy, the ordering temperature would be greater than that expected from the exchange energy (see for example ref. 134). However, due to the opposite behaviour observed in helical long range ordering, and also because the anisotropy energy could be larger than the exchange energy for low Tb concentrations (as one would expect) this argument is rejected.

We may speculate on a different approach; we have seen that both the electrical resistivity and magnetic behaviour for Sc-Gd and Y-Gd alloys are indicative of short range ordering at temperatures well above the spin glass temperature. The temperature dependence of $\Delta\rho(T)$ above the spin glass temperatures is bigger for Gd alloys (in Sc and Y) than their Tb analogs (despite the effects of Matthiessen's rule above these temperatures), and the deviations from linearity in plots of $1/X$ vs. T are more pronounced for Gd (in Sc and Y) than their Tb analogs (where the deviations in the Tb case are attributed mostly to the crystal field effects). The significance of the short range magnetic ordering is also indicated by ESR measurements mentioned earlier. We follow the discussion given by Taylor and Coles (213) for a variety of intermetallic compounds of the S-state ion for the ESR results. The nature of the interactions in the present alloys is of the RKKY type, and we may expect that coupling of (all) nearest neighbours spin down relative to spin up at the origin can not be repeated over long distances before it conflicts with the periodicity of the lattice.

It may be possible to say that this would extend the temperature range where the free energy would be minimized by the effects of short range order, and hence reduce the ordering temperature. But in the non-S-state ions such effects are reduced by the crystal field effects. The range of short range order relates to the $|\Theta|/T^*$ ratio (if Θ is related to the interactions which produce the magnetic ordering). From the tables VI, 1, 2, 3, 4, the ratio $|\Theta|/T^*$ is small (< 1) and progressively changes from negative to positive sign for Sc-Gd and Sc-Tb alloys, is also small (< 1) and positive for Y-Tb alloys, positive and approaches to unity in Y-Gd alloys. These features seem to suggest that the paramagnetic Curie temperature Θ is rather lower than that suggested by their magnetic ordering temperatures (spin freezing or helical ordering); this would not be expected from the significant amount of short range order between $|\Theta|$ and T^* . However, because of the crystal field effects (to give large pseudoparamagnetic Θ) and the change in the sign of Θ from spin glass to helical region, it might be difficult to consider the validity of the above argument. Thus, the discrepancy is still open to question.

It is clear from the magnetic phase diagrams for Tb, that the moments on the Tb ion both in Y-Tb and Sc-Tb alloys vanish at a finite concentration given by (from extrapolation) 0.65% Tb and about 0.75% Tb respectively. This is consistent with the ground state singlet of Tb in Sc, but in contrast to the case of Tb in Y where the ground state is (accidentally) degenerate; however, such a ground state is not a well defined magnetic state, and therefore one might expect such anomalies.

VI.8 Sc-Dy and Y-Dy alloy systems

In these two alloy systems, the electrical resistivity measurements are also a good indication of the type of magnetic ordering. From figures VI. 32 and 33, the effect of the magnetic superzone is clearly indicated in alloys with composition

$c \geq 25\%$ Dy in Sc and alloys $c \geq 3\%$ Dy in Y by the hump in the $\Delta\rho(T)$ curve.

It is also clear that no such effects is apparent in the resistivity of alloys with concentration 15%, 5% Dy in Sc and the 1% Dy in Y alloy. So the magnetic behaviour is expected to be analogous to that of Gd (or Tb) in Sc and Y hosts. However, because of the crystal field splitting the temperature dependence of the spin resistivity would be expected to be also complicated as in the Tb case.

No pure power law extending over an extended reasonable temperature interval has been observed. Because of the inelastic scattering setting in at a level higher than about 60 K and about 50 K for Y and Sc alloys respectively, from the ground state doublet, one would perhaps expect the spin disorder resistivity to be characterized not only by the lowest J level. The inelastic scattering is not small at temperatures compared to the magnetic ordering temperature and will cause a contribution to the resistivity above these temperatures, hence the observed complicated temperature dependence behaviour for $\Delta\rho(T)$ well below and above the magnetic ordering temperatures is attributed to this fact. The magnitude of the ordering temperatures in the spin glass region may not be deduced from the maximum in the slope of resistivity curve, because of this complex behaviour.

In the Sc-Dy alloys (25% and 30%), at low temperatures there appears to be a resistance minimum, possibly similar to that of Sc-Tb alloys.

The susceptibility of the Sc-5% Dy alloy has a maximum at about 3°K and decreases to a finite value as the temperature approaches zero (Fig. VI.34). This is interpreted as indicating a transition to a spin glass ordering state, although the maximum is not broad as in simple spin glasses. However the other characteristic spin glass effects are observed in magnetization vs. field isothermal, such as induced isothermal remanent magnetization which decays with temperature and time; and also resistivity vs. temperature curves (in the latter the magnetic superzone boundaries

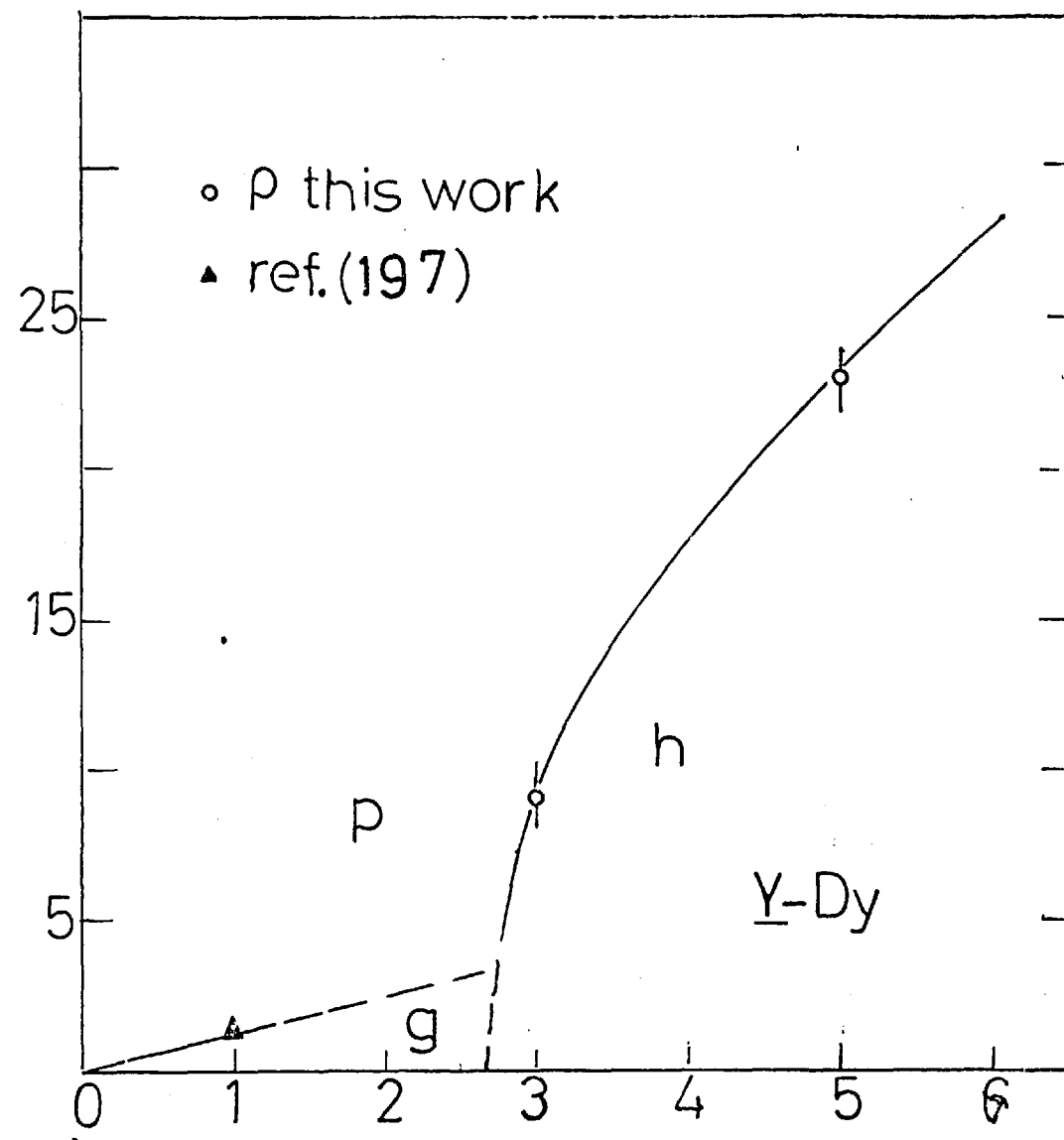
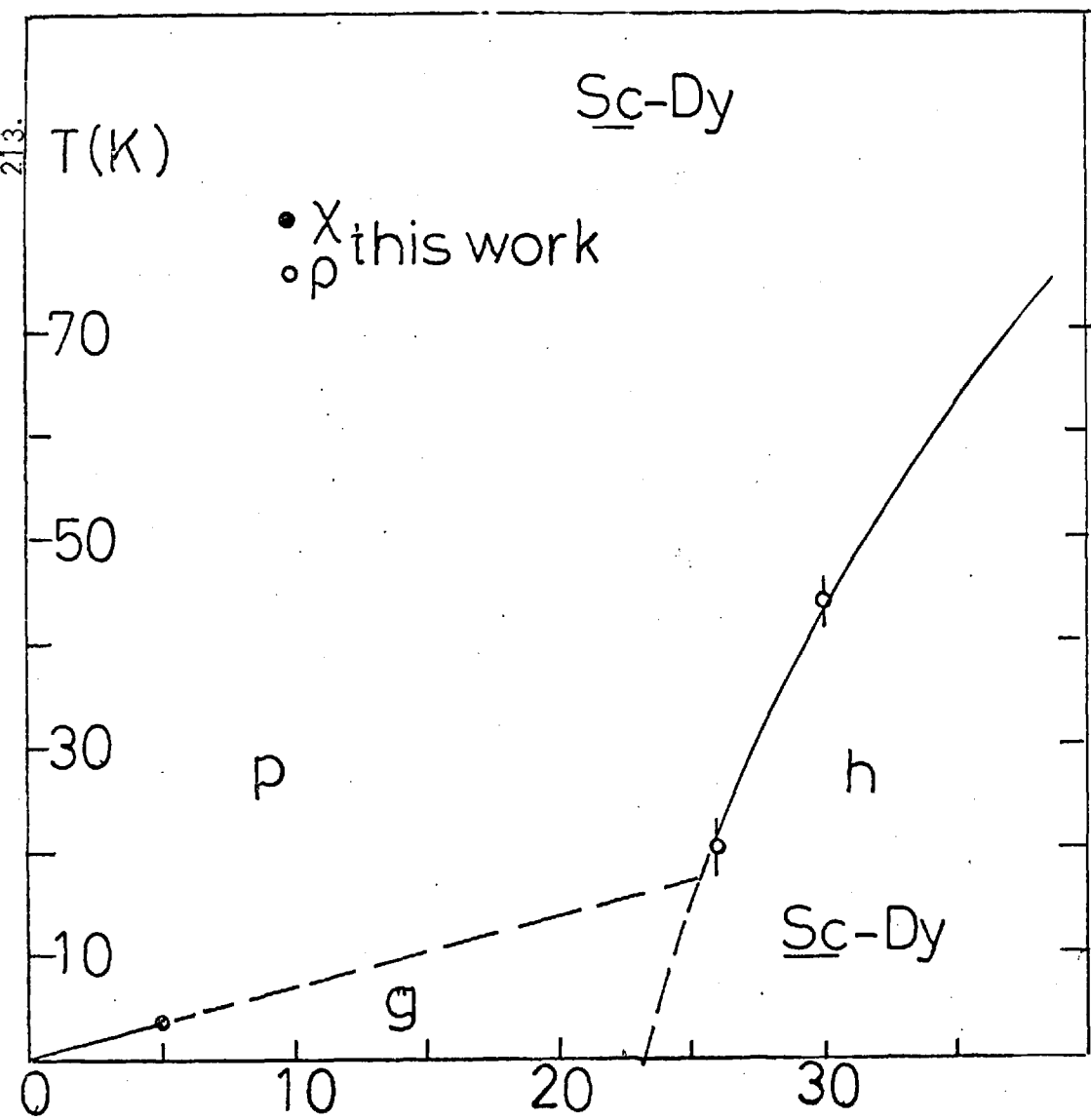


Fig VI.56

effect does not appear).

In this alloy, deviations from the Curie Weiss law occur at high temperature (45–50°K). The inverse susceptibility has a hump (dashed line) in the region of (10–25)°K where it is attributed to the crystal field and magnetic ordering effects. The straight line drawn through the higher temperature gives a positive pseudo-paramagnetic Curie temperature of 2 K. The effective paramagnetic moments per Dy ion were found to be greater than the free ion value $10.440 \mu_B$, and this is consistent with Isaacs et al (214) measurements, who again found enhanced moments in dilute Sc-Dy ($\leq 1\%$) alloys and attributed these to the polarization of the conduction electrons parallel to the Dy moment in their RKKY type interactions. However, the same worker did not report any effect of crystalline field on any of his measurements. Magnetization vs. field isotherm, shown in Fig. VI.36a is clear evidence for the magnetic ordering at low fields and level crossing at higher fields observed.

Tentative phase diagrams of Sc-Dy and Y-Dy alloys are shown in Fig. VI.56. No vanishing in the Dy moments for either case would be expected since the ground state is a Kramers doublet. Data for Y-1% Dy from ref (197) is also included. From the extrapolations we find the critical concentration for helical order for Y-Dy and Sc-Dy alloys are 23% and 2.8 % respectively.

In the preceeding sections we have considered the magnetic properties of some alloy systems and attempted to trace a conceptual path to reduce these properties to a semblance of order. We will now consider a few general points in connection with these systems. In short, there seems to be a source of information from the behaviour of the residual resistivities ($\rho_{4,2}$) with the RE contents of these systems (Sc-RE and Y-RE). In Fig. VI.1 and 2, where initially $\rho_{4,2}$ rises linearly while the concentration remains below the critical concentration and slower than linear for high RE constants, with a sharp change in the character of the curves in the Sc-RE alloy at

concentrations comparable to the critical concentration for the onset of helical ordering; this itself suggests a change in the magnetic character of these systems. It is also clear that in Y-RE alloys, in the case of Tb alloys the residual resistivities are higher and flatten off at higher concentrations (about 5%) than with the Gd or Dy analogues (about 3%). This might be an indication of a higher proportion of random frozen moments which contribute to higher residual resistivity and that the onset of long-range helical ordering occurs at higher Tb content.

As mentioned earlier, the recent theoretical calculation by Southern and Sherrington (212) for the critical concentration of the helical (periodic) long-range ordering in Y-RE alloys, is based on the stabilization of the spin wave excitations. The theory as it stands does not allow for the effect of the anisotropy on the critical concentration for the helix, and also does not consider the magnetic state below this concentration. However, the theory shows the promise of being a successful treatment since it yields an excellent agreement with our experimental results for the critical concentration of Y-Gd alloys.

Earlier, Overhauser (215) had employed spin density wave like theory in treating the magnetic behaviour of the spin glass in Cu-Mn alloys. This theory is based on the wave like order in the conduction polarization electron band where the modified Fermi surface (new zone boundaries) will stabilize self-consistently by the interelectronic exchange interaction within the conduction band. Although this interpretation was not satisfactory to account for the magnetic behaviour in Cu-Mn alloys, however, it has been subsequently shown that when rare-earth ions are present as a localized moment, this will help the new zone boundaries to be stabilized, similar to the method which has been used by Elliott and Wedgwood (141) to account for the transport properties of rare-earth metals. The analogies with our measurements seem to hold qualitatively, since the addition of little quantities of rare-earth as

localized moments to the conduction band of a non-magnetic Y (or Sc), stabilize the onset of the long-range spin density wave type antiferromagnetism within the conduction band* due to the strong response of wave vector dependence of the spin susceptibility $\chi(q)$ at a particular value of q .

We have demonstrated that there is strong evidence for a critical concentration in Sc-RE and Y-RE alloys below which long range magnetic order is not found but there exists a spin glass state (cf. Cu-Mn, Au-Fe). For non S-state solutes the behaviour is complicated by the crystal field effects. These properties have been confirmed by the electrical resistivity measurements which have distinguished the two different types of magnetic ordering. It is also shown that by a proper analysis of the magnetization data, one can distinguish the two different types of the magnetic ordering and obtain values for the critical concentrations in agreement with those obtained from the resistivity and some other physical properties reported in the literature.

Finally, the most interesting feature that emerges from our data is that qualitatively it is similar to that reported for La-RE alloys (216). These were the first observations in rare-earth alloys of the occurrence of a "magnetic glass", and the onset of long-range magnetic ordering occurs with increasing RE concentrations.

* Y and Sc may be considered as rare-earth metals without 4f electrons. The addition of a little rare-earth solute does not perturb the band structure to any marked extent. As in the pure rare-earth metals with local 4f moments, a helical type of magnetic order is established.

VI.2.2 The dilute alloys

As our understanding of the present resistivity data for the dilute S-state (Gd^{+++}) impurities in Y and Sc is not yet adequate and the application of Kondo effect with (true) exchange coupling (because $\Delta\rho = \rho_0 + A/c \log T$) is questionable, we consider the non S-state impurities data first.

(a) Non S-state impurities (Tb^{+++} , Dy^{+++}) in Y and Sc

From results presented on the dilute Sc-Tb, Sc-Dy, Y-Tb and Y-Dy alloys, the low temperature resistance is attributed to the scattering of the conduction electrons from the crystalline field energy levels. Both elastic and inelastic channels of scattering are taken into account in the calculated theoretical resistivity vs. temperature curve (see ref. (92)).

The drop in the resistance at $T \sim 8^\circ K$ ($T \sim 0.2 \delta$, where δ is the level splitting from the ground state) in Sc-Tb alloys results from the onset of inelastic scattering, the fall in the resistivity as the temperature approaches zero being attributed to the singlet ground state where no elastic or inelastic scattering contributes to the resistivity. For Y-Tb alloys where the ground state is accidentally degenerate, and with several states crossing the ground state, both elastic and inelastic contributions will contribute to the resistivity down to very low temperature.

In Sc-Dy where the ground state is a Kramers doublet, the elastic scattering has contributions to the resistivity corresponding to $|\pm 1/2\rangle$ (with admixture of $|\pm 3/2\rangle$ and $|\pm 11/2\rangle$). For both Sc-Dy and Y-Dy alloys, the difference in the curves for the two cases corresponds to different ratios of inelastic to elastic scattering.

In Sc-RE alloys the theoretical curves fit the experimental data reasonably well; minor deviations at low temperature are expected and attributed to the exchange interactions which have been neglected in the theoretical calculations. The effect of interaction is also clearly observable from $\Delta\rho/c$ vs T plots (Fig. VI.39 and 40) where we see a concentration dependence in the resistivity. We have discussed the influence of the crystal field on the Kondo effect with a negative s-f exchange interaction (Kondo minimum) in Chapter I section 1.9. Such a theory does not seem to exist for the (true) positive s-f exchange interaction. Because of the splitting of the full J value of the rare earth ion, the exchange scattering due to s-f interaction to 2nd Born approximation might not be so significant as when compared to their Gd analogues (see next section). It would be rather interesting, indeed, to consider this problem theoretically.

In Y-RE alloys exchange interaction effects are expected to be significant, and low temperature deviations from the theoretical curves in Tb and Dy alloys are attributed to these effects (see also ref. (207)).

From the spin disorder resistivities of these alloys (ρ_m) we are able to deduce a value for the exchange coupling constant J_{ex} , since it satisfies equation 1.9.6 and assuming $m^*/m = 3$, values of J_{ex} deduced as listed in table VI.5 for Sc-RE alloys and table VI.6 for Y-RE alloys. These figures do not seem to follow simply a $(\lambda - 1)^2 J(J + 1)$ law based on the Gd; we attributed this to the influence of the crystalline electric field on the spin disorder resistivity of some of the other rare-earth impurities below (or above) the $(\lambda - 1)^2 J(J + 1)$ law. It should also be pointed out that inaccuracy in determining (ρ_m) is due to the breakdown of Matthiessen's rule which yields an approximate value for the deduced J_{ex} , but the magnitude of the change is expected to be small. However, these data seem consistent with Isaacs et al (214) NMR and magnetization measurements who pointed

c% Tb	ρ_m/c $\mu\Omega$ cm/at%	J_{ex} e.v	c% Dy	ρ_m/c $\mu\Omega$ cm/at%	J_{ex} e.v
0.2	0.349	0.071	0.2	0.417	0.189
0.5	0.217	0.05	0.5	0.756	0.255
1	0.207	0.04	1	1.980	0.41

Table VI.5 (Dilute $\leq 1\%$ Sc-Tb & Dy alloys)

c% Tb	ρ_m/c $\mu\Omega$ cm/at %	J e.v	c% Dy	ρ_m/c $\mu\Omega$ cm/at %	J_{ex} e.v
0.2	6.895	0.183	0.2	2.50	0.134
0.5	1.323	0.08	0.5	1.20	0.093

Table VI. 6 (Dilute $\leq 0.5\%$ Y-Tb and Dy alloys)

out that J_{ex}^{Dy} should be more than twice that of Gd, since the enhancement of the effective moment in the case of Dy is more than Gd, and since $1/\lambda - 1/\lambda$ for Gd is twice as big as that of Dy (μ_{eff} proportional to $J_{ex} (\lambda - 1)/\lambda$).

(b) S-state impurities (Gd^{+++}) in Y and Sc

From the results presented on dilute Sc-Gd alloys ($\leq 1\%$ Gd), Fig. VI.37 and 38, below $\sim 10^0$ K the impurity resistivity is described by

$$\Delta\rho/c = \Delta\rho_0 + A/c \cdot \log T$$

and the coefficients estimated from the slope of Fig. VI.38 are listed in Table VI.7.

The non-linearity of A/c and the concentration dependence of the resistivity (Fig. VI.37) suggest that there are interactions between the Gd impurities.

We have discussed the possible origins of the positive logarithmic temperature dependence in Chapter I. Because of the well-defined moment on the Gd ions (since the $4f^7$ configuration for the Gd atom is extremely stable)

and because the effective exchange coupling (J_{ex}) between the conduction electrons of the Sc host and the magnetic 4f local electrons is expected to be small, we attribute this positive logarithmic temperature dependence to the Kondo effect with (true) ferromagnetic s-f exchange coupling J_{ex} . The spin resistivity in zero applied magnetic field is given by equation (1.3.4):

$$\rho_{spin} = c\rho_m (1 + 4 J_{ex} N(0) \log K\beta T/D)$$

where ρ_m is the spin disorder resistivity, using the estimated A/c values obtained from graph VI.38 and comparing them with the above equation, the J_{ex} has been calculated for different concentrations and listed in table VI.7 (assuming $m^*/m = 3$ and $N(0)^* = 0.61 \text{ (e.v.)}^{-1}$). The spin disorder resistivity ρ_m has then been calculated.

c% Gd	$A/c \mu\Omega \text{ cm/at } ^\circ\text{K}$	$J_{ex} \text{ e.v}$	$\rho_m/c \mu\Omega \text{ cm/at } \%$
0.22	0.084	0.052	0.286
0.5	0.126	0.06	0.380
1	0.155	0.064	0.433

Table VI.7 (Dilute $\leq 1\%$ Sc-Gd alloys)

These values for J_{ex} (and for the spin disorder resistivity) are expected to be larger in order to account for this positive temperature coefficient; because of interaction effects between impurities there is some doubt on the significance of the values. However these values are in good agreement with the J_{ex} value of 0.06 e.v given by Fradin et al (217) from NMR measurements, who concluded that the enhanced polarization of the conduction electrons is oscillatory (RKKY) form beyond the near neighbours to the impurity.

In dilute Y-Gd ($\leq 0.5\%$) alloys the exchange interaction is found to be much

*

Using free electron value.

more important than for Sc-Gd alloys in the same concentration range. The positive temperature coefficient for 0.2% alloy is also attributed to the Kondo effect with strong correlation between impurities which modified the shape of the logarithmic curve. Evidence of strong interaction effects is also given by M/M_s vs H/T plots (Fig. VI.46), where the curvature at high field arises from Brillouin saturations, but that at low fields can only arise from interactions. This alloy obeys a Curie-Weiss law (Fig. VI.16 and 17) with a paramagnetic Curie temperature ϑ where it is positive and approximates to 0.8°K . The effective moment per Gd ion μ_{eff} as determined from the paramagnetic Curie constant is larger from the free ion value (Table VI.8). This is in agreement with other reported values (197).

An attempt has nevertheless been made to estimate the exchange coupling constant from the Kondo logarithmic slope using the equation (1.3.4) again assuming $m^*/m = 3$ $N(0) = 0.61 \text{ (e.v)}^{-1}$, J_{ex} was estimated to be 0.093 eV and hence the spin disorder resistivity was determined. These are listed in table VI.2 together with other parameters.

c% Gd	$A/c_\mu \Omega \text{ cm/at } \% \text{K}$	$J_{\text{ex}} \text{ eV}$	$\rho_m/c \mu \Omega \text{ cm/at } \%$	$\mu_{\text{eff}} (\mu\beta)$	$\vartheta \text{ K}$
0.2	1.40	0.093	2.667	8.429	0.8
0.5				8.276	1.6

Table VI.8 (Dilute $\leq 0.5\%$, Y-Gd alloys)

In many ways the susceptibility and the magnetization field dependence of a 0.5% Gd alloy is similar to a 0.2% alloy, the paramagnetic Curie temperature ϑ and effective moment per Gd atom having been found to be 1.6°K and $8.276 \mu\beta$ respectively. The behaviour of the resistivity is strikingly different from that of the 0.2% alloy, the incremental resistivity $\Delta\rho/c$ can be represented by a logarithmic function (Fig. VI.15 and 45), but it can not be derived from conduction electron scattering from single impurities. Since the magnetic measurements confirm strong

interactions, we would expect magnetic ordering temperature to be below about 0.5 K (from the extrapolation vs. concentration curve from more concentrated alloys). We believe the observed behaviour can be attributed to the (expected) short-range ordering effects above the ordering temperature which yield a temperature-dependent contribution to $\Delta\rho(T)$; similar to the more concentrated alloys discussed earlier.

In conclusion, then, it would appear that in the extreme dilute limit of Sc-Gd and Y-Gd alloys, the Kondo effect with (true) exchange coupling might exist. However in the present measurements the traditional Kondo anomalies have been modified from its simplest form by the effect of RKKY type interactions as indicated by the concentration dependence of the resistivity. Such interactions stabilize the moments and lead to spin glass type spin freezing with increasing Gd concentration, hence lowering the Kondo temperature. The influence of these interactions is also indicated by measurements of susceptibility, where Curie-Weiss behaviour is observed, and by magnetization vs. field measurements which show low field Brillouin curvature.

Summary

We have found that all of the Sc-RE and Y-RE alloys examined, order magnetically to give long-range helical antiferromagnetism above some well defined critical concentrations. In the low concentration range a spin glass character was found. These properties have been confirmed by the electrical resistivity measurements which have distinguished the long range helical ordering by the associated magnetic superzone effects; these effects are absent in low concentration spin glass alloys which however show some spin glass characteristics (cf. Cu-Mn, Au-Fe).

When crystal field effects are not present, we find a T^3 behaviour in the resistivity well below T_N for the more concentrated alloys, while for the spin glass alloys a $T^{3/2}$ law was found, suggesting a different type of elementary excitation at low temperatures in different magnetic ordered states. The case of non-S-state ions is considerably more complicated; both elastic and inelastic scattering of the conduction electrons from the crystal field split levels of the solute become important at temperatures comparable to the magnetic ordering temperatures.

The alloys which show a clear sign of spin glass behaviour in their resistivity, exhibit typical spin glass features in their magnetization measurements.

The anomalous behaviour in the resistivity and the inverse susceptibility in Sc-Gd and Y-Gd alloys above the spin glass temperatures may be an indication of the presence of short range magnetic order at these temperatures; in non-S-state ion solutes this anomalous behaviour is mostly attributed to the crystal field effects.

We find that the transition temperatures of the helical antiferromagnetic states obey the simple de Gennes law whereas the spin glass temperature does not follow this behaviour. At present it is not clear why this should be the case.

We have attempted to derive estimates of J_{ex} from the spin disorder resistivity (involving J^2) and the Kondo-like $\log T$ term (involving J^3).

The values are rather low and complications due to solute-solute interactions and Matthiessen's rule effects may be present.

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LETTER TO THE EDITOR

Electrical resistivity of Pt-Mn alloys

B V B Sarkissian and R H Taylor

Physics Department, Imperial College of Science and Technology, London SW7

Received 30 August 1974

Abstract. The electrical resistivity of Pt-Mn alloys containing from 0.09 to 18 % Mn has been measured. In the most dilute alloys, a clear logarithmic region of positive slope has been observed in plots of resistivity against temperature, indicating that these Pt-Mn alloys show Coles-like behaviour. In all alloys up to about 11 at% Mn a resistance minimum has been observed which we attribute to spin glass ordering, below the minimum the resistivity follows the general $T^{3/2}$ law associated with spin glasses at low temperatures. Above this concentration there is no minimum and the resistivity is found to increase monotonically with temperature.

The magnetic properties of 3d transition metals dissolved in 4d and 5d hosts provide an interesting class of materials which can, as a function of impurity concentration, show a wide variety of magnetic property.

In the strongly exchange-enhanced metal Pd, for example, addition of Fe and Co impurities leads even at quite low concentrations (see for example, Nieuwenhuys 1974) to long-range ferromagnetism due to the strong exchange-enhancement of the host and the consequent positive polarization of the conduction band; however, addition of Mn to Pd leads to a far more complicated magnetic phase diagram (Coles *et al* 1975, Zweers and Van den Berg 1975) where the initial ferromagnetic behaviour gives way on raising the Mn concentration to spin glass behaviour, as Mn-Mn nearest-neighbour antiferromagnetic couplings become more important.

In the less strongly enhanced host, Rh, low concentrations of Fe and Mn (<0.5 at%) produce localized spin fluctuations at the impurity. In Rh-Fe (Rusby 1974) the behaviour in the dilute limit may be well understood in terms of the model of Rivier and Zlatić (1973b) with a spin fluctuation temperature, $T_{LSF} \sim 15$ K. In Rh-Mn, T_{LSF} is lower (following the usual trend in the reduction of T_{LSF} for an impurity closer to the centre of the transition series in a given host—see for example Rizzuto (1974). At higher concentrations in both of these systems, the moments are stabilized and behaviour characteristic of a spin glass is observed (Murani and Coles 1972, 1973 and particularly Rusby 1974 figure 7) without any evidence of a region where ferromagnetism is stabilized. Pt-Fe alloys appear to show similar behaviour (Loram *et al* 1972), with a value of $T_{LSF} \sim 0.4$ K in this case for the dilute limit. Spin glass behaviour is then stabilized over a fairly narrow concentration regime before the onset of long-range ferromagnetism. The Pt-Mn alloy system has until now received scant attention apart from the specific heat study of Nieuwenhuys *et al* (1973), who concluded that there was a well-defined moment on the Mn atoms at fairly low concentrations (<1 %) and that the ordering may be spin glass-like.

In this letter we report electrical resistivity measurements on Pt-Mn alloys both in the dilute limit (to 0.09 %) and for concentrated alloys (to 18 %). Resistivity, of course, provides particularly clear evidence of the magnetic character of an alloy. The presence of spin fluctuations in alloys where both the impurity and host are taken from nearby columns of the 3d, 4d and 5d transition series (Coles alloys) is manifested (Rivier and Zlatić 1972b) by an electrical resistance which increases, as the temperature is raised, as T^2 at low temperatures, then linearly with temperature, and finally, well above T_{LSF} , logarithmically approaches the unitarity limit. The behaviour of alloys where the potential is strongly modified by the difference in character between the electronic structure of the host and impurity (Kondo alloys) gives rise again to T^2 , T and $\lg T$ behaviour (Rivier and Zlatić 1972a) but this time the resistance falls as a function of increasing temperature. When well-formed moments are present on the impurity sites, ferromagnetic ordering (as in Pd-Fe, Co and Mn) is manifested by a sharp discontinuity of slope close to the Curie temperature, whilst spin glass ordering is usually manifested (as in Cu-Mn, Au-Fe and Pd-Mn) by a smooth maximum in the slope of the resistivity close to the spin freezing temperature obtained from magnetic susceptibility measurements. At low temperatures the electrical resistivity of a spin glass is expected to increase as $T^{3/2}$ but with a weak concentration dependence of the coefficient of this term (Rivier and Adkins 1975).

The alloys used in the present measurements were prepared from high-purity Mn (better than 99.99 %) and spectroscopically pure Pt, by arc-melting on a water-cooled copper hearth, turning and re-melting several times. On the initial melt, care was taken that the Pt should flow over the Mn in order to reduce Mn loss. The ingots were then drawn into wires using non-ferrous tools and given a short anneal (about half an hour) in a vacuum of 10^{-5} Torr at 750 °C. This short anneal was intended to reduce the risk of Mn depletion from the surface of the wires. Weight losses after melting were always low and electron microprobe analysis confirmed approximately the nominal concentrations. Our confidence in the composition of our alloys is also borne out by the linearity of the resistivity at 4.2 K as a function of concentration (see figure 4). The measurements were performed by a standard four terminal potentiometric technique at temperatures down to pumped ^4He and ^3He and in one case down to about 30 mK using a dilution refrigerator.

Plots of incremental resistivity against temperature are shown in figure 1 for the dilute alloys (<0.5 at %) and two particularly interesting features emerge from these data:

(i) There is clear evidence of a resistance minimum in the low concentration alloys at the lowest temperatures. Our data for the 0.5 at % alloy in figure 1 shows a clear minimum at $0.45 \text{ K} \pm 0.1$ (broken curve) and this substantiates the earlier measurements of Hansen and de Pater (private communication, see also Nieuwenhuys *et al* 1973) who found a resistance minimum in a nominal Pt 0.1 at % Mn alloy at 0.36 K.

(ii) Above the temperature of the minimum there exists a well-defined logarithmic region in the 0.09 % alloy and to a progressively lesser extent in the other alloys containing up to 0.5 % Mn. This behaviour is shown in figure 2. The positive slope of the log region shows unequivocally that the alloys are Coles-like rather than Kondo-like. It is clear from figure 2 that the region of logarithmic character is shifted to higher temperature as the concentration is increased and the temperature of the resistance minimum rises; at higher temperatures deviations from log behaviour presumably arise as a result of deviations from Matthiessen's rule, although a temperature of 6–8 K for these deviations does seem rather low in view of the fairly high Debye temperature of pure Pt (~ 230 K). However we note that similar effects in dilute Pt-Fe alloys (Loram *et al* 1972) have also been observed at about 8 K and attributed to deviations from Matthiessen's rule. Plots of

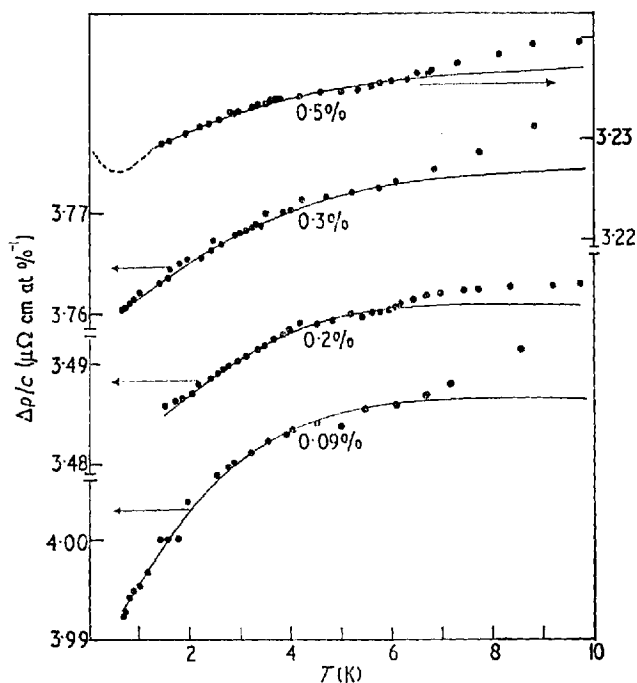


Figure 1. Excess resistivity per atomic percent, $\Delta\rho/c$, plotted against temperature. The very low temperature (dilution refrigerator range) data for the 0.5 at % alloy are shown by the broken curve.

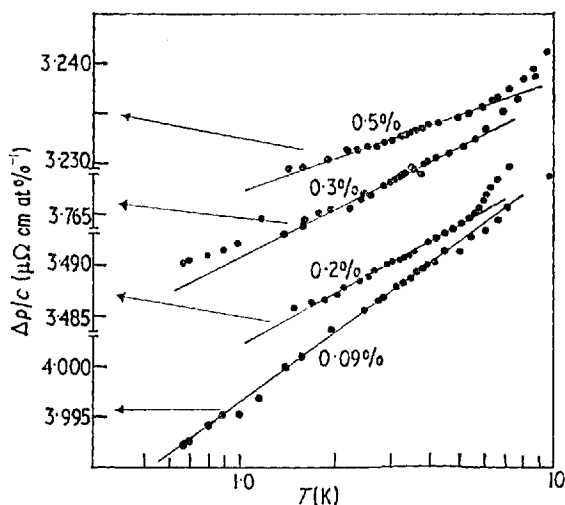


Figure 2. Excess resistivity per atomic percent, $\Delta\rho/c$, plotted against $\lg T$; the vertical scale is the same (with a shifted zero) for all the alloys.

incremental resistivity against temperature for concentrations between 1 and 12 at% are shown in figure 3. The most notable feature of these plots is now the strong resistance minimum, the temperature of which increases linearly as a function of concentration (as shown in figure 4). Below about $\frac{1}{2}T_{\min}$ the resistivity falls approximately as $T^{3/2}$ showing a temperature dependence related to that of the canonical spin glasses Cu-Mn (Ford and Mydosh 1974) and Au-Fe (Mydosh and Ford 1974 to be published). At higher concentrations still, however, we have found that the character of the resistivity undergoes a further change. In 12, 15 and 18 at% alloys, behaviour similar to that of spin glasses such as Cu-Mn and Au-Fe is observed with a monotonic increase in resistivity as a function of temperature, but with a maximum in the slope of the resistance at

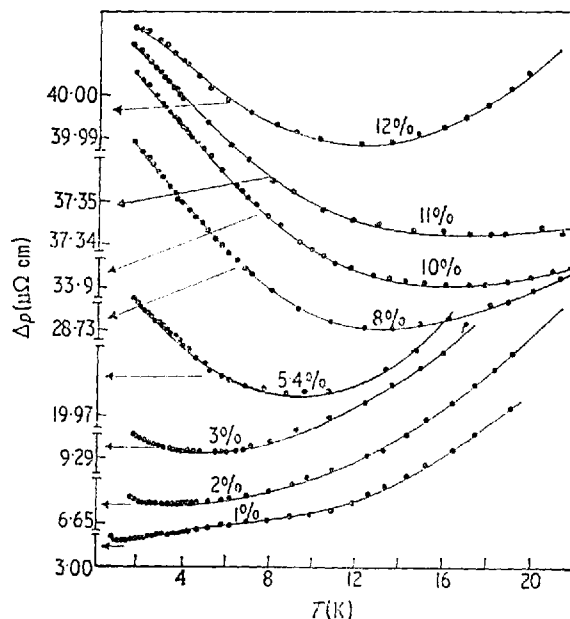


Figure 3. Excess resistivity, $\Delta\rho$, plotted against temperature for alloys in the concentration range $1 < c < 12\%$. The highest curve (12 at%) shows data for the alloy annealed at 1070 °C for 4 hours (see text). The vertical scale is the same (with a shifted zero) for all the alloys.

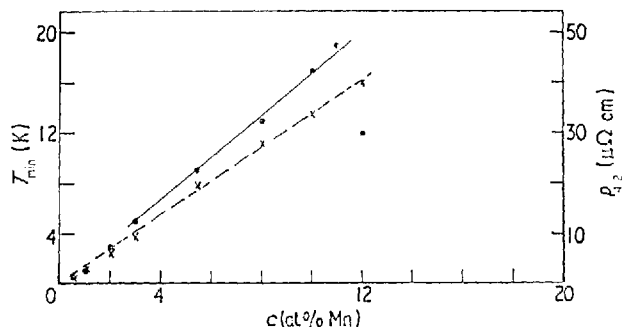


Figure 4. Solid line, temperature of the resistivity minimum plotted as a function of concentration; broken line, resistivity at 4.2 K plotted as a function of concentration.

temperatures falling on an extrapolation of the plot for the concentration dependence of the temperature of the minima in the more dilute alloys.

Preliminary magnetic susceptibility measurements made in this laboratory by Mr Pon Wei Hou on alloys containing 5.4, 8, 11 and 12 at% Mn in Pt show broad susceptibility maxima at 7, 12, 18 and 20 K respectively and all of them show a frozen-in component of the magnetization when the alloys were cooled in an applied field. The temperatures of these maxima agree fairly well with the characteristic temperatures obtained from the resistivity, and we are led to the conclusion that both the minima (as in Rh-Fe, Murani and Coles 1970) and maxima in $d\rho/dT$, signify spin glass ordering in the alloys. A theoretical justification for the origin of the minimum and the $T^{3/2}$ behaviour will be given by Rivier (1974). We note however that no AC susceptibility measurements have been performed yet and it would be interesting to see if a sharp cusp is observed as in the well-established spin glass materials.

Close to the concentration at which the resistance character changes (~ 11 at%) we were able to influence the behaviour of the resistivity by a suitable anneal. The 12 at% alloy, when annealed at 1070 °C for 4 hours and very rapidly quenched, gave a resistance minimum, but with the temperature of the minimum shifted to lower temperatures than would be suggested for a 12 at% alloy in figure 4 (by about 8 K). Analysis, in this case, did not suggest that Mn had been lost from the alloy during the anneal. We were unable, however, to produce any change in character in the 15 at% alloy. Whilst an understanding of the details of these changes in character of the resistivity at or around a critical concentration of 11 at% require a great deal more experimental investigation, the experiments that we have performed do seem to point strongly to the importance of atomic short-range order in these materials (see Coles *et al* 1975 for a fuller discussion). It is worth remarking that no similar changes have been observed in either Rh-Fe or Pd-Mn alloys at these compositions, although the critical concentration is close to the composition at which Au-Fe alloys show a change in magnetic character (Murani 1974).

Our measurements suggest that the Pt-Mn alloy system behaves quite differently from its Pd or Rh based counterparts; the alloys neither show regions of T^2 nor linear in T behaviour, characteristic of localized spin fluctuations in the dilute limit, nor a region of ferromagnetism. Instead they show behaviour, even at the lowest concentrations which we have studied, which we attribute to spin glass behaviour. Above the minimum in the most dilute alloys we have identified a clear logarithmic region and the positive slope of this indicates that, despite the fact that Pt and Mn are separated by three columns in the periodic table, Pt-Mn forms Coles alloys (unlike Mo-Co, Rh-Cr, Pt-Cr and Pd-Cr which are all Kondo-like.) The identification of the log region (which we believe is the first unequivocal identification of this behaviour in a Coles alloy) relies upon the conjunction of a low-spin fluctuation temperature and the fact that ordering effects in the relevant concentration range occur at rather low temperatures. (In Rh-Fe the inability of Rusby (1974) to identify with any certainty a logarithmic term is due here to the higher value of T_{LSF} and the consequent problems involved in separating out the effects due to deviations from Matthiessen's rule. In Pd-Mn the strong interaction between the impurities via the polarized Pd 4d band lead to higher ordering temperatures for low concentrations.) The combination of the logarithmic regime with the resistance minimum in these alloys leads to the interesting result that in Pt-Mn, the resistance behaviour is essentially an upside-down version of the data for low concentration Au-Mn alloys at low temperatures (Ford and Mydosh 1974) where, as the temperature is increased, the effect of the superposition of a rising resistivity due to spin glass behaviour on the falling Kondo resistivity leads to a maximum.

We are extremely grateful to Dr N Rivier and Professor B R Coles for many useful suggestions and discussions and to Mr Pan Wei Hou for allowing us to quote his unpublished susceptibility measurements. We also wish to thank Dr R L Rusby of the National Physics Laboratory for allowing us to use his ^3He resistance apparatus and Dr R Vaccarone for great help with the dilution refrigerator. One of us (BVBS) has received financial support from the Calouste Gulbenkian foundation during the course of this work.

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