

MAGNETIC ORDERING IN DILUTE Pd-Mn ALLOYS

by

SHANG-CHAN HO

A Thesis

presented to the University of Manitoba

in partial fulfillment of the

requirements for the degree of

Doctor of Philosophy

in

Department of Physics

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A thesis submitted to the Faculty of Graduate Studies of
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To Florence, My Love

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Magnetic Ordering in Dilute Pd-Mn Alloys

ABSTRACT

The magnetic ordering of dilute Pd-Mn alloys has been investigated for alloys with Mn concentrations from 0.5 at % to 10.45 at %, in steps of 0.5 at %. The measurements of the electrical resistivity and A.C. susceptibility have been made in the temperature range 1.5 K to 300 K and in magnetic fields from zero to 800 Oe. Three different "phases" are found: the ferromagnetic phase from 0.5 at % Mn to 2.5 at % Mn, the mixed ordering phase from 3.0 at % Mn to 4.5 at % Mn, and the spin glass phase from 5.0 at % Mn to 10.45 at % Mn. It is found that direct d-d anti-ferromagnetic coupling between nearest neighbour Mn moments comes into play besides the (enhanced) R.K.K.Y interaction usually treated in models of Edwards and Anderson, and of Sherrington and Kirkpatrick. The critical indices γ, δ and the s-d coupling constant $|J|$ are also estimated.

CHAPTER I

PURPOSE AND SCOPE OF PROJECT

The purpose of the project reported in this thesis is to investigate the magnetic ordering in dilute palladium (Pd) -manganese (Mn) alloys. Pure Pd is paramagnetic while pure Mn is antiferromagnetic. However, a host of different magnetic properties varying from spin glass to ferromagnetic behaviour appear in their alloys. Hence it is hoped that this investigation can improve one's understanding of magnetic ordering in general, and the Pd-Mn alloy system in particular. For the ferromagnetic Pd-Mn alloys, this is the first attempt to measure their critical indices γ , δ in their ferromagnet to paramagnet transition, while for the spin glass alloys one hopes to have shed more light on a subject which is still very unclear.

At the start of this project the general features of the dilute Pd-Mn alloy system were known, although there is still disagreement on the extent of the different magnetic phases. The earliest work on this system consisted of resistivity studies done by Sarachik and Shaltiel (1967) and Williams and Loram (1969b). This was followed by various magnetic measurements performed by Coles et al (1975), Star et al (1975), Nieuwenhuys and Verbeek (1977), Thomson and Thompson (1979) and others. There is general agreement that alloys with Mn concentration less than 3.0 at % are ferromagnetic, and alloys with more than 5.0 at % Mn are spin glasses. (Rault and Burger(1969) placed the ferromagnetic phase up to 8 at %, though). The range from 3.0 at % to 5.0 at % Mn, however, has variously been described as partly ferromagnetic, spin glass, and even double transition. The critical

temperatures T_C and T_{SG} also vary from investigator to investigator.

One reason for this disagreement stems from the uncertainty in the concentration of Mn and/or other impurities in the alloy. Another reason may be that the early susceptibility measurements were done in a magnetic field of ~ 1 kOe, which suppressed the cusp in the susceptibility curve of the spin glass alloys. In this project, the Mn concentration is estimated to an accuracy of ± 0.1 at %. However, as the alloys were made in steps of 0.5 at % Mn, information on the boundary of the various magnetic phases are only accurate to 0.5 at % Mn also. The driving field in the A.C. susceptibility measurement was only 0.46 Oe rms so that any cusp in the spin glass regime should be quite sharp (if it exists). Hence, it is hoped that the information obtained in this project will be more accurate.

Starting from the dilute limit, from 27 to 575 ppm Mn, Pd-Mn alloys are spin glass like (Thomson and Thompson 1979). At higher Mn concentration, from approximately 0.1 at % to 2.5 at % Mn, the alloys are ferromagnetic, (Nieuwenhuys et al 1979), while alloys with

$$2.5 \text{ at } \% < \text{Mn} < 5.0 \text{ at } \%$$

have a mixed ordering. Alloys with

$$\sim 5.0 \text{ at } \% \leq \text{Mn} \leq \sim 25 \text{ at } \%$$

are again spin glass like, and beyond 25 at % three intermediate compounds appear:

$$\beta - \text{MnPd}, \quad \beta_1 - (\text{Mn}_2\text{Pd}_3), \quad \beta_2 - \text{MnPd}_2$$

(Raub and Mahler 1954 and Yamauchi 1964). These different phases of

Pd-Mn alloys are summarized in Fig. 1.1.1. The Y-scale is only approximate to display data at low Mn concentration.

In the present project, alloys with Mn concentration from 0 to 10.45 at % were made in approximate steps of 0.5 at %. They correspond to the ferromagnetic, mixed ordering and spin glass II phases in Fig. 1.1.1. Further, these samples were measured over the temperature interval 1.5°K to 300°K, in the magnetic field from 0 to 800 Oe. The main thrust of the investigation was in the temperature range from 1.5°K to 15°K because this is the range where magnetic ordering, either ferromagnetic or spin glass like, occurs. The system was investigated via measurements of D.C. resistivity and A.C. susceptibility, supplemented by X-ray powder photography for the determination of the lattice structure of the samples.

Chapter 2 of this thesis presents some theories on the interaction between Pd and Mn in the alloys, and also on their magnetic ordering. Chapter 3 describes the experimental methods used while Chapter 4 presents the data analysis.

Because of the enormous amount of diagrams involved, the discussion in Chapter 4 will be in terms of one typical alloy whenever possible. The remaining data can be found in the Appendices.

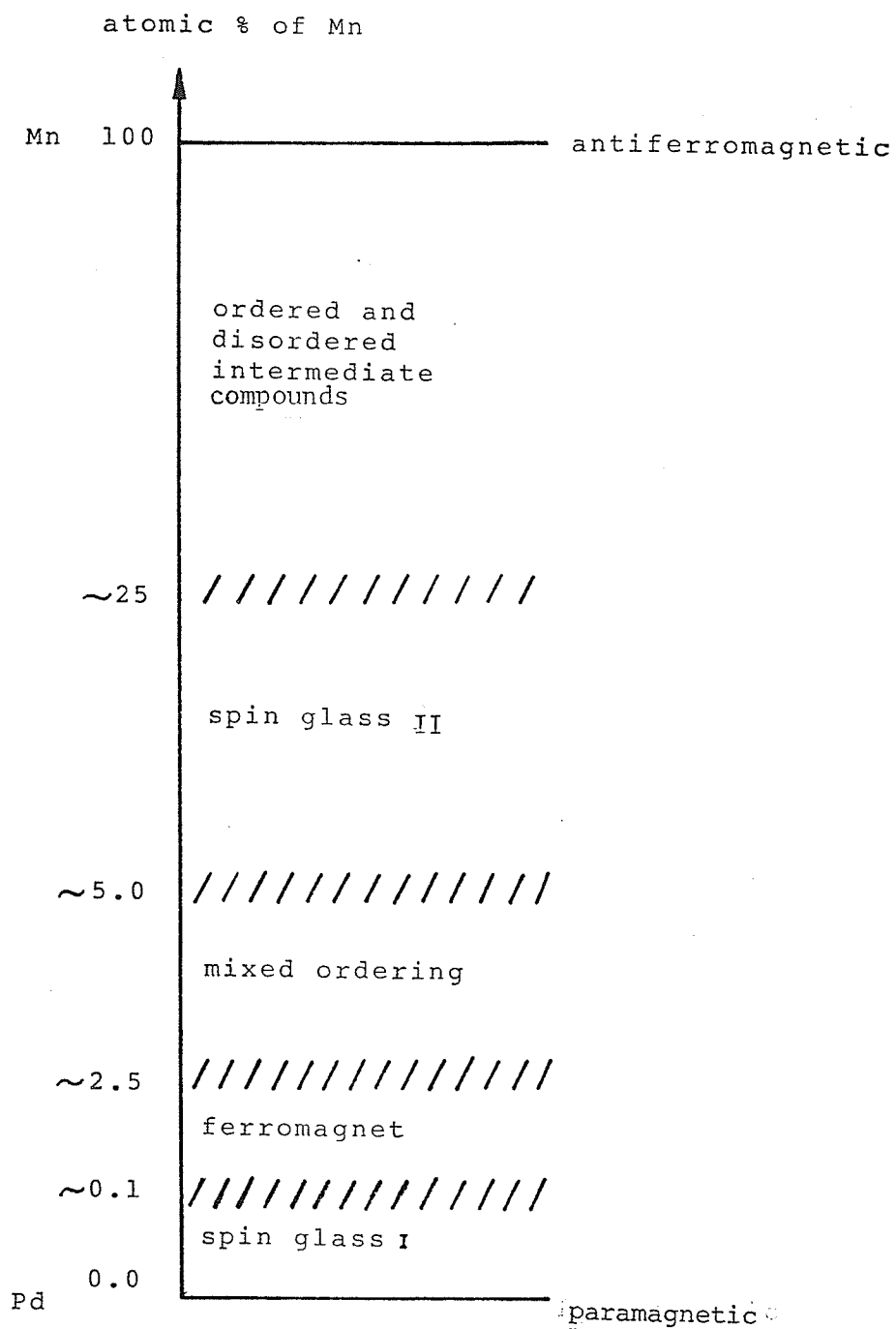


Fig. 1.1.1 Magnetic Properties of Pd-Mn Alloys
The Y-scale is only approximate.

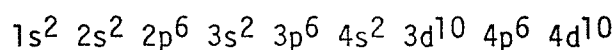
CHAPTER II

THEORIES

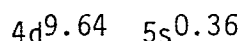
2.1 The R.K.K.Y. Interaction

2.1.1. Qualitative Description of Interactions in Pd-Mn Alloys.

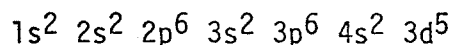
Pd and Mn are transition metals. The Pd atom has the electronic structure of $4d^{10}$ outside a closed shell of krypton-like electrons, i.e.,



In metallic Pd, some of the $4d^{10}$ electrons spill over to the 5s state. Hence instead of $4d^{10}$ one has (Vuillemin 1966)



The Mn atom has the electronic structure of $4s^2 3d^5$ outside a closed shell of argon-like electrons i.e.



In many cases the $3d^5$ configuration is quite stable, and gives rise to a magnetic moment corresponding to the spin quantum number of $S = \frac{5}{2}$, given by Hund's Rule.

When Mn is dissolved in Pd to form substitutional alloys, the magnetic moment associated with the Mn $3d^5$ configuration is preserved (Star et al 1975). This moment polarizes the Pd conduction electrons (4d and 5s) to form giant moments, via the enhanced R.K.K.Y. polarization discussed in Section 2.1.2 below. This polarization is oscillatory and at large distance r from the Mn site decreases as r^{-3} . See Fig. 2.1.1 (a). The first zero of the oscillation occurs at about 10 Å from the Mn site. This interaction is long ranged since the radius of

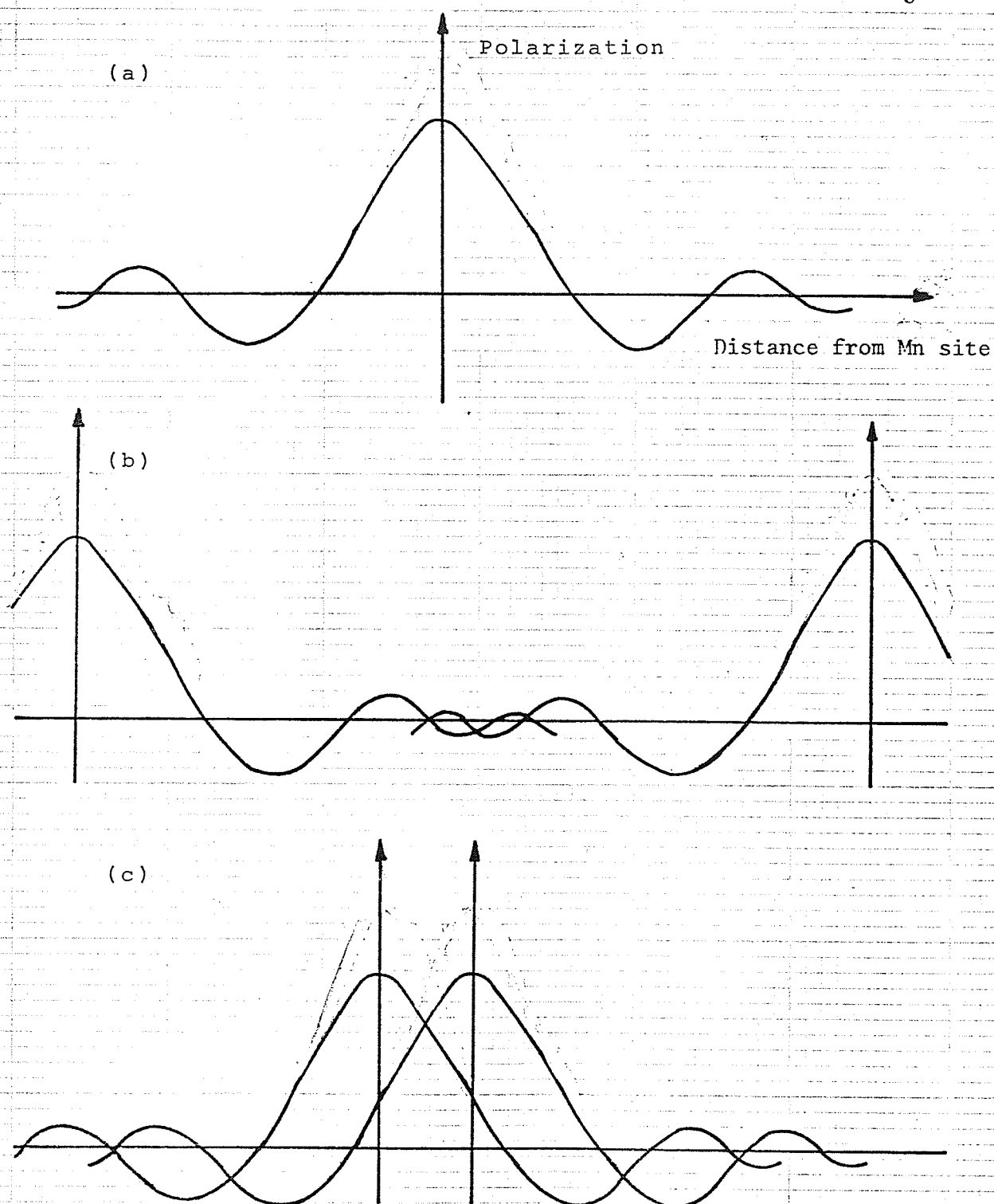


Fig. 2.1.1 (a) Enhanced R.K.K.Y. Polarization
 (b) Two Mn spins far apart; moments overlap in tails only
 (c) Giant moments overlap when two Mn spins are close together

the Pd atom is only 1.37 Å and the Mn atom 1.26 Å.

When the Mn concentration is very small, from the ppm range to less than ~0.1 at %, the Mn moments are far apart if they are evenly distributed in the alloy. Hence they interact with one another only through the tails of the R.K.K.Y. polarization. Because of the rapid change in sign in the polarization, no preferred orientational direction is established, and the alloy becomes a spin glass, as shown in Fig. 2.1.1 (b). When the Mn concentration is somewhat bigger than 0.1 at %, the average Mn-Mn moment separation falls within the first zero of the R.K.K.Y. polarization, and the giant moments begin to overlap. This produces a preferred orientation in the alloy, and makes it ferromagnetic, as depicted in Fig. 2.1.1 (c). As the Mn concentration increases further, the giant moments overlap more, and the alloy becomes more strongly ferromagnetic. This is reflected in the rise in Curie temperature T_C for the alloys from 0.5 at % to 2.5 at % Mn.

As the Mn concentration increases further, the chance of two Mn moments becoming nearest neighbors increases. When they do so, their d-electron wave functions overlap, and the direct d-d exchange for Mn atoms is expected to be anti-ferromagnetic (Moriya, 1967). One can see, roughly, that the direct Mn-Mn interaction is anti-ferromagnetic because the $3d^5$ electrons of Mn just fill up half the d-shell, and applying Hund's Rule they are all spin up. Any extra electron that can be added to the d-shell, say via covalent admixture, has to have spin down, in accordance with the Pauli Exclusion Principle. This anti-ferromagnetic interaction drives down the apparent ordering

temperature for alloys with Mn concentration between 3.0 at % and 4.5 at %, which show a mixed ordering which is not purely ferromagnetic. From 5.0 at % to ~25 at % Mn, the anti-ferromagnetic d-d interaction is in full competition with the enhanced R.K.K.Y. interaction, and the alloys are again spin glasses.

Beyond ~25 at % Mn, compounds like MnPd, Mn₂Pd₃ and MnPd₂ appear, and they are outside the scope of this investigation.

The next section outlines the R.K.K.Y. interaction used as a basis for the above discussion.

2.1.2 Derivation of R.K.K.Y. Interaction

The Ruderman-Kittel-Kasuya-Yosida (R.K.K.Y.) interaction describes the indirect interaction among magnetic moments in a metal host, via spin polarization of the host conduction electrons. In its modified form, it is responsible for giant magnetic moments inferred from magnetization measurements on some alloys, eg. PdFe and PdMn. It is believed to be able to induce ferromagnetic or spin glass like behaviour in various alloy systems. Because it is one of the main interactions in Pd-Mn alloys, an outline of the derivation is given below, based on the following references: Kittel (1968), and White, R.M. (1970).

The approach these authors use is to calculate the spin polarization $s(\vec{r})$ of a free electron gas when a magnetic moment is placed in it. The basic assumptions in the analysis are:

1. free electron model at zero temperature
2. linear response approximation

3. static magnetic field
4. energy corrected to 2nd order only, within non-degenerate perturbation theory.

Here $s(\vec{r})$ is actually $M(\vec{r})/(g\mu_B)$, where g is the Lande g -factor, and μ_B is the Bohr magneton.

The magnetization per unit volume $M(\vec{r})$ is related to the magnetic field $H(\vec{r})$ and the susceptibility $\chi(\vec{r})$ by

$$M(\vec{r}) = \int d^3r' \chi(\vec{r} - \vec{r}') H(\vec{r}')$$

Using the linear response approximation, all three quantities can be expanded into Fourier series.

$$\begin{aligned} M(\vec{r}) &= \sum_{\vec{q}} M_q \exp [i\vec{q} \cdot \vec{r}] \\ H(\vec{r}) &= \sum_{\vec{q}} h_q \exp [i\vec{q} \cdot \vec{r}] \\ \chi(\vec{r}) &= \sum_{\vec{q}} \chi_q \exp [i\vec{q} \cdot \vec{r}] \end{aligned} \quad (2.1.1)$$

$$\text{Then } M(\vec{r}) = \sum_{\vec{q}} \chi_q h_q \exp [i\vec{q} \cdot \vec{r}] \quad (2.1.2)$$

and $M_q = \chi_q h_q$, q being a reciprocal lattice vector.

Hence the problem is reduced to finding the susceptibility

χ_q of the electron gas resulting from the application of one Fourier component $h_q \cos(\vec{q} \cdot \vec{r})$ of the magnetic field.

Let the Hamiltonian of a free electron gas at zero temperature with spin σ_i be

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \mu_B \sum_i \vec{\sigma}_i \cdot \vec{h}_q \cos(\vec{q} \cdot \vec{r}_i)$$

where the first term on the right hand side is the kinetic energy and

$$\mathcal{H}_1 = \mu_B \sum_i \vec{\sigma}_i \cdot \vec{h}_q \cos(\vec{q} \cdot \vec{r}_i)$$

is the perturbation introduced by the magnetic field. To avoid difficulty arising from $q=0$, $\vec{h}_q$ is taken to lie on the x-direction i.e.

$$\vec{h}_q = h_q \hat{x}$$

$$\text{then } \mathcal{H}_1 = \frac{1}{4} \mu_B h_q \sum_i (\sigma_i^+ + \sigma_i^-) (e^{i\vec{q} \cdot \vec{r}_i} + e^{-i\vec{q} \cdot \vec{r}_i})$$

The first order correction to the energy is

$$\langle \vec{k} | \mathcal{H}_1 | \vec{k} \rangle$$

and is zero because of orthogonality of the plane wave states.

The 2nd order correction to the energy for state $\vec{k}$ is

$$\begin{aligned} \epsilon_k^{(2)} &= \sum_{\ell \neq k} \frac{|\langle \ell | \mathcal{H}_1 | k \rangle|^2}{\epsilon_k - \epsilon_\ell} \\ &= \frac{1}{4} (\mu_B h_q)^2 \left\{ \frac{1 - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} + \frac{1 - f_{k-q}}{\epsilon_k - \epsilon_{k-q}} \right\} \end{aligned}$$

where ϵ_k is the free electron energy for state $\vec{k}$,

and f_k is the Fermi-Dirac distribution.

The factors $(1 - f_{k+q})$ and $(1 - f_{k-q})$ come in because only vacant states are allowed as intermediate states in the perturbation calculation.

The total second order energy correction is a summation over all occupied $\vec{k}$ states.

$$\begin{aligned}
E^{(2)} &= \frac{1}{4} (\mu_B h_q)^2 \sum_{\vec{k}} \left\{ \frac{1 - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} + \frac{1 - f_{k-q}}{\epsilon_k - \epsilon_{k-q}} \right\} f_k \\
&= -\frac{1}{4} (\mu_B h_q)^2 \sum_{\vec{k}} \frac{f_k - f_{k+q}}{\epsilon_{k+q} - \epsilon_k} \\
&= -\frac{1}{4} (\mu_B h_q)^2 F(q)
\end{aligned}$$

where $F(q) = \sum_{\vec{k}} \frac{f_k - f_{k+q}}{\epsilon_{k+q} - \epsilon_k}$

$$= \frac{3N}{4 \epsilon_F} \left\{ 1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right\}$$

$k_F = \text{Fermi vector}, N = \frac{k_F^3}{2\pi^2} \text{ and } \epsilon_F = \frac{\hbar^2 k_F^2}{2m}$

The susceptibility for wave vector q is

$$\chi_q = - \frac{\partial^2 E^{(2)}}{\partial (\text{magnetic field})^2}$$

Because the magnetic field is $\vec{h}_q \cos(\vec{q} \cdot \vec{r}_i)$ and the spatial average of $\cos^2(\vec{q} \cdot \vec{r}_i)$ is $\frac{1}{2}$,

$$\chi_q = \mu_B^2 F(q) \quad (2.1.3)$$

The susceptibility in real space is, from Eq. 2.1.1,

$$\begin{aligned}
\chi(\vec{r}) &= \sum_{\vec{q}} \mu_B^2 F(q) \exp[i\vec{q} \cdot \vec{r}] \\
&= \frac{m \mu_B^2}{(2\pi)^3 \hbar^2} \left\{ \frac{\sin 2k_F r - 2k_F r \cos 2k_F r}{r^4} \right\}
\end{aligned}$$

If the interaction between an Mn moment $\vec{S}_\alpha$ and a Pd conduction electron $\vec{s}_i$ is assumed to be a δ -function exchange, of the form

$$- J \sum \vec{S}_\alpha \cdot \vec{s}_i \delta(\vec{r}_i)$$

then the conduction electron 'sees' an effective magnetic field of

$$H_{\text{eff}}(\vec{r}) = \frac{J}{g\mu_B} \vec{S}_\alpha \delta(\vec{r}_i)$$

with a Fourier component of

$$H_{\text{eff}}(q) = \frac{J}{g\mu_B} \vec{S}_\alpha$$

Using Eq. 2.1.2 and 2.1.3, the magnetization, and thus the spin-density

$$s(\vec{r}) = \frac{M}{g\mu_B}$$

of the conduction electron can be found

$$\begin{aligned} s(\vec{r}) &= \frac{J}{g^2 \mu_B^2} \sum_{\vec{q}} x_q e^{i\vec{q} \cdot \vec{r}} \vec{S}_\alpha \\ &= \frac{J}{g^2 \mu_B^2} \sum_{\vec{q}} \mu_B^2 F(q) e^{i\vec{q} \cdot \vec{r}} \vec{S}_\alpha \\ &= \frac{J}{g^2} \sum_{\vec{q}} F(q) e^{i\vec{q} \cdot \vec{r}} \vec{S}_\alpha \\ &= \frac{Jm}{(2\pi)^3 g^2 \hbar^2} \left\{ \frac{\sin 2k_F r - 2k_F r \cos 2k_F r}{r^4} \right\} \vec{S}_\alpha \quad (2.1.4) \end{aligned}$$

The impurity spin $\vec{S}_\alpha$ has thus induced a spin polarization in the

Pd conduction electrons. At large distances from the $\vec{S}_\alpha$ site, when $k_F r \gg 0$, the term

$$- \frac{2k_F r \cos 2k_F r}{r^4}$$

dominates the function, and the polarization oscillates with a period of πk_F^{-1} while the amplitude of the polarization decreases as r^{-3} .

Eq. 2.1.4 is called the R.K.K.Y. polarization, and is plotted in Fig. 2.1.2(a).

If there is another Mn spin $\vec{S}_\beta$ at $\vec{r}$, it will interact with $s(\vec{r})$ through a coupling of the form $-J \vec{s} \cdot \vec{S}$ and gives the R.K.K.Y. interaction energy.

$$H_{\text{R.K.K.Y.}} = - \frac{J_m^2}{(2\pi)^3 g^2 \hbar^2} \left\{ \frac{\sin 2k_F r - 2k_F r \cos 2k_F r}{r^4} \right\} \vec{S}_\alpha \cdot \vec{S}_\beta$$

The result is an indirect interaction between Mn spins $\vec{S}_\alpha$ and $\vec{S}_\beta$ via the Pd conduction electrons. If electron scattering at defects is also taken into account, then a factor $\exp(-r/\ell)$ appears, ℓ being the mean free path of the conduction electrons (de Gennes 1962). For dilute alloys $r/\ell \sim 0$. Hence the factor $\exp(-r/\ell) \sim 1$ and can usually be ignored, as explained in Section 2.4.3 below.

The above derivation makes use of the free electron gas model. For the case of the Pd d electrons in a narrow band, the electron - electron Coulomb interaction has to be taken into account. Using the random phase approximation, Wolff (1960) has shown that the spin polarization takes the form

$$s(q) = \frac{\mu_B^2 F(q)}{1 - \bar{V} F(q)} h(q)$$

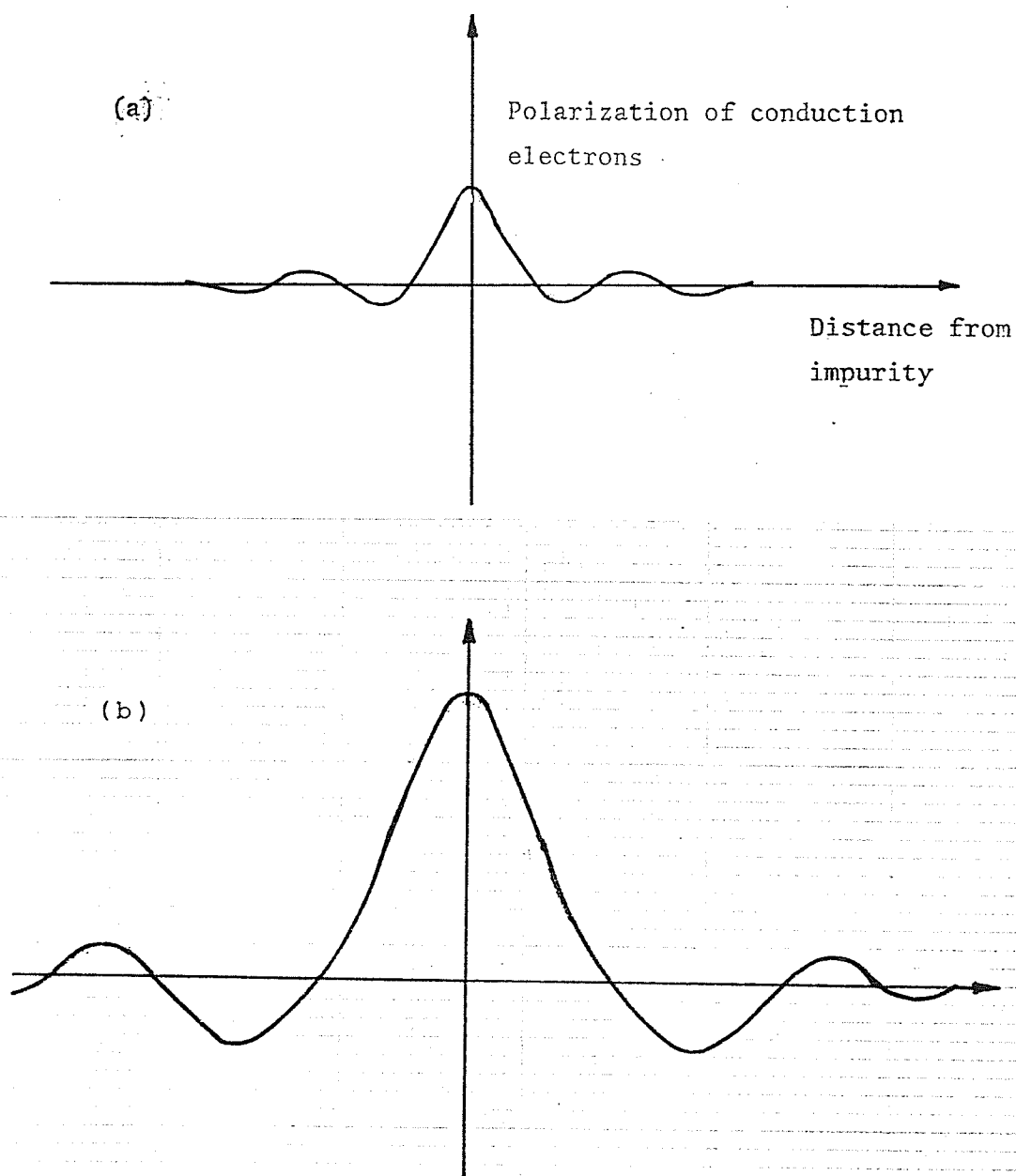


Fig. 2.1.2 (a) R.K.K.Y. polarization of conduction electrons by impurity moment
(b) Enhanced R.K.K.Y. polarization of Pd electrons by Mn spins

where $\bar{v}$ is the average of the Fourier coefficient of the screened Coulomb potential. The factor $(1 - \bar{v} F(q))^{-1}$ is called the Stoner enhancement factor and becomes very large when $\bar{v} F(q) \approx 1$, which is the case for Pd. Because $F(q) \geq 0$ and is monotonically decreasing the enhancement is greatest for small q . The result is to enhance the magnitude of the R.K.K.Y. polarization and to push out, in real space, the range of the polarization. An enhanced magnetic moment of $\sim 7.5 \mu_B$ per Mn atom resulting from such a polarization has been measured by Star et al (1975). This enhanced R.K.K.Y. polarization is plotted in Fig 2.1.2(b).

Finally, it should be pointed out that the R.K.K.Y. interaction has been derived assuming a spherical Fermi surface. Andersen (1970) has found that the Fermi surface of Pd is very much like intersecting cylinders, as reproduced in Fig. 2.1.3. For non-spherical surfaces, Roth et al (1966) show that the susceptibility at large distances r has the usual oscillating form, but that the amplitude decreases as $1/r$ for parallel regions of the Fermi surface, and as r^{-2} for cylindrical surfaces. Hence the r^{-3} dependence for R.K.K.Y. interaction for Pd-Mn alloys at large r may not be correct.

2.1.3 the R.K.K.Y. Scaling Law

One of the consequences of the r^{-3} behaviour of the R.K.K.Y. interaction at large r for spherical Fermi surfaces is the R.K.K.Y. scaling law, first suggested by Souletie and Tournier (1969). This law suggests that for a dilute alloy system with the R.K.K.Y. interaction the impurity magnetic specific heat $\Delta C_p (= C_p \text{ alloy} - C_p \text{ host})$,

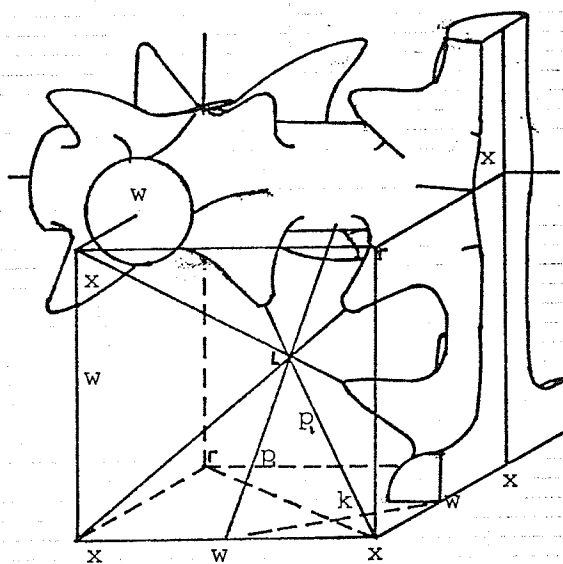


Fig. 2.1.3 Fermi surface of Pd in the periodic zone scheme. (After Andersen 1970)

the impurity magnetization M , and the susceptibility χ should be some universal functions of h/c and T/c , where h is the applied magnetic field, T is the temperature and c is the impurity concentration.

Mathematically, Souletie and Tournier (1969) find

$$\Delta C_p(T, h) = c \, \Gamma(T/c, h/c) \quad (2.1.5)$$

$$M(T, h) = c \, \zeta(T/c, h/c) \quad (2.1.6)$$

$$\chi(T, h) = K(T/c, h/c) \quad (2.1.7)$$

where Γ , ζ , K are all functions independent of c . It follows that for $h = 0$

$$\frac{\Delta C_p}{c} = \Gamma(T/c, 0)$$

$$\frac{M}{c} = \zeta(T/c, 0)$$

$$\chi = K(T/c, 0)$$

are all independent of c .

An example of R.K.K.Y. scaling is given in Fig 2.1.4, reproduced from Fig. 1 of Souletie and Tournier (1969). Here $\Delta C_p/c$ is plotted against T/c for 4 different Ag-Mn alloys. The universal function Γ is remarkably traced out. Other examples in magnetization and susceptibility can be found in the above reference.

The following is an outline of the derivation of the R.K.K.Y. scaling law.

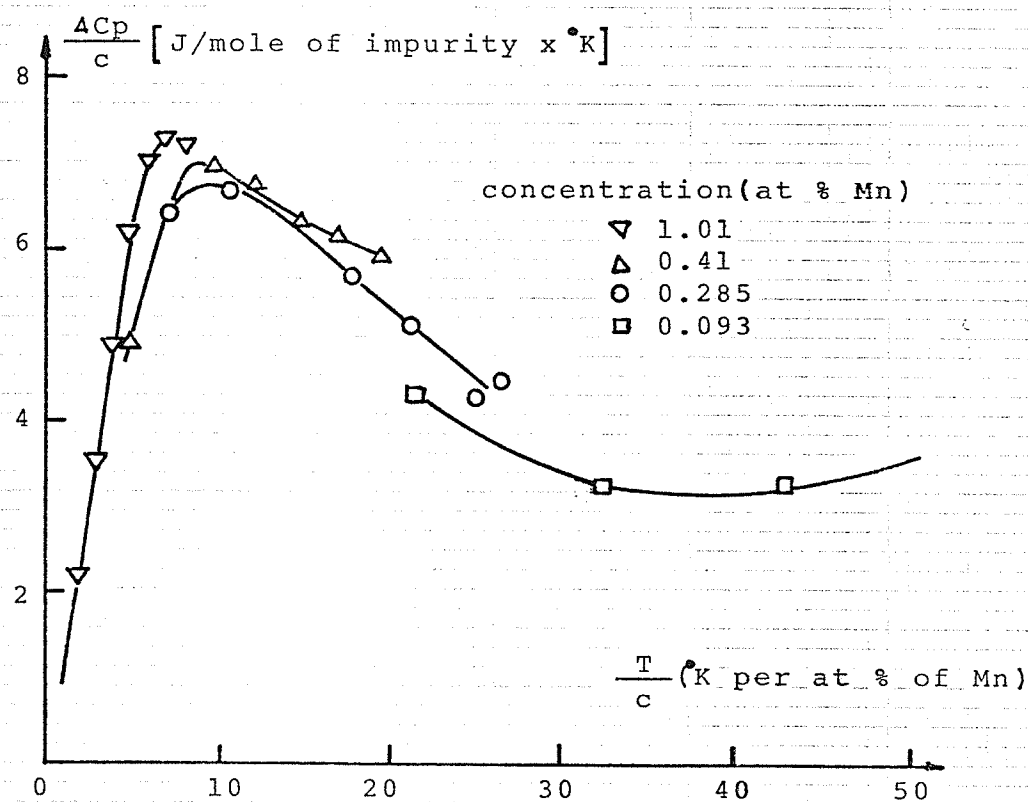


Fig. 2.1.4 Temperature dependence of the excess specific heat of Ag-Mn alloys on a "reduced diagram" $C_p/c(T/c)$. (After Souletie and Tournier 1969)

The basis of the scaling law comes from the intuitive idea that the r^{-3} decrease in the R.K.K.Y. interaction is exactly balanced by the r^3 increase in the number of impurity atoms in a sphere of radius r . Specifically, the average volume $\langle v \rangle$ associated with an impurity atom in a lattice of N sites is

$$\langle v \rangle = \frac{\text{volume of alloy}}{Nc}$$

assuming one atom per lattice site.

This $\langle v \rangle$ can also be approximated by a sphere

$$\langle v \rangle = \left\langle \frac{4}{3} \pi \left(\frac{r}{2} \right)^3 \right\rangle$$

where r is the impurity-impurity separation. Equating the two equations for $\langle v \rangle$ one gets $\left\langle \frac{4}{3} \pi \left(\frac{r}{2} \right)^3 \right\rangle = \frac{\text{volume of alloy}}{Nc}$

$$\begin{aligned} c \langle r^3 \rangle &= \frac{6}{\pi N} \times \text{volume of alloy} \\ &= \text{constant} \end{aligned} \quad (2.1.8)$$

Therefore $c \langle r^3 \rangle$ is independent of r and c .

From a molecular field model with R.K.K.Y. type interactions

$$H_i = A \sum_{j \neq i} \mu_j \frac{\cos(2k_F r_{ij})}{r_{ij}^3} \quad (2.1.9)$$

where H_i is the molecular field for spin i , μ_j is the magnetic moment for spin j , and A is the R.K.K.Y. interaction parameter.

One can recast it into the form

$$\begin{aligned} \frac{H_i}{c} &= A \sum_{j \neq i} \mu_j \frac{\cos(2k_F r_{ij})}{c r_{ij}^3} \\ &\approx \text{constant} \times \sum_{j \neq i} \frac{1}{c r_{ij}^3} \end{aligned}$$

where the cosine function is taken to be constant. Upon using Eq. 2.1.8, H_i/c becomes approximately independent of c and r . Now the normalized probability density function $P(H)$ gives the probability for the value of the molecular field on a site to be in the range dH around H . Therefore

$$P(H) = \frac{dN}{dH} = \frac{dN}{d(H/c)} \times \frac{1}{c}$$

and $cP(H) = f(H/c)$

f becomes independent of c because of H/c

Extending the definition of P to cover variations in T and h in the molecular field model, one observes that T and h enter Eq. 2.1.9 only through μ_i , in the form of a Brillouin function $B_S[\mu(H_i + h)/(k_B T)]$.

$$\text{But } B_S \left[\frac{\mu(H_i + h)}{k_B T} \right] = B_S \left[\frac{\mu \left(\frac{H_i}{c} + \frac{h}{c} \right)}{k_B T/c} \right]$$

Hence $c P(H, T, h) = f \left(\frac{H}{c}, \frac{T}{c}, \frac{h}{c} \right)$ with f independent of c .

With $P(H, T, h)$ one can calculate the magnetic specific heat, magnetization, susceptibility and other thermodynamic quantities. For example, the impurity magnetization is

$$\begin{aligned} M(T, h) &= Nc \int P(H, T, h) \mu B_S \left[\frac{\mu(H+h)}{k_B T} \right] dH \\ &= Nc \int cP(H, T, h) \mu B_S \left[\frac{\mu(H/c + h/c)}{k_B T/c} \right] d \left(\frac{H}{c} \right) \\ &= c \int Nf \left(\frac{H}{c}, \frac{T}{c}, \frac{h}{c} \right) \mu B_S \left[\frac{\mu(H/c + h/c)}{k_B T/c} \right] d \left(\frac{H}{c} \right) \\ &= c \zeta \left(\frac{T}{c}, \frac{h}{c} \right) \end{aligned}$$

Although the exact functional form of f is not known, the integration can theoretically be performed to yield the function ζ independent of c , as given in Eq. 2.1.6. Eq. 2.1.5 and 2.1.7 can be proved similarly.

It should be noted that the R.K.K.Y. scaling law is observed only in the dilute spin glass region. The lower bound is the Kondo region reached by reducing either the impurity concentration or the temperature, while the upper bound is the onset of long range ordering, when direct exchange comes into play. Larsen (1978) has discussed the applicability of R.K.K.Y. scaling to the Au-Fe alloy system. He points out that within these two boundaries the scaling is only approximately observed because of

1. concentration fluctuations in the alloy as opposed to a really homogenous situation.
2. damping of the R.K.K.Y. interaction due to electron mean free path effects. The factor $e^{-r/\lambda}$ decreases the number of impurity spins that a certain spin communicates with as the distance increases. Essentially, it invalidates Eq. 2.1.8.

For the Pd-Mn alloys investigated in this project, R.K.K.Y. scaling is not observed. Detailed discussion will be given in Chapter IV.

2.2 Theories of Ferromagnetic Ordering

2.2.1 Classification of Phase Transitions

Because of the overlap of giant moments resulting from the enhanced R.K.K.Y. interaction, some of the Pd-Mn alloys form ferromagnets at low temperatures. In this project, alloys containing between 0.5 at % and 2.5 at % Mn show a ferromagnet to paramagnet transition as the temperature is raised through their respective critical temperatures (the Curie temperature T_C). Evidence for this relatively sharp transition can be found in the sudden change in slope of the incremental resistivity vs. temperature curve, and in the appearance of the critical peak in A.C. susceptibility measurements at low magnetic fields. Following Ehrenfest (1933) one classifies a phase transition in a system according to the behavior of the system's Gibbs potential energy G . Thermodynamically

$$G = U - TS - MH$$

where U is the internal energy, T is the temperature, S is the entropy, M is the magnetization, and H is the magnetic field. In general U is a function of pressure and volume besides other variables. However, for metals in general and the Pd-Mn system in particular, the volume change in response to a pressure change of less than one atmosphere is negligible. Hence the sample volume and pressure can be considered constant throughout this thesis. Therefore $G = G(T, H)$, and $dG = -SdT - MdH$. Ehrenfest classifies a phase transition as first order if at the point of transition (T_C, H_C), the first order derivatives of G , i.e.

$$\left(\frac{\partial G}{\partial T}\right)_H \quad \text{and} \quad \left(\frac{\partial G}{\partial H}\right)_T$$

are discontinuous. One consequence of this discontinuity is the discontinuity in the entropy, and hence a non-zero latent heat of transition. ($\Delta Q = T\Delta S$). The boiling of water under normal atmospheric pressure is a good example of a first order transition. The ferromagnet to paramagnet transition in the ferromagnetic Pd-Mn alloys is classified as a second order phase transition. Hence the first order derivatives of G with respect to T and H

$$\left(\frac{\partial G}{\partial T}\right)_H \quad \text{and} \quad \left(\frac{\partial G}{\partial H}\right)_T$$

are continuous at the critical point, while the second order derivatives

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_H, \quad \left(\frac{\partial^2 G}{\partial H^2}\right)_T, \quad \left(\frac{\partial^2 G}{\partial T \partial H}\right)$$

are discontinuous at the critical point. There is no latent heat of transition, but the specific heat, the magnetization and the susceptibility, etc. diverge as T approaches T_c . One way to describe this divergence of properties is by means of critical indices.

2.2.2 Critical Indices

Experimentally it is found that the divergent behaviours of many thermodynamic properties during a second order phase transition can be adequately described by a one term power series of a thermodynamic variable, provided that the state of the sample is sufficiently close to the transition point. For example,

let
$$\chi = \chi(T, H)$$

and
$$\epsilon = \frac{T - T_c}{T_c}$$

Then $\chi(T,0)$ is found to behave as $\epsilon^{-\gamma}$ for $T > T_c$

Symbolically, $\chi(T,0) \sim \epsilon^{-\gamma}$ for $T > T_c$

γ is a constant, called a critical index.

Note that this definition of a critical index does not differentiate between the cases when

$$\chi(T,0) = \text{constant} \times \epsilon^{-\gamma}$$

and
$$\chi(T,0) = \epsilon^{-\gamma} \{ 1 + B_1 \epsilon^{x_1} + B_2 \epsilon^{x_2} + B_3 \epsilon^{x_3} + \dots \} \quad (2.2.1)$$

where $B_1, B_2, B_3, \dots$ are constants

and $x_1, x_2, x_3, \dots$ are constants > 0 .

For the latter case, when the temperature is sufficiently close to T_c the correction terms in Eq. 2.2.1 are negligible, and $\chi(T,0)$ is proportional to $\epsilon^{-\gamma}$ again.

Similarly, one can define γ' for $T < T_c$

as
$$\chi(T,0) \sim (-\epsilon)^{-\gamma'}, \quad T < T_c$$

which describes the dominant behaviour of $\chi(T,0)$ as the temperature approaches T_c from below. Other critical indices can be treated in the same manner:

For specific heat

$$C_H(T,0) \sim (-\epsilon)^{-\alpha'}, \quad T < T_c$$

$$C_H(T,0) \sim \epsilon^{-\alpha}, \quad T > T_c$$

For magnetization

$$M(T_C, H) \sim H^{1/\delta}, \quad T = T_C$$

As the spontaneous magnetization is 0 above T_C , β' is not defined.

$$M(T, 0) \sim (-\epsilon)^\beta, \quad T < T_C$$

Here, H is the internal magnetic field defined as

$$H = H_a - NM$$

where H_a is the externally applied magnetic field, N is the demagnetizing factor, and M is the magnetization per unit volume. There are other critical indices like ν, η etc., describing the behaviour of the correlation length, pair correlation function, etc. near the critical point. The reader is referred to Stanley (1971, p.45) for an extensive list of the critical indices.

It may seem that one can define one critical index for every thermodynamic function one can find. However, just as in thermodynamics where only 2 independent variables suffice to characterize the state of a sample, the critical indices are not all independent. There are many inequalities limiting their variation, eg. (Stanley 1971).

$$\alpha' + 2\beta + \gamma' \geq 2 \quad (2.2.2)$$

$$\alpha + \beta(\delta+1) \geq 2 \quad (2.2.3)$$

$$\gamma' \geq \beta(\delta-1) \quad (2.2.4)$$

If one further assumes the correctness of the scaling law hypothesis (discussed in Section 2.2.4 below), then these inequalities become equalities, and are hence solvable as simultaneous equations. The result is that only 2 of the critical indices remain unknown, and the

behavior of a sample near the critical point can be completely specified by them.

Further, the critical indices for different substances in the same dimensional space e.g. 1-D or 3-D, and having the same type of interaction, e.g. Ising or Heisenberg, have very similar critical indices. A considerable amount of theoretical and experimental research is being done to determine whether these critical indices are actually equal --- the idea of universality. Hence the understanding of critical indices becomes very important to the understanding of the second order phase transition. The simplest theory to describe these indices is the Landau theory.

2.2.3 Landau Theory

Landau and Lifshitz (1969) propose that in a second order phase transition, there is an order parameter M such that

$$M = 0 \quad , \quad T \geq T_C$$

$$0 < M \leq 1 \quad , \quad T < T_C$$

M can be the spontaneous magnetization M in a ferromagnet to paramagnet transition. As the temperature T approaches T_C , M is small, and they further postulate that the Helmholtz free energy F can be expanded as a power series in M

$$F = F_0 + AM^2 + cM^4 + O(M^6)$$

where F_0 is a constant and A, c depend on T only. Only even powers of M are necessary because F must be an even function of M . The series is truncated after the 4th power in M . Further, assume that

$$A \approx A^* (T - T_C)$$

where A^* is a constant, and that c is equal to the value of c at T_C .

Then
$$F = F_0 + A^*(T-T_C)M^2 + cM^4$$

and the Gibb's energy is

$$\begin{aligned} G &= F - MH \\ &= F_0 + A^*(T-T_C)M^2 + cM^4 - MH \end{aligned} \quad (2.2.5)$$

Landau and Lifshitz themselves point out (1969, p. 429) that

the basis for the series expansion in Eq. 2.2.5 is not clear.

Nevertheless because of its simplicity, people have built upon it a theory of critical indices under the name Landau theory.

From thermodynamics, an equilibrium state occurs at minimum G .

Hence, starting from Eq. 2.2.5

$$0 = \frac{\partial G}{\partial M} = 2A^*(T-T_C)M + 4cM^3 - H$$

$$\frac{H}{4} = \frac{A^*(T-T_C)}{2}M + cM^3$$

Define scaled parameters

$$h = H/4, \quad \epsilon = \frac{T-T_C}{T_C}, \quad a = A^*T_C/2.$$

Then
$$h = a\epsilon M + cM^3 \quad (2.2.6)$$

This is the equation of state in the Landau theory, from which the critical indices can be easily calculated, as follows:

(i) At $T = T_C$, $\epsilon = 0$

From Eq.(2.2.6) $h = cM^3$

Therefore $M \sim h^{1/3}$

and $\delta = 3.00$

(ii) As $h \rightarrow 0$, $\epsilon > 0$.

Then M is small. Taking only the leading term

$$h \sim a\epsilon M$$

$$\chi = \frac{M}{h} \sim \epsilon^{-1}$$

Therefore $\gamma = 1.00$

(iii) For $\epsilon < 0$, $h = 0$, $M \neq 0$

From Eq. 2.2.6 $0 = a\epsilon M + cM^3$

$$a(-\epsilon) M = cM^3$$

$$M \sim (-\epsilon)^{1/2}$$

Therefore $\beta = \frac{1}{2}$

One finds that Vidom's equality

$$\gamma = \beta(\delta-1)$$

is satisfied for these critical indices. Unfortunately, these critical indices do not agree with experiment close to T_c . For example, in nickel (Stanley 1971, p. 47)

$$\beta = 0.42, \quad \gamma = 1.35, \quad \delta = 4.22$$

Clearly other approaches are needed.

2.2.4 Scaling Law Hypothesis

One approach is that there are a lot of inequalities limiting the range of values the critical indices can take. Some of these inequalities are rigorous in the sense that they are only based on thermodynamics and the existence of the indices. Other inequalities require further assumptions on the properties of the sample. For example, Eq. 2.2.2 and 2.2.3 referred to above are rigorous while Eq. 2.2.4 requires two extra conditions for its existence:

$$1. \quad \left(\frac{\partial H}{\partial T} \right)_M = - \left(\frac{\partial S}{\partial M} \right)_T \geq 0 \quad \text{for } M \geq 0$$

$$2. \quad \left(\frac{\partial^2 H}{\partial M^2} \right)_T \geq 0 \quad \text{for } M \geq 0, \quad T \geq T_C$$

For further listings and proofs of these inequalities see Stanley (1971, Ch. 4).

While these inequalities are always obeyed in physical measurements, one finds that if the experimental uncertainties in the values of the critical indices are included in the analysis, the inequalities are often satisfied as equalities. Up to now, a rigorous theory to prove these equalities has not been found, but a very plausible hypothesis, the scaling law hypothesis, was proposed by Widom (1965).

The scaling law hypothesis states that Gibb's potential energy $G(\epsilon, H)$ is a generalized homogeneous function. By this, it is meant that there exist two parameters a, b such that

$$G(\lambda^a \epsilon, \lambda^b H) = \lambda G(\epsilon, H) \quad (2.2.7)$$

for any value of the number λ .

Here
$$\epsilon = \frac{T - T_C}{T_C}$$

and H is the internal magnetic field. Starting with this hypothesis, one can express all critical indices in terms of a and b . For example, by differentiating Eq. 2.2.7 with respect to H , one gets

$$\frac{\partial^b}{\partial (\lambda^b H)} \frac{\partial^a}{\partial (\lambda^a \epsilon)} G(\lambda^a \epsilon, \lambda^b H) = \lambda \frac{\partial}{\partial H} G(\epsilon, H)$$

$$\lambda^b M(\lambda^a \epsilon, \lambda^b H) = \lambda M(\epsilon, H)$$

since $M = \frac{-\partial G}{\partial H}$

$$\text{Therefore } M(\epsilon, H) = \lambda^{b-1} M(\lambda^a \epsilon, \lambda^b H) \quad (2.2.8)$$

If $H = 0$, the above equation reduces to

$$M(\epsilon, 0) = \lambda^{b-1} M(\lambda^a \epsilon, 0)$$

Since this equation is true for every λ ,

$$\text{let } \lambda = (-\epsilon)^{-1/a}$$

$$\text{Then } M(\epsilon, 0) = (-\epsilon)^{\frac{1-b}{a}} M(-1, 0)$$

$$\text{i.e. } M(\epsilon, 0) \sim (-\epsilon)^{\frac{1-b}{a}}$$

Comparing with the definition of β

$$M(\epsilon, 0) \sim (-\epsilon)^\beta, \quad \epsilon < 0$$

$$\text{one gets } \beta = \frac{1-b}{a} \quad (2.2.9)$$

Similarly from Eq. 2.2.8, take the case $\epsilon = 0$.

$$\text{Then } M(0, H) = \lambda^{b-1} M(0, \lambda^b H)$$

$$\text{Set } \lambda = H^{-1/b}$$

$$M(0, H) = H^{\frac{1-b}{b}} M(0, 1)$$

$$\text{i.e. } M(0, H) \sim H^{\frac{1-b}{b}}$$

Comparing with the definition of δ

$$M(0, H) \sim H^{1/\delta} \quad \text{for } H \rightarrow 0$$

one gets
$$\delta = \frac{b}{1-b} \quad (2.2.10)$$

γ' can be found as follows:

Differentiate Eq. 2.2.8 with respect to H again

$$\frac{\partial M(\epsilon, H)}{\partial H} = \lambda^{2b-1} \frac{\partial M(\lambda^a \epsilon, \lambda^b H)}{\partial \lambda^b H}$$

$$\chi(\epsilon, H) = \lambda^{2b-1} \chi(\lambda^a \epsilon, \lambda^b H) \quad (2.2.11)$$

since
$$\chi = \left(\frac{\partial M}{\partial H} \right)_T$$

Let $H=0$ and $\lambda = (-\epsilon)^{-1/a}$

$$\chi(\epsilon, 0) = (-\epsilon)^{-\frac{2b-1}{a}} \chi(-1, 0)$$

$$\chi(\epsilon, 0) \sim (-\epsilon)^{-\frac{2b-1}{a}}$$

Comparing with the definition of γ'

$$\chi(\epsilon, 0) \sim (-\epsilon)^{-\gamma'} \quad \text{for } \epsilon < 0$$

one gets
$$\gamma' = \frac{2b-1}{a} \quad (2.2.12)$$

It is straightforward to show that the equations 2.2.9, 2.2.10 and 2.2.12 can be combined to give

$$\gamma' = \beta(\delta-1)$$

which was first derived by Widom (1965).

Moreover, in Eq. 2.2.11 set $H=0$, and $\lambda = \epsilon^{-1/a}$

$$\text{Then } \chi(\epsilon, 0) = \epsilon^{-\frac{2b-1}{a}} \chi(1, 0)$$

Comparing with the definition of γ

$$\chi(\epsilon, 0) \sim \epsilon^{-\gamma} \quad \text{for } \epsilon > 0$$

$$\begin{aligned} \text{one gets } \gamma &= \frac{2b-1}{a} \\ &= \gamma' \end{aligned}$$

In fact, if one keeps on calculating all the critical indices in terms of a and b within the scaling law hypothesis, one finds that the two critical indices for the same thermodynamic variable below and above T_c are equal. Further, replacing a and b by the critical indices results in a host of equalities e.g.

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \\ \alpha + \beta(\delta+1) &= 2 \\ \gamma(\delta+1) &= (2-\alpha)(\delta-1) \\ \gamma &= \beta(\delta-1) \\ \beta\delta &= \beta + \gamma \end{aligned}$$

Solution of these equations as a set of simultaneous equations reduces the number of unknown indices to 2. Hence, within the scaling law hypothesis all the behaviour of a sample near the critical point can be found if one knows either a and b , or any two critical indices. In actual experiments, a and b are hard to measure, and one has to

settle for the critical indices instead.

In this project, the indices γ and δ are extracted from the A.C. susceptibility data. The scaling law hypothesis is modified to suit the experimental conditions in a manner communicated privately by Dr. B. Nickel (University of Guelph).

From Eq. 2.2.8, set $\lambda = \epsilon^{-1/a}$

$$\begin{aligned} M(\epsilon, H) &= \epsilon^{\frac{1-b}{a}} M\left(1, \frac{H}{\epsilon^{b/a}}\right) \\ &= \epsilon^{\beta} M\left(1, \frac{H}{\epsilon^{\gamma+\beta}}\right) \end{aligned} \quad (2.2.13)$$

since $\beta = \frac{1-b}{a}$ and $\gamma+\beta = \frac{b}{a}$.

This is the equation of state in the scaling law hypothesis, from which one can calculate the susceptibility as $\chi = \left(\frac{\partial M}{\partial H}\right)_T$

$$\chi = \epsilon^{\beta} \frac{1}{\epsilon^{\gamma+\beta}} M'\left(\frac{H}{\epsilon^{\gamma+\beta}}\right)$$

where $M'(x) = \frac{dM(x)}{dx}$

$$\begin{aligned} \text{Hence } \chi &= \frac{1}{\epsilon^{\gamma}} M'\left(\frac{H}{\epsilon^{\gamma+\beta}}\right) \\ &= \left(\frac{1}{\epsilon^{\gamma+\beta}}\right)^{\frac{\gamma}{\gamma+\beta}} M'\left(\frac{H}{\epsilon^{\gamma+\beta}}\right) \\ &= H^{-\frac{\gamma}{\gamma+\beta}} \left(\frac{H}{\epsilon^{\gamma+\beta}}\right)^{\frac{\gamma}{\gamma+\beta}} M'\left(\frac{H}{\epsilon^{\gamma+\beta}}\right) \end{aligned}$$

$$= H^{-\frac{\gamma}{\gamma+\beta}} G\left(\frac{H}{\epsilon^{\gamma+\beta}}\right) \quad (2.2.14)$$

$$\text{where } G\left(\frac{H}{\epsilon^{\gamma+\beta}}\right) \equiv \left(\frac{H}{\epsilon^{\gamma+\beta}}\right)^{\frac{\gamma}{\gamma+\beta}} M'\left(\frac{H}{\epsilon^{\gamma+\beta}}\right)$$

To find the maximum of χ at a fixed H , one set $\frac{d\chi}{d\epsilon} \Big|_{\epsilon = \epsilon_m} = 0$

$$0 = H^{-\frac{\gamma}{\gamma+\beta}} \left(-\frac{(\gamma+\beta)H}{\epsilon_m^{\gamma+\beta+1}} \right) G'\left(\frac{H}{\epsilon_m^{\gamma+\beta}}\right)$$

For typical values of γ and β ,

$$\begin{aligned} \gamma + \beta &\approx 1.3 + 0.5 \\ &= 1.8 \\ &\neq 0 \end{aligned}$$

The above equation then implies

$$G'\left(\frac{H}{\epsilon_m^{\gamma+\beta}}\right) = 0$$

For this equation to be true for every H and every ϵ_m , the argument of the function G' has to be constant.

$$\text{Therefore } \frac{H}{\epsilon_m^{\gamma+\beta}} = \text{constant} \quad (2.2.15)$$

$$\epsilon_m \sim H^{\frac{1}{\gamma+\beta}}$$

Using the definition of ϵ_m ,

$$\frac{T_m - T_c}{T_c} \sim H^{\frac{1}{\gamma+\beta}}$$

$$T_m \sim T_c H^{\frac{1}{\gamma+\beta}} + T_c \quad (2.2.16)$$

Hence a curve of T_m (the temperature when χ is maximum under a particular H) vs. $H^{\frac{1}{\gamma+\beta}}$ is a straight line and intercepts the Y-axis at T_c .

One can substitute Eq. 2.2.15 into Eq. 2.2.14 to obtain the behaviour of χ at T_m

$$\chi_m(T_m, H) = H^{-\frac{\gamma}{\gamma+\beta}} G(\text{constant})$$

$$\chi_m(T_m, H) \sim H^{-\frac{\gamma}{\gamma+\beta}}$$

$$\text{Using } \frac{\gamma}{\gamma+\beta} = \frac{\beta(\delta-1)}{\beta\delta} = \frac{\delta-1}{\delta} = 1 - \frac{1}{\delta}$$

one gets

$$\chi_m(T_m, H) \sim H^{\frac{1}{\delta} - 1} \quad (2.2.17)$$

It follows that χ_m , measured at temperatures $T_m \neq T_c$, obeys the same power law as one would expect from formally differentiating the equation defining δ

$$M(T_c, H) \sim H^{1/\delta}, \quad T = T_c.$$

The advantage of using Eq. (2.2.17) instead of the above equation is that a knowledge of T_C is not necessary. Eq. 2.2.17 has been experimentally verified by Gaunt et al (1981). The critical index γ can be found by using the definition

$$\chi(T,0) \sim \epsilon^{-\gamma}, \quad T > T_C$$

The description of the ferromagnet to paramagnet transition is thus complete, if one assumes the validity of the scaling law hypothesis. Experimental verification of the hypothesis is possible if one measures other critical indices and compare them with the scaling law predictions. This has been found to be generally true for other systems, e.g. Stanley (1971). For the Pd-Mn system here, this has not been followed through due to limitations in time and equipment.

Rigorous theoretical justification of the hypothesis is not available presently; but one can mention the Kadanoff construction of cells (1967) and Wilson's renormalization group method (1971) as possible candidates for a solution.

2.3 Theories of Resistivity of Ferromagnetic Pd-Mn Alloys

Besides susceptibility measurements, the ferromagnet to paramagnet transition can also be investigated through D.C. resistivity measurements. The theoretical models employed here are proposed by Yosida (1957) and by Long and Turner (1970).

2.3.1 Simple s-d Model

Yosida summarizes the interaction between Mn impurities at $\vec{R}_n$ and the host conduction electrons at $\vec{r}_i$ with the perturbation

Hamiltonian

$$\mathcal{H} = \sum_i \sum_n V(\vec{r}_i - \vec{R}_n) - 2 \sum_i \sum_n J(\vec{r}_i - \vec{R}_n) \vec{s}_i \cdot \vec{S}_n$$

where $V(\vec{r}_i - \vec{R}_n)$ is the deviation of the spin-independent potential due to the Mn ion and $J(\vec{r}_i - \vec{R}_n)$ is the effective exchange integral between the conduction electron and the Mn ion.

The main assumptions in his model are:

1. Effective mass approximation for conduction electron energy.
2. That the Fourier transformed V and J depend on $|\vec{k} - \vec{k}'|$ only, where $\vec{k}$ is the electronic wave vector.
3. Molecular field approach.
4. That Mn ions are randomly distributed, with no interference of waves scattered from different ions.

The change in Fermi sphere due to an applied electric field is calculated via the Boltzmann equation, while the transition probabilities for the elastic and the inelastic collisions are calculated to first order only using Fermi's Golden Rule. The shift in Fermi

sphere then gives rise to a resistivity expressed in Eq. 19 of Yosida's 1957 paper.

This calculation was initially applied to ordering in Cu-Mn alloys. Williams and Loram (1969b) have extended this model to include ferromagnetic ordering in Pd-Mn alloys. In the limit of strong potential scattering, they find

$$\Delta\rho(T=0) = \frac{3\pi}{2} \frac{m^*}{e^2} \frac{1}{\hbar E_F} \Omega c V^2$$

where m^* is the effective mass of conduction electrons, e is the electronic charge, Ω is the effective volume of Pd atom, E_F is the Fermi energy, c is the Mn concentration and V is the amplitude of $V(\vec{r}_i - \vec{R}_n)$. Using an effective mass approximation with $m^* = 2.2$ electron mass and 0.36 s electrons per atom (Vuillemin 1966), one finds $E_F = 1.4$ eV. Subsequently, the above equation simplifies to

$$\Delta\rho(T=0) = 5.78 c V^2 (\mu\Omega\text{cm}) \quad (2.3.1)$$

Further

$$\Delta\rho(T_C) = 5.78 c \left[|J|^2 S(1 + 4S) + V^2 \right] \quad (2.3.2)$$

$$\text{and} \quad \Delta\rho(T_C) - \Delta\rho(T=0) = 5.78 c |J|^2 S(1 + 4S) \quad (2.3.3)$$

These equations will be used to compare with experimental data in Chapter IV.

2.3.2 Simple s-d Model with Collective Excitations

This model is an improvement over Yosida's model because while Yosida considers only the interaction between s electrons and the Mn ions, Long and Turner (1970) have included the d-holes as well (0.36 holes per atom as found by Vuillemin, 1966). See Fig. 2.3.1. Interactions among the d-holes, s-electrons, and the impurity spin as calculated by the authors appear to fit the available data on the ferromagnetic phase of Pd-Mn and other alloy systems (Williams and Loram, 1969 a, 1969 b).

Long and Turner phenomenologically sum up the interactions in six terms

$$1. \quad H_{dI} = J \sum_n p_n \vec{S}_n \cdot \vec{\sigma}_d(\vec{R}_n)$$

where

$$p_n = \begin{cases} 1 & \text{if } \vec{R}_n \text{ is an impurity site} \\ 0 & \text{if } \vec{R}_n \text{ is not an impurity site} \end{cases}$$

$\vec{S}_n$ is the spin on the impurity site

$$\vec{\sigma}_d(\vec{R}_n) = \frac{1}{N} \sum_{\vec{k} \vec{q} \alpha \beta} \sum_{\vec{d} \vec{k} + \vec{q} \alpha} \sum_{\vec{d} \vec{k} \beta} c_{\vec{d} \vec{k} + \vec{q} \alpha}^\dagger c_{\vec{d} \vec{k} \beta} \vec{\sigma}_{\alpha \beta} \exp(i \vec{q} \cdot \vec{R}_n)$$

$\vec{\sigma}_d$ is the spin density of the d-band holes.

$c_{\vec{d} \vec{k} \alpha}^\dagger$ and $c_{\vec{d} \vec{k} \alpha}$ are creation and annihilation operators for the d-band

holes.

$\vec{\sigma}_{\alpha \beta}$ are the Pauli spin matrices and N is the total number of atoms in the alloy. This term represents the interaction between the d-holes of Pd and the impurity spins.

Density
of State

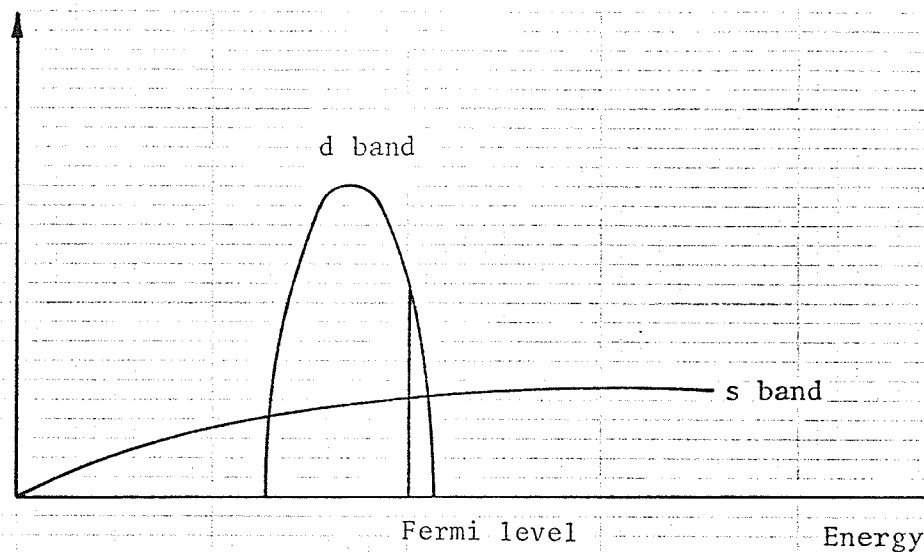


Fig. 2.3.1

Very schematic diagram of density of state of
palladium.

$$2. \quad H_d = \sum_{\vec{k}\alpha} \epsilon_d(\vec{k}) c_{\vec{k}\alpha}^\dagger c_{\vec{k}\alpha} + I \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\text{where } n_{i\uparrow} = \frac{1}{N} \sum_{\vec{k}q} c_{\vec{k}q}^\dagger c_{\vec{k}q+\vec{q}\uparrow} c_{\vec{k}\uparrow} \exp(i\vec{q} \cdot \vec{R}_i)$$

The first term in H_d sums the individual kinetic energy of the d-holes while the second term represents the strong repulsion between d-holes of opposite spin because they are highly localized on the Pd site.

$$3. \quad H_{ds} = U \sum_n \vec{\sigma}_d(\vec{R}_n) \cdot \vec{\sigma}_s(\vec{R}_n)$$

$$\text{where } \vec{\sigma}_s(\vec{R}_n) = \frac{1}{N} \sum_{\vec{k}q\alpha\beta} c_{\vec{k}q\alpha}^\dagger c_{\vec{k}q+\vec{q}\alpha} c_{\vec{k}\beta} \vec{\sigma}_{\alpha\beta} \exp(i\vec{q} \cdot \vec{R}_n)$$

$c_{\vec{k}q\alpha}^\dagger$ and $c_{\vec{k}q\alpha}$ are creation and annihilation operators for the s electrons.

This term represents the interaction between d-holes and s-electrons.

$$4. \quad H_{sI} = J \sum_n p_n \vec{S}_n \cdot \vec{\sigma}_s(\vec{R}_n)$$

Similar to H_{dI} , this term represents the exchange interaction between s electron and the impurity spin.

$$5. \quad V \sum_{\vec{k}q\alpha} \sum_n p_n c_{\vec{k}q\alpha}^\dagger c_{\vec{k}q+\vec{q}\alpha} \exp(i\vec{q} \cdot \vec{R}_n)$$

where $V = \int a^*(r) V^{\text{HF}}(r) a(r) dr$.

$a(r)$ are the Wannier functions of the s electrons on the $S_n = 0$ site.

This term represents the interaction between s electrons and the Hartree - Fock potential V^{HF} due to the valence difference between host and impurity.

$$6. \quad \sum_{\vec{k}\alpha} \epsilon_s(\vec{k}) \quad c_{s\vec{k}\alpha}^\dagger \quad c_{s\vec{k}\alpha}$$

This term sums the individual kinetic energy $\epsilon_s(\vec{k})$ of the s -electrons.

In the above 6 terms, J , I , U and J' are coupling constants to the various interactions.

The dynamical states of the impurity spins and the d -holes are approximated at low temperature by spin waves, and near the critical temperature T_c by independent spins moving in a molecular field.

The scattering of s electrons from a d -hole impurity spin pair is taken care of by substituting J_{eff} for J' .

$$J_{\text{eff}} \sim J' + U \bar{\chi}_{\text{pd}}(0,0)J$$

where $\bar{\chi}_{\text{pd}}(0,0)$ is the Pauli susceptibility χ_0 enhanced by the factor

$$(1 - I \chi_0)^{-1}$$

The incremental resistivity

$$\Delta\rho(T) = \rho(T)_{\text{alloy}} - \rho(T)_{\text{pd}}$$

is calculated using the Boltzmann equation in a similar manner to Yosida's calculation.

The result

$$\Delta\rho(T) = Ac + \frac{B}{c} T^{3/2}, \quad T \rightarrow 0 \quad (2.3.4)$$

$$\Delta\rho(T) \propto (T_C - T), \quad T \rightarrow T_C^- \quad (2.3.5)$$

$$\Delta\rho(T) = \text{constant}, \quad T \rightarrow T_C^+ \quad (2.3.6)$$

A and B are parameters independent of temperature T and Mn concentration c, but are related to various band parameters. Because of its assumption of low-lying excitations during some stages of its calculation, this theory will fail at high temperatures. For a homogeneous ferromagnet at low temperature, one expects in Eq. 2.3.4 a T^2 temperature dependence due to electron magnon scattering. The Mn moments in the alloy system are, however, randomly distributed, and the T^2 dependence gives way to a $T^{3/2}$ dependence due to breaking of translational symmetry.

The temperature dependence in Eq. 2.3.4 and 2.3.5 are well obeyed by the ferromagnetic Pd-Mn alloys investigated. The c-dependence in Eq. 2.3.4 is good for the parameter A and within 7% for B. Eq. 2.3.6 is approximately obeyed by the ferromagnetic alloys with the deviation increasing with Mn concentration. A detailed comparison between theory and data will be presented in Chapter IV.

A corollary of this theory explains the "knee" in the $\Delta\rho$ vs. T curve for ferromagnets. Experimentally, one finds that when a ferromagnet is cooled from the paramagnetic to the ferromagnetic state, the incremental resistivity in the $\Delta\rho$ vs. T curve decreases abruptly at $T = T_C$. Long and Turner's theory explains it as resulting from

the different coefficients of the same T dependence in Eq. 2.3.5 and 2.3.6. (The coefficient for T in Eq. 2.3.6 is 0.) Physically, as pointed out by Mott and Jones (1936), a magnetically ordered solid is more symmetrical than a disordered one (paramagnet), and as a symmetrical solid scatters electrons coherently, it does not contribute to electrical resistivity. Therefore the resistivity of a solid decreases with increase in orderliness.

2.4 Theories of Spin Glass Ordering

2.4.1 Introduction

From ~5.0 to ~25 at %, the Pd-Mn alloys are spin glass like. The term "spin glass" is due to Coles (1973) and is used to denote an alloy of a small amount of magnetic impurity dissolved in a noble metal host, e.g. AuFe, CuMn. Below the ordering temperature T_{sg} the impurity moments are supposed to be locked into random but fixed positions in space, resulting in zero net moment. Hence the idea of a "glass". The interaction among impurity moments is usually taken to be of the unenhanced R.K.K.Y. type, while the main observable characteristics are a cusp at T_{sg} in the A.C. susceptibility at low magnetic field, $T^{3/2}$ dependence for the incremental resistivity as $T \rightarrow 0$, and a broad incremental resistivity maximum above T_{sg} (Mydosh, 1977).

At present there is no theory that can adequately describe all the properties of spin glass systems, not to mention the Pd-Mn alloys with Mn concentration ≥ 5 at %. The main reason is that in addition to the R.K.K.Y. interaction usually discussed in spin glass theories, there is an additional short-ranged Mn-Mn interaction described in Section 2.1.1, which has not been taken into account in these theories. Further, the majority of them utilize only the long-ranged part of the R.K.K.Y. interaction, i.e.

$$\text{interaction energy} \sim \frac{\cos\left(\frac{2k_F r}{F}\right)}{(2k_F r)^3}$$

while the full interaction contains a short-ranged part also,

$$\text{interaction energy} \sim \frac{\sin(2k_F r)}{(2k_F r)^4}$$

The long-range approximation is justified for ordinary spin glasses as follows:

The Fermi vector k_F is of the order of (lattice spacing) $^{-1}$. r is of the order of several hundred lattice spacings if only a few impurity spins are evenly distributed in a macroscopic sample. Then $2k_F r \gg 1$ and $(2k_F r)^{-4}$ can be discarded in comparison to $(2k_F r)^{-3}$.

For the Pd-Mn alloys, however, the Pd conduction electrons and the Mn spins interact to form giant moments around the impurity sites, thus pushing the effective distance of the R.K.K.Y. interaction to greater distance from the Mn site, as discussed in Section 2.1.2. Thus the Mn spins have a greater chance of "seeing" one another than when giant moments are not present.

The full Hamiltonian i.e.

$$\text{energy} \sim \frac{\sin(2k_F r) - 2k_F r \cos(2k_F r)}{(2k_F r)^4}$$

should be used, and calculated to beyond next nearest neighbor distance, since the R.K.K.Y. interaction is limited only by a factor $e^{-r/\ell}$, discussed in Section 2.1.2. Published calculations, nevertheless, are usually up to nearest or next nearest neighbor distances because of the immense mathematical labour involved.

In spite of the above short-comings, the models have been

developed with some experimental characteristics of spin glasses in mind; so they correctly describe some of the characteristics. However, no single model can include all of them at the same time. Hence in this section, several of the main models have been outlined, and a detailed comparison with experimental data will be attempted in Chapter IV.

2.4.2 Elementary Excitation Model

Some of the Pd-Mn spin glass alloys show a $T^{3/2}$ dependence for their incremental resistivity at low temperature T . Rivier and Adkins (1975) have proposed a model based on the scattering of electrons by spin diffusion modes of very long lifetimes to account for such effects.

They start with the general formula for conductivity in metallic systems (Mott and Jones, 1936).

$$\sigma = \frac{2}{3} e^2 v_F^2 \rho_F \int d\epsilon \left(-\frac{\partial f}{\partial \epsilon} \right) \tau_r(\epsilon)$$

where σ is the conductivity, v_F is the Fermi velocity of conduction electrons, ρ_F is the density of state at Fermi level, $f(\epsilon)$ is the Fermi function and $\tau_r(\epsilon)$ is the relaxation time of an electron with energy ϵ . The "Fermi window" $\frac{\partial f}{\partial \epsilon}$ is approximated by a delta

function, and the approximations of isotropic medium, multiple scattering and S-wave only are applied. The interaction between spins is taken to be the usual R.K.K.Y. type,

$$\text{energy} \sim \frac{\cos r}{r^3},$$

and a Lorentzian conduction band of width Γ is assumed. For low temperatures, when only spin diffusive modes of very long wavelengths can be excited, Rivier and Adkins predict

$$\rho(T) = \rho(\infty) [1 - D(1 - CDT^{3/2})]$$

where $\rho(T)$ = resistivity due to impurity spins

$$\rho(\infty) = 3 c \Gamma / (2 e^2 v_F^2 \rho_F \hbar)$$

c = concentration of impurity

C and D are parameters.

If one identifies the impurity resistivity as the incremental resistivity $\Delta\rho$, then

$$\Delta\rho \sim T^{3/2}, \quad T \rightarrow 0$$

Rivier and Adkins expect that there will be deviations from the $T^{3/2}$ law if some of the diffusive modes with the slowest damping rates are prohibited by non-magnetic impurities, and/or surface or grain boundaries. They suggest that the new dependence will be

$$\Delta\rho \sim T^2, \quad T \rightarrow 0$$

Some of the Pd-Mn alloys studied here show a $T^{3/2}$ limiting form in their incremental resistivity, while others show a T dependence instead of $T^{3/2}$ or T^2 . The possibility of a linear T dependence is discussed in the following model.

2.4.3 Short Range Interaction Model

In Section 2.1.2 above it is claimed that the factor $e^{-r/\ell}$ used to take care of defect effects in the R.K.K.Y. interaction is approximately 1. One can visualize this by an order of magnitude estimate (Abrikosov, 1980).

In an alloy with magnetic impurities,

$$r \sim \text{average interspin distance} \sim n_m^{-1/3}$$

where n_m is the volume concentration of magnetic impurities.

In the absence of other defects

$$\ell \sim (n_m a^2)^{-1}$$

where a is the lattice parameter

$$\text{then } \frac{r}{\ell} \sim \frac{n_m^{-1/3}}{(n_m a^2)^{-1}} \sim n_m^{2/3} a^2 \sim c_m^{2/3} \ll 1,$$

where c_m is the concentration in atomic % of magnetic impurities.

Hence

$$e^{-r/\ell} \sim e^{-c_m^{2/3}} \sim 1$$

Abrikosov further argues that the case $r/\ell \gg 1$ is also possible, if non-magnetic impurities of concentration c_i are also present.

$$\text{Then } \frac{r}{\ell} \sim \frac{n_m^{-1/3}}{\ell} \sim \frac{c_i}{c_m^{1/3}}$$

If $c_i \gg c_m^{1/3}$, then $r/\ell \gg 1$, and the R.K.K.Y. interaction

becomes short-ranged. In the extreme case, only nearest neighbour interactions need to be considered.

In this model, at low temperatures, when the interaction energy among spins is much larger than the thermal energy, every spin is under the influence of only its nearest neighbour. This nearest neighbour itself is locked into another nearest neighbour, and so on. Hence the resultant effect on any spin is an effective field

$$H = V_0 S \frac{\cos 2k_F r}{r^3} e^{-r/\ell}$$

where S is the impurity spin.

V_0 is some coefficient with suitable dimensions.

Using this molecular field, the free energy is found to be

$$F = -T \ln \frac{\sinh[(S+1/2)H/T]}{\sinh(H/2T)}$$

The susceptibility χ is, for $T \ll T_0$, (T_0 is a characteristic temperature)

$$\chi = (3\pi^{3/2})^{-1} \frac{\mu}{V_0} (4\pi n_m \ell^3)^{-3/4} \\ \times \exp\left[\frac{2}{3} (4\pi n_m \ell^3)^{-1/2}\right] \ln(T_0/T).$$

where μ is such that μS is the magnetic moment of impurity spin S .

$$T_0 \sim V_0 S \ell^{-3} (4\pi n_m \ell^3)^{7/4} \exp[-(4\pi n_m \ell^3)^{-1/2}]$$

At a higher temperature, near the temperature of the susceptibility peak T_{sg} , Abrikosov uses a percolation approach. As the interaction between spins is short-ranged, he defines a thermal radius $r(T)$ such that spins separated by a distance less than $r(T)$

will interact, while those separated more than $r(T)$ will not. The percolation parameter p is defined as

$$p = n_m \frac{4\pi}{3} \left(\frac{r(T)}{2} \right)^3$$

The percolation limit is at $p_c = 0.347$.

T_{sg} is given as

$$T_{sg} = \frac{\pi}{6p_c} V_0 S^2 n_m \exp \left[- \left(\frac{6p_c}{\pi} \right)^{1/3} (n_m^{1/3} \lambda)^{-1} \right]$$

The susceptibility at T_{sg} is

$$\chi = \exp \left[- \frac{4\pi}{3} \right] \mu^2 n_m S(S+1) / 3T_{sg} \quad (2.4.1)$$

For the resistivity calculation, Abrikosov utilizes the Boltzmann equation

$$\begin{aligned} e\vec{E} \left(\frac{\partial f}{\partial \vec{p}} \right) = & -(f_p - f_p^{(0)})/\tau + \frac{1}{(2\pi)^3} \int w_{pp'} \{ -f_p(1 - f_{p'}) \\ & + f_{p'}(1 - f_p) \exp[(\epsilon_p - \epsilon_{p'})/T] \} d^3p \end{aligned}$$

where $\vec{E}$ is the applied electric field, f_p is the distribution function of electrons at any temperature. $f_p^{(0)}$ is the Fermi function, τ is the collision time corresponding to potential scattering with impurities and $w_{pp'}$ is the Born scattering probability from P to P' corresponding to exchange interaction of electrons with magnetic impurities.

f_p is then approximated by

$$f_p \sim f_p^{(0)} + f_p^{(1)} + f_p^{(2)}$$

and the Boltzmann equation is solved by iteration, assuming that

potential scattering dominates. For $T \rightarrow \infty$, he gets

$$\Delta\rho(T \rightarrow \infty) = 12\pi^4 \frac{m n_m V_o S(S+1)}{e^2 k_F^3}$$

where m = mass of electron

For $T \rightarrow 0$, Abrikosov obtains

$$\Delta\rho(T \rightarrow 0) = \Delta\rho(T = 0) + 3\pi^{7/2} \frac{m}{e^2 k_F^3} I(s)$$

$$\times (4\pi n_m)^{3-3/4} \exp\left[\frac{2}{3}(4\pi n_m)^{3-1/2}\right] T$$

$$\text{where } \Delta\rho(T = 0) = 12\pi^4 \frac{m n_m V_o S^2}{e^2 k_F^3}$$

$$I(S) = \int_0^\infty [1 - B_S(x) \frac{\sinh x - x}{\cosh x - 1}] dx$$

$B_S(x)$ is the Brillouin function for spin S .

Hence as $T \rightarrow 0$, Abrikosov predicts, that the incremental resistivity increases linearly with T ,

$$\text{and that } \frac{\Delta\rho(T \rightarrow \infty)}{\Delta\rho(T=0)} = \frac{S(S+1)}{S^2}$$

Except for giving a linear temperature dependence for the incremental resistivity at low temperature, this model is not very successful at describing the behavior of metallic spin glass.

2.4.4 Mean Field Model

The model by Edwards and Anderson (1975, 1976) is one of the most widely used models for spin glasses because it is simple

and based on the classical mean field theory.

These authors consider a spin $\vec{S}_i$ as a classical dipole interacting with another spin $\vec{S}_j$ through an interaction

$$J_{ij} \vec{S}_i \cdot \vec{S}_j$$

If the probability of finding $\vec{S}_i$ at i and $\vec{S}_j$ at j is ϵ_{ij} , then even if

$$\sum_{i,j} J_{ij} \epsilon_{ij} = 0$$

on any scale, macroscopic or microscopic, they argue that the mere existence of a ground state, which needs only be a local minimum, will enable the system to show a cusp in the susceptibility at T_{sg} . This ground state corresponds to some preferred orientation of the spin $\vec{S}_i$ at the bottom of a potential well of depth $\sim k_B T_{sg}$. For temperatures $T > T_{sg}$, the spin does not see this well; but when $T < T_{sg}$, the spin begins to settle into this preferred orientation. Hence below T_{sg} , there is a non-zero probability of finding $\vec{S}_i$ to point at the same direction if one checks it at times (1) and (2). This defines an order parameter

$$q = \langle \vec{S}_i(1) \cdot \vec{S}_i(2) \rangle$$

such that

$$q = 0 \quad T > T_{sg}$$

$$q > 0 \quad T < T_{sg}$$

$$q = 1 \quad T = 0$$

Edwards and Anderson further assumes a Gaussian distribution centered at zero for $J_{ij} \epsilon_{ij}$. The ensemble free energy is calculated

by evaluating the free energy of m replicas of the original system.

They find

$$T_{sg}^2 = \frac{2}{9} J_0^2 / k_B^2$$

where

$$J_0^2 = \sum_{\alpha} J_{i\alpha}^2 \epsilon_{i\alpha}$$

The specific heat is calculated to be

$$C_V = \lambda(1 - q^2) - 4\lambda^2 \frac{\partial q}{\partial \lambda}$$

where

$$\lambda = \rho / \rho_0$$

$$\rho = \frac{2}{3} \left(\sum_{ij} J_{ij}^2 \right) \rho_0^2 / (k_B T)^2$$

and

$$\rho_0 = \text{density of occupation of spins}$$

Edwards and Anderson themselves have pointed out that the above equation does not fit experimental data because it implies a cusp for the specific heat at T_{sg} , which is not experimentally observed.

For the susceptibility, they find

$$\chi = \frac{C}{T}, \quad T > T_{sg}$$

$$\chi = \frac{C}{T_{sg}} - 0(T_{sg} - T)^2, \quad T < T_{sg}$$

where C = Curie constant

There is thus a cusp in the susceptibility vs. temperature curve, but the cusp is not symmetrical about $T = T_{sg}$. χ varies as $1/T$ for $T > T_{sg}$ and quadratically for $T < T_{sg}$, which is not in agreement with experiment; the experimental cusp is frequently found to be symmetrical. The next model represents an improvement on the Edwards and Anderson model.

2.4.5 Improved Mean Field Model

Sherrington and Kirkpatrick (1975) and Sherrington and Southern (1975) have extended the model by Edwards and Anderson to simulate more realistic systems. They consider quantum spins with exchange interactions distributed in a Gaussian fashion about a non-zero mean J_0 .

The Hamiltonian is

$$\mathcal{H} = - \sum_{i < j} \hbar^2 J_{ij} \vec{S}_i \cdot \vec{S}_j$$

with J_{ij} distributed according to a probability distribution

$$P(J_{ij}) = \frac{1}{(2\pi)^{1/2} J} \exp\left[-\frac{(J_{ij} - J_0)^2}{2J^2}\right]$$

where J is the width of the distribution.

J_{ij} also varies with the distance between spins, eg. in R.K.K.Y. interaction

$$J_{ij} \sim \frac{1}{r^3}$$

The interaction is carried up to z neighbours of each spin. The ensemble-averaged free energy is again calculated by the method of replicas as in the previous model. The order parameter is

$$q = \langle S_i^2 \rangle$$

averaged over the J_{ij} distribution, while the magnetization is

$$m = \langle S_i \rangle$$

averaged over the same distribution.

Because of the shifted J_{ij} distribution, the phase diagram of the system under investigation becomes separated into paramagnetic,

spin glass and ferromagnetic regions with different combinations of q and m , namely

$$\begin{aligned} q \neq 0 & \Rightarrow \text{magnetic ordering} \\ q \neq 0, \quad m \neq 0 & \Rightarrow \text{ferromagnetic ordering} \\ q \neq 0, \quad m = 0 & \Rightarrow \text{spin glass behavior} \end{aligned}$$

Fig. 2.4.1 shows a schematic phase diagram in reduced units of temperature and J_0 , taken from Sherrington and Kirkpatrick (1975). In reality the phase diagram would probably be more complex.

In an extension of this model Sherrington and Southern (1975) give the spin glass temperature T_{sg} as

$$T_{sg} = \frac{\hbar^2 J_0^2 z}{3k_B} \left\{ [S(S+1)]^2 + \frac{S(S+1)}{2} \right\}^{1/2}$$

and the Curie temperature T_C as

$$T_C = \frac{S(S+1) \hbar^2 J_0 z}{6k_B} \left\{ 1 + \left[1 - \frac{3J^2}{zJ_0^2 S(S+1)} \right]^{1/2} \right\}$$

Since T_C has to be real, they predict that ferromagnetism is possible only if

$$\frac{J^2}{zJ_0^2} < \frac{S(S+1)}{3}$$

and
$$T_{C(\text{minimum})} = \frac{S(S+1) \hbar^2 J_0 z}{6k_B}$$

The susceptibility gives a cusp in zero magnetic field and a rounded maximum in applied magnetic field as shown in Fig. 2.4.2.

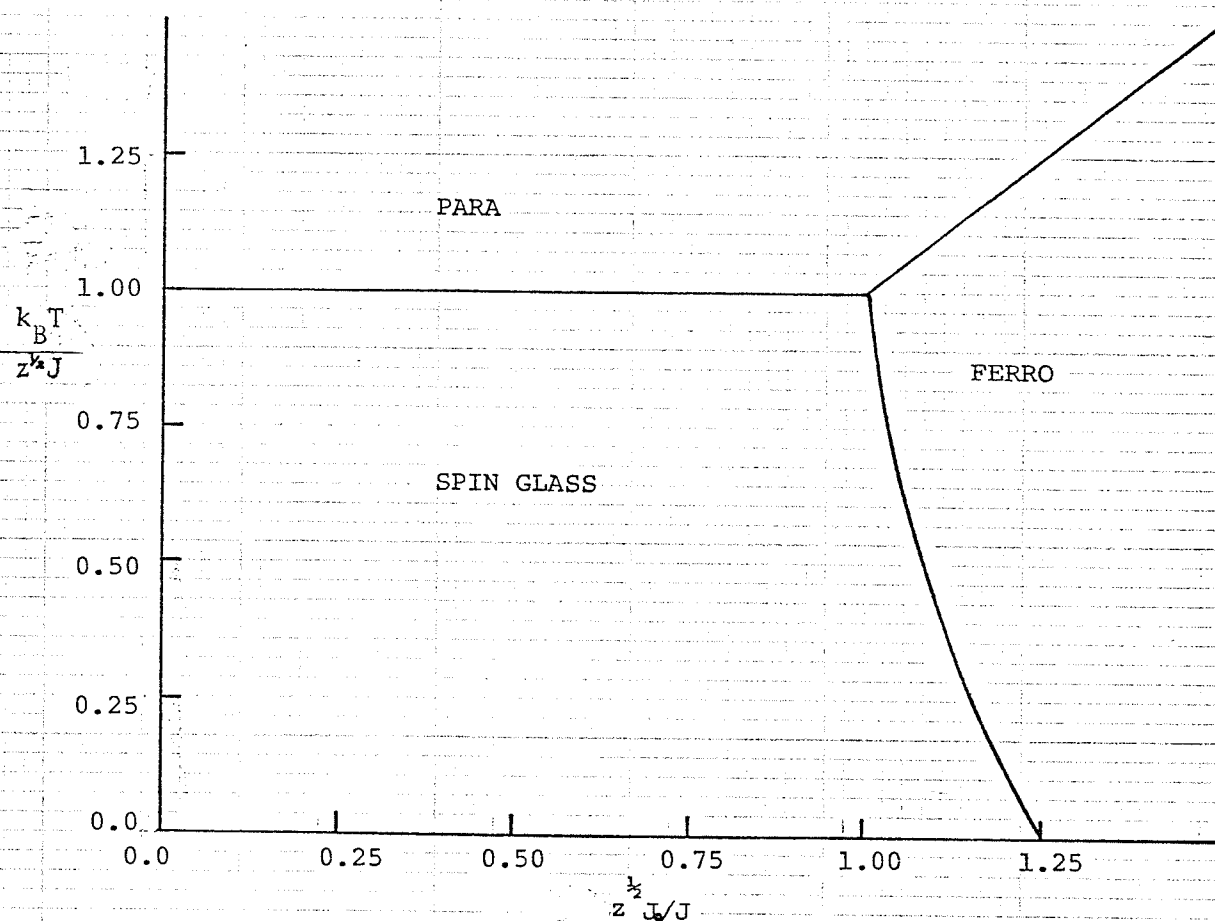


Fig.2.4.1 Phase diagram of spin-glass ferromagnet. z is the number of neighbours

From: Sherrington and Kirkpatrick (1975).

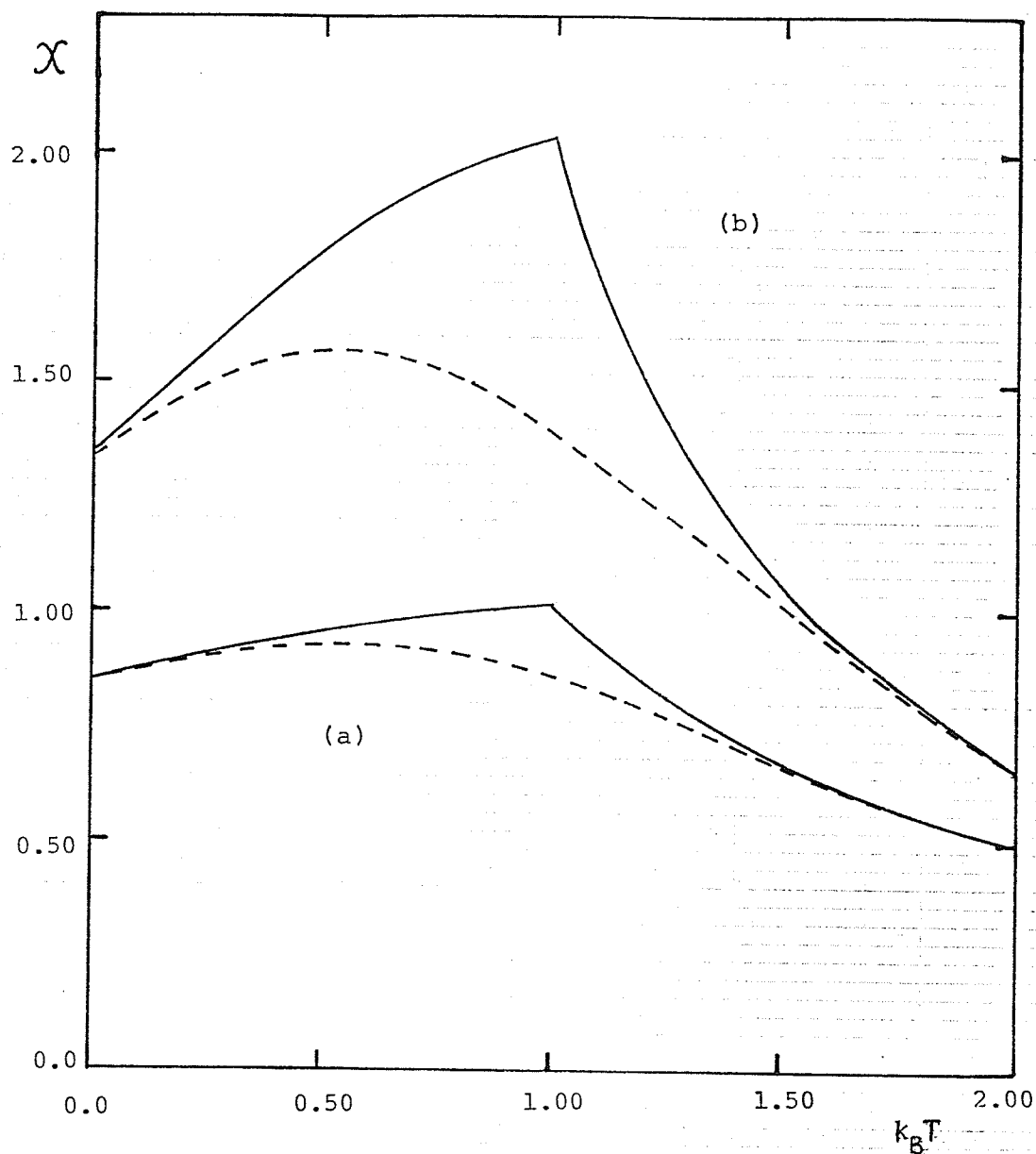


Fig. 2.4.2 Differential susceptibility without external field (solid lines) and with a field (dotted lines) for $z^{1/2}J/J=0$, curves a, and $z^{1/2}J/J=0.5$, curves b. From: Sherrington and Kirkpatrick (1975).

Unfortunately, the specific heat also shows a cusp at T_{sg} , and even worse, the entropy becomes negative at $T = 0$, both being contrary to real systems. Further improvements in the mean field models are needed.

Before discussing other theories on spin glasses, it is fair to mention other mean field models. The one by Adkins and Rivier (1974) precedes the Edwards and Anderson model while recently Walker and Walstedt (1980) have computer simulated the R.K.K.Y. interaction in spin glasses. Their analysis of the nearly degenerate ground states is noteworthy.

2.4.6. Cluster Model

Smith (1974, 1975) suggests a different approach, the cluster model, to describe the behavior of spin glasses. Smith observes that the strength of the R.K.K.Y. interaction is actually quite strong---If one takes the form

$$\text{Energy} = \sum_{ij} A \frac{\cos(2k_F r)}{(2k_F r)^3} \vec{S}_i \cdot \vec{S}_j$$

$$\text{then for Ag-Mn} \quad , \quad \frac{A}{k_B} = 7.6 \times 10^4 \text{ } ^\circ\text{K}$$

$$\text{and for Cu-Mn} \quad , \quad \frac{A}{k_B} \approx 10^5 \text{ } ^\circ\text{K}$$

Hence for the usual experimental temperatures of less than 300°K, the R.K.K.Y. interaction is able to link up spins in spite of thermal excitations. To simplify the analysis, he defines a thermal cut-off

length R_C through the relation

$$\frac{AS}{(2k_F R_C)^3} = x k_B T \quad (2.4.2)$$

where x is an undetermined parameter of order unity. A cluster is defined as a collection of spins that are connected to one another via a bond shorter than R_C and stronger than $k_B T$. All spins in a cluster, except "loose spins", are rigidly aligned colinearly in one another's internal fields, and that different clusters are comparatively free to rotate against each other. Because of the cosine factor in the numerator of the R.K.K.Y. interaction, some spins may be coupled to the cluster through a bond shorter than R_C but weaker than $k_B T$. These spins are called "loose spins" and are assumed to be small in number. This model is similar to the percolation model of Abrikosov. (Historically, Smith's model precedes that of Abrikosov by 6 years.)

From Eq. 2.4.2, as T decreases, R_C increases and the clusters grow in size. The onset of percolation, when an infinite cluster first appears, defines the spin glass temperature T_{sg} ,

$$k_B T_{sg} = \frac{cAS}{18\pi(2.7)Zx} \quad (2.4.3)$$

where c is the concentration of spins
and Z is the valency of the host.

This equation gives

$$T_{sg} \propto c$$

To account for the cusp in the susceptibility, Smith postulates a relaxation time $\tau_{n\alpha}$ needed for a cluster of n spins and type α to relax over a barrier of height $\Delta E_{n\alpha}$. The actual mechanism of relaxation is not known, but he takes a form

$$\tau_{n\alpha}^{-1} = f_{n\alpha} \exp\left(\frac{-\Delta E_{n\alpha}}{k_B T}\right)$$

where $f_{n\alpha}$ is a parameter dependent on n and α .

$\tau_{n\alpha}$ is assumed to increase with n . Hence infinite clusters will not be able to participate in any measurement made over a finite time period such as A.C. susceptibility. Further, if one ignores inter-cluster interaction, the susceptibility becomes a sum over individual cluster susceptibilities $\chi_{n\alpha}$

$$\chi(\omega) = \sum_{n\alpha} \frac{\chi_{n\alpha}}{1 + i\omega\tau_{n\alpha}}$$

This equation indicates that clusters with relaxation time greater than ω^{-1} do not contribute to the measured susceptibility. The cusp at T_{SG} thus reflects a progressive decrease in the number of finite clusters in the sample as more and more spins are frozen into the infinite cluster. The result is a frequency dependent A.C. susceptibility.

Smith has calculated the susceptibility based on the Bethe lattice model and found qualitative agreement between theory and experiment. However, he points out that a quantitative comparison with experiment is not advisable at this moment since the effects of loose spins and inter-cluster interactions are not considered.

Further, he argues that only quantities sensitive to the formation of large clusters can show anomaly at T_{sg} . Hence the resistivity does not peak at T_{sg} because the freezing out of spin flip scattering is a single spin effect.

2.4.7 Frustration Model

Toulouse (1977) has presented a totally new model on spin glasses, based on the local symmetry of the Hamiltonian

$$\mathcal{H} = - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

Take a two-dimensional square lattice with Ising spins ($S_i = \pm 1$), nearest neighbour interaction, and $|J_{ij}| = 1$. $J_{ij} = +1$ signifies ferromagnetic coupling, $J_{ij} = -1$ antiferromagnetic coupling, while $J_{ij} = \pm 1$ randomly signifies spin glass behavior. Starting from a ferromagnetic model $J_{ij} = +1$, one can make a local transformation on one particular spin $\vec{S}_i$

$$\vec{S}_i \rightarrow -\vec{S}_i$$

$$J_{ij} (j \text{ adjacent to } i) \rightarrow -J_{ij}$$

and the resultant Hamiltonian is unchanged. The above transformation is similar to the gauge transformation in electromagnetic theory.

$$\psi(x) \rightarrow e^{i\alpha(x)} \cdot \psi(x)$$

$$\vec{A}(x) \rightarrow \vec{A}(x) + \nabla\alpha$$

Thus, a considerable amount of apparent disorder can be realized by flipping the bond signs around randomly chosen sites without changing the thermodynamical properties. This is not the real disorder found

in spin glasses.

Serious disorder stems from frustration effect. Consider 4 spins situated in the corners of a square lattice as shown in Fig. 2.4.3.

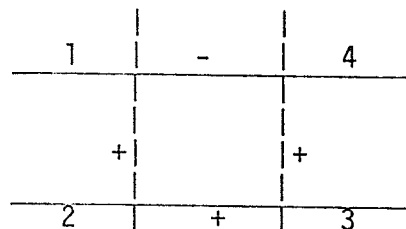


Fig. 2.4.3 Frustrated spins

Spin 1 and Spin 2 interact ferromagnetically, $J = +1$, as indicated by the "+" sign between them. Similarly for 2 and 3, and 3 and 4. However, spin 4 and spin 1 interact anti-ferromagnetically, $J = -1$, as indicated by the "-" sign between them. The energy of the system is

$$\begin{aligned} \mathcal{H} &= - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j \\ &= - \vec{S}_1 \cdot \vec{S}_2 - \vec{S}_2 \cdot \vec{S}_3 - \vec{S}_3 \cdot \vec{S}_4 - (-\vec{S}_4 \cdot \vec{S}_1) \end{aligned}$$

To achieve the ground state, lowest in energy, $\vec{S}_1$ has to be parallel to $\vec{S}_2$, because then

$$-\vec{S}_1 \cdot \vec{S}_2 = -S_1 S_2 = -(1)(1) = -1$$

Similarly $-\vec{S}_2 \cdot \vec{S}_3 = -1$

$$-\vec{S}_3 \cdot \vec{S}_4 = -1$$

Now the above 3 equations imply that $\vec{S}_1$ is parallel to $\vec{S}_2$,

$\vec{S}_2$ is parallel to $\vec{S}_3$, and $\vec{S}_3$ is parallel to $\vec{S}_4$.

The end result is that $\vec{S}_1$ is parallel to $\vec{S}_4$. Now, if $\vec{S}_1$ is parallel to S_4 , then

$$-(-\vec{S}_4 \cdot \vec{S}_1) = +\vec{S}_4 \cdot \vec{S}_1 = S_4 S_1 = (1)(1) = 1.$$

The energy of the system becomes

$$\mathcal{H} = -1-1-1+1 = -2.$$

This is much higher than the lowest possible energy.

$$\mathcal{H} = -1-1-1-1 = -4.$$

To achieve the lowest energy in the term $-(-\vec{S}_4 \cdot \vec{S}_1)$, $\vec{S}_4$ has to be anti-parallel to $\vec{S}_1$. But this will raise the energy in the term $-\vec{S}_1 \cdot \vec{S}_2, \dots$. Therefore there is conflicting information on the direction of $\vec{S}_4$ if one counts clockwise, or anticlockwise, from $\vec{S}_1$.

This situation is called frustration. One can measure the frustration function

$$\Phi = \prod_{(c)} J_{ij}$$

defined on any closed path (c) along the bonds of the lattice. If

$\Phi = +1$, there is no frustration; if $\Phi = -1$, there is.

The idea of frustration is very new, 1977, and as such is not fully developed. Kirkpatrick (1977) has investigated the ground state in a frustrated lattice, and Marland and Betts (1979) investigate the frustration effect on quantum spins. None of the above analyses, however, have yielded expressions for the susceptibility or resistivity. Hence a detailed comparison of theory with experiment is not possible at this moment.

CHAPTER III

EXPERIMENTAL METHODS

3.1 Introduction

The methods used in this investigation of magnetic ordering in the Pd-Mn system were resistivity and A. C. susceptibility measurements. In addition, room temperature X-ray powder photographs were taken to determine the lattice structure of the samples.

3.2 Sample Preparation

The concentration of manganese in the alloys was from 0 to 10.45 at %, in approximate steps of 0.5 at %. The starting materials were 99.999 % pure palladium (Pd) sponge and 99.99 % pure manganese (Mn) flake from Johnson Matthey Chemicals Limited, London. The constituents were melted on the water-cooled copper hearth of an argon arc furnace with a tungsten electrode. The atmosphere inside the furnace was about 200 torr of argon gas, gettered by molten titanium. In general each alloy was inverted and re-melted six times to ensure homogeneity, usually with negligible melting losses.

Initially, a master alloy of Pd-10.45 at % Mn was prepared. Then alloys of 0.5 at %, 1.0 at %, 1.5 at %, etc., up to 10.0 at % Mn, were obtained by diluting parts of the master alloy with the appropriate amount of palladium. The Mn concentration in each alloy was estimated to ± 0.1 at % of the nominal value. (An 0.75 at %

alloy was made later by melting together a Pd-0.5 at % Mn and a Pd-1.0 at % Mn alloy.) Following melting, the alloys were cold rolled into sheets about 0.006 cm thick, from which samples for resistivity, A. C. susceptibility and X-ray powder photographs were cut. The resistivity samples had typical dimensions of

$$10 \times 0.2 \times 0.006 \text{ cm.}^3$$

and mass of 0.06 gm, as the length was made much bigger than the cross-sectional area in order to maximise the resistance. The A. C. susceptibility samples had typical dimensions of

$$1.2 \times 0.3 \times 0.006 \text{ cm.}^3$$

and mass from 0.01 gm to 0.1 gm, although a few had a bigger surface area and were folded into hairpin shape with contacting surfaces insulated by a masking tape. The thickness of the sample (0.006 cm.) ensured that the A. C. driving field penetrated all of the sample. The X-ray powder photograph samples were thin wires.

Following cutting, the samples were etched for 1 minute to remove surface contaminants. The etching solution was:

ACIDS	PARTS BY VOLUME
Conc. nitric acid	1
Hydrochloric acid	3
Water	1
Hydrogen peroxide	a few drops

After etching, the samples were annealed for 24 hours at 650 C under continuous pumping. Typically, pressures at the end of the annealing period were 4×10^{-6} mm. Hg. After annealing, they were allowed to cool to room temperature naturally, while still being

pumped.

The master alloy of Pd-10.45 at % Mn was later analysed by the Crystal Growth Laboratory of the University of Utah, where the manganese concentration was found to be

$$(10.21 \pm 0.25) \text{ at } \%$$

The amount of iron and cobalt impurities were less than 5 ppm., and the amount of titanium impurity was less than their detection limit of 140 ppm by weight. Three different slices of the Pd-10.45 at % Mn sample were analysed and showed manganese concentrations within 0.06 at % of the mean value.

3.3 X-ray Diffraction Measurement

The resistivity ρ of a sample is defined as

$$\rho = R \left(\frac{A}{l} \right)$$

where R is the resistance, A is the cross-sectional area and l is the length over which R is measured. It is, however, difficult to measure A directly to better than 2 % because of its smallness. Hence an indirect method (Whall, et al 1972) was used, based on the equation

$$\langle A \rangle = \frac{\text{mass}}{\text{density} \times \text{sample length}}$$

where $\langle A \rangle$ is the average cross-sectional area. Measurements on mass and length were done quite satisfactorily using the balance and the travelling microscope: Masses were accurate to ± 0.0001 gm and lengths to ± 0.001 cm. The density was calculated using the lattice parameter obtained by X-ray powder diffraction photographs. As the lattice parameter was accurate to ± 0.0001 Å out of typically

3.8906 Å, the overall uncertainty of A , and hence the form factor (A/l), was limited to $\pm 0.5\%$ --- an improvement over the direct method. The following is a brief description of the X-ray measurements.

The photographs were taken on a 11.46 cm. diameter Debye-Scherrer camera which employed the Straumanis asymmetrical loading of film. The camera had the special feature of automatic compensation for film shrinkage after exposure. The X-ray source was iron, and no filter was used. Typical exposure time was 12 hours, developing time 10 minutes, and fixing time 15 minutes. The films were measured to ± 0.001 cm. with a Picker travelling micrometer. The analysis of films followed the general procedure described in standard textbooks of X-ray analysis (eg. Nuffield 1966).

Fig. 3.3.1 shows a typical powder photograph, in this case of Pd-6.5 at % Mn. There are 32 lines in the photograph, which can be grouped into K_α and K_β lines under the known wavelengths of K_α and K_β emissions from iron. The lattice is clearly face-centered cubic (fcc), and the lattice parameter estimated at (3.8906 ± 0.0001) Å.

Fig. 3.3.2 is a plot of the measured lattice parameter vs. manganese concentration in these alloys. All the alloys, and the pure palladium, were found to be fcc, and with no superlattice structure. Further, the atomic radius of Pd (1.37 Å) and that of Mn (1.26 Å) are too close to form interstitial alloys. Hence the formula for the density of fcc substitutional alloys can be used to calculate the

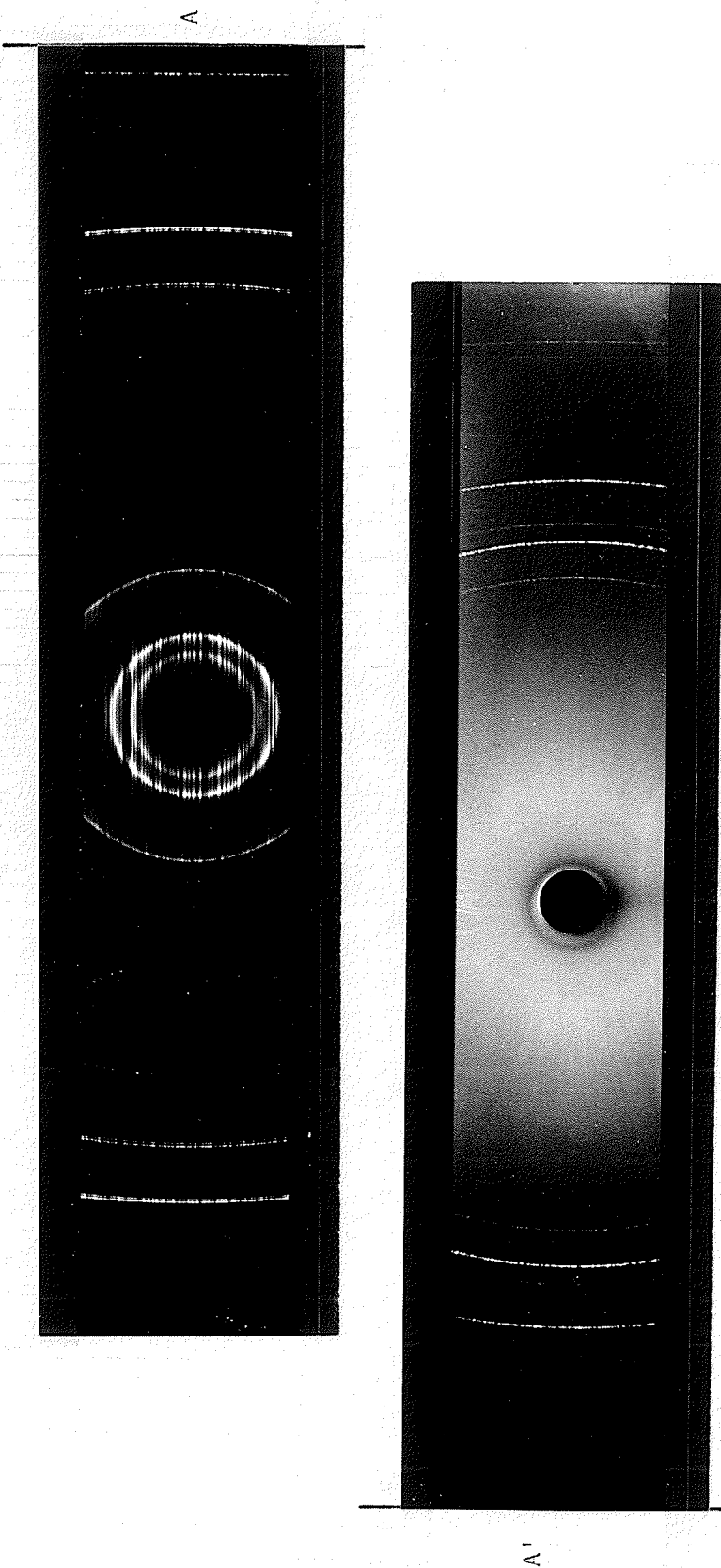


Fig. 5.3.1.1. X-ray powder photograph of Pd-6.5 at % Mn. Because it is much longer than this page, the photograph has been cut into halves for presentation. Lines A and A' should match in the original photograph.

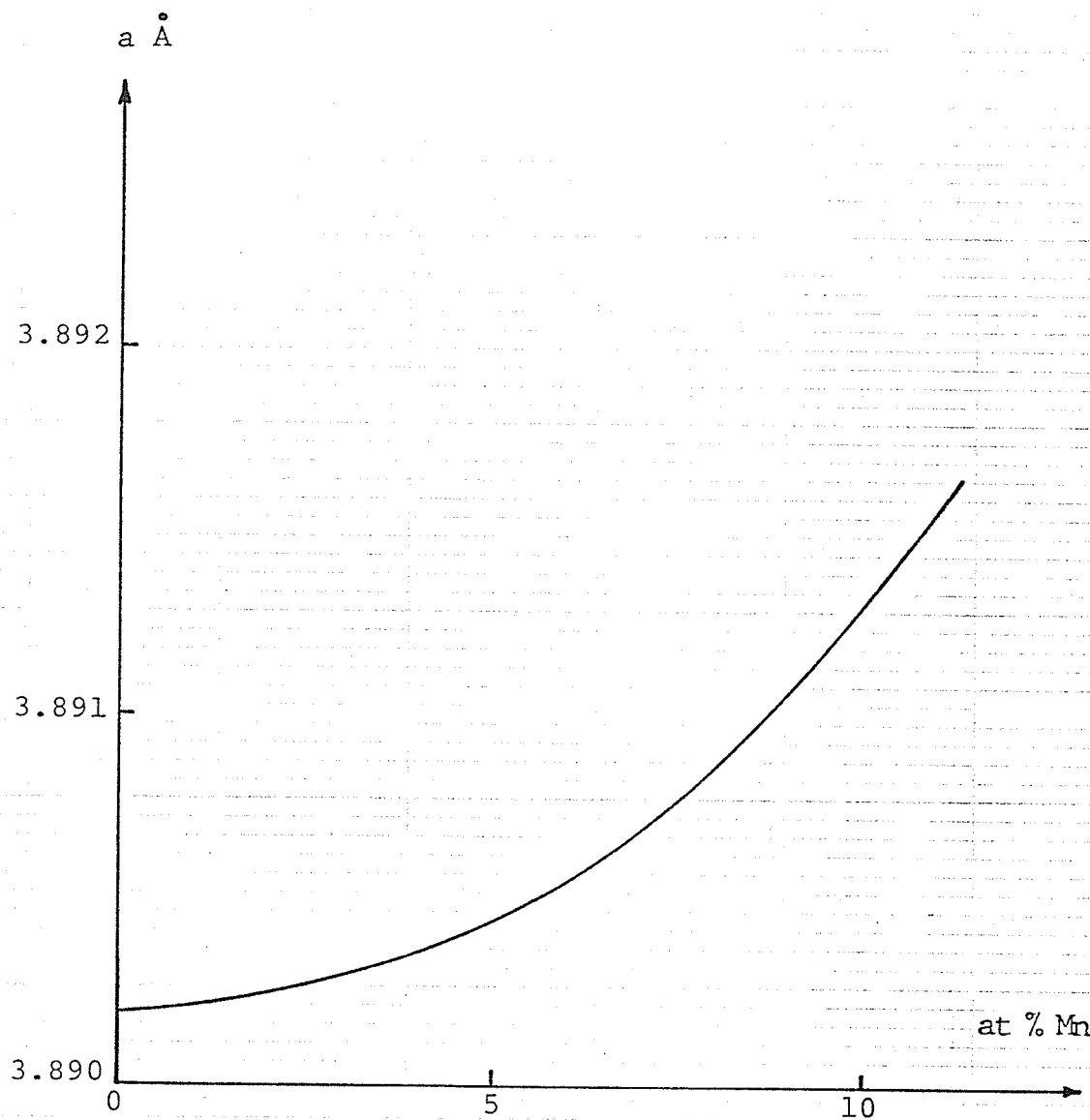


Fig. 3.3.2 Lattice parameter vs. Mn concentration.

density from the measured lattice parameter.

$$\text{Density} = \left(\frac{4}{N_A a^3} \right) (A_1 X_1 + A_2 X_2)$$

where A_1 is the atomic weight of Pd, A_2 is the atomic weight of Mn, X_1 is the atomic % of Pd, X_2 is the atomic % of Mn, N_A is the Avogadro's number and a is the lattice parameter. These densities were then used in calculating the form factors in resistivity analysis.

3.4 Measurement of Electrical Resistivity

For the purpose of discussion it is convenient to subdivide the electrical resistivity system into 7 parts:

1. the sample block to hold the samples
2. a cryostat system to achieve cooling
3. a manostat to stabilize temperature below 4.2 K
4. a manometer system to measure temperature below 4.2 K
5. an A. C. bridge circuit to stabilize temperature above 4.2 K
6. a gas thermometer to measure temperature above 4.2 K
7. the potentiometric system used to measure D. C. resistivity

3.4.1 Sample Block

The sample block was machined out of oxygen-free high conductivity (OFHC) copper in approximately the dimension shown in Fig. 3.4.1. It could accommodate up to 6 samples, usually a pure metal (host) and 5 alloys. This ensured that in calculating the in-

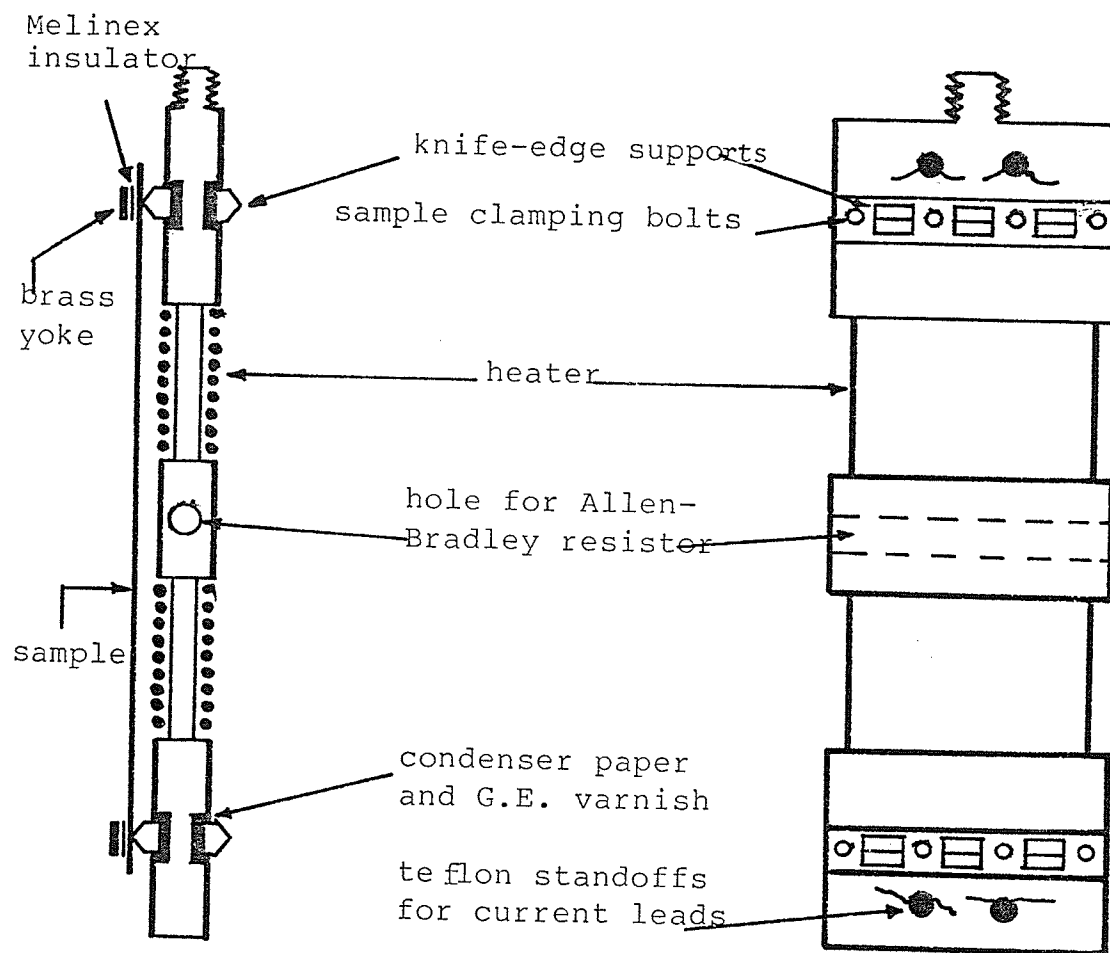


FIG. 3.4.1 (a) Edge-view of Sample Block.
(b) Face-view of Sample Block.

cremental resistivity

$$\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{host}}$$

one subtracted from ρ_{alloy} a host resistance ρ_{host} measured at the same temperature. Each sample was mounted vertically on a pair of knife-edge supports situated near the ends of the block, about 8 cm. apart. The supports were electrically insulated from the block with strips of newsprint paper, and fastened in place with generous amount of General Electric Company (G.E.) No. 7031 varnish. Wires soldered to the side of each knife-edge support provided the voltage tap-off connections. The samples were tightly clamped onto the knife-edge supports by bolts pressing onto a brass yoke, but insulated from the yoke by mylar strips. The impressions of the knife-edges induced on each sample defined the exact length across which the resistance was measured. This distance was measured to ± 0.001 cm by a travelling microscope after the samples were dismantled.

The sample block also carried two heater coils and one Allen-Bradley carbon resistor, all of which formed part of the A. C. bridge circuit used to stabilize the temperature above 4.2 K. The resistor was fitted into a hole in the middle of the sample block and was coated with generous amount of G. E. varnish to ensure good thermal contact. The sample block was screwed into the lower end of the gas thermometer bulb, and both the block and the gas thermometer bulb were sealed inside a brass inner vacuum can (IVC) with an indium O-ring. A small amount of He gas was trapped inside the IVC to ensure thermal equilibrium among the samples and the gas thermometer bulb.

The IVC itself was sealed inside a brass outer vacuum can (OVC) with Wood's metal. For temperatures from 1.5 K to 4.2 K, the OVC was filled with He gas, which served as a thermal link between the IVC and the liquid helium bath outside the OVC. Above 4.2 K the OVC was evacuated so that the samples could be heated to temperatures higher than that of liquid helium.

3.4.2 Cryostat System

The sample block, IVC and OVC were suspended from the cryostat top plate by 3 stainless steel tubes with external radiation shields. One of these tubes acted as a guide for inserting the helium transfer tube when filling the helium bath. The second was the pumping line for the OVC and also housed a 0.032 inch O. D. stainless steel tube which connected the gas thermometer bulb to an external pressure gauge. And the third tube led to the IVC and carried twenty-two electrical wires whose purpose is described in Section 3.4.7. These wires came out of the cryostat top plate through a brass 'feed-through' sealed by silicone seal and Stycast epoxy cement. Fig. 3.4.2 shows the top plate assembly.

Temperatures below 4.2 K were achieved by pumping on the helium bath surrounding the OVC with an Edwards High Vacuum Ltd. Speedivac ES 330 rotary pump. A manostat placed in its pumping line controlled the pressure of the bath. This pressure was measured by a set of mercury (Hg) and oil manometers, the reference sides of which were pumped by a Speedivac vapour diffusion pump backed by a Speedivac ES 100 rotary pump. A second diffusion pump backed by the same ES 100

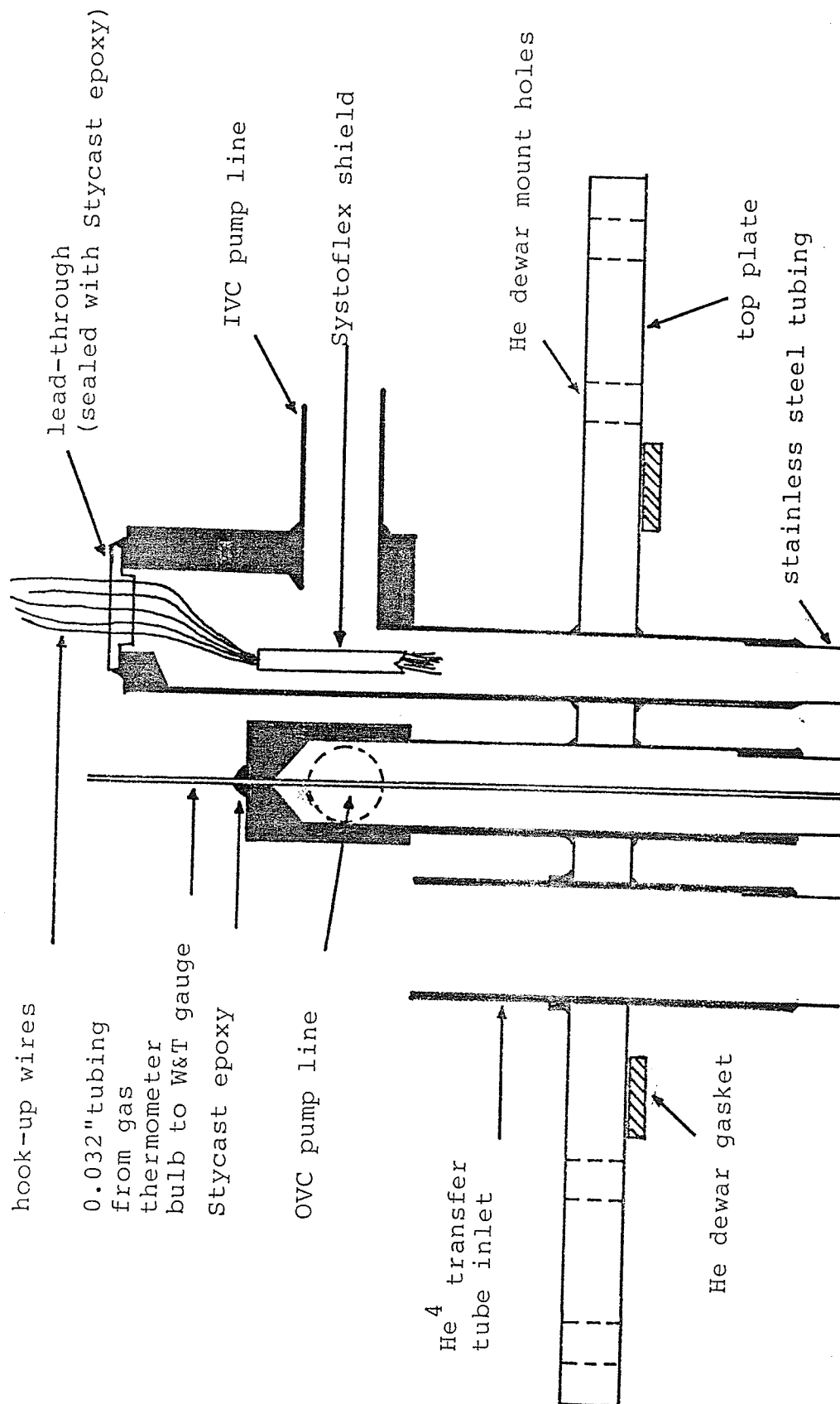


Fig. 3.4.2. Cryostat Top Plate Assembly.

pump controlled the pressure inside the IVC and OVC, which was monitored by a Pirani 11 and a Penning 8 gauge. The Pirani 11 covered the range atmosphere to 10^{-3} mm. Hg, while the Penning 8 the range 10^{-2} to 10^{-7} mm. Hg. Fig. 3.4.3 illustrates the flow diagram of the cryostat system.

3.4.3 Manostat

Temperatures below 4.2 K were stabilized by a manostat in the He bath pumping line that controlled the vapour pressure of the helium bath surrounding the OVC. Fig. 3.4.4 illustrates the construction of the manostat. It consisted of an 0.01 inch thick latex rubber membrane held between two perforated brass retaining plates. One of the plates had 177, 1/16 inch diameter holes evenly drilled in it, and led to a reservoir of gas, while the other plate was connected to the ES 330 mechanical pump and the helium bath through two perforated ports. The reservoir could be connected to the helium bath through a small valve. During pump down, this small valve was open, so that the same pressure was maintained between the reservoir and the helium bath. When a desired pressure in the reservoir was reached, the small valve was closed. Further pumping of the helium bath made the reservoir pressure higher than the helium bath pressure, forcing out the rubber membrane to seal the port to the mechanical pump. Conversely, the membrane would fall back when the bath pressure rose to the reservoir pressure through vapourization of the liquid helium, so that any further vapour build-up would be pumped away by the mechanical pump. The bath pressure, and hence the bath

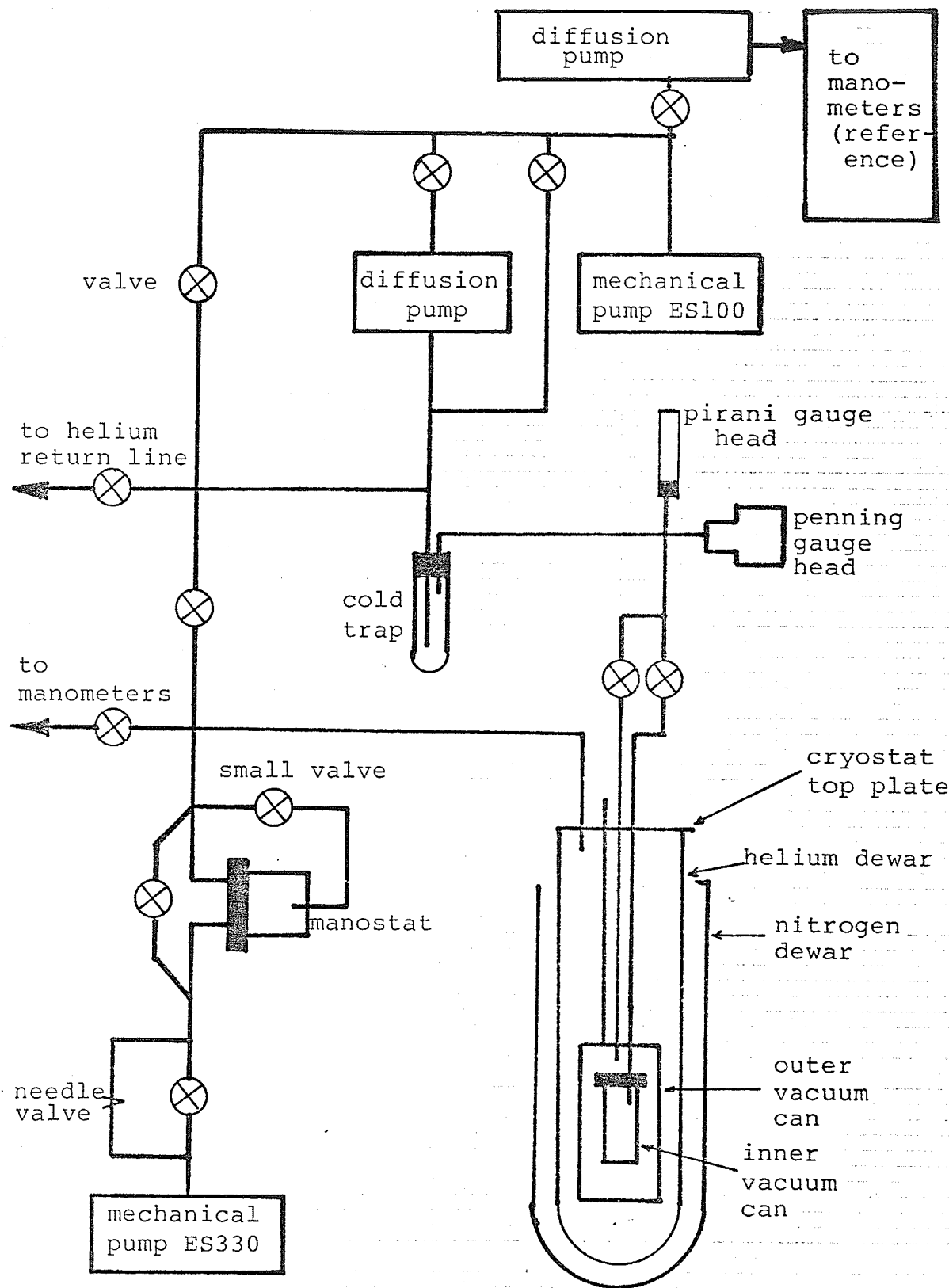


Fig. 3.4.3. Flow Diagram of the Cryostat System.

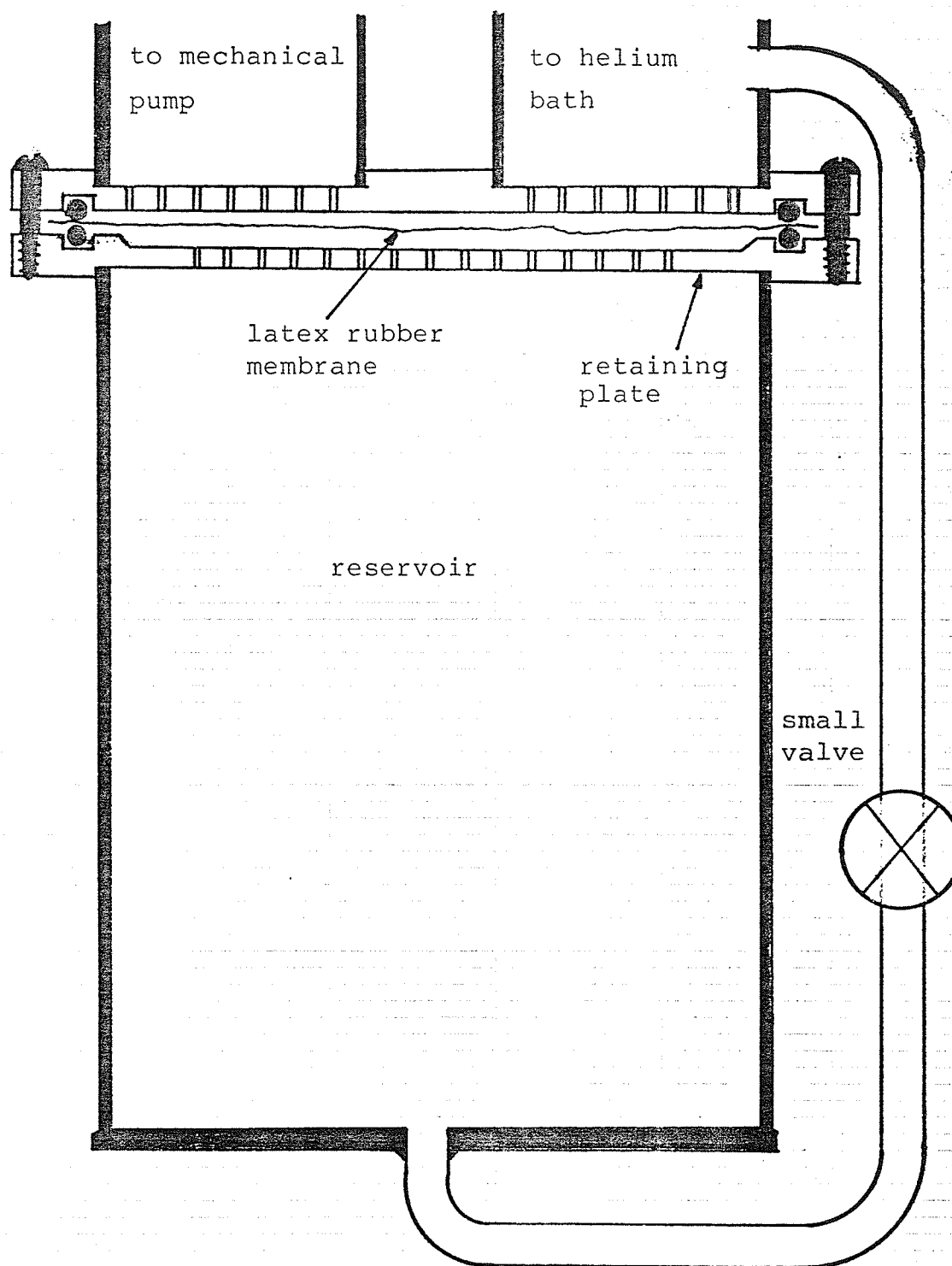


Fig.3.4.4 Manostat Construction.

temperature, were thus stabilized.

3.4.4 Manometer System

Temperatures below 4.2 K were measured by monitoring the vapour pressure of the liquid helium bath surrounding the OVC. This vapour pressure was measured by 2 manometers; one containing mercury and the other Apiezon B low vapour pressure oil. Fig. 3.4.5 shows the manometer system. The mercury manometer was used over the range 1 cm. to 85 cm. Hg, and the oil from 0.25 cm. to 3 cm. Hg, as its density was about 1/15 of that of mercury. When the bath pressure was between 1 and 3 cm. Hg, it was possible to measure this pressure on both manometers and this provided the conversion factor for oil readings below 1 cm. Hg. The heights of the liquid columns were measured to ± 0.001 cm. with a cathetometer manufactured by Griffin and George Ltd. The measured pressures were corrected for thermal expansion of the glass in the manometers, and local gravity. Temperatures corresponding to these pressures were determined from published helium vapour pressure tables. (White, G.K., 1968, p. 367)

3.4.5 A. C. Bridge Circuit

Temperatures between 4.2 K and 300 K were obtained using an A. C. Phase-Sensitive Wheatstone Bridge, the block diagram for which is shown in Fig. 3.4.6. One arm of the bridge was connected to the Allen-Bradley carbon resistor in the middle of the sample block inside the cryostat. The resistance of this carbon sensor varied from 100 ohm at room temperature, to 55000 ohm at the lowest temperature achieved (1.45 K), as shown in Fig. 3.4.7. The remaining

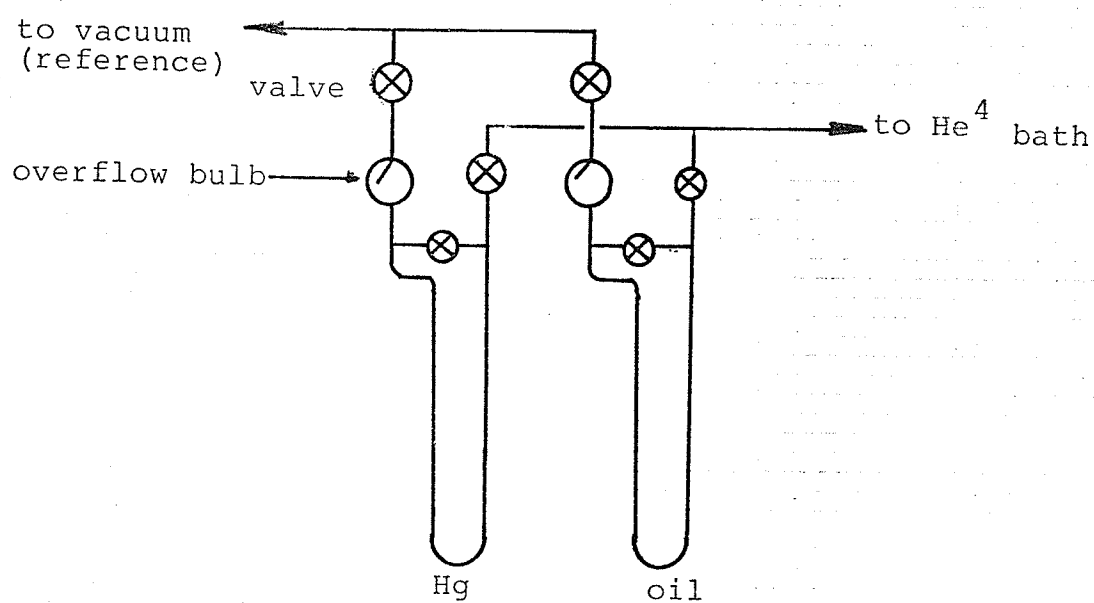


Fig.3.4.5 Manometer Arrangement.

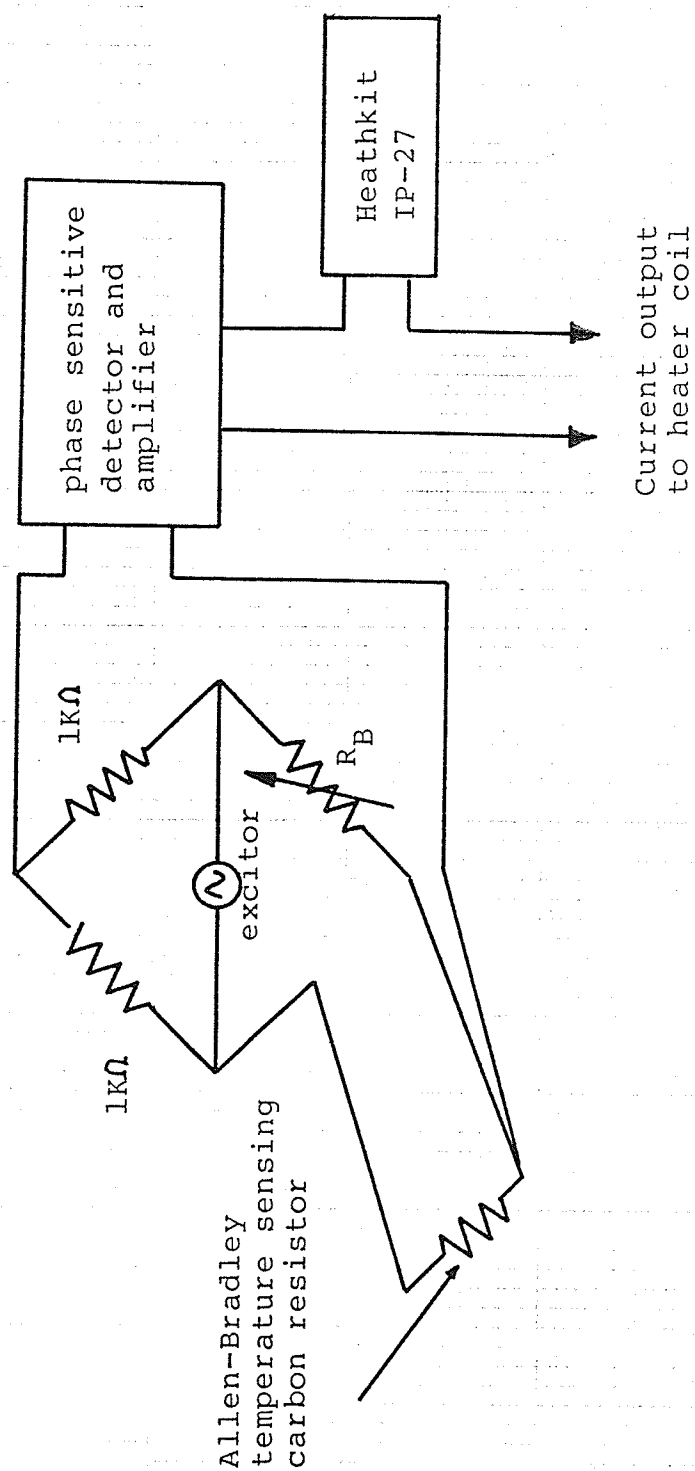


Fig.3.4.6 A.C.Phase-Sensitive Bridge Circuit.

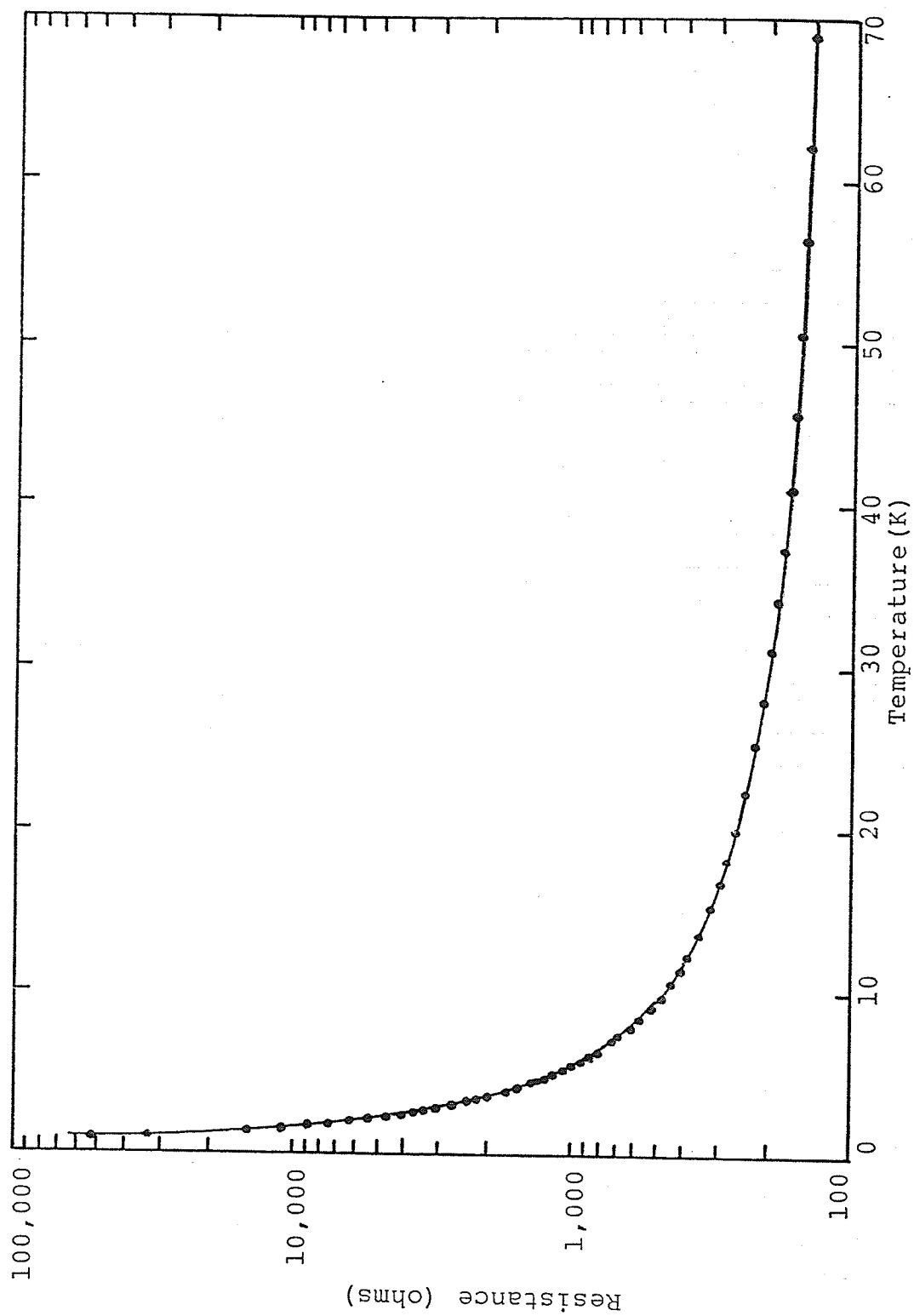


Fig.3.4.7 Resistance Versus Temperature Characteristics of the Allen-Bradley Resistor.

three arms of this bridge were located outside the cryostat and consisted of a variable resistor box and two 1000 ohm resistors.

The bridge operates as follows: When a temperature higher than the boiling point of, say, liquid helium is desired, the variable resistor box is set at a resistance R corresponding to the resistance of the carbon resistor at the required higher temperature. R is then smaller than the instantaneous resistance of the carbon resistor (still at 4.2 K). As the resistor box and the carbon resistor are part of the bridge circuit, this difference in resistance induces a difference in voltage, and a current is fed to the heater. This current is made proportional to the positive difference between the resistance of the carbon resistor and the set resistance R , so that if the carbon resistor is equal to or lower than R , the heater current is stopped.

With liquid helium surrounding the OVC, sample temperatures below about 25 K could be maintained with the current obtained directly from the bridge output. However above 25 K, a Heathkit IP-27 low voltage power supply was used to provide additional heater current. A similar situation existed above about 85 K when liquid nitrogen was used as a coolant.

Two heaters were wound around the central region of the sample block; one being actually used, the other as a spare. Each heater consisted of 20 feet of 0.036 inch diameter enamelled Cupron wire with 500 ohm resistance, which remained roughly constant as Cupron has a very small temperature coefficient of resistance.

3.4.6 Gas Thermometer

Temperatures above 4.2 K were measured with a non-linear helium gas thermometer illustrated in Fig. 3.4.8. The gas thermometer bulb was machined from brass, and formed the top of the IVC supporting the sample block. This bulb was connected to the pressure sensing capsule inside a Wallace and Tiernan (W & T) Model 62A-4C-0120 pressure gauge located outside the cryostat. The connection was provided by a continuous piece of stainless steel tubing, with 0.032 inch O.D. and 0.004 inch wall. For the sake of analysis, it was convenient to subdivide this tubing into two parts as shown in Fig. 3.4.8: L_2 (=28.7 inch) was the length of the tubing inside the cryostat, while L_1 (=109 inch) was that portion outside, which remained essentially at room temperature. The nonlinearity of the gas thermometer arose mainly from two sources: the Van der Waals-type interatomic interactions of the helium gas, and the dead spaces in L_1 and the pressure sensing capsule.

According to manufacturer's specifications, the volume V of the capsule was assumed to vary linearly with pressure P as

$$V(P) = V_0 + aP,$$

where V_0 and a are parameters to be determined. As L_1 and the capsule were always at room temperature, it was convenient to consider the volume of the capsule as aP , and add V_0 to the volume of L_1 , i.e.,

$$V_{L1} = \text{volume of } L_1 + V_0.$$

V_{L2} was the volume of L_2 only. V_{L1} and V_{L2} were assumed to remain constant throughout the experiments. The gas thermometer bulb had a volume $V_B(T)$ at the temperature T . Its value was measured to be

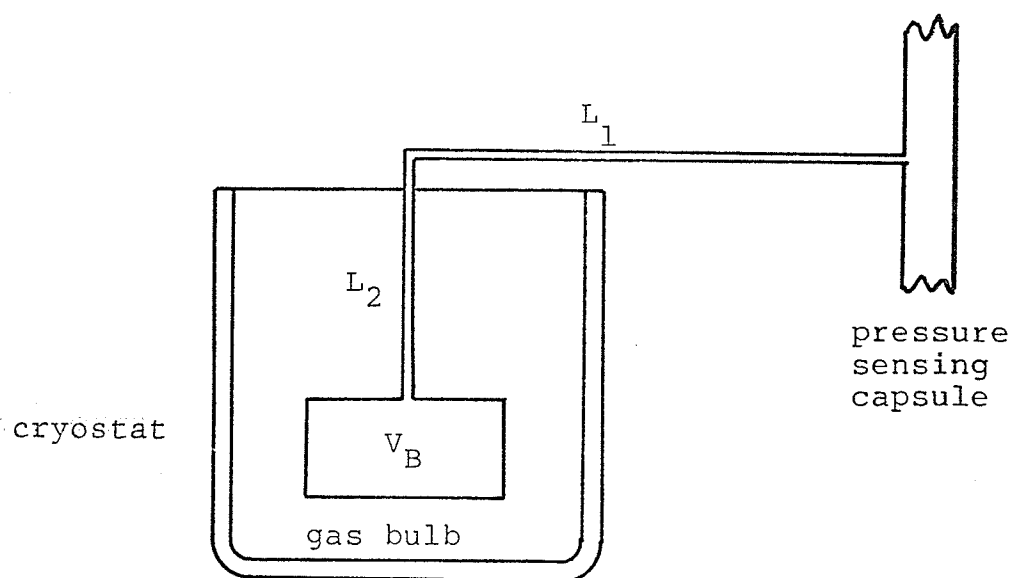


Fig.3.4.8. Schematic of Gas Thermometer.

1.497 cu. inch at room temperature, and from the tabulated values of the coefficient of linear expansion of brass (White, G.K., 1968, p. 377), it was possible to calculate its value at any temperature.

The analysis of the gas thermometer proceeds as follows:

From Appendix A the ideal gas law as applied to a container with several interconnecting compartments was

$$\sum_i \left(\frac{PV_i}{T_i} \right) = \text{constant} \quad (3.4.1)$$

where P is the pressure of the helium gas, same for all compartments V_i is the volume of i^{th} compartment and T_i is the temperature of i^{th} compartment. Following Keesom (1942, P. 30 and following), to correct for the non-ideality of the helium gas, each PV term in the summation was expanded to first order in P, i.e.,

$$PV = A + BP$$

where A and B are the first and second virial coefficients respectively. Further,

$$A = A_0 T / 273.15$$

with $A_0 = 0.999488$ in amagat units for helium. The values of B as a function of temperature were tabulated in the above reference.

$$\text{Then, } PV = A + BP = \frac{A_0 T}{273.15} + BP = \frac{A_0}{273.15} (T + 273.15 BP/A_0)$$

Therefore,

$$\frac{PV}{T + 273.15 BP/A_0} = \frac{A_0}{273.15} = \text{constant}$$

Then Eq. 3.4.1 became,

$$\sum_i \left(\frac{P V_i}{T_i + 273.15 B_i P/A_0} \right) = \text{constant} \quad (3.4.2)$$

There were 3 terms in the summation of Eq. 3.4.2:

1. The gas bulb term

$$\frac{P V_B(T=T)}{T + 273.15 B(T=T) P/A_0}$$

where T was the sample temperature

2. The cryostat tube term

$$\frac{P V_{L2}}{T_R - T} \ln \left(\frac{T_R + C}{T + C} \right) \quad (3.4.3)$$

$$\text{where } C = 273.15 B(T = \frac{T+T_R}{2}) P/A_0$$

3. The room temperature compartment term

$$\frac{P (V_{L1} + aP)}{T_R + 273.15 B(T=T_R) P/A_0}$$

where T_R was the room temperature.

The cryostat tube term was calculated assuming a linear temperature gradient from the bottom of the tube (at sample temperature T), to the top of the tube (at room temperature T_R). And the virial coefficient of the gas in the tube was approximated by B at the average temperature. See Appendix A for a detailed derivation.

To find the parameters V_{L1} and a, the gas thermometer was calibrated at the known temperatures and pressures of helium boiling

point (4.213 K) and triple point of ice (273.16 K) with a fixed amount of helium gas. Then Eq. 3.4.2 became

$$\sum_i \left(\frac{P V_i}{T_i + 273.15 B_i P/A_0} \right) \quad T = 4.213 \text{ K}$$

$$= \sum_i \left(\frac{P V_i}{T_i + 273.15 B_i P/A_0} \right) \quad T = 273.16 \text{ K}$$

Since P was given by the W & T pressure gauge, this equation simplified to an equation of 2 unknowns

$$f(V_{L1}, a)_{T=4.2 \text{ K}} = f(V_{L1}, a)_{T=273.16 \text{ K}} \quad (3.4.4)$$

Then some of the helium gas was removed from the thermometer, and the calibration at the known temperatures was repeated. This generated another equation of the form of Eq. 3.4.4. Hence V_{L1} and a could be found by solving the two simultaneous equations. The result:

$$V_{L1} = 1.0270 \text{ cu. inch}$$

$$a = 1.0557 \text{ cu. inch/atmosphere}$$

Now Eq. 3.4.2 could be used to find an unknown temperature if a fixed amount of helium gas had also been used to measure a known temperature T_0 , i.e.,

$$\sum_i \left(\frac{P V_i}{T_i + 273.15 B_i P/A_0} \right) \quad \text{unknown temperature}$$

$$= \sum_i \left(\frac{P V_i}{T_i + 273.15 B_i P/A_0} \right) \quad \text{known temperature}$$

$$= K$$

The R.H.S. of this equation could be evaluated to give a constant value K, because the only unknown variable, T, occurred on the L.H.S. of the equation only. Written in full the equation became:

$$\frac{P V_B(T=T)}{T + 273.15 B(T=T) P/A_0} + \frac{P V_{L2}}{T_R - T} \ln \left(\frac{T_R + C}{T + C} \right) + \frac{P (V_{L1} + aP)}{T_R + 273.15 B(T=T_R) P/A_0} = K \quad (3.4.5)$$

$$\text{where } C = 273.15 B(T = \frac{T+T_R}{2}) P/A_0$$

To solve this equation algebraically for T was quite difficult because of the non-linear temperature dependence of terms. Hence, a successive approximation and iteration method was used.

Initially, the following approximations were used in the gas bulb term and the cryostat tube term in the L.H.S. of Eq. 3.4.5, namely,

$$V_B(T=T) \approx V_B(T=T_0) \quad (3.4.6)$$

$$B(T=T) \approx 0 \quad (3.4.7)$$

$$\frac{1}{T - T_R} \ln \left(\frac{T_R + C}{T + C} \right) \approx \frac{1}{T + C} \approx \frac{1}{T_R} \quad (3.4.8)$$

The only 'T' variable remaining in the equation was renamed 'T₁'.

Then Eq. 3.4.5 simplified to:

$$\frac{1}{T_1} = \frac{1}{V_B(T=T_0)} \left[\frac{K}{P} - \frac{V_{L2}}{T_R} - \frac{V_{L1} + aP}{T_R + 273.15 B(T=T_R) P/A_0} \right]$$

T_1 was the first approximation to the sample temperature, and roughly corresponded to the ideal gas temperature. Next, correction was made for the neglect of the 'ln' function in Eq. 3.4.8 by substituting T_1 into the L.H.S. of Eq. 3.4.5, while keeping the approximations Eq. 3.4.6 and Eq. 3.4.7. The 'T' variable in the gas bulb term was renamed T_2 . A better estimate of the sample temperature was thus obtained.

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{V_{L2}}{V_B(T=T_0)} \left[\frac{1}{T_R} - \frac{1}{T_R - T_1} \ln \left(\frac{T_R + C_1}{T_1 + C_1} \right) \right]$$

$$\text{where } C_1 = 273.15 B(T = \frac{T_1 + T_R}{2}) P/A_0$$

Then the thermal contraction of the gas bulb and the neglect of the virial coefficient B were accounted for by substituting T_2 into the L.H.S. of the full Eq. 3.4.5, except for the one 'T' variable in the gas bulb term, which was renamed T_3 .

After some algebra, the third estimate of the sample temperature came forth

$$T_3 = \frac{V_B(T=T_2)}{V_B(T=T_0)} \left\{ \frac{1}{T_1} + \frac{V_{L2}}{V_B(T=T_0)} \left[\frac{1}{T_R} - \frac{1}{T_R - T_2} \ln \left(\frac{T_R + C_2}{T_2 + C_2} \right) \right] \right\}^{-1} - 273.15 B(T=T_2) P/A_0$$

$$\text{where } C_2 = 273.15 B(T = \frac{T_2 + T_R}{2}) P/A_0$$

The number K' defined as

$$K' = \frac{P V_B(T=T_3)}{T_3 + 273.15 B(T=T_3) P/A_0} + \frac{P V_{L2}}{T_R - T_3} \ln \left(\frac{T_R + C_3}{T_3 + C_3} \right)$$

$$+ \frac{P (V_{L1} + aP)}{T_R + 273.15 B(T=T_R) \quad P/A_0}$$

where $C_3 = 273.15 B \left(T = \frac{T_3 + T_R}{2} \right) P/A_0$

then indicated how close T_3 approached the real sample temperature T when it was compared with K . 0.001 could be added or subtracted from T_3 in succession to bring K' within $10^{-3} \%$ of K . In the end, the approximations used in deriving Eq. 3.4.5 limited the overall uncertainty of the gas thermometer temperature to $\pm 0.5 \%$.

Figure 3.4.9 illustrates the response curve of the gas thermometer with a known condition of $T_0 = 4.2^\circ \text{ K}$, $P_0 = 4.2$ inch of water, and $T_R = 24.5^\circ \text{ C}$. The deviation of this curve from the $Y = X$ line highlights the non-linearity of the gas thermometer.

3.4.7 The Potentiometric System Used to Measure D.C. Resistivity

Fig. 3.4.10 illustrates the standard four probe technique used to measure D. C. resistivity. A known current I passing through leads soldered to the ends of the sample produces a potential difference across the sample. Part of this voltage is tapped off through the knife-edge contacts. If this tapped voltage just balances a known voltage V inside the potentiometer, then the resistance R of this part of the sample defined by the knife-edges can be found by Ohm's Law:

$$R = \frac{V}{I}$$

To average out thermal voltages originating from contacts being

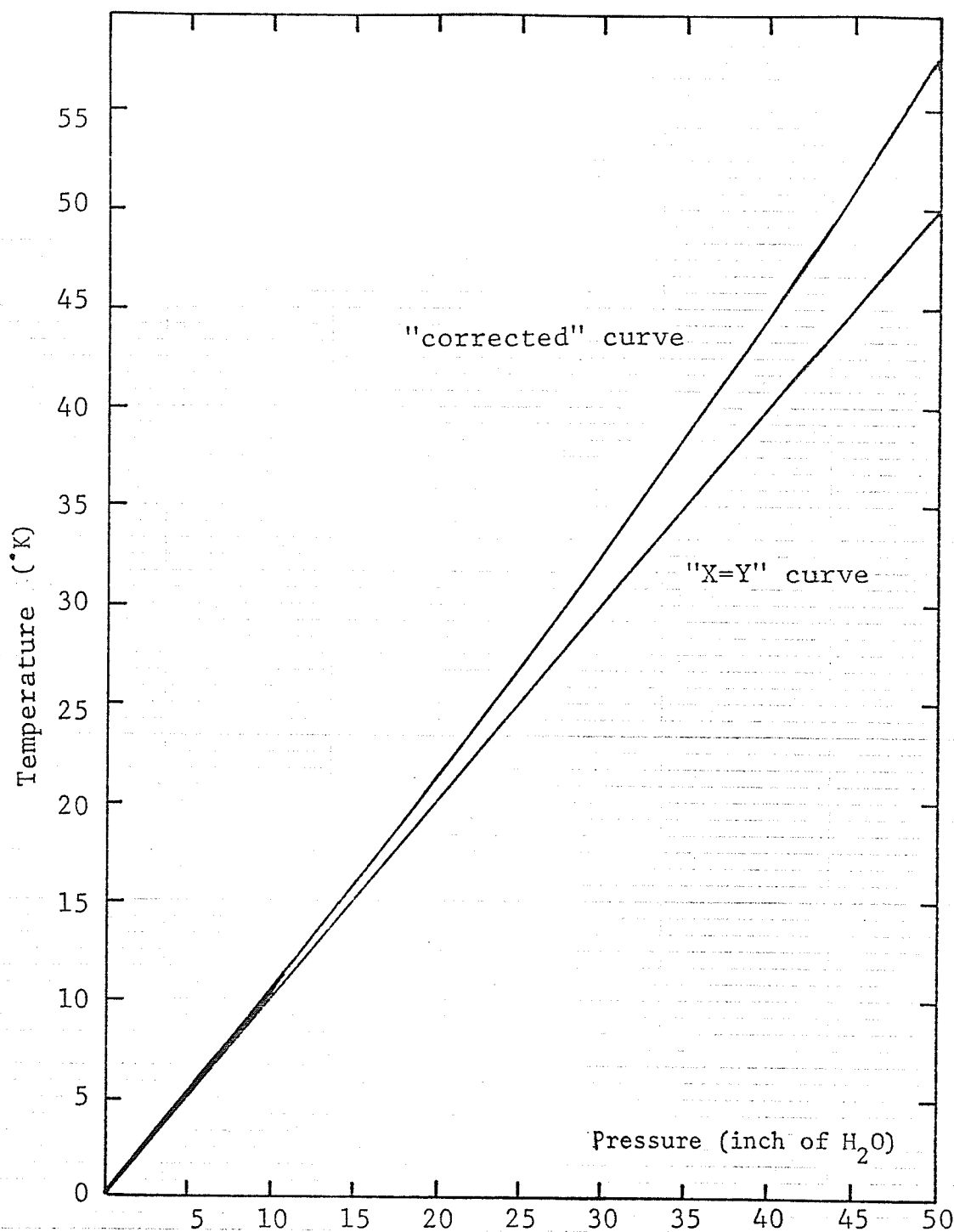


Fig. 3.4.9 Illustration of the Non-linearity of the Gas Thermometer for the Case $T_0=4.2\text{K}$, $P_0=4.2$. (Known Conditions)

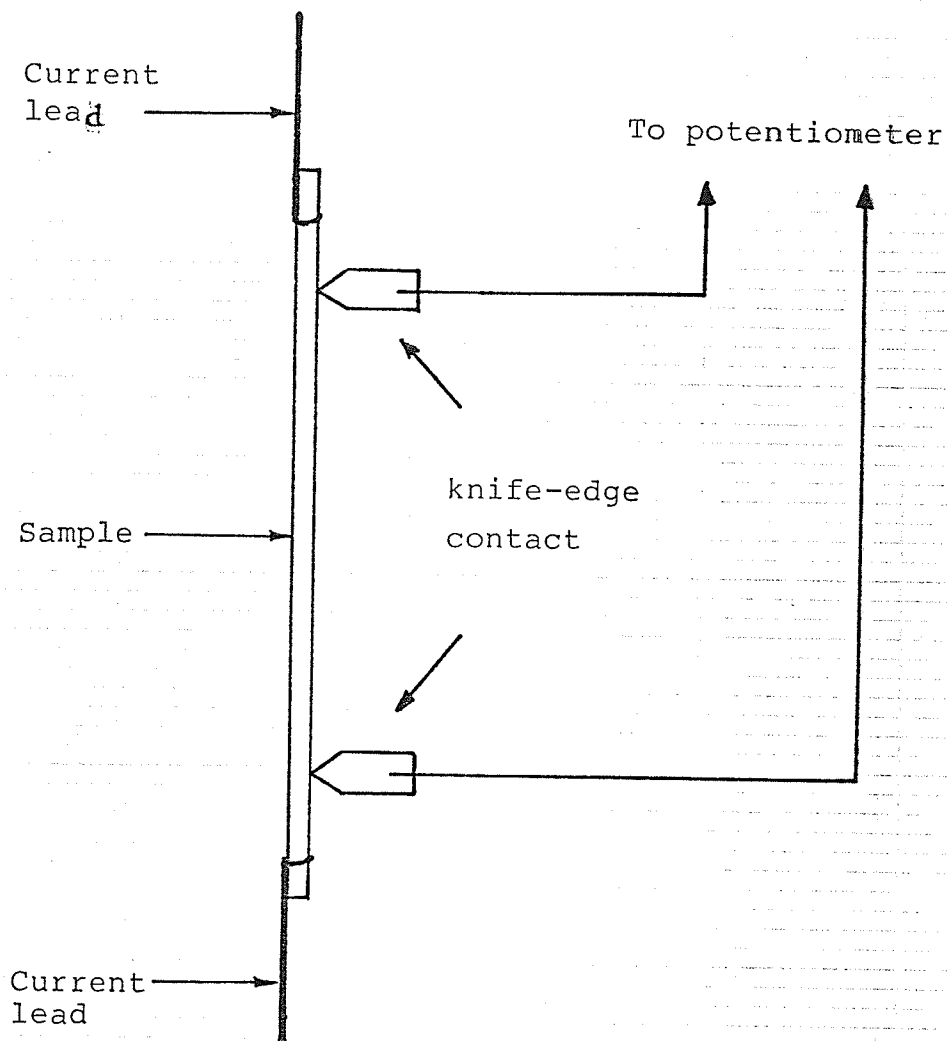


Fig.3.4.10 Four Probe Technique

switched on and off, the current I is reversed and the voltage V measured again. Then the average V and the average I will be used to calculate R for the particular temperature.

Fig. 3.4.11 shows the block diagram for the electronics used to measure D. C. resistivity. The reference voltages for various parts of the system were obtained from 6 standard cells enclosed in a temperature controlled Guildline Model 9152T6 standard cell enclosure. One of these cells referenced a Guildline 9770B constant current supply to produce a current of 10 mA stable to 2 parts in 10^6 . This current passed through a Tinsley Type 4092 reversing switch, and a Guildline 9200 standard resistor set at 0.1 ohm, before being fed via the cryostat top plate to the 6 samples on the same block. Voltages tapped from the above standard resistor and the samples, were selected by a Guildline Model 9145A10 selector switch and fed to a Tinsley Type 3589R-Auto Diesselhorst potentiometer. This potentiometer was referenced by another standard cell in the Guildline Standard cell enclosure, and powered by a Guildline Model 9781 reference voltage. The last two items were also wired through the Tinsley reversing switch so that the reversal of all relevant voltages could be synchronized. The output from the potentiometer was fed to a Tinsley Type 5214 photocell galvanometer amplifier and a Tinsley Type MS2-45E galvanometer capable of measuring to $\pm 10^{-8}$ volts. All electrical connections outside the cryostat were made with low thermal solder.

Twenty-two no. 38 enamelled copper wires in a Systoflex shield were used for electrical connections from the samples inside the cryostat to the Guildline selector switch outside. The twenty-two

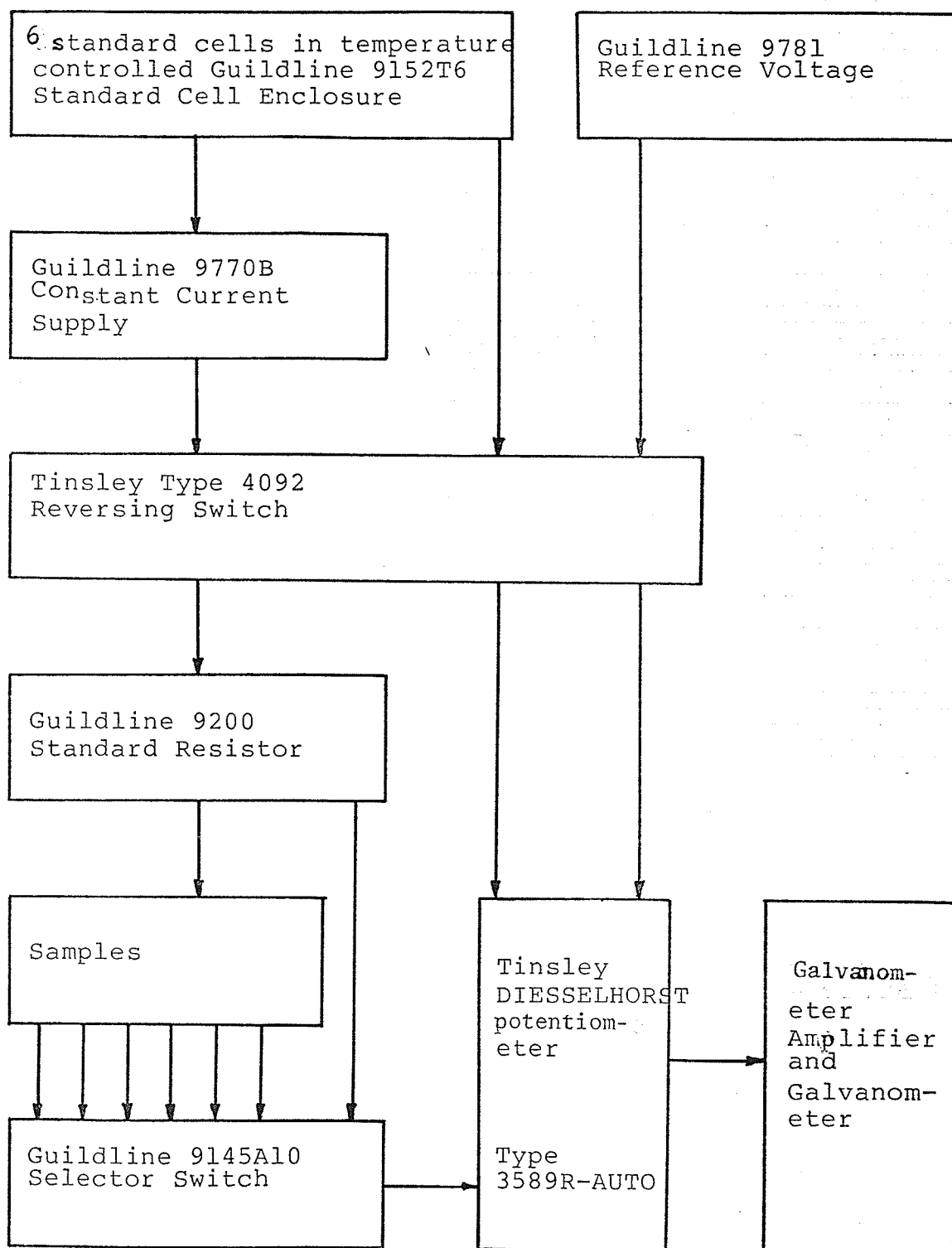


Fig. 3.4.11 Block Diagram of Electronics

comprised 12 voltage leads, 2 current leads, 3 carbon resistor leads, 2 heater and 3 spare leads. After leaving the sample block, these wires were wrapped three times around the gas thermometer bulb inside the IVC, then passed out through the OVC, and were again wrapped several times around a thermal anchor placed 4.5 inches above the OVC, as shown in Fig. 3.4.12.

This thermal anchor was a piece of solid copper rod pushed into the stainless steel tube for housing the copper wires (See Section 3.4.2). The exposed end of the rod was cut obliquely to increase surface contact with the helium bath while the enclosed end was trimmed to a smaller diameter to fit the stainless steel tube. Cigarette paper and G. E. varnish were used to ensure good thermal contact between the anchor and the wires wrapped around it. Such techniques ensured that heat originating from the top of the cryostat at room temperature would be dissipated in the helium bath rather than reaching the samples. Fig. 3.4.13 shows the relationship among the sample block, gas thermometer bulb, IVC, OVC, and thermal anchor.

3.5 Measurement of A. C. Susceptibility

The A. C. Susceptibility system is simpler to describe than the D. C. resistivity system, since it consisted of 2 essential parts only:

1. the cryostat system
2. the phase-locked magnetometer

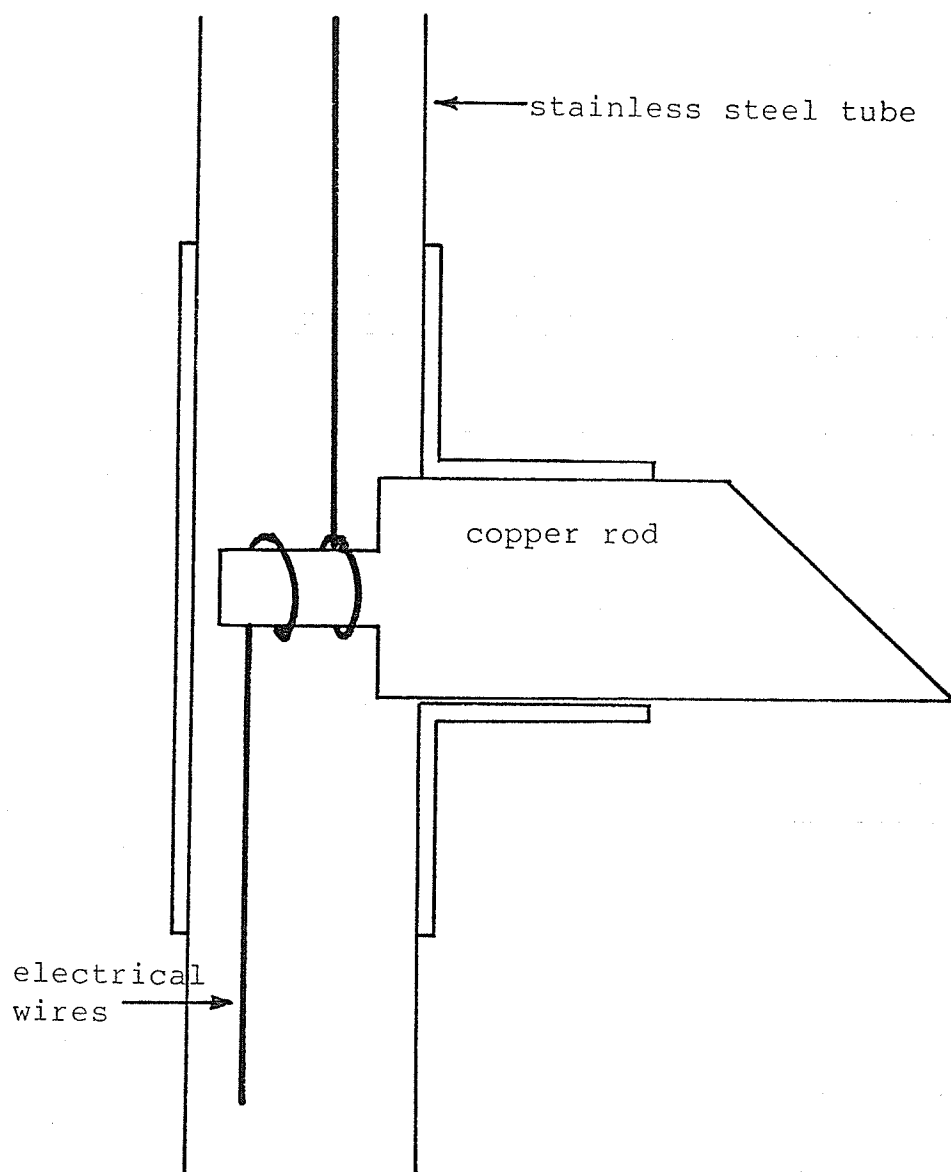


Fig.3.4.12 Thermal anchor

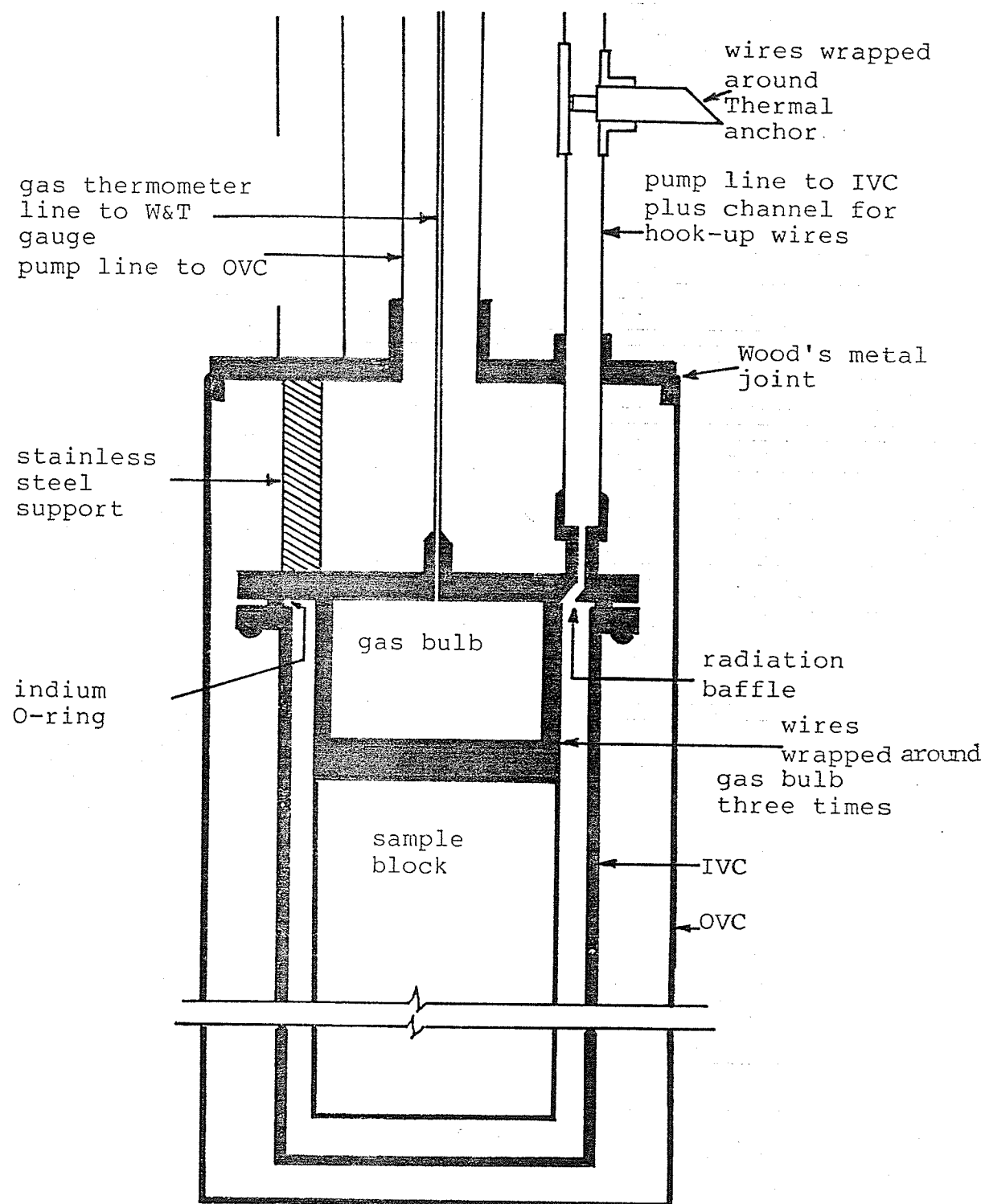


Fig.3.4.13 Details of the OVC,IVC,and Gas Bulb.

3.5.1 Cryostat System

The A. C. susceptibility system was designed to continuously measure this property over a wide range of temperature. Thus the cryostat system was not required to hold the sample at a fixed temperature. The system was cooled below 4.2 K by pumping on a helium bath surrounding the sample, while temperatures above 4.2 K were achieved by allowing the system to warm up naturally. A nichrome heater wound non-inductively around the copper block on the sample rod could accelerate the warm up rate if desired. Typically, this rate was 3 K/hour for temperatures below 4.2 K and 6 K/hour above 4.2 K. To avoid hysteresis effects, the sample was always cooled down in zero magnetic field, and measured on warming up. (Even the earth's magnetic field was balanced out.) The sample was suspended lengthwise inside a bundle of fine copper wires anchored to the bottom of the copper block. The wires provided reasonable thermal contact among the sample and two thermometers buried in the bundle close to the sample: a germanium (Ge) resistor and a Au-0.3 at % Fe vs. chromel P thermocouple. These thermometers were not magnetic, and contributed only to the background signal due to the extra leads and copper casing on the Ge resistor. See Fig. 3.5.1.

From 4.2 K to 100 K, the Ge resistor was calibrated by CryoCal, Inc. of Florida, and from 1.4 K to 4.2 K, in our laboratory against helium vapour pressure. Experience showed that the Ge resistor was not affected by magnetic or thermal cycling. The drift in resistance at the boiling point of liquid helium (4.2 K) was less than 1 % over a period of 3 years. Only the Ge resistor was used in these

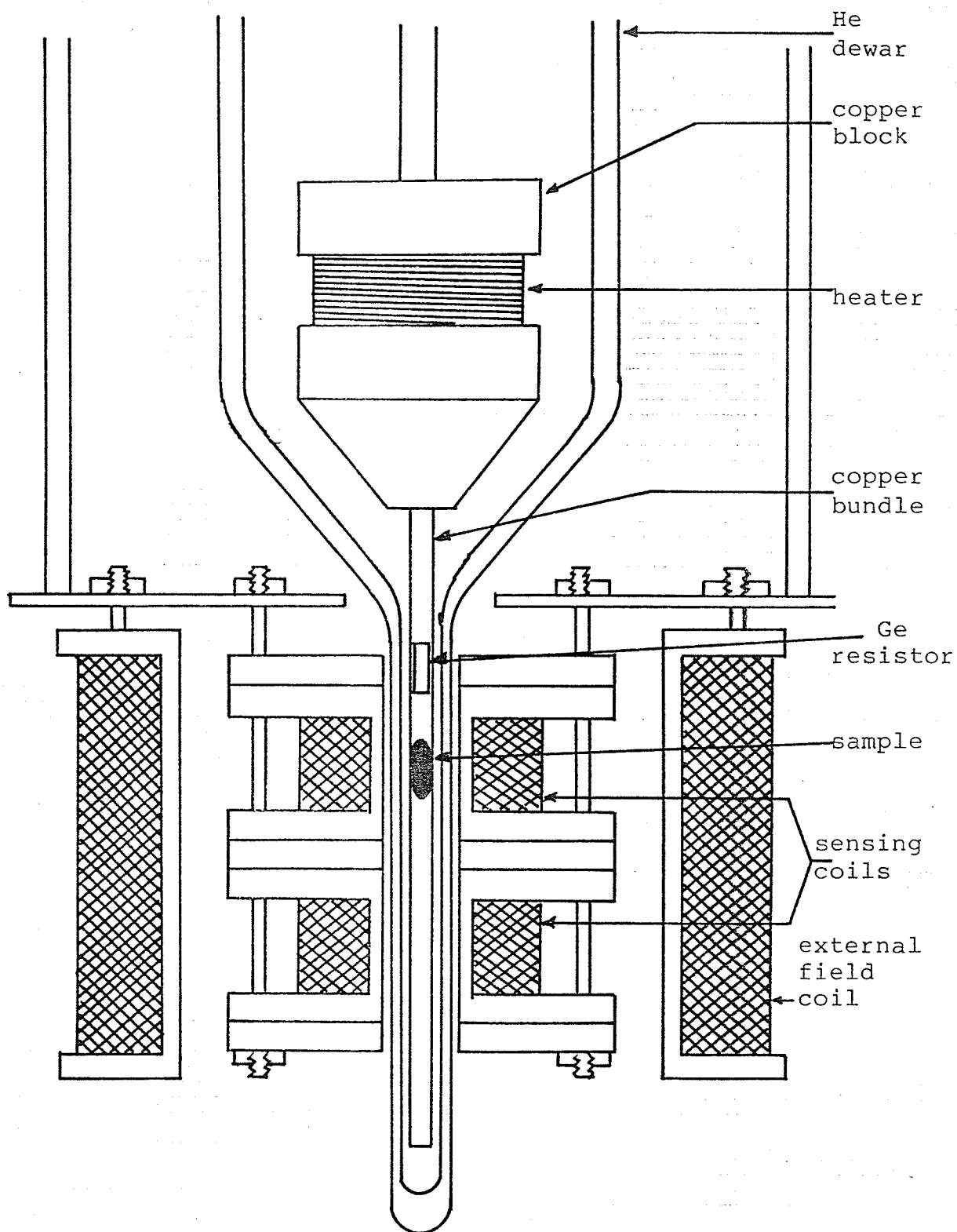


Fig.3.5.1 Arrangement of the Sensing Coils, External Field Coil, and the Sample Probe in the A.C. Susceptibility Cryostat.

experiments.

3.5.2 Phase-Locked Magnetometer

A. C. susceptibility as a function of temperature was measured by a phase-locked magnetometer designed by I. Maartense (1970). Fig. 3.5.2 shows the block diagram of the magnetometer. The first LC circuit consisted of a sensing coil L_1 inside the cryostat connected in series with a capacitor C_1 outside. This circuit was allowed to resonate at its natural frequency

$$\omega_1 = (L_1 C_1)^{-1/2}$$

This frequency was used by an oscillator to drive a second similar LC circuit whose natural frequency was

$$\omega_2 = (L_2 C_2)^{-1/2}$$

These two frequencies were compared in a phase detector which was sensitive to signal phase, but not amplitude. If $\omega_1 = \omega_2$, then the output from the phase detector would be zero. If a sample with a permeability was inserted into the coil of the 2nd LC circuit, the effective value of L_2 would be changed, and the two frequencies would be different. The phase detector would then generate a voltage to correct the frequency of the 2nd LC circuit by means of a voltage controlled reactance. This voltage was proportional to the A. C. susceptibility of the sample, and could be recorded on the Y-input of an X-Y recorder. The X-input was the voltage from the Ge resistor thermometer.

Each sensing coil in the two circuits consisted of 4000 turns of 35 gauge enamelled copper wire wound on a nylon coil former. Their inductances were measured to be 205 mh and 202 mh respectively.

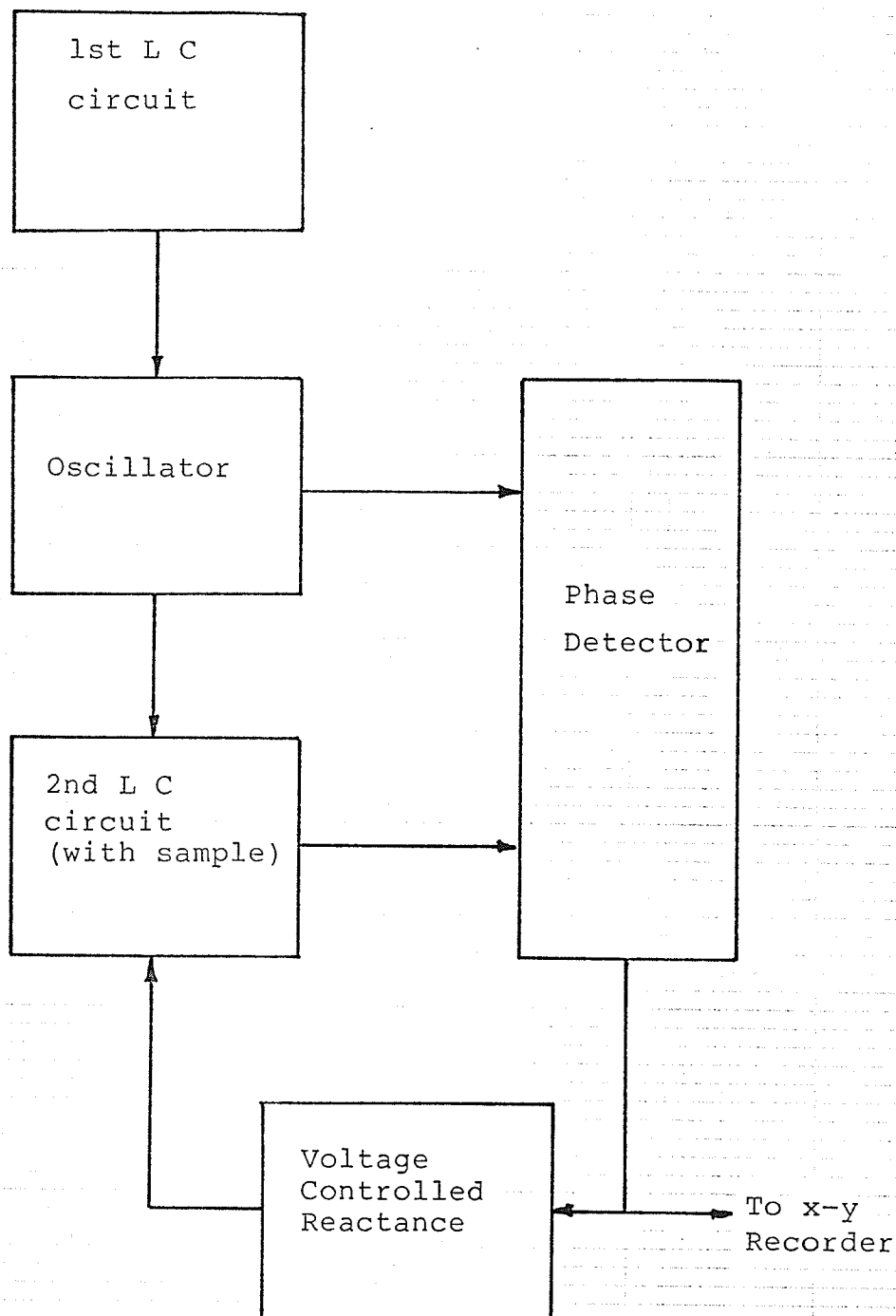


Fig.3.5.2 Block Diagram of Phase Locked Magnetometer.

A coaxial field coil of 3500 turns of 22 gauge enamelled copper wire provided the external magnetic field up to 800 Oe. All 3 coils were immersed in liquid nitrogen to minimize temperature difference between the sensing coils and to cool the field coil. At high currents, however, joule heating of the field coil caused so much bubbling of the liquid nitrogen that small drifts in the temperature and/or position of the sensing coils were inevitable. To correct for this background drift, the sample was periodically raised out of the sensing coils to indicate the true 'zero' of the magnetometer output.

3.5.3 Calibration

The measured volume susceptibility $\Delta\chi$ was related to the inductance ΔL of the sensing coil through the equation (Maartense 1970)

$$\Delta\chi = \frac{\Delta L}{4\pi L \eta}$$

where ΔL was the change in L , and η was the filling factor of the sample in the coil. To use this equation directly required accurate measurement of the sample volume, which was deemed too difficult to do. Hence the magnetometer was calibrated with Gd_2O_3 powder at 77 K.

Gd_2O_3 is a paramagnet at 77 K, and its susceptibility can be described by the Curie law satisfactorily.

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

where χ is the susceptibility per unit volume, N is the number of magnetic atoms per unit volume, g is the g -factor, μ_B is the Bohr magneton, J is the spin of magnetic atom, k_B is the Boltzmann's constant, T is the temperature and $g = 2$ and $J = 3.5$ for Gd ions in Gd_2O_3 .

The Gd_2O_3 powder was enclosed in a small glass tube whose size was chosen to approximate the average sample size. The position of the tube inside the sensing coil was adjusted to give the maximum signal from the magnetometer. It was found that 1 mV of magnetometer signal corresponded to a susceptibility of 8.58×10^{-7} emu/Oe. It follows that

$$\text{susceptibility per unit mass} = \frac{\text{signal} \times 8.58 \times 10^{-7}}{\text{mass of sample}} \quad (\text{emu/gm/Oe})$$

and

$$\text{susceptibility per unit volume} = \frac{\text{signal} \times 8.58 \times 10^{-7}}{\text{mass of sample}} \times \text{density} \quad (\text{emu/c.c./Oe})$$

However, the spread in filling factors among samples, and changes in demagnetising field if the sample shapes varied, placed a possible error of $\pm 10\%$ on the absolute value of the measured susceptibility. When changes in susceptibility of the same sample are concerned, the data are much more accurate. Nevertheless, the resolution of the magnetometer itself, $\sim 10^{-8}$ emu/Oe, placed a lower limit on the detectable signal, so that for alloys with more than 9.0 at % Mn, their weak susceptibilities are less accurately measured.

In addition, for every alloy one made a background run of the magnetometer with no sample to determine the background signal. This background signal has already been subtracted in the data in Chapter IV.

3.5.4 Corrections for Demagnetizing Factor and Internal Magnetic Field

With the magnetometer used in this project, the output is the measured susceptibility χ_{meas} , defined as

$$\chi_{\text{meas}} = \frac{dM}{dH_a}$$

where M is the magnetization of sample and H_a is the applied magnetic field. The data one looks for are the real susceptibility χ measured with respect to the internal magnetic field H_i

$$\chi = \frac{dM}{dH_i}$$

H_i and H_a are related by the scalar equation

$$H_i = H_a - NM \quad (3.5.1)$$

assuming an elliptical form for the samples. N is the demagnetizing factor.

Now $H_i = H_a - NM$

$$\text{Therefore } \frac{\partial H_i}{\partial M} = \frac{\partial H_a}{\partial M} - N$$

$$\frac{1}{\chi} = \frac{1}{\chi_{\text{meas}}} - N \quad (3.5.2)$$

$$\chi = \frac{\chi_{\text{meas}}}{1 - N\chi_{\text{meas}}} \quad (3.5.3)$$

Since the samples investigated have positive susceptibilities, the above equation implies that

$$\frac{1}{\chi_{\text{meas}}} > \frac{1}{\chi} .$$

It follows that provided $\frac{1}{\chi_{(maxi)}}$ can be ignored in comparison with N

$$\frac{1}{\chi_{meas (maxi)}} \approx N \quad (3.5.4)$$

This gives a better estimate of N than the formula of Osborn (1945) since the samples are not real ellipsoids.

Substituting this results into Eq. 3.5.2 one gets

$$\chi \approx \frac{\chi_{meas}}{1 - \frac{\chi_{meas}}{\chi_{meas (maximum)}}} \quad (3.5.5)$$

Because of the approximation used in Eq. 3.5.4, Eq. 3.5.5 will fail when $\chi_{meas} \approx \chi_{meas(maxi)}$. Fortunately, with the ferromagnetic Pd-Mn alloys even the earth's field, ~ 0.65 Oe, reduces χ_{meas} to half of $\chi_{meas(maxi)}$. Hence Eq. 3.5.5 is acceptable for correcting the data for demagnetising factor.

To correct for the internal field H_i for the ferromagnetic Pd-Mn alloys, one notes that after correcting for demagnetising factor, the height of the critical peak χ_m , under an applied field H_a , follows the empirical formula

$$\chi_m = AH_a^{-n} \quad (3.5.6)$$

where A and n are constants such that

$$A > 0, \quad 1 > n > 0$$

For examples see Fig. 4.2.7 and other diagrams in the Appendices.

Hence from Eq. 3.5.2,

$$AH_a^{-n} = \frac{dM}{dH_a} (1 + NAH_a^{-n})$$

$$M = A \int_0^{H_a} \frac{1}{H_a^n + NA} dH_a$$

A power series expansion for the integrand

$$(H_a^n + NA)^{-1} = \sum_{i=1}^{\infty} (NA)^{i-1} H_a^{-in} (-1)^{i+1}$$

converges absolutely whenever $x_m < \frac{1}{2N}$, using the ratio test of series (Sokolnikoff and Redheffer 1966, p. 19). This condition is always satisfied because the critical peak heights are never more than 20% of $1/N$.

Interchanging the order of summation and integration, one gets

$$M = \frac{H_a}{N} \sum_{i=1}^{\infty} N^i x_m^i \frac{(-1)^{i+1}}{1 - in}$$

Hence

$$H_i = H_a \left\{ 1 - \sum_{i=1}^{\infty} N^i x_m^i \frac{(-1)^{i+1}}{1 - in} \right\} \quad (3.5.7)$$

This is the equation used to extract H_i from H_a . In practice, the difference between H_i and H_a increased from ~ 0.2 Oe at low applied fields to ~ 4 Oe at high fields. The procedure is only approximate because of the assumption of an ellipsoid for each sample and of the temperature dependence of Eq. 3.5.6. This dependence is given by Eq. 2.2.16, but is ignored in the above analysis. For Pd-Mn alloys with Mn ≥ 5.0 at %, the internal field is not calculated because there is no critical peak.

3.5.5 Frequency Dependence of Output

The magnetometer was operated at an A. C. driving field of 0.46 Oe rms. and a frequency of 2400 Hz. for all the measurements. The frequency dependence of the susceptibility signal was checked on the calibration sample and the Pd-1.0 at % Mn sample. When the frequency was changed from 2400 Hz. to 714 Hz., at the same driving field and at the same temperature of 77 K, the signal for Gd₂O₃ decreased by 6.6 %. As the susceptibility of Gd₂O₃ had no frequency dependence at 77 K, this decrease had to be instrumental in origin. When the same frequency change was applied to Pd-1.0 at % Mn, at a temperature when Pd-1.0 at % Mn was ferromagnetic, the signal decreased by 6.0 %. Hence the susceptibility signal of Pd-Mn alloys could not be significantly changed by changing the frequency from 2400 Hz to 714 Hz. The magnetometer was set at 2400 Hz because the higher frequency provided better signal to noise ratio.

In surveying the literature, it is found that substantial frequency dependence of susceptibility of other alloys usually occurs at the MHz level. Further, as found by Smit et al (1979), the frequency dependence of Pd-Mn alloys in this concentration range is negligible. Hence one can safely state that the A. C. susceptibility data presented here approximate the static susceptibility theory of this thesis within an error of $\pm 10\%$ if absolute values are concerned, while the error becomes smaller, probably $\pm 0.1\%$ if changes in susceptibility of the same sample is concerned. For alloys with more than 9.0 at % Mn, the data are not so accurate though.

CHAPTER IV

DATA ANALYSIS

4.1 From 0.5 at % to 2.5 at % Mn

4.1.1 Low field susceptibility data

There is general agreement that Pd-Mn alloys in this range are ferromagnetic. One evidence for the ferromagnetism is the susceptibility data, shown in Fig. 4.1.1 for Pd-2.5 at % Mn. Note that the number beside each curve indicates the net applied magnetic field, measured in Oe. In zero D.C. biasing field, as the temperature decreases, the measured susceptibility increases rapidly in the vicinity of T_c , peaking at a value $\chi_{\text{meas(maxi)}}$ close to N^{-1} , N being the demagnetising factor. At lower temperature, the susceptibility decreases with decreasing temperature, indicating the presence of anisotropy effects. The effect of an applied field is quite striking, as a result of the sample's small N (≈ 0.05) and low saturation moment (Star et al 1975). The earth's field (the vertical component of which is 0.65 Oe in this laboratory) is sufficient to round off the main peak to a broad peak with about half its original height. A slightly stronger field, 9.3 Oe, pushes the main peak below the low temperature limit of 1.45°K of the magnetometer, while bringing out a small peak at a temperature close to the inflexion point of the original zero field curve. This small peak, only 3% of $\chi_{\text{meas(maxi)}}$, is called a critical peak because its position T_m and height χ_m are related to the critical indices of the ferromagnet to paramagnet transition as discussed in Section 2.2.4.

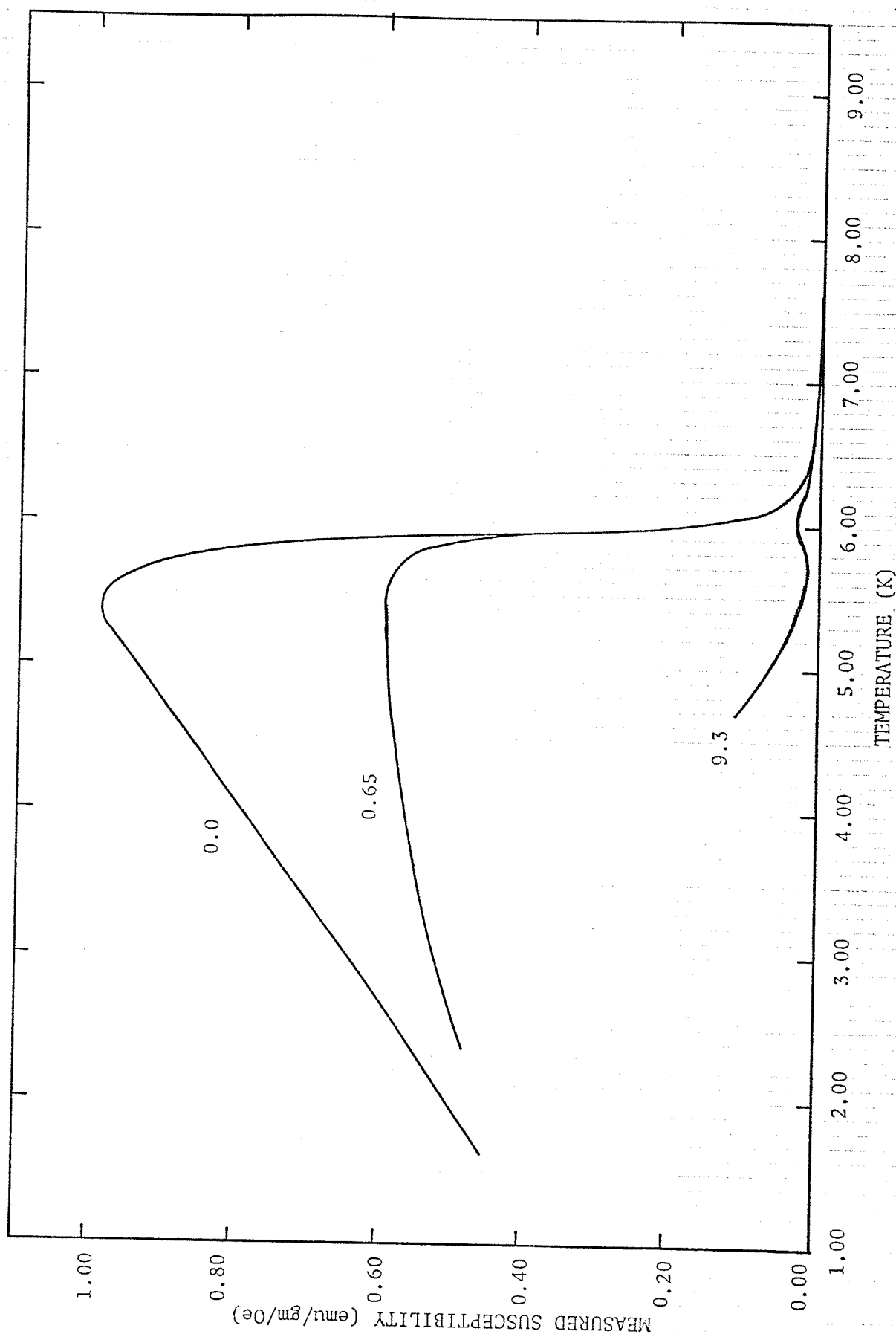


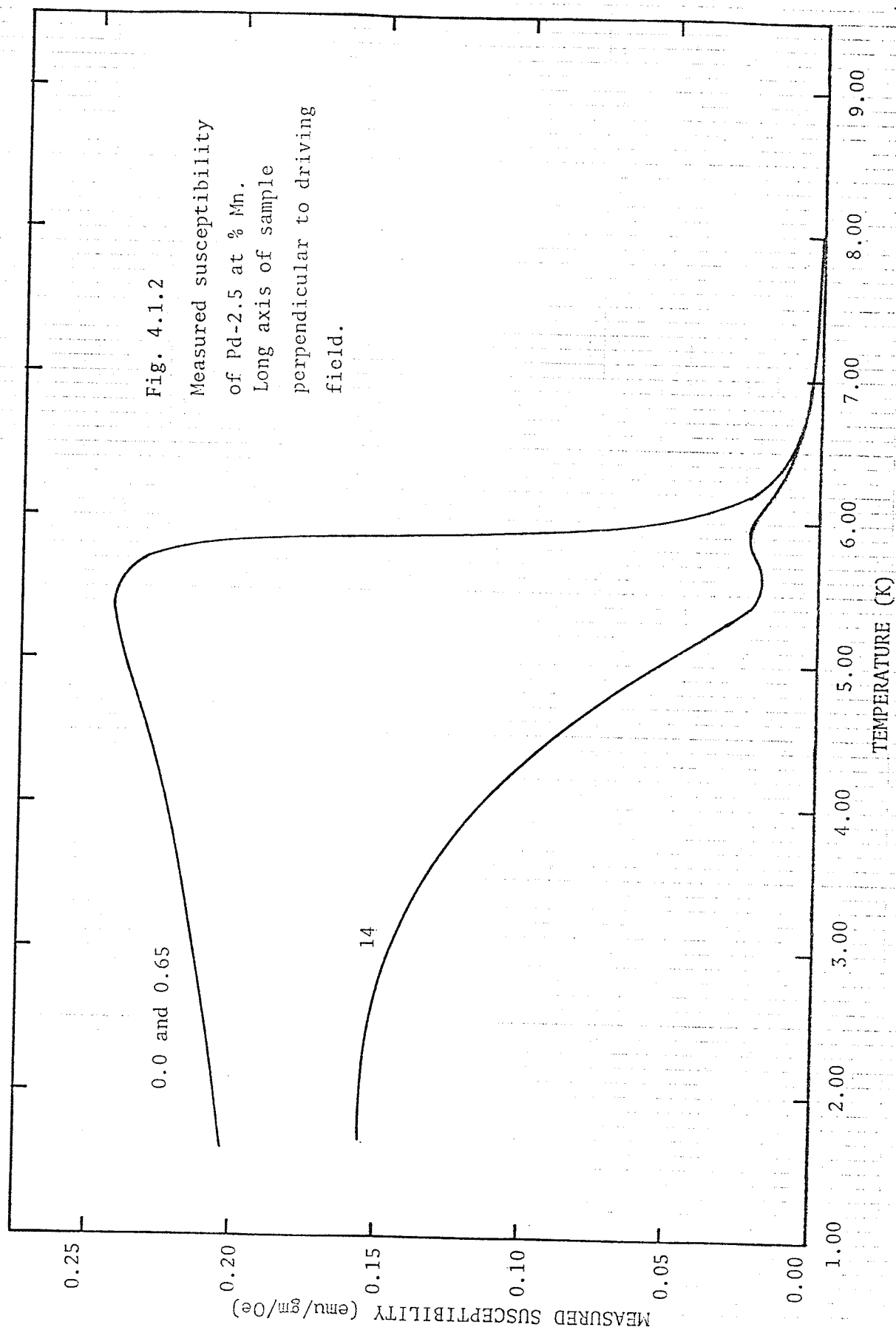
Fig. 4.1.1 Measured susceptibility of Pd-2.5 at % Mn.

If the sample is rotated so that its long axis is perpendicular to the driving field, the changes in susceptibility is less dramatic, due to the increase in N (≈ 0.3). Fig. 4.1.2. depicts the case for a Pd-2.5 at % Mn sample measured in this manner. The 0.0 Oe and 0.65 Oe curves actually coincide within experimental error, while an applied field of 14 Oe brings out a critical peak which is 10% of $\chi_{\text{meas(maxi)}}$ for this orientation. The critical index γ obtained from the $\chi(T,0)$ curve in Fig. 4.1.2 is 1.33 while it changes to 1.36 if taken from the $\chi(T,0)$ curve in Fig. 4.1.1. Fig. 4.1.2 is the only case when the long axis of the sample is perpendicular to the driving field; all others are measured in the parallel orientation.

As pointed out in Section 3.5.4, $\chi_{\text{meas(maxi)}}$ approaches N^{-1} . Hence a measure of the relative saturation moment of Mn in each alloy is the ratio $\chi_{\text{meas(maxi)}}/N^{-1}$, plotted in Fig. 4.1.3 for $\text{Mn} \leq 5.0$ at %. Here N^{-1} is calculated following Osborn (1945). The maximum value, 80%, occurs at Pd-2.0 at % Mn, and decreases almost exponentially for alloys above and below this concentration, reaching only 4% for Pd-5.0 at % Mn. That this maximum does not reach 100% indicates the difficulty in approximating the sample shape by an ellipsoid, and also the limitation of Eq. 3.5.4.

4.1.2 Medium to high field susceptibility data

With increase in magnetic field, the main peak is further reduced, while the critical peak becomes more prominent with respect to the background. The critical peak height χ_m , however, decreases



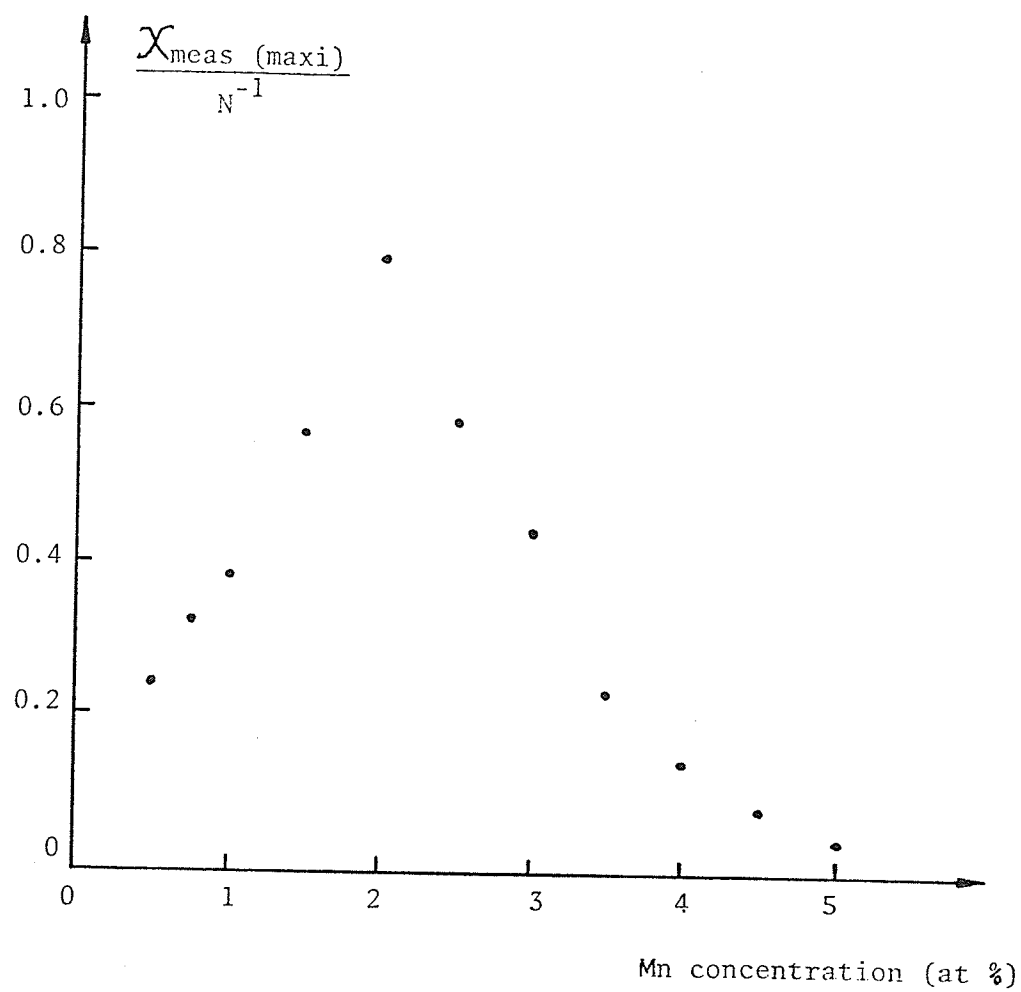


Fig. 4.1.3 $\frac{\chi_{\text{meas}} (\text{maxi})}{N^{-1}}$ of Pd-Mn alloys.

with field, and the peak position T_m moves up in temperature, as shown in Fig. 4.1.4 and 4.1.5. Note that χ_m always stays within the envelope of the original zero field curve. Above ~ 150 Oe applied field, even the critical peak begins to broaden, so that although χ_m remains well defined, T_m does not. As discussed in Section 2.2.4 above, T_m follows Eq. 2.2.16 within the scaling law hypothesis. This is borne out in Fig. 4.1.6, where typical values of γ and β are used in Eq. 2.2.16:

$$\gamma = 1.35, \quad \beta = 0.45, \quad (\gamma + \beta)^{-1} = 0.556$$

The relatively big error bars in T_m at high H_i points to the difficulty in estimating the position of the maximum of a broad peak. The curve is a straight line intercepting the Y-axis at T_c . This value of T_c is acceptable since from Eq. 2.2.16 $T_m(H_i = 0)$ is independent of $\gamma + \beta$, although for some alloys an adjustment of a few hundredths of a degree Kelvin is needed to give a satisfactory γ -plot. The Pd-2.5 at % Mn sample, however, requires a somewhat larger shift.

An interesting point which was not anticipated is that the height of the critical peak χ_m , after correcting for demagnetising factor, follows a power law of H_a , similar to H_i , namely

$$\chi_m(T_m, H_a) = A H_a^{-n}$$

with $A > 0$, $1 > n > 0$.

Figure 4.1.7 presents the typical case. Hence a $\ln\text{-}\ln$ plot of χ_m vs. H_a gives a straight line with a slope of $-n$. This n is then used to extract H_i for H_a as outlined in Section 3.5.4 above. With H_i one can proceed to extract the critical index δ using $\ln\text{-}\ln$ plots

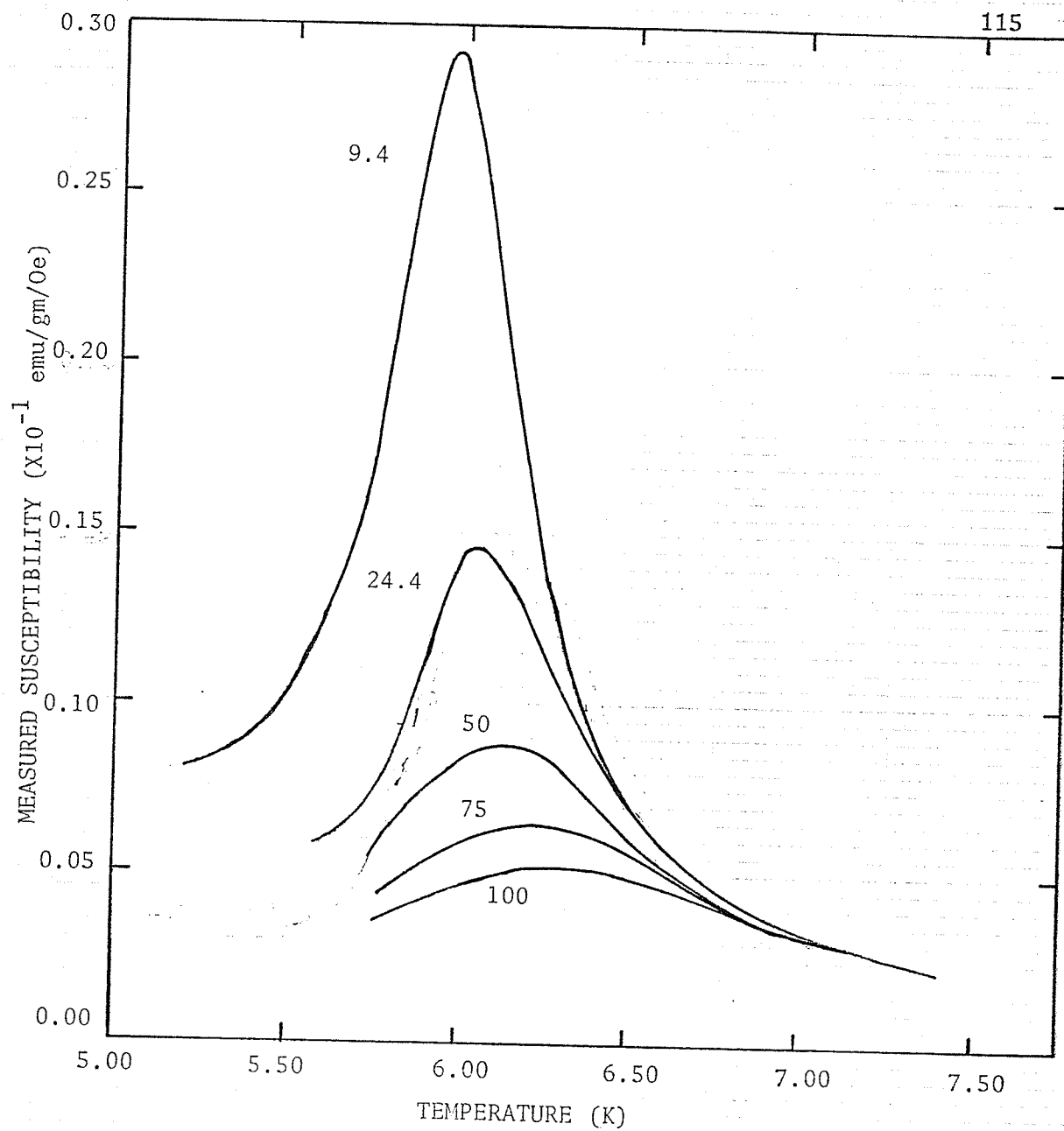


Fig. 4.1.4 Measured susceptibility of Pd-2.5 at % Mn.

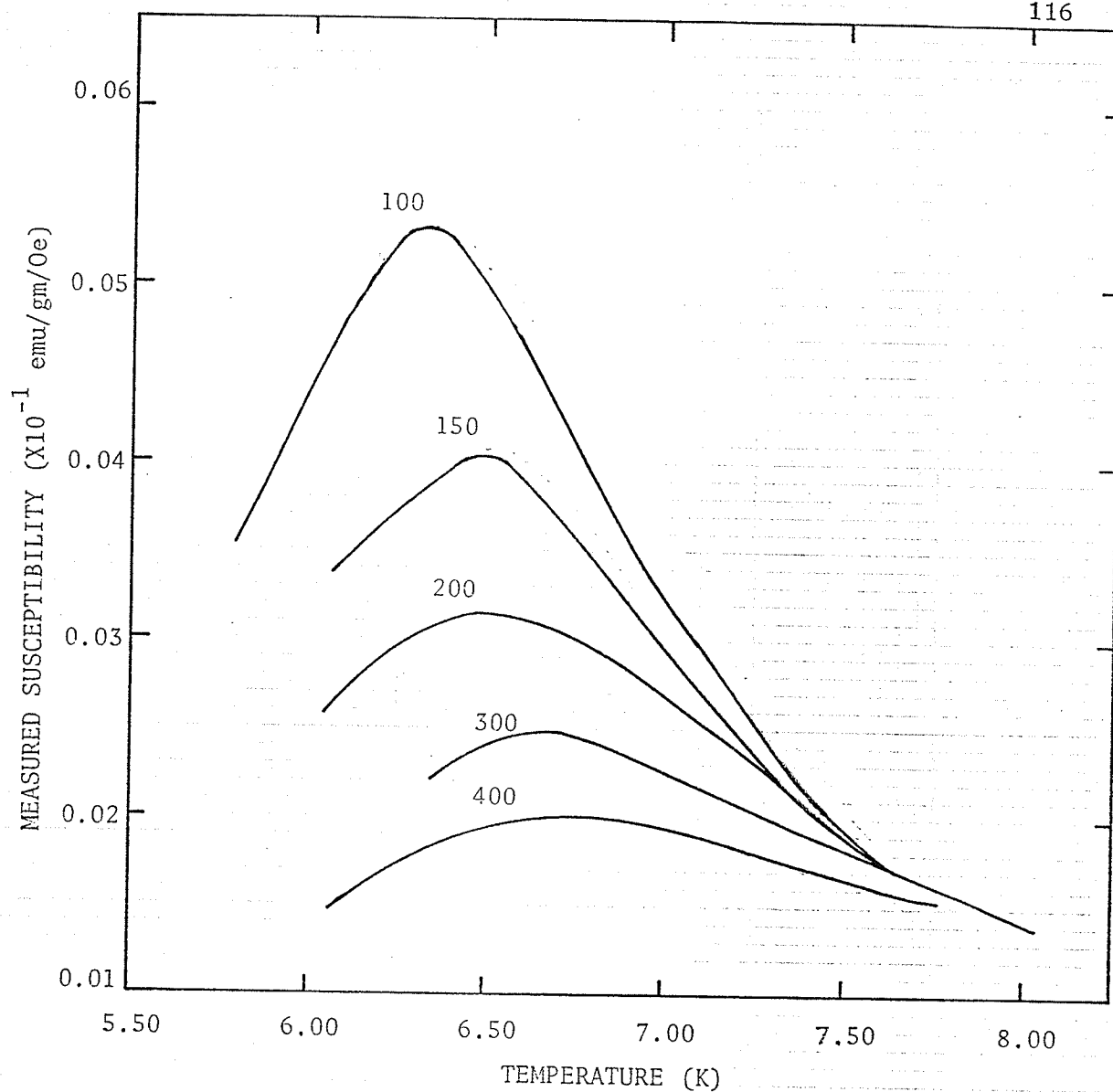


Fig. 4.1.5 Measured susceptibility of Pd-2.5 at % Mn.

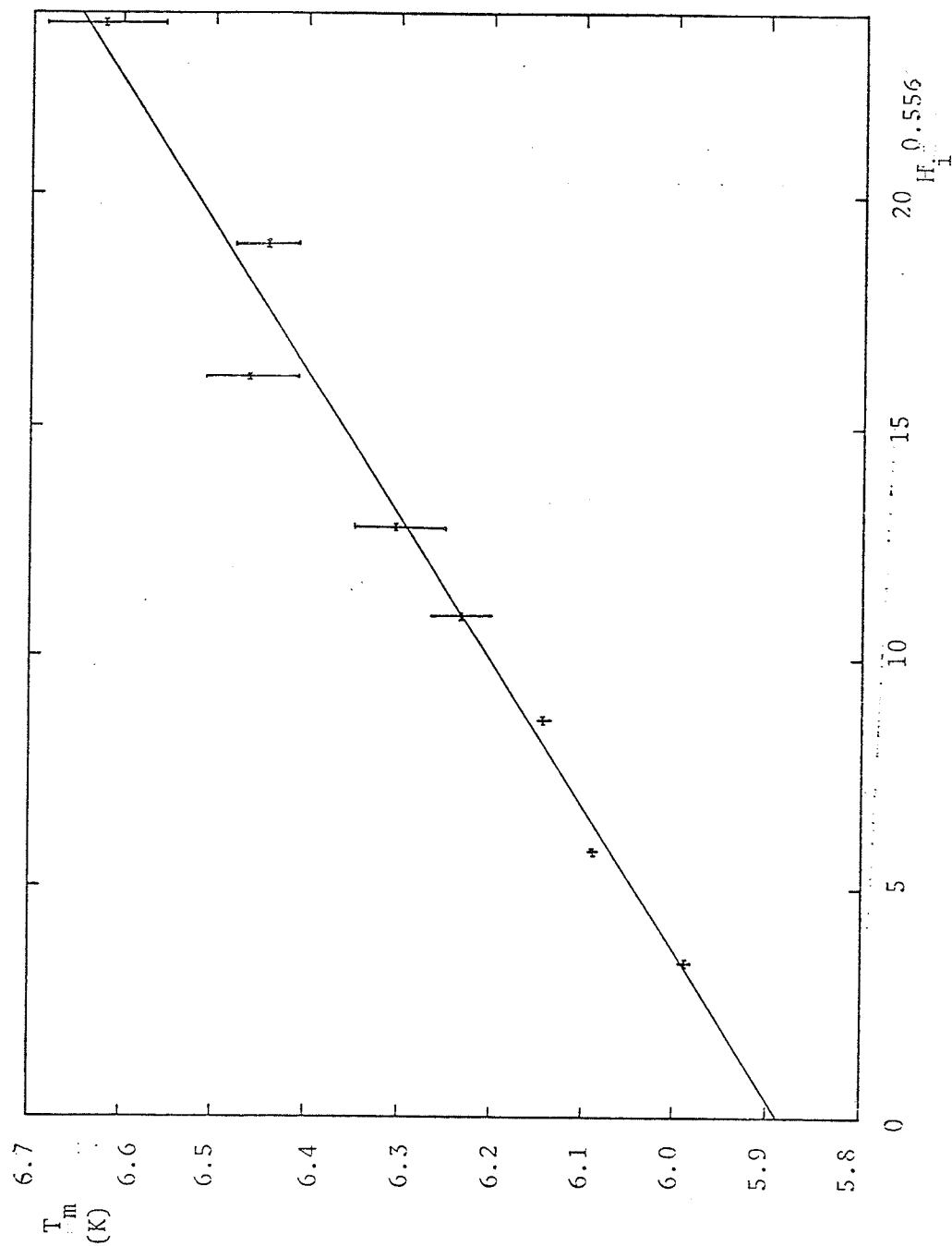


Fig. 4.1.6 T_m vs. $H_i^{0.556}$ for Pd-2.5 at % Mn.

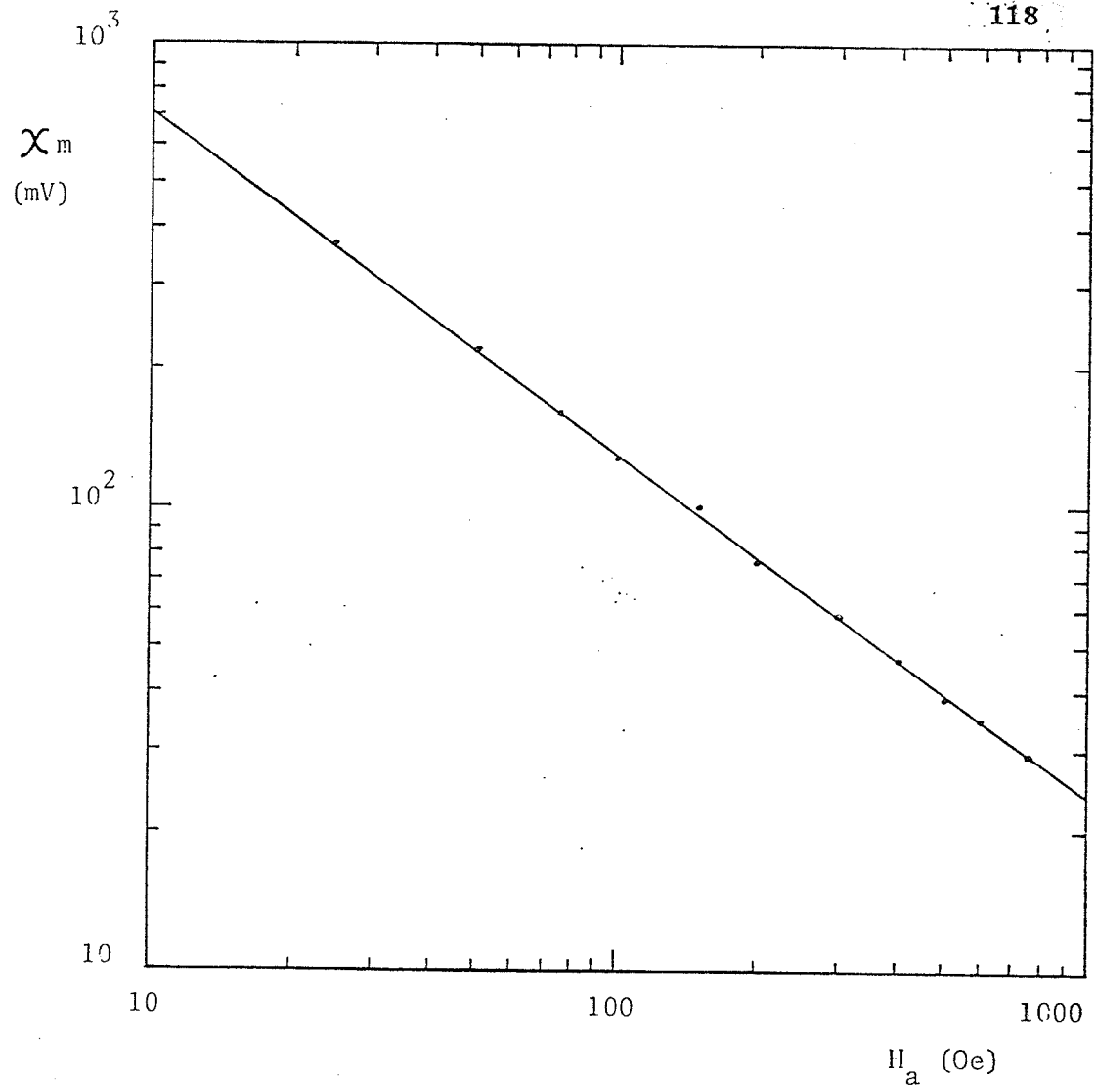


Fig. 4.1.7 Susceptibility vs. H_a for Pd-2.5 at % Mn.

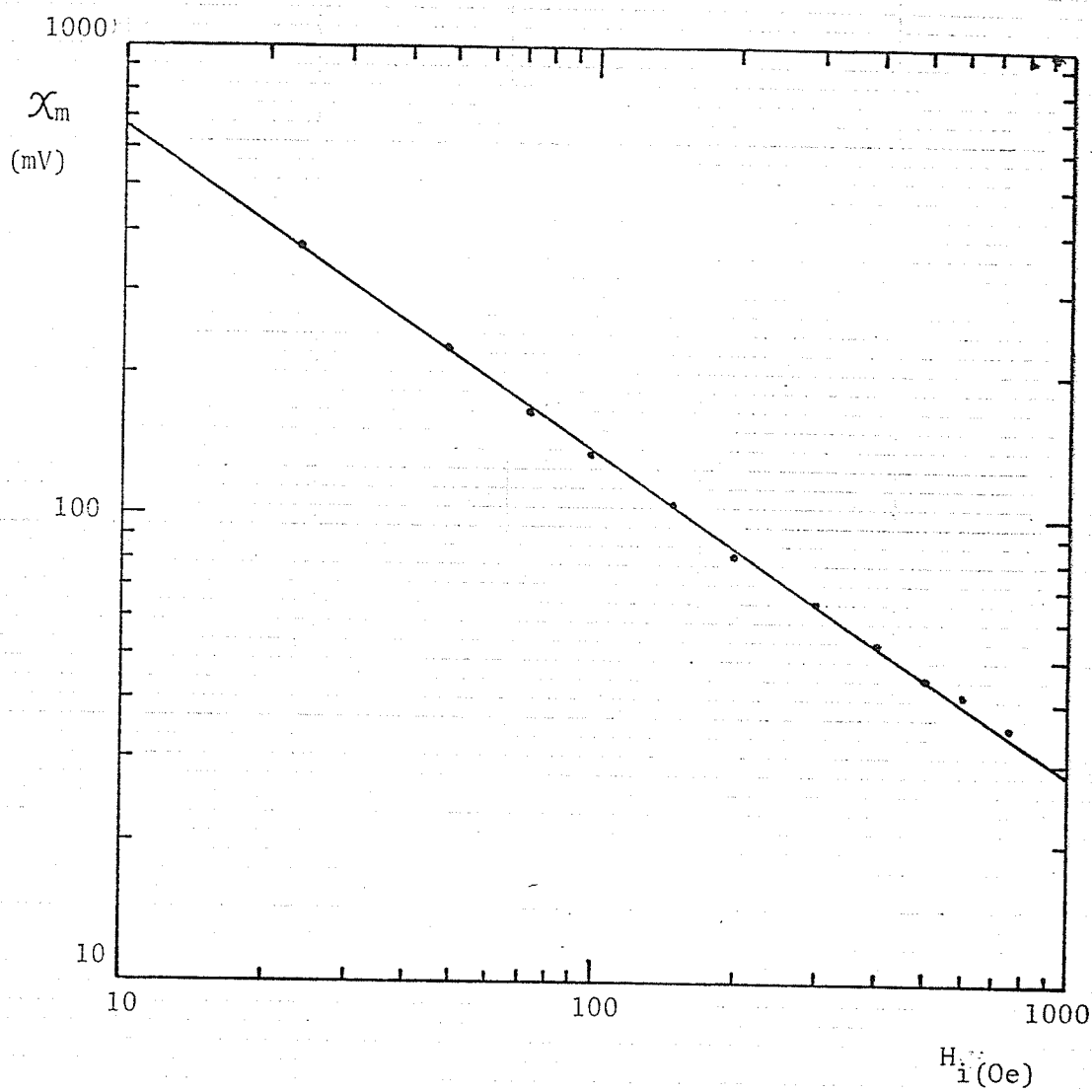


Fig. 4.1.8 Susceptibility vs. internal field for Pd-2.5 at % Mn.
(δ -plot)

of χ_m vs. H_i (See Fig. 4.1.8). As mentioned before, the value of δ obtained is free from any error in T_C . The value of δ decreases smoothly from 4.0 for Pd-0.5 at % Mn to 3.3 for Pd-2.5 at % Mn. With

With T_C and δ found, one might attempt to obtain β by recasting Eq. 2.2.15 as

$$\epsilon_m \sim H_i^{\frac{1}{\beta\delta}}$$

since $\beta\delta = \gamma + \beta$.

Then ideally, an ln-ln plot of ϵ_m vs. H_i will generate a straight line with slope $(\beta\delta)^{-1}$. The difficulties in this approach are that at low H_i , such a plot is very sensitive to uncertainties in T_C since $T_m - T_C$ is small, and that at high H_i , T_m itself is not well defined as the critical peaks broadened. Hence the β 's are not estimated.

4.1.3 γ Plots

Another critical index that can be extracted from the susceptibility data is γ . From the definition of γ

$$\chi(T,0) \sim \epsilon^{-\gamma}, \quad T > T_C$$

where $\epsilon = \frac{T - T_C}{T_C}$.

Hence a ln-ln plot of the susceptibility data, after correcting for demagnetising factor, vs ϵ gives a straight line with a slope of $-\gamma$. See Fig. 4.1.9. Such a plot suffers from the inherent errors of uncertainties in $(T - T_C)$ and in the resolution of the magnetometer used since the susceptibility data used are recorded in one sweep of

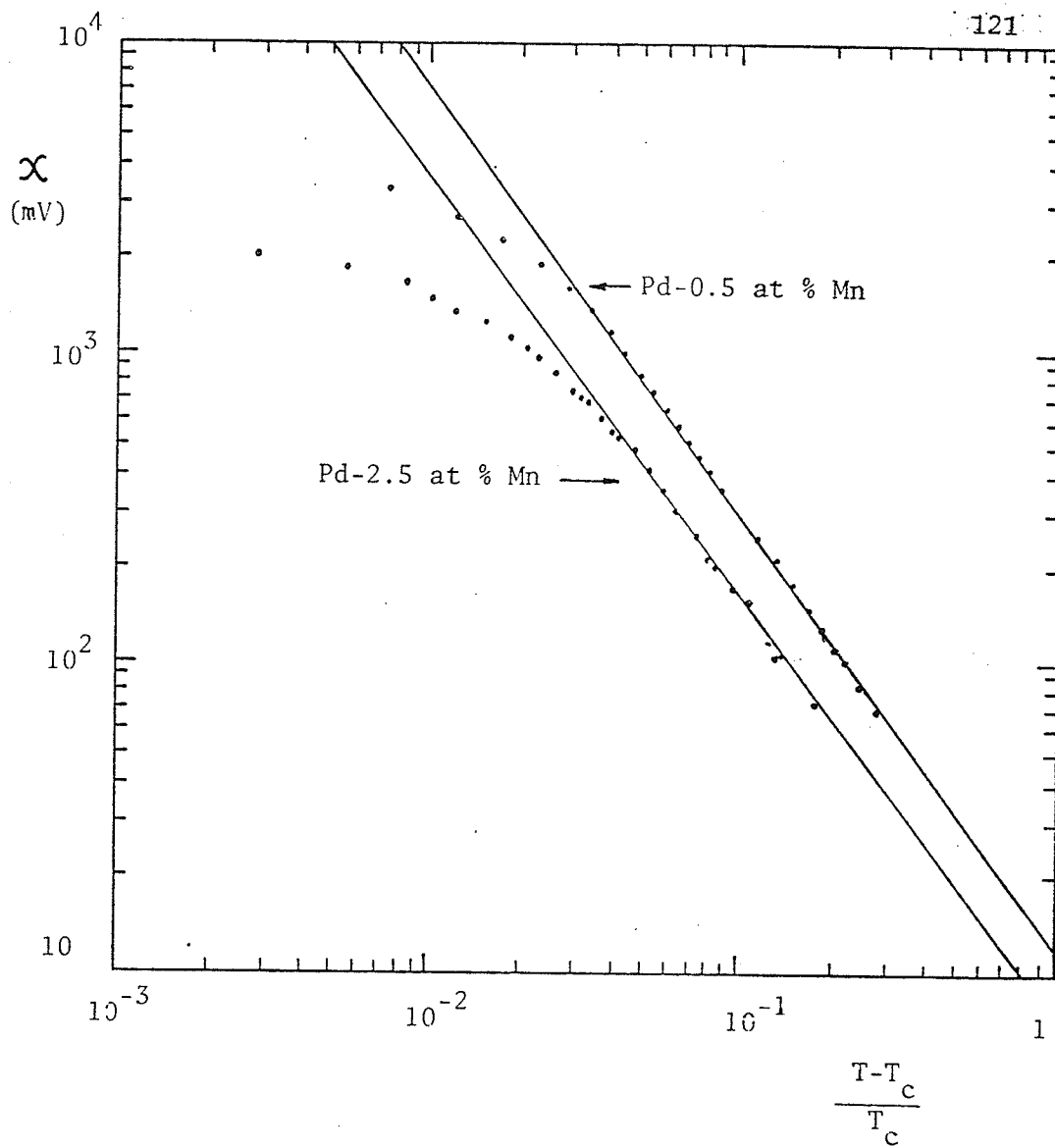


Fig. 4.1.9 Susceptibility vs. $\frac{T - T_c}{T_c}$ for Pd-0.5 at % Mn and Pd-2.5 at % Mn. (χ -plot)

the magnetometer at zero magnetic field. By comparison, each δ -plot contains $\chi_m(T_m, H_i)$ data taken from different sweeps of H_i , each taken with an optimum scale. Hence the γ -plot is not as good a straight line as the δ -plot. The γ 's obtained vary from 1.30 to 1.37, encompassing the value of 1.33 usually quoted for 3-D Heisenberg magnets.

These γ -plots can be used to estimate the effective magnetic moment of the Mn atom, as outlined by Maartense and Williams (1978):

In the mean-field approximation (MFA)

$$\chi = \frac{N \mu_{\text{eff}}^2}{3k_B(T - T_c)}$$

where N is the number of magnetic atoms per unit volume, and

μ_{eff} is the effective magnetic moment.

Since $\gamma = 1$ in MFA;

$$\begin{aligned} \chi &= \frac{N \mu_{\text{eff}}^2}{3k_B (T - T_c)} \left(\frac{T - T_c}{T_c} \right)^{1-\gamma} = \frac{N \mu_{\text{eff}}^2}{3k_B T_c} \left(\frac{T - T_c}{T_c} \right)^{-\gamma} \\ &= A \left(\frac{T - T_c}{T_c} \right)^{-\gamma} \end{aligned} \quad (4.1.1)$$

$$\text{where } A \equiv \frac{N \mu_{\text{eff}}^2}{3k_B T_c} \quad (4.1.2.)$$

Eq. 4.1.1 is equivalent to the equation defining γ . Hence A can be found from the γ -plots and μ_{eff} estimated via Eq. 4.1.2. The μ_{eff} values decreases systematically from 12.3 $\mu_B/\text{Mn atom}$ for Pd-0.5 at % Mn to 7.5 $\mu_B/\text{Mn atom}$ for Pd-2.5 at % Mn. While most of them are higher than the 7.5 $\mu_B/\text{Mn atom}$ quoted by Star et al (1975) and Thom-

son and Thompson (1979), due to the approximations of MFA, the decrease in effective magnetic moment with increasing Mn concentration is unmistakable. This can be taken as one piece of evidence supporting increase in direct Mn-Mn anti-ferromagnetic coupling with increase in Mn concentration.

Further support can be found in the systematic increase in width of the critical peaks with increase in Mn concentration. Under an applied field of, say 9.4 Oe, the spread in temperature of the critical peak heights measured at 75% of peak value, increased from 0.21 degrees K for the Pd-0.5 at % Mn alloy to 0.41 degree K for the Pd-3.0 at % Mn alloy. For the 3.5 at %, 4.0 at % and 4.5 at % alloys, the critical peaks are not yet separated from the main peaks at 75% peak height. Alloys with Mn concentration larger than or equal to 5 at % do not show critical peaks, but the same trend can be found for the main peak height at zero field, measured at 75% of

$\chi_{\text{meas(maxi)}}$. Fig. 4.1.10 presents the above data.

4.1.4 Resistivity Data

The ferromagnet to paramagnet transition is also reflected in the resistivity data. The most prominent feature is the sudden decrease in slope, the "knee", in the incremental resistivity curve near T_C , as shown in Fig. 4.1.11. Within experimental error the position of this knee coincides with T_C from the susceptibility data. As discussed in Section 2.3.2, Long and Turner explain this knee as resulting from the intersection of two straight line sections of the curve, at T_C . The one above T_C is predicted to be flat, i.e. the

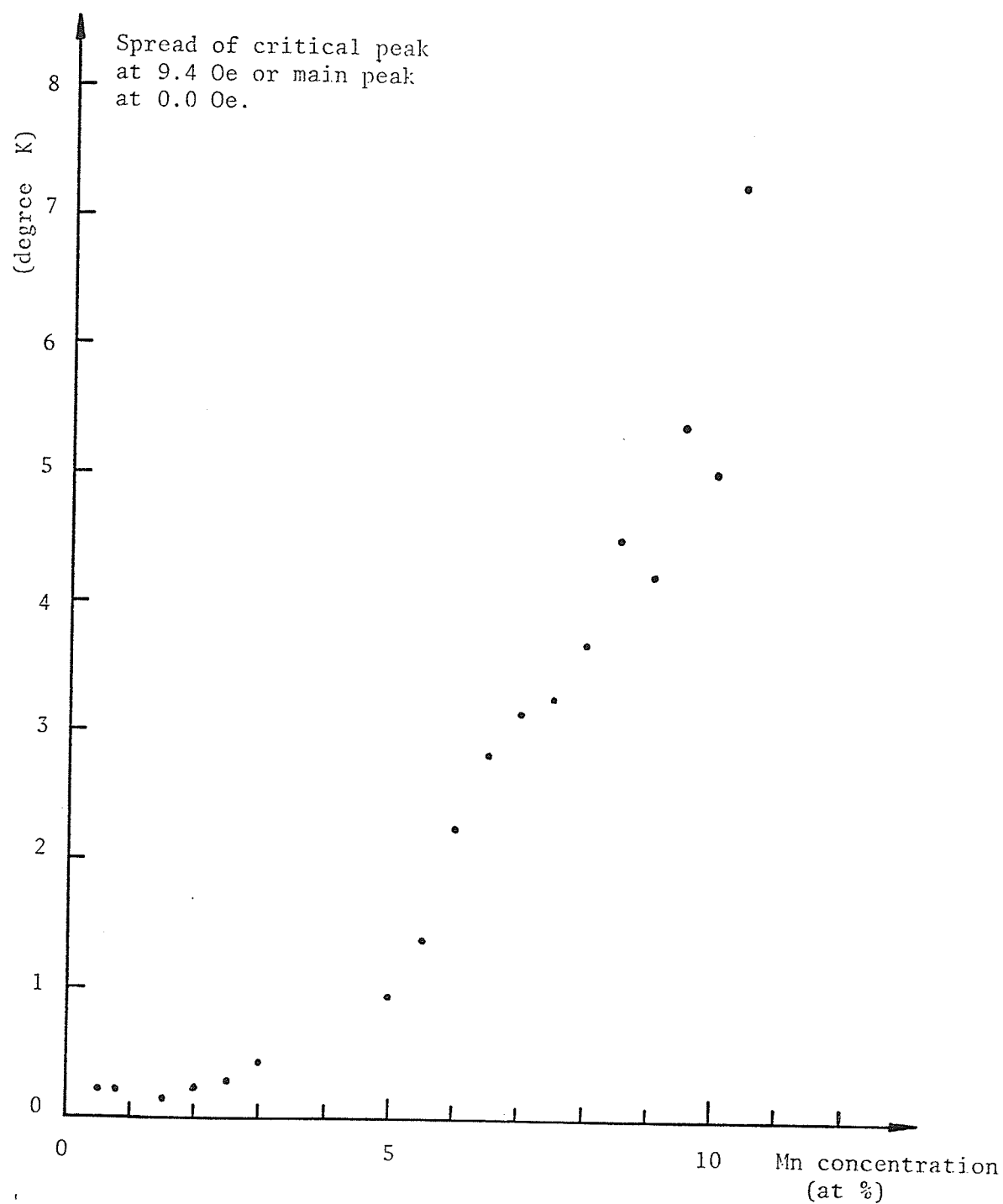


Fig. 4.1.10

Width of critical peak at 9.4 Oe for alloys with less than 3.5 at % Mn, and width of main peak at zero field for alloys with more than 4.5 at % Mn, measured at 75% of peak height.

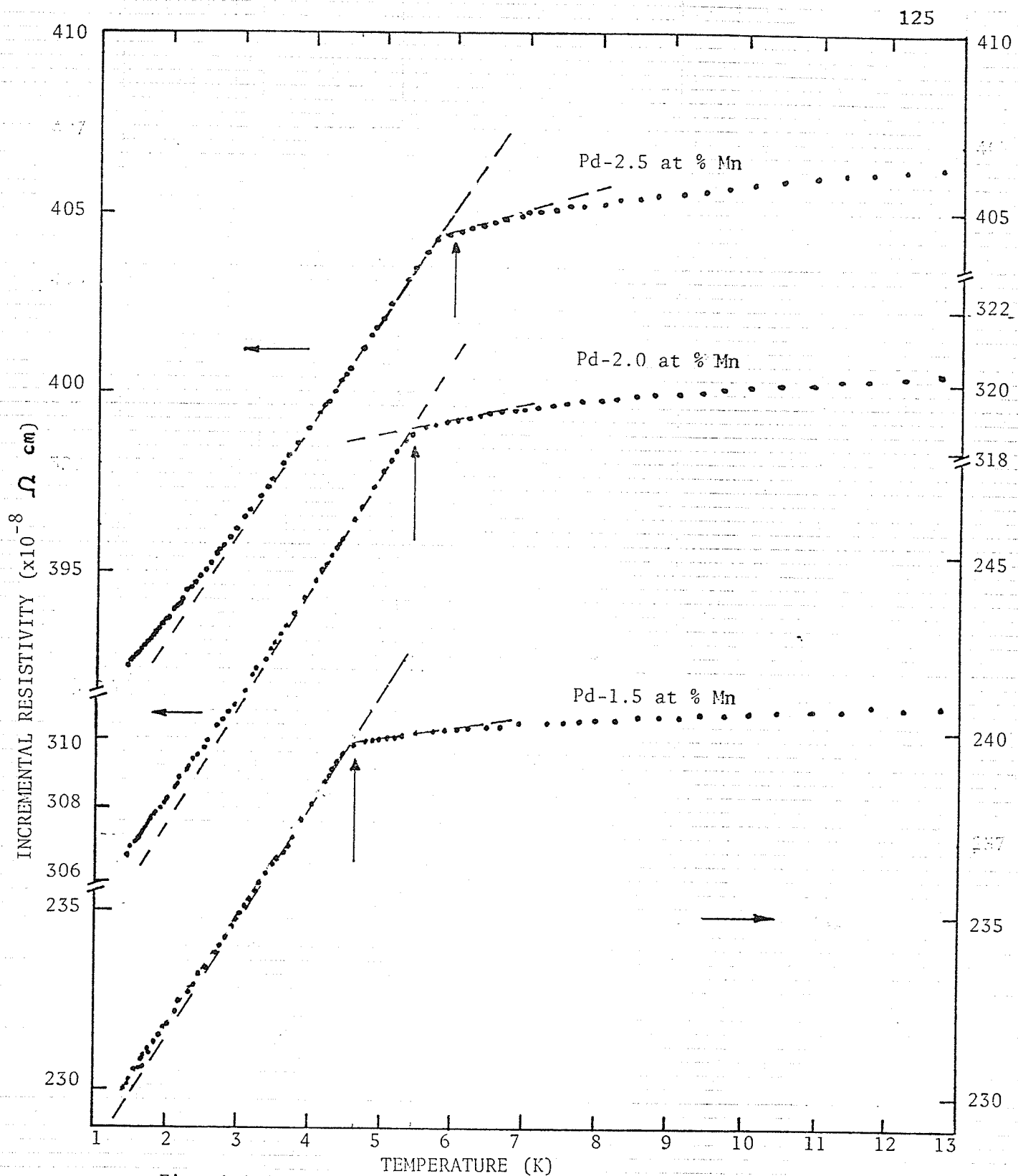


Fig. 4.1.11

Incremental resistivity data of Pd-1.5 at % Mn, Pd-2.0 at % Mn, and Pd-2.5 at % Mn.

Vertical arrow indicates position of T_c from susceptibility data.

coefficient of T is zero, while the one below T_C varies as $(T_C - T)$. Experimentally, one observes an increasing temperature dependence of $\Delta\rho(T)$ for the supposedly flat region above T_C . Only the Pd-0.5 at % Mn alloy is flat from T_C to $\sim 10^\circ\text{K}$, after which phonon contribution begins to dominate the resistivity. For alloys with higher Mn concentration, this linear region keeps getting steeper. The effect is seen clearly by plotting

$$\frac{\Delta\rho(10^\circ\text{K}) - \Delta\rho(T_C)}{\Delta\rho(T_C) - \Delta\rho(0)}$$

as a function of Mn concentration as done in Fig. 4.1.12. The value for Pd-4.5 at % is 1.92, too big to be included in the diagram.

Qualitatively, the increasing antiferromagnetic Mn-Mn coupling has the result of smearing out the internal field distribution $P(H)$, so that there are more spins coupled with higher than average energy. The alloy is hence less homogeneous, and the temperature dependence in $\Delta\rho(T)$ just above T_C goes up, as observed experimentally.

Long and Turner's model further predicts that at low temperature, the incremental resistivity for each alloy varies as Eq. 2.3.4

$$\Delta\rho(T) = A c + \frac{B}{c^{1/2}} T^{3/2} \quad T \rightarrow 0$$

Hence a plot of $\Delta\rho(T)$ vs $T^{3/2}$ should yield a straight line, at least in the low temperature limit. See Fig. 4.1.13 for examples. The coefficients of the $T^{3/2}$ terms for all the ferromagnetic alloys can then be plotted vs. $c^{-1/2}$, as done in Fig. 4.1.14, although the small T_C of the Pd-0.5 at % Mn has prevented its $T^{3/2}$ region from being observed in this project. Within 7% error, the $T^{3/2}$ coefficients for

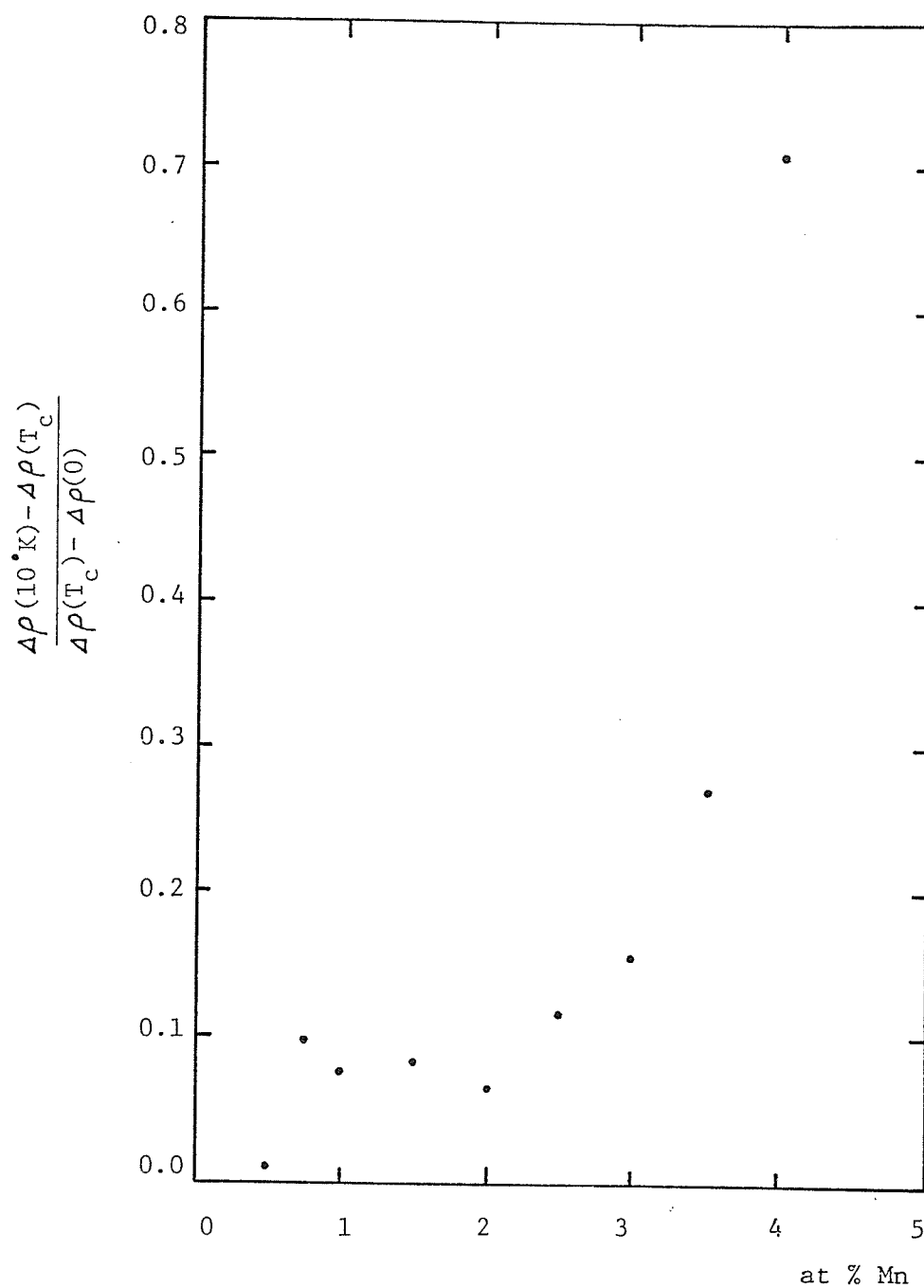


Fig. 4.1.12 $\frac{\Delta\rho(10^\circ\text{K}) - \Delta\rho(T_c)}{\Delta\rho(T_c) - \Delta\rho(0)}$ vs. Mn concentration. For alloys with Mn > 2.5 at %, T_c changes to T_c^* .

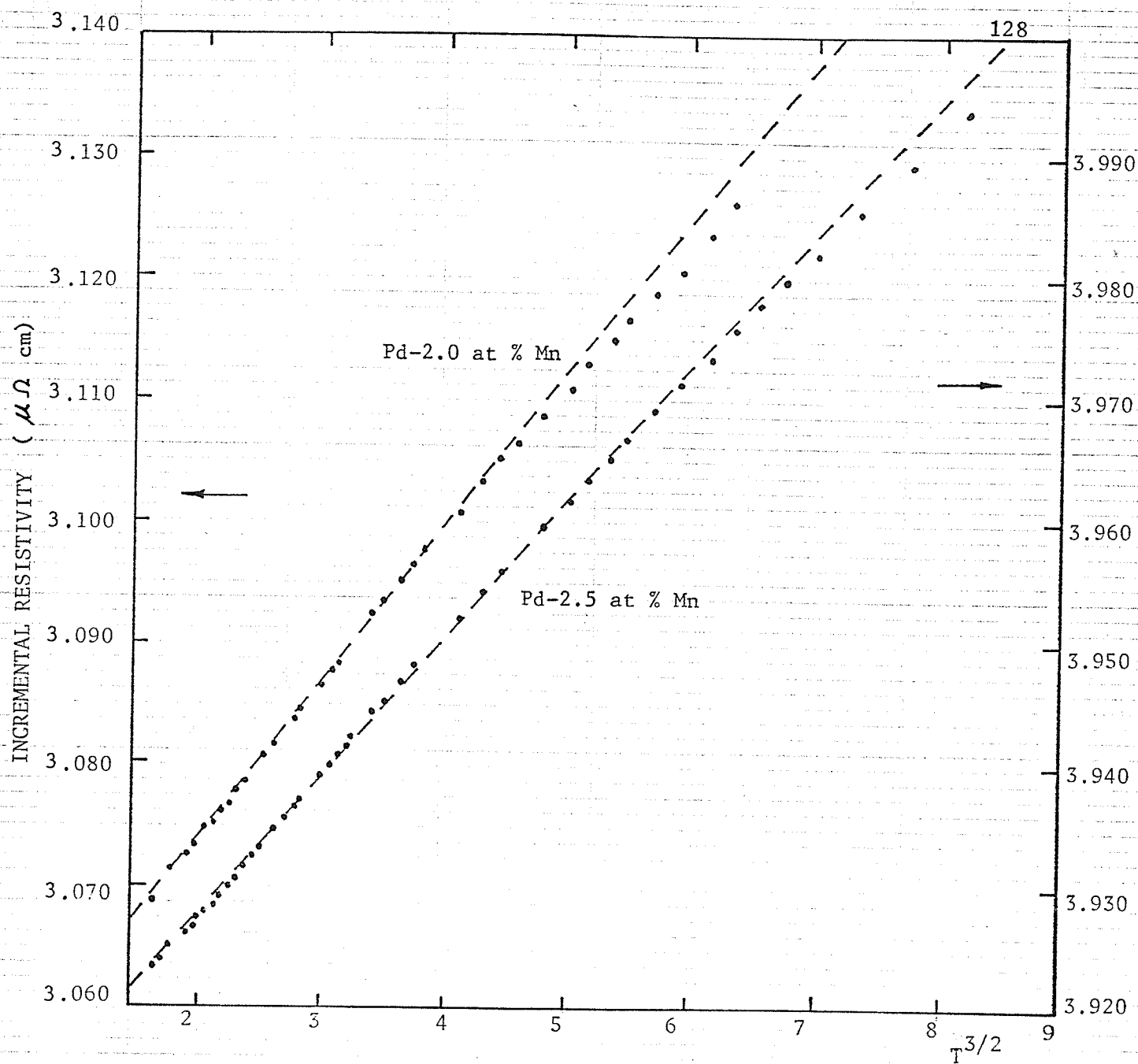


Fig. 4.1.13

Incremental resistivity vs. $T^{3/2}$ for Pd-2.0 at % Mn and Pd-2.5 at % Mn.

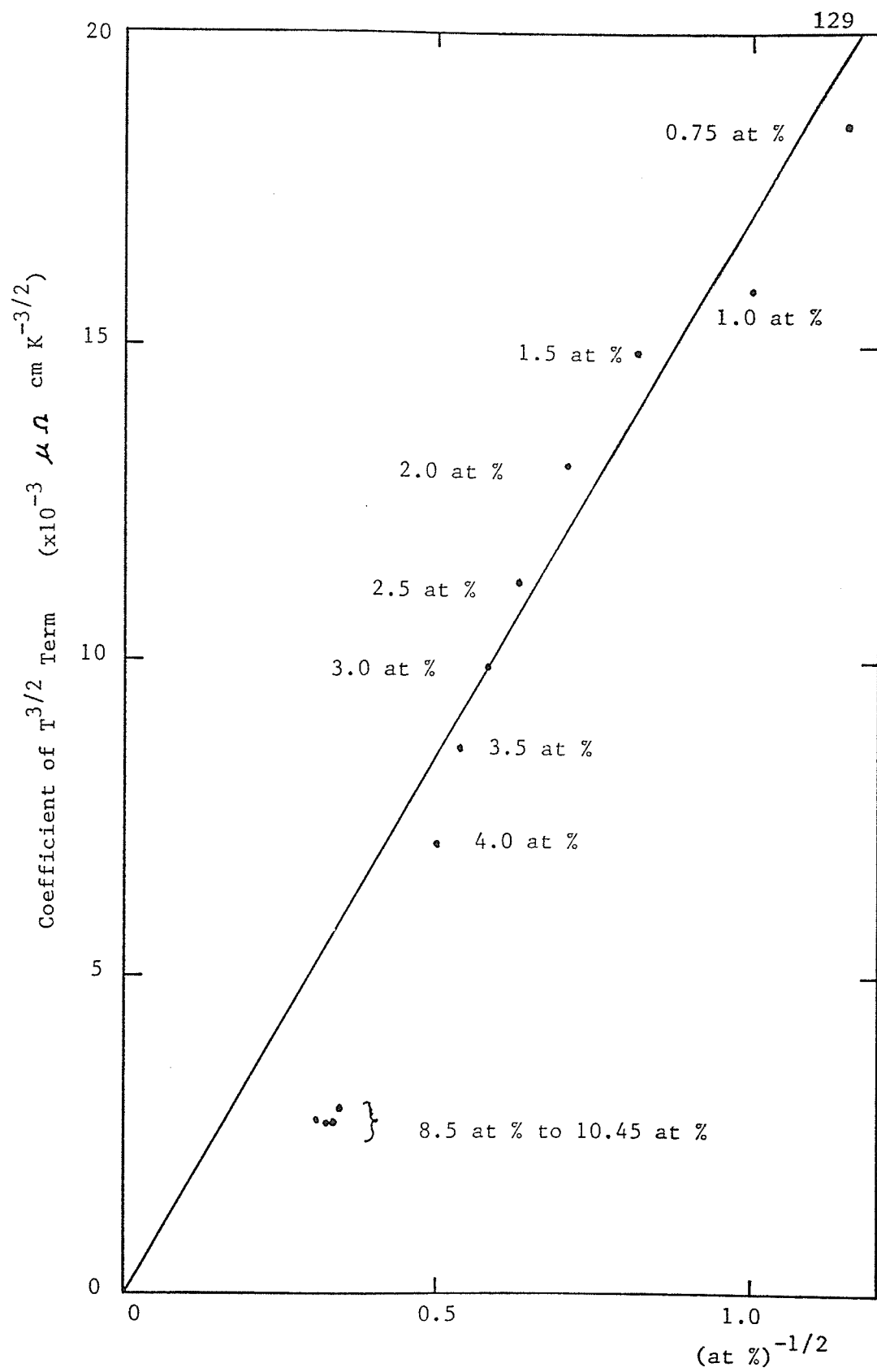


Fig. 4.1.14 Coefficient of $T^{3/2}$ Term vs. (Mn concentration) $^{-1/2}$.

alloys with less than 4.5 at % Mn follow a straight line with a slope of B equal to $0.017 \mu\Omega \text{ cm K}^{-3/2} (\text{at } \%)^{1/2}$. Incidentally, some of the spin glass alloys also show a $T^{3/2}$ limiting form in their incremental resistivities, but for a different reason than treated in Long and Turner's model. Hence these coefficients do not scale with $c^{-1/2}$, as shown in the above diagram.

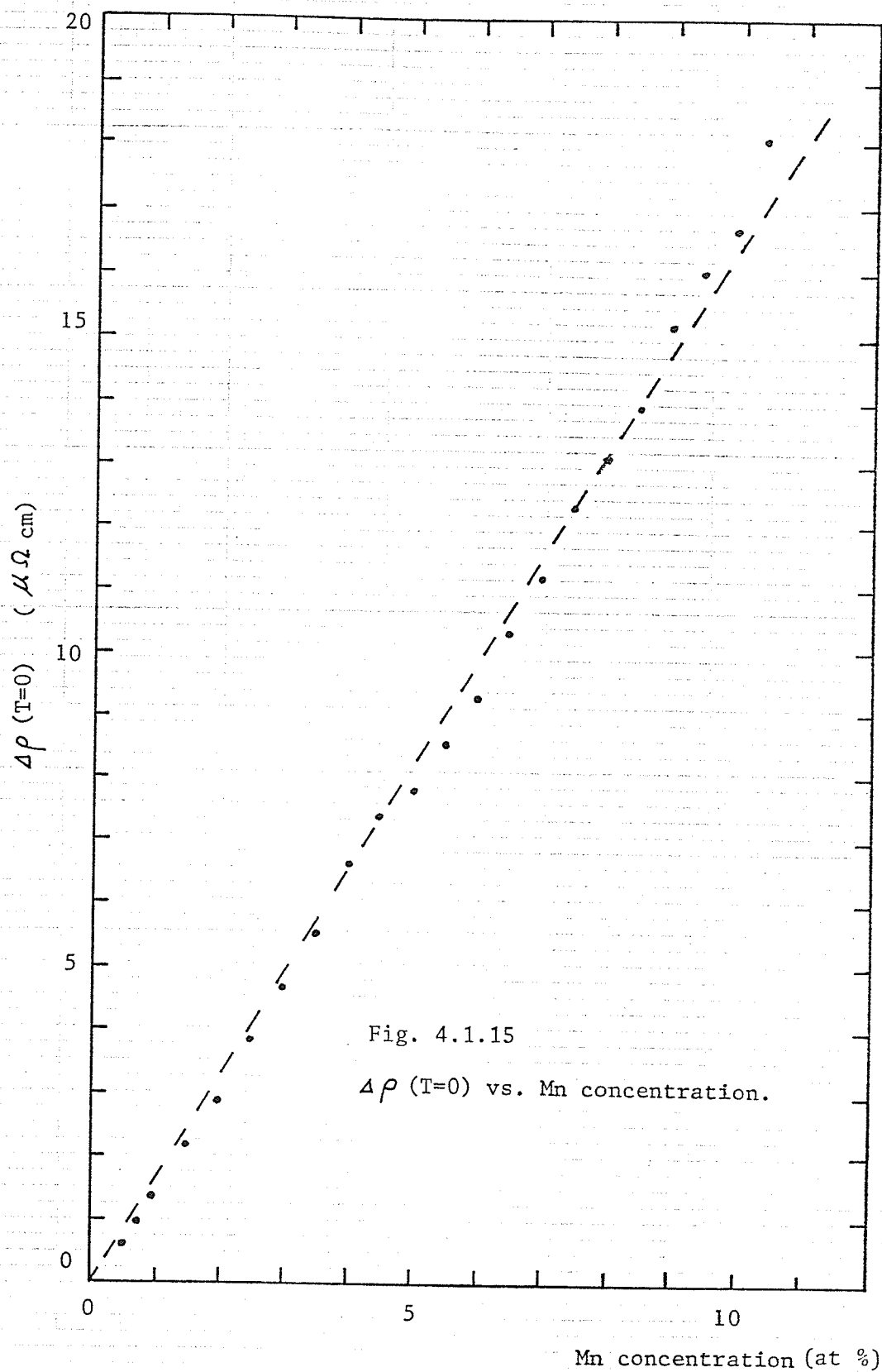
By extrapolating the $T^{3/2}$ region to $T=0$, one can get the residual resistivity $\Delta\rho(T=0)$ of each alloy. The parameter A in Eq. 2.3.4 is then found to be $1.62 \mu\Omega \text{ cm/at } \%$ by plotting $\Delta\rho(T=0)$ vs. c . Fig. 4.1.15 shows the data for all alloys investigated. It is remarkable that for all alloys except the 10.45 at % Mn the residual resistivities follow to within 4% a straight line passing through the origin, although strictly speaking, the model applies to ferromagnetic alloys only.

The residual resistivities can also be used to estimate the deviation from periodic potential due to Mn ions, using Yosida's formula

$$\Delta\rho(T=0) = 5.78 cV^2 \quad (2.3.1)$$

The value of V increases smoothly from 0.47 eV for Pd-0.5 at % Mn to 0.52 eV for 2.5 at % Mn. The corresponding V for 3.0 at % Mn is 0.52 eV and increases to 0.54 eV for 4.5 at % Mn, although the applicability of the model to alloys with $\text{Mn} > 2.5$ at % is doubtful. The above values of V compare favourably with the results of Williams and Loram (1969 b).

Yosida's model further furnishes estimate of the exchange inte-



gral J between Pd conduction electrons, and Mn ions.

$$\Delta\rho(T_C) - \Delta\rho(T=0) = 5.78 c |J|^2 S(1 + 4 S) \quad (2.3.3)$$

Using $S = \frac{5}{2}$ for Mn ions, one can extract estimates of $|J|$ from the incremental resistivity data. $|J|$ varies from 0.020 eV for 0.5 at % Mn to a maximum of 0.035 eV at 2.0 at % Mn, then decreases to 0.029 eV at 2.5 at % Mn. Similar to the V estimates above, applying Eq. 2.3.3 to alloys with Mn > 2.5 at % yields a $|J|$ decreasing monotonically from 0.028 eV at 3.0 at % Mn to 0.013 eV at 4.5 at % Mn. These numbers show more variation than those given by Williams and Loram (1969 b), but are of the same order of magnitude. Because the ordering is ferromagnetic, J is actually positive.

4.1.5 Summary of Results

The following tables summaries the parameters deduced from the A.C. susceptibility and the D.C. resistivity data for alloys with Mn $\leq$ 2.5 at %.

Table 4.1.1. Parameters deduced from A.C. susceptibility data.

Alloy at % Mn)	T_C (K)	δ	γ	μ_{eff} (μ_B per Mn)
0.5	1.65 $\pm$ 0.01	4.0 $\pm$ 0.15	1.37	12.3
0.75	2.59 $\pm$ 0.01	4.0 $\pm$ 0.15	1.32	10.2
1.0	3.37 $\pm$ 0.01	3.7 $\pm$ 0.15	1.34	9.6
1.5	4.65 $\pm$ 0.01	3.6 $\pm$ 0.15	1.30	9.0
2.0	5.46 $\pm$ 0.01	3.4 $\pm$ 0.15	1.34	8.3
2.5	6.00 $\pm$ 0.01	3.3 $\pm$ 0.15	1.36	7.5

Table 4.1.2. Summary of parameters taken from the resistivity data.

Alloy (at % Mn)	T_c (K)	$\Delta\rho(0)$ ($\mu\Omega$ cm)	Coefficient of the linear term ($\mu\Omega$ cm K^{-1})	Coefficient of the $T^{3/2}$ term ($\mu\Omega$ cm $K^{-3/2}$)
0.5	1.70 ± 0.10	0.650†	0.039	---
0.75	2.60 ± 0.10	1.037	0.037	0.0185
1.0	3.30 ± 0.05	1.427	0.034	0.0159
1.5	4.55 ± 0.05	2.276	0.032	0.0149
2.0	5.40 ± 0.05	2.987	0.032	0.0131
2.5	5.85 ± 0.05	3.905	0.031	0.0112

†Estimated, as no $T^{3/2}$ term was observed from which an extrapolation could be made.

Table 4.1.2 (con't)

Alloy (at % Mn)	V (eV)	$ J $ (eV)
0.5	0.47	0.020
0.75	0.49	0.021
1.0	0.50	0.023
1.5	0.51	0.027
2.0	0.51	0.035
2.5	0.52	0.029

4.2 From 3.0 at % Mn to 5.0 at % Mn

4.2.1 Susceptibility Data

As pointed out above, alloys in this Mn concentration range have stronger direct d-d antiferromagnetic coupling, due to their higher Mn concentration. The consequence is clearly seen in the susceptibility data presented in Fig. 4.2.1 to 4.2.5. While the 3.0 at % alloy resembles the ferromagnetic alloys in most respects, the discrepancy increases with increasing Mn concentration until at 5.0 %, the susceptibility curve does not yield a critical peak at all. The decrease in $\chi_{\text{meas(max)}}/N^{-1}$ has already been presented in Fig. 4.1.3 above. Here, anisotropy effects are more prominent.

The expression $\frac{1}{\chi_{\text{meas(max)}}} \frac{dx}{dT}$

evaluated below the main peak temperature climbs from a value of 0.2 at 3.0 at % Mn to about 0.7 at 5 at % Mn. Further, whereas with the ferromagnetic Pd-Mn alloys, the main peak is pushed to below 1.45°K by a small magnetic field, now it moves down in temperature so slowly that for the 4.0 at % Mn and the 4.5 at % Mn samples, the main peak and the critical peak are both visible (>1.45K) and comparable in height under an applied field of ~10 Oe. Fig. 4.2.6 traces the change in position of the two peaks for Pd-4.5 at % Mn. It can be seen that the main peak moves down in temperature with increase in magnetic field while the critical peak moves up.

The effect of applied magnetic field on the susceptibility of the present alloys is also smaller compared to the ferromagnetic alloys, although their demagnetising factors are comparable. Whereas

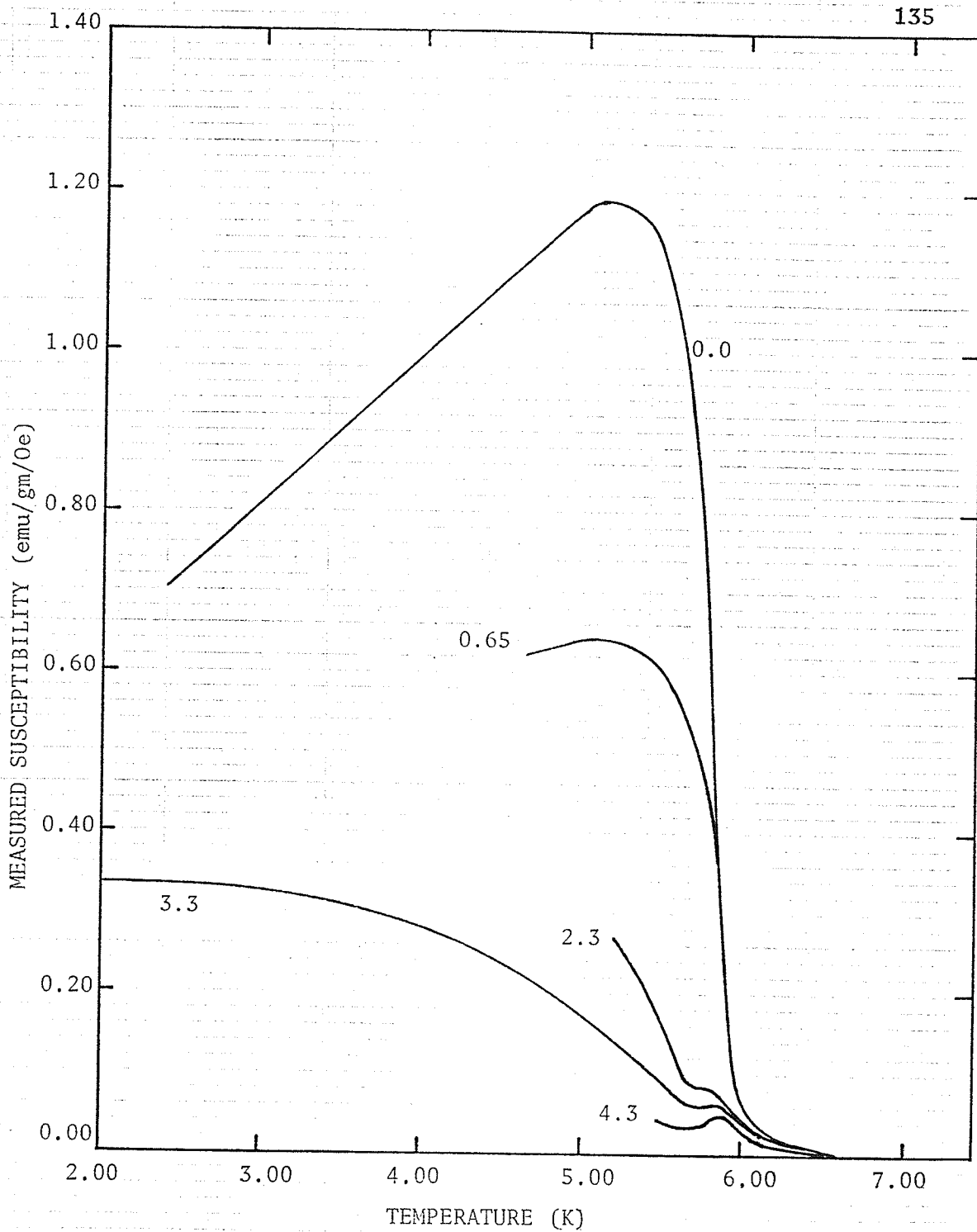
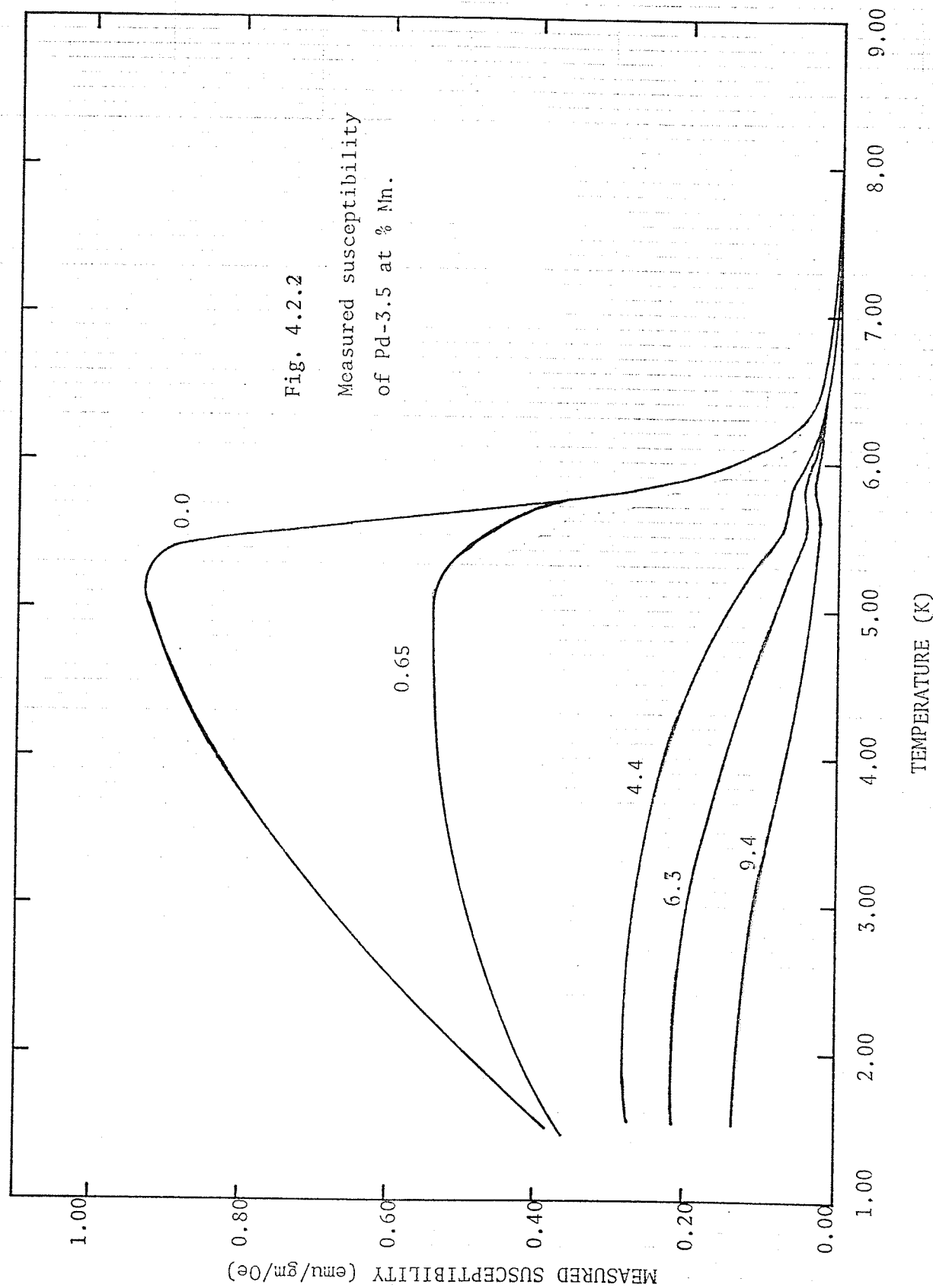
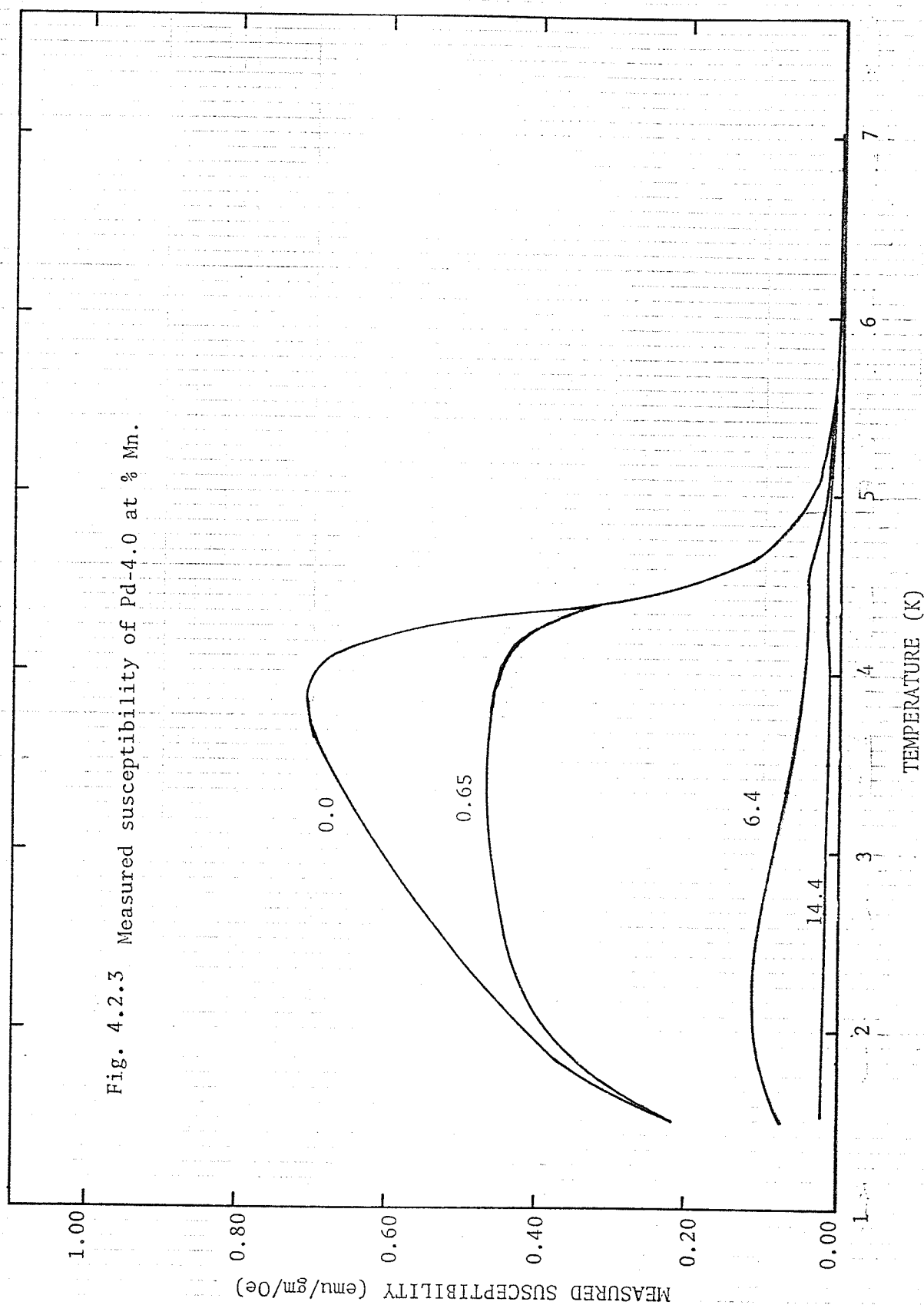


Fig. 4.2.1 Measured susceptibility of Pd-3.0at % Mn.





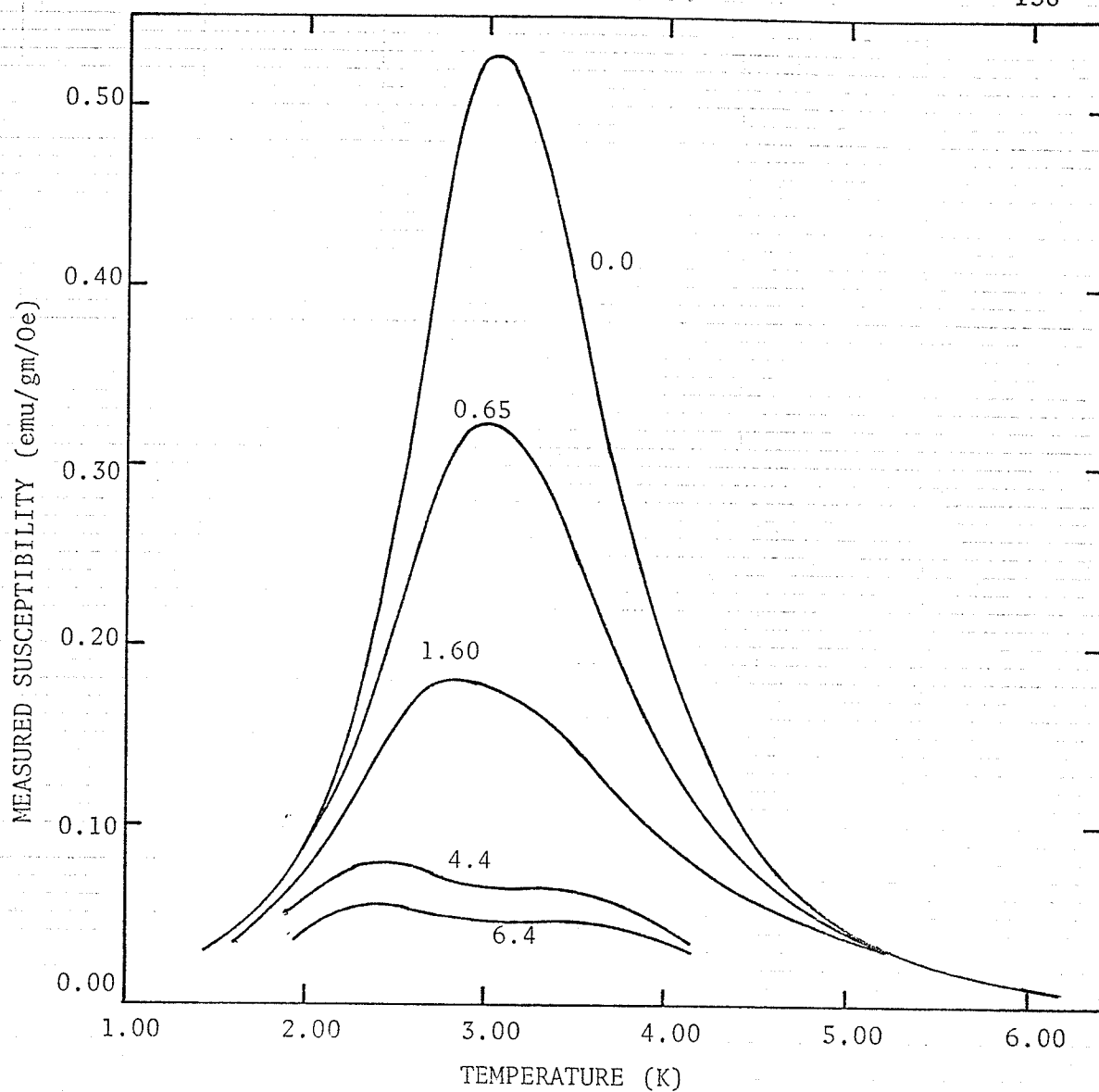
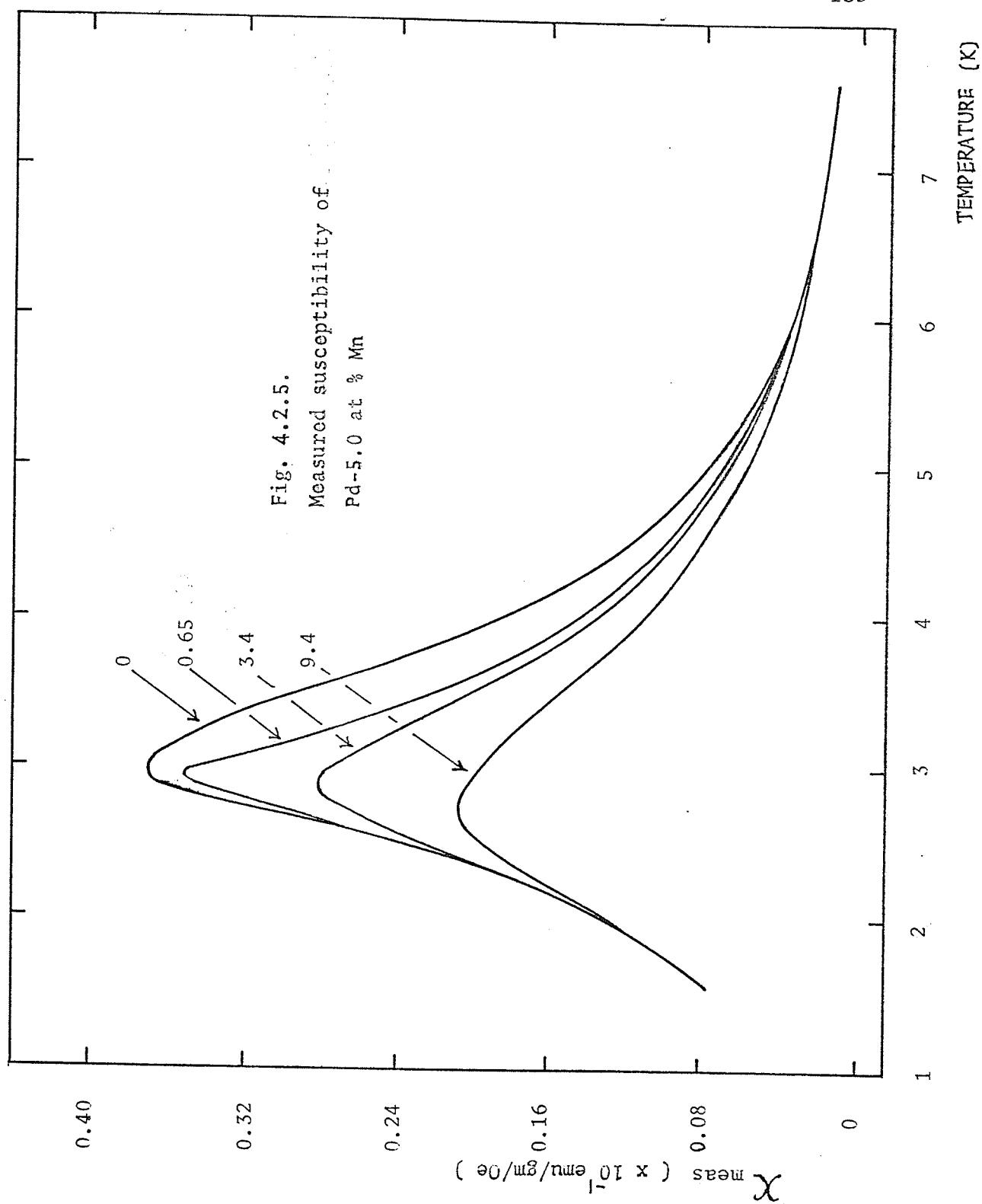


Fig. 4.2.4 Measured susceptibility of Pd-4.5 at % Mn.



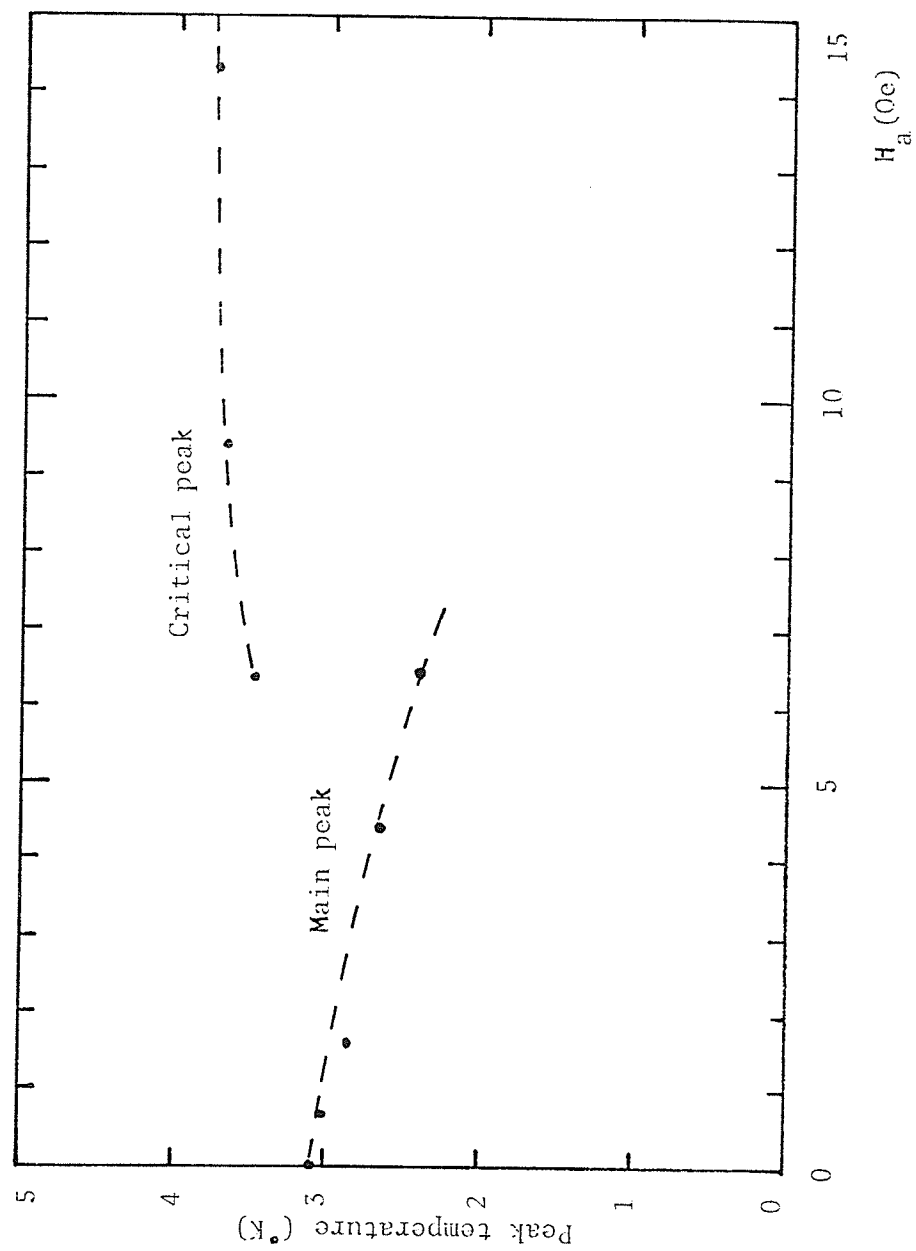


Fig. 4.2.6 Changes of peak temperatures with applied magnetic field for Pd-4.5 at % Mn.

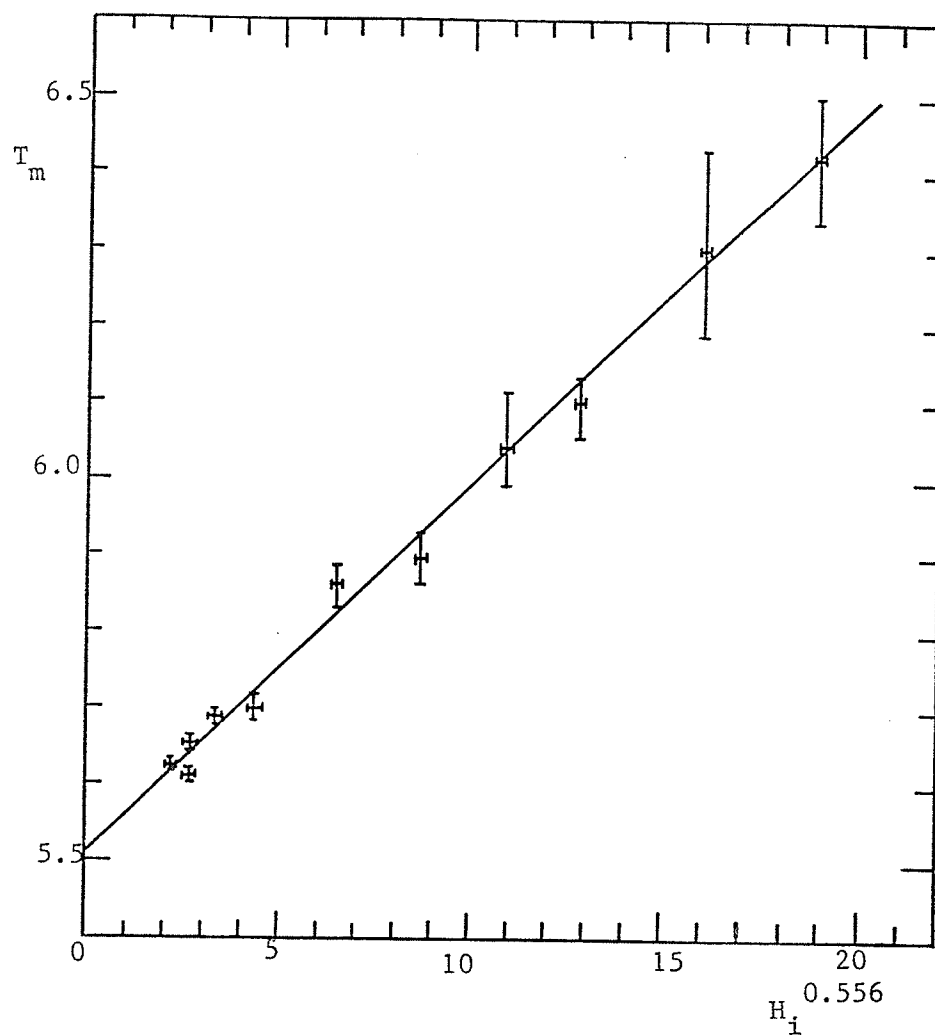


Fig. 4.2.7 T_m vs. $H_i^{0.556}$ for Pd-3.5 at % Mn.

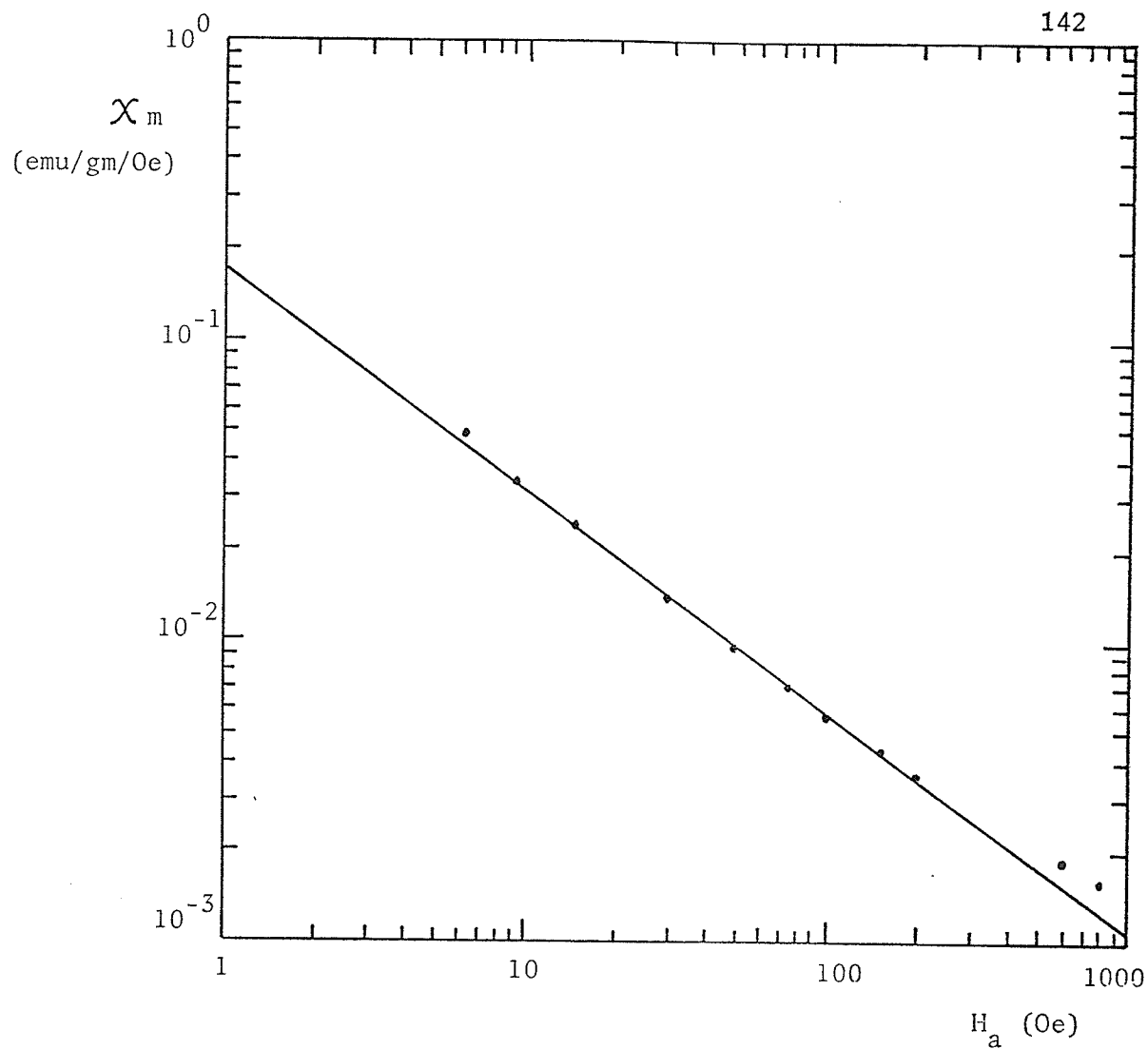


Fig. 4.2.8 Susceptibility vs. H_a for Pd-3.5 at % Mn.

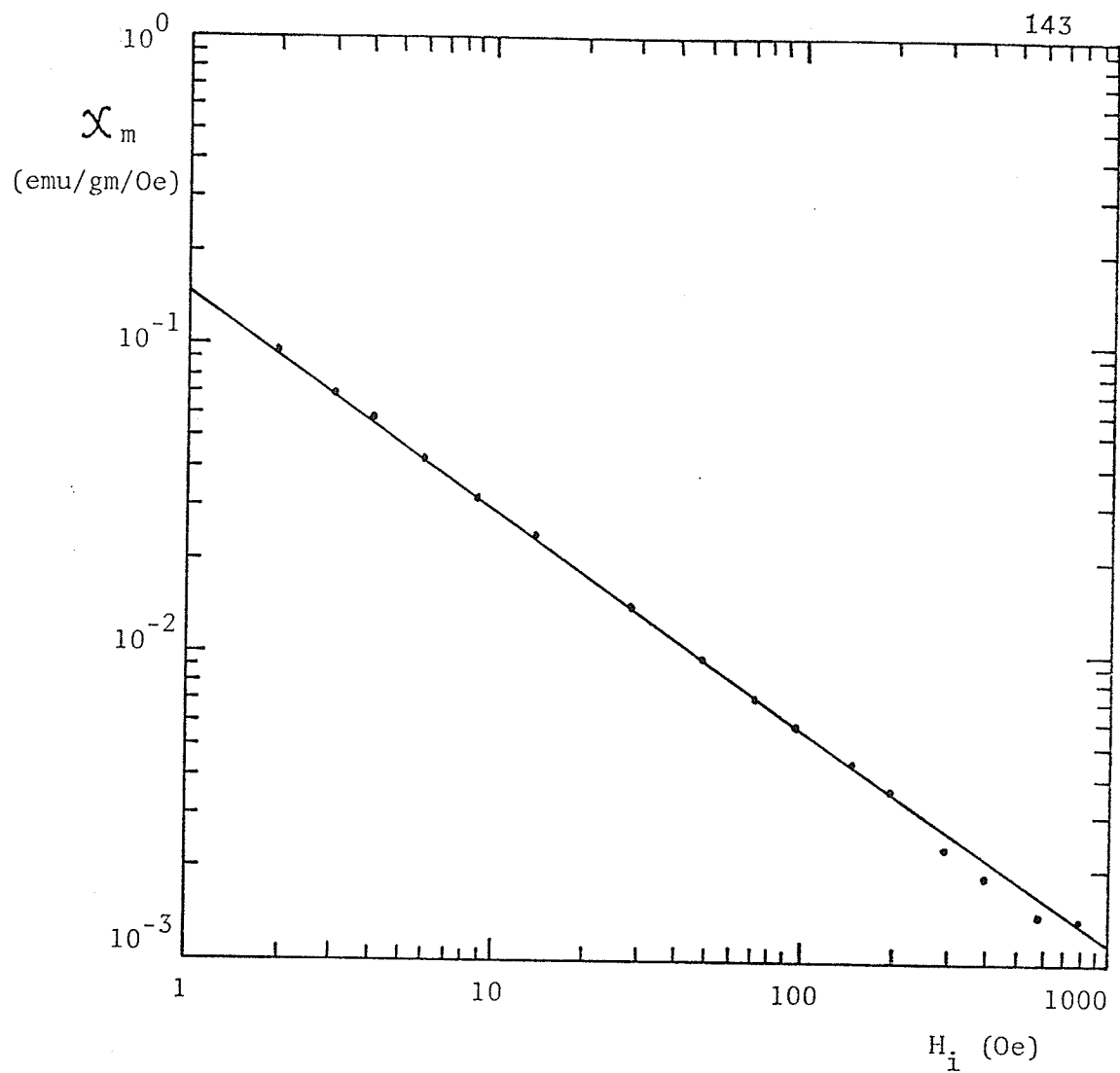


Fig. 4.2.9 Susceptibility vs. H_i for Pd-3.0 at % Mn. (δ -plot)

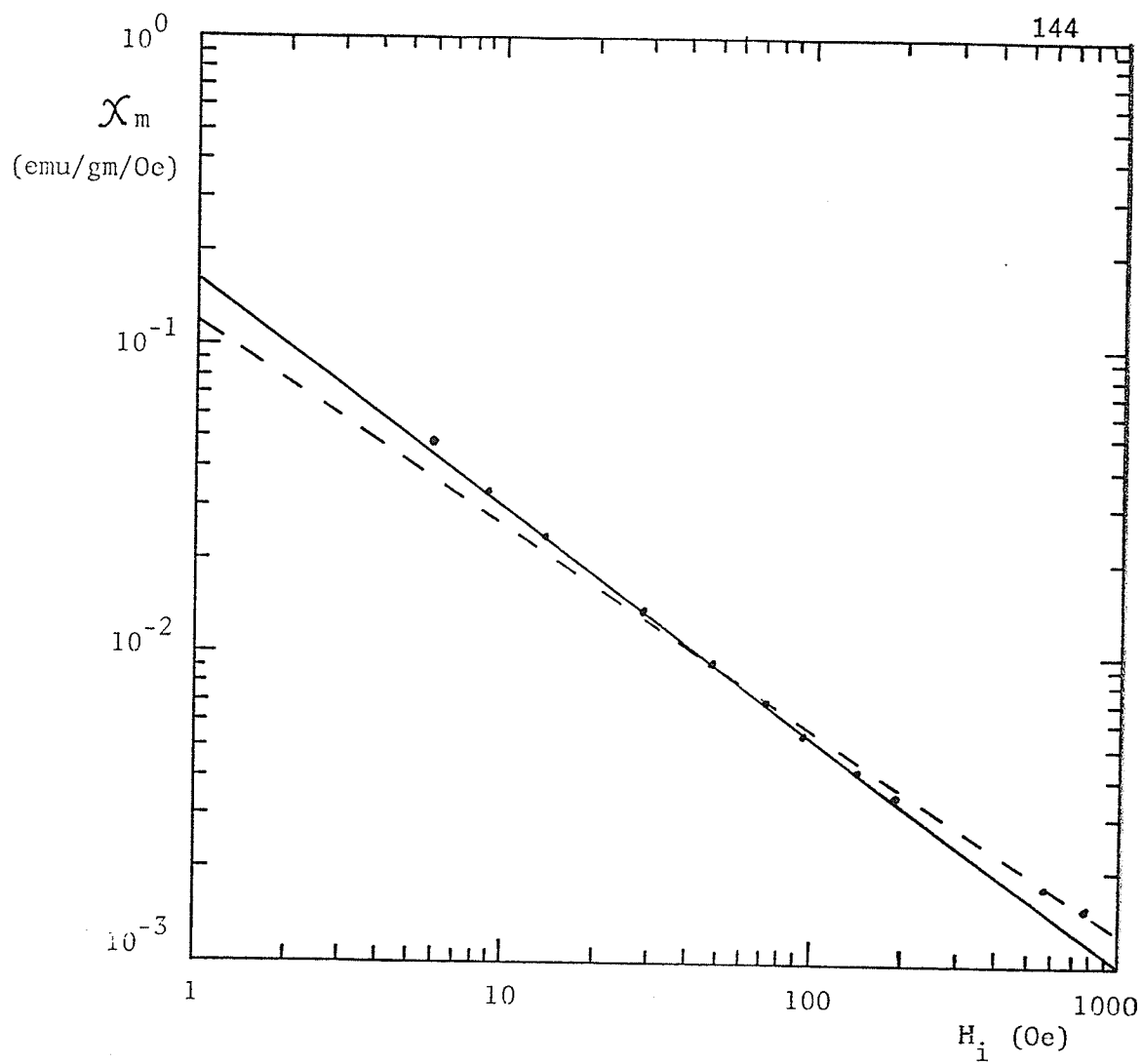


Fig. 4.2.10 Susceptibility vs. H_i for Pd- 3.5 at % Mn. (δ -plot)

for the 3.0 at % Mn sample, the earth's field is still strong enough to roughly halve the main peak, its effect decreases progressively to a reduction of only 3% for the 5.0 at % alloy. As before, one can test the applicability of the scaling law hypothesis on these alloys, by extracting the parameters T_C^* , δ^* and γ^* from the susceptibility data. The asterisk on these parameters is to distinguish them from those of true ferromagnetic ordering. Fig. 4.2.7 shows the plot T_m^* vs. $H_i^{0.556}$ for Pd-3.5 at % Mn. The slope of the straight line fit is considerably higher than that of similar plots for the ferromagnetic alloys. Moreover, the T_C^* obtained is close to zero field inflexion point only for the 3.0 at % alloy. As Mn concentration increases, T_C^* falls progressively below the inflexion point, while remaining above the main peak temperature. What is worse, the T_C^* 's obtained do not give a well-defined straight line in the γ -plots.

The critical index δ^* can also be obtained as before. However, one immediate difficulty is the scatter in the χ_m vs. H_a plots, shown in Fig. 4.2.8 for Pd-3.5 at % Mn. In addition, the resultant δ^* -plot yields a reasonable straight line only for Pd-3.0 at % Mn, as shown in Fig. 4.2.9, from which δ^* is estimated to be 3.4 for the whole range of H_i 's. For the 3.5 at %, 4.0 at %, and 4.5 at % alloys, each δ^* -plot exhibits two straight line sections from which a "low field" and a "high field" δ^* have been estimated. See Fig. 4.2.10 for the 3.5 at % alloy.

$$\delta^*(\text{low field}) \approx 4.0$$

$$\delta^*(\text{high field}) \approx 2.9$$

The average of these two δ^* 's is 3.4; the same argument applies to

the other alloys in this Mn range. This is quite a change from the trend of decreasing δ with increasing Mn for the ferromagnetic alloys.

The γ^* -plots, too, show more curvature than before. In the 3.0 at % alloy, if T_C^* is taken to be 5.80°K from the T_m^* vs. $H_i^{0.556}$ plot, then the γ^* -plot in Fig. 4.2.11 yields two straight line sections, with two γ^* 's.

$$\gamma^* \approx 3 \text{ for } 2 \times 10^{-2} \leq \epsilon \leq 5 \times 10^{-2}$$

$$\gamma^* \approx 2 \text{ for } 5 \times 10^{-2} \leq \epsilon \leq 3 \times 10^{-1}$$

Raising T_C^* to 5.95°K produces the curve in Fig. 4.2.12 with a γ^* of $\sim 4/3$. However, 5.95°K is too far from the inflexion point of the zero field curve, and outside the estimated certainty in T_C^* for this alloy. Similar situations for the 3.5 at %, 4.0 at % and 4.5 at % alloys yield γ^* 's up to 2.5. In face of the usually quoted γ of 1.33 for 3-D Heisenberg ferromagnets, the γ^* 's are rejected in this project. The Pd-5.0 at % Mn alloy does not yield a critical peak under any applied magnetic field. Its main peak decreases in height and moves down in temperature under applied magnetic fields---all characteristics of spin glasses. In view of the above analysis, it can be said that the scaling law hypothesis does not hold for Pd-Mn alloys in this Mn range.

4.2.2 Resistivity Data

The resistivity data, too, show a gradual breaking down of ferromagnetic ordering with increase in Mn concentration. As shown in Fig. 4.2.13, the "knee" in the incremental resistivity vs. temperature curve gets progressively washed out from 3.0 at % Mn, until at

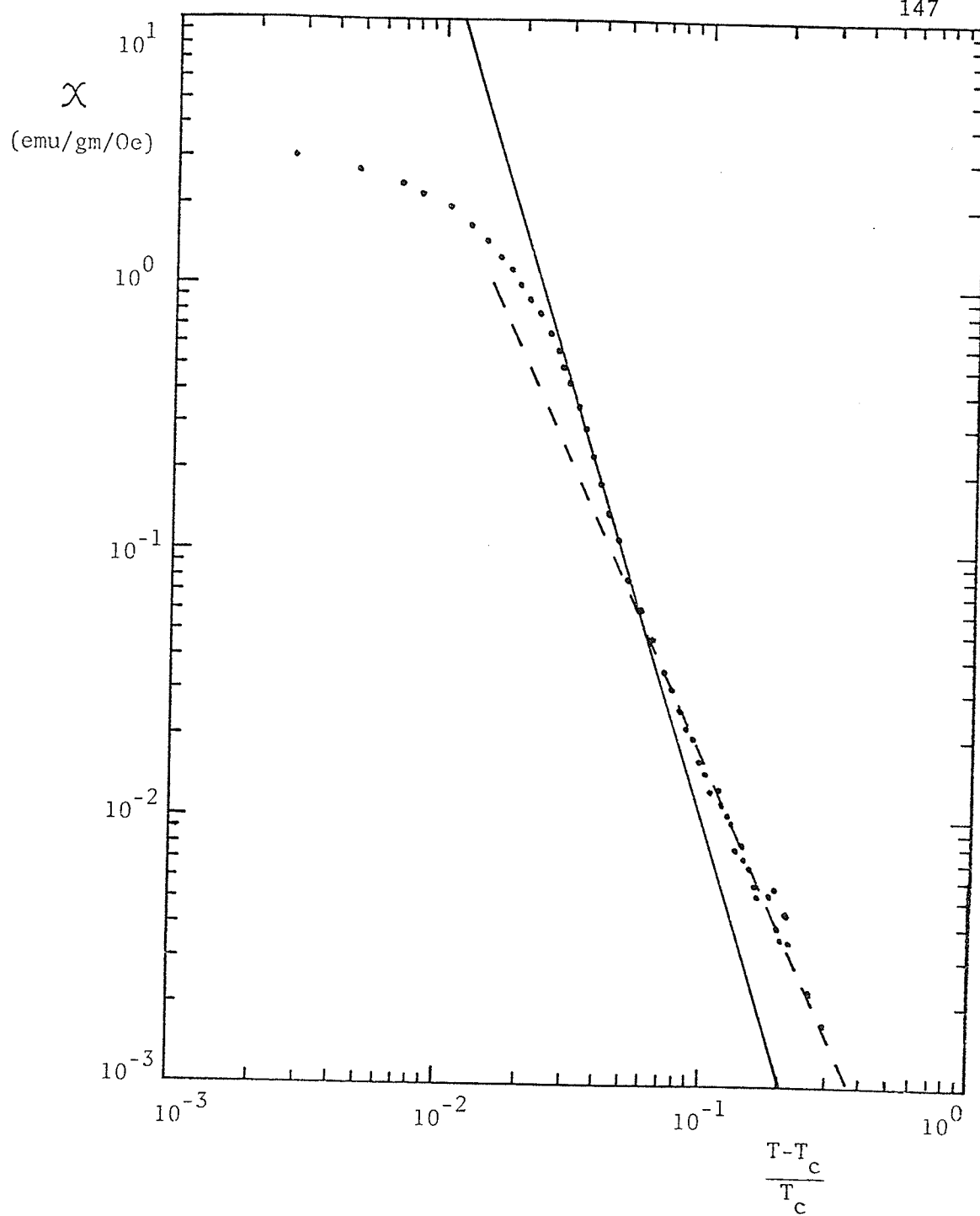


Fig. 4.2.11 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-3.0 at % Mn. (χ -plot)

$$T_c = 5.80 \text{ K}$$

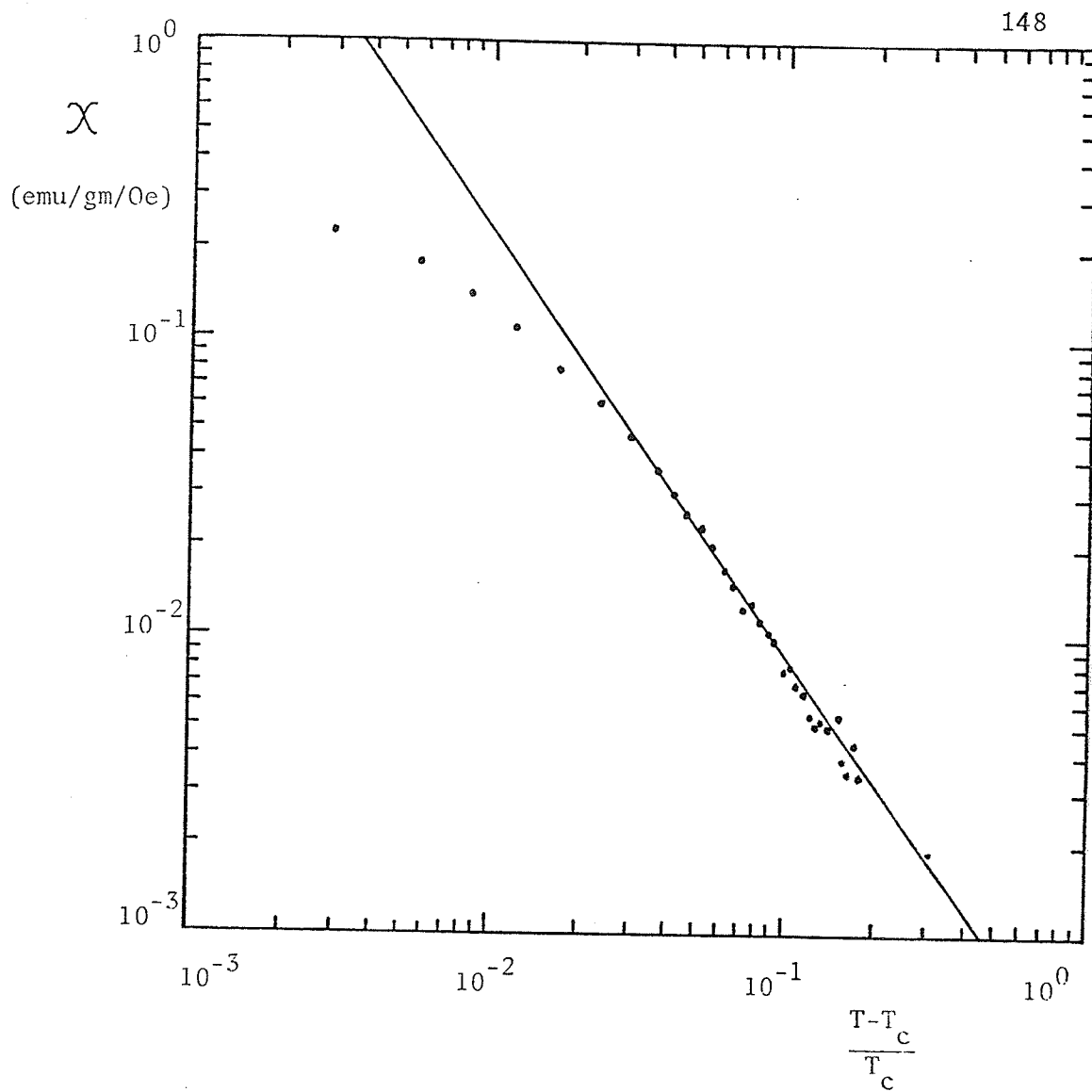


Fig. 4.2.12 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-3.0 at % Mn. (γ -plot)

$T_c = 5.95$ K

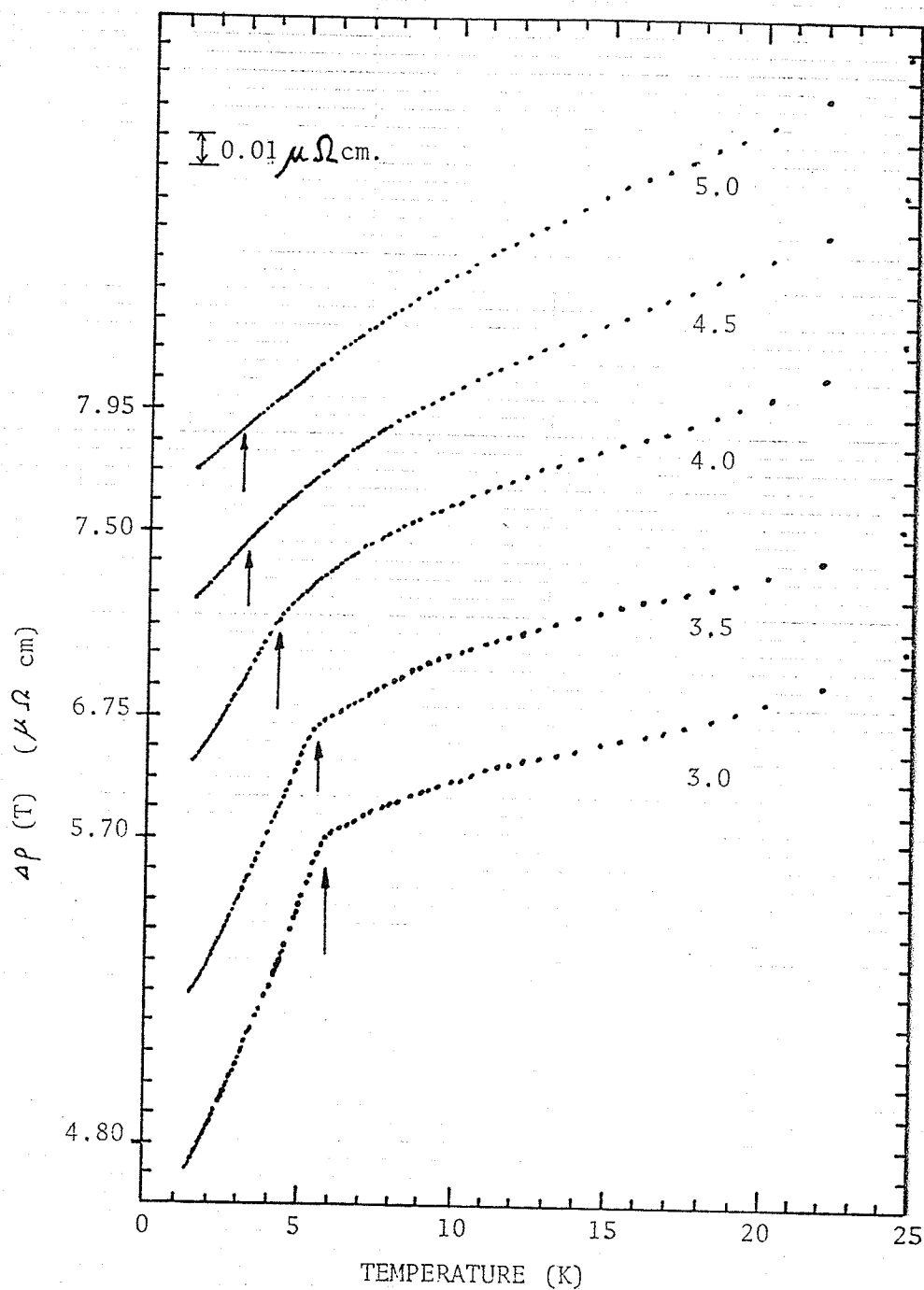


Fig. 4.2.13

Incremental resistivity data of Pd-5.0 at% Mn, Pd-4.5 at% Mn, Pd-4.0 at% Mn, Pd-3.5 at% Mn, and Pd-3.0 at% Mn.

Number on Y-axis indicates appropriate magnitude for each sample.

Vertical arrow indicates position of T_C^* or T_{sg} from susceptibility data.

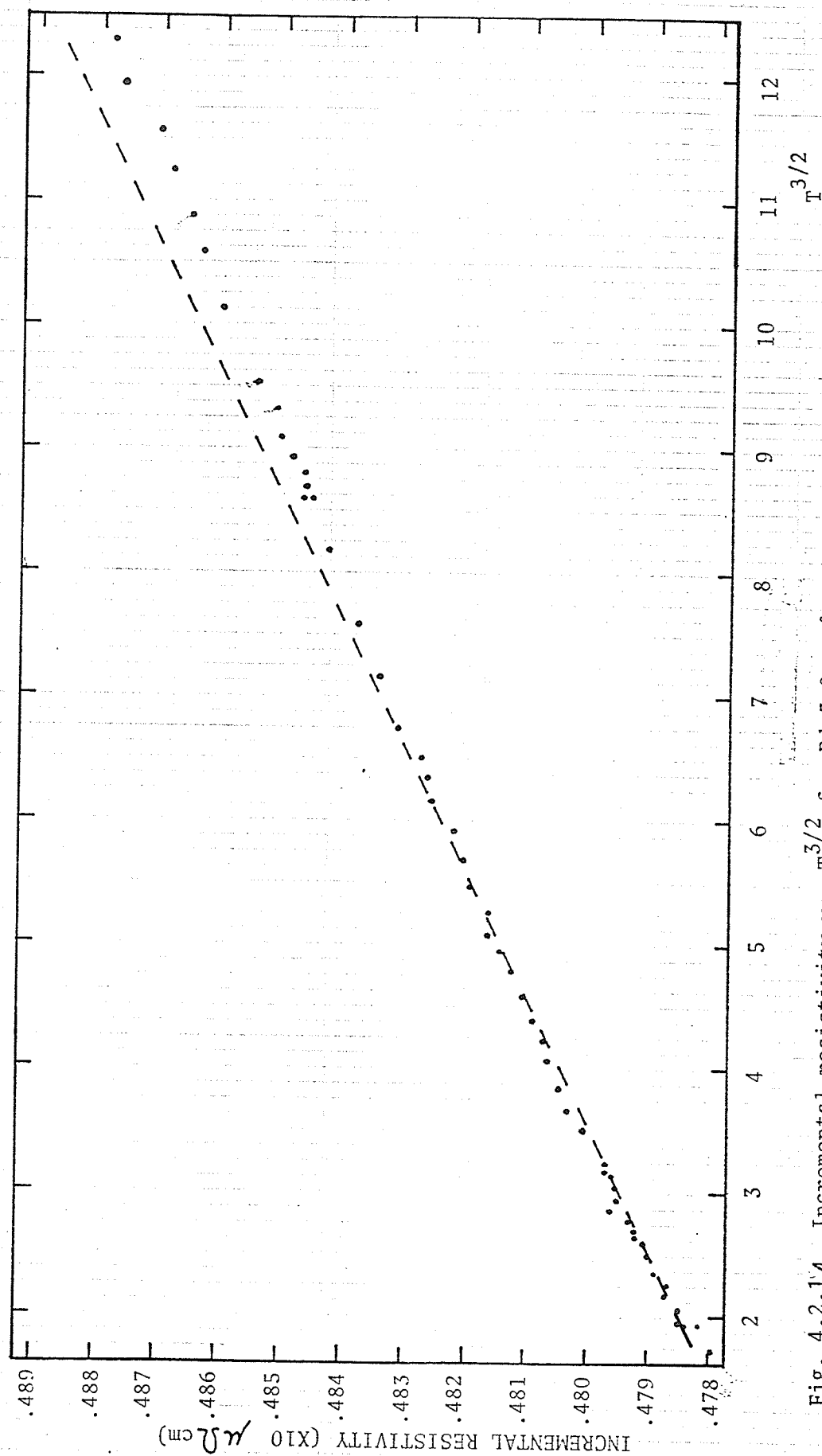


Fig. 4.2.1.4 Incremental resistivity vs. $T^{3/2}$ for Pd-3.0 at % Mn.

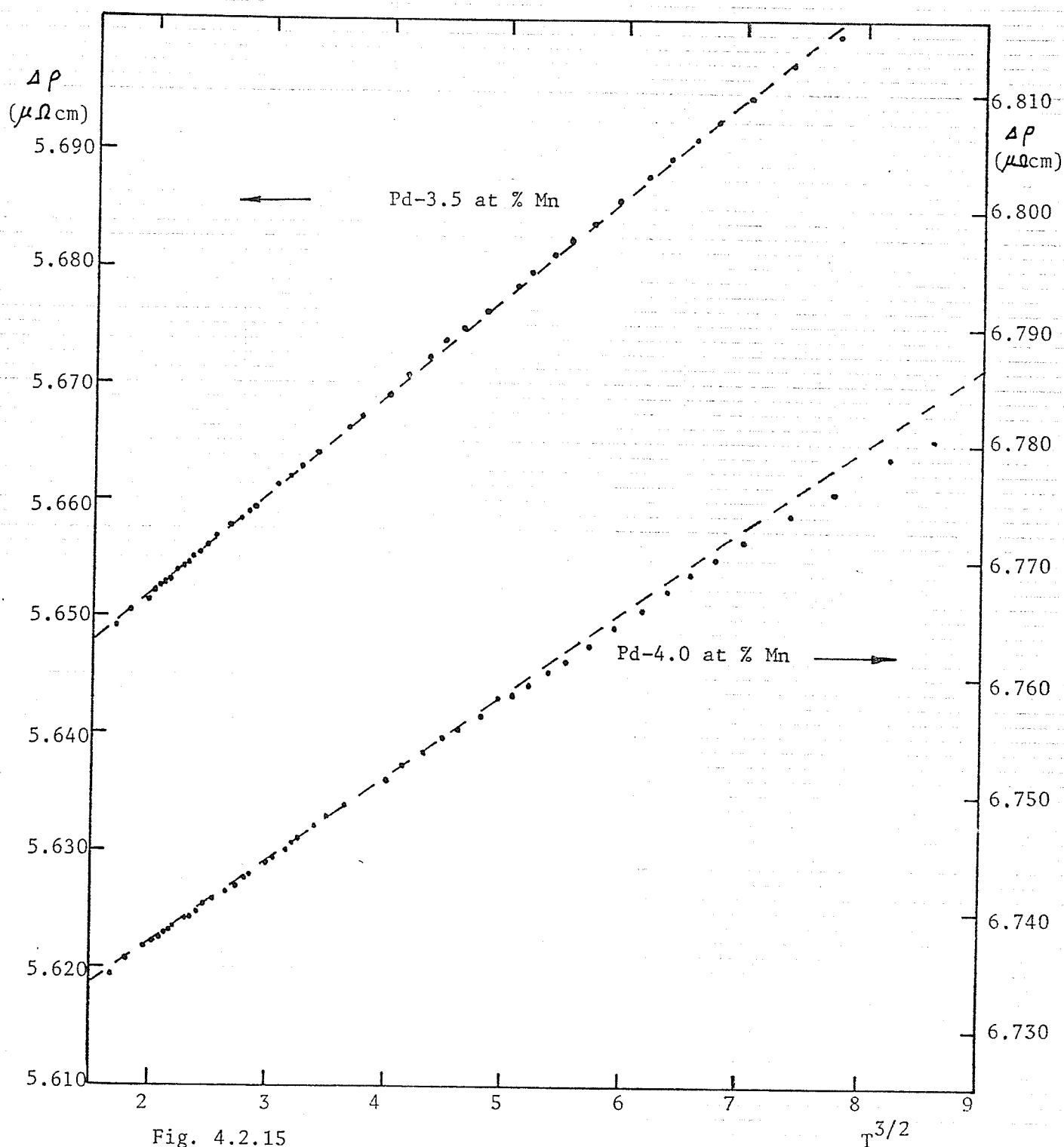


Fig. 4.2.15

Incremental resistivity vs. $T^{3/2}$ for Pd-3.5 at % Mn and Pd-4.0 at % Mn.

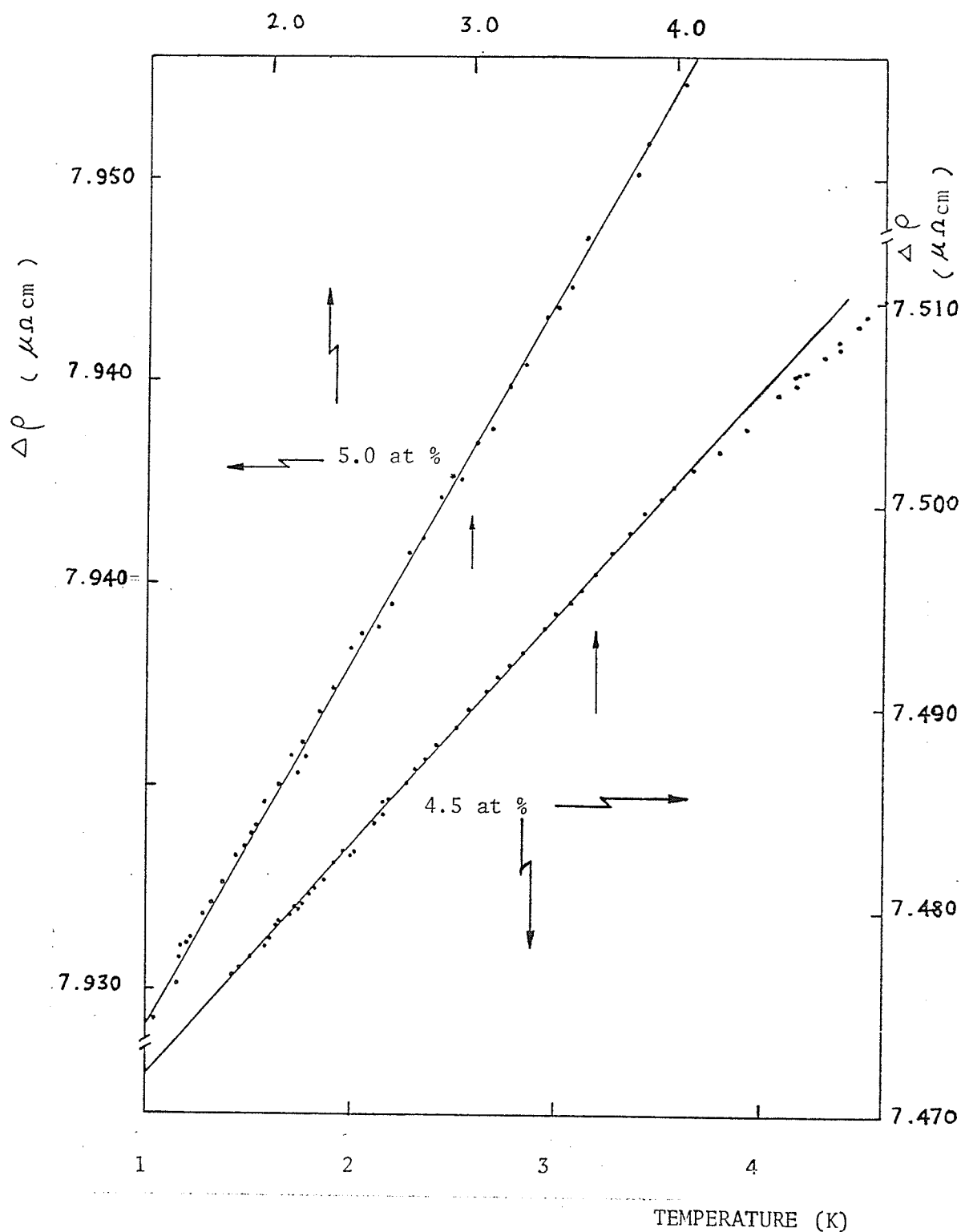


Fig. 4.2.16

Incremental resistivity vs. temperature for Pd-4.5 at % Mn and Pd-5.0 at % Mn.

The vertical arrows indicate T_c^* or T_{sg} from susceptibility data.

5.0 at % Mn, no anomaly is detected around $3^{\circ}\text{K}(T_{\text{sg}})$, coinciding with the disappearance of the critical peak in this alloy. The position of the knee still agrees within experimental error with T_{C}^* from the susceptibility data. The two linear temperature range above and below T_{C} are still visible while the ratio

$$\frac{\Delta\rho(10^{\circ}\text{K}) - \Delta\rho(T_{\text{C}}^*)}{\Delta\rho(T_{\text{C}}) - \Delta\rho(0)}$$

keeps increasing with increasing Mn concentration, as shown in Fig. 4.1.12 above.

The second feature of Long and Turner's model, the $T^{3/2}$ dependence, is found for alloys from 3.0 at % to 4.0 at %, as shown in Fig. 4.2.14 and 4.2.15, while the 4.5 at % and the 5.0 at % alloy show a linear temperature dependence from 4 K to 1.5 K, the lowest temperature measured, as shown in detail in Fig. 4.2.16. The $T^{3/2}$ coefficients have already been plotted in Fig. 4.1.14. It is not clear whether the 4.5 at % Mn alloy will actually yield a $T^{3/2}$ dependence if the temperature is much lower. For the 5.0 at % Mn, see the discussion in Section 4.3.2.

4.2.3 Summary of Results

The following tables summarise the parameters deduced from A.C. susceptibility and the D.C. resistivity data for alloys with 3.0 at % $\leq$ Mn $\leq$ 5.0 at %.

Table 4.2.1. Summary of parameters taken from the AC susceptibility data.

Alloy (at % Mn)	T_C^* (K)	δ^*	
		Low field	High Field
3.0	5.8 ± 0.1	3.4 ± 0.15	3.4 ± 0.15
3.5	5.5 ± 0.1	3.8	3.1
4.0	4.2 ± 0.1	4.0	2.9
4.5	3.2 ± 0.1	4.2	2.8
5.0	$2.97 \pm 0.05(T_{sg})$	---	---

Table 4.2.2. Summary of parameters taken from the resistivity data

Alloy at % Mn	$T_C^{*†}$ (K)	$\Delta\rho(T=0)$ $\mu\Omega\text{cm}$	Coefficient of the linear term ($\mu\Omega\text{cm K}^{-1}$)	Coefficient of the $T^{3/2}$ term ($\mu\Omega\text{cm K}^{-3/2}$)	$\frac{\Delta\rho(10\text{K}) - \Delta\rho(T_C^*)}{\Delta\rho(T_C^*) - \Delta\rho(0)}$
3.0	5.8 ± 0.1	4.765	0.029	0.0099	0.16
3.5	5.35 ± 0.1	5.635	0.024	0.0086	0.27
4.0	4.1 ± 0.1	6.723	0.018(5)	0.0071	0.71
4.5	3.3 ± 0.2	7.472	0.011(2)	----	1.92
5.0	----	7.917	0.0089	----	2.02

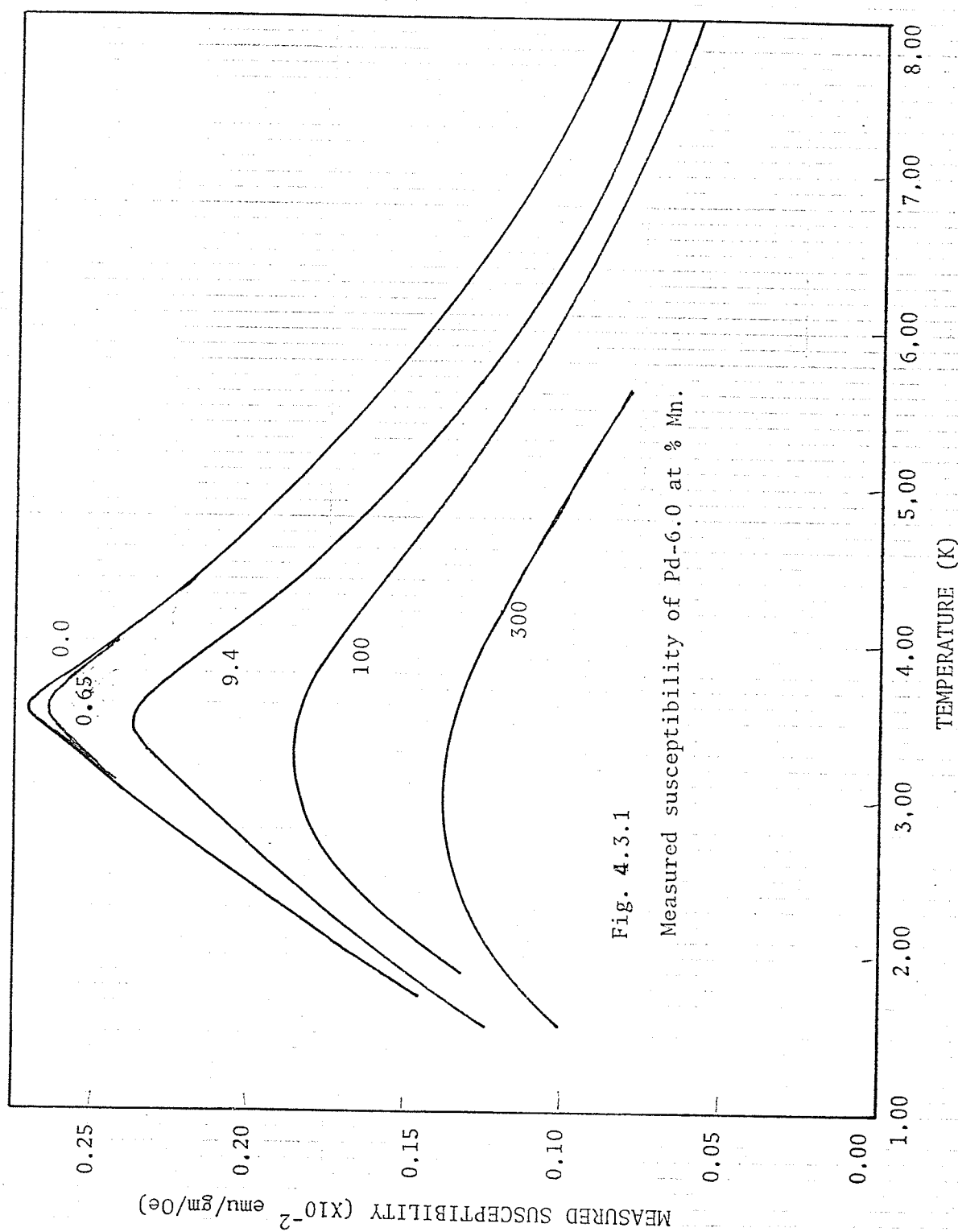
$†T_C^*$ above is taken as the temperature at which $d(\Delta\rho)/dT$ begins to decrease rapidly with increasing temperature.

4.3 From 5.5 at % Mn to 10.45 at % Mn

4.3.1 Susceptibility Data

Starting from 5.0 at % Mn, the critical peak seen in the more dilute alloys disappears altogether, while the main peak sharpens to a cusp at a temperature usually called T_{sg} . See the susceptibility data for Pd-6.0 at % Mn and Pd-10.45 at % Mn in Fig. 4.3.1 and 4.3.2 for examples. The cusp is symmetrical with respect to T_{sg} , contrary to the predictions of Edwards and Anderson, given in Section 2.4.4, and of Sherrington and Kirkpatrick, in Section 2.4.5. Similar to conventional spin glasses such as CuMn, the magnitude of the measured susceptibility of the present alloys is much smaller than that of the ferromagnetic alloys, so that it is now not necessary to correct for demagnetising effects. The reason can be found in Eq. 3.5.3, where N is now ignored in comparison with $1/\chi$.

The effect of an applied magnetic field is to decrease the overall signal while also rounding off the cusp to a broad maximum peaking at a lower temperature. Note that the earth's field still has a visible effect on the 6.0 at % Mn but not on the more concentrated alloys. The decrease in susceptibility becomes so small that for alloys with $Mn \geq 7.0$ at %, curves for different applied fields partly overlap one another. For clarity of presentation, the Y-scale for such a diagram is labelled for the curve with the maximum applied field (the bottom curve), and each successive curve above one another (corresponding to a smaller field) has been artificially raised by a constant amount given in the caption of the diagram.



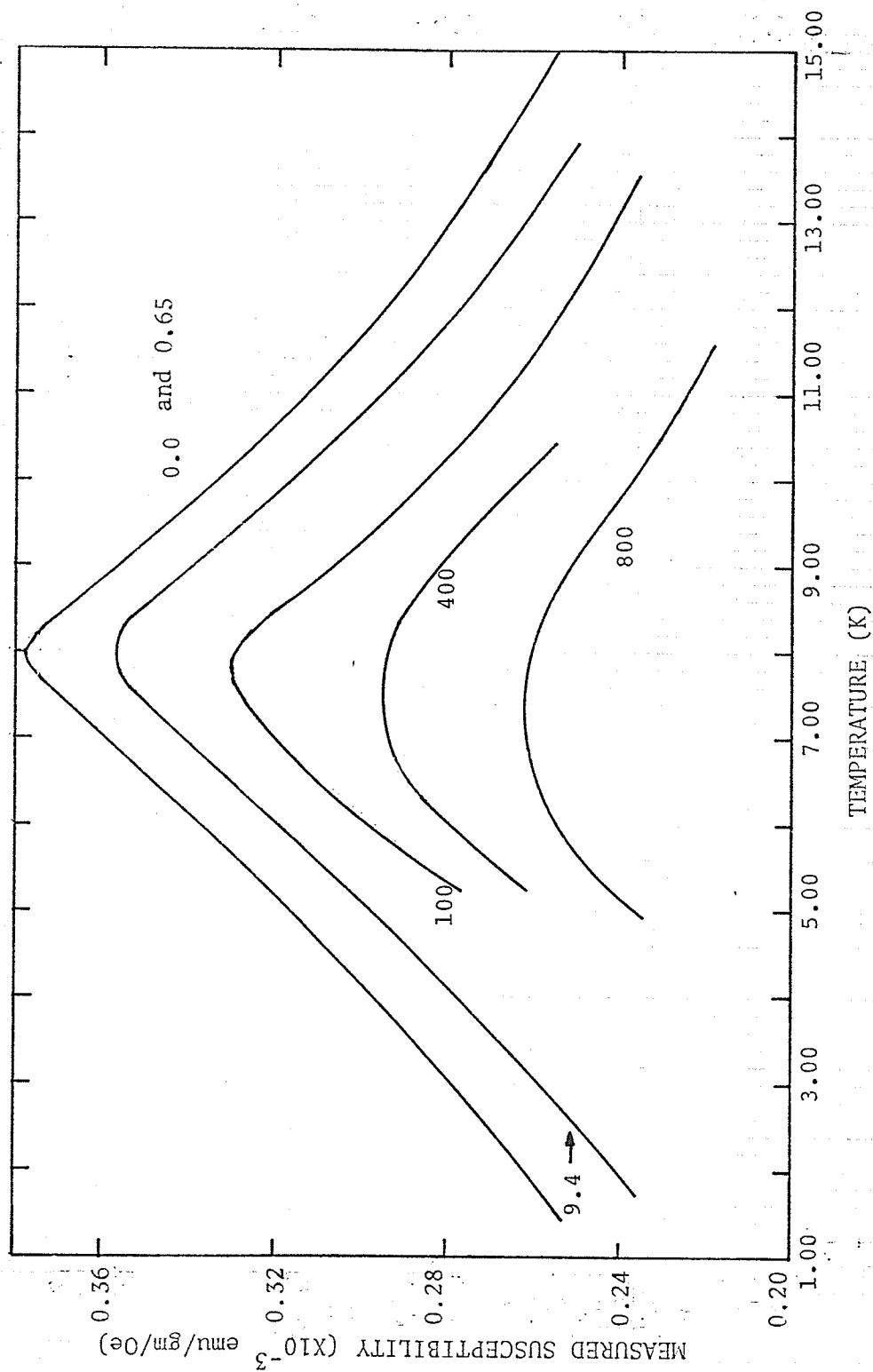


Fig. 4.3.2 Measured susceptibility of Pd-10.45 at % Mn.

The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.2×10^{-4} emu/gm/Oe for clarity.

The decrease in $\chi_{\text{meas(maxi)}}/N^{-1}$ for alloys with Mn > 5.0 at % is shown in Fig. 4.3.3. Note the use of logarithm scale to bring out the small signals. Although there are some scatter in the data near 7 at % and 9.5 at %, the general trend of decrease in susceptibility signal with increase in Mn concentration is clear, corresponding to a decrease in magnetic moment in these alloys.

As pointed out in Section 2.1.3, if R.K.K.Y scaling holds, $\chi(T,0)$, when plotted against the variable T/c , should bring out the universal function K . However, this is not the case, as shown in Fig. 4.3.4, where the susceptibility data of several alloys are presented. That they tend to fill up the whole page as opposed to falling into a single curve, highlights the failure of R.K.K.Y. scaling. Besides the reason given at the end of Section 2.1.3, one notes the extra direct d-d anti-ferromagnetic coupling as discussed in Section 2.1.1. Hence this failure is anticipated.

More comparisons with theoretical models follow.

Abrikosov's model predicts that

$$\chi(T_{\text{sg}},0) \cdot T_{\text{sg}}/c = \text{constant}$$

as deduced from Eq. 2.4.1.

This expression is, however, found to be a decreasing function of Mn concentration c , as given in Table 4.3.1 below.

The model of Edwards and Anderson predicts that

$$\chi = \frac{C}{T} \quad \text{for } T > T_{\text{sg}}$$

Hence a plot of $1/\chi$ vs. T should yield a straight line passing through

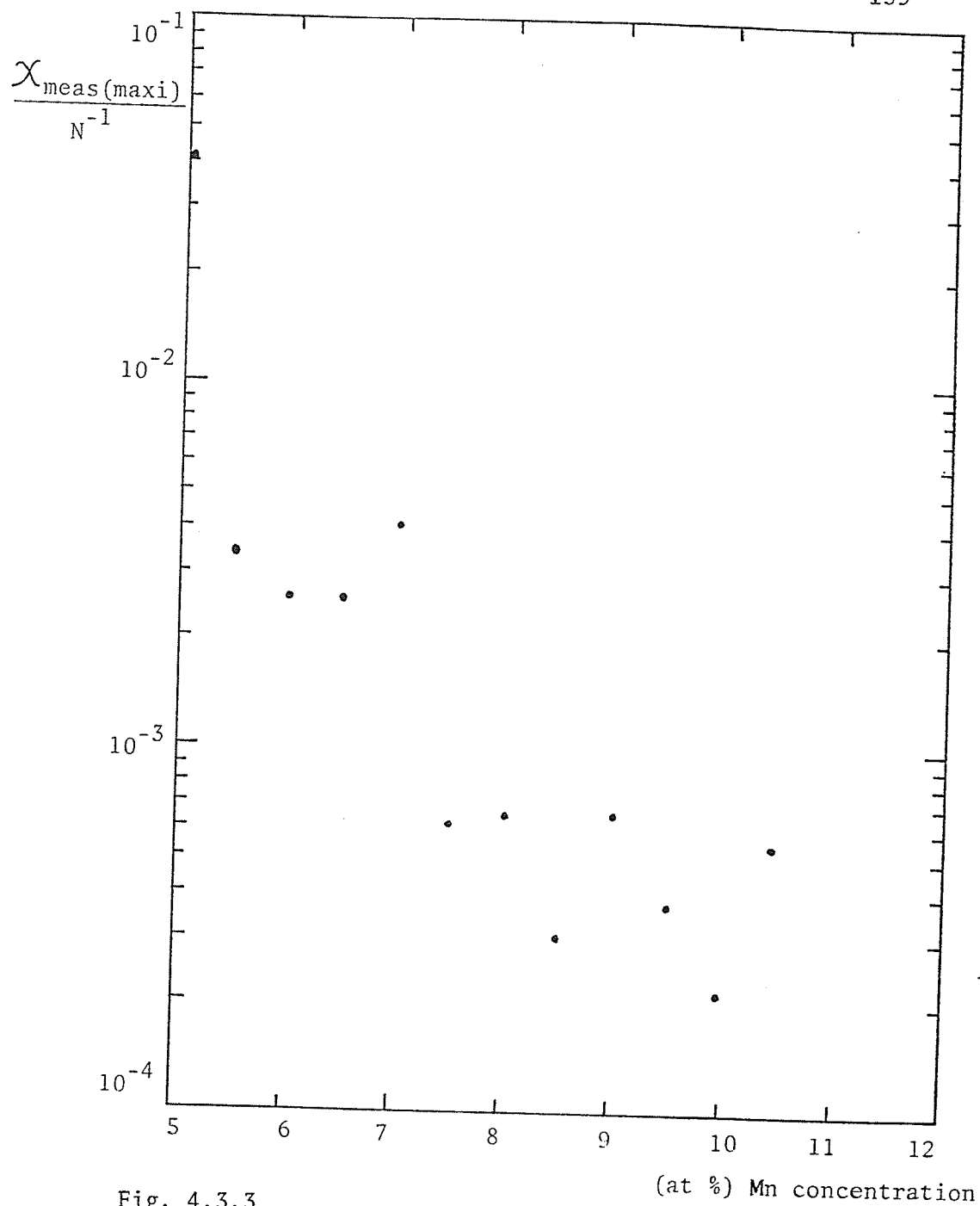


Fig. 4.3.3

(at %) Mn concentration

$\chi_{meas(maxi)} / N^{-1}$ for alloys with $Mn \geq 5.0$ at %.

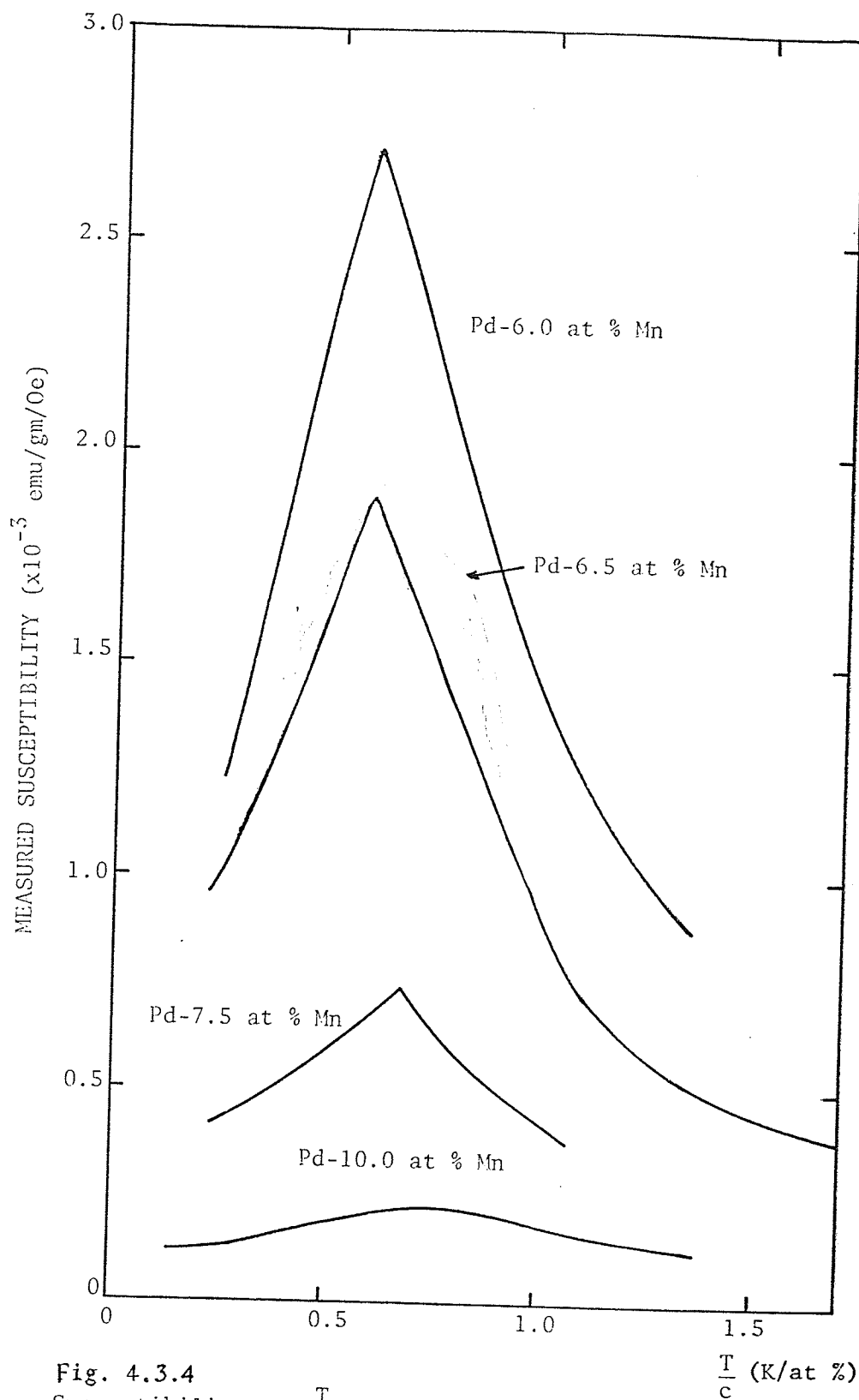


Fig. 4.3.4
Susceptibility vs. $\frac{T}{C}$ for Pd-6.0 at % Mn, Pd-6.5 at % Mn,
Pd-7.5 at % Mn, and Pd-10.0 at % Mn.
Note the failure of RKKY scaling.

the origin. This is found to be only approximately true for Pd-10.0 at % Mn, as shown in Fig. 4.3.5. $1/\chi$ vs. T is a straight line only in the temperature range $7.5 \text{ K} \leq T \leq 12^\circ \text{ K}$. Above 12° K , the line becomes curved. Hence the straight line may actually be an artifact of fitting data to too small a temperature interval, as remarked by Mulder et al (1981). The same range dependence is also found for plots of 8.0 at % Mn and 10.45 at % Mn. Further, the x-intercept of the line is positive (1.7° K) for the former alloy but negative (-1.4 K) for the latter, as shown in Fig. 4.3.6. Hence, no significance is attached to these $1/\chi$ vs. T plots.

A major failure of both the Edwards and Anderson model, and the Sherrington and Kirkpatrick model, is their prediction of a cusp in the specific heat, which is not experimentally observed. The reason, as pointed out by Abrikosov (1980), is that in order to account for a cusp in susceptibility, these models have assumed the existence of an order parameter, which necessarily brings about a cusp in the theoretical specific heat.

Finally the cluster model (Smith 1974) predicts that $T_{\text{sg}} \propto c$ using an r^{-3} type interaction. If, however, the interaction is r^{-2} , it predicts that $T_{\text{sg}} \propto c^{2/3}$. Experimentally one finds that $T_{\text{sg}} \propto (c-2.5)$. Hence the real interaction in the Pd-Mn alloy system is neither r^{-3} , nor r^{-2} . More discussion on this point will be given in Section 4.4.1.

4.3.2 Resistivity Data

For the resistivity data for alloys within this Mn range, the

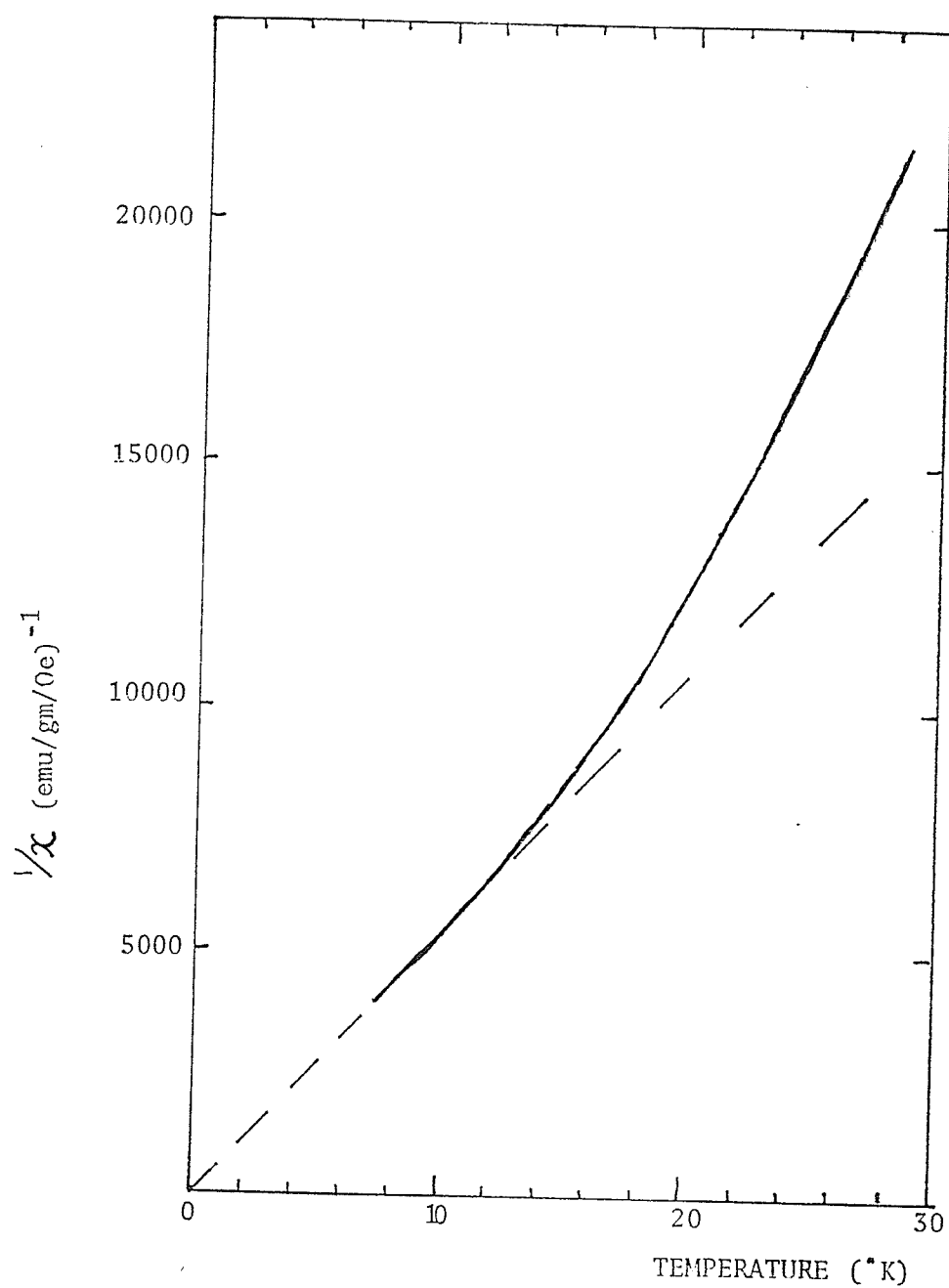


Fig. 4.3.5 $1/\chi$ vs temperature for Pd-10.0 at 2% Mn.
Note the apparent Curie law behaviour near T_{sg} .

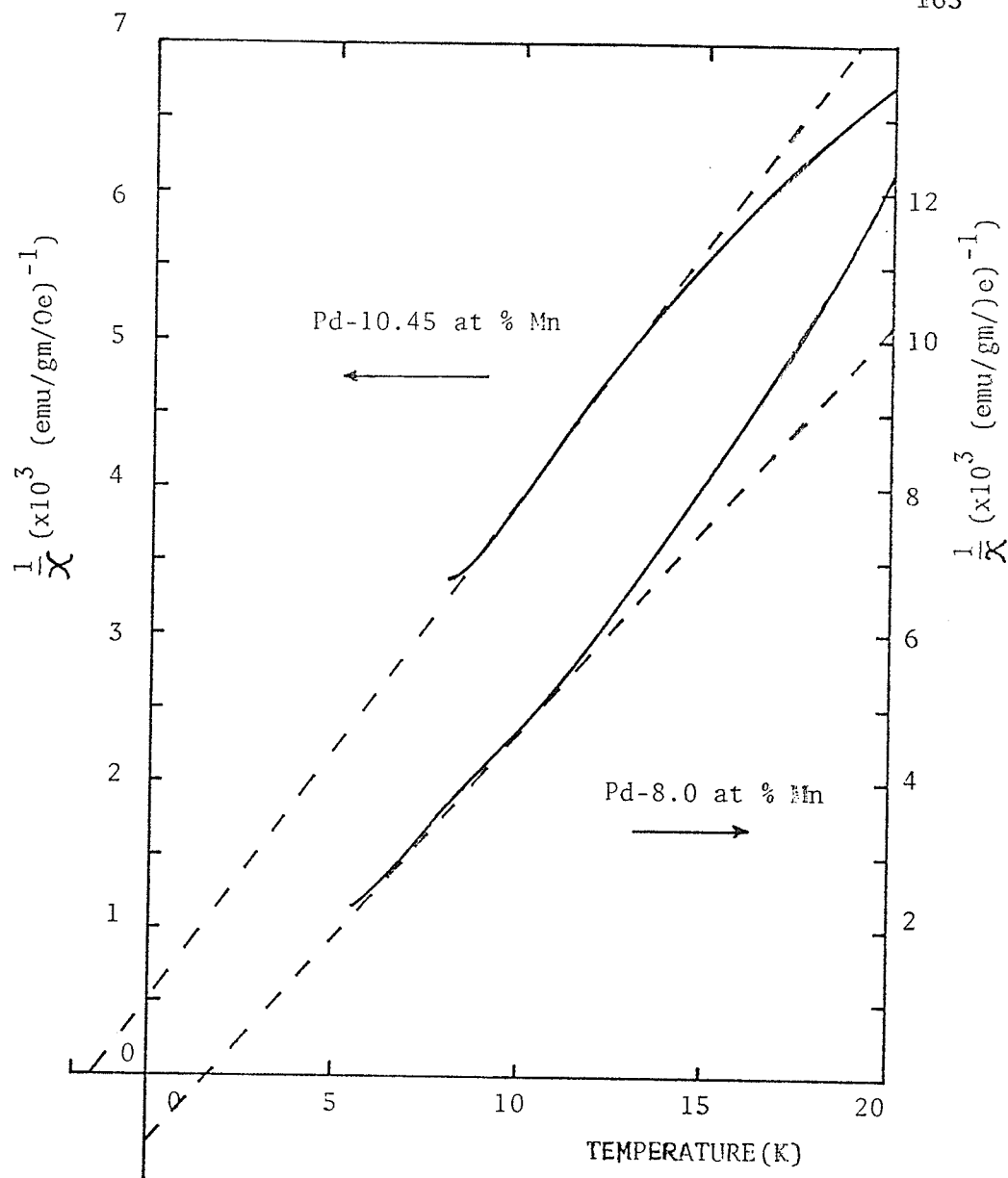


Fig. 4.3.6

$\frac{1}{\chi}$ vs. temperature for Pd-8.0 at % Mn and Pd-10.45 at % Mn.

Instead, one finds a broad maximum above T_{sg} , near 60° K , as shown in Fig. 4.3.7. The fact that this broad maximum does not change position with change in Mn concentration indicates that it is probably associated with breakdown in Matthiessen's Rule (Bass 1972), so that

$$\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{host}}$$

no longer faithfully represents the impurity resistivity. Unfortunately at present there is no better way of extracting the impurity resistivity from ρ_{alloy} for high impurity concentrations. This broad maximum has been repeatedly checked in this laboratory.

Similar to conventional spin glasses (Ford and Mydosh, 1976) the incremental resistivity is found to be linear in temperature at T_{sg} for all the spin glass-like Pd-Mn alloys investigated. The limiting form ($T \rightarrow 0$) of the incremental resistivity is linear in T for alloys with $5.0 \text{ at } \% \leq \text{Mn} \leq 8.0 \text{ at } \%$, and $T^{3/2}$ for alloys with $\text{Mn} > 8.0 \text{ at } \%$. (See Fig. 4.3.8 and 4.3.9 for examples). The coefficient of the linear term decreases slightly at $6.5 \text{ at } \% \text{ Mn}$ and then increases slowly with increase in Mn concentration. The coefficient of the $T^{3/2}$ term is constant within experimental error, in sharp contrast to the behaviour of its counterpart for the ferromagnetic Pd-Mn alloys, as already shown in Fig. 4.1.14 above.

The models of Abrikosov and of Rivier and Adkins have respectively predicted a T and a $T^{3/2}$ limiting form for the incremental resistivity of a spin glass. Both have, however, based their arguments on the process of scattering of conduction electrons from thermally generated excited states close to the ground state. The

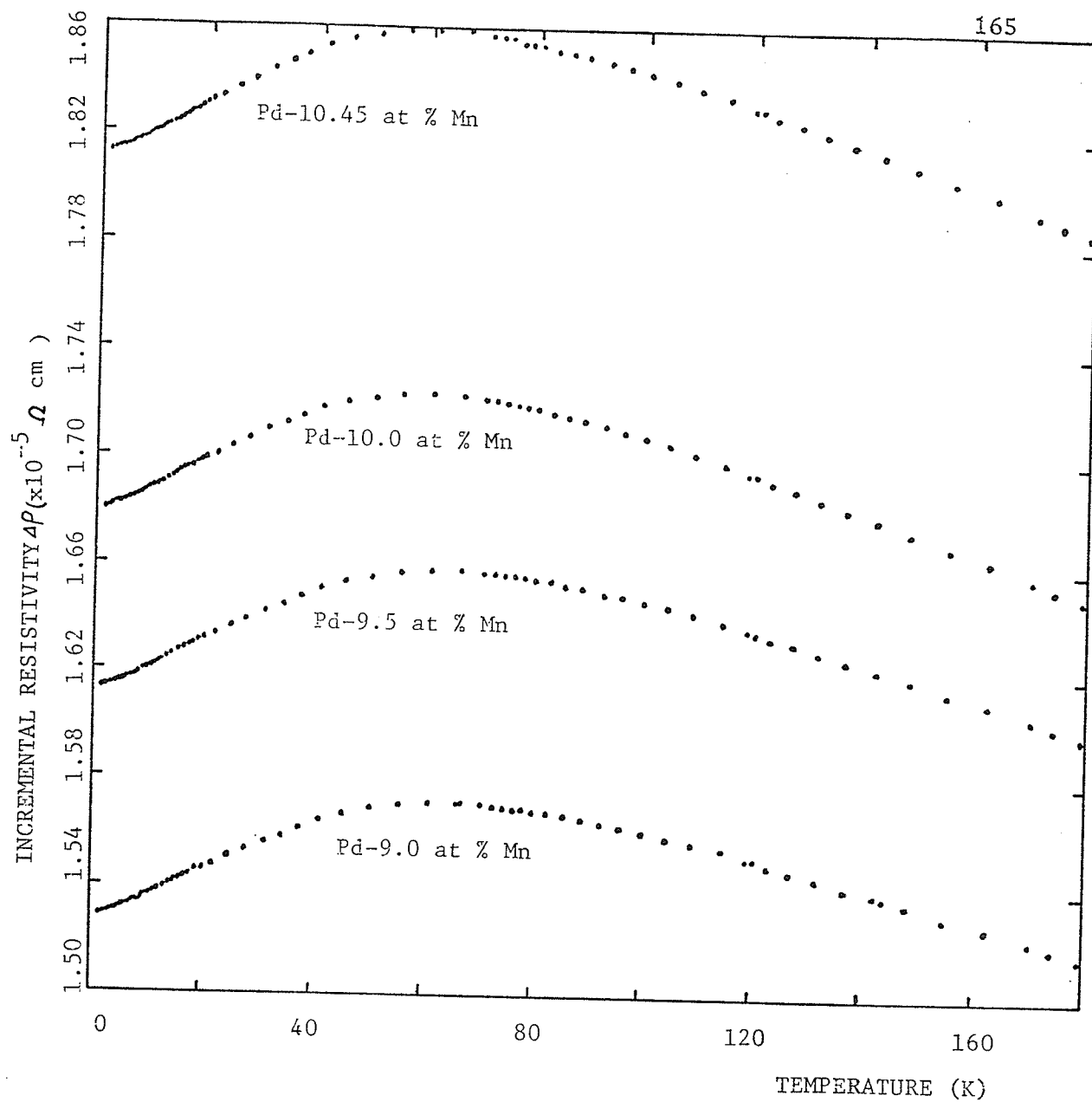


Fig. 4.3.7 Incremental resistivity of Pd-Mn alloys.

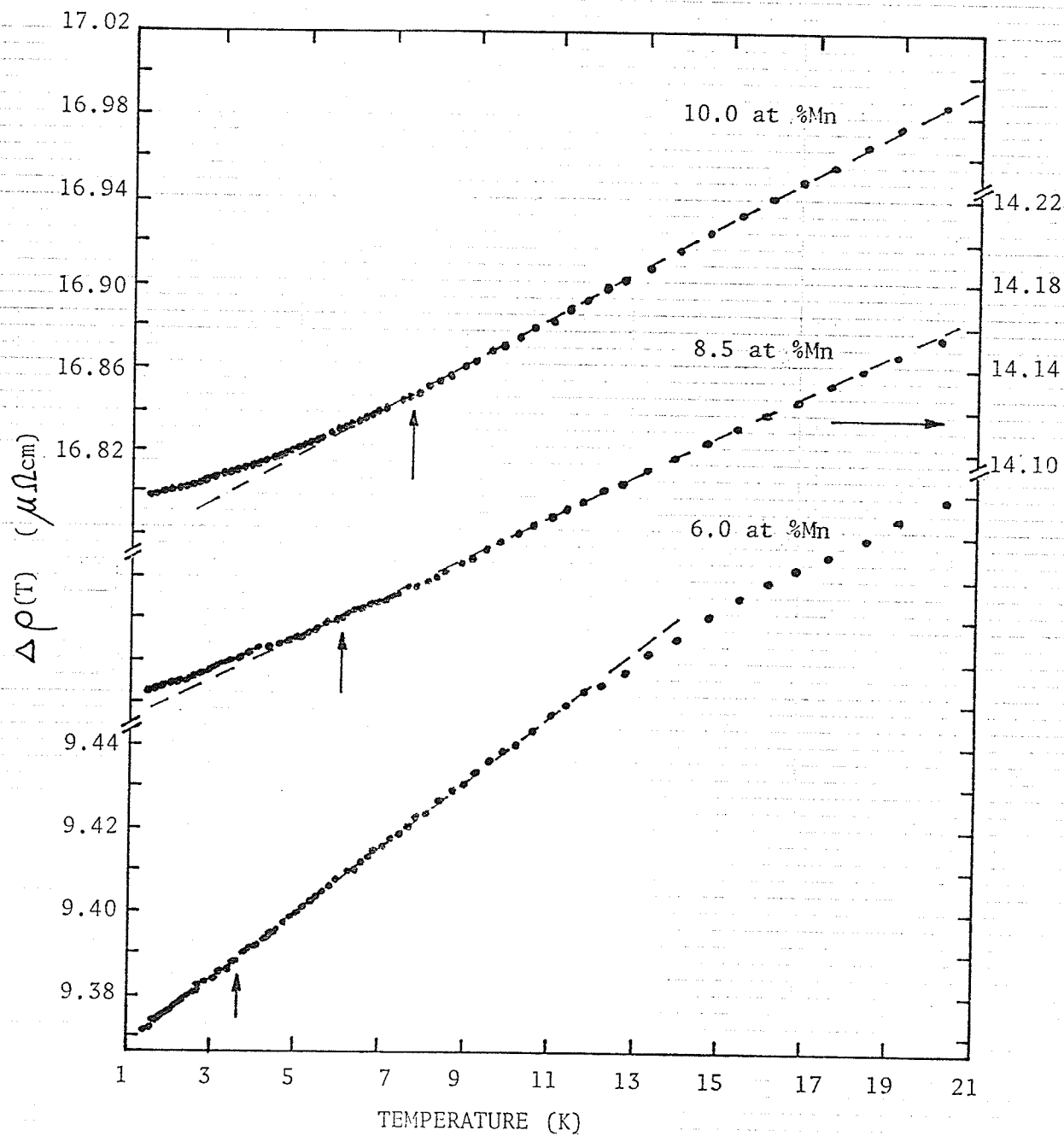


Fig. 4.3.8 Incremental resistivity data of Pd-6.0 at % Mn, Pd-8.5 at % Mn, Pd-10.0 at % Mn.

Vertical arrow indicates position of susceptibility peak.

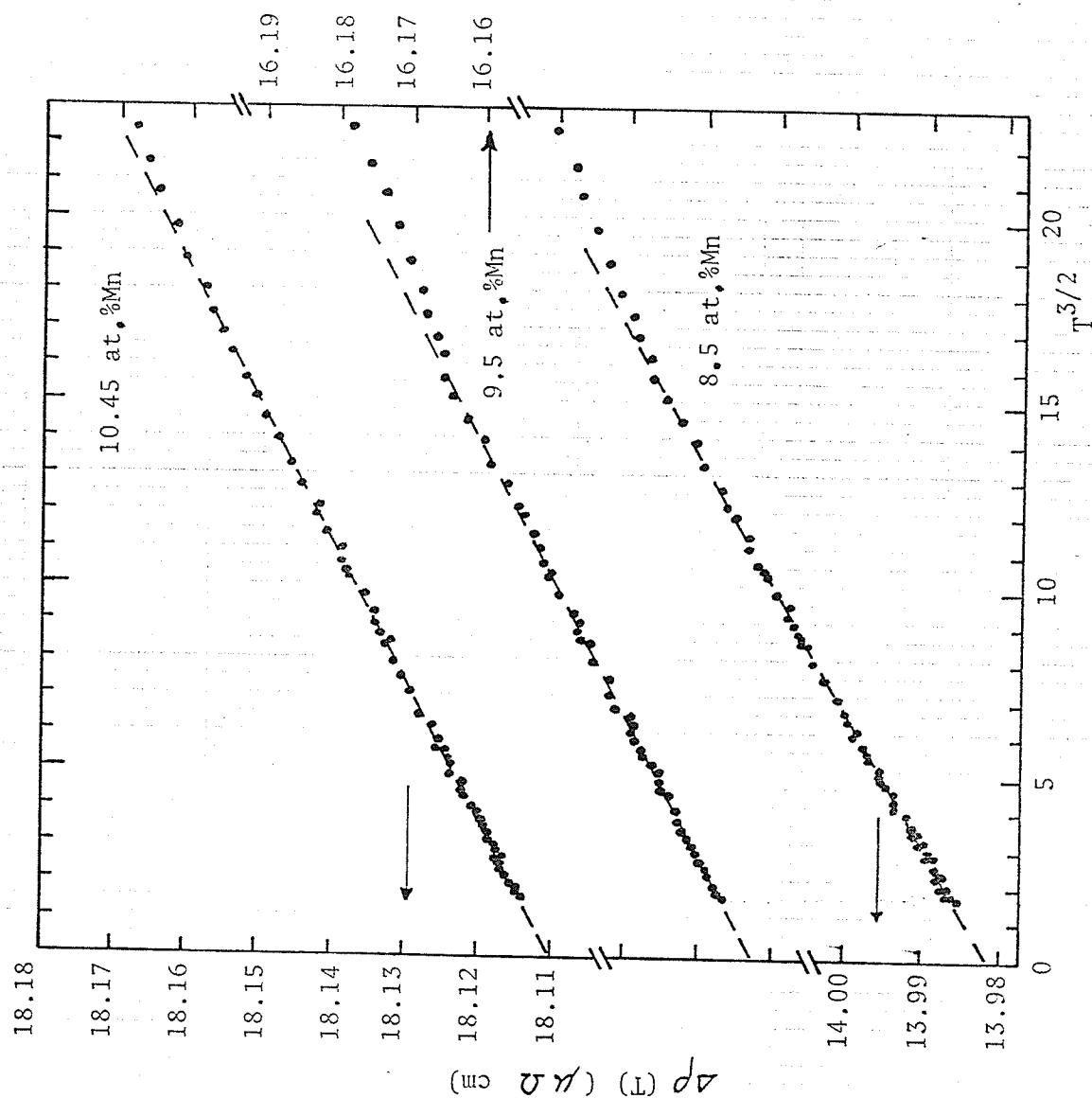


Fig. 4.3.9 Incremental resistivity vs. $T^{3/2}$ for Pd-10.45 at % Mn, Pd-9.5 at % Mn, and Pd-8.5 at % Mn.

T-dependence is found to be true for conventional spin glasses where the range of validity is roughly 15 to 30% of T_{sg} . For Pd-Mn spin glass with a linear T dependence, e.g. the 7.0 at % Mn, the linear region extends from 1.5° K to 7° K, while its T_{sg} is only 4.3° K. For alloys with a $T^{3/2}$ dependence, e.g. the 9.5 at % Mn, the $T^{3/2}$ region extends from 1.5°K to 6.5°K, a temperature 90% of its T_{sg} (7.05°K). Hence, for the present alloys, one should also consider scattering at energy levels much higher than those treated in the above two models. Moreover, as the $T^{3/2}$ region for 8.5 at % Mn extends up to its T_{sg} (5.9°K), one expects to find a $T^{3/2}$ region for the 8.0 at % Mn near its T_{sg} (5.5°K) too, since the two alloys differ by only half a percent of Mn concentration. Instead, one finds that the linear region for the 8.0 at % Mn extends from 1.5°K to 8.0°K, as shown in Fig. 4.3.10. Therefore, the missing $T^{3/2}$ region for this alloy, and similarly for other Pd-Mn spin glass alloys, is not an error of not looking in the right temperature interval.

4.3.3 Summary of Results

The following tables summarise the parameters deduced from the A.C. susceptibility and D.C. resistivity data for alloys with 5.5 at % $\leq$ Mn $\leq$ 10.45 at %.

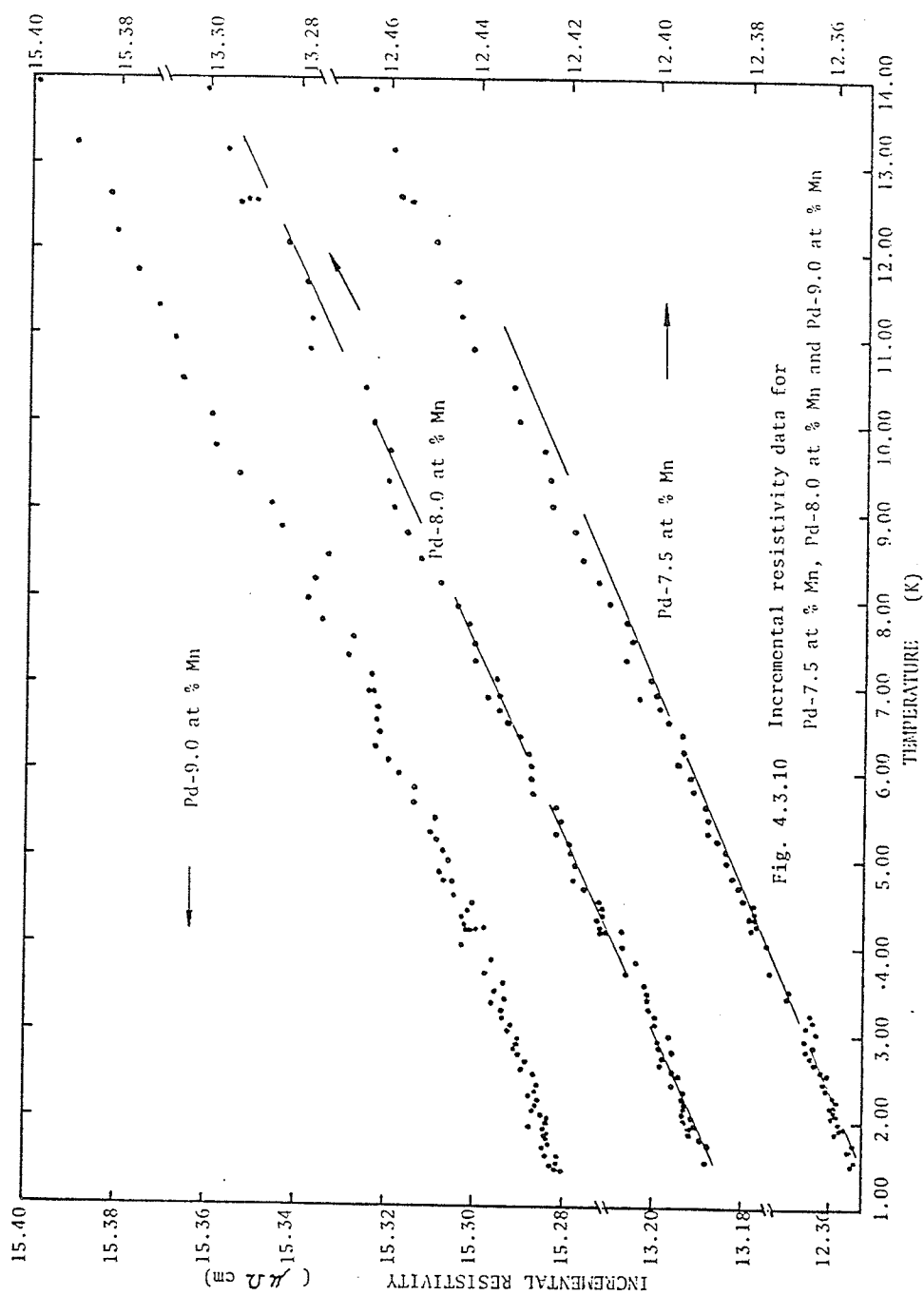


Fig. 4.3.10 Incremental resistivity data for
Pd-7.5 at % Mn, Pd-8.0 at % Mn and Pd-9.0 at % Mn

Table 4.3.1 Summary of the A.C. susceptibility data

Alloy	T_{sg}	$\chi(T_{sg}, 0)$	$\chi(T_{sg}, 0)T_{sg}/c$
(at % Mn)	(K)	(10^{-3} emu/gm/Oe)	($\times 10^{-3}$)
5.5	3.15 ± 0.05	4.6 ± 0.5	2.63
6.0	3.6 ± 0.05	2.7 ± 0.3	1.62
6.5	3.9 ± 0.05	2.0 ± 0.2	1.20
7.0	4.3 ± 0.05	1.7 ± 0.2	1.04
7.5	5.1 ± 0.05	0.74 ± 0.07	0.503
8.0	5.55 ± 0.05	0.44 ± 0.04	0.305
8.5	5.9 ± 0.05	0.39 ± 0.04	0.271
9.0	6.5 ± 0.05	0.37 ± 0.04	0.267
9.5	7.05 ± 0.05	0.31 ± 0.03	0.230
10.0	7.55 ± 0.05	0.26 ± 0.03	0.196
10.45	8.05 ± 0.05	0.29 ± 0.03	0.223

Table 4.3.2. Summary of Parameters from the Resistivity Data

Alloy (at % Mn)	$\Delta\rho(T=0)$ ($\mu\Omega\text{cm}$)	Coefficient of the the linear term ($\mu\Omega\text{cm K}^{-1}$)	Coefficient of the $T^{3/2}$ term ($\mu\Omega\text{cm K}^{3/2}$)
5.5	8.61	0.008(4)	-----
6.0	9.37	0.008(0)	-----
6.5	10.38	0.007(6)	-----
7.0	11.25	0.008(4)	-----
7.5	12.35	0.008(8)	-----
8.0	13.18	0.009(0)	-----
8.5	13.98	0.009(5)	0.002(9)
9.0	15.28	0.010(4)	0.002(7)
9.5	16.12	0.010(8)	0.002(7)
10.0	16.79	0.011(0)	0.002(7)
10.45	18.11	0.011(2)	0.002(7)

4.4 Conclusion

4.4.1 Phase Diagram

Fig. 4.4.1 summarises the critical temperatures T_C , T_C^* , and T_{Sg} found in this project. The data are more reliable than those obtained previously because of the reasons given in Chapter I. The ferromagnetic phase extends from 0.5 at % Mn to 2.5 at % Mn, and has been examined via the behaviour of the critical peak of the susceptibility data, as well as the "knee" in the resistivity data. Similarly, the mixed ordering phase lies in the range of 3.0 at % Mn to 4.5 at % Mn, although the phase is only quasi-ferromagnetic as discussed in Section 4.2.1 above. The spin glass phase lies in the range of 5.0 at % Mn to 10.45 at % (and beyond) and has been examined via the cusp of the susceptibility data. As noted before, the actual boundary of the phase may lie within the half per cent interval of the given value. The highest temperature for ferromagnetic transition T_C is 6.0 K for the 2.5 at % Mn, and the highest spin glass temperature T_{Sg} is 8.05 K for 10.45 at % Mn. The lowest T_C is 1.64 K for 0.5 at % Mn, and the lowest T_{Sg} is 2.97 K for 5.0 at % Mn. Considering that there is another spin glass phase at very dilute Mn concentration (500 ppm), the co-existence of two spin glass phases in the same alloy system is very rare in nature, while the co-existence of spin glass and ferromagnetic phases are believed to be more common, e.g. AuFe.

Of the theories presented in this thesis, only the model of Sherrington and Kirkpatrick predicts a phase diagram, Fig. 2.4.1, similar to the present system, with a twist. If their phase diagram is plotted with $J_0 \rightarrow -J_0$ then their theoretical prediction would appear

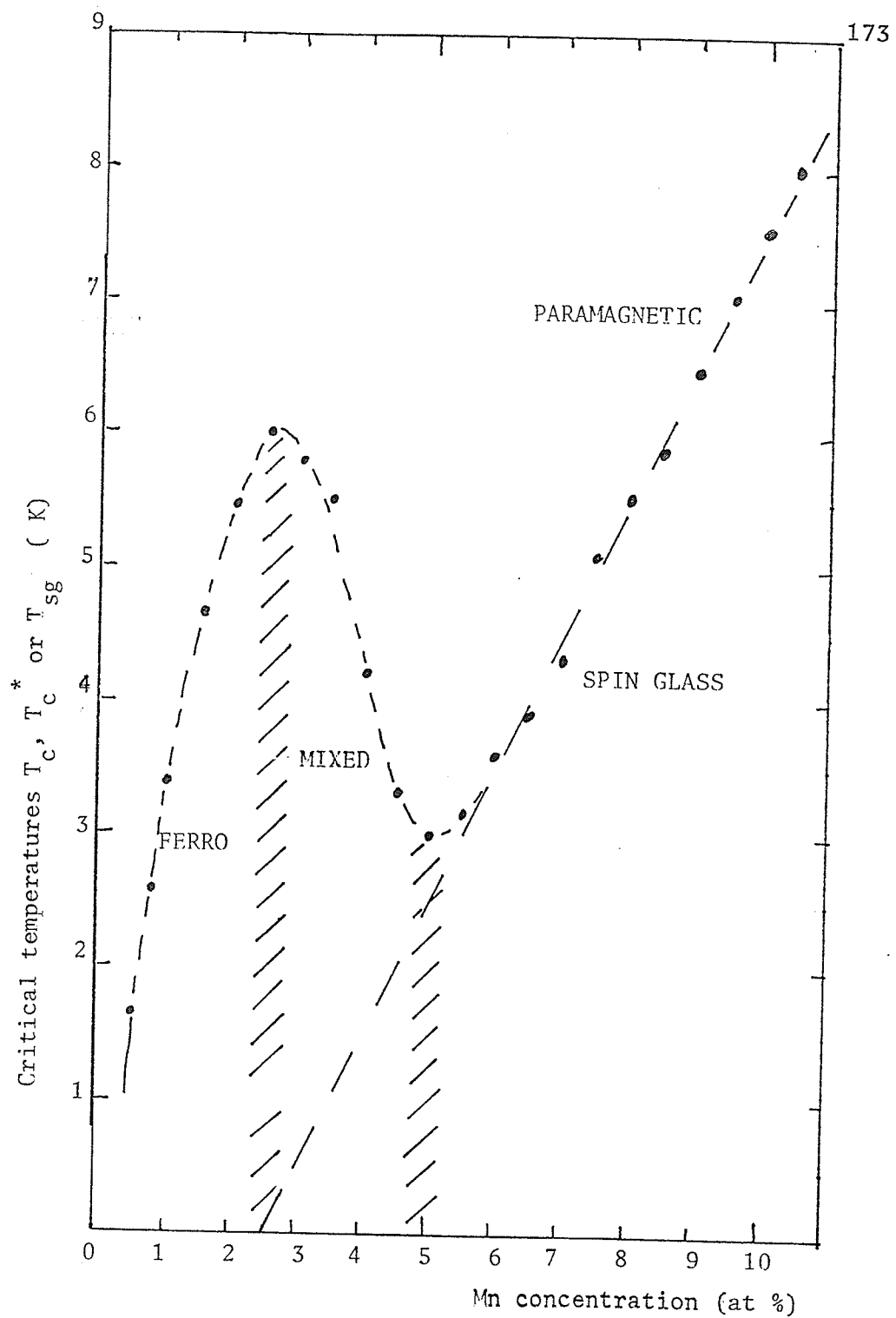


Fig. 4.4.1 Critical temperatures as a function of Mn concentration.

The data plotted are T_c for $0.5 \text{ at } \% \leq \text{Mn} \leq 2.5 \text{ at } \%$, T_c^* for $3.0 \text{ at } \% \leq \text{Mn} \leq 4.5 \text{ at } \%$ and T_{sg} for $\text{Mn} \geq 5.0 \text{ at } \%$.

to resemble the experimental situation, as shown in Fig. 4.4.2. However, more recent calculations by Kirkpatrick and Sherrington (1978) show that such a situation does not lead to a simple mirror reflection of the phase diagram, and further leads to the prediction of an antiferromagnetic state. This clearly does not reproduce the situation discussed above. It therefore seems that the competing interactions in the Pd-Mn system, viz., a long-ranged ferromagnetic coupling via the enhanced R.K.K.Y. polarization and a short-ranged direct d-d anti-ferromagnetic coupling cannot be described by a simple modification of the Sherrington and Kirkpatrick model. However, some aspects of this model suit the Pd-Mn system better because it includes interactions beyond pure R.K.K.Y.

4.4.2 Double Transitions?

Fig. 4.4.1 shows that the spin glass temperature T_{sg} of alloys with Mn > 5.0 at % follows a straight line of the form

$$T_{sg} \propto (c - 2.5)$$

where c is the Mn concentration in atomic %.

If this is extended, it intercepts the x-axis at 2.5 at % Mn. Hence for alloys with 2.5 at % < Mn < 5.0 at %, two possible phase transitions can be proposed, one quasi-ferromagnetic from the behaviour of the critical peak as noted in Section 4.4.1, and one spin glass like by inference from the behaviour of the spin glass alloys. This idea has been suggested by Verbeek and Mydosh (1978) and Verbeek et al (1978) for AuFe and Pd(Fe,Mn). Actually, the susceptibility data of

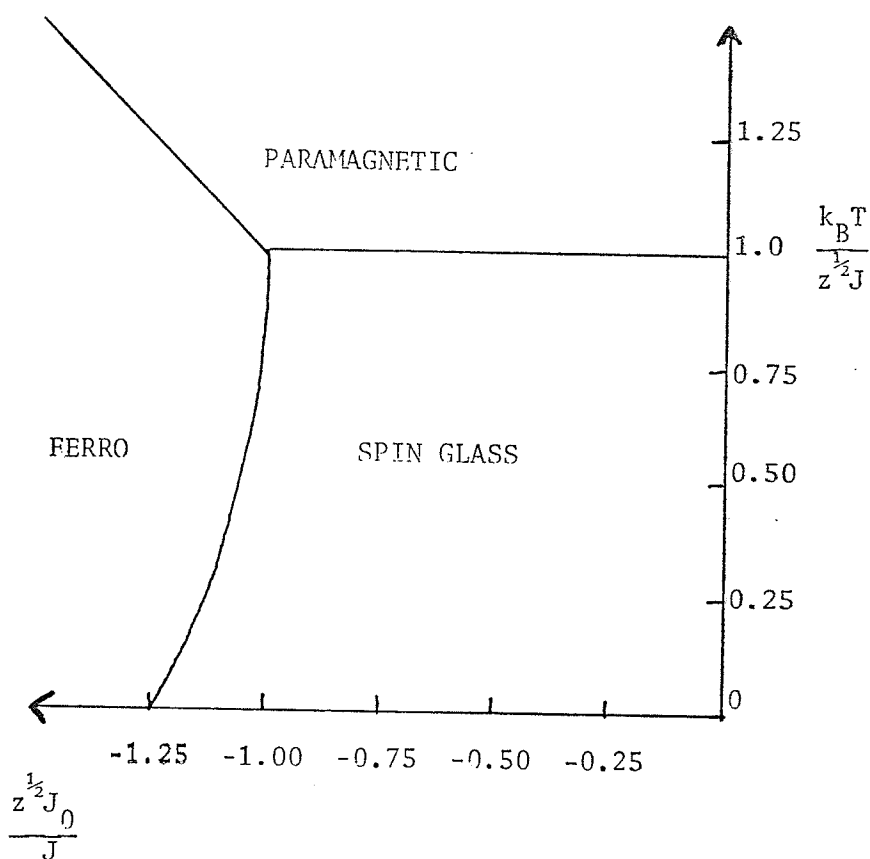


Fig. 4.4.2 Adapted phase diagram of spin-glass ferromagnet (adapted from Sherrington & Kirkpatrick 1975)

z is the number of neighbours, J is the spin-spin coupling parameter, J_0 is the deviation from the center in the probability distribution of J .

these alloys show two peaks only under a small magnetic field. As shown in Fig. 4.2.6 for Pd-4.5 at % Mn, with increase in field strength, the high temperature peak moves up in temperature, while the low temperature peak moves down. The high temperature peak provides information on critical behaviour on T_C^* , γ^* , δ^* by virtue of its height and position in a magnetic field, and has been closely examined in Section 4.2.1. The low temperature peak extrapolates to the zero field main peak $\chi_{\text{meas(maxi)}}$, which occurs at a temperature (3.1°K) slightly lower than T_C^* (3.2°K), but much higher than the temperature predicted by the relation

$$T_{\text{sg}} \propto (c-2.5)$$

while no other peaks are visible in the whole temperature range examined. The same argument applies to Pd-4.0 at % Mn. Hence the zero field main peak, $\chi_{\text{meas(maxi)}}$, of alloys with 2.5 at % < Mn < 5.0 at % does not indicate a continuation of the spin glass transition for alloys with Mn > 5.0 at %. In conclusion, the idea of double transitions for alloys in this Mn concentration range is not supported in this project.

4.4.3 Recommendations for Further Study

A. It is hoped that a better way of isolating the impurity contribution from the alloy data can be found. For example, at present, there is no better way than assuming that

$$\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{host}}$$

faithfully represents the resistivity due to the Mn impurities.

However, this approximation should not be good at high Mn concentration, as evidenced by the incremental resistivity data of alloys with Mn > 5.0 at %.

B. All the data of this project reflect the importance of the antiferromagnetic direct d-d coupling of the Mn ions. Hence, further study should concentrate on a theoretical model that includes this interaction as well as the R.K.K.Y. interaction. The model of Sherrington and Kirkpatrick is a good start. However, more detailed calculation of the R.K.K.Y interaction itself is also needed, as discussed in Section 2.4.1.

C. On the experimental side, one hopes to understand better the effect anisotropy has on the A.C. susceptibility data. This effect is amplified by the small demagnetising factors of the samples. In particular, the measured A.C. susceptibility signal always decreases if the sample's coercive force is greater than the driving field of the magnetometer. It is questionable whether the zero field main peak is real, or just an artifact of the A.C. technique. because the ferromagnetic Pd-Mn alloys have coercive forces, too. In this respect, measurements of the real and the imaginary susceptibilities will help to clear up the picture. If a range of driving field frequencies are employed, one gets contact between these two susceptibilities via the Kramers-Kronig relationships.

D. Finally, it will be nice to prepare more samples near the Mn concentrations of 0.5 at %, 2.5 at % and 5.0 at % to further study

the transition among the various phases. A dilution refrigerator will be needed to investigate the more dilute alloys as their T_c 's are too low for the present equipment.

Appendix A

THE IDEAL GAS LAW

As applied to a container with several interconnecting compartments V_i , each with different temperature T_i .

Assume that a steady state is reached so that the pressure P is the same throughout the container. From the kinetic theory of an ideal gas, one has

$$P = \frac{1}{3} \frac{m n_i}{V_i} \overline{v_i^2} \quad (\text{A.1})$$

where m = mass of ideal gas molecule

n_i = number of molecules in i^{th} compartment

V_i = volume of i^{th} compartment

$\overline{v_i^2}$ = mean squared velocity of molecules in i^{th} compartment

If one is only concerned with situations far away from the boundary of the compartments (and so ignore the discontinuity in temperature across the boundary) the average kinetic energy of each molecule is:

$$\frac{1}{2} m \overline{v_i^2} = \frac{3}{2} k_B T_i$$

where k_B = Boltzmann's constant

T_i = temperature of i^{th} compartment

Substituting into Eq. A.1

$$P = \frac{n_i}{V_i} k_B T_i$$

$$\frac{PV_i}{T_i} = n_i k_B$$

$$\sum_i \left(\frac{PV_i}{T_i} \right) = \sum_i n_i k_B = \text{constant}$$

because $\sum_i n_i$ is the total number of molecules in the container. This is the ideal gas law used in Eq. 3.4.1.

In practice, the non-ideality of the gas was taken care of by using Eq. 3.4.2 instead of Eq. 3.4.1. The three terms in the summation represented 3 compartments: the gas bulb at sample temperature T , the room temperature compartment at T_R , and the cryostat tube at some temperature(s) between T and T_R .

To approximate the real spread of temperatures along the whole length L of the cryostat tube, the tube was mentally divided into many small compartments, each of volume

$$\Delta V = A \Delta x$$

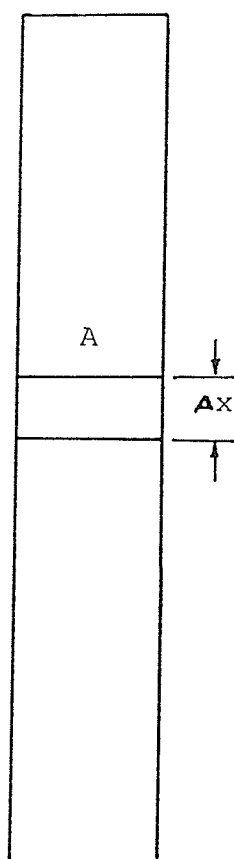
where A = cross-sectional area of the tube

x = variable along the length of the tube

See Fig. A.1. A linear temperature gradient along the tube was assumed so that

$$T_i = T + (T_R - T) x/L$$

Temperature = T_R (room temperature)



Temperature = T (sample temperature)

Fig.A.1 Analysis of the Cryostat Tube Term.

Further, assume the second virial coefficient B was the same for all compartments along the tube, and was equal to

$$B \left(T = \frac{T + T_R}{2} \right).$$

Then for the cryostat tube

$$\sum_i \frac{PV_i}{T_i + 273.15 B_i P/A_0} = \sum_i \frac{PA \Delta x_i}{T_i + C}$$

where $C = 273.15 B \left(T = \frac{T + T_R}{2} \right) P/A_0$

In the limit Δx_i approached dx

$$\sum_i \text{approached } \int_0^L$$

and the above summation became

$$\begin{aligned} & \int_0^L \frac{PA \, dx}{T_i + C} \\ &= PA \int_0^L \left(T + \left(\frac{T_R - T}{L} \right) x + C \right)^{-1} dx \\ &= \frac{PV_{L2}}{T_R - T} \ln \left(\frac{T_R + C}{T + C} \right) \end{aligned}$$

where $V_{L2} = AL =$ volume of cryostat tube.

This is the cryostat tube term used in Eq. 3.4.3

APPENDIX B

MEASURED SUSCEPTIBILITY DATA FOR
ALLOYS WITH Mn $\leq$ 2.5 at %

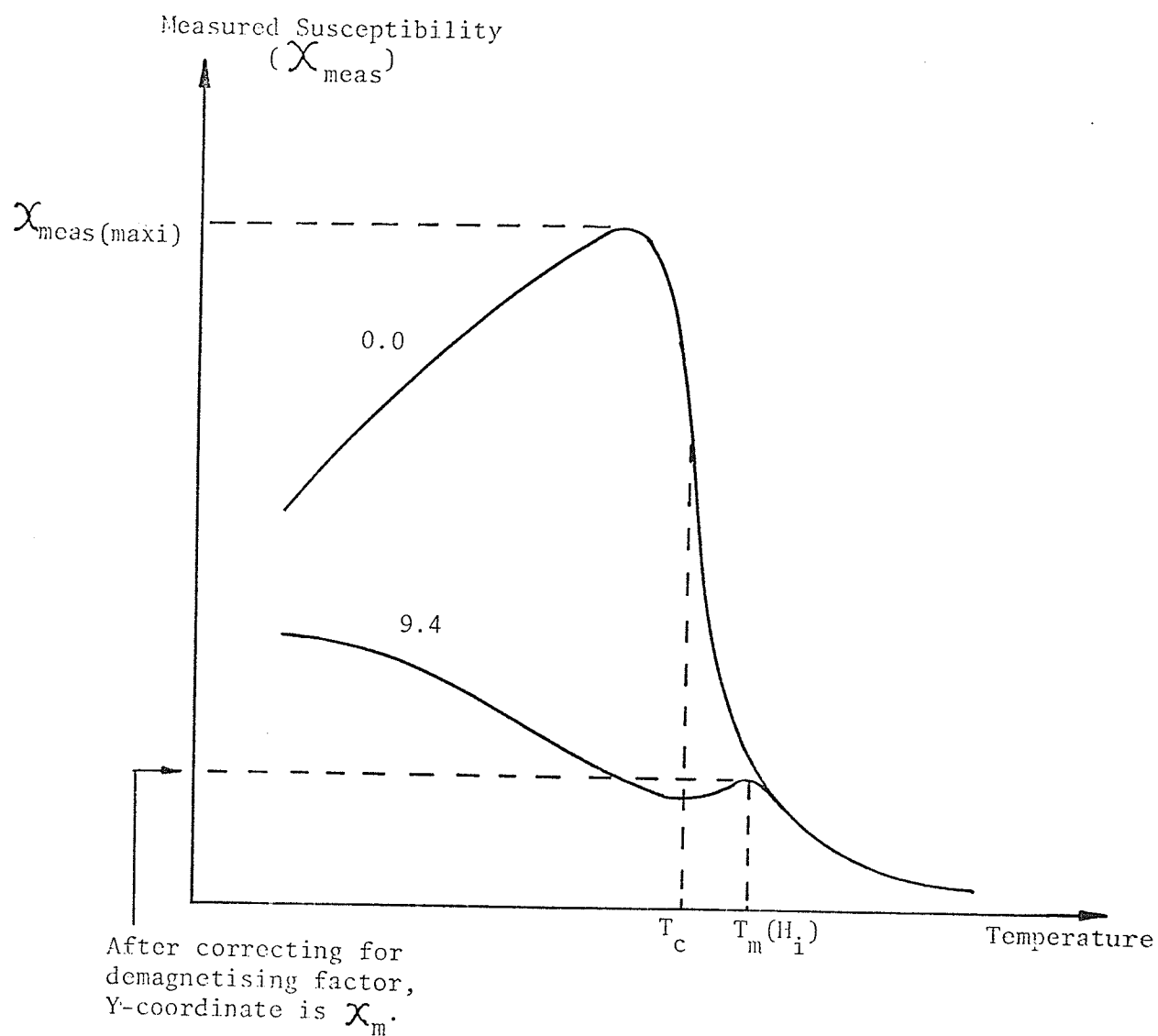


Fig. B.1 Explanation of symbols in susceptibility data.
The number beside each curve indicates the net applied magnetic field, measured in Oe.

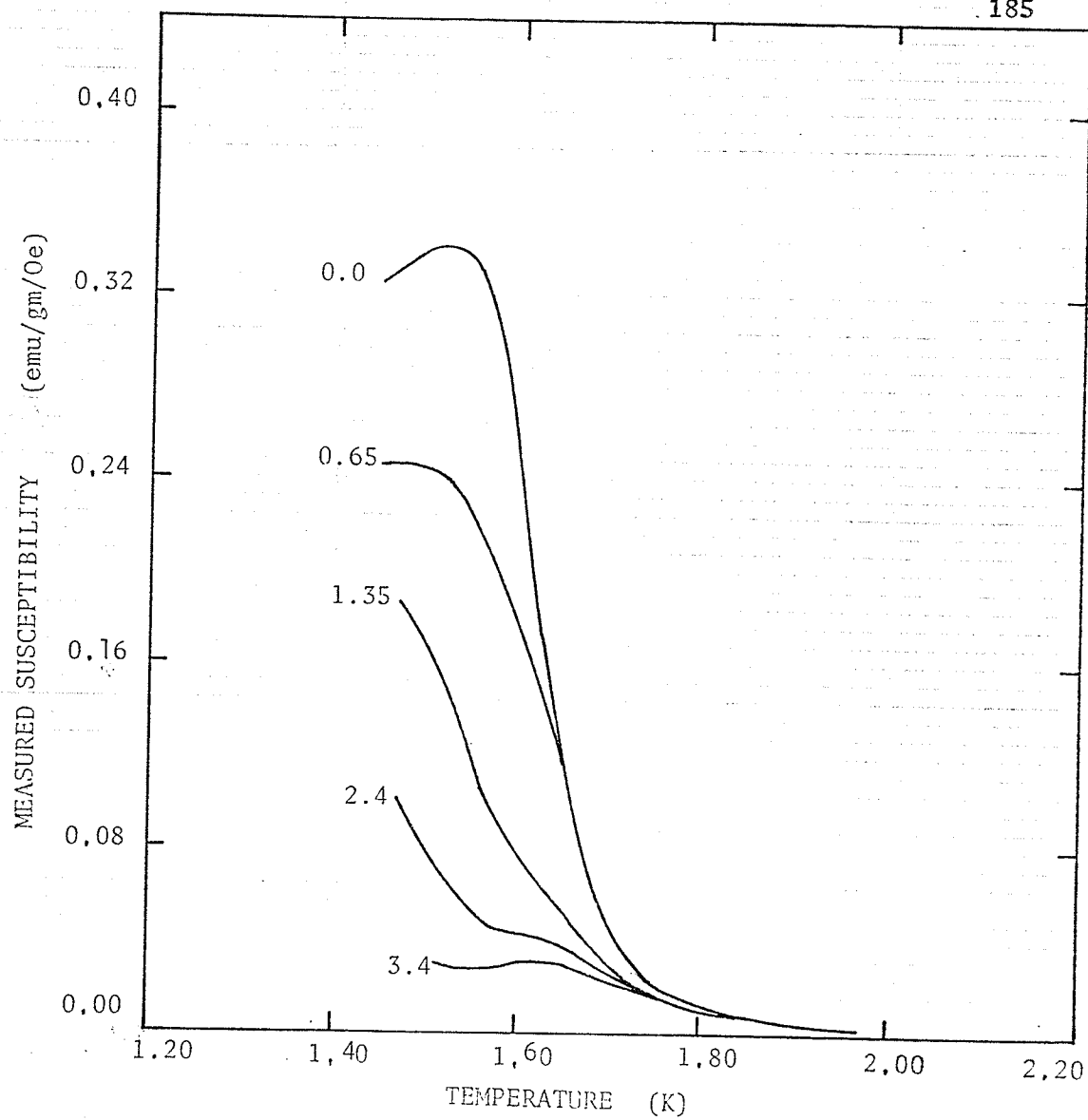


Fig. B.2 Measured susceptibility of Pd-0.5 at % Mn.

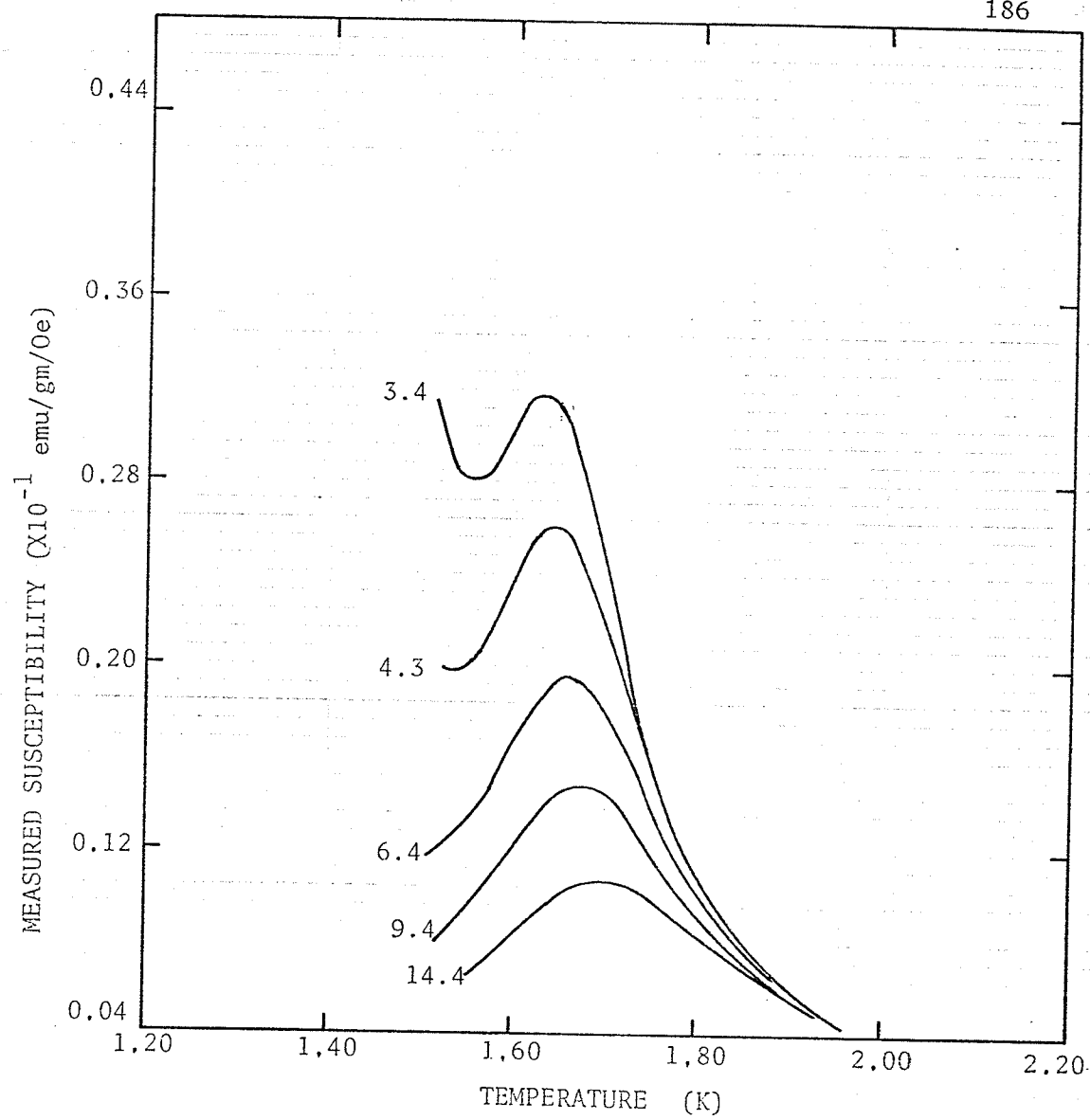


Fig. B.3 Measured susceptibility of Pd-0.5 at % Mn.

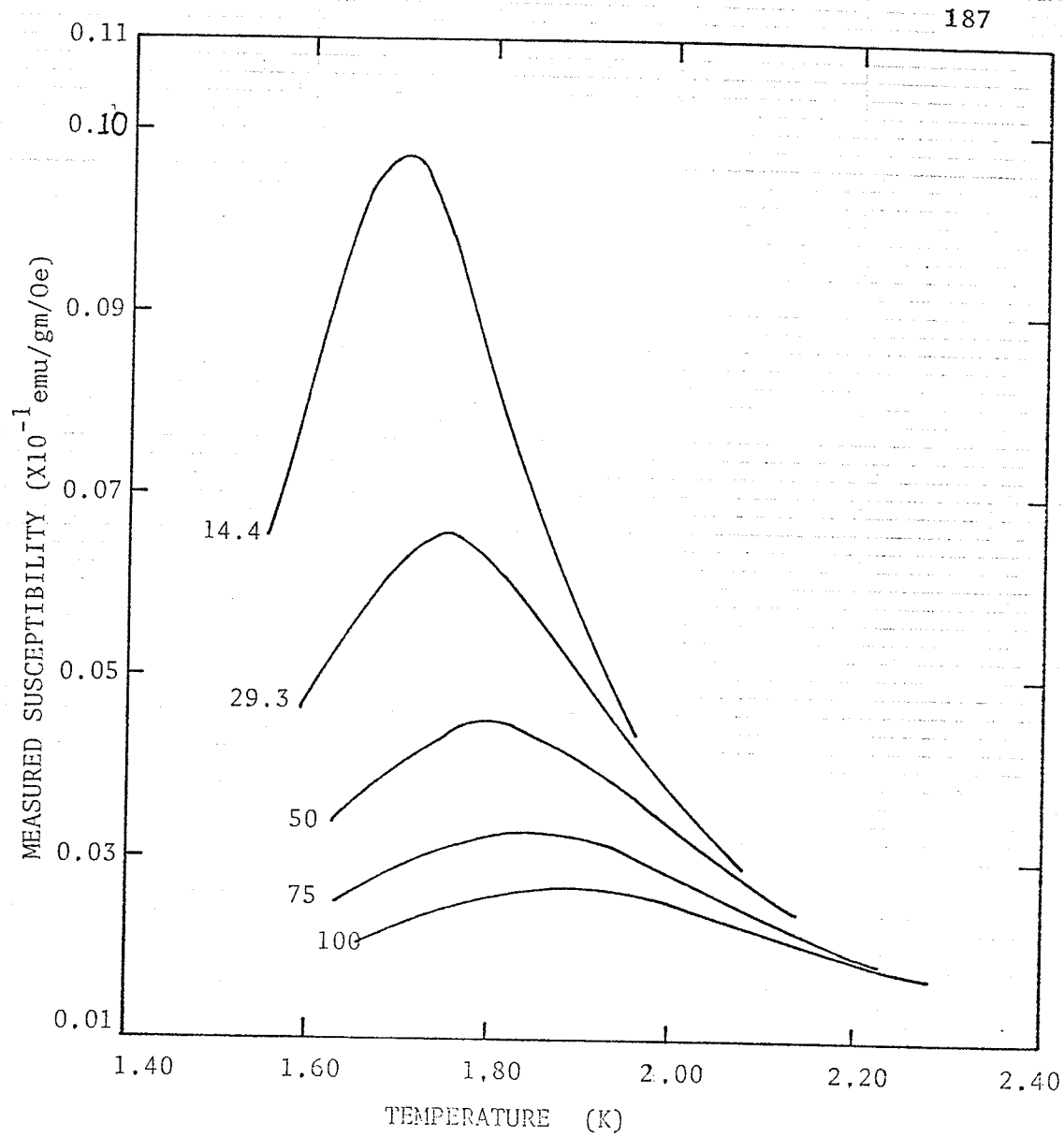


Fig. B.4 Measured susceptibility of Pd-0.5 at % Mn.

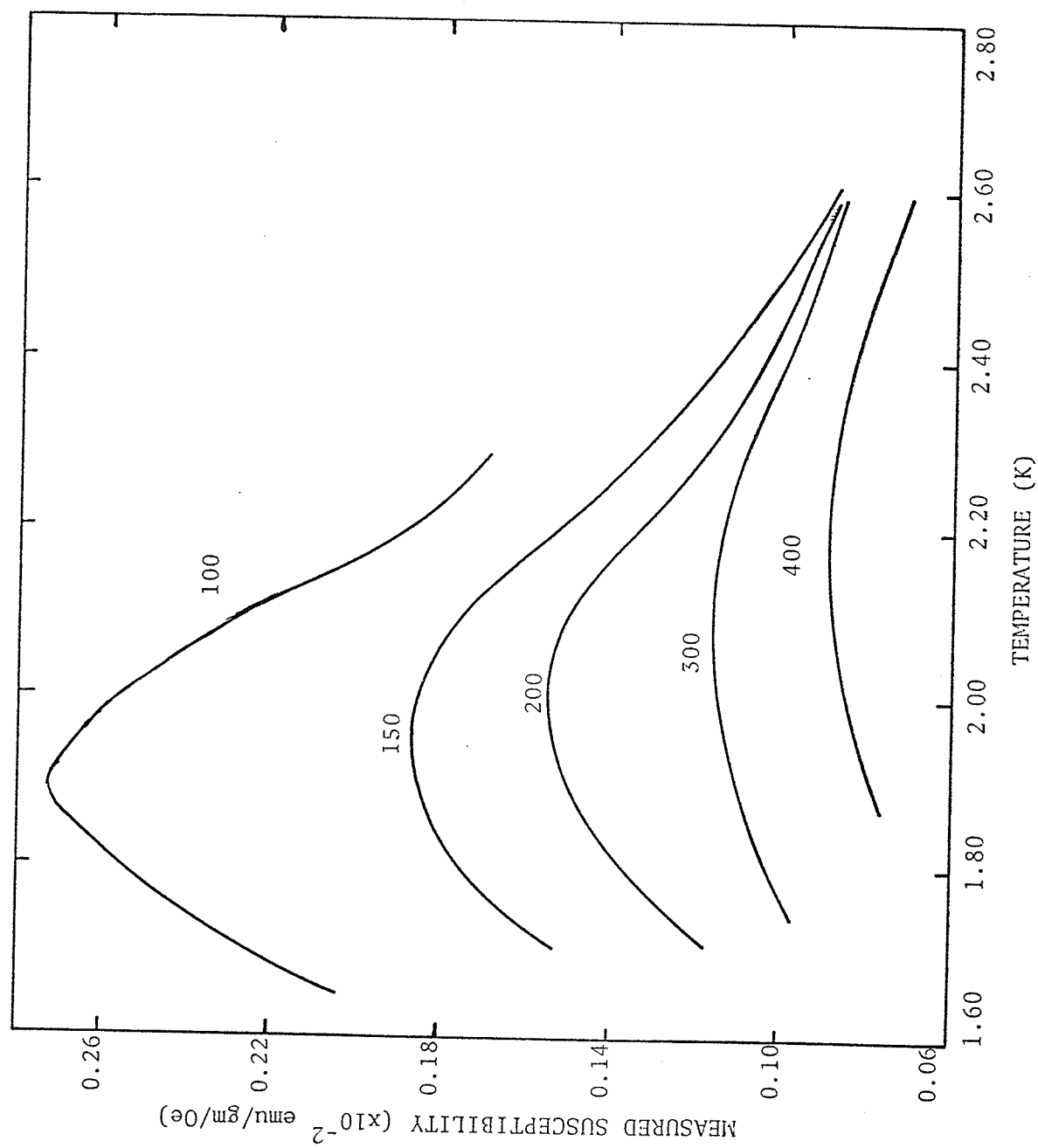
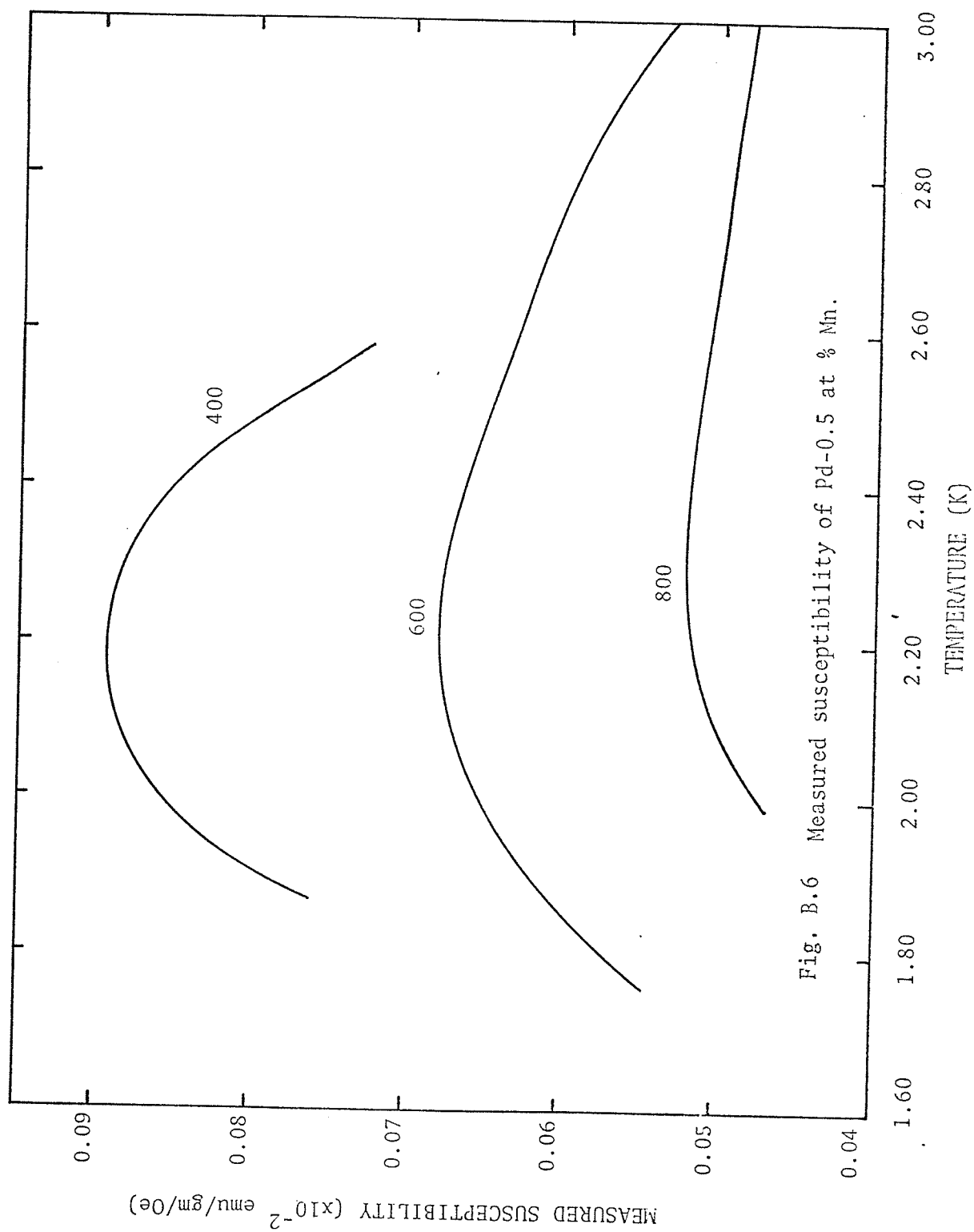


Fig. B.5 Measured susceptibility of Pd-0.5 at % Mn.



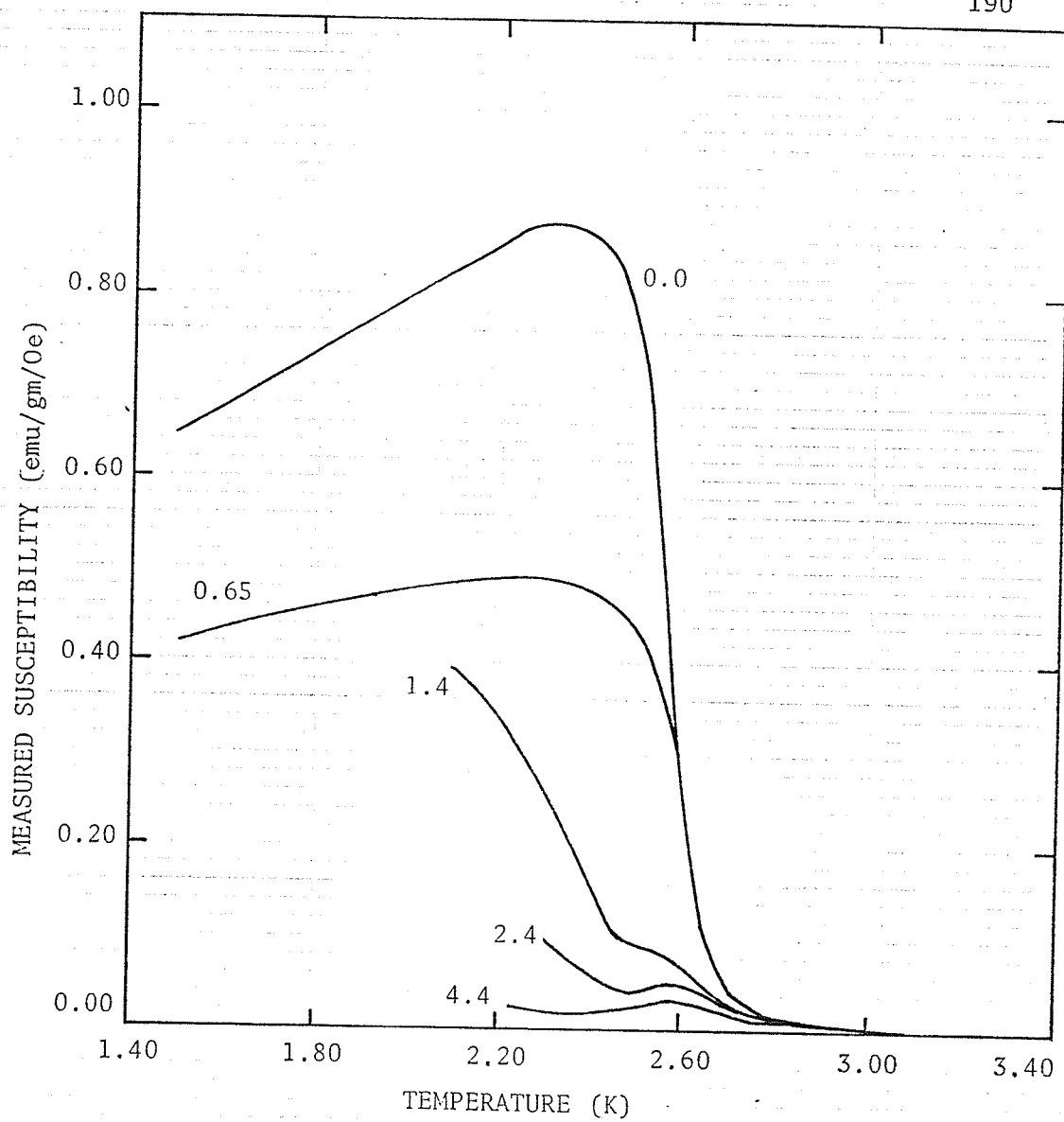
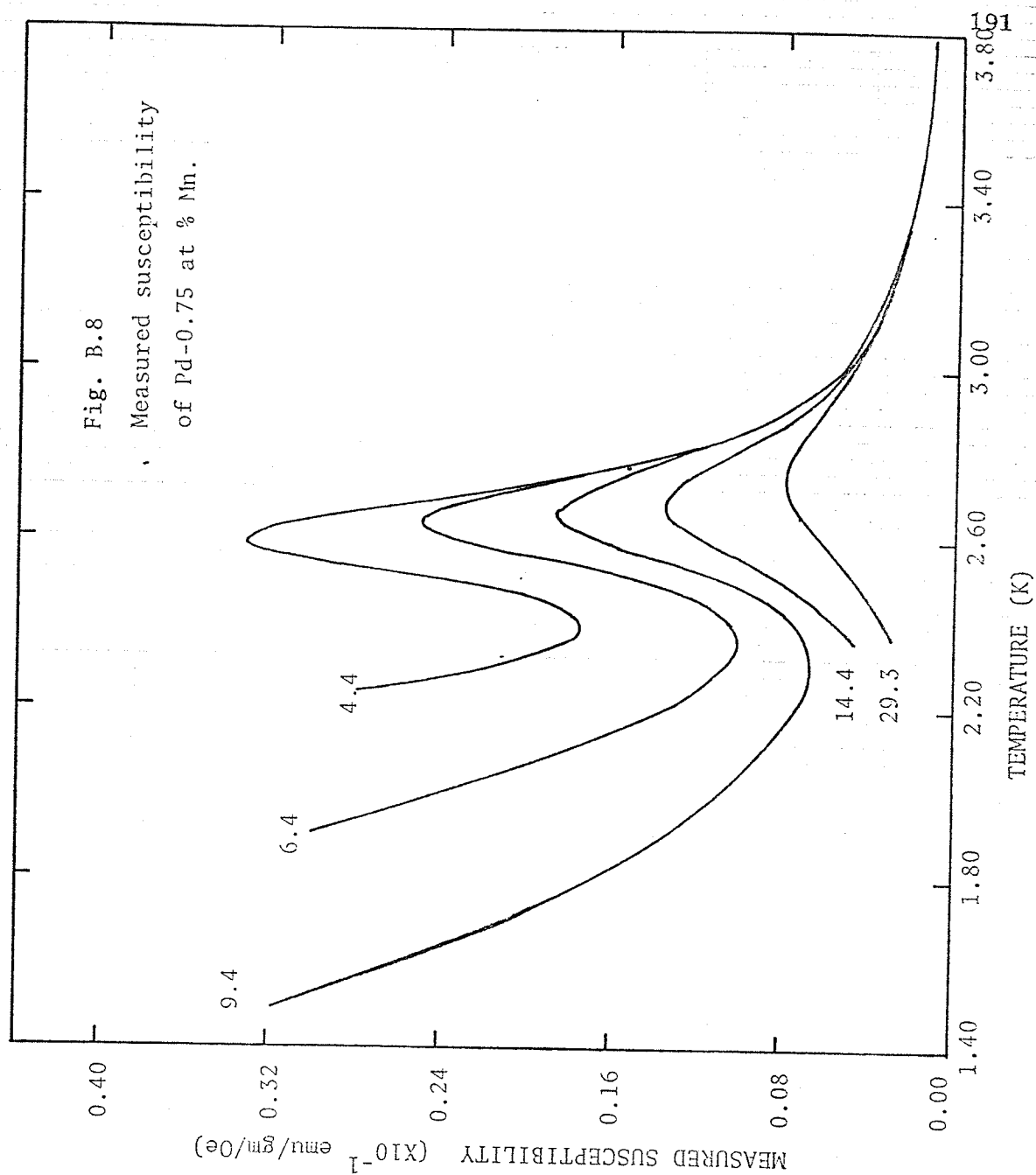


Fig. B.7-- Measured susceptibility of Pd-0.75 at % Mn.



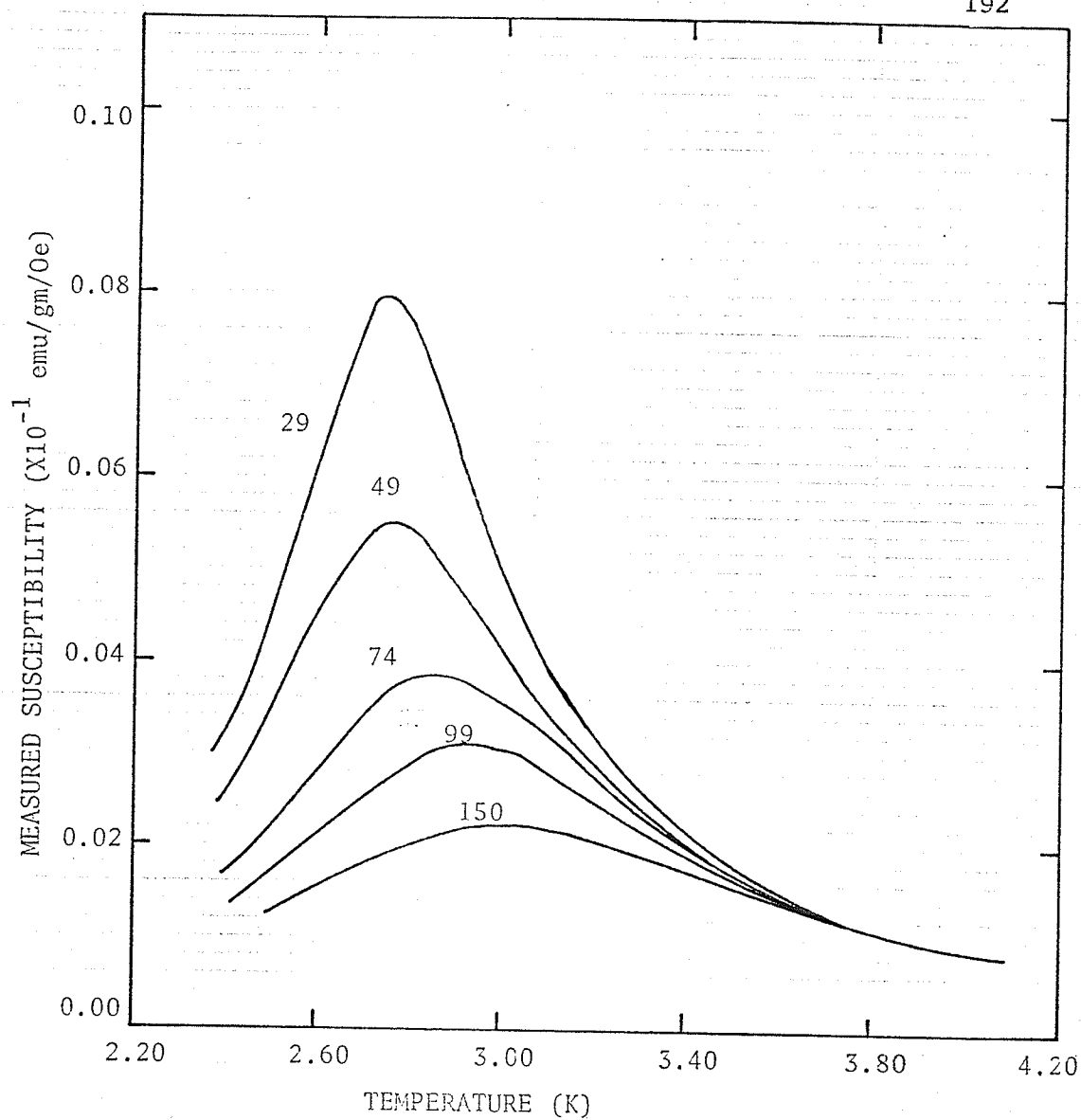


Fig. B.9 Measured susceptibility of Pd-0.75 at % Mn.

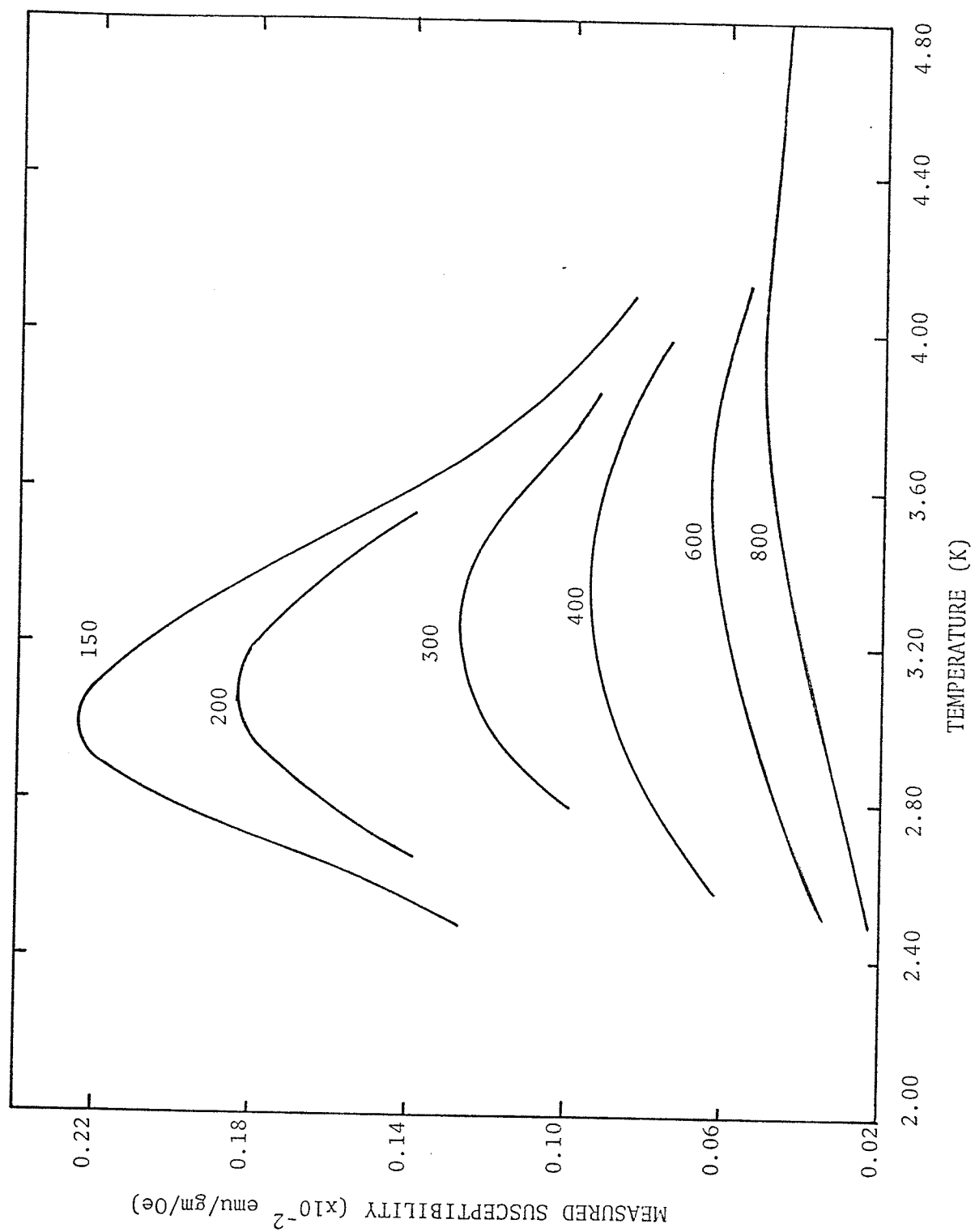


Fig. B.10 Measured susceptibility of Pd-0.75 at % Mn.

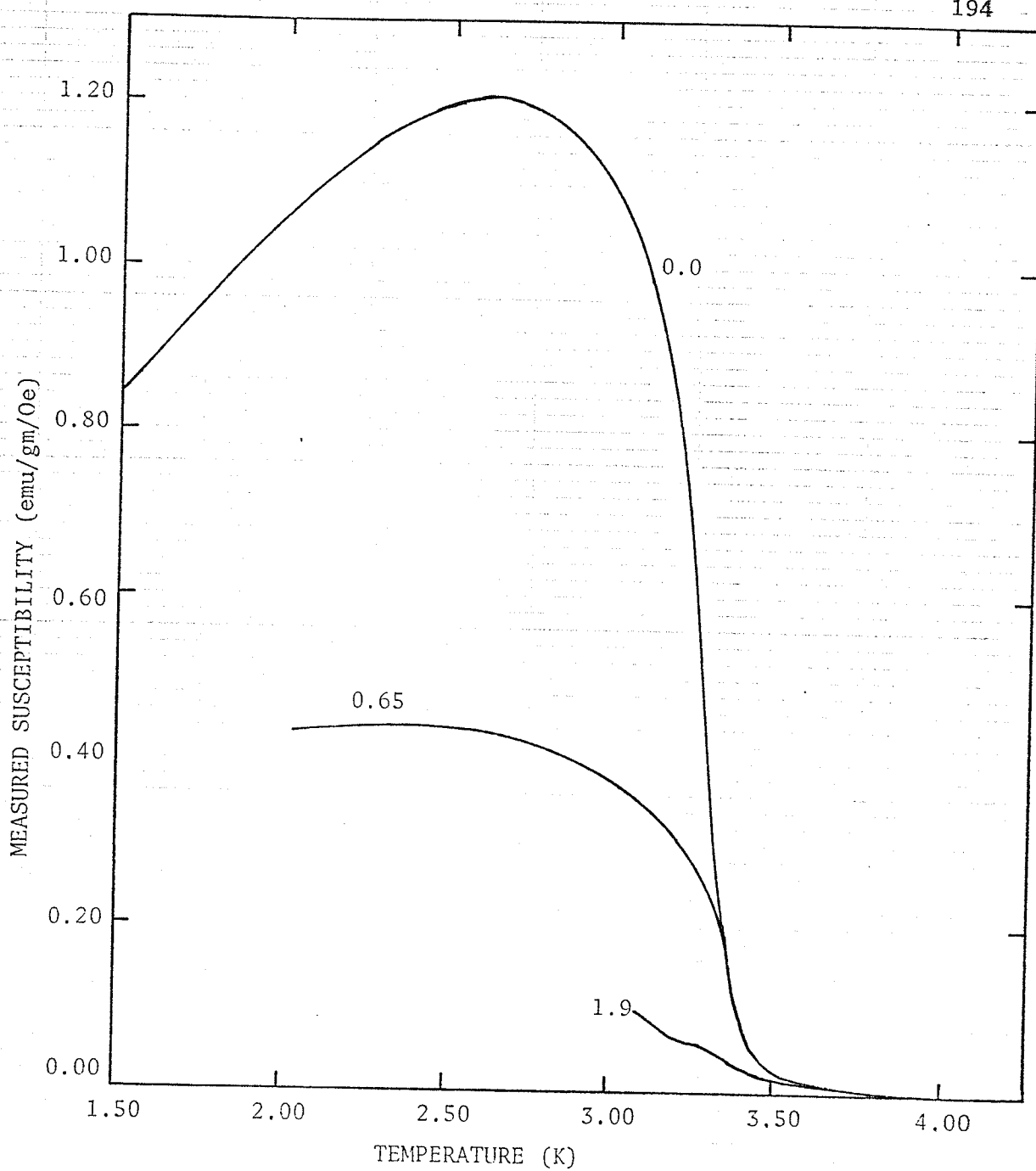


Fig. B.11 Measured susceptibility of Pd-1.0 at % Mn.

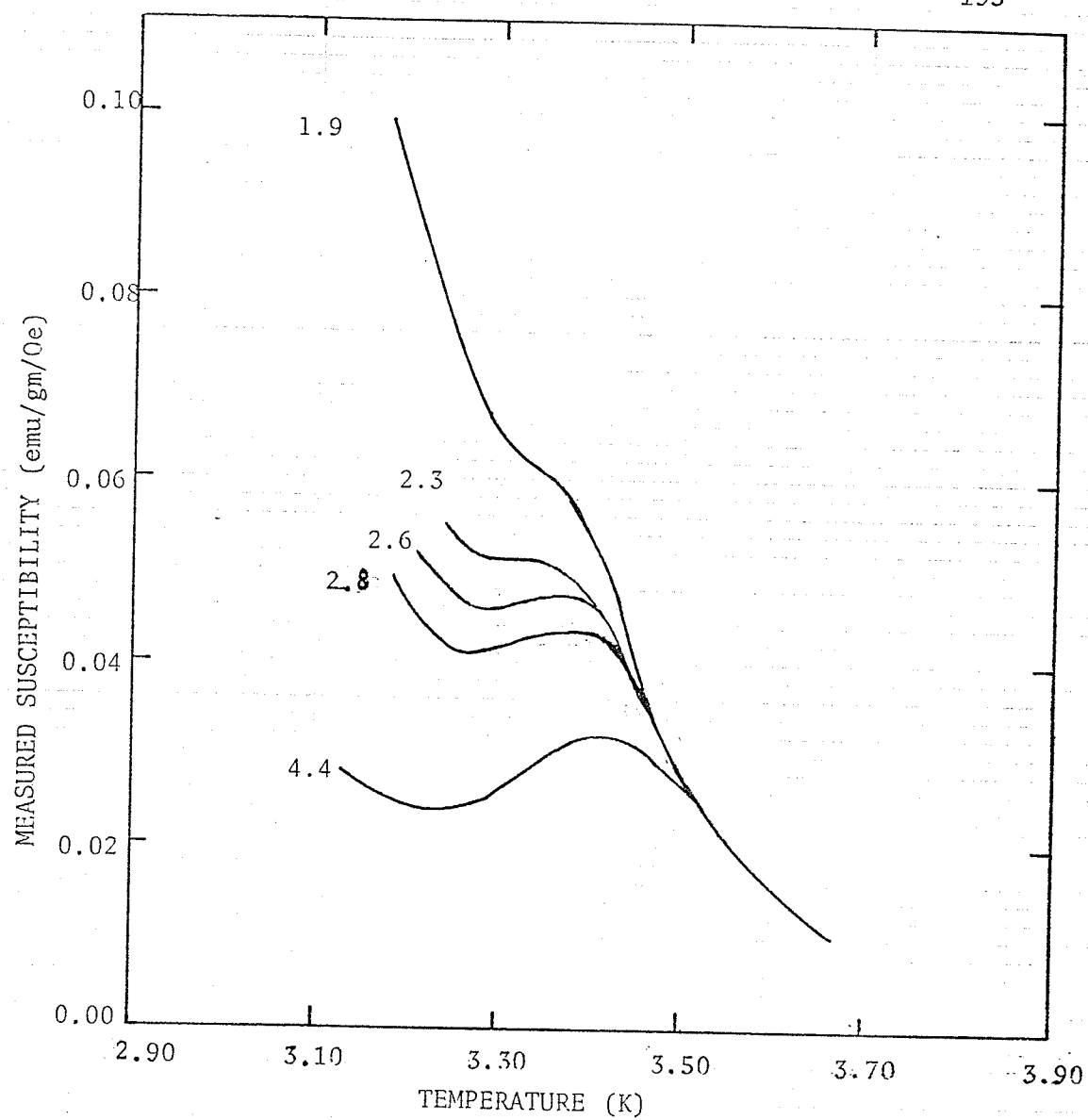


Fig. B.12 Measured susceptibility of Pd-1.0 at % Mn.

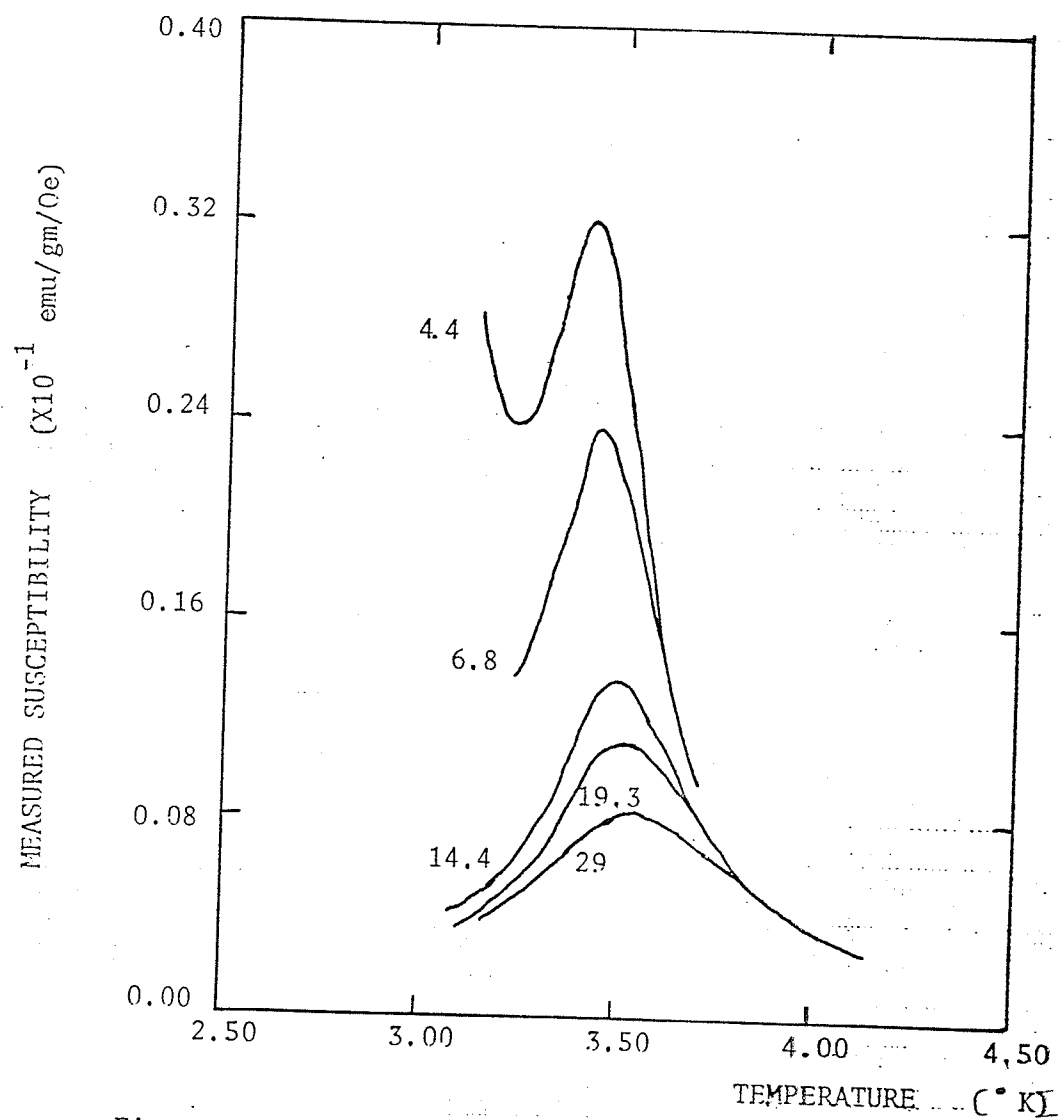


Fig. B.13 Measured susceptibility of Pd-1.0 at % Mn.

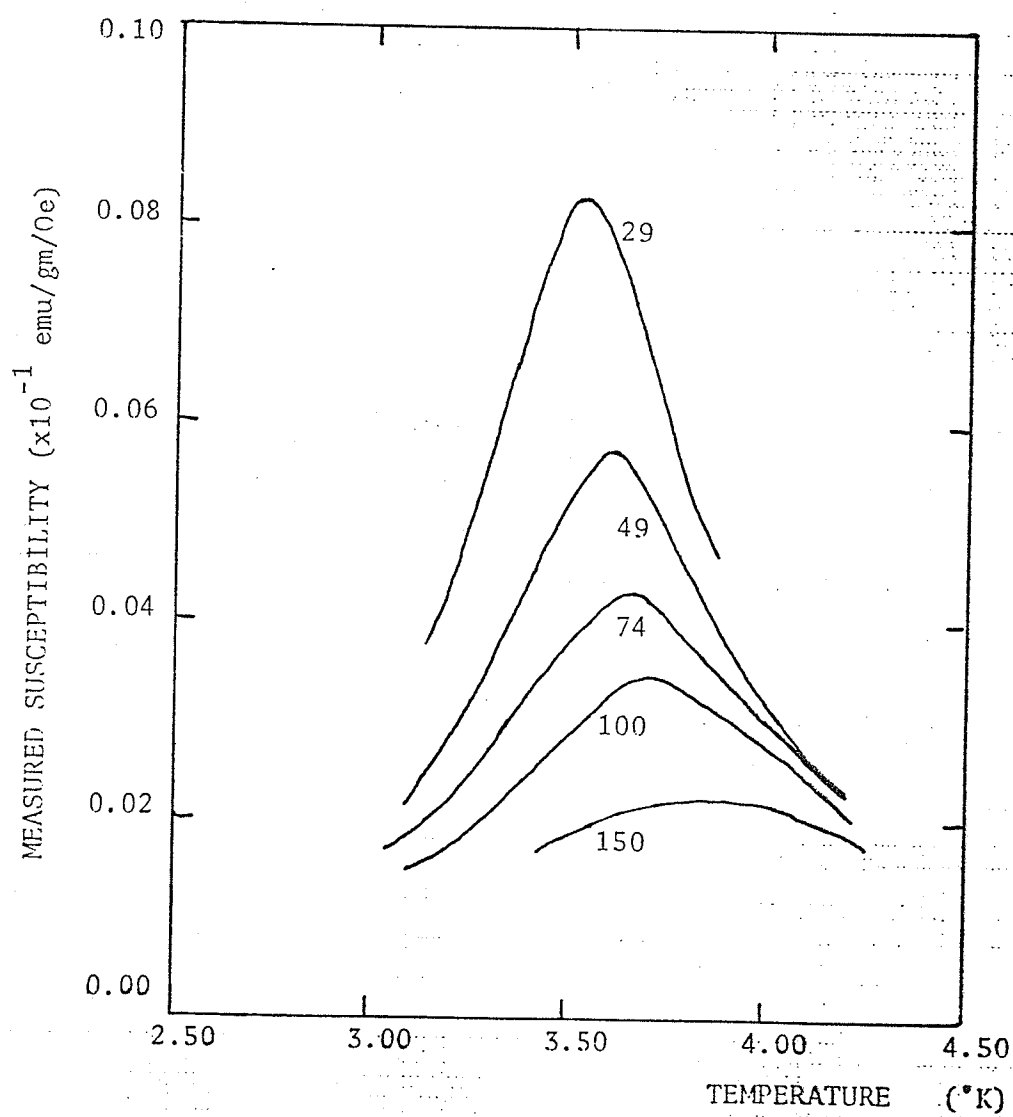


Fig. B.14 Measured susceptibility of Pd-1.0 at % Mn.

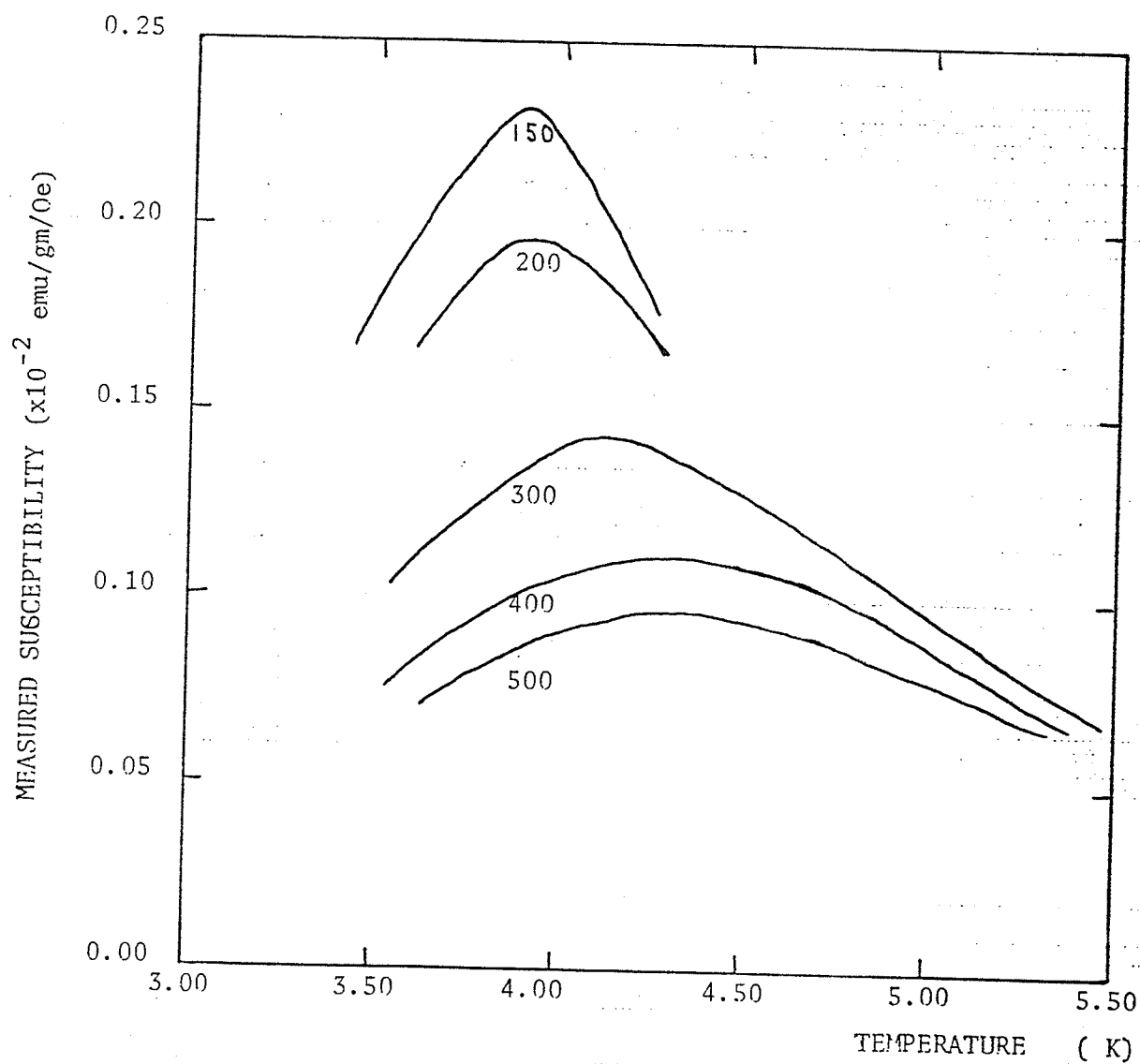


Fig. B.15 Measured susceptibility of Pd-1.0 at % Mn.

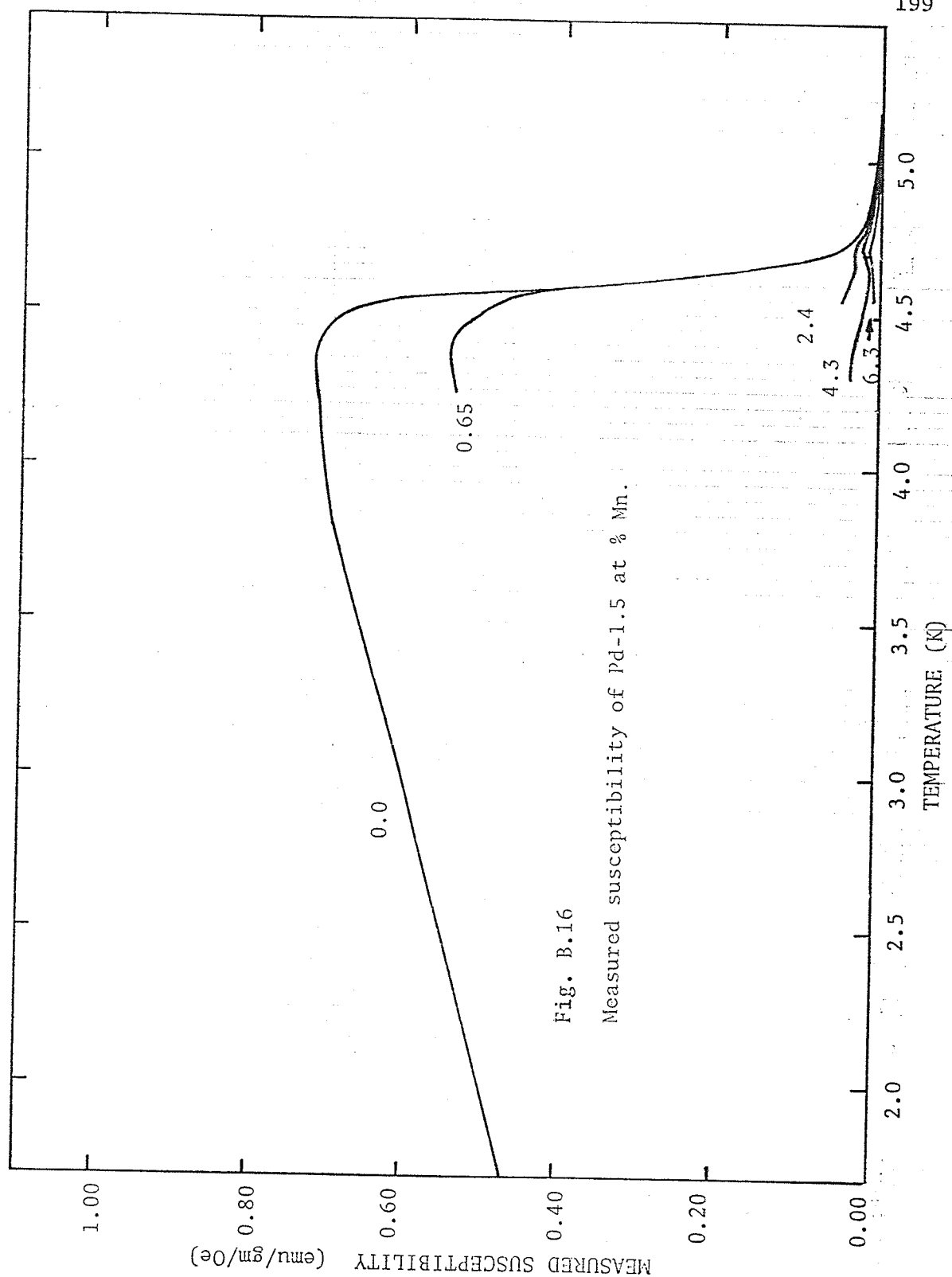


Fig. B.16
Measured susceptibility of Pd-1.5 at % Mn.

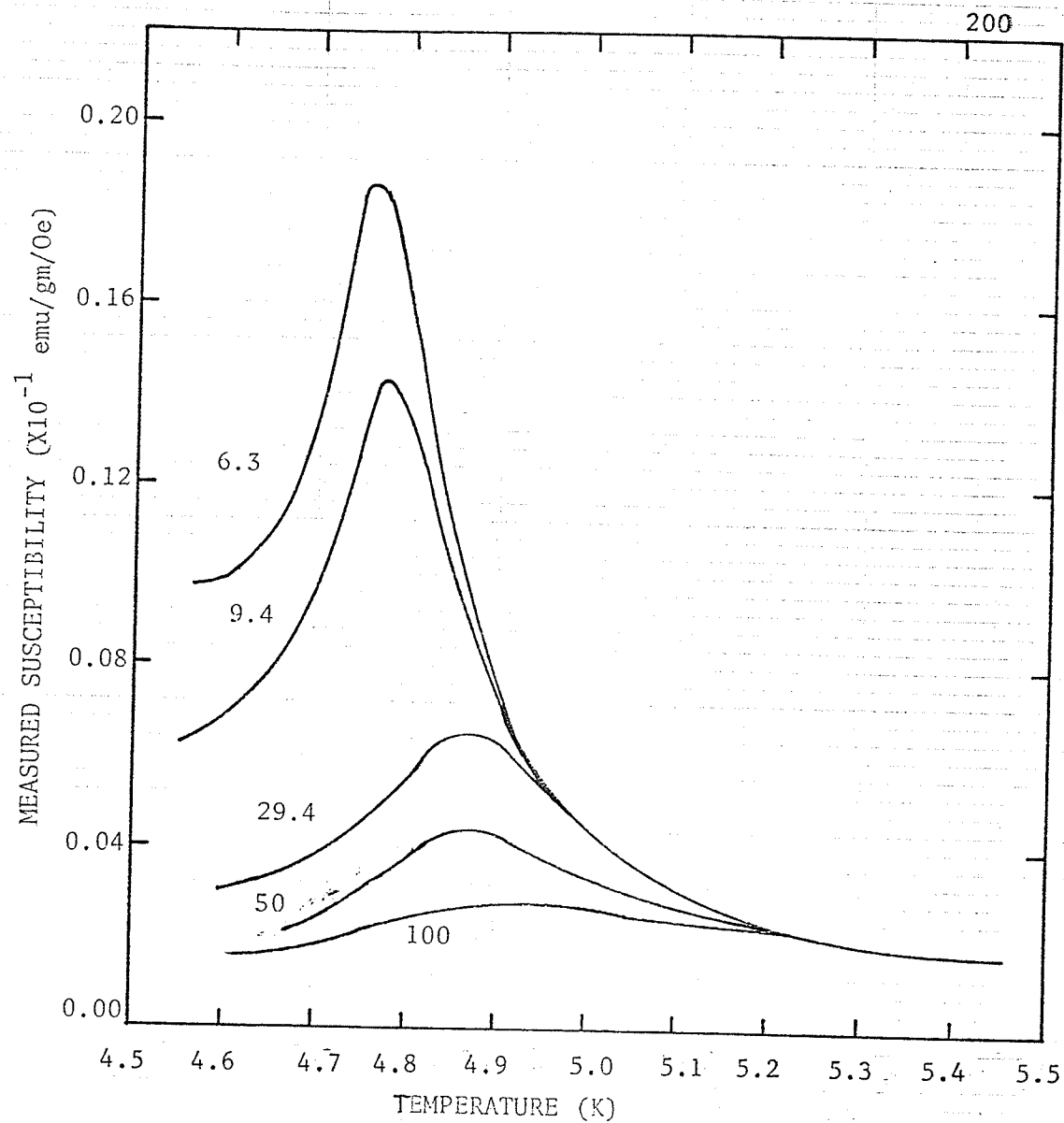


Fig. B.17 Measured susceptibility of Pd-1.5 at % Mn.

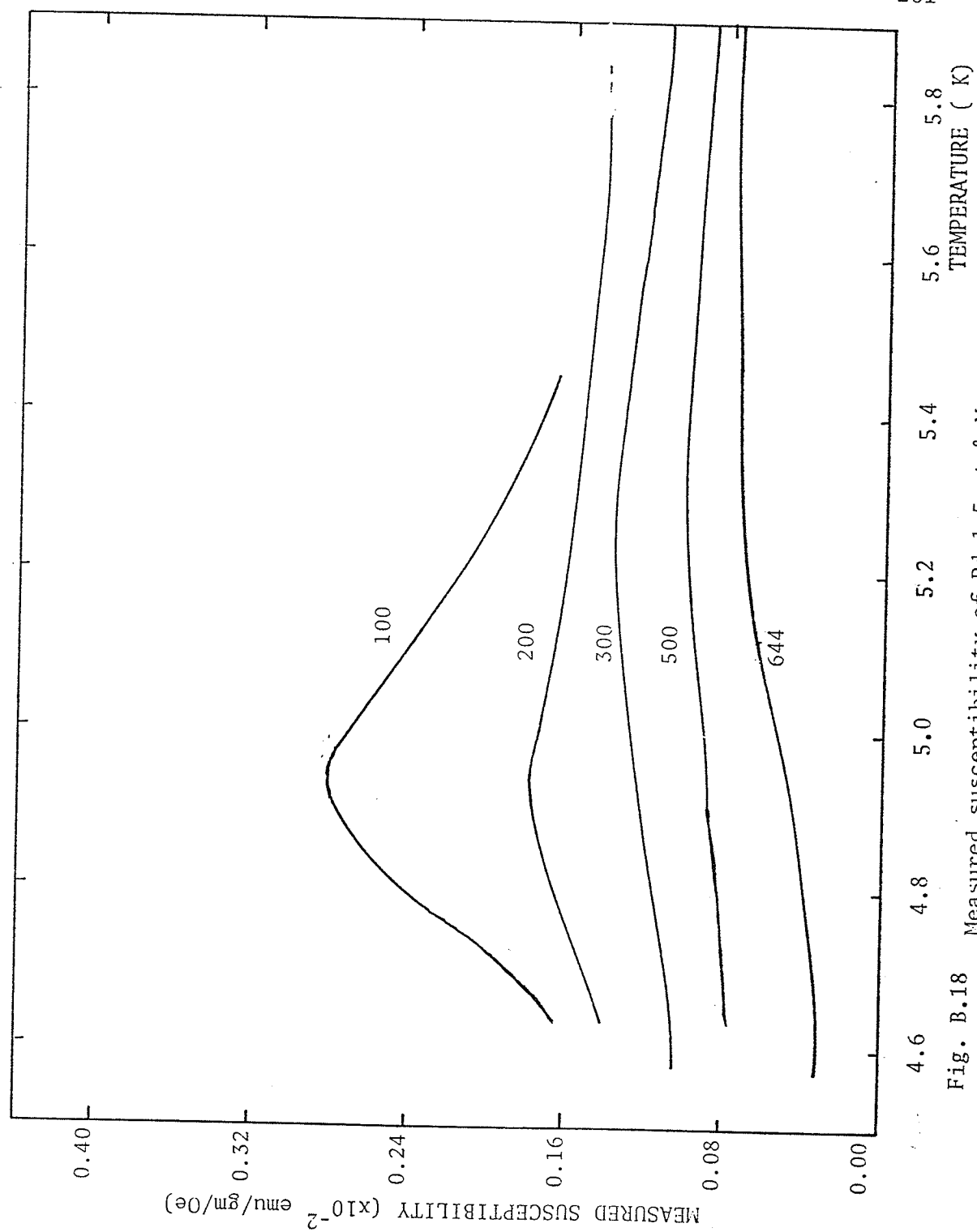


Fig. B.18 Measured susceptibility of Pd-1.5 at % Mn.

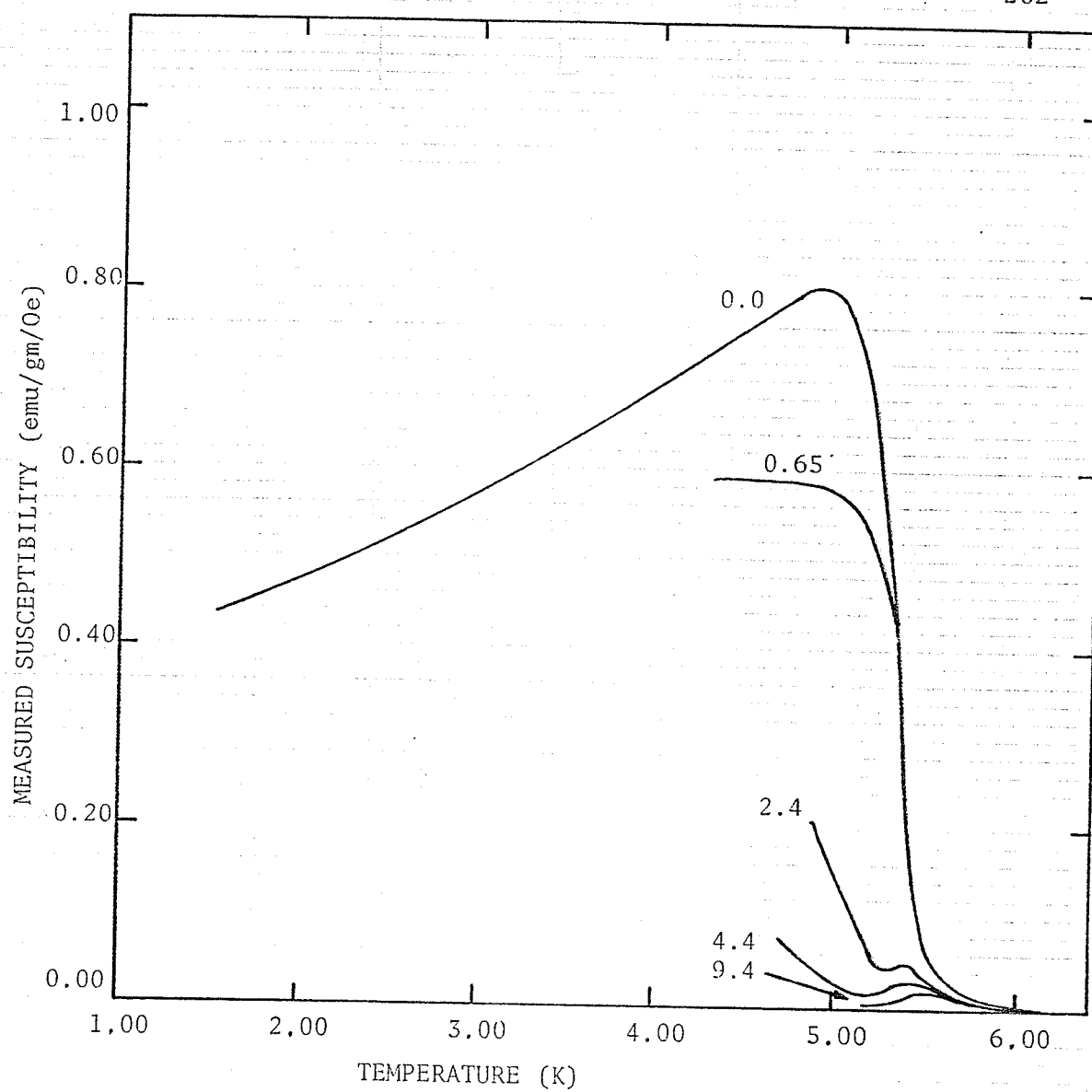


Fig. B.19 Measured susceptibility of Pd-2.0 at % Mn.

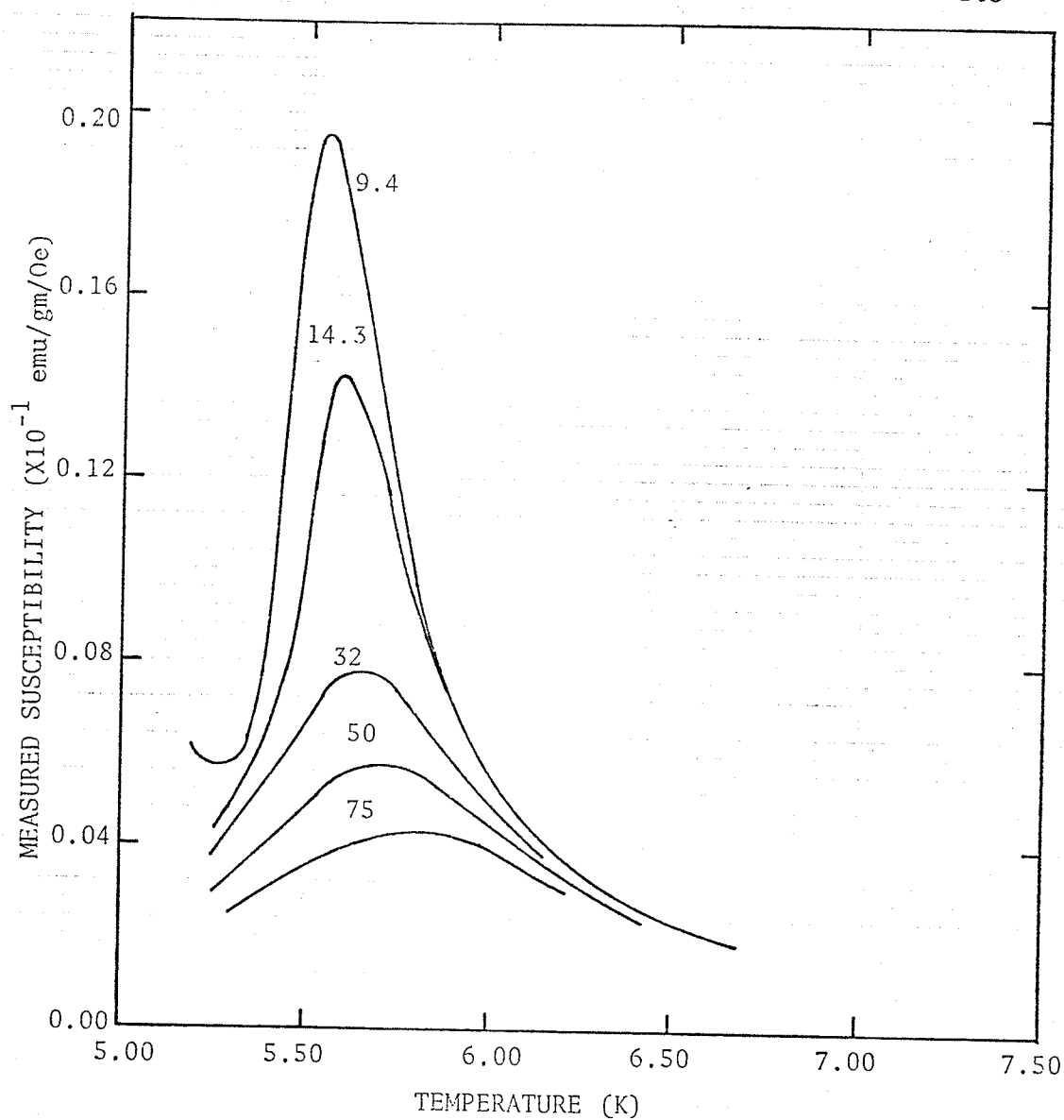


Fig. B.20 Measured susceptibility of Pd-2.0 at % Mn.

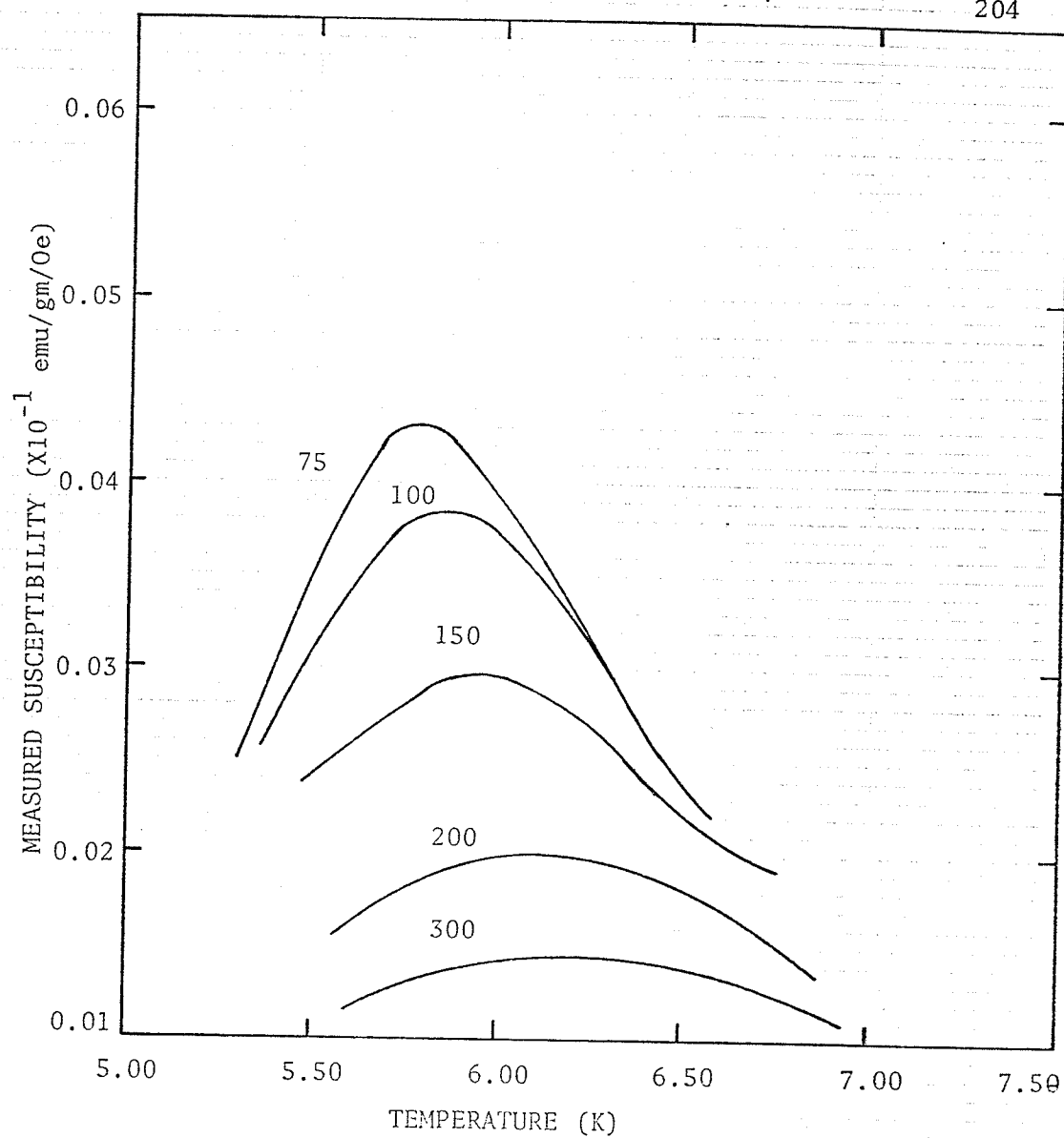


Fig. B.21 Measured susceptibility of Pd-2.0 at % Mn.

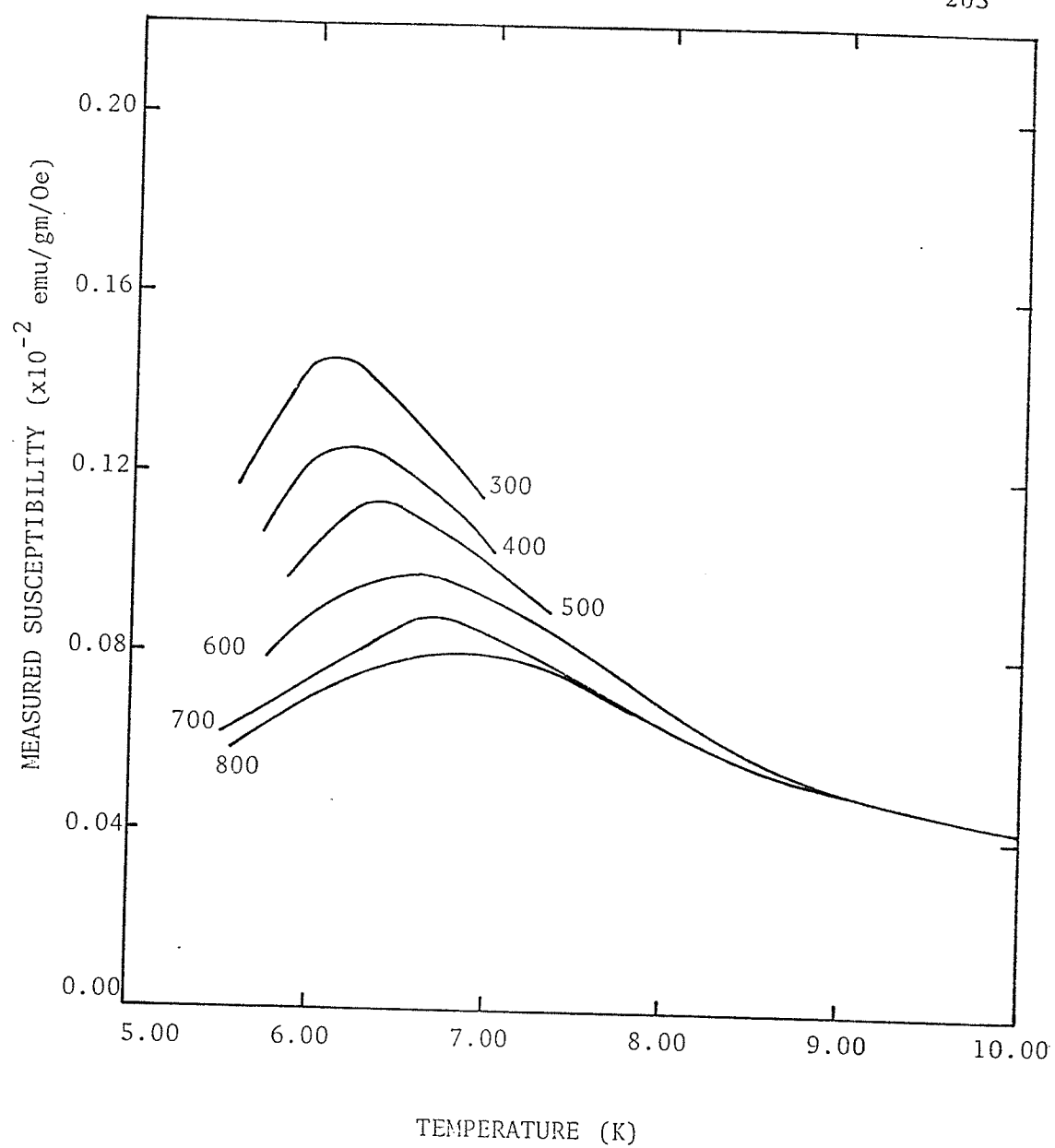


Fig. B.22 Measured susceptibility of Pd-2.0 at % Mn.

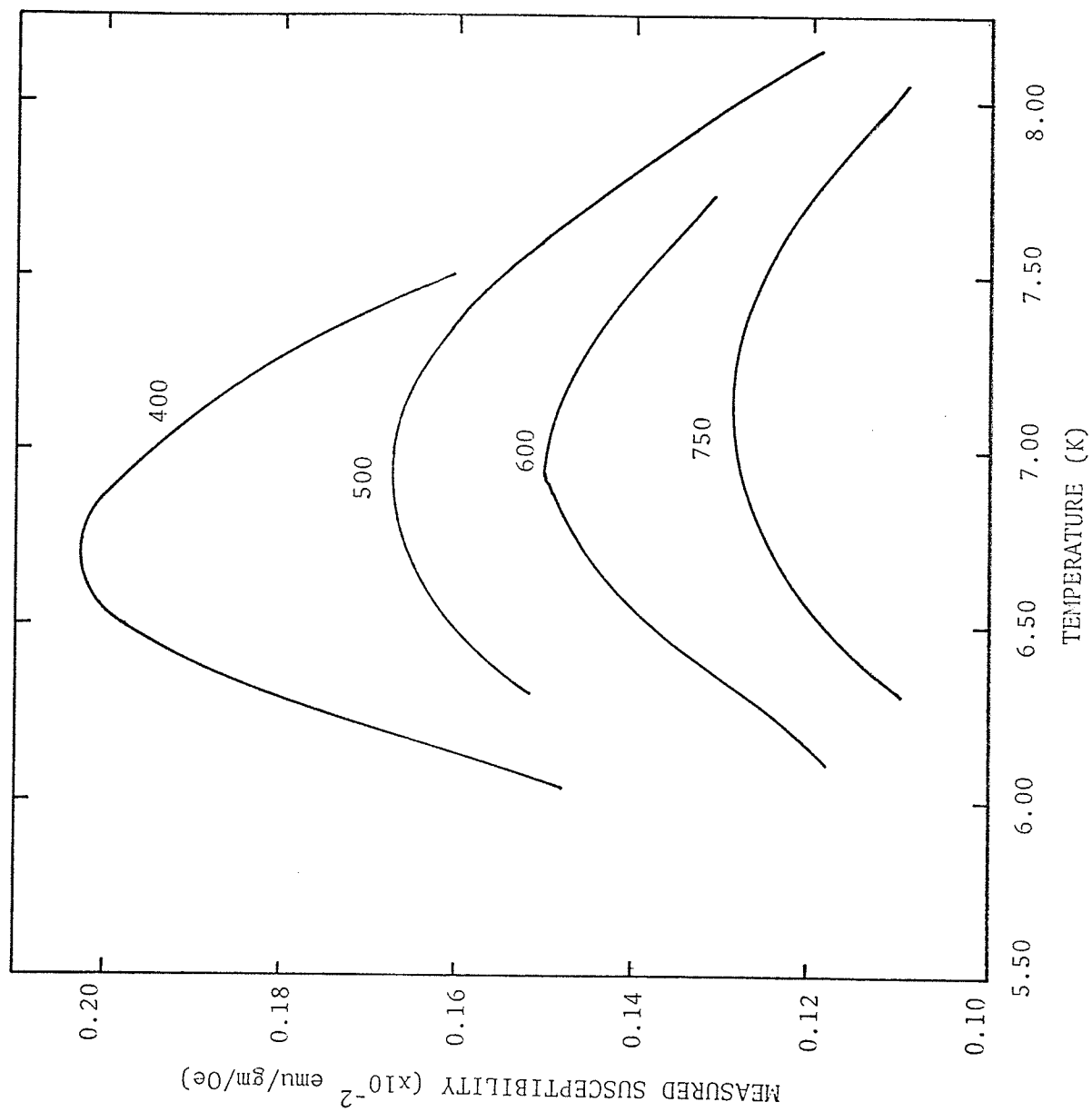
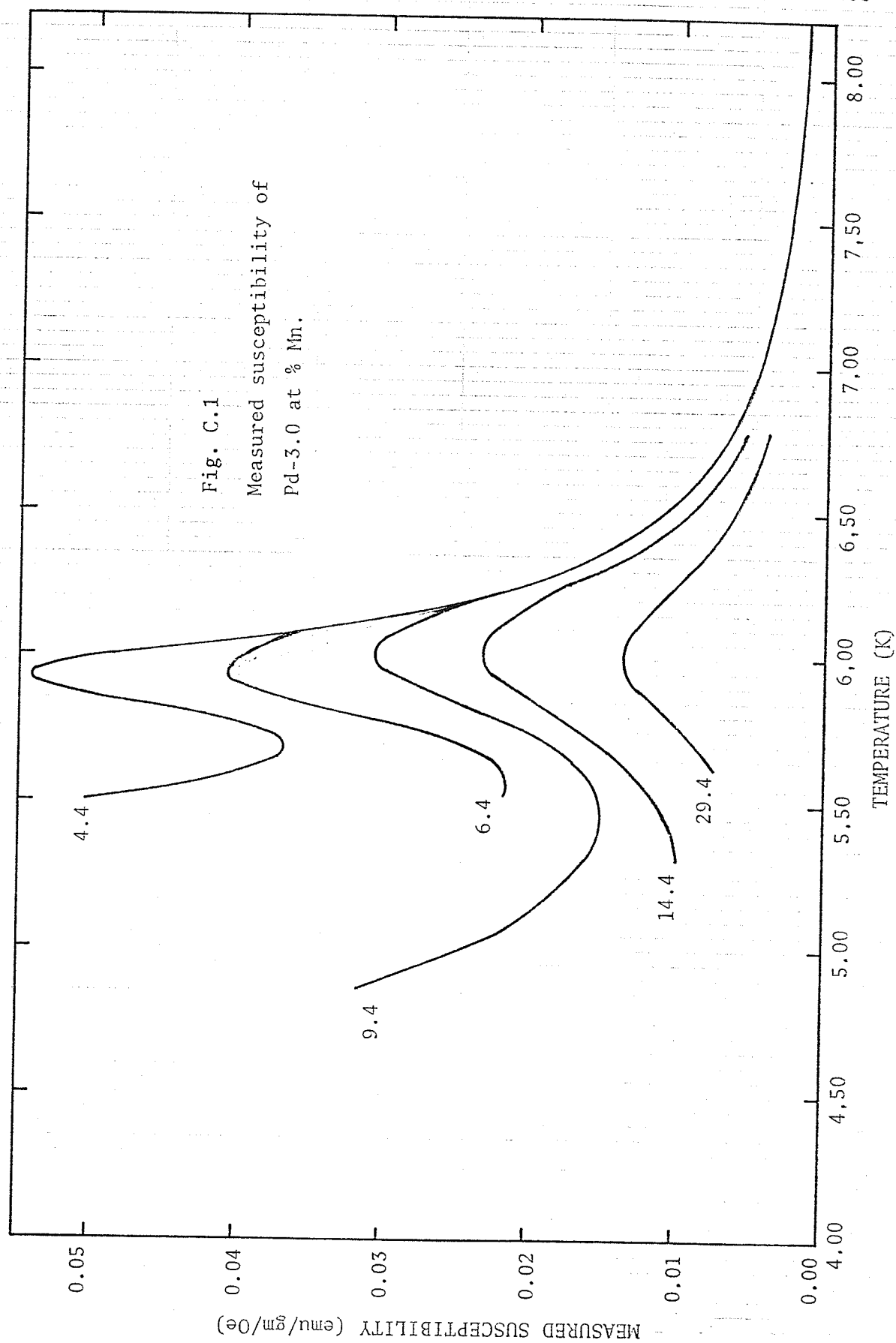
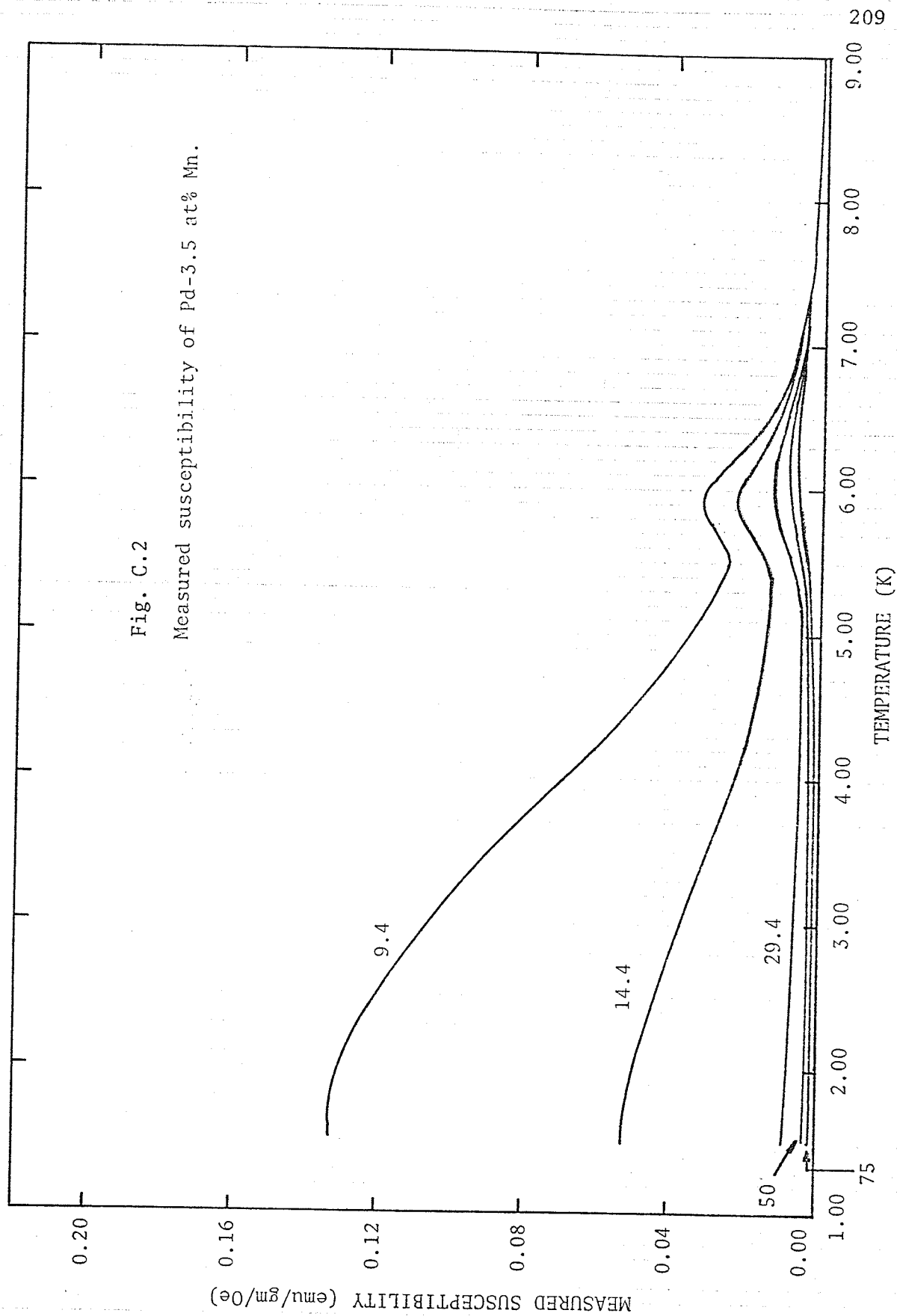


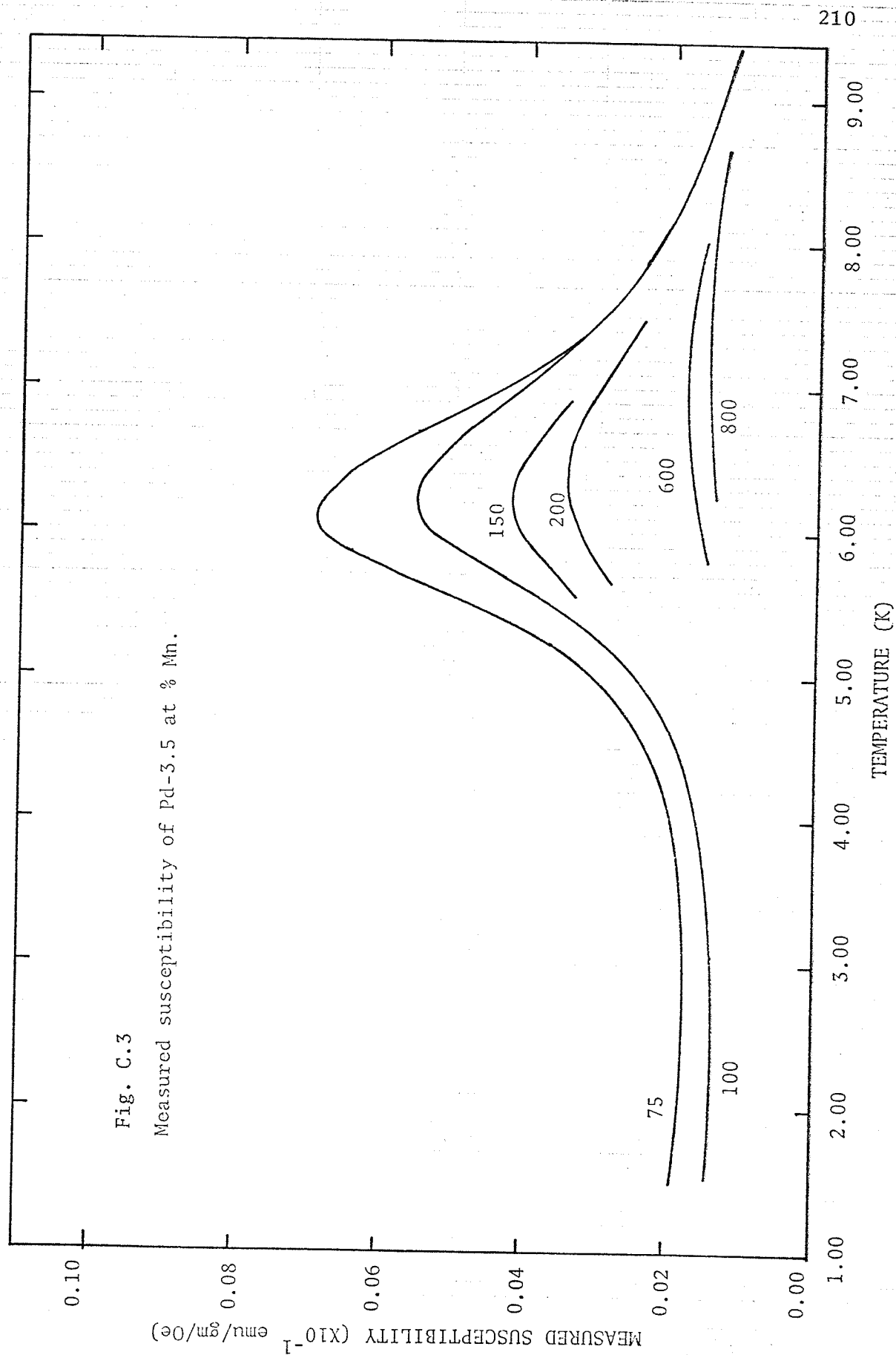
Fig. B.23 Measured susceptibility of Pd-2.5 at % Mn.

APPENDIX C

MEASURED SUSCEPTIBILITY DATA FOR
ALLOYS WITH $3.0 \text{ at } \% \leq \text{Mn} \leq 4.5 \text{ at } \%$







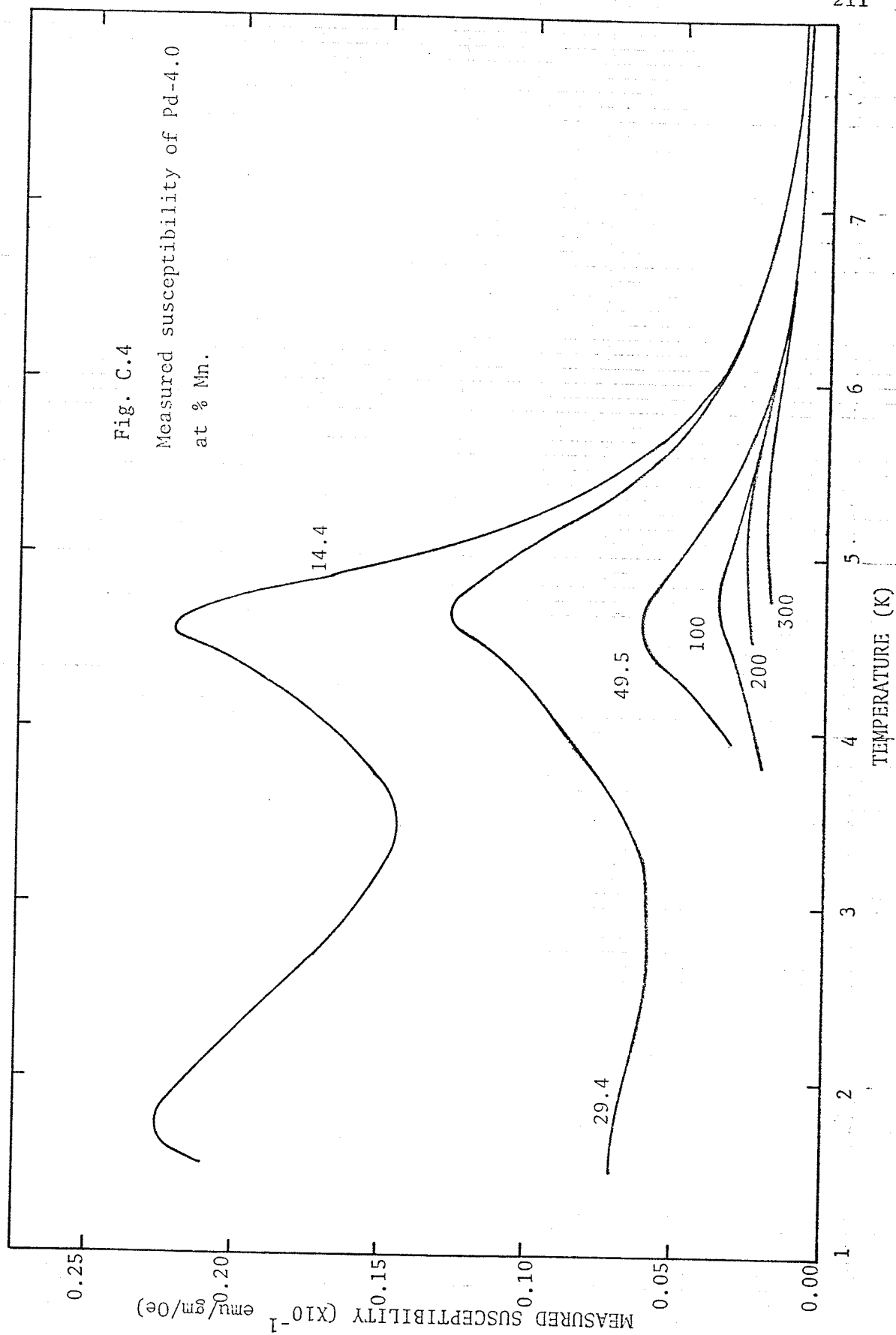
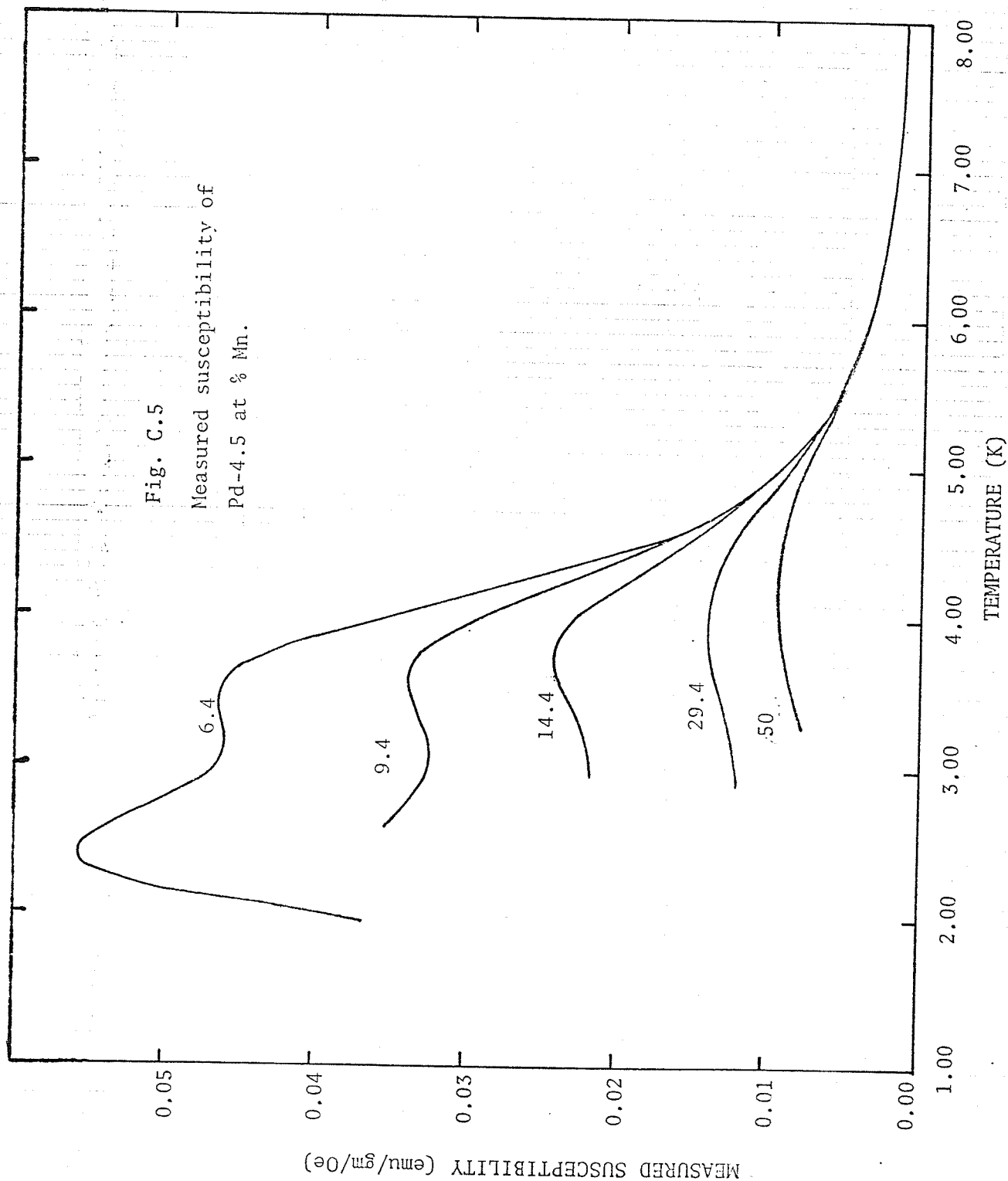
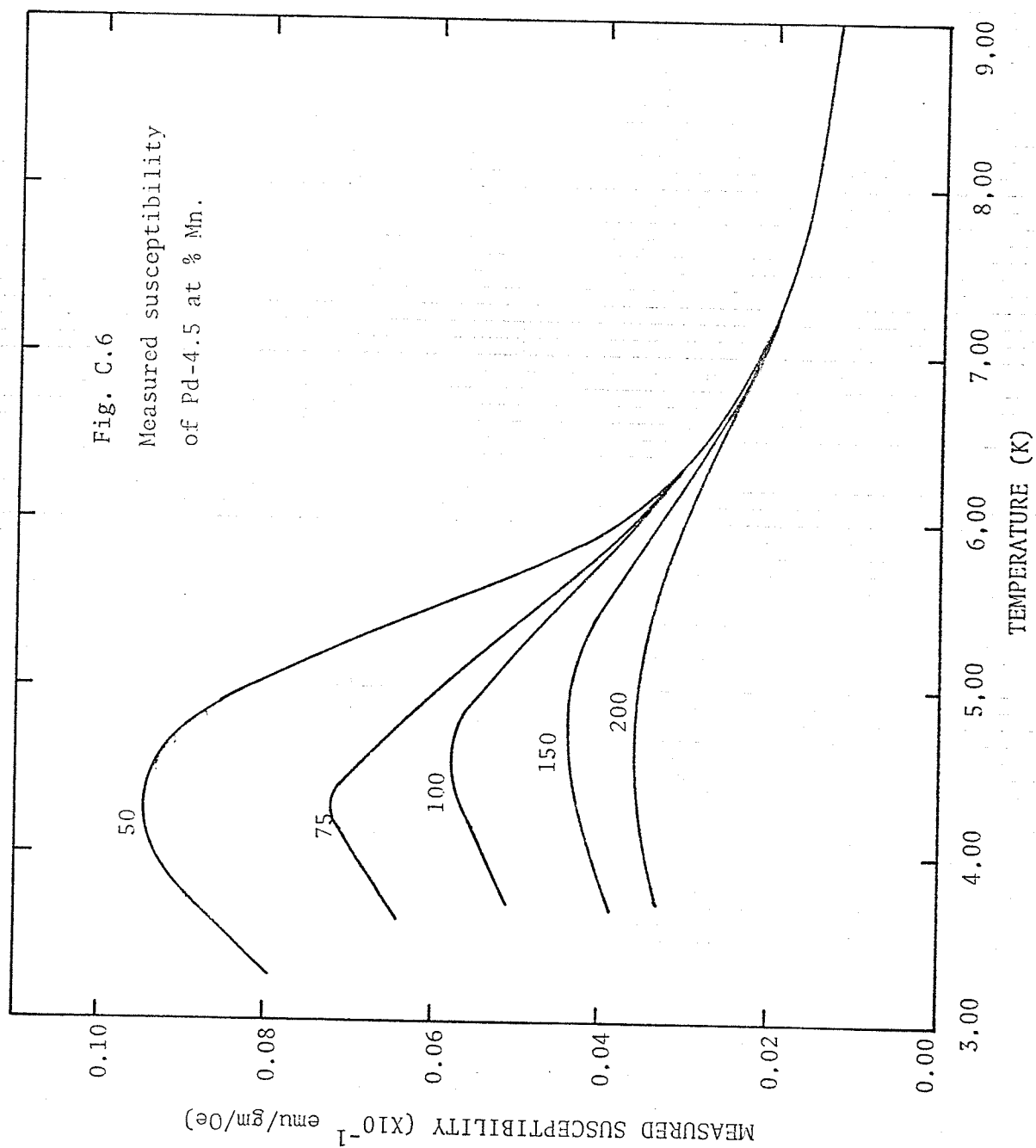
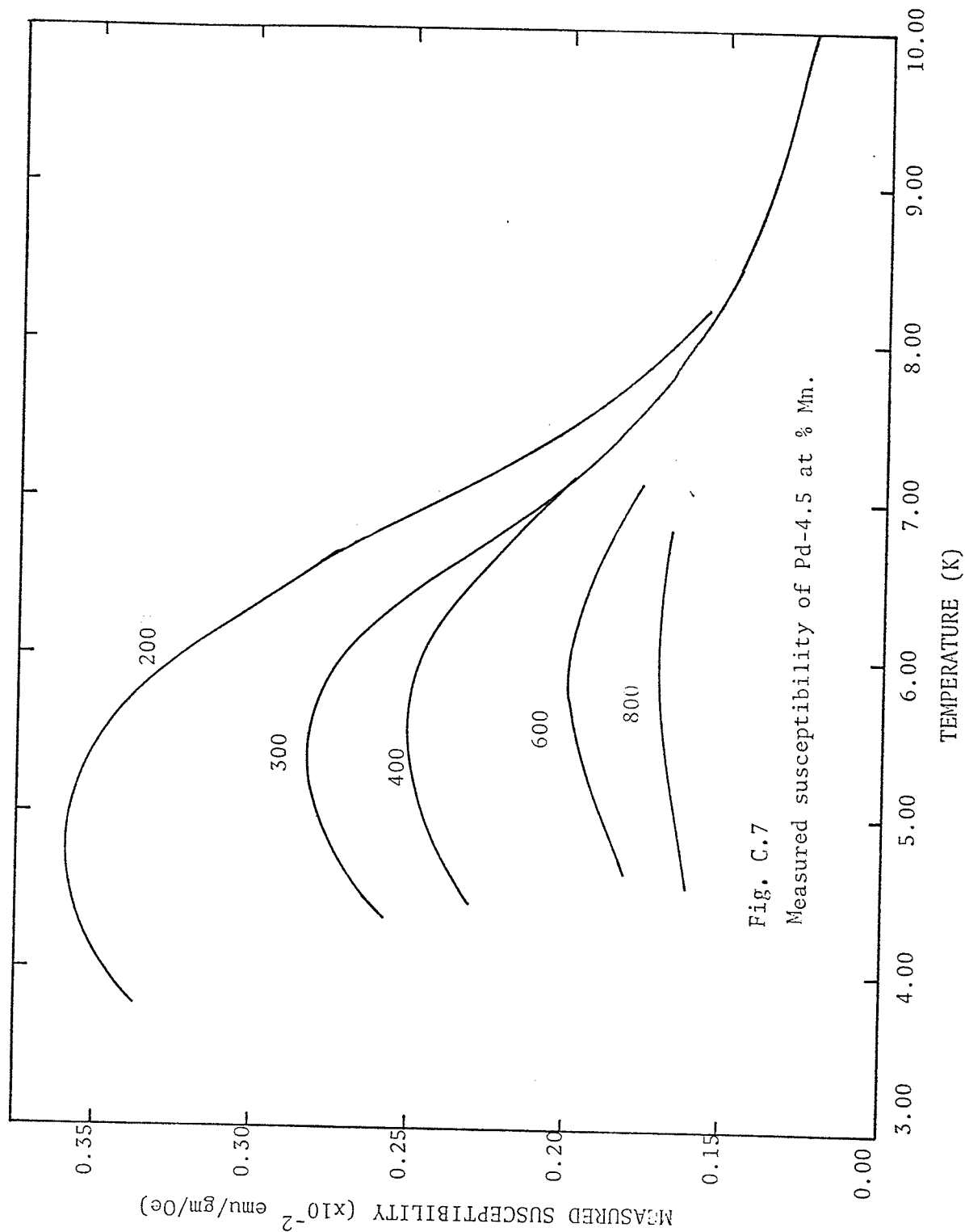
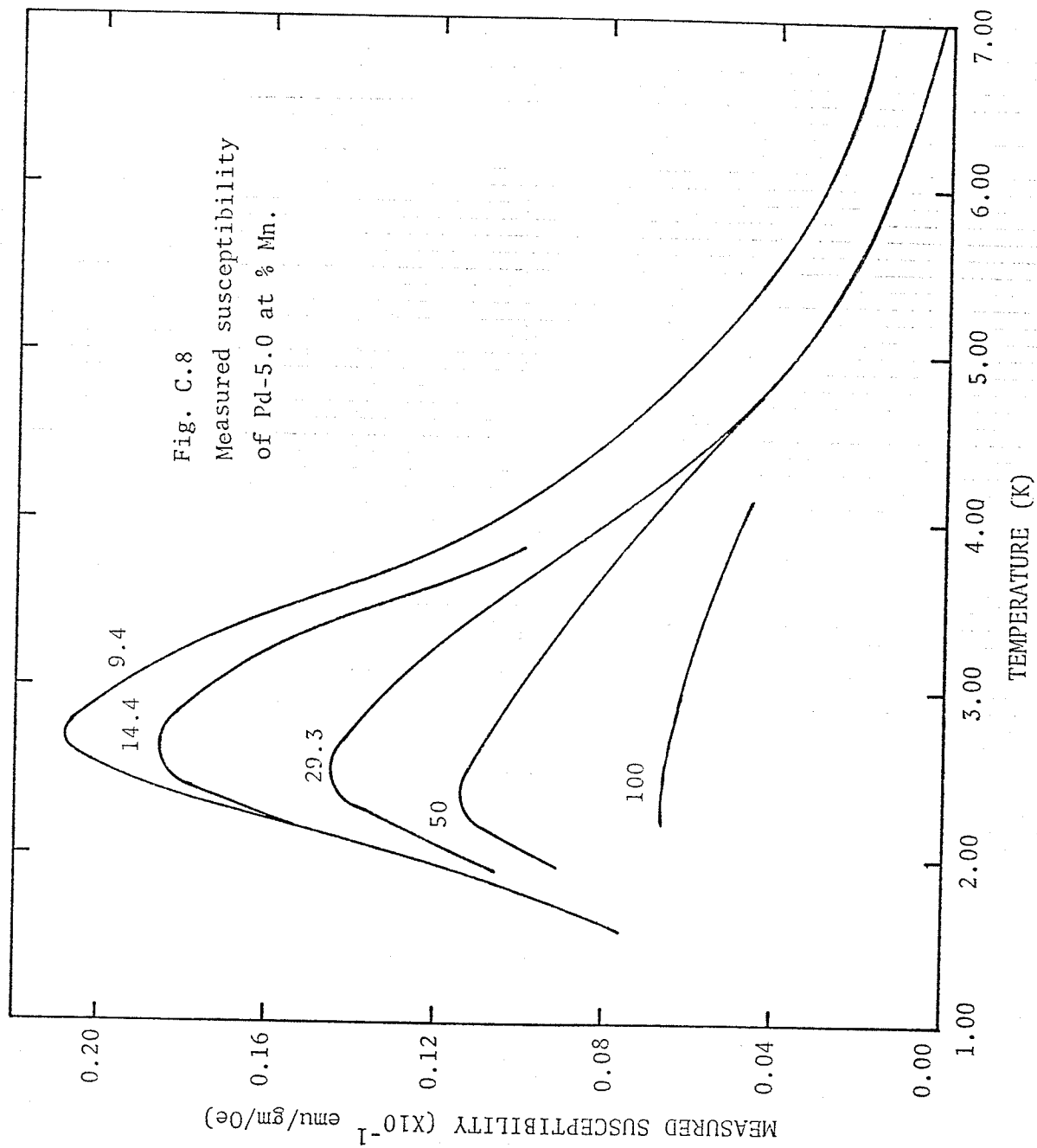


Fig. C.5
Measured susceptibility of
Pd-4.5 at % Mn.









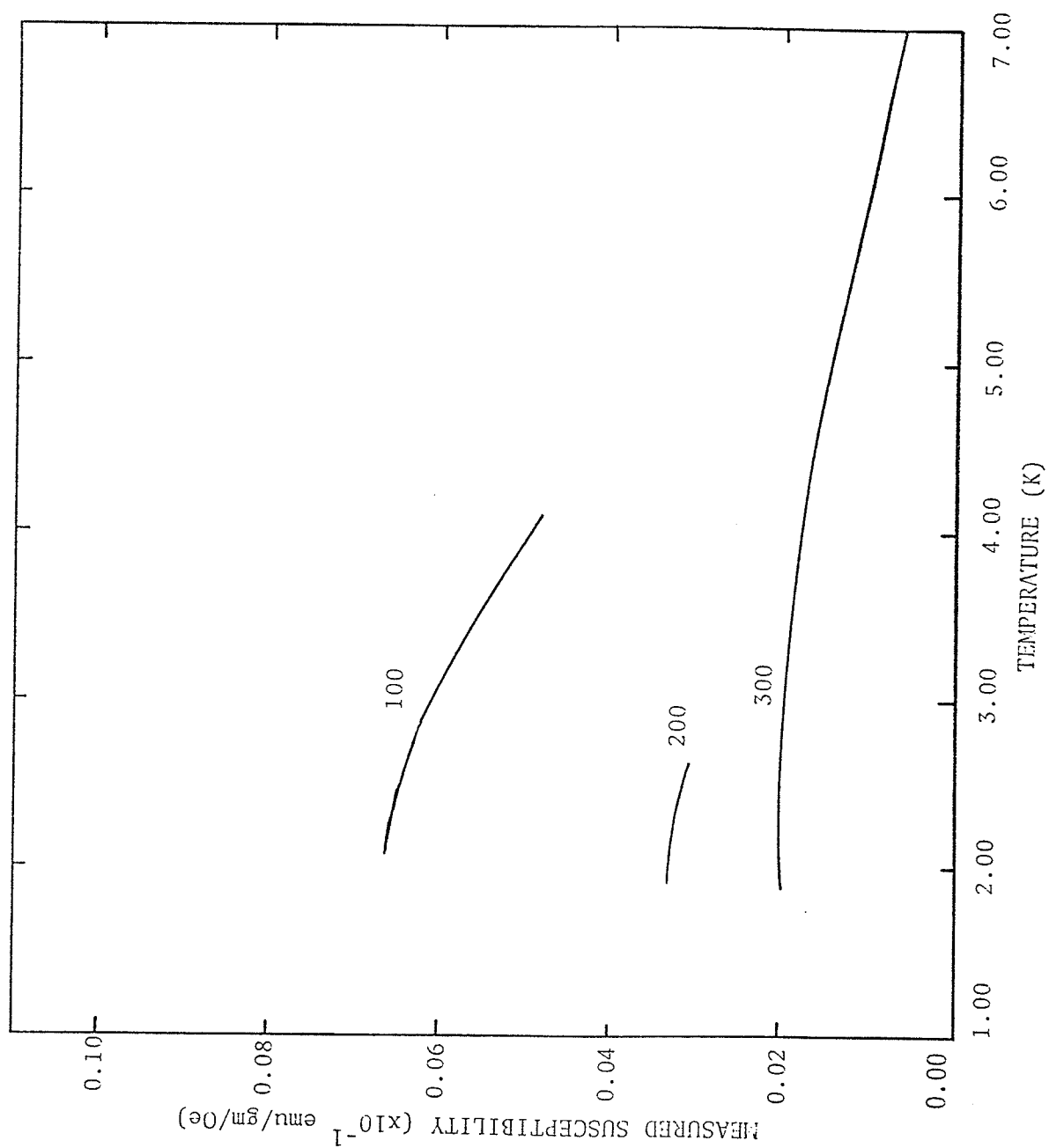
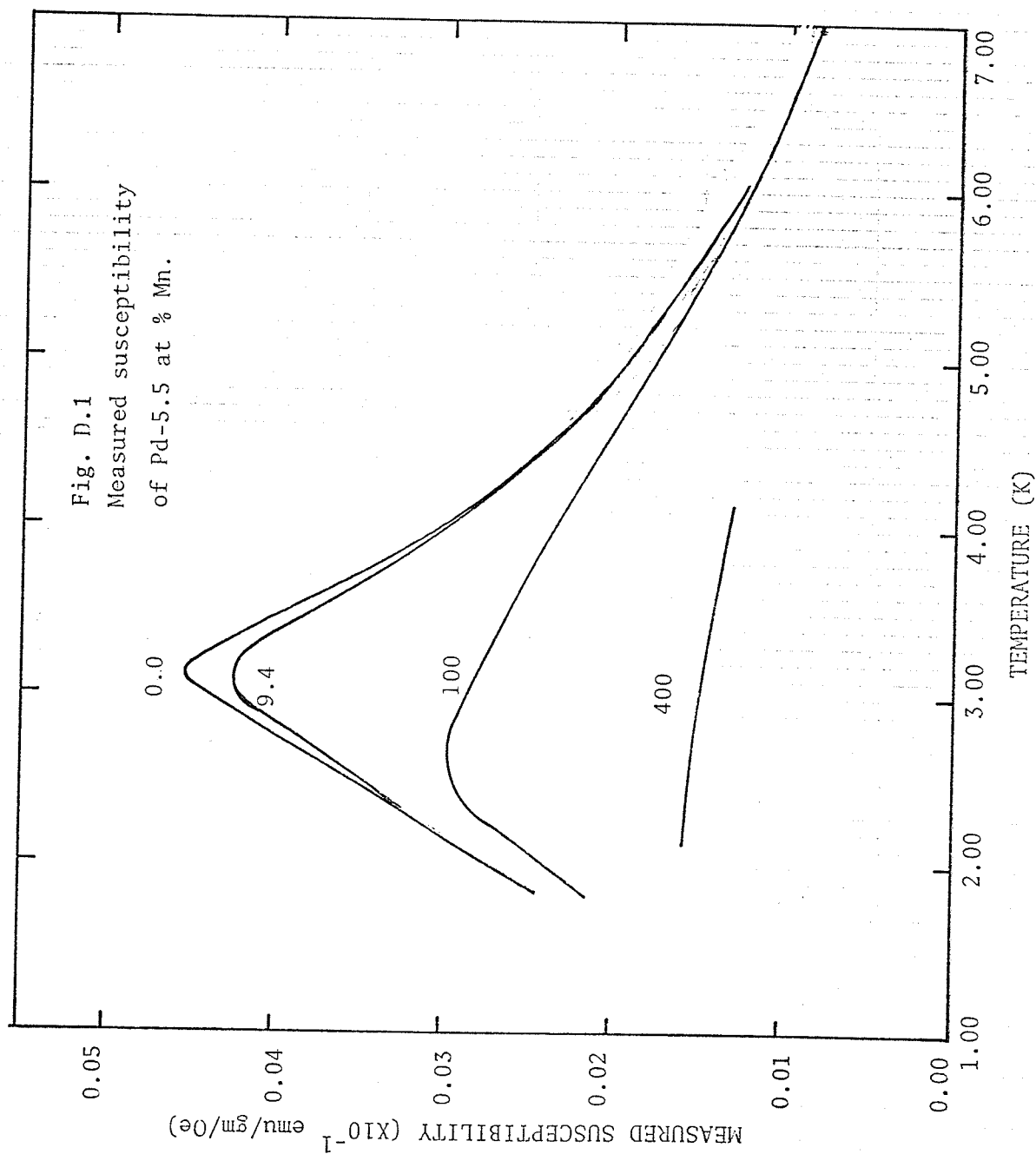


Fig. C.9 Measured susceptibility of Pd-5.0 at % Mn.

APPENDIX D

MEASURED SUSCEPTIBILITY DATA FOR ALLOYS

WITH Mn $\geq$ 5.0 at %



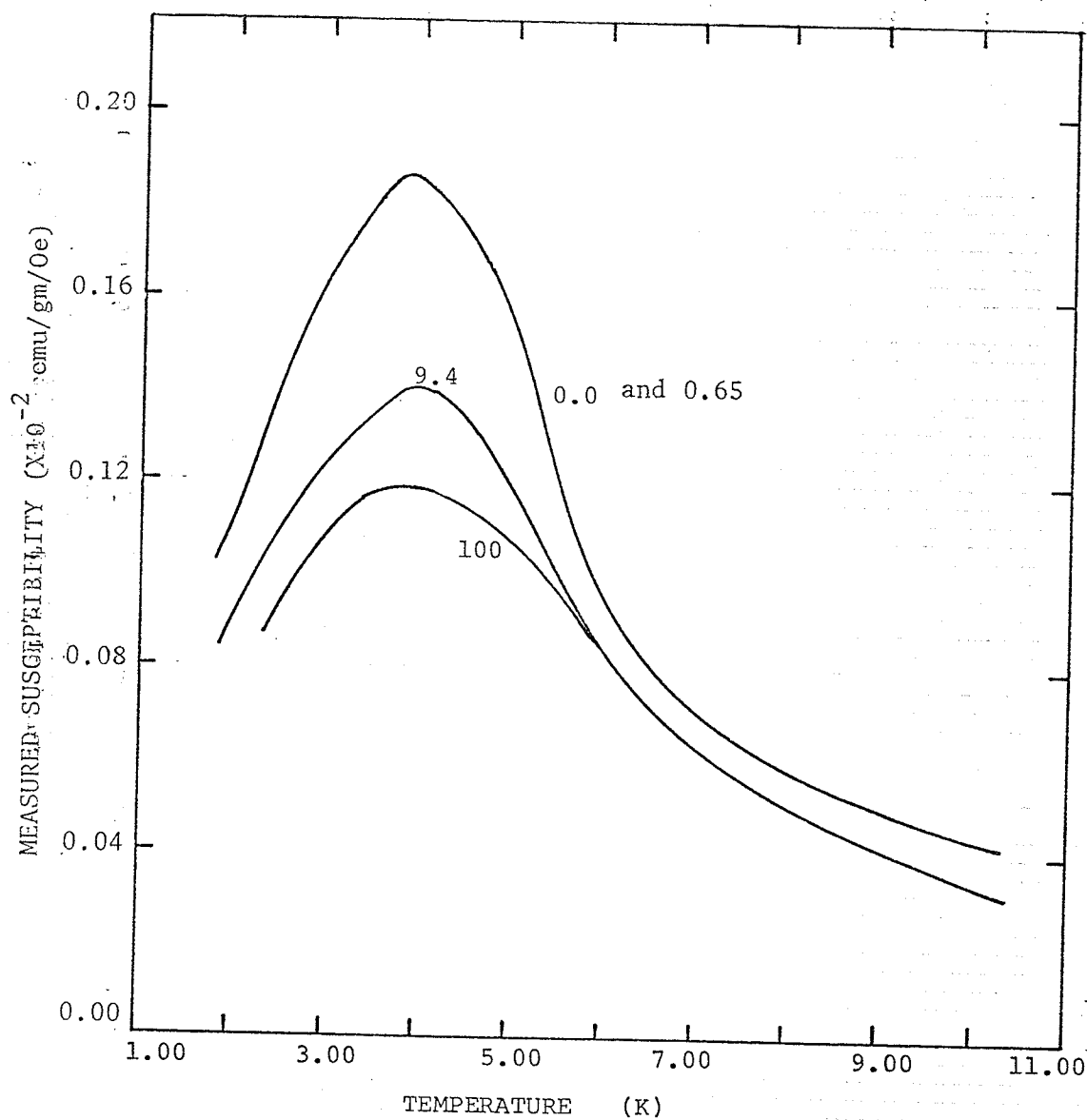


Fig. D,2 Measured susceptibility of Pd-6.5 at % Mn.

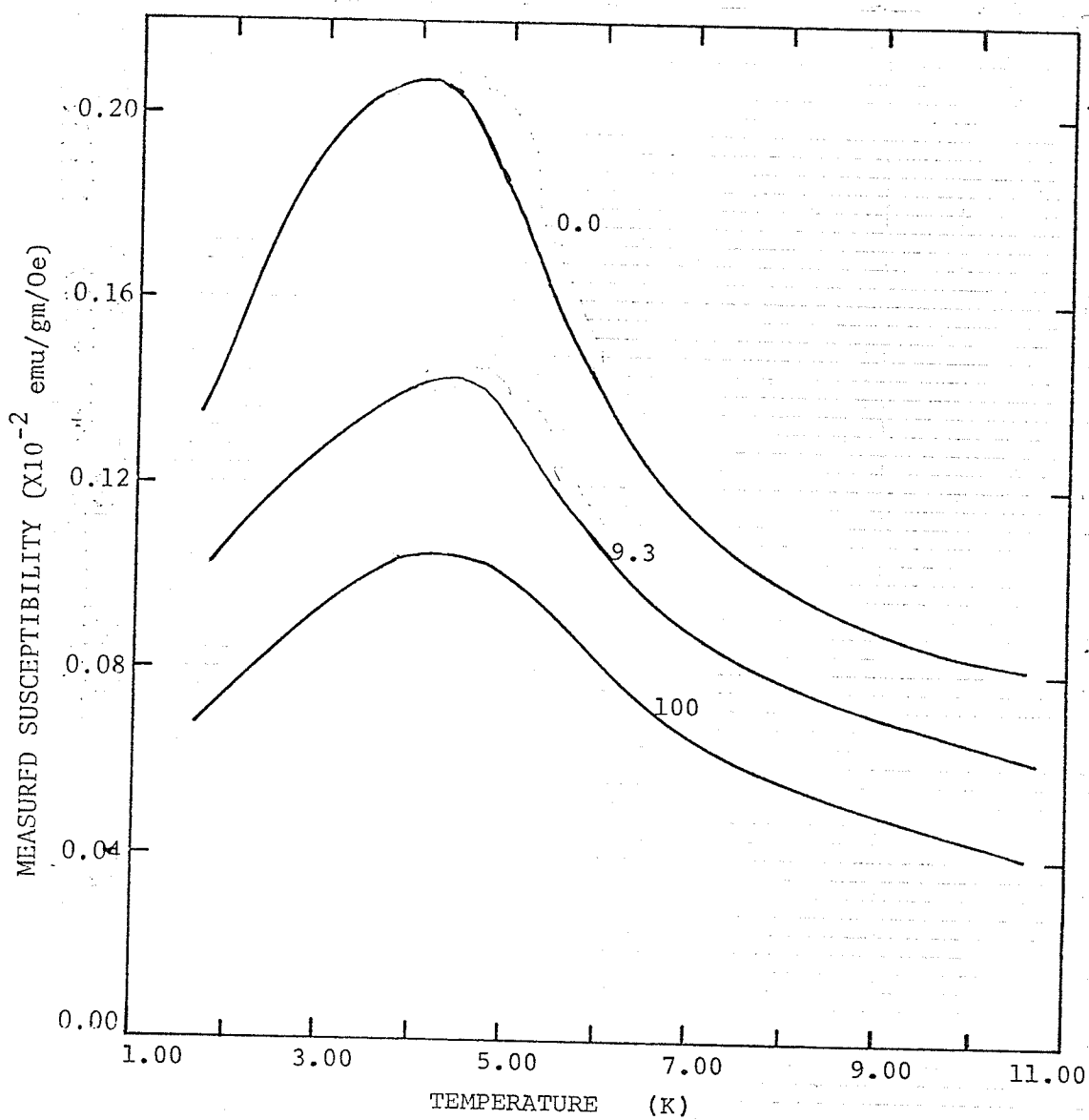


Fig. D.3 Measured susceptibility of Pd-7.0 at % Mn. The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.2×10^{-3} emu/gm/Oe for clarity.

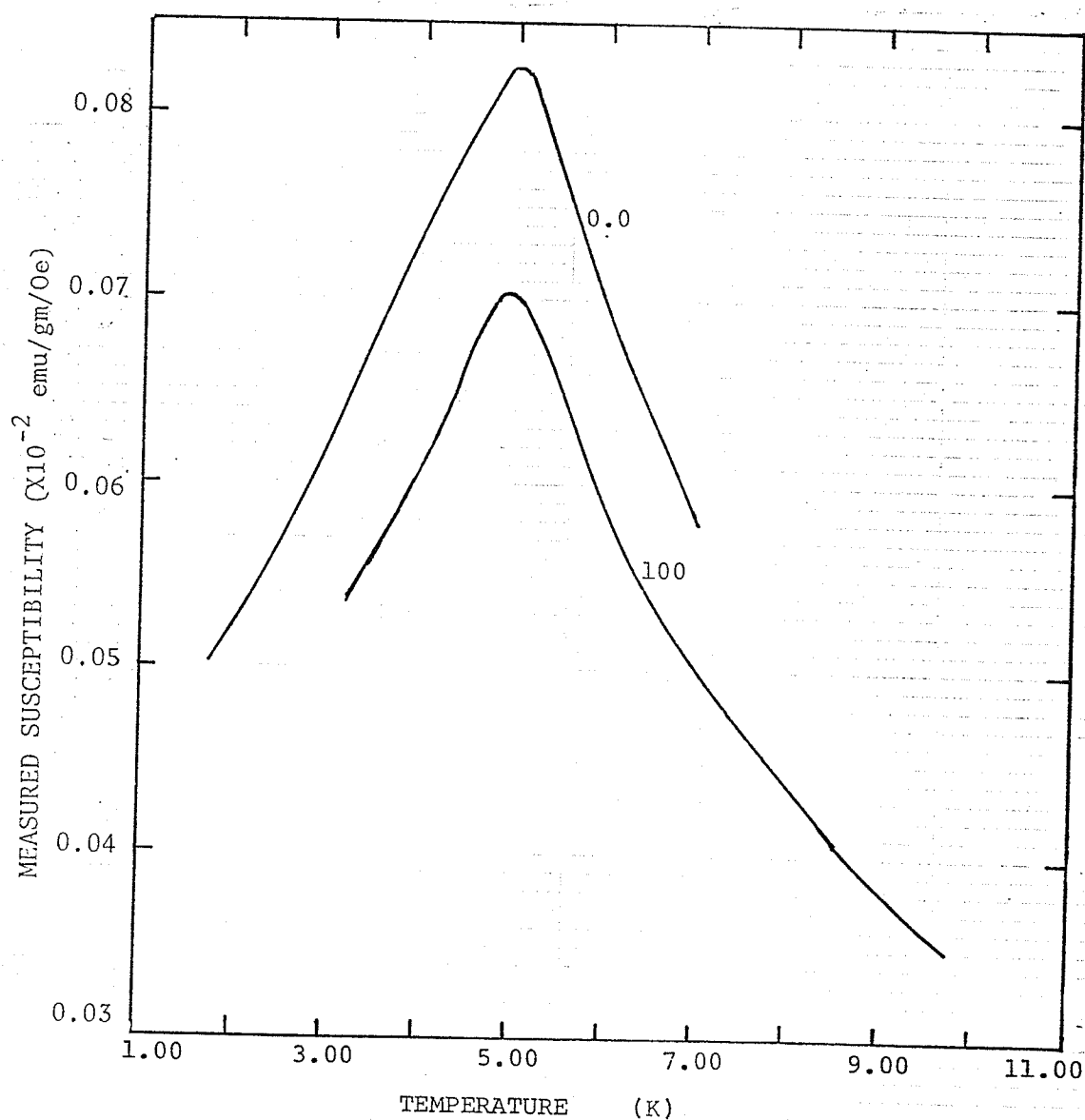


Fig. D.4 Measured susceptibility of Pd-7.5 at % Mn.
The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.1×10^{-3} emu/gm/Oe for clarity.

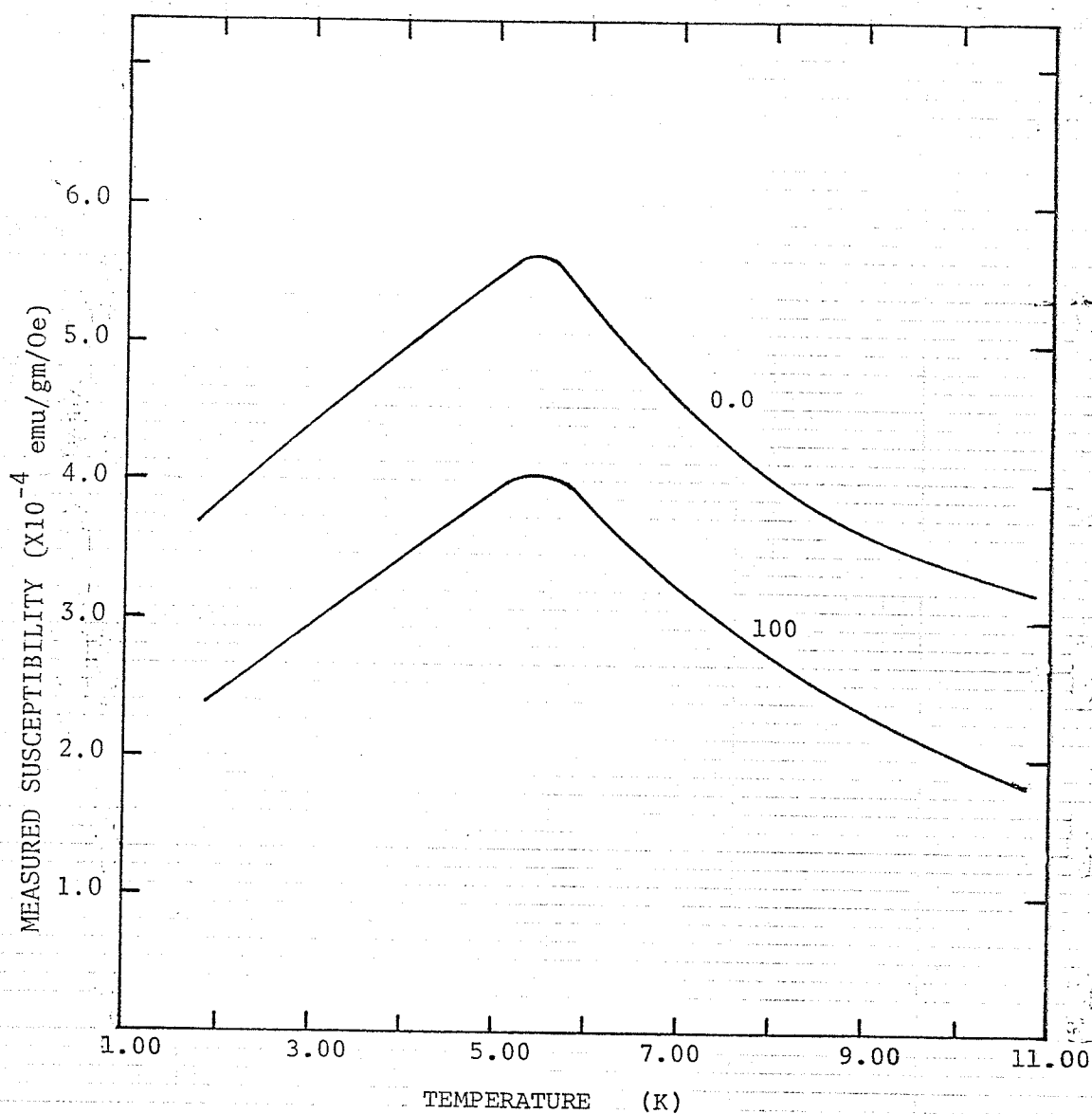


Fig. D.5 Measured susceptibility of Pd-8.0 at % Mn.

The Y-scale corresponds to the lower curve.

The upper curve has been raised by 1.33×10^{-4} emu/gm/Oe for clarity.

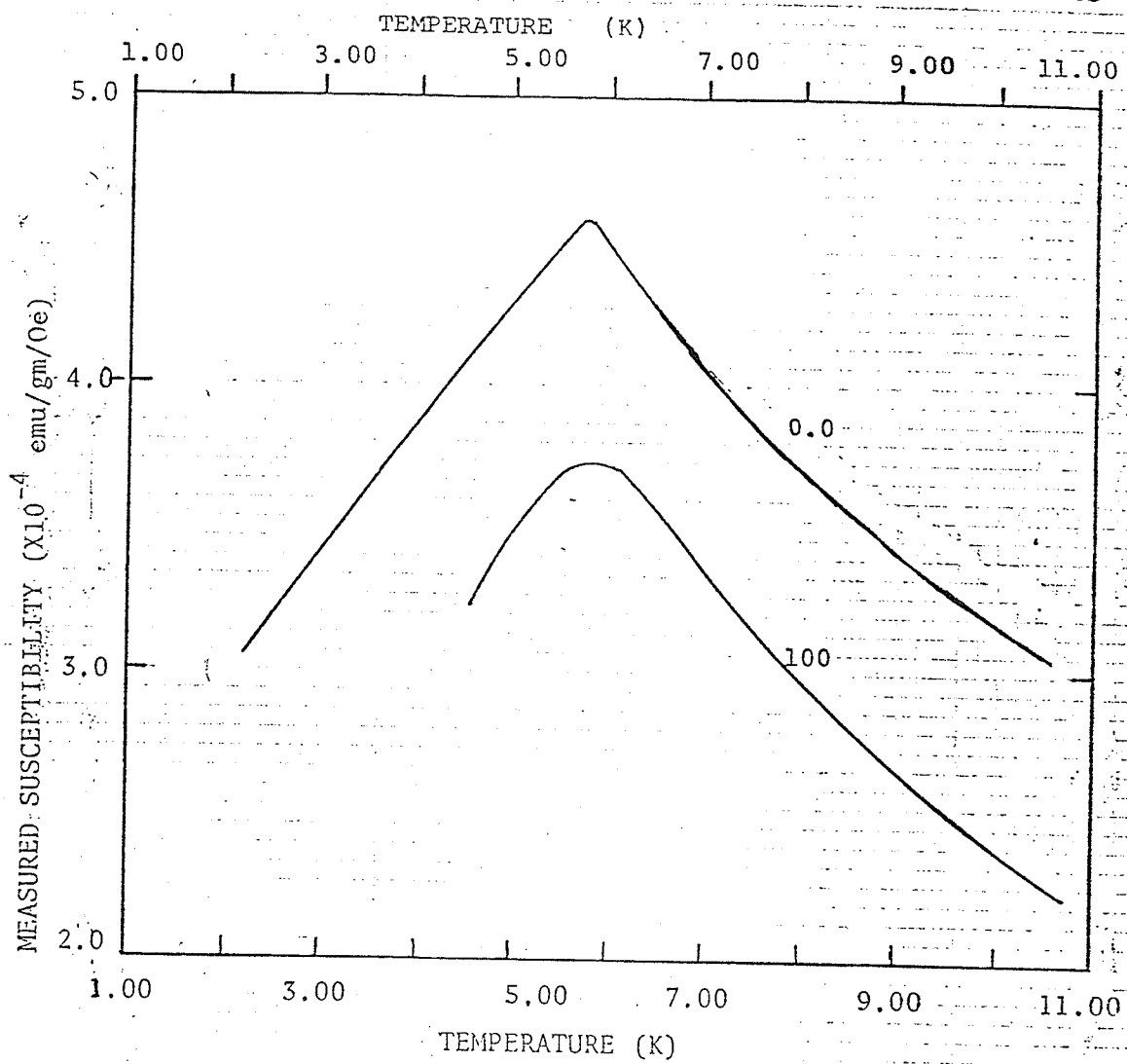


Fig. D.6 Measured susceptibility of Pd-8.5 at % Mn.

The Y-scale corresponds to the lower curve.

The upper curve has been raised by 0.667×10^{-4} emu/gm/Oe for clarity.

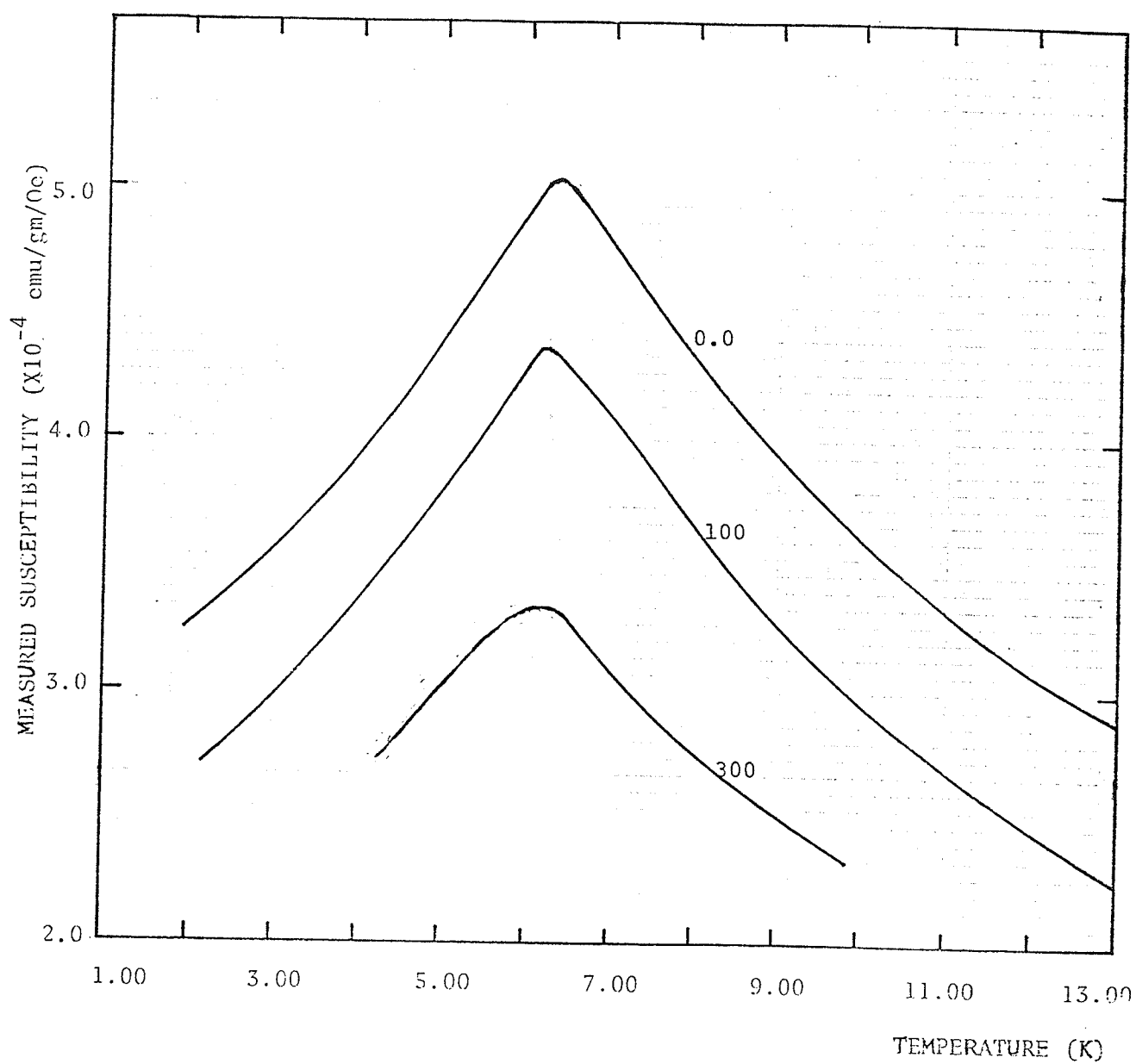


Fig. D.7

Measured Susceptibility data of Pd-9.0 at % Mn.

The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.667×10^{-4} emu/gm/Oe for clarity.

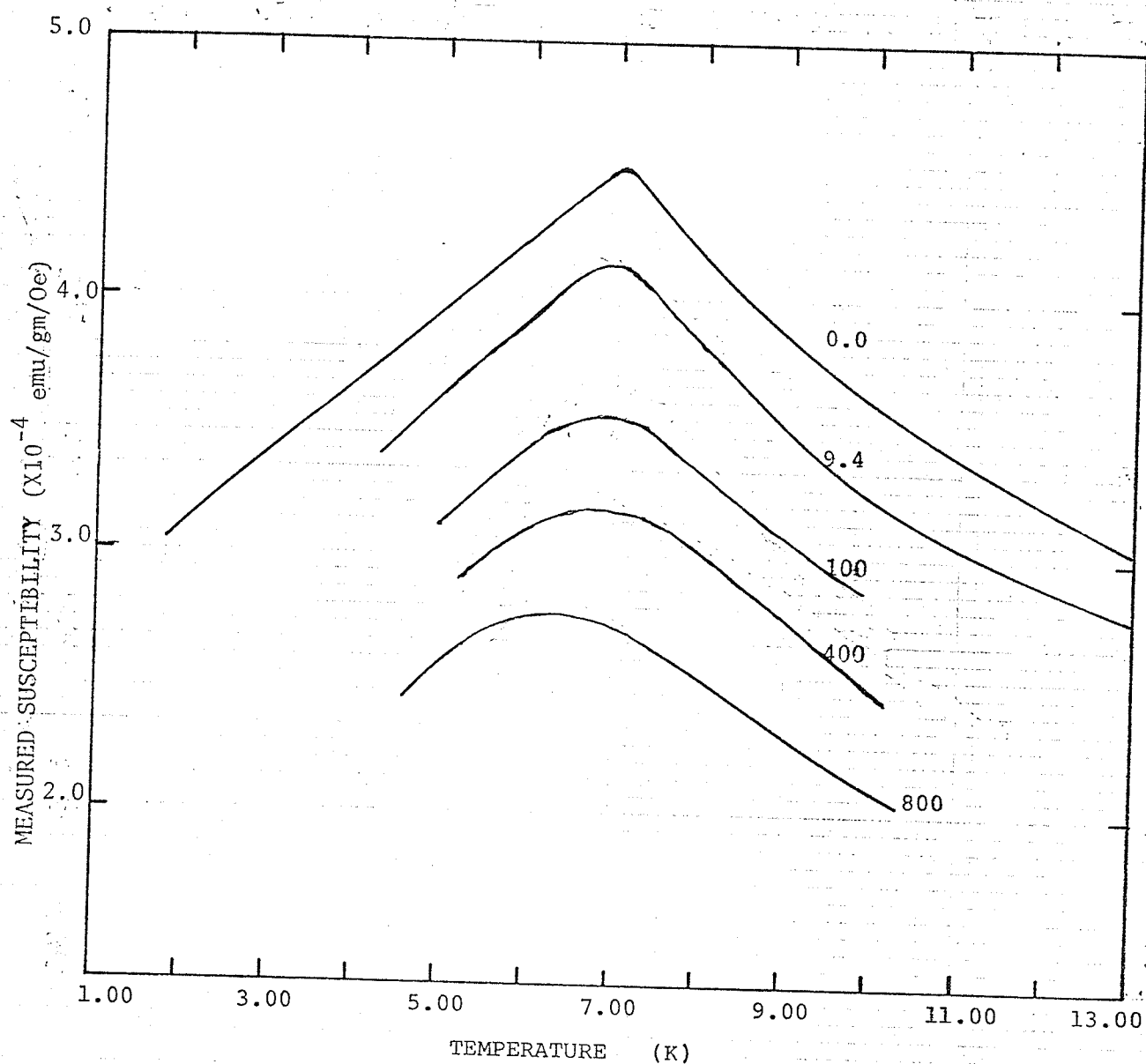


Fig. D.8 Measured susceptibility of Pd-9.5 at % Mn.

The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.333×10^{-4} emu/gm/Oe for clarity.

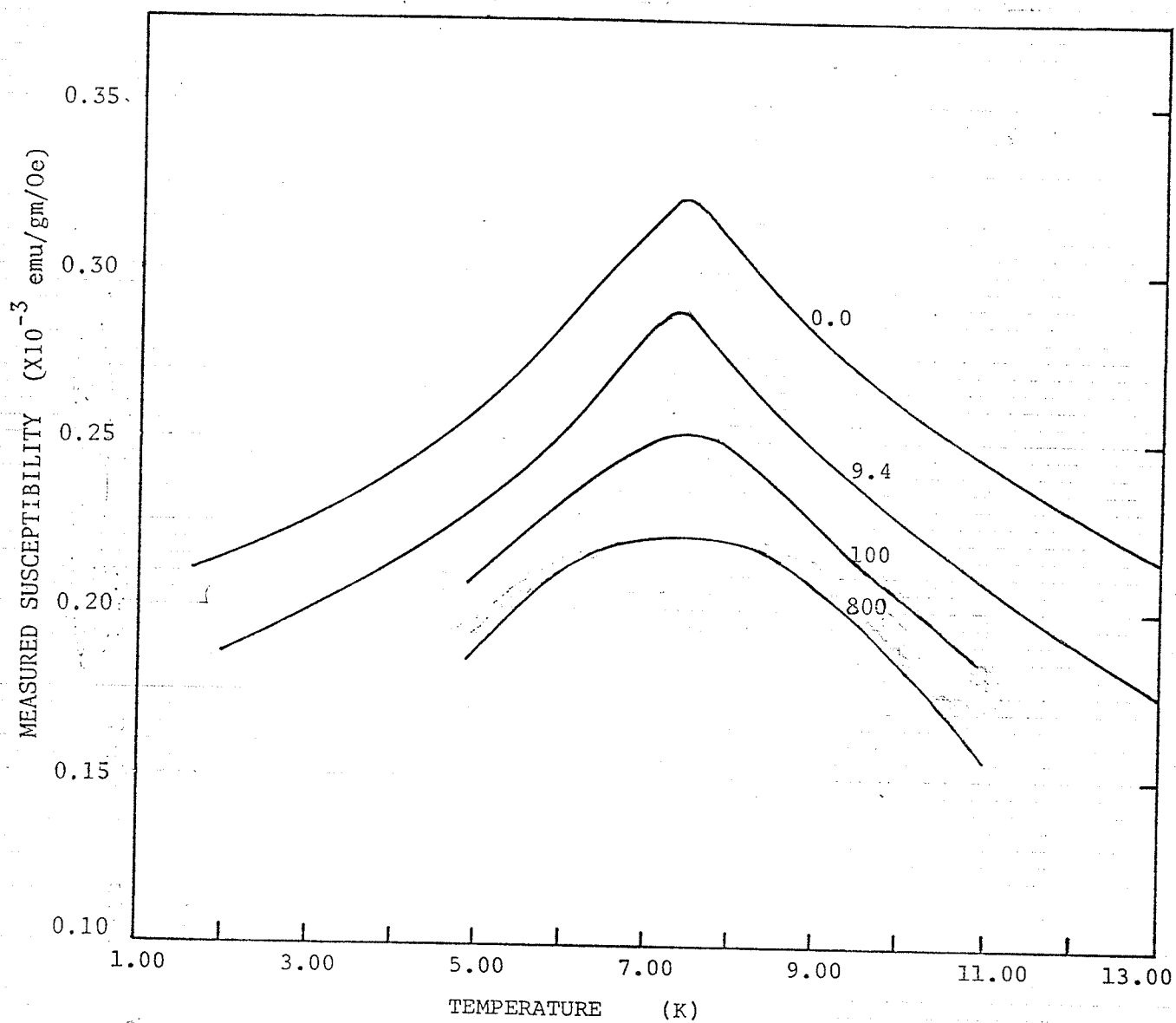


Fig. D.9 Measured susceptibility of Pd-10 at % Mn.

The Y-scale corresponds to the bottom curve. Each successive curve above one another has been raised by 0.25×10^{-4} emu/gm/Oe for clarity.

APPENDIX E

RELATED PLOTS OF SUSCEPTIBILITY

DATA FOR ALL ALLOYS

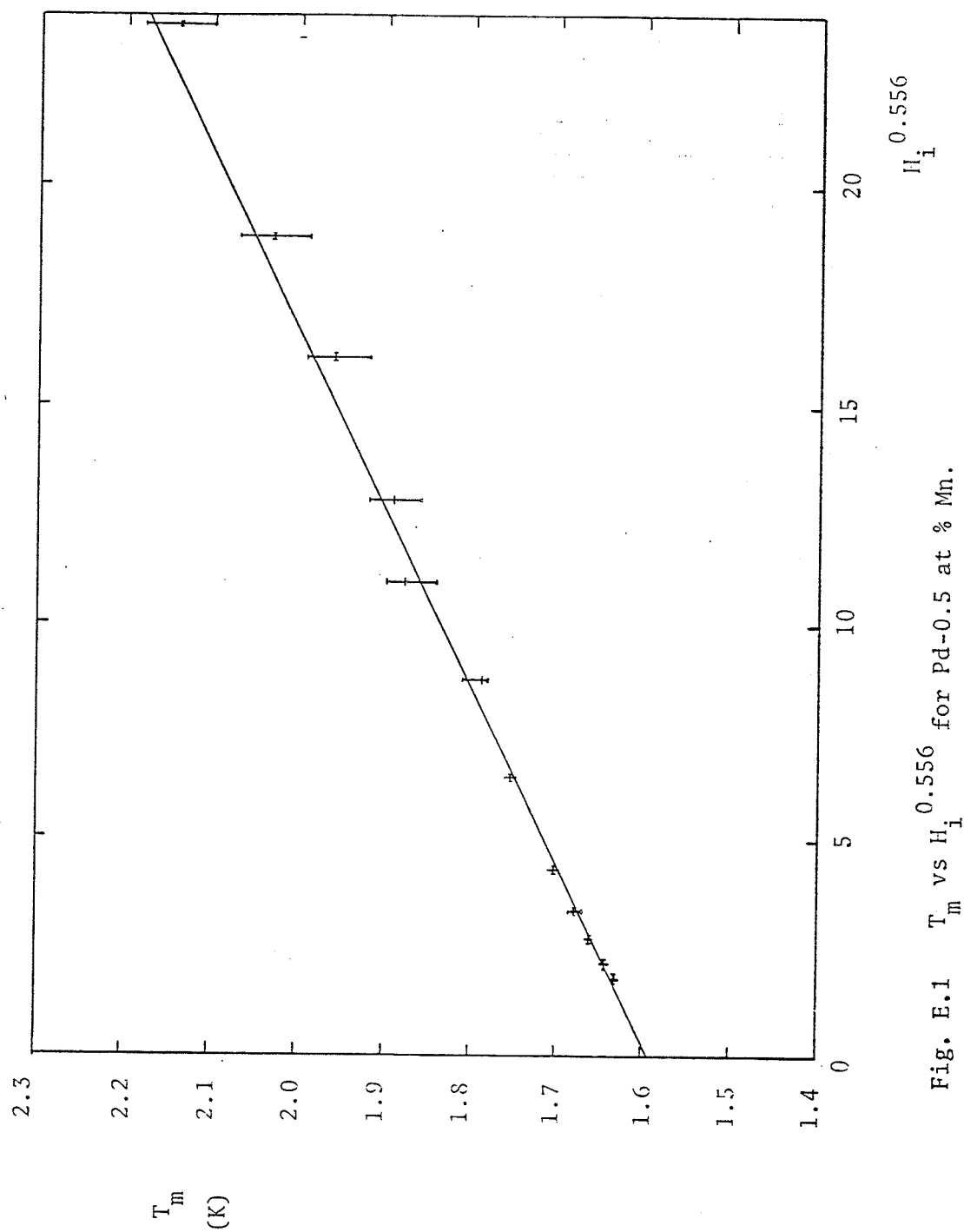


Fig. E.1 T_m vs $H_i^{0.556}$ for Pd-0.5 at % Mn.

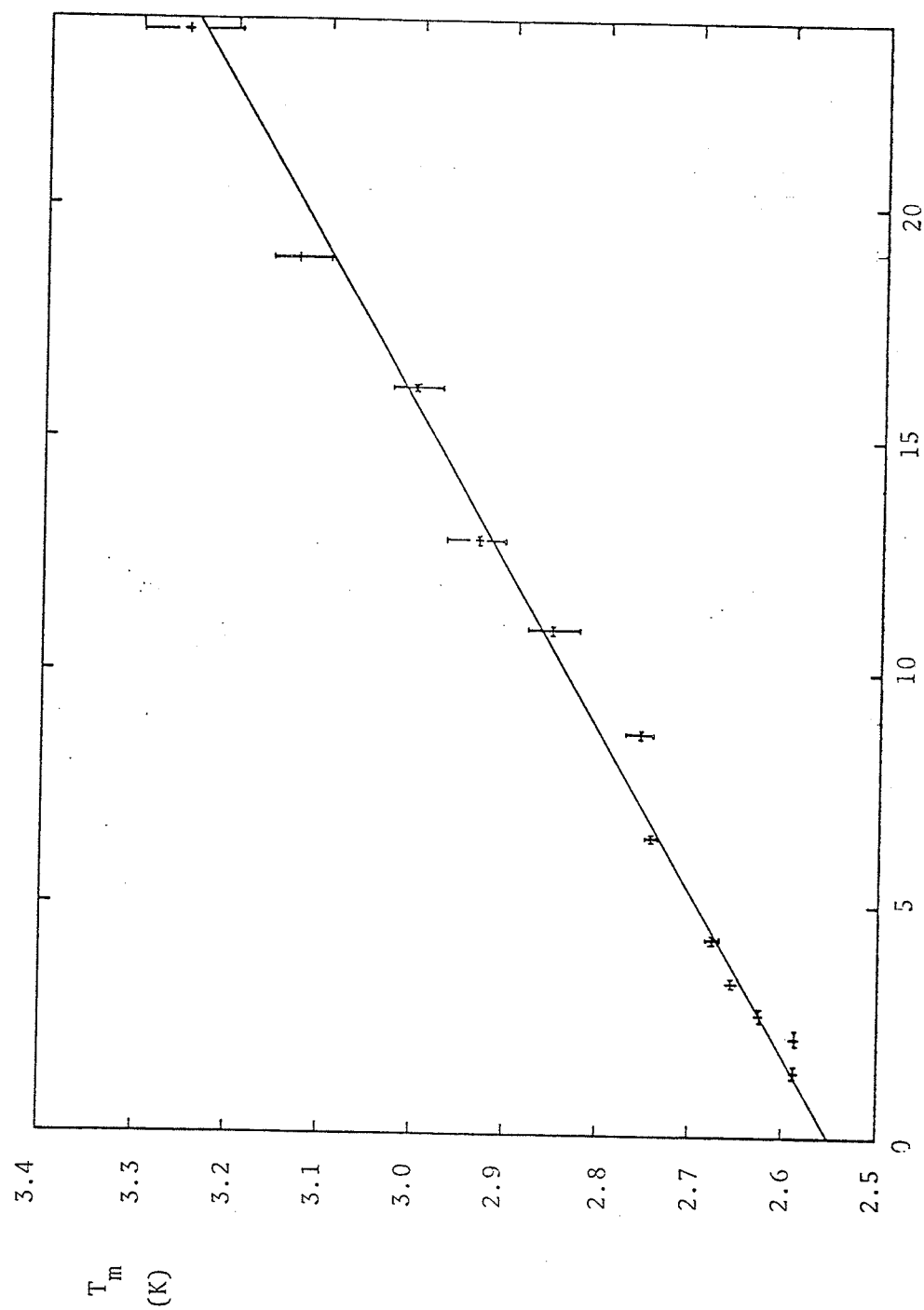


Fig. B.2 T_m vs $H_i^{0.556}$ for Pd-0.75 at % Mn.

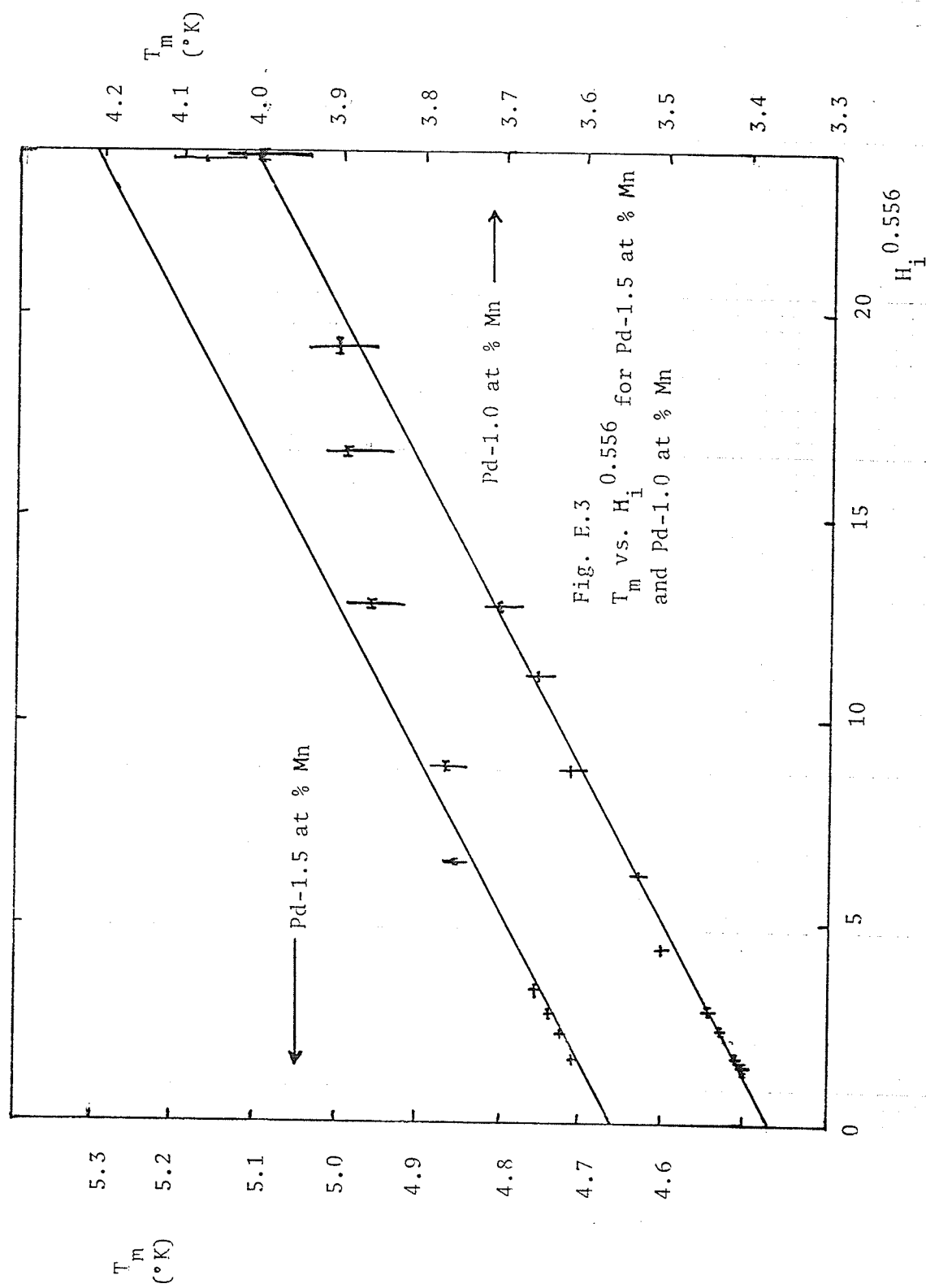


Fig. E.3 T_m vs. H_i for Pd-1.5 at % Mn and Pd-1.0 at % Mn

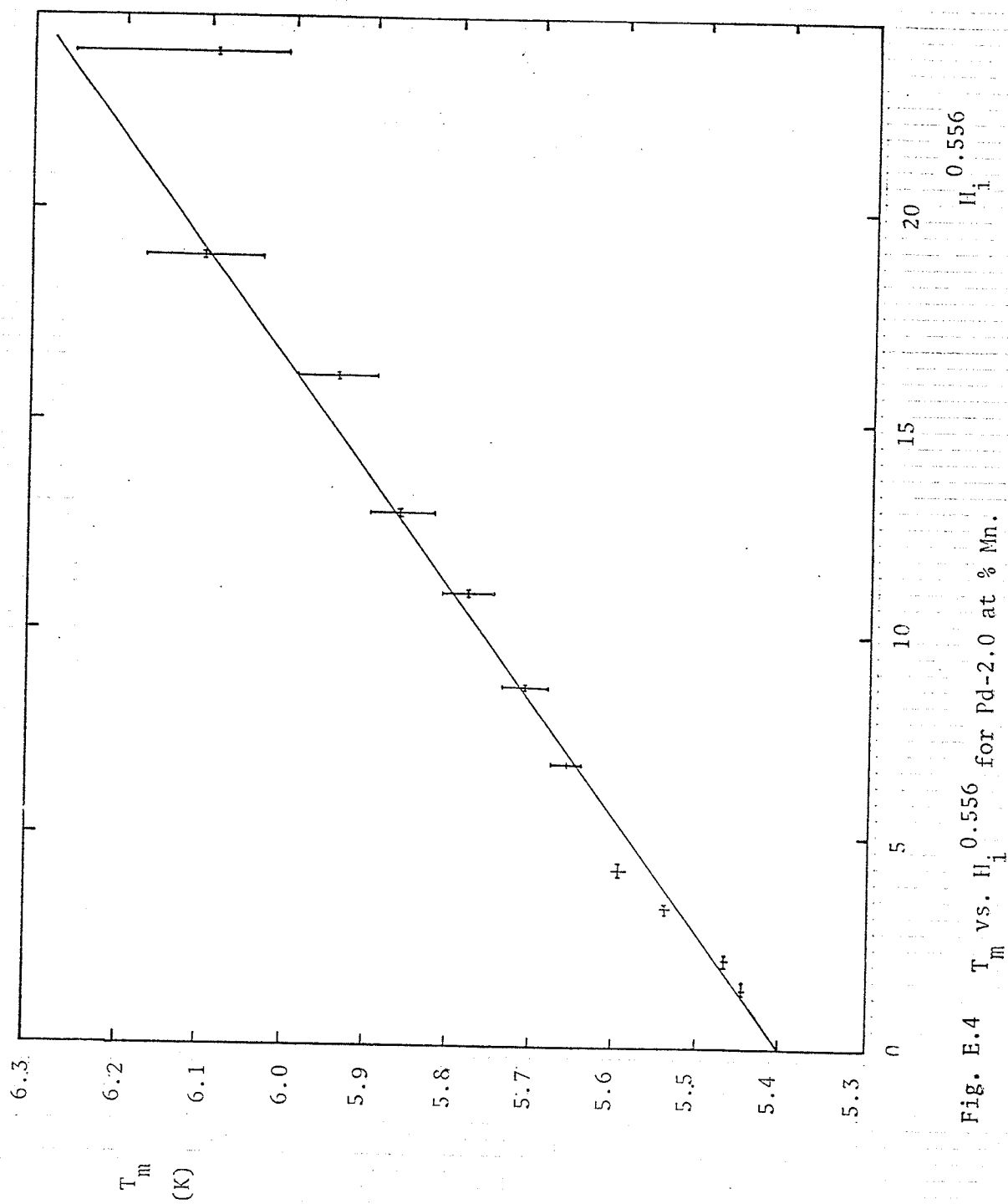


Fig. E.4 T_m vs. H_i for Pd-2.0 at % Mn.

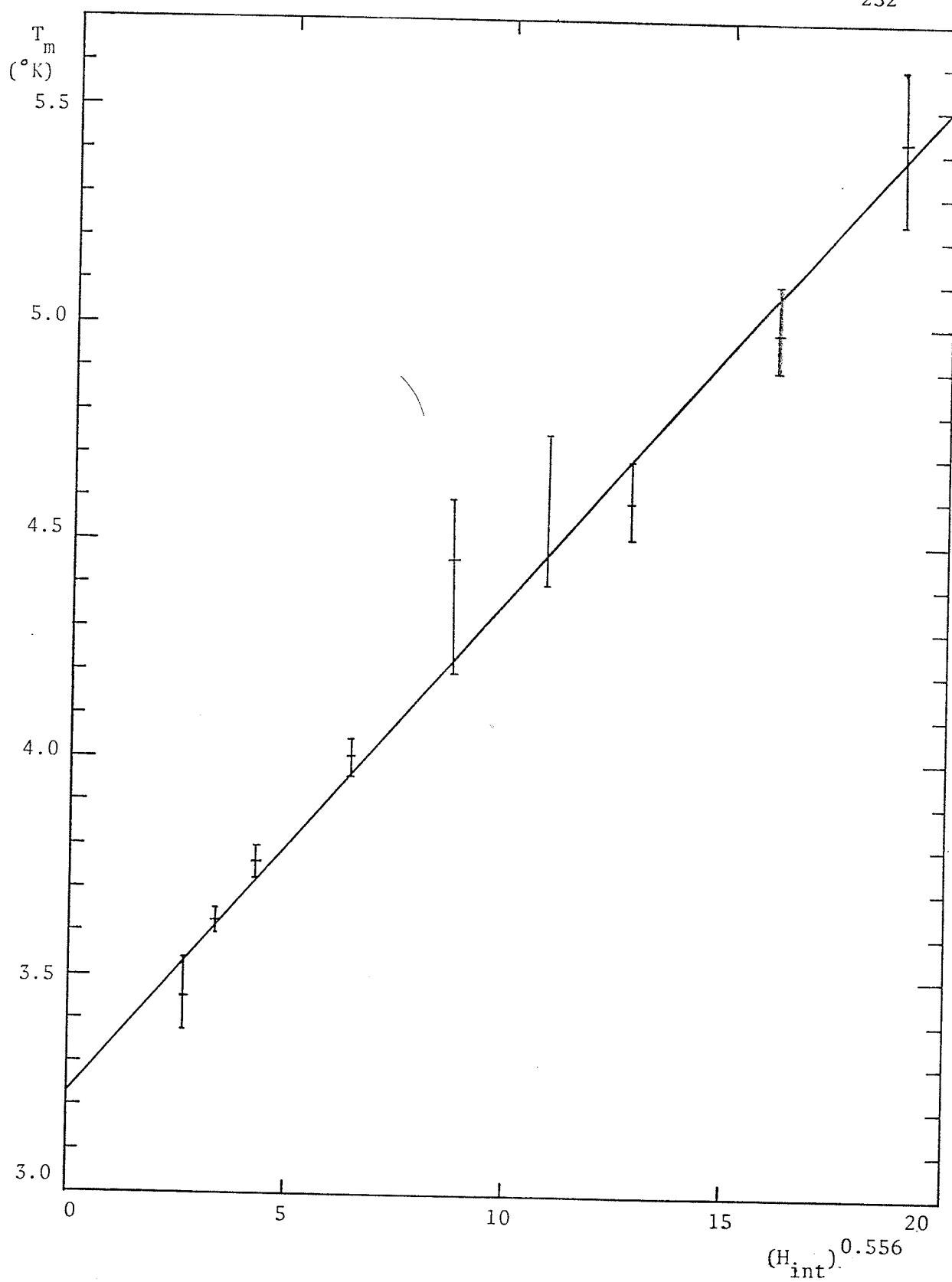


Fig. E.5 T_m vs. $H_i^{0.556}$ for Pd-4.5 at % Mn.

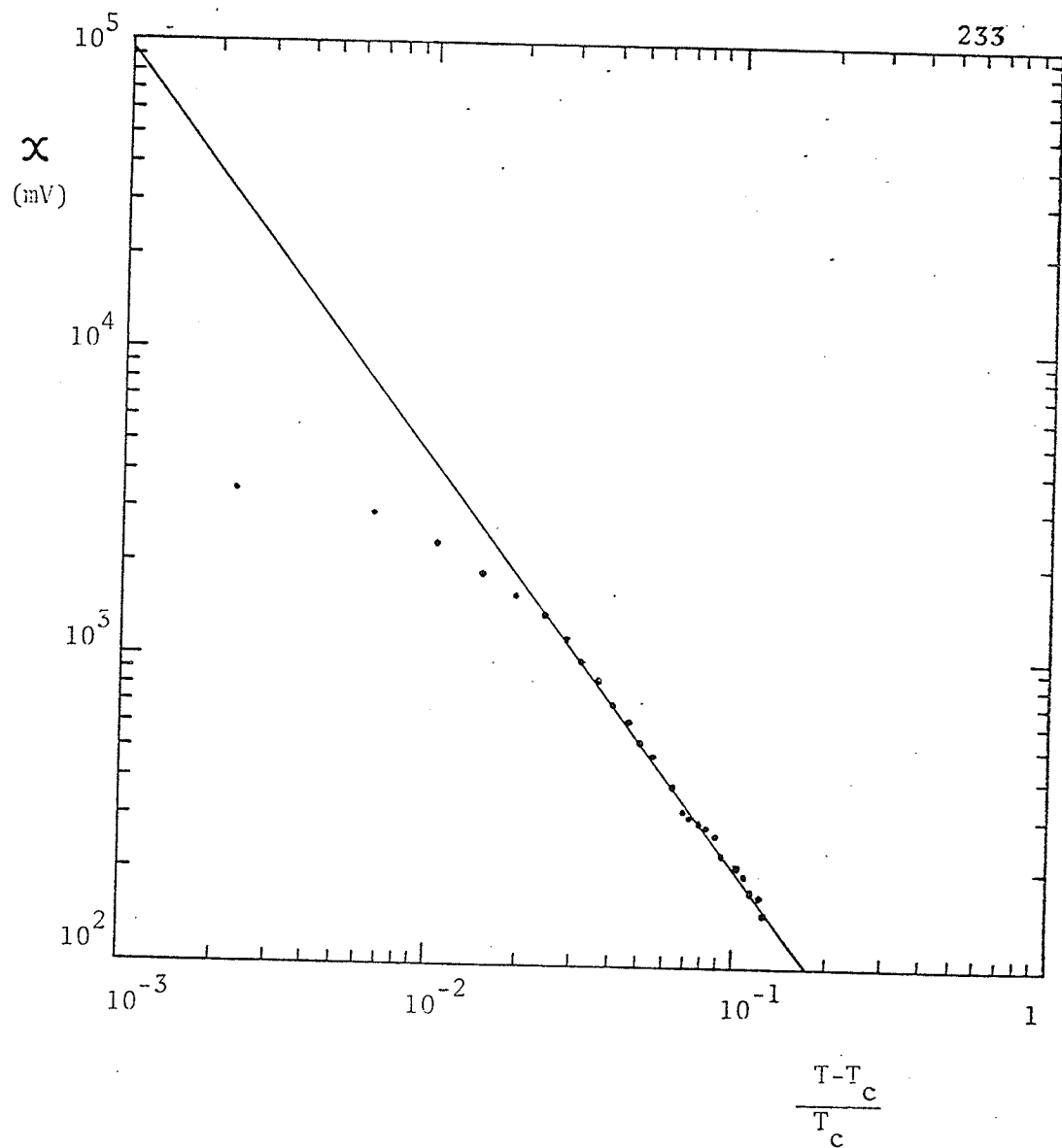


Fig. E.6 Susceptibility vs. $\frac{T - T_c}{T_c}$ for Pd-0.75 at % Mn. (γ -plot)

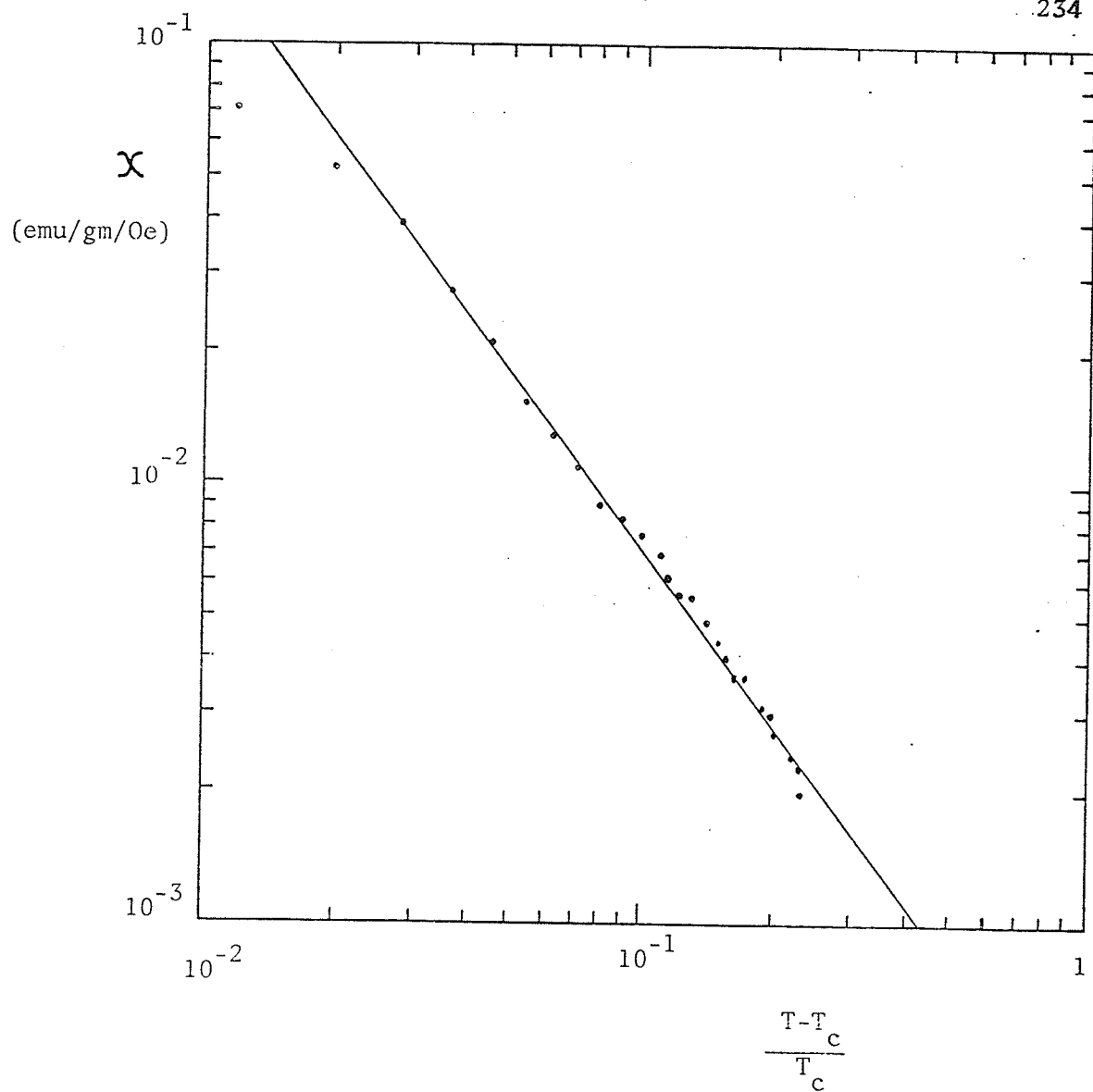


Fig. E.7 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-1.0 at % Mn. (χ -plot)

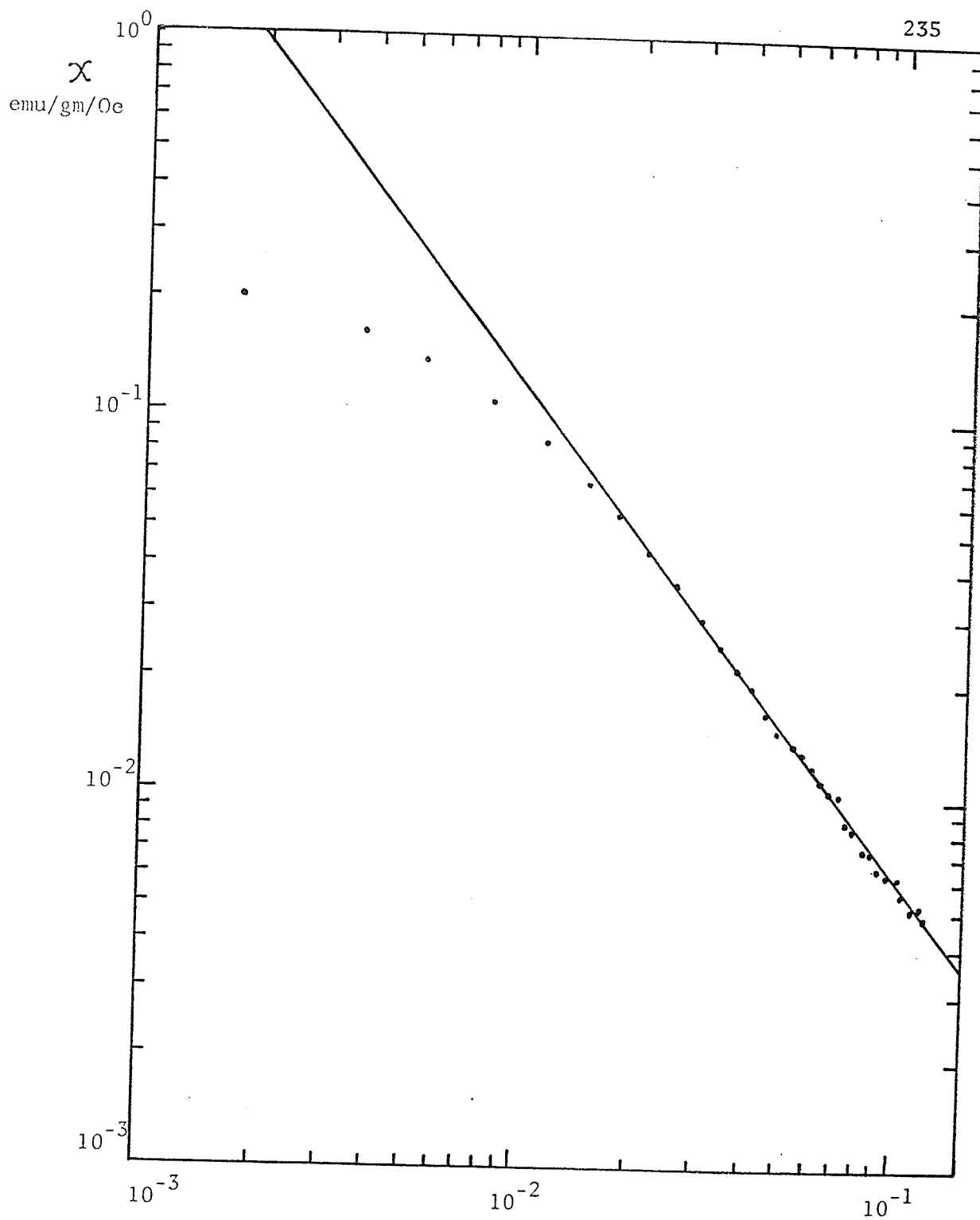


Fig. E.8 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-1.5 at % Mn.
(χ -plot)

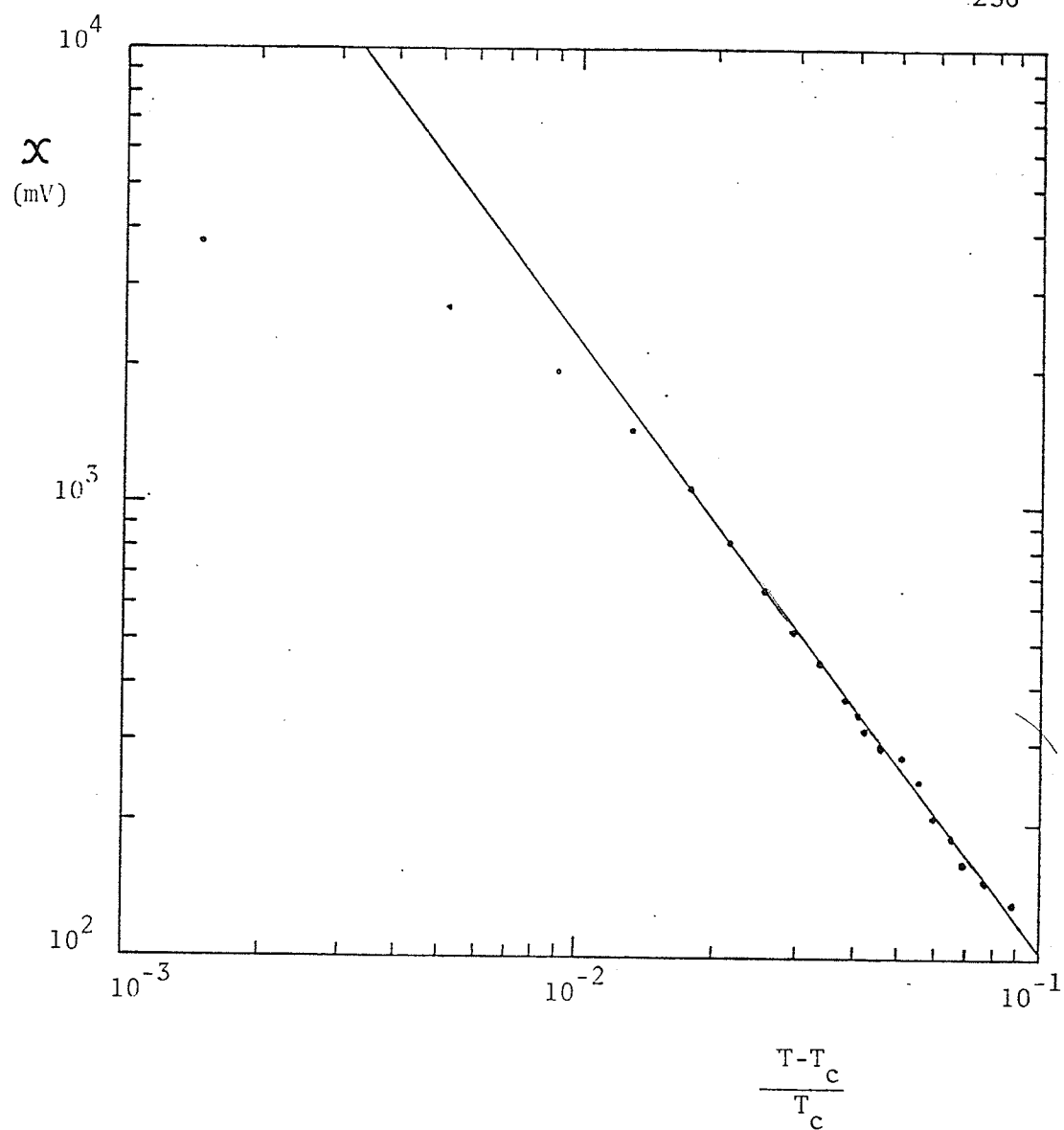


Fig. E.9 Susceptibility vs. $\frac{T - T_c}{T_c}$ for Pd-2.0 at % Mn. (χ -plot)

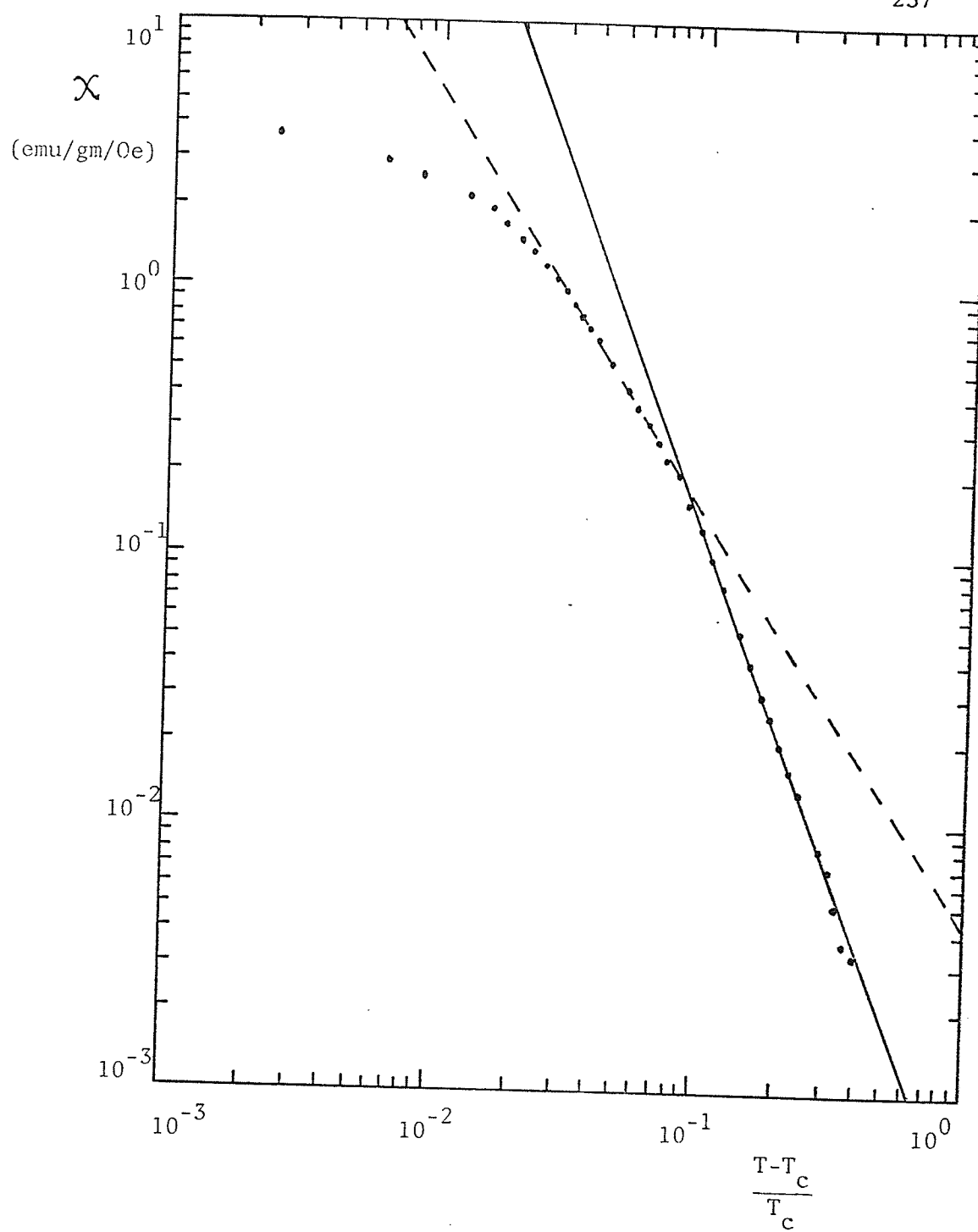


Fig. E.10 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-3.5 at % Mn. (γ -plot)

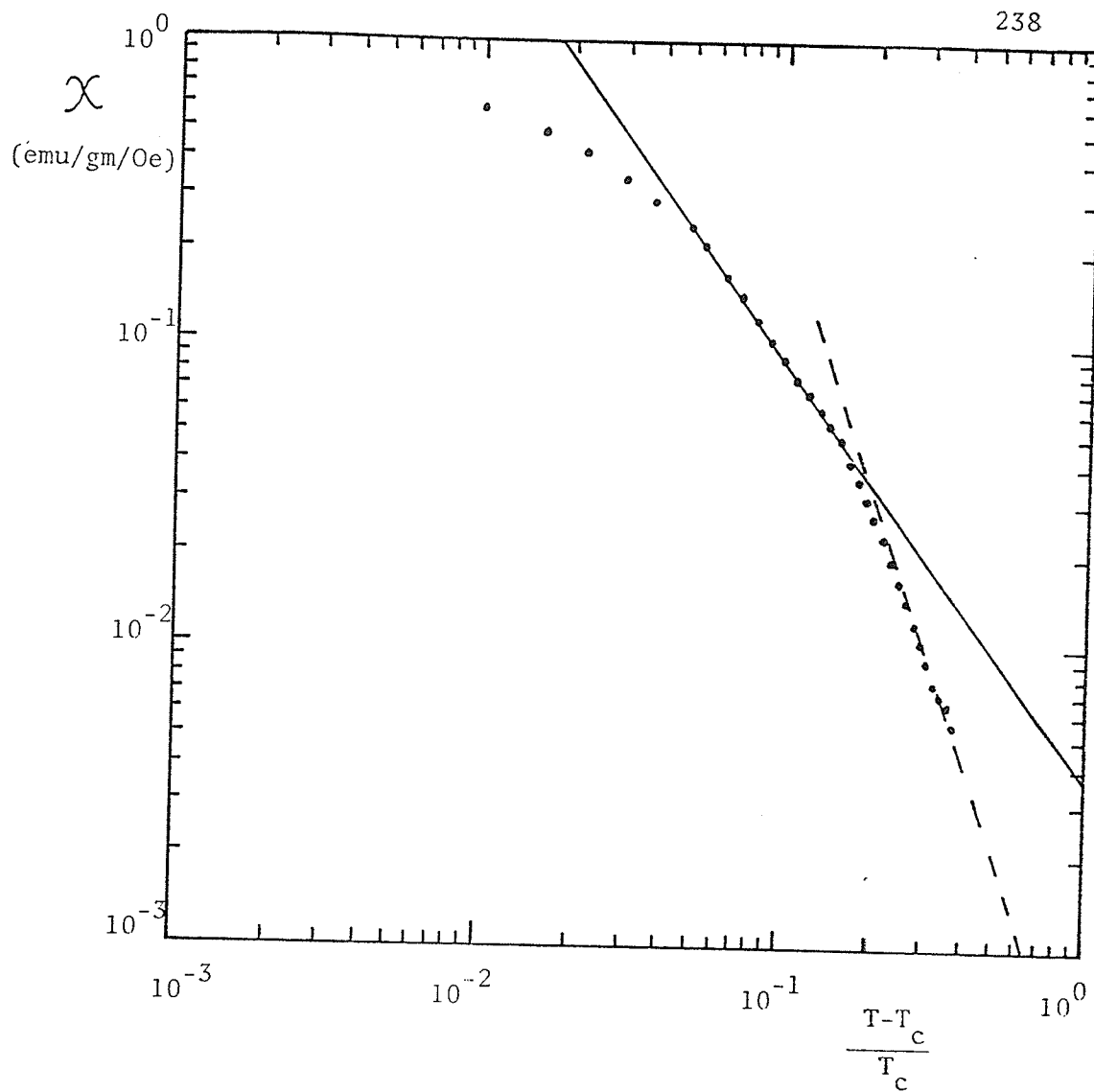


Fig. E.11 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-4.0 at % Mn. (γ -plot)

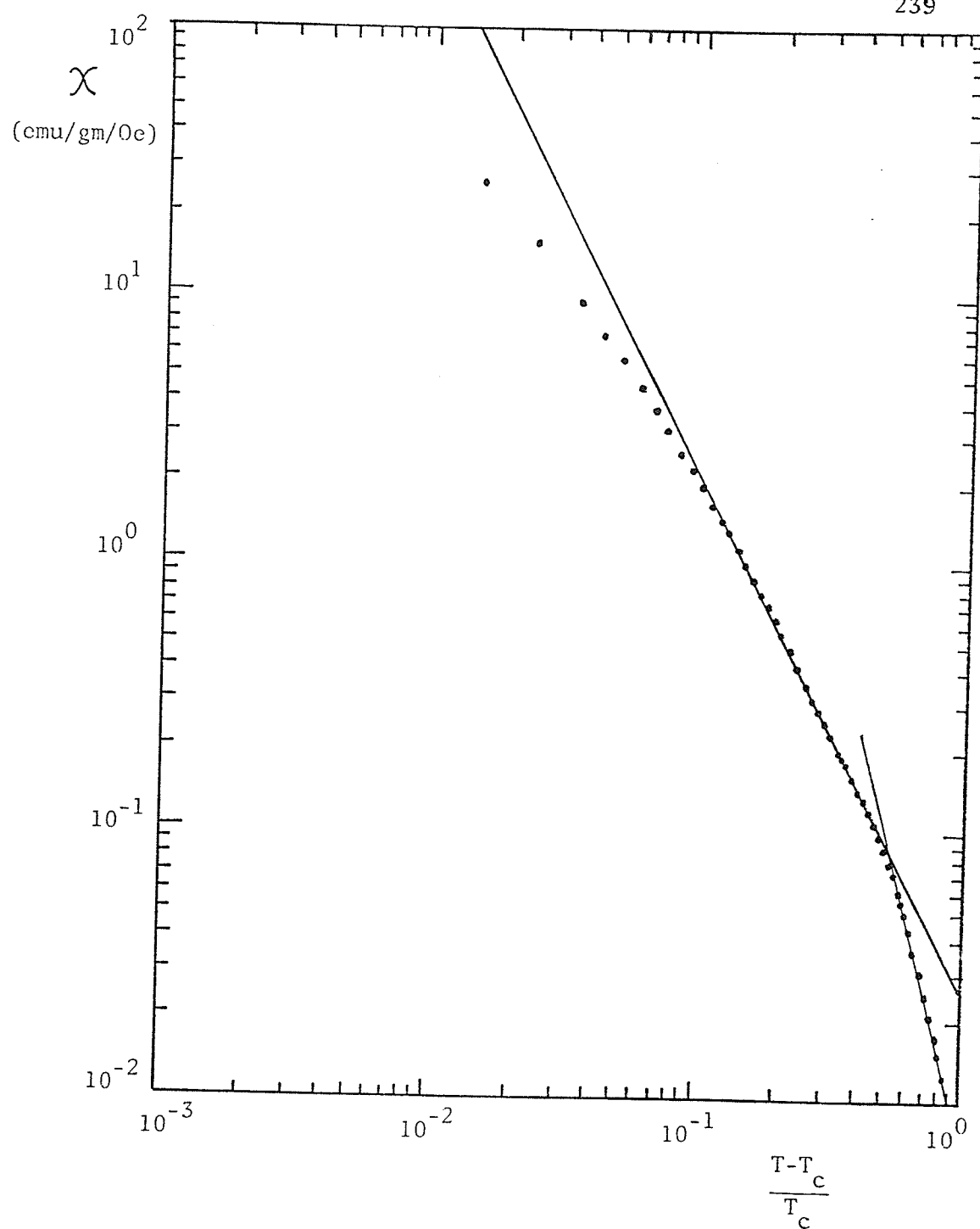


Fig. E.12 Susceptibility vs. $\frac{T-T_c}{T_c}$ for Pd-4.5 at % Mn. (γ -plot)

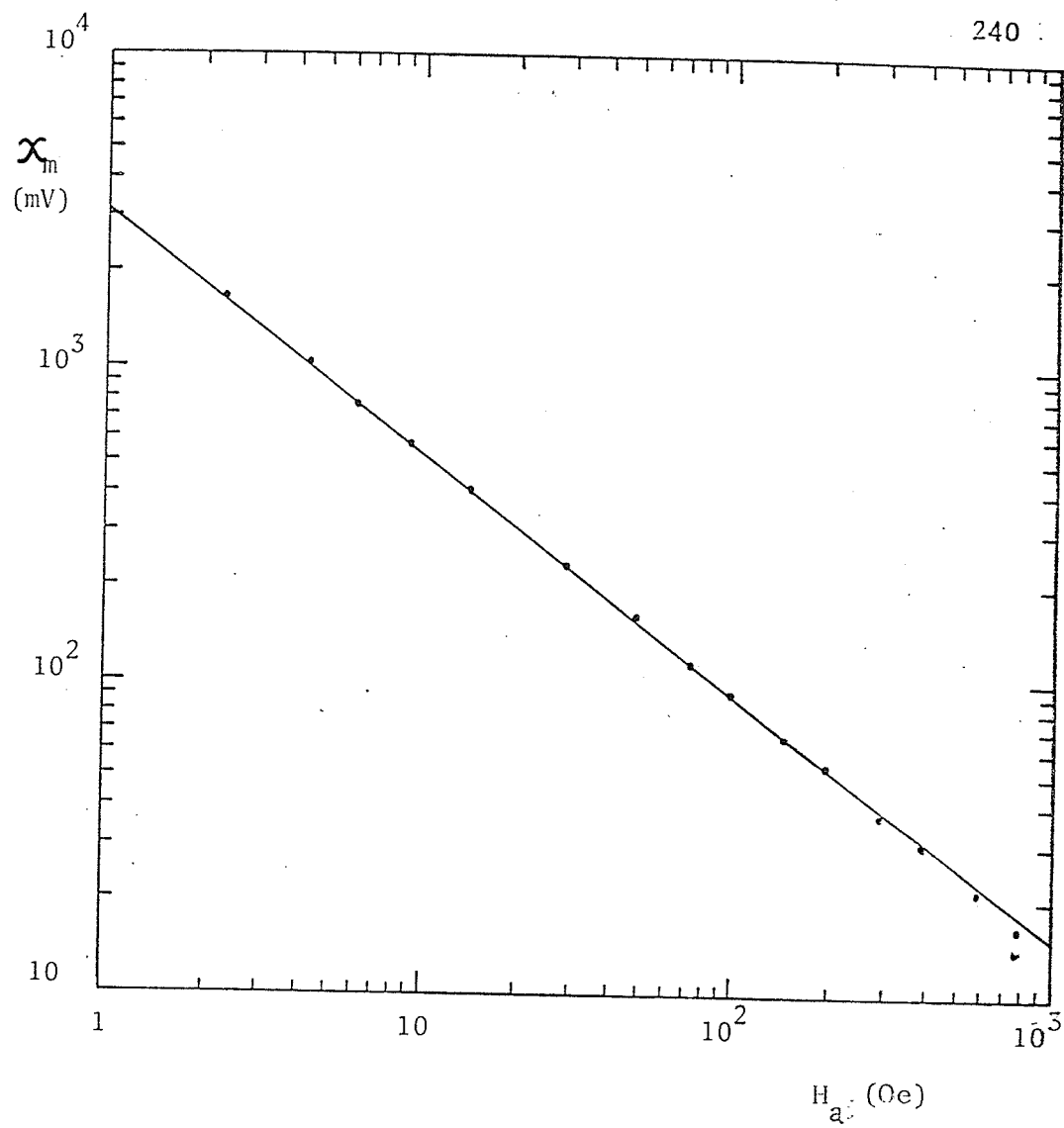


Fig. E.13 Susceptibility vs. H_a for Pd-0.75 at % Mn.

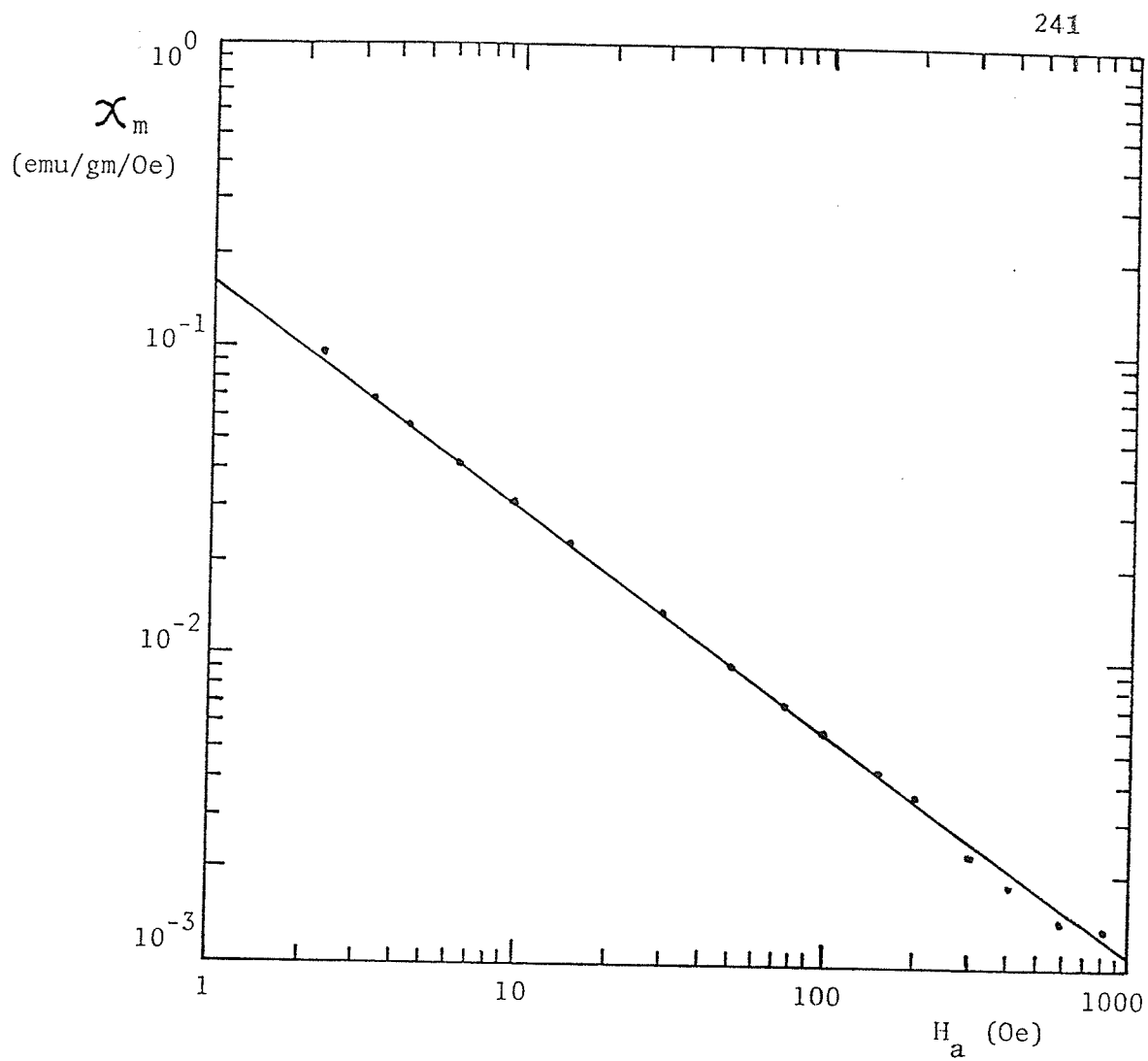


Fig. E.14 Susceptibility vs. H_a for Pd-3.0 at % Mn.

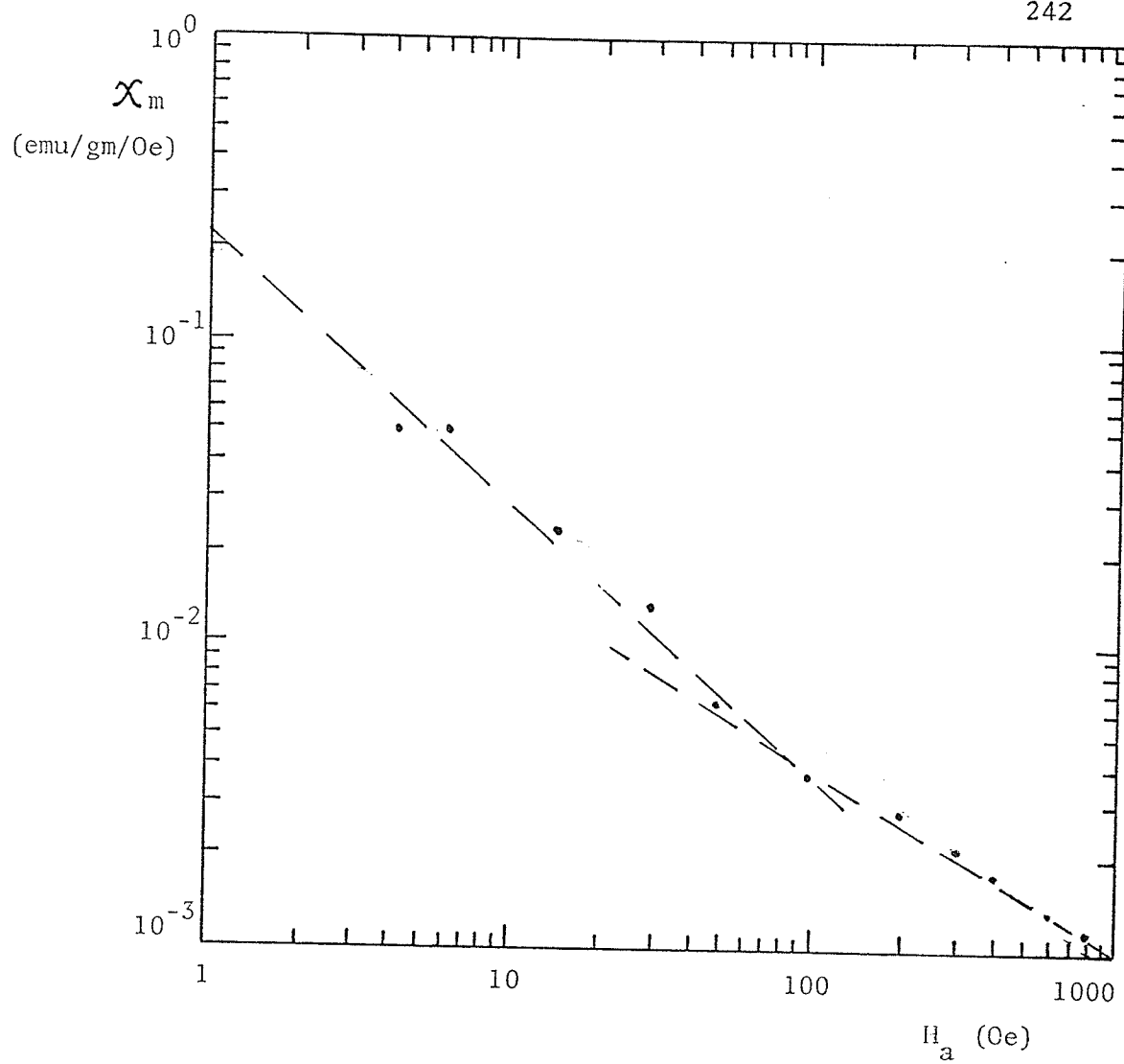


Fig. E.15 Susceptibility vs. H_a for Pd-4.0 at % Mn.

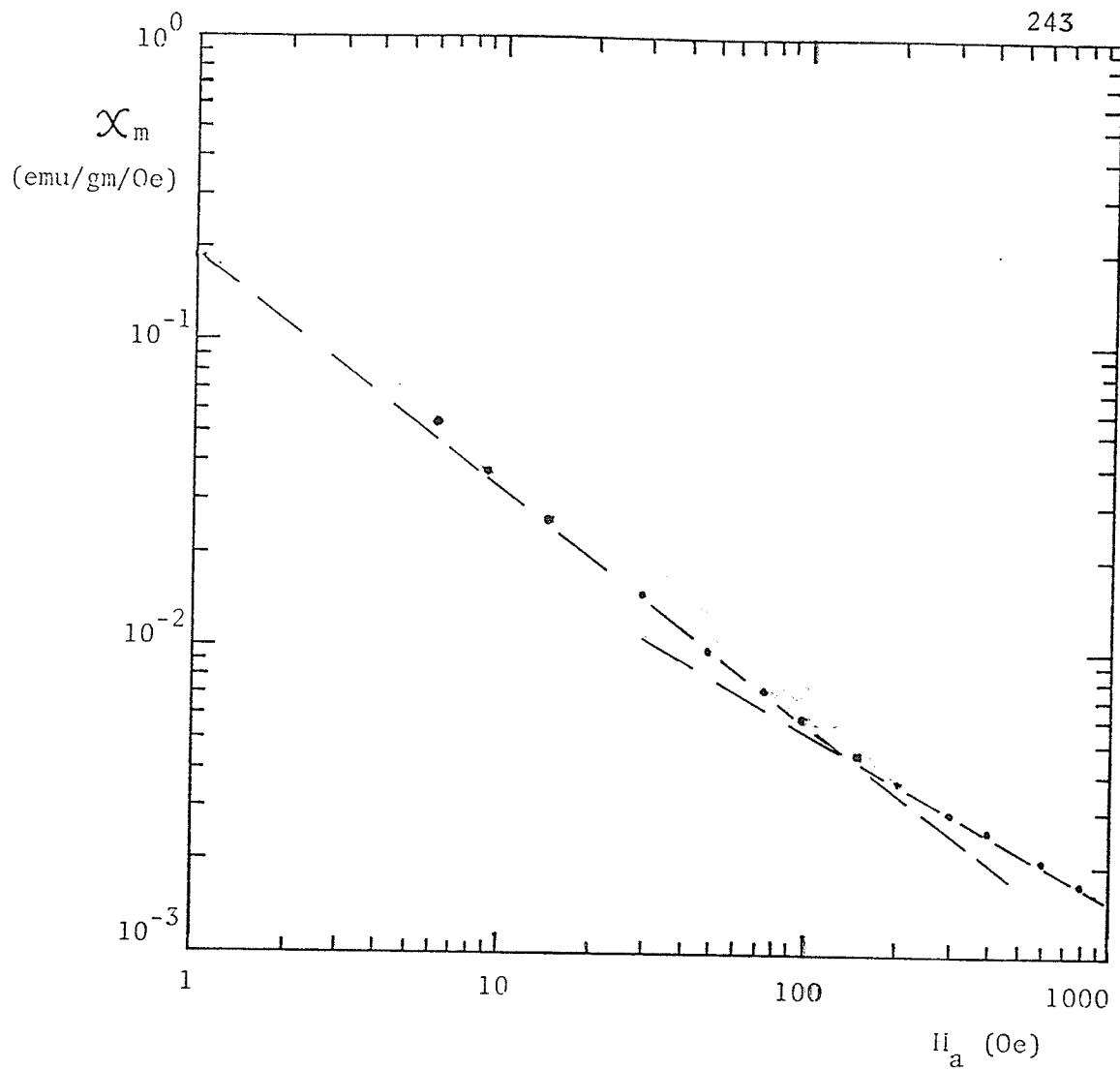


Fig. E.16 Susceptibility vs. H_a for Pd-4.5 at % Mn.

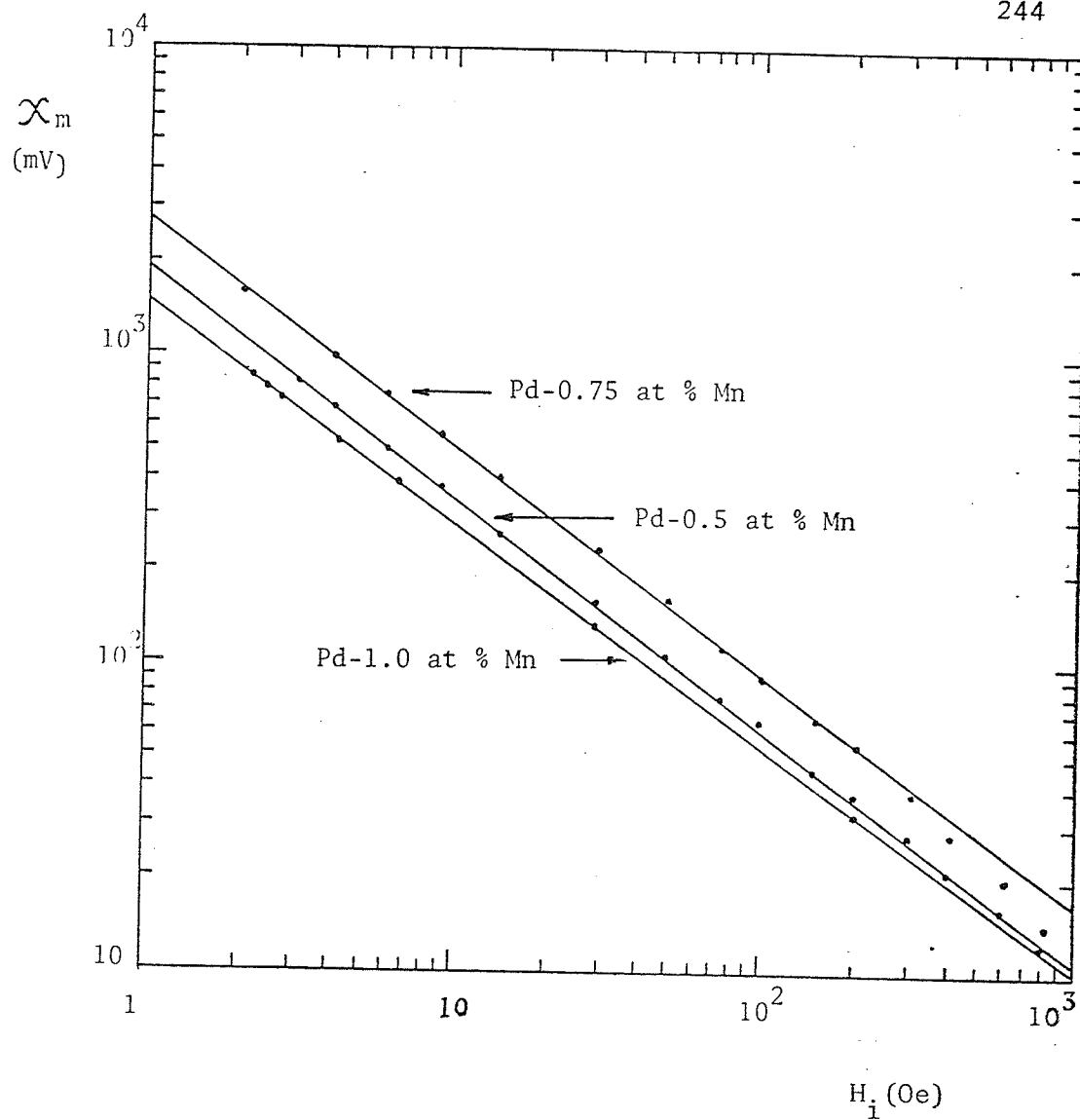


Fig. E.17 Susceptibility vs. internal field for Pd-0.5 at % Mn, Pd-0.75 at % Mn, and Pd-1.0 at % Mn. (δ -plot)

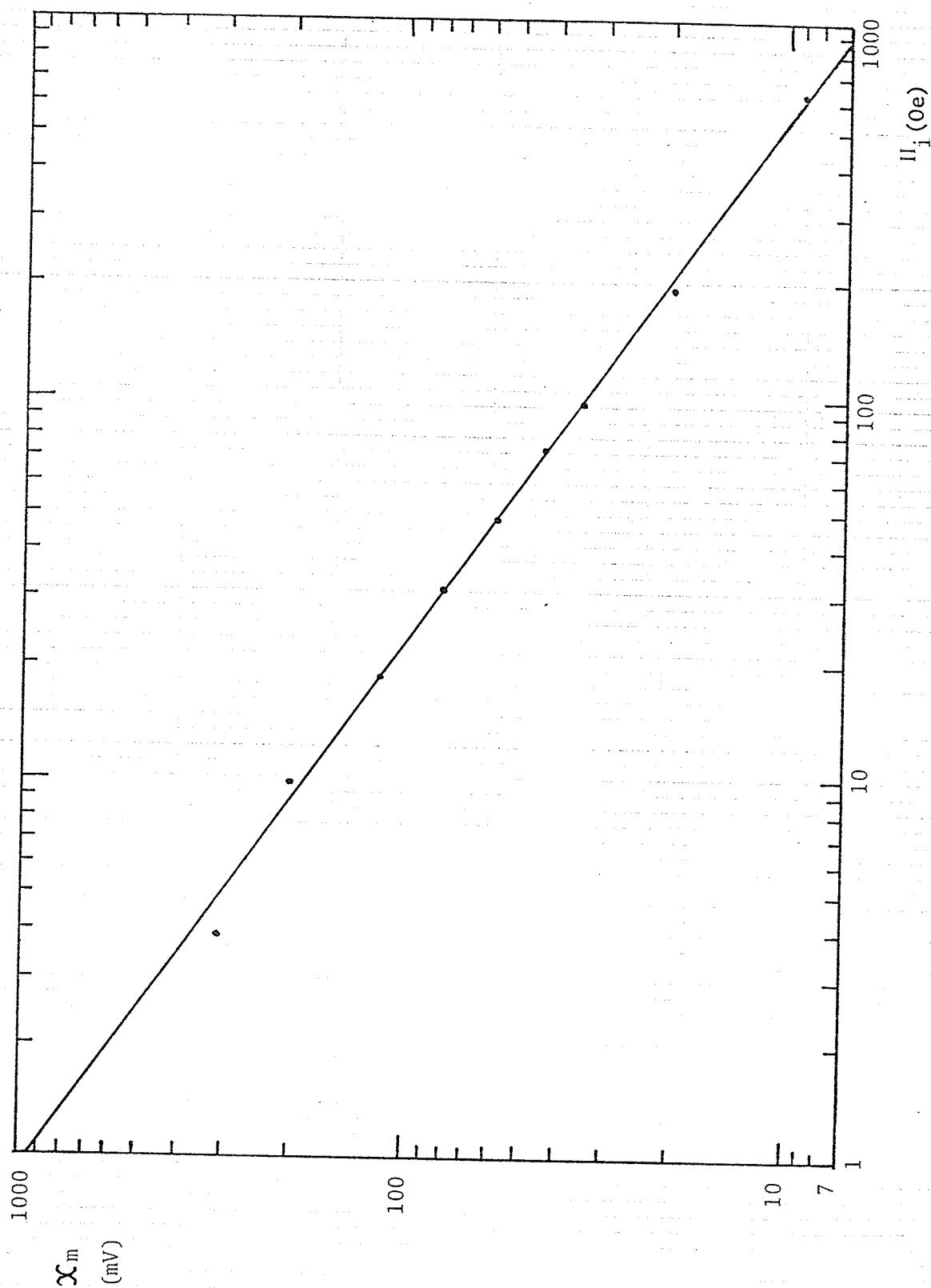


Fig. E.18 χ_m vs. H_i for Pd-1.5 at % Mn. (δ -plot)

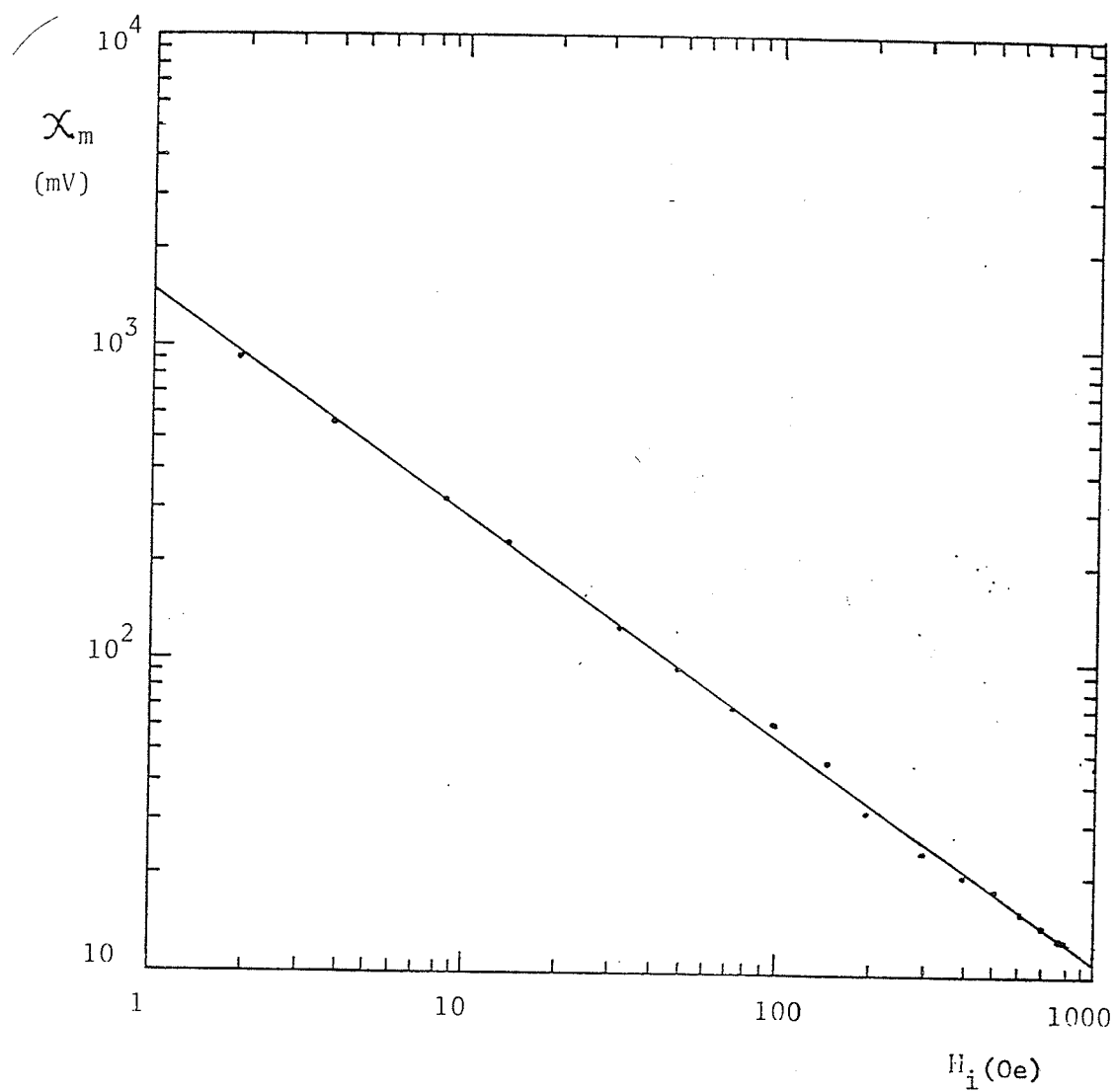


Fig. E.19 Susceptibility vs. H_i for Pd-2.0 at % Mn. (δ -plot)

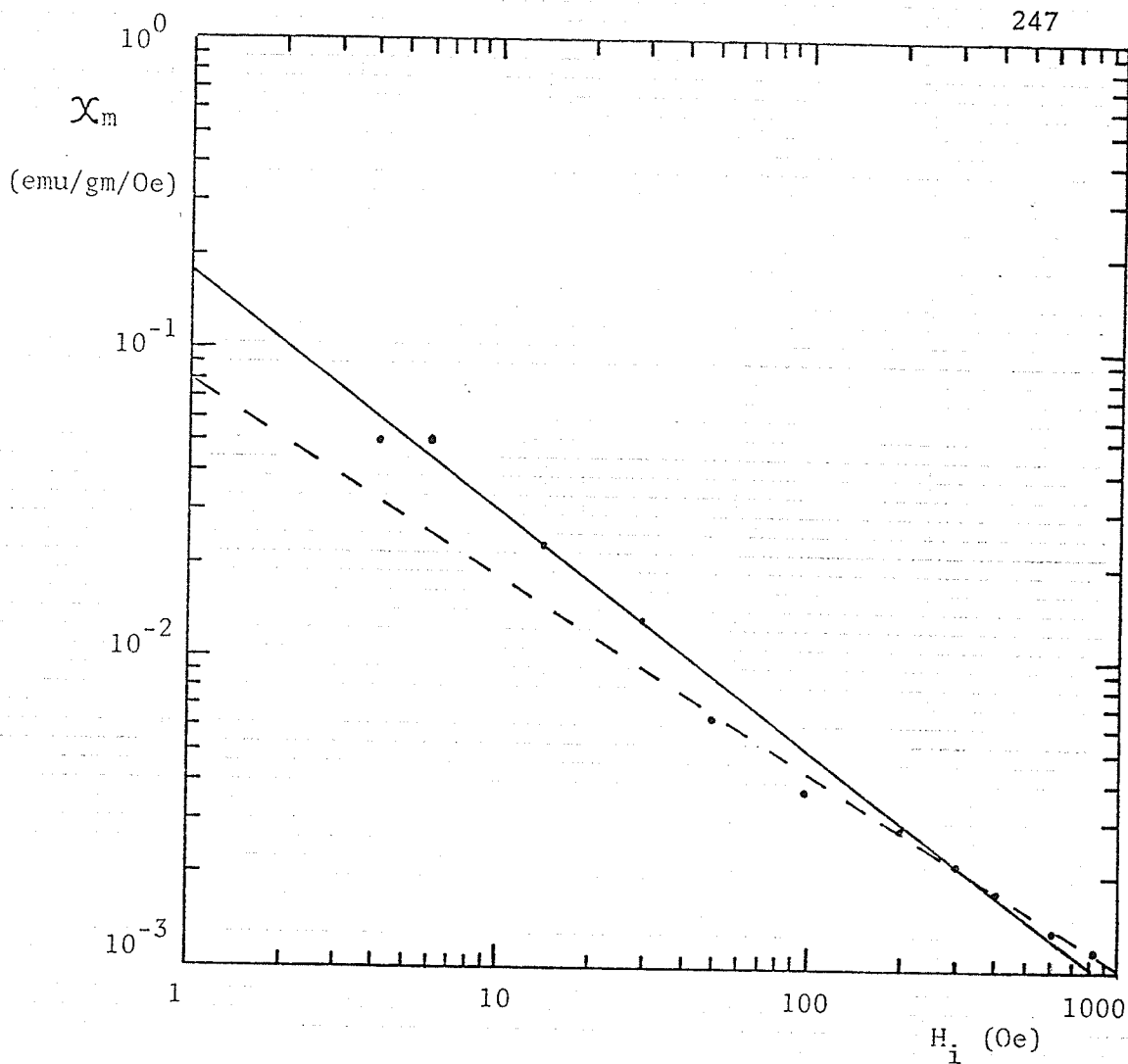


Fig. E.20 Susceptibility vs. H_i for Pd-4.0 at % Mn. ($\int$ -plot)

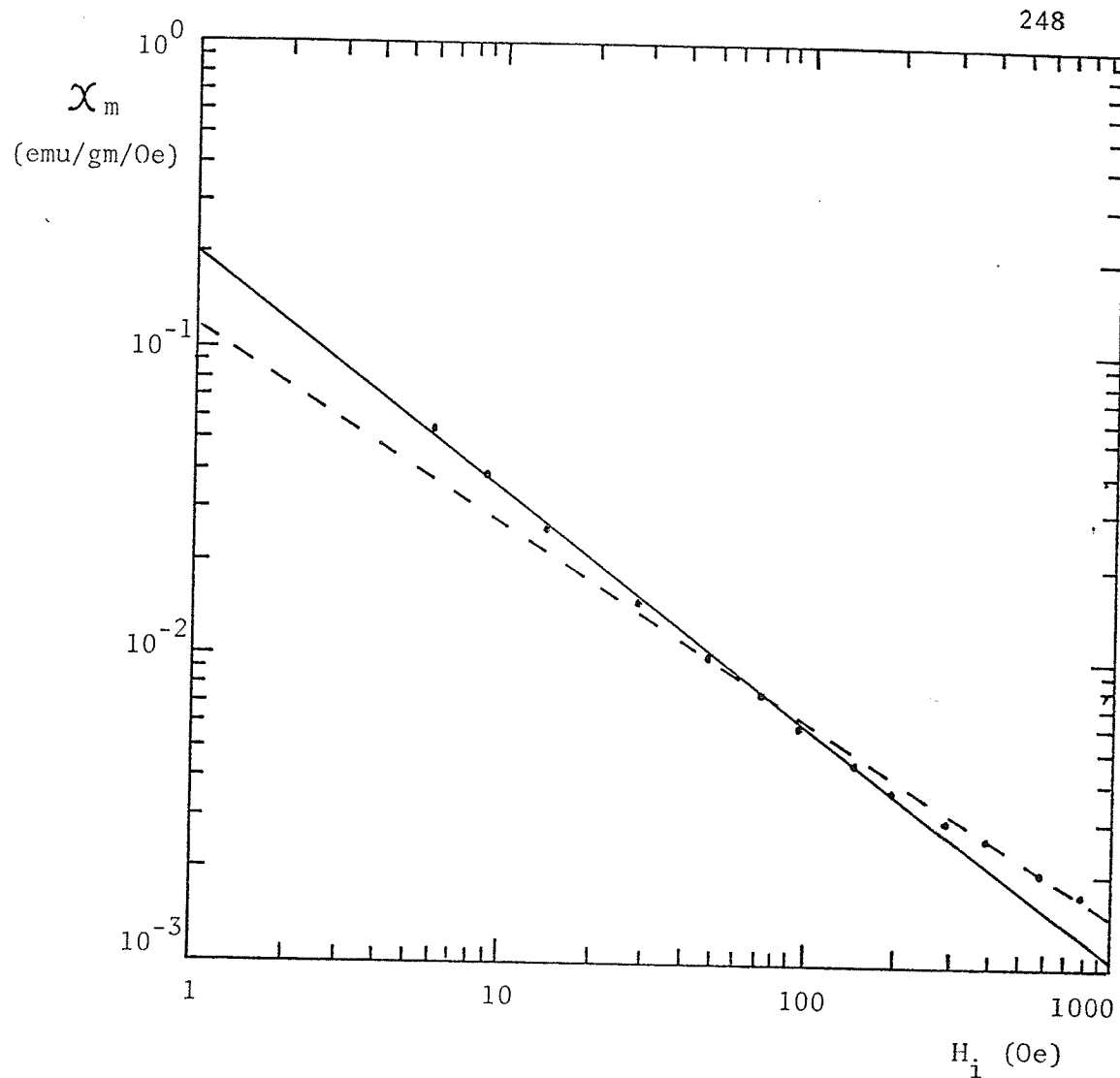


Fig. E.21 Susceptibility vs. H_i for Pd-4.5 at % Mn. (δ -plot)

APPENDIX F

RESISTIVITY DATA FOR ALL ALLOYS

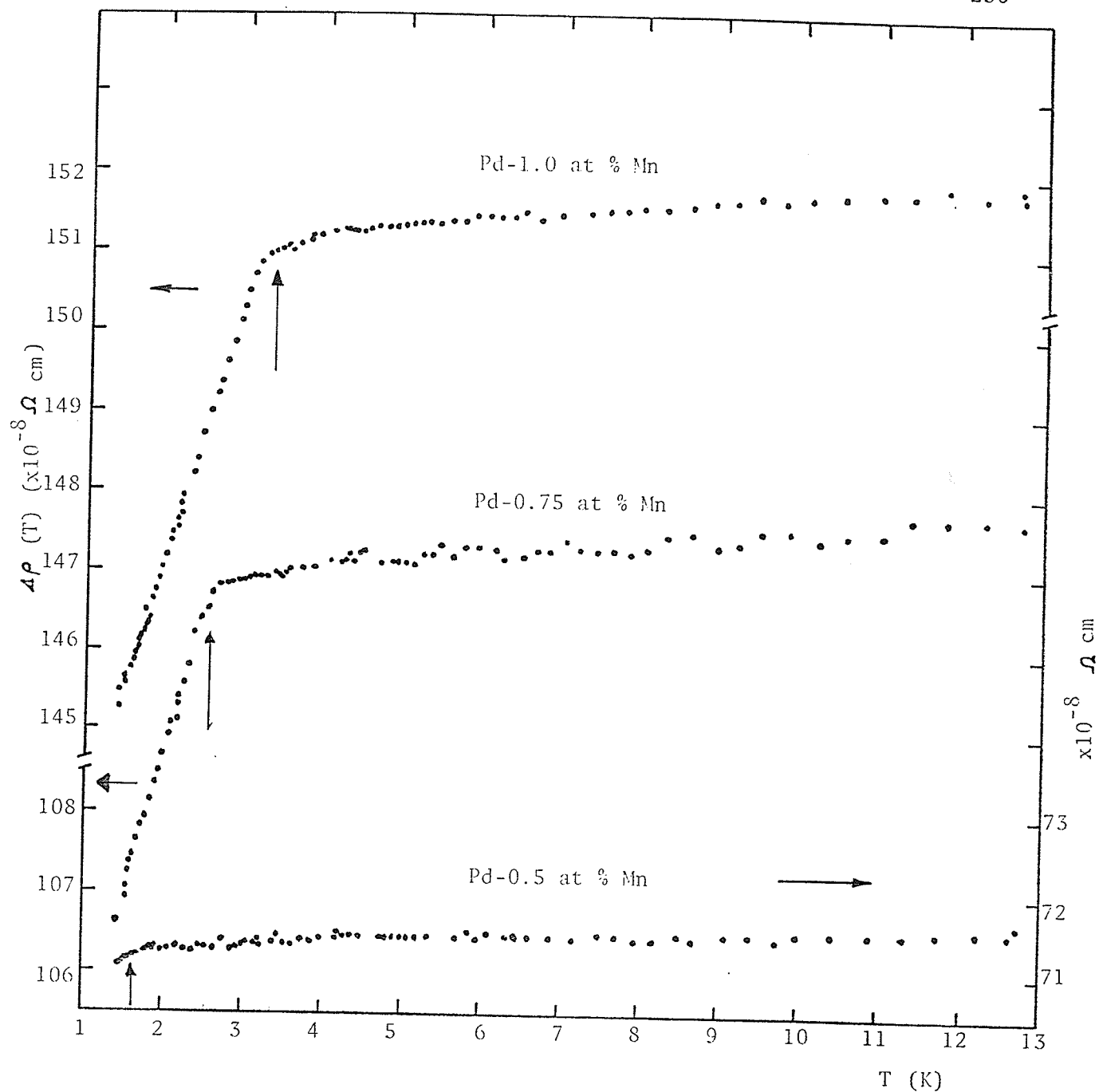


Fig. F.1

Incremental resistivity of Pd-0.5 at % Mn, Pd-0.75 at % Mn, and Pd-1.0 at % Mn. Vertical arrow indicates position of T_C from susceptibility data.

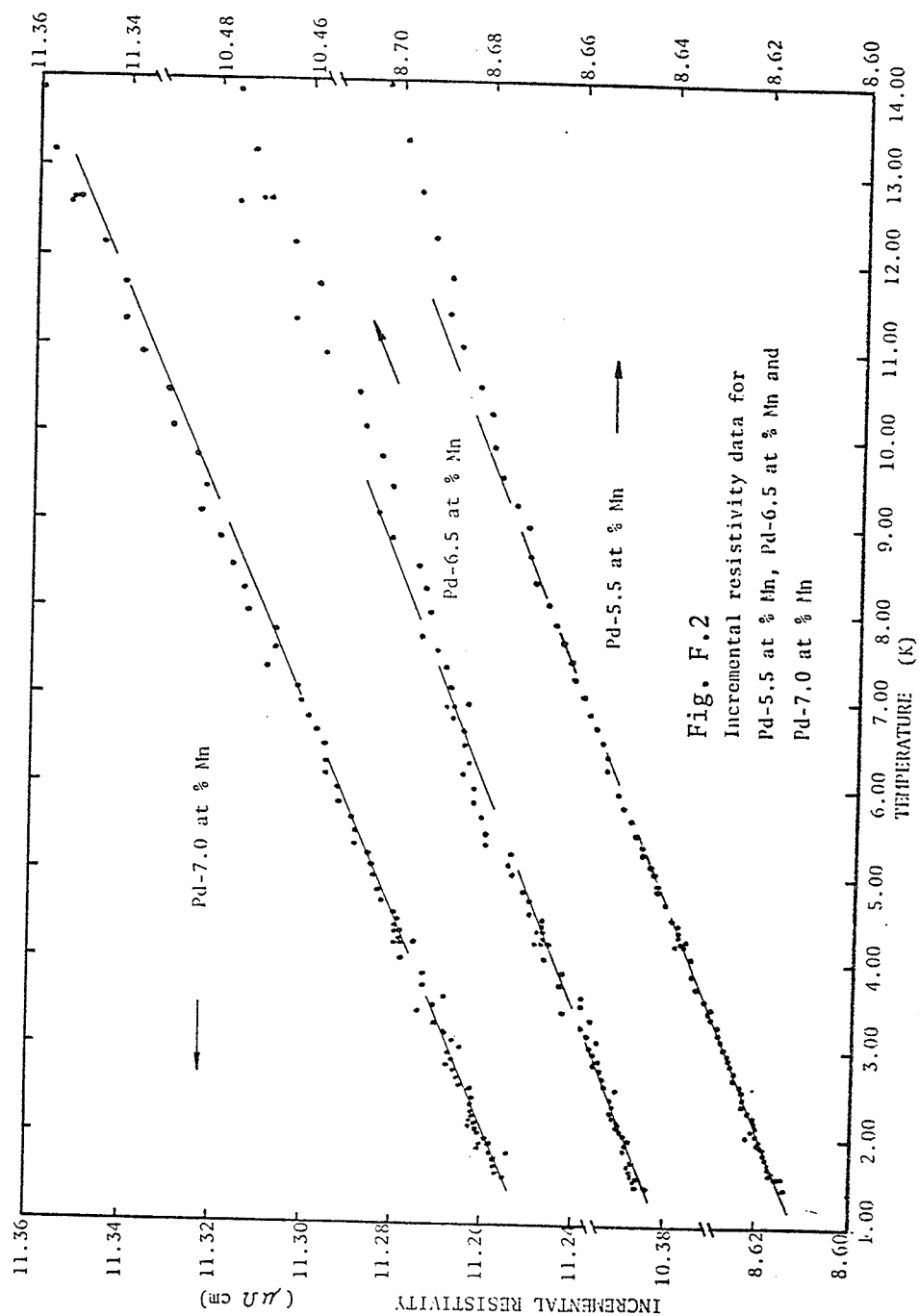
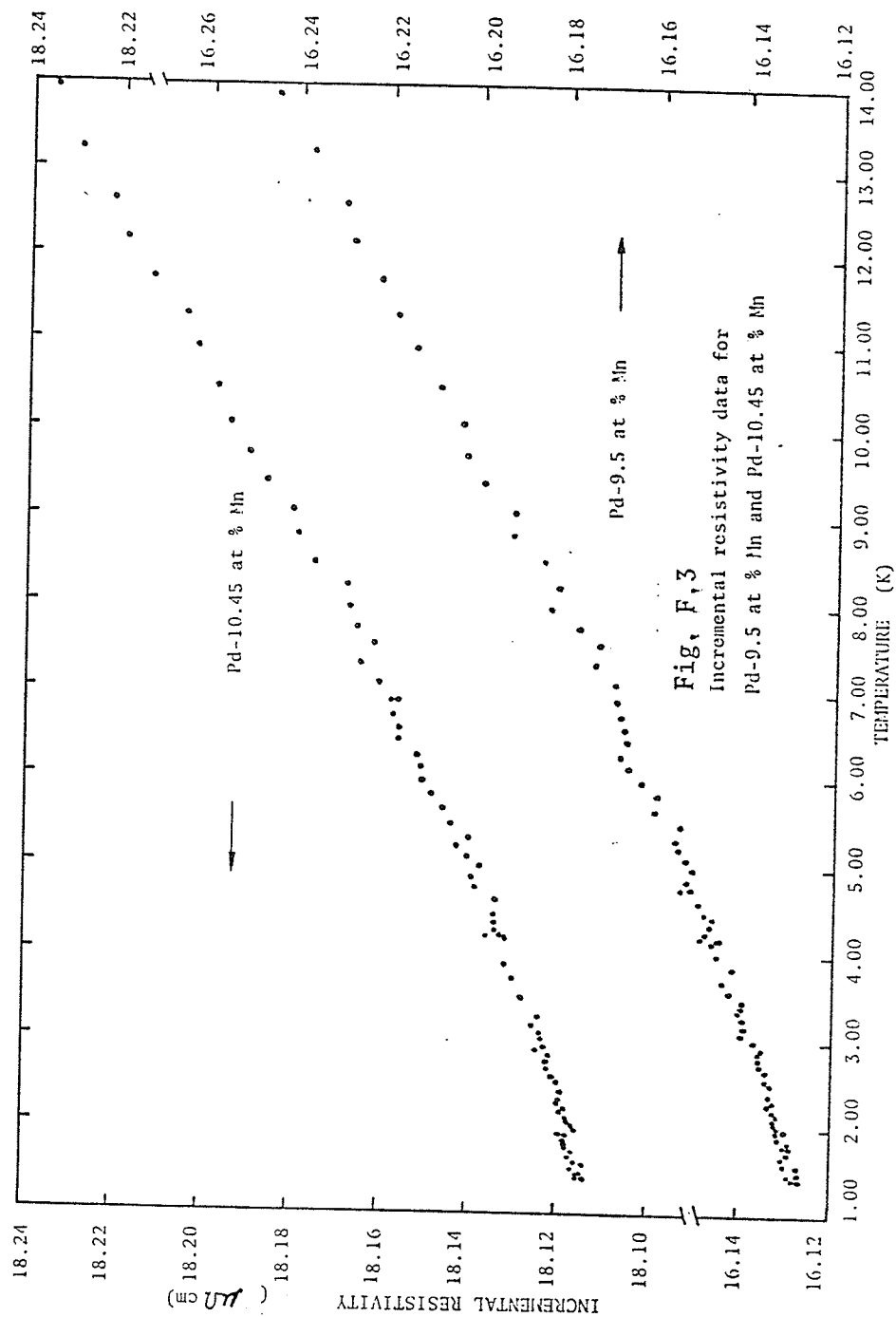


Fig. F.2
Incremental resistivity data for
Pd-5.5 at % Mn, Pd-6.5 at % Mn and
Pd-7.0 at % Mn



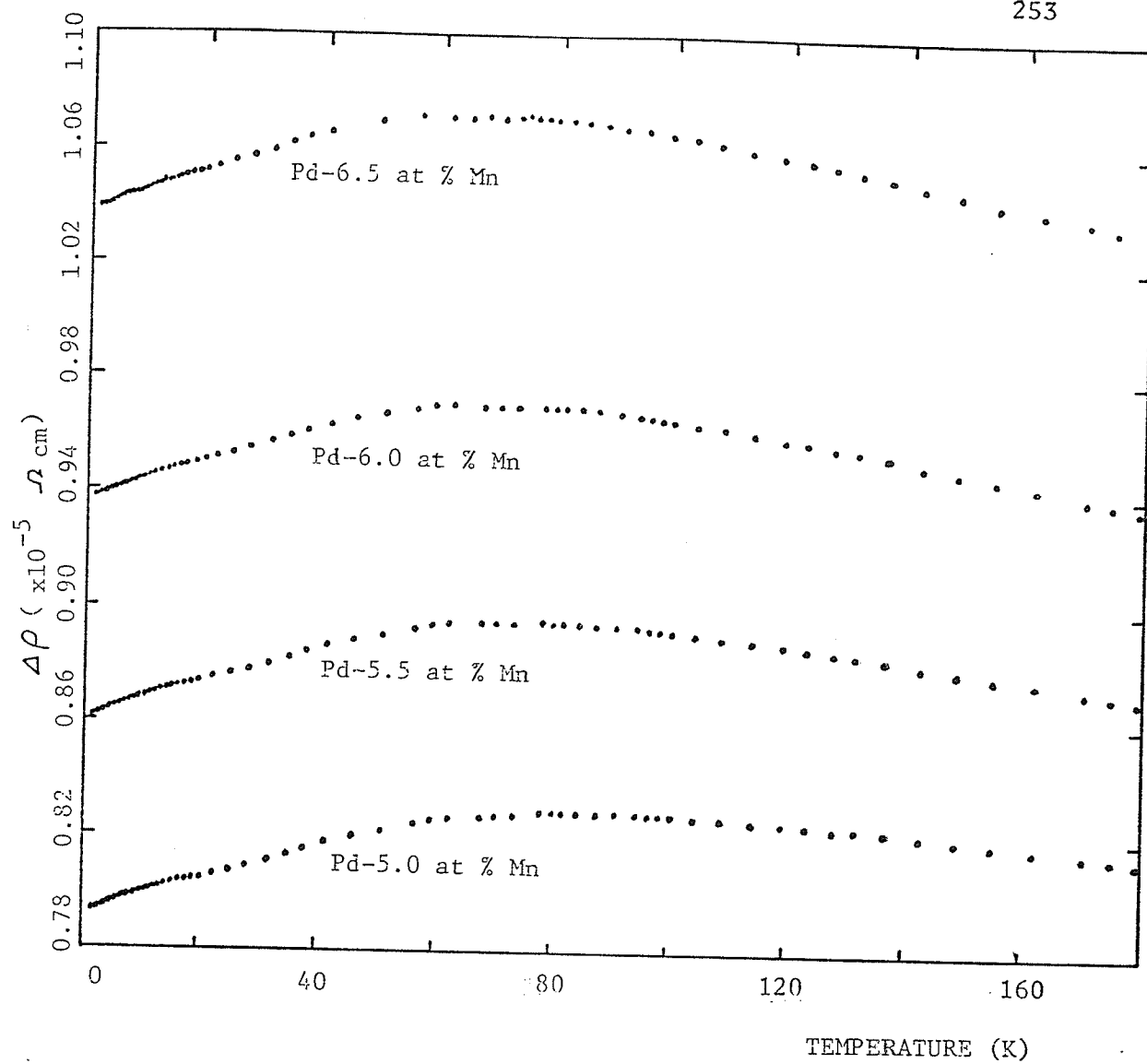


Fig. F.4 Incremental resistivity of Pd-Mn alloys.

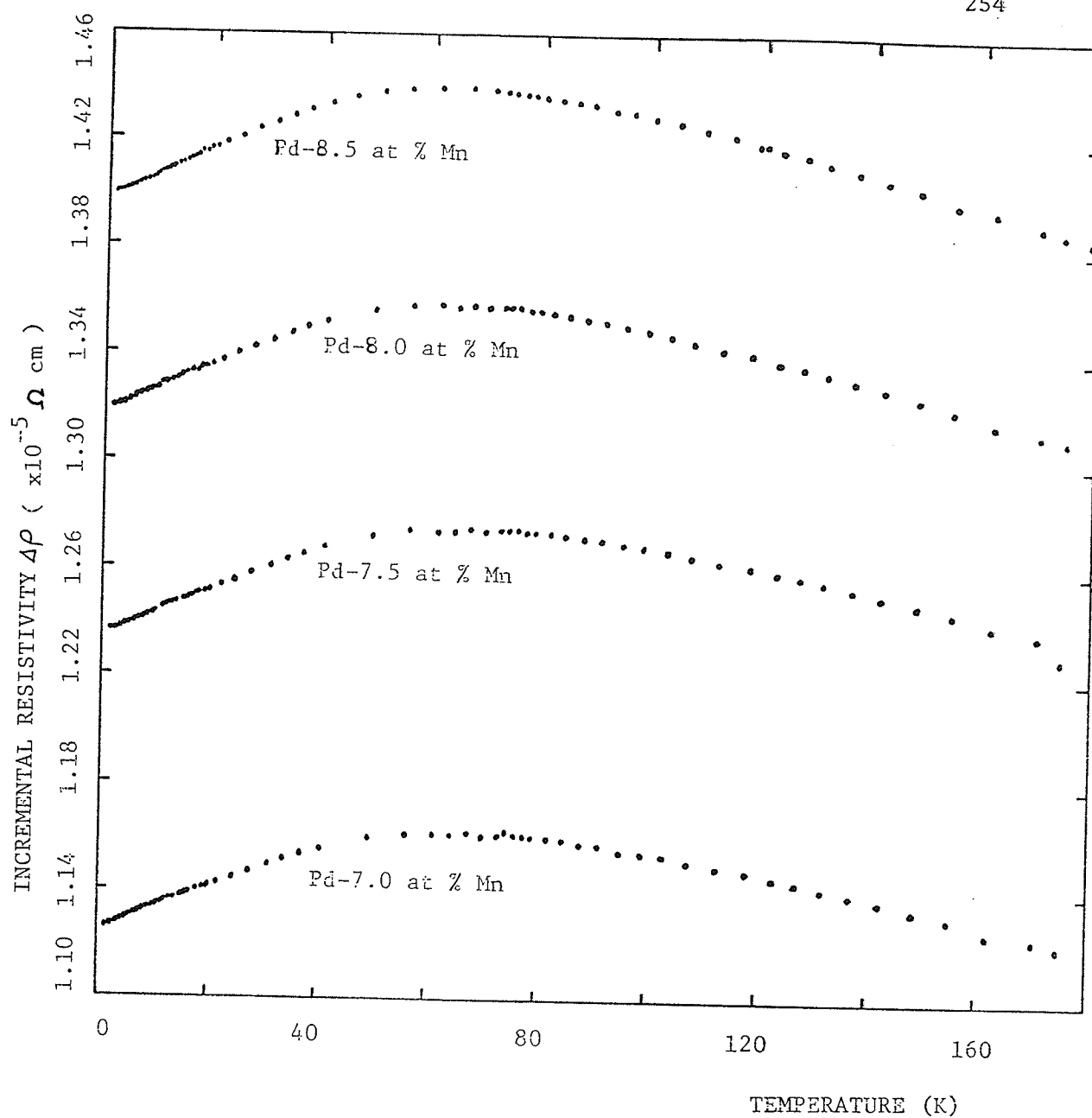


Fig. F.5 Incremental resistivity of Pd-Mn alloys.

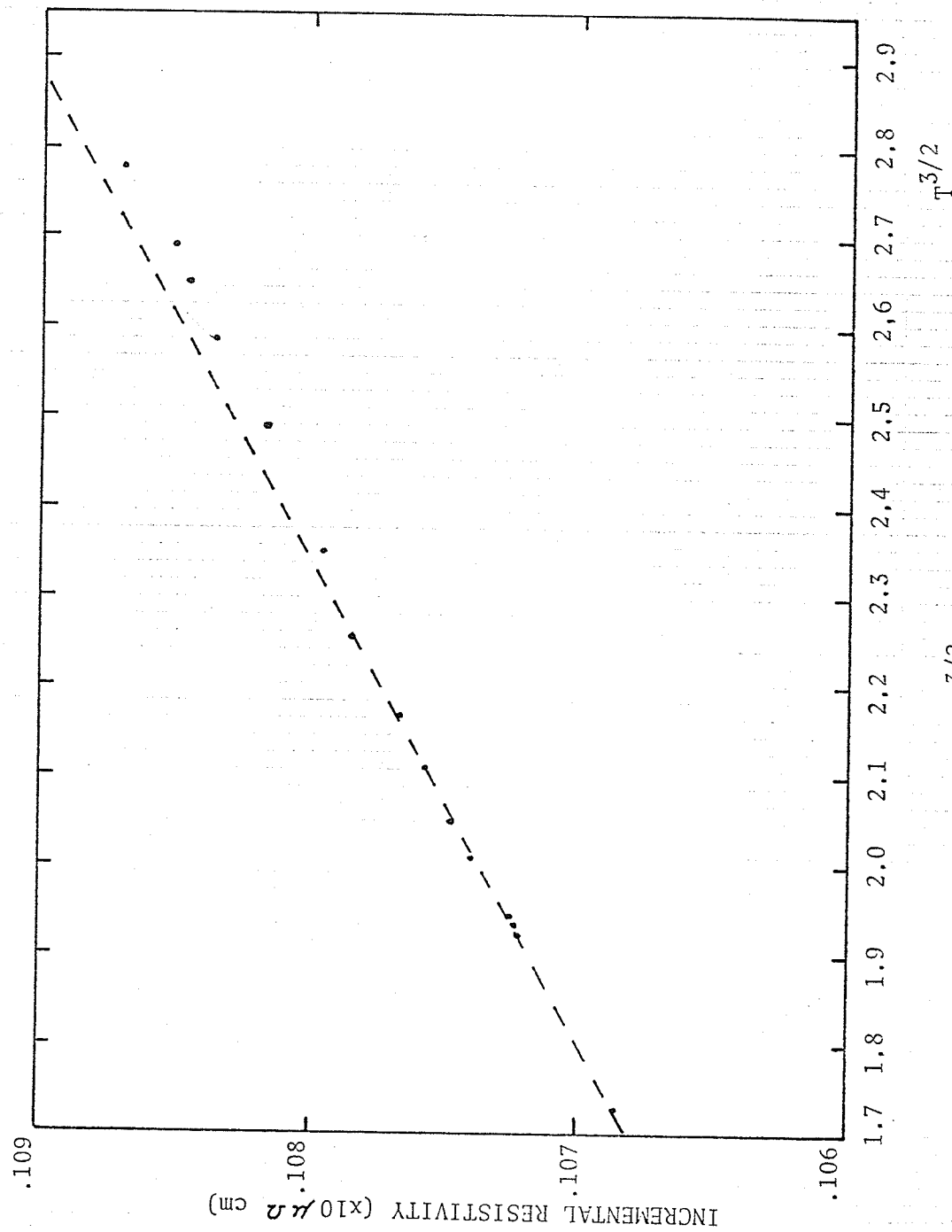
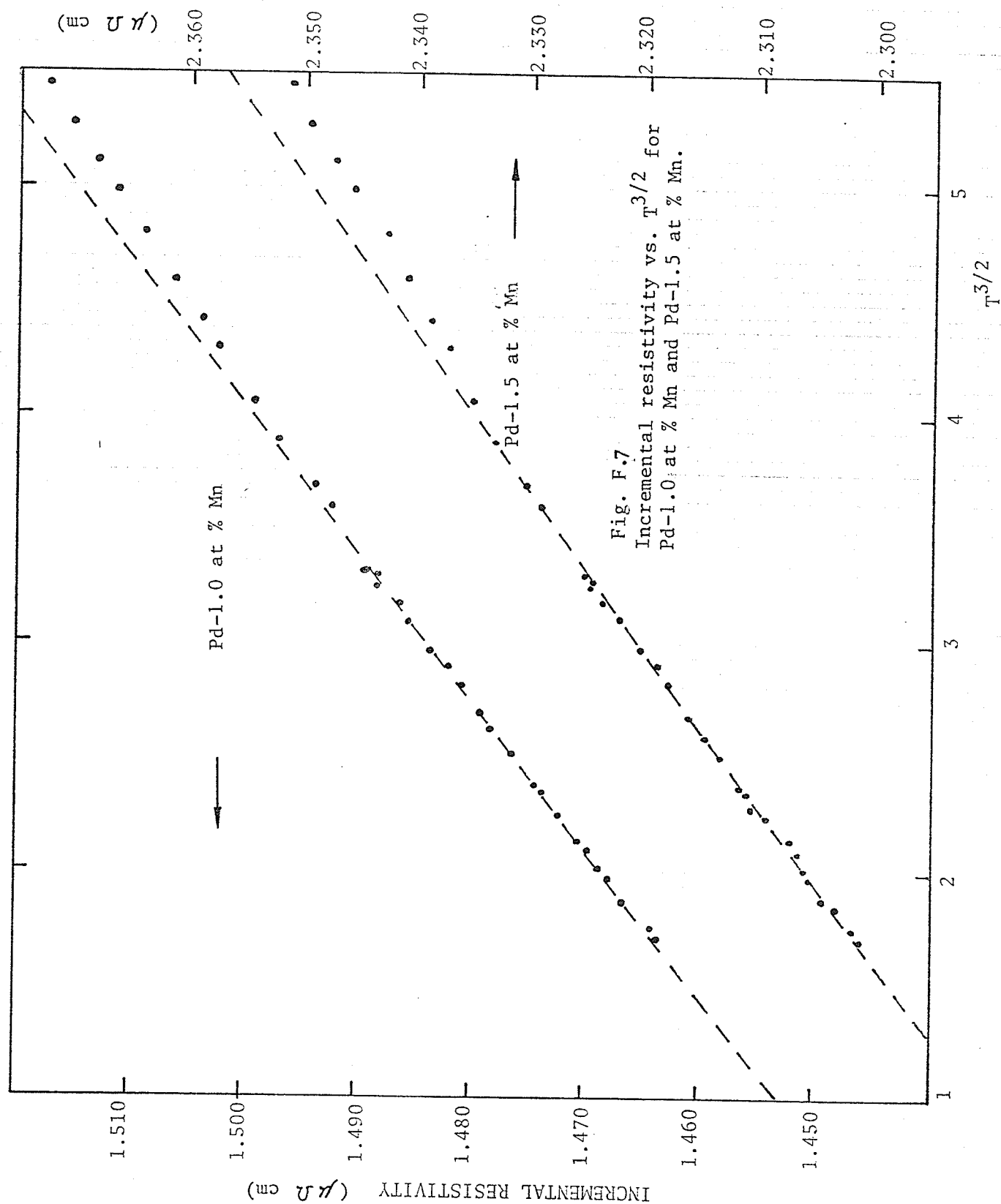


Fig. F.6 Incremental resistivity vs. $T^{3/2}$ for Pd-0.75 at % Mn.



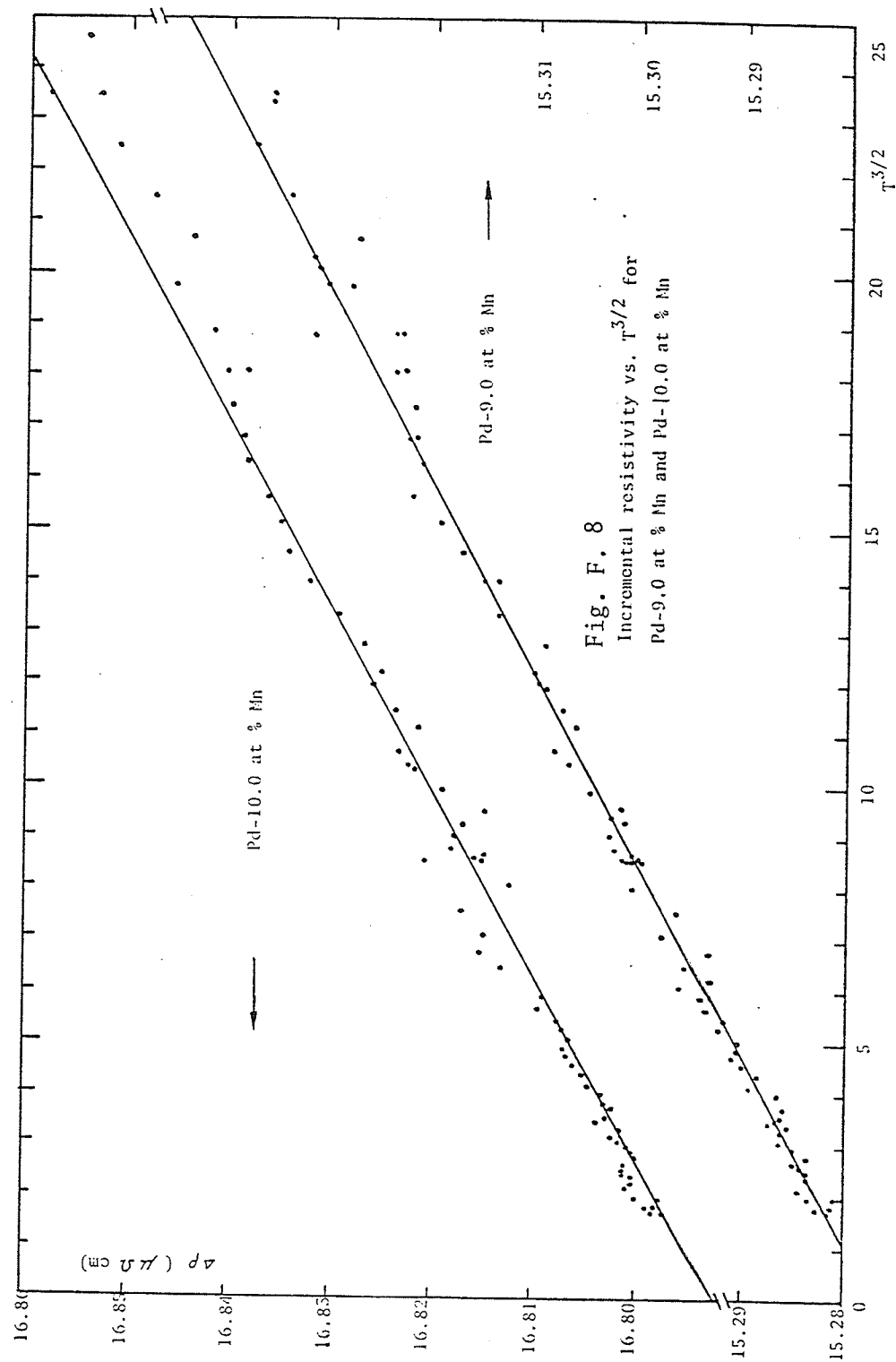


Fig. F. 8
Incremental resistivity vs. $T^{3/2}$ for
Pd-9.0 at % Mn and Pd-10.0 at % Mn

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