3846

NAME OF AUTHOR..*CHARLES THOMAS HAYWOOD*.......

TITLE OF THESIS..*ELECTRICAL RESISTIVITY MEASUREMENTS*

IN PALLADIUM AND PALLADIUM/

HYDROGEN ALLOYS.................

UNIVERSITY...*OF ALBERTA*..........................

DEGREE...*PH. D.*..............YEAR GRANTED...*1969*..........

Permission is hereby granted to THE NATIONAL

LIBRARY OF CANADA to microfilm this thesis and to

lend or sell copies of the film.

The author reserves other publication rights,

and neither the thesis nor extensive extracts from

it may be printed or otherwise reproduced without

the author's written permission.

(Signed)*C. T. Haywood*

PERMANENT ADDRESS:

439 Michener Park

Edmonton, Alberta

....

DATED*May 8*........19*69*

THE UNIVERSITY OF ALBERTA

ELECTRICAL RESISTIVITY MEASUREMENTS IN

PALLADIUM AND PALLADIUM/HYDROGEN ALLOYS

by

© CHARLES THOMAS HAYWOOD

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

EDMONTON, ALBERTA

SPRING, 1969

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled ELECTRICAL RESISTIVITY
MEASUREMENTS IN PALLADIUM AND PALLADIUM/HYDROGEN ALLOYS
submitted by Charles Thomas Haywood in partial fulfilment
of the requirements for the degree of Doctor of Philosophy.

....
Supervisor

....

....

....

....
External Examiner

Date ....May 2, 1969.....   ....

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled ELECTRICAL RESISTIVITY
MEASUREMENTS IN PALLADIUM AND PALLADIUM/HYDROGEN ALLOYS
submitted by Charles Thomas Haywood in partial fulfilment
of the requirements for the degree of Doctor of Philosophy.

....
Supervisor

....

....

....
External Examiner

Date ....May 2, 1969.....   ....

ACKNOWLEDGEMENTS

ABSTRACT

The resistivity of palladium and palladium/hydrogen alloys has been studied from liquid helium temperatures to room temperature. At low temperatures ($10^{\circ}K < T < 60^{\circ}K$), ρ_i was found to be well-represented by aT^n up to $H/Pd = 0.25$. For high concentrations and at low temperatures, the resistivity was found to be dependent upon time and upon the rate of cooling. These effects are presumed to be due to the transformation which produces a resistivity maximum near $55^{\circ}K$. The residual resistivity was lower for faster cooling rates. The characteristic temperature θ_r has been calculated for pure palladium and for the alloys. It was found to be in general accord with available results in the literature.

The resistivity in the presence of both a transverse and a longitudinal magnetic field has also been studied. The fractional change in resistivity, $\rho(H)-\rho(0)/\rho(0)$, is positive in all cases and decreases as the hydrogen content increases. The decrease, however, does not conform with Kohler's rule.

Finally, experiments on the systems tantalum/hydrogen and niobium/hydrogen showed that the increase in

resistivity due to 1 at. % of hydrogen in these metals is the same order of magnitude as for palladium. This indicates that comparison of these three systems would be worthwhile if the experimental difficulties in obtaining high hydrogen to metal ratios can be overcome.

TABLE OF CONTENTS

LIST OF FIGURES

Figure I-1

Plots of pressure-concentration isotherms for
palladium/hydrogen. The region to the left of
of the dashed curve corresponds to the α-phase.
The region to the right of the dashed curve cor-
responds to the β-phase. The region inside the
dashed curve corresponds to the mixed phase region
(Lewis,1967 p. 17)
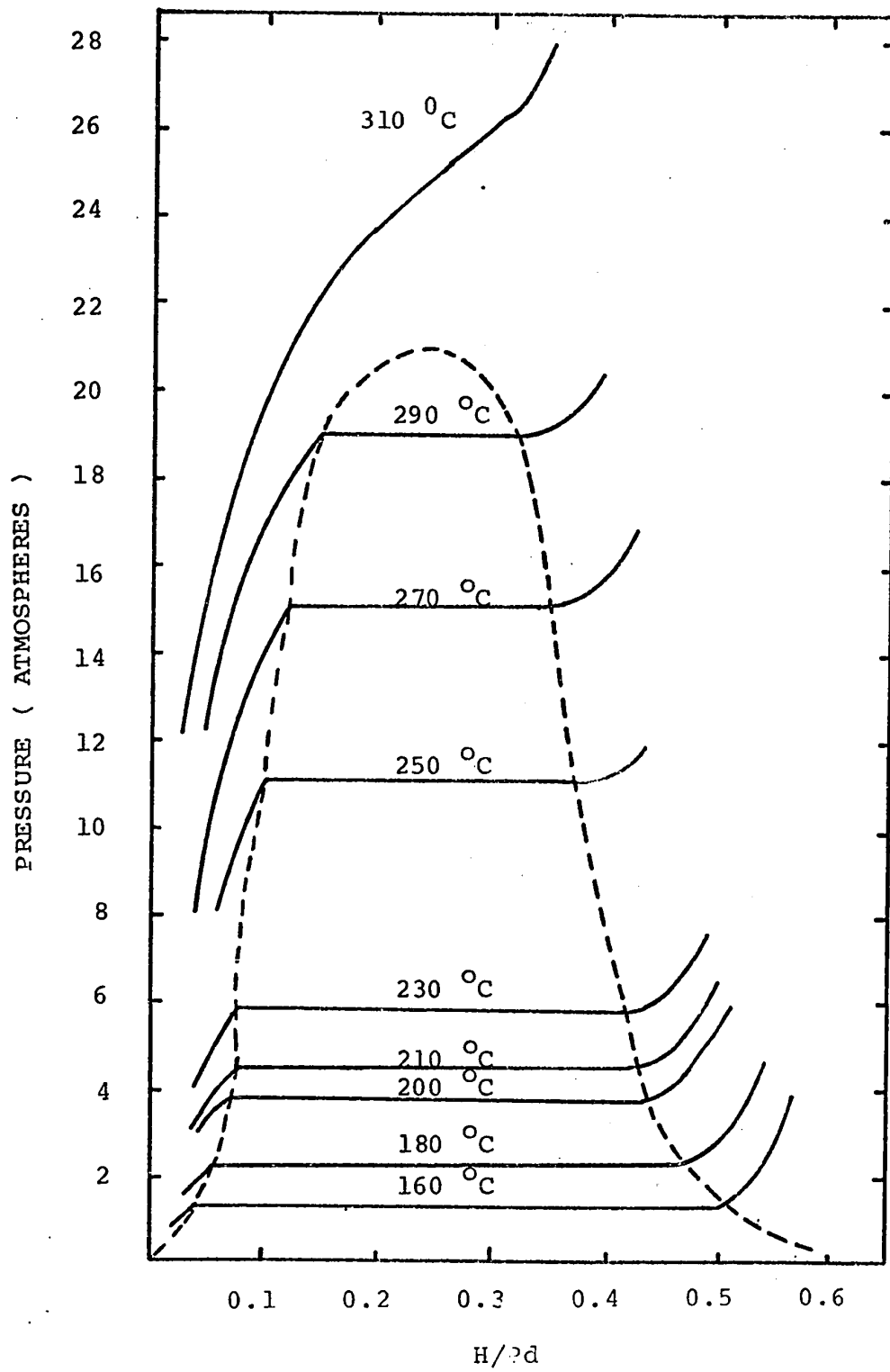
1967), nuclear magnetic resonance (Norberg, 1952), specific
heat (Mitacek and Aston, 1961), transport effects (Smith
et al., 1962; Schindler et al., 1959; Ho and Manchester,
1968), magnetic susceptibility (Gibb et al., 1966), para-
magnetic resonance (Shaltiel, 1963), de Haas-van Alphen
effect (Vuillemin and Priestley, 1965) have yielded interest-
ing, though often ambiguous and sometimes conflicting,
results.

Yet, many facets of the problem had not been
investigated. In particular, detailed data on the hydrogen
concentration dependence of the electrical resistivity for
a wide range of temperatures and concentrations were not
readily available; no time dependence of the electrical
resistivity due to the transformation near $50^{\circ}K$ had been
reported; nor were any data concerning the effect of this
transformation on the resistivity at other temperatures
available (particularly the residual resistivity). Also,
the effects of a magnetic field had been investigated only
in the low hydrogen concentration range. Furthermore,
palladium, being one of the homologous group known as the
transition metals, is not really well understood even in
its pure state.

It was felt that further progress in understanding
the general characteristics of the palladium/hydrogen

system required that broad investigations be carried out on samples with well documented histories. In order to carry this out, detailed measurements of the electrical resistivity of palladium and palladium/hydrogen alloys over the range of temperature from $4^{\circ}K$ to $300^{\circ}K$ were made. The specimens used were of high purity and, as far as possible, had similar histories. In addition, the magnetoresistance, both longitudinal and transverse, was studied. Finally, a limited number of measurements on niobium, tantalum, and their hydrogen alloys were made in order to see what similarities there might be among the three alloys systems.

Although these experiments constitute one of the most comprehensive investigations of transport properties of palladium/hydrogen alloys, other properties must be as thoroughly studied before the eventual interpretation becomes clear. It is felt by this author that the present experiments have clarified directions for future work.

CHAPTER I

A. The Mott Model

In terms of electronic behavior, the transition metals all possess the following properties:

      a. high electrical resistivity

      b. strong paramagnetism or ferromagnetism

The first successful attempts to explain these properties of the transition elements using the concepts of band theory in solids were made by N. F. Mott (Mott, 1936a; Mott, 1936b; Mott and Jones, 1936). His original ideas are still used and have been modified only slightly in most cases.

Mott started with the fact that the free atoms of the transition metals have an incomplete d shell either in the ground state or (in the case of palladium) in excited states of small energy. Thus, if one considers a small range of energy about the ground state energy, it is apparent that there is more than one atomic state which can exist in this range.

By definition, the transition metals have a Fermi surface lying in at least two zones. In some of them, for example palladium, it is probably a good approximation to

say that for the states near the Fermi surface, the wave
functions of states in one zone must be largely derived
from the 4d atomic functions and in the other from 5s
(and to a lesser extent 5p, 5d, etc.).

For palladium there are ten electrons to be shared
among these states. Probable configurations are:

$$4d^{10} \qquad\qquad 4d^9\,5s^1 \qquad\qquad 4d^8\,5s^2 \,.$$
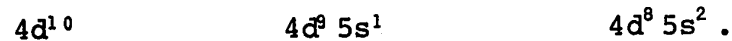
These configurations represent states with closed d-shells,
one positive hole in the d-shell, and two positive holes
in the d-shell, respectively.

It is characteristic of these metals that the
radius of the wave function of the d-states is considerably
smaller than that of the s-states. Thus, the s-electrons
account for nearly all of the binding energy and are the
more mobile carriers. A schematic graph of energy versus
the reciprocal of the atomic separation (after Mott and
Jones, 1936 p. 191) is given in Fig. 1.1 for the 4d and
5s states of palladium. The states lie close together in
the free atoms. However, when the atoms are brought together
to form a lattice, each quantized state broadens out into
a band of allowed energies; but, because the 4d orbits
are small, the broadening will be considerably less in the
d-band than the s-band. The density of states is thus

Figure 1.1

Schematic graph of energy versus the
reciprocal of atomic separation.

ENERGY
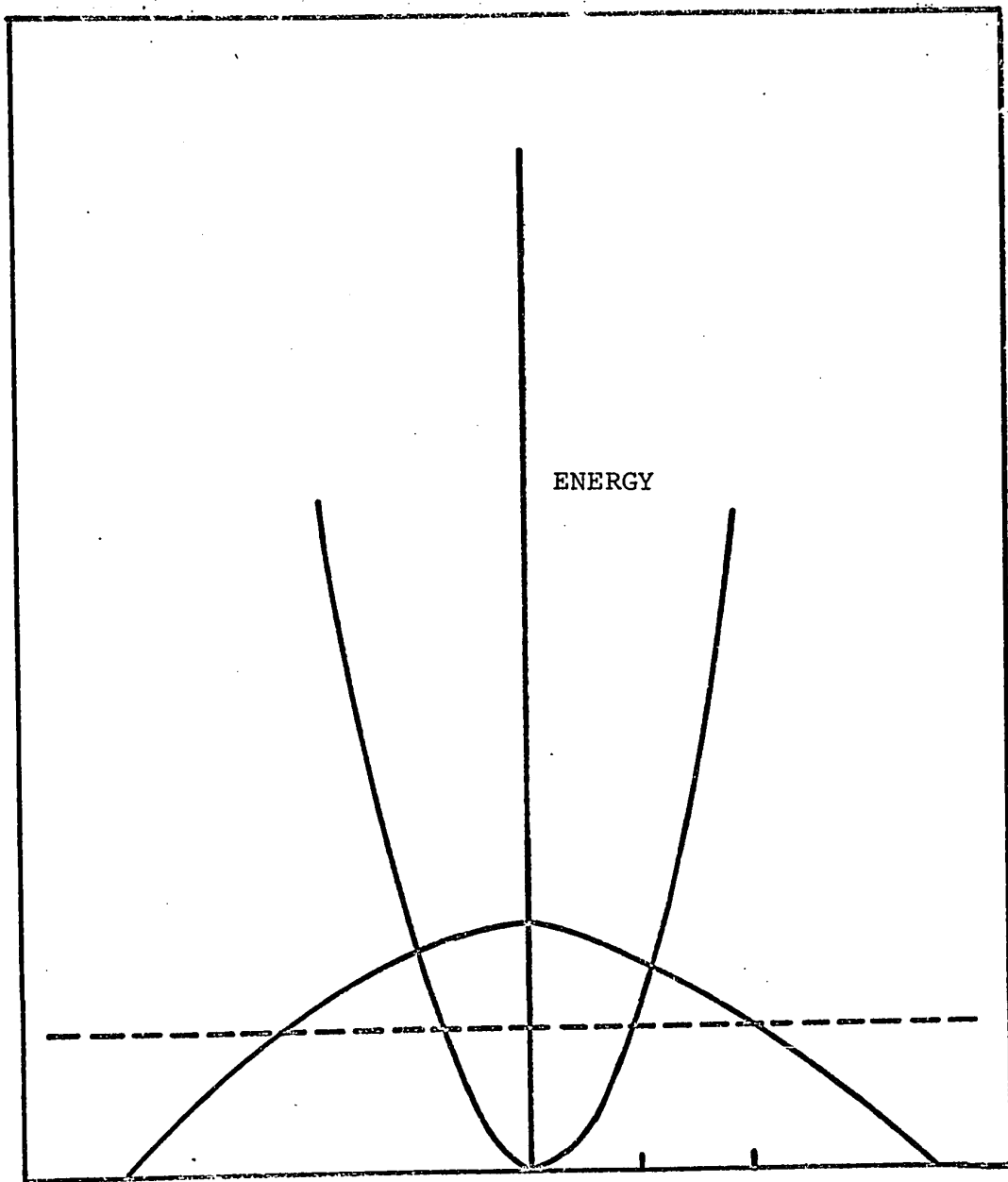
WAVE VECTOR $\vec{k}$

much higher in the d-band. Furthermore, if in a crystal of N atoms there are pN s-electrons, then there will also be pN positive holes in the d-band.

Were it not for the complications caused by the vacant states in the transition metals, one would expect to be able to describe their conduction properties fairly well, as is done with the monovalent metals, by the free-electron model. In this model the interaction with the ion cores is completely neglected. Using this model, the electrical conductivity σ is given by the well-known relation $\sigma = ne^2\tau/m$, where n is the number of electrons per unit volume, e the electronic charge, τ the relaxation time, and m the electronic mass.

Mott's explanation of the comparatively low electrical conductivity of these metals follows from the above picture of their band structure (Mott model). The d-electrons have a large effective mass and contribute a negligible amount to the conductivity. However, the vacant levels in the d-band have a considerable effect upon the conductivity of the s-electrons through inter-band transitions. That is, not only can a conduction electron be scattered into energy levels in the s-band (s-s transitions) but also into energy levels in the d-band

(s-d transitions). The s-d transition probability (Mott argued) is proportional to the density of empty states at the Fermi level in the d-band ; and, since this density of states is high, the s-d transition can be expected to give rise to a scattering probability which is much greater than normal. The d-band , then, acts as a trap into which s-electrons are scattered and lost from the current. It is this mechanism, absent from such metals as copper and silver (possessing filled d-bands) which decreases the electrical conductivity of the transition metals. It should be mentioned that the magnetic properties of the transition metals, though not of major importance to the present work, are also due to the presence of the unfilled d-states (Mott, 1964).

In order to describe quantitatively the electrical resistivity of a metal, one must consider in detail the three separate mechanisms which give rise to the resistance:

    a. scattering of electrons by phonons,

    b. scattering of electrons by other electrons,

    c. scattering of electrons by impurities
       or defects.

B. Electron-Phonon Scattering in Transition Metals

Wilson (1938, 1953) was able to develop equations describing the effects of electron-phonon interactions on the resistance. These results, though they cannot be used to predict the exact magnitude of this contribution to the resistance of metals, do predict a temperature dependence for the electron-phonon contribution. The salient features of this theory are worthy of review.

Using the wave vector $\vec{k}$ to define the states of the electrons, the number of electrons per unit volume whose wave vectors lie in the interval $d\vec{k} = dk_1 dk_2 dk_3$ is

$$\frac{1}{4\pi^3} f(\vec{k},\vec{r}) d\vec{k} \tag{1}$$

where $f(\vec{k},\vec{r})$ is the electronic distribution function. The net rate of increase of f due to collisions can be written as

$$\frac{df}{dt}\bigg|_{coll.} = \int W(\vec{k}',\vec{k}) f(\vec{k}') \{1-f(\vec{k})\} - W(\vec{k},\vec{k}') f(\vec{k}) \{1-f(k')\} \ dk', \tag{2}$$

where $W(\vec{k}',\vec{k})$ is the probability per unit time that an electron makes a transition from the state $\vec{k}'$ to the

state $\vec{k}$. The first term on the right hand side of (2) is the number of electrons per unit time forced into the state $\vec{k}$ and the second term is the number of electrons per unit time leaving the state $\vec{k}$. If the transitions are due to lattice vibrations with wave vector $\vec{q}$ and one assumes that the distribution function can be written $f = f_0 - \Phi \frac{\partial f_0}{\partial E}$, then (2) can be written

$$\frac{\partial f}{\partial t}\Big|_{coll.} = \frac{C^2 \Delta}{8\pi^3 MhkT} \int \frac{|\vec{q}|^2}{\nu_q} N_{\vec{q}} [f_0(\vec{k})\{1-f_0(\vec{k}+\vec{q})\}$$

$$\Omega(E_{\vec{k}}-E_{\vec{k}+\vec{q}}+h\nu_{\vec{q}}) + f_0(\vec{k}+\vec{q})\{1-f_0(\vec{k})\}\Omega(E_{\vec{k}}-E_{\vec{k}+\vec{q}}-h\nu_{\vec{q}})]$$

$$\{\Phi(\vec{k}+\vec{q}) - \Phi(\vec{k})\}d\vec{q} \quad , \tag{3}$$

if the initial and final states are in the same band (Wilson, 1953 p. 260). The quantity C is a constant with units of energy, M and Δ are the mass and volume of a unit cell respectively, $N_{\vec{q}}$ is the average number of phonons with wave-vector $\vec{q}$, and the quantity Ω is defined by

$$\Omega = \frac{\sin xt/h}{x/h} \quad . \tag{4}$$

In order to generalize equation (3) to describe the case of an electron transition from the s-band to the d-band

of a transition metal, Wilson assumes that both bands are parabolic. Taking the zero energy at the bottom of the s-band, the bands are then described by

$$E_s(\vec{k}) = \frac{h^2|\vec{k}|^2}{8\pi^2 m_s} \tag{5}$$

and

$$E_d(\vec{k}) = \frac{A-h^2|\vec{k}|^2}{8\pi^2 m_d} \qquad A > 0 \tag{6}$$

as shown in Fig. 1.2. The generalization then simply consists of a careful labelling of the initial and final states as to whether they are s- or d- states. The result is

$$\left[\frac{df_s}{dt}\right]_{s-d} = \frac{\bar{\omega}_d C_{sd}^2 \Delta}{8\pi^3 MhkT} \int \frac{|\vec{q}|^2}{v_{\vec{q}}} N_q [f_{os}(\vec{k})\{1-f_{od}(\vec{k}+\vec{q})\}$$

$$\times \ \Omega(E_{\vec{k},s}-E_{\vec{k}+\vec{q},d}+h\nu_q)+ f_{od}(\vec{k}+\vec{q})\{1-f_{os}(\vec{k})\}\Omega(E_{\vec{k},s}-E_{k+\vec{q},d}-h\nu_q)]$$

$$\times \ \{\Phi_d(\vec{k}+\vec{q}) - \Phi_s(\vec{k})\}d\vec{q} \ , \tag{7}$$

where $\bar{\omega}_d$ is a weight factor for the d-band. The integration of (7) is outlined by Wilson and leads to an integral of the form

Figure 1.2

The assumed form of the energy bands in
a transition metal.

ENERGY

5s

4d

1/d
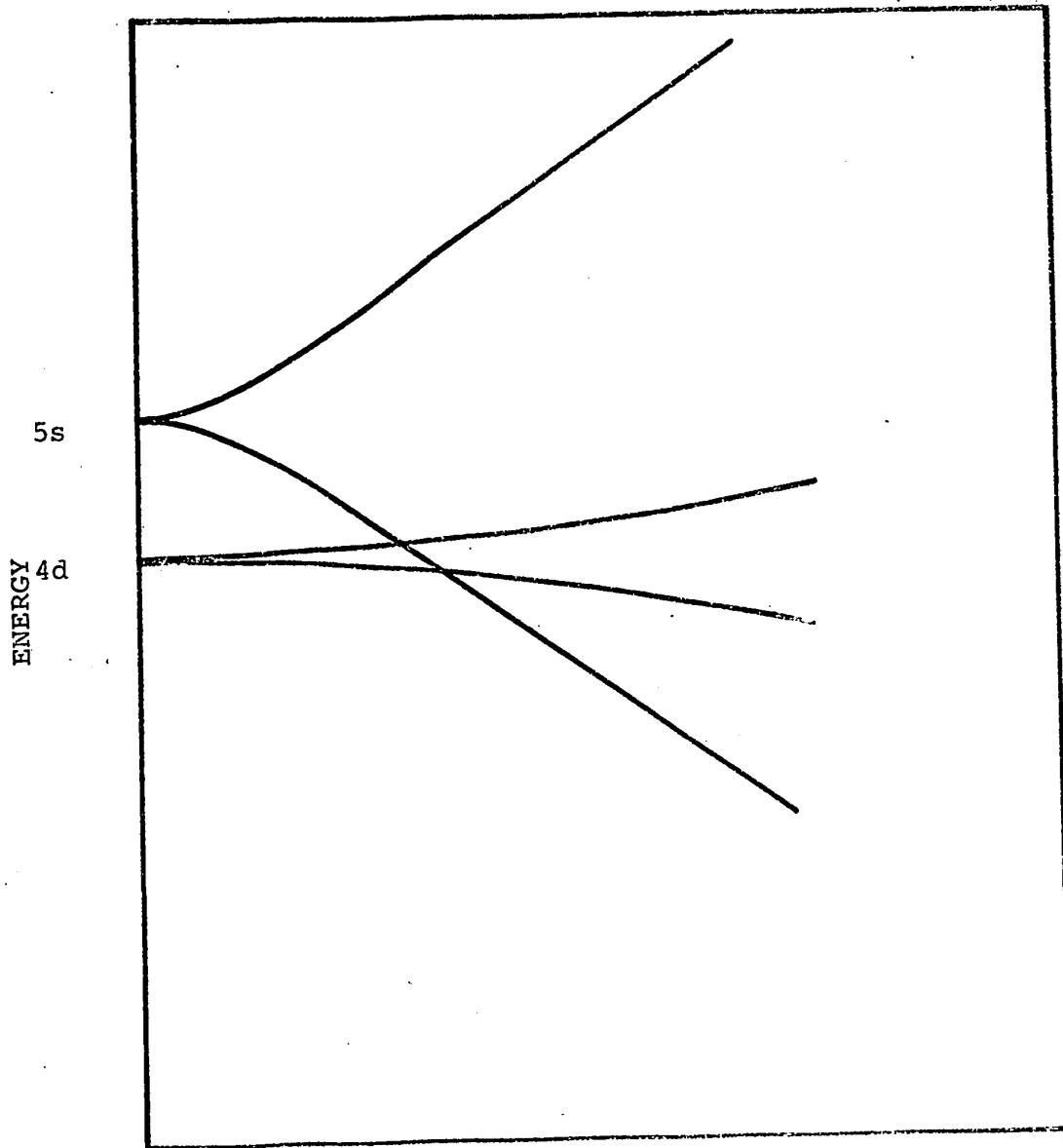
$$\int_{\phi=\pi}^{\phi=0} \frac{\sin y}{y} \, dy \tag{8}$$

where ϕ is the angle between the vectors $\vec{k}$ and $\vec{q}$, and y is defined by

$$y = 2\pi t(E_{\vec{k},s} - E_{\vec{k}+\vec{q},d} \pm h\nu_q)/h = \frac{2\pi t}{h}[\frac{h^2}{2}(\frac{1}{m_s} + \frac{1}{m_d})k^2$$

$$\frac{h^2}{2m_d}(2k_q\cos\phi + q^2) - A \pm h\nu_q] \tag{9}$$

The integral (8) is zero unless the limits of integration are of opposite signs. Neglecting the term $h\nu_q$, the upper limit is positive if

$$q > \sqrt{\frac{2Am_d}{h^2} - \frac{m_d}{m_s}k^2} - k \tag{10}$$

Since only electrons near the top of the Fermi distribution may contribute to the conductivity, k may be replaced by k_s. Using (5) and (6), k_s and k_d can be related by noting that at $T = 0°K$

$$\frac{h^2|\vec{k}_s|^2}{8\pi^2 m_s} = \frac{A - h^2|\vec{k}_d|^2}{8\pi^2 m_d} \quad .$$

The condition (10) then becomes

$$q > k_d - k_s \ . \tag{11}$$

Similarly, the lower limit is negative if

$$q > k_s - k_d \ . \tag{12}$$

The condition for an s-d transition to be possible then becomes

$$q > |k_d - k_s| \ . \tag{13}$$

The condition (13) can be understood from Fig. 1.2, by noting that when an electron jumps from a point on the s-sphere in k-space to the nearest point on the d-sphere, $\vec{k}$ and $\vec{k}'$ will have the same direction and thus

$$q = |k_d - k_s| \ .$$

Wilson is also able to obtain the temperature dependence of the contribution to the electrical resistivity due to phonon induced s-d transitions. The result is (Wilson, 1953, p. 272; Colquitt, 1965)

$$\rho_{phonon})_{s-d} = \frac{3h^3 \omega_d m_d P_{sd}}{8\pi^2 (2m_s)^{1/2} e^2 E_F} \left(\frac{T}{\theta_D}\right)^3 [J_3(\frac{\theta_D}{T}) - J_3(\frac{\theta_E}{T})] \tag{14}$$

where

$$J_n(x) = \int_o^x \frac{z^n \, dz}{(e^z-1)(1-e^{-z})} \tag{15}$$

and θ_D is the Debye characteristic temperature. P is a matrix element connecting the states labelled by its subscripts. θ_E is defined through the relation $k\theta_E = h\nu_E$, ν_E being the frequency corresponding to the minimum value of $\vec{q}$ necessary for a phonon-induced transition.

The phonon-induced resistivity also consists of a part due to s-s transitions. This can be written (Wilson, 1953, p. 263; Colquitt, 1965)

$$\rho_{phonon}\bigg|_{s-s} = \frac{2m_s P_{ss} 3h^3}{16\pi(2m_s)^{1/2} e^2 E_F} (\frac{T}{\theta_D})^5 2^{-1/3} n^{-2/3} J_5(\frac{\theta_D}{T}) \quad . \tag{16}$$

C. Electron-Electron Interactions

The contribution to the resistivity due to the scattering of electrons by other electrons was described first by Baber (1937) and later by Appel (1963). Baber's results are obtained by calculating an expression for $1/\tau$, the reciprocal of the relaxation time, by assuming a screened coulomb interaction between the s-electrons and the d-holes. Using the Mott model for the band structure and the Born approximation to describe the scattering, he obtains an expression for ρ which may be

written in the form

$$\rho = \text{const.} \left(\frac{kT}{\xi}\right)^2 \qquad (17)$$

ξ is the breadth of the s-band and the constant depends only on such factors as the screening constant, mass ratio for the carriers in the s-band and d-band, and number of electrons per unit volume.

Baber explains this T^2 dependence for the resistivity due to electron-electron scattering qualitatively in the following manner. In a transition the s-electron cannot lose energy greater than about kT since it must jump into an unoccupied state. Conservation of energy then dictates that the d-electron with which it makes a collision cannot gain more energy than kT. It follows that this d-electron must, both before and after the collision, be in a state lying in a range kT at the surface of the Fermi distribution. If ξ_2 is the Fermi energy for the d-electrons, then, roughly, out of all of the possible collisions with d-electrons, only a fraction $(kT/\xi_2)^2$ is allowed by the exclusion principle.

Appel (1963) uses a formalism quite different from that of Baber, but Appel also obtains a T^2 dependence for the electron-electron interband scattering

contribution to the resistivity. Appel's calculations do not depend on the assumption of a relaxation time, which is usually not justified at low temperatures (Howarth and Sandheimer, 1953). He considers the charge carriers to be quasi-particles described by a collision operator and uses the variational principle to calculate their interactions.

D. Matthiessen's Rule

The part of the electrical resistivity due to the scattering of electrons by impurities or lattice defects is usually handled by simply considering it to be temperature independent. Thus one writes $\rho = \rho_o + \rho_i(T)$, ρ_o being the residual resistivity $\rho(T=0^oK)$ due to impurities and lattice defects and $\rho_i(T)$ being the temperature dependent portion of the resistivity which appears at finite temperatures. If Matthiessen's rule is valid, $\rho_i(T)$ will be the same function regardless of the state of the metal, i.e. independent of ρ_o. Though basically an experimental law, Matthiessen's rule has some theoretical basis and is only expected to hold provided (Jones, 1956):

   i.   the temperature is high enough that all thermal scattering is elastic,

   ii. the electrons may be considered quasi-free, i.e. $E \alpha k^2$,

iii.   the thermal motion of the lattice does not

       affect the scattering potential,

iv.   the impurity atoms do not affect the thermal

       motion of the lattice,

v.   the impurity atoms do not change the

       effective number of conduction electrons.

E.   The Non-Rigid Band Theory of Palladium Alloys

A simple interpretation of experiments on certain palladium alloys implies that there must be approximately 0.55 holes/atom in the palladium d-band. This may be inferred from magnetic susceptibility studies on palladium/hydrogen, palladium/gold, and palladium/silver (Mott and Jones 1936, pp 199-200). In these alloys, the magnetic susceptibility vanishes near atomic concentrations of 0.55. This vanishing of the magnetic susceptibility, presumably, is due to the filling of the palladium d-band. Thus, using the rigid band model, it has been assumed that there must be 0.55 holes/atom to be filled.

It was these results which lent credibility to the Mott model for the band structure of the transition metals and aided Coles and Taylor (1962) in explaining the transport properties of the palladium/silver alloy series with striking success. However, Vuillemin and Priestley (1965)

investigated the Fermi surface of palladium using
de Haas-Van Alphen measurements and found that it contains
0.36±0.01 s-electrons per atom. This implies that there
are also 0.36 holes/atom in the d-band. This result is
consistent with the measurements of the high field Hall
coefficient by Alekseevskii et al. (1964), leaving little
doubt that the correct value for the number of d-holes per
atom is 0.36 instead of the previously accepted 0.55.

Dugdale and Guénault (1966) modified the Mott
model slightly and were able to explain satisfactorily both
the electrical resistivity and thermoelectric power of
palladium/silver. They assumed that when palladium is
alloyed the s-band moves relative to the d-band in such a
way as to accomodate the additional s-electrons. This is
the basic idea of non-rigid bands and was suggested by
earlier work of Lettington (1965) on the optical properties
of α-brasses.

The important point for the present work is that
Dugdale and Guénault have shown that it is possible to
account for the difference in the number of d-holes in pure
palladium and the number deduced from results in palladium/
silver by making very simple assumptions about the palladium
band structure.

F.   Conduction in the Presence of a Magnetic Field—

Magnetoresistance

The theory of magnetoresistance effects has been reviewed by Jan (1957), Chambers (1960), Fawcett (1964) and others. Jan (1957) pointed out that any theory of the change in resistance in a magnetic field should account for the following experimental facts:

(a) the change is usually an increase which is larger for transverse fields than for longitudinal fields, but the same order of magnitude in both cases

(b) in small fields it is usually quadratic with the applied field and linear (or saturates) in very large fields.

In specimens with geometry such as that presently used, the simple free-electron model gives zero magneto-resistance due to the cancellation of the Lorentz force on the electrons by the transverse Hall electric field. Thus magnetoresistance is said to be a measure of the departure from the free-electron model. The simplest model which gives a nonvanishing (transverse) magnetoresistance is the two-band model. The two bands are assumed to be of the normal form and overlap. This model is representative of

the transition metals.

Let $\vec{j}_e$ and $\vec{j}_h$ be the current densities in each band due to electrons and holes respectively. Both currents are subject to the same electric field $\vec{E}$ and make angles ϕ_e and ϕ_h with this field (these are the Hall angles). The net current $\vec{j} = \vec{j}_e + \vec{j}_h$ makes an angle ϕ with the field $\vec{E}$. Using purely geometric arguments, one can show (Jan, 1957)

$$\frac{\rho(H) - \rho(0)}{\rho(0)} = \frac{\Delta\rho}{\rho(0)} = \frac{\dfrac{\sigma_e \sigma_h}{e^2 (\sigma_e + \sigma_h)^2}\left(\dfrac{\sigma_e}{n_e} + \dfrac{\sigma_h}{n_h}\right)^2 H^2}{1 + \dfrac{\sigma_e^2 \sigma_h^2 (n_e - n_h)^2}{e^2 (\sigma_e + \sigma_h)^2 n_e^2 n_h^2} H^2} , \qquad (18)$$

assuming that the conductivity in zero field is given by $\sigma_e + \sigma_h$. This equation predicts some of the phenomena observed experimentally. For low fields $\Delta\rho$ is proportional to H^2, while for higher fields this quadratic behavior still holds if $n_e = n_h$; but $\Delta\rho/\rho(0)$ becomes independent of field otherwise. Furthermore, $\Delta\rho/\rho(0)$ in equation (18) can only have positive values.

Kohler (1938) was able to show theoretically that the dependence of the magnetoresistance on temperature, magnetic field and purity of the sample should be a function of τH alone. Noting that $\tau \propto \dfrac{1}{\rho}$, Kohler's rule can be

written as

$$\frac{\Delta\rho}{\rho(0)} = f\left(\frac{H}{\rho(0)}\right) \qquad (19)$$

for both transverse and longitudinal magnetoresistance. Kohler's rule is only an approximation, and deviations indicate that different types of scattering mechanisms have different effects on different groups of carriers (Ziman, 1964, p 218).

CHAPTER II   EXPERIMENTAL METHODS

A.   Palladium and the Palladium/Hydrogen Alloys

All palladium specimens (pure and hydrided) were prepared from the same roll of 0.01 inch diameter were obtained from Johnson, Matthey and Co. Ltd.   This wire had a stated purity of 99.999%.   A spectographic analysis of the impurities is given in Appendix II.

Potential and current leads of the same palladium wire were attached to the specimens by fusion in a vacuum. To accomplish this, the ends of the leads were wrapped tightly around the specimen and this junction was bombarded by electrons ejected from an electron gun.   The junction was melted by setting the accelerating potential at approximately 2 kilovolts and increasing the filament current until it was white hot.   This resulted in a beam current of approximately 50 ma.   A pressure of less than 10^{-5} mm of Hg. was required to prevent sparking.

For annealing, the specimens were placed in an alumina tube which was inserted in a wire-wound furnace available in the physics department.   It was found that annealing in helium at one atmosphere produced specimens with the lowest residual resistivity.   Annealing in vacuum

was not satisfactory because the results, as determined by
the residual resistivity ratio, were not reproducible. If
the annealed specimens were allowed to cool to room tempera-
ture in the presence of the helium gas, however, the metal
surface was left with a slight blueish deposit. In order
to obtain the minimum value of the ratio $R_{4.2^oK}/R_{293^oK}$
and a clean specimen surface, the following procedure was
adopted: (1) the alumina tube containing the specimen was
first evacuated and then helium gas was passed through a
liquid nitrogen trap into the tube; (2) the oven was then
turned on and brought to a temperature of approximately
900^oC which was maintained for 4 hours; (3) the oven was
then allowed to cool to 400^oC;(4) at 400^oC the oven was
evacuated to a pressure of less than 10^{-5} mm of Hg., and
the oven was allowed to cool to room temperature. To
illustrate the effects of this treatment, typical resistivity
values for a specimen are given in Table 2.1.

After annealing, the specimen (including leads)
was charged to the desired hydrogen concentration by using
it as the cathode in an electrolytic cell containing 0.1 N
sulfuric acid as the electrolyte and a platinum wire as the
anode. A current of 1 ma was used in most cases; however,
for the higher concentrations 0.5 ma was used. The hydrogen
concentration was determined both from the electrolysis

TABLE 2.1

ELECTRICAL RESISTIVITY $(\mu\Omega\text{-cm})$ OF TYPICAL SAMPLE

Conditions	$\rho_{273^{\circ}K}$	$\rho_{4.2^{\circ}K}$	$\rho_{4.2^{\circ}K}/\rho_{273^{\circ}K}$
As received	10.14	17.5×10^{-2}	17.2×10^{-3}
After annealing	10.03	0.961×10^{-2}	0.958×10^{-3}

data and from the change in resistivity at $0^{\circ}C$ (Barton, Lewis, and Woodward, 1963; Simons and Flanagan, 1966). As revealed by the data in Table 2.2, for low concentrations the electrolysis data can be a good indication of the hydrogen concentration; while for higher concentrations they are not reliable. In general, when one attempts to add the hydrogen too rapidly the electrolysis data will always indicate more than the true hydrogen content, even at fairly low concentrations. It was found that, at or below room temperature, the rate of loss of hydrogen was negligible after the specimens were removed from the electrolytic cell.

For the temperature dependent studies, typical specimen length was 20 cm. The specimens were coiled before the annealing treatment and occupied a length of approximately 5 cm in the cryostat. The specimens that were used for the longitudinal magnetoresistance were approximately 9 cm in length. In order to have specimens in which the electrical current was at right angles to the magnetic field, specimens of about 20 cm were wound on a threaded nylon coil of about 1.5 cm length. Placing the axis of the coil parallel to the axis of the superconducting solenoid resulted in approximately transverse configuration. The degree to which this geometry can be considered transverse

TABLE 2.2

DETERMINATION OF THE HYDROGEN CONTENT

Sample No.	H/Pd from electrolysis	R/R_o	H/Pd from Barton et al.(1963)	Assumed H/Pd
19	−	−	−	0.02
17	0.08	1.09	0.075	0.08
18	0.16	1.20	0.18	0.16
18	0.32	1.29	0.25	0.25
20	0.40	1.48	0.41	0.40
19	0.55	1.76	0.56	0.55
19	0.57	1.79	0.59	0.57
19	0.59	1.82	0.64	0.59
19	0.61	1.83	0.65	0.61
19	0.63	1.83	0.65	0.63
19	0.65	1.84	0.65_5	0.65
19	0.67	1.85	0.66	0.66
19	0.77	1.86	0.67	0.67
19	2.03	1.91	0.70	0.70

is discussed in Appendix I, where the results of magneto-
resistance measurements in iron are presented.

B. The Tantalum and Niobium Specimens

It was necessary to anneal these two metals in
vacuum since, if they were heated to high temperatures in
the presence of helium, a fragmentary state resulted. The
annealing temperature used for both of these metals was
$1000^{\circ}C$. The hydrogen was introduced in a manner similar
to that used for palladium and the concentration was
estimated using available data on the change in resistivity
at room temperature (Verani-Borgucci and Verdini, 1965).
Tantalum and niobium become quite brittle when hydrogen is
introduced even in small quantities and thus it was not
possible to use specimens with a hydrogen to metal ratio of
greater than 0.025 for niobium and 0.011 for tantalum. Verani-
Borgucci and Verdini (1965) were able to use specimens with
concentrations as high as 0.06 for niobium and 0.05 for
tantalum. However, these specimens were of a diameter
larger than the present 0.01 inch samples and this may account
for their ability to absorb more hydrogen and not break.

Results of the spectrographic analysis of the
specimens used in the present experiments are included in
Appendix II.

C. The Cryostat and Temperature Controller

The main body of the data on the temperature dependence of the resistivity was obtained using the cryostat described by White and Woods (1955). Later measurements, due to the introduction of a magnetic field, were made on a new——but similar——cryostat. The outer can of the new cryostat had a diameter of only 1.25 inches. The inner can limited the working space to about 1 inch by 5 inches. Due to the severe space limitations, it was not possible to include a pumping chamber for lowering the temperature of the specimen below that of the bath.

A stainless steel insert dewar was available for thermally isolating the superconducting solenoid to permit magnetoresistance measurements at 77°K. Despite the use of the insert dewar, it was found that there was a steady downward drift in the specimen temperature even with liquid nitrogen inside the insert dewar. However, the temperature of the liquid nitrogen could be stabilized by placing a 100 ohm resistor carrying a current of 1 ampere in the liquid nitrogen. This procedure was followed to be certain that temperature drifts did not mask the magnetoresistance effect. It was only for the ferromagnetic metals, nickel and iron, that any effect in the magnetoresistance at 77°K

was observable and, for this reason, the insert dewar was seldom used. Most measurements were made at or near $4.2^{\circ}K$.

In order to increase the specimen temperature above the bath temperature, an electronic temperature controller (Dauphinee and Woods, 1955) was used. Baths of liquid helium, liquid nitrogen, dry ice in ethyl alcohol, and ice water were used. During each measurement, thermal stability was easily maintained and temperature drifts were negligible. On the first cryostat the heating element used was a carbon resistor placed on the top of the inner can. On the second cryostat, a length of constantan wire was wrapped around the inner can to form a heating element. The first advantage of this procedure was that it saved space. The second advantage was that the resulting heat distribution was more uniform than in the case of the single resistor, and this seemed to reduce the time necessary for thermal equilibrium.

D. Temperature Measurement

Initially, the temperature was measured using a thermocouple of copper vs. gold +2.1 at. % cobalt. This thermocouple has been described in the literature (Powell et al., 1961) and is widely employed. The thermocouple was calibrated by measuring the thermal emf at the boiling

points of liquid helium and liquid oxygen with a reference junction in a bath of ice with distilled water. These data were compared with Powell et al. (1961) to obtain a factor f which would bring the published data into agreement with the measured emf. The published data were then everywhere reduced by the factor f giving a temperature vs. emf curve for the presently used thermocouple. The factor f used was 0.979. Thus, the necessary correction was not large. The variation of the thermal emf at 4.2°K for different runs corresponded to a temperature difference of less than 0.3°K. A germanium resistor, obtained from Solitron, Inc., calibrated in the range 4.2°K—100°K (guaranteed to $\pm 0.1^{\circ}$K) was later used and confirmed the accuracy of the previous temperature measurements. Subsequently, the germanium resistor was used up to 100°K, and a copper vs. constantan thermocouple was used above 100°K.

E.   The Potentiometer-Galvanometer System

Initially, a Guildline, Inc. Type 9160 Potentiometer with a Type 9460 Photo-Cell Galvanometer Amplifier, and a Type 9461-A Galvanometer were used. Later a Cambridge Type 44246 Potentiometer was used in conjunction with a Cambridge L398767 short-period galvanometer. The sensitivity of both systems was such that a change in

potential of 0.1 µv was easily detectable. The specimen current was measured by means of a Leeds and Northrup model 4015-B standard resistor with a nominal resistance of 0.01 ohms.

F. The Superconducting Solenoid

A Westinghouse, Inc. superconducting solenoid with a rated field of 20,000 gauss at 15.1 amperes was used to provide the magnetic fields. The field was determined by reading the ammeter in the magnet control and applying the coil constant 20,000 gauss/15.1 amperes or by monitoring the potential due to the current passing through the ammeter movement and using this to calculate the current. This latter procedure was particularly useful for small values of current. The magnetic field could always be determined to an accuracy of better than 3% by these procedures.

G. Accuracy of the Results

Due to the wide range of temperature and resistance of the various alloys it is impossible to assign a unique limit of accuracy for all of the results. However, for pure palladium near $4.2^{\circ}K$ the resistance could be determined to an accuracy of approximately $\pm 0.1\%$. The

alloys, because of their higher resistance, were subject to less uncertainty. At higher temperatures, the uncertainty in resistance was less than ±0.1%.

In order to convert resistance measurements to resistivity values, it was necessary to use the geometrical factor, cross-sectional area/length. This factor is estimated to be known to an accuracy of ±2% for all cases. No corrections have been made for changes in dimensions due to thermal expansion or hydrogen absorption. Changes in dimension due to hydrogen absorption could be expected to change the ratio cross-sectional area/length by as much as 4%, judging from lattice expansion results (Aben and Burgers, 1962).

The magnetoresistance effect varied by a factor of approximately 10^4 between pure palladium and the highest concentration alloys. Fortunately, the effect is maximum when the specimen resistance is minimum. For pure palladium at 20,000 gauss, the change in sample resistance corresponded to a change in potential which was typically 100 μv; while for the highest concentration alloy this change was approximately 1 μv. Comparing these numbers to the limiting accuracy of the potentiometer, 0.1 μv, the limits of accuracy are set at 1% and 10% for pure palladium and the highest concentration alloy, respectively.

CHAPTER III EXPERIMENTAL RESULTS

A. Temperature Dependence of the Resistivity of Pd
and Pd-H

Experimental results of the resistivity as a function of the hydrogen concentration in palladium are given in Fig. 2.1. For clarity, the data points are not shown and the scale has been deliberately compressed in order to show the entire range of concentrations. The symbol α is used to represent the ratio H/Pd in this and subsequent graphs. In Figs. 2.2 and 2.3, the same data are shown on an enlarged scale. The high concentration data have been corrected for an anomaly which appeared at low temperatures. This anomaly has been shown in detail (Haywood and Verdini, 1968; Appendix III) and at that time it was assumed to be due to the surface contamination of the specimens by some superconducting impurity. Since then, the presence of surface contamination has been confirmed by a detailed examination of the specimen surface under a low-power microscope. This contamination, probably Wood's metal, was removed and the anomalous behavior, manifested by an approximate 2% sharp decrease in resistivity as the temperature decreased past $7.5^{O}K$, disappeared. Effects due to this impurity would not be important at

Figure 3.1

Electrical resistivity as a function of temperature for pure palladium and palladium/ hydrogen alloys up to H/Pd = 0.70.
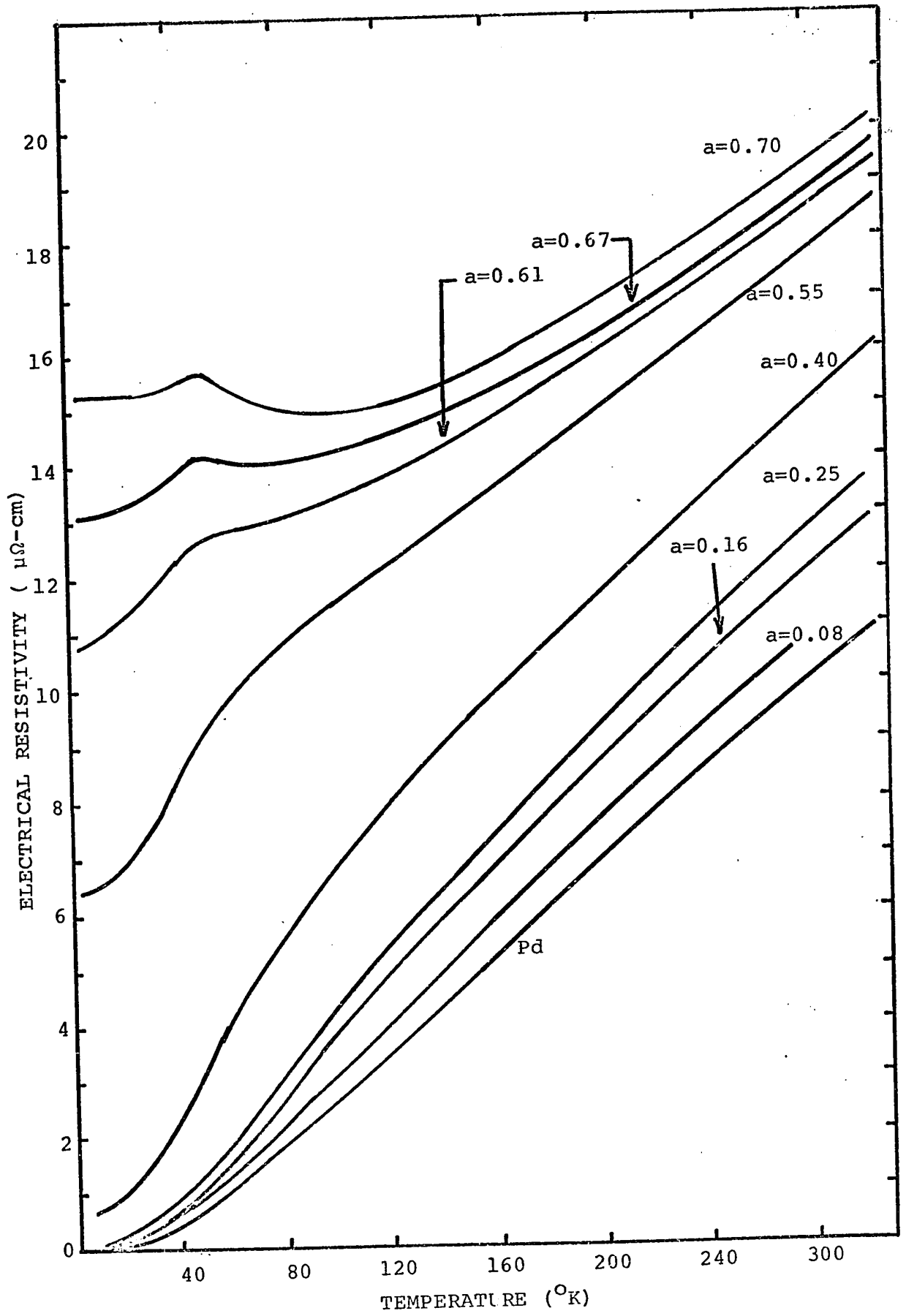
Figure 3.2

Electrical resistivity as a function of
temperature showing the details of the
transformation near 50°K.
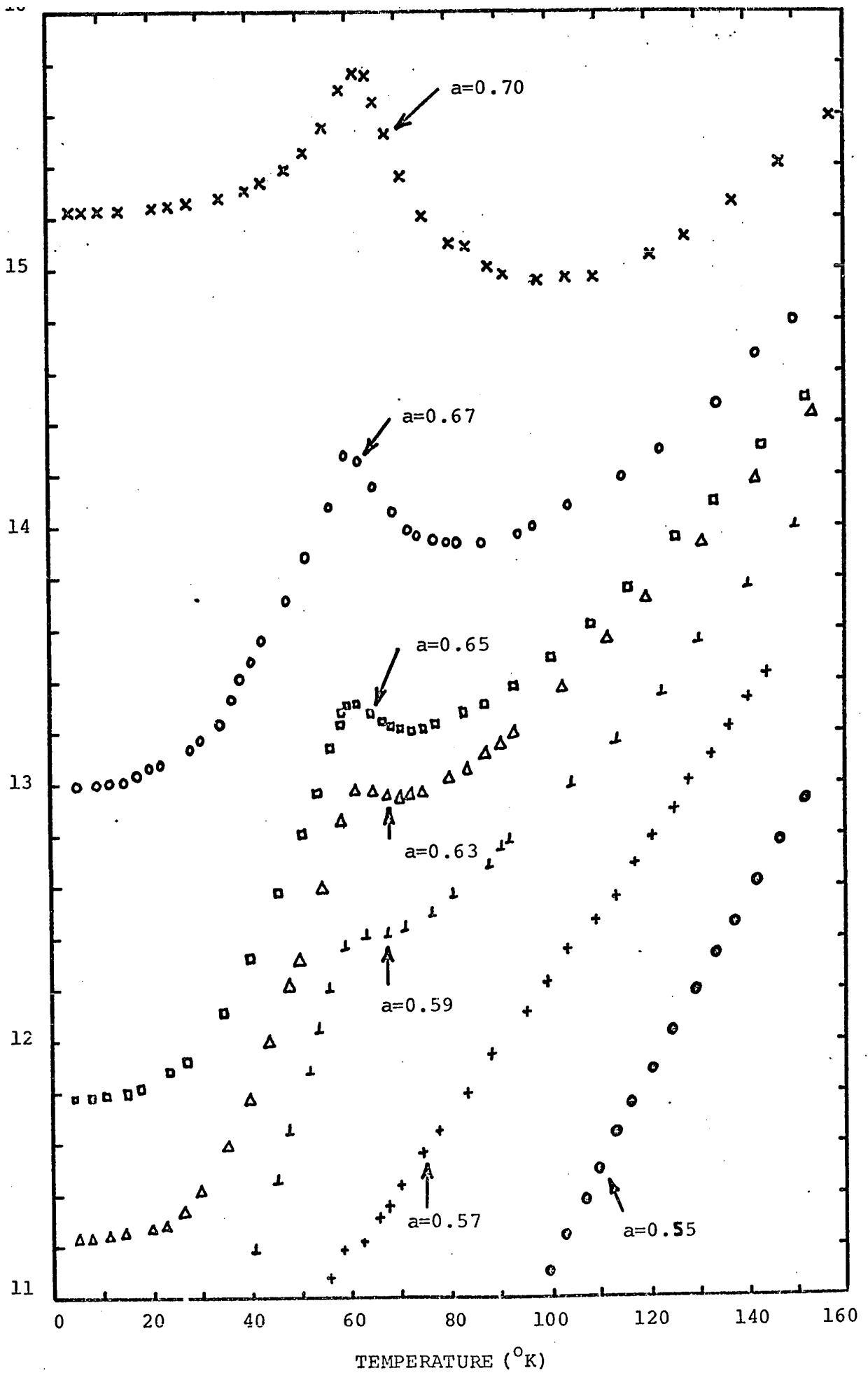
Figure 3.3

Electrical resistivity as a function of
temperature for high-concentration alloys
at high temperatures.
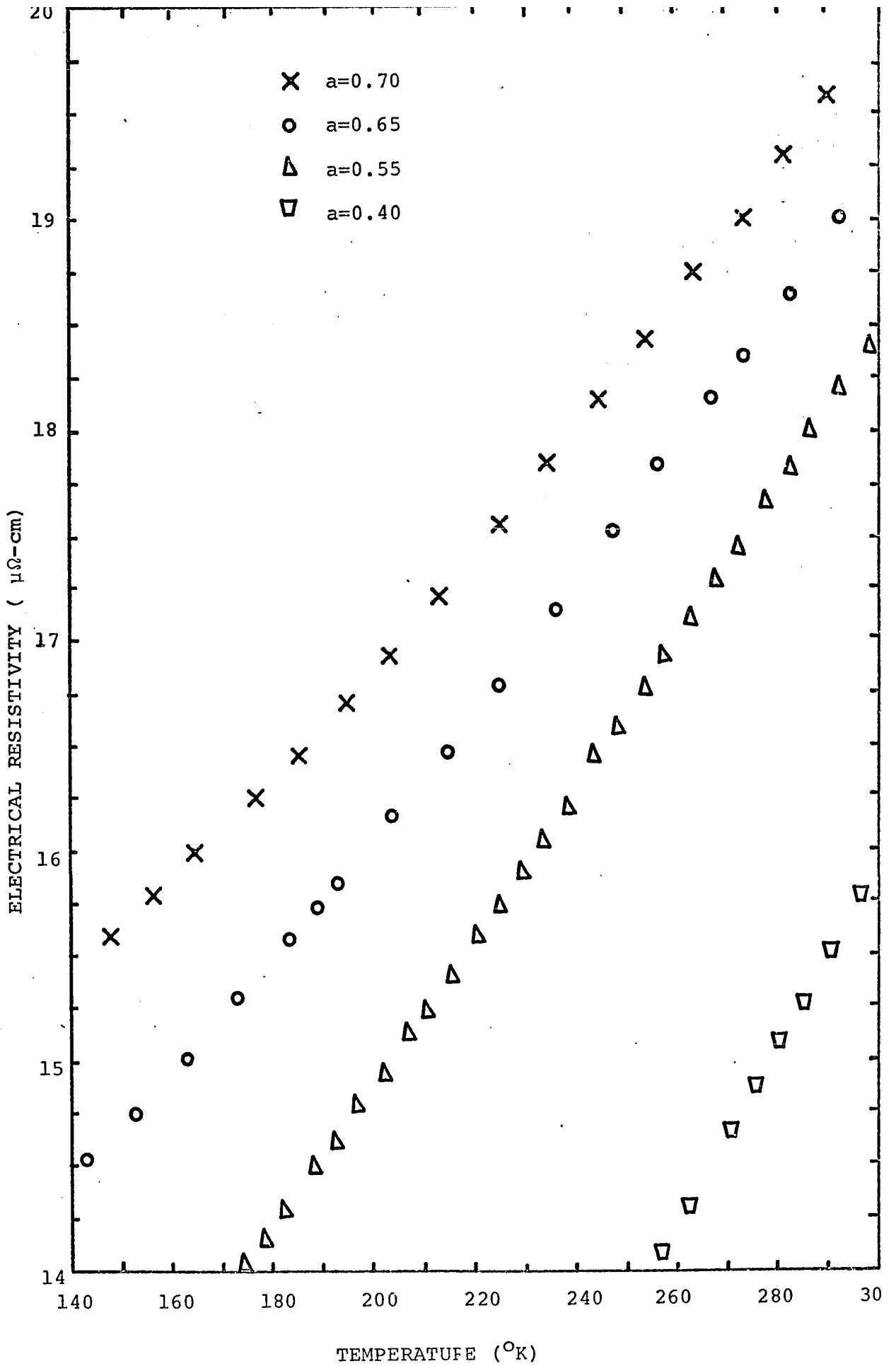
higher temperatures and thus no corrections above $7.5^{O}K$ were necessary.

At low temperatures, $10^{O}K<T<60^{O}K$, the ideal resistivity is found to be well represented by aT^{n}. The exponent n depends upon the hydrogen content and decreases with increasing H/Pd ratio, as shown in Table 3.1. There is a similarity in the effect on the exponent n due to the addition of a small amount of hydrogen and due to cold working (as-received), since in both cases the exponent is increased. However, when the hydrogen is further increased, the exponent n begins to decrease. The change in exponent must be interpreted as due to either a shift in relative importance of one or more of the scattering mechanisms or the introduction of a new scattering mechanism.

In order to pursue this point further, it is instructive to consider the data using the scheme of renormalization introduced by Colquitt (1965). Using the equations of Wilson (1953), presented in Chapter 1 of the present work, to describe the electron-phonon contribution to the resistivity, Colquitt projects out the temperature dependence of the s-s transitions in a renormalization of $\rho_{Pho.}$. The result can be written

TABLE 3.1

EXPERIMENTAL VALUES FOR THE EXPONENT n OF

$$\rho_i \propto T^n \text{ at } T < 60^\circ K$$

H/Pd	n
0 (as received)	2.7 ± 0.1
0 (annealed)	3.1
0.02	3.0
0.08	2.8
0.16	2.7
0.25	2.3

$$\tilde{\rho}_{pho.} = \text{const.}_{[} \frac{2^{-1/3} \; n^{-2/3}}{\omega_d m_d \; P_{sd}/m_s P_{ss}} + \frac{J_3(\frac{\theta_D}{T}) - J_3(\frac{\theta_E}{T})}{(T/\theta_D)^2 \quad J_s(\theta_D/T)}] \quad (20)$$

or,

$$\tilde{\rho}_{pho} = \text{const.} \; [\tilde{\rho}_{s-s} + \tilde{\rho}_{s-d}(T)] \quad . \quad (21)$$

Assuming $\tilde{\rho}_{s-s} \ll \tilde{\rho}_{s-d}$ at $T = \theta_D$, $\rho_{pho.}(\theta_D)$ is approximately the same as $\rho_{s-d}(\theta_D)$. Then the const. is removed by writing

$$\frac{\tilde{\rho}_{pho}(T)}{\tilde{\rho}_{pho}(\theta_D)} = \frac{\tilde{\rho}_{s-s}}{\rho_{s-d}(\theta_D)} + \frac{\tilde{\rho}_{s-d}(T)}{\tilde{\rho}_{s-d}(\theta_D)} \quad , \quad (22)$$

The momentum gap parameter θ_E becomes an important parameter when the theory is put in this form. Colquitt is able to fit the data of White and Woods (1959) for pure palladium by choosing $\theta_E \simeq 0.1 \; \theta_D$ and neglecting any effects due to s-s transitions. In Fig. 3.4, the present results have been plotted in this form and are compared with the theoretical curves. The Debye characteristic temperature has been taken to be $280^O K$ in all cases. This is an accepted value for pure palladium (Meaden 1965; Rayne 1960). The present results for pure palladium are seen to fit the theoretical curve for $\theta_E \simeq 0.1 \; \theta_D$, but

Figure 3.4

Comparison of experimental results of the
temperature dependence of the resistivity
of palladium and palladium/hydrogen alloys
with theory for various values of the
momentum gap parameter θ_E .
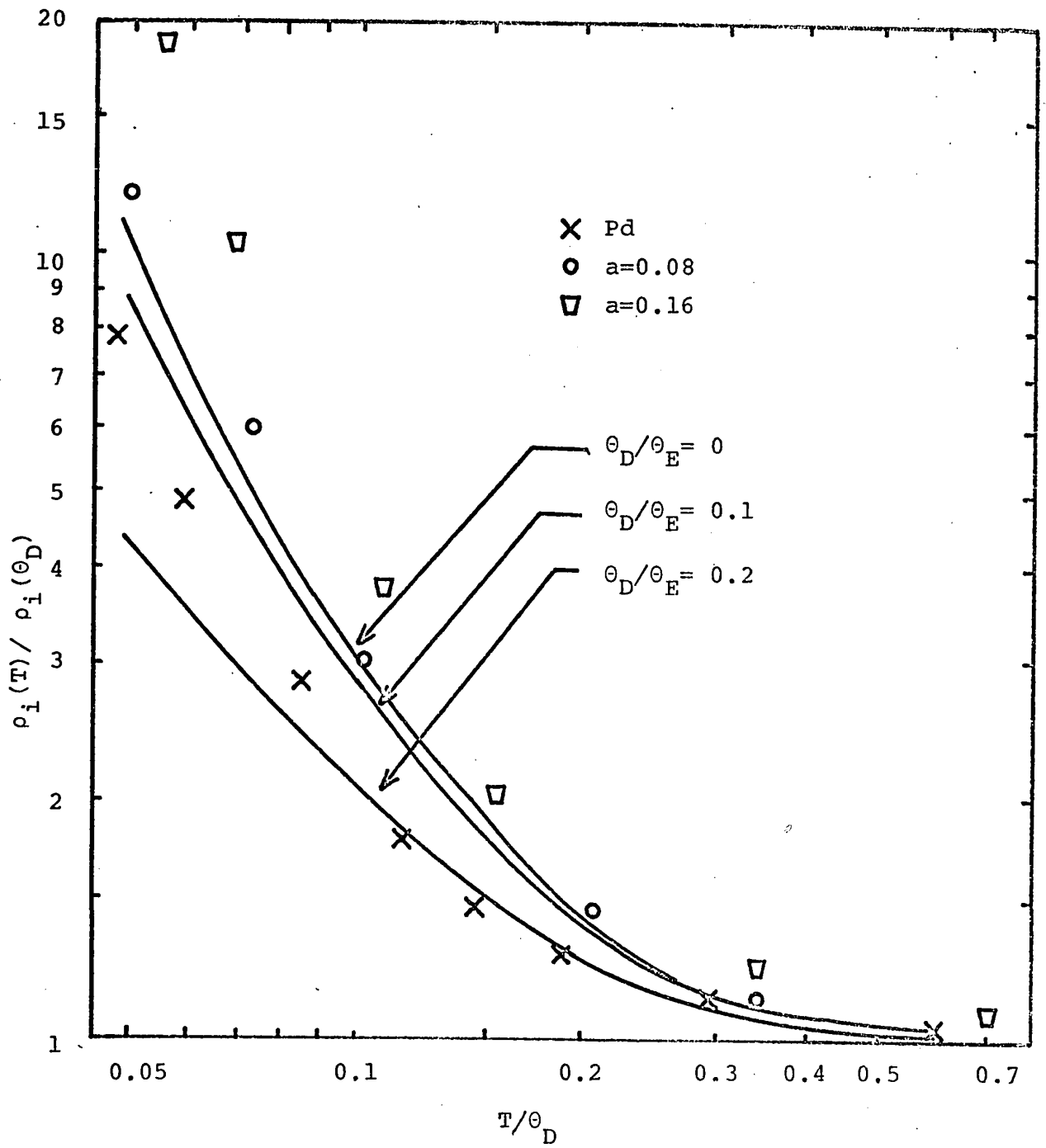
the alloys do not. The results for H/Pd = 0.08 could be made to agree more closely with the theoretical curves by choosing a value of θ_D smaller than that chosen for pure palladium. Such a procedure is not justified, however, for reasons discussed in the section of this thesis dealing with the Gruneisen characteristic temperature. Effects due to electron-electron scattering which would give a T^{-3} contribution to the resistivity in the renormalized scheme, do not appear to be important in the range of temperatures shown, $15^{\circ}K < T < 300^{\circ}K$.

From these results one may conclude that the change in temperature dependence of the electrical resistivity as palladium is alloyed with hydrogen is not due to a shift in relative importance of electron-phonon, either s-s or s-d, or electron-electron induced transitions and is not due to changes in the momentum gap parameter. It is then reasonable to assume that such effects, though they are undoubtedly present, are masked by the scattering of the electrons due to the occluded protons.

Bambakidis et. al. (1969) have calculated the structural resistivity for the case of the palladium/ deuterium system. These results should apply equally well to the palladium/hydrogen system. They assume that

initially the deuterium atoms contribute their electrons
to filling the holes in the d-band, resulting in a strong
screening of the deuterium ion. As more deuterium is added,
the additional electrons are assumed to be contributed
instead to the s-band, whose states are delocalized and
hence do not screen as strongly. This model then gives three
different types of scattering centers. A palladium atom
with a hole, a palladium atom associated with a strongly
screened deuterium ion, and a palladium atom associated with
a weakly screened deuterium ion. In the extremely high
concentration range, i.e. above $D/Pd \simeq 0.75$, they consider
only the two latter types of scattering centers existing as
independent superlattices. Since it is expected that s-d
scattering must go to zero as the palladium d-band is filled,
only s-s scattering is taken into account. The results are
given for two assumptions about the energy bands in
palladium. One theoretical curve is derived assuming that
the number of holes, n_h , is equal to 0.55 per atom. This
choice is consistent with the nearly zero value of the
magnetic susceptibility observed for $H/Pd = 0.55$ as dis-
cussed by Mott and Jones (1936). A second theoretical
curve is presented assuming $n_h = 0.36$. This assumption
is consistent with the deHaas-Van Alphen experiments of
Vuillemin and Priestley (1965) on pure palladium.

In order to compare the results of the present experiments with those of Banbakidis et. al. (1969) the residual resistivity of the specimens used in the two experiments must be considered. The results are presented in the form of $[\rho(x)/\rho(0)]_{4.2^{\circ}K}$ vs. x , where x is the atomic ratio of the alloy. The resistivity at 4.2°K for the samples used in the present experiments was typically 0.0096 $\mu\Omega$-cm. The corresponding value for the specimens of Banbakidis et. al. (1969) was 0.105 $\mu\Omega$-cm. Their specimens were not as pure as the ones used in this work and were annealed by passing a large electric current through the sample. This method of annealing usually does not result in a uniform heating of the specimen. These values can be compared to the value 0.01 $\mu\Omega$-cm, reported by White and Woods (1959) for a specimen of annealed palladium at 4.2°K.

For purposes of comparison, the results of Bambakidis et al. (1969) have been adjusted by a factor of 10 as a correction for the difference in residual resistivity between the two sets of experiments, and are presented in Fig. 3.5 along with the present results. The experimental results for palladium/deuterium agree well with the theoretical curve for n_h = 0.55. The present results indicate that the palladium/hydrogen

Figure 3.5

Comparison of the concentration dependence
of the resistance ratio $[\rho(x)/\rho(0)]_{4.2^\circ K}$
for the cases $x = D/Pd$ (Bambakidis et al.,
1968) and $x = H/Pd$, present results. The
solid curves are theoretical predictions
for this ratio.
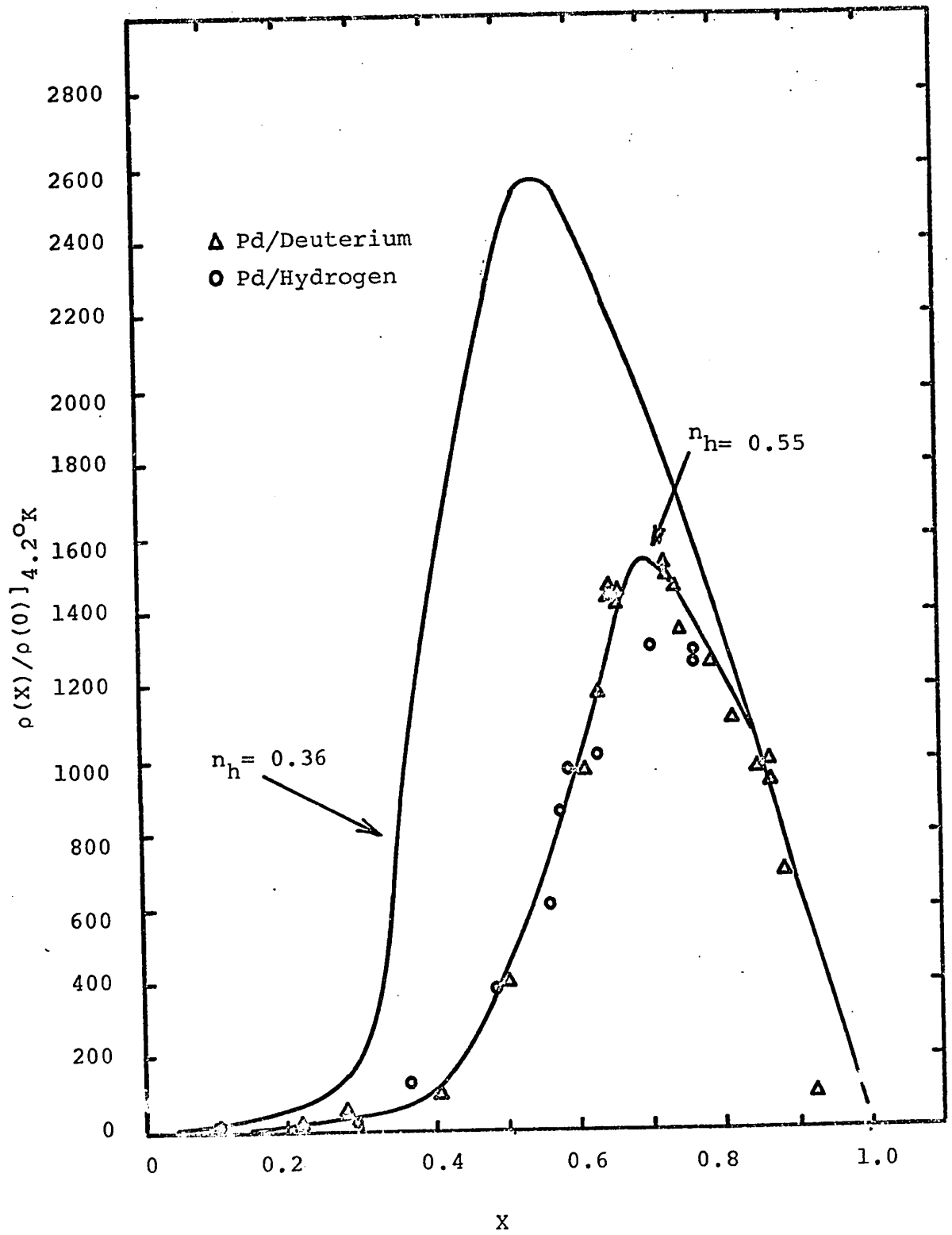
system also behaves as if there were 0.55 holes/atom in the palladium d-band. The position of the maximum in the resistivity ratio for the present results cannot be precisely determined since the guide for determining the concentration (Barton et al. 1963) gives data only up to H/Pd = 0.69. Concentrations above H/Pd = 0.70 are estimated from these results, however. Skóskiewicz and Baranowski (1968) found that the residual resistivity of palladium/hydrogen increased up to H/Pd = 0.74 but, that for H/Pd = 0.89, there was a considerable decrease. The present results are consistent with these findings.

The quantity $\Delta\rho = \rho_{Alloy} - \rho_{Palladium}$, calculated from the present measurements at different temperatures for the low concentration alloys and for a cold-worked pure palladium wire in the "as-received" condition, is shown in Fig. 3.6. Matthiessen's rule, which requires a temperature independent value of the parameter $\Delta\rho$, is applicable neither to the alloys nor to the cold-worked specimen. In the latter case, the graph of the extra resistivity as a function of temperature has a slight maximum around $50^{\circ}K$ and is very similar to that found in pure strained copper (Dugdale and Basinski, 1967). For the alloy of concentration H/Pd = 0.02, the quantity $\Delta\rho$ increases almost linearly with temperature over the

Figure 3.6

The temperature dependence of the extra
resistivity, $\Delta\rho$, for low-concentration
palladium/hydrogen alloys and for palladium
in the "as-received" condition.
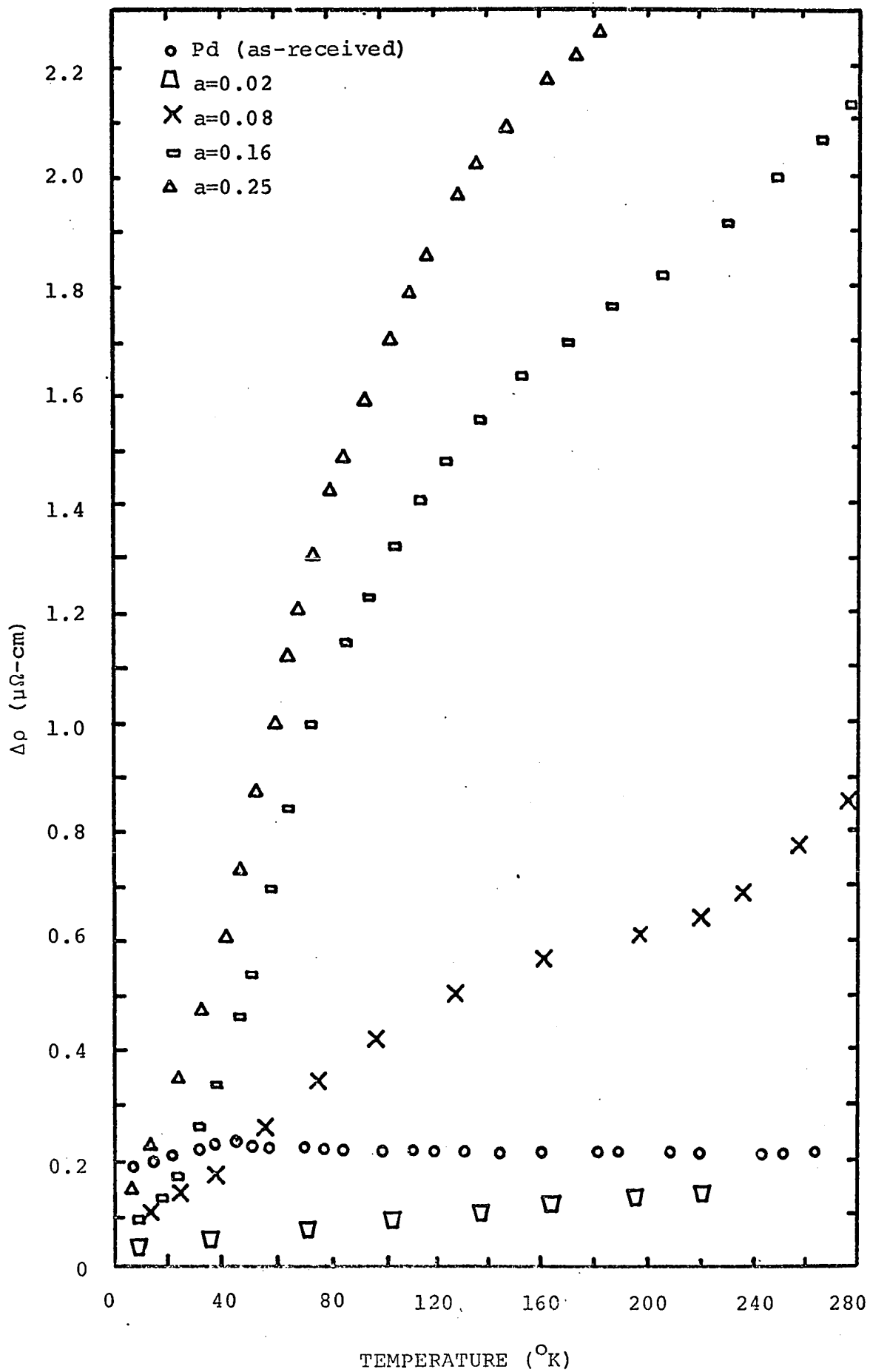
whole temperature range. For higher concentrations, $\Delta\rho$ is almost linear for $T>220^{\circ}K$.

B. The Characteristic Temperature θ_r of Palladium and Palladium/Hydrogen Alloys

The electrical resistivity and specific heat of a metal are frequently discussed in terms of a characteristic temperature. In the case of specific heat measurements, the characteristic temperature used is the Debye characteristic temperature, θ_D. The Debye temperature is obtained by fitting the experimental heat capacity results to the Debye function. Similarly, the lattice interaction with the electrons can be described by a characteristic temperature obtained by fitting the experimentally observed ideal resistivity data to the Gruneisen-Bloch relation

$$\rho_i(T) = \frac{KT}{\theta_r^2} \ G \left(\frac{\theta_r}{T}\right)$$

(Gruneisen,1933; Kelly and MacDonald,1953; Meaden,1965, p.97). The parameter K is usually taken to be a constant and must be eliminated before the characteristic temperature can be determined. The Gruneisen and Debye temperatures are usually similar in magnitude. The Debye approximation is better at low temperatures and the calculated value of θ_D is usually

fairly constant at low temperatures. The calculated θ_r values, in contrast, frequently drop rapidly at low temperatures. In the case of the transition metals, this happens because the resistivity at low temperatures is much higher than that predicted by the Gruneisen-Bloch equation. This is due to the presence of s-d scattering, of course.

Kelly and MacDonald (1953) have given various methods for calculating θ_r and θ_D. In the case of θ_r, Meaden (1965) has also discussed the assumptions underlying the methods and their degree of reliability. If θ_r is treated as a temperature-dependent parameter, one may calculate its value from the relation

$$\left(\frac{T_1}{\theta_1}\right)^2 G\left(\frac{\theta_1}{T_1}\right) = T_1 \, \rho_{i_{T_1}} \left[\frac{T_o}{\theta_o^2 \rho_{i_{T_o}}} \, G\left(\frac{\theta_o}{T_o}\right)\right] .$$

T_o is a reference temperature, θ_o is an estimate of the Gruneisen temperature, T_1 is the temperature at which one wishes to know the value of the characteristic temperature, θ_1. The appropriate functions are tabulated by Meaden (1965, pp. 97, 104).

In Fig. 3.7 the derived values of θ_r as a function of temperature are shown for palladium and the various

Figure 3.7

Calculated values of the parameter θ_r for pure palladium and representative palladium/hydrogen alloys.
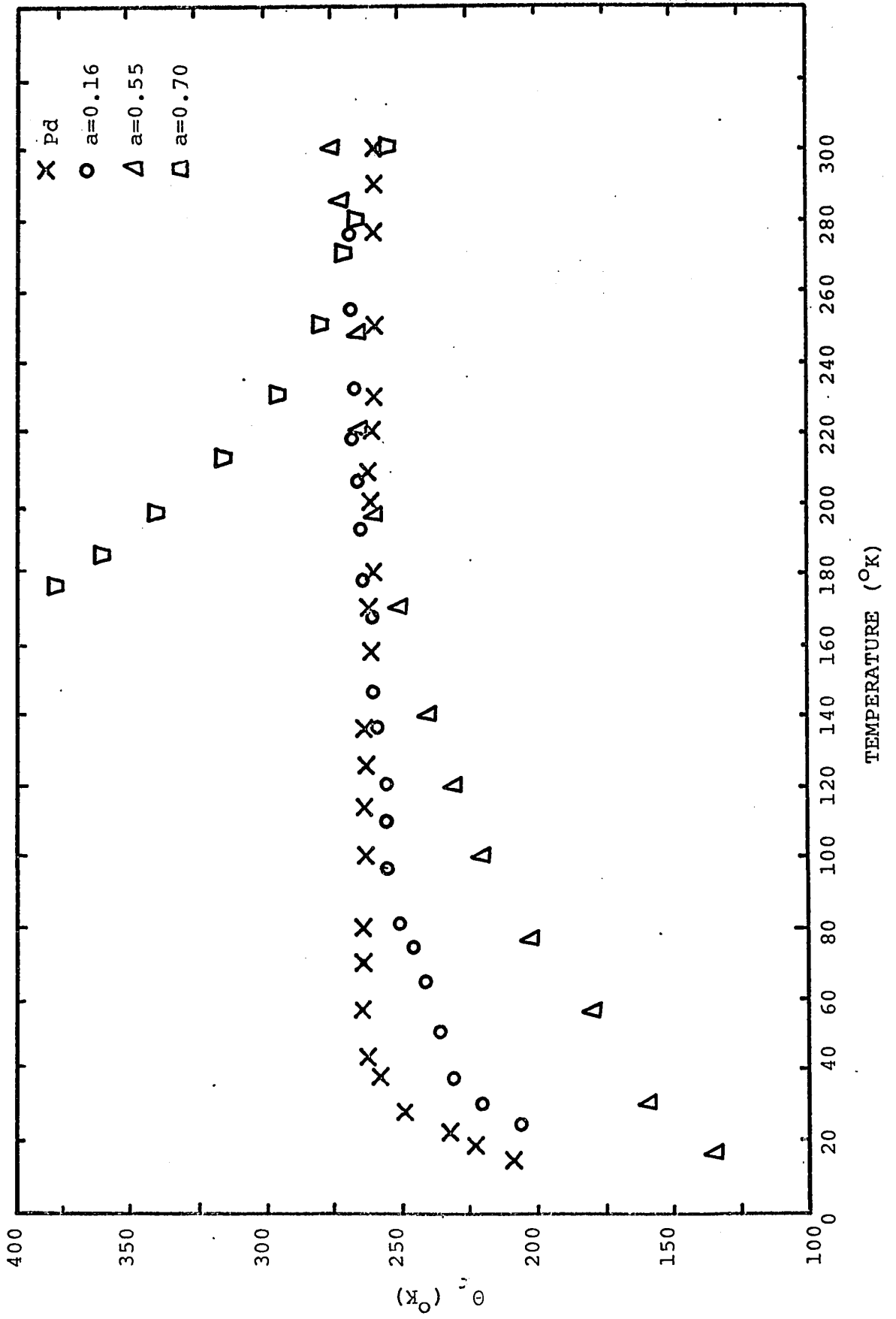
palladium/hydrogen alloys measured here. For pure palladium the value of θ_r is consistent with the value $270^\circ K$ quoted by Meaden (1965), for the temperature range $\theta_r/3$ to θ_r. Smith, et al. (1962) have calculated θ_r for pure annealed palladium and for palladium after desorption of hydrogen by another of the methods of Kelly and MacDonald (1953). Their results were lower than the present results by about $20^\circ K$, but, varied considerably with temperature, even near θ_r, due to their method of calculation. Owen and Evans (1967) have determined the characteristic temperature by measuring the fall of intensity of reflected x-rays with increasing temperature. For pure palladium their result is $\theta = 267^\circ K$ at $293^\circ K$. Furthermore, they found that θ increased to a value of $311^\circ K$ for $H/Pd = 0.07$, their highest concentration. No analogue to this latter result is seen in the present experiments. For $H/Pd \leq 0.55$, the present results may be described in the following manner:

(1) near $300^\circ K$, θ_r is not sensitive to the hydrogen concentration, but does increase slightly with increasing hydrogen content

(2) for temperatures less than $100^\circ K$ the characteristic temperature decreases with increasing hydrogen content

(3) the range of temperature in which θ_r may be considered constant decreases with increasing hydrogen content

For the alloy with $H/Pd = 0.70$, the behavior is drastically different. θ_r increases rapidly as the temperature is lowered. This behavior has been ascribed by Ho and Manchester (1968) to electron scattering from optical phonon modes due to the presence of the protons. The presence of such local modes has been verified by neutron scattering by Kley et al. (1967) at low hydrogen concentrations and by Bergsma and Goedkoop (1960) at high concentrations. The importance of these local modes at high concentrations is probably due to the beginnings of the formation of a super-lattice of protons. Assuming this, one would expect the resistivity versus concentration curve to show a decrease in this range of concentrations. Such a decrease has been seen by Bambakidis et al. (1969) in palladium/deuterium above $D/Pd = 0.76$ at room temperature and at $4.2^{\circ}K$. Skóskiewicz and Baranowski have seen this effect above $H/Pd = 0.74$ at $4.2^{\circ}K$, as previously discussed. The presence of optical modes in the case of zirconium/hydrogen has been reported by Bickel and Berlincourt (1960). Their results were interpreted using the theory developed by Sondheimer and Howarth (1953) to describe the effects of optical

scattering on resistivity. There is little doubt that the optical modes are present in both palladium/hydrogen and zirconium/hydrogen, but a detailed investigation of this effect should employ techniques other than electrical resistivity studies.

C. The Resistivity Anomaly

In Fig. 3.2 the anomalous region near $50^\circ K$ is shown in detail. The maximum is present only for $H/Pd \geq 0.57$. Other authors have reported the presence of this maximum in the electrical resistivity at lower concentrations. Schindler et al. (1959) report a small, but definite, maximum for $H/Pd = 0.50$ and the results of Ho and Manchester (1968) show a maximum for $H/Pd = 0.51$. The results of Barton et al. (1963), from which the present concentrations were determined, suggest an uncertainty in concentration of only about $\pm.02$ in the high concentration range.

The position of the maximum is largely independent of concentration. The position of the subsequent minimum is, however, noticeably concentration dependent. For $H/Pd = 0.61$ it occurs at $58^\circ K$ and for $H/Pd = 0.70$ it occurs at $92^\circ K$. These results are in agreement with

Schindler et al. (1959) and Rota (unpublished Ph.D. thesis, University of Rome, 1967). It is also of interest to note that the value of the resistivity at the minimum is less than the residual value obtained at $4.2^{O}K$.

There have been three attempts to explain this anomaly. Nace and Aston (1957) view the anomaly which they have observed in the specific heat at approximately the same temperature as being due to the onset of a rotational or re-orientation process of some type of Pd-H molecule. They cite similar behavior in NH_4Cl, NH_4NO_3 and others (Hildenbrand and Giaque, 1953). Mitacek and Aston (1961) point out that such a process might produce an anomaly in the phonon distribution and thus the anomaly in the resistivity. Neutron diffraction studies have been made on β palladium/hydrogen by Ferguson et al. (1965). The results show that at high temperatures, $T >> 55^{O}K$, the protons are located in octahedral $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites (β PdH). At low temperatures, $T << 55^{O}K$, there has been a partial migration to the nearby tetrahedral $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ sites (β^{*}PdH). The anomaly in the electrical resistivity near $55^{O}K$ is then viewed as arising from increased electronic scattering produced by the disordered arrangement of the hydrogen atoms among octahedral and nearby tetrahedral sites in the palladium lattice.

Skóskiewicz and Baranowski (1968) have been able to produce specimens with H/Pd as high as 0.89 by using gaseous hydrogen at 10,000 atmospheres. Their results show that the anomaly is not present for H/Pd = 0.89 but is present when the concentration is reduced to H/Pd = 0.74 and disappears again at lower concentrations. They believe that this behavior can be explained by assuming that the hydrogen in palladium is randomly distributed at high temperatures; but that at low temperatures, islands of stoichiometric PdH appear. This model is consistent with the disappearance of the resistivity anomaly since one would expect that the formation of such islands would be less likely when the atomic concentration approaches unity. What is not clear, however, is why the formation of such islands would increase the resistivity. One would expect that the formation of regions of high proton density would leave the surrounding metal with decreased impurity con- centration and possibly result in a decrease in resistivity. However, it seems that the model of Mitacek and Aston is really quite similar to the model of Skóskiewicz and Baranowski in that they both assume the presence of some type palladium-hydrogen molecule. The details of both of these models are required before their ability to explain the phenomena can be examined closely.

Fig. 3.8 shows some effects that are directly attributable to the transformation. For the top curve, the sample was brought rapidly (in about 9 minutes) from $77^{\circ}K$ to $41^{\circ}K$ and the resistivity was studied as a function of time. The resistivity increased with time. After 235 minutes the temperature was brought to $46^{\circ}K$ and the resistivity was observed to increase faster with time. This behavior is to be contrasted with the lower curve, where the sample temperature was quickly changed from $77^{\circ}K$ to $55^{\circ}K$, again in about 9 minutes. Under these conditions, the resistivity decreased with time. After 260 minutes the temperature was reduced to $50^{\circ}K$ and the resistivity decreased at a faster rate.

The results shown in Fig. 3.9 again emphasize the pronounced effect which the transformation can have on the electrical resistivity. The "fast-cooling" results were obtained by first cooling the sample from liquid nitrogen to liquid helium temperature in about 4 minutes and then measuring the temperature dependence of the resistivity as the temperature was slowly increased. The resistivity maximum thus obtained occurred at $52^{\circ}K$ and its value was 15.76 $\mu\Omega$-cm. The "slow-cooling" results were obtained by taking resistivity measurements while the temperature was slowly decreased during a

Figure 3.8

Time dependence of the resistivity of a
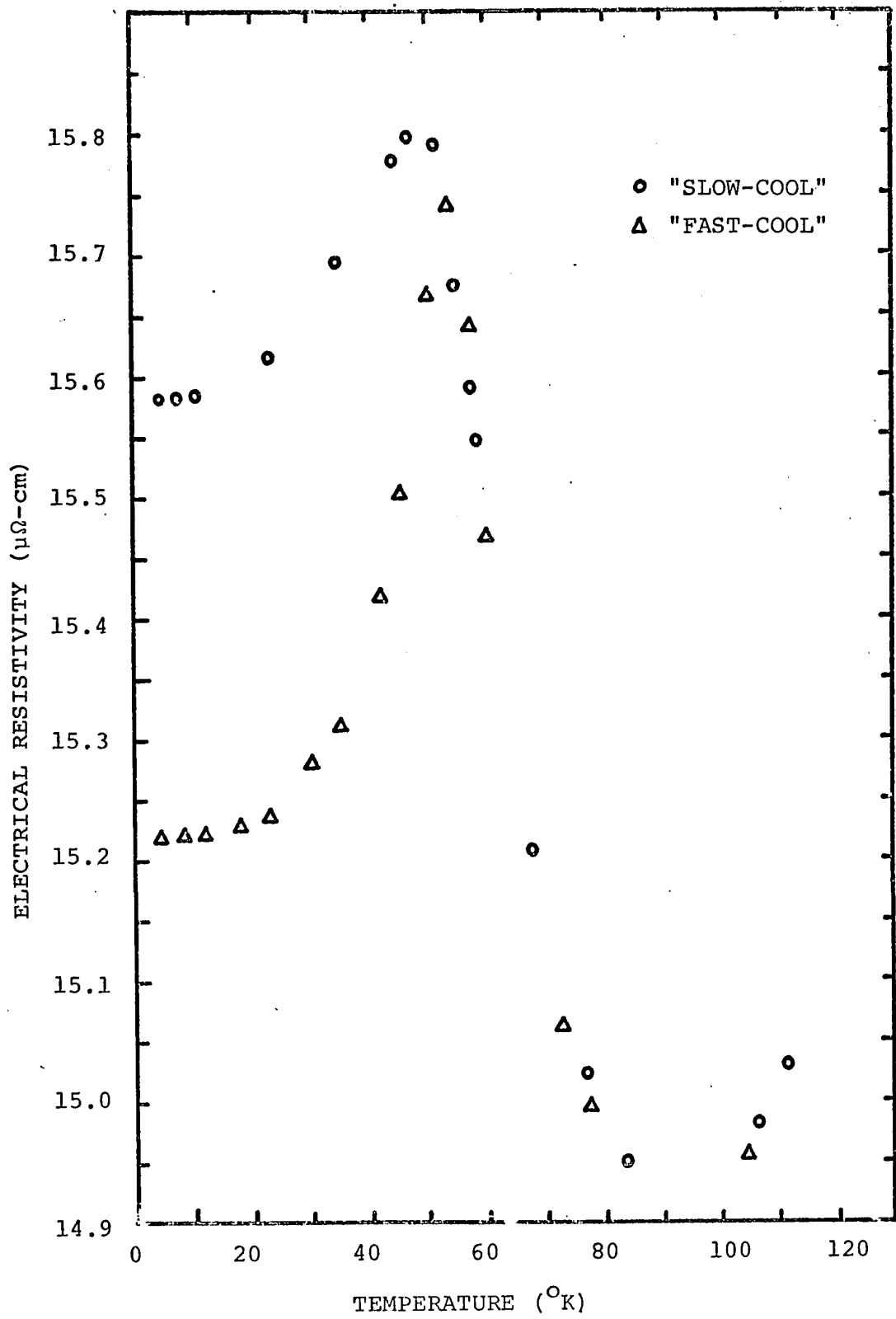palladium/hydrogen alloy with concentration
H/Pd = 0.70 .
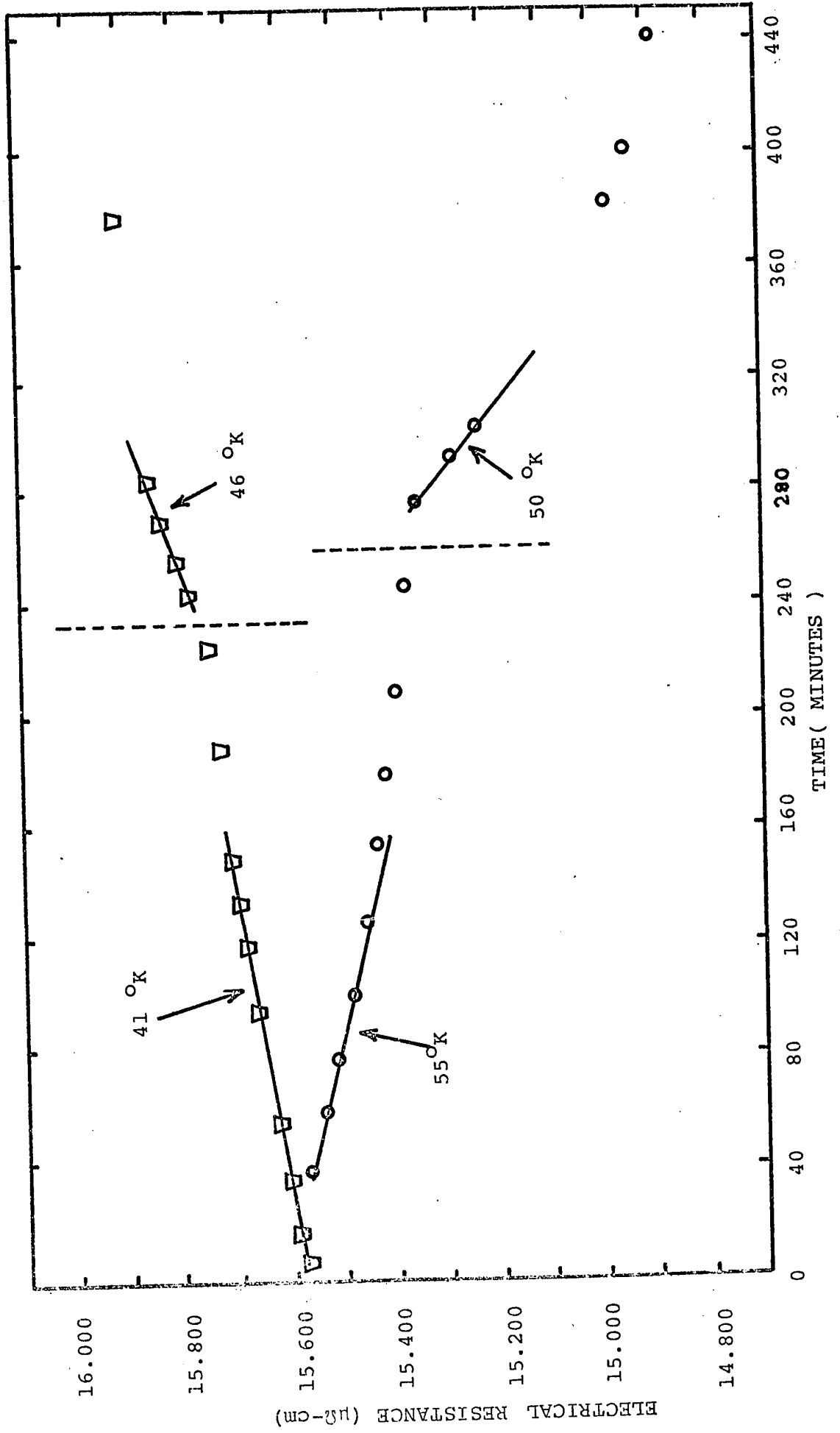
Figure 3.9

Resistivity as a function of temperature
showing effects due to the cooling rate of
the specimen for H/Pd = 0.70 .

5-hour period. The resistivity maximum occurred at 44^OK, with a value of 15.77 $\mu\Omega$-cm in this case. The resistivity was also measured while the sample temperature was slowly increased after the measurement of the "slow-cooling" behavior. This resulted in a maximum at 46.5^OK with a value of 15.81 $\mu\Omega$-cm. Except for the differences near the maximum, there was no important hysteresis effect observed during this cycle. In contrast to the usual behavior of metallic alloys, the residual resistivity is higher for the slower cooling rate.

It is impossible to use the above data to state unequivocally which, if any, of the three models advanced to explain the anomaly is correct. However, it is clear that the rapid cooling could be expected to reduce the $\beta \rightarrow \beta^*$ transformation suggested by Ferguson et al. (1965). Likewise, using their suggestion that it is the disorder of occupancy of both tetrahedral and octahedral lattice sites which is responsible for the increased resistivity, the residual resistivity would be expected to be lowered. This behavior is not implicit in the models of Mitacek and Aston (1963) or Skóskiewicz and Baranowski (1968).

Data on the time dependence of the resistivity at constant temperature for palladium/deuterium are not available for comparison with the present results. Equilibrium

times for palladium/hydrogen are known to be much less
however (Smith, 1969). The results in Fig. 3.8 indicate
that a detailed explanation of the resistivity maximum
must take into account changes in electron scattering due
to (1) the motion of the protons per se and (2) effects
due to the new location or configuration of the protons,
i.e. a dynamic rather than static theory is required.

D. Magnetoresistance

The quantity $\omega_c \tau$ is important in magnetoresistance
measurements since it determines whether the magnetic
field is to be considered as small, $\omega_c \tau \leq 1$, or large,
$\omega_c \tau \gg 1$. For H = 20,000 Oe., ω_c is of the order of
$3 \times 10^{11} \text{sec}^{-1}$. Using the free-electron expression for
the conductivity, $\sigma = \dfrac{Ne^2 \tau}{m}$, one can estimate the relaxa-
tion time to be 5×10^{-12} sec. for pure palladium at
4.2°K. The value of $\omega_c \tau$ is then of the order 1 and
it is clear that the fields presently used must be
considered weak. The conductivity decreases rapidly with
increasing hydrogen concentration; so, the results for the
alloys are even deeper in the weak field realm.

The experiments in a magnetic field yielded
results which were reproducible in terms of the magnetic

field dependence of $\Delta\rho/\rho(0)$, but which gave some variation in the magnitude of the effect. This variation in magnitude could always be partially attributed to changes in the value of $\rho(0)$ at 4.2°K. It was not possible to produce specimens with exactly the same residual resistivity, even when they were annealed under identical conditions. And, for the alloys, the value of the resistivity at 4.2°K was found to depend upon the conditions under which the specimen was brought to the low temperature. The behavior for pure palladium in a transverse field is illustrated by the results in Fig. 3.10.

Figs. 3.11, 3.12 and 3.13 show the results for representative palladium/hydrogen alloys in a transverse magnetic field. For pure palladium and the alloys, $\Delta\rho/\rho(0)$ is positive and there is no indication of saturation. The magnitude of the effect is greatly dependent upon the concentration, but the slope is not. The results show that $\Delta\rho/\rho(0)$ is not proportional to H^2; the form being approximately $\Delta\rho/\rho(0) \propto H^{1.2}$. Ziman (1960) has pointed out that the magnetoresistance of polycrystalline materials is a result of averaging over many crystallite orientations. He was able to explain satisfactorily the nearly linear behavior observed by Chambers (1956) in polycrystalline specimens of copper, silver, and gold on

Figure 3.10

Transverse magnetoresistance in three different
pure palladium specimens at 4.2^{O}K.
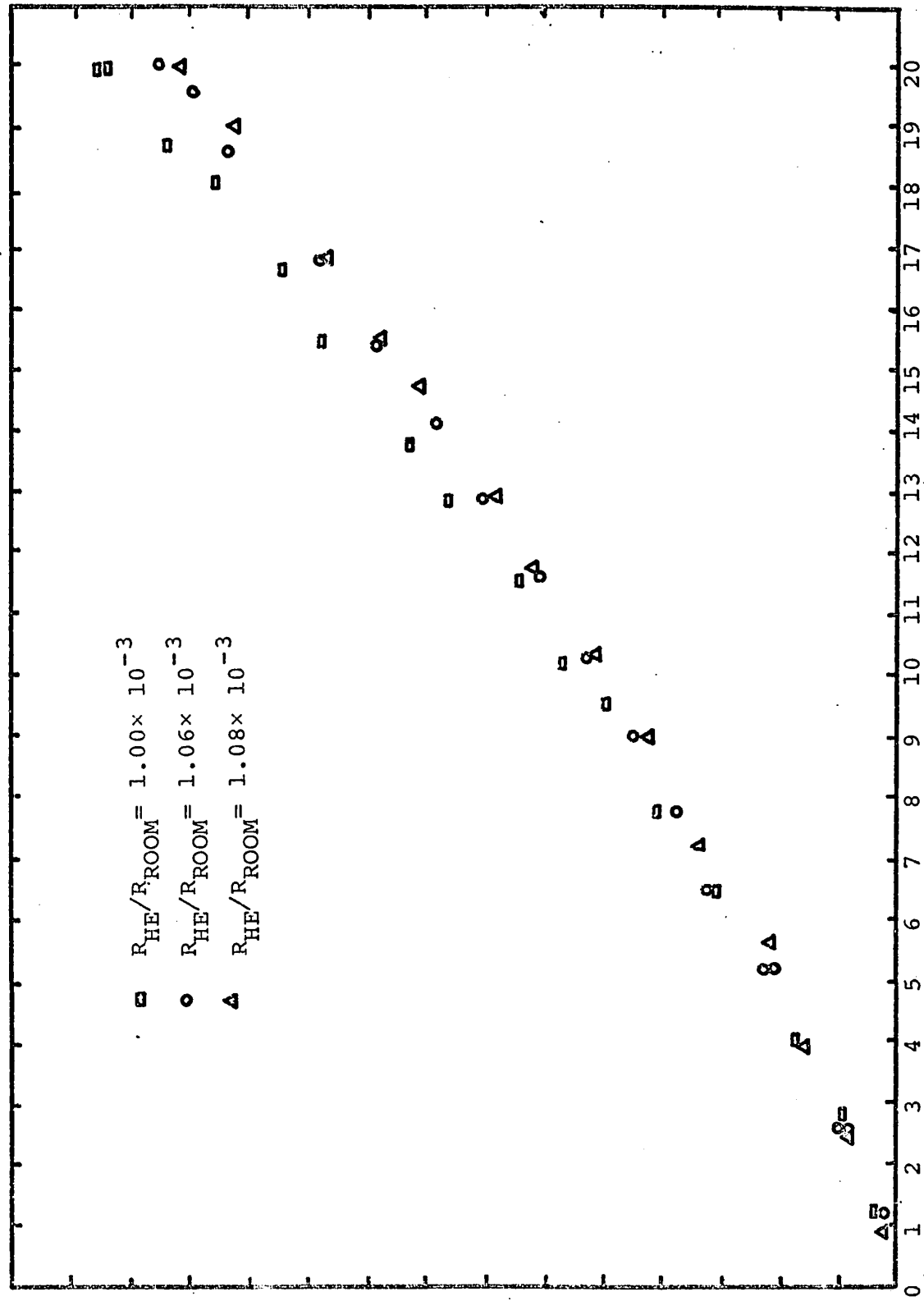
Figure 3.11

Transverse magnetoresistance for alloys
of concentration H/Pd = 0.001, 0.009, and
0.02   at   4.2°K.
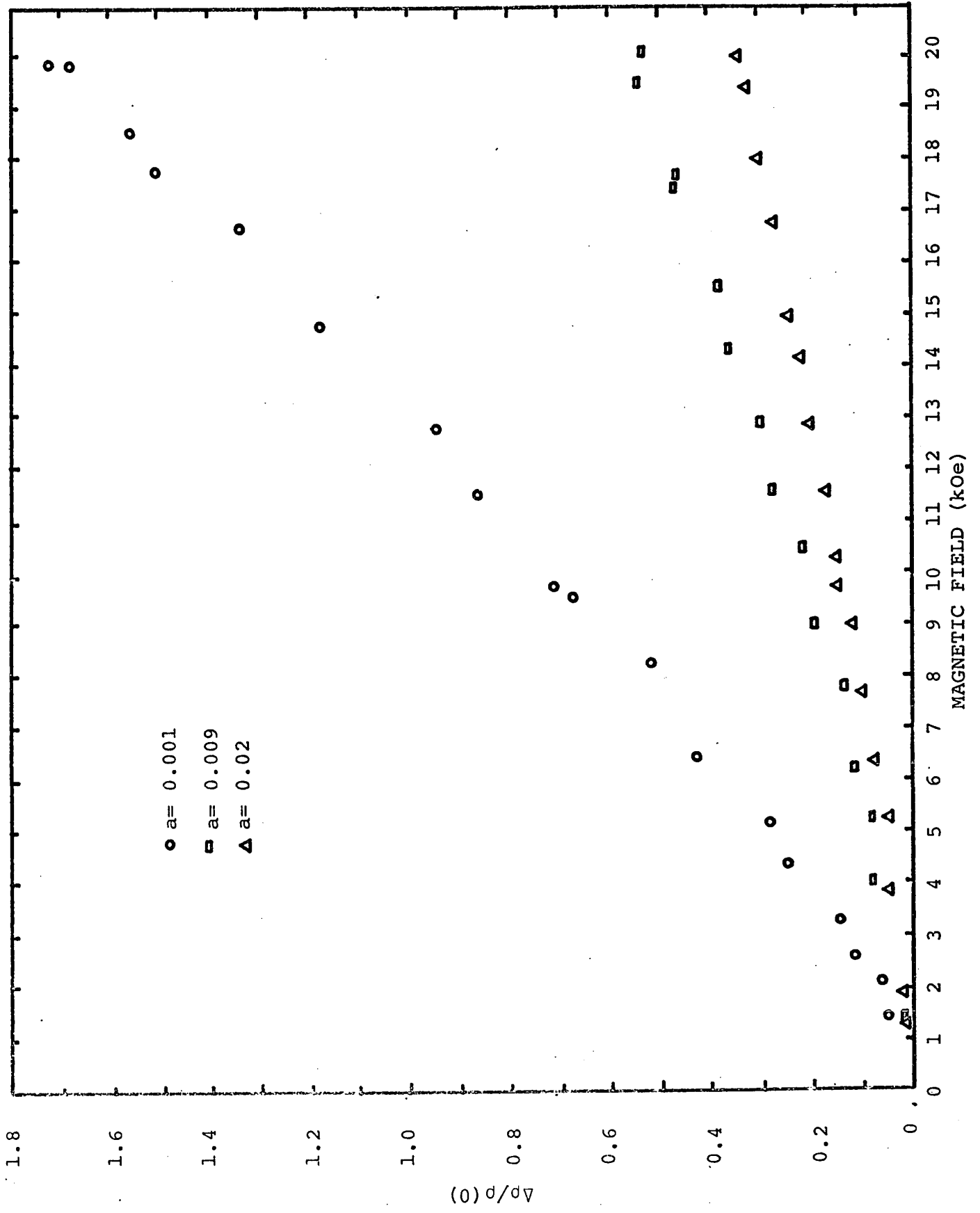
Figure 3.12

Transverse magnetoresistance for alloys

of concentration H/Pd = 0.37, 0.48, and

0.51 at 4.2^{O}K.

MAGNETIC FIELD (kOe)

Δρ/ρ(0)

o a= 0.37
□ a= 0.48
△ a= 0.51
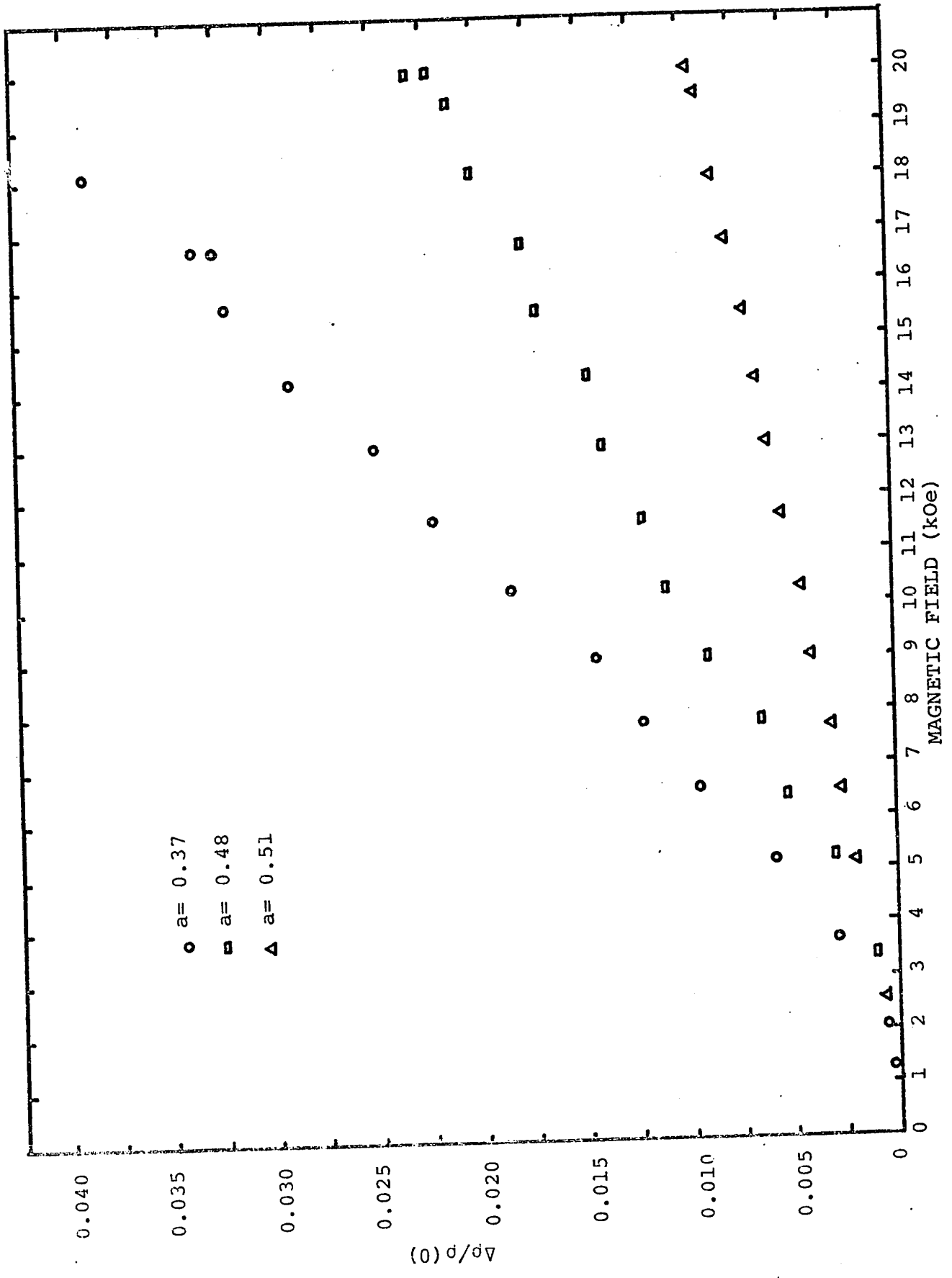
Figure 3.13

Transverse magnetoresistance for alloys of
concentration H/Pd = 0.64 and 0.76 at
4.2°K.

$\Delta\rho/\rho(0) \times 10^3$

o a = 0.64

△ a = 0.76
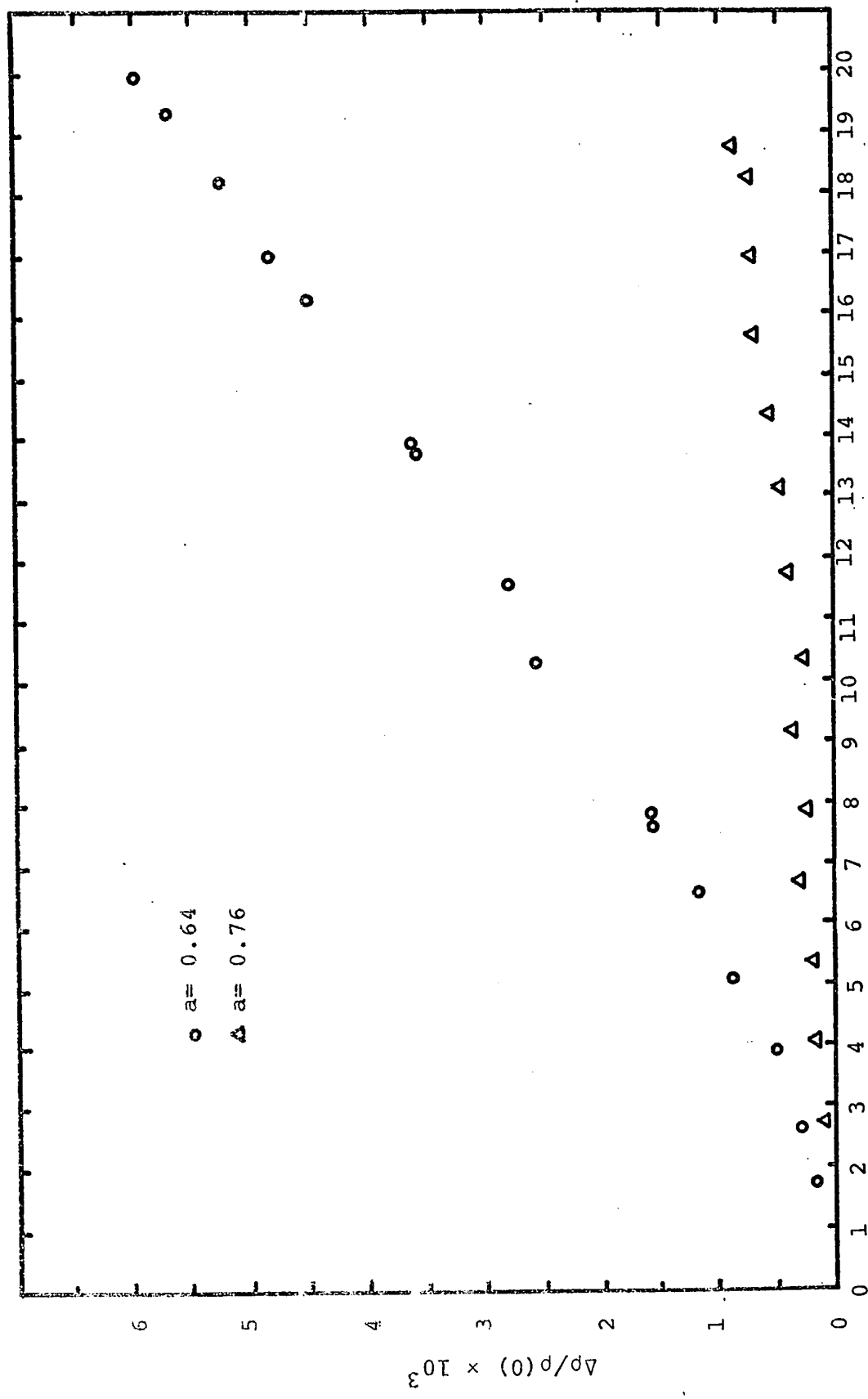
MAGNETIC FIELD (kOe)

this basis. The situation is somewhat more complicated in
the transition metals, but it may be assumed that the
explanation is similar.

In weak magnetic fields the nature of the collision
processes determines the magnetoresistance. The results
in a transverse magnetic field, because of the observed
similarity of palladium and the palladium/hydrogen alloys,
indicate that there is no large scale change in collision
processes. This is surprising, especially in the high
concentration alloys where the d-band becomes filled and
s-d scattering must go to zero. However, it is likely that
this effect is obscured by the scattering effect of the
protons and that this method is not sensitive enough to
detect the change in s-d scattering.

Figs. 3.14, 3.15, 3.16, and 3.17 show results for
longitudinal fields. Pure palladium in a longitudinal
field behaves quite differently from pure palladium in a
transverse field. Theory predicts that the longitudinal
magnetoresistance must saturate at high fields. This result
is indicated even in the relatively weak fields used here
(a similar contrast in the behavior of platinum in longi-
tudinal and transverse magnetic fields was observed; the
results are not included in this thesis, however). The

Figure 3.14

Longitudinal magnetoresistance in pure
palladium at 4.2^{O}K.

Figure 3.15

Longitudinal magnetoresistance for alloys
of concentration H/Pd = 0.018 and 0.195
at 4.2°K.
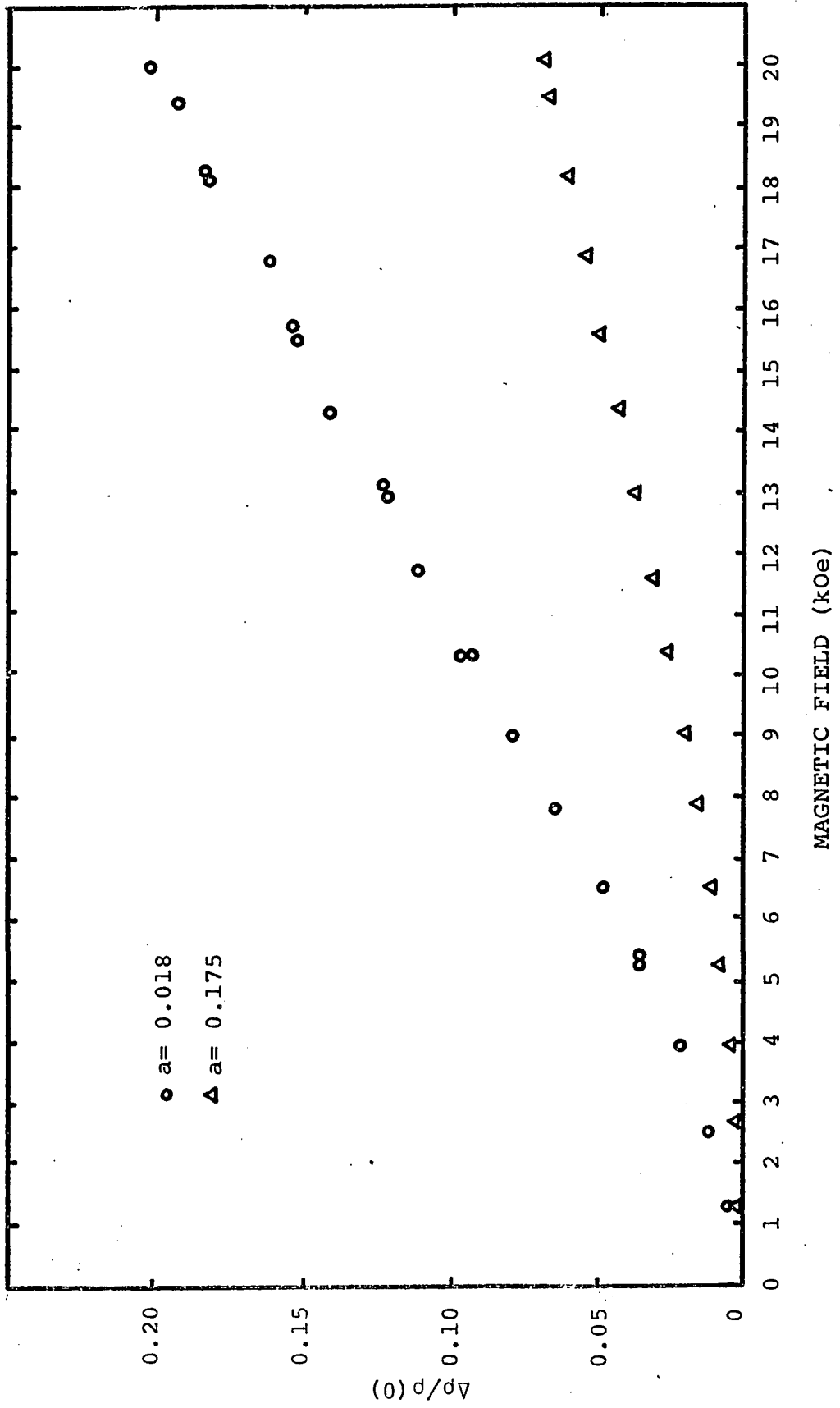
Figure 3.16

Longitudinal magnetoresistance for alloys
of concentration H/Pd = 0.29 and 0.37
at 4.2^{O}K.
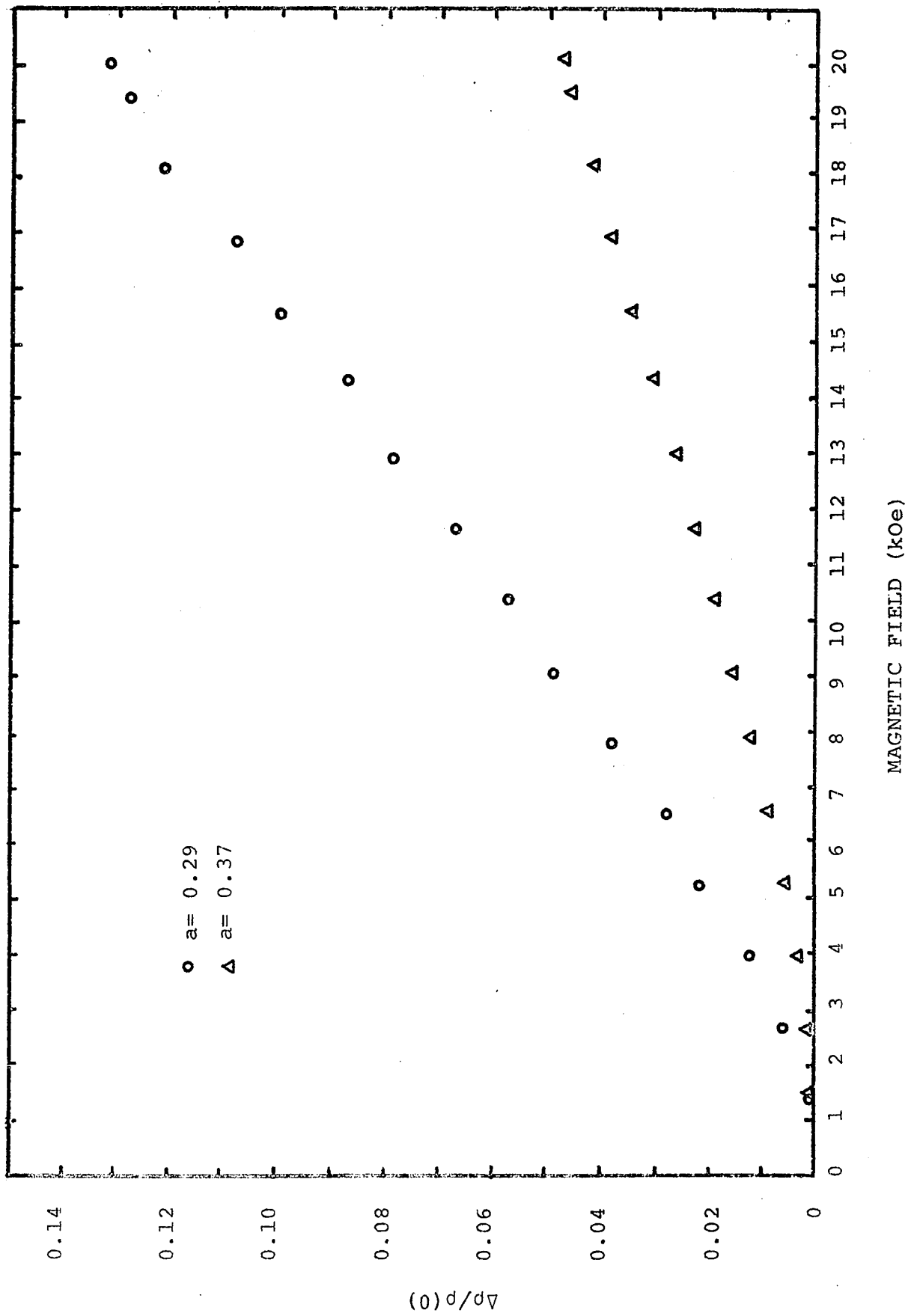
Figure 3.17

Longitudinal magnetoresistance for alloys of concentration H/Pd = 0.50 and 0.61 at 4.2°K.

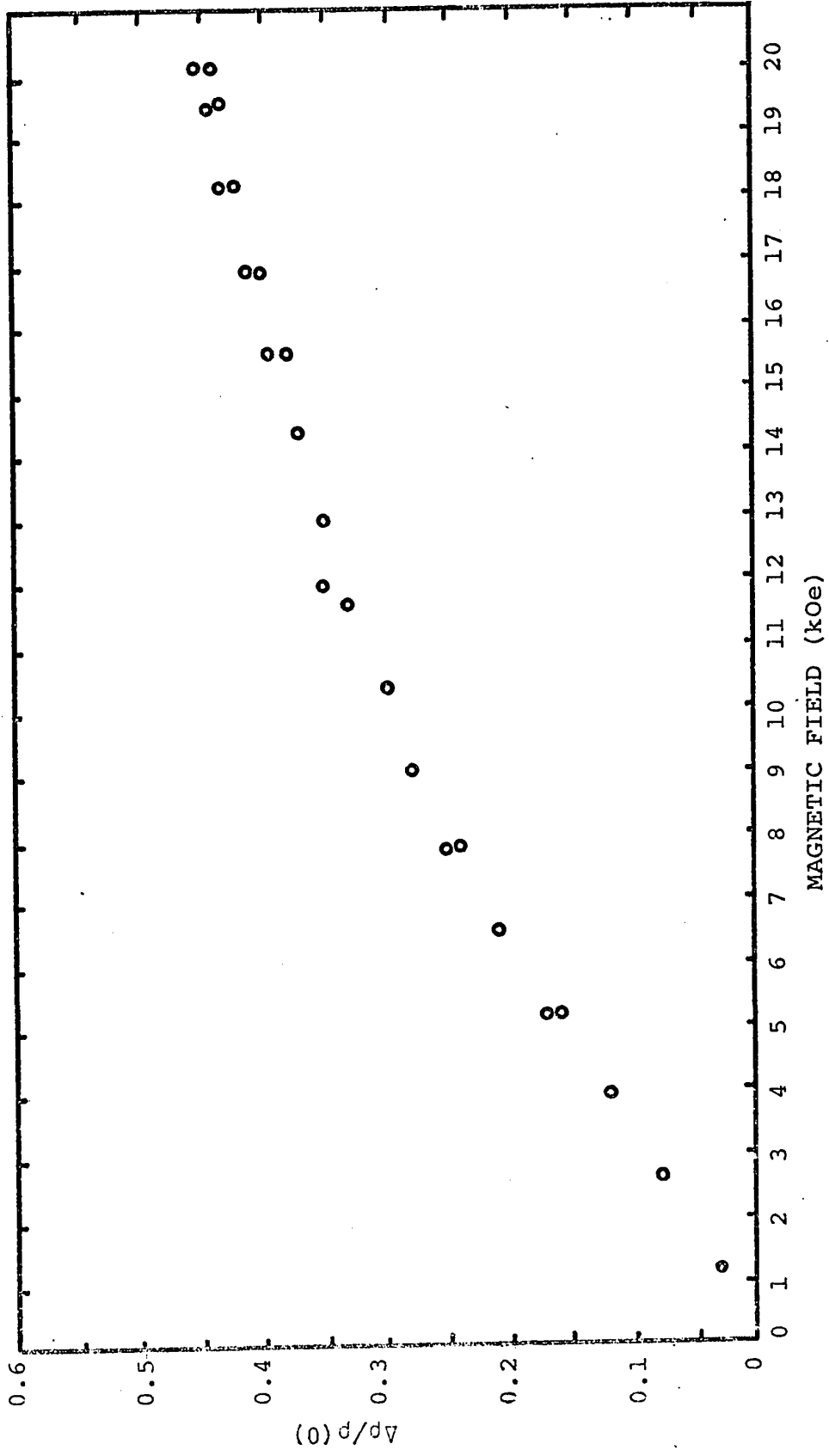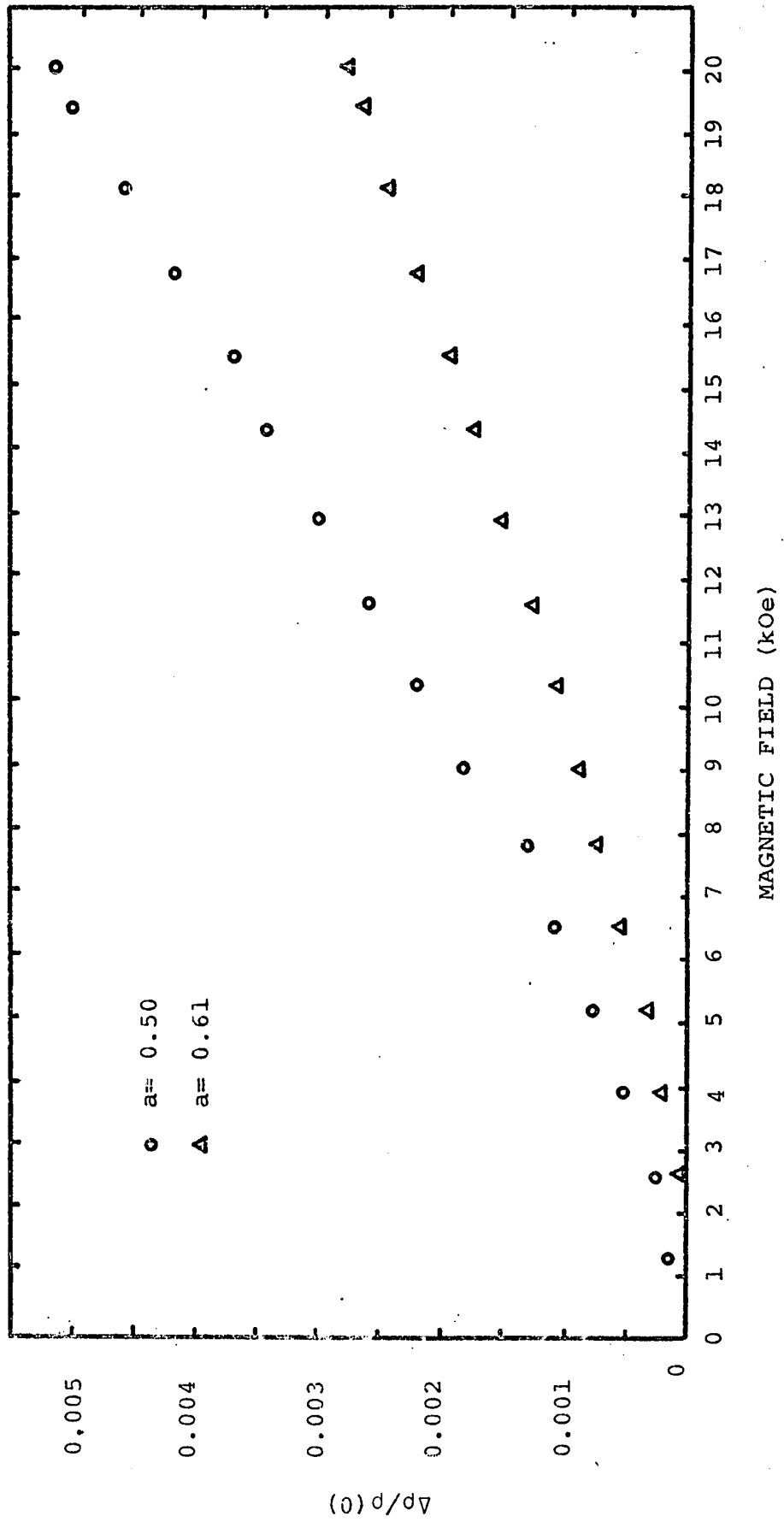remarkable effect seen in the palladium/hydrogen alloys is that small concentrations of hydrogen alter the magnetic field dependence so as to make it very similar to the results in a transverse magnetic field. The saturation field of the longitudinal effect is, evidently, shifted to a higher value since no indication of its presence is seen in the alloys in fields up to $20,000 \, kO_e$.

Alekseevskii et al. (1964) have reported the results of measurements on single crystal palladium in a transverse magnetic field. They found palladium to be a compensated metal whose Fermi surface consists of two parts, an open hole surface, and a closed electron surface. Based on the linear decrease of the magnetic susceptibility with increasing H/Pd ratio (Wucher, 1949), Alekseevskii et al. (1966) made measurements on single crystal low-concentration palladium/hydrogen alloys expecting to see changes in the Fermi surface. Their conclusion was that the open (hole) region of the Fermi surface was not changed by the presence of hydrogen in small concentrations, up to H/Pd = 0.03 . The Hall effect was not altered in this range of concentrations, but was altered at higher concentrations, above H/Pd = 0.05. This indicates that the scattering processes can become important in galvano-magnetic phenomena when hydrogen is added to palladium.

The present results indicate that there may be changes in the Fermi surface which are not detectable in transverse fields but are detectable in longitudinal fields. Using the present picture of palladium/hydrogen alloys, i.e. filling of the d-band, such a change is most likely to take place in the open (hole) portion of the Fermi surface.

To illustrate the behavior of the palladium/hydrogen system in terms of Kohler's rule, a Kohler plot of results in a longitudinal magnetic field is shown in Fig. 3.18. If Kohler's rule were obeyed, all points would lie on the same curve. Kohler's rule is not obeyed, particularly for the high concentration alloys. These deviations are probably indicative of a difference in relaxation time between impurity scattering and phonon scattering.

Magnetoresistance measurements at temperatures as high as 15°K in palladium and some of the low-concentration alloys revealed no new behavior in the magnetoresistance, the only change being a decrease in $\Delta\rho/\rho(0)$. Measurements at 77°K showed no measureable magnetoresistance, indicating that the effect is less than one part in 10^{5} .

Figure 3.18

Kohler plot for the palladium/hydrogen system
in a longitudinal magnetic field at 4.2^{O}K.
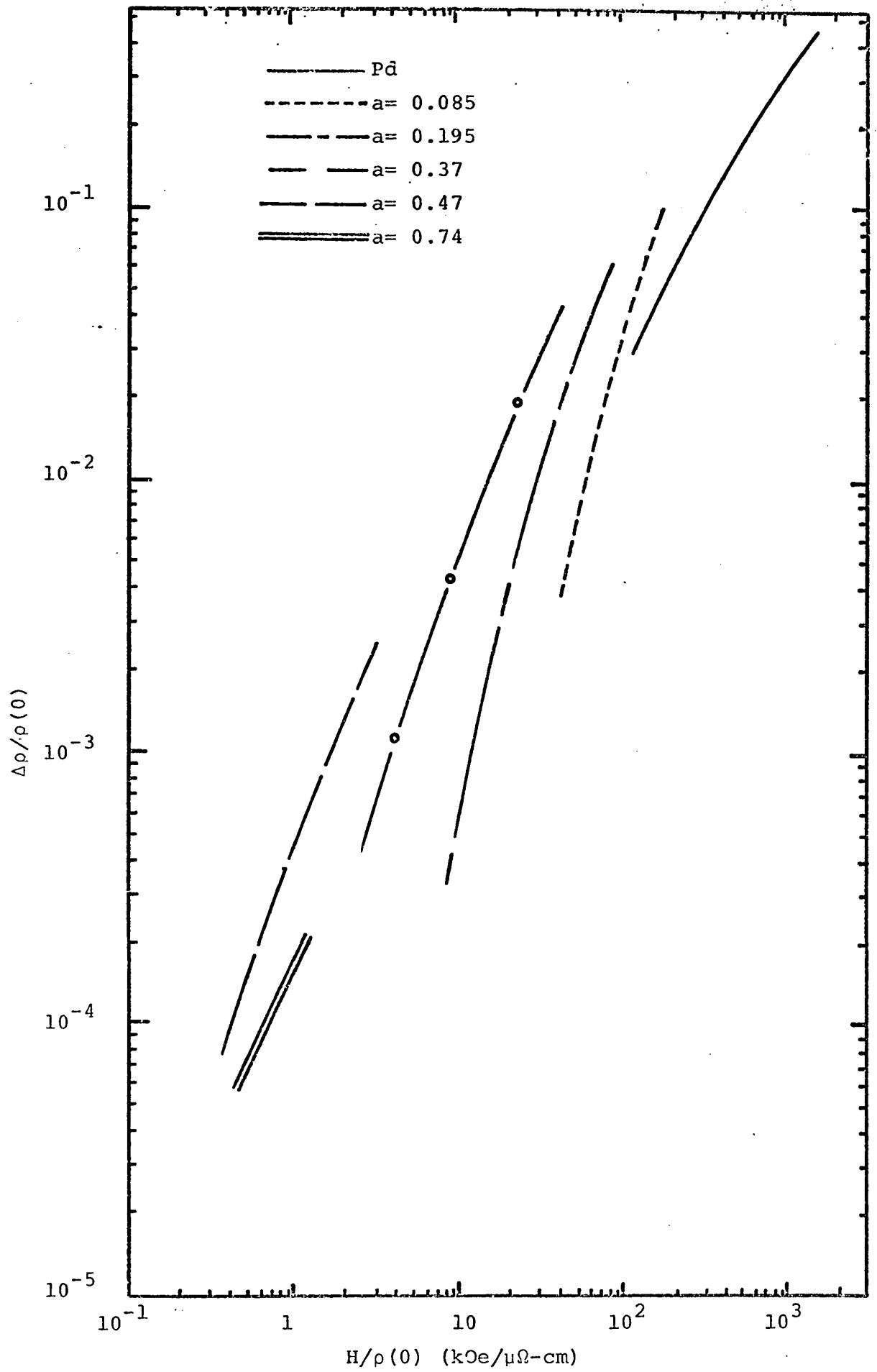
E.   Effects of Hydrogen Occlusion on Tantalum and
     Niobium

A detailed comparison of the results with palladium
is difficult because of the very slight amounts of hydrogen
which can be added to tantalum and niobium by the presently
employed methods. In addition to pure niobium, three
niobium/hydrogen alloys were prepared having concentrations
H/Nb = 0.0045, 0.012, and 0.025. Pure tantalum was studied
as well as alloys of concentration H/Ta = 0.0024, 0.0065, and
0.0114. The temperature dependence of resistivity of the
pure metals followed closely the results of White and Woods
(1959). The simplest way to compare the results of hydrogen
in tantalum and niobium to the results for hydrogen in
palladium is to compare the quantity $\delta\rho$, the change in
resistivity per atomic per cent of hydrogen. For palladium,
at 4.2°K, $\delta\rho$ was found to be 0.02 $\frac{\mu\Omega\text{-cm.}}{\text{at per cent}}$.
For niobium at 9.5°K (niobium is superconducting below
8.8°K), $\delta\rho$ was found to be 0.1 $\frac{\mu\Omega\text{-cm}}{\text{at per cent}}$ and for tantalum
at 5.6°K (tantalum is superconducting below 4.4°K), $\delta\rho$ was
found to be 0.04 $\frac{\mu\Omega\text{-cm}}{\text{at per cent}}$. The value for palladium agrees
well with that quoted by Ho and Manchester (1968) and may
be compared with their value of 0.044 $\frac{\mu\Omega\text{-cm}}{\text{at per cent}}$ for the
case of deuterium in palladium. From these results, it is
clear that comparison of the results for palladium/hydrogen

to other systems, such as tantalum/hydrogen and niobium/ hydrogen at higher concentrations would be of interest.

CONCLUSION

The effects of hydrogen occlusion on the resistivity
of palladium in the low temperature region show that the
hydrogen causes a shift in the exponent n of the expres-
sion $\rho_i \propto T^n$, which is probably characteristic of tempera-
ture dependent electron scattering due to the presence of
the protons. The dominance of this scattering mechanism
makes it impossible to detect a change in the s-d scattering
probability through a change in the momentum gap parameter
θ_E .

Calculations of the characteristic temperature,
θ_r , for palladium and the alloys, show that θ_r is not
affected strongly by the hydrogen in concentrations up to
H/Pd = 0.55 at high temperatures (T $\geq$ θ_r/3) ; but that the
range of temperature in which θ_r can be considered
constant decreases as the hydrogen content increases. For
H/Pd = 0.70 , θ_r increases rapidly as the temperature
decreases, indicating that high frequency local modes due
to the presence of hydrogen become important.

Studies of the residual resistivity as a function
of hydrogen concentration show that the palladium/hydrogen
alloys behave as if the palladium d-band had 0.55 holes/

atom. These results are in agreement with those of palladium/deuterium (Bambakidis et. al. 1969) and support the concept of non-rigid bands proposed by Dugdale and Guénault (1960).

The resistivity anomaly near 55^OK was investigated in detail. Time dependence in the resistivity near the position of the peak was studied. The effect of rapid cooling of the specimen on the residual resistivity was investigated and found to be in qualitative agreement with the theory of Ferguson et al. (1963) on the origin of this anomaly.

Studies of the resistance in transverse and longitudinal magnetic fields showed that the addition of hydrogen to palladium reduces the magnetoresistance, but not in a manner consistent with Kohler's rule. In pure palladium there is no indication of saturation in transverse magnetic fields, but saturation occurs in longitudinal fields. The form of the magnetoresistance is not appreciably altered by the presence of hydrogen; but in the case of longitudinal fields, the hydrogen causes the field dependence to change so that it is much the same as in the transverse case. The saturation field, if it still exists, is shifted to much higher values by the addition of hydrogen.

It is the opinion of this author that further elucidation of the phenomena observed in palladium/hydrogen might be achieved by looking at other alloy systems and using different techniques. For example, Shaltiel (1963) has suggested that the decrease in magnetic susceptibility with increasing hydrogen content in palladium is intimately related to the growth of the β-phase at the expense of the α-phase. This suggestion is contradictory to Mott's hypothesis concerning the filling of the palladium d-band with the hydrogen electrons. This could be investigated in palladium/silver or palladium/gold with hydrogen since these systems retain the α-phase for high concentrations (Maeland, 1968). The resistivity anomaly near $55^{\circ}K$ needs further study to determine its nature. More work on the time dependence of this effect might prove useful. Furthermore, it seems that the use of pressure or impurities (possibly magnetic) might produce an interaction which could help in understanding the phenomena.

APPENDIX I

MAGNETORESISTANCE IN IRON

Galvanomagnetic effects in metals are often sensitive to misalignments between the specimen and the magnetic field. This is especially true when the specimens are single crystals. Effects of misalignment and thermal emf's can usually be corrected by using two directions of sample current for a given magnetic field direction and then reversing the direction of the magnetic field and repeating the procedure.

It is obvious that by cooling a specimen and placing the coil axis parallel to the magnetic field there is always a longitudinal magnetoresistance effect appearing in addition to the transverse effect. In the present experiments the ratio of the specimen length to the coil length was approximately 20 to 1.5, indicating a 7% contribution of longitudinal magnetoresistance to the observed magnetoresistance.

The possible effects of misalignment were first checked by the usual method of reversing the magnetic field direction. Results showed that this reversal produced no significant change. The reversal of the sample current

was important, however, to cancel the effect of thermal emf's.

During the course of the present experiments, measurements were made on transition metals other than palladium, iron being one of these. A further check on misalignment is possible using the results on iron. Berger and DeVroomen (1965) described the importance of the Weiss domains on the magnetoresistance of iron. They point out that in zero applied field the Weiss domains have a random orientation. The local internal field $\vec{B}$ is therefore approximately parallel to the current density in certain domains and perpendicular in other domains. This results in an average resistivity of the sample which is intermediate between the low value corresponding to longitudinal magnetoresistance and the higher value corresponding to transverse magnetoresistance. When a small longitudinal external field is applied, it tends to align all domains giving rise to a situation where only longitudinal magnetoresistance is present. This causes the experimentally observed decrease in resistance (Smit, 1951). Similarly, a small transverse field produces a resistance increase (Smit, 1951). However, when the specimen used is ferromagnetic, the sample geometry is especially important because of the demagnetizing factor, N.

The magnetic field $\vec{H}$, the magnetic induction $\vec{B}$, and the intensity of magnetization $\vec{J}$ are related by

$$\mu_o \vec{H} = \vec{B}_e - N\vec{J}$$

and $N = 0$ for a long straight wire parallel to the magnetic field, $N = \frac{1}{2}$ for a wire perpendicular to the magnetic field. Then, in an approximate transverse magnetic field the longitudinal contribution of the magnetic field can have an appreciable effect.

Fig. 1. shows results obtained using iron in the transverse geometry previously described. The inset is a schematic diagram taken from Berger and DeVroomen (1965) showing the expected form of the magnetoresistance effect for a transverse field. Comparison shows that the present experimental results, though displaying some inconsistencies with the expected behavior, must be put in the category of an approximately transverse field. It is interesting to note that reversing the direction of the magnetic field did not alter the magnetoresistance of iron in the presently employed geometry. Thus it could not be used to correct for the misalignment.

One may conclude that the geometry used for obtaining a transverse magnetic field in the present experi-

Fig. Appendix 1.1

Magnetoresistance of iron in transverse and longitudinal

fields at 4.2^{O}K. The inset shows the expected form of

the magnetoresistance of iron for the cases indicated.

Resistance of a very pure ferromagnet in a small applied field H_0, at low temperature. Curve (a) refers to a longitudinal applied field, and curve (b) to an exactly transverse applied field. Curve (c) refers to an approximately transverse applied field.
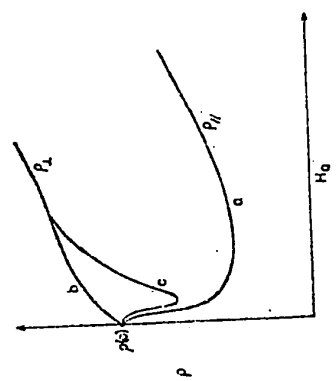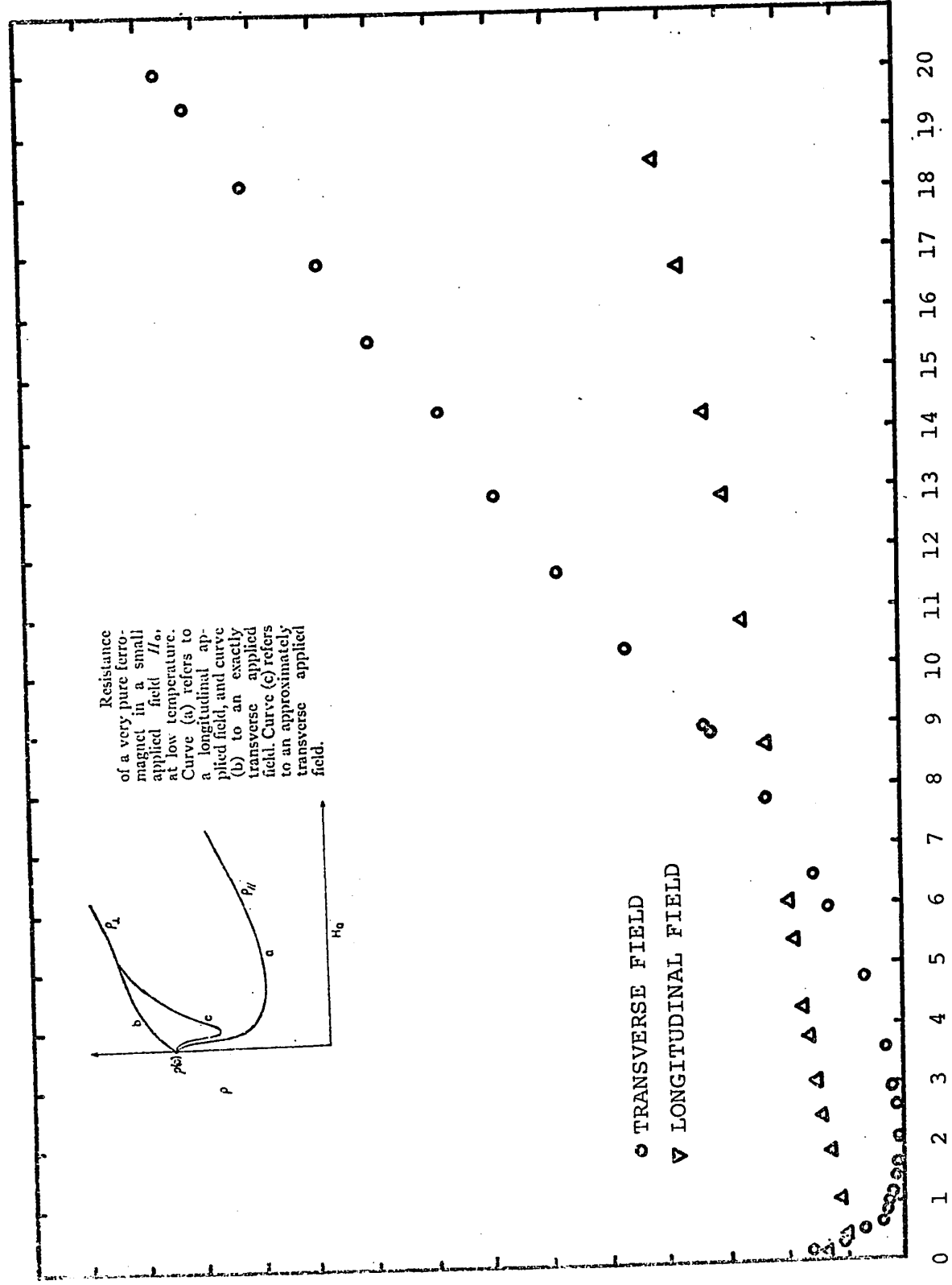
○ TRANSVERSE FIELD

▽ LONGITUDINAL FIELD

MAGNETIC FIELD (kOe)

$\Delta\rho/\rho(0)$

ments must be used with caution if the specimens are

ferromagnetic.

APPENDIX II

SPECTROGRAPHIC ANALYSIS

OF THE

SPECIMENS

<u>Palladium</u>   Supplied by Johnson, Matthey and Co. Ltd.

Impurities detected:

Element	Quantity Present (parts per million)
Silicon	10
Platinum	5
Rhodium	3
Copper	2
Iron	1
Magnesium	1

<u>Niobium</u>   Supplied by Materials Research Corporation.

Primary Impurities Detected:

Element	Quantity Present (parts per million)
C	8
N	23.4
O	4
Ta	100
W	6.4

<u>Tantalum</u>   Supplied by Materials Research Corporation.

Primary Impurities Detected:	Quantity (parts per million)
C	10
O	3.5
N	2.3
Nb	25
Ni	1.5
W	1.2

APPENDIX III

Electrical Resistivity Measurements

in

Palladium-Hydrogen Alloys

C. T. Haywood and L. Verdini

Electrical resistivity measurements in palladium–hydrogen alloys

C. T. HAYWOOD AND L. VERDINI

Department of Physics, University of Alberta, Edmonton, Alberta

The resistivity of palladium and palladium–hydrogen alloys has been studied in the temperature range 2–300 °K. At low temperatures (10 °K $< T <$ 60 °K), it is found that ρ_i is proportional to T^n, with $n = 3.1$ for pure palladium; but n decreases to 2.3 for an alloy with H/Pd $= 0.25$. For high concentrations and at low temperatures, the resistivity is found to be dependent upon the time and rate of cooling through the $\beta \rightleftarrows \beta^*$ transformation. The residual resistivity is lower for faster cooling rates.

The increase in resistivity due to 1 at. % hydrogen in palladium is calculated and found to be of the same order of magnitude as that for interstitials in other f.c.c. metals, but less then that found for hydrogen in the b.c.c. transition metals tantalum and niobium at room temperature.

Introduction

The palladium–hydrogen alloy system has been extensively studied in the past and the existence of two face-centered cubic phases, termed α and β, has been verified (McKeehan 1923). At concentrations with an atomic ratio less than H/Pd ≈ 0.015, only the α phase, characterized by a lattice parameter that varies continuously from 3.890 to 3.895 Å, exists. Above H/Pd ≈ 0.53, only the β phase, characterized by a lattice parameter of approximately 4.02 Å, exists. For intermediate concentrations the two phases coexist (Simons and Flanagan 1965; Aben and Burgers 1962). Neutron diffraction studies (Ferguson et al. 1965) have been most revealing. In the β phase, the occluded protons occupy the octahedral crystallographic sites at high temperatures ($T > 55$ °K), while at low temperatures ($T < 55$ °K) there is a partial migration to the tetrahedral sites, giving rise to the β^* phase. The resistivity (Schindler et al. 1959) and heat-capacity anomalies (Mitacek and Aston 1961) seen in the region of 55 °K have been explained on the basis of this transformation from the β to the β^* phase.

Despite the present abundance of data on this system, it was felt that a systematic investigation of the electrical resistivity over a wide range of concentrations was justified in order to see more clearly the effects of the $\beta \rightleftarrows \beta^*$ transformation on the electrical conduction properties. A detailed investigation from helium temperatures to room temperature was thus initiated.

Experimental Technique

Samples of 99.999% spec-pure palladium obtained from Johnson, Matthey and Co.

Limited were used for all measurements. The diameter of the wire was 0.025 cm. Potential and current leads of palladium were attached by fusion in a vacuum. This was accomplished by wrapping the leads around each end of the specimen and bombarding the junction with electrons ejected by an electron gun. This method was chosen in order to avoid the possibility of contamination of the specimen. Typical specimen length was 20 cm, with leads about 2 cm long.

The specimens were coiled and placed in an oven for annealing. It was found that annealing in helium at one atmosphere produced a lower residual resistivity than annealing in a vacuum. The annealing temperature was 900 °C and the time about 4 hours. In order to be certain that no helium was retained by the sample, the helium atmosphere was removed when the oven temperature had decreased to 400 °C, and the sample was then allowed to cool to room temperature in a vacuum of 10^{-6} mm Hg. To illustrate the effects of this treatment, typical resistivity values for a specimen are given in Table I.

After annealing, the specimen (including leads) was charged to the desired hydrogen concentration by electrolysis in 0.1 N sulphuric acid. A current of 1 mA was used in most cases; however, for the higher concentrations 0.5 mA was used.

TABLE I

Electrical resistivity ($\mu\Omega$-cm) of typical sample

Conditions	$\rho_{273\ °K}$	$\rho_{4.2\ °K}$	$\rho_{4.2\ °K}/\rho_{273\ °K}$
As received	10.14	17.5×10^{-2}	17.2×10^{-3}
After annealing	10.03	0.961×10^{-2}	0.958×10^{-3}

TABLE II

Determination of the hydrogen content

Sample No.	H/Pd from electrolysis	R/R_0	H/Pd from Barton *et al.* (1963)	Assumed H/Pd
19	—	—	—	0.02
17	0.08	1.09	0.075	0.08
18	0.16	1.20	0.18	0.16
18	0.32*	1.29	0.25	0.25
20	0.40	1.48	0.41	0.40
19	0.55	1.76	0.56	0.55
19	0.57	1.79	0.59	0.57
19	0.59	1.82	0.64	0.59
19	0.61	1.83	0.65	0.61
19	0.63	1.83	0.65	0.63
19	0.65	1.84	0.65$_5$	0.65
19	0.67	1.85	0.66	0.66
19	0.77	1.86	0.67	0.67
19	2.03*	1.91	0.70	0.70

*Bubbles observed on the wire during electrolysis.

The hydrogen concentration was determined both from the electrolysis data and from the change in resistivity at 0 °C (Barton, Lewis, and Woodward 1963). As seen in Table II, for low concentrations the electrolysis data are reliable, while for higher concentrations they are no longer reliable (bubbles were seen to form on the sample surface at high concentrations). For high concentrations the value of R/R_0, where R_0 and R are the values of the resistance at 0 °C before and after charging, was used to determine the hydrogen content.

After being charged, the specimen was placed in the cryostat described by White and Woods (1955) and left in vacuum for at least 24 hours in order to be certain that the hydrogen was in equilibrium within the palladium lattice. A reference specimen of pure palladium was in thermal contact with the hydrogenated sample during all measurements so that resistance values could be obtained for both specimens at the same temperature. An electronic temperature controller (Dauphinee and Woods 1955) was used to achieve temperatures above 4.2 °K. Below 100 °K the temperature was determined by measuring the resistance of a calibrated germanium resistor obtained from Solitron, Inc., and above 100 °K a thermocouple of copper vs. gold + 2.1 at. % cobalt was used. Data were taken at intervals of approximately 5 °K when the resistance was fairly constant and at intervals as small as 0.5 °K when the resistance was changing rapidly with temperature.

All electrical potentials were measured by using a Guildline, Inc., Type 9160 Potentiometer with a Type 5214/9460 Photo-Cell Galvanometer Amplifier, and a Type 9461-A Galvanometer. Such a system is capable of detecting a change in potential of 0.01 μV. Effects due to thermal e.m.f.'s were avoided by making measurements with the current in the forward and reverse directions and averaging appropriately. The resistance of pure palladium, taking into account current and temperature fluctuations, could thus be determined to 0.1 % near helium temperatures, with less uncertainty for the charged specimens.

Comparison of the present resistivity values with those given by White and Woods (1959) shows that the room-temperature resistivity of the pure palladium samples used in the present experiments deviates from their measurements by 2%. This is undoubtedly due to determinations of the geometrical factor (cross-sectional area/length). This error was considered unimportant and no attempts were made to correct it.

Experimental Results and Discussion

Experimental results of the resistivity as a function of temperature for various concentrations are given in Fig. 1. For purposes of clarity the data points have been omitted. It is seen that the addition of hydrogen to palladium increases the resistivity at all temperatures and that this increase is substantial at high concentrations. The behavior of the resistivity as a function of
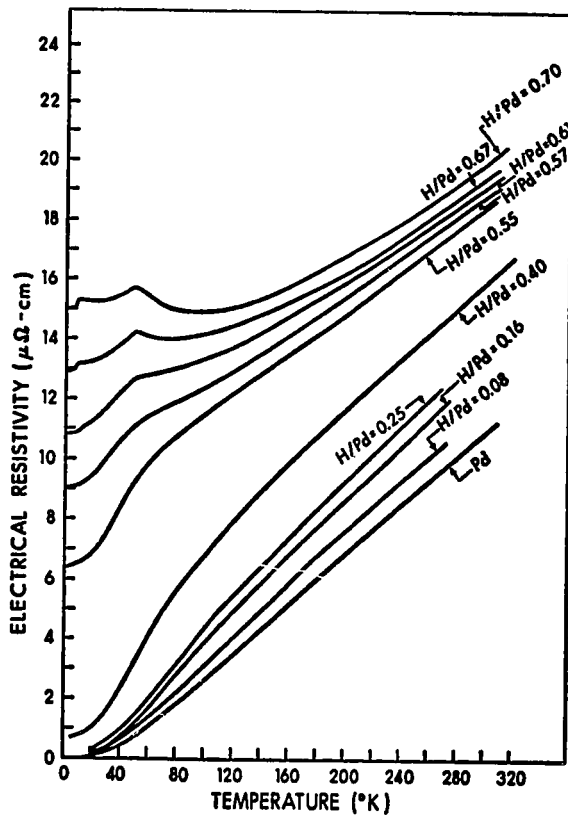
FIG. 1. Electrical resistivity as a function of temperature for pure palladium and various palladium-hydrogen alloys.

temperature for the alloys with H/Pd ≤ 0.40 is very similar to that of the pure metal. At low temperatures $(10\ ^\circ K < T < 60\ ^\circ K)$ the ideal resistivity $\rho_i(T) = \rho(T) - \rho_r$, ρ_r being the residual resistivity, is proportional to T^n. The exponent n depends on the hydrogen content and decreases with increasing H/Pd ratio, as shown in Table III. Between 120 and 300 °K the dominant mechanism affecting the resistivity seems to be scattering between the s and d bands of palladium, as predicted by the Mott model. The d band should be filled by the s electrons of the hydrogen atoms at H/Pd $\simeq$ 0.55,

TABLE III

Experimental values for the exponent n of
$\rho_i \propto T^n$ at $T < 60\ ^\circ K$

H/Pd	ρ_r ($\mu\Omega$-cm)	n
0 (as received)	17.5×10^{-2}	2.7 ± 0.1
0 (annealed)	0.76×10^{-2}	3.1
0.02	4.7×10^{-2}	3.0
0.08	8.8×10^{-2}	2.8
0.16	8.2×10^{-2}	2.7
0.25	13.0×10^{-2}	2.3

resulting in ρ proportional to T (Gerritsen 1956). For pure palladium ρ is seen to be concave towards the temperature axis. This same behavior holds for H/Pd ≤ 0.40. For H/Pd = 0.55, ρ is very nearly proportional to the temperature and for H/Pd = 0.57, ρ is concave away from the temperature axis. Thus, qualitative agreement with the present theory seems to be obtained.

In Fig. 2 the anomalous region near 50 °K is seen in detail. The maximum is present only for H/Pd ≥ 0.57, with the position of the peak largely independent of concentration. The position of the subsequent minimum is, however, noticeably concentration dependent. For H/Pd = 0.61 it occurs at 58 °K and for H/Pd = 0.70 it occurs at 92 °K. This is in general agreement with Schindler et al. (1959) and Rota (unpublished Ph.D. thesis, University of Rome, 1967). It is also of interest to note that for H/Pd = 0.70 the value of the resistivity at the minimum is less than the residual value obtained at 4.2 °K.
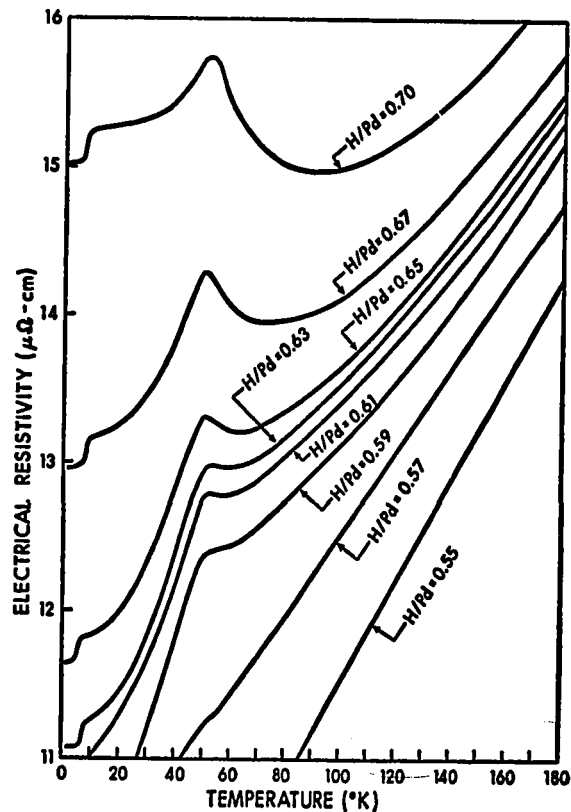

FIG. 2. Electrical resistivity as a function of temperature for high-concentration palladium-hydrogen alloys, showing the anomaly near 55 °K due to the $\beta \rightleftarrows \beta^*$ transformation.
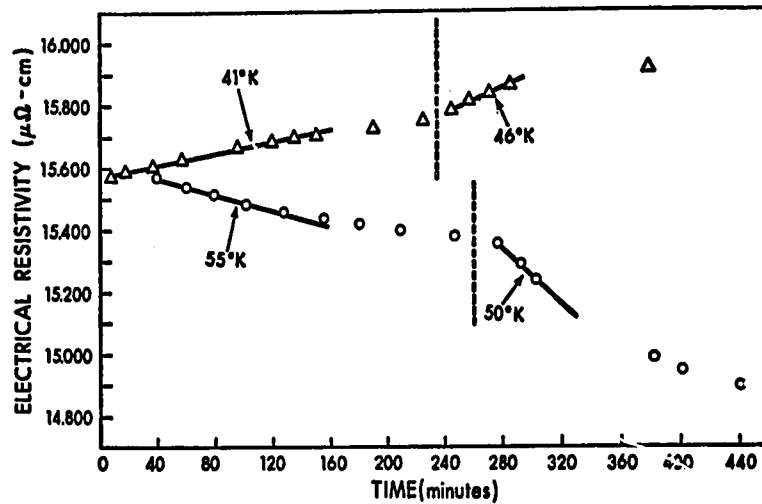
Fig. 3. Time dependence of the electrical resistivity of a hydrogen–palladium alloy with H/Pd = 0.70. The dotted vertical lines indicate the times at which the temperature was changed.

Figure 3 shows some effects that are directly attributable to the β ⇄ β* transformation. For the top curve, the sample was brought rapidly (in about 9 minutes) from 77 to 41 °K and the resistivity was studied as a function of time. The resistivity is seen to increase with time. After 235 minutes the temperature was brought to 46 °K and then the resistivity was observed to increase faster with time. This behavior is to be contrasted with the lower curve, where the sample temperature was quickly changed from 77 to 55 °K, again in about 9 minutes. Here, the resistivity decreased with time. After 260 minutes the temperature was reduced to 50 °K and the resistivity decreased at a faster rate.

Figure 4 again emphasizes the large effect which the β ⇄ β* transformation can have on the electrical resistivity. The "fast-cooling" results were obtained by first cooling the sample from liquid nitrogen to liquid helium temperatures in about 4 minutes and then measuring the resistivity as a function of temperature as the temperature was slowly increased. The resistivity maximum thus obtained occurred at 52 °K and its value was 15.76 μΩ-cm. The "slow-cooling" results were obtained by taking resistivity measurements as the temperature was slowly decreased during a 5-hour period. The resistivity maximum occurred at 44 °K, with a value of 15.77 μΩ-cm in this case. The resistivity was also measured while the sample temperature was slowly increased after the measurement of the "slow-cooling" behavior. This resulted in a

maximum at 46.5 °K, with a value of 15.81 μΩ-cm. Except for the differences near the maximum, there was no important hysteresis effect observed during this cycle. In contrast
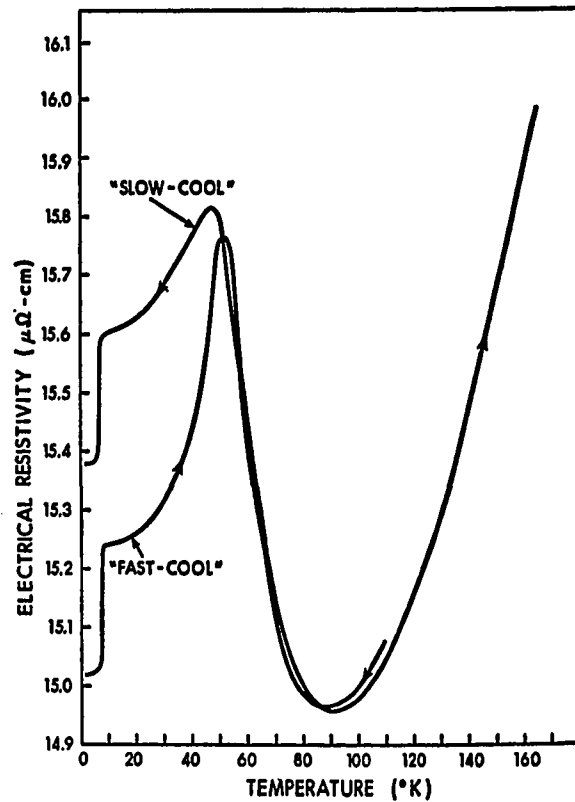

Fig. 4. Electrical resistivity as a function of temperature for the alloy with H/Pd = 0.70 for two different rates of cooling. The jump below 10 °K is probably due to some superconducting impurities.
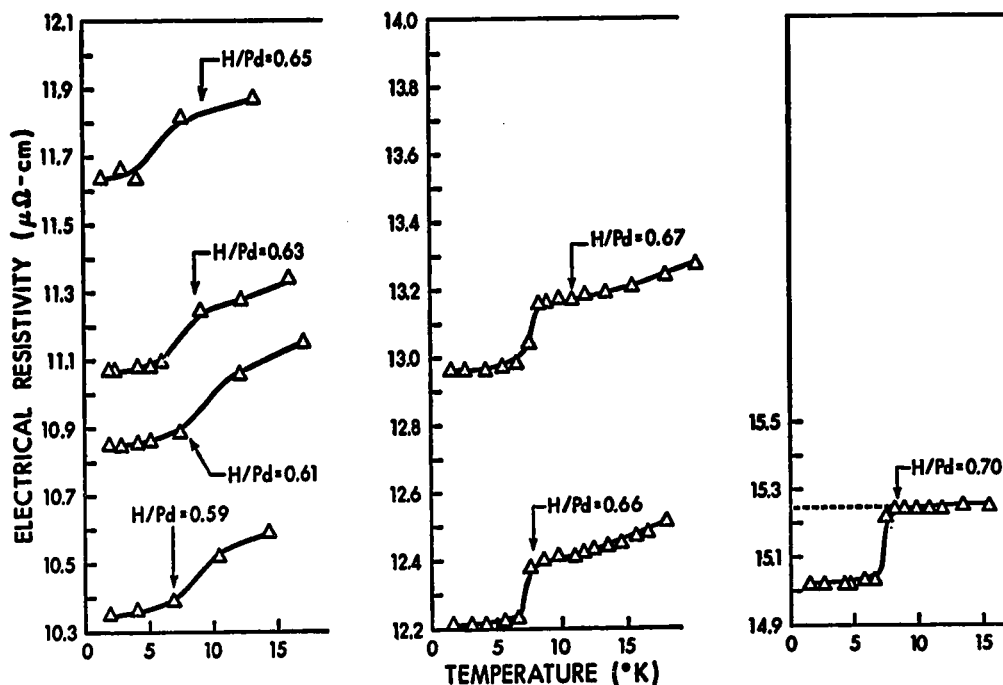
FIG. 5. Low-temperature anomaly observed in a single specimen for different concentrations.

to the usual behavior of metallic alloys, the residual resistivity is higher for the slower cooling rate. However, this can be explained by the work of Nace and Aston (1957). Their specific-heat data indicate a high residual entropy ($S_0 = 0.59 \pm 0.18$ e.u.) for this alloy, suggesting that the β^* phase is a rather disordered state. Thus, it is not surprising that the residual resistivity of this configuration should be so high.

Figure 5 shows the resistivity as a function of temperature for temperatures less than 15 °K. There is a resistivity jump near 7.5 °K which becomes more pronounced as the hydrogen concentration is increased. Cycling in this temperature region produced no evidence of hysteresis in the electrical resistivity, and, as evidenced by Fig. 4, the $\beta \rightleftarrows \beta^*$ transformation does not seem to be important. This behavior has been observed only in one specimen and it is assumed that this effect is due to the unwanted presence of some superconducting impurities. It is possible that some impurities were introduced during the annealing treatment, but this is unlikely, since other specimens annealed in the same manner exhibited normal behavior. The results in Fig. 5 indicate a hydrogen-concentration dependence, suggesting that the

impurities might have been introduced during the electrolytic charging. However, subsequent attempts to reproduce this effect by purposely contaminating the electrolytic solution with the soft-soldering alloy used to connect the palladium leads to copper leads have failed. The resistivity jump has been investigated in the presence of a magnetic field produced by a superconducting solenoid. As seen in Fig. 6, there is a temperature-dependent critical field for this effect. When the field is sufficiently high, the resistivity assumes a value very close to the extrapolated value shown on the right side of Fig. 5.

The quantity $\Delta\rho = \rho_{alloy} - \rho_{palladium}$, calculated from the present measurements at different temperatures for the low-concentration alloys and for a cold-worked pure palladium wire in the "as-received" conditions, is shown in Fig. 7. It is seen that Matthiessen's rule, which requires a constant value of the parameter $\Delta\rho(T)$ for a given substitutional alloy, is applicable neither to the alloys nor to the cold-worked specimen. In the latter case, the graph of the extra resistivity as a function of temperature has a slight maximum around 50 °K and is very similar to that recently found in pure strained copper (Dugdale and Basinski 1967). For the alloy of
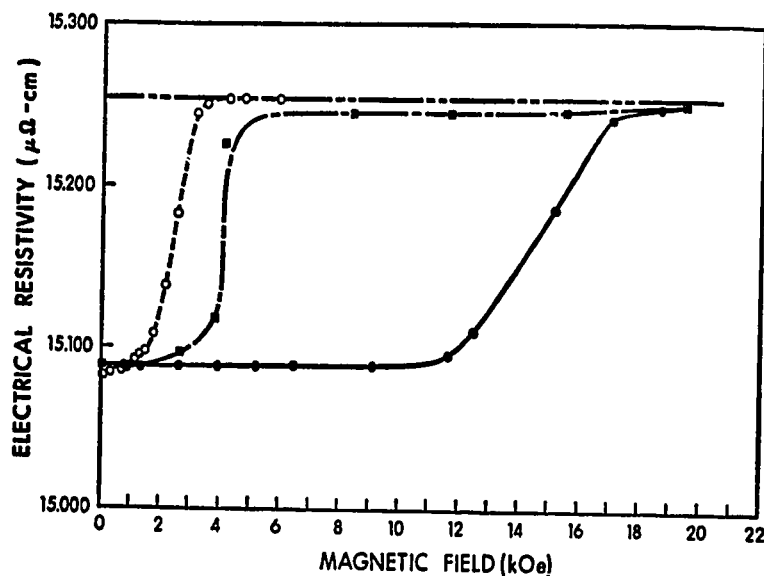
FIG. 6. Electrical resistivity as a function of magnetic field for the "anomalous" specimen at H/Pd = 0.70 showing the existence of a temperature-dependent critical field: ●, T = 4.15 °K; ■, T = 6.95 °K; O, T = 7.56 °K. There are no data points shown for 11.4 °K since the resistivity remained constant with field (— - - —).
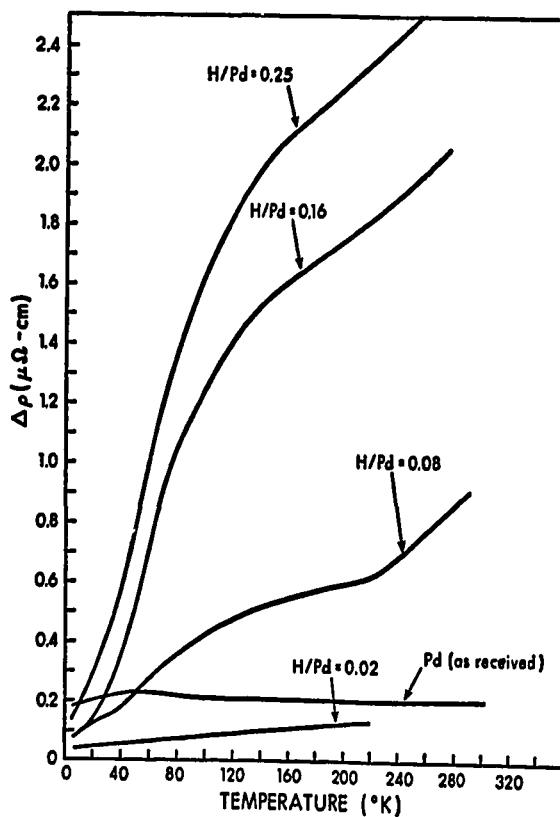

FIG. 7. The change of electrical resistivity due to the presence of hydrogen in palladium as a function of temperature for different concentrations.

concentration H/Pd $\simeq$ 0.02, the quantity $\Delta\rho$ increases almost linearly with temperature over the whole temperature range, having only a small bump between 80 and 120 °K. For higher concentrations (H/Pd $\leqslant$ 0.40), $\Delta\rho$ increases rapidly with temperature, showing an almost linear increment for T > 220 °K. This behavior may be considered similar in some aspects to that found in substitutional alloys (Gerritsen 1956, p. 206).

The change in resistivity at 4.2 and 273 °K due to the presence of hydrogen has been tabulated in Table IV for some of the alloys. It is interesting to note the large discrepancy in the increase $\delta\rho$ due to 1 at.% of hydrogen for the different alloys at 4.2 °K. This is probably due to the fact that the results are largely affected by lateral effects such as the creation of dislocations or other lattice defects (Verani-Borgucci and Verdini 1965) which may give a contribution of the same order of magnitude (Hunter and Nabarro 1953), i.e. 10^{-2} $\mu\Omega$-cm. The values $\delta\rho$ found at 273 °K are in good agreement with those given in the case of interstitial atoms in other f.c.c. metals such as copper, silver, and gold (Dexter 1952). For copper, silver, and gold in substitutional alloys with palladium, the atomic resistivity increase was 0.89 $\mu\Omega$-cm/at.%,

TABLE IV

Change in electrical resistivity due to the presence of hydrogen in palladium

T (°K)	H/Pd	H (%)	ρ_0 (μΩ-cm)	$\Delta\rho$ (μΩ-cm)	$\delta\rho$ (μΩ-cm/at. %)
4.2	0.02	1.96	1.18×10^{-2}	3.7×10^{-2}	1.9×10^{-2}
	0.08	7.4	0.89×10^{-2}	7.9×10^{-2}	1.07×10^{-2}
	0.16	13.8	1.57×10^{-2}	5.6×10^{-2}	0.48×10^{-2}
	0.25	20.0	1.57×10^{-2}	11.4×10^{-2}	0.57×10^{-2}
273.15	0.02	1.96	9.9	0.16	8.0×10^{-2}
	0.08	7.4	9.8	0.86	11.6×10^{-2}
	0.16	13.8	9.9	2.07	14.5×10^{-2}
	0.25	20.0	9.9	2.87	14.4×10^{-2}

0.44 μΩ-cm/at. %, and 0.41 μΩ-cm/at. %, respectively (Gerritsen 1956). In the case of hydrogen in tantalum and niobium, it was found that $\delta\rho = 0.80$ μΩ-cm/at. % and $\delta\rho = 0.75$ μΩ-cm/at. % respectively (Verani-Borgucci and Verdini 1965).

Conclusions

The behavior of the electrical resistivity of the alloys of the hydrogen–palladium system has been investigated as a function of temperature. The β ⇌ β* transformation is seen to dominate the resistivity below 100 °K for specimens with a high concentration of hydrogen. Time dependence in the resistivity of the palladium–deuterium system has been reported (Smith 1964), but no such time dependence has previously been reported in the palladium–hydrogen system. Present results show that this time dependence is observable and that measurements of the residual resistivity of the palladium–hydrogen alloys are in doubt, unless care is taken to ensure an equilibrium state. The β ⇌ β* transformation is responsible for the resistivity peak near 55 °K and for the history dependence of the electrical resistivity.

Acknowledgments

The authors are indebted to Dr. S. B. Woods

for the use of his cryostat and to the National Research Council of Canada for financial support.

ABEN, P. C. and BURGERS, W. G. 1962. Trans. Faraday Soc. **58**, 1989.

BARTON, J. C., LEWIS, F. A., and WOODWARD, I. 1963. Trans. Faraday Soc. **59**, 1201.

DAUPHINEE, T. M. and WOODS, S. B. 1955. Rev. Sci. Instr. **31**, 253.

DEXTER, D. L. 1952. Phys. Rev. **87**, 768.

DUGDALE, J. S. and BASINSKI, Z. S. 1967. Phys. Rev. **157**, 552.

FERGUSON, G. A., SCHINDLER, A. I., TANAKA, T., and MORITA, T. 1965. Phys. Rev. **137**, 483.

GERRITSEN, A. N. 1956. Handbuch der Physik, Vol. XIX (Springer Verlag, Berlin).

HUNTER, S. C. and NABARRO, F. R. N. 1953. Proc. Roy. Soc. (London), Ser. A, **220**, 542.

McKEEHAN, L. W. 1923. Phys. Rev. **21**, 334.

MITACEK, P. and ASTON, J. G. 1961. Nature, **191**, 271.

NACE, D. M. and ASTON, J. G. 1957. J. Am. Chem. Soc. **79**, 3623.

SCHINDLER, A. I., SMITH, R. J., and KRAMER, E. W. 1959. Tenth Intern. Conf. on Refrigeration, Copenhagen, p. 74.

SIMONS, J. W. and FLANAGAN, T. B. 1965. J. Phys. Chem. **69**, 3581, 3773.

SMITH, ROBERT J. 1964. National Aeronautics and Space Administration Rept. (E-2785).

VERANI-BORGUCCI, M. and VERDINI, L. 1965. Phys. Stat. Sol. **9**, 243.

WHITE, G. K. and WOODS, S. B. 1955. Can. J. Phys. **33**, 58.

———— 1959. Phil. Trans. Roy. Soc. (London), Ser. A, **251**, 274.

BIBLIOGRAPHY

Aben, P.C. and Burgers, W.G., (1962) Trans. Faraday Soc. 58, 1989.

Alekseevskii, N.E., Karstens, G.E., and Mozhaev, V.V., (1966) Soviet Physics JETP 23, 798.

Alekseevskii, N.E., Karstens, G.E., and Mozhaev, V.V., (1964) Soviet Phys. JETP 19, 1333.

Appel, J., (1963) Phil. Mag. 8, 1071.

Arons, R.R., Bouman, J., Wizenbeek, M., Klaase, P.T.A., Tuyn, C., Leferink, G., and DeVries, G., (1967) Acta Metallurgica 15, 144.

Baber, W.G., (1937) Proc. Roy. Soc. (London) A158, 383.

Bambakidis, G., Smith, R.J., and Otterson, D.A., (1969) Phys. Rev. 177, 1044.

Barton, J.C., Lewis, F.A., and Woodward, I. (1963) Trans. Faraday Soc. 59, 1201.

Berger, L. and deVroomen, A.R., (1965) Journal of Applied Physics 36, 2777.

Bergsma, J. and Goedkoop, J.A., 1960. Physica 26, 744.

Bickel, P.W. and Berlincourt, T.G., 1960. Phys. Rev. 119, 1603.

Chambers, R.G., 1956. Proc. Roy. Soc. (London), Ser. A238, 344.

Coles, B.R., and Taylor, J.C., 1962. Proc. Roy. Soc. A, 267, 139.

Colquitt, Leroy, Jr., (1965) Journal of Applied Physics, 36, 2454.

Dauphinee, T.M., and Woods, S.B., (1955) Rev. Sci. Instr. 31, 253.

Dugdale, J.S., and Basinski, Z.S., (1967) Phys. Rev. 157, 552.

Dugdale, J.S., and Guénault, A.M., 1966. Phil. Mag. 13, 503.

Ferguson, G.A., Schindler, A.I., Tanaka, T., and Morita, T., (1965) Phys. Rev. 137, 483.

Gibb, R.P., MacMillan, J., and Roy, R.J., 1966. Phys. Chem. 70, 3024.

Gruneisen, E., (1933) Ann. Physik 16, 530.

Haywood, C.T., and Verdini, L. (1968) Can. J. Phys. 46, 2065.

Hildenbrand, D.L. and Giaque, W.F., (1953) J. Am. Chem. Soc. 75, 2811.

Ho, N.S., and Manchester, F.D., (1968) Canadian Journal of Physics 46, 1341.

Howarth, D.J., and Sondheimer, E.N.,Proc Roy.Soc. A219 53 (1953).

Jan, J.-P., "Solid State Physics" vol. 5, Academic Press, New York.

Jones, H. Handbuck der Physik, Vol. XIX, Springer Verlag, Berlin.

Kelly, F.M. and MacDonald, D.K.C. (1953) Can. J. Phys. 31, 147.

Kley, W., Peretti, J., Rubin, R. and Verdan G., (1967) Journal de Physique, Supplement 2 C1-26.

Kohler, M., (1938) Ann Physik 32, 211.

Lettington, A.H., 1965, Phil Mag., 11, 863.

Lewis, F.A., (1967) "The Palladium/Hydrogen System" Academic Press, New York.

Maeland, Arnulf, J. 1968. Canadian Journal of Physics, 46, 111.

McKeehan , L.W., (1923) Phys. Rev. 21, 334.

Meaden, G.T., (1965) "Electrical Resistance of Metals" Plenum Press, New York.

Mitacek, P. and Aston, J.G., (1961) Nature, Lond. 191, 271.

Mott, N.F., (1936a) Proc. Roy. Soc., 153, 699.

Mott. N.F., (1936b) Proc. Roy. Soc., 156, 368.

Mott, N.F. and Jones, H., (1936) "Theory of the Properties of Metals and Alloys", Oxford University Press, Oxford.

Nace, G.M. and Aston, J.G. (1957), J.Am. Chem. Soc. 79 3623.

Norberg , R.E. (1952), Phys. Rev. 86, 745.

Owen, E.A. and Evans, E.W., (1967) Brit. J. Appl. Phys. 18, 605.

Powell, R.L., Bunch, M.D., and Corruccini, R.J., (1961) Cryogenics, 1, 139.

Rayne, J.A. Phys. Rev. 118, 1545 (1960).

Schindler, A.I., Smith, R.J., and Kammer, E.W. (1959) Tenth Int. Conf. on Refrigeration at Copenhagen, p.74.

Shaltiel, D., (1963) J. Appl. Phys. 34, 1190.

Simons, J.W., and Flanagan, T.B., (1965) J. Phys. Chem 69 3581, 3773.

Simons, J.W. and Flanagan, T.B., (1966) J. Chem. Phys. 44, 3486.

Skóskiewicz, T., and Baranowski, B. (1968) Phys. Stat. Sol. 30, K33.

Smit, J., (1951) Physica 17, 612 (1951).

Smith, D.P., (1947) "Hydrogen in Metals", University of Chicago Press, Chicago.

Smith, Robert, J. 1964. National Aeronautics and Space Administration Rept. (E-2785).

Smith, R.J., Schindler, A.I., Kammer, E.W., (1962) Phys. Rev. 127, 179.

Sondheimer, E.H., and Howarth, D.J., (1953) Proc. Roy. Soc. (London) A219, 53.

Smit, J., (1955) Physica 21, 877.

Verani-Borguicci, M., and Verdini, L., (1965) Phys. Stat. Sol. 9, 243.

Vuillemin, J.J., and Priestley, M.G., 1965, Phys. Rev. Letters, 14, 307.

White, G.K., and Woods, S.B., (1959) Phil. Trans. Roy. Soc. (London), Ser A, 251, 274.

Wilson, A.H., (1938) Proc. Roy. Soc. A, 167, 580.

Wilson, A.H., (1953) "Theory of Metals" Cambridge University Press, Cambridge.

Wucher, J. (1949) Compt. rend. 229, 175.

Ziman, J.M. (1964) "Principles of the Theory of Solids", Cambridge University Press, Cambridge.