THERMOELECTRICITY IN MAGNETIC ALLOYS

by

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ABSTRACT

Mechanisms leading to giant Seebeck coefficients in metallic alloys were studied. Experimental measurements were made in Fe doped $Ag_{1-x}Pd_x$ alloys between 4.2 and 520°K. The resistance minimum phenomenon (Kondo effect) and giant thermopower was discovered in Ag(Fe) alloys and estimates of the Kondo temperature and exchange scattering parameter are 15°K and -0.53 eV, respectively. The $Ag_{1-x}Pd_x$(Fe) alloys show large negative thermopowers (~-40 μV/deg) in the region above room temperature. The experimental results in conjunction with recent theories of thermoelectricity in the presence of s-d scattering suggest that the exchange parameter remains negative (antiferromagnetic) for all values of x between 0 and 1. This result contradicts the interpretation recently given to Kondo effect behavior in $Cu_{1-x}Pd_x$(Fe) alloys in which a change in sign of the exchange parameter was suggested.

Certain principles of designing metallic thermoelectric devices were given. These were based on systematics of parameters, as a function of the position of the magnetic solute and solvent in the periodic table, of known materials and on recent theories of s-d exchange scattering and the Kondo effect. Using these principles it was shown how devices with Seebeck coefficients of ~100 μV/deg could be obtained. In addition other potentially useful metallic thermoelectric materials are suggested for further investigation.

TABLE OF CONTENTS

LIST OF FIGURES

ACKNOWLEDGEMENTS

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I. INTRODUCTION

The work described in this report was stimulated by research at the NASA-Electronics Research Center, which indicated that metallic alloys might prove to be more suitable for certain thermoelectric heat pumping applications than currently available materials. It has been known for some time that nonmagnetic metals such as the noble metals, when doped with small concentrations of magnetic impurities, exhibit giant Seebeck coefficients S over a wide temperature range(1). In fact Au(Fe) versus chromel thermocouples are now widely used as sensitive thermometers between liquid helium and room temperatures(2). The magnitude of S in these alloys is orders of magnitude larger than one would expect on the basis of simple free electron ideas. One can inquire into the fundamental reasons for these large thermopowers and, in particular, ask if materials can be designed to give values of S which are so large that significant Peltier applications will result. The present work was an attempt to try to define the fundamental parameters of a metallic alloy that control the magnitude of the thermoelectric power.

From a rather general point of view, we expect on theoretical grounds that the thermopower of a metal due to electron diffusion is(1)

$$S = \frac{\pi^2 k^2 T}{3e} \left(\frac{\partial \ell n\ n(E)}{\partial E} + \frac{\partial \ell n\ v^2(E)}{\partial E} + \frac{\partial \ell n\ \tau(E)}{\partial E} \right)_{E_F}, \quad (1)$$

where T is the absolute temperature, n(E) the electronic density of states at energy E, v an average electron velocity, τ the electronic relaxation time, and E_F the Fermi energy. Thus it is clear that giant values of S might be expected if n(E), $v^2(E)$, or $\tau(E)$ are abnormally sensitive functions of energy. Equation (1) already gives an indication of the source of the high values of S when magnetic impurities are present. In these circumstances, an electron scattering from a localized magnetic moment will have its spin flipped and this will be an inelastic scattering process because of the Zeeman energy required. Under these conditions it is clear that $\tau(E)$ could be a sharp function of (E) so that a large derivative could result.

It has also become clear recently(3,4) that the presence of giant thermoelectric powers at low temperatures in magnetic alloys - is intimately connected with the resistance minimum often found in these alloys at low temperatures. Kondo in 1964 showed that these minima could be explained by assuming an interaction between the localized magnetic impurity of spin S and the conduction electron of spin s, the so-called s-d exchange interaction, of the form

$$H_{s-d} = - J \underset{\sim}{S} \cdot \underset{\sim}{s} \qquad (2)$$

where J is the exchange parameter. A perturbation calculation, carried to second order in the Born

approximation, gave a resistivity of the form(3)

$$\rho_{spin} = c\,\rho_m[1 + (3zJ/E_F)\ln T] \qquad (3)$$

$$\rho_m = 3\pi m J^2 S(S+1)(V/N)/2e^2 h E_F ,$$

where m is the free electron mass, V the crystal volume, N the total number of atoms, z the electron per atom ratio, and c the atomic fraction of impurity atoms. It is clear that this expression, and therefore perturbation theory, diverges as T approaches zero. It is thought that the temperature at which perturbation theory diverges,

$$T_K \simeq (E_F/k)\exp(-1/n(E_F)J) , \qquad (4)$$

gives the temperature at which there is a form of phase transition to a spin-compensated, many-body state(4). Estimates of T_K may be obtained from anomalies in the magnetic susceptibility, specific heat, and, most importantly for the present work, the thermoelectric power(5,6). The thermopower shows a characteristic peak, of very large magnitude, in the region of T_K.

The results of Equations (1) and (4), along with the preceding discussion, suggest therefore that giant thermopowers are likely to be obtained in magnetic alloys and that the density of states plays a major role in determining the magnitude of the thermopower and also the temperature at

which the effect is to be maximized. For practical devices it would be of obvious benefit if T_K were in the vicinity of room temperature.

With the above ideas in mind, the present work has focused on measurements of S and ρ in the Fe doped AgPd alloy system. This system was chosen because we know Fe in Pd forms giant magnetic moments of magnitude $\simeq 12\ \mu_B$(4) and we expect Fe in Ag also to form a moment though no definitive work has been done on the Kondo effect in Ag(Fe). In addition, Ag and Pd are adjoining neighbors in the periodic table so that their masses and sizes are similar. This suggests that one can control the density of states at the Fermi level, $n(E_F)$, and thus control T_K through Equation (4). Whether one can treat the host metal (AgPd) in an average band model and neglect the local environments of the individual magnetic moments is, of course, open to question. But, because of the similarities of Ag and Pd mentioned above, this assumption probably holds better than in any other alloy system which still allows $n(E_F)$ to be varied greatly. Since $n(E_F)$ for Pd is much larger than for Ag because of the holes in the d band, Equation (4), taken at face value, suggests that T_K should increase as one alloys Ag(Fe) with Pd.

The plan of the research was as follows. First it was necessary to demonstrate the existence of the Kondo effect in the Ag(Fe) system. This was done and, as expected, the phenomenon turned out to be a low temperature one. The second

major part of the investigation was to measure ρ(T) and S(T) at high temperatures (to ~500^{o}K), in order to study the spin dependent scattering effects on the thermopower and resistivity in the temperature region of practical interest.

Because there are an infinite number of possible binary and ternary alloys of the form A(M) and AB(M), where A and B are nonmagnetic metals and where M is a magnetic impurity, it is clearly not possible to simply adopt a trial and error method for determining alloys and concentrations which give significant values of S. Therefore the present work has concentrated on a single ternary alloy system in an attempt to understand the principles underlying giant thermoelectric effects. Nevertheless, in addition to presenting results on the AgPd(Fe) system, some general comments on other alloy systems will be made in the concluding section of this report.

II. EXPERIMENTAL PROCEDURES

A. Sample Preparation

The alloys were made from high purity silver ingot (69 pure) and palladium sponge (59 pure), supplied by Johnson Matthey Chemicals, Ltd. Samples were prepared by induction melting in an inert gas atmosphere, chill casting, and mechanical swaging. The weighed charge was melted in a zirconium oxide crucible by induction heating from a graphite susceptor mounted vertically in a vycor tube. The temperature of the charge was monitored by a thermocouple inside a zirconia thermocouple protection tube, which also acted as a plunger covering a hole in the crucible. The charge was held at the melting point of its highest melting component for 15 minutes, and the plunger was lifted by a magnet, permitting the melt to drop 2 inches into a carbon-coated copper mold, chilled by circulating liquid nitrogen. The sample thus obtained was cleaned in an ultrasonic bath, inserted in a stainless steel tube and swaged to a diameter of about 2 mm. The stainless steel sheath was then filed off.

Each specimen was analyzed for silver-palladium composition and iron content by the M.I.T. quantitative analysis laboratory.

The sample notation used throughout this report is as follows:

$$(Ag_{1-x}Pd_x)_{10^6-y}(Fe)_y \equiv Ag_{1-x}Pd_x(Fe)_y \quad (x,y)$$

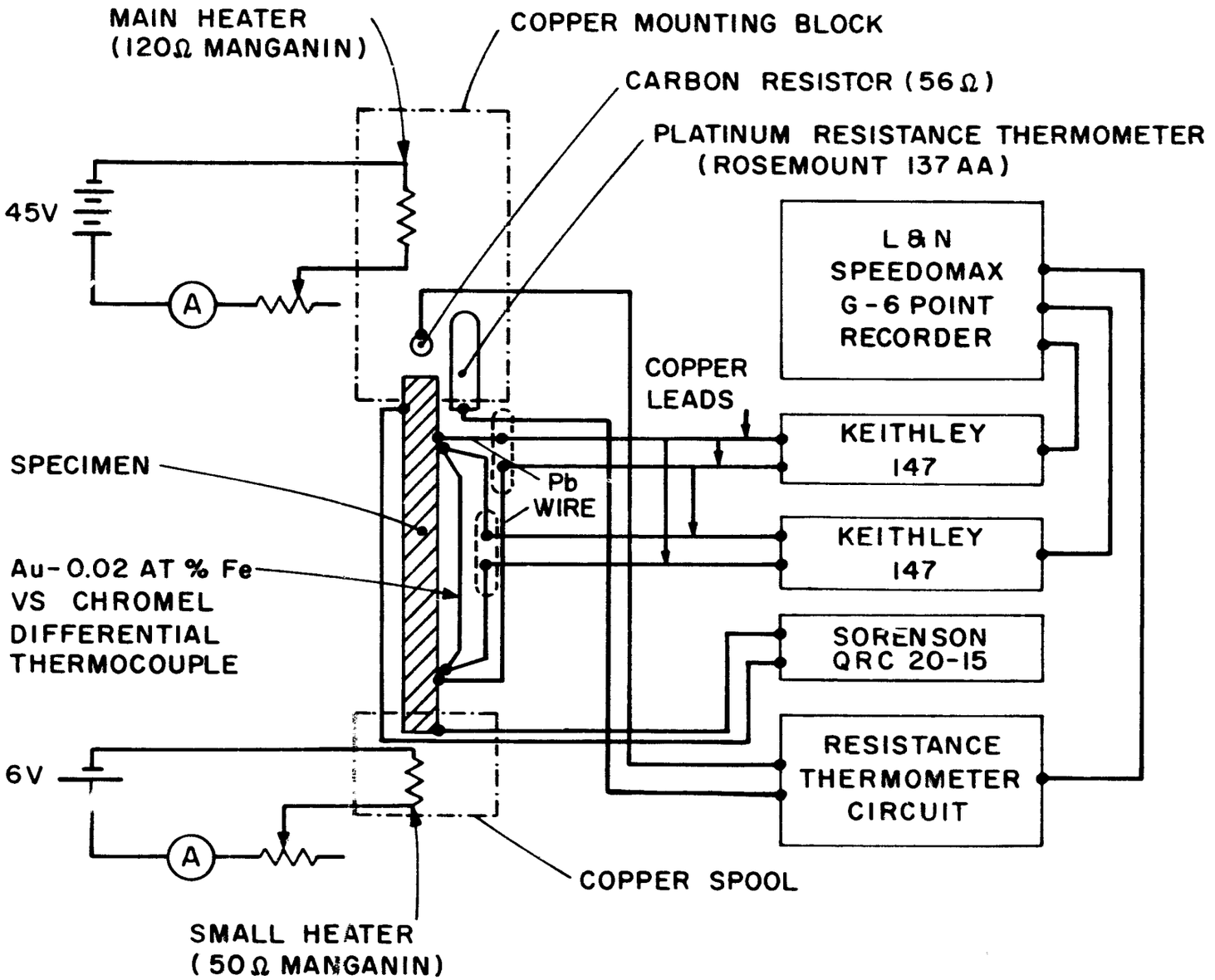
The shorthand notation (x,y) thus denotes the atomic fraction of Pd (x) in the host metal and y denotes the fraction of Fe in the total alloy, in parts per million.

B. Measurement Techniques

Measurements of both resistivity and thermopower consist of the measurement of a voltage across the sample, the former caused by a superposed current and the latter by a temperature gradient produced by a small heater mounted on one end of the sample. These measurements were made using the electronics shown in Figure 1 from below the liquid helium boiling point up to room temperature in a cryostat, and from room temperature up to 500°K in a furnace. Measurements were recorded on perforated paper tape in an automatic readout system, and analyzed by computor. These measurement techniques have been described previously(7).

The cryostat consists of two concentric cylindrical vacuum cans suspended on stainless steel tubes from a brass flange at the dewar head, with independent vacuum control in each can. The inner can was sealed with pressure on a lead wire; the outer can was sealed with Wood's metal solder. Approximately one atmosphere of helium gas was maintained within the inner can throughout the run, in order to help minimize changing thermal voltages in probe contacts.

Figure 1: Schematic of sample and electronics used to measure S(T) and ρ(T) in low temperature apparatus.


MAIN HEATER
(120Ω MANGANIN)
COPPER MOUNTING BLOCK
CARBON RESISTOR (56Ω)
PLATINUM RESISTANCE THERMOMETER
(ROSEMOUNT 137 AA)
45V
A
L & N
SPEEDOMAX
G-6 POINT
RECORDER
COPPER
LEADS
KEITHLEY
147
SPECIMEN
Pb
WIRE
KEITHLEY
147
Au-0.02 AT % Fe
VS CHROMEL
DIFFERENTIAL
THERMOCOUPLE
SORENSON
QRC 20-15
RESISTANCE
THERMOMETER
CIRCUIT
6V
A
COPPER SPOOL
SMALL HEATER
(50Ω MANGANIN)

Temperature was controlled by manipulation of the pressure of helium gas in the outer can for heat conduction to the cryogen, by a main heater wrapped around the inner can, and by a control heater, wrapped around the flange of the inner can. The main heater was manually adjusted; the control heater, via a cryogenic temperature controller built by I.R.I. Co., by a GaAs diode mounted near it. Measurements could be made below the liquid helium boiling point by a facility for regulated pumping on the dewar. The temperature was monitored by calibrated carbon and platinum resistance thermometers.

A simple sample holder was built for a horizontal furnace for measurements above room temperature. Two copper cylinders, one-inch diameter, clamp onto each end of the sample and contain insulated pressure contact probes for the voltage measurement and each a junction of an iron-constantan thermocouple for the temperature gradient measurement. One cylinder was wrapped with a 10 watt nichrome heater for producing the temperature gradient, and a constant current supply was connected across the two cylinders for the resistance measurement.

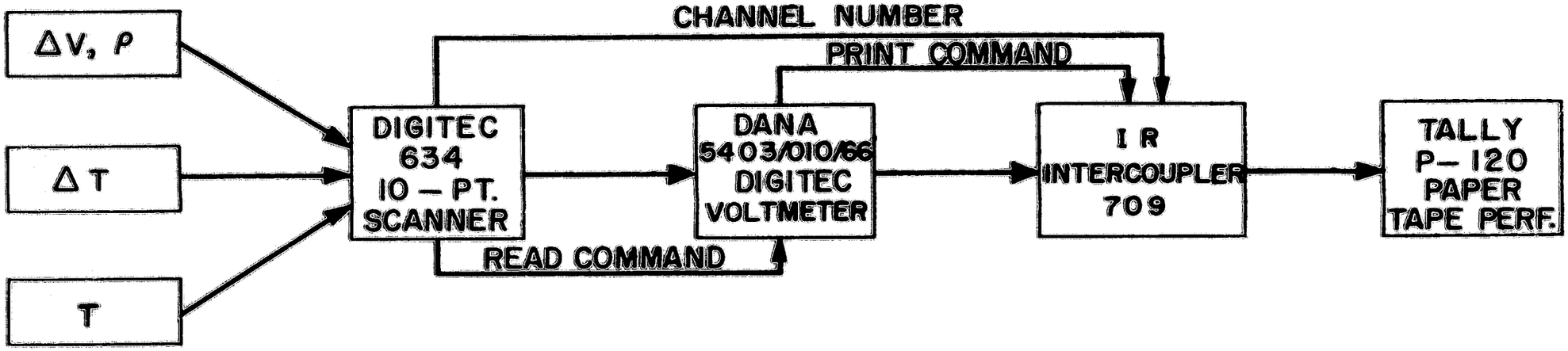
Thermopower measurements in the cryostat were made as follows. After the specimen reached thermal equilibrium at a given temperature, a small transient temperature gradient was generated by passing current through the small heater on one end of the specimen. The three signals,

temperature, temperature differential, and voltage, were recorded sequentially on a strip chart recorder and on paper tape (Figure 2). This data was processed by a computer program which averaged the sample voltage-to-thermocouple voltage ratio over the duration of the measurement, and converted this to the absolute thermopower of the specimen by a calculation involving the thermopowers of the calibrated Au-Fe-chromel differential thermocouple and the lead voltage leads(7).

For resistance measurements in the cryostat, current leads were soldered to the ends of the specimens and specimen voltage was measured on the same lead leads as for the thermopower measurements. A current of 1 A was supplied by a PAR Princeton TC602CR power supply. Voltages for both directions of current were recorded on paper tape at five readings in each direction for a given temperature, and averaged by computer.

Thermopower and resistance measurements in the high temperature apparatus were made in a manner similar to the low temperature apparatus. The data were recorded and analyzed manually, however.

Figure 2: Block diagram of data acquisition system.


ΔV, ρ
ΔT
T
DIGITEC
634
10 – PT.
SCANNER
CHANNEL NUMBER
PRINT COMMAND
READ COMMAND
DANA
5403/010/66
DIGITEC
VOLTMETER
I R
INTERCOUPLER
709
TALLY
P – 120
PAPER
TAPE PERF.

III. RESULTS AND DISCUSSION

A. Low Temperature Results

As indicated earlier, it was first necessary to prove the existence of the s-d exchange scattering mechanism in the Ag(Fe) alloys. Figure 3 shows the resistivity for 537 and 600 ppm Fe samples and for a pure Ag sample ($\lesssim$1 ppm impurities) in the low temperature region. A resistance minimum is obvious. The spin part of the resistivity per unit impurity, $\Delta\rho/c = (\rho_{alloy} - \rho_{pure})/c$, is plotted for a 600 ppm and 537 ppm alloy in Figure 4. That the curves are not congruent indicates an error in the Fe concentration in solid solution. Equation (3) gives

$$\frac{\partial \Delta\rho/c}{\partial \ell n T} = \frac{9\pi m z (V/N)\, S(S+1)}{2e^2 h E_F^2} J^3, \qquad (5)$$

from which J may be calculated. The average value obtained from the two curves is

$$J = -0.53 \text{ eV},$$

which is a reasonable value for this antiferromagnetic interaction strength. It is not possible to estimate the Kondo temperature T_K from the resistivity results for Ag(Fe) because $\rho(T)$ has not approached the low temperature unitarity limit(4). However, an anomalously high value of the thermoelectric power of Ag(Fe) is seen at low temperatures in

Figure 3: Low temperature resistivity of 537 and 600 ppm Fe in Ag and pure Ag samples.

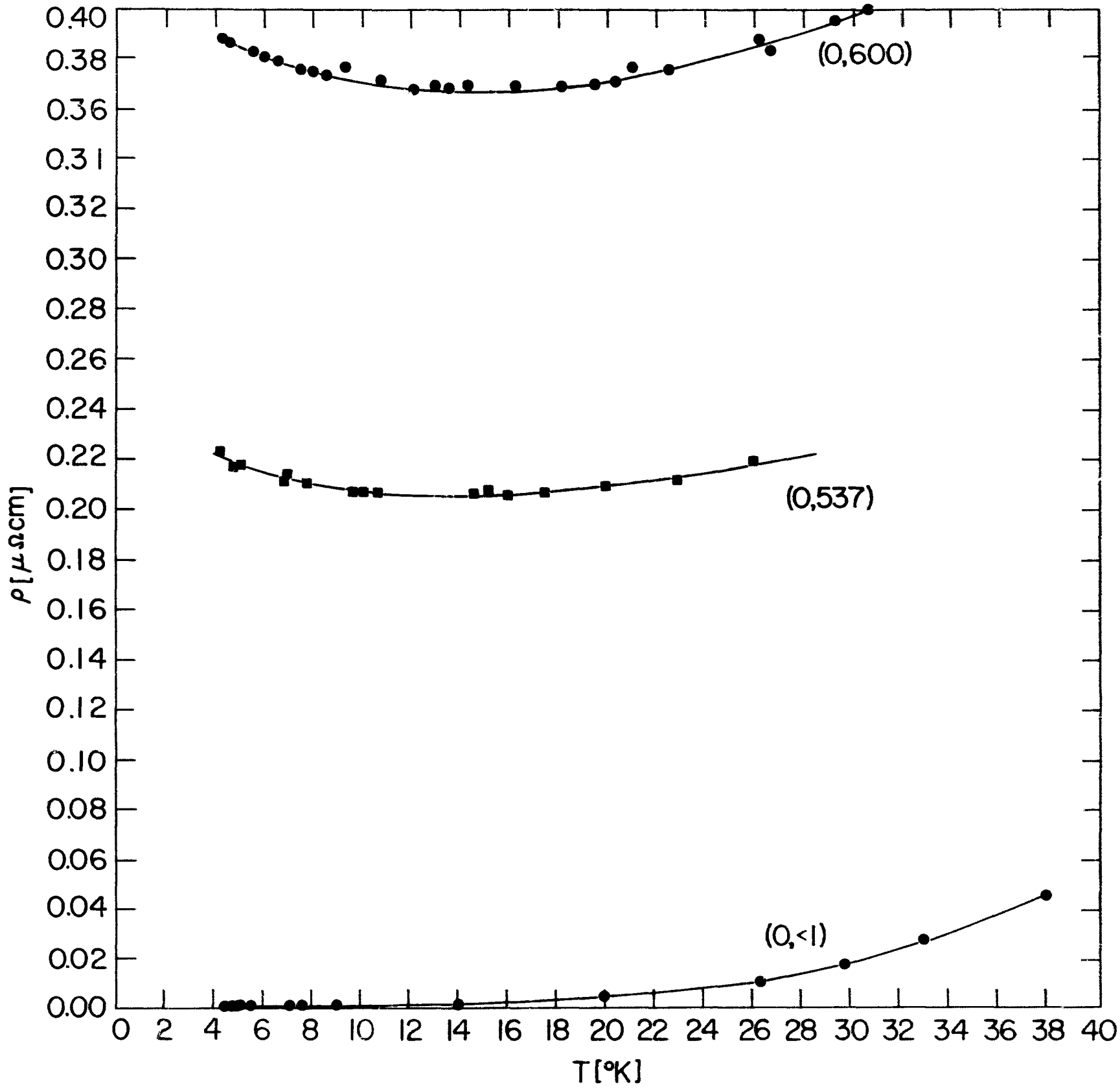

0.40
0.38
0.36
0.31
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
ρ[μΩcm]
(0,600)
(0,537)
(0,<1)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
T[°K]

Figure 4: Incremental resistivity per ppm of Fe in Ag(Fe) alloys.

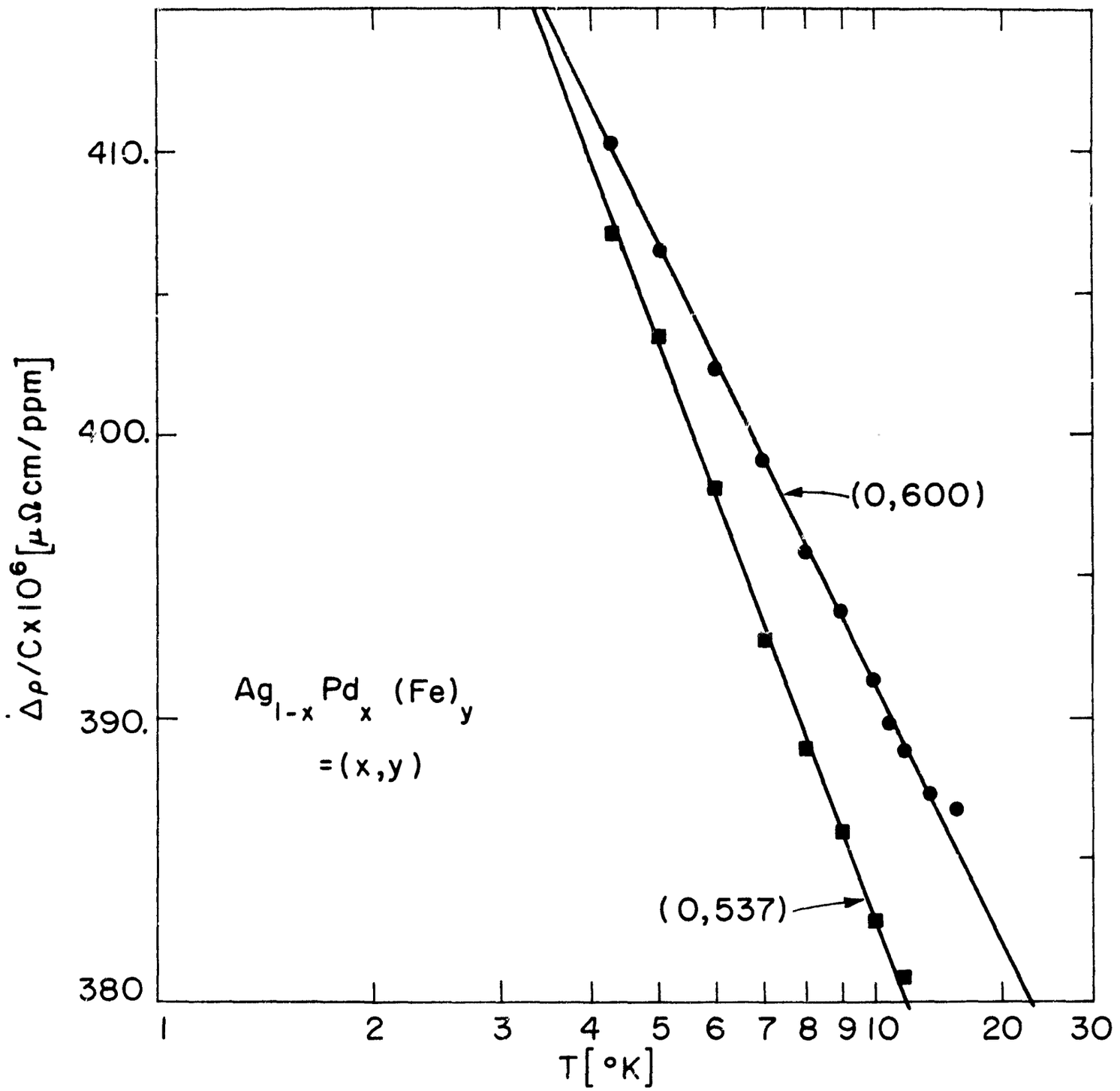

410.
400.
390.
380
$\Delta\rho/C \times 10^6 [\mu\Omega cm/ppm]$
$Ag_{1-x}Pd_x(Fe)_y$
=(x,y)
(0,600)
(0,537)
1
2
3
4
5
6
7
8
9
10
20
30
T[°K]

Figure 5. The large negative peak at T ≈ 15°K suggests that its origin is also the s-d exchange scattering mechanism which gives rise to the Kondo effect. Thus we estimate the Kondo temperature for the Ag(Fe) system to be

$$T_K \approx 15^{\circ}K \ .$$

This value is similar to that of Cu(Fe) and this is reasonable because of the similarity in the electronic structures of Ag and Cu. The above two pieces of evidence, *viz.* the resistance minimum and giant thermopower, provide the first convincing proof of the Kondo effect in this alloy system.

B. High Temperature Results

The second part of the investigation consisted of detailed temperature and concentration dependent measurements of Fe doped AgPd alloys. Figures 6 and 7 exhibit the temperature dependence of $\rho(T)$ and $S(T)$ for the alloys between ~280°K and 520°K. Figures 8 and 9 exhibit the concentration dependence of ρ and S at 273°K. In these two figures the solid curve represents data on nominally *pure* AgPd(8,9). There are several interesting points to be made concerning Figures 6 - 9.

First, clearly there are some very large values of thermoelectric power in these alloys. The order of magnitude is ~40 μV/deg. This confirms our expectations of larger

Figure 5: S(T) for pure Ag and $Ag(Fe)_{600}$ in low temperature region.

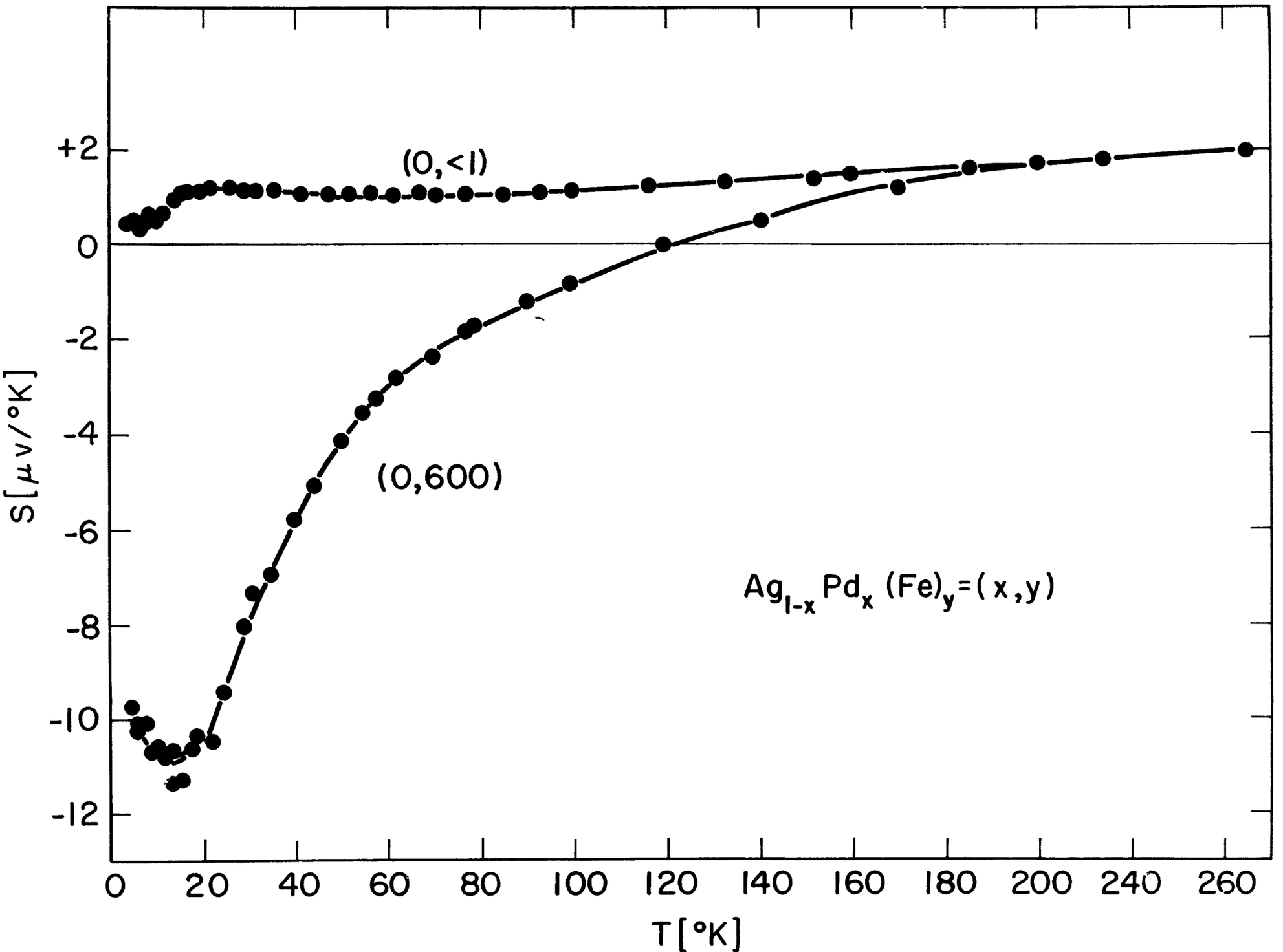

+2
0
-2
-4
-6
-8
-10
-12
S[μv/°K]
(0,<1)
(0,600)
Ag1-x Pdx (Fe)y=(x,y)
0
20
40
60
80
100
120
140
160
180
200
240
260
T[°K]

Figure 6: High temperature resistivity of AgPd(Fe) alloys.

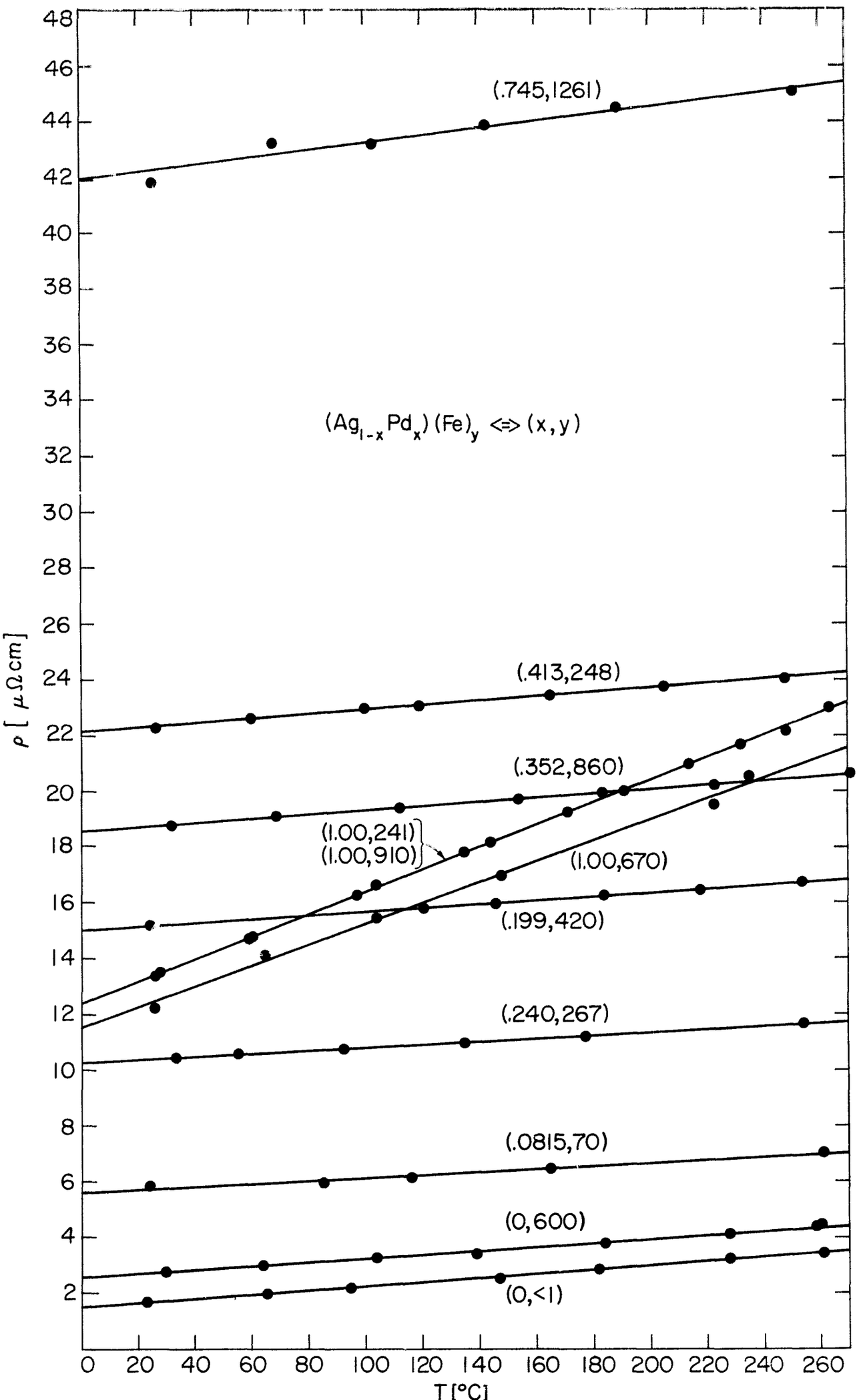

(.745,1261)
(Ag1-xPdx)(Fe)y <=> (x,y)
(.413,248)
(.352,860)
(1.00,241)
(1.00,910)
(1.00,670)
(.199,420)
(.240,267)
(.0815,70)
(0,600)
(0,<1)
ρ [μΩcm]
T [°C]
0 20 40 60 80 100 120 140 160 180 200 220 240 260
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48

Figure 7: High temperature thermopower of AgPd(Fe) alloys.

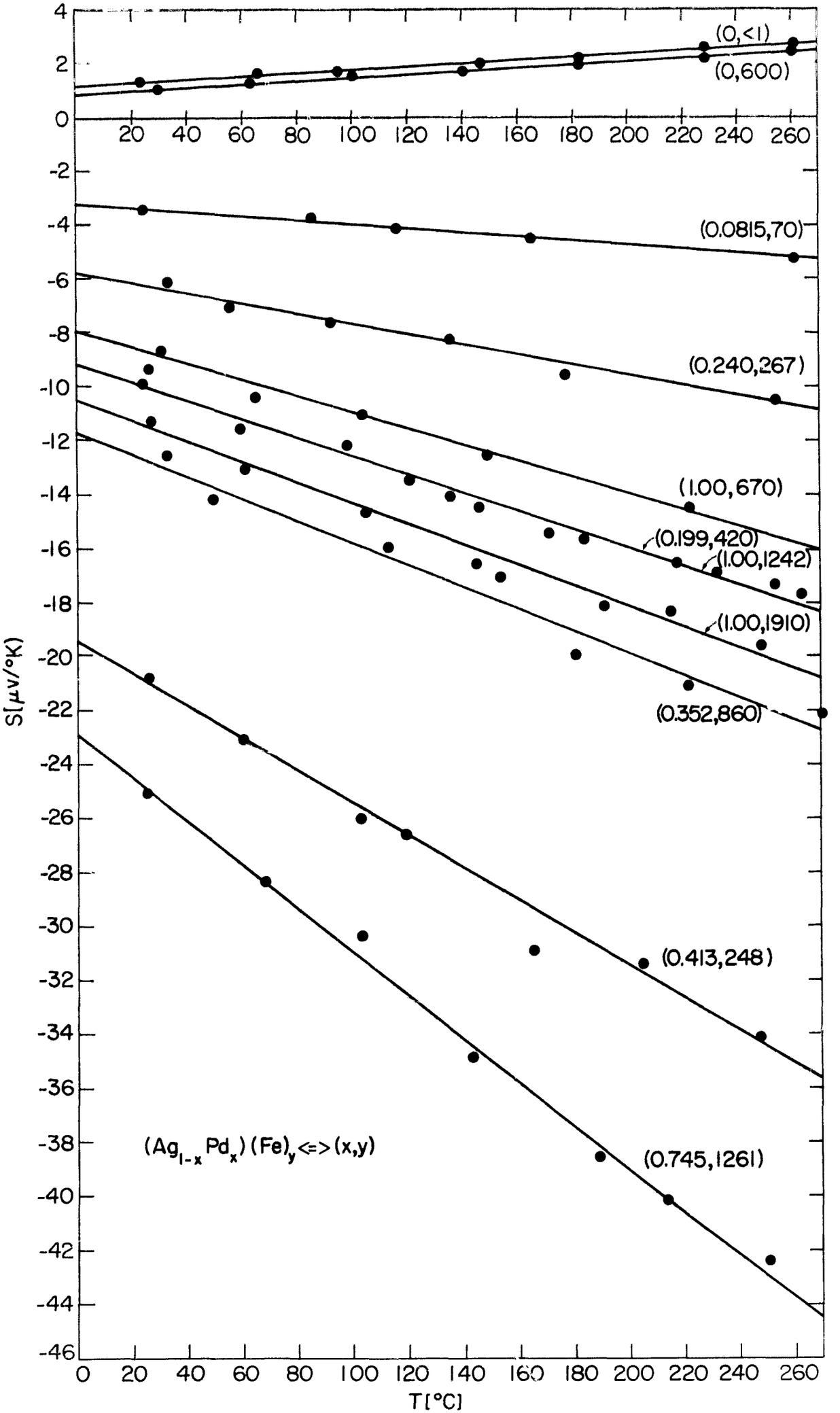

(0,<1)
(0,600)
(0.0815,70)
(0.240,267)
(1.00,670)
(0.199,420)
(1.00,1242)
(1.00,1910)
(0.352,860)
(0.413,248)
(0.745,1261)
(Ag1-x Pdx) (Fe)y <=> (x,y)
S[μv/°K)
T[°C]

Figure 8: Concentration dependent of ρ at ($273^{o}K$). The numbers in parenthesis are the Fe concentrations in ppm. The heavy line represents data of reference (9).

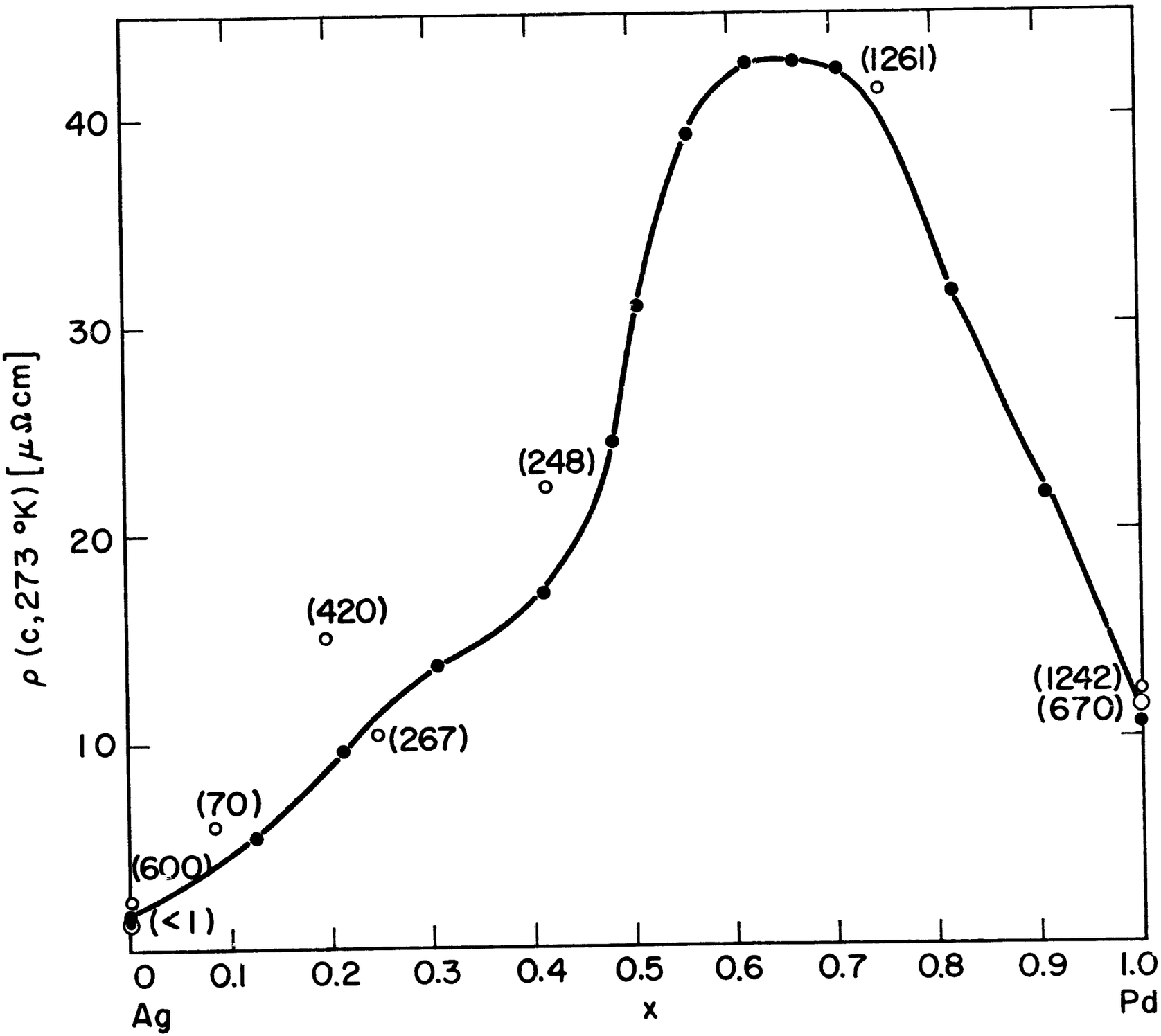
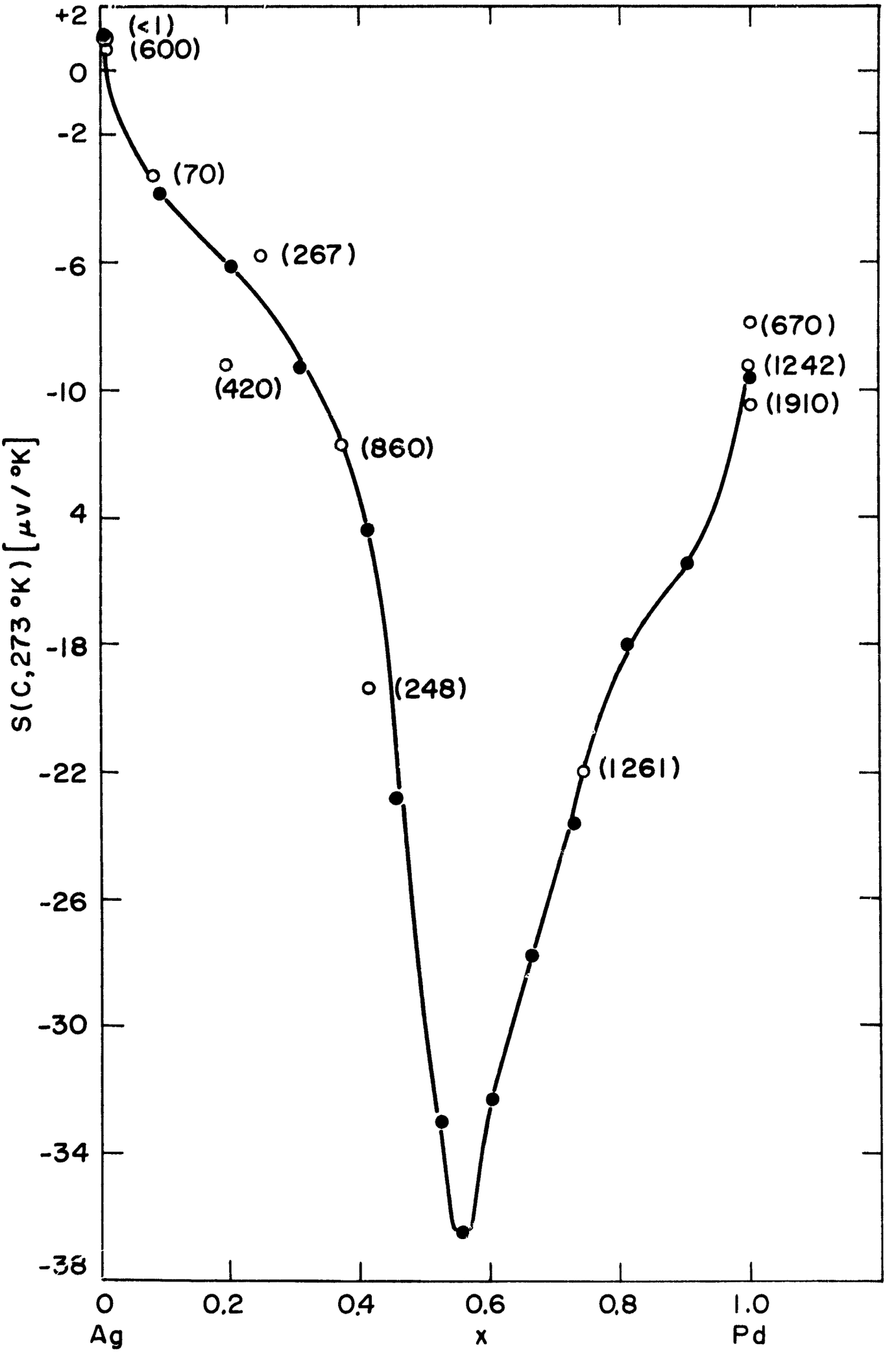

ρ (c, 273 °K) [μΩcm]
40
30
20
10
(1261)
(248)
(420)
(267)
(70)
(600)
(<1)
(1242)
(670)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Ag
x
Pd

Figure 9: Concentration dependence of S at ($273^{o}K$). The numbers in parenthesis are the Fe concentrations in ppm. The heavy line represents data of reference (8).


+2
0
-2
-6
-10
4
-18
-22
-26
-30
-34
-38
S(C,273 °K) [μv/°K]
(<1)
(600)
(70)
(267)
(420)
(860)
(248)
(1261)
(670)
(1242)
(1910)
0
0.2
0.4
0.6
0.8
1.0
Ag
x
Pd

thermopowers when there are d band holes and also localized magnetic moments present.

Second, Figure 9 seems to indicate that the major influence on the thermopower in this system comes from the host AgPd alloy rather than the Fe impurities added. Now Fe was added only up to ~1000 ppm so that the influence of single magnetic impurities could be studied. At higher magnetic impurity concentrations, interactions of these moments would undoubtedly occur and the task of analysis would become very difficult indeed. If we define ΔS as the difference in the thermopower of the Fe doped and "pure" AgPd, then we can discern in Figure 9 a definite trend for negative values of ΔS. This is particularly true for the Ag(Fe) and Pd(Fe) alloys while for the $Ag_{1-x}Pd_x(Fe)_y$ alloys the evidence is not so clear. The reason for this latter circumstance is that the undoped samples of Taylor and Coles had as much as ~500 ppm of impurities in them(8,9). It is likely that the solid curve has an uncertainty of ~2 μV/deg and from our data on either end of Figure 9, it appears that the solid curve is only lower bound on the true S(x) curve for $Ag_{1-x}Pd_x$. We therefore have that $dS/dy < 0$ for $x = 0$ and $x = 1.0$ and it is probably true for all x between 0 and 1.0. This apparent negative contribution to the thermopower from electron scattering from localized magnetic moments suggests that a current viewpoint of magnetic moments in exchange enhanced metals such as Pd is incorrect.

This viewpoint suggests that the exchange interaction J in such a system is positive (ferromagnetic) since a magnetic impurity such as Fe in Pd appears to polarize its nearest neighbors positively to produce a giant magnetic moment of ~12 μ_B. However the neutron scattering results in Pd(Fe) show that the moment localized on the Fe itself is only ~2 μ_B. Thus the suggested view of an alloy such as $Ag_{1-x}Pd_x(Fe)$ would be that the exchange parameter J would start out negative for x = 0 and turn positive at some intermediate value of x < 1. In fact recent work on the resistance minimum phenomenon in $Cu_{1-x}Pd_x(Fe)_y$ has been interpreted precisely in this way(10). According to this work J changed sign between 20 and 30 percent Pd. However, the theoretical expression for the thermopower due to spin-flip scattering is(11)

$$S = -\left(\frac{\pi}{2e}\right) \sin 2\eta \;\; g(\tau)/f(\tau) \;, \qquad (6)$$

where

$$f(\tau) = 1 - \cos 2\eta \; \{\tau/[\tau^2 + \pi^2 S(S+1)]^{1/2}\}$$

$$g(\tau) = [\tau^2 + \pi^2 S(S+1)]^{-3/2}$$

$$\sin 2\eta = \frac{2\pi n(E_F)U}{1 + (\pi n(E_F)U)^2} \;; \quad T >> T_K$$

$$\tau = \ell n \; T/T_K .$$

In these equations η is the phase shift due to potential scattering of coupling constant U. Thus, the sign of the thermopower peak, which comes essentially from the $g(\tau)$ term, is determined by sign of U. An antiferromagnetic exchange parameter is assumed. Suhl and Wong(6) have obtained further information on the thermopower in these systems in the form of calculated curves for various values of J and U with S = 1/2. What is important for our purposes is that the giant thermopower peaks occur only for $J < 0$ and, in agreement with Equation (6), the sign of the peak is opposite to that of the potential coupling constant. The order of magnitude of the thermopower peaks is $S \sim k/e \sim 87\ \mu V/deg$. These theoretical results, in conjunction with our experimental findings, suggest that the exchange parameter J is negative over the whole concentration region x in the $Ag_{1-x}Pd_x(Fe)$ system. Also the potential scattering coefficient seems to be positive in agreement with its sign in Cu(Fe) and Au(Fe) alloys. According to this interpretation the loss of resistance minimum in the $Cu_{1-x}Pd_x(Fe)$ alloys is the result of a change in the potential scattering phase shift factor, following the theories of Fisher(12) and Kondo(13). These questions of sign of the coefficients U and J will be discussed further in the following section, when design considerations of high thermopower couples are discussed.

The final point to be made concerning Figures 6 - 9 is that of the fundamental origin of the large value of S seen at $x \simeq 0.55$ in Figure 9. The usual explanation has been to attribute this to a large energy dependent change in the d-band density of states. Thus in Equation (1), the important term is assumed to be the first term which, in this case, is proportional to $\partial \ell n\, \eta_d / \partial E$.(14) However, recent low temperature work on undoped $Ag_{1-x}Pd_x$ alloys casts doubt on this explanation. Recently Edwards et al. have discovered a low temperature resistance minimum in undoped $Ag_{1-x}Pd_x$(15). Although the evidence is not entirely convincing, the explanation advanced for this phenomenon is scattering from spin fluctuations, i.e. short lived near-moments on Pd rich regions of the sample. It is quite possible that the large thermopowers observed at $x \simeq 0.6$ are thus the result of a "spin-scattering" similar to the s-d scattering mechanism discussed earlier. The relationship between these two problems, i.e., that of a well defined moment as opposed to a short-lived moment, is an active area for research currently(4). Therefore we do not intend to comment on it further here except to point out that explanations of transport phenomena based on the Mott, two-band, model(14) should be taken only with considerable reservations in the light of this recent work.

IV. SUMMARY AND CONCLUSIONS

The major results and conclusions of this study can be summarized as follows:

1. The Kondo effect was investigated in Ag(Fe) alloys with thermoelectric power and electrical resistivity measurements. Estimates of J and T_K are -0.53 eV and 15°K, respectively. These are the first determinations of these parameters for this system, so far as the authors are aware.

2. $dS/dy < 0$ for x = 0 and 100 and probably for $0 \leq x \leq 1$, where x and y are defined by $Ag_{1-x}Pd_x(Fe)_y$. Since very large negative thermopowers are observed for x = 0 and x = 100, the theory of thermoelectricity due to the s-d exchange scattering mechanism implies that J < 0 (antiferromagnetic) over the whole range of x. This in turn implies that recent interpretations of Pd based and other exchange enhanced magnetic alloys in terms of a positive J (ferromagnetic) may have to be revised.

3. In terms of practical thermoelectric materials with high Seebeck coefficients, we can come to the following conclusions. The $Ag_{1-x}Pd_x(Fe)$ system does provide some rather large values of the Seebeck coefficient. It appears that the main contribution to these large values comes from the host matrix ($Ag_{1-x}Pd_x$) rather than from the Fe doping. However, in view of recent transport anomalies detected in $Ag_{1-x}Pd_x$ alloys(15), it is quite possible that the giant

thermopowers observed in these alloys are due to spin-fluctuation effects rather than simple, one-electron, energy dependences of the density of states. Thus the giant thermopowers of undoped AgPd alloys probably have their origins in scattering mechanisms similar to those of the better understood s-d interaction giving rise to the Kondo effect. So far as the authors are aware, a theoretical treatment of thermopower in the presence of spin-fluctuations is, at present, nonexistent.

When it comes to designing thermoelectric devices with high values of S, we can now make some specific recommendations. While we cannot calculate the magnitudes of the expected giant thermopowers because we do not know fundamental parameters of most alloys such as $n(E_F)$, J, and U, we can, nevertheless, use present experimental results coupled with existing theory to design thermocouples having Seebeck coefficients of the order of 100 μV/deg. The theoretical results have shown that the sign of the giant thermopower peak is determined essentially by the sign of the potential scattering coefficient U. Therefore to make couples with very high values of S we must in general make a couple of the form $A(T_1):A(T_2)$ where A is the base metal (solvent) of the couple and where T_1 is on the left hand side of Mn in the transition series and where T_2 is on the right hand side of Mn. The distance of T_1 and T_2 from Mn, which is at the center of the 3d series, determines the characteristic

temperature at which the maximum value of S will occur. This follows from the relation $T_K \sim (E_F/k)\exp(-n(E_F)J)^{-1}$ and from the observed values of J as a function of solute position in the periodic table. For example T_k for Mn in the noble metals is of the order of 10^{-2}°K while for V or Co in the noble metals, $T_K \sim 10^3$ K(4,5). In addition it is important that the solutes T_1 and T_2 be chosen so the sign of the absolute thermopower of $A(T_1)$ and $A(T_2)$ is opposite. This can be done in terms of the theory presented in the previous section. As an example, it is known that Au with V or Cr impurities gives a positive peak while Au with Fe or Co gives a negative peak(16). Another example is the alloy couple $Pd_{.92}V_{.08}$:$Pd_{.93}Mn_{.07}$. The absolute values of S for the two components at 500°C are +25 μV/°K and -45 μV/°K. Thus this couple gives a Seebeck coefficient of 70 μV/°K which is the largest value for a metallic couple based on a single solvent known to the authors. The work of Aldred on $Pd(T)_c$ where T is one of the 3d transition elements also shows a systematic change of dS/dc from small negative at T = Ni to large negative at T = Mn to large positive at T = V. This accounts for the very large value of S in the Pd based couple mentioned above, and can be explained in terms of a change in sign of the potential scattering coefficient on changing the solute from V to Mn.

Another class of metallic alloys may also prove to be interesting to investigate. Metallic compounds of

the form T·M, where T is a 3d transition metal and M is a nontransition metal, have been shown to exhibit the Kondo effect and other transport anomalies(18,19). These result from slight deviations from exact stoichiometry which lead to localized magnetic moments on excess T sites. Earlier work in our laboratories has shown that the thermopower of $Fe_{56.5}Al_{43.5}$ is ~+35 μV/°K and that of $Co_{50.6}Al_{49.4}$ is -40 μV/°K at ~300°K. In alloys of this class it is likely that excess or substitutional magnetic impurity atoms have giant values of magnetic moment which lead to giant thermopower values. This would seem to be a fertile area for further research.

In conclusion, we have shown that magnetic impurity excitations lead to giant thermopowers in AgPd(Fe) alloys and in several other alloy systems. Guided by present theoretical work on these effects we were able to give several design principles for metallic thermoelectric devices. It was shown how to construct devices giving Seebeck coefficients of ~100 μV/deg. There seems to be no reason for believing that further experimentation guided by these principles could not produce metallic devices with Seebeck coefficients of several hundred microvolts per degree.

REFERENCES

1. D. K. C. MacDonald, Thermoelectricity (John Wiley and Sons, New York, 1962).

2. R. L. Rosenblum, Rev. Sci. Instr. 39, 890 (1968).

3. J. Kondo, in Solid State Physics, Vol. 23, F. Seitz, D. Turnbull, and H. Ehrenreich, eds. (Academic Press, New York, 1969), p. 183.

4. A. J. Heeger, in Solid State Physics, Vol. 23, F. Seitz, D. Turnbull, and H. Ehrenreich, eds. (Academic Press, New York, 1969), p. 283.

5. M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. 40, 380 (1968).

6. H. Suhl and D. Wong, Physics 3, 17 (1967).

7. G. R. Caskey, D. J. Sellmyer, and L. G. Rubin, Rev. Sci. Instr. 40, 1280 (1969).

8. J. C. Taylor and B. R. Coles, Phys. Rev. 102, 27 (1956).

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

10. N. V. Volkenshtein, L. A. Ugodnikova, and Yu. N. Tsiovkin, ZhETF Pis. Red. 9, 189 (1969).

11. K. Maki, Prog. Theor. Phys. 41, 586 (1969).

12. K. Fischer, Phys. Rev. 158, 613 (1967).

13. J. Kondo, Phys. Rev. 169, 437 (1968).

14. J. S. Dugdale and A. M. Guenault, Phil. Mag. 13, 503 (1966).

15. L. R. Edwards, C. W. Chen, and S. Legvold, to be published.

16. K. Kume and O. Kogure, J. Phys. Soc. Jap. 25, 930 (1968).

17. A. T. Aldred, J. Phys. Soc. Jap. 22, 762 (1967).

18. G. R. Caskey and D. J. Sellmyer, J. Appl. Phys. 40, 1476 (1969).

19. D. J. Sellmyer, J. Franz, G. R. Caskey, and J. Ahn, Proc. Twelfth International Conference on Low Temperature Physics, Kyoto, Japan (1970).