Comparison of the resistivity of PdCr with canonical spin-glass systems*

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The electrical resistivity of several PdCr alloys, with between 11- and 18-at.% Cr, has been investigated between 1.4 and 300 K, and found to resemble that of canonical spin glasses (CSG). At low temperatures $\Delta\rho(T) \propto AT^{3/2}$, with $A \propto -\log c$ over the concentration range investigated; the range of validity of this $T^{3/2}$ variation ($T < T_1$) is small in PdCr (where A is comparatively large) as in AgMn. At higher temperatures $\Delta\rho(T)$ passes through an inflection point (at T_m) reaching a maximum (at T_μ) above which it decreases with increasing temperature. The ratio T_m/T_1 is found to be roughly constant, as predicted by recent spin-glass theories, but as in CSG its magnitude is smaller than predicted. There are, however, several quantitative differences between PdCr and CSG; specifically both T_μ and $\Delta\rho(T_\mu) - \Delta\rho(0)$ are typically an order of magnitude smaller than in CSG of comparable concentration, whereas the slope of $\Delta\rho(T)$ above T_μ is about an order of magnitude larger than in CSG. This latter point in particular lends support to the assertion that such differences may arise from the fact that CSG are good moment systems (T_K or $T_S \ll T_m$), but PdCr is not ($T_S \sim T_m$).

I. INTRODUCTION

Traditional interpretation[1,2] of existing transport data[3-5] on the PdCr system appear to indicate that resonances in the band structure are important [$\Delta\rho(T=0) \simeq 4.2$-$\mu\Omega$ cm/at.% Cr in the dilute limit], with the effect of finite temperature reducing the incremental resistivity $\Delta\rho(T)$ below its zero-temperature value, this decrease exhibiting a T^2 dependence in the single-impurity limit.[3] This latter effect has been interpreted[4,6,7] as signifying the presence of localized spin fluctuations at the Cr sites, which push the scattering away from the resonant peak. Estimates of the localized-spin-fluctuation characteristic temperature T_S from the observed T^2 coefficients in the low-concentration (c) limit vary, typically, from 120 K using[7]

$$\Delta\rho(T) = \Delta\rho(0)[1 - (T/T_S)^2] \tag{1}$$

to 30 K, using the low-temperature expansion of[4]

$$\Delta\rho(T) = Ac + Bc \ln[(T^2 + T_S^2)^{1/2}], \tag{2}$$

with a value for $B = -0.67$ extrapolated from higher concentration data. It is worth noting that with either estimate the characteristic energies ($k_B T_S \lesssim 0.01$ eV) are such that they lend support to recent contentions[8] that, for magnetic impurities at least, the itinerant aspects of local moment retention should be deemphasized as in configurational based approaches.[9,10] This point, however, is not the prime objective of this paper.

In the PdCr system the effect of impurity interactions is such as to render Eqs. (1) and (2) invalid at low temperatures, with the observed value for the temperature derivative of $\Delta\rho(T)$ being substantially larger than that predicted by

either equation. Further, the appearance of magnetic order in this system, as signalled by a maximum in $\Delta\rho(T)$ or an inflection point (at lower temperatures) in $\Delta\rho(T)$, or $\rho(T)$, requires[3,4] a Cr concentration close to 7 at.%, thus resembling the behavior reported[11] for ternary alloys of Fe in (VCr). It has been inferred[12] from such observations that long-range coupling via Ruderman-Kittel-Kasuya-Yosida oscillations is relatively ineffective, with the result that the ordered ground state is principally determined by near-neighbor d-d overlap. However, the structure of this ground state is currently not well understood, viz., is PdCr a spin glass? Spin glasses have been the subject of extensive analysis recently, however, the most significant segment of this work has concentrated on systems in which the characteristic single-impurity energies ($k_B T_S$ or $k_B T_K$) are well below typical spin glass "freezing" temperatures. In the PdCr system this is not the case, and the attendant effect on the ground state is unclear. In an attempt to clarify this point we have performed measurements on PdCr specimens containing between 11- and 18-at.% Cr, and these are reported here.

II. EXPERIMENTAL DETAILS

Alloys containing nominally 11-, 12-, 14-, 16-, and 18-at.% Cr were individually prepared in the form of 5-g buttons by melting together the appropriate amounts of 99.999% pure Pd wire and 99.999% pure Cr beads (both obtained from Matthey, London, U.K.) on the water-cooled Cu hearth of an argon arc furnace. Weight losses were typically less than 5 mg after inverting and remelting each alloy six times. Resistivity specimens were cut from cold rolled sheets, which,

after etching, were annealed for 20 h at 650 °C
in a vacuum of 10^{-6} Torr. Details of the resist-
ance and temperature measuring techniques have
been given previously.[13]

III. RESULTS AND DISCUSSION

The results for the resistivities $\rho(T)$ of the
alloys examined are summarized in Fig. 1. The
data for the 11-at.% Cr specimen exhibits the
semblance of a weak local minimum around 55 K
(actually a minimum slope rather than zero slope),
below which appears a broad maximum in the
temperature range 30–35 K. Such structure be-
comes less pronounced as the Cr concentration
is increased, with the resistivity of the most
concentrated alloy examined (18-at.% Cr) in-
creasing monotonically with temperature above
4.2 K. Below 4.2 K however the situation is some-
what reversed, with alloys containing more than
14-at.% Cr displaying a very weak minimum, the
position and depth of which increase with increasing
concentration as summarized in Fig. 2. Table I
lists the various characteristic features in the
resistivity of alloys containing between 4- and
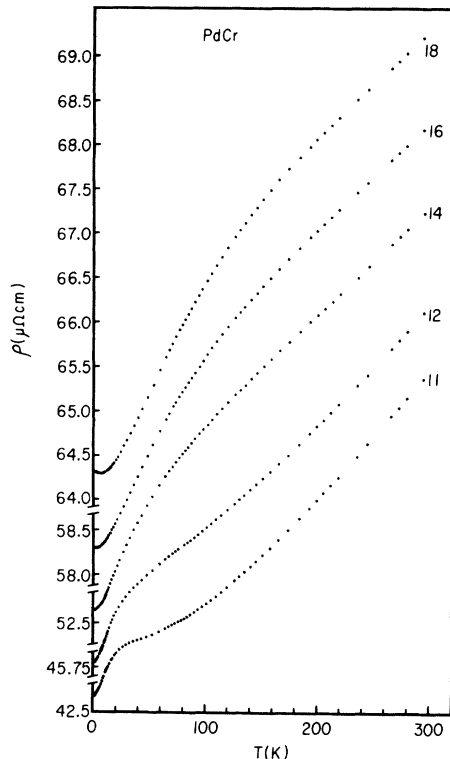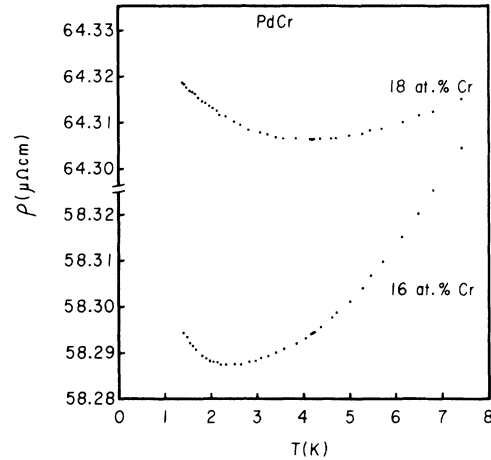18-at.% Cr, the range 4–10 at.% having been

FIG. 2. Resistivity of the two most concentrated alloys
examined, showing details of the resistivity minima be-
low 8 K.

covered by our previous study.[4] The incremental
resistivities $\Delta\rho(T)$ are displayed in Fig. 3; below
4.2 K weak minima are observed in $\Delta\rho(T)$ in the more
concentrated alloys, as outlined above. Above 4.2 K
$\Delta\rho(T)$ initially increases faster than linearly with in-
creasing temperature, then passes through an inflec-
tion point before reaching a maximum (at temperature
T_μ), the estimated temperature of both of which are
listed in Table II for each alloy. Above the maximum
$\Delta\rho(T)$ decreases approximately linearly with in-
creasing temperature; there is in fact some cur-
vature in $\Delta\rho(T)$ above T_μ the extent of which can
be seen by comparing $(d\Delta\rho(T)/dT)_{T\sim 2T_\mu}$, with
$(d\Delta\rho(T)/dT)_{T\gg T_\mu}$ both of which are listed in Table
II.

FIG. 1. Resistivity $\rho(T)$ (in $\mu\Omega$ cm) plotted against
temperature T (in K) up to 300 K. The numbers marked
against each curve is the Cr concentration (in at.%).

A. Behavior of T_μ and $\Delta\rho(T_\mu) - \Delta\rho(0)$

The behavior outlined above typifies the onset
of magnetic ordering in many dilute alloy sys-
tems,[14] although T_μ for the present system is
roughly an order of magnitude smaller than that
associated with archtypical spin-glass systems[14]
(Fe, Cr, or Mn in Ag or Au), but is comparable
with the corresponding temperature[15] for similar
amounts of transition metal impurity in PtMn
[in this system however, sizeable potential scat-
tering coupled with a narrow band[16] appear to
invert the behavior of $\Delta\rho(T)$ relative to the usual
spin glasses; the appropriate temperature here
is that of the minimum]. Various concentration
dependences for T_μ have been reported; in the
noble-metal-based spin glasses T_μ has been found
to be[14] approximately proportional to $c^{1/2}$; in
PtMn below 12 at.% T_μ is proportional to c,
whereas above 12 at.% a change in character is
observed[15] with the resistivity increasing mono-

TABLE I. Summary of the resistivity data.

Concentration (at.% Cr)	4.05	5.05	6.05	8.1	10.1	11	12	14	16	18
T_{min} (K)	65	70	75	75–80	55[a]	55[a]	···	···	···	···
T_{max} (K)	···	···	···	4±0.5	21±1	30–35[a]	···	···	···	···
Inflection point (K)	···	···	···	2.5±0.75	4±1.5	6±2.5	9±3	16±3	30±5	50±7

[a] Local, not absolute.

tonically with increasing temperature but with the inflection point in the resistivity falling on an extrapolation of the T_μ-vs-c line for the more dilute alloys. The behavior of T_μ in *Pd*Cr is shown in Fig. 4, which suggests

$$T_\mu \propto c - c_0, \qquad (3)$$

with $c_0 \simeq 7$ at.%; as in *Pt*Mn a distinct reduction in the rate of increase of T_μ occurs at 13-at.% impurity, but unlike the latter system the inflection points in $\rho(T)$ for *Pd*Cr (see Table I) do not lie on an extrapolation of the T_μ-vs-c curve for the less concentrated alloys.

It is also of interest to compare the difference $\Delta\rho(T_\mu) - \Delta\rho(0)$ in *Pd*Cr with the spin glass systems. As is clear from the data in Table II, not only is this difference a strongly nonlinear function of Cr concentration, but it is also up to an order of magnitude smaller here (0.4 $\mu\Omega$ cm for 10-at.%

Cr) compared with canonical spin glasses (4 $\mu\Omega$ cm for 10-at.% Fe in Au).

B. Behavior of $\Delta\rho(T)$ below T_μ

In the noble-metal-based spin glasses, which have been the subject of the most extensive analyses,[14] it has been found that the spin "freezing" temperature T_0 estimated from a number of measurements correlates quite well with the temperature at which the derivative $d(\Delta\rho)/dT$ exhibits a maximum. In Fig. 5 the details of $\Delta\rho(T)$ below T_μ are displayed to afford further comparison with archtypical spin glasses. The vertical arrows in this figure mark the estimated inflection points in $\Delta\rho(T)$ for the various alloys; the rapid rise in $\Delta\rho(T)$ with increasing temperature above 4.2 K is evident in this figure, however there is not an extended region around T_m where $\Delta\rho(T)$ is nearly linear. Such a difference may simply arise due to the compressed temperature scale over which spin glass like behavior is evident in *Pd*Cr compared with other systems. These estimates for T_m are plotted in Fig. 4, which indicates

$$T_m \propto c - c_0 \qquad (4)$$

over the range examined, with $c_0 \simeq 7$ at.%.

One of the characteristic signatures of spin-glass ordering has been the observation of a $T^{3/2}$ term in $\Delta\rho(T)$ at temperatures below T_m, the coefficient A of this term being only weakly concentration dependent ($A \propto -\log_{10}c$ or $c^{-1/5}$). The origin of this term in such systems is currently attributed[17] to conduction electrons scattering inelastically from long-wavelength, weakly damped spin-diffusion modes (the low-temperature elementary excitations of spin glasses), specifically the existence of the $T^{3/2}$ term relies on the presence of modes of zero damping without which this limiting form would be T^2. Figure 6 summarizes the results of a $\Delta\rho(T)$ vs $T^{3/2}$ plot for the alloys examined here; as can be seen from this figure $\Delta\rho(T)$ does indeed vary as $T^{3/2}$ down to the lowest temperatures examined for the 11- and 12-at.% Cr specimens. In the 14-at.% Cr
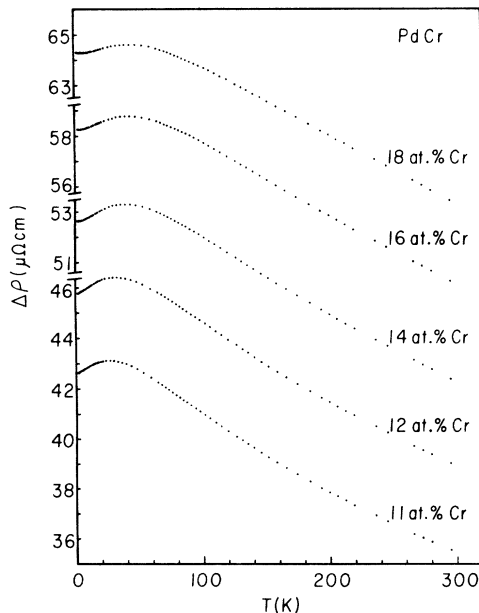

Fig. 3. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$ cm) plotted against temperature T (in K) up to 300 K.

TABLE II. Incremental resistivity data.

| Concentration (at.% Cr)	4.05	5.05	6.05	8.1	10.1	11	12	14	16	18
$\Delta\rho$ (T=0) ($\mu\Omega$ cm)	20.09±0.03	24.80±0.03	28.07±0.03	34.12(5)±0.03	40.21±0.03	42.63±0.03	45.77±0.03	52.61±0.03	58.27±0.03	64.30±0.03
T_μ (K)	···	···	···	4±1	20±1.5	25±1.5	31.5±1.5	39±1.5	41.5±1.5	43±1.5
$\Delta\rho$ (T_μ) ($\mu\Omega$ cm)				34.17	40.60	43.11	46.40	53.30	58.77	64.61
Inflection point [T_m, (K)]				2.5±0.75	4±1.5	9±2	12±3	17±4	19±4	25±4.5
$\left(\dfrac{d\Delta\rho}{dT}\right)_{T\sim 2T_\mu}$ ($\mu\Omega$ cm/K)				4.97×10^{-2}	3.54×10^{-2}	3.49×10^{-2}	3.42×10^{-2}	3.21×10^{-2}	2.95×10^{-2}	2.75×10^{-2}
$\left(\dfrac{d\Delta\rho}{dT}\right)_{T\gg T_\mu}$ ($\mu\Omega$ cm/K)				1.86×10^{-2}	2.28×10^{-2}	2.49×10^{-2}	2.54×10^{-2}	2.66×10^{-2}	2.70×10^{-2}	2.75×10^{-2}
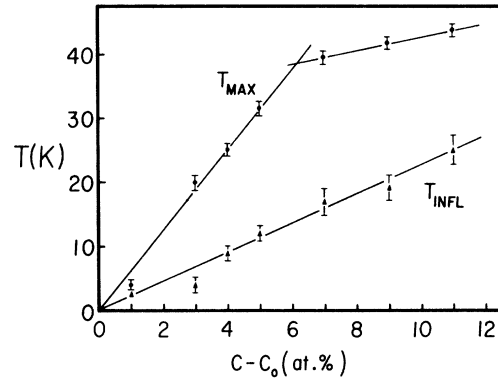
FIG. 4. Plots of the temperature T_{max} (in K; designated T_μ in the text) at which the incremental resistivity displays a maximum, and the temperature T_{infl} (in K; designated T_m in the text) the estimated position of the inflection point in $\Delta\rho(T)$, against the reduced concentration $c-c_0$ (in at.%).

sample deviations away from $T^{3/2}$ (towards T^2) are observed, resembling the situation reported[14,18] for comparable amounts of Cr in Au, and smaller amounts of[19] Mn in Cu. Of course, for the 16- and 18-at.% Cr specimens which possess a weak minimum below 4 K, there can be no such limiting temperature dependence, however at temperatures above these minima $\Delta\rho(T)$ does follow a $T^{3/2}$ dependence over a substantial range. In Table III we list the coefficients A estimated from the data in Fig. 6, along with the temperature T_1 above which deviations from the initial $T^{3/2}$ dependence occur. Figure 7 shows that the
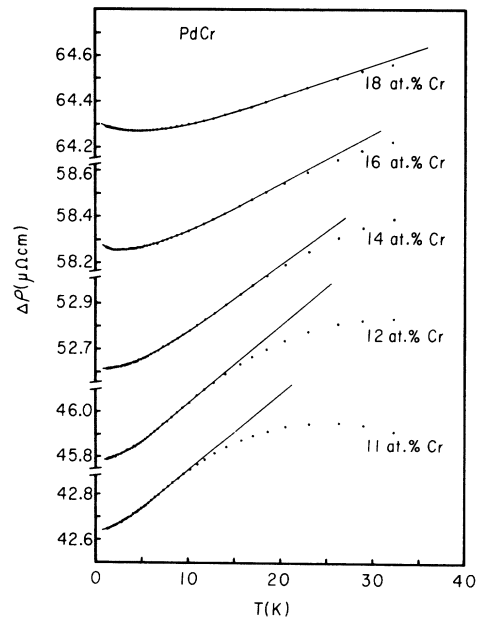

FIG. 5. Details of the incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$ cm) at temperatures below T_μ.
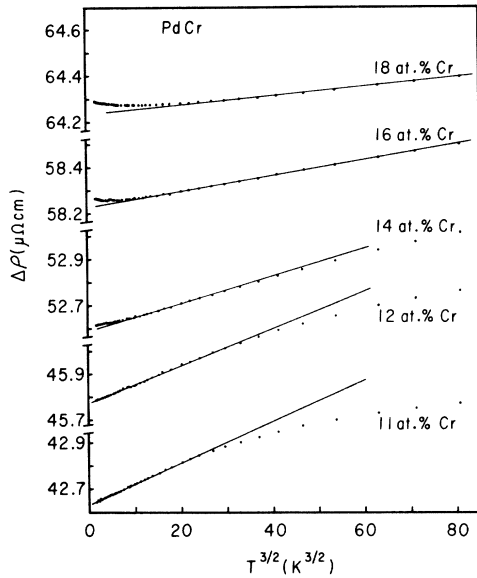
FIG. 6. Plots of the incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$ cm) against $T^{3/2}$ (in $K^{3/2}$).

coefficient A follows a $-\log_{10}c$ dependence as in canonical spin glasses (CSG); certainly the concentration range covered by the present investigation is very much smaller than that covered in CSG (especially when expressed on a $\log_{10}c$ scale), this however can hardly be avoided since PdCr does not order below 7 at.% and consequently exhibits a measurable $T^{3/2}$ term only above about 10 at.%. In PdCr A exhibits a concentration variation (36 $n\Omega$ cm/$K^{3/2}$ per decade of concentration) which is an order of magnitude more rapid than in AuFe (3 $n\Omega$ cms/$K^{3/2}$ per decade), but this does not conflict with existing systematics of spin glasses in that there appears to be an inverse correlation[14] between A and T_1 (the latter, along with T_m and T_μ are comparatively small in the present system, as in AgMn).

It may appear tempting to attribute the $T^{3/2}$ to T^2 transition in the limiting form for $\Delta\rho(T)$ in the 14-at.% specimen as being due to the slowest spin-diffusion modes becoming inoperative (possibly due to conduction-electron mean-free-path

limitations as the impurity content increases), as has already been done[17] for CuMn and AuCr. Such an approach, however, does not seem capable of explaining the occurrence of resistivity minima at slightly higher Cr concentrations in both the present system and[20] AuCr. The appearance of weak minima at low temperatures (often below the magnetic ordering temperature) in reasonably concentrated alloys is not confined to the two systems mentioned above (AuCr and PdCr), but have also been observed in PdNi,[21] PdAg,[3,22] and PtCo.[23] Considering the concentration and temperature range in which such effects occur (along with the magnetic field independence[3] of the minima in PdCr), inelastic spin-flip scattering mechanisms appear unlikely as their source, but an analog of the recently proposed[24] structural source for minima of nonmagnetic origin in amorphous conductors warrants consideration.

C. Spin-glass consistency tests

While the magnetic properties of spin glasses have been the subject of extensive theoretical speculation,[25] the electrical properties have received comparatively little theoretical attention. The work that has been done in this latter category has been directed towards understanding "good moment" systems (with T_K or $T_S \ll T_m$), for which two consistency tests have been suggested[17]; while PdCr (with $T_S \sim T_m$) is not a good moment system, it still appeared instructive to apply these tests to it: The first is

$$T_m = 2.23\,T_1. \tag{5}$$

An inspection of the data in Tables II and III indicate that while this ratio is roughly constant in the present system its magnitude ($\sim$1.5) is rather less than that given by Eq. (5). It should be emphasized however (see Fig. 6) that T_1 is not easy to estimate with certainty, particularly when there are weak minima at low temperature, but in spite of these, the discrepancies between observation and prediction are no greater in PdCr than in CSG.[14] Second

$$[\Delta\rho(T_m) - \Delta\rho(0)]/[\Delta\rho(\infty) - \Delta\rho(0)] = \tfrac{1}{6}. \tag{6}$$

TABLE III. Incremental resistivity data below T_μ.

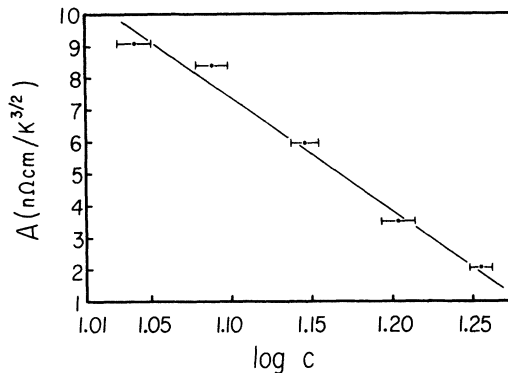| Concentration (at.% Cr)	8.1	10.1	11	12	14	16	18
A ($n\Omega$ cm/$K^{3/2}$)	$\cdots$	$\cdots$	9.07 ± 0.15	8.38 ± 0.15	5.94 ± 0.15	3.50 ± 0.15	2.05 ± 0.15
T_1 (K)	$\cdots$	$\cdots$	8 ± 1	8 ± 1	8.5 ± 1	13.3 ± 1	17.5 ± 1
$\Delta\rho$ (T_m) ($\mu\Omega$ cm)	34.16	40.30	42.86	46.08	52.97	58.51	64.48

FIG. 7. Coefficient A of the $T^{3/2}$ term (in $n\Omega$ cm/K$^{3/2}$) plotted against $\log_{10}c$.

This test is more difficult to implement than the first; the numerator is easily extracted from the experimental data whereas the denominator is not. Even in good moment systems $(T_K, T_S \ll T_m)$ the logarithmic nature of single impurity scattering of conduction electrons (the Kondo effect) produces a resistivity maximum at high temperatures (T_μ) by depressing the resistivity below its temperature-independent spin disorder plateau, even when the latter is attained at temperatures several orders of magnitude larger than T_K or T_S. This causes[17] some uncertainties in $\Delta\rho(\infty) - \Delta\rho(0)$, but such uncertainties are substantially greater in systems where $T_S \sim T_m$ when the high-temperature slopes are up to an order of magnitude larger than in CSG (see Table II and the data in Ref. 14). This effect is the clearest indication of the influence of single-impurity characteristics via a high T_S on the transport properties above the ordering temperature. As a result, in the present system one can only use Eq. (6) to "predict" $\Delta\rho(\infty) - \Delta\rho(0)$ for each alloy using the measured $\Delta\rho(T_m)$ and $\Delta\rho(0)$; while the concentration dependence of this difference can be complicated,[17] it is at least observed to scale monotonically with increasing concentration in GSG. The data listed in Tables II and III indicate that this is not the case in PdCr. Even if an attempt is made to account for the effect of weak minima by taking $\Delta\rho(0)$ as the incremental resistivity found by extrapolating the $T^{3/2}$ dependence to $T = 0$ (giving values of 52.59, 58.22, and 64.23 $\mu\Omega$ cm, respectively, for the three most concentrated alloys), the predicted difference $\Delta\rho(\infty) - \Delta\rho(0)$ increases with increasing concentration to 14-at.% Cr, but increasing the concentration beyond the percolation limit results in the difference declining. No comparable effect has been reported for CSG. As mentioned above, the most likely candidate for explaining such differences is the significantly larger T_S in PdCr,

although quantitative comparisons must clearly await the arrival of a comprehensive theoretical approach to this area.

IV. SUMMARY AND CONCLUSIONS

The electrical properties of PdCr alloys containing between 10- and 18-at.% Cr exhibit several features which resemble those of spin glasses; in summary they are the following: (i) $\Delta\rho(T)$ displays a $T^{3/2}$ temperature dependence at low temperatures, the coefficient A of which varies as $-\log_{10}c$ over the range examined. (ii) The range of validity $(T < T_1)$ of this $T^{3/2}$ variation correlates inversely with A, being small in PdCr (where A is comparatively large) as in AgMn. (iii) At higher temperatures $\Delta\rho(T)$ passes through an inflection point (at T_m), climbing to a maximum (at T_μ) above which it falls away with increasing temperature. (iv) The ratio T_m/T_1 is roughly constant for the concentration range examined, as predicted by recent spin-glass theories, although as in CSG the magnitude of this ratio is smaller than the theoretical estimate. (v) In the more concentrated alloys deviations away from $T^{3/2}$ appear at the lowest temperatures; in fact weak minima (which we suspect to be of nonmagnetic origin) occur in our most concentrated alloys. Such minima have been reported in a variety of reasonably concentrated alloys, including spin glasses. The most marked differences between PdCr and CSG arise from quantitative comparisons, viz., (vi) The temperature T_μ of the maximum in $\Delta\rho(T)$ is nearly an order of magnitude smaller than in CSG of comparable concentration, as is (vii) the difference $\Delta\rho(T_\mu) - \Delta\rho(0)$. (viii) However the slope of the incremental resistivity *above* T_μ is nearly an order of magnitude larger in PdCr than in CSG.

We suspect that these quantitative differences arise from the fact that CSG have T_K or $T_S \ll T_m$, whereas in PdCr $T_S \sim T_m$. Point (viii) above provides strong support for such an assertion in that even in good moment systems the logarithmic nature of conduction-electron–single-impurity scattering (the Kondo effect) causes the high-temperature resistivity to be depressed below its spin disorder plateau in spite of the fact that this plateau is approached at temperatures several orders of magnitude above T_K. With T_K (or T_S) $\sim T_m$ one expects such effects to be more pronounced, and this is indeed observed.

We hope that the measurements reported in this paper will provide some motivation for a spin-glass theory which is valid in the region where $T_S \sim T_m$, so that quantitative comparisons become possible. We realize however that the difficulties inherent in such an approach are substantial.

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