COHERENCE IN $CEPD_3$

Jon Lawrence and Yang-Yuan Chen

Physics Department
University of California
Irvine, CA 92717 USA

Joe Thompson

Los Alamos National Laboratory
Los Alamos, NM 87545 USA

INTRODUCTION

At high temperatures in periodic cerium valence fluctuation compounds[1,2,3] the cerium atoms act as a set of uncorrelated scattering centers. In the archetypal compound $CePd_3$ the resistivity ρ at high temperatures has a negative slope (Fig. 1a) as expected in the single-ion Kondo limit. Use of the inelastic neutron scattering linewidth[4] as a measure of the Kondo temperature yields $T_K \simeq 250K$. At the temperature $T_{max} = 125K$ the resistivity exhibits a maximum indicating the onset of coherence, i.e., of correlations amongst the 4f scattering centers resulting in strong renormalization of the conduction electrons. The nature of this coherence is loudly debated at present.

In this paper we present results[5] of resistivity and susceptibility measurements on $CePd_3$ and its alloys which support the existence of a third significant temperature, $T_* = 40K$. Anomalous pressure dependence of $\rho(T)$ occurs and nonmagnetic impurities cause large increases in $\rho(T)$ on this scale, which we emphasize is distinct from (and smaller than) the scale T_{max} over which coherence first appears. We give evidence that the magnetic form factor anomaly known[6] to exist in $CePd_3$ arises on the same scale T_* suggesting that the 5d spin susceptibility which is responsible for the form factor anomaly is connected with the low temperature transport anomalies. We restrict the discussion to the relationship of these results to other experimental measurements in $CePd_3$. In particular, we stress the relationship of these results to those of recent optical conductivity measurements[7] which show that the quasi-particle effective mass is strongly renormalized at low temperatures. This occurs over a temperature scale which we propose is T_*.

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EXPERIMENTAL RESULTS AND ANALYSIS

In this section we present both new results[5] (e.g., the pressure dependence of $\rho(T)$) and new analysis of experiments reported earlier by others.[8-15] For the latter case we perform the analysis for experiments repeated on a set of our own samples which were manufactured and characterized in a consistent fashion. This latter is particularly important in the light of the known[8-10] extreme stoichiometry dependence of $CePd_3$ shown in Fig. 2a where we plot the resistivity of $CePd_{3+y}$. These results, in agreement with earlier studies,[16] show a large residual resistivity ρ_o when $y > 0$ and a vanishing ρ_o when $y < 0$. (To determine y we assumed that all weight loss on arc melting arose from vaporization of Pd. X-ray diffraction on the soot remaining on the arc furnace hearth yielded a Pd spectrum, in confirmation of this assumption. The consistency of the variation of the lattice parameter $a_o(y)$ with stoichiometry (Fig. 2b) strengthens our case that we correctly measure y in this fashion.) In all the experiments reported below we held y slightly negative to eliminate the effect of stoichiometry on the measurement. We believe that insuf-

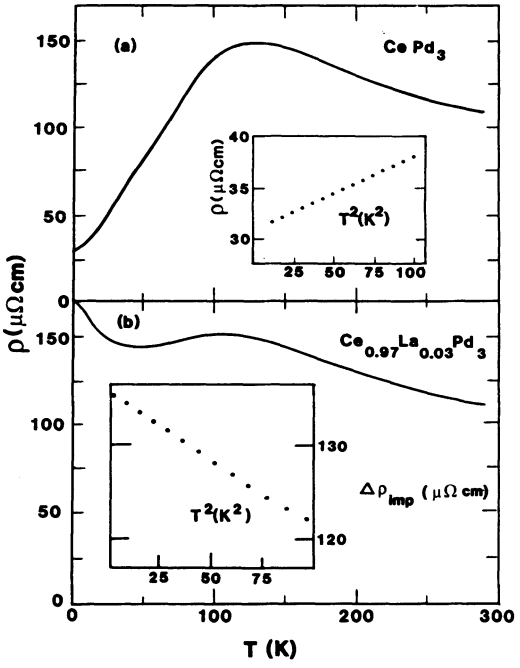

Fig. 1. Resistivity at ambient pressure for (a) $CePd_3$ and (b) $Ce_{0.97}La_{0.03}Pd_3$. This inset in (a) shows the low temperature resistivity of $CePd_3$ plotted vs. T^2. The inset in (b) shows the impurity contribution (i.e., with the resistivity of $CePd_3$ subtracted out) to the resistivity of $Ce_{0.97}La_{0.03}Pd_3$ plotted vs. T^2. (From Ref. 5)

ficient attention to this effect can lead to inconsistencies in the experimental outcome.[17]

Close examination of Fig. 1a reveals the existence of a shoulder in the curve near 40K. This feature has been observed before, even in very high quality single crystals.[12] For T < 10K the resistivity follows a T^2 power law (Fig. 1a, inset). Assuming that the resistivity should rise to its saturation value ρ_s as $\rho_o + \rho_s(T/T_*)^2$ and taking $\rho(T_{max}) = 150\ \mu\Omega$-cm as an estimate of ρ_s leads to a value $T_* = 45$K. The resistance of $CePd_3$ at several pressures is shown in Fig. 3.[5,13] As the pressure is increased large changes are observed above 50K but for T < 40K the resistivity is essentially unaffected.

It is well known[8,11] that minute amounts of nonmagnetic solute lead to very large increases in the low temperature resistivity of $CePd_3$. This is shown in Fig. 1b where it can be seen that merely 3% substitution of La for Ce increases the residual resistivity to large values $\rho_o > \rho(T_{max})$. In Fig. 4 and 5 we exhibit results for $Ce_{1-x}M_xPd_3$ where M = Y, Sc, La. As shown earlier[11] the residual resistivity increases rapidly with x and is essentially independent of solute. In each case for fixed x = 0.03 the resistivity rises to essentially the same value $\rho_o \approx 175\ \mu\Omega$-cm, there is a minimum near 50K and the low temperature variation is as $\rho(T) = \rho_o[1-(T/T_*)^2]$ with $T_* \approx 40$-45K. In Fig. 5 we show that as x is increased in $Ce_{1-x}La_xPd_3$ the residual resistivity increases rapidly up to $x \approx 0.06$ and begins to saturate for larger x; but T_* increases very slowly as x increases.

In Fig. 6 we plot the susceptibility of $Ce_{1-x}La_xPd_3$ for x = 0, 0.03 and 0.06. The susceptibility has been corrected in a standard fashion[18] for a Curie "tail" which arises below 10K probably due to the presence of Ce_2O_3.[9] (We detected the existence of a very weak trace (< 0.4%) of this impurity phase in neutron diffraction on one of our samples.) After this correction our results are in agreement with those of other groups[12,14]

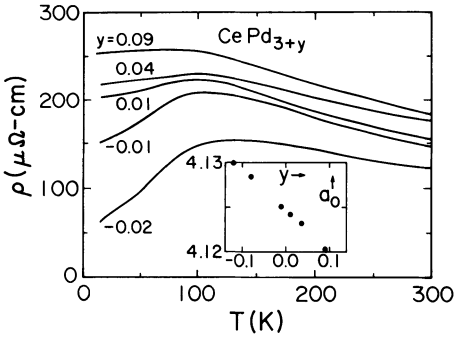

Fig. 2. Resistivity of $CePd_{3+y}$ for several values of y. The inset shows the lattice constants as a function of y.

who suppressed the tail by application of a magnetic field. Above 50K the susceptibility is similar to other valence fluctuation compounds, showing a broad maximum centered near 125K and a Curie-Weiss susceptibility $C/(T+\theta)$ at higher temperature. Below 50K there is an upturn in the susceptibility presently believed[12,14] to be intrinsic. Our analysis shows that at the lowest temperatures the susceptibility obeys a T^2 law, i.e., $\chi(T) = \chi(0)\ [1-(T/T_*)^2]$ with $T_* \approx 40K$. On alloying with La the susceptibility does not change significantly and it retains the T^2 law, with T_* essentially constant. We have also measured $\chi(T)$ for $CePd_{3+y}$ and, in agreement with others,[15] we find a similar result. Apart from a small constant shift the susceptibility is unaffected by stoichiometry variations or by alloying.

DISCUSSION

The existence of the shoulder near 40K in the resistivity of $CePd_3$, the coefficient $T_* \approx 40K$ of the law $\rho(T) = \rho_o + \rho_{max}(T/T_*)^2$ and the

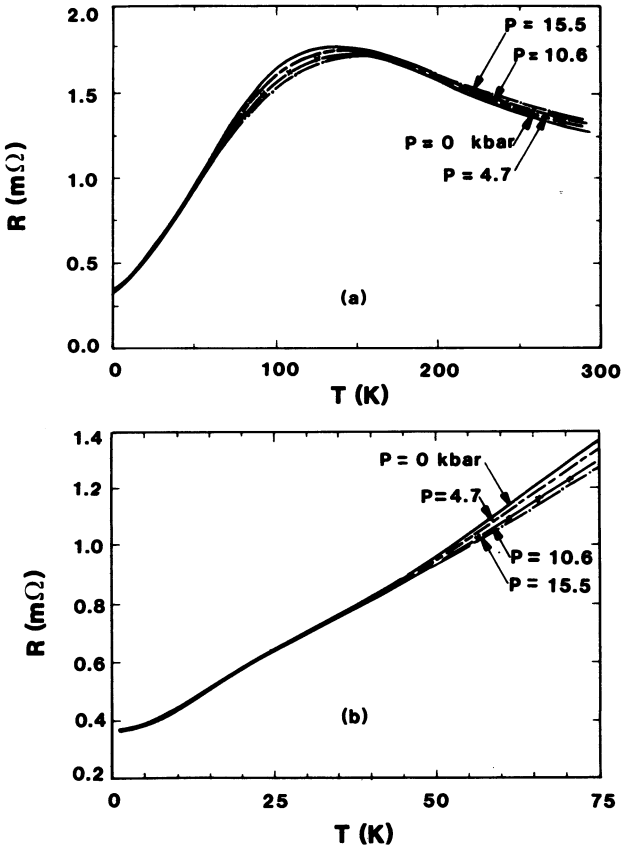

Fig. 3. (a) The resistance of $CePd_3$ versus temperature for four pressures; (b) Low temperature region of the data for the same four pressures showing the insensitivity to pressure below 40K. (From Ref. 5)

radically different pressure dependence of $\rho(T)$ above and below 40K all point to the existence of a temperature scale $T_* \approx 40K$ below which the transport behavior changes its character. Anomalies in other transport phenomena are known to occur in the same temperature range. For example, the thermopower[19] peaks near 125K but exhibits a very marked shoulder near 40K. The Hall mobility[20] is constant above 40K but decreases rapidly at lower temperature, changing sign at 10K.

It is clear[8] that minute amounts of nonmagnetic impurities lead to enormous increases in the residual resistivity ρ_o. The issue we address here is the temperature scale over which this occurs. One point of view is that the impurity destroys coherence, which should occur on the scale T_{max}. If this were so, then for x large enough that $\rho_o(x) > \rho(T_{max})$ we would expect the resistivity to be simply that of noninteracting Kondo impurities: monotone decreasing as T increases. The clear existence of two maxima separated by a minimum near 50K for $Ce_{0.97}M_{0.03}Pd_3$ belies this interpretation. The impurity clearly affects ρ on a scale smaller than T_{max}. The existence of the quadratic power law $\rho(T) = \rho_o[1-(T/T_*)^2]$ with $T_* \simeq 40K$ suggests that the scale for the impurities is the same as for the anomalies in pure $CePd_3$.

We have seen that the resistivity of $Ce_{1-x}M_xPd_3$ for fixed x is independent of solute[11] (M = La, Y, Sc); $\rho_o(x)$ has the same value and the quadratic temperature dependence is basically identical. On removal of a cerium atom from site i a "Kondo hole" term $H_{hole}(i)$ is created in the

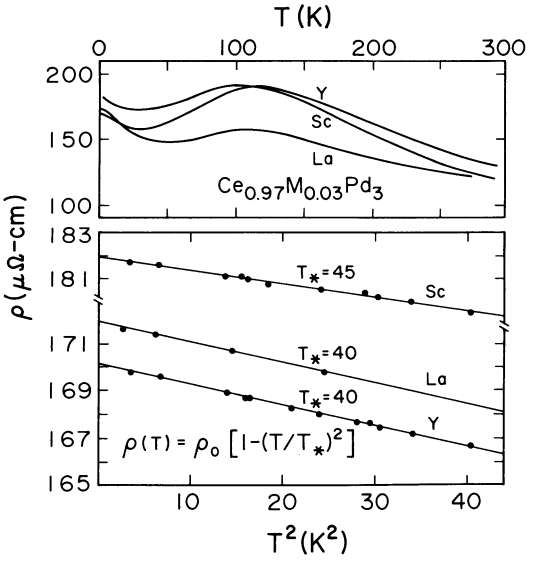

Fig. 4. (Top) The resistivity of $Ce_{1-x}M_xPd_3$ plotted versus temperature for M = Y, Sc, La; (bottom) The low temperature resistivity of the same three compounds plotted vs. T^2. These demonstrate the power law behavior $\rho(T) = \rho_o[1-(T/T_*)^2]$ with T_* given in the plot.

Hamiltonian[5]:

$$H = H_o - H_{hole}(i) + \delta V(i)$$

where H_o is the Hamiltonian for pure $CePd_3$, δV represents potential scattering from the impurity and

$$H_{hole}(i) = \sum_{\sigma} E_f n_{fi\sigma} + U n_{fi\uparrow} n_{fi\downarrow} + \sum_{k\sigma} (V_{kf} f^{+}_{i\sigma} c_{k\sigma} + cc)$$

in the usual Anderson-model notation. Assuming that the potential term δV (which should vary from solute to solute) is much weaker than the Kondo hole term, then the resistivity would be insensitive to which element is substituted. It is the absence of a cerium atom from its appropriate site that governs the alloy resistivity.

This same mechanism can explain the stoichiometry dependence of $\rho(T)$ in $CePd_{3+y}$; these alloys show[16] a large residual resistivity ρ_o when $y > 0$ and a small ρ_o when $y < 0$ (Fig. 2). When $y > 0$ there will be vacancies and/or Pd atoms on the cerium sublattice, which will lead to scattering

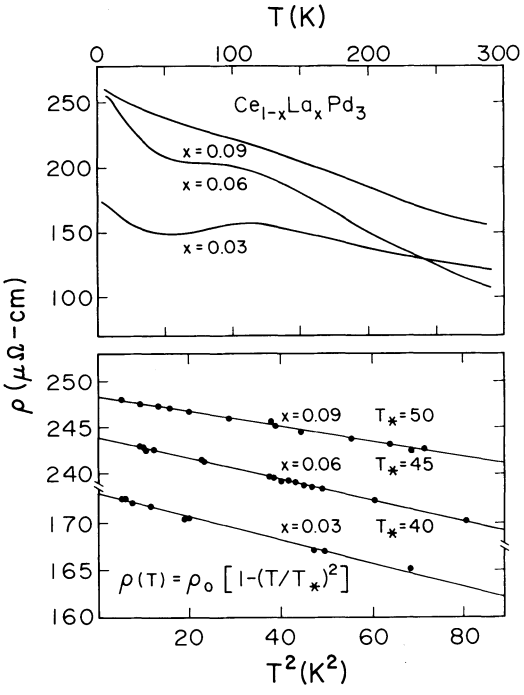

Fig. 5. (Top) Resistivity of $Ce_{1-x}La_xPd_3$ for x = 0.03, 0.06 and 0.09; (bottom) Low temperature resistivity plotted vs. T^2. Values of T_* are given in the figure.

from the Kondo hole. (Site disorder within the $AuCu_3$ structure would lead to the same effect.) On the other hand, when $y < 0$ the imperfection would reside on the Pd sublattice, giving a substantially weaker effect.

The susceptibility of $CePd_3$ shows an intrinsic rise[12,14] with a quadratic temperature dependence $\chi = \chi(0)[1-(T/T_*)^2]$ at low temperatures. This effect is connected to the existence of a neutron form factor anomaly[6] which arises from the growth of a 5d contribution at low temperatures. The induced magnetization is about 17% 5d character and 83% 4f character. The rise in $\chi(T)$ below 50K thus arises from this 5d susceptibility. The T = 0 4f susceptibility has the approximate value 1.5×10^{-3} emu/mole and χ_{4f} initially increases with increasing T, reaching a maximum at 125K (at which temperature the 5d susceptibility is negligible). Our results show that this 5d susceptibility exists on the same temperature scale T_* as (and is undoubtedly implicated in) the transport anomalies. We note that the 5d susceptibility is unchanged by alloying in $Ce_{1-x}La_xPd_3$ for x as large as 0.06: whereas the cerium sublattice disorder has an enormous effect on the transport behavior it has very little on the susceptibility.

To improve the microscopic understanding of these issues requires spectroscopic measurements. For example, it is desirable to measure the inelastic magnetic neutron cross section of $CePd_3$ at low temperatures. Ideally this would be done on a single crystal, would include the low energy region (0.1 - 10 meV) and would be performed at several temperatures. In this experimental mode a search could be made for several possibilities for changes in the spin fluctuation spectrum occurring on the scale T_*. These include the onset of antiferromagnetic correlations (as

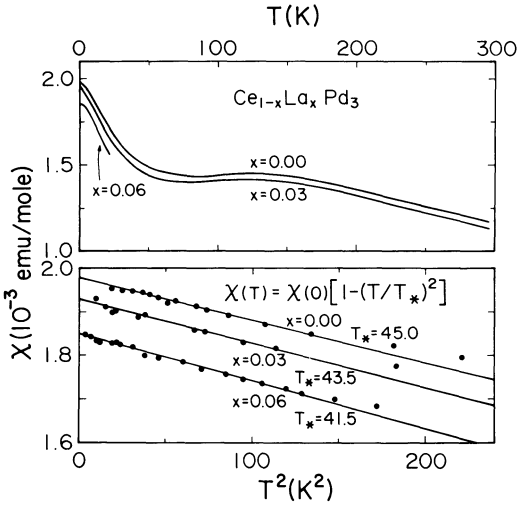

Fig. 6. (Top) The susceptibility of $Ce_{1-x}La_xPd_3$ vs. temperature for x = 0, 0.03 and 0.06; (bottom) The low temperature susceptibility plotted versus T^2. The power law is $\chi(T) = \chi_o(0)[1-(T/T*)^2]$, with T* given in the plot.

seen recently[21] in heavy fermion compounds at very low temperature), renormalization of the spectrum as T is lowered below T_* and/or the onset of an excitation on a low energy scale (~ 3 mev) comparable to kT_*.

Recent polarized neutron results[22] in polycrystal $CePd_3$ do suggest large renormalizations in the spectrum over a broad energy scale (0-100 meV) at low temperatures. In particular, the spectrum is quasielastic at 250K ($\chi'' \propto \Gamma\omega/(\Gamma^2 + \omega^2)$), but a broad inelastic peak centered at 55 meV grows as the temperature is lowered. The polarized inelastic scattering technique has the advantage that the nonmagnetic background is removed unambiguously but suffers from poor statistics; we therefore recently sought to confirm these results using unpolarized neutrons in the time-of-flight mode where the opposite conditions apply. We found[23] considerable magnetic scattering but depending on which assumption we made about the Q dependence of multiple scattering we found we could fit the spectrum either as a single quasielastic peak or as the sum of quasielastic and inelastic peaks with parameters as reported by Galera. However, we found no detectable change on this broad energy scale (10-120 meV) between the spectra at 10 and 100K. We are thus uncertain as to the relevance of these results for the existence of the low temperature scale T_*. In any case these results should be verified in single crystals.

The far infrared optical conductivity experiment[7] recently reported for $CePd_3$ is of great relevance to this discussion. The spectra can be understood as arising from frequency-dependent scattering of a very small number of carriers (0.3 per formula unit) due to the coupling of the electrons to a bosonic excitation spectrum (presumably the spin fluctuations). The quasiparticle effective mass m^* is strongly renormalized over the optical band mass m_b; at 4.2K $m^* = 40m_b$; at 75K the effective mass falls to 17 m_b. The lack of enhancement at room temperature (recall T_K = 250K) implies that the renormalization is not a single ion effect, but arises from the interactions which are also responsible for coherence. The temperature scale of this effect (i.e., whether T_* or T_{max}) is not clear -- spectra at more temperatures and with somewhat better statistics would be required to determine this. Nevertheless the large drop in m^* between 4.2 and 75K suggests that T_* is the correct scale for the onset of the renormalization; we shall take this point of view in the rest of the discussion.

Under this assumption the low temperature behavior of the resistivity ($\rho \sim \rho_s (T/T_*)^2$ and the shoulder near T_*) is understandable. It also gives a clue as to the effect of nonmagnetic impurities. A very small number of very heavy electrons carry the current; apparently these are very strongly scattered by any imperfection in the cerium sublattice (i.e., by the "Kondo hole"). This effect disappears when the heavy mass renormalizes to the bare mass for $T > T_*$.

Impurities have a much greater effect on $CePd_3$ than on other valence fluctuation compounds with comparable T_K -- particularly $CeSn_3$. We believe that this extreme sensitivity is due to the small number of carriers (0.3 per formula unit as mentioned above) and arises ultimately from a band structure effect. Photoelectron spectra (XPS and BIS)[24] for $LaPd_3$, $CePd_3$ (and YPd_3) show that the Pd 4d states are full and that the lanthanide 5d (4d for Y) states are split off above the Fermi level. This leaves a very low density of carriers at the Fermi level. This is in contrast to the $CeSn_3$ where there is a healthy density of tin 5 sp states to carry the current and shunt the 4f channel.

The connection between the onset of large mass renormalizations and of the 5d susceptibility (i.e., the form factor anomaly) both occurring on the same scale T_* is an open question. We emphasize that in our interpretation small amounts of imperfection (for $x \lesssim 0.06$) do not destroy coherence, but do strongly scatter the heavy electrons. Hence, the 5d susceptibility (insofar as it is connected to coherence) can remain insensitive to low levels of alloying as observed.

The lack of pressure dependence for $T < T_*$ (as opposed to large pressure dependence at higher T) also remains open. In this context recent work[25] on the specific heat of $CeAl_3$ is worth mentioning. The volume dependence of the linear coefficient γ has the value expected for the single-ion Kondo effect for $T > T_K$ but at low temperatures $T < T_K$ the quantity $\partial \ln \gamma / \partial \ln V$ actually changes sign. The system responds very differently to pressure in the coherence regime than in the single-ion regime.

A final question concerns the distinction between the two scales $T_* = 40K$ and $T_{max} = 125K$. It appears that coherence first sets in on the scale T_{max}, but the interactions responsible for the large renormalizations occur on the scale T_*. The two scales are distinct, as evidenced for example by the very different pressure dependence over the two ranges. The question is, how can coherence in the transport behavior occur at T_{max} independent of interactions? One conjecture is that for $T < T_K = 250K$ the scattering phase shifts at all sites become identical so that even in the absence of interactions, Bloch's law will hold and the resistivity will approach the value zero. A second conjecture is that the phonons are implicated in the existence of the scale T_{max}; it is known,[1] for example, that the thermal expansion has a broad maximum at this temperature.

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17. Perhaps this is the reason that the data in Ref. 8, in contast to our results and those of Ref. 11, show no minimum in the resistivity of $Ce_{1-x}M_xPd_3$ for x = 0.03.
18. At low temperatures $\chi \rightarrow \chi(0)$ and the measured susceptibility satisfies $T\chi_{meas} \rightarrow T\chi(0) + C_{imp}$ where C_{imp} is the impurity phase Curie constant.
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