Kondo hole behavior in $Ce_{0.97}La_{0.03}Pd_3$

J. M. Lawrence,* T. Graf,† M. F. Hundley, D. Mandrus,‡ and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

A. Lacerda and M. S. Torikachvili§
National High Magnetic Field Laboratory, Pulse Facility, Los Alamos, New Mexico 87545

J. L. Sarrao and Z. Fisk
National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306

(Received 4 December 1995)

We present results for the resistivity, the magnetoresistance, and the specific heat of $Ce_{0.97}La_{0.03}Pd_3$ and $CePd_3$. The impurity contributions to these measurements follow the predictions of the single-impurity Kondo model for a Kondo temperature $T_L \approx 65$ K, assuming that the impurity behaves as a crystal-field split (Γ_7) doublet. Assuming a $J=\frac{5}{2}$ impurity, the value of T_L needed to fit these experiments varies from 65 to 125 K. The contribution to the susceptibility may be too small to be explained by the model. These results address whether the nonmagnetic impurity behaves as a Kondo hole. [S0163-1829(96)08919-9]

When nonmagnetic impurities are placed in an otherwise periodic heavy-fermion compound, the impurities can behave as though they are Kondo impurities. A classic example[1] is the alloy system $Ce_{1-x}La_xPd_3$: for $CePd_3$ the resistivity $\rho(T)$ falls to a small residual value as the temperature approaches $T=0$; but for $x=0.03$ the resistivity increases with decreasing temperature for $T<50$ K and the residual resistivity is large, of order 50 $\mu\Omega$ cm/at. % La [Fig. 1(a)]. Subtracting the host resistivity to obtain the impurity contribution yields a resistivity that is qualitatively similar to that expected for a Kondo impurity [Fig. 1(b)]. This effect is not very sensitive to which particular element is added, as long as it resides on the Ce site,[2] so that it is the *absence* of the Ce atom that causes the effect, hence the terminology Kondo hole.

The basic idea is that for systems where the heavy renormalized electrons carry the electric current in the ground state, said electrons will be strongly scattered by impurities on the Ce sublattice. That is, the nonmagnetic impurities destroy ''coherence.'' At higher temperatures where the coherence is absent, and the unrenormalized conduction electrons carry the current, the effect of the nonmagnetic impurity will disappear.[3] Hence the resistivity should vanish on the same temperature scale as the coherence. This has also been shown[4] (in the single-site approximation) to yield a *magnetoresistance* of the same form as for a Kondo impurity. Since calculations[3] show that the nonmagnetic dopant induces a resonance in the pseudogap that has much the same form as a Kondo resonance, the impurity also might be expected to give rise to a Kondo-like contribution to the specific heat and susceptibility. In this paper we present results for $Ce_{1-x}La_xPd_3$ for the magnetic field dependence of the transport, and for the specific heat and magnetization. Our focus is to test the extent to which the results can be fit to the predictions of the single-impurity Kondo model.

Samples of $CePd_3$ and $Ce_{0.97}La_{0.03}Pd_3$ were made by zone refining arc-melted polycrystal rods. The susceptibility χ of two representative samples, measured in a superconducting quantum interference device magnetometer in fields of 0.1–0.5 T, is shown in Fig. 2; the low-temperature magnetization M of two other samples (measured for several values of temperature using a vibrating sample magnetometer and an 18-T superconducting magnet at the National High Magnetic

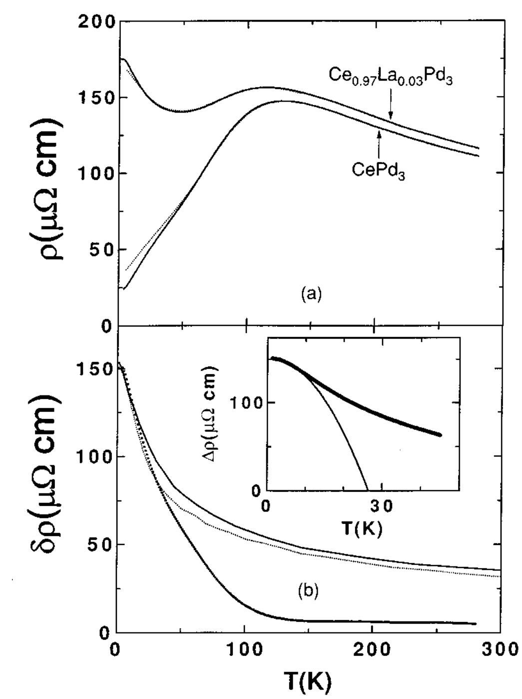

FIG. 1. (a) Resistivity vs temperature for $Ce_{1-x}La_xPd_3$ for $x=0$ and 0.03, for $B=0$ (solid lines) and $B=18$ T (dotted lines). (b) The impurity contribution to the resistivity for $B=0$ (small squares), found by subtracting the data for $x=0$ from that for $x=0.03$. The solid (dotted) line is the prediction for a $J=\frac{1}{2}$ ($J=\frac{5}{2}$) Kondo impurity with Kondo temperature $T_L=65$ K. The inset compares the impurity contribution (heavy line) to the form $\rho_0(1-AT^2)$ (thin line) where the coefficient A has the value expected for either a $J=\frac{1}{2}$ or $\frac{5}{2}$ Kondo impurity with $T_L=65$ K.

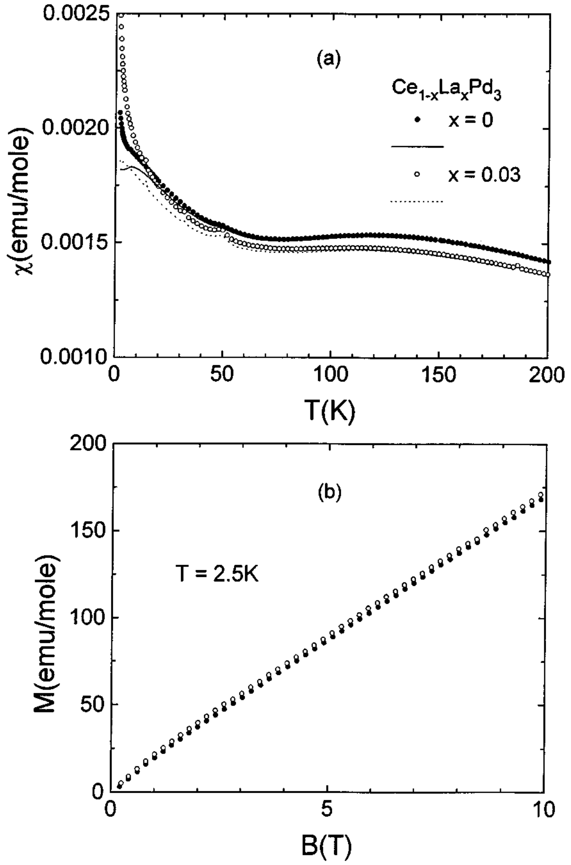

FIG. 2. (a) The susceptibility vs temperature for two representative samples of $Ce_{1-x}La_xPd_3$, with $x=0$ and 0.03, before (circles) and after (lines) subtraction of a small Curie term. If the data for $x=0.03$ are scaled to be equal to those of $CePd_3$ at high temperature (see text), the low-temperature intrinsic susceptibility for $x=0.03$ is then larger than that for $x=0$ by an amount 0.06×10^{-3} emu/mole, corresponding to the value expected for a $J=\frac{1}{2}$ Kondo impurity with $T_L=97$ K. (b) The magnetization vs magnetic field at 2.5 K for two other samples with $x=0$ and 0.03.

Field Laboratory) is shown in Fig. 2(b). It has been shown[5,6] that the increase in χ with decreasing temperature below 50 K is largely intrinsic; only the small additional increase below 10 K is extrinsic. This extrinsic contribution can be fit with a Curie law, and its (small) contribution to the magnetization can be saturated in small magnetic fields [Fig. 2(b)]. The susceptibilities of four zone-refined samples all had extrinsic Curie tails that were as small as those of the best samples reported in the literature.[5,6] The saturation magnetization and Curie constants correspond (under the assumption that they arise from an effective spin-$\frac{1}{2}$ impurity) to impurity contents of a few tenths of a percent. The room-temperature susceptibility for different samples at fixed x typically varied by $\pm3\%$; this reflects both field inhomogeneities, and uncertainties in the background susceptibility for small samples.

The specific heat $C_p(T)$ (Fig. 3), measured using a thermal relaxation technique, shows a small peak near 6.5 K. Past studies[7] suggest this arises from the presence of Ce_2O_3, which orders antiferromagnetically at approximately this temperature.[8] The entropy under the peak measured for several zone-refined samples showed that the amount of Ce in the samples in this second phase is of order 0.1%. We found

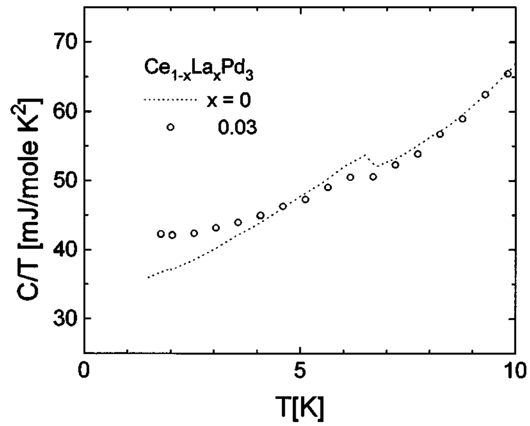

FIG. 3. The linear coefficient C_p/T of specific heat of $Ce_{1-x}La_xPd_3$ for $x=0$ and 0.03. The small peak near 6.5 K arises from a small amount (0.1%) of Ce_2O_3 in the sample; the value of C_p/T for $T\rightarrow0$ has the same value, independent of the magnitude of the Ce_2O_3 contribution. The nonmagnetic impurity induces a positive contribution to the specific-heat coefficient, of magnitude 6 mJ/mole K^2; this is the value expected for a $J=\frac{1}{2}$ Kondo impurity with $T_L=68$ K (or a $J=\frac{5}{2}$ impurity with $T_L=114$ K).

that, in the range 10–15 K, the specific heat of different samples disagreed by 2–3 %; the agreement was much better near 20 K, and was excellent for $T<4$ K.

The temperature dependence of the resistivity for $B=18$ T [Fig. 1(a)] and the field dependence of ρ at fixed temperatures (Fig. 4) was measured using the same 18-T magnet as for the magnetization. The rates for heating and cooling and increasing and decreasing the magnetic field were kept sufficiently low that no hysteresis was observed. We ran two samples each for $x=0$ and 0.03, establishing reproducibility of the field dependence. The absolute values are uncertain by roughly 15%, due to the uncertainty in determining the precise dimensions of the small ($0.5\times1\times3$ mm) rods used for the measurement.

We wish to test the extent to which all the data can be fit within the framework of the Kondo impurity model. In the Kondo limit ($n_f\rightarrow1$) of the Anderson model the theoretical predictions scale with T_K, i.e., a single Kondo temperature should scale the data for the different measurements. For strong mixed valence ($n_f<0.85$) two energy scales are required. Although $CePd_3$ is actually a mixed valent compound ($n_f\sim0.80$–0.85) we will for simplicity compare to theory in the Kondo limit. It is not obvious to us which value of the impurity spin ($J=\frac{1}{2}$ or $\frac{5}{2}$) should be used in the comparison: it depends on whether crystal fields affect the Kondo hole. If so, the cubic environment might give rise to a Γ_7 doublet Kondo hole. We will compare to theory for both values of J. In comparing to theory we use the Kondo temperature T_L defined[9] in relation to the linear coefficient of specific heat γ via $T_L\equiv(2J/2J+1)\pi^2R/3\gamma$, where R is the gas constant. For this definition, in the Coqblin-Schrieffer (i.e., Kondo) theory the low-temperature susceptibility has the value $\chi(0)=C/T_L$.[10] Here the Curie constant is $C=N_AJ(J+1)(g\mu_B)^2/3k_B$; for Ce, g is $\frac{6}{7}$ for $J=\frac{5}{2}$ and $C=0.807$ emu K/mole, while for a $J=\frac{1}{2}$ Γ_7 doublet, $g=\frac{10}{7}$ and $C=0.192$ emu K/mole.

In Fig. 1(b) we plot the temperature dependence of the impurity contribution to the resistivity, found by subtracting

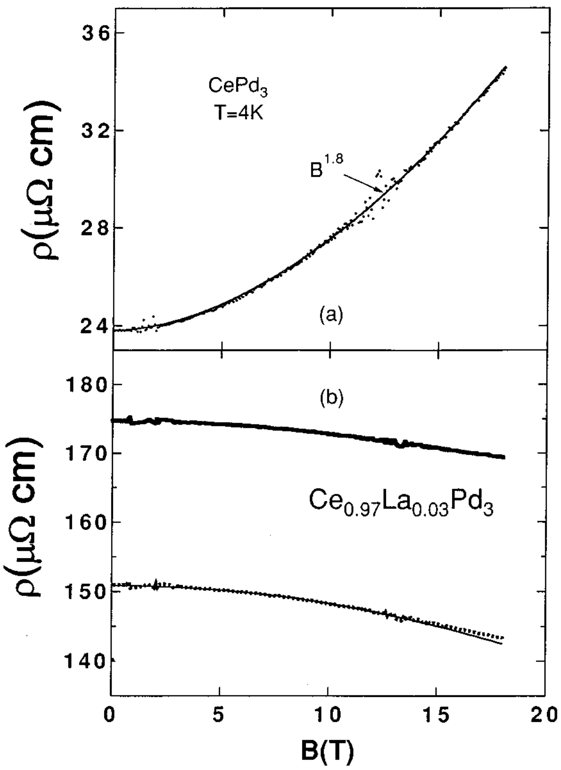

FIG. 4. (a) The magnetoresistance of $CePd_3$ at 4 K. The solid line represents a fit to the form $\Delta\rho/\rho_0 \propto B^{1.8}$. (b) The magnetoresistance of $Ce_{0.97}La_{0.03}Pd_3$ at 4 K (thick line). The thick dashed line represents an estimate of the effect of the reduction of the scattering rate by the field on the resistance; the effect of the field on the cyclotron orbits is estimated by applying a generalization of Kohler's rule (Ref. 13) and subtracted out. The thin line, representing the form $\rho = \rho_0(1-\alpha B^2)$, is the form expected for the low field magnetoresistivity of a $J=\frac{1}{2}$ Kondo impurity for $T_L=58$ K (or a $J=\frac{5}{2}$ impurity with $T_L=125$ K).

the resistivity of $CePd_3$ from that of $Ce_{0.97}La_{0.03}Pd_3$ (square symbols). The solid and dotted lines are predictions for the Kondo impurity model for $J=\frac{1}{2}$ (Ref. 11) and $\frac{5}{2}$ (Ref. 12), respectively; for both cases a value $T_L=65$ K is used in the comparison to the data. In the inset, the data (thick curve) at low temperature are shown to vary as the square of the temperature: $\rho(T)=\rho_0(1-AT^2)$ with $A=1.42\times10^{-3}/\mathrm{K}^2$ (thin curve). When compared to the Fermi-liquid predictions [$A=\pi^4/16T_L^2$ for $J=\frac{1}{2}$ (Ref. 11) and $A\approx 6.0/T_L^2$ for $J=\frac{5}{2}$ (Ref. 12)] this value also implies the value $T_L=65$ K for both $J=\frac{1}{2}$ and $\frac{5}{2}$. Hence at the lowest temperatures the resistivity behaves as an Anderson impurity, with Kondo temperature 65 K. For $T>20-30$ K the data appear to fall off far more rapidly than the predictions of the impurity model [Fig. 1(b)]; however, this may be an artifact arising from the above-mentioned uncertainty in determination of the geometric factors.

The magnetoresistivity of $CePd_3$ is positive, varying nearly quadratically in field [Fig. 4(a)]; this is ordinary magnetoresistance due to the creation of conduction-electron cyclotron orbits by the field. The magnetoresistance of $Ce_{0.97}La_{0.03}Pd_3$ is *negative* [Fig. 4(b)], in striking qualitative agreement with the Kondo model, for which the magnetic field causes a decrease in the spin-flip scattering rate.[9] To test for quantitative agreement, the cyclotron-orbital contribution must be separated out. Unfortunately, this is an extremely difficult problem, depending in detail on band structure and momentum dependence of the scattering. We attempt a qualitative analysis only, of the same form as used[13] in a recent study of $YbAgCu_4$, where we used a generalization of Kohler's rule to effect the separation. The result is shown as the dashed curve in Fig. 4(b). The solid line through the data represents the quadratic field dependence $\rho(B)=\rho_0\,(1-\alpha B^2)$ with $\alpha=1.7\times10^{-4}$. For $S=\frac{1}{2}$, low-field expansion (Sec. 4.4 of Ref. 10) of the Bethe ansatz results gives $\alpha=(1/16)(\pi g\mu_B/k_BT_L)^2$; for a Γ_7 doublet with $g=1.43$ the experimental value of α implies $T_L=58$ K. For the case $J=\frac{5}{2}$ the theoretical prediction is $\alpha=(175/216)(\pi g\mu_B/k_BT_L)^2$; here a value $T_L=125$ K fits the data.

The use[13] of Kohler's rule $\Delta\rho/\rho_0=\beta(B/\rho_0)^{1.8}$ to estimate the orbital contribution to the magnetoresistance acknowledges that, in the presence of the larger scattering rate and residual resistivity that prevails for $x=0.03$ the electrons complete a much smaller fraction of a cyclotron orbit before scattering, and hence the orbital contribution will be smaller than for $CePd_3$. To get a sense for the resulting uncertainty in the value of T_L derived from the magnetoresistance measurement we note that were we to ignore this and simply subtract the magnetoresistance of $CePd_3$ from that of $Ce_{0.97}La_{0.03}Pd_3$, the value of T_L needed to describe the data would be smaller (44 K for $J=\frac{1}{2}$ and 93 K for $J=\frac{5}{2}$). Alternatively, if we assume no orbital contribution at all and directly fit the data for $x=0.03$ without subtracting the data for $CePd_3$, we obtain $T_L=73$ K for $J=\frac{1}{2}$ and 159 K for $J=\frac{5}{2}$.

We next consider the specific heat. The low-temperature specific heat of antiferromagnets typically varies as $C_P\sim T^3$; hence we assume that the Ce_2O_3 impurity phase will not contribute to C_p/T in the limit $T\to0$. (In confirmation of this, we find that the value of C_p/T for $T\to0$ reproduces well for different samples and does not depend on the magnitude of the small maximum.) The addition of 3% La to $CePd_3$ increases the linear coefficient by 6 mJ/mole K^2 (Fig. 3). Assuming this arises from a concentration $x=0.03$ of Kondo impurities, the corresponding Kondo temperature (see above) is $T_L=68$ K for $J=\frac{1}{2}$ and $T_L=114$ for $J=\frac{5}{2}$.

In the Kondo theory, the susceptibility should be related to the Kondo temperature by $\chi(0)=xC/T_L$;[10] for $x=0.03$, $J=\frac{5}{2}$ and $T_L=65$ K the impurity contribution to the susceptibility should be 0.4×10^{-3} emu/mole, while for a Γ_7 doublet ($J=\frac{1}{2}$) it should be 0.09×10^{-3} emu/mole. For the samples shown in Fig. 2, the *intrinsic* susceptibility for both $CePd_3$ and $Ce_{0.97}La_{0.03}Pd_3$ is identical. That is, after subtraction of the Curie tail, the resulting value for the low-field susceptibility $\chi(0)$ is 1.82×10^{-3} emu/mole for both samples [solid and dashed lines in Fig. 2(a)]. Furthermore the magnetization curves for two samples differ by a constant amount for $B>2$ T, while the slopes are identical [Fig. 2(b)]; this implies that the impurity phase saturation magnetization is larger for the La-doped sample, but that the intrinsic susceptibilities are equal. Hence, the impurity does not appear to give a simple Kondo hole contribution to the susceptibility.

As stated above, the measured absolute value of susceptibility can be in error by a few percent. We now argue that the high-temperature susceptibility for $x=0.03$ should equal that of $CePd_3$: the 3% reduction in the susceptibility due to the smaller number of Ce atoms in the alloy should be nearly compensated by the decrease in characteristic energy on alloying. [At high temperature we expect $\chi = C/(T+\theta)$ with $\theta \propto T_{\max}$; and $T_{\max}$ decreases from 120 K for $CePd_3$ to 113 K for $x=0.03$.] Indeed, we found that the room-temperature susceptibility of a polycrystalline sample for $x=0.03$ equaled that of $CePd_3$. For the sample of $Ce_{0.97}La_{0.03}Pd_3$ shown in Fig. 2 the susceptibility at 350 K is lower than that of $CePd_3$ by a factor 1.033; if the two should be equal, the intrinsic susceptibility at low temperature should be increased by this factor, to 1.88×10^{-3} emu/mole. This is consistent with a Kondo hole contribution of 0.06×10^{-3} emu/mole, which is the value expected for a Γ_7 doublet with $T_L=97$ K, but is too small for a $J=\frac{5}{2}$ Kondo hole.

To summarize, for $Ce_{0.97}La_{0.03}Pd_3$ the low-temperature impurity contribution to the temperature dependence of the resistivity has the same form as a Kondo impurity with Kondo temperature $T_L=65$ K. For $T>50$ K the contribution appears to decrease with temperature more rapidly than the theoretical prediction, but this may be a consequence of error in the determination of the sample geometry. The magnetoresistance is negative, in important qualitative agreement with the prediction of Kondo theory. The precise magnitude of the effect depends in detail on the method used to separate out the ordinary, positive orbital magnetoresistance; the result can be fit by Kondo theory with a Kondo temperature 58 K for $J=\frac{1}{2}$ and 125 K for $J=\frac{5}{2}$. The linear coefficient of specific heat is larger than that of $CePd_3$, by an amount 6 mJ/mole K^2, which is consistent with an impurity Kondo temperature 68 K for $J=\frac{1}{2}$ and 114 K for $J=\frac{5}{2}$. Hence, these measurements support the concept of a Kondo hole, in the simple sense that the impurity contributions to $\rho(T)$, $\rho(H)$, and $\gamma = C_p/T$ behave similarly to those expected for a Kondo impurity. For $J=\frac{5}{2}$ the Kondo temperatures 65–125 K derived from the different measurements agree to within a factor of 2; for the $J=\frac{1}{2}$ (Γ_7 doublet) case, the agreement (58–68 K) is better. Finally, the susceptibility does not appear to have the extra contribution expected for a Kondo hole; however, this may be a consequence of error (~3%) in the determination of the magnetic field, or of the low-temperature Curie tail, and if so the contribution is of same order of magnitude as that expected for a Γ_7 doublet Kondo hole.

The single-ion Kondo temperature T_K of $CePd_3$ is greater than 500 K. In the single-site approximation,[4] the scale for the Kondo hole should be the same as T_K. The fact that the Kondo hole scale T_L is an order of magnitude smaller than T_K is a key part of the argument[1,2] that the full ground-state coherence sets in on a much smaller temperature scale than T_K in $CePd_3$. The fact that $T_L \ll T_K$ also allows the negative temperature coefficient of $\rho(T)$ to be observable. We know of no other heavy-fermion systems for which such a small concentration of impurities induces a negative $d\rho/dT$ at low temperature. As discussed in earlier work,[1,2] it is possible that the large magnitude of the effect reflects the low carrier density in $CePd_3$; it is almost a ''Kondo insulator.''

Work at Los Alamos was performed under the auspices of the U.S. Department of Energy. Work at the National High Magnetic Field Laboratory was supported by the National Science Foundation and Florida State University. Work by J.M.L. was supported by the Center for Materials Science at Los Alamos under the UC Personnel Assignment Program; work by MST was supported by the Superconducting Technology Center at Los Alamos.

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*Permanent address: Department of Physics and Astronomy, University of California, Irvine, CA 92717.

†Permanent address: Departmento de Física, Universidad Autónoma de Madrid, Madrid, Spain.

‡Permanent address: Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

§Permanent address: Physics Department, San Diego State University, San Diego, CA 92182.

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