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Two Energy Scales in $CePd_3$

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We report anomalies in the temperature- and pressure-dependent electrical resistivity of $CePd_3$ and its alloys that occur on a temperature scale ≈ 40 K, which correlates with the scale for the neutron-scattering form-factor ($5d$ susceptibility) anomaly. We outline an argument that the reported effects demonstrate the existence of an energy scale T_{coh} [related to the single-ion spin-fluctuation scale T_{sf} by a factor $1/(2J+1)$] over which coherence develops among spin fluctuations on different sites.

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The susceptibilities of a large class of cerium and ytterbium valence-fluctuation compounds vary with temperature as universal functions of a scaled temperature T/T_{sf}, where $k_B T_{sf}$ is the spin-fluctuation energy.[1] Single-ion models of mixed valence[2,3] predict such single-energy scaling, with Bethe-*Ansatz* calculations[4] for $J=\frac{5}{2}$ and $\frac{7}{2}$ Kondo impurities yielding susceptibilities in good agreement with those observed experimentally over a wide temperature range. Indeed, many of the properties of these materials can be understood in models[5] that treat the compounds as a collection of $4f$ impurities. However, at low temperatures ($T << T_{sf}$), coherence among the valence and spin fluctuations on different sites must set in. Such coherence is a necessary condition for the observation of de Haas–van Alphen oscillations, which have been seen in $CeSn_3$.[6] Several years ago Anderson[7] suggested that the energy scale T_{coh} over which the resulting quasiparticle bands arise might differ from the single-ion scale T_{sf} by a factor $1/N$, where $N=2J+1$ is the oribtal degeneracy; recent theories based on the large-N limit support this idea.[8]

Experimental properties should differ in the narrow-band regime from those predicted by single-ion theory. One of the first indications that there might be such differences can be found in neutron form-factor measurements in $CeSn_3$ and $CePd_3$.[9] At temperatures above 40 K, both compounds exhibit susceptibilities consistent with single-ion scaling with $T_{sf} \approx 100$–200 K, but below 40 K the susceptibility increases as a result of an increasing $5d$ susceptibility component. The electrical resistivity is also a very sensitive measure of coherence in that, for the single-ion case, it saturates to a large value at low temperatures, while for the periodic case, it must vanish at $T=0$. In this paper we report resistivity data for $CePd_3$ and the alloy $Ce_{0.97}La_{0.03}Pd_3$. Anomalies in the pressure and temperature dependence occur on a scale ≈ 40 K, correlating with that of the form-factor (susceptibility) anomalies. We give evidence that these anomalies reflect the onset of coherence as opposed to being a spurious property of $CePd_3$.

The results[10] at ambient pressure for $CePd_3$ are shown in Fig. 1; they are in good agreement with those of other investigators.[11-13] In the pure compound the

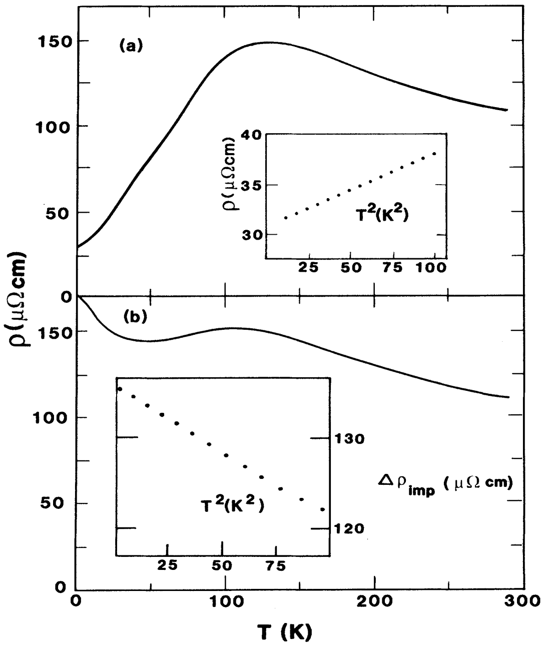

FIG. 1. Resistivity at ambient pressure for (a) $CePd_3$ and (b) $Ce_{0.97}La_{0.03}Pd_3$. The inset in (a) shows the low-temperature resistivity of $CePd_3$ plotted vs T^2. The inset in (b) shows the impurity contribution to $Ce_{0.97}La_{0.03}Pd_3$ ($\Delta\rho_{imp}$; see text) plotted vs T^2.

resistivity exhibits a maximum at a temperature $T_{max} = 124$ K, which is very close to the temperature of the susceptibility maximum. Because it equals the inelastic magnetic neutron linewidth Γ, we can use $2T_{max}$ as a measure of the spin-fluctuation temperature T_{sf}.[1] At lower temperatures, the resistivity decreases as coherence sets in. Closer examination of Fig. 1(a) reveals the existence of a shoulder in the curve near 30 K. This feature has been observed before, even in very high-quality single crystals.[11] For $T < 10$ K, the resistivity follows a T^2 power law [Fig. 1(a), inset] of the form $\rho(T) = (30.65 + 0.072T^2)$ $\mu\Omega$-cm. To extract a temperature scale T^* from the T^2 law, we note that the resistivity should climb to its saturation value ρ_s as $\rho(T) = \rho_0 + \rho_s(T/T^*)^2$. Taking $\rho(T_{max}) = 150$ $\mu\Omega$-cm as an estimate of ρ_s, we obtain $T^* = 45$ K.

The resistance of $CePd_3$ at several pressures up to 15 kbar is shown in Fig. 2. Above 50 K the resistivity changes markedly with pressure: T_{max} increases at a rate $dT_{max}/dP \approx 1$ K/kbar, and the room-temperature resistivity increases at a rate 0.5%/kbar. The data nicely demonstrate single-energy scaling[14] in that if we plot $R(T,P)/R_{max}(P)$ vs $T/T_{max}(P)$, as in Fig. 2(c), we find that the data collapse onto a single curve. However, closer examination of the low-temperature data [Fig. 2(b)] shows that for $T < 40$ K the resistivity is essentially unaffected by pressure.

Hence, the temperature of the shoulder, the coefficient of the T^2 law, and the difference in pressure dependence above and below 40 K all indicate that the transport behavior is anomalous on the same temperature interval as the susceptibility anomaly. To give evidence that the anomalies are associated with the onset of coherence, we turn next to alloy studies.

Consider the resistivity of $(Ce,La)Pd_3$ [Fig. 1(b)]. On alloying with lanthanum, T_{max} decreases to 102 K. (The tendency of lanthanum solutes to decrease the characteristic energy of cerium is well documented.[1]) In addition, the low-temperature resistivity increases drastically. To determine the temperature scale of the increase, we estimate the impurity contribution to the resistivity by subtracting the pure $CePd_3$ background:

$$\Delta\rho_{imp} = \rho(Ce_{0.97}La_{0.03}Pd_3) - \rho(CePd_3).$$

We then find that the impurity contribution varies as

$$\Delta\rho_{imp} = 135\{1 - [T/(31\text{ K})]^2\}\ \mu\Omega\text{-cm}.$$

This is the behavior expected of a Kondo impurity with T_K of order 30–40 K. Consider next the pressure dependence (Fig. 3): The resistivity for $T > 50$ K changes shape quite markedly with pressure, but, while there is a constant shift (i.e., 2% decrease in residual resistivity), the temperature dependence of the resistivity below 40 K is unaltered by pressure. This makes it clear that the temperature scale of the impurity resistivity is intimately related to the temperature scale of the anomalies in the host matrix.

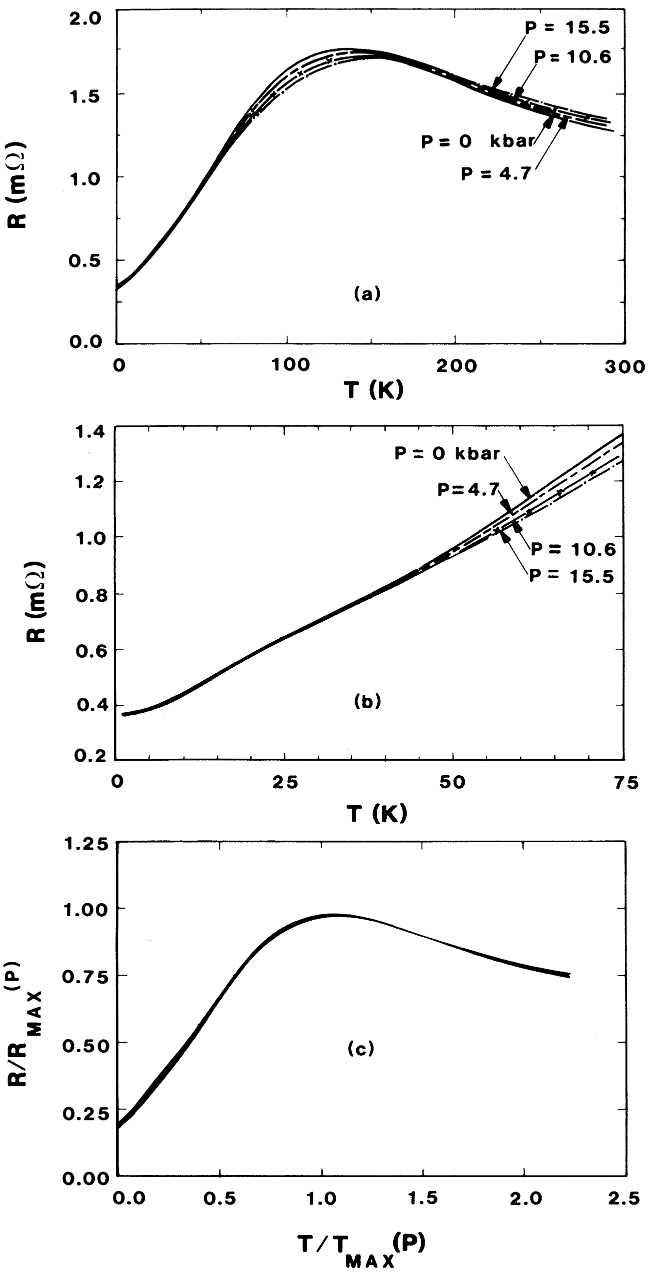

FIG. 2. (a) Resistance of $CePd_3$ for four pressures. (b) Low-temperature region of the data for the same four pressures, showing the variance of the resistance with pressure below 30 K for all four pressures. (c) Plot of the resistance for all four pressures scaled to its maximum value $[R/R_{max}(P)]$, demonstrating single-energy scaling of the resistivity over a broad temperature range.

Now, why should it be that nonmagnetic lanthanum gives a Kondo effect with T_K the same as the tempera-

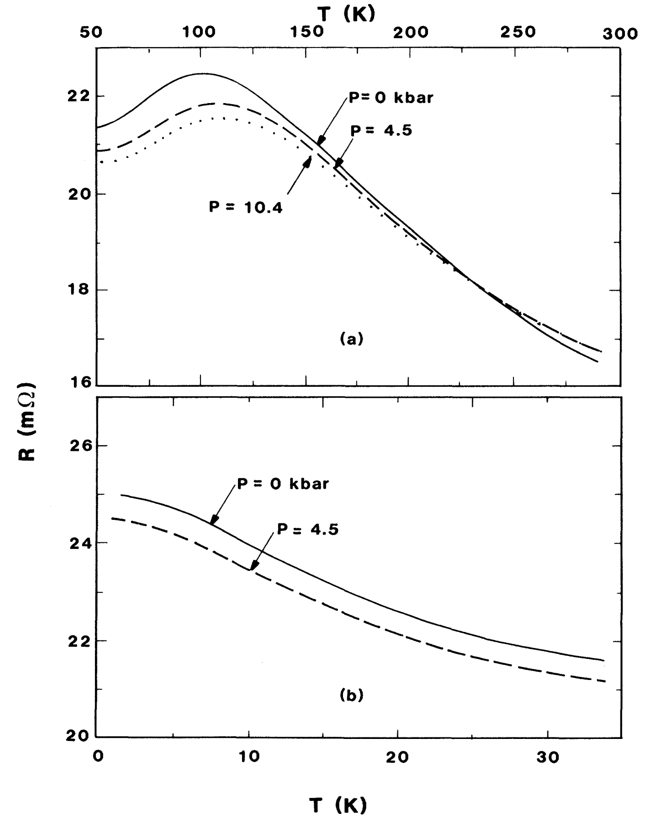

FIG. 3. Resistance of $Ce_{0.97}La_{0.03}Pd_3$ for several pressures (a) in the range 50–300 K, where the resistivity changes shape as a function of pressure, and (b) in the range 0–35 K, where apart from a constant shift, the temperature dependence is unaffected by pressure.

ture of the form-factor and transport anomalies in pure $CePd_3$? The answer, we believe, is that by removing the cerium atom from the solute site i, a "Kondo hole" is created; i.e., the impurity Hamiltonian can be written

$$H_{\rm imp} = H_0 - H_{\rm K} + H_{\rm pot},$$

where H_0 is the Hamiltonian for $CePd_3$, and

$$H_{\rm K}^i = E_f n_f^i + U n_{f\uparrow}^i n_{f\downarrow}^i + \sum\nolimits_{k\sigma} V_{kf}(f_{i\sigma}^\dagger c_{k\sigma} + \text{c.c.})$$

(in the usual notation), and $H_{\rm pot}$ is a weak term representing potential scattering from the lanthanum atom. The Kondo-hole term $-H_{\rm K}^i$ gives rise to a Kondo effect in the regime where H_0 demonstrates narrow-band behavior; i.e., for $T < T_{\rm coh}$, the heavy quasiparticles scatter from the Kondo hole. For $T > T_{\rm coh}$, this is no longer true; rather, the bare s,d electrons now scatter from all the $4f$ electrons, and the lanthanum site gives only potential scattering. Hence the temperature scale for the lanthanum Kondo-hole impurity should be $T_{\rm coh}$. There is further experimental evidence for this: Recent work[12] on $Ce_{1-x}R_xPd_3$ alloys (R = Y,Gd,Pr) shows that for fixed x the resistivity is *independent of solute.* For $x = 0.03$, it has the same large value of residual resistivity ρ_0 and the same temperature dependence as exhibited here for the lanthanum solute. This dramatic result has a natural explanation in terms of the Kondo-hole effect: Any solute gives rise to the same Kondo-hole term.

This completes the outline of our argument that the reported effects demonstrate the existence of a second energy scale $T_{\rm coh} \approx 40$ K over which coherence develops. From the estimate $T_{\rm sf} = 2T_{\rm max} = 250$ K, we see that it is indeed true that $T_{\rm coh} \approx T_{\rm sf}/(2J+1)$, since $J = \frac{5}{2}$ for cerium.

We now wish to discuss the generality of these results. The development of coherence is clearly indicated by vanishing resistivities in most valence fluctuators. A key question is whether it will give rise to similar effects as in $CePd_3$. To answer this, we must distinguish between effects.

First, we consider the form-factor anomaly. This is also observed in $CeSn_3$ and on a temperature scale $O(T_{\rm sf}/(2J+1))$. We have no answer to the question as to why the $5d$ susceptibility should grow large below $T_{\rm coh}$, except to point out that it is quite reasonable that the $5d$ wave functions should suffer changes as coherence develops. This is especially true if the latter involves growth of a hybridization gap, as proposed by several theories.[15,16] Without a more definitive answer, we cannot know whether form-factor anomalies are a general phenomenon. [That the susceptibility and resistivity anomalies should be related is more straightforward; it is well known[17] that the relaxation rate is a weighted Fermi-surface integral over $T\chi(Q)$ when the transport is dominated by spin scattering.]

Consider next the fact, implied by our analysis, that $T_{\rm coh}$ is independent of pressure, while $T_{\rm sf}$ changes substantially. This suggests immediately that, while $T_{\rm coh}$ is $O(T_{\rm sf}/(2J+1))$, the two scales are not uniquely related, but that the relation depends on details of crystal structure, cation wave functions, etc. Recent work[18] on the specific heat of $CeAl_3$ indicates that the volume dependence of the linear coefficient γ has the value expected for the single-ion Kondo effect for $T > T_{\rm sf}$, but that at low temperatures $T < T_{\rm sf}$, the quantity $\partial \ln\gamma / \partial \ln V$ actually changes sign. The system responds very differently to pressures in the coherence regime than in the single-ion regime. To determine the case of $CeSn_3$, we have recently[10] studied $\rho(T)$ at pressures up to 15 kbar. Between 20 and 50 K the resistivity varies as $\rho_{\rm HI}(T) = \rho_0 + \rho_{\rm max}(T/T^*)^2$, where $T^* = 170$ K at $P = 0$ and $dT^*/dp = 2.5$ K/kbar. Here the observed T^* is consistent with the single-ion temperature $T_{\rm sf}$. Below 30 K, however, there is an upturn in the resistivity, and the deviation $\Delta\rho(T)$ [defined through the formula $\rho(T)=\rho_{\mathrm{HI}}+\Delta\rho$] is found to be independent of pressure. Hence, while the details differ from $CePd_3$, the resistivity again has a contribution, on a scale comparable to that of the form factor, whose pressure dependence differs from that at high temperatures.

What is *not* general is the detailed shape and magnitude of the resistivity. Although $CeSn_3$ and $CePd_3$ have comparable T_{sf} (~ 250 K) and valences $n_f \sim 0.9$), their resistivities are very different. We think that this reflects band-structure effects: In $CeSn_3$ there is a healthy density of tin $5sp$ states to carry the current, while in $CePd_3$, the palladium states are full and the cerium $5d$ states split off above the Fermi level, leaving a very low density of carriers at E_{F}.[19] This is a key reason why the effects on the resistivity of $CePd_3$ are so large.[10]

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