Charge dynamics of Ce-based compounds: Connection between the mixed valent and Kondo-insulator states

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The reflectivities of the mixed-valent compounds $CeSn_3$ and $CePd_3$ have been measured to obtain the optical conductivity as a function of temperature. Both compounds show a renormalization of the low-energy Drude conductivity at low temperatures. In addition, for the low-carrier-density compound $CePd_3$, but not for high-carrier-density $CeSn_3$, substantial spectral weight lost from the conductivity below 1000 cm^{-1} reappears in the frequency range 2000–10 000 cm^{-1}, indicating that $CePd_3$ can be considered a lightly doped Kondo insulator.

$CePd_3$ is the most celebrated mixed-valent metal and as such, has been examined by essentially all techniques of modern condensed-matter physics. Of particular interest have been measurements of the electronic density of states using optical,[1] photoemission (PES),[2] and bremsstrahlung isochromat (BIS) (Ref. 3) spectroscopies. The latter measure the single particle density of states (DOS) below and above the Fermi level by removing and adding one particle, respectively. In contrast, the optical conductivity, which is measurable with better energy resolution, is basically a convolution of the PES and BIS spectra. The key result of the optical experiments performed to date are: (1) at low frequencies, $CePd_3$ behaves as a low-carrier-density Fermi liquid whose effective mass is enhanced below a coherence temperature of $T^* \sim 40$ K and (2) at the intermediate frequency ($0.1 < \hbar\omega < 1$ eV) electronic response has considerable structure. Because band theory[4] can account for (2), one might fairly conclude that (1) represents the extent to which interesting many body effects occur in $CePd_3$. It is the purpose of this paper to argue otherwise. In particular, we show that the interband transitions in $CePd_3$ are extraordinarily temperature (T) dependent for k_BT one to two orders of magnitude below the interband transition energies. On cooling, the most striking change in the optical conductivity is the formation of a pseudogap, accompanied by a large shift of spectral weight to high energy. Thus, the data are reminiscent of those for optical gap formation in the correlated insulators FeSi (Ref. 5) and $Ce_3Bi_4Pt_3$ (Ref. 6) and when taken together with the low carrier density of $CePd_3$ support the idea that $CePd_3$ is a lightly doped Kondo insulator.[7] Optical conductivity data which we have collected for $CeSn_3$, an isostructural mixed-valent compound with a substantially higher carrier density,[8] further support this idea: the spectral weight redistribution of $CeSn_3$ on cooling from room temperature is largely confined to frequencies below 1000 cm^{-1}.

We prepared polycrystalline $CePd_3$ from stoichiometric amounts of the constituents by arc melting, while we grew single crystals of $CeSn_3$ in a tri-arc furnace using the Czochralski method; tungsten studs were used as seeds. Four-probe dc resistivity measurements on $CePd_3$ were performed using silver paste contacts.

Near normal incidence reflectivity was measured using a Fourier interferometer for the range 15–5000 cm^{-1}, a grating spectrometer for the near infrared and visible range, 1000–25 000 cm^{-1}, and a double-beam McPherson instrument for the ultraviolet range up to 100 000 cm^{-1}. We mounted the samples in a circulating He cryostat with a lever allowing interchange of reference and sample at any temperature. To deduce the optical conductivity from the reflectivity, we applied Kramers-Kronig (KK) transforms. The low-frequency termination was the Hagen-Rubens relation, and the high-energy extrapolation was an ω^2 followed by an ω^4. The zero-frequency conductivities, obtained from the KK extrapolation, agree within 20% with the bulk dc measurements (see inset to Fig. 3).

Figure 1 shows the reflectivity and the real part of the conductivity for $CeSn_3$ at selected temperatures. Changes in the low-frequency region reflect a narrowing of the Drude peak with decreasing temperature. As with $CePd_3$,[1] the data at low ω and T can be understood in terms of a scattering rate depending strongly on both frequency and temperature. The narrowing and the frequency dependence of the scattering rate at low T are intimately related to the renormalization of the effective mass, which is of order ten free-electron masses for this mixed-valent compound.[9] In Fig. 1(b) one also sees the growth and sharpening of two weak peaks as

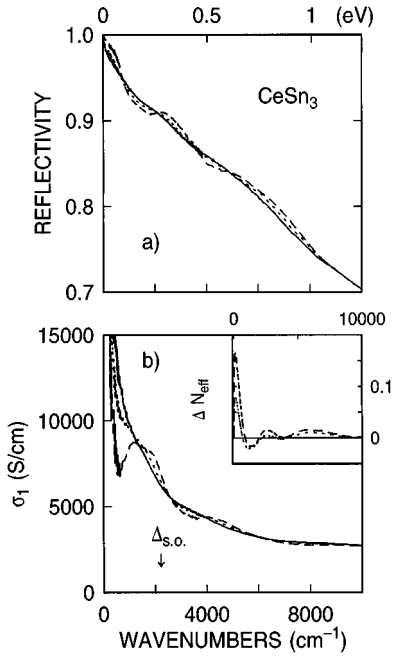

FIG. 1. (a): Reflectivity of $CeSn_3$ at 250 K (solid), 150 K (dotted), and 25 K (dashed). (b) Optical conductivity of $CeSn_3$ as calculated from the reflectivity. Below 1000 cm^{-1} spectral weight shifts to lower energy as the temperature decreases. The inset shows $\Delta N_{\rm eff}$ [see Eq. (1) in text] for temperatures of 150 K (dotted) and 25 K (dashed). The positive $N_{\rm eff}$ shows the shift of spectral weight to lower energy.

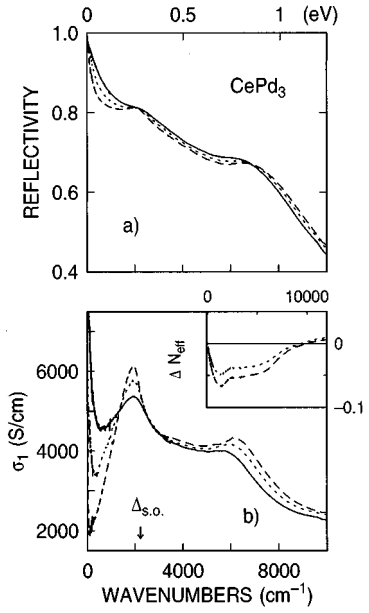

FIG. 2. (a): Reflectivity of $CePd_3$ at 250 K (solid), 150 K (dotted), and 25 K (dashed). The spectra below 75 K and above 2000 cm^{-1} nearly coincide. (b) Optical conductivity of $CePd_3$ at 250, 150, and 25 K. Spectral weight below 1000 cm^{-1} shifts to higher energy. The inset shows $\Delta N_{\rm eff}$ as calculated by Eq. (1) (see text) for temperatures of 150 K (dotted) and 25 K (dashed).

the temperature is lowered: one occurring at about 2000 cm^{-1}, the other at 4500 cm^{-1}.

Since carrier density is related to the integral of $\sigma_1(\omega)$, it is useful to define the quantity

$$\Delta N_{\rm eff}(\omega,T)=\frac{2m_eV_{\rm f.u.}}{\pi e^2}\int_0^{\omega}[\sigma_1(\tilde{\omega},T)-\sigma_1(\tilde{\omega},250\ \ {\rm K})]d\tilde{\omega} \tag{1}$$

(with $V_{\rm f.u.}$ the volume per formula unit and m_e the free-electron mass), which is the difference between the effective carrier density $N_{\rm eff}$ (per formula unit) at arbitrary temperature T and at 250 K. As can be seen in the inset to Fig. 1(b), for $T=25$ and 150 K, $\Delta N_{\rm eff}$ grows rapidly near $\omega=0$, and then drops to essentially zero in the vicinity of 1000 cm^{-1}. This behavior reflects the sharpening of the low-frequency conductivity resonance, i.e., an increase in $\sigma_1(\omega)$ near $\omega=0$ and a concomitant decrease at higher frequency. We conclude that on lowering T below 250 K, spectral weight is most obviously rearranged for $\omega\leqslant$ 800 cm^{-1}. Thus, for $CeSn_3$ we find that electronic spectral weight is largely conserved over a frequency scale of order $5k_BT$.

Figure 2 shows the reflectivity and the real part of the conductivity for $CePd_3$ at selected temperatures. Like $CeSn_3$, $CePd_3$ displays the renormalization (sharpening) of the Drude peak at low temperature associated with the onset of coherence. This has been well studied and described in terms of a renormalized scattering rate and mass.[1,10,11] In this paper we concentrate on the high-energy features: the growth of structures in the conductivity as the temperature is reduced. Such structures can be seen for $CePd_3$ at $\sim$ 2000 and 6000 cm^{-1}, as compared to $\sim$ 2000 and $\sim$ 4500 cm^{-1} in $CeSn_3$. Previous workers have variously assigned them to spin-orbit splittings and interband transitions. Indeed, Koenig and Khan[4] find features at both energies in the joint density of states obtained from their band structure calculation for $CePd_3$. On the other hand, 2000 cm^{-1} coincides with the spin-orbit energy $\Delta_{\rm SO}=2050$ cm^{-1} for a free Ce^{3+} ion and, indeed, a temperature dependence due to many body effects has been calculated[12] for the DOS around $\Delta_{\rm SO}$. The unequivocal crossing of the reflectivities for different temperatures around 7000 cm^{-1} causes the temperature dependence in the optical conductivity around 8000 cm^{-1}. The higher energy structures (around 8000 and 4500 cm^{-1}) could be derived from Kondo lattice effects[13] often postulated for mixed-valence and heavy-fermion compounds.

Although the reduction of the conductivity in the intermediate frequency range may seem similar in $CePd_3$ and $CeSn_3$, there is, in fact, a significant difference. For $CePd_3$, the spectral weight lost from the region around 800 cm^{-1} does not shift to low-frequency. The weight of the narrow low-frequency resonance is quite small, barely observable in the inset of Fig. 2(b). Figure 2, in fact, demonstrates that the spectral weight missing from the range $\omega\leqslant$ 1000 cm^{-1} is *shifted upward*, primarily to the higher frequency range, $\omega\sim$ 6000–8000 cm^{-1}. The result that $\Delta N_{\rm eff}$ returns to zero by about 10 000 cm^{-1} shows that the charge conservation sum rule is ultimately satisfied. It is quite surprising, however, that one has to go to such a high frequency ($\sim 50k_BT$) to achieve this result.

For $CeSn_3$, as well as UPt_3 (Ref. 14) and $YbAl_3$,[15] the dc resistivity is a monotonic function of T, decreasing gradually between room temperature and the coherence tempera-

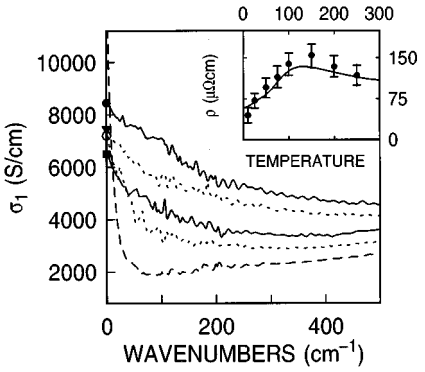

FIG. 3. Infrared conductivity of $CePd_3$ for selected temperatures in the far infrared [from top: 250 (solid), 200 (dotted), 150 (solid), 100 (dotted), 25 K (dashed)]. σ_{dc} as extrapolated from the KK transform is shown along the vertical abscissa for: 250 (●), 200 (▼), 150 (■), and 100 (○) K. The data for 150 K $\leqslant T$ show a uniform decrease of the conductivity, reflecting the shift of spectral weight to high energy. At 25 K, the development of a sharp (renormalized) Drude peak is also evident. The inset shows the dc resistivity as extrapolated from the infrared data ρ_{dc}^{IR} (●) together with the measured dc resistivity ρ_{dc}^{trans} (solid line) taken on a sample from the same batch.

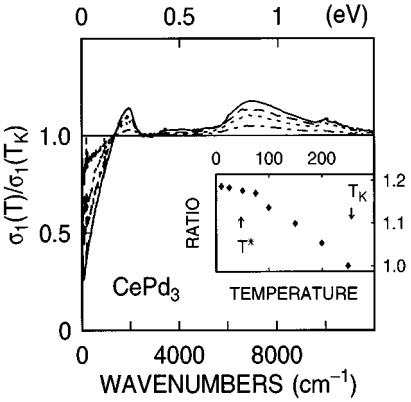

FIG. 4. Relative change of the optical conductivity with respect to the Kondo temperature T_K=250 K (200 K: dot-dashed; 150 K: dotted; 100 K: dashed; 25 K: line). The inset shows the ratio $\sigma_1(T)/\sigma_1(T_K)$ at 7000 cm^{-1}, demonstrating the strong temperature dependence *above* T^*.

ture T^* and rapidly below T^*. For $CePd_3$ and certain other compounds such as $CeCu_2Si_2$ (Ref. 16) and $CeAl_3$,[17] however, the temperature dependence of ρ_{dc} is more complex. Between room temperature and T_{max}=120 K, ρ_{dc} increases with decreasing T, leading to a maximum before a rapid decrease associated with the onset of coherence (see inset of Fig. 3). The increase of ρ_{dc} might be attributed to an enhanced scattering rate, Γ, which would cause characteristic *crossings* of $\sigma_1(\omega,T)$ at frequencies around Γ for different temperatures T. The data of Fig. 3, however, show that cooling from 250 K to T_{max} yields no such crossing, nor any apparent broadening of the Drude part of the conductivity. Instead they indicate an overall reduction of the spectral weight at low frequency, i.e., a *reduced effective carrier density*. Our infrared measurements reveal further that this spectral weight shifts to high energy, thus establishing a surprising connection between the dc resistivity anomaly of $CePd_3$ and the development of the high-energy structure around 7000 cm^{-1}. We emphasize that this physics is distinct from renormalization effects on the scattering rate and mass associated with the formation of the coherent heavy-fermion ground state,[18] in which the Drude peak narrows dramatically due to the coherent hybridization of the f states to the Fermi surface. For $CePd_3$ the spectral weight of the coherence peak at $\omega \approx 0$ is negligible compared to the shifted spectral weight under discussion here, and would appear only as a very small positive spike in ΔN_{eff} at very low frequency (below about 5 cm^{-1}).

The appearance of the pseudogap suggests a proximity to an insulating instability for $CePd_3$, where the carriers responsible for the negative $d\rho/dT$ at room temperature ultimately reside in filled bands while a small number of electrons account for the coherent transport, seen as $T \rightarrow 0$. The crossover between the two regimes is also responsible for the change in the sign of the Hall constant[19] near T_{max}. Thus, $CePd_3$ can be regarded as an intrinsically doped Kondo insulator,[7] with a carrier concentration, at low temperature, of $n \approx 0.5 \times 10^{21}$ cm^{-3} in contrast to the higher $n \approx 0.5 \times 10^{22}$ cm^{-3} of conventional heavy fermion or mixed-valent compounds such as $CeSn_3$.[19] A shift of spectral weight to high frequencies accompanying pseudogap development has been inferred for the Ce-based Kondo insulator, $Ce_3Bi_4Pt_3$ (Ref. 6), and for FeSi.[5] In $CePd_3$, the spectral weight has been successfully recovered and thus, this is a compound for which the upper energy scale can be identified. We suggest that this phenomenon of shifting spectral weight, which connects very low- and high-energy scales, lies at the heart of understanding the nature of gap development in strongly correlated insulators. The coincidence of the energies of the piled-up spectral weight with the spin-orbit coupling energy and the single-ion $4f$ energy (≈ -1 eV) gives hints to the localizing effects.

In Fig. 4 we show the relative change of $\sigma_1(\omega)$ of $CePd_3$ for different temperatures with respect to $\sigma_1(\omega)$ at 250 K which coincides with the Kondo temperature T_K of $CePd_3$.[20] The inset, in which we plot the detailed temperature dependence of the ratio $\sigma_1(\omega,T)/\sigma_1(\omega,T_K)$ for ω= 7000 cm^{-1}, demonstrates that the high-frequency response evolves at temperatures above the coherence temperature T^*, i.e., is not directly connected to the coherence effect. The strong temperature dependence of the ratio $\sigma_1(T)/\sigma_1(250\ K)$ is only possible if either the initial or final DOS of the optical transition is *sharp and temperature dependent.* Growth of a broad peak around 0.8 eV in the BIS spectra of $CePd_3$ has also been reported recently and it has been assigned to the temperature dependence of the f density of states.[3] Ordinary band theory can not account for large changes in the electronic response at energies much higher than the measuring temperatures.[21] Thus, both the BIS and our optical data indicate many body effects in $CePd_3$ which are shared with FeSi (Ref. 5) and $Ce_3Bi_4Pt_3$ (Ref. 6) but not with higher-carrier-density $CeSn_3$.

We have performed detailed measurements of the temperature- and frequency-dependent optical conductivities of the classic mixed-valence metals $CeSn_3$ and $CePd_3$. Below their coherence temperatures T^*, both $CeSn_3$ and $CePd_3$ show a renormalization of the low-frequency Drude

response. For $CePd_3$ there is, in addition, the development of a pseudogap involving a significant shift of spectral weight to ~ 1 eV $\gg k_B T$. This is reminiscent of how the optical gaps form in the correlated insulators FeSi (Ref. 5) and $Ce_3Bi_4Pt_3$.[6] The similarity is probably not accidental given that the spectral weight associated with pseudogap formation dwarfs the weight of the Drude term in $CePd_3$. In contrast, $CeSn_3$ exhibits a Drude term with spectral weight an order of magnitude larger and relatively little redistribution of weight to high frequencies. Thus, $CePd_3$ behaves as a lightly doped Kondo insulator, a description which accounts for the well-known anomalous transport properties of this compound, while $CeSn_3$, on the other hand, appears to be a conventional metal with a renormalized conduction band. We conclude that by virtue of its being an easily prepared stoichiometric metal, $CePd_3$ affords a unique opportunity to understand lightly doped Kondo insulators without the complications of disorder.

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