Kondo Coupling Induced Charge Gap in $Ce_3Bi_4Pt_3$

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Measurements of the infrared reflectivity of the Kondo insulator $Ce_3Bi_4Pt_3$ as reported. Near room temperature the charge dynamics are comparable to those of a heavy fermion compound in the incoherent regime; however, below 100 K the depletion of the low frequency conductivity signifies the development of a charge gap at low frequency (~ 300 cm^{-1}). The temperature dependence of the depleted spectral weight scales with the quenching of the Ce $4f$ moments, demonstrating that the gap formation is due to the local Kondo coupling of charge carriers to the Ce magnetic moments. The spectral weight which disappears as the gap forms must be displaced to energies much larger than the gap.

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For 30 years the manifestation and interaction of localized and itinerant electron states in transition metals, actinide, and rare earth compounds have challenged experimentalists as well as theoreticians. New types of ground states have been discovered as, e.g., magnetic semiconductors, Kondo metals, mixed valent compounds, heavy fermion metals, and, most spectacular, high temperature superconductors. A common label for this area of solid state physics has been strongly correlated electron systems. Specific topics of research include mixed valent and heavy fermion compounds. Both classes of materials might be comprehensively described by the periodic Anderson model. For the mixed valent substances the f electron energy E_f is adjacent to the Fermi energy E_F resulting in a strong Kondo coupling J. In the heavy fermion compounds E_f lies well below E_F, allowing the application of the Kondo lattice Hamiltonian (KLH). High temperature properties can be understood as the incoherent response of a dense single impurity Kondo system, while below a material specific temperature T^* a coherence of the Kondo singlets develops, giving rise to a Fermi liquid with a strongly enhanced effective electron mass m^*. At even lower temperatures the Fermi liquid can become unstable to magnetic ordering or superconductivity. A new instability became evident recently [1] in which the Fermi liquid exhibits an insulating ground state. Since the KLH is applied the notion Kondo insulator has been coined [2].

In this Letter we use infrared measurements of the charge dynamics to address the crucial issue of the nature of the Kondo insulator gap. With no electron-electron interaction ($U=0$), the half-filled periodic Anderson Hamiltonian reveals a small gap due to the coherent hybridization between d and f bands [3]. Essentially this gap is not different from bonding-antibonding gaps of conventional band structure calculations, although it may be smeared out thermally due to the very small gap value. The situation turns elaborate when the correlation is switched on ($U_{ff} \neq 0$). For illustration, in the extreme case of a very strong Kondo coupling J, each localized state binds one conduction electron to form a local singlet, and the energy for the excitation of the captured electron, i.e., the charge gap, is governed and stabilized by the local antiferromagnetic (Kondo) coupling [4]. In contrast to conventional band structure gaps, one then expects a temperature dependence of the gap correlated with the temperature dependence of the magnetic interactions. For 1D systems the ground state has been exactly calculated being a singlet with a spin gap that might be smaller than the charge gap [5]. However, because of the restricted dimension the real substances may reveal more subtle aspects. With far-infrared measurements [6] we probe the temperature dependent evolution of the charge response [$\sigma_1(\omega)$] and gap formation and address the postulated energy difference for spin and charge excitation.

We investigated single crystals of $Ce_3Bi_4Pt_3$ of dimensions like $1.5 \times 1.5 \times 1$ mm^3. This alloy has a cubic ($I\bar{4}3d$) symmetry with lattice constant $a_0 = 9.998 \pm 0.005$ Å. In order to prevent any oxidization of the reactive Ce we worked inside a dry Ar chamber for polishing the sample and mounting it in a circulating He cryostat. Near normal incidence reflectivity was performed using a Fourier interferometer for the range 50–5000 cm^{-1}. A grating spectrometer was used for the near-infrared and visible range (1000–25000 cm^{-1}). As a reference mirror we evaporated a Ag film adjacent to the sample; a lever mechanism allowed the interchange of reference and sample at any temperature without breaking the vacuum.

In Fig. 1 the infrared reflectivity for $Ce_3Bi_4Pt_3$ is shown for selected temperatures. In the high temperature region (100 to 300 K) the reflectivity resembles that of a low conductivity metal, and does not show much temperature dependence. Below 100 K the reflectivity begins to show strong temperature dependence, and exhibits characteristics of gap development at low frequency. On the reflectivity we performed the Kramers-Kronig transformation to extract the infrared conductivity. To this end the reflectivity was extrapolated to lower frequencies us-

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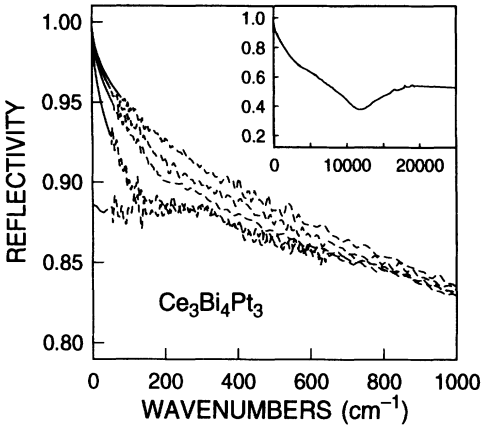

FIG. 1. Far-infrared reflectivity of $Ce_3Bi_4Pt_3$ at selected temperatures (from bottom to top: 25, 50, 75, 100, and 300 K). The thin lines show the low frequency terminations. The inset depicts the optical range of the reflectivity.

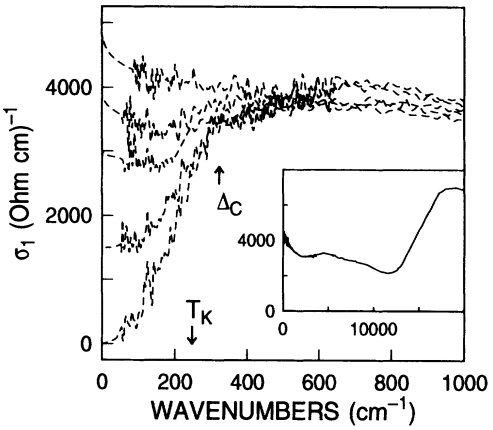

FIG. 2. Real part of the optical conductivity $\sigma_1(\omega)$ for different temperatures (from below: 25, 50, 75, 100, and 300 K). A gap is opening below 100 K; the prominent feature at Δ_c seems to be independent of temperature. The inset presents the optical region of σ_1.

ing the Hagen-Rubens relation. For the 25 K data we did not notice any free carrier contribution to the reflectivity down to 50 cm^{-1}; therefore, we assumed the reflectivity to be constant below 50 cm^{-1}. The high frequency reflectivity is adopted from $CePd_3$ which shows a similar interband transition pertaining to the d bands of the transition metal. The termination does not significantly affect the conductivity in the infrared range (60 to 15000 cm^{-1}) of relevance to this work.

In Fig. 2, the real part of the optical conductivity, $\sigma_1(\omega)$, is shown as a function of frequency for several temperatures. Between 100 and 300 K the conductivity is nearly constant as a function of frequency in the far infrared. Changes of the conductivity are modest above 100 K. Below this temperature, however, spectral weight begins to disappear from the low frequency region, signifying the development of a charge gap or pseudogap. Aspects of both the frequency and temperature dependence of these data are unusual, as discussed below.

Regarding the frequency dependence, one observes that while a significant amount of spectral weight (integrated conductivity) is depleted from the low frequency region at the lowest temperature, it is not apparent to where this conductivity has been displaced. It does not appear directly above the gap, as in a charge density wave system, nor is it shifted to low frequency, as in a superconductor. Since there is a sum rule on the integrated conductivity [7], the data instead suggest that the spectral weight displaced upon gap formation must be distributed over a wide range of energy, e.g., extending up to about 1 eV. This unusual behavior is reminiscent of recent results [8] on the d-band Kondo insulator analog, FeSi, suggesting that it is a characteristic aspect of Kondo insulator charge gap formation. But, on a microscopic scale, FeSi differs significantly from $Ce_3Bi_4Pt_3$. FeSi shows a temperature induced magnetism [9], whereas $Ce_3Bi_4Pt_3$ reveals a highly correlated singlet ground state [10]. The gap renormalization of FeSi above 300 K may be attributed to a "thermally activated Kondo lattice." In contrast, the ground state and charge localization of $Ce_3Bi_4Pt_3$ is governed by a correlation (Kondo) energy as thoroughly described below.

Several aspects of the temperature dependence of the infrared conductivity are also interesting and unusual. First we note that the conductivity is strongly depleted up to a characteristic frequency of about 300 cm^{-1} at low temperature, which corresponds to roughly 400 K. The data show, however, that the development of the gap primarily occurs only below the much lower temperature of 100 K. The discrepancy between these temperature scales indicates a severe departure from a picture of gap disappearance based on rigid bands and simple thermal activation of carriers. One observes also that the gap disappears by filling in from below, and that there is no discernible shift of the gap to lower energy.

To further explore the unusual nature of the temperature dependence of $\sigma_1(\omega,T)$, it is of interest to connect the gap formation with a phase transition. However, $Ce_3Bi_4Pt_3$ does not exhibit a well-defined phase transition, but rather a gradual magnetic-nonmagnetic transition of mixed valent, dense Kondo systems [10]. Inelastic neutron scattering measurements [11] have detected a spin gap at an energy of $\Delta_s \sim 160$ cm^{-1} opening at temperatures below 100 K. The simultaneous formation of spin and charge gap below 100 K provokes the proposition that the charge gap is triggered by the magnetic-nonmagnetic transition. The following quantitative calculations strongly support this idea.

On assuming the Curie law with a temperature dependent effective magnetic moment $\mu_{\rm eff}(T)$,

$$\chi = \mu_{\rm eff}^2(T)/3k_BT\,, \tag{1}$$

we can calculate $\mu_{\rm eff}(T)$ of the localized $4f$ states exploit-

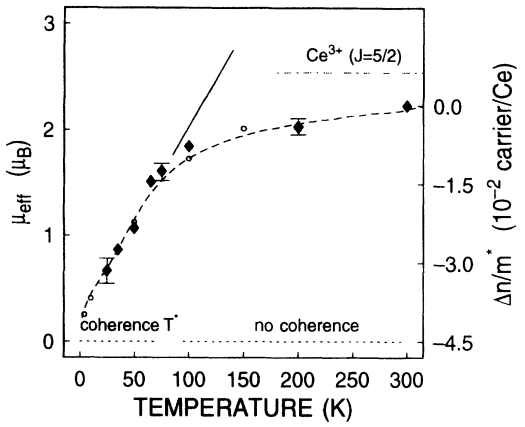

FIG. 3. Left axis: Effective magnetic moment μ_{eff} on the Ce ions of $Ce_3Bi_4Pt_3$ in units of the Bohr magneton μ_B. The dashed line gives the magnetic susceptibility data from Ref. [10]; the round points are from the neutron data of Ref. [11]. Also indicated is the Hund's rule value of the free ion Ce^{3+}. Right axis: The diamond-shaped points represent the localized charge carrier as a function of temperature as calculated by the optical sum rule [Eq. (2)]. The thin line indicates the linear temperature dependence below T^*.

ing the experimental [10] magnetic susceptibility χ (see Fig. 3). The optical sum rule provides a formula to calculate the number of localizing charge carrier upon the gap (singlet) formation,

$$\frac{\Delta n(T)}{m^*} \propto \int_0^{\Delta_c} \sigma_1(\omega,T)d\omega - \int_0^{\Delta_c} \sigma_1(\omega,300\text{ K})d\omega . \tag{2}$$

Proposing that the opening of the charge gap, i.e., the localization of charge carrier, is due to the involvement of the d electrons into the singlet formation, the number of disappearing charge carriers should scale with the amount of the quenched magnetic moment μ_{eff}. As depicted in Fig. 3 a convincing agreement has emerged [12]. In contrast to heavy fermions where the local $4f$ states delocalize below the coherence temperature T^*, the Kondo insulator shows a localization of charge carrier to the local $4f$ moments. In both cases the ground state is a singlet due to the Kondo coupling but a fundamental competition between localization of free carriers and delocalization of $4f$ electrons seems to be going on. The corroboration of the local Kondo interaction and localization in $Ce_3Bi_4Pt_3$ comes also from the relation of μ_{eff} to n^{free}. Normally the plot χT vs T gives the density of localized carriers n^{4f}, but in our case we have found a correlation of $\sqrt{\chi T}$ to the density n. We attribute it to the fact that *free* carriers, n^{free}, compensate the local magnetic moment $\mu_{\text{eff}} \propto \sqrt{\chi T}$, which itself enters the susceptibility as a square.

One can discuss $\sigma_1(\omega,T)$ in terms of comparison with and contrast to the behavior of ordinary metals and semiconductors. Normally a good metal would exhibit a peak in $\sigma_1(\omega)$ at $\omega=0$. The absence of such a peak for

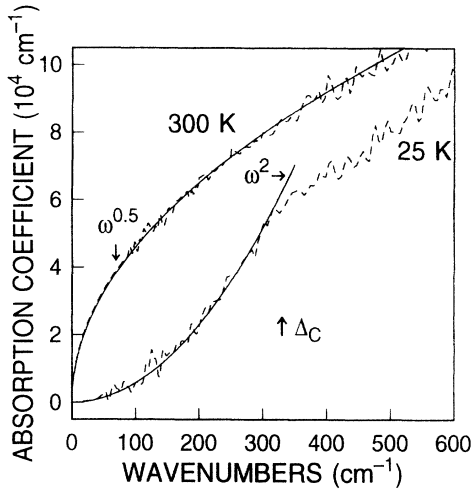

FIG. 4. Absorption coefficient at 300 K (upper curve) and 25 K (lower curve) as calculated from the optical constants. The thin lines are a square root (Drude-like) and a square fit, respectively.

$Ce_3Bi_4Pt_3$ above T^* can be interpreted in terms of the incoherent scattering of charge carriers within a dense Kondo impurity system, similar to an ordinary heavy fermion or mixed valent compound [13] above T^*. Differences emerge as the temperature is lowered below T^*. In HF's, a narrow resonance in $\sigma_1(\omega)$ evolves at $\omega \approx 0$ associated with the transport of the renormalized quasiparticles. Infrared measurements allow the direct observation of the crossover from the coherent region at low frequency, where the particles are highly renormalized and the scattering is weak, to the incoherent region at high ω, where the charge carriers are ordinary electrons which scatter strongly from the localized spins. In the Kondo insulator case, the spectral weight disappears linearly in temperatures below T^* (see thin line in Fig. 3). The remaining spectral weight within the gap is attended with σ_{dc} in the coherent state. It shows no Drude-like peak inside the gap at $\omega \approx 0$ as would be expected for a semiconductor. It might imply a charge transport below T^* which is of a collective nature rather than of a quasiparticle charge dynamics. In Fig. 4 we have plotted the absorption coefficient for 300 and 25 K. The thin lines give a square root fit (Drude-like) for the high temperature data and a square fit for the low temperature spectrum [14]. The 25 K data show a fundamental dependence which might be ascribed to a gapless, collective excitation spectrum of the charge system. Another interpretation is to relate the remaining spectral weight with extrinsic effects. However, the high amount of the spectral weight as well as the well-defined functional dependence ($\alpha \sim \omega^2$) seems unlikely for extrinsic impurities.

We address now the physical nature of Δ_c. Theoretical estimations [15] of hybridization gaps give a direct gap Δ^{direct} of the order of tenths of eV and an indirect gap $\Delta^{\text{indirect}} \sim T_K$ [1]. With $T_K = 320$ K and a gap tempera-

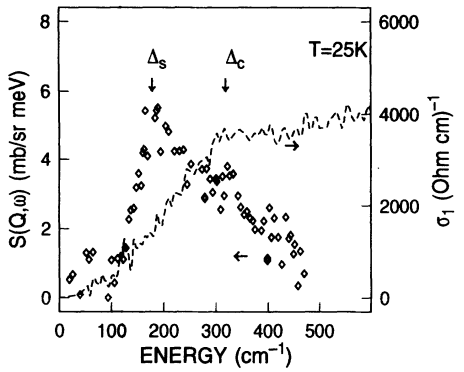

FIG. 5. Comparison of spin gap Δ_s (squares, left axis) from neutron measurements of Severing *et al.* [11] and charge gap Δ_c (dashed line, right axis) from optical conductivity σ_1.

ture $\Delta_c/k_B = 450$ K, arguing that the optical gap coinciding with the transport gap seems reasonable. On the other hand, the linear extrapolation of the steep part of $\sigma_1(\omega)$ to zero gives a value on the order of 100 K. Similar temperatures have been predicted for a temperature dependent transport gap [16].

Another possibility is to interpret Δ_c as the energy needed to excite a bound charge out from a *local* Kondo singlet ($\Delta_c \sim k_B T_K$). The temperature independence of Δ_c follows naturally from the fixed Kondo energy T_K. For the spin excitation of the singlet a local triplet [5] is predicted with an additional energy needed to delocalize the charge: $\Delta_s \leq \Delta_c$. In Fig. 5 we compare Δ_s from neutron data with the optical conductivity; the ratio $\Delta_c/\Delta_s \approx 1.8$ points to the strong coupling Kondo limit. The strong coupling regime also emerges from neutron spectroscopy because $Ce_3Bi_4Pt_3$ has revealed an order of magnitude higher spin gap, which increases [17] due to an enhanced Kondo coupling J, than has been reported [18] for the Kondo insulator CeNiSn.

The local formation of singlets with a following coherence might also be expressed with notions like excitons, Wigner crystallization, excitonic insulator, etc., as was shown successfully [19] for the Kondo insulator $TmSe_{1-x}Te_x$. A similar approach has been suggested [20] for the Kondo insulators SmB_6 and YbB_{12}.

In conclusion, we have presented explicitly the formation of a charge gap for the mixed valent Kondo insulator $Ce_3Bi_4Pt_3$ at low temperature. The gap formation is characterized by (i) a temperature independent gap with an energy Δ_c similar to the single ion Kondo energy $k_B T_K$ and (ii) a loss of spectral weight scaling with the quenching of the local $4f$ moments. The spectral weight within the gap grows linearly with temperature which may hint to an unconventional charge dynamics below Δ_c as, e.g., gapless collective charge modes.

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