Hybridization Gap in Heavy Fermion Compounds

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We report the results of optical studies of new heavy fermion compounds YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$. We show that these compounds, as well as several other heavy fermion materials with a nonmagnetic ground state, obey a universal scaling relationship between the quasiparticle effective mass $m^*$ and the magnitude of the energy gap $\Delta$ in the excitation spectrum. This result is in accord with the picture of hybridization of localized $f$-electron and free carrier states.

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Intermetallic compounds containing elements with $f$-electrons show a rich variety of effects, including a large enhancement of the quasiparticle effective mass [so-called “heavy fermion” (HF) behavior], a Kondo insulating state, and unconventional superconductivity [1–3]. These effects have been at the focus of condensed matter physics over the last two decades. The qualitative picture of both HF and the Kondo insulating state is based on the idea that ground state results from a competition between Kondo and RKKY interactions [4]. If the RKKY interaction dominates, various magnetic ground states can occur. However, if the Kondo interaction dominates, theory predicts that hybridization between localized $f$-electron and conducting carrier states should lead to the opening of a charge gap (or pseudogap) at the Fermi energy [5–9]. While this picture is not in dispute, the well-defined predictions of the hybridization scenario have so far escaped direct experimental verification. One of the key predictions is a simple scaling relationship between the magnitude of the direct energy gap $\Delta$ in the excitation spectrum and the enhancement of the effective mass of conducting carriers $m^*$ in the coherent regime [10]. Several HF materials, such as CeAl$_3$ [11], show no evidence of such a gap, whereas in prototypal compounds such as UPt$_3$ and URu$_2$Si$_2$ the gap is attributed to a magnetic ground state [12–15].

In this paper, we present results for two new HF materials that belong to the filled skutterudite family, YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$ [16–18]. In our view, YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$ are perfectly suited to test the hybridization gap paradigm because the characteristic temperature $T^*$ of the crossover to the coherent regime in the electronic transport in both compounds is as high as 50 K, permitting one to examine transport and optical properties at $T \ll T^*$. Based on magnetic susceptibility and electrical resistivity measurements [17,20], CeRu$_4$Sb$_{12}$ is speculated to order magnetically below 10 K, but in this work we studied only its paramagnetic phase.

Infrared spectroscopy is an ideal method to explore the heavy fermion ground state. This technique enables one to measure directly the magnitude of the gap in the density of states, while the analysis of the optical constants allows evaluation of the mass enhancement $m^*$ over the free electron mass $m_0$ or the carrier band mass $m_0$ [1,2]. The complex conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ was determined through Kramers-Kronig analysis from the reflectivity measurements carried out over the frequency range from 40 to 30 000 cm$^{-1}$. As a high energy extrapolation we used the data for the metallic skutterudite compound LaFe$_4$P$_{12}$, measured up to 12 eV [21]. As a low-frequency extension, we used the Hagen-Rubens formula and the dc resistivity values obtained for samples from the same batch.

Insight into the changes of the electronic structure and the carrier dynamics of YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$ associated with the crossover to coherent transport is provided by the spectra of the dissipative part of the optical conductivity $\sigma_1(\omega)$ (Figs. 1 and 2). At $T > T^*$, the frequency dependence of the conductivity can be described with a simple Drude formula: $\sigma_1(\omega) = \sigma_0/(1 + \omega^2\tau^2)$, where $\sigma_0$ is the dc conductivity and $\tau$ is the carrier relaxation time. Besides this free electron contribution, in both compounds we observe an interband feature at $\sim 10 000$ cm$^{-1}$, typical for a variety of skutterudites [21]. In addition, sharp peaks due to infrared active phonons were seen at 114 and 267 cm$^{-1}$ for YbFe$_4$Sb$_{12}$ and at 116, 221, and 248 cm$^{-1}$ for CeRu$_4$Sb$_{12}$. At $\omega < 90$ cm$^{-1}$ for YbFe$_4$Sb$_{12}$, and $\omega < 400$ cm$^{-1}$ for CeRu$_4$Sb$_{12}$, the low-$T$ conductivity is suppressed compared to the spectrum at $T \approx T^*$ and shows a gap-like threshold at $\Delta$ (Figs. 1 and 2). The location of the gap feature is the same at all $T < T^*$, whereas the amount of the spectral weight $N_{\text{eff}}(\omega) = \int_0^\omega d\omega' \sigma_1(\omega')$ in the intragap region is strongly $T$ dependent. The spectral weight from the intragap region is transferred primarily to higher energies and is completely recovered for $\omega < 0.2$ eV for YbFe$_4$Sb$_{12}$ and 0.6 eV for CeRu$_4$Sb$_{12}$. Interestingly, the energy scale involved in the redistribution of the spectral weight exceeds both $\Delta$ and $T^*$ by at least a factor of 10. Such a mismatch
has been previously detected in both metals and insulators with hybridization gaps in the density of states [22,23]. It is noteworthy that in the Yb-based compound, the gap affects only a small part of the Fermi surface, whereas the gap-free regions are responsible for a metallic background in the spectra of $\sigma_1(\omega)$ which is only weakly $T$ dependent. In the Ce-based compound, the background is very small, and therefore the gap is likely to affect most of the Fermi surface.

Another distinct feature of the optical conductivity of both YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$ in the coherent regime is a narrow resonance at $\omega = 0$. At $T > T^*$, we find good agreement between $\sigma_1(\omega)$ at the lowest measured frequency ($40 \text{ cm}^{-1}$) and the dc value. Below $T^*$, such an agreement is no longer observed and dc values systematically exceed $\sigma_1(\omega = 40 \text{ cm}^{-1})$. This behavior is consistent with the development of a narrow (Drude-like) mode in the response of our samples. Such narrow modes, with half-widths of only a few wave numbers, are also suggested by the frequency dependence of the conductivity in the extrapolated region (thin lines in Figs. 1 and 2). Similar and even narrower resonances are found in the low-temperature conductivity of all HF metals [1,2]. Usually, these features are attributed to the renormalization of the quasiparticle scattering rate $1/\tau(\omega)$ and the effective mass $m^*(\omega)$. The extended Drude formalism is the canonical way to quantify renormalization:

$$m^*(\omega) = \frac{\omega_p^2}{4\pi} \frac{\sigma_2(\omega)}{\sigma_1^2(\omega) + \sigma_3^2(\omega)} \frac{1}{\omega},$$

$$\frac{1}{\tau(\omega)} = \frac{\omega_p^2}{4\pi} \frac{\sigma_1(\omega)}{\sigma_1^2(\omega) + \sigma_3^2(\omega)},$$

where the plasma frequency $\omega_p^2 = 4\pi e^2 n/m_p$ is estimated from the integration of $\sigma_1(\omega)$ up to the frequency of the onset of interband absorption. The spectra of the effective mass and of the scattering rate calculated from Eqs. (1) and (2) are plotted in Fig. 3. At $T > T^*$, the spectra of $1/\tau(\omega)$ are nearly frequency independent. As temperature is lowered below $T^*$, the absolute value of $1/\tau(\omega)$ in the intragap region is suppressed and a threshold feature emerges in the spectrum. Notably, the “optical resistivity” $\rho_{opt} = 4\pi/\omega_p \tau^2(\omega \rightarrow 0)$, calculated from the data at the lowest measured frequency, reveals excellent agreement with the direct dc measurements. Suppression of the scattering rate is in accord with the strong enhancement of the effective mass in YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$. We observe $m^*/m_0 \sim 25$ and 80 for the Yb- and Ce-based compounds, respectively. These results are consistent with the specific heat measurements which yield $m^*/m_0 = 27$ and 90 [16]. The conclusion of electronic mass enhancement in YbFe$_4$Sb$_{12}$ and CeRu$_4$Sb$_{12}$ is robust and was tested using other approaches towards the analysis of the optical constants, i.e., “sum rule arguments” [24] and the ratio of zero crossings (Fig. 3) in the dielectric function $\varepsilon_1$ [1].

It is generally accepted that the essential physics of the HF metals and Kondo insulators is captured in the
gives excellent account of the behavior of YbFe
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FIG. 3. Frequency dependence of the quasiparticle effective
mass and scattering rate (top and middle panel, respectively)
and real part of the dielectric constant \( \varepsilon_1 \) (bottom panel) for both
YbFe

Sb

12

and CeRu

Sb

12
. The symbols on the left indicate the
effective masses obtained from specific heat measurements. The
arrows point to low-frequency plasmons, which are due to heavy
quasiparticles.

Anderson lattice Hamiltonian [1,6,9,25], describing a
band of conduction electrons which hybridizes with
localized \( f \)-electrons. Calculations show that for \( T < T^* \),
hybridization leads to a dispersion relation schematically
shown in the inset in Fig. 1 [5,7,8]. This band structure
gives excellent account of the behavior of YbFe
Sb
12
and CeRu
Sb
12
. The hole-like character of conducting carriers, as inferred from Hall effect measurements [20],
suggests that the Fermi level is in the lower band \( E_K \). At
the Fermi energy the band is flat, in agreement with the
renormalization of the effective mass and the scattering
rate at low \( T \) (Fig. 3). The existence of heavy quasiparticles is confirmed by the observation of a low
frequency plasmon in the spectra of the real part of the di-
electric constant \( \varepsilon_1(\omega) \), Fig. 3. The hybridization picture also implies a gap in the density of states, giving rise to a
second absorption channel in the conductivity spectra. A
low-lying gap is found in both compounds (Figs. 1 and 2).
Several numerical calculations of the optical conductivity exist [26,27] that are in qualitative agreement with our
data. To determine the gap value accurately, we have
performed a simple simulation of \( [\sigma_{coh}/\sigma_{incoh}] \), the ratio
of the optical conductivities in the coherent and incoherent states. The method follows closely the BCS calculation
[28], except that the coherence factors are of type I,
as opposed to type II, in conventional superconductors [29]. The low-temperature conductivity is obtained as
\( \sigma(\omega, 10 \, \text{K}) = [\sigma_{coh}/\sigma_{incoh}] \cdot \sigma(\omega, 50 \, \text{K}) \). In the insets
in Fig. 4, we show the final results of the simulation,
indicated by gray lines. The excellent agreement allows
very accurate determination of the magnitude of the gap.

From the band structure shown in the inset in Fig. 1, it
is clear that there must be a relation between quasi-particle
effective mass (\( m^* \sim d^2E/dk^2 \)) and the magnitude of the gap.
Indeed, calculations yield [5]

\[
\frac{m^*}{m_b} \approx \left( \frac{\Delta}{T^*} \right)^2.
\]

As can be seen from Fig. 4, this scaling is in good agree-
ment with our experimental data. The relation described by
Eq. (3) is general and should hold for all paramagnetic HF
materials. Indeed, we were able to identify similar scal-
ing in at least two other paramagnetic compounds: CeCu
[30] and CeCu
[31–33]. If the correlation were to hold
for another nonmagnetic HF compound CeAl
3
, then the magnitude of the gap \( \Delta \) can be expected to be as wide as
500 cm\(^{-1}\). However, in the latter system the gap has not
been observed [11], indicating that the quasiparticle con-
cept may break down at such high energies.

It is noteworthy that HF materials with a magnetic
ground state show systematic deviations from the scaling
implied by Eq. (3), falling both above (CePd
3
[34]) and
below (UPt
3
[14], URu
2
Si
2
[13], U
2
PtC
2
[2], and UCu
5
[12]) the universal line [35]. It is likely that magnetic
excitations further enhance the effective mass compared to the value derived from the hybridization mechanism. Alternatively, one can suggest that magnetic ordering may lead to the suppression of the energy gap. Both scenarios are consistent with the notion that in magnetic HF compounds the RKKY interaction overwhelms the Kondo coupling which is responsible for Eq. (3) [4]. One way to distinguish between the role of the two competing mechanisms in the formation of the heavy quasiparticle ground state is to explore the response of the HF compounds in which magnetic ordering at \( T = T_M \) emerges out of the coherent state at \( T < T^* \). At least two materials from Fig. 4 belong to this class: CeRu\(_4\)Sb\(_{12}\) (\( T_M = 7 \) K, \( T^* = 60 \) K) and CeCu\(_5\) (\( T_M = 4 \) K, \( T^* = 6 \) K); low-\( T \) experimental data are not available at the moment.

In conclusion, infrared experiments have revealed a scaling relationship between the magnitude of the effective mass \( m^* \) and the gap \( \Delta \) that is followed by most nonmagnetic HF systems. In contrast, HF compounds which order magnetically show distinct deviations from this pattern, signaling the possibility of more than one single route to the heavy fermion state [36].

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[10] Temperature dependence of the electrical resistivity in the HF materials usually shows two distinct regions separated by \( T^* \). At \( T > T^* \), the absolute value of \( \rho_{dc} \) is high and is only weakly dependent on \( T^* \). In several compounds \( d\rho_{dc}/dT \) is positive in this region. At \( T < T^* \), \( \rho_{dc} \) is strongly suppressed and in many HF systems varies quadratically with \( T \). This latter behavior is often referred to as the “coherent regime”. The coherence temperature can be determined (inset in Fig. 2) either as a point where the resistivity suddenly drops or as a peak in the first derivative of resistivity (infection point).
[18] Filled skutterudites are a family of compounds with the general structural formula \( M_4X_{12} \) (\( M = \) alkaline earth, rare earth, actinide; \( T = \) Fe, Ru, Os; \( X = \) P, As, Sb). The bonding within the \( T_4X_{12} \) “cage” is primarily covalent, similar to Zintl phases (Ref. [19]). However, previous studies have shown that physical and chemical properties of filled skutterudites are in large part determined by the filling atom \( M \), which has been shown to be loosely bonded to the cubic cages in the skutterudites’ structure. Heavy fermion behavior has been found only in those members of the family which have rare earths as their filling atoms.
[24] Quasiparticle mass enhancement \( m^* \) with respect to the band value \( m_b \) can be determined by taking a ratio of the spectral weight of the narrow Drude component to the total intraband spectral weight at \( T > T^* \), as discussed in detail in Ref. [1], Section IIE2.
[32] CeCu\(_5\) shows long-range magnetic order below \( T_N = 4 \) K [31], but the data shown in Fig. 4 were taken at \( T = 5 \) K.
[33] The spectra of CeCu\(_5\) [30] reveal a resonance at 5 meV previously attributed to the transitions across the hybridization gap. However, the spectral weight removed from a much broader region indicates that the gap could be as high as 200 meV.
[35] Note that UPd\(_2\)Al\(_3\) [12] is not very far from the line. This does not contradict the prediction of the hybridization theory. The theory merely predicts that nonmagnetic HF compounds should be on the universal line.