Observation of a new excitation in the mixed-valent state of YbInCu$_4$

S. R. Garner, Y.W. Rodriguez, and Z. Schlesinger

Department of Physics, University of California
Santa Cruz, California 95064

B. Bucher

Department of Physics, ITR
Oberseestrasse 10; 8640 Rapperswil Switzerland

Z. Fisk

Department of Physics and NHMFL, Florida State University
Tallahassee, Florida 32310

J. L. Sarrao

Los Alamos National Laboratory, Los Alamos
New Mexico, 84545
(September 19, 1999)

Infrared measurements are used to obtain conductivity as a function of temperature and frequency in YbInCu$_4$, which exhibits an isostructural transition to a mixed-valent state at $T_v \simeq 42 K$. In addition to a gradual loss of spectral weight with decreasing temperature extending up to 1.5 eV, sharp resonances appear in the mixed-valent state at 0 and 0.25 eV. These features may be key to understanding both YbInCu$_4$ and the nature of the mixed-valent Kondo state.

The presence of local moments in metallic systems is associated with a variety of interesting phenomena, including the Kondo effect, heavy-fermion physics and mixed-valence. In rare cases, an isostructural first-order transition at which a discontinuous change in valence and volume accompanies an abrupt disappearance of the local moment is observed. This moment disappearance can be described in terms of the formation of a mixed-valent Kondo-singlet state, in which the f-level moment is compensated due to a Kondo-like screening by conduction electrons. The transition to such a state provides an exceptional opportunity to probe a range of fundamental phenomena, including moment compensation, Kondo singlet formation, and mixed-valence.

The prototypical example of a volume/valence transition is the $\gamma - \alpha$ transition of Ce, in which a valence change from about 3 to 3.2 occurs in concert with a volume reduction of about 15% at $T_v \sim 200 K$. According to the Kondo-volume-collapse model, the reduced lattice constant in the low temperature phase is associated with an increase in hybridization between local moment and conduction electron states. This results in an enhanced Kondo energy, which drives the transition to a Kondo-singlet ground state. The energy reduction associated with the formation of the singlet ground state justifies the loss of entropy associated with the disappearance of the local-moment degrees-of-freedom. Technical difficulties associated with an intermediate phase make it very difficult to study the intrinsic physics of this transition in Ce.

YbInCu$_4$ also exhibits a transition to a mixed-valent Kondo-singlet ground state, which is isostructural to its high-temperature local moment state. In this compound the intrinsic physics is more accessible, as there is no intervening phase, and the transition occurs at $T_v \simeq 42 K$ at ambient pressure. At this transition the Yb valence decreases from $\sim$3 to $\sim$2.85, and the local moment vanishes. The volume change is of opposite sign to that of Ce— a difference consonant with the observation that Yb has one hole in the f-level, whereas Ce has only one f electron; however the magnitude of the volume change in YbInCu$_4$ ($\sim$0.5%) is too small to provide a basis for an increase in hybridization that would drive the transition. YbInCu$_4$ is thus a very interesting system, with a transition from a magnetic state to a mixed-valent ground state that is not well understood.

In this letter, we focus on changes in the infrared conductivity of YbInCu$_4$ associated with the transition into the mixed-valent state. The abrupt increase of the Kondo scale below $T_v$ may allow us to identify key features of the Kondo state, and thus shed light on fundamental phenomena of Anderson lattice systems. This work is complementary to previous optical work which addressed the relationship between spectral features and band-structure calculations.

At the transition two resonances appear. The first is a Drude-like peak centered at zero frequency which is qualitatively similar to low-temperature behavior seen in certain cerium compounds (c.f. ref. 21). The second is a resonance at $\sim 0.25$ eV, which is present only in the mixed-valent state. We discuss the interpretation of these resonances as intra- and inter-band excitations of coherent Kondo-state quasiparticles, respectively, for which the substantial increase of $T_K$ at $T_v$ is critical.
FIG. 1. The reflectivity and the real part of the conductivity at low frequency are shown for YbInCu$_4$ at T = 250 K (long dashes), 55 K (shorter dashes) and 20 K (solid). The low-frequency resonance at 20 K is associated with the intra-band excitations of a long-lived quasi-particle (Kondo) resonance. The inset shows the scattering rate (solid), $\tau^{-1}$, in cm$^{-1}$, and effective mass enhancement (dotted), $m^*$, vs frequency at 20 K.

Also of interest are spectral weight changes extending beyond 1 eV, which may have implications regarding the energy, time and length scales associated with moment compensation and Kondo singlet formation.

The samples used in these experiments are high-quality single crystals grown from an In-Cu flux. For these samples a sharp transition occurs at about 42 K in the absence of strain. At the transition the volume increases by about 0.5 % as the sample is cooled, and the susceptibility and resistivity drop abruptly by an order of magnitude. Thermal cycling tends to induce strain in the samples, which can broaden the transition and move it to higher temperature. Infrared and optical measurements are performed using a combination of Fourier transform and grating spectrometers to cover the range from 50 to 50,000 cm$^{-1}$. In these measurements we have gone to great efforts to measure in all ranges before going through the transition to avoid disorder effects influencing the infrared data significantly. The conductivity as a function of frequency is obtained from a Kramers-Kronig transform of the reflectivity data. For the purpose of performing this transform, the measured reflectivity is extended from 50,000 to 200,000 cm$^{-1}$ as a constant, and above that it is made to decrease like $1/\omega^2$. At low frequency a Hagen-Rubens termination is attached to the data. In the region of the actual data, the conductivity is insensitive to the details of these terminations.

Figure 1 shows the reflectivity and the real part of the conductivity in the low-frequency region in which a narrow Drude-like peak appears at low temperature. Above $T_v$ the conductivity is suppressed and only weakly dependent on frequency, due to the the strong scattering of the conduction electrons by the dense magnetic “impurities” (local moments). Below $T_v$ this scattering is suppressed, the d.c. resistivity decreases abruptly and a narrow resonance appears in $\sigma_1(\omega)$, as shown in figure 1. Extrapolated values of $\sigma_1(\omega)$ to $\omega = 0$ of about $\sigma_{d.c.} \approx 10,000 \Omega^{-1}cm^{-1}$ above $T_v$, and $\approx 40,000$ to 80,000 $\Omega^{-1}cm^{-1}$ below $T_v$ are consistent with d.c. resistivity measurements.

FIG. 2. The reflectivity and the real part of the conductivity at low frequency are shown for YbInCu$_4$ at T = 250 K (long dashes), 55 K (shorter dashes) and 20 K (solid). Gradual reduction of spectral weight with cooling occurs in the vicinity of 8,000 cm$^{-1}$ (1 eV). A well-defined resonance appears at 2,000 cm$^{-1}$ (1/4 eV) in the low temperature Kondo state.

One can view this low-temperature behavior in terms of a frequency dependent scattering rate and effective mass, as shown in figure 1b (inset). At 20 K the scattering rate rises rapidly between about 25 and 200 cm$^{-1}$ exhibiting a change in slope in the vicinity of 200 cm$^{-1}$, which is comparable to the Kondo scale ($\approx 280$ cm$^{-1}$) of the low-T state of YbInCu$_4$. The effective mass enhancement increases with decreasing $\omega$ over the same range and approaches an asymptotic value of about $m^* \approx 10$ at low frequency. These low temperature quantities
exhibit a crossover from a low energy regime where the compensated moments are ineffective scatterers, to a high energy regime in which conduction electrons are strongly scattered by uncompensated moments. This reflects the evolution of the dynamics from that of dressed, heavy quasiparticles to that of the undressed band-like carriers, which is fundamental to systems with a local moment resonance not too far from the chemical potential.

Figure 2 shows reflectivity and conductivity to higher frequency (12,000 cm$^{-1}$). These data show the persistence of significant temperature dependence to very high frequency (compared to $T$ or $T_K$) in YbInCu$_4$. For example, between about 5,000 to 12,000 cm$^{-1}$ $\sigma_1(\omega)$ decreases substantially as $T$ is reduced both above and below $T_v$. In addition, a prominent resonance appears in the mixed-valent (low-T) state near 2,000 cm$^{-1}$. The spectral sharpness and abrupt appearance of this feature at $\omega \approx 2,000$ cm$^{-1}$ ($\sim 1/4eV$) as a function of temperature are striking.

Figure 3 shows spectral weight, which is the indefinite integral of $\sigma_1(\omega)$, $n(\omega) = \frac{\sigma_1(\omega)}{\omega} \int_0^\omega \sigma_1(\omega') d\omega'$, as a function of frequency. In this figure (and figure 2) we see that there is a net loss of spectral weight as the temperature is lowered from 250 K to 55 K. The loss amounts to about 10% of the strength of the broad mode centered around 9,000 cm$^{-1}$, and corresponds to $\approx 1$ carrier/Yb atom with the reasonable assumption of a band mass of 3 (times the free-electron mass). Since spectral weight is ultimately conserved (if one integrates to high enough frequency), these data imply that it must be displaced to still higher frequency (above 16,000 cm$^{-1}$ $\approx 2$ eV) as $T$ is reduced from 250 to 55 K. Recent theoretical work has explored possible origins of such high energy spectral weight shifts (involving energies vastly larger than $K_BT$ and $K_BT_K$) in strongly correlated systems.

The coalescence of the 20 and 55 K curves at the high frequency end of figure 3 indicates that the increase in spectral weight associated with the appearance below $T_v$ of the resonance at $\sim 2000$ cm$^{-1}$ is balanced by a general reduction of $\sigma_1(\omega)$ up to $\sim 12,000$ cm$^{-1}$. The displaced spectral weight corresponds to about 1.5 carriers/Yb.

Although the spectral weight of the very narrow low temperature resonance at $\omega = 0$ (figure 1) is quite small, it is significant to the correspondence between the infrared data and Hall effect data for YbInCu$_4$. Hall effect, when corrected for skew scattering, reflects an increase from about 0.7 carriers/Yb above $T_v$ to a much higher value ($\sim 4$ carriers/Yb) below the transition. Above $T_v$, the low frequency rise of the conductivity (figure 2) can be fit with a broad ($\sim 700$ cm$^{-1}$) resonance with a strength which corresponds to about one carrier per Yb, which is roughly consistent with recent high-temperature Hall data. Below $T_v$, a much sharper ($\sim 25$ cm$^{-1}$) additional peak appears in $\sigma_1(\omega)$ at $\omega \sim 0$, as seen in figure 1b. With the inclusion of the frequency dependent, low-temperature mass enhancement of $m^*\approx 10$ (figure 1b, inset), this narrow peak represents an additional 2.5 carriers/Yb, consistent with the substantial increase in carrier density inferred from the low T Hall effect data.

Both the starting Hamiltonian and the mechanism that drives the transition to the mixed-valent state remain areas of active research for YbInCu$_4$. With regard to the mechanism, it has been argued that the lattice expansion is too small to explain the large change in Kondo temperature (from $\sim 25$ K to 400 K) at the transition. The Falikov-Kimball model is capable of producing a quasi Hubbard-like first-order transition, and may be relevant to high-temperature properties of YbInCu$_4$, however it ignores hybridization, which is certainly important in the low-T state. In the mixed-valent state, where the Kondo scale is large, the dynamics of the Periodic Anderson Model (PAM) are expected to be relevant. Within the PAM context, the 1/4 eV excitation can be associated with a quasiparticle interband transition involving Kondo resonance states near $E_F$. The abrupt change of $T_K$ at the transition and the abrupt appearance of the resonance are consistent with this interpretation. The study of YbInCu$_4$, with its first-order transition at which $T_K$ increases by an order of magnitude, thus appears to allow the first clear identification of this fundamental excitation.

The energy scale for this interband excitation involving the dynamically generated quasi-particle states at $E_f$ (the Kondo resonance) is expected to be $\sim \sqrt{T_K}$, which is reasonable. One can estimate the hybridization broadening, $\Gamma$, using its relationship to $\sqrt{\Gamma}$, to be $\Gamma \approx 0.25$ eV. Further,
one can use $\Gamma$ in NCA formulae involving $n_f(T)$ along with $L_{III}$ edge measurements of valence to infer that the $f$-level is about 0.5 eV away from the chemical potential. These values are quite reasonable for this mixed-valent system.

The observation that the growth of the resonance at $\simeq 1/4$ eV comes from a redistribution of spectral weight from essentially the entire range below 1.5 eV (comparable to the bandwidth) may have implications for questions related to exhaustion and the EDOS scales relevant to screening in Kondo lattice systems. Does it suggest that conduction electrons further than $K_B T_K$ from the chemical potential are significantly involved in screening in the Kondo lattice? Further work can be expected to address such questions. It is also intriguing to note that an excitation of similar frequency is present in YbB$_6$ [41] for which $T_K \simeq 300$ K, and that related features may also be present in spectra from mixed-valent Ce compounds [28].

In summary, YbInCu$_4$ is of interest because of the rarity of valence transitions, a lack of understanding of their underlying mechanism, and due to the opportunity to observe the effect of dramatic changes of $T/T_K$ on physical properties. We observe high-energy spectral weight changes, which may be relevant to the mechanism, and the abrupt appearance of a sharp excitation near 1/4 eV, present only in the high $T_K/T$ state, which is interpreted as the Kondo-charge-particle interband excitation.

Acknowledgements: The authors acknowledge valuable conversations with J. W. Allen, D. L. Cox, P. Coleman, J. K. Freericks, D. H. Lee and A. P. Young, and technical assistance from Todd Lorey, Sonya Hoobler, Jason Hancock and Petar Kostic. Work at UCSC is supported by the NSF through grant # DMR-97-05442. Work at Los Alamos is performed under the auspice of the U.S. Dept. of Energy. NHMFL is supported by the NSF and the state of Florida. ZF and JLS also acknowledge partial support from the NSF under grant # DMR-9501529.

1. A.C. Hewson. The Kondo Problem to Heavy Fermions. Cambridge University Press, (1993).
2. J.M. Lawrence, P.S. Riseborough, and R.D. Parks. Rep. Prog. Phys., 44:1, (1981).
3. J.W. Allen and I.Z. Liu. Phys. Rev. B, 46:5047, (1992).
4. I. Felner and I. Nowik. Phys. Rev. B, 33:617, (1986).
5. I. Felner et al. Phys. Rev. B, 35:6956, (1987).
6. J.L. Sarrao. Physica B, 259:261:128, (1999).
7. B. Kindler, R. Graf, F. Ritter, W. Assmus, and B. Luthi. Phys. Rev. B, 50:704, (1994).
8. J.M. Lawrence, G.H. Kwei, J.L. Sarrao, Z. Fisk, D. Mandrus, and J.D. Thompson. Phys. Rev. B, 54:6011, (1996).
9. J.L. Sarrao, C.D. Immer, C.L. Benton, Z. Fisk, J.M. Lawrence, D. Mandrus, and J.D. Thompson. Phys. Rev. B, 54:12207, (1996).
10. C.D. Immer, J.L. Sarrao, Z. Fisk, A. Lacerda, C. Mielke, and J.D. Thompson. Phys. Rev. B, 56:71, (1997).
11. J.M. Lawrence, S.M. Shapiro, J.L. Sarrao, and Z. Fisk. Phys. Rev. B, 55:14467, (1997).
12. A.L. Cornelius, J.M. Lawrence, J.L. Sarrao, Z. Fisk, M.F. Hundley, G.H. Kwei, J.D. Thompson, Both C.H., and Bridges F. Phys. Rev. B, 56:7993, (1997).
13. E. Figueroa, J.M. Lawrence, J.L. Sarrao, Z. Fisk, M.F. Hundley, and J.D. Thompson. Solid State Commun., 106:347, (1998).
14. J.L. Sarrao, A.P. Ramirez, T.W. Darling, Freibert, A. Migliori, C.D. Immer, Z. Fisk, and Y. Uwatoko. Phys. Rev. B, 58:409, (1998).
15. F. Marabelli and E. Bauer. J. Appl. Phys., 73:5418, (1993).
16. M. Galli, F. Marabelli, and E. Bauer. Physica B, 206-207:355, (1995).
17. A. Continenza, P. Monachesi, M. Galli, F. Marabelli, and E. Bauer. J. Appl. Phys., 79:6423, (1996).
18. A. Continenza, P. Monachesi, M. Galli, F. Marabelli, and E. Bauer. Physica Scripta, T66:177, (1996).
19. J.W. Allen and J.C. Mikkelsen. Phys. Rev. B, 15:2952, (1977).
20. F.E. Pinkerton, A.J. Sievers, J.W. Wilkins, M.B. Maple, and B.C. Sales. Phys. Rev. Lett., 47:1018, (1981).
21. B.C. Webb, A.J. Sievers, and T. Mihalisin. Phys. Rev. Lett., 57:1951, (1986).
22. A.C. Wooten. Optical Properties of Solids. Academic Press, (1972).
23. M.J. Rozenberg, G. Kotliar, and H. Kajueter. Phys. Rev. B, 54:8452, (1996).
24. V. Zlatic and J.K. Freericks. preprint, xx, (1999).
25. J.K. Freericks and V. Zlatic. Phys. Rev. B, 58:322, (1998).
26. Peirs Coleman. Phys. Rev. Lett., 59:1026, (1987).
27. A.N. Tahvildar-Zadeh, M. Jarrell, Th. Pruschke, and J.K. Freericks. Phys. Rev. B, 6x:to be published, (1999).
28. N.E. Bickers, D.L. Cox, and J.W. Wilkins. Phys. Rev. B, 36:2036, (1987).
29. J.L. Sarrao et al. Phys. Rev. B, 59:6855, (1999).
30. A.J. Millis. Physica B, 259-261:259, (1999).
31. H. Okamura, S. Kimura, H. Shinozaki, T. Nanba, F. Iga, N. Shimizu, and T. Takabatake. Phys. Rev. B, 58:7496, (1998).
32. B. Bucher, Z. Schlesinger, D. Mandrus, Z. Fisk, J.L. Sarrao, J.F. DiTusa, C.S. Oglesby, G. Aeppli, and E. Bucher. Phys. Rev. B, 53:2948, (1996).