Title
High-Resolution, Low-Temperature, Photoemission Studies of Heavy-Fermion Systems: UBe13 and UPt3

Journal
Physical Review Letters, 53(21)

ISSN
0031-9007

Authors
Arko, AJ
Olson, CG
Wieliczka, DM
et al.

Publication Date
1984-11-19

DOI
10.1103/physrevlett.53.2050

High-Resolution, Low-Temperature, Photoemission Studies of Heavy-Fermion Systems: UBe_{13} and UPt_3

A. J. Arko
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

and

C. G. Olson and D. M. Wieliczka
Ames Laboratory–U. S. Department of Energy, Iowa State University, Ames, Iowa 50011

and

Z. Fisk and J. L. Smith
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 6 August 1984)

High-resolution (0.13 eV) photoemission measurements performed at low temperatures (≈ 20 K) show that a sharp feature (measured width $\simeq 0.15$ eV at full width at half maximum) exists at the Fermi edge in the electronic structures of UBe_{13} and UPt_3. In UBe_{13} the feature shows some temperature dependence.

PACS numbers: 79.60.Cn, 71.25.Pi

The unusual properties of the recently discovered heavy-fermion superconductors[1,2] are presently the subject of considerable investigation,[3] primarily because of the prospect of *p*-wave superconductivity. The similarity to the *p*-wave superfluid ^{3}He has been pointed out by a number of investigators.[4–6] While the theoretical models are not yet on firm ground it appears that a common feature of all models[5–8] is the existence of a very narrow band at E_F which is primarily *f*-like in nature and only very slightly hybridized with the *s*-*p* bands of the neighboring atoms. It is this narrow band at E_F which yields the astonishingly large specific-heat γ values[1,2,9–11] and effective masses (two or three orders of magnitude larger than values of typical metals), which are characteristic of heavy-fermion systems. One of the current models[6] states that the magnetism in this nearly localized state is suppressed by the Kondo effect so that the materials can be described as "Kondo lattices"[8,12] characterized by a Fermi liquid of extremely heavy electrons.

The coexistence of superconductivity and spin fluctuations has been demonstrated recently[10,11] in UPt_3. The spin-fluctuation temperature T^* can be deduced experimentally as the degeneracy temperature in the specific-heat vs temperature curve. For both UBe_{13} and UPt_3 it is found[2,10] that $T^* \approx 10$ K. Since in heavy-fermion compounds $T^* \approx T_F$, i.e., the bandwidth of the narrow feature,[5] this translates into a bandwidth of order 0.001 eV. The first photoemission study of heavy-fermion systems[13] was undertaken in the hope of observing this narrow band. None was observed. Indeed the resonant photoemission data on UBe_{13} pointed to a 5-eV-wide $5f$ band, which is anomalously large for actinide systems. A subsequent study[14] pointed out that at least part of the problem in the initial work on UBe_{13} was rapid oxygen diffusion from the bulk onto the surface. In addition to suppressing any narrow features this also led to an erroneous interpretation of the oxygen peak at -7 eV as being due to Be $2p$ bands. Parks *et al.*[14] pointed out that the large width of the $5f$ band is probably due to strong *p*-*f* hybridization and not the lack of hybridization as initially assumed.[13] However, they too failed to see any narrow features at E_F because of insufficient resolution.

The failure of photoemission measurements on heavy-fermion systems thus far to observe sharp peaks at E_F has been disappointing. A narrow band surely must exist at E_F to yield the extremely large γ values. It is difficult to believe that a 5-eV-wide band as measured in UBe_{13}[13,14] condenses into a state only 10^{-3} eV wide. A reasonable assumption must be that in these systems we have a narrow, nearly pure, $5f$ subband at E_F, while the remaining $5f$ electrons strongly hybridize with the ligand p or d electrons below E_F. Recent results by Wuilloud *et al.*[15] point out that most of the high density at E_F is on uranium sites only, consistent with this point of view.

In order for photoemission measurements to make a critical contribution to the heavy-fermion investigation, it would be necessary to obtain resolutions on the order of the bandwidth of the sharp feature and work at $T < T^*$. Clearly, this is not possible with present day technology if the condensed bandwidth is indeed 10^{-13} eV. On the other hand the temperature dependence of the Kondo effect often goes as $\log T$ so that we would expect some remnant of this state at temperatures presently obtainable (≈ 20 K) in photoemission experiments. At the very least we can look for the narrow band at E_F which possibly condenses into this state,[8] assuming of course that such condensation actually occurs and the Kondo model applies to heavy-fermion systems.

In this paper we report measurements on UBe_{13} and UPt_3 at temperatures down to 20 K and with a resolution of 0.13 eV. Low temperatures were used in the hope that some remnant of a temperature-dependent narrow resonance could be seen at 20 K. The low temperature had the added benefit in UBe_{13} in that it prevented oxygen diffusion from the bulk, thus enabling us to maintain a contamination-free surface for several hours. A sharp feature having a measured width ≈ 0.15 eV was observed in both materials at E_F.

The measurements were done at the Tantalus storage ring of the Synchrotron Radiation Center in Stoughton, Wisconsin. Polycrystalline samples of UPt_3 and UBe_{13} were mounted onto the cold head of a closed-cycle helium refrigerator. Temperatures were monitored via a AuFe-Chromel thermocouple embedded in the copper holder in close proximity to the sample. The typical operating vacuum was $\approx 5\times10^{-11}$ Torr. Samples were fractured at temperature *in situ.* It was found that any change in temperature (up or down) resulted in some surface contamination, as evidence by a deterioration of the spectrum quality. The analyzer was a double-pass cylindrical-mirror analyzer operated at 0.095-eV resolution (6-eV pass energy). The resolution of the monochromator ranged from 0.05 eV at 40-eV photon energy to 0.3 eV at 100-eV photon energy. The sharp feature thus could not be properly studied at resonance, but rather only at 40 eV (i.e., at maximum resolution). Fortunately the $5f$ cross section at 40 eV is sufficient to yield all necessary information.

In Fig. 1, we show data on both UBe_{13} and UPt_3 obtained at 40-eV photon energy. The long (10-eV) scans are at 0.3-eV resolution (15-eV pass energy) and their primary aim is to demonstrate the oxygen-free surface as evidenced by a lack of structure in the 6–7-eV binding-energy region. Additional broad features are observed in the long-scan spectra of both compounds which were not reported in earlier investigations.[13,14] As a result of space

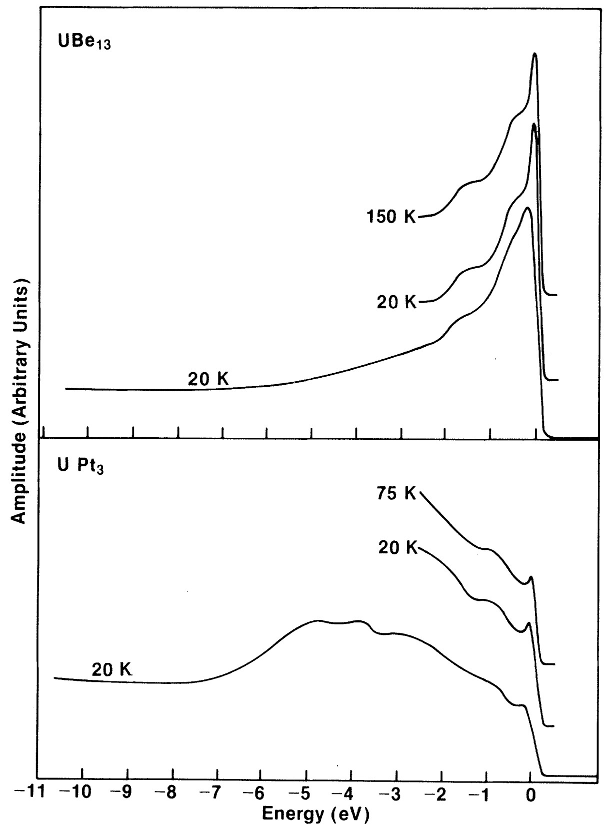

FIG. 1. Energy distribution curves (EDC's) for UBe_{13} and UPt_3 at 40-eV photon energy. The long scans are at 20 K and 0.3-eV resolution. The short scans are at 0.13-eV resolution at the temperature indicated.

limitations we will discuss the broad features in a later publication. Resonance work, however, shows that in UBe_{13} these broad features are f-like, but probably Pt derived in UPt_3.

We wish to focus attention on the short (3 eV wide) scans in Fig. 1, taken at ≈ 0.13-eV resolution. In both UBe_{13} and UPt_3 a sharp peak is observed precisely at the Fermi energy, with a measured half-width of 0.15 eV. At 0.3-eV resolution this peak is drastically diminished so that failure to observe it previously[13–15] is understandable. Moreover, even a slight oxygen contamination substantially distorts all valence-band features. Thus it is nearly impossible to observe this sharp peak at room temperature.

This sharp feature at E_F almost certainly must be associated with the band resulting in the heavy-mass electrons. Since the measured peak is only slightly broader than our resolution we can in principle determine its true width. We have done a modeling study using a Lorentzian peak centered at E_F, multiplied by a temperature-gradient Fermi function and broadened by a Gaussian instrument function. A best comparison to the data was obtained with a full width at half maximum of 0.15 eV for the Lorentzian. We associate the filled part of this Lorentzian (0.075 eV) with the true width of the narrow feature, which of course still makes it nearly 2 orders of magnitude broader than the 10^{-3}-eV-wide band inferred from specific-heat data. One possible explanation for the large width is that at 20 K the "Kondo lattice" no longer exists and we are observing only the "broad" band which condenses into the Kondo state and which is stabilized by slight hybridization with the Be-derived *s-p* bands. Another possibility, however, is that of hole-lifetime broadening of a much narrower peak. Such broadening is of course expected to be small at E_F, but certainly is not negligible. Such a feature would show a temperature dependence for the amplitude, but not the width of the photoemission peak. Indeed the *amplitude* of the sharp feature in UBe_{13} in Fig. 1 decreases by 10%–15% between 20 and 150 K. While this is less than anticipated from a Kondo-type system, modeling studies show that this decrease is considerably larger than one would expect from thermal broadening of a 0.075-eV-wide Lorentzian-shaped peak ($\approx 3\%$). The *width* of the narrow feature, however, does *not* change up to 150 K and neither do the remaining features in UBe_{13}. This would seem to rule in favor of the lifetime-broadening picture with the assumption that no experimental artifact contributes to the amplitude of this sensitive feature. Possible strains induced during sample fracture may also broaden the spectra. Obviously these data need to be taken with better than 0.075-eV resolution and $T \approx 10$ K.

The amount of hybridization can be inferred from the constant-initial-state (CIS) scans of Fig. 2. Curve I is for UPt_3 while curves II and III are for UBe_{13}. For curves I and II in Fig. 2 the initial state, E_i at which the CIS scan is obtained, is at the point of the maximum in the EDC near E_F. Curve III is taken at $E_i = -5.0$ eV where the Be *s-p* bands are prominent. We note that at E_F we obtain the standard two-peaked structure in the CIS spectra (features *B* and *D* in Fig. 2) characteristic of 5*f*-electron emission at resonance. In addition, there are features *A* and *C* for both UPt_3 and UBe_{13}, and feature *E* for UBe_{13} only. Features *A* and *C* are most likely associated with uranium 6*d* resonant emission on the basis of the observation that in the rare-earth elements it is found[16] that valence electrons of different orbital character have cross-section maxima at different energies. Moreover, Iwan, Koch, and Himpsel[17] reported the existence

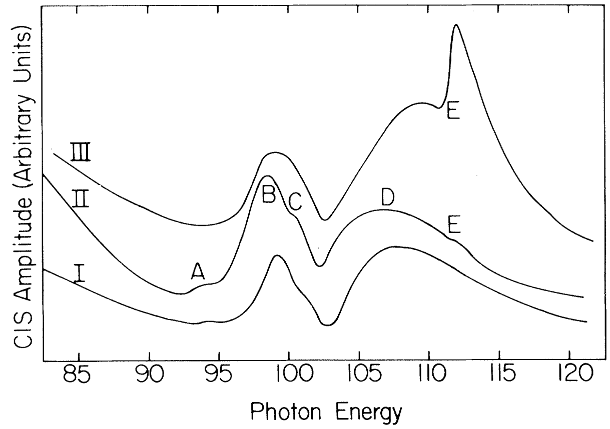

FIg. 2. Constant-initial-state scans at 20 K: curve I, UPt_3, E_i is the maximum in the EDC at E_F; curve II, UBe_{13}, E_i is the maximum in the EDC at E_F; curve III, UBe_{13}, $E_i = -0.5$ eV. The 5*f* resonances in curve III are due to secondary electrons.

of a "satellite" in uranium metal which resonates at the antiresonance of the uranium 5*f*'s (i.e., ≈ 94 eV). The energy position of the satellite matches the position of the 6*d* states in uranium.[18] A difference spectrum between an EDC at 94-eV photon energy (maximum in 6*d* emission) and an EDC at 92-eV photon energy in UBe_{13} shows that the 6*d* intensity is peaked at E_F and is already of zero intensity at -1.5 eV. Clearly, uranium 6*d* character exists at E_F in UBe_{13}, and to a lesser extent in UPt_3. Band-structure calculations for UBe_{13} bear out this observation.[19] EDC's were not measured at the *d* resonance in UPt_3. A substantial amount of Pt-derived *d* density exists at E_F, however, on the basis of the 92-eV scans.

Perhaps a more interesting peak in Fig. 2 is feature *E* at 112-eV photon energy in UBe_{13}, which is just barely discernible near E_F but is quite prominent in the -5-eV scan. This is the beryllium 1*s*-2*p* resonance which enhances the Be-derived part of the spectrum. Clearly the amount of Be-derived density at E_F is very small, of the order of 1% of the density at -5 eV. This is consistent with the results of Wuilloud *et al.*[15] who find that most of the high density is confined to the U atom with only weak hybridization with the *s-p* bands from Be. Thus, it appears likely from our data that the sharp peak at E_F is primarily *f*-like, with the *f* band stabilized by a very small amount ($\approx 1\%$) of *p* admixing from Be atoms. Such weak hybridization has been found sufficient to stabilize the *f* band[20] in $CeSn_3$ where the Ce atoms are also too far apart for direct *f-f* overlap. The metallic behavior of UBe_{13} at high temperatuers probably comes from the broader $6d$ band at E_F.

While the narrow band at E_F is almost purely f-like, the remaining f electrons are apparently strongly hybridized with the s-p bands of Be and most likely do not condense into the Fermi liquid. Indeed both f- and p-derived features have substantial amplitude at -2 eV, which indicates maximum hybridization at this energy.

In summary, we have observed a narrow feature at the Fermi energy in the photoemission spectra of UBe_{13} and UPt_3 which we believe can be associated with the narrow f band responsible for the heavy-fermion superconductivity. This feature is only slightly hybridized with the Be s-p bands in UBe_{13} and it shows a temperature dependence larger than expected from thermal broadening. A uranium-derived $6d$ band likewise exists at E_F in UBe_{13} and in UPt_3.

We wish to thank G. W. Crabtree, D. D. Koelling, and B. W. Veal for helpful discussions. We also wish to thank the staff at the Synchrotron Radiation Center for their assistance. The Synchrotron Radiation Center is operated through National Science Foundation Grant No. DMR-83-13523. This work was also supported by the U. S. Department of Energy. Ames Laboratory is operated for the U. S. Department of Energy by the Iowa State University under Contract No. W-7405-ENG-82.

[1]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[2]H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).

[3]For a review, see G. R. Stewart, Rev. Mod. Phys. (to be published).

[4]H. R. Ott, H. Rudigier, T. M. Rice, K. Ueda, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. **21**, 1917 (1984).

[5]O. T. Valls and Z. Tesanović, Phys. Rev. Lett. **53**, 1497 (1984).

[6]P. W. Anderson, Phys. Rev. B **30**, 1549 (1984).

[7]H. Razafimandiby, P. Fulde, and J. Keller, to be published.

[8]M. Tachiki and S. Maekawa, Phys. Rev. B **29**, 2497 (1984).

[9]K. Andres, J. E. Graebner, and H. R. Ott, Phys. Rev. Lett. **35**, 1779 (1975).

[10]G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).

[11]Z. Fisk, G. R. Stewart, J. O. Willis, H. R. Ott, and F. Hulliger, Phys. Rev. B (to be published).

[12]A. Yoshimori and H. Kasai, J. Magn. Magn. Mater. **31–34**, 475 (1983).

[13]G. Landgren, Y. Jugnet, J. F. Morar, A. J. Arko, Z. Fisk, J. L. Smith, H. R. Ott, and B. Reihl, Phys. Rev. B **29**, 493 (1984).

[14]R. D. Parks, M. L. denBoer, S. Raaen, J. L. Smith, and G. P. Williams, Phys. Rev. B **30**, 1580 (1984).

[15]E. Wuilloud, Y. Baer, H. R. Ott, Z. Fisk, and J. L. Smith, Phys. Rev. B **29**, 5228 (1984).

[16]A. Zangwill and Paul Soven, Phys. Rev. Lett. **45**, 204 (1980).

[17]M. Iwan, E. E. Koch, and F.-J. Himpsel, Phys. Rev. B **24**, 613 (1981).

[18]B. Reihl, private communication.

[19]D. D. Koelling, private communication.

[20]D. D. Koelling, Solid State Commun. **43**, 247 (1982).