RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 3 1 AUGUST 1984

Resonant photoemission studies of the heavy-fermion superconductors $CeCu_2Si_2$, UBe_{13}, and UPt_3

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(Received 25 April 1984)

Valence-band photoemission studies, using synchrotron light and employing Fano resonances to enhance f-derived features, were made of the three known heavy-fermion superconductors: $CeCu_2Si_2$, UBe_{13}, and UPt_3. The results for $CeCu_2Si_2$ and UBe_{13} contrast markedly with those reported earlier, reflecting closer control of surface contamination in the present study. We infer from the present study and other considerations that in all three systems there is significant hybridization between the f electrons and the nearest-neighbor ligands, which may be essential to the phenomenon of heavy-fermion superconductivity.

The remarkable phenomenon of heavy-fermion superconductivity has been reported for three systems: $CeCu_2Si_2$,[1] UBe_{13},[2] and UPt_3.[3] In all three systems the electrons responsible for the superconductivity have effective masses $m^* \gtrsim 200 m_e$. It is assumed that the f electrons play an essential role, and speculations have been made[3,4] about triplet superconductivity (as in ^3He). However, the microscopic origin of heavy-fermion superconductivity remains at this time a completely open question. The motivation for the valence photoemission experiments reported herein was to provide information about the electronic structure, which might contribute to the solution of this problem.

The experiments were performed on Station U14 of the 750-MeV VUV Ring at the National Synchrotron Light Source (NSLS). A plane grating monochromator[5] together with a double-pass cylindrical mirror analyzer gave a combined (electrons plus photons) resolution of 0.25–0.3 eV at $h\nu = 30$ eV, 0.4–0.5 eV at 100 eV, and 0.5–0.6 eV at 120 eV. Polycrystalline, single-phase samples of $CeCu_2Si_2$, UBe_{13}, and UPt_3 were prepared by arc-melting the constituents in an inert atmosphere. Clean sample surfaces were prepared by fracturing the samples *in situ* in the measuring chamber, where the pressure was $\sim 1 \times 10^{-10}$ Torr.

In order to isolate the $4f$- or $5f$-derived features from other features in the valence band, Fano resonances were employed, as in previous studies (see, e.g., Refs. 6–9, and references cited therein), at the $4d$ threshold in $CeCu_2Si_2$ and the $5d$ threshold in the U compounds. The corresponding excitations, responsible for enhanced f emission, are

$$4d^{10}4f^n \rightarrow 4d^9 4f^{n+1} \rightarrow 4d^{10}4f^{n-1} + e_{4f}$$

and

$$5d^{10}5f^n \rightarrow 5d^9 5f^{n+1} \rightarrow 5d^{10}5f^{n-1} + e_{5f} \ .$$

These resonances are exhibited for the three systems in constant-initial-state (CIS) spectra in Fig. 1, taken at binding energies of 2 eV for $CeCu_2Si_2$ and 1 eV for the U com-

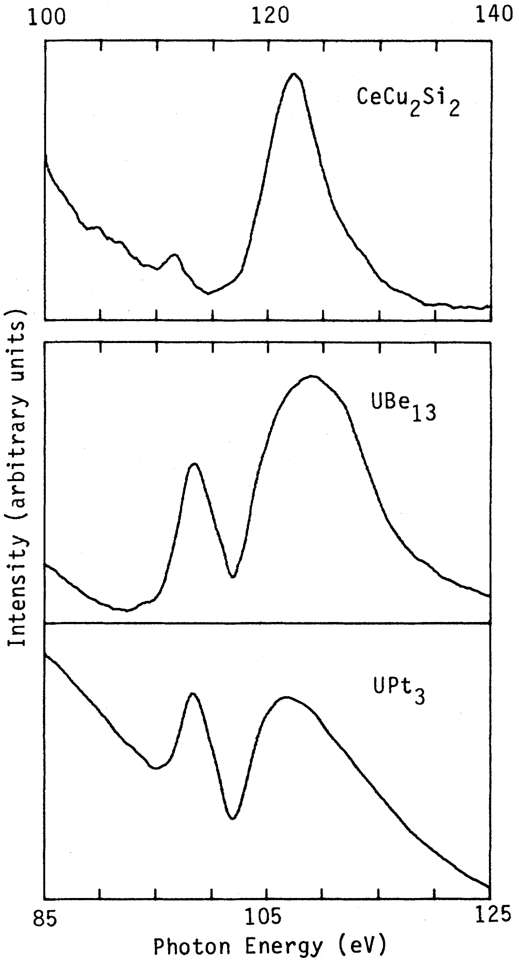

FIG. 1. Constant initial state (CIS) spectra taken at the binding energy $E_b = 2$ eV for $CeCu_2Si_2$ and at $E_b = 1$ eV for UBe_{13} and UPt_3.

pounds. CIS spectra obtained for other binding energies in the range 0–3 eV were found to be virtually identical to those shown in Fig. 1. In UPt_3 the relatively strong photon energy dependence of the Pt-derived 5*d* emission is seen in the energy interval 85–95 eV. The precursive fingerprint structure in the Ce-derived CIS reflects the (L,S) multiplet structure of the intermediate configuration $4d^9 4f^2$ (Ref. 10) and the split peak in the U-derived CIS's is due to strongly nonstatistical absorption from the spin-orbit-split 5*d* shell.[11] The anomalous broadening of the higher-energy peak of the UBe_{13} CIS is caused by Be-derived Auger emission at photon energies above 112 eV (the Be *K*-shell ionization energy).

In Fig. 2 are shown the photoemission spectra (energy distribution curves) taken on-resonance (122 eV for $CeCu_2Si_2$ and 109 eV for the U compounds) and off-resonance (112 eV for $CeCu_2Si_2$ and 92 eV for the U compounds). Also plotted are the difference spectra, which are dominated by 4*f* or 5*f* emission, respectively. For $CeCu_2Si_2$ and UPt_3 the off-resonance spectra were normalized in intensity in order to erase the Cu 3*d* signature (the peak at 4 eV) or the Pt 5*d* signature (i.e., the shoulder at 5 eV) in the difference spectra. This required multiplying the off-resonance spectra by the factors 0.77 and 0.39 for $CeCu_2Si_2$ and UPt_3, respectively. These factors correspond to the off-resonance to on-resonance ratios of the respective *d* emission cross sections. The ratio 0.39 for UPt_3 is similar to the 5*d* ratio for elemental gold[12] in the same energy range. The off-resonance spectrum for UPt_3 is nearly identical to that observed in $CePt_2$ (Ref. 13), which implies that the Pt-derived 5*d* bands in the two systems are similar. No normalization was used for the off-resonance UBe_{13} spectrum. The weak maximum at ~7 eV in the latter is attributed to a trace ($\lesssim 0.2$ monolayer) of oxygen (see discussion below). For the two U compounds, difference spectra obtained by subtracting the 92-eV spectrum from the 98-eV spectrum are essentially identical to those shown in Fig. 2. The backgrounds due to secondary electrons were not subtracted in any of the spectra in Fig. 2, since the salient features of the spectra are unaltered by such a (necessarily somewhat arbitrary) procedure.

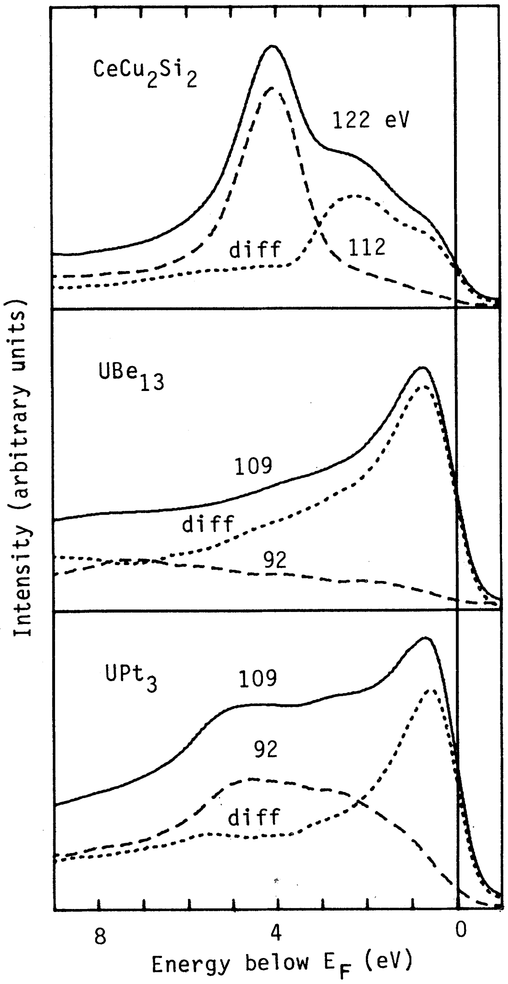

FIG. 2. Photoemission spectra (energy distribution curves) taken on-resonance and off-resonance at the indicated photon energies, and the difference spectra (which highlights *f*-derived emission) for $CeCu_2Si_2$, UBe_{13}, and UPt_3.

The results shown in Fig. 2 for $CeCu_2Si_2$ are drastically different from those reported earlier,[14] which we attribute to a small amount of surface oxygen contamination in the earlier study. We have since established from controlled oxygen chemisorption experiments that $\lesssim 0.2$ monolayer oxygen coverage severely distorts the bimodal 4*f*-derived difference spectrum in $CeCu_2Si_2$.[15] The satellite feature is rapidly suppressed and the main peak is narrowed. This distortion scales linearly with the oxygenation of the Si bands as monitored by Si 2*p* core-hole emission. This suggests that there is strong hybridization between the Ce 4*f* electrons and the Si atoms, which are the nearest neighbors to Ce in the $CeCu_2Si_2$ crystal structure. Similarly, the anomalously large width of the main *f*-derived peak in the clean specimen, in contrast to that seen for example in γ-Ce and α-Ce,[16,17] also implies a large hybridization.

The results shown in Fig. 2 for UBe_{13} are also dramatically different from those reported earlier.[9] Again, we attribute this to oxygen contamination in the earlier study. This is best illustrated in Fig. 3(b) which shows the spectrum obtained after subjecting a freshly fractured surface to 1 L oxygen (1 L = 1 Langmuir = 10^{-6} Torr sec). This spectrum is similar in appearance to those reported in Ref. 9, which exhibit the same maximum at ~7 eV, which was interpreted as a Be-derived feature. In UBe_{13} the rate of oxygen appearance on the surface is too rapid to be explained by chemisorption from residual oxygen in the chamber—the oxygen must come from the bulk of the sample to the surface. A similar phenomenon has been observed for $CeRu_2$.[18] This problem means that relatively oxygen-free spectra can only be obtained within a few minutes after fracturing the sample. In Fig. 3(a) is shown a spectrum taken at $h\nu = 30$ eV within 3 min after the sample was fractured. At this energy the 5*f* emission is drastically reduced and the spectrum should be dominated by Be-derived *s* and *p* features. The spectrum is relatively flat, apart from the parasitic growth of secondary electron emission with increasing binding energy (decreasing kinetic energy of the emitted electrons). The flattening of the Be-derived spectrum relative to its peaked density of states (at ~7 eV) in Be metal (Ref. 9, and references cited therein), coupled with the anomalously tailing out of 5*f* spectral weight to large binding energy, suggests strong hybridization between the U 5*f* electrons and the Be valence electrons. The conclusion in Ref. 9 that such hybridization effects are negligibly small

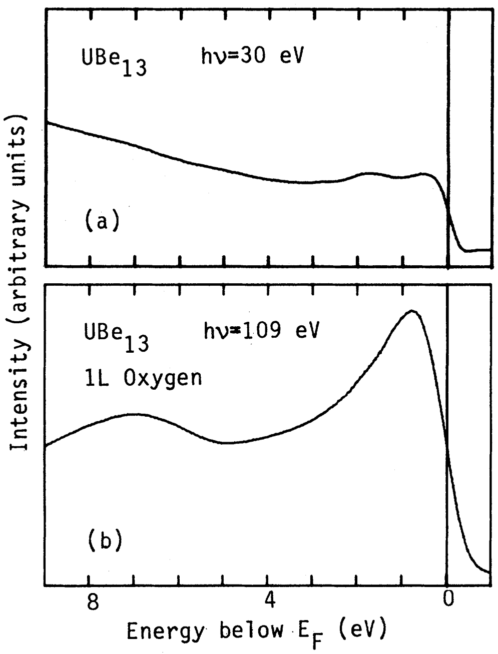

FIG. 3. Photoemission spectra taken at photon energies of (a) 30 eV for clean UBe$_{13}$ and (b) 109 eV for UBe$_{13}$ exposed to 1 L oxygen.

resulted from the interpretation of the oxygen-derived feature as a Be feature.

Finally we consider UPt$_3$, for which the width of the $5f$ feature is much narrower than in UBe$_{13}$ (Fig. 2). The growth in its intensity at the top of the articulated Pt $5d$ band is consistent with,[8] but not proof for, strong hybridization between the U $5f$ and Pt $5d$ electrons. However, we can infer indirectly that such hybridization is large by analogy with the behavior of Ce-based intermetallics. It is possible in the latter case to measure the hybridization energy between the $4f$ electrons and conduction electrons (or neighboring ligands) by studying shakedown satellites in Ce-derived three-core emission. It is a general rule in these studies that when the nearest neighbors to Ce are transition-metal atoms, the hybridization is large.[19] Of particular relevance, we have found[20] such hybridization effects to be large in CePt$_2$, in which, as discussed above, the Pt $5d$ band appears very similar to that in UPt$_3$. The above analogy is strengthened by the fact that the U $5f$ electrons have larger radial extent that the Ce $4f$ electrons, which would lead to stronger hybridization with neighboring ligands.

No attempt was made to determine the $5f$-electron count in the U compounds by comparing the spectra to that of a standard. The principal difficulty with this approach is the uncertainty in the sampling area of the fractured samples.

A common property of the spectra of the three systems (Fig. 2) is the presence of f spectral weight at or near E_F, which would seem to be necessary to account for the high density of states at E_F (large effective mass) inferred from the low-temperature Fermi-liquid behavior.[1-3] It should be noted, however, that the observed f spectral weight at or near E_F is, in all three systems, considerably larger than that predicted for the Kondo (or Kondo lattice) model (see, e.g., Ref. 21, and references cited therein), which has been sometimes invoked in the description of these materials.

The major point we wish to make is that for each of the three heavy-fermion superconductors there is, as we have argued above, evidence (either direct or indirect) for significant hybridization between the f electrons and the nearest-neighbor ligands, these being the Si $3p$, the Be $2p$, and the Pt $5d$ electrons for CeCu$_2$Si$_2$, UBe$_{13}$, and UPt$_3$, respectively.[22] This we offer as a possible clue to the mystery of the occurrence of heavy-fermion superconductivity in these systems.

The work at Polytechnic and National Synchrotron Light Source (Brookhaven) was supported by the U.S. Department of Energy under Contracts No. DE-AC02-81ER10862 and No. DE-AC02-76CH00016, respectively. The work at Los Alamos was also performed under the auspices of the U.S. Department of Energy.

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[1] F. Steglich, J. Aarts, C. B. 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] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).

[4] C. M. Varma, Bull. Am. Phys. Soc. **29**, 404 (1984).

[5] G. P. Williams and M. Howells, Nucl. Instrum. Methods **208**, 37 (1983).

[6] A. Franciosi, J. H. Weaver, N. Mårtensson, and M. Croft, Phys. Rev. B **24**, 3651 (1981).

[7] J. W. Allen, S.-J. Oh, M. B. Maple, and M. S. Torikachvili, Phys. Rev. B **28**, 5347 (1983).

[8] B. Reihl, N. Mårtensson, D. E. Eastman, A. J. Arko, and O. Vogt, Phys. Rev. B **26**, 1842 (1982).

[9] 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).

[10] J. Sugar, Phys. Rev. B **5**, 1785 (1972).

[11] A. Zangwill, D. Lieberman, and R. Cowan (unpublished).

[12] S. T. Manson, in *Photoemission in Solids,* edited by M. Cardona and L. Ley (Springer, Berlin, 1978), Vol. 1, p. 135.

[13] R. D. Parks, S. Raaen, M. L. denBoer, and G. P. Williams (unpublished).

[14] R. D. Parks, B. Reihl, N. Mårtensson, and F. Steglich, Phys. Rev. B **27**, 6052 (1983).

[15] M. L. denBoer, S. Raaen, R. D. Parks, and G. P. Williams (unpublished).

[16] R. D. Parks, B. Reihl, and N. Mårtensson, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 299.

[17] D. Wieliczka, J. H. Weaver, D. W. Lynch, and C. G. Olson, Phys. Rev. B **26**, 7056 (1982).

[18] W. Wuilloud, Y. Baer, and M. B. Maple, Phys. Lett. **97A**, 65 (1983).

[19] J. C. Fuggle, F. U. Hillebrecht, Z. Zolnierek, R. Lasser, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983).

[20] S. Raaen and R. D. Parks (unpublished).

[21] C. Lacroix, J. Appl. Phys. **53**, 2131 (1981).

[22] Implicit in our use of the work "ligand" is our assumption that covalent bonding is an important component in the bonding scheme in these materials, a concept alien to the basic structure of the Kondo (or Kondo lattice) model. See discussions in A. Fujimori, Phys. Rev. B **28**, 2281 (1983), and references cited therein.