Electronic structure of superconducting UBe$_{13}$

G. Landgren, Y. Jugnet, and J. F. Morar

IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

A. J. Arko

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Z. Fisk and J. L. Smith

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

H. R. Ott

*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich,
CH-8093 Zurich, Switzerland*

B. Reihl

IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

(Received 25 July 1983)

We have studied the actinide superconductor UBe$_{13}$ with resonant photoemission using synchrotron radiation $30 \leq h\nu \leq 120$ eV. In agreement with the anomalously high γ value of 1.1 J/mole K^2, we find a high density of $5f$ states at the Fermi level E_F. Uranium $6d$ electrons are not present at E_F as can be derived from the zero intensity at E_F in the off-resonance spectrum. The close resemblance of this off-resonance curve to a photoemission spectrum of pure Be suggests that the hybridization of U $5f$ electrons with Be s,p electrons is small. Indeed, the UBe$_{13}$ photoemission curves look like a superposition of U and Be curves. By using photoemission results from UO$_2$ as a reference, we find that the valence-band emission contains about one $5f$ electron. The present results on UBe$_{13}$ are compared with those of CeCu$_2$Si$_2$, another member of the family of exotic superconductors.

I. INTRODUCTION

It was very recently discovered[1] that UBe$_{13}$ becomes superconducting below 0.85 K, and below 1 K exhibits an anomalously high electronic specific-heat value of $\gamma = 1.1$ J/mole K^2. Therewith, UBe$_{13}$ is the first example of an actinide system containing $5f$ electrons which falls into the class of so-called exotic superconductors. Another example is the $4f$ system CeCu$_2$Si$_2$ ($\gamma \simeq 1$ J/mole K^2),[2] in which superconductivity is claimed to be mediated by heavy fermions generated presumably by interactions between the localized $4f$ electron and the conduction electrons.[3] A clear understanding on a microscopic scale, however, is still lacking and the relevance of this understanding to the problem of "intermediate valence" in cerium- and uranium-based systems is evident. For CeT_2Si$_2$ (T = Cu, Ag, Au, Pd), it is the hybridization of Ce $4f$ electrons with T-derived d states which determines the ground-state properties (superconductivity for T = Cu, ordered magnetism for T = Ag, Au, Pd). This was concluded from resonant photoemission studies on these systems.[4] Here, we apply the same technique to UBe$_{13}$ using synchrotron radiation 30 eV $< h\nu \leq 120$ eV from the National Synchrotron Light Source at the Brookhaven National Laboratory.

II. METHOD

Resonant photoemission provides a means to extract the n,l character our of the valence-band emission which usually consists of overlapping contributions, provided an $n, (l-1)$ core level is available.[5] Here, the electronic states are characterized by their main quantum number n and their orbital quantum number l. Experimentally, the resonance manifests itself as a minimum in the photoemission-intensity-versus-$h\nu$ curve, which is followed by a maximum when $h\nu$ is tuned through the core absorption edge. In case of an atomiclike uranium configuration, the minimum reflects Fano-type interference effects[6] between direct valence-band photoemission

$$5d^{10}5f^36d^17s^2 + h\nu \rightarrow 5d^{10}5f^26d^17s^2 + e_{5f} \; ,$$

and the $5d$ core-hole absorption into intermediate excited states

$$5d^{10}5f^36d^17s^2 + h\nu \rightarrow [5d^95f^46d^17s^2]^* \; ,$$

while the maximum is due to the subsequent decay of the excited states

$$[5d^95f^46d^17s^2]^* \rightarrow 5d^{10}5f^26d^17s^2 + e_{5f} \; .$$

This technique has been applied successfully to the localized $5f$ systems USb$_x$Te$_{1-x}$, UO$_2$ and UPd$_3$,[5] the itinerant $5f$ alloy UIr$_3$,[7] the $4f$ systems CeT_2Si$_2$ (T = Cu, Ag, Au, Pd),[4] and the $4f$ superconductors CeRu$_2$ and CeCo$_2$ (Ref. 8). It is particularly successful in materials in which the U $5f$ electrons are energetically degenerate with U $6d$'s (as in USb$_x$Te$_{1-x}$) or transition-metal d's (as in UPd$_3$), or when the f electrons are even hybridized with transition-metal d's as in UIr$_3$ and CeT_2Si$_2$. UO$_2$ serves as a prototype since the

U $5f$ and the O $2p$ photoemission features are completely separated[5] and hence provide a way to determine quite accurately the $5f$ to $2p$ photoemission cross-section ratio as well as the "pure" $5f$ resonance behavior.

III. EXPERIMENTAL

The experiment was performed with the IBM two-dimensional spectrometer[9] now installed at the Brookhaven National Laboratory. The synchrotron radiation from the 750-MeV storage ring was monochromatized with a 3-m toroidal grating monochromator yielding a total energy resolution (electrons and photons) of 0.3 eV at $h\nu = 40$ eV and 0.75 eV at $h\nu = 100$ eV. Single crystals of UBe_{13} were fractured in a vacuum of 2×10^{-10} Torr and then immediately transferred to the measuring position which held a vacuum better than 1×10^{-10} Torr. Angle-integrated ($\Delta\Omega = 86°$) energy-distribution curves (EDC's) were taken within two hours after cleavage.

IV. RESULTS AND DISCUSSION

In Fig. 1(a), we present an EDC of UBe_{13} at $h\nu = 40$ eV, a photon energy at which the p, d, and f photoemission cross sections are roughly equal,[10] and hence a picture of the total density of states (DOS) is obtained. We note two spectral features in Fig. 1(a), one sharp peak right at E_F and a broader one centered at about -7-eV initial energy. From the cross-section dependence at low excitation energies $h\nu < 60$ eV, as well as the resonance behavior (to be discussed below), we can immediately assign U $5f, 6d$ character to the Fermi peak, and Be s,p character to the second feature at -7 eV. So far, no theoretical DOS calculation has been performed. Therefore, in Fig. 1(b), we compare our

results for UBe_{13} with an EDC from beryllium[11] taken at $h\nu = 1487$ eV, again a photon energy which provides a good overall picture of the DOS of Be. The justification for this comparison is taken from the fact that the Be-Be and next-nearest Be distances are 2.16 and 2.59 Å in fcc UBe_{13},[12] while they are 2.23 and 2.29 Å, respectively, in hexagonal Be.[13] Inoue and Yamashita[14] have performed band-structure calculations for Be as a function of the lattice constant. They find essentially no change of the DOS when varying the lattice constant from 0.8 to 1.2 times its nominal value. In addition, hypothetically fcc Be has a DOS almost equal to hcp Be.[14] Hence, to a first approximation, the s- and p-like electrons of Be will have the same wave-function overlap and form bands at approximately the same energy positions in UBe_{13} as they were determined for Be [cf. Fig. 1(b)]. Noteworthy is the low DOS of Be at E_F, exactly where we recognize the U $5f$ contribution in Fig. 1(a). In addition, the $2s$-like maximum of states in Be corresponds to the -7-eV feature in UBe_{13} to which we had already previously assigned s,p character (see above).

To derive the mere $5f$ contribution, in Fig. 2 we use the EDC's of UBe_{13} at $h\nu = 98$ eV (on resonance) and $h\nu = 92$ eV (off resonance). These photon energies were determined from the maximum and minimum, respectively, in the $5f$ intensity-versus-$h\nu$ curve (constant initial-state spectrum) obtained from EDC's measured in steps of 2 eV through the $5d$ absorption edge and then normalized to the photon flux.[5] The EDC's in Fig. 2(a) have been normalized to equal Be $2s$ intensity at -7 eV. The Be $2s$ emission does not change at the $5d \rightarrow 5f$ Fano resonance (because of different atoms, different main quantum numbers, and the Δl-selection rule). Most striking is the zero intensity at E_F in the off-resonance spectrum of Fig. 2(a). Such a zero intensity at $h\nu = 92$ eV has so far only been observed in UO_2,[5] which is known to be purely f-like with no other overlapping states. Usually, at least some U $6d$ contribution accounts for some spectral intensity (see, e.g., UTe in Ref. 5 or α-uranium in Ref. 15). Therefore, we conclude that no U $6d$ states are present at E_F. In going away from the
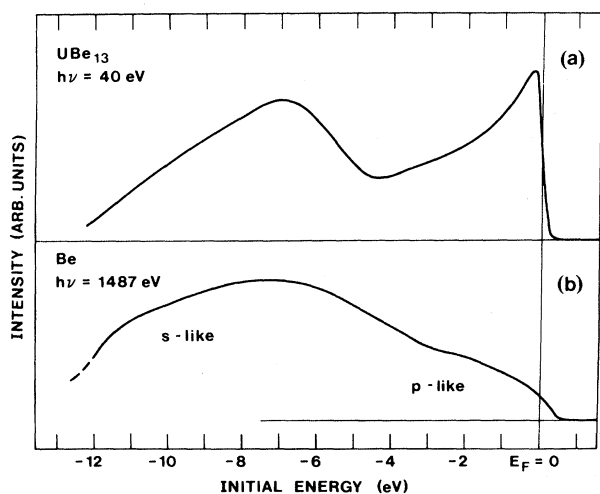

FIG. 1. (a) Energy-distribution curve of photoelectrons from UBe_{13} at $h\nu = 40$ eV. The background due to the secondary electrons has been subtracted. (b) EDC of photoelectrons from beryllium at $h\nu = 1487$ eV after background subtraction [from Höchst, Steiner, and Hüfner (Ref. 11)]. The notations s- and p-like were derived by comparison with the calculations of Inoue and Yamashita (Ref. 14).
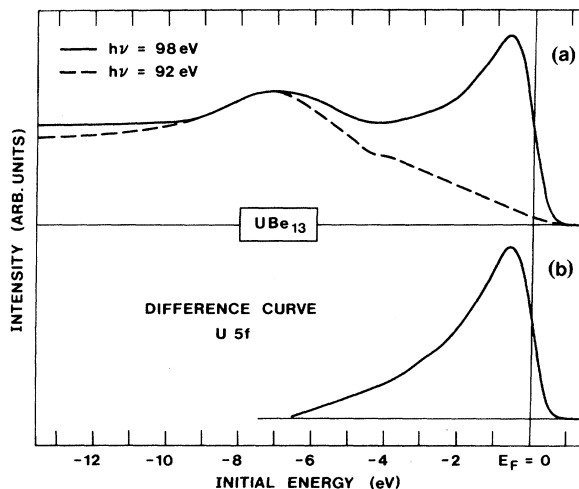

FIG. 2. (a) EDC at $h\nu = 98$ eV (on-resonance, solid line) and $h\nu = 92$ eV (off-resonance, dashed line) normalized to equal peak heights at -7 eV. (b) The difference curve resulting from the upper panel represents the $5f$ emission (see also text).

Fermi level, increasing spectral intensity can be seen in the off-resonance EDC of Fig. 2(a). Although, in principle, some U $6d$'s could account for this emission, comparison of this EDC at $h\nu=92$ eV with the pure Be spectrum of Fig. 1(b) reveals a lot of resemblance. As pointed out above, Be $2s$ or $2p$ states are not affected by the $5d \to 5f$ resonance. Therefore it is tempting to attribute $5f$ character to the entire difference curve of the on- and off-resonance curves, which is shown in Fig. 2(b). This is in contrast to the $4f$ electron systems CeT$_2$Si$_2$ (T=Cu, Ag, Au, Pd),[4] in which the f-intensity scales with T-derived d intensity at E_F. This has led to the conclusion[4] that the hybridization of the f's with the d's of the transition metal determines the ground-state properties. The nearest U-U distance[12] of 5.13 Å in UBe$_{13}$ (for comparison UO$_2$: 3.9 Å) points towards localized $5f$ electronic states, and very small or no direct $5f$ wavefunction overlap is expected. Hybridization of U f electrons with Be p's, however, cannot be derived from our resonant photoemission results and the comparison with Be. The tailing of the $5f$ intensity away from the Fermi level as can be seen from the difference curve of Fig. 2(b) allows for some hybridization effects at higher binding energies.

To obtain a measure for the number of $5f$ electrons per formula unit n_{5f}(UBe$_{13}$) in UBe$_{13}$, we use as a reference the photoemission spectrum of UO$_2$ at $h\nu=40$ eV,[5,16] obtained under the same conditions as the EDC in Fig. 1(a). For the intensity ratio, we find $I_{5f}/I_{2p}=0.5$ in UO$_2$. This ratio can also be expressed in terms of the photoemission cross sections σ_f and σ_p and the number of electrons per formula unit n_{5f}(UO$_2$) and n_{2p}(UO$_2$):

$$I_{5f}/I_{2p} = \sigma_f n_{5f}(\text{UO}_2)/\sigma_p n_{2p}(\text{UO}_2) \ .$$

Separating the UBe$_{13}$ EDC of Fig. 1(a) at the intensity minimum at -4.45 eV into a U $5f$ and a Be $2s$ contribution, we obtain a ratio

$$I_{5f}/I_{2s} = \sigma_f n_{5f}(\text{UBe}_{13})/\sigma_s n_{2s}(\text{UBe}_{13}) = 0.35 \ .$$

Hence, n_{5f}(UBe$_{13}$) can be written as

$$n_{5f}(\text{UBe}_{13}) = \frac{0.35}{0.5} \frac{\sigma_s}{\sigma_p} n_{2s}(\text{UBe}_{13}) \frac{n_{5f}(\text{UO}_2)}{n_{2p}(\text{UO}_2)} \ . \tag{1}$$

The ratio of the $2s$ to $2p$ photoemission cross sections has been calculated[10] for carbon at $h\nu=40.8$ eV: $\sigma_s/\sigma_p=0.788$. The total number of s and p electrons in UBe$_{13}$ is $2\times13=26$. From the x-ray photoemission spectroscopy results on Be, it was deduced[11] that 40% of the total number of electrons is contained in the s-like emission feature yielding n_{2s}(UBe$_{13}$) $=10.4$. Finally, it is well known[5] that n_{2p}(UO$_2$) $=2\times6=12$ and n_{5f}(UO$_2$) $=2$. Inserting all the numbers in Eq. (1) results in n_{5f}(UBe$_{13}$) $=0.96$, i.e., about one electron. With all the approximations used in obtaining this number [comparison with Be to get n_{2s}(UBe$_{13}$), the

ambiguity in the background subtraction in UO$_2$ and UBe$_{13}$, etc.], it is not surprising that n_{5f} deviates from the paramagnetic effective moment[1] at room temperature $\mu_p=3.1\mu_B$. From one localized f electron, a free-ion moment of $2.54\mu_B$ is derived in Russel-Saunders coupling. Finally, the f number obtained at $h\nu=40$ eV [cf. Fig. 1(a)] is consistent with the pure f contribution derived from the resonance curves (see above).

One $5f$ electron in UBe$_{13}$ points towards a very close resemblance to CeCu$_2$Si$_2$ (and Ce systems, in general) which presumably has one $4f$ electron.[2,3] Although the width of the $5f$ emission in the 40-eV EDC [Fig. 1(a)] is rather broad (~2eV) as compared with the expectedly narrow f band of millivolt width in the ground state, it is known that the $4f$ photoemission in Ce systems is very broad (2–3) eV and exhibits the anomalous two-peak structure (cf., e.g., Refs. 4 and 8) which is currently a matter of great interest.[17] So, in principle, effects similar to those proposed[17,18] for photoemission from Ce systems may account for the broad width of the $5f$ emission in UBe$_{13}$.

The high-f DOS is compatible with the anomalously high γ value, while some localized character manifests itself in the effective moment of $3.1\mu_B$ per U ion. Such localization effects and the degree of correlation can be studied by high-energy photoemission on the $4f$ core levels in $5f$ systems.[19] It is the possible existence of a satellite and its intensity relative to the $4f$ main line which gives a measure for the localization of the $5f$'s. In the valence-band region,[15] no such satellites are discernible (cf. Figs. 1 and 2), therefore future x-ray photoemission experiments on the core levels are welcomed. Complementary bremsstrahlung isochromat spectroscopy will allow[20] determination of the effective Coulomb correlation energy.

As a final remark, it is worthwhile recalling that the band-structure calculation for Be (Refs. 11 and 14), as well as the photoemission DOS [cf. Fig. 1(b)], shows a very low DOS (of p states) at E_F. According to our findings, the huge $5f$ DOS falls into this minimum. Indeed, our photoemission spectra of UBe$_{13}$ look like a superposition of the spectra of its constituents U (Ref. 15) and Be (Ref. 11). Clearly, the $5f$ electrons play a role for the superconductivity in UBe$_{13}$, since related ThBe$_{13}$ does not exhibit[21] a superconducting transition down to 0.45 K. On the other hand, the similar Be-Be spacing in Be and UBe$_{13}$ may explain why UBe$_{13}$ is metallic like Be, but not why it is a superconductor.

[1]H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. Lett. 50, 1595 (1983).
[2]F. Steglich, J. Aarts, C. B. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. 43, 1892 (1979).
[3]W. Lieke, U. Rauchschwalbe, C. B. Bredl, F. Steglich, J. Aarts, and

F. R. de Boer, J. Appl. Phys. 53, 2111 (1982).
[4]R. D. Parks, B. Reihl, N. Mårtensson, and F. Steglich, Phys. Rev. B 27, 6052 (1983).
[5]B. Reihl, N. Mårtensson, D. E. Eastman, A. J. Arko, and O. Vogt, Phys. Rev. B 26, 1842 (1982), and references therein.

[6]U. Fano, Phys. Rev. 124, 1886 (1961).

[7]A. J. Arko, D. D. Koelling, and B. Reihl, Phys. Rev. B 27, 3955 (1983).

[8]J. W. Allen, S. J. Oh, I. Lindau, M. B. Maple, J. S. Suassuna, and S. B. Hagström, Phys. Rev. B 26, 445 (1982).

[9]D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods 172, 327 (1980).

[10]S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. 21, 285 (1981).

[11]H. Höchst, P. Steiner, and S. Hüfner, Z. Phys. B 30, 145 (1978).

[12]N. C. Baenziger and R. E. Rundle, Acta Crystallogr. 2, 258 (1949).

[13]K. J. H. MacKay and N. A. Hill, J. Nucl. Mater. 8, 263 (1963).

[14]S. T. Inoue and J. Yamashita, J. Phys. Soc. Jpn. 35, 677 (1973).

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

[16]B. Reihl (unpublished results).

[17]O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. 50, 604 (1983).

[18]S. Hüfner and P. Steiner, Z. Phys. B 46, 37 (1982); S. H. Liu and K. M. Ho, Phys. Rev. B 26, 7052 (1982); A. Fujimori, *ibid.* 27, 3992 (1983).

[19]W. D. Schneider and C. Laubschat, Phys. Rev. Lett. 46, 1023 (1981).

[20]Y. Baer, H. R. Ott, J. C. Fuggle, and L. E. DeLong, Phys. Rev. B 24, 5384 (1981).

[21]E. Bucher, J. P. Maita, G. W. Hull, P. C. Fulton, and A. S. Cooper, Phys. Rev. B 11, 440 (1973).