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High-energy spectroscopic study of the electronic structure of UBe_{13}

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X-ray photoemission and bremsstrahlung isochromat spectroscopies have been used to probe the occupied and unoccupied states of UBe_{13}. Between two and three electrons are found to populate the tail of a surprisingly broad $5f$ band (~ 5 eV) of extended states. With our resolution ($\lesssim 0.5$ eV) it is not possible to observe directly at the Fermi energy any peculiarity of the density of states explaining the extraordinary properties of this compound. However, the drastic differences between the core-level spectra of U and Be indicate that the $5f$ states remain essentially confined around the U atoms and are only weakly hybridized with the *sp*-band states originating from the Be atoms.

The recent discovery of bulk superconductivity in UBe_{13} below 1 K (Ref. 1) has given clear evidence for the existence of strongly interacting electrons in some metallic materials, giving rise to anomalous properties at low temperatures. Other examples for this type of materials are $CeAl_3$ (Ref. 2) and $CeCu_2Si_2$ (Ref. 3), again two compounds containing f electrons, obviously a prerequisite for the observation of the behavior to be discussed here. All these compounds show an anomalously large specific heat $c_p(T)$ at low temperatures. In $CeAl_3$, $c_p(T)$ decreases linearly with decreasing temperature below 1 K but, in comparison with normal metals, with a very large coefficient γ of the order of 1.5 J/mole K^2,[2] indicating a considerable renormalization of the electronic subsystem. In UBe_{13} (Ref. 1) and $CeCu_2Si_2$,[3] this linear decrease with a slope of about 1 J/mole K^2 is intercepted by a discontinuity Δc due to a superconducting transition. In both cases, the magnitude of Δc is compatible with the large values of c_p/T just above the transitions and the experimental verification that the entropy difference between the superconducting and the normal state is zero below T_c demonstrates that it is indeed the strongly interacting electrons that are involved in the superconducting state.

These high γ values are necessarily also based on large densities of electronic states at the Fermi energy E_F, implying very narrow features in the energy dependence of the electronic structure at E_F. The possible occurrence of such features is well known from theoretical work concerning the electronic structure of simple metals containing transition-metal impurities in the dilute limit.[4] Recent work considering concentrated systems[5] claims that similar narrow resonances at E_F also appear in this case. Information on the energy dependence of the electronic structure of a metal is provided by using photoemission techniques. A first attempt concerning UBe_{13} involved resonant photoemission, favoring the emission of electrons with f symmetry, by scanning the energy range below E_F to about 12-eV binding energy.[6] Since also core-electron spectra and particularly the energy distribution of empty electron states provide valuable information, we chose to map parts of the electronic spectrum of UBe_{13} by using x-ray photoemission (XPS) and bremsstrahlung-isochromat spectroscopy (BIS).

The sample investigated in the present study was a platelet cut from the same polycrystalline batch of material that was used for previous specific-heat measurements.[7] The XPS and BIS spectra were obtained in a combined instrument described elsewhere.[8,9] The contamination was removed from the sample surface by scraping it *in situ* with an Al_2O_3 file until the O 1*s* and C 1*s* XPS signals could no longer be detected in a 5-min scan. The base pressure of 1×10^{-11} Torr in the instrument allowed us to accumulate the different spectra during periods of many hours without any sizable degradation of the surface cleanliness.

The occupied valence-band states of UBe_{13} have recently been studied by resonant photoemission.[6] The spectra have been interpreted as revealing a UBe_{13} density of states (DOS) looking rather like a superposition of the DOS of the two pure constituents U and Be. A calibration procedure of the intensity of the different signals in the spectra has yielded a $5f$ population of roughly one electron. Our XPS valence band spectrum of UBe_{13} is shown on the left side of Fig. 1. In the energy range from the Fermi energy E_F to -4 eV it is in good agreement with the previously published spectrum excited at 40 eV.[6] The *sp* states of Be forming a broad band[10] have a very weak cross section at the Al $K\alpha$ photon energy. From atomic cross-section calculations[11] they are estimated to represent less than 10% of the total intensity of the XPS spectrum and for this reason they do not emerge from the background of inelastically scattered electrons extending at higher binding energies. In U, the atomic cross section for the $5f$ states is substantially larger than the one for the $6d$ states $[\sigma(5f^1)/\sigma(6d^1)=6]$ (Ref. 11) and the XPS peak must be mainly attributed to the tail of the $5f$ band cut by E_F. This spectrum of UBe_{13} shows a striking similarity with the spectrum of α-U metal[12] despite the different environment of the U atoms and their

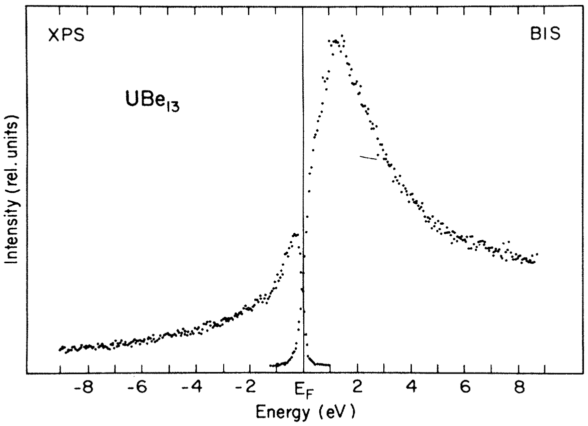

FIG. 1. Combined XPS–BIS spectrum of UBe_{13}. The relative intensities below and above E_F have been scaled by a continuity criterion (see text).

separation which is more than 50% larger in UBe_{13} than in α-U.

In a limited energy range above E_F the unoccupied states have been probed by BIS and the corresponding spectrum is shown on the right side of Fig. 1. Since the matrix elements for the BIS transitions are practically the same as those accounting for XPS transitions, also the BIS spectrum represents nearly exclusively the empty $5f$ states superimposed on a background increasing toward higher energies and attributable to electrons which have been scattered inelastically prior to the BIS process. Whereas two marked peaks are observed in α-U,[12] the BIS spectrum of UBe_{13} shows a single and featureless peak with its maximum at 1.3 eV. On the low-energy side, the clear change of slope at 0.4 eV allows us to observe the position of the Fermi edge which is found to coincide with the position determined by the usual energy-scale calibration performed with Au. The Koopmans's approximation is very accurate at the Fermi energy of metals,[13] so that it is well justified to join the XPS and BIS spectra at E_F in order to depict the whole $5f$ band. The main uncertainty in this attempt is the calibration of the relative intensities observed with the two different techniques. In the present situation, the comparison of the Fermi-edge intensities is not suitable: the two techniques have different line shapes and linewidths[8,9] and, furthermore, E_F is located in a very steep DOS. A more reliable approach in determining the relative intensities consists in joining the two spectra above and below the range affected by the Fermi cutoff by a smooth curve. As shown in Fig. 1, this criterion allows us to represent rather precisely a continuous DOS crossing E_F. After subtraction in both spectra of a background proportional to the integrated signal intensity from E_F to the respective energy and joining smoothly the spectra away from E_F, the area of the two curves represent the total band intensity.

As mentioned previously, the contribution of the $l=2$ projected DOS to the spectra is small but not entirely negligible. For this reason the experimental intensity ratio $I_{BIS}/I_{XPS}=3.7$ does not directly represent the ratio of the empty to occupied $5f$ states but it must be corrected for the presence of the ten $6d$ states located in the same energy range. It is straightforward to express I_{BIS}/I_{XPS} as a function of the numbers of the occupied states (n_f, n_d) and of the cross-section ratio $\sigma(5f^1)/\sigma(6d^1)=6$ (Ref. 11):

$$\frac{I_{BIS}}{I_{XPS}}=\frac{(10-n_d)+(14-n_f)\sigma_f/\sigma_d}{n_d+n_f\sigma_f/\sigma_d} . \tag{1}$$

In a metallic bond, only a very small charge transfer is expected between the Be and U atoms, as confirmed below in the discussion of the core level binding energies. The approximate neutrality around the U atoms yields the additional condition for the number of occupied f and d states $n_d+n_f\cong 6$ which allows us to extract the value $n_f\cong 2.8$. The uncertainties affecting the numbers used in this estimation are not influencing markedly the value found for n_f. In order to demonstrate this fact, we have calculated the range of each parameter for which n_f varies from 2 to 3:

$$3.5\leq I_{BIS}/I_{XPS}\leq 4.9 \ ;$$

$$1.75\leq \sigma(5f^1)/\sigma(6d^1)\leq 19 \ ;$$

$$5.4\leq n_d+n_f\leq 10.4 \ .$$

The variation of (n_d+n_f) describes implicitly the neglected presence in U of s and p states which have different cross sections than the d states. The acceptable errors in these numbers are smaller than these limits and we can safely conclude that the metallic band of UBe_{13} is occupied by a number of $5f$ electrons not far from 3, but in any case between 2 and 3. This result is in disagreement with the value of $n_f\cong 1$ derived from previous photoemission spectra excited by low-energy photons.[6] Less surprising is the discrepancy with the value of n_f between 1 and 2 predicted by a free-ion interpretation of the effective paramagnetic moment of $3.08\mu_B$.[7]

Figure 2 shows the XPS spectrum of the $5f$ core level of U. The maximum of the $4f_{7/2}$ line located at 377.35 eV can be considered to yield accurately the binding energy of this level. It lies in the narrow energy range from 377.1 to 377.4 eV where the $4f_{7/2}$ binding energies of α-U, US, UAs, USb are found.[14] It is interesting to note that the peculiar behavior of UTe manifests itself by a binding energy of 378.1 eV (Ref. 14) and the tetravalence of the U ions containing two $5f$ localized electrons in UPd_3 (Ref. 15) and UO_2 (Ref. 16) by the still higher values of 379.0 and 380.25

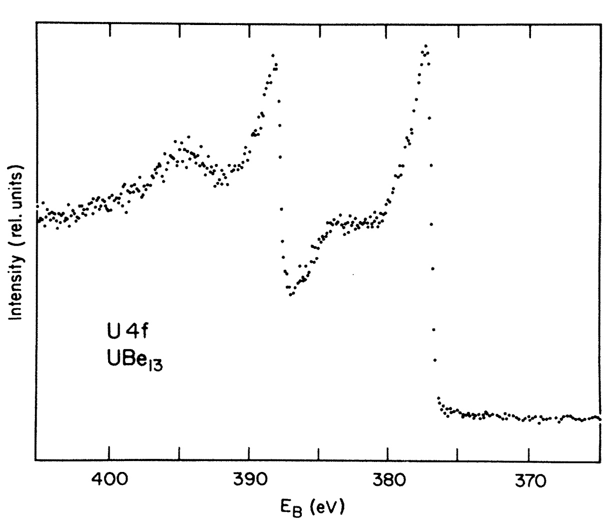

FIG. 2. XPS spectrum of the U $4f$ levels in UBe_{13}.

eV, respectively. These observations confirm our intensity analysis of the outer level spectra leading to the conclusion that the $5f$ population is undoubtedly larger than 2. The very pronounced asymmetrical shape of the lines shown in Fig. 2 reflects a high metallic DOS around E_F allowing the excitation of a great number of low-energy electron-hole pairs in the screening mechanism of the core hole around the U ions.

An intense and broad satellite is also observed at about a 7 eV larger binding energy than each main $4f$ signal. The satellites most likely account for an atomiclike reaction of the outer electrons to the deep hole creation and are due to a local breakdown of the band behavior around the ionized atom. Such effects are particularly intense in narrow bands where the correlation is so important that the large relaxation energy requires the existence of such highly excited final states. The exact nature of this puzzling final state is not established but it may correspond to an integral $5f$ occupation ($5f^2$ or $5f^3$). It has been pointed out[17] that the intensity of this satellite observed in many different U compounds is to some extent correlated with the value of the effective paramagnetic moment, a fact which is also verified in UBe_{13}. Probably the hybridization strength of the $5f$ states of U with the sp orbitals of the numerous surrounding Be atoms is the key parameter of this problem and not the U-U spacing.[17,18] In UBe_{13} this hybridization seems to be just strong enough to involve the $5f$ states in the band but can still be locally broken by the atomic potential increase resulting from the core-level ionization. This situation could provide an explanation for the correlation observed between high values of the effective paramagnetic moment and intense satellites.[17] Finally, the absence of shake-down satellite is a further confirmation of the extended nature of the $5f$ states.[14]

So far we have been concerned essentially with the local DOS around the U atoms and originating from $5f$ and $6d$ states. Interesting information on the Be valence states can be obtained indirectly from the Be $1s$ spectrum shown in Fig. 3. The binding energy of 111.2 eV is identical to that found in pure Be metal,[10] at least within the uncertainty associated with the absolute energy calibration. Compared to the drastic asymmetry of the U $4f$ lines shown in Fig. 2, this narrow line [observed full width at half maximum (FWHM) = 0.70 eV] contains obviously only a moderate amount of electron-hole pairs. As expected, the satellite associated with the localized U final state is not excited in the Be $1s$ ionization process. The spectrum of Fig. 3 confirms[6] that around the Be atoms the local DOS is very little disturbed by the presence of the U atoms. This observation is not surprising in view of the high dilution of the U atoms in the Be matrix.

The essential feature of the UBe_{13} electronic structure emerging from this study is that the $5f$ states of U can only get a delocalized character by a weak hybridization with the sp wave function tails of the four Be atoms located on the cube faces midway between two nearest U atoms which are too far apart to form a band by direct f-f overlap.[19] The densities of states deriving from U and Be atoms remain rather well separated in space as demonstrated by the dramatically different line shapes observed for the core-level excitations of the two different kinds of atoms. The outer level spectra presented here reflect nearly exclusively the U states which are obviously responsible for the unconventional properties of UBe_{13}. The limited resolutions of XPS (0.3 eV) and BIS (0.5 eV) allow us to obtain only an overall picture of the DOS which cannot provide any evidence for the mechanism driving the transition from a paramagnetic regime to a superconducting state or for the origin of the enormous low-temperature electronic specific heat. With decreasing temperature one might anticipate a further weakening of the coupling between sp and f states resulting in an increase of the correlation and effective mass of the $5f$ states. This situation can be thought to favor a ground state dominated by an interaction of magnetic origin.[7] In view of the unexpected broad XPS–BIS $5f$ spectrum recorded at room temperature, it seems illusory to develop models where the total $5f$ bandwidth is supposed to be of the order of 1 meV to explain the exciting low-temperature properties of UBe_{13}. Only the electrons in the immediate vicinity of E_F can be expected to display an extraordinary behavior. Spectroscopic measurements with higher resolution and at low temperature should help to elucidate the mechanisms responsible for this puzzling problem.

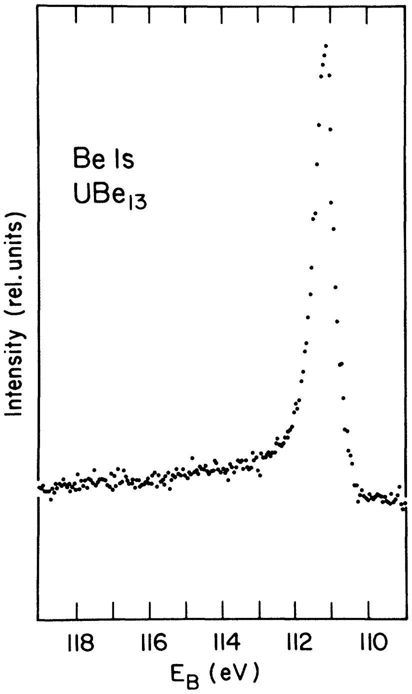

FIG. 3. XPS spectrum of the Be $1s$ level in UBe_{13}.

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