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# $CeB_6$ and $CeCu_6$ single crystals probed by resonant photoemission spectroscopy: A comparison between the two electronic structures

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The electronic structure of $CeB_6$ and $CeCu_6$ single crystals is investigated by means of valence-band resonant photoemission spectroscopy at the Ce $3d$-$4f$ and Ce $4d$-$4f$ thresholds. From the direct comparison between these two heavy fermions compounds, the role of the hybridization between the atomiclike Ce $4f$ orbitals and the delocalized valence band states has been studied. Particular attention has been focused on the differences in the electronic structure between bulk and surface layers. A conceivable additional hybridization between Cu $3d$ and Ce $4f$ states in $CeCu_6$ is discussed, and the possibility of a spectroscopic evaluation of the Kondo temperature, in comparison with results from electrical resistivity measurements, is also addressed. [S0163-1829(97)02315-1]

The role of the hybridization between the Ce $4f$ orbitals and more delocalized states in determining the electronic structure of Ce compounds has been thoroughly studied in recent years,[1] remaining at the same time in the center of a strong controversy regarding the best theoretical model to describe these systems.[2–6]

The possibility for a serious comparison between the different theoretical interpretations and the experimental results depends strongly on the availability of several Ce compositions, together with more powerful and better controlled spectroscopic techniques. It is, for example, interesting to focus the interpretation of the experimental data on those changes that are correlated to changes in the sample stoichiometry, e.g., by comparing the results from different binary Ce compounds in a single phase diagram[7] or by comparing isostructural Ce compounds with different Ce partners.[8]

Concerning the experimental methods, it is furthermore important to compare photoemission measurements with different degree of surface sensitivity in order to detect changes in the electronic structure of a given Ce compound which are connected to the decreasing Ce $4f$ surface hybridization.[9–11] In addition, highly resolved photoemission data close to the Fermi edge have been extensively used for a direct verification of the theoretical predictions.[12–14]

In this work we investigate the electronic structures of $CeB_6$ and $CeCu_6$ by comparing resonant photoemission measurements both at the Ce $4d$-$4f$ and $3d$-$4f$ thresholds. In order to achieve better insight into the valence-band (VB) structure of these materials, the experiments have been performed with the best energy resolution available for the two photon energy ranges corresponding to the above-mentioned thresholds ($\sim$120 eV for $4d$-$4f$ and $\sim$880 eV for $3d$-$4f$). For this purpose, the resonant photoemission measurements at the Ce $4d$-$4f$ threshold reported here have been recorded at the soft x-ray beamline 22 of the MAX synchrotron radiation laboratory in Lund, Sweden,[15] with energy resolution ranging between 50 and 100 meV at $\sim$120 eV of photon energy. Resonant photoemission measurements on the same compounds at the Ce $3d$-$4f$ threshold have been taken at the Super-ESCA beamline of the ELETTRA facility in Trieste, Italy,[16] with energy resolution of the order of 600 meV at $\sim$880 eV of photon energy.

Several measurements of the bulk properties of these compounds, electrical resistivity for both $CeB_6$ (Ref. 17) and $CeCu_6$ (Refs. 18 and 19) and magnetic susceptibility for $CeB_6$ (Ref. 20), report comparable Kondo temperatures ($T_K$) below 10 K. Furthermore, direct and inverse photoemission measurements on $CeCu_6$ result in a very low value for the estimated $f$ hybridization with delocalized states, and in a nearly unitary (0.995) $f$ occupancy in the ground state.[21] As a matter of fact, low values for $T_K$ are rather common for other Ce compounds with partners having $sp$ valence orbitals [e.g., CeAl and CeSi (Ref. 1)] and reflect the ineffective mixing of the $f$ and $sp$ states, particularly when the Ce-to-Ce nearest-neighbor distance does not allow overlapping of the $4f$ orbitals. The case of $CeCu_6$ is of particular interest since a contribution from a possible Cu $3d$–Ce $4f$ hybridization, in the case of a not completely filled Cu $3d$ shell, could

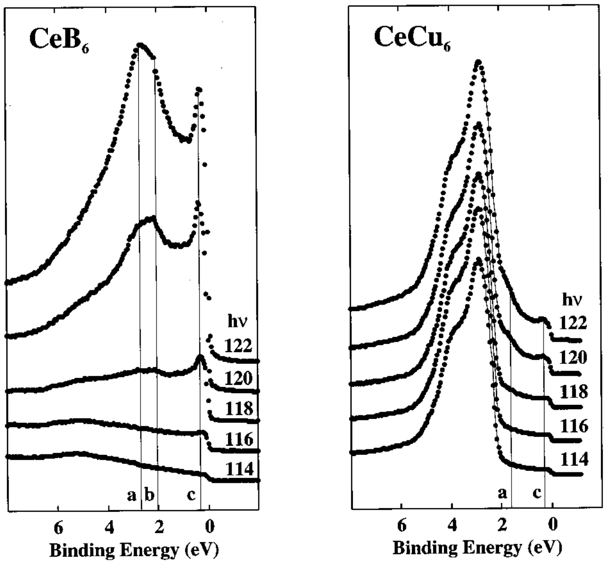

FIG. 1. Resonant valence-band photoemission spectra of CeB$_6$ (left) and CeCu$_6$ (right) at the Ce $4d$-$4f$ threshold. The photon energies for each spectrum are also shown. The overall energy resolution is about 100 meV.

contribute substantially to higher values of $T_K$, which happens for all the other Ce $3d$ transition-metals compounds.[1] Furthermore, the Cu neighbors in CeCu$_6$ have approximately the same distance as in Cu metal,[22] which has a calculated $d$ occupancy of 9.91.[23] It is therefore interesting to ask if a residual $d$-$f$ mixing could result in a strengthening of the overall hybridization. With this work we intend to give a spectroscopic answer to this problem by comparing CeCu$_6$ with an isostoichiometric compound, CeB$_6$, which has a pure $sp$-$f$ mixing in the valence band.

Single crystals of CeB$_6$ and CeCu$_6$ were grown by the floating-zone method[20] and Czochralski method,[18] respectively. CeB$_6$ has a LaB$_6$ crystal structure while CeCu$_6$ is orthorhombic, and both were oriented to expose the (110) surface. Fresh surfaces are obtained *in situ* by scraping with a diamond file in ultrahigh vacuum conditions (UHV) at a base pressure in the $10^{-11}$-mbar range. The samples were continuously cooled at liquid N$_2$ during both the surface scraping and measurements, in order to avoid surface contamination due to the segregation of impurities from the bulk.

Figure 1 displays the photoemission spectra across the Ce $4d$-$4f$ threshold for CeB$_6$ (left panel) and CeCu$_6$ (right panel). In the case of CeB$_6$ a strong enhancement across the threshold is clearly visible and can be easily exploited to extract the Ce related spectral weight in the valence band. Two main resonating features can be distinguished: a narrow peak at the Fermi edge ($c$) and a broad feature at about 2–3 eV of binding energy (BE), which can be further resolved into a peak and a shoulder ($a$ and $b$). According to the interpretation given by the Anderson single impurity Hamiltonian (AIH) approach,[24] the higher BE feature is assigned to a $4f^0$ final-state configuration. The strong peak at the Fermi level has instead a dominant $4f^1$ final-state character, which reflects the hybridization between the $4f$ orbitals and the delocalized valence states.

In the case of CeCu$_6$, presented in the right panel of Fig. 1, all the spectra are dominated by an intense Cu $3d$ emission, and very weak resonance features from the Ce $4f$ states are seen ($a$ and $c$). This different behavior is easily explained by taking into account the calculated atomic photoemission cross section[25] of Cu $3d$ states, which, once normalized to the sample stoichiometry, is almost two orders of magnitude larger than that of Ce $4f$ at 100 eV of photon energy.

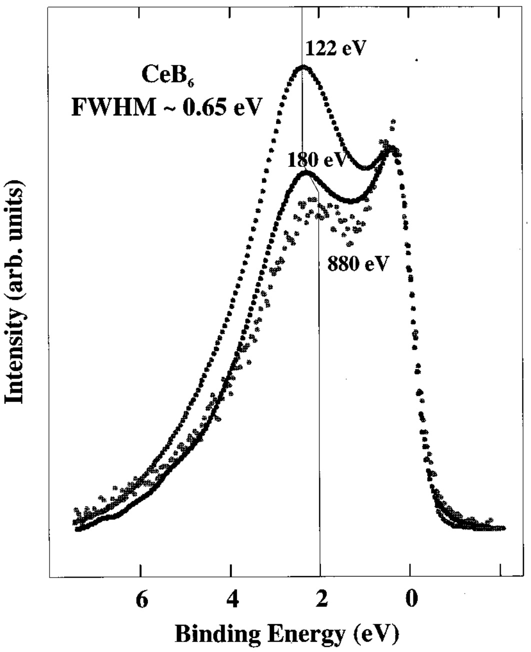

FIG. 2. Evolution of the Ce $4f$ spectral weight in CeB$_6$ from bulk to surface layers: bottom curve (880 eV), bulk sensitive, corresponding to the Ce $3d$-$4f$ threshold; middle curve recorded at a photon energy of 180 eV; upper curve (122 eV), more surface sensitive, corresponding to the Ce $4d$-$4f$ threshold.

The evolution of the $4f$ spectral weight in CeB$_6$, on going from the bulk to the surface layers, is illustrated in Fig. 2, where three VB measurements with different degrees of surface sensitivity are compared. The lower curve is the difference between spectral on- and off-resonance conditions, respectively, at the Ce $3d$-$4f$ threshold (882–875 eV). The middle curve corresponds to a photoemission spectrum excited by 180-eV energy photons. In this photon energy range the Ce $4f$ cross section is dominant and therefore this spectrum can be considered as representative of the Ce $4f$ spectral weight.[25] The upper curve is the difference spectrum (122–114 eV) at the Ce $4d$-$4f$ threshold. All three curves have been background subtracted, and the last two convoluted with a Gaussian function to achieve the same energy resolution as the first curve. The estimated electron mean free paths[26] are 17, 5.7, and 4.5 Å, respectively, for the three curves and therefore the evolution of the $4f$ states from bulk (bottom curve) to surface (top) can be followed. The first evidence is a shift of about 0.3 eV for the center of gravity of the $f^0$ peak to higher energy on going from bulk to surface sensitive spectra, which is consistent with the separation of features $a$ and $b$ in the left panel of Fig. 1 (0.6 eV). This suggests the assignment of $a$ and $b$ to the surface and bulk contributions in the $4f^0$ final state, respectively, as further supported by previous observations of a surface core-level shift in other low-$T_K$ compounds.[27] The second evidence is a

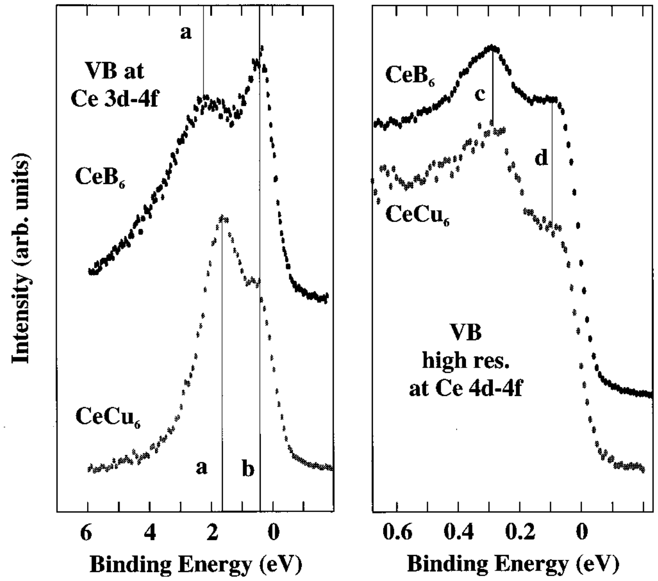

FIG. 3. Left: VB photoemission of $CeB_6$ and $CeCu_6$ at the Ce $3d$-$4f$ threshold (650 meV of energy resolution). Both curves are differences between on (~882 eV) and off-resonance (~875 eV) spectra, and background subtracted. Right: Highly resolved (50 meV of energy resolution) resonant valence-band edges for $CeCu_6$ and $CeB_6$ extracted at Ce $4d$-$4f$ threshold (on-off resonance).

progressive increase of the $f^0/f^1$ intensity ratio on going from bulk to surface, which witnesses the decrease of the surface $4f$ hybridization due to the lowered surface coordination.

In order to exploit the AIH model in the prediction of macroscopic properties connected to the Kondo temperature, the photoemission results for $CeCu_6$ and $CeB_6$ are compared in Fig. 3. In the left panel, the $4f$ spectral weights of the two compounds are plotted, as extracted at the deep Ce $3d$-$4f$ threshold by subtracting the off-resonance spectrum (~875 eV of photon energy) from the on-resonance one (~882 eV), and performing an integral background subtraction. In the right panel the valence-band-edge fine structures are plotted, as extracted at the shallow $4d$-$4f$ threshold (by on-off resonance subtraction). It is noteworthy that, concerning the Ce $4f$ electronic structure, only the measurements at the deep Ce threshold ($3d$-$4f$) allow a straightforward comparison in the full VB region, since the same comparison is somehow hindered at the shallow $4d$-$4f$ threshold by the intense Cu $3d$ signal of $CeCu_6$. Besides, the measurements at the deep threshold are more bulk sensitive, therefore facilitating the comparison with the bulk property measurements, such as the temperature dependence of the electrical resistivity.

In the comparison at the Ce $3d$-$4f$ thresholds (left), the higher $f^0/f^1$ intensity ratio ($a/b$) for $CeCu_6$ should be noted. This, within the framework of the AIH interpretation, would imply a weaker hybridization strength between the $f$ and the valence-band states for $CeCu_6$ as compared to $CeB_6$, since a weaker hybridization would cause a lower intensity for the screened feature ($f^1$) as compared to the unscreened one ($f^0$). Consequently this fact suggests a lower Kondo temperature for $CeCu_6$ than for $CeB_6$.

The highly resolved resonant valence-band edges of $CeB_6$ and $CeCu_6$ are shown in the right panel of Fig. 3. For both spectra two features are clearly resolved: a shoulder at the Fermi edge ($d$) and a peak at about 300 meV of higher binding energy ($c$). These features correspond to the spin-orbit split $4f^1$ final state ($4f_{7/2}$ for feature $c$ and $4f_{5/2}$ for $d$) and their relative intensity ratio ($d/c$) can be used for a qualitative spectroscopic evaluation of the Kondo temperature.[12] As a matter of fact, while $d$ lies on the tail of the Kondo resonance, located above the Fermi level for Ce compounds and originating from the mixing between $f$ and VB states, $c$ is too far in energy to be affected by the Kondo peak spectral intensity. Therefore the spectroscopic ratio $d/c$ reflects indirectly the hybridization strength, and therefore $T_K$. In analogy with the conclusion drawn from the left panel of Fig. 3, also starting from the highly resolved valence-band edges it is possible to assess a higher hybridization for $CeB_6$ as compared to $CeCu_6$, since the near edge feature ($d$) is more intense for the former than for the latter.

These results seem to discard the possibility of a significant $d$-$f$ hybridization in $CeCu_6$, as originally postulated. To confirm even further this conclusion we performed VB photoemission measurements at the Cu $2p$-$3d$ absorption threshold, finding no visible enhancement in the VB region, substantially implying a filled Cu $3d$ shell in the ground state. Therefore a slightly lower $T_K$ value for $CeCu_6$ as compared to $CeB_6$ should instead be attributed to a less efficient mixing of the Cu $4s$ state with Ce $4f$ states, as compared to the B $2sp$–Ce $4f$ mixing, because of crystallographic considerations. Actually the Ce ion in $CeB_6$ is surrounded by 24 first neighbors at a distance of 3.04 Å, while in the orthorhombic structure of $CeCu_6$ there is a cage of 19 Cu ions surrounding the Ce ion at an average distance of 3.15 Å. Therefore, both for the higher coordination number and the lower distance, the $sp$-$f$ mixing is expected to be stronger in $CeB_6$ than in $CeCu_6$.

In conclusion, the controversial AIH model allows a qualitative interpretation of the photoemission measurements of $CeB_6$ and $CeCu_6$ in a consistent way: both VB results at the Ce $3d$-$4f$ absorption threshold and highly resolved VB edges at the Ce $4d$-$4f$ threshold concur in attributing a slightly stronger hybridization between $4f$ and delocalized valence states for $CeB_6$, and discard the possibility of a strong $d$-$f$ mixing in $CeCu_6$.

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