PHYSICAL REVIEW B, VOLUME 64, 075119

# Electronic structure and the x-ray photoemission spectrum of the Kondo-dense compound $UCu_5Al$

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(Received 21 November 2000; published 31 July 2001)

$UCu_5Al$ belongs to a class of Kondo-dense compounds. The electronic structure has been studied by combining x-ray photoemission spectroscopy results with those obtained in the band structure calculation. The latter was carried out by using the tight-binding linear muffin-tin orbital method in the atomic sphere approximation. Reasonable agreement between the experimental and calculated data has been achieved. A complex satellite structure observed in the core-level spectra may suggest that the uranium atoms have some mixed valence character, as is the case of other uranium heavy fermion systems.

DOI: 10.1103/PhysRevB.64.075119 PACS number(s): 71.20.−b, 82.80.Pv

## I. INTRODUCTION

Uranium intermetallic compounds, especially those containing a transition metal $T$ and a $p$-metal $M$, form an interesting class of materials. In recent two decades they attracted particular interest because of their frequent anomalous behavior at low temperatures, mainly caused by the simultaneous occurrence of the magnetically ordered (MO) state together with heavy fermion and sometimes even with superconducting states. In such materials the uranium $5f$ electrons are a subject of large hybridization with the $U(6d)$ and *spd* valence-conduction electrons contributed by the other atoms. Thus, this kind of interactions may lead to exotic many-body phenomena such as the Kondo lattice (KL) and heavy fermion (HF) behavior.[1,2] The hybridization is particularly strong because of the large extension of the $5f$ radial wave functions comparing to that of $4f$ electrons of rare earth atoms. This special nature of the $5f$ electrons is also reflected in their strong interactions with the surrounding ligands creating crystal field potential. All these circumstances lead to a less or more extended delocalization of these electrons which is realized by forming the $f$-originating narrow bands near the Fermi energy $E_F$. The width of the $5f$ band, being usually intermediate between those in the $3d$- and $4f$-electron systems is attributed to the degree of the $5f$-electron delocalization. The bands located approximately around 0.6 eV below $E_F$ can be considered as quasilocalized states. However, for quite a number of uranium intermetallics, it has been found that the $5f$ electrons are really neither localized nor they are fully delocalized. For the fully itinerant $5f$ electrons the spin orbit coupling interaction has the same order of magnitude as the width of the $5f$ band, which means that we deal also here with usually large orbital magnetic moment but antiparallel oriented to the spin one. Moreover, in some heavy-fermion systems a dual nature model, i.e., the presence of itinerant and localized $5f$ electrons in the band structure of strongly correlated f electrons has been considered in recent years.[3] Such an approach with some success has been made, e.g., for the superconducting, antiferromagnetic HF system $UPd_2Al_3$,[4] where the $5f$ itinerant states are responsible for the former properties while the $5f$ localized states for the latter ones.

Experimentally, the $5f$ states in great variety of actinide intermetallics have been probed by different techniques. Among others, UPS and XPS measurements are now among the most powerful methods which offer information on the DOS of occupied states as well as about high-binding-energy core levels. Surprisingly, the recently experimentally observed dispersion of the $U(5f)$ states has been first of all attributed rather to the direct $f$-$f$ interaction (such overlap of the $5f$ wave functions concerns rather small distant uranium atoms occurring rather in metallic uranium) than to the hybridization between the $f$ and $d$ orbitals.[5] Hence in many cases of uranium intermetallics the $5f$ bands are dispersionless. To clarify the situation it is important to obtain more information about the electronic structures of such uranium materials, particularly to establish the partial density of states (DOS) of the $5f$ electrons and compare it with the experimental data, as for example are provided by photoemission (PE) measurements. Note that the hybridization effects in PE measurements are usually reflected by satellite structures of the $4f$-core-electron spectra.

In our study to establish a model which can account for the experimental facts we have chosen first the newly discovered medium HF system, namely the uranium ternary compound $UCu_5Al$, crystallizing in its own tetragonal structure.[6] A linear coefficient of specific heat $\gamma$ is $170\ \mathrm{mJ/K^2\ mole}$.[7] A large anisotropy of susceptibility even in the paramagnetic state[8] indicates large interactions of the $5f$ electrons in this ternary compound with crystal electric field of surrounding atoms. A notable feature is a peculiar magnetic structure of this compound observed by neutron diffraction measurements. Below $T_N$ (18 K) $UCu_5Al$ orders in sine-modulated structure along the $c$ axis with an incommensurate propagation vector $\vec{k}=[0,0,0.55]$.[6]

Up to now the electronic structure for only a few ternary uranium compounds containing transition metals have been considered in the literature. The compound $UCu_5Al$ belongs to a family of uranium ternaries with general chemical formula $UCu_5M$, where $M$ in addition to Al stands for In, In-Ga, and Sn,[9] for which we are going to perform systematically both PE experiments and band structure calculations. The Kondo-like behavior of all these ternaries has been documented by numerous experiments.[9] These type ground state properties presented for the $UCu_5M$ family compounds are a result of an interplay of the Kondo effect, crystal field splitting and Ruderman-Kittel-Kasuya-Yosida (RKKY)-type exchange interactions.

The paper is organized as follows: First, the sample characterization and the experimental procedure is outlined. Then the band structure calculations are described and the photoemission spectra are calculated. The photoemission spectrum for the broad binding energy range was measured. Attention is paid to analyzing profiles of the core $4f$ lines and to compare the valence spectrum with band structure calculations.

## II. EXPERIMENT

The $UCu_5Al$ sample was obtained by arc melting of the constituent metals in high purity helium atmosphere. The sample was remelted several times and then annealed at 850°C for one week. The x-ray powder diffraction examination showed that the compound was single phase material, crystallizing in the tetragonal system of its own type (space group $I4/mmm$).

The x-ray photoemission (XPS) spectra in a broad range of binding energy (0 – 1300 eV) were obtained with monochromatized Al $K_\alpha$ radiation at room temperature, using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with an energy resolution about 0.3 eV. The Fermi level ($E_F=0$) was referred to the gold $4f$-levels binding energy at 84.0 eV. The emission spectra of the uranium and copper elements were measured after mechanical cleaning in the sample preparation chamber under UHV conditions ($1\times10^{-9}$ Torr) and then introduced into spectrometer ($5\times10^{-10}$ Torr). Each spectrum of the $UCu_5Al$ was measured immediately after breaking the sample in vacuum of $5\times10^{-10}$ Torr. The oxidation of the sample was checked by observing the O($1s$) spectra before and after each measurement. All core-level and valence band spectra of the $UCu_5Al$ sample were measured with the aquisition time about 5 min and we had not observed the oxidation effect during that time.

## III. COMPUTATIONAL METHOD

The electronic structure was calculated based on the tight-binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA).[10,11] The calculations were performed without spin polarization because of the low $T_N=25$ K and the XPS measurements made at room temperature only. In the ASA the unit cell is filled by Wigner-Seitz spheres having the same total volume

TABLE I. The crystallographic characteristics of the $UCu_5Al$ compound, and positions of atoms as reported in Ref. 6.

| Atoms (positions) | $X$/a | $Y$/b | $Z$/c | Wigner-Seitz radii [a.u.] |
|---|---|---|---|---|
| U($b$) | 0 | 0 | 0.5 | 3.59072 |
| Cu($h$) | 0.1908 | 0.1908 | 0 | 2.65677 |
| Cu($d$) | 0.5 | 0 | 0.25 | 2.61198 |
| Al($d$) | 0 | 0.5 | 0.25 | 2.90727 |

$$\frac{4}{3}\pi\sum_{j=1}^{N} S_j^3=V,$$

where $j$ is the index of atom in the unit cell, $N$ is number of atoms in the cell, $S_j$ is the Wigner-Seitz radius of the $j$th atom and $V$ is the volume of the unit cell. In our case the unit cell contains one formula unit ($N=7$ atoms). The tetragonal unit cell as depicted in Fig. 2 of Ref. 6 was used in the computations. The coordinates of the atoms in the unit cell were taken from Ref. 6 and are summarized in Table I. The overlap volume of the muffin-tin spheres is about 8.1%. The standard combined corrections[10] for overlapping were used to compensate for errors due to the ASA. The scalar relativistic approximation for band electrons and the fully relativistic treatment for the frozen core electrons were used. The spin-orbit interactions were taken into account in the form proposed by Min and Jang.[12] The exchange correlation potential was assumed in the form proposed by Perdew *et al.*[13] with nonlocal corrections. The starting atomic configurations were taken as core $+6p^65f^36d^17s^2$ for U, core $+3d^{10}4s^1$ for Cu, and core $+3s^23p^1$ for Al atom. The experimental values of the lattice parameters, as given in Ref. 6 were used in the calculations. The crystallographic characteristics are collected in Table I. The self-consistent calculations were performed for 1116 $k$ points in the irreducible wedge of the Brillouin zone. The tetrahedron method[14–16] was used for integration over the Brillouin zone. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps were the same within an error 0.01 mRy.

To confirm the band structure calculations, the valence band XPS spectrum was measured and compared with computed photoemission spectra (PES). The method used here consists of weighting the density of states (DOS) with appropriate atomic cross sections ($c_{i,l}$) for photon scattering[17] and applying a convolution with a Gaussian function which accounts for a finite experimental resolution $\delta$. In our case the photon energy is equal to 1486.6 eV (Al $K_\alpha$ source) and the parameter $\delta=0.3$ eV is equal to the experimental resolution.

## IV. RESULTS AND DISCUSSION

The calculated electronic band structure, summarized in the DOS plots in Fig. 1, is characterized by the three distinct features: (i) the band of width of an order of 1 eV from the

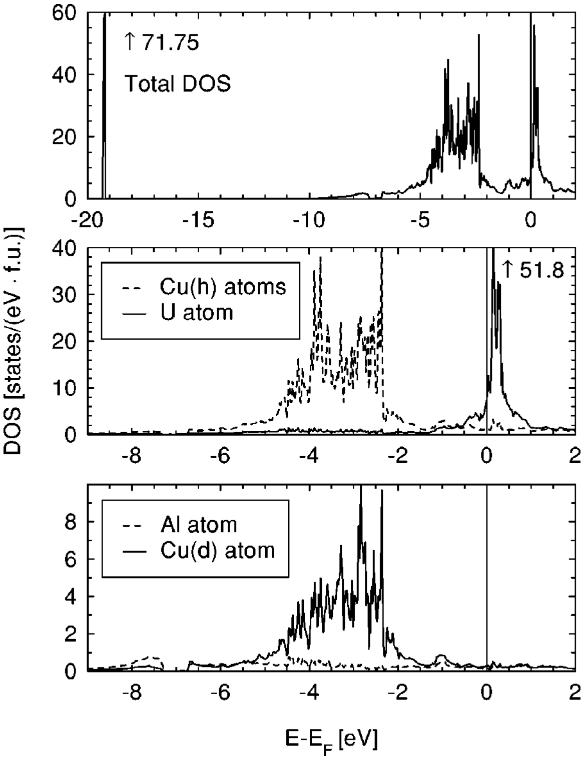

FIG. 1. The total and local DOS plots for $UCu_5Al$. Arrows indicate the heights of peaks, which run out of scale. Note the change of scale in the middle and the bottom panels made to visualize clearly details, especially the spin-orbit splitting of the *f* band from U.

$5f$-derived electrons from U, lying mostly above the Fermi level $E_F$, (ii) the band of width of an order of 3 eV dominated by the $3d$-derived electrons from Cu, and, finally, (iii) by a narrow sharp peak from the $6p$ electrons of U. The two latter lying below the $E_F$.

These features are well reproduced by the measured XPS spectra. The Cu atoms in the two nonequivalent positions ("*d*" and "*h*") provide contributions to the DOS with slightly different structure but with the same overall band width and positions, as depicted in Fig. 1. Because of hybridization the peak located about 19 eV below $E_F$ does not have a pure *p* character but represents a mixture of *s* states [$\sim$0.9%, mainly from Cu($h$) atoms], *p* states ($\sim$98.1%, mainly from U atoms), and finally *d* states [$\sim$1%, mainly from Cu($h$) atoms]. Contribution of the Al and Cu($d$) atoms to this peak is negligible. The Al atoms change the DOS in the energy range between about $-10$ eV and the Fermi level. They facilitate hybridization because the Al($3p$) electrons enhance overlapping of the wave functions. The Cu atoms introduce only one *s*-symmetry electron to the valence band, and the *d* band is almost completely filled ($\sim$9.5 electrons) and is localized well below $E_F$ with the center of gravity located about 3 eV below the Fermi level. The symmetry of Al($3p$) electrons is important because of large distance between the U atoms (about 5 Å compared to only $\sim$2.8 Å in the case of $\alpha$-U). This observation is supported by our electronic structure calculations (unpublished) for hypothetical compounds $UCu_6$ and $UCu_4Al_2$ with an assumed crystallographic structure identical to the one of $UCu_5Al$. The results showed that adding one more Al atom causes broadening of the DOS peak for the U($5f$) electrons which are responsible for the onset of magnetic ordering.

Detailed information on the DOS at the Fermi level and the integrated number of electrons up to the Fermi level is provided in Table II. The total DOS at the Fermi level is equal to 9.141 states/(eV f.u.). The uranium atoms provide the main contribution to the total DOS at the Fermi level, i.e., about 82% while the *f* electrons themselves contribute 79%. The *f* electrons form a band containing about 3.15 electrons with the center of gravity lying 0.23 eV above $E_F$. Occupations of electrons for U and Cu($h$) atoms are enhanced because of charge transfer from the Cu($d$) and Al atoms. Comparing the measured value of the linear electronic specific heat parameter $\gamma$(170 mJ/K$^2$ mol)[6] and the value obtained from our band structure calculations $\gamma_0$(21.5 mJ/K$^2$ mol) one can calculate the ratio $\gamma/\gamma_0$, the value of which was found to be 7.91. This can be compared with a remarkable enhancement of the specific heat coefficient in $UPt_3$, where $\gamma/\gamma_0 \approx 24$.[18] It is well known that if the Fermi surface topology of many uranium compounds can be provided by the LDA band calculations, the large $\gamma_0$ enhancement can not be explained within the LDA approach due to a strong correlation among the U($5f$) electrons.

The XPS spectrum for valence band (VB) of the compound $UCu_5Al$ (Fig. 2, middle panel), is compared in the same figure (the lowest panel) with the corresponding spectra for pure (orthorhombic) U and (fcc) Cu. All spectra are normalized to the maximum intensity. The peak at about 5 eV for pure U is enhanced by the unavoidable presence of oxygen. The VB spectrum of $UCu_5Al$ clearly shows the resemblance to a superposition of those for pure Cu and U metal. Due to the hybridization of U($5f$) electrons with the Cu(3d) and spd valence electrons a band about 6 eV wide is

TABLE II. Partial density of states (DOS) [states/(eV f.u.)] and the number of states (NOS) [electrons/atom] at the Fermi level calculated for the $UCu_5Al$ compound. Total DOS ($E_F$)=9.141.

| Atoms | *s* electrons | | *p* electrons | | *d* electrons | | *f* electrons | |
|---|---|---|---|---|---|---|---|---|
| (positions) | NOS | DOS | NOS | DOS | NOS | DOS | NOS | DOS |
| U($b$) | 0.5821 | 0.0237 | 6.1777 | 0.0249 | 2.1651 | 0.2160 | 3.1487 | 7.2435 |
| Cu($h$) | 0.7689 | 0.1269 | 0.7677 | 0.5317 | 9.4947 | 0.5600 | | |
| Cu($d$) | 0.6871 | 0.0173 | 0.7547 | 0.0576 | 9.4987 | 0.2001 | | |
| Al($d$) | 1.0735 | 0.0156 | 1.5722 | 0.0949 | 0.2152 | 0.0289 | | |

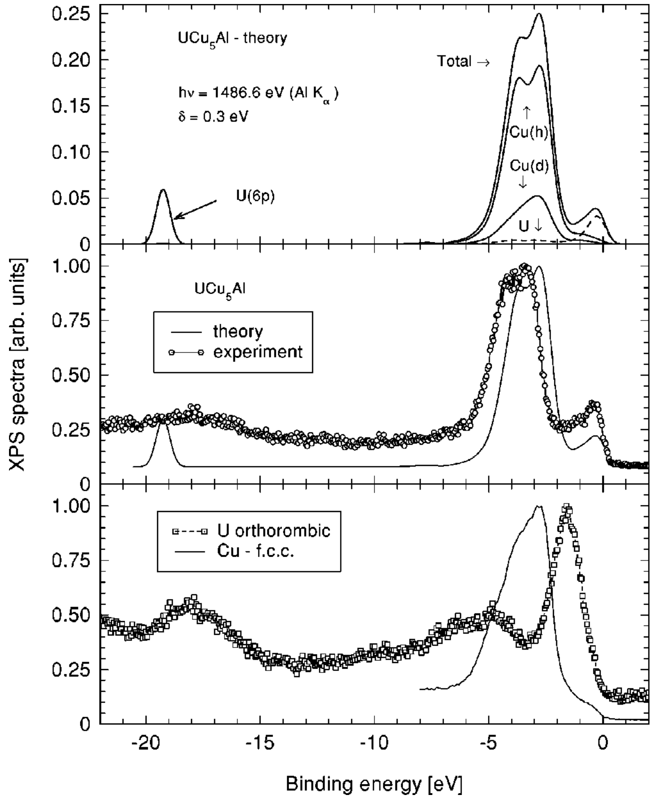

FIG. 2. The calculated photoemission spectra (total and local contributions) for $UCu_5Al$ (the uppermost panel); experimental Al $K_\alpha$ XPS spectrum of the valence band for $UCu_5Al$ (middle panel) and the reference spectra for pure metals of fcc. Cu and orthorhombic U (the lowest panel).

formed. The position of the maximum in the VB spectrum of $UCu_5Al$ is shifted by 0.45 eV in the binding energy as compared to the VB of pure Cu. The band of width of an order of 1 eV from U($5f$) derived electrons is lying predominantly above the Fermi level while the occupied part, contributing to XPS, gives rise to the maximum at about $-0.33$ eV.

Figure 3 shows the U($4f$) core-level spectrum of $UCu_5Al$ and its decomposition. The background is subtracted by the Tougaard method.[19] The spectrum shows an 11-eV spin-orbit splitting corresponding to the $4f_{7/2}$ and $4f_{5/2}$ components and each of them consists of a dominant asymmetric line and two broad satellites at higher binding energy sides. The position of the one of the satellites, which is symmetric, is 7.3 eV higher in the binding energy. The structure consisting of the main line and this 7 eV satellite has been observed in the XPS core-level spectra of a number of binary uranium intermetallic compounds.[20] The only observed difference in the core level spectra between various binary intermetallic uranium compounds is the occurrence of the different degree of asymmetry of the main lines and the difference in the intensity of the 7-eV satellite. An origin of the large asymmetry of the main line has been frequently referred to the screening of the core-hole potential by neighboring U($5f$) electrons.[21,22] This leads to the conclusion that the main line is more asymmetric and the intensity of a broad 7.3 eV satellite is larger for more localized $5f$ system, i.e., for the case with smaller $f$-ligand hybridization. In our work we have observed additional asymmetric satellites at about 3 eV in higher binding energy with respect to the main lines. The shape of these asymmetric lines was fitted according to the Sunjič-Doniach theory,[23] where the asymmetry of the line is described by the singularity index $\alpha$, which is a function of angular-dependent partial screening charges. In turn, the origin of the satellites at about 3 eV higher binding energy is not yet quite clear. Similar satellites are also reported in other studies. For example, the presence of symmetric line at about 380 eV is interpreted as due to oxidation, while for the pseudobinary solid solutions $URh_{1-x}Pd_x$ as a result of contribution of the three $5f^2$, $5f^3$, and $5f^4$ final states, which can be attributed to the presence in the initial state of some mixed valence character of uranium atoms with the $5f^2$ and $5f^3$ states.[24] A similar situation was, for example, reported for the heavy fermion ternary system $UM_2Al_3$ ($M=$Ni and Pd).[25] The contribution of the strongly asymmetric 3 eV ($5f^3$) satellite is probably enhanced by slight presence of uranium oxides, which just gives near its position a line but being quite symmetric.[26]

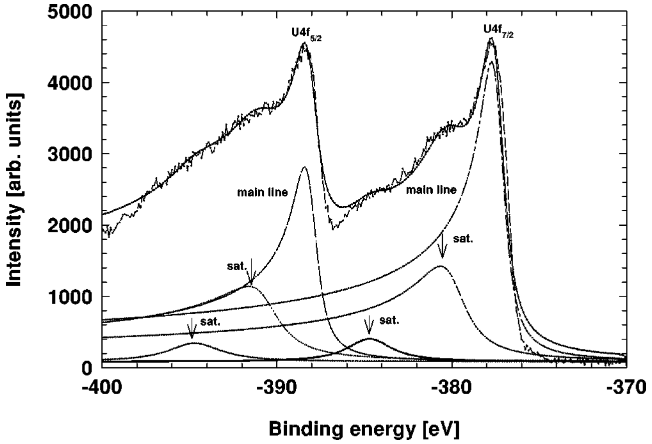

FIG. 3. The U($4f$) core-level spectrum of $UCu_5Al$ with the background subtracted and its decomposition. The structure observed is assigned to the final state $5f^4$, $5f^3$, and $5f^2$ configuration with increasing binding energy.

Finally, the calculated XPS spectrum is presented in Fig. 2 (the uppermost panel), together with the extracted contributions inferred for U and Cu in both crystallographical ($d$ and $h$) sites. There are four Cu atoms at the $h$ sites, whereas only one at the $d$ site what explains the differences in their relative contributions. The contribution of Al atoms was not drawn in Fig. 2 because it appeared negligible. This is due to small contribution of Al atoms to the DOS, additionally reduced by small values of cross sections for the Al($s$) and Al($p$) electrons. The agreement with the experimental curve of Fig. 2 is reasonably good.

## V. CONCLUSIONS

It can be concluded that in $UCu_5Al$ the $5f$ electrons are to some extent delocalized due to the $5f$-$3d$ hybridization which especially is reflected in the spectra of core levels. Following conclusions of other authors studying the uranium pseudobinary and ternary alloys containing also the transition metal, the three peak structure of the latter may suggest some mixed valence character of the initial state in $UCu_5Al$. Furthermore, the XPS valence band of $UCu_5Al$ is quite well reproduced by the one-electron band structure calculations which have been done within the density functional theory. The enhancement of parameters depending on the density of states at the Fermi level is moderate thus implying a moderate role of many body effects.

## ACKNOWLEDGMENTS

A.S. and J.M. thank Dr. L. Smardz for useful discussions on experimental aspects of XPS spectrum. The part of A.S. and J.M. was supported by the KBN Grant No. 2P03B 118 14, whereas that of R.T. by Grant No. 2P03B 150 17. The band calculations were performed in the Supercomputer and Networking Center in Poznań (PCSS).

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