Electronic structure of cage-type ternaries ARu_2Al_{10} – Theory and XPS experiment (A = Ce and U)

M. Samsel-Czekała [a], E. Talik [b], M. Pasturel [c], R. Troć [a,*]

[a] W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-422 Wrocław, Poland
[b] A. Chełkowski Institute of Physics, University of Silesia, ul. Uniwersytecka 4, Katowice 40-007, Poland
[c] Institut des Sciences Chimiques de Rennes, Université Rennes 1, UMR CNRS 6226, Campus de Beaulieu, 263 Av. Général Leclerc, 35042 Rennes Cedex, France

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ABSTRACT

The electronic structure of the isomorphic, orthorhombic URu_2Al_{10} and $CeRu_2Al_{10}$ aluminides have been studied by X-ray photoelectron spectroscopy (XPS) and *ab initio* calculations using the fully relativistic full-potential local-orbital (FPLO) method within the local density approximation (LDA). The calculated data of the former system revealed fairly sharp triple-peaks of the U $5f$ states around the Fermi level (E_F) and a large broad contribution from the Ru $4d$ states expanded from E_F to about 6.5 eV of binding energy. Although the size and positions of the Ru $4d$ bands for the latter compound are quite similar to those of the U-based one, the double Ce $4f$ sharp peaks are placed almost completely above E_F underlying their mostly localized character. We have also analyzed the Fermi surfaces (FSs) in these two aluminides. The calculated results of both ternaries were then compared with our experimental XPS data for URu_2Al_{10} and with such data for $CeRu_2Al_{10}$ available in the literature. The results are in fairly good agreement between the theory and experiment. Especially, the fact that the spectrum weight of the Ce $4f$ electrons below E_F turned out to be very much reduced, reflecting rather a small f–c hybridization of these electrons compared to considerably larger one in the U-based compound.

1. Introduction

The discovered in 1998 large group of ternary intermetallic compounds RT_2Al_{10}, where R is a rare earth element and T is Fe, Ru and Os, unexpectedly adopt the orthorhombic crystal structure of the $YbFe_2Al_{10}$ – type (*Cmcm*, $Z = 4$) [1] instead of a well known tetragonal $ThMn_{12}$–type (see Ref. [2] for a discussion). The distinctive feature of this orthorhombic structure is a cage type of the atom coordination around the centered R atom composed of 16 Al and 4 T atoms. In turn, the T-icosahedron consists of 10 Al and two R atoms. In this structure the nearest distance between R atoms, $d_{R–R}$ is even larger than 0.5 nm. This makes that any magnetic order induced by the Rudermann–Kittel–Kasuya–Yoshida (RKKY) interaction is possible only at very low temperatures. For example, the isostructural to Ce-counterparts $Nd(Ru;Os)_2Al_{10}$ having similar cation–cation separations order antiferromagnetically, but only below $T_N = 2.5$ K [3]. However it turned out that among these ternaries, $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$ have anomalous second order antiferromagnetic phase transitions, namely at 27.3 and 28.7 K, respectively [4,5]. This quite unexpected behavior has been then confirmed by neutron diffraction and muon spin relaxation experiments [6–8]. Recently the two isostructural uranium ter-

naries UFe_2Al_{10} [9] and URu_2Al_{10} [10] have been synthesized and their cage-type structure refined. In contrast to the aforementioned Ce-based ternaries, they are non-magnetically ordered compounds down to 2 K in similar way to $CeFe_2Al_{10}$ [8,11]. The latter is well-determined a valence fluctuation compound (see Ref. [7]) due to the largest $4f$-conduction electron (f–c) hybridization in the whole CeT_2Al_{10} group. Moreover, this compound is treated as a classical Kondo-semiconductor. Contrastingly, $CeRu_2Al_{10}$, is metallic at low temperatures [4,12]. Likely, the striking feature of the U-based compounds is a strong hybridization existing between their mostly localized f- and mostly itinerant d-electrons, which emerges from their specific electronic structure around the Fermi energy (E_F), as we will discuss below. Thus, this feature in the case of URu_2Al_{10} leads to the occurrence of mixed-valence properties [10], confirmed by both the observed tendency to form a maximum in the susceptibility at about 50 K and the electrical resistivity that changes with temperature in the expected way, i.e., as a S-shaped curve. In addition, the large positive values of the transverse magnetoresistivity observed at low temperatures differentiate this system from any magnetic fluctuators. Nevertheless, the further studies, as inelastic neutron scattering are needed to finally rule out also possible here a spin fluctuation effect (see Ref. [10] for discussion).

Very recently the optical conductivity spectra, Ce $3d$ XPS measurements and LDA band-structure calculations [13] have shown

* Corresponding author. Tel.: +48 71 3954 206; fax. +48 71 344 10 29.
E-mail address: R.Troc@int.pan.wroc.pl (R. Troć).

that the anisotropic electronic structure is responsible for the AFM transition in both $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$. Next, it was found for the Ru- and Os-based aluminides that their electronic structure can be characterized by a rather weak one-dimensional f–c hybridization between Ce–$4f$ and conduction states along the b axis, and stronger two-dimensional hybridization in the ac plane, which thus causes the occurrence of charge density wave (CDW) instability, slightly above T_0 [13]. Thus, this kind of instability is responsible for inducing the AFM ordering with a possible spin density wave (SDW) character with such high transition temperatures, while an usual RKKY interaction would lead to the magnetic phase transition not higher than around 2 K with respect to quite large $d_{Ce–Ce}$ = 0.52 nm. Hence, $CeRu_2Al_{10}$ has been classified as a system with the antiferromagnetically arranged magnetic moments being coupled linearly along the c axis with rather small magnitude of ordered moment [7]. Alternatively, Kondo et al. [14] pointed out that this type of AFM order may be explained also by strong coupling between spin and charge degrees of electron freedom. Moreover, these authors have observed the Shubnikov-de Haas (SdH) oscillations in this system. Thus, this is direct evidence of the existence of the Fermi surface in such a material [15]. The problem of magnetic state and electronic structure in $CeRu_2Al_{10}$ has been considered quite recently by Goraus and Ślebarski [16]. Their use of the LSDA + U approach with a small U value stabilizes an AFM state, otherwise for large U, the ferromagnetic ground state is preferred. Moreover, the performed structure relaxation of atomic positions with the $Cmcm$ unit cell gave rise to noticeable displacement of the Al atoms in the unit cell (u.c.). The authors except for valence band (VB) spectra also carried out the analysis of a f–c hybridization, based on deconvolution of the measured Ce $3d$ XPS spectra. This analysis gave a moderate change in a value of the Ce valence of about 3.05 at room temperature (RT) and small hybridization energy Δ of about 60 meV [16].

In this paper, we present the results of band structure calculations for both $(U;Ce)Ru_2Al_{10}$, containing also topology of the Fermi surfaces, and XPS spectra in the non-magnetic state to recognize in greater detail the electronic structure of the above two intriguing ternary aluminides. We focus also on the Ru bands in these two aluminides. The electronic structures determined by us for both these ternaries were then employed in an interpretation of our XPS experimental data for URu_2Al_{10}, but in the case of $CeRu_2Al_{10}$, the valence band XPS data were taken from Ref. [16]. Despite the specific cage-type crystal structure of these ternaries and similar large interatomic $d_{U–U}$ and $d_{Ce–Ce}$ distances (exceeding 0.5 nm), these two species show, however, different and highly intriguing physical properties.

2. Experimental

To carry out an XPS experiment, we have synthesized both single-crystalline and polycrystalline samples. The single crystals of URu_2Al_{10} were prepared by an Al flux method. Unfortunately, the obtained single-crystals were extremely brittle and, hence, very difficult in handling. The polycrystalline sample of URu_2Al_{10} was prepared by melting constituents in an arc furnace under Ti–Zr gettered argon atmosphere. The purity (in wt.%) of elements was: U (99.98), Ru (99.9) and Al (99.999). The sample was remelted several times to improve homogeneity and annealed at 800 °C for one week. The X-ray pattern showed no evidence of any foreign phases. The lattice parameters were close to those given in Ref. [10].

The XPS spectrum of URu_2Al_{10} was collected in a broad range of 0–1400 eV binding energy (BE) with monochromatized Al K$_\alpha$, $h\nu$ = 1486.6 eV, radiation taken at room temperature (RT) using a PHI 5700 ESCA spectrometer. The small single crystal of $2 \times 1 \times 1$ mm^2 in size was repeatedly cleaved in situ about every 10 min while the polycrystalline sample in a form of thin stick was broken several times under high vacuum of 5×10^{-10} Torr immediately before taking measurements. The oxygen and carbon contaminations were checked by monitoring the intensity of the O 1s and C 1s photoemission peaks visualized on the total XPS spectrum measured in a wide binding energy range. We found rather negligible contamination of our samples by oxygen and carbon. The latter was in somewhat larger quantity for the polycrystalline sample. The spectrum was referred to gold, to its

$4f$-level binding energy 84.0 eV. The energy spectrum of emitted electrons were analyzed by a hemispherical mirror analyzer with an energy resolution of about 0.3 eV. Both obtained spectra on single-crystalline and polycrystalline materials were very similar to each other exhibiting only slightly worse statistics for the latter sample. Moreover, due to an arc electrode the overview spectrum displayed some distinct presence of C 1s peak especially for the polycrystalline sample.

3. Calculation details

The band structures of URu_2Al_{10} and $CeRu_2Al_{10}$ have been computed by the fully relativistic version of the FPLO method [17]. In this approach all electrons were treated by the 4-component Kohn–Sham–Dirac equation, containing implicitly spin-orbit (SO) coupling up to all orders, and solved self-consistently. The Perdew–Wang parameterization [18] of the LDA exchange-correlation potential was utilized. In the calculations the experimental values of both lattice parameters and the atomic positions in the u.c. of the $Cmcm$-type (Nr. 63) were used for U- and Ce-based compounds from Refs. [10,19], respectively. Except for one position of U or Ce atoms in 4c and Ru atom in 8d, there are five distinctive atomic positions of Al[10], namely Al(1) in 8e, Al(2) and Al(3) in 8f, Al(4) and Al(5) in 8g. Only the Ru and Al(1) atoms have two equivalent nearest-neighbours Ce sites, while the remaining Al(2-5) sites have only one such a U(Ce) site. This makes certain uniqueness of Al(5) site among Al sites in consideration of possible lattice distortion [20]. The position of the central atom in 4c is somewhat special. The U(Ce) atoms in this position form a one dimensional (1D) zig-zag chains with an angle between bonds of 122°. In view of the magnetic exchange interaction just the 1D problem must be taken into account, though the whole structure is 3D.

In our calculations the valence basis sets were used as follows: the U $5s5p5d;6s6p$ (pseudo-core), and $6d;5f;7s7p$ (pure valence) or Ce $4f;5s5p$ (pseudo-core) and $5d;6s6p$ (pure valence); Ru $4s4p$ (pseudo-core) and $4d;5s5p$ (pure valence); Al $2s2p$ (pseudo-core) and $3s3p3d$ (pure valence) states. The size of the k-point mesh in the irreducible wedge of the Brillouin zone (BZ) was $8 \times 8 \times 8$ (105 points). The FPLO method being atomic orbital based, provide the Mulliken decomposition of charges, which is somewhat dependent on the orbitals used.

The band energies, FSs as well as total and partial densities of states (DOS) have been computed per the u.c. The partial DOSs were determined for different atomic sites (in u.c.) or electron orbitals and are presented per formula unit (f.u.). For comparison with the experimental XPS spectra, the corresponding theoretical valence band XPS spectra were calculated for both compounds by the standard procedure. Namely, the partial DOSs for the constituent atoms were multiplied by the respective weight factors proportional to atomic subshell photoionization cross-sections [21]. The outputs were summed up and convoluted with a Gaussian of full width at the half maximum (FWHW) being equal to 0.3 eV to simulate the instrumental energy resolution of the experimental analyzer.

4. Results and discussion

4.1. DOS

The calculated DOS in URu_2Al_{10} and $CeRu_2Al_{10}$ are displayed in Figs. 1 and 2, respectively. As the DOS and FS visualized in Fig. 3(a) indicate, URu_2Al_{10} exhibits a metallic-type behavior in agreement with previous low temperature transport measurements [10]. The three Kramers double-degenerate bands, numbered 345, 347, 349, crossing E$_F$ are dominated by the narrow-peak contributions of the U $5f$ states being strongly hybridized with the U $6d$ and Ru $4d$ as well as the Al $3spd$ states originating from all five aluminum atomic sites in the u.c. It demonstrates that all atoms in the URu_2Al_{10} contribute to the metallic bond. This feature is clearly visible