Core-Level Photoelectron Spectroscopy Study of UTe$_2$

Shin-ichi Fujimori$^{1,4}$, Ikuto Kawasaki$^1$, Yukiharu Takeda$^1$, Hiroshi Yamagami$^{1,2}$, Ai Nakamura$^1$, Yoshiha Homma$^3$, and Dai Aoki$^3$

$^1$Materials Sciences Research Center, Japan Atomic Energy Agency, Sayo, Hyogo 679-5148, Japan
$^2$Department of Physics, Faculty of Science, Kyoto Sangyo University, Kyoto 603-8555, Japan
$^3$Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan

The valence state of UTe$_2$ was studied by core-level photoelectron spectroscopy. The main peak position of the U 4f core-level spectrum of UTe$_2$ coincides with that of UB$_2$, which is an itinerant compound with a nearly 5f$^3$ configuration. However, the main peak of UTe$_2$ is broader than that of UB$_2$, and satellite structures are observed in the higher binding energy side of the main peak, which are characteristics of mixed-valence uranium compounds. These results suggest that the U 5f state in UTe$_2$ is in a mixed valence state with a dominant contribution from the itinerant 5f$^3$ configuration.

The unconventional superconductivity in UTe$_2$ has attracted much attention in recent years. Its electronic structure is essential to understand the origin of its superconductivity, and angle resolved photoelectron spectroscopy (ARPES) has been applied using soft X-ray (SX, hν = 30–150 eV) and vacuum ultraviolet (VUV, hν = 800 eV) synchrotron radiation. However, these two ARPES studies presented contradicting views of the electronic structure of UTe$_2$.

The SX ARPES study concluded that the band-structure calculation treating all U 5f states as valence electrons can explain the overall electronic structure of UTe$_2$ while the VUV ARPES study argued that the near-E$_F$ electronic structure is very similar to that of the band-structure calculation of ThTe$_2$ although there exist heavy bands around the Z point. In addition, the partial U 5f density of states (DOS) obtained by resonant photoelectron spectroscopy (RPES) at the 4d $\sim$ 5f absorption edge (hν = 736 eV) has a dominant sharp peak at the Fermi energy, while the on-resonant RPES spectrum measured at the 5d $\sim$ 5f absorption edge (hν = 98 eV) has a dominant peak at a higher binding energy of E$_B$ $\sim$ 0.7 eV.

To solve this discrepancy, additional electronic structure studies on UTe$_2$ are required. Recently, Thomas et al. reported X-ray absorption spectrum (XAS) of UTe$_2$ under ambient and high pressures. They argued that UTe$_2$ exhibits intermediate valence at ambient pressure, suggesting that the U 5f state in UTe$_2$ is hybridized with the ligand states. In the present study, we further studied the U 5f valence state of UTe$_2$ using core-level spectroscopy, which has the ability to probe the valence state of the local uranium site.

The U 4f spectrum of UTe$_2$ was compared with that of a typical itinerant compound, UB$_2$, and localized compound, UPd$_3$, as well as ferromagnetic superconductors UGe$_2$, UCoGe, URhGe, and UPt$_3$.

Photoemission experiments were conducted on the SX beamline BL23SU at SPring-8. The overall energy resolution in the angle-integrated photoelectron spectroscopy experiment at hν = 800 eV was approximately 140 meV. The kinetic energy of photoelectrons is about 400 eV, which is considered to have enough bulk sensitivity since the U 4f spectra of URu$_2$Si$_2$ measured at hν = 800 eV$^{5,7}$ and hν = 5945 eV$^{9,10}$ are essentially identical. The sample temperature was kept at 20 K for all measurements. Other experimental conditions are described in Ref. 3.

Figure 1 (a) presents a comparison of the U 4f core-level spectra of UB$_2$, UTe$_2$, UGe$_2$, UCoGe, URhGe, UPt$_3$, and UPd$_3$. Their negative second derivatives of U 4f$_{3/2}$ spectra are also provided in Fig. 1 (b) to indicate the locations of peaks in the spectra. Data of UB$_2$, UGe$_2$, UCoGe, URhGe, UPt$_3$, and UPd$_3$ are depicted from Refs 6 and 7. UB$_2$ and UPd$_3$ are typical itinerant and localized compounds, respectively. The band structure and Fermi surface of UB$_2$ are well explained by the band-structure calculation treating all U 5f electrons as itinerant. The occupation number of the U 5f state within the Muffin-Tin sphere is 2.82 in the calculation; thus, the local U 5f electronic configuration of UB$_2$ can be considered the dominant 5f$^3$ configuration. In contrast, UPd$_3$ is a uranium compound with a localized 5f$^2$ configuration.

These spectra all generally consist of a dominant main peak located at E$_B$ = 377 $\pm$ 379 eV and a broad satellite structure distributed at E$_B$ = 381 $\pm$ 387 eV. These complex spectral shape originate from the transition from the ground state to multiple final states with different local U 5f electronic configurations. There are several theoretical models of the origin of the U 4f spectral profiles; however, the quantitative analysis has not yet been established. Nevertheless, dif-
ferent final states have different binding energies, which can be used to identify the local electronic configuration in the ground state. Here, we discuss the electronic structure of UT$_2$ based on a comparison with typical uranium compounds.

The main peak positions of UT$_2$, UGe$_2$, UCd$_2$, and URhGe are almost identical ($E_F = 377 \pm 377.3$ eV), and have a similar asymmetric peak structure with a long tail toward higher binding energies. Their main peak positions are very similar to that of the itinerant U 5f compound UB$_3$ (designated as A in Fig. 1 (b)), and are very different from the spectrum of UPd$_3$ (designated as B in Fig. 1 (b)). This indicates that the dominant final state configurations in UT$_2$ as well as UGe$_2$, UCd$_2$, and URhGe are identical to that of UB$_3$, and the dominant U 5f configurations in the ground states of UT$_2$, UGe$_2$, UCd$_2$, and URhGe are also similar to that of UB$_3$. In contrast, the main peaks of UT$_2$ as well as ferromagnetic superconductors are broader than that of UB$_3$. As seen in the spectrum of UPd$_3$, the main peak consists of two peaks ($E_F = 378.9$ and 377.2 eV), and the broadening in the main peaks of UT$_2$, UGe$_2$, UCd$_2$, and URhGe may originate from a small contribution from the UPd$_3$-type peak on the higher binding energy side of the main peaks, although this has not been resolved experimentally. Moreover, the core-level spectrum of UT$_2$ is accompanied by a satellite, which has been observed in the U 4f core-level spectra of strongly-correlated or localized 5f$^2$ uranium compounds. Thus, these results indicate that the ground state of UT$_2$ is a mixed valence state with a dominant contribution from the 5f$^3$ configuration and some contribution from the 5f$^2$ configuration. These results are consistent with the result of SX-ARPES study\(^3\) and the XAS study.\(^5\) In addition, the core-level spectral shape of UT$_2$ is similar to that of UGe$_2$, UCd$_2$, and URhGe, which have essentially itinerant but correlated U 5f states,\(^7,14,15\) suggesting that UT$_2$ should be similar to them.

Here, we consider the relationship between the present result and the results of other studies on the electronic structure of UT$_2$. In density functional theory (DFT) plus Hubbard U (DFT+U) and generalized gradient approximation plus U (GGA+U) with $U \geq 2$ eV, quasi-two-dimensional Fermi surfaces have been predicted.\(^16,17\) In these calculations, most of the U 5f weight was away from the Fermi level by the introduction of the U, and the topology of the Fermi surface becomes almost identical to that of the DFT calculation for ThTe$_2$. Experimentally, the VUV ARPES study reported very similar near-$E_F$ electronic structure, although the existence of a heavy band around the Z point was claimed.\(^3\) Furthermore, the VUV-RPES spectrum was interpreted based on the ground state with the dominant 5f$^2$ Hund’s rule ground state, which is based on the slightly mixed valent but essentially localized 5f$^3$ state.\(^4\) In such a situation, its core-level spectrum should be similar to those of the localized compound UPd$_3$ or weakly hybridized compound UPt$_3$. However, the present result indicates that the hybridized (itinerant) 5f$^3$ configuration is dominant in the ground state of UT$_2$, and the U 5f states should thus make dominant contributions to the state at the Fermi level. The very different nature of U 5f states observed in the VUV ARPES study may originate from the enhanced surface sensitivity of VUV PES ($\leq 5$ Å) compared with XPS ($\geq 15$ Å), as similar discrepancies have been observed in strongly correlated f-electron materials.\(^7,18,19\)

In summary, we applied core-level spectroscopy to UT$_2$. A comparison between the core-level spectral shape of UT$_2$ and that of typical compounds demonstrated that the local electronic configuration of the U 5f state in UT$_2$ is in the mixed valence state with a dominant contribution from the 5f$^3$ configuration. Furthermore, the spectrum of UT$_2$ is very similar to that of UGe$_2$, UCd$_2$, and URhGe, suggesting that U 5f should essentially have itinerant character, although there exist electron correlation effects. The result indicates that the topology of the Fermi surface of UT$_2$ should be considerably different from the localized model, such as the DFT calculation for ThTe$_2$.

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