Core-Level Photoelectron Spectroscopy Study of UTe_2

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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.[1,2)] 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, $h\nu = 565 - 800$ eV)[3)] and vacuum ultraviolet (VUV, $h\nu = 30 - 150$ eV)[4)] 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 U $5f$ states as valence electrons can explain the overall electronic structure of UTe_2[3)] 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.[4)] In addition, the partial U $5f$ density of states (DOS) obtained by resonant photoelectron spectroscopy (RPES) at the $4d - 5f$ absorption edge ($h\nu = 736$ eV) has a dominant sharp peak at the Fermi energy,[3)] while the on-resonant RPES spectrum measured at the $5d - 5f$ absorption edge ($h\nu = 98$ eV) has a dominant peak at a higher binding energy of $E_B \sim 0.7$ eV.[4)] 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.[5)] 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.[6,7)] 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.[8)] The overall energy resolution in the angle-integrated photoelectron spectroscopy experiments at $h\nu = 800$ 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_2Si_2 measured at $h\nu = 800$ eV[6,7)] and $h\nu = 5945$ eV[9)] are essentially identical. The sample temperature was kept at 20 K for all measurements. Other experimental conditions are described in Ref. 3.

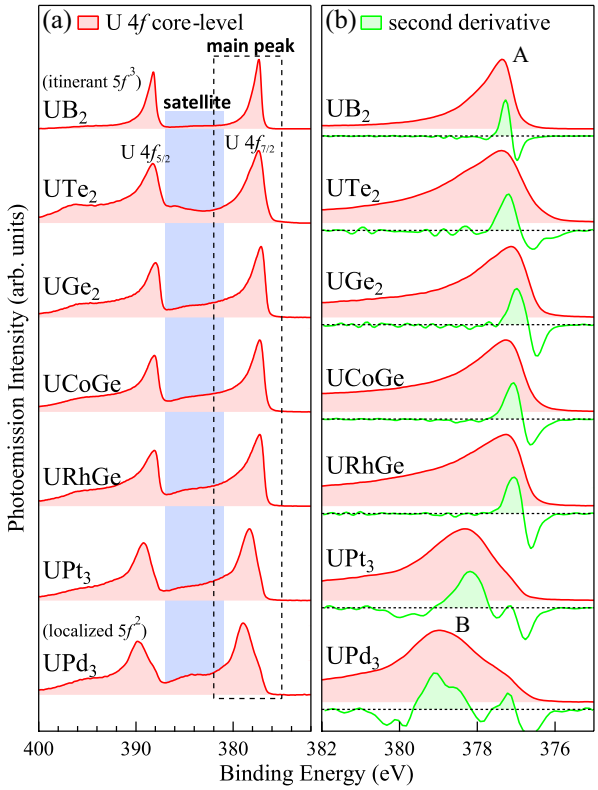

Fig. 1. U $4f$ core-level spectra of UTe_2 and reference compounds. Data of UB_2, UGe_2, UCoGe, URhGe, UPt_3, and UPd_3 are depicted from Refs 6 and 7. (a) U $4f$ core-level spectra of UB_2, UTe_2, UGe_2, UCoGe, URhGe, UPt_3, and UPd_3. (b) Blow up of the main peaks of U $4f_{7/2}$ spectra and their negative second derivatives

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 $4f_{7/2}$ 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.[10)] 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 $E_B = 377 - 379$ eV and a broad satellite structure distributed at $E_B = 381 - 387$ eV. These complex spectral shape originate from the transition from the ground state to multiple final states with different local U $5f$ electronic configurations.[11)] There are several theoretical models of the origin of the U $4f$ spectral profiles;[12,13)] however, the quantitative analysis has not yet been established. Nevertheless, dif-

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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 UTe_2 based on a comparison with typical uranium compounds.

The main peak positions of UTe_2, UGe_2, UCoGe, and URhGe are almost identical (E_B = 377 – 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_2 (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 UTe_2 as well as UGe_2, UCoGe, and URhGe are identical to that of UB_2, and the dominant U $5f$ configurations in the ground states of UTe_2, UGe_2, UCoGe, and URhGe are also similar to that of UB_2. In contrast, the main peaks of UTe_2 as well as ferromagnetic superconductors are broader than that of UB_2. As seen in the spectrum of UPd_3, the main peak consists of two peaks (E_B = 378.9 and 377.2 eV), and the broadening in the main peaks of UTe_2, UGe_2, UCoGe, 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 UTe_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 UTe_2 is a mixed valence state with a dominant contribution from the $5f^3$ configuration and some contribution from the $5f^2$ configuration. These result are consistent with the result of SX-ARPES study[3] and the XAS study.[5] In addition, the core-level spectral shape of UTe_2 is similar to that of UGe_2, UCoGe, and URhGe, which have essentially itinerant but correlated U $5f$ states,[7,14,15] suggesting that UTe_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 UTe_2. In density functional theory (DFT) plus Hubbard U (DFT+U) and generalized gradient approximation plus U (GGA+U) with $U \gtrsim 2$ 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.[4] 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 $5f^2$ state.[4] In such 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 UTe_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 ($\lesssim$ 5 Å) compared with SX-PES ($\gtrsim$ 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 UTe_2. A comparison between the core-level spectral shape of UTe_2 and that of typical compounds demonstrated that the local electronic configuration of the U $5f$ state in UTe_2 is in the mixed valence state with a dominant contribution from the $5f^3$ configuration. Furthermore, the spectrum of UTe_2 is very similar to that of UGe_2, UCoGe, 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 UTe_2 should be considerably different from the localized model, such as the DFT calculation for $ThTe_2$.

Acknowledgment The authors thank A. B. Shick and W. E. Pickett for stimulating discussion. The experiment was performed under Proposal Nos. 2019A3811 at SPring-8 BL23SU. The present work was financially supported by JSPS KAKENHI Grant Numbers JP15H05882, JP15H05884, JP15H05745, JP15K21732, JP16H01084, JP16H04006, JP18K03553, and JP19H00646.

1) S. Ran, C. Eckberg, Q.-P. Ding, Y. Furukawa, T. Metz, S. R. Saha, I.-L. Liu, M. Zic, H. Kim, J. Paglione, and N. P. Butch: Science **365** (2019) 684.
2) D. Aoki, A. Nakamura, F. Honda, D. Li, Y. Homma, Y. Shimizu, Y. J. Sato, G. Knebel, J.-P. Brison, A. Pourret, D. Braithwaite, G. Lapertot, Q. Niu, M. Vališka, H. Harima, and J. Flouquet: J. Phys. Soc. Jpn. **88** (2019) 043702.
3) S.-i. Fujimori, I. Kawasaki, Y. Takeda, H. Yamagami, A. Nakamura, Y. Homma, and D. Aoki: J. Phys. Soc. Jpn. **88** (2019) 103701.
4) L. Miao, S. Liu, Y. Xu, E. C. Kotta, C.-J. Kang, S. Ran, J. Paglione, G. Kotliar, N. P. Butch, J. D. Denlinger, and L. A. Wray: Phys. Rev. Lett. **124** (2020) 076401.
5) S. Thomas, F. Santos, M. Christensen, T. Asaba, F. Ronning, J. Thompson, E. Bauer, R. Fernandes, G. Fabbris, and P. Rosa: arXiv:2005.01659 (2020).
6) S. Fujimori, T. Ohkochi, I. Kawasaki, A. Yasui, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, Y. Tokiwa, S. Ikeda, T. Sugai, H. Ohkuni, N. Kimura, and Y. Ōnuki: J. Phys. Soc. Jpn. **81** (2012) 014703.
7) S.-i. Fujimori, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, and Y. Ōnuki: J. Phys. Soc. Jpn. **85** (2016) 062001.
8) Y. Saitoh, Y. Fukuda, Y. Takeda, H. Yamagami, S. Takahashi, Y. Asano, T. Hara, K. Shirasawa, M. Takeuchi, T. Tanaka, and H. Kitamura: J. Synchrotron Rad. **19** (2012) 388.
9) A. Amorese, M. Sundermann, B. Leedahl, A. Marino, D. Takegami, H. Gretarsson, A. Gloskovskii, C. Schlueter, M. W. Haverkort, Y. Huang, M. Szlawska, D. Kaczorowski, S. Ran, M. B. Maple, E. D. Bauer, A. Leithe-Jasper, P. Hansmann, P. Thalmeier, L. H. Tjeng, and A. Severing: P. Natl. Acad. Sci. U.S.A. **117** (2020) 30220.
10) T. Ohkochi, S.-i. Fujimori, H. Yamagami, T. Okane, Y. Saitoh, A. Fujimori, Y. Haga, E. Yamamoto, and Y. Ōnuki: Phys. Rev. B **78** (2008) 165110.
11) S. Fujimori, Y. Saito, N. Sato, T. Komatsubara, S. Suzuki, S. Sato, and T. Ishii: Solid State Commun. **105** (1998) 185.
12) K. Okada: J. Phys. Soc. Jpn. **68** (1999) 752.
13) G. Zwicknagl: Phys. Status Solidi B **250** (2013) 634.
14) S.-i. Fujimori, I. Kawasaki, A. Yasui, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, and Y. Ōnuki: Phys. Rev. B **89** (2014) 104518.
15) S. Fujimori, T. Ohkochi, I. Kawasaki, A. Yasui, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, and Y. Ōnuki: Phys. Rev. B **91** (2015) 174503.
16) Y. Xu, Y. Sheng, and Y.-f. Yang: Phys. Rev. Lett. **123** (2019) 217002.
17) J. Ishizuka, S. Sumita, A. Daido, and Y. Yanase: Phys. Rev. Lett. **123** (2019) 217001.
18) Y. Takeda, T. Okane, T. Ohkochi, Y. Saitoh, H. Yamagami, A. Fujimori, and A. Ochiai: Phys. Rev. B **80** (2009) 161101.
19) S.-i. Fujimori: J. Phys. Condens. Matter **28** (2016) 153002.