Photoemission Evidence for Valence Fluctuations and Kondo Resonance in YbAl$_2$

Masaharu Matsunami$^{1,2,*}$, Ashish Chainani$^2$, Munetaka Taguchi$^2$, Ritsuko Eguchi$^{2,1}$, Yasutaka Takata$^2$, Masaki Oura$^2$, Makina Yabashi$^2$, Kenji Tamasaki$^2$, Yoshinori Nishino$^{2,1}$, Tetsuya Ishikawa$^2$, Masashi Kosaka$^3$, and Shik Shin$^{1,2,4}$

$^1$Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
$^2$RIKEN SPring-8 Center, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan
$^3$Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan
$^4$Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST), Chiyoda-ku, Tokyo 102-0075, Japan

We use hard x-ray photoemission spectroscopy (HAXPES) to investigate the electronic structure of YbAl$_2$, for which the Yb valence has not been consistently reported to date. The bulk sensitivity and the analytical simplicity provided by the Yb 3$d$ core-level HAXPES allow a reliable determination of the mean valence of Yb ions. For YbAl$_2$, it is evaluated to be +2.20, which remains nearly unchanged below 300 K. The Kondo resonance peak with an extremely high Kondo temperature (above 2000 K) is clearly identified in the valence-band spectra. The results indicate that a coherent Kondo state can be robust even in a nearly divalent system.

KEYWORDS: YbAl$_2$, valence fluctuation, photoemission spectroscopy, HAXPES

For a long time, rare-earth intermetallic compounds have attracted much attention, since they exhibit a wide variety of strongly correlated electronic phenomena associated with the valence instability of these rare-earth ions. Recently, the concept of valence fluctuations has received renewed interest in relation to the unconventional quantum critical phenomena, particularly for Yb-based compounds such as YbRh$_2$Si$_2$ or $\beta$-YbAlB$_4$. Theoretically, the role of the critical valence fluctuations has been invoked to explain their properties. The importance of critical valence fluctuations provides us with an opportunity to reexamine the valence fluctuation phenomena. Experimentally, the most fundamental issue is to precisely determine the mean valence, which is a measure of the $f$-electron occupation and localization.

Hard x-ray photoemission spectroscopy (HAXPES) with an excitation energy of 5–8 keV is one of the best-suited techniques. Apart from the well-known bulk sensitivity, HAXPES can probe the Yb 3$d$ core levels, located at a binding energy ($E_b$) of 1500–1600 eV, which is usually not possible with laboratory sources. For the Yb 3$d$ core-level spectra, the divalent (4$d^1$, fully occupied) and the trivalent (4$d^{10}$, one-hole localized) features are well separated, thus allowing highly reliable valence determination. Indeed, HAXPES has been applied to various Yb-based compounds, such as the valence transition system YbInCu$_4$, the valence fluctuation systems YbAl$_3$ and YbCu$_2$Si$_2$, the divalent systems Yb metal and YbS, the Kondo semiconductor YbB$_{12}$, and the heavy-fermion superconductor YbAlB$_4$. In this letter, we demonstrate a precise determination of the Yb valence for YbAl$_2$, which has also been considered as a prototypical valence fluctuation system.

YbAl$_2$ crystallizes in the cubic Laves MgCu$_2$ structure. The electrical resistivity shows a normal metallic behavior without a coherence peak in the temperature ($T$) range below 300 K. The electronic specific-heat coefficient, which provides a measure of effective electron mass, exhibits a slightly enhanced value, $\sim$10–17 mJ/K$^2$mol. The magnetic susceptibility has a broad maximum ($T_{\text{max}}$) at 800–850 K and is nearly independent of $T$ below 300 K after subtracting the impurity contribution. The Kondo $T$ ($T_K$) has been estimated as 2000–2600 K from the $3T_{\text{max}}$ or the inelastic neutron scattering. The Yb valence has been investigated by some techniques such as the lattice parameters and the x-ray absorption spectroscopy (XAS) at the Yb-$L_{III}$ edge. In addition, the valence-band photoemission spectroscopy (PES) using $h\nu = 70, 1487$ (Al-$K\alpha$), and 1254 eV (Mg-$K\alpha$) has also been applied to study Yb valence. The reported valence values, however, have considerably large variation between +2.0 and +2.6. Such a large discrepancy may be caused by surface effects, or the inelastic neutron scattering. After carefully overcoming such considerations, our HAXPES results provide a conclusive Yb mean valence and consistency with its estimated $T_K$. Furthermore, the Kondo resonance peak is identified in the valence-band spectra, indicating that a coherent Kondo ground state can be robust even in a nearly divalent system such as YbAl$_2$.

The single crystals of YbAl$_2$ were grown by the lithium flux method. Clean sample surfaces were obtained by fracturing in situ. Synchrotron-based HAXPES experiments were carried out at the undulator beamline BL29XUL in SPring-8, using $h\nu = 7940$ eV and a hemi-
spherical electron analyzer, Scienta R4000-10kV.27 The total energy resolution was set to 250 and 170 meV for the measurements of the core-level and valence-band spectra, respectively. To obtain the higher-resolution (50 meV) valence-band spectrum, we also performed soft x-ray (SX-) PES at the undulator beamline BL17SU using $h\nu=580$ eV and Scienta SES-2002.28 The $E_B$ of samples was calibrated using the Fermi level ($E_F$) of an evaporated Au film.

Figure 1 shows the Yb $3d$ core-level spectrum of YbAl$_2$ at 20 K, compared with that of YbCu$_2$Si$_2$, which is known to show a Yb valence of $+2.8$.10 The sharp peak at $E_B=1559$ eV is due to the Al 1$s$ core level. The Yb $3d$ core-level spectra are separated into the $3d_{5/2}$ region at 1515–1540 eV and the $3d_{3/2}$ region at 1560–1585 eV owing to spin-orbit splitting. Both the spin-orbit components in YbCu$_2$Si$_2$ show two final-state configurations: the 3$d^9$4$f^{14}$ (Yb$^{2+}$) line at $\sim1520$ and $\sim1568$ eV, and the 3$d^9$4$f^{13}$ (Yb$^{3+}$) multiplets at $\sim1525$–1538 and $\sim1572$–1583 eV, which are due to the valence fluctuations. Similarly for YbAl$_2$, a clear Yb$^{2+}$ line and weak Yb$^{3+}$ multiplets can be observed, although we also find the Al 1$s$ core level positioned between the $3d_{5/2}$ and $3d_{3/2}$ regions and overlapped satellite features. The satellite features are caused by the energy loss due to plasmon excitations ($h\omega_p=14.32$ eV), as confirmed by measuring the Al 1$s$ core-level spectrum shown in the inset of Fig. 1.

In order to determine the Yb mean valence for YbAl$_2$, the obtained spectra were analyzed in terms of the atomic multiplet model for free Yb$^{2+}$ and Yb$^{3+}$ ions.29

Figure 2 shows the Yb $3d_{5/2}$ core-level spectra at 300 and 20 K, in comparison with those obtained from the atomic-multiplet calculation. The calculated discrete spectra were broadened by a Doniach–Sunjić function convoluted with a Gaussian representing the experimental energy resolution. The energy-loss satellites were fitted with a Lorentzian for the relatively intense peak at $\sim1534$ eV and a Gaussian for the broad peak at $\sim1548$ eV. As a background, the standard integral type one was used. The experimental spectra for both $T$ are well reproduced by the calculation with the Yb mean valence of $+2.20$, which is obtained from the weight ratio between Yb$^{2+}$ and Yb$^{3+}$ components. As can be confirmed in the expanded panel in Fig. 2, the experimental spectra are located well between the calculated reference spectra, and hence, the accuracy in determining the Yb mean valence is estimated as $\pm0.02$.

Figure 3 shows the $T$-dependent Yb valence in YbAl$_2$ evaluated from the lattice parameters,17,20 the XAS at the $L_{III}$ edge,20–22 the valence-band PES,23–25 and the above-described HAXPES. In the following, we discuss the origin of the large discrepancy among the results of these techniques. Since the lattice parameters as well as the magnetic susceptibility probe an average signal of Yb$^{2+}$ and Yb$^{3+}$ components, it is intrinsically difficult to estimate a precise Yb valence. This difficulty may be related to the large variation among two results for YbAl$_2$.17,20 On the other hand, using spectroscopies such as XAS and PES, each component can be separately probed. The Yb $L_{III}$-edge XAS is a well-known powerful tool for investigating the electronic structure, including the Yb-valence determination, and can be performed even under magnetic field and/or external pressure. However, Yb$^{2+}$ and Yb$^{3+}$ components in spectra are rela-
Most include signals from orbitals other than Yb 4d in measurements using XAS. Next, the HAXPES results can be due to the surface oxidation effects can have a serious impact on the Yb valence even with the bulk sensitive probe. Such a problem has been pointed out in terms of an extra trivalent signal derived from the surface Yb component is consistent with the fact that YbAl is not a purely divalent system. It can be understood in terms of the extremely high Tc (=2000–2600 K) in YbAl, since the valence should vary significantly around Tc. This finding is consistent with the electrical resistivity showing no coherence peak and the constant magnetic susceptibility below 300 K.

We now discuss the electronic structure of YbAl2 on the basis of the valence-band spectra, which also reflects the fluctuating Yb valence. Figure 4 shows the T-dependent valence-band HAXPES spectra and the high-resolution SX-PES spectrum at 25 K, which are normalized for integrated intensity up to E=A=13 eV. The most prominent features are two sharp peaks between E=A=12–18 eV, which are derived from the Yb2+–4f doublet (J=7/2 and 5/2) corresponding to the 4f13 final state. Next, two weak structures are observed at 2–5 eV in the HAXPES spectra, but not in the SX-PES spectrum. According to the band calculation and taking into account the photoionization cross sections, these can be attributed to Al13s and 3p states. The multiple peak feature observed at 5–12 eV is due to the Yb3+–4f multiplet corresponding to the 4f12 final state. The existence of a fractional Yb3+ component is consistent with the fact that YbAl2 is not a purely divalent system. It is important to note that the Yb2+–4f/2 peak crosses E=F, in contrast to the case of purely divalent Yb systems in which this peak is located significantly below E=F.
In order to analyze this peak, the $\text{Yb}^{2+}-4f$ doublet in the SX-PES spectrum was fitted by two Doniach–Šunjic functions multiplied with a Fermi-Dirac distribution at $T=25$ K and convoluted with a Gaussian, as shown in the left inset of Fig. 4. The spectrum is reproduced well by this simple fitting, which does not include any background and/or surface components. The obtained position and the intrinsic width (FWHM) of the $4f_{7/2}$ peak are 180 and 170 meV, respectively, both of which are in excellent agreement with the estimated $T_K$ ($=2000–2600$ K) and, in particular, the characteristic peak position ($=180$ meV) in inelastic neutron scattering.\(^{19}\) Therefore, the $\text{Yb}^{2+}-4f_{7/2}$ peak can be identified as the Kondo resonance peak, thereby providing conclusive evidence for Kondo screening in YbAl$_2$ and consistency with the $T_{\text{max}}$ behavior in the magnetic susceptibility.\(^{13,18}\) This finding establishes that the coherent Kondo ground state can be robust even in a nearly divalent regime.

Although the $T$ dependence is small in the valence-band spectra as well as the core-level spectra, the $\text{Yb}^{2+}-4f$ peaks slightly shift by $\sim 30$ meV toward lower $E_B$ with cooling, as shown in the right inset of Fig. 4, in contrast to the unshifted behavior of the $\text{Yb}^{3+}-4f$ multiplet. Such $T$ variation has also been observed in YbAl$_3$, and it was suggested to be a signature of the deviation from the framework of the single-impurity Anderson model.\(^{9}\) In addition, the weight of the $\text{Yb}^{2+}$ component slightly increases with cooling, suggesting a slight reduction of Yb valence within the error bar.\(^{20}\) It is noted that since the Kondo effect is intrinsically associated with the hybridization between conduction band and $f$-electron states and since the estimated $T_K$ of YbAl$_2$ is very high, it is expected difficulty to estimate the small change in $T$-dependent hybridization between 20 and 300 K.

In conclusion, we performed HAXPES and SX-PES on YbAl$_3$. From the Yb 3$d$ core-level spectra, the mean valence of Yb ions was evaluated to be $+2.20$, which remained nearly unchanged below 300 K. Through the comparison with those obtained by other techniques, the reliability of the valence determined by HAXPES was demonstrated. Furthermore, the Kondo resonance peak was identified in the valence-band spectra, indicating that a coherent Kondo ground state can be robust even in a nearly divalent system such as YbAl$_2$.

Acknowledgment We thank H. Okamura and S. Kimura for valuable comments. The measurements of HAXPES and SX-PES were carried out with the approval of the RIKEN SPring-8 Center (Proposals No. 200900011 and No. 20090003, respectively). This research is supported by the Japan Society for the Promotion of Science (JSPS) through its Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) Program.

1) C. M. Varma: Rev. Mod. Phys. 48 (1976) 219.
2) J. M. Lawrence, P. S. Riseborough, and R. D. Parks: Rep. Prog. Phys. 44 (1981) 1.
3) O. Trovarelli, C. Geibel, S. Mederle, C. Langhammer, F. M. Grosche, P. Gegenwart, M. Lang, G. Sparn, and F. Steglich: Phys. Rev. Lett. 85 (2000) 626.
4) S. Nakatsuji, K. Kuga, Y. Machida, T. Tayama, T. Sakakibara, Y. Karaki, H. Ishimoto, S. Yonezawa, Y. Maeno, E. Pearson, G. G. Lonzarich, L. Balicas, H. Lee, and Z. Fisk: Nature Phys. 4 (2008) 603.
5) S. Watanabe and K. Miyake: Phys. Rev. Lett. 105 (2010) 186403.
6) H. Sato, K. Shimada, M. Arita, K. Hiraoka, K. Kojima, Y. Takada, K. Yoshikawa, M. Sawada, M. Nakatake, H. Namatame, M. Taniguchi, Y. Takata, E. Ikenuga, S. Shih, K. Kobayashi, K. Tamasaku, Y. Nishino, D. Miwa, M. Yabashi, and T. Ishikawa: Phys. Rev. Lett. 93 (2004) 246404.
7) I. Moreschini, C. Dallera, J. J. Joyce, J. L. Sarrao, E. D. Bauer, V. Fritsch, S. Bobev, E. Carpene, S. Huotari, G. Vankò, G. Monaco, P. Lacovig, G. Panaccione, A. Fondacaro, G. Paolicelli, P. Torelli, and M. Grioni: Phys. Rev. B 75 (2007) 035113.
8) S. Suga, A. Sekiyama, S. Imada, J. Yamaguchi, A. Shimamoto, A. Izirawa, K. Yoshimura, M. Yabashi, K. Tamasaku, A. Higashiyama, and T. Ishikawa: J. Phys. Soc. Jpn. 78 (2009) 074704.
9) S. Suga, A. Sekiyama, S. Imada, A. Shimamoto, A. Yamashiki, M. Tsunekawa, C. Dallera, L. Braicovich, T.-L. Lee, O. Sakai, T. Ebihara and Y. Ônuki: J. Phys. Soc. Jpn. 74 (2005) 2880.
10) M. Matsunami, A. Chainani, M. Taguchi, R. Eguchi, Y. Ishida, Y. Takata, H. Okamura, T. Nanba, M. Yabashi, K. Tamasaku, Y. Nishino, T. Ishikawa, Y. Senba, H. Ohashi, N. Tsujii, A. Ochiai, and S. Shih: Phys. Rev. B 78 (2008) 155118.
11) J. Yamaguchi, A. Sekiyama, S. Imada, H. Fujiwara, M. Yano, T. Miyamachi, G. Funabashi, M. Obara, A. Higashiyama, K. Tamasaku, M. Yabashi, T. Ishikawa, F. Iga, T. Takabatake, and S. Suga: Phys. Rev. B 79 (2009) 125121.
12) M. Okawa, M. Matsunami, K. Ikizaka, R. Eguchi, M. Taguchi, A. Chainani, Y. Takata, M. Yabashi, K. Tamasaku, Y. Nishino, T. Ishikawa, K. Kuga, N. Horie, S. Nakatsuji, and S. Shih: Phys. Rev. Lett. 104 (2010) 247201.
13) E. E. Havinga, K. H. J. Buschow, and H. J. van Dal: Solid State Commun. 13 (1973) 621.
14) N. Tsujii, K. Yoshimura, and K. Kosuge: J. Phys.: Condens. Matter 15 (2003) 1993.
15) T. Görlich, C. Pfei¨ederer, K. Grube, and H. v. Löhneysen: Phys. Rev. B 71 (2005) 033101.
16) H. Nowatari, Y. Saiga, Y. Kato, K. Iwata, S. Katano, T. Fujiwara, Y. Uwatoko, and M. Kosaka: J. Phys. Soc. Jpn. 76 (2007) Suppl. A, 80.
17) A. Iandelli and A. Palenzona: J. Less-Common Met. 29 (1972) 293.
18) J. C. P. Klaasse, J. W. E. Sterkenburg, A. H. M. Bleyendaal, and F. R. de Boer: Solid State Commun. 12 (1973) 561.
19) A. P. Murani, A. D. Taylor, R. Osborne, and Z. A. Bowden: Philos. Mag. B 65 (1992) 1333.
20) K. R. Bauchspies, W. Boksch, E. Holland-Moritz, H. Launöes, R. Pott, and D. Wohlfoten: in Valence Fluctuations in Solids, ed. L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981).
21) J. Röhrle, G. Kirl, J.-P. Kappler, M.-F. Ravet, and D. Wohlfoten: in Valence Instabilities, ed. P. Wachtler and H. Boppart (North-Holland, Amsterdam, 1982).
22) C. Dallera, E. Annese, J.-P. Ruffe, A. Palenzona, G. Vankò, L. Braicovich, A. Shukla, and M. Grioni: Phys. Rev. B 68 (2003) 245114.
23) G. Kaindl, B. Reihl, D. E. Eastman, R. A. Polik, N. Märtensson, B. Barbara, T. Penney, and T. S. Plaskett: Solid State Commun. 41 (1982) 157.
24) S.-J. Oh, J. W. Allen, B. Barbara, T. Penney, and T. S. Plaskett: J. Magn. Magn. Mater. 52 (1985) 183.
25) I. Abatti, B. DeMichielis, A. Fasana, M. Sancrotti, A. Iandelli, G. L. Olcese, and R. Eggenhöffer: Solid State Commun. 65 (1988) 743.
26) The probing depth in low-energy (VUV-SX) PES, HAXPES, and LiF/edge (fluorescence-yield) XAS is generally considered as $<20$ and $\sim 80$ Å, and $\sim 10$ μm, respectively.
27) T. Ishikawa, K. Tamasaku, and M. Yabashi: Nucl. Instrum. Methods Phys. Res., Sect. A 547 (2005) 42; Y. Takata, M. Yabashi, K. Tamasaku, Y. Nishino, D. Miwa, T. Ishikawa,
28) K. Horiba, R. Eguchi, N. Kamakura, K. Yamamoto, M. Matsumani, Y. Takata, Y. Senba, H. Ohashi, and S. Shin: AIP Conf. Proc. 879 (2007) 1611.

29) The details of the calculations are shown in R. Cowan: The Theory of Atomic Structure and Spectra (University of California Press, Berkeley, CA, 1981). The Slater integrals $F_k(4f, 4f)$, $F_k(3d, 4f)$, and $G_k(3d, 4f)$ were scaled to 80, 93, and 81%, respectively.

30) The Yb mean valence estimated from the valence-band spectra in Fig. 4 is $+2.30\pm0.05$ (20 K) and $+2.31\pm0.05$ (300 K) for HAXPES and $+2.13\pm0.03$ (25 K) for SX-PES. The discrepancy with the valence estimated with Yb 3d core-level HAXPES can be attributed to the existence of orbitals other than Yb 4f electrons spread over a wide energy, which cannot be accurately separated, in valence-band spectra.

31) S. J. Lee, S. Y. Hong, I. R. Fisher, P. C. Canfield, B. N. Harmon, and D. W. Lynch: Phys. Rev. B 61 (2000) 10076.

32) J. J. Yeh and I. Lindau: At. Data Nucl. Data Tables 32 (1985) 1.