

Strong Valence Fluctuation in the Quantum Critical Heavy Fermion Superconductor β -YbAlB₄: A Hard X-Ray Photoemission Study

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Electronic structures of the quantum critical superconductor β -YbAlB₄ and its polymorph α -YbAlB₄ are investigated by using bulk-sensitive hard x-ray photoemission spectroscopy. From the Yb 3d core level spectra, the values of the Yb valence are estimated to be ~ 2.73 and ~ 2.75 for α - and β -YbAlB₄, respectively, thus providing clear evidence for valence fluctuations. The valence band spectra of these compounds also show Yb²⁺ peaks at the Fermi level. These observations establish an unambiguous case of a strong mixed valence at quantum criticality for the first time among heavy fermion systems, calling for a novel scheme for a quantum critical model beyond the conventional Doniach picture in β -YbAlB₄.

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Rare-earth compounds possess rich f -electron physics such as heavy fermion formation, magnetic transitions, valence fluctuation phenomena, and quantum criticality [1–8]. In particular, near the quantum critical point (QCP: a non-thermal-parameter-induced phase transition point at absolute zero), a quantum fluctuation can lead to unusual behaviors such as a non-Fermi liquid ground state and unconventional superconductivity; therefore, quantum criticality is one of the most active problems in the study of correlated electrons. Around the antiferromagnetic QCP, exotic superconductivity is actually found in many Ce-based heavy fermion systems, which is considered to be mediated by magnetic fluctuation [3,5,7,8]. Recently, on the other hand, the valence fluctuation-mediated superconductivity around the valence transition quantum critical end point has also been discussed in CeCu₂(Si, Ge)₂ [9–11]. Thus, f -electron systems exhibit complex exotic superconductivity, providing a variety of examples for the study on other unconventional superconductivity including high-temperature superconductivity.

The magnetic QCP is frequently explained by the Doniach picture [12], considering the competition between two different energy scales of Rudermann-Kittel-Kasuya-Yosida (RKKY) exchange interaction and Kondo screening effect. The former causes the local moment magnetism of f electrons, while the latter induces the itinerancy of f electrons accompanying heavy effective mass via the hybridization with the conduction band (c - f hybridization). The c - f hybridization involves the valence fluctuation in rare-earth ions, raising the deviation from the integral valence of 3. In the case of Yb-based systems, the 4f-electron configuration fluctuates between 4f¹³ (Yb³⁺) and 4f¹⁴ (Yb²⁺). The Yb²⁺ component gives the direct measure of the c - f hybridization strength, which can be quantitatively evaluated using high-energy spectroscopic

methods [13–19]. Preceding studies have revealed intriguing aspects of QCP and valence fluctuation in some Yb-based heavy fermion systems. In the chemically tuned quantum critical YbCu_{5-x}Al_x, for example, the Yb valence increases to 3 approaching the antiferromagnetic region. Nevertheless, the small deviation from the trivalent configuration is known to remain at the antiferromagnetic QCP [13,14]. In such systems, the role of the valence fluctuation in the quantum critical phenomena is under active discussion [13,14,20], which is not considered in the conventional QCP's picture.

A newly discovered polymorph of LnAlB₄ system [21] has special attraction in heavy fermions. β -YbAlB₄ shows non-Fermi liquid behavior under zero-field and ambient pressure, indicating the immediate existence of a QCP without any external tuning (i.e., pressure, magnetic field, or chemical doping) [22]. Furthermore, this compound shows superconductivity with the transition temperature T_c of 80 mK, which was found for the first time in Yb-based systems [22,23]. In terms of the electron-hole parallelism between Ce³⁺ (4f¹; one electron) and Yb³⁺ (4f¹³; one hole), β -YbAlB₄ is a unique model compound to study the superconductivity and its relation to the QCP in heavy fermion systems. In addition, the Curie-Weiss temperature $|\Theta_{CW}|$ and the crossover temperature T^* where the hybridized f -electron coherence emerges show relatively higher values of order of 100 K, suggesting that the RKKY and Kondo energy scales compete at a higher energy [22]. The susceptibility shows the Curie-Weiss behavior with the effective moment $\mu_{\text{eff}} \sim 2.9\mu_B/\text{Yb}$, and its temperature dependence over the entire T range can be fit by a crystalline electric field scheme, suggesting a local nature of 4f moment [21,24]. In contrast, a quantum oscillation study confirmed that heavy 4f electrons contribute to the Fermi surface below large T^* [25]. The origin of the quantum

criticality and superconductivity occurring in β -YbAlB₄ is not yet clarified. It has been recently discussed whether the QCP can be fully explained by the conventional Doniach picture or not [24,26]. The particular quantum critical behavior in β -YbAlB₄ motivates us to reveal the Yb valence state as an indicator of the Kondo effect's supremacy over the RKKY interaction and to discuss its role for quantum criticality and superconductivity.

The progress of hard x-ray photoemission spectroscopy (HX-PES) in recent years has enabled us to probe the bulk-sensitive core level and valence band electronic structure [15]. A photoelectron with kinetic energies of 5–8 keV attains an escape depth of 50–100 Å from a crystal surface [27]; thus HX-PES can reveal the bulk electronic structure of *f*-electron systems, which are known to exhibit strong surface effects. In particular, quantitative estimations of the valence state have been reported by HX-PES [16–19,28,29]. Since β -YbAlB₄ exhibits a QCP without external parameter tuning, this is an appropriate compound for a photoemission study related to quantum critical phenomena.

In this Letter, we report the bulk-sensitive HX-PES measurements of β -YbAlB₄ and its polymorph α -YbAlB₄. In contrast to β -YbAlB₄, the ground state of α -YbAlB₄ is a heavy Fermi liquid without QCP behavior and superconductivity, though the values of T^* , Θ_{CW} , and μ_{eff} are very similar [21,30]. In order to understand the essential difference between α - and β -YbAlB₄, the measurements of both polymorphs should be beneficial. Yb³⁺ and Yb²⁺ components were observed in Yb 3*d* spectra for both α - and β -YbAlB₄, which is direct evidence for the valence fluctuation. The valence band spectrum of β -YbAlB₄ also clearly shows the Yb²⁺ 4*f* peaks contributing to the electronic state at the Fermi level. Our results suggest the breakdown of the conventional Doniach picture in β -YbAlB₄. We discuss the possible relationship between the strong valence fluctuation and superconductivity at the QCP in β -YbAlB₄.

High-quality single crystals of α - and β -YbAlB₄ were grown by the Al-flux method as described in the literature [21]. HX-PES experiments were performed at the undulator beam line BL29XUL of SPring-8 synchrotron facility using a Scienta R4000-10kV hemispherical electron spectrometer [31]. We chose the photon energy of $h\nu = 7.94$ keV. We obtained clean surfaces of the samples by fracturing *in situ* under the base pressure of $\sim 10^{-8}$ Pa at room temperature. Data acquisition was carried out at 20 K. The energy resolution ΔE was set to ~ 250 meV. The Fermi level E_F was determined by the Fermi edge of an evaporated Au film connected electrically to the sample.

Figure 1 shows Yb 3*d* core level spectra of α - and β -YbAlB₄. The obtained spectra are very similar to each other. The Yb 3*d* level is split into 3*d*_{5/2} and 3*d*_{3/2} levels by the spin-orbit coupling. The sharp peak at 1560 eV is the Al 1*s* level, while the weak broad peaks at 1550 eV and

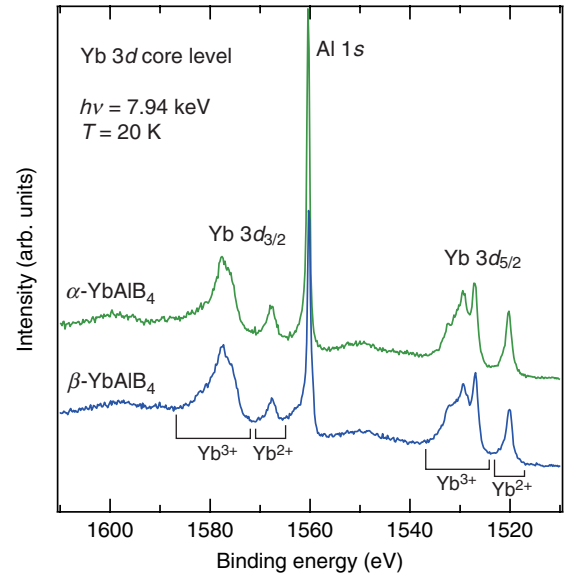


FIG. 1 (color online). HX-PES spectra of Yb 3*d* and Al 1*s* core levels in α -YbAlB₄ (upper) and β -YbAlB₄ (lower).

1600 eV may be due to plasmon satellites of Yb 3*d*_{5/2} and 3*d*_{3/2} core levels, respectively. The 3*d*⁹4*f*¹³ final state (corresponding to Yb³⁺) multiplets are found at the energy region of 1524–1538 eV for the 3*d*_{5/2} component and at 1572–1587 eV for the 3*d*_{3/2} component. The 3*d*⁹4*f*¹⁴ final state (corresponding to Yb²⁺) lines are also observed at 1520 eV and 1567.5 eV as 3*d*_{5/2} and 3*d*_{3/2} components, respectively. This result, showing the coexistence of Yb²⁺ and Yb³⁺ levels, is clear evidence of the valence fluctuation in α - and β -YbAlB₄. Note that all Yb sites in these compounds are crystallographically equivalent [21]; therefore, we can exclude the possibility of spatial separation of divalent and trivalent Yb sites.

To evaluate the values of Yb valence, we analyzed Yb 3*d*_{5/2} level spectra which are not affected by the Al 1*s* peak and its satellite as shown in Fig. 2. Yb³⁺ peaks were reproduced by the result of the atomic multiplet calculation [32]. To consider the electron lifetime and the asymmetric spectral shape due to the conduction electron scattering, each calculated line was broadened using the Doniach-Šunjić line shape [33]. For the broad plasmon satellites and the background components, we assumed a Gaussian peak and the Shirley-type integral background [34], respectively. The instrumental energy resolution effect was considered as the Gaussian convolution with the full width of ΔE . We can estimate the value of the Yb valence as the ratio of peak intensity areas (shown as shaded areas in Fig. 2) of Yb²⁺ and Yb³⁺ components, thus obtaining 2.73 ± 0.02 and 2.75 ± 0.02 as Yb valences for α - and β -YbAlB₄, respectively. These values, significantly deviating from 3, are consistent with high T^* reflecting the strong *c-f* hybridization in both compounds. Considering the similarity in Yb valence, T^* , Θ_{CW} , and μ_{eff} , the ground

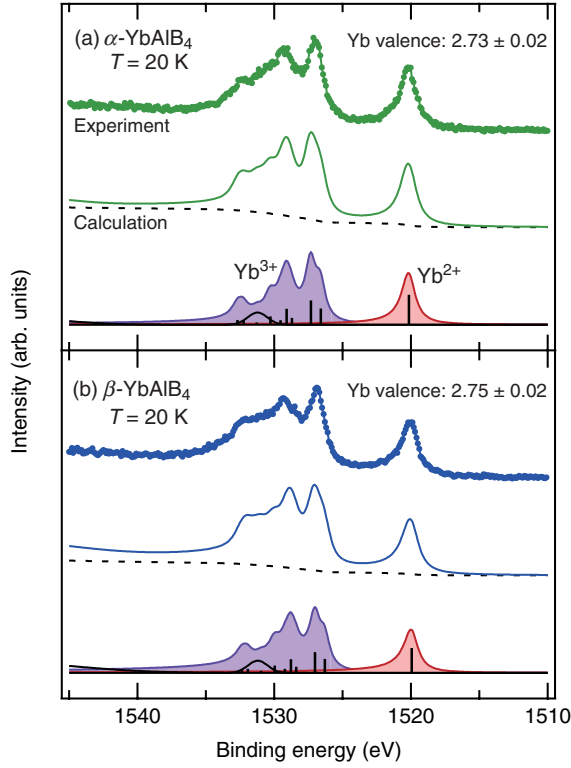


FIG. 2 (color online). Comparison of experimental spectra for Yb $3d_{5/2}$ core level with calculation in (a) α -YbAlB₄ and (b) β -YbAlB₄. Experimental data and fitting results are shown as upper and middle spectra, respectively. Dashed curves represent the integral background. Lower spectra represent calculated Yb $3d_{5/2}$ multiplet lines and the broadened (shaded curves) and plasmon satellites (solid curves).

state of the YbAlB₄ system seems sensitive to the difference of the crystal structure. The strong deviation of Yb valence is also qualitatively consistent with local density approximation calculations for β -YbAlB₄ (the $4f$ -electron number of $n_f \sim 13.4$) [24,25], though electronic correlations should also be considered to make a more precise comparison.

This valence fluctuation behavior in α - and β -YbAlB₄ is also clearly found in the valence band spectrum shown as Fig. 3. The observed peaks at E_F and 1.3 eV correspond to the $J = 7/2$ and $5/2$ levels of the $4f^{13}$ final state (Yb²⁺) split by the spin-orbit coupling, respectively. This split width of 1.3 eV is a typical value in Yb-based compounds [16,18]. The $J = 7/2$ level is peaked at E_F and is hybridized with the s - p derived conduction band states, thus acquiring itinerancy, and participating in the Fermi surface. This indicates that Yb $4f$ electrons become itinerant and its number fluctuates via the c - f hybridization, which is consistent with the core level spectra in Fig. 1.

Now we discuss the valence fluctuation behavior in the vicinity of the QCP in β -YbAlB₄. Since the Yb valence reflects the degree of $4f$ -hole localization, the valence fluctuation suggests a strong hybridization effect of Yb

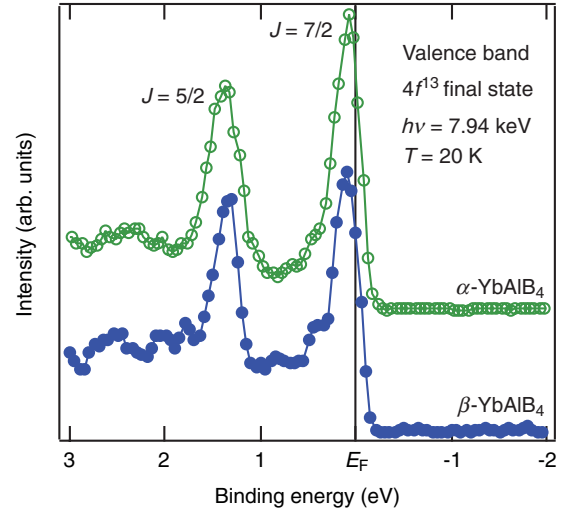


FIG. 3 (color online). HX-PES spectra of the $4f^{13}$ final state in the valence band of α - and β -YbAlB₄.

$4f$ holes with the conduction bands for both α - and β -YbAlB₄. Here, we should note that the valence value of ~ 2.75 in the non-Fermi liquid β -YbAlB₄ is similar to ~ 2.73 in β -YbAlB₄ with normal heavy Fermi liquid behavior [30]. Indeed, the amount of the divalent component in β -YbAlB₄ is very large in comparison with other quantum critical Yb-based compounds such as YbCu_{5-x}Al_x (Yb ^{$\sim 2.95+$}) [13] and YbRh₂Si₂ (Yb ^{$\sim 2.9+$}) [35]. We should also note that other comparable valence fluctuation systems such as YbInCu₄ (Yb ^{$\sim 2.74+$}) [16] and YbAl₃ (Yb ^{$\sim 2.71+$}) [18] show Pauli paramagnetic Fermi liquid behavior at low temperature [36,37], indicating disappearance of the magnetic moment of localized Yb $4f$ electrons due to complete Kondo screening. Since the magnetic susceptibility of the quantum critical β -YbAlB₄ indicates the existence of the local moment with Ising anisotropy along the c axis [22], such a strong valence fluctuation indicative of the itinerant $4f$ electrons is very unique in β -YbAlB₄.

This unprecedented dual character of f electrons in β -YbAlB₄ confronts us with difficulty in the conventional scheme. In the conventional Doniach phase diagram described by the competition between Kondo screening and RKKY interaction, the valence fluctuation gets suppressed on approaching QCP. Here, we conclude that the simple Doniach picture cannot be applied to the quantum critical phenomena in β -YbAlB₄. It is worth noting that such strong mixed valence has been unambiguously established for the first time in heavy fermion compounds, thus showing its possible relation to the unique superconductivity. Our finding in β -YbAlB₄ raises the question of how one can microscopically describe the superconducting mechanism where the f -electrons have both itinerant and localized character. Furthermore, it is an interesting question to check whether α -YbAlB₄ also show QCP behavior and the dual localized-itinerant character, varying an external pa-

parameter such as pressure or magnetic field. To uncover the nature of the QCP and superconductivity in YbAlB₄ system, further investigations using detailed magnetic and theoretical studies across the global phase diagram are highly desired.

In summary, we have investigated the electronic structure in quantum critical β -YbAlB₄ and the Fermi liquid system α -YbAlB₄ using bulk-sensitive HX-PES with $h\nu = 7.94$ keV. Both Yb²⁺ and Yb³⁺ components were clearly observed in the Yb 3*d* core level spectra, providing direct evidence for the noninteger valence values of ~ 2.73 and ~ 2.75 for α - and β -YbAlB₄, respectively. The valence band spectra of these compounds also show the Yb²⁺ peaks at the Fermi level. We have found the unique valence fluctuation feature at the QCP with the superconductivity in β -YbAlB₄, thus indicating the possible role of the valence fluctuation in addition to the magnetic fluctuation, requiring the novel quantum critical scheme beyond the Doniach picture.

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- [1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
- [2] C. M. Varma, *Rev. Mod. Phys.* **48**, 219 (1976).
- [3] N. D. Mathur *et al.*, *Nature (London)* **394**, 39 (1998).
- [4] G. R. Stewart, *Rev. Mod. Phys.* **73**, 797 (2001).

- [5] R. Settai, T. Takeuchi, and Y. Ōnuki, *J. Phys. Soc. Jpn.* **76**, 051003 (2007).
- [6] H. v. Löhneysen *et al.*, *Rev. Mod. Phys.* **79**, 1015 (2007).
- [7] P. Monthoux, D. Pines, and G. G. Lonzarich, *Nature (London)* **450**, 1177 (2007).
- [8] P. Gegenwart, Q. Si, and F. Steglich, *Nature Phys.* **4**, 186 (2008).
- [9] H. Q. Yuan *et al.*, *Science* **302**, 2104 (2003).
- [10] A. T. Holmes, D. Jaccard, and K. Miyake, *Phys. Rev. B* **69**, 024508 (2004).
- [11] K. Miyake, *J. Phys. Condens. Matter* **19**, 125201 (2007).
- [12] S. Doniach, *Physica B+C (Amsterdam)* **91**, 231 (1977).
- [13] K. Yamamoto *et al.*, *J. Phys. Soc. Jpn.* **76**, 124705 (2007).
- [14] H. Yamaoka *et al.*, *Phys. Rev. B* **80**, 035120 (2009).
- [15] Y. Takata, in *Very High Resolution Photoelectron Spectroscopy*, edited by S. Hüfner (Springer, Berlin, 2007), pp. 373–397.
- [16] H. Sato *et al.*, *Phys. Rev. Lett.* **93**, 246404 (2004).
- [17] L. Moreschini *et al.*, *Phys. Rev. B* **75**, 035113 (2007).
- [18] S. Suga *et al.*, *J. Phys. Soc. Jpn.* **74**, 2880 (2005).
- [19] M. Matsunami *et al.*, *Phys. Rev. B* **78**, 195118 (2008).
- [20] G. Knebel *et al.*, *J. Phys. Soc. Jpn.* **75**, 114709 (2006); G. Knebel *et al.*, *Physica (Amsterdam)* **378–380B**, 68 (2006).
- [21] R. T. Macaluso *et al.*, *Chem. Mater.* **19**, 1918 (2007).
- [22] S. Nakatsuji *et al.*, *Nature Phys.* **4**, 603 (2008).
- [23] K. Kuga *et al.*, *Phys. Rev. Lett.* **101**, 137004 (2008).
- [24] A. H. Nevidomskyy and P. Coleman, *Phys. Rev. Lett.* **102**, 077202 (2009).
- [25] E. C. T. O’Farrell *et al.*, *Phys. Rev. Lett.* **102**, 216402 (2009).
- [26] S. Friedemann *et al.*, *Nature Phys.* **5**, 465 (2009).
- [27] K. Kobayashi *et al.*, *Appl. Phys. Lett.* **83**, 1005 (2003).
- [28] K. Yamamoto *et al.*, *J. Phys. Soc. Jpn.* **73**, 2616 (2004).
- [29] A. Yamasaki *et al.*, *Phys. Rev. Lett.* **98**, 156402 (2007).
- [30] N. Horie *et al.*, in *Meeting Abstracts of the Physical Society of Japan* (The Physical Society of Japan, Tokyo, 2009), Vol. 64, part 3, p. 651.
- [31] T. Ishikawa, K. Tamasaku, and M. Yabashi, *Nucl. Instrum. Methods Phys. Res., Sect. A* **547**, 42 (2005); Y. Takata *et al.*, *ibid.* **547**, 50 (2005).
- [32] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
- [33] S. Doniach and M. Šunjić, *J. Phys. C* **3**, 285 (1970).
- [34] D. A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- [35] C. Dallera as discussed in Ref. [20].
- [36] J. L. Sarrao *et al.*, *Phys. Rev. B* **54**, 12 207 (1996).
- [37] A. L. Cornelius *et al.*, *Phys. Rev. Lett.* **88**, 117201 (2002).