Evidence for $\Gamma_8$ Ground-State Symmetry of Cubic YbB$_{12}$ Probed by Linear Dichroism in Core-Level Photoemission

Yuina Kanai$^{1,2}$, Takeo Mori$^1$, Sho Naimen$^1$, Kohei Yamagami$^{1,2}$, Hidenori Fujiwara$^{1,2}$, Atsushi Higashiyama$^{2,3}$, Toshiharu Kadono$^{2,4}$, Shin Imada$^{2,4}$, Takayuki Kiss$^{1,2,5}$, Arata Tanaka$^6$, Kenji Tamasaku$^{2,5}$, Makina Yabashi$^2$, Tetsuya Ishikawa$^2$, Fumitoshi Iga$^7$, and Akira Sekiyama$^{1,2,5}$

$^1$Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.
$^2$RIKEN SPring-8 Center, Sayo, Hyogo 679-5148, Japan.
$^3$Faculty of Science and Engineering, Setonan University, Neyagawa, Osaka 572-8508, Japan.
$^4$Department of Physical Science, Ritsumeikan University, Kusatsu, Shiga 525-0058, Japan.
$^5$Center for Promotion of Advanced and Interdisciplinary Research, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.
$^6$Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530, Japan.
$^7$College of Science, Ibaraki University, Mito, Ibaraki 310-8512, Japan.

We have successfully observed linear dichroism in angle-resolved Yb$^{3+}$ 3$d_{3/2}$ core-level photoemission spectra for YbB$_{12}$ in cubic symmetry. Its anisotropic 4$f$ charge distribution due to the crystal-field splitting is responsible for the linear dichroism which has been verified by spectral simulations for a single-site Yb$^{3+}$ ion in cubic symmetry. The observed linear dichroism as well as the polarization-dependent spectra at two different photoelectron directions for YbB$_{12}$ is quantitatively reproduced by the theoretical analysis for $\Gamma_8$ ground state, indicating the $\Gamma_8$ ground-state symmetry for the Yb$^{3+}$ ions mixed with the Yb$^{2+}$ state.

Rare-earth-based strongly correlated electron systems show various interesting phenomena such as competition between magnetism and unconventional superconductivity, charge and/or multipole ordering, and formation of a narrow ($\sim$meV) gap at low temperatures. Among them, YbB$_{12}$ is known as a Kondo semiconductor$^{1–5}$, which has recently been recognized as a candidate for topological insulators$^{12}$, as intensively discussed for another Kondo semiconductor SmB$_6$$^{7–10}$. The mean valence of YbB$_{12}$ has been estimated as $\sim 2.9+$ by bulk-sensitive 3$d$ core-level hard X-ray photoemission (HAXPES) spectroscopy$^{10}$. In order to discuss mechanisms of the gap opening at low temperatures$^{5,11–19}$ and the possibility of topological insulator, it is essential to verify the ground-state symmetry of the Yb$^{3+}$ [4$f^{13}$ (one hole)] state determined by crystal-field (CF) splitting. Nevertheless, it is unclear for YbB$_{12}$. Its eight-fold degenerated Yb$^{3+}$ 4$f_{7/2}$ levels are considered to be split into two quartets$^{20}$(normally, two doublets and a quartet) due to CF in YbB$_{12}$. The ground state of the Yb$^{3+}$ ions is commonly asserted to be in a so-called $\Gamma_8$ symmetry$^{5,18}$, but a possible accidentally degenerated $\Gamma_0 + \Gamma_7$ ground state is not completely excluded. In this letter, we show the evidence for the $\Gamma_8$ symmetry of the Yb$^{3+}$ sites in the ground state of YbB$_{12}$ on the basis of linear dichroism in angle-resolved core-level photoemission.

Generally, it is difficult to experimentally determine the 4$f$ ground-state symmetry. Inelastic neutron scattering is useful but other excitations like phonon excitations often hamper to observe magnetic 4$f–4$f excitations. Linear dichroism (LD) in 3$d$–to–4$f$ soft X-ray absorption spectroscopy (XAS) for single crystals is powerful owing to the dipole selection rules, as reported for Ce compounds$^{19,22}$. However, it is not applicable for compounds in cubic symmetry, in which there is no anisotropic axis relative to the electric field of an incident light. On the other hand, the selection rules work also in photoemission process while the excited electron energy is much higher than that in the absorption. Furthermore, there is another controllable measurement parameter as “photoelectron detection direction” relative to the single-crystalline axis in addition to the polarization direction of the excitation lights in photoemission. Indeed, using LD in 3$d$ core-level HAXPES spectra, determination of the Yb$^{3+}$ 4$f$ ground state have been succeeded for tetragonal YbCu$_2$Si$_2$ and YbRh$_2$Si$_2$$^{23}$. LD in the core-level HAXPES for cubic Yb compounds is also expected to be observed, as discussed below.

In the case of Yb$^{3+}$ ions in tetragonal symmetry, the eightfold degenerate $J = 7/2$ state splits into four dou-
FIG. 1. (Color online) (a) Simulated polarization-dependent 3d_{5/2} photoemission spectra of Yb^{3+} ions assuming the crystal-field-split ground state in cubic symmetry along the [100] direction, together with the corresponding experimental geometry. (b) Same as (a) but for the photoelectron along the [111] direction. The 4f-hole spatial distributions for the corresponding states are also shown.

The Γ_6 and Γ_7 states correspond to the tetragonal Γ_{6}^{1} (with b = \sqrt{7/12}) and Γ_{7}^{2} (with c = 1/2) states, respectively. Since the CF splitting in the cubic symmetry can be recognized as the special case for the tetragonal symmetry, it is natural to expect the observation of LD in core-level photoemission for cubic Yb compounds at least Γ_6 or Γ_7 ground state, for which the 4f charge distribution is deviated from a spherical symmetry and thus anisotropic as shown in Fig. 1. The Γ_6, Γ_7, and Γ_8 4f charge distributions are elongated along the [100], [111], and [110] directions, respectively. Actually, we have performed ionic calculations including the full multiplet theory and the local CF splitting using the XTLS 9.0 program. All atomic parameters such as the 4f-4f and 3d-4f Coulomb and exchange interactions (Slater integrals) and the 3d and 4f spin-orbit couplings have been obtained using Cowan’s code based on the Hartree-Fock method. The Slater integrals (spin-orbit couplings) are reduced to 88% (98%) to fit the core-level photoemission spectra.

Simulated polarization-dependent Yb^{3+} 3d_{5/2} core-level HAXPES spectra in the cubic symmetry at two photoelectron directions ([100], [111]) are shown in Fig. 1. In the case of YbB_{12}, since the accidentally degenerated Γ_6 + Γ_7 states could be a candidate for the ground state, the simulations assuming the Γ_6 + Γ_7 ground state and its 4f hole spatial distribution are also shown. LD defined by the difference in spectral weight between the s- and p-polarization configurations is reversed between the [100] and [111] directions for all states displayed here. LD for the Γ_6 ground state has the same tendency as that for the Γ_8 ground state. On the other hand, LD for Γ_8 is the smallest since the 4f hole spatial distribution for the Γ_8 state is the nearest to a spherical shape among these three eigenfunctions. LD assuming the Γ_6 + Γ_7 state is reversed to that for the Γ_8 state. These simulations indicate that the symmetry of Yb^{3+} state can be determined by LD in the core-level photoemission.

We have performed LD in HAXPES at BL19LXU of SPring-8 using a MBS A1-HE hemispherical photoelectron spectrometer. A Si(111) double-crystal monochromator selected linearly polarized 7.9 keV radiation within the horizontal plane, which was further monochromatized by a Si(620) channel-cut crystal. In order to switch the linear polarization of the excitation light from the horizontal direction to the vertical direction, two single-crystalline (100) diamonds were used as a phase retarder placed downstream of the channel-cut crystal. P_L of the polarization-switched X-ray after the phase retarder was estimated as −0.93, corresponding to the vertically linear polarization components of 96.5%. Since the detection direction of photoelectrons was set in the horizontal plane with an angle to incident photons of 60°, as shown in Figs. 1(a), (b), the experimental configuration at the horizontally (vertically) polarized light exci-
FIG. 2. (Color online) (a) Polarization-dependent Yb $3d_{5/2}$ core-level HAXPES raw spectra (solid lines) of YbB$_{12}$ along the [100] direction and optimized Shirley-type background which we have subtracted from the raw spectra (dashed lines). (b) Same as (a) but in an expanded scale.

The polarization light was focused onto the samples using an ellipsoidal Kirkpatrick-Baez mirror. In order to precisely detect LD in the Yb $3d$ core-level photoemission spectra, we optimized the photon flux so as to set comparable photoelectron count rates between the $s$- and $p$-polarization configurations. Single crystals of YbB$_{12}$ synthesized by the traveling-solvent floating-zone method were fluctuated along the (100) plane in situ, where the base pressure was $\approx 1 \times 10^{-7}$ Pa. The experimental geometry was controlled by using a newly developed two-axes manipulator, where the normal emission direction parallel to the [100] direction in Fig. 1(a) was changed to the photoelectron detection of the [111] direction in Fig. 1(b) by azimuthal rotation of 45° and polar rotation by $\sim 55^\circ$.

The sample and surface qualities were checked on the basis of the absence of any core-level spectral weight caused by possible impurities including oxygen and carbon. The energy resolution was set to 400 meV. The measuring temperature is 9 K that is sufficiently lower than the excited state ($\gtrsim 250$ K).

The polarization-dependent Yb$^{3+}$ $3d_{5/2}$ HAXPES spectra along the [100] direction of YbB$_{12}$ are shown in Fig. 2. A single peak at a binding energy of $\sim 1519$ eV and a multiple-peak ranging from 1524 to 1534 eV exist in all the spectra. Since the 4$f$ subshell is fully occupied in the Yb$^{3+}$ sites with a spherically symmetric 4$f$ distribution, the former single peak is ascribed to the Yb$^{2+}$ states. The $3d^84f^{13}$ final states for the Yb$^{3+}$ components show an atomic-like multiplet-split peak structure in the 1524–1534 eV range. We show the spectra in the expanded scale ranging from 1524.5 to 1530.5 eV in the Fig. 2(b). A slight but intrinsic LD is seen in the highest and second-highest peaks in the raw spectra.

Comparison of the polarization-dependent Yb$^{3+}$ $3d_{5/2}$...
HAXPES spectra of YbB$_{12}$ and their LD with the photoelectron directions of [100] and [111] to the simulated ones for the $\Gamma_6$ ground state are shown in Fig. 3. So-called Shirley-type backgrounds are subtracted from the raw spectra as shown in Fig. 2 and the background-subtracted spectra are normalized by both Yb$^{3+}$ and Yb$^{3+}$ 3d$_{5/2}$ spectral weights. The highest peak is slightly stronger in the p-polarization configuration (p-pol.) than in s-polarization one (s-pol.), and the second highest peak is stronger in the s-pol. for both experimental and simulated spectra along the [100] direction. These tendencies are reversed for the data along the [111] direction. As shown in Figs. 3(a) and (b), the observed LD as well as the spectra are quantitatively reproduced by the simulations for the $\Gamma_8$ ground state, for which the 4f charge distribution is shown in Fig. 3(c). If the 4f ground state of YbB$_{12}$ were in the $\Gamma_6$ symmetry, LD would much larger than the experimental one. The sign of LD for the $\Gamma_6$ or the accidental degenerated $\Gamma_6 + \Gamma_7$ ground states is completely inconsistent with our experimental results. Such a quantitative reproducibility of LD as well as the core-level spectra by the simulations surely indicates the Yb$^{3+}$ (4f$^{13}$) ions in the $\Gamma_8$ symmetry mixed with a small quantity ($\sim 10\%$) of the Yb$^{2+}$ (4f$^{14}$) component$^{12}$ in the ground state of YbB$_{12}$.

Our finding of the $\Gamma_8$ 4f symmetry for the Yb$^{3+}$ sites in the ground state is consistent with the prediction by a band-structure (local density approximation + on-site Coulomb repulsion, LDA+$U$) calculation, where the $\Gamma_6$ and $\Gamma_7$ states are in the occupied side$^{2}$. One might consider that the $\Gamma_6$ and $\Gamma_7$ states are possibly mixed in the ground state for the valence-fluctuating system due to the hybridization between the 4f and valence-band orbitals at low temperatures well below the Kondo temperature ($\sim$ 240 K for YbB$_{12}$). As widely recognized for the local electronic structures of transition metal-oxides, on the other hand, it should be noted that the so-called crystal-field splitting actually seen for realistic materials is a consequence of the anisotropic hybridization effects in addition to static ligand potentials. The latter would be much smaller than the former for YbB$_{12}$ since the ligand-field potential on the Yb sites is to some extent nearer to a spherically symmetric one, being caused by the crystal structure$^{12,23}$, where the Yb ion is surrounded by the truncated octahedron made of 24 boron ions as shown in Fig. 3(d). The 4f-hole spatial distributions are elongated along the centers of the truncated octahedron faces for the $\Gamma_6$ and $\Gamma_7$ states whereas they are along the edges of the hexagonal faces for the $\Gamma_7$ state, which leads to the conclusion that the 4f holes in the $\Gamma_8$ state are relatively stabilized by the hybridizations compared to those in the $\Gamma_6$ and $\Gamma_7$ states with different symmetry, as suggested by the LDA+$U$ calculation. The possible $\Gamma_6$ and/or $\Gamma_7$ state mixture would be experimentally insignificant in our data.

In summary, we have successfully determined the 4f symmetry of the Yb$^{3+}$ sites in the ground state for cubic YbB$_{12}$ as the $\Gamma_8$ symmetry by the LD in Yb$^{3+}$ core-level HAXPES at two different photoelectron directions. Our result also suggests that the Yb$^{3+}$ ion model under the effective CF, in which the hybridization effects are implicitly taken into account, is available even for the valence-fluctuating system at low temperatures well below the Kondo temperature. The applicability of LD in the core-level HAXPES even to the system in cubic symmetry (not restricted to systems with lower symmetry) demonstrated here would be promising for revealing the strongly correlated orbital symmetry of the ground state in partially filled subshell, of which the charge distributions are deviated from the spherical symmetry.

We thank H. Yomosa, S. Fujioka, K. Yano, Y. Nakata, Y. Nakatani, T. Yagi, S. Tachibana, Y. Nakamura, H. Aratani, and K. Kodera for supporting the experiments. We are also grateful to K. Miyake, A. Tsuruta, Y. Saitoh, A. Yasui, and A. Fujimori for fruitful discussions. This work was supported by a Grant-in-Aid for Scientific Research (23654121), Grants-in-Aid for Young Scientists (23684027, 23740240), and a Grant-in-Aid for Innovative Areas (20102003) from MEXT and JSPS, Japan, and by Toray Science Foundation. The hard X-ray photoemission was performed at SPring-8 under the approval of JASRI (2014A1149, 2014B1305).

1. M. Kasaya, F. Iga, K. Negishi, S. Nakai, and T. Kasuya, J. Magn. Magn. Mater. 31-34, 437 (1983).
2. M. Kasaya, F. Iga, M. Takigawa, and T. Kasuya, J. Magn. Magn. Mater. 47-48, 429 (1985).
3. F. Iga, N. Shimizu, and T. Takabatake, J. Magn. Magn. Mater. 177-181, 337 (1998).
4. T. Susaki, Y. Takeda, M. Arita, K. Mamiya, A. Fujimori, K. Shimada, H. Namatame, M. Taniguchi, N. Shimizu, F. Iga, and T. Takabatake, Phys. Rev. Lett. 82, 992 (1999).
5. T. Saso and H. Harima, J. Phys. Soc. Jpn. 72, 1131 (2003).
6. H. Weng, J. Zhao, Z. Wang, Z. Fang, and X. Dai, Phys. Rev. Lett. 112, 016403 (2014).
7. M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. 104, 106408 (2010).
8. T. Takimoto, J. Phys. Soc. Jpn. 80, 123710 (2011).
9. S. Suga, K. Sakamoto, T. Okuda, K. Miyamoto, K. Kuroda, A. Sekiyama, J. Yamaguchi, H. Fujiwara, A. Iriizawa, T. Ito, S. Kimura, T. Balashov, W. Wulfhekel, S. Yeo, F. Iga, and S. Imada, J. Phys. Soc. Jpn. 83, 014705 (2014).
10. 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, 125121 (2009).
11. K. A. Kikoin and A. S. Mishchenko, J. Phys.: Condens. Matter 7, 307 (1995).
12. P. S. Riseborough, Phys. Rev. B 68, 235213 (2003).
13. J. C. Cooley, M. C. Aronson, Z. Fisk, and P. C. Canfield, Phys. Rev. Lett. 74, 1629 (1995).
14. V. N. Antonov, B. N. Harmon, and A. N. Yaresko, Phys.
Rev. B 66, 165209 (2002).

15 P. Thunström, I. Di Marco, A. Grechnev, S. Lebègue, M. I. Katsnelson, A. Svane, and O. Eriksson, Phys. Rev. B 79, 165104 (2009).

16 J. Yamaguchi, A. Sekiyama, M. Y. Kimura, H. Sugiyama, Y. Tomida, G. Funabashi, S. Komori, T. Balashov, W. Wulfhekel, T. Ito, S. Kimura, A. Higashiya, K. Tamasaku, M. Yabashi, T. Ishikawa, S. Yeo, S.-I. Lee, F. Iga, T. Takabatake and S. Suga, New J. Phys. 15, 043042 (2013).

17 A. Akabari and P. Thalmeier, J. Korean Phys. Soc. 62, 1418-1422 (2012).

18 K. S. Nemkovski, J. -M. Mignot, P. A. Ivanov, E.V. Nefedova, A. V. Rybina, L. -P. Regnault, F. Iga, and T. Takabatake, Phys. Rev. Lett. 99, 137204 (2007).

19 T. Willers, B. Fäk, N. Hollmann, P. O. Körner, Z. Hu, A. Tanaka, D. Schmitz, M. Enderle, G. Lapertot, L. H. Tjeng, and A. Severing, Phys. Rev. B 80, 115106 (2009).

20 P. Hansmann, A. Severing, Z. Hu, M. W. Haverkort, C. F. Chang, S. Klein, A. Tanaka, H. H. Hsieh, H.-J. Lin, C. T. Chen, B. Fäk, P. Lejay, and L. H. Tjeng, Phys. Rev. Lett. 100, 066405 (2008).

21 T. Willers, Z. Hu, N. Hollmann, P. O. Körner, J. Gergner, T. Burnus, H. Fujiwara, A. Tanaka, D. Schmitz, H. H. Hieh, H.-J. Lin, C. T. Chen, E. D. Bauer, J. L. Sarro, E. Goremychkin, M. Koza, L. H. Tjeng, and A. Severing, Phys. Rev. B 81, 195114 (2010).

22 T. Willers, D. T. Adroja, B. D. Rainford, Z. Hu, N. Hollmann, P. O. Körner, Y.-Y. Chin, D. Schmitz, H. H. Hieh, H.-J. Lin, C. T. Chen, E. D. Bauer, J. L. Sarro, K. J. McClellan, D. Byler, C. Geibel, F. Steglich, H. Aoki, P. Lejay, A. Tanaka, L. H. Tjeng, and A. Severing, Phys. Rev. B 85, 035117 (2012).

23 T. Mori, S. Kitayama, Y. Kanai, S. Naimen, H. Fujiwara, A. Higashiya, K. Tamasaku, A. Tanaka, K. Terashima, S. Imada, A. Yasui, Y. Saitoh, K. Yamagami, K. Yano, T. Matsumoto, T. Kiss, M. Yabashi, T. Ishikawa, S. Suga, Y. Onuki, T. Ebihara, and A. Sekiyama, J. Phys. Soc. Jpn. 83, 123702 (2014).

24 K.W. H. Stevens, Proc. Phys. Soc. London Sect. A 65, 209 (1952).

25 B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J-M. Esteve, Phys. Rev. B 32, 5107 (1985).

26 A. Tanaka and T. Jo, J. Phys. Soc. Jpn. 63, 2788 (1994).

27 R. D. Cowan, The Theory of Atomic Structure and Spectra (University of California Press, Berkeley, 1981).

28 A. Sekiyama, J. Yamaguchi, A. Higashiya, M. Obara, H. Sugiyama, M. Y. Kimura, S. Suga, S. Imada, I. A. Nekrasov, M. Yabashi, K. Tamasaku, and T. Ishikawa, New J. Phys. 12, 043045 (2010).

29 A. Sekiyama, A. Higashiya, and S. Imada, J. Electron Spectrosc. Relat. Phenom. 190, 201 (2013).

30 M. Yabashi, K. Tamasaku, and T. Ishikawa, Phys. Rev. Lett. 87, 140801 (2001).

31 H. Fujiwara, S. Naimen, A. Higashiya, Y. Kanai, H. Yomosa, K. Yamagami, T. Kiss, T. Kadono, S. Imada, A. Yamasaki, K. Takase, S. Otsuka, T. Shimizu, S. Shinbara, S. Suga, M. Yabashi, K. Tamasaku, T. Ishikawa, and A. Sekiyama, to be submitted for publication.

32 A. Czopnik, N. Shitsevalova, A. Krivchikov, Y. Paderno, and Y. Onuki, J. Phys.: Condens. Matter 17, 5971 (2005).