

Strongly correlated ground-state orbital symmetry of tetragonal and cubic Yb compounds probed by linear dichroism in *angle-resolved* core-level photoemission

Strongly correlated electron systems show a variety of intriguing phenomena such as unconventional superconductivity, nontrivial semiconducting behavior, and quantum criticality. Among them, the Yb-based single-crystalline YbRh₂Si₂, the Kondo semiconductor YbB₁₂, and the valence-fluctuating YbCu₂Si₂ have been synthesized and thus intensively studied over the past few decades. Since strong Coulomb repulsion (effective value of 5–10 eV order) acts between 4*f* electrons in Yb sites, an ionic picture is a good starting point for discussing and revealing their electronic structure as well as the origins of various phenomena. The majority of Yb ions in the above-mentioned materials are in Yb³⁺ (4*f*¹³, one 4*f* hole in other words) configurations. Yb³⁺ 4*f* levels are split by spin-orbit coupling (~1.3 eV) and further split by a crystalline electric field (CEF, <0.1 eV) in solids, as shown in Fig. 1.

Ground-state 4*f*-orbital symmetry determined by CEF splitting is very basic information on realistic strongly correlated electron systems. However, such ground-state symmetry is not straightforwardly revealed. Inelastic neutron scattering is useful, but other excitations such as phonon excitations often overlap with the 4*f*-4*f* excitation contributions [1]. Linear dichroism (LD) in 3*d*-4*f* X-ray absorption (XAS) is powerful for revealing the orbital symmetry owing to the dipole selection rules, as reported for heavy-fermion systems with nearly Ce³⁺ configurations [2,3]. However, LD in XAS is no longer available for compounds with cubic symmetry in which there is no anisotropic axis relative to the electric field of the incident light. Recently, we have discovered that the multiple-peak structure in *angle-resolved* core-level photoemission spectra relative to the crystal axis shows detectable LD reflecting the outer spatial distribution not only for tetragonal [4] but also for cubic [5] Yb compounds. This originates from the anisotropy in electron-electron Coulomb interactions and exchange interactions in the ionic 4*f* sites.

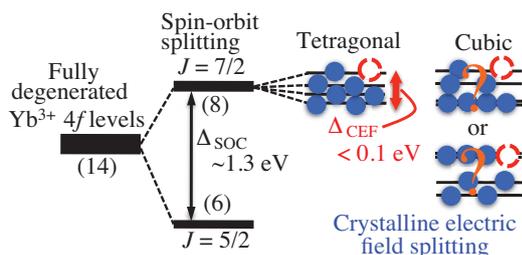


Fig. 1. Energy levels of Yb³⁺ ions in crystalline solids.

We have observed LD in hard X-ray photoemission spectroscopy (HAXPES) at beamline BL19LXU. In order to switch the linear polarization of the excitation light from the horizontal direction to the vertical direction, two single-crystalline (110) diamonds were used as a phase retarder. The experimental configuration for horizontally (vertically) polarized light excitation corresponds to *p*-polarization (*s*-polarization), in which the incident-light propagation and photoelectron detection directions are within the horizontal plane. Single crystals of the Yb compounds were cleaved or fractured *in situ*.

The polarization-dependent angle-resolved Yb³⁺ 3*d*_{5/2} core-level HAXPES spectra of YbCu₂Si₂ and YbRh₂Si₂ are shown in Fig. 2. There is a multiple-peak structure characteristic of ionic Yb³⁺ states yielding the 3*d*⁹4*f*¹³ multiplet-split peaks in the photoemission final states in all the spectra. Clear LD, defined by the difference in spectral weight between the *s*- and *p*-polarization configurations, is seen in the spectra depending on the material. For instance, in the spectra at $\theta = 0^\circ$, the peak at 1527 eV is stronger in

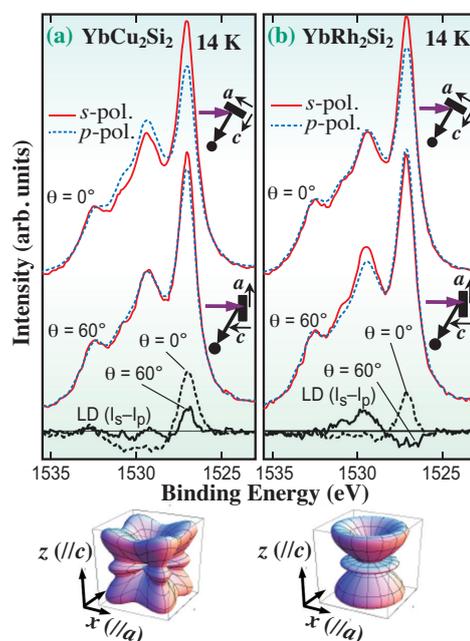


Fig. 2. (Upper) Polarization-dependent *angle-resolved* [$\theta = 0^\circ$ and 60° , where θ denotes the angle between the photoelectron detection and the [001] direction] Yb³⁺ 3*d*_{5/2} core-level HAXPES spectra and their LD for tetragonal YbCu₂Si₂ (a) and YbRh₂Si₂ (b). The inset illustrations denote the experimental configurations. (Lower) Yb³⁺ 4*f* charge spatial distributions corresponding to the ground-state wave functions (see text) for each compound obtained by our study.

the *s*-polarization configuration (*s*-pol.) than in the *p*-polarization configuration (*p*-pol.), whereas the structure with the 1529.5 eV peak and 1530.5 eV shoulder is stronger in the *p*-pol. for both compounds. On the other hand, the obtained LD is mutually different at $\theta = 60^\circ$ (incident light along the *c*-axis); whereas the LD is reduced at $\theta = 60^\circ$ while keeping the same sign as that at the same binding energy with $\theta = 0^\circ$ for YbCu₂Si₂, the sign of the LD is flipped at $\theta = 60^\circ$ relative to that at $\theta = 0^\circ$ for YbRh₂Si₂. In the case of Yb³⁺ ions with tetragonal symmetry, the eightfold degenerate $J = 7/2$ state splits into four doublets as

$$|\Gamma_7^1\rangle = c|J_z = \pm 5/2\rangle + \sqrt{1-c^2}|J_z = \mp 3/2\rangle,$$

$$|\Gamma_7^2\rangle = -\sqrt{1-c^2}|\pm 5/2\rangle + c|\mp 3/2\rangle,$$

$$|\Gamma_6^1\rangle = b|\pm 1/2\rangle + \sqrt{1-b^2}|\mp 7/2\rangle,$$

$$|\Gamma_6^2\rangle = -\sqrt{1-b^2}|\pm 1/2\rangle - b|\mp 7/2\rangle,$$

where the coefficients $0 \leq b \leq 1$, $0 \leq c \leq 1$ define the actual *4f* charge distributions and CEF splitting energies. In order to determine the ground-state symmetry on the basis of our experimental data, we have performed ionic calculations including the full multiplets and the local CEF splitting. We found that the polarization-dependent HAXPES data for YbCu₂Si₂ is best described by the ground state of $|\Gamma_7^2\rangle = -0.36|\pm 5/2\rangle + 0.93|\mp 3/2\rangle$. The LD and spectra of YbRh₂Si₂ are found to be best reproduced by the simulations for the pure $|J_z| = \pm 3/2$ state with the Γ_7 symmetry.

In the cubic symmetry, the $J = 7/2$ state splits into two doublets and one quartet as

$$|\Gamma_6\rangle = \sqrt{5/12}|\pm 7/2\rangle + \sqrt{7/12}|\mp 1/2\rangle,$$

$$|\Gamma_7\rangle = -\sqrt{3/2}|\pm 5/2\rangle + 1/2|\mp 3/2\rangle,$$

$$|\Gamma_8\rangle = \begin{cases} -\sqrt{7/12}|\pm 7/2\rangle + \sqrt{5/12}|\mp 1/2\rangle \\ 1/2|\pm 5/2\rangle + \sqrt{3/2}|\mp 3/2\rangle \end{cases}.$$

Since their *4f* charge distributions deviate from spherical symmetry even in the cubic symmetry, it is natural to expect the observation of LD in core-level photoemission for cubic Yb compounds. Indeed, LD in core-level HAXPES has been successfully detected for cubic YbB₁₂ as shown in Fig. 3. Slight but intrinsic LD can be seen in the Yb³⁺ *3d*_{5/2} spectra, where the sign of the LD is flipped at the same binding energy between the data along the [100] and [111] directions. The observed LD and spectra for YbB₁₂ are well reproduced by the simulations for the Γ_8 ground state.

The applicability of the LD in the core-level HAXPES even to the system with cubic symmetry, as demonstrated here, is promising for revealing the strongly correlated orbital symmetry of the ground state in a partially filled subshell.

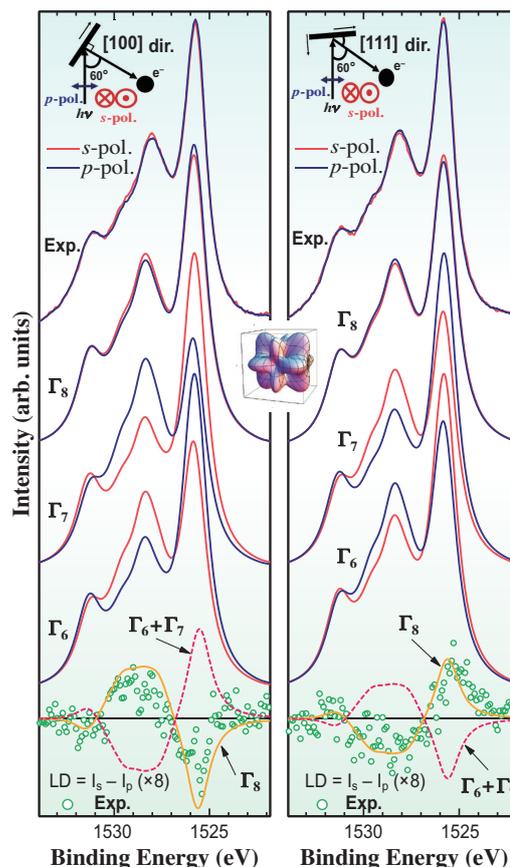


Fig. 3. Comparison of the polarization-dependent angle-resolved Yb³⁺ *3d*_{5/2} core-level HAXPES spectra and their LD for cubic YbB₁₂ with the theoretically simulated spectra for cubic symmetry. The Yb³⁺ *4f* charge distribution corresponding to the ground-state wave function (see text) for the Yb³⁺ Γ_8 symmetry realized for YbB₁₂ is also shown.

Akira Sekiyama^{a,b,*}, Yuina Kanai^{a,b} and Shin Imada^{b,c}

^a Division of Materials Physics, Osaka University

^b RIKEN SPring-8 Center

^c Department of Physical Sciences, Ritsumeikan University

*E-mail: sekiyama@mp.es.osaka-u.ac.jp

References

- [1] E. Holland-Moritz *et al.*: Phys. Rev. B **25** (1982) 7482.
- [2] P. Hansmann *et al.*: Phys. Rev. Lett. **100** (2008) 066405.
- [3] T. Willers *et al.*: Phys. Rev. B **80** (2009) 115106.
- [4] 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** (2014) 123702.
- [5] Y. Kanai, T. Mori, S. Naimen, K. Yamagami, H. Fujiwara, A. Higashiya, T. Kadono, S. Imada, T. Kiss, A. Tanaka, K. Tamasaku, M. Yabashi, T. Ishikawa, F. Iga and A. Sekiyama: J. Phys. Soc. Jpn. **84** (2015) 073705.