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Revising the $4f$ symmetry in CeCu_2Ge_2 : Soft x-ray absorption and hard x-ray photoemission spectroscopy

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We present a detailed study on the $4f$ ground-state symmetry of the pressure-induced superconductor CeCu_2Ge_2 probed by soft x-ray absorption and hard x-ray photoemission spectroscopy. The revised $4f$ ground states are determined as $|\Gamma_7\rangle = \sqrt{0.45}|J_z = \pm\frac{5}{2}\rangle - \sqrt{0.55}|\mp\frac{3}{2}\rangle$ with Σ -type in-plane rotational symmetry. This gives an in-plane magnetic moment consistent with the antiferromagnetic moment as reported in neutron measurements. Since the in-plane symmetry is the same as that for the superconductor CeCu_2Si_2 , we propose that the charge distribution along the c axis plays an essential role in driving the system into a superconducting phase.

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The discovery of the first heavy fermion superconductor CeCu_2Si_2 has attracted considerable attention to quantum critical phenomena in strongly correlated electron systems [1–4] such as high- T_c superconductivity and topological phases with strong spin-orbit interactions [5,6]. The superconductivity in CeCu_2Si_2 is suppressed by the isostructural substitution of Ge for Si [7,8]. The end-member compound tetragonal CeCu_2Ge_2 shows an antiferromagnetic long-range order below a Néel temperature (T_N) of ~ 4.2 K at ambient pressure [9]. The Sommerfeld coefficient γ is as high as 100 mJ/(mol K²), suggesting that the energy scale of the on-site Kondo fluctuation is the same order of magnitude as that of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [9]. An external pressure above 7.6 GPa induces superconductivity below 0.6 K due largely to an increase of the hybridization between the localized $4f$ and conduction electrons. Moreover, a different type of superconducting phase emerges at around 12 GPa, where an abrupt change into the critical $4f$ valence fluctuation in the presence of a strong on-site Coulomb repulsion has been proposed to understand its origin [10–12].

The low-temperature properties of these compounds are mostly determined by the $4f$ ground-state

symmetry for Ce^{3+} ions in the tetragonal crystalline electric field (CEF). The $4f$ states with a total angular momentum $J = 5/2$ split into three Kramers doublets equated to $|\Gamma_6\rangle = |J_z = \pm\frac{1}{2}\rangle$, $|\Gamma_7^1\rangle = \alpha|\pm\frac{5}{2}\rangle - \sqrt{1-\alpha^2}|\mp\frac{3}{2}\rangle$, and $|\Gamma_7^2\rangle = \sqrt{1-\alpha^2}|\pm\frac{5}{2}\rangle + \alpha|\mp\frac{3}{2}\rangle$, where α^2 denotes the mixing factor reflecting the out-of-plane (parallel to the crystal c axis) anisotropy in the spatial distribution of the $4f$ states. The α^2 value is also connected to the anisotropy in magnetic moments per Ce ion as shown in Fig. 1 [13,14]. The out-of-plane anisotropy can be determined by linearly polarized soft x-ray absorption spectroscopy (XAS) [15–17], and the phase diagram of tetragonal $\text{CeIr}_{1-x}\text{Rh}_x\text{In}_5$ has shown to be scaled by α^2 [17]. Therefore, it has been recognized that proving ground-state symmetry is of great importance to elucidate the origin of quantum critical phenomena. In addition, the sign of α gives the in-plane (perpendicular to the c axis) rotational symmetry labeled as Σ -type (Π -type) Γ_7 , whose charge distribution has valleys (crests) in the [100] direction as shown in Fig. 1(b). The in-plane symmetry for both CeCu_2Si_2 and CeCu_2Ge_2 has been determined as Σ -type Γ_7 using nonresonant inelastic x-ray scattering (NIXS) [18,19].

However, the CEF ground-state symmetry of CeCu_2Ge_2 is still puzzling. It has been reported that the $4f$ symmetry is described as $|\Gamma_7\rangle = 0.9|\pm\frac{5}{2}\rangle \pm 0.435|\mp\frac{3}{2}\rangle$ [20]. The corresponding α^2 value of 0.81 yields an expected magnetic moment of $\sim 1.5\mu_B/\text{Ce}$ along the c axis as obtained from

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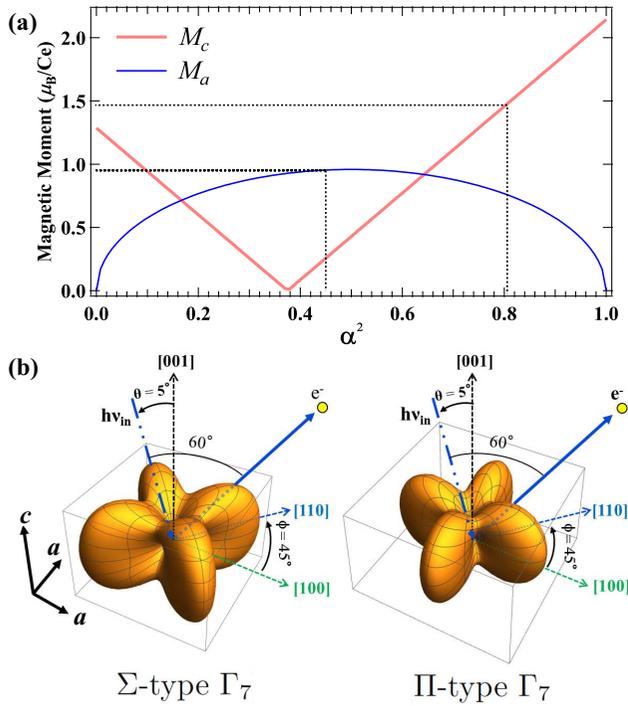


FIG. 1. (a) Expectation values of magnetic moments along the a and c axes per a Ce^{3+} ion denoted as M_a and M_c for the $|\Gamma_7\rangle = \alpha |\pm \frac{3}{2}\rangle \pm \sqrt{1 - \alpha^2} |\mp \frac{3}{2}\rangle$ ground states plotted as a function of α^2 . Dashed lines are guides for the eye for $\alpha^2 = 0.45$ and 0.81 . (b) Angular distribution of charge density plot of the Γ_7 states with the possible rotational symmetry of Σ type (left) and Π type (right). In the HAXPES measurements, the angle between the incoming x ray (projection from an outgoing photoelectron to the ab plane) and the $[001]$ direction ($[100]$ direction) is defined as θ (ϕ).

Fig. 1, which is much larger than a magnetic ordered moment of $1.04\mu_B/\text{Ce}$ below T_N observed in neutron measurements [21–23]. It is also in sharp contrast to the Ce moments pointing in the ab plane [22,23]. Therefore, it is essential to determine the $4f$ ground-state symmetry of CeCu_2Ge_2 by utilizing advanced spectroscopy.

In this Rapid Communication, we report a revising ground-state symmetry of CeCu_2Ge_2 studied by the polarized XAS and hard x-ray photoemission spectroscopy (HAXPES). The mixing parameter α^2 , obtained by XAS, successfully explains the magnetic susceptibility. By analyzing the Ce $3d$ core-level HAXPES spectra using the same α^2 value [24–26], in-plane symmetry of the $4f$ states is determined as Σ -type Γ_7 , which is consistent with the results obtained from NIXS measurements [19].

High-quality CeCu_2Ge_2 single crystals were grown by the Cu-Ge flux method [27]. Magnetic susceptibility was measured by means of a superconducting quantum interface device (SQUID) magnetometer (Quantum Design, MPMS3). XAS measurements were performed at the twin-helical undulator beamline BL23SU of SPring-8 [28]. The XAS spectra were obtained in total-electron-yield mode with an energy resolution of 80 meV, and the base pressure was about 1.1×10^{-8} Pa. The HAXPES measurements were performed at BL19LXU of SPring-8 [29], where a MBS A1-HE hemispher-

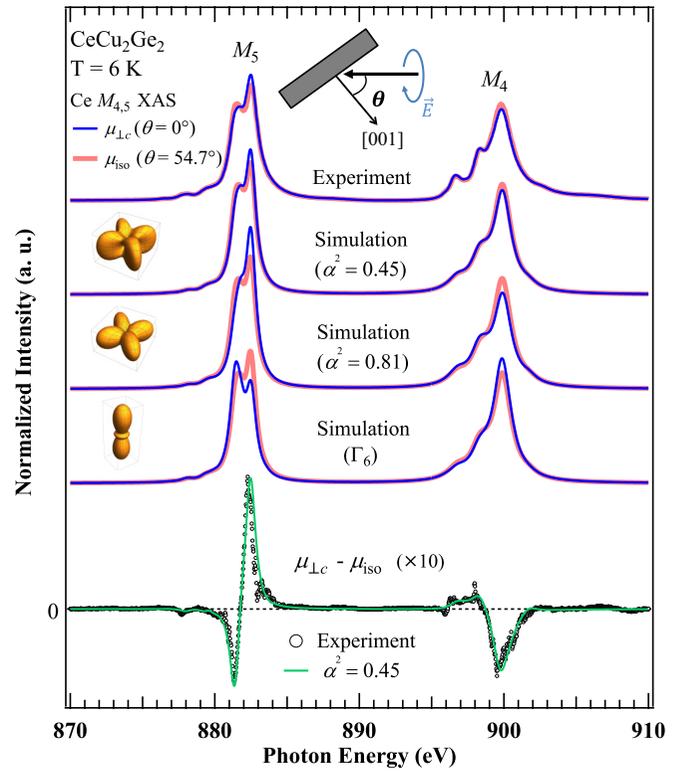


FIG. 2. Circularly polarized XAS spectra of CeCu_2Ge_2 at the Ce $M_{4,5}$ absorption edges (top) obtained for x-ray incidence angles of $\theta = 0^\circ$ ($\mu_{\perp c}$) and 54.7° (μ_{iso}) with respect to the c axis parallel to the surface normal. The spectral simulations assuming the ground state of Γ_7 ($\alpha^2 = 0.45$), Γ_7 ($\alpha^2 = 0.81$), and Γ_6 symmetry together with the initial-state $4f$ charge distributions. The $\mu_{\perp c} - \mu_{\text{iso}}$ spectrum is compared with the best-fit simulation assuming Γ_7 ground states with $\alpha^2 = 0.45$ (bottom). The error bar of the experimental $\mu_{\perp c} - \mu_{\text{iso}}$ spectrum is within the size of the markers.

ical electron analyzer and transmission-type phase retarders were installed [30]. The degree of linear polarization (P_L) of the polarization-switched x ray was estimated as -0.93 , corresponding to the vertically linear polarization components of 96.5%. The energy resolution was set to 500 meV, and the base pressure was 1.8×10^{-7} Pa. The samples were cleaved to expose clean (001) surfaces and the measurement temperatures were set to 6 and 10 K for XAS and HAXPES measurements, respectively, both of which were sufficiently lower than the excited states at ~ 200 K [31].

The XAS and HAXPES spectra were simulated by making use of full multiplet calculations for $\text{Ce}^{3+} 3d^{10}4f^1 \rightarrow 3d^94f^2$ and $3d^{10}4f^1 \rightarrow 3d^94f^1 + e^-$ electric-dipole transitions, respectively, with the XTLS 9.0 program [32]. The atomic parameters of the $4f$ - $4f$ and $3d$ - $4f$ Coulomb interactions, the $3d$ and $4f$ spin-orbit couplings, were obtained from the Hartree-Fock values for Ce^{3+} [33]. We obtained a reduction factor of 58% (97% and 75%) for the $4f$ - $4f$ interaction (spin-orbit couplings for $3d$ and $4f$) by fitting our experimental isotropic Ce $M_{4,5}$ XAS spectrum [15]. The CEF energy for the first (second) excited state ΔE_1 (ΔE_2) = 197 (212) K have been obtained from inelastic neutron scattering (INS) measurements [31].

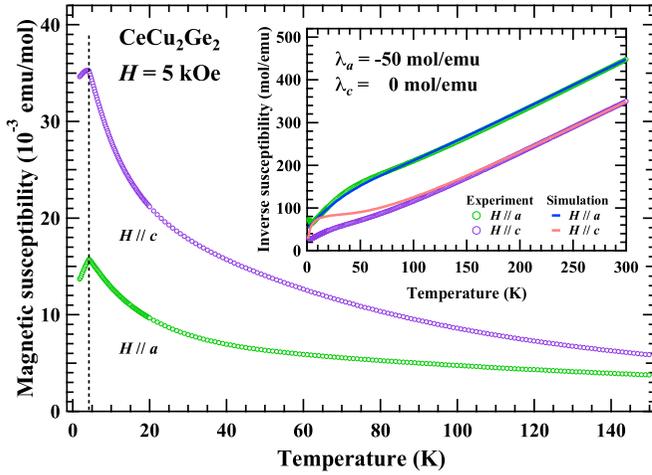


FIG. 3. Anisotropic magnetic susceptibility obtained by applying a magnetic field parallel to the a and c axes. The vertical dashed line indicates T_N . The inset shows the inverse magnetic susceptibility with those obtained by simulation based on the CEF model (solid lines). An anisotropic molecular field parameter of λ_a (λ_c) = -50 (0) mol/emu is taken into account in the simulation along the a (c) axis.

Figure 2 shows the circularly polarized Ce $M_{4,5}$ XAS data of CeCu₂Ge₂ (top) measured for photon incidence angles of $\theta = 0^\circ$ and 54.7° relative to the c axis (surface normal). The $\theta = 0^\circ$ geometry yields the XAS intensity with the linear polarization \vec{E} perpendicular to the tetragonal c axis, labeled as $\mu_{\perp c}$, since the electric field vector \vec{E} must be transverse to the direction of light propagation [34]. The spectrum for $\theta = 54.7^\circ$ provides the polarization-averaged isotropic XAS spectrum $\mu_{\text{iso}} = (2\mu_{\perp c} + \mu_{\parallel c})/3$, where $\mu_{\parallel c}$ denotes the XAS intensity with \vec{E} parallel to the c axis. The initial-state $4f^0$ components at around 888 eV are negligibly small, indicating a highly localized character of the $4f$ states [18,34]. The $\mu_{\perp c}$ signals deviate from the isotropic spectrum, as shown in the difference spectrum defined as $\mu_{\perp c} - \mu_{\text{iso}}$ (bottom), reflecting the orbital anisotropy of the Ce $4f$ states. The spectral simulation rules out the $|\Gamma_7\rangle = \alpha |\pm \frac{5}{2}\rangle \pm \sqrt{1-\alpha^2} |\mp \frac{3}{2}\rangle$ ground states with $\alpha^2 = 0.81$, since the polarization dependence of the simulated spectra at $M_{4,5}$ edges is too large to account for the experimental data. By fitting the $\mu_{\perp c} - \mu_{\text{iso}}$ spectrum (bottom), we find the best-fit parameter of $\alpha^2 = 0.45 \pm 0.05$ for the Γ_7 states, yielding a magnetic moment along the a axis (M_a) of $0.95\mu_B/\text{Ce}$ as obtained from Fig. 1(a). This value agrees well with the in-plane Ce moment of $1.04\mu_B$ as reported in INS measurements [9,21,23]. Note that a spectral simulation for Γ_6 ground states results in the relative intensity of two multiplet peaks at the M_5 edge different from the experimental signals and thus the possibility of the Γ_6 ground states is excluded.

Figure 3 displays the magnetic susceptibility obtained under an external magnetic field of $H = 5$ kOe parallel to the a and c axes. In the antiferromagnetically ordered phase below T_N , the c -axis susceptibility χ_c is nearly constant, while the a -axis susceptibility χ_a tends to decrease with temperature. This is consistent with the ordered magnetic moment aligned in the ab plane as reported in neutron measurements [23], although

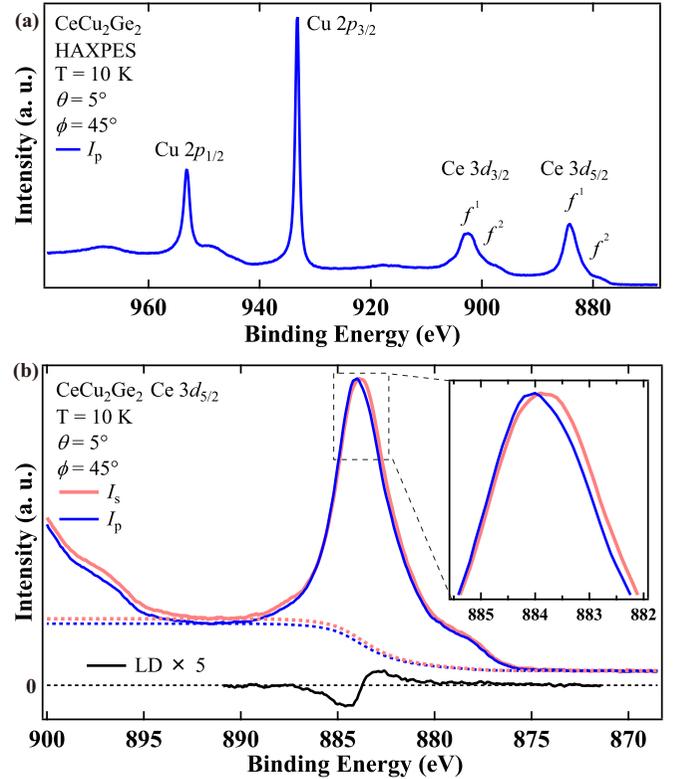


FIG. 4. (a) Ce $3d$ core-level spectrum together with Cu $2p$ states. (b) Polarized Ce $3d_{5/2}$ HAXPES (solid lines) with the backgrounds (dashed line) obtained by the experimental geometry as shown in Fig. 1(b). The thin and thick solid lines denote the photoelectron intensities of I_s and I_p , and corresponding LD is plotted in the bottom. The inset shows an enlarged view around the main $3d_{5/2}$ peak.

χ_a is smaller than χ_c . As shown in the inset, χ_c^{-1} is well reproduced by the simulation of χ_{CEF}^{-1} given by a standard CEF calculation assuming the Γ_7 ground states with $\alpha^2 = 0.45$ as determined by XAS and the CEF energy of ΔE_1 (ΔE_2) = 197 (212) K [31]. On the other hand, χ_a^{-1} is fitted by using $\chi^{-1} = \chi_{\text{CEF}}^{-1} - \lambda_a$, where λ_a is the anisotropic molecular field parameter along the a axis of -50 mol/emu. This suggests that anisotropy of the magnetic exchange interactions between the Ce ions is important for the antiferromagnetic structure.

To determine the rotational symmetry of the Γ_7 ground state, we have performed the Ce $3d$ core-level HAXPES measurements. Figure 4(a) shows an overview of the Ce $3d$ and Cu $2p$ core-level spectra. The Ce $3d$ spectrum shows atomlike multiplets mainly due to the $3d^9 4f^1$ and $3d^9 4f^2$ final states [35]. The Cu $2p$ spectrum shows sharp peaks without satellite $2p^5 3d^9$ final-state multiplet structures [36,37], indicating that the Cu $3d$ states are fully occupied. Thus the Cu $3d$ states hardly hybridize with the Ce $4f$ states. Figure 4(b) shows the Ce $3d_{5/2}$ spectra obtained by using linearly polarized x rays. As shown in the inset, the intensity obtained with s - and p -polarized configurations labeled as I_s and I_p is switched around the peak top at ~ 884 eV. This is highlighted in the linear dichroism (LD) spectrum defined here by the difference of intensity normalized from 871.4 to

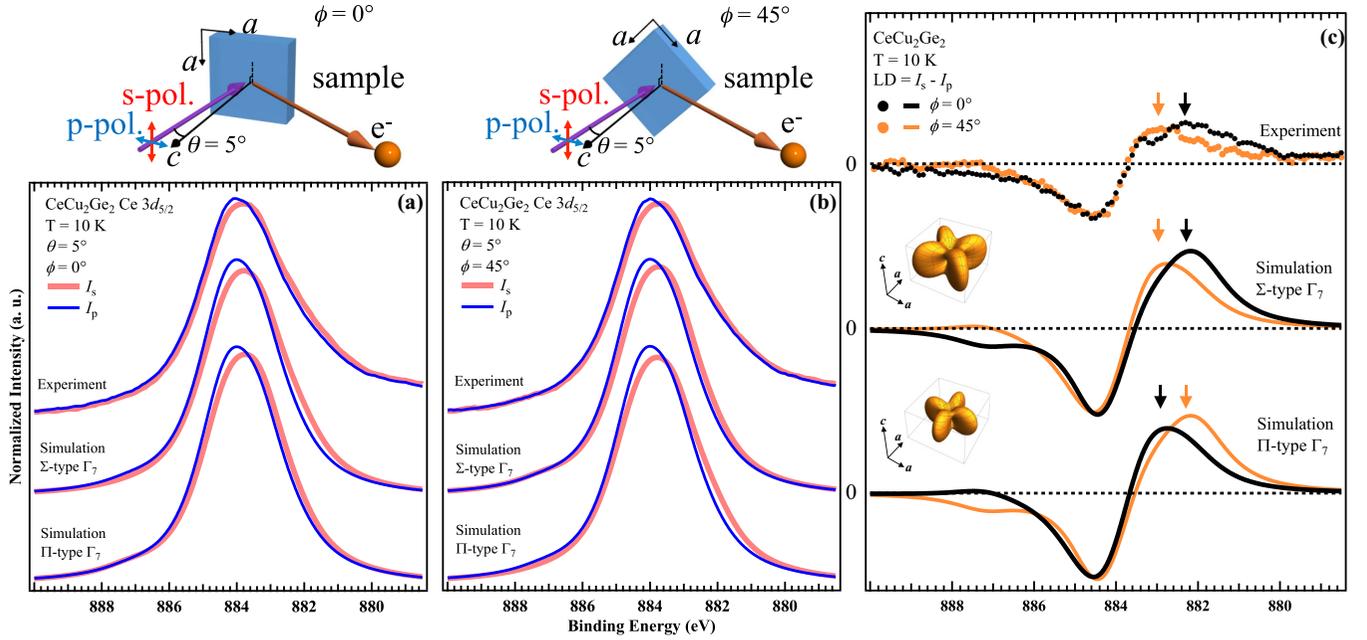


FIG. 5. (a), (b) Linearly polarized Ce $3d_{5/2}$ core-level HAXPES spectra recorded by s - and p -polarized photons together with the spectral simulations assuming the Σ -type Γ_7 and Π -type Γ_7 ground states for the $\phi = 0^\circ$ and 45° configurations. The experimental geometries are illustrated on the top, where the angle between the c axis and the detected photoelectron direction is set to 55° . (c) ϕ -dependent LD obtained by HAXPES and spectral simulations. The error bar of experimental LD spectra is indicated by the size of the markers.

841.6 eV as $I_s - I_p$, after subtracting the background. The sign change of the LD spectrum is attributed to the anisotropic charge distribution of the $4f$ states.

Figures 5(a) and 5(b) show the experimentally observed azimuthal rotation dependence of Ce $3d_{5/2}$ spectra (top) obtained at $\phi = 0^\circ$ and 45° , respectively. Although the difference between I_s and I_p at the higher-energy side of the peak top is similar to each configuration, the dichroism at the low-energy tail around 882 eV in the $\phi = 0^\circ$ configuration is slightly stronger than that in the $\phi = 45^\circ$ spectrum. This tendency is clearly observed in the azimuthal angle dependence of the LD spectra as shown in Fig. 5(c). The major difference between $\phi = 0^\circ$ and 45° configurations is observed in the region with a positive sign of LD spectra between 880 and 883.5 eV, and the positive peak indicated by the arrow of the 45° spectrum is located at the higher-energy side than that of the 0° spectrum. Azimuthal dependence of the LD spectra is clearly reproduced by the spectral simulation assuming the Σ -type Γ_7 ground states with the same mixing parameter as that obtained by the XAS. Note that Π -type symmetry is obviously ruled out since the spectral simulation shows the opposite trend around 882 eV for the experimental LD spectra. Thus we can identify the in-plane rotational symmetry of Σ -type Γ_7 , which is in line with the results of NIXS measurements [19].

The $4f$ symmetry of CEF ground states of the Ce^{3+} ion in CeCu_2Ge_2 is thus successfully determined as

$$|\Sigma\text{-type } \Gamma_7\rangle = \sqrt{0.45} |\pm\frac{5}{2}\rangle - \sqrt{0.55} |\mp\frac{3}{2}\rangle.$$

The in-plane symmetry of CeCu_2Ge_2 is the same as that of CeCu_2Si_2 , which has been reported as $|\Sigma\text{-type } \Gamma_7\rangle = \sqrt{0.77} |\pm\frac{5}{2}\rangle - \sqrt{0.23} |\mp\frac{3}{2}\rangle$ [18,38]. Note that the $4f$ charge

distribution of CeCu_2Si_2 is rather compressed along the c axis in comparison with that of CeCu_2Ge_2 . Our findings suggest that the c -axis anisotropy of the $4f$ states could play an important role in emerging unconventional superconductivity. Most interesting is that the c -axis anisotropy of CeCu_2X_2 ($X = \text{Si}, \text{Ge}$) shows a trend opposite to that of $\text{CeIr}_{1-x}\text{Rh}_x\text{In}_5$ [17], where the $4f$ charge distribution in the superconducting phase expands to the c axis to gain the hybridization with conduction electrons [17]. Therefore, it would be important to take into account the anisotropic hybridization effects, which induce the momentum-dependent heavy electronic structures as reported in the superconductor CeNi_2Ge_2 [39]. This motivates us the systematic investigation of $4f$ symmetry for the $\text{Ce}M_2X_2$ ($M =$ transition metal) systems to reveal the origin of the quantum criticality.

In conclusion, we have determined the Ce $4f$ symmetry of CeCu_2Ge_2 using the combined technique of polarized XAS and core-level HAXPES. The revised out-of-plane anisotropy parameter of α^2 was estimated as 0.45 ± 0.05 , which can explain the magnetic properties. The in-plane $4f$ symmetry is Σ type, the same as that of the superconducting CeCu_2Si_2 , suggesting that the out-of-plane anisotropy plays an essential role in driving the system into the superconducting phase.

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