Possible multi-orbital ground state in CeCu$_2$Si$_2$.

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The crystal-field ground state wave function of CeCu$_2$Si$_2$ has been investigated with linear polarized $M$-edge x-ray absorption spectroscopy from 250 mK to 250 K, thus covering the superconducting ($T_c=0.6$ K), the Kondo ($T_K \approx 20$ K) as well as the Curie-Weiss regime. The comparison with full-multiplet calculations shows that the temperature dependence of the experimental linear dichroism is well explained with a $\Gamma_{4}^{(1)}$ crystal-field ground-state and the thermal population of excited states at around 30 meV. The crystal-field scheme does not change throughout the entire temperature range thus making the scenario of orbital switching unlikely. Spectroscopic evidence for the presence of the Ce $4f$ configuration in the ground state is consistent with the possibility for a multi-orbital character of the ground state. We estimate from the Kondo temperature and crystal-field splitting energies that several percents of the higher lying $\Gamma_6$ state and $\Gamma_7$ crystal-field states are mixed into the primarily $\Gamma_4^{(3)}$ ground state. This estimate is also supported by re-normalized band-structure calculations that uses the experimentally determined crystal-field scheme.

I. INTRODUCTION

Heavy fermion compounds are $f$ electron systems where, at low temperatures, the hybridization of localized $4f$ or $5f$ and conduction electrons ($c/f$-hybridization) forms an entangled ground state with quasiparticles that can have effective masses up to three orders of magnitude larger than the free electron mass$^{[1,2]}$. The $c/f$-hybridization goes along with a certain delocalization of the $f$ electrons and depending on the degree of delocalization magnetic order, unconventional superconductivity or intermediate valence occurs. Here superconductivity usually occurs in the vicinity of the quantum critical point where the magnetic order transitions are suppressed to zero Kelvin$^{[3,4]}$. In the heavy fermion compound CeCu$_2$Si$_2$, a material with a Kondo temperature of $T_K \approx 20$ K$^{[5,6]}$, unconventional superconductivity was observed for the first time$^{[7]}$ opening up an entire new field of research. Superconductivity in CeCu$_2$Si$_2$ appears at ambient pressure but also in a wider range of applied pressures where two superconducting domes have been observed with maxima at 0.45 GPa ($T_c = 0.6$ K) and 4.5 GPa ($T_c = 2$ K) in the pressure($P$)/temperature($T$) phase diagram$^{[8]}$. The substitution of Si by the larger Ge separates the two domes$^{[9]}$ suggesting the two superconducting phases may be of different origin.

The ambient or low pressure superconducting phase is close to antiferromagnetism; small changes in the Si stoichiometry lead to an antiferromagnetic ground state$^{[10]}$. It is therefore likely that spin fluctuations are responsible for the formation of Cooper pairs and there is strong evidence for the $d$-wave character of this superconducting phase$^{[11,12]}$. For the high pressure superconducting phase, however, valence fluctuations were proposed to provide the pairing mechanism$^{[13]}$ but so far a valence transition at applied pressure has not been experimentally confirmed$^{[14]}$.

The $d$-wave character of the ambient pressure superconductivity in CeCu$_2$Si$_2$ has been contested recently$^{[15]}$ and here the determination of the crystal-field wave functions of the crystal-field split Hund’s rule ground state has become important. Is the ground state a multiorbital state as suggested by Ref.$^{[16]}$? Or does an orbital switching as function of temperature take place as suggested in another scenario to model the double dome structure of the two superconducting phases$^{[17]}$? For further clarification it is therefore indispensable to revisit spectroscopically the crystal-field problem of CeCu$_2$Si$_2$ and its temperature dependence.

We recall the $J = 5/2$ Hund’s rule ground state of Ce in CeCu$_2$Si$_2$ is split by the tetragonal crystal field into two
and one \( \Gamma_6 \) Kramers doublet which can be written in \( J_z \) representation with \( 0 \leq |\alpha| \leq 1 \):

\[
\begin{align*}
\Gamma_7^{(1)} &= |\pm 5/2 \rangle + \sqrt{1 - \alpha^2}| \mp 3/2 \rangle, \\
\Gamma_7^{(2)} &= \sqrt{1 - \alpha^2}| \pm 5/2 \rangle - |\mp 3/2 \rangle, \\
\Gamma_6 &= | \pm 1/2 \rangle
\end{align*}
\] (1)

Here the \( \Gamma_7^{1,2} \) orbital states distinguish each other in their \( J_z \) admixture and orientation within the unit cell; for \( \alpha > 0 \) the lobes of the angular distribution of the \( \Gamma_7 \) state points along [100] and for \( \alpha < 0 \) along [110] (see Fig.1), for \( \alpha = 0 \) i.e. in case of a pure \( J_z \) state the orbital has full rotational symmetry around the [001] axis. Goremychkin et al. found with inelastic neutron scattering two strongly broadened and almost degenerate crystal-field excitations at about 30 meV [21]. In the Goremychkin neutron experiment the crystal-field wave functions were, however, determined from the anisotropy of the static susceptibility \( \chi_{\text{stat}} \) which is well described with a \( \Gamma_7^{(1)} \) ground state with \( |\alpha| = 0.88 \). Note, inelastic neutron scattering cannot determine the sign of \( \alpha \) in the wave function since it is dipole limited. Non-resonant inelastic x-ray scattering (NIXS) overcomes this dipole limitation [22] and Willers et al. found that \( \alpha \) in \( \Gamma_7^{(1)} \) is negative at 20 K i.e. the \( \Gamma_7^{(1)} \) with its lobes along the (110) direction forms the ground state at 20 K [25]. The NIXS experiment was performed well above \( T_K \) and \( T_c \) without looking explicitly at the \( J_z \) admixture (ac anisotropy). Hence, till today, there is no spectroscopic information available about the \( J_z \) admixture of the ground-state wave function of CeCu$_2$Si$_2$, nor about the possibility of a cf-hybridization induced multiorbital ground state [19] or orbital reoccupation [20].

The present work addresses this lack of information. We set up an experiment with the aim to investigate the crystal-field wave functions of the ground state, below \( T_K \) and \( T_c \), and well above, looking also for any changes in the orbital occupation that cannot be explained with the Boltzmann-type thermal occupation of excited crystal-field states.

II. METHOD

X-ray absorption spectroscopy (XAS) is an element specific probe for valence, spin and orbital degrees of freedom [20–28]. In particular, the linear dichroism (LD) of linear polarized XAS (XLD) at the rare earth \( M_{4,5} \) edges \((3d^{10}4f^1 \rightarrow 3d^34f^2) \) measures the anisotropy of the \( 4f^1 \) wave function of the crystal-field ground split Hund’s rule ground state of Ce$^{3+}$ \((J = 5/2) \) with unprecedented accuracy [29, 33]. XAS is element specific and the signal to background ratio is very good. XLD probes specifically the ground-state symmetry when working at low \( T \). Excited crystal-field states contribute via thermal occupation.

XLD is based on dipole selection rules and each \( J_z \) state exhibits its own specific directional dependence [29] resulting in a specific dichroism LD\(_J_z\) that relate to each other as \( \text{LD}_{J_z} = -5 \text{LD}_{J_z} \approx -1.25 \text{LD}_{J_z} \). Although the data analysis was performed with a full multiplet calculation (see below), the analysis becomes more intuitive when expressing the LD of each crystal-field state in terms of incoherent sums of the individual LD\(_J_z\). This is only possible when the rotational symmetry is higher than twofold and as long as the crystal-field splitting is small with respect to the spin orbit splitting [29]. Both are fulfilled for CeCu$_2$Si$_2$ so that we can write for the LD of the \( \Gamma_7^{(1)} \) state:

\[
\text{LD}_{\Gamma_7^{(1)}} = \alpha^2 \text{LD}_{5/2} + (1 - \alpha^2) \text{LD}_{3/2}
\] (4)

The LD\(_{\Gamma_7^{(1)}}\) of the \( \Gamma_7^{(2)} \) state can be written accordingly. This little exercise demonstrates that XLD is sensitive to the square of \( \alpha \) and therefore not to its sign. When excited states get populated with rising temperature the total LD(\( T \)) signal is the superposition of the individual LDs of each crystal-field state, weighted by thermal occupation.

![Fig. 1. ThCr$_2$Si$_2$ structure of CeCu$_2$Si$_2$ with Ce $\Gamma_7^{(1)}$ (left) and $\Gamma_7^{(2)}$ orbital (right) at the body center of the unit cell. The aspect ratios of the orbitals correspond to eq.(1) and (2) with $\alpha = 0.59$ and the orientation to $\alpha < 0$.](image-url)
III. EXPERIMENT AND SIMULATIONS

The XLD experiment was performed on well characterized superconducting CeCu$_2$Si$_2$ single crystals [33] at the DEIMOS beamline at synchrotron SOLEIL in France [39] between 0.25 and 5 K, at the BOREAS beamline at synchrotron ALBA in Spain [37] between 3.2 and 150 K and the DRAGON beamline of the NSRRC in Taiwan between 100 and 250 K. The energy resolution at the Ce $M_{4,5}$ edge at $h\nu \approx 870$-910 eV was about 0.4 eV. The DEIMOS beamline is quite unique in the world since its cryomagnet is equipped with an insert for cooling to 250 mK in ultra high vacuum (UHV) [38]. The temperature stability is within a few percent and the temperature difference between thermocouple and sample surface amounts to 50 to 100 mK depending on thermal contact. The BOREAS beamline has the advantage of a reference sample in the beam so that small drifts in energy can be easily corrected. At all beamlines the samples were cleaved in situ in ultra high vacuum and then transferred to a main chamber ($10^{-10}$ mbar) where the signal was recorded in the total-electron-yield (TEY) mode by measuring the drain current. The cleaved $ac$ surface was perpendicular to the Poynting vector, with $c$ being the fourfold tetragonal axis, so that data could be taken with the electric field vector $\vec{E} \parallel c$ and $\vec{E} \perp c$. This was achieved at the DEIMOS and BOREAS beamline by changing the polarization of the light impinging on the sample. At the DRAGON beamline the polarization cannot be changed and, instead, the sample is turned to achieve the polarization parallel and perpendicular to the $c$-axis. All samples were aligned with the Laue method prior to the experiment.

The data were normalized to the integrated intensity of the experimental isotropic spectra, constructed as $I_{iso} = (I_{E \parallel c} + 2I_{E \perp c})/3$, and compared with simulations obtained with the full multiplet code Quanty [39]. The atomic parameters for the 4$f$-4$f$ and 3$d$-4$f$ Coulomb interactions were calculated with the Cowan code [40] and reduced by about 21% and 39%, respectively, to account for configuration interaction effects that are not included in the Hartee-Fock scheme. The reduction factors are determined by optimizing the XAS simulation to $I_{iso}$ without taking into account the crystal-field splitting of the Hund’s rule ground state. Configuration interaction effects are not considered. For obtaining the best crystal-field description of the linear polarized data the linear dichroism $LD = I_{E \parallel c} - I_{E \perp c}$ was fitted because the background due to the edge jump as well as the 4$f^0$ satellite do not show any dichroism and so they cancel out in the LD.

IV. RESULTS

Figure 2(a) shows the XLD data of CeCu$_2$Si$_2$ at 0.25 K and panel (b) the simulation based on a single ion crystal-field model with a ground state $\Gamma_V^{(1)}$ (eq. (1)) with $\alpha = 0.59 \pm 0.1$. The comparison of the experimental and simulated dichroism $LD = I_{E \parallel c} - I_{E \perp c}$ in Fig. 2(c) establishes how well the data are reproduced.

The temperature dependence of the LD is displayed in Fig. 3(a)-(d); for $T = 0.25$ to 5 K in panel (a) and (b), for $T = 3.2$ to 150 K in panel (c) and (d), and for $T = 100$ to 250 K in panel (e) and (f). Within the accuracy of the experiment, there is no change in the LD up to 75 K. At 150 K, however, the LD decreases a fair amount. Figure 3(g) and (h) show the simulated LD on the basis of a $\Gamma_V^{(1)}$ ground-state wave function with $\alpha = 0.59$ and excited states $\Gamma_6$ and $\Gamma_V^{(2)}$ at around 30 meV: The latter crystal-field splitting energies are from the neutron
FIG. 3. (color online) Experimental linear dichroism $\text{LD} = I_{\parallel} - I_{\perp}$ at the $M_5$ and $M_4$ edges for $T = 0.25$ to 5 K (SOLEIL data) in panel (a) and (b) and for $T = 3.2$ to 150 K (ALBA data) in panel (c) and (d), and $T = 100$ to 250 K (NSRRC data) in panel (e) and (f). Panel (g) and (h) shows the full multiplet simulations taking into account the thermal population of crystal-field states at around 30 meV.

The question is now whether the ground state is given by just one crystal-field state or whether higher lying crystal-field states contribute. The answer to this question is of relevance for the development of multi-orbital based models [13] that perhaps could explain why the d-wave superconductor CeCu$_2$Si$_2$ may be fully gapped at sufficiently low temperatures [16-18].

The experimental XAS spectra, see Fig.4(a), exhibit the small but distinct feature at about 880 eV photon energy which can be attributed to the presence of the Ce 4$f^0$ configuration in the ground state [31]. This in turn signals that the $cf$-hybridization is active and thus also provides a channel for the higher lying crystal-field states to mix into the ground state. The amount of mixing-in is not negligible for systems with high Kondo temperatures such as CeRu$_4$Sn$_8$ [12] and also CeCoIn$_5$ [13] where the crystal-field splittings are not much larger than the Kondo energy scale. For CeCu$_2$Si$_2$, however, we expect that the involvement of the higher crystal-field states will be quite small because transport and thermodynamic measurements indicate a Kondo temperature of about 20 K [3, 6] which is small with respect to the crystal-field splitting $\Delta_f \approx 30$ meV [21].

In the following we will utilize our spectroscopy to obtain an independent check on the Kondo energy scale by looking at the evolution of the relative 4$f^0$ spectral weight as function of temperature. Panel (b)-(e) of Fig.4 display the $f^0$ satellites (see rectangles in panel (a) and (b)) on an enlarged scale. We find that the 4$f^0$ spectral weight remains unchanged up to 5 K (panel (b) and (c)) within the accuracy of the data, decreases slightly at 50 and 75 K (panel (d) and (e)), and is strongly reduced at 150 K. Panel (f) and (g) of Fig.4 show $\tilde{n}(T)$, the integrated intensity of the $f^0$ satellite between $T = 3.2$ and 150 K after subtracting a linear background. According to a self consistent large-orbital-degeneracy theory by Bickers, Cox and Wilkins [41] the presence of the Kondo effect is reflected in the temperature dependence of $\tilde{n}(T)$. It should show a gradual decrease with temperature followed by a flattening out for $T = \infty \gg T_K$. In particular, at $T_K$ it exhibits an inflection point at 1/2 of the difference of its high and low temperature value. Although here we do not observe the flattening out of $\tilde{n}(T)$, possibly because of the population of excited crystal-field states (see Ref.42), we do observe a strong drop of $\tilde{n}(T)$ not far from the literature value of $T_K = 20$ K [2, 6]. We thus find CeCu$_2$Si$_2$ is indeed a material with a relatively low $T_K$.

We now carry out an analysis using a simple approximation scheme for the Anderson impurity Hamiltonian [46] in order to estimate how much of the higher lying $\Gamma_6$ and $\Gamma_7^{(2)}$ crystal-field states contribute to the spectral changes while going from the superconducting, via the Kondo, to the Curie-Weiss regime up to 75 K. This strongly suggest that the orbital switching as function of temperature as suggested in Ref. [20] does not take place. Instead, the XAS/LD results point towards a robust static crystal-field scheme.

The XAS spectra and the LD therein of In CeCu$_2$Si$_2$ have been measured in the wide temperature range from 250 mK to 250 K. The data are all well described with the single-orbital crystal-field ground state wave function

$$\Gamma_f^{(1)} = -0.59|5/2\rangle + 0.81|3/2\rangle$$

and the Boltzmann occupation of the excited states at $\approx 30$ meV. We especially note that there are no noticeable results in Ref [21]. The simulations reproduce the experimental data very well. A crystal-field state at e.g. 12 meV as suggested by Horn et al [41] on the other hand would lead to a much faster reduction of LD and can therefore be excluded.

V. DISCUSSION
primarily \( \Gamma_{7}^{(1)} \) ground state. The approximate description is valid at temperatures \( T \lesssim T_{0} \) where \( T_{0} \) is the characteristic temperature of heavy fermion or valence fluctuating systems and the results smoothly reduce to the predictions of the variational treatment \cite{34, 47}. Assuming a constant density of conduction states \( N\left(0\right) \), the occupancies of the crystal-field split \( 4f \)-states are given by

\[ n_{f\Gamma} \sim \left(1 - n_{f}\right) |V_{\Gamma}|^{2} N\left(0\right) \frac{1}{k_{B}T_{0} + \Delta_{\Gamma}} \]

where \( \Gamma \) refers to the representation, i.e., \( \Gamma = \Gamma_{7}^{(1)}, \Gamma_{6}, \) or \( \Gamma_{7}^{(2)} \), \( \tau = \pm \) accounts for the Kramers degeneracy, and \( \Delta_{\Gamma} \) is the crystal-field excitation energy relative to the crystal-field ground state. In the systems under consideration, the crystal-field splitting largely exceeds the characteristic energy \( \Delta_{\Gamma} \gg k_{B}T_{0} \). The cf hybridization \( |V_{\Gamma}| \) may depend on the symmetry of the crystal-field state \( \Gamma \) and the weight of the \( f^{0} \)-configuration in the ground state is given by

\[ (1 - n_{f}) = \frac{1}{1 + \sum_{\tau'} \frac{2|V_{\tau'}|^{2} N(0)}{k_{B}T_{0} + \Delta_{\Gamma_{\tau}}} } \]

In \( \text{CeCu}_{2}\text{Si}_{2} \), \( (1 - n_{f}) \sim 0.01 - 0.03 \) and the dominant contribution to the low-energy states comes from the \( \Gamma_{7}^{(1)} \) crystal-field ground state. We anticipate, however, a \( \Gamma_{6} \)-contribution

\[ \sum_{\tau = \pm} n_{f\Gamma_{6}} = \sum_{\tau = \pm} \frac{2|V_{\tau}|^{2} N(0)}{k_{B}T_{0} + \Delta_{\Gamma_{6}}} \sim \frac{|V_{\Gamma_{6}|^{2}}}{k_{B}T_{0} + \Delta_{\Gamma_{6}}} \sim \frac{k_{B}T_{0}}{\Delta_{\Gamma_{6}}} \]

since the hybridization strengths are comparable (see Figure 5 below, renormalized quasiparticle bands). Taking \( T_{0} = T_{K} \sim 20 \text{K} \) and \( \Delta_{\Gamma_{6}} \sim 30 \text{meV} \), we find about 6% \( \Gamma_{6} \)-contribution. Similarly, with \( \Delta_{\Gamma_{7}^{(2)}} \sim 30 \text{meV} \), we may also expect to find about 6% of \( \Gamma_{7}^{(2)} \)-contribution in the ground state. These are small amounts but not negligible, and perhaps sufficient to justify the multi-orbital model \cite{19} that explains the symmetry of the superconducting gap at very low temperatures.

The small but non-negligible amount of hybridization-induced mixing-in of the excited states into the ground state is also very much supported by the results of renormalized band-structure calculations \cite{48}. Here the present ground-state symmetry and excited \( 4f \) states at 30 meV are taken into account and the contributions of the three crystal-field states are projected out to the respective bands (see Fig. 5). The Fermi surface has two major sheets with quasiparticle masses that differ profoundly in which the Fermi surface sheet with the light quasiparticles very much resembles that of the LDA standard band structure calculations. It indeed turns out that the heavy band at zero energy has mainly \( \Gamma_{7}^{(1)} \) character with some minor contributions in the few percent range of the \( \Gamma_{6} \) and \( \Gamma_{7}^{(2)} \) states.

Finally, for completeness, we need to examine the consequences of having a mixed-orbital ground state for the analysis of the LD in XAS. We calculated the XAS spectra for a ground state which consists of 88% \( \Gamma_{7}^{(1)} \), 6% of \( \Gamma_{6} \), and 6% of \( \Gamma_{7}^{(2)} \) states. This requires the adjustment of the \( \alpha \) value to [0.62] in order to still reproduce the experiment. The correction is minor not only because the
contribution of the higher lying states is small, in addition, the LD of the $\Gamma_6$ and $\Gamma_7^{(2)}$ states partially cancel each other out. The small correction to $\alpha$ makes us confident that the crystal-field model with the Boltzmann occupation of the excited states is of more than sufficient accuracy to support our conclusion that no orbital switching as function of temperature takes place. Instead, we can safely infer the presence of a robust static crystal-field scheme although, in principle, the analysis of the temperature dependence of the LD would require a temperature dependent Anderson impurity calculation. It would also be very interesting to study quantitatively in the same framework the impact of the mixing in of the $\Gamma_6$ and $\Gamma_7^{(2)}$ on the magnetic susceptibility.

VI. SUMMARY

CeCu$_2$Si$_2$ has been investigated with soft x-ray absorption spectroscopy in the temperature range from 250 mK to 250 K and the $J_\alpha$ admixture of the $\Gamma_7$ ground state wave function has been determined. The overall temperature dependence of the experimental linear dichroism LD($\Gamma$) is well reproduced by the thermal occupation of excited crystal-field states so that the scenario of orbital switching seems unlikely. The spectra indicate the presence of the Ce $4f^0$ configuration in the ground state so that in principle the ground state can have a multi-orbital character. Based on the experimentally confirmed Kondo temperature and the crystal-field energies, the contribution of the higher lying $\Gamma_9$ and $\Gamma_7^{(2)}$ crystal-field states to the primarily $\Gamma_7^{(1)}$ ground state is estimated to be about 6% within the $4f^1$ manifold. This estimate is supported by re-normalized band structure calculations that uses the experimentally determined crystal-field scheme.

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