Determining the Crystal-Field Ground State in Rare Earth Heavy Fermion Materials Using Soft-X-Ray Absorption Spectroscopy

P. Hansmann,[1] A. Severing,[1] Z. Hu,[1] M. W. Haverkort,[1] C. F. Chang,[1] S. Klein,[1] A. Tanaka,[2] H. H. Hsieh,[3] H.-J. Lin,[4]
C. T. Chen,[4] B. Fåk,[5] P. Lejay,[6] and L. H. Tjeng[1]

[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln, Germany*
[2]*Department of Quantum Matter, ADSM Hiroshima University, Higashi-Hiroshima 739-8530, Japan*
[3]*Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan*
[4]*National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30077, Taiwan*
[5]*CEA, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS, 38054, Grenoble, France*
[6]*Institut Néel, CNRS, BP 166, 38042 Grenoble Cedex 9, France*

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We infer that soft-x-ray absorption spectroscopy is a versatile method for the determination of the crystal-field ground state symmetry of rare earth heavy fermion systems, complementing neutron scattering. Using realistic and universal parameters, we provide a theoretical mapping between the polarization dependence of Ce $M_{4,5}$ spectra and the charge distribution of the Ce $4f$ states. The experimental resolution can be orders of magnitude larger than the $4f$ crystal-field splitting itself. To demonstrate the experimental feasibility of the method, we investigated $\mathrm{CePd_2Si_2}$, thereby settling an existing disagreement about its crystal-field ground state.

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Heavy fermion materials are strongly correlated rare earth or actinide materials where the atomiclike f electrons interact with conduction electrons giving rise to extraordinary low energy properties. There has been a revival of interest in many of these well-studied compounds along with an intense search for new materials at the border between magnetic order and superconductivity. When driven through a quantum critical point by either magnetic field or pressure, they exhibit non-Fermi liquid behavior [1–9]. There are indications that the unconventional superconductivity in these compounds is triggered by antiferromagnetic correlations leading to the interesting aspect of competing magnetic and superconducting order parameters which may involve a momentum dependent hybridization of f and conduction electrons [10–13]. Therefore, any microscopic understanding of how the wealth of properties in Heavy Fermion materials evolves out of the strongly interacting f ground state requires the knowledge of the spatial distribution of the f state involved. For example Zwicknagl [14] pointed out that the Fermi surface of several systems depends strongly on the crystal-field symmetries and also Maehira *et al.* [15] showed the importance of crystal-field effects for the electronic properties of the Ce 115 compounds [11]. Other effects like the quadrupolar ordering reflect the charge distribution of the f ground state [16–19], but so far reliable input from experiment is scarce.

The standard experimental technique to determine the crystal-field energy level scheme is inelastic neutron scattering on polycrystalline samples. The additional information of quasi- and inelastic intensities should be sufficient to extract information about the f spatial distribution as well, but the analysis of magnetic intensities is often hampered by broadened lines, phonons in the same energy window as the magnetic excitations, or strong absorption of one of the sample's constituents (e.g., Rh, In, B, or Sm). Therefore, the wave functions of the crystal-field states are often determined from a combined analysis of neutron and single crystal static susceptibility data [20–22]. However, as pointed out by Witte *et al.* [23] and Janoušová *et al.* [24], even this combined method often fails due to the powder and thermal averaging in either technique. Moreover, in the presence of magnetic order anisotropic molecular field parameters have to be introduced in order to fit the static susceptibility, ending up with too many free parameters for a unique description of the crystal-field potential, leaving ambiguities and unresolved debates in the present literature. One then has to resort to time consuming inelastic polarized neutron scattering experiments with their demand for large single crystals [23,24], or, equally time consuming, to elastic scattering experiments with polarized neutrons to determine the f magnetic form factor [25].

We will show in this report at the example of $\mathrm{CePd_2Si_2}$ that polarization dependent soft-x-ray absorption spectroscopy at the rare earth $M_{4,5}$ edges (soft-XAS) is a powerful tool to give undisguised direct information concerning the $4f$ charge distribution in the ground state. This technique is complementary to neutron scattering, but has the advantage of having orders of magnitude better signal-to-noise/background ratio and of requiring only small amounts of sample material. It is capable of measuring materials which are strongly absorbing for neutrons, and it is element specific, so that the presence of more than one type of magnetic ion is no limitation.

Over the last 20 years soft-XAS has developed into a powerful technique for studying the element-specific local electronic structure of $3d$ transition metal and $4f$ rare earth compounds. The respective $2p$-to-$3d$ ($L_{2,3}$) and $3d$-to-$4f$ ($M_{4,5}$) absorption processes can be well understood in terms of atomiclike transitions into multiplet-split final states [26–29]. Unique is that the dipole selection rules are very effective in determining which of those final states can be reached and with what intensity for a given initial state symmetry. This makes the technique an extremely sensitive local probe, ideal to study the valence, spin, and orbital state of the ions of interest.

The majority of soft-XAS studies on rare earth materials was so far focused on their magnetism [30]. Surprisingly, only little attention had been paid on orbital symmetry or crystal-field issues in rare earths: there are a few soft-XAS reports early on addressing surface and interface crystal fields [31–33]. As a bulk material, only the giant crystal-field system $\mathrm{CeRh_3B_2}$ has been investigated [34–38]. The analysis reported, however, used an Anderson impurity model with a much too high Kondo temperature [39], thereby giving the impression that the effects in the XAS would vanish for small crystal fields. Moreover, that analysis did not take the full crystal-field symmetry [40] into account. Here we follow a different route by using an ionic ansatz since for most heavy fermion systems the Kondo energy scale is much smaller than the crystal-field splittings. In addition we include the full symmetry of the crystal fields. We then arrive at the new insight that for small crystal-fields in rare earth systems a simple and general mapping can be found between the ground state orbital symmetry and the polarization dependence of the spectra, allowing for an accurate and quick quantitative analysis.

The spin-orbit interaction in the f shell of rare earth compounds is much larger than the crystal-field splitting due to its small spatial distribution. J in the LS coupling is therefore a good quantum number, and the eigenstates in the presence of crystal fields can be expressed in terms of linear combinations of the corresponding $|J_z\rangle$ states. In the case of Ce^{3+} with f^1 in tetragonal site symmetry, the sixfold degenerate $J = 5/2$ state splits into three doublets: $|1\rangle = a|\pm 5/2\rangle - b|\mp 3/2\rangle$, $|2\rangle = |\pm 1/2\rangle$, and $|3\rangle = b|\pm 5/2\rangle + a|\mp 3/2\rangle$ with Γ_7^1, Γ_6, and Γ_7^2 symmetry. The crucial question is which state forms the ground state and what are the a and b coefficients ($a^2 + b^2 = 1$), thus defining the actual charge distribution. In Stevens formalism [41] the tetragonal crystal-field potential of an f^1 is given by the crystal-field parameters B_2^0, B_4^0, and B_4^4, and can be expressed alternatively through the transition energies ΔE_{12} and ΔE_{13}, and the coefficient a.

To study the sensitivity of the Ce $M_{4,5}$ spectra to the $4f$ charge distribution of the ground state, we performed ionic calculations which include the full multiplet theory [26–30] using the XTLS 8.3 program [27]. It accounts for the intra-atomic $4f$-$4f$ and $3d$-$4f$ Coulomb and exchange interactions, the $3d$ and $4f$ spin-orbit couplings, and the local crystal-field parameters [42]. All atomic parameters were given by the Hartree-Fock values, with a reduction of about 35% for the $4f$-$4f$ parameters and 25% for the $3d$-$4f$ to reproduce best the experimental isotropic spectra of Ce materials with low Kondo temperatures, thereby accounting for configuration interaction effects not included in the Hartree-Fock scheme [27].

We start with calculating the $M_{4,5}$ spectra for the pure $|J_z\rangle$ states of the Ce^{3+} with $4f^1$ and $J = 5/2$ for two polarizations of the electric field vector $\vec{E}$, $\vec{E} \parallel \mathbf{c}$ and $\vec{E} \perp \mathbf{c}$, where the tetragonal $\mathbf{c}$ axis is aligned along the $\mathbf{z}$ direction. Figure 1 shows the results of these calculations. The spectra are dominated by the Ce $3d$ core-hole spin-orbit coupling which splits the spectrum roughly in two parts, namely, the M_5 ($h\nu \approx 877$–887 eV) and M_4 ($h\nu \approx 895$–905 eV) white lines regions. Crucial is the strong polarization dependence which is characteristic for each of the states. This polarization dependence is intuitively clear when looking at the spatial distributions of the f electrons of each $|J_z\rangle$ state, see Fig. 1: the distributions differ remarkably between the different $|J_z\rangle$ states.

The results in Fig. 1 are a nice demonstration of the so-called initial state symmetry effect, an important concept for the determination of the ground state orbital symmetry in real materials: the splitting between the various crystal-field states can be small, e.g., smaller than the broadening of the spectra due to lifetime, phonon, or experimental resolution, and yet the polarization dependence can be very large. Important is that the temperature is sufficiently low so that primarily only the lowest state is populated. In fact, we can make use of the fact that the crystal-field splittings in rare earth materials are typically much smaller than the ≈ 400 meV spectral broadening. When calculating the polarization dependence of the states $|1\rangle$ or $|3\rangle$, we find they can be well approximated by an incoherent sum of the $|3/2\rangle$ and $|5/2\rangle$ spectra, weighted with the proper a^2 and b^2 parameters. The results are shown in Fig. 2, where we let a^2 run from 0 to 1, with $a^2 = 0$ corresponding to a pure $|3/2\rangle$ and $a^2 = 1$ to a pure $|5/2\rangle$ state. Figure 2 can serve as a map to find the coefficient a^2 directly from experiment. It should be generally applicable for tetragonal Ce materials without the need to know the crystal-field

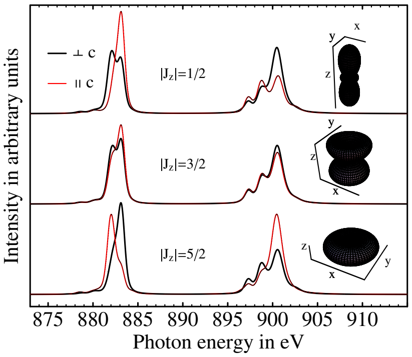

FIG. 1 (color online). Calculated $M_{4,5}$ soft-x-ray absorption spectra for pure $|J_z\rangle$ states of Ce^{3+} for the incoming light polarized $\parallel$ and $\perp$ $\mathbf{c}$ ($\mathbf{z} \parallel \mathbf{c}$ in tetragonal symmetry), together with the corresponding $4f$ spatial distributions.

splittings themselves as long as the total crystal-field splitting is small in comparison to the spin-orbit splitting of 230 meV. Yet, having knowledge of the crystal-field energies, e.g., from neutron scattering, this XAS technique will also enable us to give a clear and unique set of crystal-field parameters, independent of molecular fields. Important is that this ionic approach is only accurate for materials in which the Kondo temperature is sufficiently smaller than the splitting between the lowest and first excited crystal-field state, otherwise the analysis needs to be extended by using the Anderson impurity model.

We have measured the linear polarized soft-XAS spectra of $\mathrm{CePd_2Si_2}$ in order to prove the feasibility of the technique. Several groups measured the crystal-fields scheme of $\mathrm{CePd_2Si_2}$ with neutron scattering [21,22,43,44] and agree in the energy splitting but end up with considerably different ground state wave functions. The authors of [21,22] both took the energy splitting from neutron data and fitted the single crystal static susceptibility in order to obtain the ground state wave function. Both groups obtained decent fits although different ground state coefficients were assumed. This is due to the fact that anisotropic molecular field parameters were introduced in order to take into account the antiferromagnetic order at 10 K. The $\mathrm{CePd_2Si_2}$ single crystal used was grown by the Czochralski method as described in [21]. It orders at $T_N \approx$ 10 K. The XAS measurements were performed at the Dragon beam line of the NSRRC in Taiwan. The spectra were recorded using the total electron yield method in a chamber with a pressure of 2×10^{-10} mbar. Clean sample areas were obtained by cleaving the crystals *in situ*. The energy resolution at the Ce $M_{4,5}$ edges ($h\nu \approx 875$–910 eV) was set at 0.4 eV, and the degree of linear polarization was $\approx 98\%$. The $\mathrm{CePd_2Si_2}$ single crystal was mounted with the **c** axis perpendicular to the Poynting vector of the light. By rotating the sample around this Poynting vector, the polarization of the electric field can be varied continuously from $\vec{E} \parallel \mathbf{c}$ to $\vec{E} \perp \mathbf{c}$. This measurement geometry allows for an optical path of the incoming beam which is independent of the polarization, guaranteeing a reliable comparison of the spectral line shapes.

The bottom curves of Fig. 3 show the measured soft-XAS spectra of $\mathrm{CePd_2Si_2}$ at $T = 50$ K for the light polarized parallel and perpendicular to the **c** axis. The spectral features are well resolved and their sharpness can be taken as a confirmation for the atomic character of the Ce states. A polarization dependence can be clearly seen due to the excellent signal-to-noise/background ratio. Comparing these experimental spectra to the simulations in Figs. 1 and 2, one can immediately deduce that the ground state must be state $|1\rangle$ with a^2 close to 0.3. Indeed, a more detailed simulation analysis yields the best fit for $a^2 = 0.29$. We know from neutron data [43,44] that the first excited crystal-field level is above 19 meV, i.e., well above 200 K, so that at $T = 50$ K only the ground state contributes to the spectra. When simulating the data the Boltzmann factor was nevertheless taken into account. The value found for a^2 corresponds to $a = 0.54$ and $b = 0.84$, so that we essentially confirm the ground state of

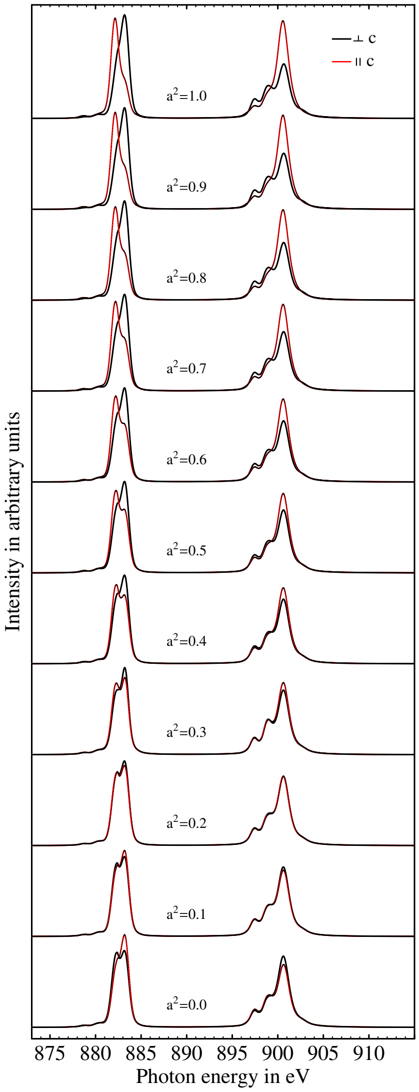

FIG. 2 (color online). Top: Calculated $M_{4,5}$ soft-x-ray absorption spectra for the mixed states $a|\pm 5/2\rangle - b|\mp 3/2\rangle$ for mixing factors a^2 from 0 to 1 for light polarized $\parallel$ and $\perp$ **c**.

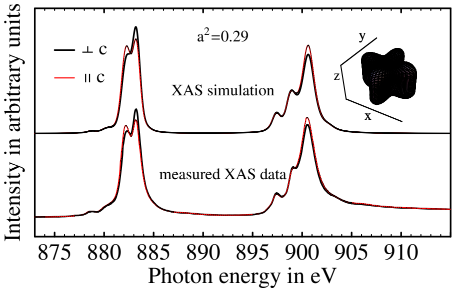

FIG. 3 (color online). Bottom: experimental $M_{4,5}$ soft-x-ray absorption spectra of $\mathrm{CePd_2Si_2}$ at $T = 50$ K for light polarized $\parallel$ and $\perp$ **c**. Top: simulated $M_{4,5}$ spectra with $a^2 = 0.29$ and corresponding $4f$ spatial distribution.

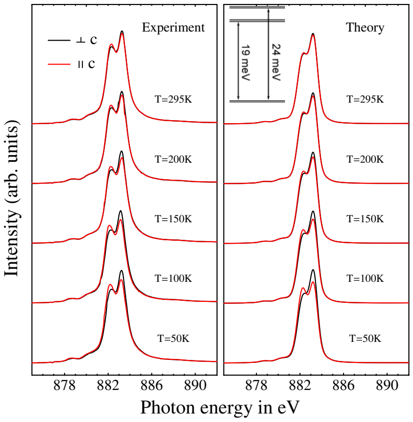

FIG. 4 (color online). Temperature dependence of the experimental (left) and calculated (right) M_5 soft-x-ray absorption edge of $CePd_2Si_2$. Inset: crystal-field energies as in [21].

$CePd_2Si_2$ as proposed by [21]: $|1\rangle = 0.55|\pm5/2\rangle - 0.84|\pm3/2\rangle$. The corresponding spatial distribution of the $4f$ electron in this ground state is shown in the inset of Fig. 3.

To confirm the crystal-field nature of the polarization effect, we have also carried out measurements at elevated temperatures. The polarization dependence in the spectra diminishes as the temperature rises as is shown in Fig. 4 for 50, 100, 150, 200, and 295 K. This is in accordance with the increased population of higher crystal-field levels, resulting eventually in an isotropic spectrum at sufficiently high temperatures. These elevated temperature spectra can be well described using the ground state symmetry and coefficient from the 50 K spectrum, the crystal-field energies from neutron data [21], and the Boltzmann factor for each respective temperature.

In conclusion we have shown that the Ce $M_{4,5}$ spectra have a polarization dependence which is characteristic for the charge distribution of the Ce $4f$ states. We have provided a set of reference spectra (Figs. 1 and 2) from which one can find the ground state parameters directly from the experiment, without the need to know the crystal-field energies themselves as long as they are small. Using this method we have investigated the local electronic structure $CePd_2Si_2$ and settled the debate concerning the ground state wave function of this compound, demonstrating that soft-x-ray absorption spectroscopy is a powerful method complementing neutron scattering.

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