Pressure-Induced Valence Crossover in Superconducting $CeCu_2Si_2$

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Measurement of the Ce valence in the heavy fermion $CeCu_2Si_2$ is reported for the first time under pressure and at low temperature ($T = 14$ K) in proximity of the superconducting region. $CeCu_2Si_2$ is considered as a strong candidate for a new type of pairing mechanism related to critical valence fluctuations which could set in at high pressure in the vicinity of the second superconducting dome. A quantitative estimate of the valence in this pressure region was achieved from the measurements of the Ce L_3 edge in the high-resolution partial-fluorescence yield mode and subsequent analysis of the spectra within the Anderson impurity model. While a clear increase of the Ce valence is found, the weak electron transfer and the continuous valence change under pressure suggests a crossover regime with the hypothetical valence line terminating at a critical end point T_{cr} close to zero.

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Low energy magnetic fluctuations are suggested to mediate electron pairing in various unconventional superconductors, ranging from heavy fermion (HF) and cuprates to iron pnictides compounds. In most of these systems, a magnetically ordered phase is adjacent to the superconducting (SC) phase and the magnetic ordering temperature is driven to zero when approaching the so-called magnetic quantum critical point (QCP) by an external control parameter such as doping, magnetic field, or pressure around which superconductivity emerges. The critical magnetic fluctuations that build up around the QCP are held responsible for electron pairing. In some HF materials, however, the superconducting phase extends beyond the QCP, in a region of the phase diagram sufficiently far from magnetic ordering to consider other pairing mechanisms. $CeCu_2Si_2$, the first discovered HF superconductor [1], exhibits such a two-dome SC region [2,3] under pressure as schematically illustrated in Fig. 1 with the critical temperature T_c peaking at $P_c \sim 4$ and $P_v \sim 45$ kbar. Around P_c, the proximity of $CeCu_2Si_2$ to a QCP is established by (i) a subtle metallurgy that yields either antiferromagnetic (AF) or SC samples depending on stoichiometry [4], (ii) the recovery of magnetism through substitution of Si by Ge [5,6] and retrieval of the two SC domes under pressure, (iii) proofs of magnetic fluctuations and their interplay with superconductivity [7,8]. Increasing pressure however suppresses magnetism [7] while superconductivity is enhanced, therefore suggesting another pairing mechanism around P_v, probably having a different order parameter symmetry as recently proposed [9]. Early transport measurements show hints of intermediate valence behavior under pressure [2,6] and the hypothesis that critical valence fluctuations (CVF) may mediate electron pairing in this compound was more recently put on a quantitative basis [10]. Thus, the second anomaly at P_v in $CeCu_2Si_2$ could be associated to a CVF-driven SC state, providing that the Coulomb interaction U_{fc} between the f and conduction states is sufficiently strong. The hypothetical first-order valence transition line

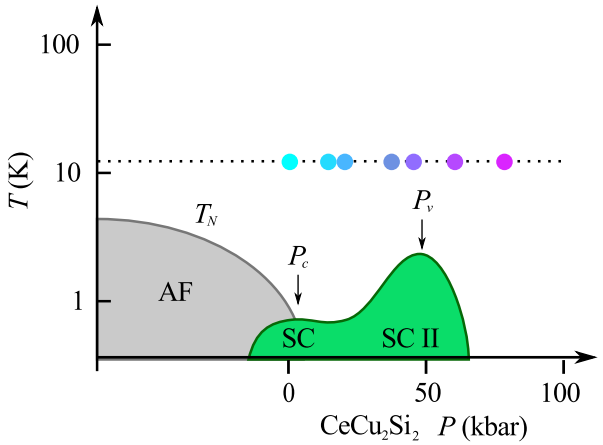

FIG. 1 (color online). Schematic view of the P-T phase diagram of $CeCu_2Si_2$ (adapted from Ref. [10]). T_N is the Néel temperature; P_c and P_v are the pressure location of the two superconducting domes. The circles show the locations in the phase diagram where the sample was measured.

supposedly ends up at a critical terminal point at $P_{cr} \sim P_v$ and T_{cr} yet to be defined—in Ce, for instance, it occurs at ≈ 20 kbar and 600 K [11]. Across the phase line, we expect enhanced valence fluctuations under pressure and change of degeneracy of the ground state. But no direct assessment of the Ce valence in $CeCu_2Si_2$ near P_v at low temperature is reported. In fact, as for $CeCu_2Si_2$ most of the knowledge about the valence change in heavy fermion materials is indirectly deduced from thermodynamic and transport measurements [10]. We present here the first attempt to extract quantitatively the Ce valence in heavy fermion from spectroscopic measurements at low temperature ($T = 14$ K) in the very proximity of the SC region. While our results demonstrate clear valence changes, the smooth pressure dependence is indicative of superconductivity emerging from the crossover regime with $T_{cr} \approx 0$.

An efficient way of estimating the f valence is to use core-hole spectroscopy. The method relies on the core-hole potential to lift the degenerated mixed valent ground sate. As the screening acts differently on the different f states, information about the f-electron count can be retrieved. In the hard x-ray range, the sizable penetration depth of photons allows these measurements in samples contained in a pressure cell. Although the method has been widely used in photoemission and x-ray absorption spectroscopy (XAS) over the past, the emergence of resonant inelastic x-ray scattering as a probe of mixed valent materials has brought up a new level of accuracy in the measurements that was severely lacking [12]. Especially, the early estimate of the Ce valence in $CeCu_2Si_2$ at room T under pressure contained an inevitable large uncertainty [13].

The experiment was performed on the ID-26 beam line at the European Synchrotron Radiation Facility (ESRF). A 20 μm thick single crystal of $CeCu_2Si_2$ was loaded in a membrane-driven diamond anvil cell (DAC) with silicon oil as the pressure transmitting medium. Small crystals were obtained by slow cooling from the melt under 50 bar of Ar in a $BaZrO_3$ crucible [10]. The sample is the same as in Ref. [10], ensuring its superconducting properties. To enhance transmission, the DAC was equipped with a pair of perforated diamonds capped with 500 μm thick anvils. The gain in transmission with respect to standard DAC setup is as high as ~6–7 orders of magnitude. For low temperature measurements, the DAC was mounted in a liquid He cryostat. The lowest temperature that could be reached was 14 K as measured on the outer face of the diamond. Pressure was estimated by standard ruby fluorescence spectroscopy. The L_3 XAS spectra were acquired in partial-fluorescence yield mode (PFY) where the Ce $L\alpha_1$ ($3d_{5/2} \rightarrow 2p_{3/2}$) line is monitored while the incident energy is swept across the absorption edge. The spectra thus obtained are almost free from core-hole lifetime broadening effects, and show enhanced resolution compared to standard XAS. Figure 2 shows the

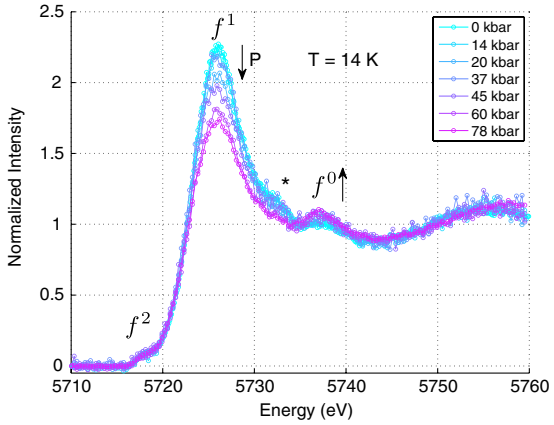

FIG. 2 (color online). X-ray absorption spectra in $CeCu_2Si_2$ as a function of pressure at 14 K. The spectra were acquired in the partial-fluorescence yield, high-resolution mode PFY-XAS. The arrows show the evolution of main spectral features with increasing pressure.

PFY-XAS spectra in $CeCu_2Si_2$ measured at 14 K as a function of increasing pressure. The spectra have been normalized to an edge jump of unity. They can be decomposed in three components subsequently identified as f^0, f^1, and f^2, although these are not pure spectral features (see below). Notice that the f^2 feature that shows up in the preedge region is solely observable thanks to the PFY spectral sharpening effect. Upon pressure increase, the f^0 feature grows in intensity; at the same time, the f^1 component decreases along with the shoulder (*) on the high energy side that seemingly belongs to the same family of states; the f^2 feature stays mostly unchanged. The transfer of spectral weight from f^1 to the f^0 component is significative of a valence transition from Ce^{3+} towards Ce^{4+} as expected from electron delocalization under pressure in f-electron systems.

An accurate estimate of the electron transfer, and more generally of the electronic changes under compression in f-electron systems, can be retrieved from simulation of the spectra within the Anderson impurity model. The method was successfully adopted to spectroscopic measurements in Ce mixed valent materials [14], and later applied to volume collapse transition under pressure [15]. The ground state is described as a degenerated mixed valent configuration $c_0|4f^0\rangle + c_1|4f^1\rangle + c_2|4f^2\rangle$, where the $||c_i||^2 (i = 0, 1, 2)$ are the weights of the different f states. The main interaction terms in the Hamiltonian are the hybridization V between the f electrons and the valence band, and the Coulomb interactions between the $4f$ electrons U_{ff}, $2p$ core hole and $4f$ electrons $U_{f\underline{2p}}$, and $3p$ core hole and $4f$ electrons $U_{f\underline{3p}}$. Correction factors for the hybridization term in the presence of a core hole (R_c) and $4f$ electrons ($1/R_v$) are introduced to account for configuration dependence of the hybridization. The impurity state is defined by its binding energy ϵ_f^0, and W simulates the bandwidth of

the conduction electrons. The parameters are fitted to the experiment starting from the values of γ-Ce [16]. The spectra are computed from the energy spread and intensity of the multiplet states (cf. ticks in Fig. 3) and dipolar transition matrix elements after lifetime broadening and addition of a steplike background. The weights of the different f states composing the ground state and the parameters ϵ_f^0, V, and W are adjusted to fit the spectral changes while the intra-atomic parameters are kept constant since they are insensitive to volume changes. The quality of the fits is illustrated in the inset to Fig. 3.

The parameters derived from the calculations are listed in Table I for the different pressures, and the corresponding calculated x-ray absorption spectra shown in Fig. 3. The calculations describe well the spectral changes observed as a function of pressure with the reduction of the white line intensity and enhancement of the postedge features. More importantly, they provide a quantitative estimate of the electronic changes as a function of pressure in the ground state, which can be summarized as follows : The proportion of the f^0 configuration significantly increases at high pressure at the expense of the f^1 configuration; at the same time, there is a small increase of the doubly occupied state f^2 occupation which was already observed in elemental Ce under pressure. While the f^0 , f^1 balance inversion is consistent with the valence increase at high pressure, the rise of the f^2 occupation is a manifestation of decrease correlation in the compressed lattice already observed in Ce [15]. The variation of the Ce valence, or equivalently of the electron count n_f, can be estimated from the weighted sum over the f states. The

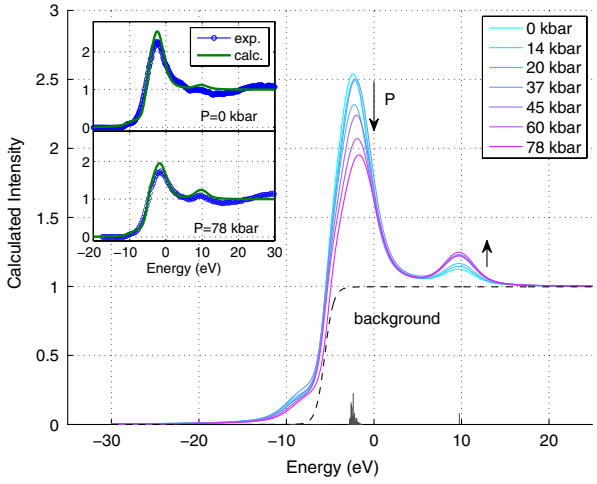

FIG. 3 (color online). Computed x-ray absorption spectra in $CeCu_2Si_2$ as a function of pressure within the Anderson impurity model (solid lines); see text for details. Ticks show the multiplet states for the lowest pressure. An arctan background (dashed line) is added to all the spectra to mimic the edge jump; arrows show the tendency upon pressure increase. Inset: comparison between calculated (lines) and measured (circles) spectra at the two extreme pressures.

TABLE I. Parameters used in the calculations, f states weights, and electron count as a function of pressure; the other parameters $U_{ff} = 6.0$ eV, $U_{f\underline{2p}} = 10.4$ eV, $U_{f\underline{3d}} = 10.4$ eV, $R_c = 0.6$, $R_v = 1.0$ are constant.

P (kbar)	0	14	20	37	45	60	78
ϵ_f^0 (eV)	−2.1	−2.1	−2.15	−2.15	−2.15	−2.15	−2.15
V (eV)	0.2	0.22	0.22	0.24	0.25	0.26	0.28
W (eV)	0.8	0.9	1.0	1.1	1.3	1.4	1.5
f^0 (%)	7.5	10.2	10.1	13.7	15.6	17.6	21.2
f^1 (%)	89.1	85.8	86.0	82.0	80.0	77.9	74.1
f^2 (%)	3.4	4.0	3.9	4.3	4.4	4.5	4.6
n_f	0.96	0.94	0.94	0.91	0.89	0.87	0.83

total valence change is estimated around 0.13 from ambient pressure to 78 kbar.

To further investigate the relevance of valence fluctuations for the superconducting properties of $CeCu_2Si_2$, we represent the evolution of the number of f electrons per site, $\bar{n}_f = n_f/2$ in Fig. 4, on the same energy scale ϵ_f^0/D as utilized in Ref. [10], Fig. 2. D is the Fermi energy of conduction electrons as "if it were decoupled from the f electrons" [10]. We used the relationship $D = 2V$ introduced in the CVF model. The most striking result is the absence of sharp valence transition across P_v and the weak change in f-electron count. In the CVF model, $\bar{n}_f$ is expected to decrease by 45% in the low correlation limit (U_{fc} small), and reach a nearly 90% decrease in the highly correlated case (U_{fc} large) in order to account for a significant increase of T_c and the formation of a superconducting dome under pressure. The total variation in $\bar{n}_f$ of 14% obtained from our data seemingly contrasts with this description; from Fig. 4, it is also clear that the nature of

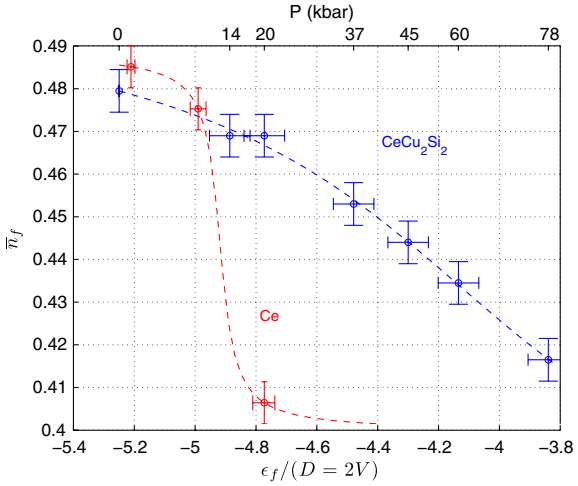

FIG. 4 (color online). f-electron number per site $\bar{n}_f$ as function of pressure (top scale). The lower scale refers to the dimensionless unit of Ref. [10]; we use the approximation $D = 2V$. The dashed lines are guides to the eyes. The Ce data were borrowed from Ref. [15].

the transition in $CeCu_2Si_2$ strongly differs from that of Ce considered as prototypical of first-order valence transition in $4f$ systems [15].

This established, are there any intrinsic limitations in our methodology or analysis that would conceal or damp the valence fluctuations? The lowest temperature reached in this study is significantly higher than T_c (~ 1.5 K at P_v). This is a primarily due to technical limitations of membrane-driven pressure cells combined with the need of an optical access that necessarily limits the cooling power of our cryostat. In contrast, resistivity or specific heat measurement can be carried out at much lower temperatures. It is based on such investigations that valence fluctuations mediated mechanism was initially proposed. Nevertheless, critical behaviors are expected to extend far beyond the critical point [17] so that signs of valence fluctuations should be observable at $T \gg T_c$; in $CeCu_2Si_2$, signatures of P_c already exist at $\sim 10 \times T_c$ [10]. We notice also that the temperature at which we carried out the measurement is lower than the pressure-dependent characteristic temperatures (referred to as $T_1^{\max}$ and $T_2^{\max}$ in the literature) that sign the interplay between the Kondo effect and the crystal field excitations so that we really probe the ground state properties [18]. Our results primarily suggest that U_{fc} is small and the calculated variation of n_f in the CVF model is too large. A known limitation of the CVF model is to neglect the mixing of conduction electrons of different crystal field symmetry at different sites which tends to overestimate the valence change. A more refined approach would possibly agree better with our data. It is possible in fact to reconcile the CVF model, resistivity and specific heat data, and our observations by considering that the critical end point temperature $T_{\rm cr}$ is located at very low temperature. Superconductivity would then occur in the crossover regime from the Kondo state to mixed valency as initially predicted for $CeCu_2Si_2$ [10,20] while being consistent with our finding of a smooth valence decrease under pressure and low temperature.

In conclusion, we have investigated by x-ray spectroscopy at the Ce L_3 edge the valence properties of $CeCu_2Si_2$ near the region of expected valence instability, at low temperature and high pressure. The results have been analyzed within the Anderson impurity model. While we could demonstrate a clear change of the number of f electrons as pressure increases, the continuous variation in the f-electron count under pressure is consistent with superconductivity emerging from the crossover region between the Kondo and mixed valent states, and a nearly zero critical temperature. The results prove that direct estimation of the valence properties in a heavy fermion compound at low temperature and high pressure is possible and opens the way for further investigations along this line. They call also for supplementary theoretical effort to understand the physics and pairing mechanism of f-electron superconductors.

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