Absence of magnetic field effect on the cerium valence in $CeCu_2Si_2$ at its optimum superconducting critical temperature

M. Barbier,[1,2] M. Sundermann,[3,4] A. Poux,[2,5] A. Rogalev,[2] D. Braithwaite,[6] J.-P. Sanchez,[6] and F. Wilhelm[2]

[1]*Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France*
[2]*European Synchrotron Radiation Facility (ESRF), B.P. 220, F-38043 Grenoble cedex, France*
[3]*Institute of Physics II, University of Cologne, Zülpicher Strasse 77, D-50937 Cologne, Germany*
[4]*Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany*
[5]*Laboratoire National des Champs Magnétiques Intenses (LNCMI) Toulouse, 143 avenue de Rangueil, F-31400 Toulouse, France*
[6]*Univ. Grenoble Alpes, Grenoble INP, CEA, IRIG-Pheliqs, F-38000 Grenoble, France*

(Received 7 July 2021; revised 15 October 2021; accepted 5 November 2021; published 29 November 2021)

The archetypical heavy-fermion superconductor $CeCu_2Si_2$ is known to present two distinct superconducting phases under pressure. In the low-pressure region, the superconductivity is mediated by spin fluctuations while the superconducting phase observed in the high-pressure region could be associated with a first-order valence transition (FOVT). However, the critical end point (CEP) of the FOVT was shown to be located at negative temperature and only a continuous valence change (crossover regime) was so far observed at 14 K, i.e., far above the optimal superconducting temperature ($T_c = 2.3$ K). Here we present x-ray absorption measurements under pressure and applied magnetic field at the Ce L_3 edge at 2.7 K, i.e., close to the optimal T_c. It was expected that the applied magnetic field could shift the CEP to positive temperature with the possibility to observe a FOVT. Our data indicate the valence of Ce increases continuously (crossover regime) from 3.11 at ambient pressure up to 3.20 at 8.5 GPa likewise for any applied magnetic field up to 6 T.

DOI: 10.1103/PhysRevB.104.205136

I. INTRODUCTION

The heavy-fermion superconductor $CeCu_2Si_2$, discovered in 1979, marks a keystone in the history of superconductivity as the first unconventional superconductor [1]. This opened a vast area of research on the relation between magnetism and superconductivity, mainly in heavy-fermion systems, but with implications to all known unconventional superconductors, including high-T_C cuprates, organic superconductors, and more recently iron-based superconductors. It also remains one of the most studied systems today as it is suspected that in $CeCu_2Si_2$, not one but two distinct unconventional mechanisms of superconductivity may play a role [2]. This was revealed by its nontrivial phase diagram under pressure. Indeed, under pressure the critical temperature initially remains close to its ambient pressure value of 0.7 K, then increases sharply up to about 2.3 K at a pressure of 4 GPa, before decreasing and vanishing [3]. Further studies and comparison with other systems showed that in fact this phase diagram emerges from two distinct superconducting zones (Fig. 1).

As $CeCu_2Si_2$ at ambient pressure is known to lie just at the border of antiferromagnetic (AFM) order, the low-pressure dome of superconductivity is generally accepted to be mediated by AFM spin fluctuations, similar to the superconducting phase found at the quantum critical point (QCP) in other systems like $CePd_2Si_2$ or $CeIn_3$ [5], and centered at slightly negative pressure $P \leqslant 0$. This superconducting pairing mechanism at ambient pressure was confirmed by the identification of antiferromagnetic excitations by inelastic neutron scattering [6]. The second dome centered at a critical pressure P_V located around 4–5 GPa (see Fig. 1) is rather far from the QCP, and therefore it seems probable that a separate mechanism for superconductivity is at play. Furthermore, heat-capacity measurements suggest that the thermodynamic properties of the two superconducting regions are different and have even possibly different pairing symmetries [7]. The mechanism behind the second superconducting dome, which additionally leads to one of the highest critical temperatures found in heavy-fermion systems (2.3–2.4 K), is however still an enigma. Indeed, the absence of spin fluctuations around P_V was inferred via Cu-nuclear quadrupole resonance measurements [8]. The most attractive proposals, supported by the observation near P_V of a linear temperature dependence of the resistivity and an enhancement of the residual resistivity, is that charge or valence fluctuations could mediate superconductivity [9,10]. Moreover, the second superconducting dome could be linked to the critical pressure of a first-order valence transition (FOVT) where the valence shows a discontinuity below the critical end point (CEP), while at $T > T_{CEP}$, in the crossover regime (VCO), the valence changes continuously. This phenomenon is well known in elementary cerium (γ-α transition), with $T_{CEP} = 480$ K at $P = 1.5$ GPa, where under pressure the isothermal resistivity exhibits a discontinuous anomaly below T_{CEP} and a rapid but continuous decrease above T_{CEP} (see Fig. 3(b) in Ref. [11]). So, extensive theoretical developments based on the periodic Anderson model including the Coulomb repulsion between f and conduction electrons have studied the effect that valence fluctuations

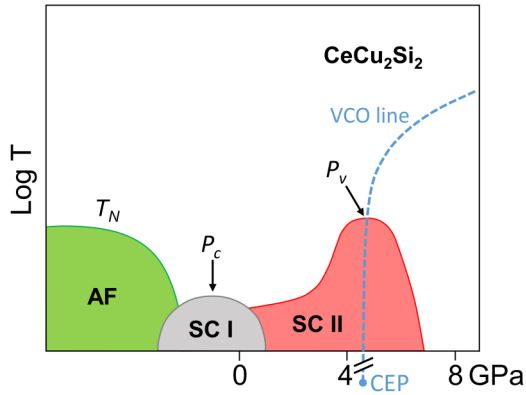

FIG. 1. Schematic P-T phase diagram of $CeCu_2Si_2$ showing the critical pressure P_C and P_V where the superconductivity is mediated either by antiferromagnetic fluctuations (SCI) or critical valence fluctuations. (SCII). P_C where T_N goes to zero appears to be at slightly negative pressure for $CeCu_2Si_2$ samples with tiny Cu excess. The negative pressure where AFM order sets in has been explored by substituting Si by Ge. The VCO line (blue) and the location of the CEP at about 8 K and 4.5 GPa $\sim P_V$ are obtained from resistivity measurements (adapted from Ref. [4]).

linked to this transition could induce superconductivity [12]. The valence crossover line and the critical pressure P_V for $CeCu_2Si_2$ are inferred from the midpoint of the normalized resistivity, ($\rho^* = \rho - \rho_0$), drop at different temperatures above 4 GPa (see Fig. 5(a) in Ref. [4]). The critical temperature T_{CEP} is estimated from the divergence for $T \rightarrow T_{CEP}$ of the slope $d\rho^*/dP_{Pvco}$ (see Fig. 5(c) in Ref. [4]). So far direct measurements of the cerium valence change with pressure are inconclusive. Early studies performed at room temperature [13] gave the first indication of the cerium valence change, but obviously the behavior at such high temperature is not necessarily indicative of what is happening at the superconducting temperature. More recently, a resonant inelastic x-ray scattering study was performed at 14 K [14]. The results found are in fact similar to the high-temperature measurements, showing a significant change of the cerium valence (about 0.10) with pressure, similar in amplitude to that found in elementary cerium, and with the strongest slope in the pressure region where T_C is maximum. On the other hand no sharp change corresponding to the FOVT that is at the basis for the model of valence fluctuation-induced superconductivity is seen. This is not however conclusive evidence against the valence fluctuation pairing mechanism as the FOVT could occur at very low or even at negative temperature. Meticulous analysis of transport and thermodynamic measurements [4] suggested that the CEP of the FOVT would be located at about $T_{CEP} = -8(3)$ K and $P_v \approx 4.5$ GPa [4]. A more recent work gives a full overview of superconductivity in $CeCu_2Si_2$ and related systems, as well as an analysis of more accurate resistivity data indicating that T_{CEP} for $CeCu_2Si_2$ is even less negative [$-3.7(7)$ K] and the optimum T_C is controlled by T_{CEP} (the highest T_C is observed for the least negative T_{CEP}) [11]. In this case superconductivity could still be mediated by the valence fluctuations in the VCO regime at higher temperature where the valence changes continuously. Clearly direct measurement of the cerium valence at the lowest possible temperatures is desirable. Another interesting prediction of the FOVT is that it could be controlled by magnetic field. The rare-earth valence in correlated electron systems is generally rather insensitive to magnetic fields. This field of research is developing fast due to the recent possibility to perform absorption spectroscopy measurements in pulsed magnetic fields up to typically 30 T, so very much extending the previously accessible field range. However, except in rare cases where for example a metamagnetic transition is induced [15], even with such high fields the effects are generally small. If a FOVT is present, theoretical studies show that the critical point will be sensitive to field. If the system can be tuned, for example with pressure, just beyond the critical pressure, the application of field should quite efficiently increase the critical temperature of the FOVT [16,17]. By extension, if the FOVT lies at a negative temperature, a high enough magnetic field can drive it towards zero or positive temperatures (for more details see the discussion). An accurate quantitative prediction is not available, but naively with the deduced T_{CEP}, one might expect that a field of a few tesla could have a significant effect on the cerium valence in $CeCu_2Si_2$, at low but positive temperature, if the system is tuned just to the critical point. The aims of this experiment were therefore twofold: first to reinvestigate the pressure dependence of the valence at lower temperature, if possible below or close to the superconducting critical temperature, and secondly to look for an effect of magnetic field on the cerium valence in the critical pressure region.

II. EXPERIMENT

The x-ray absorption near-edge structure (XANES) experiments were carried out on the beamline ID12 at the European Synchrotron Radiation Facility in Grenoble [18,19] which offers a possibility to combine high pressure, high magnetic field, and low temperature. A single crystal with good superconducting properties was obtained by slow cooling from the melt under 50 bar of Ar in a BaZrO3 crucible [10] and polished to a thickness of 10 μm. The magnetic field of up to 6 T and the x-ray beam were applied along the (magnetic easy) c axis. The sample was loaded in a membrane-driven diamond-anvil cell with a helium transmitting pressure medium. A stainless-steel gasket with a hole diameter size of 300 μm and a thickness of 60 μm was used. Pressure could be changed *in situ*, and was measured using the ruby fluorescence technique. In order to have a good signal level at the cerium L_3 edge ($2p_{3/2} \rightarrow 5d$ transition at $\sim$5.7 keV), we used a fully perforated diamond with a culet size of 600 μm on the incident beam side in combination with a diamond disc window (thickness 80 μm for sample S1 and 150 μm for sample S2) behind it. The cell was placed in a constant helium flow cryostat able to achieve temperatures down to 2 K. The lowest temperature on the sample is 2.7 K. As focalization system, we used a single 2D Be lens (with 50-μm radius of curvature) and two pinholes with 400-μm holes placed at both side of the lens. The x-ray absorption spectra at the Ce L_3 edge were collected in the total fluorescence yield (TFY) mode measured in backscattering geometry. The XANES spectra were then corrected for self-absorption effects. The signal measured in the transmission mode was much less intense due to passing

through the full thickness of the second diamond, and was therefore not used for the analysis. Difficulties were encountered to smoothly increase the pressure; large jumps were often obtained, and it was impossible to decrease the pressure, possibly due to a partial blockage of the membrane circuit. For this reason the experiment was repeated on a second sample (S2) to obtain more pressure points. This allowed five different pressures to be measured comprising points at low pressure, points around the optimum T_C, and one point well above this optimum. The results on both samples are similar and all analyzed together. For all pressures the spectra were measured at zero magnetic field and with an applied field of 6 T. For some pressure points an intermediate field of 3 T was also applied.

III. RESULTS AND DISCUSSION

The shape of the XANES spectra arises from the excitation of a Ce $2p_{3/2}$ core electron into the unoccupied Ce $5d$-derived states. The ground state of the Ce ion in the intermediate valence compound is a hybrid state $|\psi_0\rangle = a|4f^0\rangle + b|4f^1\rangle$ [20]. In the final state in the x-ray absorption process, the $2p^5 4f^0$ and $2p^5 4f^1$ states are partially split by the strong Coulomb interaction between the $2p$ core hole and the $4f$ electrons. The XANES spectra can then be described by the superposition of two white lines corresponding to the $4f^0$ (Ce^{4+}) and $4f^1$(Ce^{3+}) states separated by about 9 eV. Actually, a $4f^2$ contribution could also be present in the Ce ground state as shown when recording the spectra in the partial fluorescence yield mode which allows better resolution [14]. This very weak contribution, on the order of a few percent which appears at the left side of the $4f^1$ main peak, is hardly seen in our TFY spectra. In the following we will neglect this contribution as it does not affect our conclusions.

In Fig. 2(a) we show the XANES spectra obtained at 2.7 K for different pressures. The applied curve-fitting procedure is similar to the one reported recently in the literature [21,22].The normalization of XANES spectra is done using the standard procedure based on a linear fit to remove the preedge background and a postedge linear fit to obtain an absorption edge jump of unity using the ATHENA data-processing software [23]. The main shape of the spectra arises from the $4f^1$(Ce^{3+}) contribution and the much weaker feature at the right flank is due to the $4f^0$(Ce^{4+}) contribution. One observes a strong variation of the Ce^{3+} to Ce^{4+} intensity ratio with increasing pressure, signaling the conversion of the valence towards Ce^{4+}. Figure 2(b) shows a typical analysis of the experimental spectra. The XANES spectra are fitted in the fixed energy range (5.703–5.743 eV) using a set of two Gaussians and an arctangent function for each electronic configuration ($4f^1$ and $4f^0$) taking into account the lifetime and instrumental broadenings to deconvolute the white lines. The full width at half maximum of the four Gaussian functions was kept constant (5.8 eV) as well as the broadening of the arctangent functions (3.5 eV) for all spectra. Similar procedure is commonly applied in the analysis of Ce L_3-edge XANES spectra of CeP and CeO_2-based systems [21,22]. High-energy resolution fluorescence-detected x-ray absorption applied to Ce L_3 edge of CeO_2 revealed fine structures clearly demonstrating four distinct features above the absorption edge [24,25]. Those measurements may justify the use of four Gaussian peaks (G1–G4) deconvolution of the features above the edge in our analysis. For the sake of comparison, we used also a procedure based on two Gaussian peaks deconvolution and found that both procedures lead to essentially the same results despite the latter being less accurate due to the larger residuals.

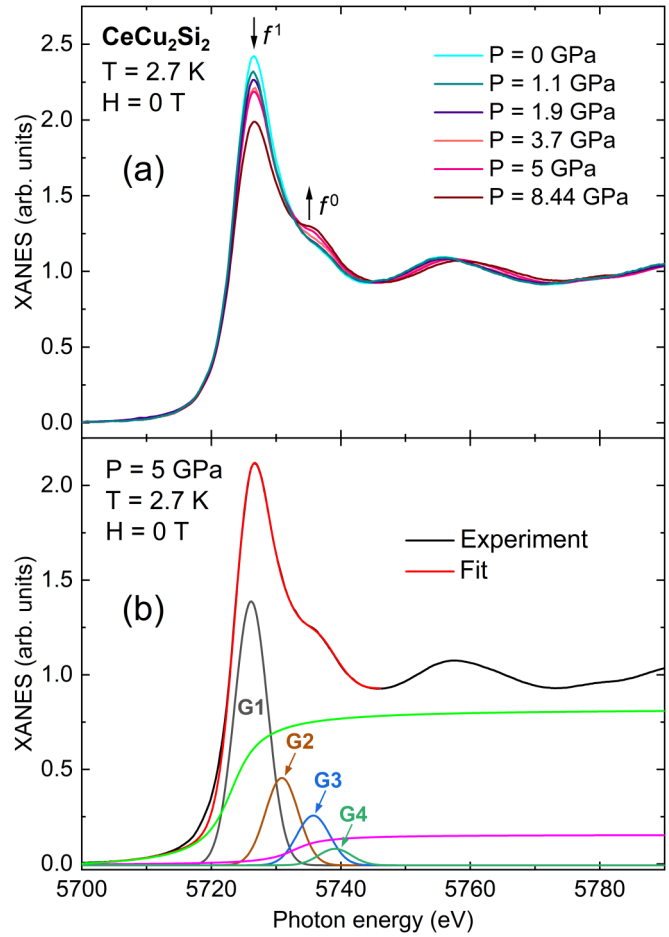

FIG. 2. (a) XANES spectra in $CeCu_2Si_2$ as a function of pressure at 2.7 K. The arrows show the evolution of the f^1(Ce^{3+}) and f^0(Ce^{4+}) features with increasing pressure. The broad bump centered at about 5757 eV is attributed to the extended x-ray absorption fine structure (EXAFS) contribution. (b) Typical fit (red curve) of $CeCu_2Si_2$ XANES spectra (black line) with the combination of Gaussians (white lines) and arctangent functions for $Ce^{3+}(4f^1)$ and $Ce^{4+}(4f^0)$ contributions. The couples of G1–G2 and G3–G4 Gaussians are attributed to the Ce^{3+} and Ce^{4+} contributions, respectively.

Since the $4f^2$ contribution is neglected, the valence $v \approx 3 + I^{4+}/(I^{3+} + I^{4+})$, where I^{4+} and I^{3+} are the area of the Ce^{4+}(G3 + G4) and Ce^{3+}(G1 + G2) white lines, respectively [21]. Figure 3 represents the pressure dependence at 2.7 K of the spectral weight of the Ce^{3+} contribution $4f^1/(4f^1 + 4f^0)$ or in other words the $4f$ electron count n_f, which is equal to 1 for Ce^{3+}. It is shown that n_f (valence v) decreases (increases) smoothly and continuously with pressure without any sizable anomaly at P_V. The valence changes from 3.11 at ambient pressure up to 3.20 at 8.5 GPa. Note that the data obtained at 2.7 K, i.e., very close to the highest T_C value observed

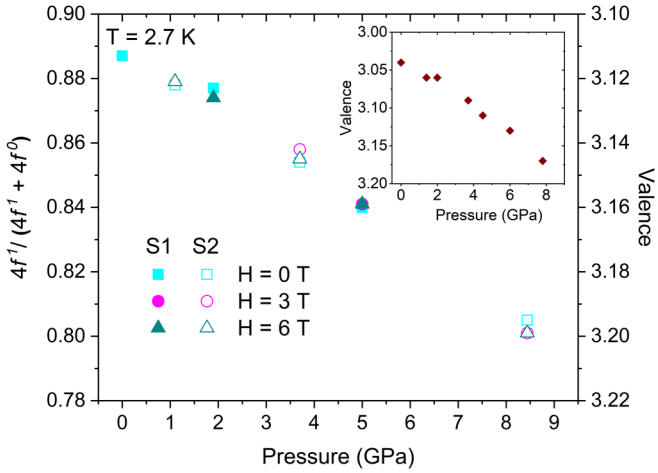

FIG. 3. Pressure dependence of the weight of the Ce^{3+}, $4f^1/(4f^1+4f^0)$, contribution at 2.7 K, i.e., close to the superconducting temperature T_C for different applied fields. The inset represents the pressure dependence at zero applied field of the Ce valence at 14 K obtained previously from the analysis of the x-ray absorption spectra taken in the partial fluorescence mode within the Anderson impurity model [14].

in $CeCu_2Si_2$, do not differ significantly from those obtained previously at 14 K (see inset in Fig. 3) [14]. Thus $CeCu_2Si_2$ exhibits only a crossover valence transition, i.e., it lies in the VCO regime down to the lowest temperature. This observation is in line with the slightly negative (−3.7 K) T_{CEP} deduced from resistivity measurements [14]. This behavior appears to be a common feature of the Ce heavy-fermion superconductors where the most negative T_{CEP} correspond to the lowest T_C [14]. The observation of a FOVT in elemental Ce at finite temperature is due to the short Ce-Ce distances, which lead to a strong U_{fc} Coulomb repulsion between $4f$ and $5d$ conduction electrons at the same Ce site. This Coulomb repulsion is much smaller in the Ce-based heavy-fermion superconductors with conduction electrons supplied by other elements than Ce because of its intersite origin [12]. Figure 4(a) displays XANES spectra recorded at 5 GPa (i.e., close to the optimal pressure where T_c reaches its maximum value), 1.1 GPa at 2.7 K and zero applied magnetic field, and under 6 T. The difference spectra clearly indicate that the application of a magnetic field does not change the shape of the spectra and in turn the Ce valence. Figure 4(b) shows the magnetic field dependences of $4f^1/(4f^1+4f^0)$ at 2.7 K and different pressures below and above P_V. Within the experimental errors, which are about the size of the symbols, the Ce^{3+} contribution does not depend on the application of a magnetic field up to 6 T. $CeCu_2Si_2$ remains thus in the VCO regime as at zero field.

The pressure and magnetic field behavior of $CeCu_2Si_2$ can be understood if one considers the schematic ground state ($T = 0$ K) in the U_{fc}-E_f plane where E_f is the f-level energy which is negative and U_{fc} stands for the Coulomb repulsion between the f and conduction electrons [16,17]. The first-order transition lines (bold) are shown to be shifted to smaller $|E_f|$, whereas the critical U_{fc} of the CEP (represented by filled circles) first decreases and then increases. The intriguing result is the nonmonotonic field dependence of the CEP. For

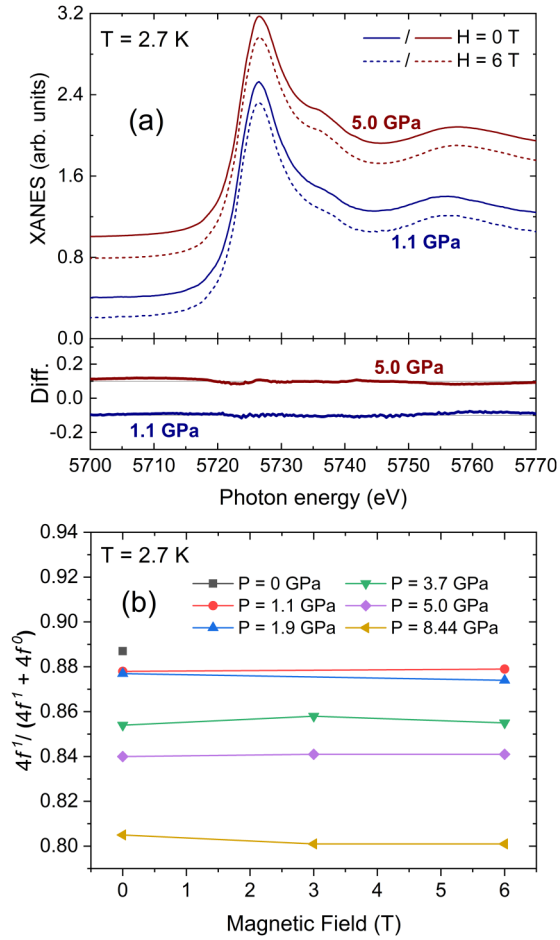

FIG. 4. (a) XANES spectra recorded at 1.1 and 5.0 GPa and 2.7 K for zero field and 6 T together with the result of the subtraction. (b) Pressure dependence of the weight of the Ce^{3+}, $4f^1/(4f^1+4f^0)$, contribution at 2.7 K, i.e., close to the superconducting temperature T_C for different applied fields.

small H values U_{fc} decreases and in turn T_{CEP} is expected to decrease too, i.e., it becomes more negative. At higher H, one observes an upturn and U_{fc} (T_{CEP}) increases. In the investigated field range (up to 6 T), T_{CEP} remains below 2.7 K (the temperature of our measurements). The filled square represents the location of $CeCu_2Si_2$ in the phase diagram at ambient pressure and zero field and the point-dashed line mimics its evolution with increasing pressure. $CeCu_2Si_2$ lies, whatever the pressure or the field, below the FOVT lines, i.e., it is in the VCO regime (Fig. 5).

IV. CONCLUSION

The heavy-fermion $CeCu_2Si_2$ superconductor was investigated by XANES measurements under high pressure and applied magnetic field at a temperature close to the optimal superconducting temperature. The data provide a microscopic view of the pressure and field dependence of the Ce valence. It is shown that pressure does not lead to a first-order valence transition, even in the temperature range where superconductivity occurs, and with applied field. This is in line with the slightly negative critical temperature T_{CEP} deduced from

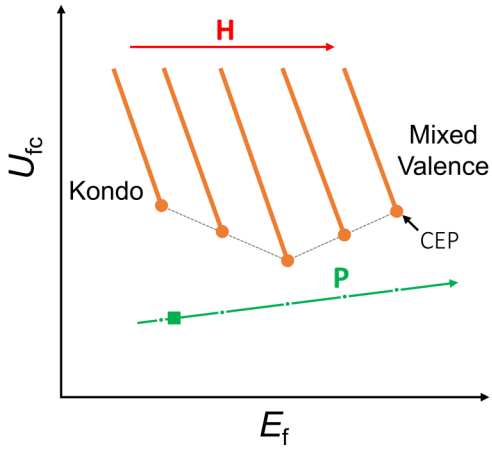

FIG. 5. Schematic ground-state diagram in the U_{fc}-E_f plane. The bold solid lines represent the first-order valence transition lines and the filled circles stand for the critical end point. The shaded line connects the CEP under magnetic field. The filled square stands for the location of $CeCu_2Si_2$ in the phase diagram. The point-dashed line mimics the pressure dependence of its location (adapted from Refs. [16,17]).

resistivity measurements. $CeCu_2Si_2$ belongs to the valence crossover regime in the whole investigated (P,H,T) range. The valence fluctuation mechanism remains however the most plausible scenario for the enhancement of superconductivity in the high-pressure regime; indeed, it is worth to mention that an alternative model for the observation of a second superconducting dome based on critical fluctuations associated with an orbital (crystal-field) transition [26] was recently invalidated by linear polarized M-edge x-ray absorption measurements [27]. The absence of a magnetic field-induced FOVT in $CeCu_2Si_2$ does not invalidate the critical valence fluctuation theory (CVF) model. We observe simply that T_{CEP} (H) stays below our measurement temperature of 2.7 K at 6 T. Quantitative predictions from the CVF model seem almost impossible at the present state of the art. Even although the magnitude of the valence jump is about 0.1 at the FOVT in elementary Ce, its expected magnitude in a hypothetical FOVT in $CeCu_2Si_2$ is an open issue. Extending this study to much higher fields is an interesting but challenging proposition. A more quantitative theoretical estimation of the expected effects would certainly be interesting. At present it seems that the high-pressure superconducting phase diagram of $CeCu_2Si_2$ remains a noncompletely solved question.

ACKNOWLEDGMENTS

We thank D. Jaccard for providing the single crystal of $CeCu_2Si_2$. M.S. is grateful for support from the German funding agency Deutsche Forschungsgemeinschaft (DFG) through Project No. 600575. High-pressure XANES was measured at ESRF through Proposal No. HC-1476. We are grateful to the technical support offered at ID12 beamline.

[1] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).
[2] H. Q. Yuan, F. M. Grosche, M. Deppe, C. Geibel, G. Sparn, and F. Steglich, Science **302**, 2104 (2003).
[3] F. Thomas, C. Ayache, I. A. Fomine, J. Thomasson, and C. Geibel, J. Phys.: Condens. Matter **8**, L51 (1996).
[4] G. Seyfarth, A.-S. Rüetschi, K. Sengupta, A. Georges, D. Jaccard, S. Wanatabe, and K. Miyake, Phys. Rev. B **85**, 205105 (2012).
[5] N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. Haselwimmer, and G. G. Lonzarich, Nature (London) **394**, 39 (1998).
[6] O. Stockert, J. Arndt, E. Faulhaber, C. Geibel, H. S. Jeevan, S. Kirchner, M. Loewenhaupt, K. Schmalzl, W. Schmidt, Q. Si, and F. Stegligh, Nat. Phys. **7**, 119 (2011).
[7] E. Lengyel, M. Nicklas, H. S. Jeevan, G. Sparn, C. Geibel, F. Steiglich, Y. Yoshioka, and K. Miyake, Phys. Rev. B **80**, 140513(R) (2009).
[8] K. Fugiwara, Y. Hata, K. Miyoshi, J. Takeuchi, Y. Shimaoka, H. Kotegawa, T. C. Kobayashi, C. Geibel, and F. Steglich, J. Phys. Soc. Jpn. **77**, 123711 (2008).
[9] D. Jaccard, H. Wilhelm, K. Alami-Yadri, and E. Vargoz, Physica B **259–261**, 1 (1999).
[10] A. T. Holmes, D. Jaccard, and K. Miyake, J. Phys. Soc. Jpn. **76**, 051002 (2007).
[11] G. W. Scheerer, Z. Ren, S. Watanabe, G. Lapertot, D. Aoki, D. Jaccard, and K. Miyake, npj Quantum Mater. **3**, 41 (2018).
[12] S. Watanabe and K. Miyake, J. Phys.: Condens. Matter **23**, 094217 (2011).
[13] J. Röhler, J. Klug, and K. Keulerz, J. Magn. Magn. Mater. **76–77**, 340 (1988).
[14] J.-P. Rueff, S. Raymond, M. Taguchi, M. Sikora, J.-P. Itié, F. Baudelet, D. Braithwaite, G. Knebel, and D. Jaccard, Phys. Rev. Lett. **106**, 186405 (2011).
[15] A. Kotani, J. Electron. Spectrosc. Relat. Phenom. **181**, 168 (2010).
[16] S. Wanatabe, A. Tsuruta, K. Miyake, and J. Flouquet, Physica B **404**, 2942 (2009).
[17] S. Wanatabe, A. Tsuruta, K. Miyake, and J. Flouquet, Phys. Rev. Lett. **100**, 236401 (2008).
[18] A. Rogalev and F. Wilhelm, Physics Met. Metallogr. **116**, 1285 (2015).
[19] F. Wilhelm, G. Garbarino, J. Jacobs, H. Vitoux, R. Steinmann, F. Guillou, A. Snigirev, I. Snigireva, P. Voisin, D. Braithwaite, D. Aoki, J.-P. Brison, I. Kantor, I. Lyatun, and A. Rogalev, High Pressure Res. **36**, 445 (2016).
[20] A. Kotani, K. O. Kvashnina, P. Glatzel, J. C. Parlebas, and G. Schmerber, Phys. Rev. Lett. **108**, 036403 (2012).
[21] B. Joseph, T. Torchio, C. Benndorf, T. Irifune, T. Shinmei, R. Pöttgen, and A. Zerr, Phys. Chem. Chem. Phys. **19**, 17526 (2017).
[22] J.-D. Cafun, K. O. Kvashnina, E. Casals, V. F. Puntes, and P. Glatzel, ACS Nano **7**, 10726 (2013).
[23] B. Ravel and M. Newville, J. Synchrotron Radiat. **12**, 537 (2005).

[24] A. V. Soldatov, T. S. Ivanchenko, S. Della Longa, A. Kotani, Y. Iwamoto, and A. Bianconi, Phys. Rev. B **50**, 5074 (1994).

[25] A. Kotani, K. O. Kvashinina, S. M. Butorin, and P. Glatzel, Eur. Phys. J. B **85**, 257 (2012).

[26] L. V. Pourovskii, P. Hansmann, M. Ferrero, and A. Georges, Phys. Rev. Lett. **112**, 106407 (2014).

[27] A. Amorese, A. Marino, M. Sundermann, K. Chen, Z. Hu, T. Willers, F. Choukani, P. Ohresser, J. Herrero-Martin, S. Agrestini, C.-T. Chen, H. J. Lin, M. W. Haverkort, S. Seiro, C. Geibel, F. Steglich, L. H. Tjeng, G. Zwicknagl, and A. Severing, Phys. Rev. B **102**, 245146 (2020).