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Pressure-induced change of the pairing symmetry in superconducting $CeCu_2Si_2$

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Low-temperature (T) heat-capacity measurements under hydrostatic pressure of up to $p \approx 2.1$ GPa have been performed on single-crystalline $CeCu_2Si_2$. A broad superconducting (SC) region exists in the T-p phase diagram. In the low-pressure region antiferromagnetic spin fluctuations and in the high-pressure region valence fluctuations had previously been proposed to mediate Cooper pairing. We could identify these two distinct SC regions. We found different thermodynamic properties of the SC phase in both regions, supporting the proposal that different mechanisms might be implied in the formation of superconductivity. We suggest that different SC order parameters are characterizing the two distinct SC regions.

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The ongoing interest in unconventional, i.e., non-*s*-wave, superconductors was initiated 30 years ago by the discovery of superconductivity in the heavy-fermion (HF) metal $CeCu_2Si_2$.[1] While for conventional (BCS) superconductors a very low concentration of magnetic impurities is generally detrimental to superconductivity, for $CeCu_2Si_2$ 100 at.% of magnetic Ce^{3+} ions turned out to be prerequisite to form the superconducting (SC) phase:[1] the nonmagnetic reference compound $LaCu_2Si_2$ is not a superconductor,[1] and doping with a small amount of nonmagnetic impurities was found to suppress the SC state completely.[2] Because of their small effective Fermi velocity, the heavy quasiparticles forming the Cooper pairs in $CeCu_2Si_2$ cannot escape their own "polarization cloud" which discards the BCS-type electron-phonon coupling mechanism.[1] Soon after the discovery of HF superconductivity, magnetic couplings were considered to mediate the pairing in these materials.[3] As early as 1986, antiferromagnetic (AF) spin fluctuations, including those at low frequencies near a spin-density-wave (SDW) instability [or quantum critical point (QCP)], were proposed to act as SC glue in HF metals.[4] The pressure-induced superconductor $CePd_2Si_2$ may be considered of prototype for this type of superconductors:[5] it exhibits a very narrow "dome" of superconductivity centered around its QCP at a critical pressure $p_c \approx 2.8$ GPa and, further on, shows pronounced non-Fermi-liquid (NFL) behavior in its low-temperature normal state.[5] Remarkably, in $CeCu_2Si_2$ superconductivity extends well beyond the AF instability, suggesting that a mechanism, other than AF spin fluctuations, might be involved in the formation of the Cooper pairs in the high-pressure region. There, valence fluctuations were supposed to mediate the formation of superconductivity.[6,7] The extended SC state of $CeCu_2Si_2$, schematically depicted in Fig. 1, results from the merging of two distinct SC regions:[8] the one on the low-pressure side (SC1) appears to be similar to that observed in other NFL superconductors, such as $CePd_2Si_2$,[5] while in the high-pressure region, another type of SC state (SC2) seems to form. Even though valence-fluctuation mediated superconductivity has been predicted theoretically (e.g., Refs. 9 and 10), its experimental observation is so far limited to the $CeCu_2(Si_{1-x}Ge_x)_2$ family.[7,8] In these materials the two instabilities, i.e., an AF one at low pressure and a low-lying critical end point of the first-order valence-transition line at elevated pressure,[11] are sufficiently separated in order to be distinguishable and, at the same time, show up in an experimentally accessible pressure range. While superconductivity in the regions SC1 and SC2 has been presumed to be mediated by AF spin fluctuations and critical valence fluctuations, respectively,[6–8] the pairing mechanism in the crossover region (hatched area in Fig. 1) from the HF to the intermediate valence (IV) state is still a matter of discussion: while both types of fluctuations may be involved together in forming the SC state on the one hand, a first-order transition line might separate the two distinct regions of superconductivity on the other.

In this paper, we study the thermodynamic properties in SC $CeCu_2Si_2$ by specific-heat experiments under pressure. For the present study we have chosen a $CeCu_2Si_2$ single crystal of stoichiometric composition, in which superconductivity expels SDW order at low magnetic field but where the SDW is recovered in an overcritical magnetic field for superconductivity ("A/S-type" $CeCu_2Si_2$).[12] We find different thermodynamic properties in the two distinct SC regions, SC1 and SC2. This hints at a pressure-induced change of the pairing symmetry.

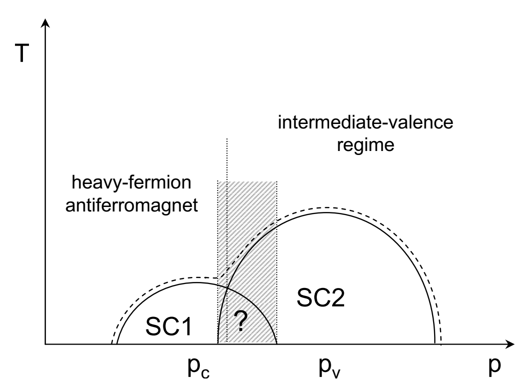

FIG. 1. Schematic T-p phase diagram of $CeCu_2Si_2$. The dashed line depicts the shape of the SC phase line observed experimentally. p_c and p_v indicate the critical pressures for the magnetic and the valence instabilities, respectively.

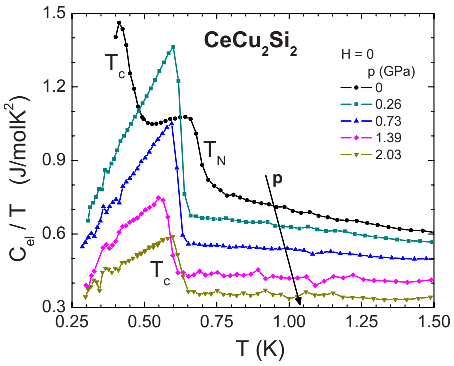

FIG. 2. (Color online) Low-temperature $C_{el}(T)/T$ versus T of A/S-type $CeCu_2Si_2$ at $H=0$ for pressures as indicated in the figure.

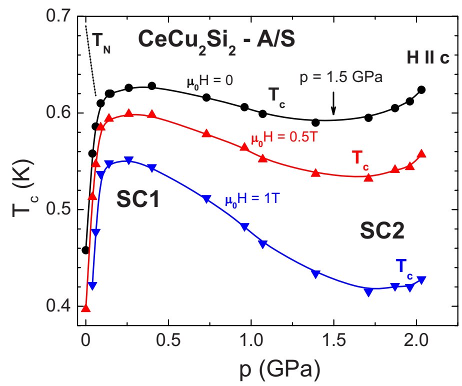

FIG. 3. (Color online) Pressure dependence of T_c for different values of $\mu_0 H$. The pressure dependence of T_N at $H=0$ is shown by the dotted line. The arrow indicates the estimated border between the low-pressure (SC1) and the high-pressure (SC2) SC regions at $H=0$.

The A/S-type $CeCu_2Si_2$ single crystal was grown in an aluminum-oxide crucible by a modified Bridgman technique, using Cu excess as flux medium. Powder x-ray diffraction patterns confirmed the proper tetragonal $ThCr_2Si_2$ structure with lattice parameters $a=0.4099$ nm and $c=0.9923$ nm at 295 K. Heat-capacity measurements under hydrostatic pressure have been performed in a single-shot ^{3}He evaporation cryostat by employing a compensated quasiadiabatic heat-pulse technique. In addition, the SC transition in $CeCu_2Si_2$ was detected through magnetocaloric and ac-susceptibility measurements on the same sample and at the same pressures. A single piece of A/S-type $CeCu_2Si_2$ weighing about $m \approx 0.4$ g was used for the experiments. Its residual resistivity was $\rho_0 \approx 10$ $\mu\Omega$ cm, indicating a good sample quality.[13] The magnetic field was always applied parallel to the c axis. The measurements at low pressures ($p<1.1$ GPa) were carried out in a CuBe piston-cylinder pressure cell, while for the high-pressure range ($p \geq 1.1$ GPa) a double layer NiCrAl-CuBe-type piston-cylinder pressure cell was utilized. For the entire experiment, Flourinert FC72 was used as pressure transmitting medium. A piece of tin served as pressure gauge. For the whole pressure range, the electronic specific heat (C_{el}) was obtained by subtracting the ambient pressure lattice specific heat of the isostructural nonmagnetic reference compound $LaCu_2Si_2$.[14]

The temperature dependence of the low-temperature C_{el} of $CeCu_2Si_2$ for selected pressures is shown in Fig. 2. Characteristic for A/S-type $CeCu_2Si_2$, two consecutive phase transitions, can be observed at $p=0$, an upper one at $T_N \approx 0.69$ K to an incommensurate SDW order[15] and a lower one marking the onset of superconductivity at $T_c \approx 0.46$ K. Upon increasing pressure, the AF order is gradually suppressed while superconductivity is stabilized. Above $p=0.07$ GPa no anomaly indicating the onset of AF order can be observed anymore. In the normal state, C_{el} of $CeCu_2Si_2$ decreases with increasing pressure in the entire pressure range. This is expected for Ce-based HF systems, where application of pressure leads to an increase of the hybridization strength between the Ce $4f$ and the conduction electrons and hence to a decrease of the effective mass of the quasiparticles.

Figure 3 displays the evolution of T_c as a function of pressure for different magnetic fields as obtained from the heat-capacity measurements. With increasing pressure, a steep initial rise of $T_c(p)$ is followed by a pronounced maximum and, at elevated pressure, a shallow minimum. For $H=0$, $T_{c,max} \approx 0.63$ K at $p \approx 0.4$ GPa and $T_{c,min} \approx 0.59$ K at $p \approx 1.5$ GPa. We use the pressure value of $T_{c,min}$ to delineate the border between the two regions SC1 and SC2. With increasing magnetic field the T_c values become reduced and $T_{c,min}$ shifts to higher pressures, suggesting an increasing separation between the two SC regions. As can be seen in Fig. 3, superconductivity in the SC2 region is suppressed more efficiently by the magnetic field than in the SC1 region. At $\mu_0 H=2$ T, superconductivity still exists in a very narrow pressure range at low pressures, while in the high-pressure region there is no superconductivity up to $p \approx 2.1$ GPa. Here, the upper-critical field, $\mu_0 H_{c2}(0)$, is smaller than 1.5 T. In the low-temperature normal state ($T<1$ K, $\mu_0 H=2$ T), $C_{el}(T)/T=\text{const}[\approx 0.4\ \text{J}/(\text{mol K}^2)]$ at $p>1.5$ GPa, indicating a moderately heavy Landau Fermi-liquid state. This leads us to conclude that in this pressure and magnetic field range A/S-type $CeCu_2Si_2$ is situated far away from a QCP.

Figure 4 depicts the evolution of the $H=0$ normalized low-temperature electronic specific heat under pressure. The data are presented as $C_{el}(T)/(\gamma_n T)$ versus T/T_c, where γ_n is $C_{el}/T|_{T=T_c^+}$ in the normal state. The specific-heat data obtained on SC $CeCu_2Si_2$ do not follow the BCS prediction (dashed line), and the $\Delta C_{el}/(\gamma_n T_c)|_{T=T_c}$ ratio exhibits values smaller than the BCS value of 1.43. A quasilinear temperature dependence of $C_{el}(T)/T$ can be observed at $0.5T_c<T<T_c$ for all pressures above 0.09 GPa. A comparison with numerical calculations of $C_{el}(T)/T$ (Ref. 16) suggests that the SC state in $CeCu_2Si_2$ has an unconventional nature and is characterized by a gap function having line nodes.

The normalized specific-heat data, $C_{el}(T)/(\gamma_n T)$ versus T/T_c, fall on a single curve for pressures 0.09 GPa $\leq p \leq 0.4$ GPa; in the same way, the data in the high-pressure range, 1.71 GPa$\leq p \leq 2.03$ GPa, collapse also on a single (but different) curve as can be seen in Fig. 4(a). Figure 4(b) displaying the data for the intermediate pressure range 0.73 GPa$\leq p \leq 1.39$ GPa reveals a gradual shift of the data from the low-pressure to the high-pressure scaling curve.

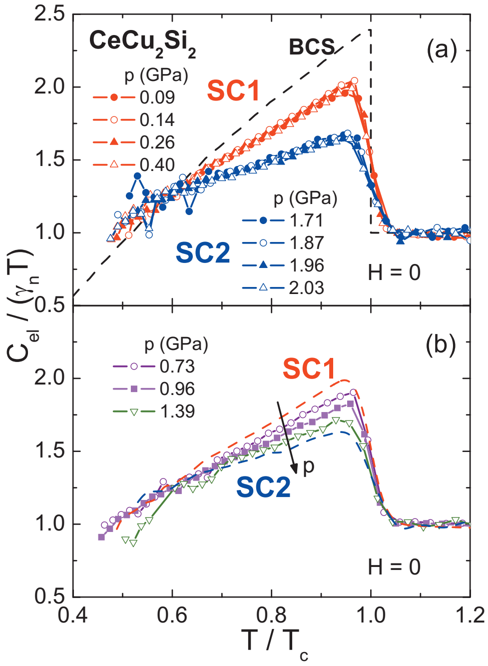

FIG. 4. (Color) Normalized electronic specific-heat data obtained on $CeCu_2Si_2$ under pressure. The dashed line in panel (a) corresponds to the theoretically calculated dependence for the case of a conventional BCS-type superconductor. The two dashed lines in panel (b) serve as references and they reproduce the data for the two distinct groups presented in panel (a).

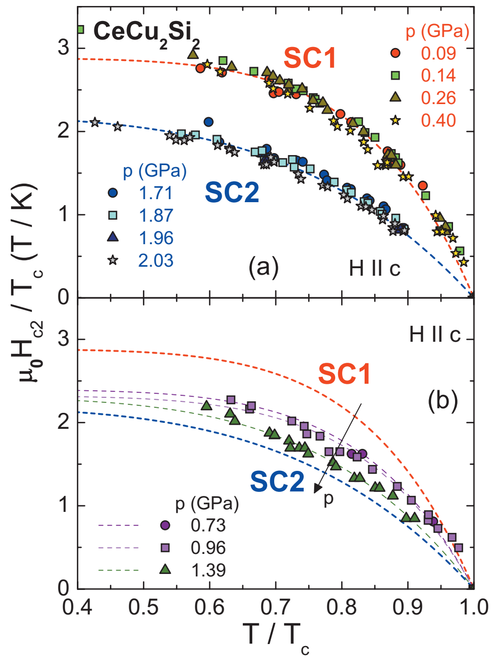

FIG. 5. (Color) $\mu_0 H_{c2}(T)/T_c$ versus T/T_c for different pressures obtained for $H \parallel c$. Lines are guides for the eyes. The red and blue lines from panel (b) reproduce the corresponding lines from panel (a) and serve as references for regions SC1 and SC2 presented in panel (a).

Figure 5 presents the normalized upper-critical field $\mu_0 H_{c2}(T)/T_c$ as a function of the normalized temperature T/T_c. These data display a similar pressure evolution as observed in the case of $C_{el}(T)/(\gamma_n T)$: two distinct scaling curves are found for the two SC regions, and the data in the intermediate pressure range shift gradually on increasing pressure from the scaling curve corresponding to region SC1 to the one corresponding to region SC2. These findings highlight that the SC order parameters in regions SC1 and SC2 are different. The continuous evolution of the data from SC1 to SC2 favors an overlap region between SC1 and SC2 where a smooth crossover takes place rather than a first-order transition line between SC1 and SC2.

At $p \geq 0.09$ GPa, the values estimated for the Pauli-limiting field are slightly smaller than those experimentally obtained for the upper-critical field, while for the orbital-limiting field we estimate values three to four times larger than $H_{c2}(0)$. This proves that $H_{c2}(T)$ is strongly Pauli limited in the pressure range 0.09 GPa $\leq p <$ 2.1 GPa, indicating a SC order parameter of even parity, consistent with d-wave pairing symmetry as we will discuss in the following.

Our conclusion of different SC order parameters in $CeCu_2Si_2$ at low and high pressures is corroborated by theoretical considerations. The experimental results presented in Figs. 4(a) and 5(a) show that $\Delta C_{el}/(\gamma_n T_c)|^{SC1}_{T=T_c}/\Delta C_{el}/(\gamma_n T_c)|^{SC2}_{T=T_c} \approx 1.6$ and $(dH_{c2}/dT)^{SC1}_{T=T_c}/(dH_{c2}/dT)^{SC2}_{T=T_c} \approx 1.9$. A theoretical analysis shows that even within the manifold of d symmetry the above mentioned ratios can be different from 1 for different symmetries of pairing:[17] by choosing the $d_{x^2-y^2}$ and the d_{xy} type pairings for the SC1 and SC2 regions, respectively, one estimates theoretically $\Delta C_{el}/(\gamma_n T_c)|^{d_{x^2-y^2}}_{T=T_c}/\Delta C_{el}/(\gamma_n T_c)|^{d_{xy}}_{T=T_c} \approx 1.6$ and $(dH_{c2}/dT)^{d_{x^2-y^2}}_{T=T_c}/(dH_{c2}/dT)^{d_{xy}}_{T=T_c} \approx 1.8$.[17] The good agreement between the experimental results and the theoretical estimation for these quantities suggests that $d_{x^2-y^2}$ pairing is realized at the lower pressure side (region SC1) and d_{xy} pairing is realized at the higher pressure side (region SC2). It is reasonable that $d_{x^2-y^2}$ pairing is realized in the lower pressure region where the AF fluctuations develop due to AF quantum criticality around ambient pressure because the AF correlations among f electrons at adjacent sites in the basal plane are expected to promote the pairing with $d_{x^2-y^2}$ symmetry.[18] The origin of the d_{xy} pairing in the higher pressure region should be assigned to a SC glue different from AF fluctuations. As mentioned earlier, a promising candidate may be valence fluctuations which are enhanced in the higher pressure region around $p \simeq 5$ GPa.[6,19]

In conclusion, we found different thermodynamic properties in the two distinct SC regions of $CeCu_2Si_2$. Our results support the previously made suggestion[6–10] that two different mechanisms are involved in the formation of the Cooper pairs in these two regions: in the SC1 state, pairing is likely to be mediated by AF spin fluctuations; in the high-pressure SC state (SC2), valence fluctuations are supposed to mediate the formation of the Cooper pairs. Superconductivity in the low-pressure region is more robust against application of magnetic field than in the SC2 region as indicated by the larger upper-critical fields. Further on, we observed distinct scaling laws of $C_{el}(T)/(\gamma_n T)$ versus T/T_c and of $\mu_0 H_{c2}(T)/T_c$ versus T/T_c in the two different SC regions. Therefore, we suggest the existence of different SC order parameters in SC1 and SC2. A theoretical analysis of our data proposes $d_{x^2-y^2}$-type Cooper pairing for the SC1 region and d_{xy}-type pairing for the SC2 region. The existence of different SC order parameters is highly consistent with the different mechanisms supposed to be implied in the formation of Cooper pairs in $CeCu_2Si_2$. We find a smooth crossover from the SC1 to the SC2 region. Thus, this crossover region should be characterized by a SC state where both AF spin and valence fluctuations are involved together in the Cooper pairing. However, for a precise experimental determination of the SC order parameters in the low- and high-pressure regimes, field-angle dependent specific-heat experiments at low temperatures have to be performed in the future.

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