Strain enhancement of superconductivity in CePd$_2$Si$_2$ under pressure

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We report resistivity and calorimetric measurements on two single crystals of CePd$_2$Si$_2$ pressurized up to 7.4 GPa. A weak uniaxial stress induced in the pressure cell demonstrates the sensitivity of the physics to anisotropy. Stress applied along the c-axis extends the whole phase diagram to higher pressures and enhances the superconducting phase emerging around the magnetic instability, with a 40% increase of the maximum superconducting temperature, $T_c$, and a doubled pressure range. Calorimetric measurements demonstrate the bulk nature of the superconductivity.

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By varying an external control parameter, such as magnetic field, composition or pressure, many heavy-fermion systems may be pushed through a quantum critical point (QCP), where their magnetic ordering temperature goes to zero. In the immediate vicinity of this point, transport and thermodynamic measurements show striking deviations from standard Fermi-liquid behavior. In particular, the low temperature resistivity, $\rho(T)$, exhibits a $T^n$ behavior with $1<n<1.5$ over a wide temperature range. The nature of this non-Fermi-liquid (NFL) behavior remains an open question. Is the spin-fluctuation description appropriate, with itinerant magnetism developing below a characteristic temperature such as the Kondo temperature, $T_K$? Alternatively, this characteristic temperature may collapse at the QCP, leading to localized magnetism down to the lowest temperatures. Particular attention has been paid to the case of stoichiometric compounds, whose weak disorder permits the observation of superconductivity around the magnetic instability. Due to the enhancement of low-lying magnetic excitations in this region, it is commonly believed that Cooper pairs are magnetically formed. In one of these systems, CePd$_2$Si$_2$, superconductivity was discovered in a window of about 1 GPa around the QCP at a critical pressure $P_c \approx 2.8$ GPa. Simultaneously, NFL behavior was found in resistivity measurements with a $T^{1.2-1.3}$ law over two decades in temperature. As an exponent $d/2$ is predicted for a $d$-dimensional antiferromagnet by spin-fluctuation theory, it has been suggested that the magnetic excitation spectrum has an effective dimension close to 2. This assumption is supported by the quasi-linear pressure dependence of the Néel temperature, $T_N$, predicted to be $(P_c - P)^{2/d}$, by the tetragonal symmetry (I4/mmm) and by the magnetic structure containing a frustrated moment in the center of the elementary cell.

The results quoted above were obtained in hydrostatic conditions using a “liquid” pressure transmitting medium. Another investigation was carried out in a Bridgman anvil cell, using a soft solid (steatite) as a pressure transmitting medium. This showed a rather different phase diagram: around a higher critical pressure $P_c \approx 3.6$ GPa, a strikingly expanded superconducting region was found, lying from 2 to 7 GPa with a maximum of $T_c$ apparently disconnected from $P_c$, casting doubt upon spin fluctuations as the only mediation mechanism for superconductivity. As this pressure technique is suspected to provide higher pressure gradients, a residual stress along the cell axis could be at the origin of these differences. Our motivation was thus to demonstrate and understand the effect of uniaxial stress under pressure.

In this letter, we report resistivity and calorimetric measurements performed on two samples in a Bridgman anvil cell up to 7.4 GPa. The samples were set in the pressure cell with the force load direction perpendicular and parallel to the c-axis (ref. being the latter). These measurements demonstrate the high sensitivity of the physics in CePd$_2$Si$_2$ to pressure conditions, and the crucial influence of anisotropy on the emerging superconductivity. The differences between the previously observed phase diagrams can be explained by the results from these two samples, with an enhancement of superconductivity when uniaxial stress is applied along the c-axis. Calorimetric measurements demonstrate the bulk nature of this superconductivity; a combination of both types of measurement leads to further insight into the quantum critical point and its associated energy scale.

The samples were extracted from the same single crystalline platelet used in refs. A. Demuer, A. T. Holmes, and D. Jaccard. A parallelepiped sample (510×75×60 µm$^3$), with a residual resistivity ratio $RRR \approx 62$, was cut into two pieces of length 250 µm. These were polished to a small cross-section (~70×20 µm$^2$), and spot-welded with 5 µm diameter gold wires, giving $\rho(293 K)= 45 \mu\Omega$ cm to within 10% for both samples and $RRR$ values of 48 and 103. The corresponding residual resistivities, $\rho_0$, were respectively 1 and 0.48 $\mu\Omega$ cm. The samples will be referred to as (higher $\rho_0$) and ⊥ (lower $\rho_0$) in relation to the orientation of their c-axis with respect to the force load direction (and the additive uniaxial stress). Both samples were connected for four-point DC resistivity measurements, with sample having additional connections for a constantan resistive heater and a thermocouple Au/Au-0.67 at.% Fe suitable for AC calorimetric measurements. The pressure was determined by the superconducting transition of a lead
Sample $\perp$ gave rise to a phase diagram similar to that obtained in hydrostatic conditions (Fig. 1). The superconductivity was limited to the range 2.14–3.25 GPa around $P_{c\perp} \simeq 2.7$ GPa, with $T_c$ having a maximum of 375 mK (mid-point criterion). In contrast, the phase diagram of sample $//$ seems to be stretched towards higher pressures. $T_N$ collapses at $P_{c//} = 3.9$ GPa with a critical behavior $(P - P_c)^\alpha$, $\alpha = 0.60 \pm 0.05$, as distinct from the quasi-linear dependence in the hydrostatic case. Superconductivity occurred between 2.14 and 5.0 GPa (using a mid-point criterion). As in the previous investigation in a Bridgman cell [7], $T_c$ reached a higher value, 520 mK in our case. This maximum of $T_c$ coincides with $P_c$, suggesting that this extended superconductivity is still related to the QCP. The apparent discrepancy between $P_c$ and the maximum of $T_c$ in ref. [7] can be explained by the criterion chosen (onset), sensitive to the large transition widths at extremes pressures.

Fig. 2 shows $\rho(T)$ curves from sample $//$ for selected pressures with a phononic linear contribution (0.17 $\mu\Omega$ cm/K) subtracted. The first pressure, 0.1 GPa, corresponds mainly to a small uniaxial stress along the force load direction. With increasing temperature, one can distinguish a clear kink at $T_N \simeq 11$ K, a maximum at $T_{max}$ attributed to the Kondo effect and a “shoulder” reflecting the influence of excited crystal-field (CF) levels. At high temperature, the $-\ln T$ dependence is characteristic of Kondo scattering. As the pressure rises, $T_{max}$ increases continuously whereas the excited CF anomaly is rather pressure independent. This latter progressively merges with the Kondo peak around 1.5 GPa and seems to collapse at higher pressures. $T_{max}(P)$ shows no anomaly at $P_c$ and identical values $T_{max}(P_c)$ in both samples (Fig. 1).

The resistivity was analyzed at low temperature in terms of a power law $\rho(T) = \rho_0 + AT^n$. Such dependencies are not stable over a wide temperature range except for pressures close to $P_c$, where these power laws extend up to 30 K. The fits were therefore limited to a window of 0.5–2 K, in order to compare data over the entire pressure range. Fig. 3 shows the pressure dependence of the coefficient $A$ and the exponent $n$ (inset). $A$ behaves as $(d\rho/dT)^\gamma |_{T\to0}$ and may be interpreted as a Fermi-liquid contribution prefactor. As expected from the spin-fluctuation model SCR [10], $A(P)$ shows a sharp maximum at $P_c$. This maximum is similar in both samples with $A(P_c)/A(0) \simeq 5$. At 7.4 GPa, the $A$ coefficient of sample $\perp$ has fallen by a factor of 100 compared to its value at $P_c$. A small anomaly was found in $A(P)$ at about 1 GPa in sample $\perp$, and 2 GPa in sample $//$, possibly corresponding to a pressure induced magnetic phase transition. Such an anomaly seems to be present in the isoelectronic compound CePd$_2$Ge$_2$ at about 12 GPa just below $P_c \simeq 13.8$ GPa [14].

An additional curve in Fig. 3 shows the pressure dependence of $\gamma^2 = (C/T)^2 |_{T\to0}$ in sample $\perp$; this also has a maximum at $P_c$. For each pressure, $\gamma^2$ was estimated at 100 mK by subtraction of $1/V^2$ taken at two frequencies (16 and 256 Hz) where $V$ is the thermocouple voltage amplitude [13]. To obtain a reliable pressure dependence, the same working parameters were used for all pressures. Far from the instability, $A$ and $\gamma$, both related to the square of the effective mass of quasi-particles, $m^*^2$, are expected to follow the Kadowaki-Woods relation, $A \propto \gamma^2$ [3]. The peak in $\gamma^2$ at $P_c$ is less pronounced than in $A(P)$ with $\gamma^2(P_c)/\gamma^2(7.4$ GPa)$\simeq 18$, but $\gamma$ may well include a contribution from the pressure transmitt-
ting medium, reducing the relative size of the peak.

In both samples, a sharp dip in the resistivity exponent \( n(P) \) (inset of Fig. 3) is associated with the magnetic instability, reaching values lower than the 2 expected for Fermi-liquid behavior. The minimum values obtained were 1.32 and 1.42 (±0.03) for samples \( \perp \) and // respectively. As in the \( A(P) \) curves, a small anomaly appears around 1 and 2 GPa.

The superconducting transition appears in the calorimetric measurement only at 2.68 GPa, the closest pressure to \( P_c \). Fig. 4 shows a comparison between superconducting transitions in \( \rho(T) \) and the calorimetric signal \( 1/V \) (\( \sim C_p/T \)). The onset of the calorimetric transition occurs at the temperature for which \( \rho \) reaches zero. In sample \( \perp \) at 2.68 GPa \( \approx P_c \), we studied the effect of an external magnetic field on the superconductivity using the two types of measurement. The large initial slope of the upper critical magnetic field in the basal plane, \( dH^c_\perp/dT \approx -6 \) T/K, indicates that heavy quasiparticles are involved in superconductivity. The size of the calorimetric anomaly collapses rapidly with increasing field and becomes undetectable above 0.5 T. If the calorimetric anomaly at \( H=0 \) indicates a bulk transition, one cannot rule out the magnetic field revealing a non-homogeneous situation in the sample, as suggested by the large transition widths in \( \rho(T) \) and disappearance of the anomaly in calorimetric measurement for pressures away from \( P_c \). The inset in Fig. 4 shows the superconducting transition in \( \rho(T) \) for sample // close to its \( P_c \). A striking point is that the highest value of \( T_c \) is obtained in the sample with the larger residual resistivity, demonstrating that the superconductivity enhancement is not related to the crystal purity.

The following discussion is supported by the unprecedented quality of our samples, with \( RRR \) values as high as 130 at \( P_c \). Bearing this in mind, one should be aware that variations on a submillimetric scale exist even within a single crystal - the present samples and those of ref. [5, 6] were cut from the same tiny single-crystalline platelet with \( RRR \) values varying by a factor of 3 at \( P = 0 \). Furthermore, we claim to have an accurate value for the resistivity, with a well-defined geometric factor enabling the determination of the absolute resistivity to within 10%. As suggested earlier, the temperature \( T_{max} \) of the maximum in the magnetic contribution to the resistivity should be related to the Kondo temperature, \( T_K \). \( T_{max} \) takes the same value at \( P_c \) for both samples, supporting the idea that \( T_{max} \) is a reliable characteristic energy for the QCP. Its pressure dependence allows us to take part in the heated debate about the nature of the QCP illustrated by another heavy-fermion system, \( CeCu_{6-x}Au_{x} \). While neutron measurements on the substituted compound \( CeCu_{5.9}Au_{0.1} \) seem to reveal localized magnetism at the lowest temperature \( 3 \), measurements under pressure on the stoichiometric compound \( CeCu_{5}Au \) [7] showed no anomaly in \( T_K \) at \( P_c \), suggesting that the magnetism remains itinerant around the QCP. As the latter behavior is observed in our investigation, spin-fluctuation theory should also apply in the vicinity of the QCP of \( CePd_2Si_2 \). In both of our samples, the QCP occurred in a pressure domain where the characteristic Kondo energy \( k_B T_K \) (\( T_K \propto T_{max} \)) typically reaches the crystal-field splitting energy (see Fig. 1). Furthermore, \( \ln A \) is found to behave as \( -\alpha \ln(T_{max}) \) with a slope \( \alpha \approx 4 \), instead of the value of 2 expected for a normal heavy-fermion regime. This indicates the entrance into an intermediate valence regime, probably leading to deviations from the simple spin-fluctuation model. The fact that \( \gamma^2(P) \) decreases slower than \( A(P) \) above \( P_c \) might tempt us to invoke the predictions of ref. [8], but our calorimetric measurement is not quantitative enough.
does allows us to demonstrate clearly a relationship between $A$ and $\gamma$, showing in both a peak at $P_c$, but the $\gamma$ value extracted probably includes undefined addenda obscuring the physics.

As in previous measurements, NFL behavior was observed in $\rho(T)$ at $P_c$ in both samples over more than one decade in temperature. The stability of this behavior in temperature has been proposed to result from a crossover between “clean” and “dirty” limit regimes for a specific amount of disorder [18]. However, this explanation disagrees with the systematic observation of power laws in $\rho(T)$ at $P_c$ over a large temperature range for samples with residual resistivities spread over almost one decade [19, 20]. The exponent in $\rho(T) = \rho_0 + AT^n$ in all cases reaches remarkably low values with $n \simeq 1.2 - 1.3$, a value generally attributed to a non 3D spin-fluctuation spectrum. However, let us recall that in other compounds such as CeCu$_2$Ge$_2$, a minimum of $n$ close to 1 was found only for $P > P_c$, in a pressure domain where $k_BT_K$ reaches the CF splitting energy [19]. As this happens for $P \simeq P_c$ in CePd$_2$Si$_2$, one may wonder if the low exponent observed is not a consequence of this change of regime.

Hydrostatic pressure reduces both lattice parameters $a$ and $c$. At a given pressure, an additional uniaxial stress, $\sigma$, along one axis further reduces that lattice parameter while expanding the others. A description of the physical properties as a function only of the cell volume fails in this system, as shown by the various phase diagrams obtained on samples / / . Whereas the situation remains mostly unchanged when $\sigma$ is applied in the basal plane, the clear extension of the phase diagram for $\sigma$ along the $c$-axis shows that the ratio $c/a$, reflecting the anisotropy of the system, is also a key parameter. Considering the spin-fluctuation prediction $T_N(P) \propto (P_c - P)^{2/d}$, the exponent $0.60 \pm 0.05$ obtained for sample / / suggests that applying $\sigma$ along the $c$-axis restores a 3D spin-fluctuation spectrum. With the same theoretical approach, the minimum value of the exponent in the $\rho(T)$ power law at $P_c$, predicted to be $T^{2/3}$, should be different in the two samples. However, the differences observed in $n(P_c)$ and in $A(P_c)$ (Fig. 3) are smaller than we might expect. The most striking consequence of this change in anisotropy is the apparent enhancement of superconductivity for $\sigma$ applied along the $c$-axis with a 40% higher maximum value of $T_c$ and a doubling of its pressure range. This enhancement is not related to a larger electronic mean free path due to reduced disorder, since the sample with a higher $T_c$ also has the higher $\rho_0$. As spin fluctuations are thought to be at the origin of the Cooper pairing, one may attribute the enhancement of superconductivity to different features of the spin-fluctuation spectrum. The values of the critical exponents in $T_N(P)$ suggests that 3D spin fluctuations would be more favorable for superconductivity, though many scenarios such as an increase in carriers density associated with a band modification under uniaxial stress remain possible.

Our measurements demonstrate the complexity of the physics in CePd$_2$Si$_2$ in the vicinity of its quantum critical point. At this pressure $P_c \simeq 2.7 - 2.8$GPa, several energy scales such as the Kondo and excited crystal-field energies interact, leading to a complex ground state. While the other archetypical system for a superconducting phase induced around its critical point, the cubic CeNi$_3$, is insensitive to pressure conditions [15, 20], the physical properties of the tetragonal CePd$_2$Si$_2$ are strongly affected by modification of anisotropy resulting from additional uniaxial strain along the $c$-axis. The quasi 2D-behavior evoked for spin-fluctuations seems to be destroyed and superconductivity is enhanced around $P_c \sim 3.9$GPa. As pure uniaxial stress experiments are extremely difficult to perform under pressure, the effect of the anisotropy on superconductivity around a quantum critical point should be checked on a compound close to its instability at ambient pressure. CeNi$_3$Ge$_2$, where traces of superconductivity as well as quasi-2D behavior for spin fluctuations were found [21, 22], appears as one of the best candidates.

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