Superconductivity beyond the Pauli limit in high-pressure CeSb$_2$

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We report the discovery of superconductivity at a pressure-induced magnetic quantum critical point in the Kondo-lattice system CeSb$_2$, sustained up to magnetic fields that exceed the conventional Pauli limit eight-fold. Like CeRh$_2$As$_2$, CeSb$_2$ is locally non-centrosymmetric around the Ce-site, but the evolution of critical fields and normal state properties as CeSb$_2$ is tuned through the quantum critical point motivates a fundamentally different explanation for its resilience to applied field.

In an increasing number of materials – notably the new unconventional superconductors CeRh$_2$As$_2$ [1] and UTe$_2$ [2, 3] – superconductivity is surprisingly resilient to magnetic field, and the temperature dependence of the upper critical field shows a rich and unexpected structure. This is important not just for applications in which high magnetic fields are required but also because the field resilience suggests that the superconducting Cooper pairs form triplet states, which may be exploited for quantum computing. In CeRh$_2$As$_2$, the postulated high field triplet state has been linked to a structural peculiarity, namely the lack of inversion symmetry around the crucially important Ce atoms, which underpin the electronic structure and the superconducting pairing mechanism.

In the related, clean Kondo lattice material CeSb$_2$, we here report the discovery of superconductivity over a narrow pressure range that envelopes a magnetic quantum critical point (qcp). CeSb$_2$ displays a complex magnetic phase diagram with at least four magnetic phases and a ferromagnetic ground state [4–8], all of which are initially robust under pressure, but its electronic and magnetic properties change profoundly [9, 10] at the high pressures considered here. Like CeRh$_2$As$_2$, high pressure CeSb$_2$ lacks inversion symmetry around the Ce sites, and its upper critical field is strongly enhanced over expectations from elementary theory. In contrast to CeRh$_2$As$_2$, however, signatures of a singlet-triplet transition under applied field are not observed in CeSb$_2$, suggesting that the critical field is instead boosted by a more general mechanism intrinsic to strong-coupling superconductivity involving ultra-heavy quasiparticles.

**Methods.** High quality crystals of CeSb$_2$ with residual resistivity ratios RRR = $\rho_{300}/\rho_0 \simeq 100$ were grown using standard self-flux techniques [5] and characterised by powder x-ray diffraction techniques [5] and heat capacity measurements. Piston-cylinder pressure cell measurements up to about 28 kbar were carried out in a compound BeCu/MP35 cell [12] with the superconducting transition temperature of Sn as the pressure gauge [13], whereas a wider pressure range up to 40 kbar was accessed in moissanite anvil cells using room temperature ruby fluorescence to determine the pressure. Glycerol was used as the pressure medium in both types of pressure cell. The crystal orientation reported in magnetic field studies (c-axis vs. in-plane) refers to the low pressure structure. The electrical resistivity was determined using a standard 4-terminal AC technique with a 3 μA current at the lowest temperatures, and the magnetic susceptibility was measured using a mutual inductance technique with a pickup microcoil inside the high pressure sample volume [14]. The heat capacity was obtained from a 3ω temperature modulation technique, oscillating the current in a thick film metal heater and in a Cernox thermometer closely connected to the sample at a frequency $\omega$, and picking up the third harmonic $\omega_3 = 3\omega$ of the resulting thermometer signal [15]. Measurements in a QD PPMS in the range 2 K-300 K were complemented...
by low temperature studies in a cryogen-free ADR system (Drogetic Measurement System, DMS) to < 0.1 K and in fields of up to 6 T.

**Superconductivity and anomalous normal state.**

The normal state in-plane resistivity in CeSb$_2$ at an applied pressure $p \simeq 31.6$ kbar displays a distinctly non-Fermi liquid, sub-linear temperature dependence $\rho(T)$ (Fig. 1). The resistivity rises steeply at low $T$ and reaches a shallow maximum at 22.5 K, above which it stays roughly constant up to room temperature (left inset in Fig. 1), following a form familiar from other Ce or Yb-based Kondo lattice materials such as CeCu$_2$Si$_2$, CeCoIn$_5$, and YbRh$_2$Si$_2$ [16–19]. It approaches saturation well below 10 K, reaching 80% of the maximum resistivity at $T^* \simeq 8.2$ K. These temperatures are similar to those recorded in CeCu$_2$Si$_2$, CeCoIn$_5$, and YbRh$_2$Si$_2$, suggesting extremely strong electronic correlations, narrow renormalised bands and high quasiparticle masses in high-pressure CeSb$_2$.

A sharp resistive transition with mid-point $T_c \simeq 0.22$ K (main plot in Fig. 1) indicates superconductivity at very low temperatures, in line with the low electronic energy scales suggested by the normal state $\rho(T)$. Superconductivity proves surprisingly robust to applied magnetic fields along the crystallographic $c$ direction (right inset in Fig. 1). It persists to $> 3$ T at low $T$, exceeding the Pauli paramagnetic limiting field, which is conventionally written as $B_{\text{Pauli}} = 1.84 T K^{-1} T_c$ [20, 21], by nearly an order of magnitude. The in-plane upper critical field is similarly enhanced [15].

For small applied fields, $T_c$ is initially reduced, then rises again to a value slightly higher than the zero-field $T_c$, for $B \approx 1.5$ T. This produces an unusual, inverted ‘S’-shaped structure in the $B_{c2}$($T$) curve. The inverted ‘S’ structure is observed at several other pressures $\leq 32.2$ kbar but vanishes at higher pressures (see below). The sign reversal of $dB_{c2}/dT$, which is $> 0$ over an intermediate field range, points towards an underlying, field tuned phase transition within the normal state [15].

**Quantum critical point.** Distinct transition anomalies are indeed observed at pressures less than $p_c \simeq 32$ kbar (Fig. 2a-c). Electric transport measurements for $p < p_c$ find a kink in $\rho(T)$ at low $T$, which causes a jump in the $T$-derivative of the resistivity $\rho'(T)$ (Fig. 2a-b). Heat capacity measurements under pressure likewise display a jump in $C(T)$ (Fig. 2c) at a transition temperature $T_N$ that is consistent with that of the kink in $\rho(T)$. Heat capacity data furthermore show evidence for a weaker, second transition at a lower temperature $T_{N2}$, which

![Figure 2](image-url)
merges with $T_N$ as pressure is increased. Both step-like heat capacity signatures suggest second-order transitions. High pressure muon spin rotation studies indicate two distinct magnetically ordered states associated with $T_N$ and $T_{xy}$ [11]. The detection of two magnetic transitions is reminiscent of the CeCu$_2$(Si/Ge)$_2$ system [22] and of YbRh$_2$Si$_2$ under pressure [19]. The magnetic transition signatures extrapolate to zero temperature at a magnetic quantum critical point near 32 kbar. The superconducting transition has likewise been tracked in high pressure transport measurements using two anvil cells and a susceptibility measurement in a third anvil cell (inset of Fig. 2e). Following the magnetic and superconducting transition signatures as functions of pressure results in the phase diagram (Fig. 2d), which shows a superconducting dome tightly confined to the immediate vicinity of a magnetic quantum critical point, indicating a prominent role for magnetic fluctuations in the superconducting pairing mechanism.

Normal and superconducting properties of CeSb$_2$ evolve rapidly with pressure (Fig. 2e-g). The low $T$ resistivity takes a quasi-linear $T$ dependence near $p_c$ (Fig. 2e), which saturates to a nearly constant resistivity (Fig. 2f) above a low $T^* \sim 10$ K. The low $T$ slope of $\rho(T)$, measured by the resistivity increment $\Delta \rho_{1K} = \rho(1K) - \rho_0$ over the extrapolated residual resistivity $\rho_0$ diminishes rapidly with increasing pressure. This is accompanied by a steep increase in $T^*$, demonstrating that compression under applied pressure strongly increases the effective electronic bandwidth in CeSb$_2$ (Fig. 2g).

**High pressure structure.** CeSb$_2$ forms in the orthorhombic SmSb$_2$ structure (space group $D_4h$), which lacks inversion symmetry around the Ce site but is centrosymmetric around the center of the unit cell. Transport measurements at intermediate pressures 6 kbar $< p < 17$ kbar show a highly hysteretic resistivity anomaly (e.g. 8 kbar data in Fig. 2f), which shifts to lower temperature with increasing pressure [9] and disappears beyond 17 kbar, where the low-$T$ state differs profoundly from the low-$T$ state at ambient pressure [10]. High pressure X-ray diffraction [11] has established that this anomaly signals a first-order structural phase transition, which at low $T$ is complete by about 17 kbar. The superconducting and magnetic states discussed above are therefore all associated with the high pressure structure of CeSb$_2$. The rare earth (R) diantimonides RSb$_2$ adopt a variety of structure types, all of which lack inversion symmetry around the rare earth site: SmSb$_2$ (like CeSb$_2$ at $p = 0$), HoSb$_2$ (orthorhombic, space-group 21), EuSb$_2$ (monoclinic, space-group 11) and YbSb$_2$ (orthorhombic, space-group 63). The X-ray data and $ab$ initio DFT calculations in [11] unambiguously rule out the SmSb$_2$ and HoSb$_2$ structures for high pressure CeSb$_2$ and favour the YbSb$_2$ structure (inset in Fig. 2d).

**Critical fields.** The locally non-centrosymmetric structure of high pressure CeSb$_2$ invites comparison to CeRh$_2$As$_2$ [1, 23–27] and other unconventional superconductors such as UTe$_2$, UGe$_2$ and UPt$_3$ (e.g. [28]) when considering the response to applied magnetic field. Both the form of the critical field curve $B_{c2}(T)$ in CeSb$_2$ and the magnitude of the upper critical field are unusual. We consider first the inverted ‘S’-shaped form for $B_{c2}(T)$ displayed in the inset of Fig. 1. The initial reduction, then increase of $T_c$ with field is most pronounced at the lowest pressure at which full resistive transitions could be observed (28.2 kbar, Fig. 3a). It is already weaker at 31.6 kbar (Fig. 1) and weaker still close to the qcp, at 32.2 kbar (Fig. 3b, e). Comparing $B_{c2}(T)$ at these last two pressures (Fig. 3e) shows that near the qcp, the critical field curves converge on a single line at high fields but differ at low fields. At pressures above $p_c$, the critical field curves gradually change into the conventional form (Fig. 3f). The relative reduction of $T_c$ at low fields $< 0.5$ T for $p < p_c$ could be seen as a signature of a field-induced transition between two distinct superconducting states, as in CeRh$_2$As$_2$ [1], or it might result from a field-induced magnetic transition. The step-like...
magnetoresistance anomaly at 28.2 kbar shown in Fig. 3d points towards the second scenario. The transition field of ≃ 0.5 T (vertical arrow) corresponds to the minimum \( T_c \) in the 28.2 kbar critical field curve in Fig. 3e (horizontal arrow). These findings suggest that the inverted ‘S’ shape of \( B_{c2}(T) \) on the ordered side of the qcp results from the interplay between applied field and the magnetic spin fluctuation spectrum: tuning the system out of the magnetically ordered state with increasing field enhances order parameter fluctuations and the associated pairing interaction, thereby strengthening superconductivity. A similar explanation has been advanced in pressured UGe\(_2\) [29].

Considering next the eight-fold enhancement of \( B_{c2} \) over the conventional Pauli limit \( B_{Pauli} = 1.84 \text{ T K}^{-1} T_c \) [21, 34] in CeSb\(_2\), we note that moderate violations of the Pauli limit are common in Ce-based heavy fermion materials such as CeCoIn\(_5\) and CeCu\(_2\)Si\(_2\) (Table I) without necessarily being taken as evidence for triplet pairing. The ratio of the high initial slope \( B'_{c2} \) over \( T_c \) in compressed CeSb\(_2\) indicates a very high Sommerfeld ratio \( C/T \sim 1.2 J/\text{molK}^2 \) (Table I) [15]. It is larger than the corresponding ratios in UPt\(_3\), CeIn\(_5\), CeCu\(_2\)Si\(_2\), and UBe\(_{13}\), suggesting that the quasiparticles underlying superconductivity in high pressure CeSb\(_2\) are among the heaviest ever recorded in a superconducting heavy fermion material. This is significant, because theoretical studies [35, 36] indicate that violations of Pauli limiting may generally be expected in superconductors with large mass renormalisation, irrespective of whether the pairing is mediated by phonons or spin-fluctuations and whether the pairing state has s-wave or d-wave symmetry [37]. The original calculation of the conventional Pauli limiting field [21, 34] balances the superconducting condensation energy against the magnetic energy involved in changing the spin alignment of the paired electrons in an applied field. The former depends on the energy gap, the latter on the spin susceptibility. Although some uncertainty in the latter arises from imprecise knowledge of the conduction electron g-factor, this would have to be << 1 to explain substantially enhanced Pauli limiting fields, which is difficult to justify: strong anisotropy of the g-factor is ruled out by the large \( B_{c2} \) observed for \( B \perp c \) [15]. In strong-coupling superconductors the balance between condensation energy and magnetic energy needs to be modified both on the side of the condensation energy, because the energy gap may be far larger than the BCS relation \( \Delta = 1.76k_BT_c \), suggests, and on the side of the magnetic energy, because the spin susceptibility is reduced below the Pauli susceptibility indicated by the quasiparticle density of states by as much as the interaction-induced mass enhancement. In model calculations, this causes the Pauli limit to be boosted to about 1.5T\( T_k \leftarrow 1.2J/\text{molK}^2 \), with \( m^* \) the renormalised quasiparticle mass and \( m_b \) the bare band mass [35]. In UBe\(_{13}\), the eight-fold enhancement of \( B_{c2} \) over the conventional Pauli limit (Table I) has been interpreted likewise [33] in terms of a strong-coupling calculation, and a similar boost to the limiting field was found in a calculation for spin-fluctuation induced d-wave pairing [37]. In this approach, resilience to high fields is achieved by gradually admixing a frequency-odd triplet pairing state into the underlying frequency-even singlet pairing state [38, 39] (see also [40, 41] for material-specific calculations). This general route contrasts starkly with the scenario advanced for CeRh\(_2\)As\(_2\) (e.g. [1]), which is predicated on its locally non-centrosymmetric structure. In heavy fermion materials such as CeSb\(_2\), a quantitative calculation is hindered by the similar magnitudes of the Zeeman energy at \( B_{c2} \) and electronic as well as bosonic energy scales, by the effect of the applied field on the pairing interaction, by the highly anomalous normal state, which deviates profoundly from expectations of Fermi liquid theory, and by our incomplete understanding of the origins of mass renormalization and pairing interaction, which do not align completely. The intriguing suggestion that increasing admixture of odd-frequency, triplet superconductivity can boost the critical field in strongly correlated materials should be tested in more detailed theoretical and computational investigations.

High-pressure CeSb\(_2\) emerges as a clean, ultra-heavy fermion system with superconductivity forming out of a pronounced non-Fermi liquid state and an upper critical field far beyond the Pauli limit. Because the qcp underlying the superconducting dome can in CeSb\(_2\) be crossed under pressure, this material supplies an excellent test case for refining our understanding of unconventional superconductivity. Our findings suggest that strong mass renormalization boosts the magnitude of \( B_{c2} \) without the need for a singlet-triplet phase transition as reported in CeRh\(_2\)As\(_2\), and that the interplay between applied field, magnetic order and the associated magnetic fluctuations can explain the evolution of \( B_{c2}(T) \) across the qcp.

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