Letter

Pressure dependence of superconductivity in $CeRh_2As_2$

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In the recently discovered heavy fermion superconductor $CeRh_2As_2$, a magnetic-field-induced phase transition has been observed inside the superconducting state, which is proposed to be a transition from an even- to an odd-parity superconducting state. The odd-parity superconducting state and its large upper critical field has been explained by local inversion symmetry breaking and consequent Rashba spin-orbit coupling. Here, we report the experimental tuning of the superconductivity in $CeRh_2As_2$ via applied pressure. Superconductivity is continuously suppressed up to 2.5 GPa. The kink in the upper critical field, which has been used to indicated the even- to odd-parity transition, is also suppressed, indicating the odd-parity state is suppressed faster than the even-parity state. Above 2.5 GPa, there might be a second dome of superconductivity, which requires further investigation.

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I. INTRODUCTION

The discovery of odd-parity superconductors with spin-triplet pairing is a central goal of quantum materials research, as they potentially host nontrivial topological excitations. Conventional wisdom has been to look for superconductivity in the vicinity of ferromagnetism. This route has led to the discovery of a collection of promising candidates, including the ferromagnetic superconductors UCoGe [1], URhGe [2], UGe_2 [3], and the nearly ferromagnetic superconductor UTe_2 [4]. Recently, an avenue has opened with the discovery of the heavy fermion superconductor $CeRh_2As_2$ with critical temperature T_c of 0.3 K, in which the odd-parity superconducting state is established by local inversion symmetry breaking and consequent Rashba-like spin-orbit coupling [5].

A striking feature of the superconducting state of $CeRh_2As_2$ is the very high upper critical field H_{c2} [5]. When a magnetic field is applied along the *c* axis, H_{c2} reaches $\sim$14 T at base temperature of 10 mK, far exceeding the Pauli limit of 0.6 T. Inside the superconducting state, a phase transition induced by applying a magnetic field along the *c* axis was observed, which has been interpreted as a transition from a low-field, even-parity to a high-field, odd-parity state. In addition, recent nuclear magnetic resonance (NMR) measurements on $CeRh_2As_2$ have suggested an antiferromagnetic order within the superconducting state in zero magnetic field [6,7] that disappears for magnetic field >4 T applied along the *c* axis.

Authors of theoretical studies have suggested that local inversion symmetry breaking plays an essential role in establishing the odd-parity superconducting state in $CeRh_2As_2$ [5,8]. The tetragonal $CaBe_2Ge_2$-type structure of $CeRh_2As_2$ is globally centrosymmetric but breaks inversion symmetry locally at the Ce site, enabling a Rashba spin-orbit coupling with an alternating sign on neighboring Ce layers. When a magnetic field is applied perpendicular to the Ce layers, the superconducting gap function on adjacent Ce layers related by inversion symmetry can have an opposite sign, leading to an odd-parity state. The $\vec{d}$ vector of the odd-parity state due to the Rashba spin-orbit coupling is in the plane, causing the absence of the Pauli paramagnetic limit for $H \parallel c$. The angle dependence of the upper critical fields agrees well with the theoretical model, further confirming the superconductivity in higher magnetic fields is indeed the odd-parity state [9].

This model originates from a theory developed in the context of layered superconductors with local inversion symmetry breaking that predicts a pair-density wave state [10–12]. In principle, it could apply to other quasi-two-dimensional superconductors with sublattice structure, However, the field-induced transition has not been widely observed. It turns out that the even- to odd-parity transition is also suppressed by hopping between the two sublattices. For this transition to occur, the spin-orbit coupling needs to be larger than the intersublattice hopping, and it is not intuitively clear whether this condition can be realized in a bulk material. As a matter of fact, a relatively strong Rashba-like spin texture has been observed in a bilayer cuprate superconductor, but there is no evidence of a field-induced odd-parity state [13]. To account for the observed transition in $CeRh_2As_2$, it has been proposed that, in addition to the local inversion symmetry breaking, the nonsymmorphic crystal structure allows the Rashba spin-orbit coupling to be larger than the interlayer hopping [8].

Applied pressure provides a possible route to experimentally tune the relative strength between the spin-orbit coupling and the interlayer hopping by changing the lattice constant. From a simple tight-binding point of view, interlayer hopping will increase as the lattice parameters decrease under pressure, while spin-orbit coupling will remain the same, leading to a continuous decrease of the relative strength between

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spin-orbit coupling and interlayer hopping. In this letter, we investigate the superconductivity of $CeRh_2As_2$ under applied pressure. Critical temperature of superconductivity, as well as the kink in the upper critical field, which has been used to indicate the even- to odd-parity transition, is continuously suppressed by pressure up to 2.5 GPa. Fitting to the upper critical field indicates that the odd-parity state is suppressed faster than the even-parity state. Above 2.5 GPa, T_c seems to abruptly increase, forming a second dome of superconductivity. This dome might be dominated by the odd-parity state. However, the pressure medium used in this letter also solidifies at room temperature in this pressure range, potentially causing issues with hydrostaticity. Further investigation is highly demanded to fully understand the superconductivity of $CeRh_2As_2$ in the high-pressure range.

II. METHODS

Single crystals of $CeRh_2As_2$ were grown using Bi flux following previous studies [5]. A nonmagnetic piston-cylinder pressure cell was used for electrical transport measurements under pressures up to 3.0 GPa, with Daphne oil 7373 as the pressure medium. Low-temperature resistance measurements were performed in a Bluefors dilution fridge down to 12 mK and up to 14 T. The current was applied along the *a* axis, and the magnetic field was applied along the *c* axis. Pressure produced on the single-crystal sample at low temperatures was calibrated by measuring the superconducting transition temperature of lead placed in the cell. The known pressure dependencies of the superconducting transition temperature of Pb [14,15] were used for this purpose.

III. RESULTS

Figure 1(a) shows the resistivity data as a function of temperature under various pressures up to 3.0 GPa. The superconducting transition is initially suppressed to lower temperatures upon increasing pressure and then sharply enhanced to higher temperatures after 2.5 GPa, leading to a nonmonotonic pressure dependence. The T_c-P phase diagram constructed from $\rho(T)$ data is presented in Fig. 1(d). Here, T_c is determined as the midpoint of the resistivity drop upon the transition, with the onset and offset of T_c setting the error bar. The most important feature of the T_c-P phase diagram is the double superconducting dome. The first dome has a maximum T_c at ambient pressure, and the second dome has a maximum T_c at ~2.7 GPa. Close to ambient pressure, T_c is suppressed at a very slow rate of −0.03 K/GPa. This is in sharp contrast to the estimation based on the Ehrenfest relation using thermal expansion and specific heat measurements, which yields a suppression rate of −0.21 K/GPa [16], an order of magnitude higher than our experimental results. Here, T_c reaches a minimum value of 0.12 K at 2.5 GPa, and we did not find a pressure <3 GPa where superconductivity is completely suppressed between the two domes. When the pressure is released from 3 to 2.5 GPa, T_c of 0.12 K is recovered [open data point on Fig. 1(d)]. Note that the pressure medium used in this letter, Daphne oil 7373, starts to solidify at room temperature at ~2.5 GPa. It is not clear whether the sudden jump of T_c in the same pressure range is caused by the solidification of the

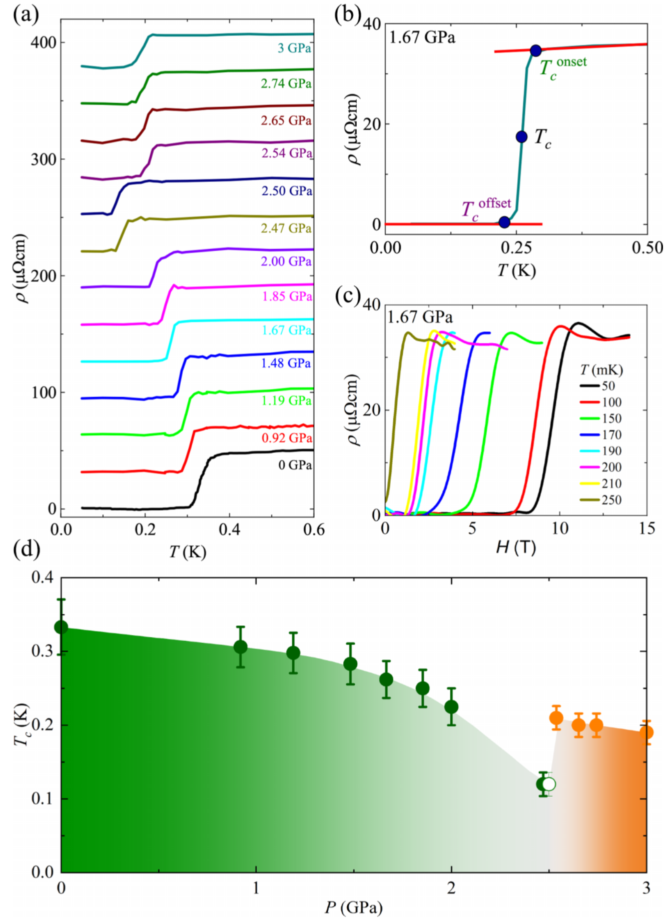

FIG. 1. (a) Resistivity ρ of $CeRh_2As_2$ as a function of temperature for different pressures. For clarity, the curves are shifted vertically by 33 μΩ cm. (b) $\rho(T)$ data at 1.67 GPa as an example to illustrate the criteria used to determine the T_c, which is taken as the midpoint of resistivity drop upon the transition. The deviation from the zero resistivity is taken as the offset of T_c, while the deviation from the normal state is taken as the onset of T_c. (c) Resistivity ρ of $CeRh_2As_2$ as a function of magnetic field for different temperatures between 50 and 250 mK at 1.67 GPa. (d) T_c-P phase diagram of $CeRh_2As_2$ showing a double superconducting dome. Open circle represents the data taken upon decreasing the pressure.

pressure medium. It will be beneficial to perform an additional pressure study of $CeRh_2As_2$ with a different pressure medium for comparison in the future.

Having established the T_c-P phase diagram, we now investigate the parity of the superconductivity inside the two domes. For this purpose, we measured resistivity as a function of magnetic field at various temperatures and extracted the upper critical field H_{c2} for each pressure as shown in Fig. 2. Here, $\rho(H)$ shows hysteresis going through the superconducting transition, and in Fig. 2, we use the data upon downsweep of magnetic field to extract H_{c2}-T for all the pressures for consistency. At ambient pressure, when the magnetic field is applied along the *c* axis, there is a transition from even- to odd-parity superconducting state, evidenced in ac magnetic susceptibility and specific heat measurements [5]. Resistivity does not show the transition, as it is always zero inside the superconducting state. However, H_{c2}-T shows a clear kink at

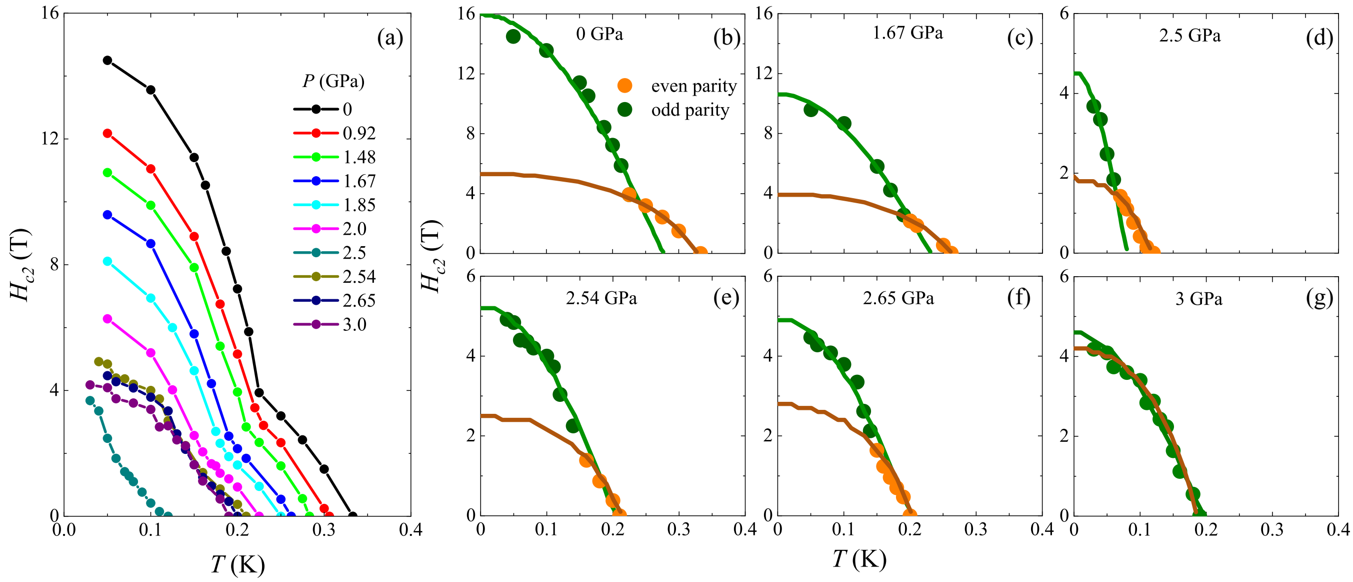

FIG. 2. (a) H_{c2} vs T for different pressures. (b)–(g) Fits to the upper critical fields for even-parity (orange line) and odd-parity (green line) states for 0, 1.67, 2.5, 2.54, 2.65, and 3 GPa.

H^* separating the even- and odd-parity states, which can be used to infer the even-to-odd state transition. Under pressure, the even-to-odd transition clearly manifests up to 2.5 GPa, and H^* is suppressed to lower magnetic fields. Above 2.5 GPa, the kink in H_{c2}-T is diminished, and a more detailed analysis is required to investigate whether there is still a transition from even- to odd-parity state.

To investigate the nature of the superconductivity in more detail, we fit the H_{c2}-T curve to the following expression that includes both Pauli paramagentic effect and orbital effect [5,9]:

$$\ln(t) = \int_0^\infty du \frac{\left[1 - F + F\cos\left(\frac{Hgu}{H_P t}\right)\right]\exp\left(\frac{-Hu^2}{\sqrt{2}H_{\rm orb}t^2}\right) - 1}{\sinh u}, \tag{1}$$

where $t = T/T_c$, H_P and $H_{\rm orb}$ are Pauli and orbital limits, and F quantifies the pair breaking due to the Pauli paramagnetic effect ($F = 1$ for even-parity state and $F = 0$ for odd-parity state). The representative H_{c2}-T curve and the fit for pressures below and above 2.5 GPa are shown in Fig. 2. In the low-pressure range, e.g., 1.67 GPa, the low-field part can fit well to the expression for the even-parity state, while the high-field part can fit well to the expression for odd-parity state, like the ambient pressure results. At 2.5 GPa where T_c is suppressed to a minimum value, we can still fit the low-field part to the even-parity state and the high-field part to the odd-parity state. Above 2.5 GPa, an interesting situation happens: while the low-field part can still fit to the expression for the even-parity state, the whole data range can also fit well to the expression for the odd-parity state. In other words, the low-field part of the data can fit to both even- and odd-parity states. As pressure increases, the range of data that can fit to both expressions increases. At 3 GPa, almost the entire data range can fit to both even- and odd-parity states.

Although we cannot exclusively tell the parity of the superconducting state at 3 GPa, the hysteresis of $\rho(H)$ might shed some light on it. As mentioned above, $\rho(H)$ shows hysteresis going through the superconducting transition. The representative data for below and above 2.5 GPa are shown in Fig. 3. Below 2.5 GPa, a clear hysteresis is seen but only in the odd-parity state. In the even-parity state, there is no obvious hysteresis. It is worth noting that the hysteresis loop is clockwise (higher critical field for downsweep), like that observed in previous torque measurements at ambient pressure [9]. At 3 GPa, hysteresis is observed in the entire temperature range, indicating the dominating odd-parity state. Moreover, the H_{c2}-T curve for upsweep of the magnetic field actually shows a clear kink, at rather low magnetic field, 0.2 T. Following the same analysis method, we can fit the data in the high-field range to the odd-parity state and the data in the low-field range to the even-parity state. The even-parity state has a very low upper critical field of 0.5 T. Analyzing both downsweep and upsweep, it is likely that the superconducting state is dominated by the odd-parity phase. The small portion of the even-parity state seen upon upsweep could even be due to the imhomogeneity of the pressure.

IV. DISCUSSION

Figure 4(a) summarizes the pressure dependence of the upper critical field of even- and odd-parity states from the fitting. The odd-parity state is suppressed faster than the even-parity state in the pressure range up to 2.5 GPa. Above 2.5 GPa, our results seem to indicate that odd-parity state eventually dominates. At ambient pressure, the odd-parity state is quickly suppressed when the magnetic field is turned away from the c axis [9]. This has been explained in terms of the in-plane $\vec{d}$ vector of the odd-parity superconductivity which leads to an absence of Pauli limiting for $H \parallel c$ and the presence of Pauli limiting for $H \parallel ab$. In this letter, the magnetic field is always applied along the c axis. The suppression of both even- and odd-parity states must be due to a different mechanism. Note that, in the context of layered superconductors with local inversion symmetry breaking, the amplitude of the odd-parity

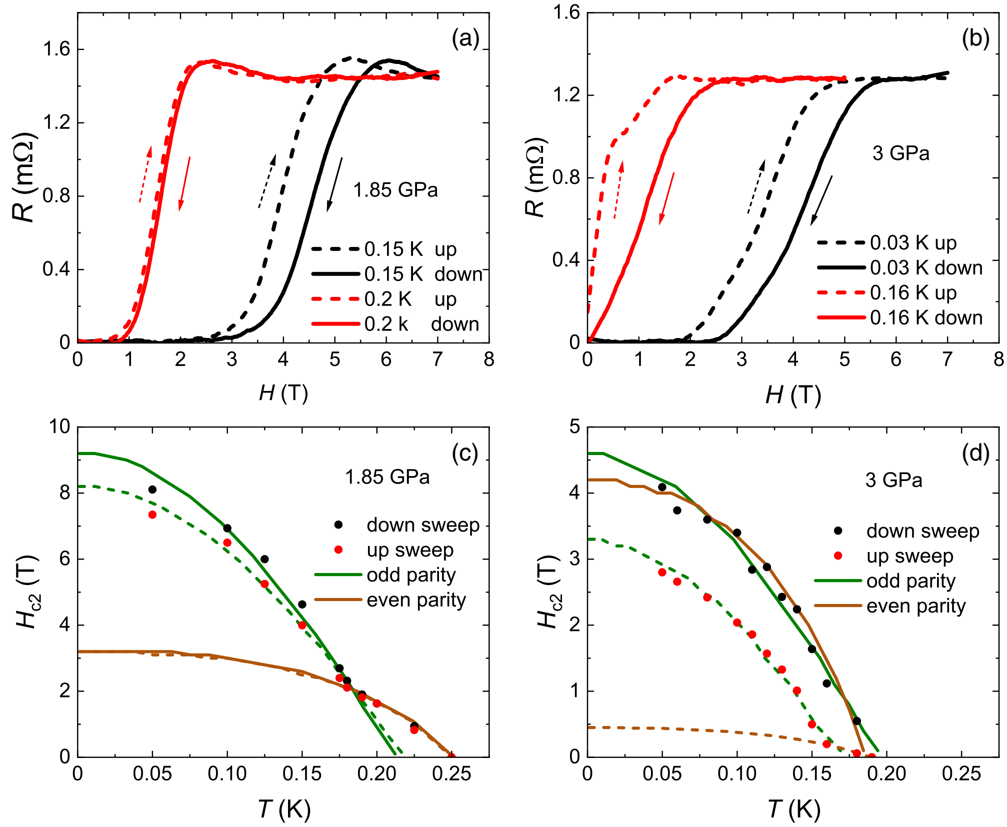

FIG. 3. Resistance $R(H)$ data at (a) 1.85 GPa and (b) 3 GPa as function of magnetic field at 0.15 and 0.2 K, for both upsweep (red line) and downsweep (black line) of magnetic field. Fits to the upper critical fields for even-parity (orange line) and odd-parity (green line) states for (c) 1.85 GPa and (d) 3 GPa.

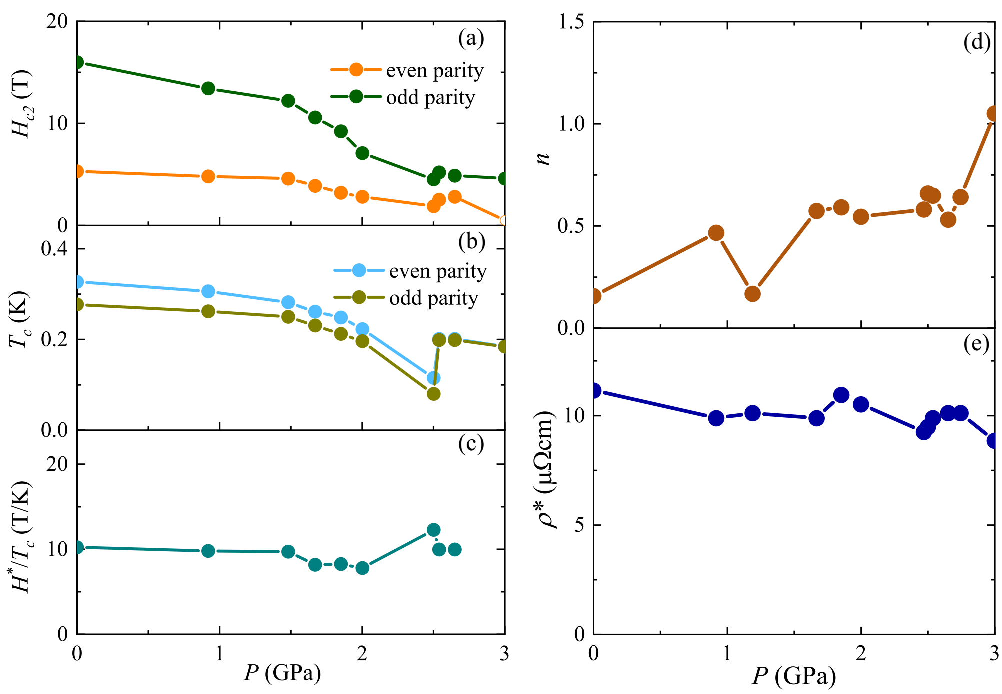

FIG. 4. (a) H_{c2} extracted from the fit as a function of P for even- and odd-parity superconducting state. (b) T_c as a function of P for even- and odd-parity superconducting state. T_c of the odd-parity state is extracted from the fit. (c) H^*/T_c as a function of P, where H^* is critical field for the even-to-odd transition and T_c is the critical temperature of the even-parity state. (d) Power-law exponent of the fit to the normal state as a function of P. (e) $\rho^* = \rho - \rho_0$ as a function of P showing no obvious decrease.

state is proportional to $\alpha_R/\sqrt{\alpha_R^2+t^2}$, where α_R is the strength of Rashba spin-orbit coupling and t is the strength of the interlayer hopping [8]. Clearly, the odd-parity state is enhanced by the spin-orbit coupling and suppressed by the interlayer hopping. Under applied pressure, the spin-orbit coupling will remain more or less the same, while interlayer hopping is expected to increase as the lattice constant decreases. Therefore, the even- to odd-parity transition is naturally expected to be suppressed by pressure, which seems to be consistent with our data <2.5 GPa.

We also investigated the evolution of the quantum fluctuations under pressure. The relation between the quantum fluctuations and the superconductivity in $CeRh_2As_2$ has not been extensively studied, even though $CeRh_2As_2$ is close to a quantum critical point at ambient pressure, as evidenced by the normal state non-Fermi-liquid behavior, i.e., $C/T \sim T^{0.6}$ and $\rho(T) \sim \sqrt{T}$. This quantum critical point is proposed to be associated with a quadrupole order [16]. Antiferromagnetic fluctuations have been observed from NMR measurements [7]. Theoretical calculations have shown that the critical field for the even-to-odd transition H^* is enhanced by antiferromagnetic fluctuations, and H^*/T_c stays nearly constant as $\widetilde{\alpha}$ varies [17]. Our results show that H^*/T_c slightly decreases under pressure, then increases at 2.5 GPa. This seems to indicate a change of the strength in the antiferromagnetic fluctuations, in addition to the suppression of $\widetilde{\alpha}$. What this does to the parity of the superconducting state is yet to be explored theoretically.

In addition to the spin fluctuations, under high pressure, valence fluctuations could develop in Ce-based compounds. A few other Ce-based superconductors also exhibit enhanced superconductivity under pressure [18–23], which is attributed to the valence fluctuations associated with the valence crossover [24,25]. A method has been developed based on resistivity measurements to investigate the valence crossover and has been applied to a wide range of Ce-based systems [19]. It shows that, when the system is tuned through the valence crossover by pressure, $\rho^* = \rho - \rho_0$ is strongly reduced by 1–2 order(s) of magnitude, which is attributed to a sudden delocalization of $4f$ electrons. We applied this analysis to $CeRh_2As_2$, as shown in Fig. 3. Here, ρ^* is pressure independent in the whole pressure range without a clear indication of sudden drop crossing 2.5 GPa. A valence crossover is still possible at higher pressure, which will be investigated in future experiments.

To summarize, we observed a continuous suppression of superconductivity in $CeRh_2As_2$ under pressure up to 2.5 GPa. The odd-parity is suppressed faster than the even-parity state, which could be consistent with the competition between the Rashba spin-orbit coupling and the interlayer hopping in determining the parity of superconducting states of systems with local symmetry breaking. At higher pressure, >2.5 GPa, there might be a second dome of superconductivity, where the odd-parity state seems to gradually dominate. Due to the solidification of the pressure medium at room temperature >2.5 GPa in this letter, superconductivity of $CeRh_2As_2$ at higher pressure requires future investigation (see Supplemental Material [26]).

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[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.108.L020504 for complete dataset of resistance as a function of magnetic field and resulting H_{c2} for all pressure values.