Pressure-Induced Heavy Fermion Superconductivity in the Nonmagnetic Quadrupolar System $PrTi_2Al_{20}$

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We report the discovery of a pressure-induced heavy fermion superconductivity in a nonmagnetic orbital ordering state in the cubic compound $PrTi_2Al_{20}$. In particular, we found that the transition temperature and the effective mass associated with the superconductivity are dramatically enhanced as the system approaches the putative quantum critical point of the orbital order. Our experiment indicates that the strong orbital fluctuations may provide a nonmagnetic glue for Cooper pairing.

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Unconventional superconductivity has been intensively studied in strongly correlated electron systems [1–5]. In particular, $4f$-electron based materials have provided archetypical examples of the heavy fermion superconductivity. In these systems, the quantum criticality arises by tuning the competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect that screens $4f$ moments through hybridization with conduction electrons. Without the disadvantage of introducing disorder, pressure is one of the cleanest tuning parameters. A number of pressure-induced heavy fermion superconductors have been found in the vicinity of a magnetic quantum critical point (QCP), providing strong evidence that critical magnetic fluctuations mediate Cooper pairing. Motivated by this, the search for superconductivity near a different form of instability such as orbital ordering has been vigorously made so far [6–10]. While the coupling between spin and orbital degrees of freedom is unavoidable in transition metal systems, f-electron systems may provide an ideal nonmagnetic state where orbitals are the only active degree of freedom.

One such nonmagnetic state can be found in the cubic $4f^2$ systems such as praseodymium (Pr) and uranium (U) based compounds when the crystal electric field (CEF) stabilizes the so-called Γ_3 doublet state with an electric quadrupole moment [11]. Here, because of strong intra-atomic spin-orbit coupling, the magnetic and orbital states are represented by the total angular moment $\boldsymbol{J}$. Thus, the orbital degree of freedom takes the form of the electric quadrupole moment (irreducible tensor operators of the total angular momentum $\boldsymbol{J}$), which may form a variety of electric ground states such as the uniform (ferroquadrupolar) and commensurate or incommensurate staggered (antiferroquadrupolar) order through indirect RKKY-type interaction [11,12]. Moreover, its hybridization with a conduction electron may also induce a nonmagnetic form of the Kondo effect that quenches the quadrupolar moment and leads to an anomalous metallic state [13–15].

Recent work on $\mathrm{Pr}Tr_2\mathrm{Al}_{20}$ (Tr = Ti, V), which crystallizes in a cubic structure (the space group $Fd\bar{3}m$; see the inset of Fig. 3), has demonstrated the interplay of the quadrupole order and Kondo effect through the strong hybridization between the Γ_3 ground doublet and conduction electrons [16–20]. $PrTi_2Al_{20}$ undergoes a ferroquadrupole transition at $T_Q = 2$ K. Furthermore, it exhibits superconductivity (SC) at $T_{SC} = 0.2$ K with the associated enhanced effective mass of the order of $10m_0$, which can be suppressed by the application of the magnetic field of $\sim$6 mT [18]. On the other hand, the high temperature properties are dominated by a low-lying Γ_4 triplet CEF excited state located at $\sim$65 K [16,19]. By contrast, PrV_2Al_{20}, which possesses a smaller unit cell volume than $PrTi_2Al_{20}$, exhibits anomalous behavior similar to what is predicted for the quadrupolar Kondo effect. In addition, PrV_2Al_{20} shows a weaker anomaly associated with quadrupole order at a lower $T_Q = 0.6$ K, most likely due to partial quenching of the quadrupole moment by the larger hybridization [16]. These suggest that further increase of the hybridization in these systems, which is experimentally possible by applying pressure or chemical substitution, may well provide the rare opportunity to approach a putative QCP of the quadrupole order [21]. Moreover, the proximity to the QCP may enhance the effective mass as well as the transition temperature T_{SC} of the superconductivity observed under ambient pressure. However, it is known that the multipole order is sensitive to the structural disorder [14,16], and, hence, we employed external pressure as a control parameter. Here we report the discovery of the heavy fermion superconductivity in $PrTi_2Al_{20}$ that reaches $\sim$1 K under highly hydrostatic conditions.

$PrTi_2Al_{20}$ single crystals were grown by the Al-flux method as described in the literature [16]. The phase purity was verified by powder x-ray diffraction measurements, and the residual resistivity ratio (RRR $\sim$ 76) reflects the high quality of the single crystals. High pressure experiments were performed by using a cubic anvil cell, which is known to generate hydrostatic pressure owing to the multiple-anvil geometry [22], with glycerol as a pressure transmitting medium. Pressure at low temperature was determined by the pressure dependence of the superconducting transition temperature of lead. Electrical resistivity was measured by a dc 4-probe method for an applied magnetic field along the [111] axis. ac magnetic susceptibility was measured at a fixed frequency of 307 Hz with a modulation field of 0.1 mT applied along the [111] axis. Specific heat measurements under pressure were performed by the ac calorimetry technique with an AuFe/Au thermocouple [23].

Figure 1(a) shows the temperature dependence of the magnetic part of the resistivity ρ_{mag} (defined in the figure caption) measured under various pressures. At high temperatures under ambient pressure, ρ_{mag} shows the $-\ln T$ dependence due to the magnetic Kondo effect using the excited magnetic CEF levels [16]. On cooling, as the nonmagnetic Γ_3 doublet state becomes predominantly populated, the resistivity decreases, forming a peak at $T_{\mathrm{max}} \sim 50$ K set by the CEF splitting (~ 65 K) between the ground doublet and the first magnetic excited state [16,19]. At lower temperatures, a clear resistive drop due

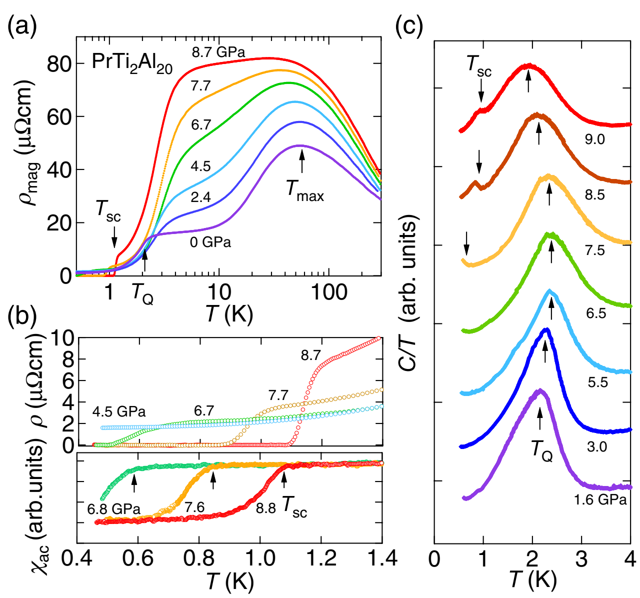

FIG. 1 (color online). (a) Magnetic part of the resistivity, ρ_{mag}, versus the logarithm of the temperature under various pressures. Here, ρ_{mag} is obtained by subtracting the resistivity of $\mathrm{LaTi_2Al_{20}}$ obtained under ambient pressure from that of $\mathrm{PrTi_2Al_{20}}$. (b) Temperature dependence of the resistivity and the ac magnetic susceptibility at low temperatures. A large diamagnetic signal due to the SC transition is observed at a lower temperature, which corresponds to nearly 60% superconducting shielding, estimated by comparing to the diamagnetic signal of lead with almost the same size as the sample of $\mathrm{PrTi_2Al_{20}}$. (c) Temperature dependence of the ac specific heat divided by temperature for different pressures. The curves are shifted vertically for clarity.

to the quadrupole ordering is observed at $T_Q = 2$ K at ambient pressure [16]. As pressure promotes hybridization, the overall resistivity including the maximum value at T_{max} increases in magnitude. On the other hand, T_{max} decreases with pressure, suggesting that pressure slightly reduces the CEF splitting. The ordering temperature T_Q can be traced as a sharp resistivity drop up to $P \sim 4.5$ GPa and shows a slight increase with pressure. Beyond this, the anomaly becomes significantly broadened accompanied by the unusual enhancement of the resistivity, probably originating from partial quenching of the quadrupole moment due to the strong hybridization between the Γ_3 and conduction electrons. Surprisingly, above 6.7 GPa, another anomaly was observed at lower temperatures: The resistivity shows an abrupt drop to zero at $\sim$0.7 K at 6.7 GPa, indicating the onset of superconductivity. With further increasing pressure, the resistivity drop due to the superconducting transition becomes sharper, and T_{SC} increases up to 1.1 K at $P = 8.7$ GPa. The observation of a large diamagnetic response in the ac magnetic susceptibility at almost the same temperature as the onset of the zero resistance state indicates that pressure-induced superconductivity is of bulk origin [Fig. 1(b)].

To further elucidate the interplay between the superconductivity and ferroquadrupole order, we measured the specific heat under pressure [Fig. 1(c)]. At 1.6 GPa, the specific heat divided by temperature C/T shows a peak due to the quadrupolar ordering at the same $T_{\mathrm{Q}} \sim 2$ K as in the ambient case. With increasing the pressure, T_Q monotonically goes up and the anomaly becomes sharper. Beyond $P = 5.5$ GPa, however, further increase of the pressure starts broadening and shifting the transition to a lower temperature and instead induces a well-defined subsequent anomaly on cooling associated with the superconducting transition. The superconducting anomaly appears at the temperature in full agreement with those found in the resistivity and ac magnetic susceptibility measurements, providing further evidence for the bulk superconductivity.

To determine the superconducting critical field B_{c2}, the temperature dependence of the resistivity was measured under various fields [Figs. 2(a) and 2(b)]. With increasing magnetic field, the superconducting transition broadens and moves to a lower temperature. Here B_{c2} is defined as the field values where the resistivity becomes zero. At 8.7 GPa with the highest $T_{\mathrm{SC}} = 1.1$ K, B_{c2} is estimated to be more than 3 T by extrapolating its temperature dependence. Besides, a linear fit to the data near T_{SC} provides the initial slope $B'_{c2} = dB_{c2}/dT \sim 6.0$ T/K, which is the highest value among Pr-based heavy fermion superconductors [6,18,24] and similar to the case found in the heavy fermion superconductors such as $\mathrm{CeCu_2Si_2}$ [25]. The zero temperature orbital critical field can be determined from the relation $B_{c2}(0) = -0.727\, B'_{c2} T_{\mathrm{SC}}$ [26,27], yielding $B_{c2}(0) \sim 4.7$ T. Furthermore, this value of $B_{c2}(0)$ allows us to estimate the Ginzburg-Landau coherence

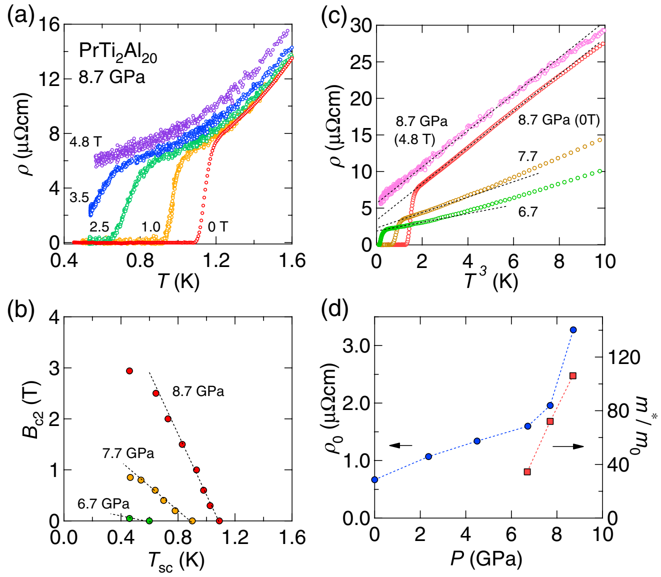

FIG. 2 (color online). (a) Temperature dependence of the electrical resistivity $\rho(T)$ of $PrTi_2Al_{20}$ at 8.7 GPa under various magnetic fields. (b) Superconducting phase diagram, i.e., the critical magnetic field B_{c2} as a function of temperature, derived from the zero resistivity temperature. (c) $\rho(T)$ versus T^3 at various pressures. (d) Pressure dependence of the residual resistivity ρ_0 and the effective mass m^* estimated by using the slope of the critical field curve, assuming a spherical Fermi surface.

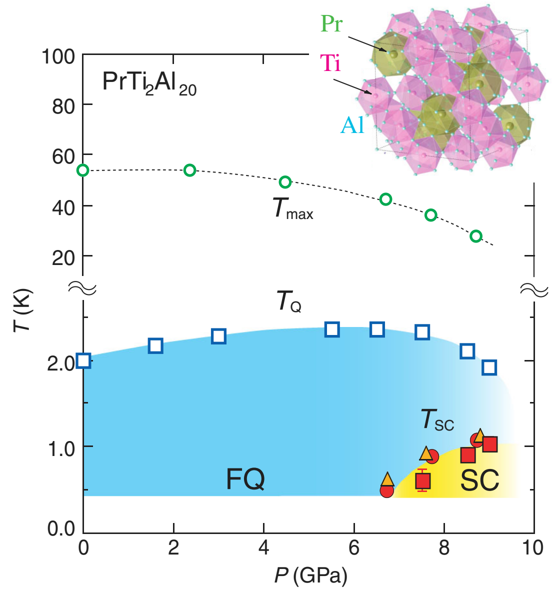

FIG. 3 (color online). Open circles and squares represent the position of T_{max} determined from the maximum in the temperature dependence of the resistivity and the ferroquadrupole ordering temperature T_Q, respectively. The SC transition temperatures T_{SC} are deduced from the temperature dependence of the resistivity (closed circles), the ac magnetic susceptibility (closed triangles), and the ac specific heat (closed squares), respectively. The inset shows the cubic crystal structure of $PrTi_2Al_{20}$. Cages made by $PrAl_{16}$ and $TiAl_{12}$ are indicated in green (larger cages) and purple (smaller cages), respectively.

length from the equation $B_{c2}(0) = \Phi_0/2\pi\xi_0^2$. This yields the small value of $\xi_0 \sim 84$ Å, and a large electronic effective mass $m^* \sim 106 m_0$, indicating heavy fermion character of the superconductivity.

Now we turn to the temperature dependence of the normal-state resistivity at 8.7 GPa. Unlike the typical temperature dependence appearing in the proximity to the magnetic QCP, neither standard Fermi-liquid ($\rho \propto T^2$) nor typical non-Fermi-liquid ($\rho \propto T^n$; $n < 2$) behaviors were observed, but the resistivity above T_{SC} is best fitted by a single power-law dependence $\rho_0 + AT^n$ with $n \sim 3.0$. Furthermore, the T^3 dependence survives under magnetic fields exceeding the upper critical field and extends to the lowest temperature measured [Fig. 2(c)]. This is in sharp contrast with the ambient pressure case where the resistivity shows an exponential decrease below T_Q, reflecting freezing of the quadrupole moment forming an anisotropic gap of the collective mode of the ferroquadrupole order [18]. Therefore, the T^3 dependence indicates the gapless nature of the excitations, most likely of quadrupole fluctuations. Indeed, although in a limited field region, the T^3 dependence was also observed in the Pr-based heavy fermion superconductor $PrOs_4Sb_{12}$ at the border of the field-induced quadrupole order [6]. Moreover, this asymptotic T^3 behavior becomes more prominent with pressure. As pressure starts suppressing the quadrupolar order above 6 GPa, it dominates over the entire temperature region below T_Q, suggesting that T^3 behavior comes from the critical fluctuations of the quadrupolar order. Compared to the $PrOs_4Sb_{12}$ case, the T^3 dependence in $PrTi_2Al_{20}$ is much more robust against a magnetic field up to at least 4.8 T, consistent with the nonmagnetic nature of the quadrupole moment. We obtained residual resistivity ρ_0 by assuming the power-law equation $\rho = \rho_0 + AT^3$ for different pressures and summarized the pressure variation of ρ_0 together with m^* [Fig. 2(d)]. The pressure evolution of ρ_0 and m^* upon suppression of T_Q indicates the emergence of heavy fermion superconductivity with a large electronic effective mass that comes from critical fluctuations associated with the ferroquadrupole order.

Pressure-induced evolution of ferroquadrupolar and superconducting phases of $PrTi_2Al_{20}$ is summarized in the temperature-pressure phase diagram (Fig. 3). After peaking at $P \sim 6$ GPa, the ferroquadrupole ordering temperature becomes suppressed with significant broadening, indicating the presence of the associated QCP. The most prominent feature is that ferroquadrupole order coexists with the pressure-induced heavy fermion superconductivity in a wide pressure region. The coexistence of quadrupole order and the superconductivity can be compared to that observed in $PrIr_2Zn_{20}$, which is isostructural to $PrTi_2Al_{20}$. $PrIr_2Zn_{20}$ exhibits an antiferroquadrupole ordering at $T_Q = 0.11$ K and undergoes a subsequent superconducting transition at $T_{SC} = 0.05$ K [24]. However, the small upper critical field $B_{c2} < 2$ mT implies that Cooper pairs are not formed by heavy quasiparticles [28]. While similar coexistence between the low temperature superconductivity and ferroquadrupole order is observed in $PrTi_2Al_{20}$ at ambient pressure [18], the high pressure superconducting state is qualitatively different, given 3 orders of magnitude enhancement in B_{c2} by approaching the putative ferroquadrupolar QCP.

It is interesting to note that the phase diagram of $PrTi_2Al_{20}$ closely resembles those of Ce-based heavy fermion superconductors. For instance, in $CeRhIn_5$ [3,29], the antiferromagnetic order of Ce ions shows the maximum and is rapidly suppressed under higher pressures where the superconducting state develops. A magnetic QCP of heavy fermion compounds arises as a result of competition between the RKKY and the magnetic Kondo interactions [1–4]. In analogy, it is suggested that RKKY-type quadrupole intersite interaction mediated by a conduction electron competes with the quadrupolar Kondo effect, which screens quadrupole moments of a nonmagnetic Γ_3 doublet state [11,13,14]. Here, it is important to note that T_{max} retains a large value ~30 K even at ~9 GPa, although it gradually decreases with pressure. This suggests that the CEF splitting remains 1 order of magnitude larger than both ferroquadrupole and superconducting transition temperatures and the excitation between the Γ_3 ground doublet and the Γ_4 low-lying excited state may be negligible. These further suggest that the pairing glue for the heavy fermion superconductivity found in $PrTi_2Al_{20}$ is the critical fluctuations of quadrupoles, which may possibly come from the competition between the quadrupolar order and Kondo effect.

Superconductivity mediated by orbital fluctuations has been discussed for a possible mechanism of the heavy fermion superconductivity in $PrOs_4Sb_{12}$ [6,7,30,31] and the high temperature superconductivity in the iron pnictides [9,10]. However, orbital fluctuations in these systems have strong coupling with magnetic excitations because of a low-lying magnetic CEF state in $PrOs_4Sb_{12}$ and iron moments exhibiting spin density wave order in pnictides. The observation of heavy fermion superconductivity accompanied by critical fluctuations of a purely nonmagnetic orbital degree of freedom is unprecedented. Therefore, the superconductivity in $PrTi_2Al_{20}$ will provide the direct test bench for further theoretical research of pairing mechanisms due to orbital fluctuations, providing useful information for the study of the superconductivity in other systems such as $PrOs_4Sb_{12}$ and the iron pnictides. Our results suggest a generic phase diagram hosting unconventional superconductivity on the border of orbital order, paving a new path for further research on novel quantum criticality and superconductivity due to orbital fluctuations.

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