Heavy-fermion superconductivity in Ce$_2$PdIn$_8$

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Abstract
The compound Ce$_2$PdIn$_8$ is a recently discovered novel member of the series Ce$_n$TIn$_{3n+2}$, where $T = d$-electron transition metal, and $n = 1$ or 2. So far, only the phases with $T = \text{Co}$, Rh and Ir have been intensively studied for their unconventional superconducting behaviors at low temperatures. By means of magnetic susceptibility, electrical resistivity and heat capacity measurements we provide evidence that also Ce$_2$PdIn$_8$ has a superconducting ground state with strong heavy-fermion character. The clean-limit superconductivity sets in at $T_c = 0.7$ K at ambient pressure, likely at a verge of a quantum phase transition that manifests itself in a form of distinct non-Fermi liquid features in the bulk normal state characteristics.

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1. Introduction

Since the discovery of pressure-induced superconductivity in the heavy-fermion antiferromagnet CeRhIn$_5$ [1], the series of compounds Ce$_n$TIn$_{3n+2}$ ($T = \text{Co, Rh and Ir}$) has became one of the most intensively studied strongly correlated electron system. The indides CeCoIn$_5$ and CeIrIn$_5$ have been characterized as ambient-pressure heavy-fermion superconductors ($T_c = 2.3$ and 0.4 K, respectively) with paramagnetic normal state properties [2, 3]. Moreover, in CeCoIn$_5$ a Fulde-Ferrell-Larkin-Ovchinnikov phase has been observed in strong magnetic fields, in which the electrons form Cooper pairs with nonzero total momentum [4]. In turn, in CeRhIn$_5$ the heavy-fermion superconductivity emerges out of an antiferromagnetic state ($T_N = 3.8$ K at ambient pressure) upon application of hydrostatic pressure ($T_c = 2$ K at $p = 1.6$ GPa) [5]. Similar properties have been found for the structurally closely related phases Ce$_2$TIn$_8$ with $T = \text{Co, Rh and Ir}$. Both Ce$_2$CoIn$_5$ and Ce$_2$RhIn$_5$ are heavy-fermion superconductors. In the former indide, the ambient-pressure superconductivity emerges at $T_c = 0.4$ K out of the paramagnetic normal state [6], while in Ce$_2$RhIn$_8$ an antiferromagnetic ordering below $T_N = 2.8$ K occurs at ambient pressure, and the superconducting properties set in under applied pressure that suppresses the magnetism and yields $T_c = 2$ K at $p = 2.3$ GPa [6]. Ce$_2$IrIn$_8$, as the only material from the series, does not exhibit any cooperative phase transition and remains a heavy-fermion paramagnet down to 50 mK [7].

Very recently, we reported for the first time on the formation and the main physical properties of a novel representative of the Ce$_2$TIn$_8$ family with $T = \text{Pd}$ [8, 9]. Single crystals of Ce$_2$PdIn$_8$ have been found to exhibit heavy-fermion clean-limit superconductivity below $T_c = 0.68$ K. In contrast, the compound studied in polycrystalline form has not revealed any phase transition at low temperatures, and has been characterized as a paramagnetic heavy-fermion system with a non-Fermi liquid character of its electronic ground state.

In this paper, we communicate on the superconductivity in high quality polycrystals of Ce$_2$PdIn$_8$. Based on the results of electrical resistivity and specific heat measurements performed down to 350 mK, we provide evidence for the heavy-fermion superconducting state below $T_c = 0.7$ K that emerges likely due to proximity of the system to an antiferromagnetic quantum critical instability.
2. Experimental details

Polycrystalline sample of Ce$_2$PdIn$_8$ was synthesized by arc melting the stoichiometric amounts of the elemental components (Ce - 3N, Ames Laboratory, Pd - 3N, Chempur and In - 6N, Chempur) in a copper-hearth furnace installed inside a glove-box filled with ultra-pure argon gas with continuously controlled partial pressures of O$_2$ and H$_2$O to be lower than 1 ppm. The button was flipped over and remelted several times to ensure good homogeneity. The weight losses after the final melting were negligible (less than 0.2%). Subsequently, the sample was wrapped with tantalum foil, sealed an evacuated quartz tube and annealed at 700 °C for 5 weeks.

Quality of the obtained alloy was checked by x-ray powder diffraction using an X’pert Pro PanAnalytical diffractometer with CuK$_α$ radiation and by energy dispersive x-ray (EDX) analysis employing a Phillips 515 scanning electron microscope equipped with an EDAX PV 9800 spectrometer. Both techniques proved single-phase character of the sample, with the proper stoichiometry and the primitive tetragonal crystal structure of the Ho$_2$CoGa$_4$-type (space group $P4/mmm$). The structural refinement done using the program FULLPROF yielded the lattice parameters and the positional parameters very close to those reported in Ref. 8.

Magnetic measurements were carried out in the temperature range 1.71 - 400 K and in applied magnetic fields up to 5 T using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The heat capacity and the electrical resistivity were measured by the relaxation method and the ac technique, respectively, over the temperature interval 350 mK - 300 K and in fields up to 9 T employing a Quantum Design PPMS platform.

3. Results and discussion

All the main results of the present experimental study of polycrystalline Ce$_2$PdIn$_8$ are summarized in the tree panels of Fig. 1. Apparently, the compound is a well localized magnetic system with no long-range magnetic order down to the lowest temperatures studied. Above 70 K, the magnetic susceptibility (see Fig. 1a) obeys the Curie-Weiss law with a large negative paramagnetic Curie temperature $θ_p = -41.8$ K and the effective magnetic moment $μ_{eff} = 2.41$ $μ_B$ being close to that expected for trivalent Ce ions. At lower temperatures, an upward deviation of the inverse magnetic susceptibility from the Curie-Weiss law is seen, which likely manifests crystalline electric field (CEF) interactions. Below ca. 6 K, the magnetic susceptibility shows an additional distinct upturn (see the inset to Fig. 1a), which may hint at the presence of some critical spin fluctuations. The magnetization taken at 1.71 K is a linear function of magnetic field without any hysteresis effect (not shown here), as expected for paramagnetic state. In general, the new magnetic data of Ce$_2$PdIn$_8$ are nearly identical to those reported before for the polycrystalline sample [2].

As may be inferred from Fig. 1b, nearly the entire temperature dependence of the electrical resistivity of Ce$_2$PdIn$_8$ is mainly governed by the Kondo effect (note the solid curve). Above 50 K, the $ρ(T)$ variation can be approximated by the formula $ρ(T) = (ρ_0 + ρ_0^c) + ε_{ph} T + c_k ln T$, in which the first term accounts for the conduction electrons scattering on static defects and disordered spins, the second term represents the phonon contribution, whereas the third one results from the spin-flip Kondo scattering. From the least-squares fitting one derives the parameters: $ρ_0 + ρ_0^c = 127.5$ $μΩcm$, $ε_{ph} = 0.11$ $μΩcm/K$ and $c_k = -18.6$ $μΩcm$. These values are almost identical to those derived previously [8]. The broad maximum in $ρ(T)$, seen around 30 K, can likely be associated with a transition from incoherent to coherent Kondo regime. This crossover maximum occurs at slightly higher temperature than that found for the polycrystal reported in Ref. [2], which is in line with higher metallurgical quality of the new sample (cf. the Summary). In the coherent state, the resistivity rapidly decreases with decreasing temperature down to $T_c = 0.7$ K, at which point an onset of the superconducting state is observed with a sharp resistivity drop to zero value. Remarkably, above $T_c$ the resistivity changes with temperature according to the formula $ρ(T) = ρ_0 + aT^n$ with $ρ_0 = 6.4$ $μΩcm$, $a = 4.1$ $μΩcm/K$ and $n = 1$ (note the dashed line in Fig. 1b). It is worthwhile emphasizing that this linear dependence of $ρ(T)$ is observed up to 9 K, i.e. over more than a decade in the temperature. Such a distinct non-Fermi-liquid (NFL) character of the resistivity is usually considered as a hallmark of quantum critical spin fluctuations in two-dimensional systems with inherent antiferromagnetic correlations [11].

The superconducting transition at $T_c = 0.7$
K manifests itself as a sharp peak in the low-temperature specific heat of Ce$_2$PdIn$_8$ (see Fig. 2c). At higher temperatures, $C(T)$ can be analyzed in terms of a sum of the electronic, Schottky and phonon contributions, $C(T) = C_e + C_{Sh} + C_{ph}$, where $C_e$ has the NFL form $C_e(T) = aT \ln(T_0/T)$, $C_{Sh}$ is written for a system of three Kramers doublets and $C_{ph}$ is represented by the Debye model. As shown in Fig. 2c, adopting the values derived in Ref. [8] for the critical spin-fluctuation temperature ($T_0 = 38$ K) and for the energies of the excited crystal field levels ($\Delta_1 = 60$ K and $\Delta_2 = 198$ K), and also taking the Debye temperature $\Theta_D = 193$ K, i.e. very close to that estimated in Ref. [8] ($\Theta_D = 184$ K), one may reasonably well describe the experimental $C/T$ data nearly in the entire temperature range above $T_c$.

The magnetic entropy, calculated from the excess specific heat due to the cerium 4f electrons (not shown here), reaches a value of $R \ln 2$ per Ce atom (expected for a doubly degenerated ground state) not below 20 K. This distinct entropy reduction presumably results from Kondo screening interactions. The Bethe Ansatz approach (for effective spin $s = 1/2$) yields the Kondo temperature of about 10 K, in perfect agreement with the value $T_K \approx [\theta_p/4] \approx 10$ K, estimated from the magnetic susceptibility data shown. The very same value of $T_K$ was derived for Ce$_2$PdIn$_8$ in the previous studies [9].

The low-temperature resistivity and the specific heat data of Ce$_2$PdIn$_8$ are shown in Figs. 2a and 2b, respectively. Upon applying magnetic field the superconducting transition, defined as a midpoint in $\rho(T)$ and as an inflexion point above the peak in $C(T)$, shifts to lower temperatures and gets suppressed below 0.35 K (the terminal temperature in this study) in a field of 2 T. In strong magnetic fields the $C/T$ ratio shows a tendency to saturate at a strongly enhanced value $\gamma_n$ of 1220 mJ/(mol K$^2$), thus proving heavy Fermi liquid character of the compound studied. In zero field, the specific heat jump at $T_c = 0.7$ K amounts to about 1.5 J/(mol K$^2$), and hence the ratio $\Delta C/\gamma_n T_c$ is about 1.74, which is larger than a value of 1.43 predicted by the BCS theory.

The temperature dependence of the upper critical field $\mu_0 H_{c2}$ is shown in Fig. 2c. The initial slope $d\mu_0 H_{c2}/dT$ attains as large value as -13.5 T/K, and extrapolation to zero temperature yields $\mu_0 H_{c2}(0) = 2.5$ T. These parameters, especially $\mu_0 H_{c2}(0)$, are somewhat lower than those reported for single-crystalline Ce$_2$PdIn$_8$, derived for the magnetic field applied along the c-axis [3]. Nevertheless, their magnitudes clearly corroborate the heavy fermion character of the superconducting state. In the framework of the model developed by Orlando et al. (Ref. [12]), one may calculate the the effective mass $m^* \approx 193 m_e$, the electronic mean free path of the quasiparticles $l \approx 27$ nm and the BCS coherence length $\xi_0 \approx 4.9$ nm. The so-derived relation $l \gg \xi_0$ clearly indicates that Ce$_2$PdIn$_8$ exhibits clean limit superconductivity. Furthermore, from the formulas given in Ref. [13], one may also determine the Ginzburg–Landau coherence length $\xi_{GL}$ and the penetration depth $\lambda_{GL}$ to be equal to 11.5 and 422 nm, respectively. Hence, the Ginzburg-Landau parameter $\kappa_{GL}$ is estimated to be about 37, well within the range for type II superconductivity. In general, all these key characteristics of the superconducting state in polycrystalline Ce$_2$PdIn$_8$ are similar to those calculated for the single crystals (compare Table I in Ref. [9]). Some differences in the two sets of the superconducting parameters should likely be attributed to anisotropy in the electrical transport behavior, inherent to the tetragonal crystal structure of the compound studied.

4. Summary

The experimental data obtained in this work undoubtedly demonstrate that high-quality polycrystals of Ce$_2$PdIn$_8$ exhibit at low temperatures the heavy-fermion superconductivity, which emerges out of the paramagnetic normal state with distinct non-Fermi liquid character. This finding contrasts with the previous report on the properties of polycrystalline Ce$_2$PdIn$_8$ that has been characterized as a paramagnet down to 0.35 mK. The lack of superconductivity in the previously studied polycrystals can be rationalized by their poorer metallurgical quality in comparison to the sample investigated in the present work. Extreme sensibility of the superconducting properties to internal strains, structural disorder and non-stoichiometry is a well known characteristic feature of unconventional coupling of Cooper pairs (it is enough to recall here the case of CeCu$_2$Si$_2$ [14]). The new polycrystalline sample of Ce$_2$PdIn$_8$ was synthesized using higher-purity cerium (3N instead of 99.8 wt.%) in precisely controlled argon atmosphere (arc-furnace installed in an glove-box) and then annealed at higher temperature (700 °C viz. 600 °C applied before) and for longer time (five instead of four weeks). This
procedure yielded the electrical resistivity of ca. 10 \(\mu\Omega\text{cm}\) just above the onset of superconductivity in the new specimen, as compared to the residual resistivity of about 40 \(\mu\Omega\text{cm}\), reported in Ref. [8].

The superconducting temperature measured for the present polycrystalline sample of Ce\(_2\)PdIn\(_8\) is equal to that reported in Ref. [9] for the single crystal. Also the other main characteristics of the superconducting state are similar in both crystalline forms of the compound. Thus, the new experimental data definitely corroborate all our previous statements on the heavy-fermion superconductivity in Ce\(_2\)PdIn\(_8\). On the other hand, the present work does not support our arguments for the antiferromagnetic ordering above \(T_c\). In contrast to the behavior of the single-crystalline sample studied in Ref. [8], the polycrystals of Ce\(_2\)PdIn\(_8\) are paramagnetic in the entire normal state. This apparent contradiction has recently been solved by Uhlirova et al. [15], who demonstrated that the antiferromagnetism observed in as-grown single crystals of Ce\(_2\)PdIn\(_8\) is always due to small admixture of the impurity phase CeIn\(_3\). Our own on-going studies seem confirm the presence of a thin layer of the latter compound, sandwiched in between single-crystalline slabs of the parent indide. Full account on the metallurgical problems encountered in growing single crystals of Ce\(_2\)PdIn\(_8\) will be given in our forthcoming paper.

To conclude, Ce\(_2\)PdIn\(_8\) is a novel heavy-fermion superconductor with \(T_c = 0.7\ \text{K}\) at ambient pressure. Its main superconducting parameters are fairly similar to those reported for the closely related compounds CeCoIn\(_5\), CeIrIn\(_5\) and Ce\(_2\)CoIn\(_8\) [2, 3, 5]. The non-Fermi liquid character of the normal state hints at the presence of critical spin fluctuations of antiferromagnetic type. It seems very likely that the superconductivity in Ce\(_2\)PdIn\(_8\) emerges at the verge of underlying quantum critical point instability, similarly to the case of the CeTIn\(_5\) and Ce\(_2\)TIn\(_8\) relatives.

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Figure 1: (a) Temperature dependence of the inverse magnetic susceptibility of Ce$_2$PdIn$_8$ measured in a magnetic field of 0.5 T. The solid line represents the Curie-Weiss fit. The inset shows the magnetic susceptibility at low temperatures. (b) Temperature variation of the electrical resistivity of Ce$_2$PdIn$_8$. The solid line stands for the fits discussed in the text. (c) Temperature dependence of the specific heat over temperature ratio of Ce$_2$PdIn$_8$. The lines represent the specific heat contributions discussed in the text.

Figure 2: Temperature dependencies of (a) the electrical resistivity (taken with the current $j = 0.1$ mA) and (b) the specific heat over temperature ratio of Ce$_2$PdIn$_8$, measured in various magnetic fields. (c) Temperature variation of the upper critical field in Ce$_2$PdIn$_8$, determined from the data presented in panels (a) and (b).