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Broken Time-Reversal Symmetry in Superconducting Partially Filled Skutterudite $Pr_{1-\delta}Pt_4Ge_{12}$ *

Jia-Wei Zang(臧佳伟)[1], Jian Zhang(张建)[1,2], Zi-Hao Zhu(朱子浩)[1], Zhao-Feng Ding(丁兆峰)[1], Kevin Huang[1], Xiao-Ran Peng(彭小冉)[1], Adrian D. Hillier[3], Lei Shu(殳蕾)[1,4]**

[1]*State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433*
[2]*Geballe Laboratory for Advanced Materials, Stanford University, Stanford, CA 94305, USA*
[3]*ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Chilton, Didcot, Oxon OX11 0QX, United Kingdom*
[4]*Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093*

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Time reversal symmetry (TRS) is a key symmetry for classification of unconventional superconductors, and the violation of TRS often results in a wealth of novel properties. Here we report the synthesis and superconducting properties of the partially filled skutterudite $Pr_{1-\delta}Pt_4Ge_{12}$. The results from x-ray diffraction and magnetization measurements show that the $[Pt_4Ge_{12}]$ cage-forming structure survives and bulk superconductivity is preserved below the superconducting transition temperature $T_c = 7.80$ K. The temperature dependence of both the upper critical field and the electronic specific heat can be described in terms of a two-gap model, providing strong evidence of multi-band superconductivity. TRS breaking is observed using zero field muon-spin relaxation experiments, and the magnitude of the spontaneous field is nearly half of that in $PrPt_4Ge_{12}$.

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One of the key challenges in the study of unconventional superconductivity is to discover more materials with extra broken symmetries in addition to gauge symmetry breaking.[1] Broken time reversal symmetry (TRS) often leads to novel properties in superconductors and the possible existence of multiple superconducting phases.[2] For example, the existence of a second superconducting phase was found in the TRS breaking superconductors UPt_3 and $U_{1-x}Th_xBe_{13}$.[3–5] The filled skutterudite compounds RT_4X_{12} (R=rare-earth or alkaline-earth metals, T=Fe, Ru, Os, and X=P, As, Sb),[6] including the first discovered Pr-based heavy fermion superconductor $PrOs_4Sb_{12}$ and the iso-structural $PrPt_4Ge_{12}$,[7,8] provide a remarkable playground for studying broken TRS superconductivity. Moreover, the $4f$ electron-filled skutterudite family displays an astonishing diversity of physical properties, including unconventional superconductivity, quadrupolar ordering, heavy fermion, and non-Fermi liquid behaviors.[9–11]

$PrPt_4Ge_{12}$ has a much higher superconducting transition temperature (T_c = 7.9 K) than $PrOs_4Sb_{12}$ (T_c = 1.8 K),[9] but shows no heavy-fermion behavior.[8] Specific-heat and transverse filled muon-spin relaxation (μSR) experiments suggested strongly coupled unconventional superconductivity with point-like nodes in the energy gap.[12] A spontaneous static local magnetic field B_s below $T_m \simeq 6.8$ K ($T_m < T_c$) was observed by performing a zero-field μSR experiment, signaling a TRS breaking superconducting state.[8] Remarkably, due to the observation of the point-like nodes and broken TRS, $PrOs_4Sb_{12}$ and $PrPt_4Ge_{12}$ were proposed to be the candidates to host 3D gapless Majorana fermions.[13] However, a ^{73}Ge-NQR study revealed that $PrPt_4Ge_{12}$ is a weakly coupled BCS superconductor,[14] while analysis on the critical fields[15] and photoemission spectroscopy[16] provided evidence of multi-band superconductivity. Thus the superconducting gap structure in $PrPt_4Ge_{12}$ remains controversial. The behavior that TRS breaks at temperature T_m, which is below T_c, is also puzzling. It is crucial to shed new light on the superconducting order parameter of $PrPt_4Ge_{12}$ and clarify the origin of the broken TRS state.

It is confirmed that in ternary skutterudite compounds the polyanionic $[T_4X_{12}]$ host structure remains stable despite marked deviations from the required 72 electrons count per formula unit, providing a great deal of freedom to explore skutterudite structures composed with partially filled host elements.[17,18] Following this idea, we report a study of an imperfectly filled skutterudite $Pr_{1-\delta}Pt_4Ge_{12}$ to investigate (i) whether the cage-forming structure and superconductivity survive with partially filled ^{141}Pr nuclei, (ii) the effect of the insufficiently filled ^{141}Pr nuclei on TRS breaking in $PrPt_4Ge_{12}$, and (iii) the gap symmetry of $Pr_{1-\delta}Pt_4Ge_{12}$ and implications of the superconducting order parameter of $PrPt_4Ge_{12}$.

Polycrystalline samples of $Pr_{1-\delta}Pt_4Ge_{12}$ were synthesized by mixing Pr ingots (Alfa Aesar 99.9%), Pt sponge (99.9999%), and Ge pieces (Alfa Aesar 99.9999%) with the ratio of y:4:12 (y = 0.5, 0.6,

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**Corresponding author. Email: leishu@fudan.edu.cn

0.7, 0.8, and 1).[19] The samples were annealed at 800℃ for 14 days in a sealed quartz tube (containing 200 Torr Ar at room temperature). XRD measurements were performed by a Bruker D8 x-ray diffractometer using a Cu K_α source. Rietveld refinements were conducted on powder XRD patterns using GSAS and EXPGUI.[20,21] Magnetization measurements were performed by a Quantum Design superconducting quantum interference device. Heat capacity measurements were performed on a Quantum Design physical properties measurement system, which employs a standard thermal relaxation technique. ZF-μSR experiments were carried out at the ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, Chilton, UK.

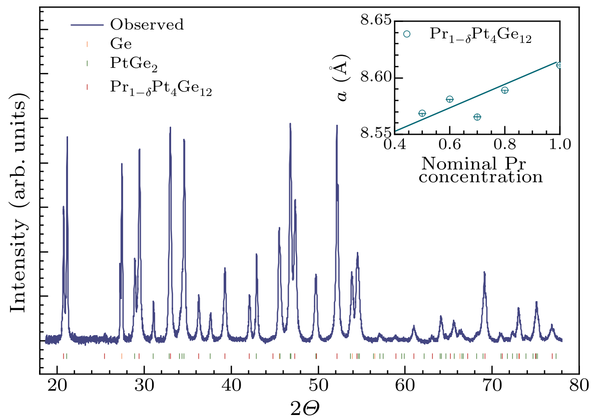

Fig. 1. A representative powder XRD pattern of the grown polycrystalline sample. Orange, green and red tick marks below the pattern indicate the positions of expected Bragg peaks for the refined ordered crystal structures of Ge, $PtGe_2$, and $Pr_{1-\delta}Pt_4Ge_{12}$, respectively. Inset: the lattice parameter a of $Pr_{1-\delta}Pt_4Ge_{12}$ derived from the fitting of the $PrPt_4Ge_{12}$ structure. The abscissa is the nominal Pr concentration.

XRD phase analysis for the obtained powder patterns reveals the presence of three phases in the samples: $Pr_{1-\delta}Pt_4Ge_{12}$, Ge and $PtGe_2$. A representative XRD pattern (for the nominal Pr concentration $y = 0.5$ sample) is displayed in Fig. 1, with the weight ratios of $Pr_{1-\delta}Pt_4Ge_{12}$, Ge and $PtGe_2$ equalling to 37.0%, 24.3%, and 38.7%, respectively. The patterns and their refinement with the three phases agree well with each other for all the samples (fits not shown). The inset of Fig. 1 indicates that the lattice parameter a derived from the fitting of the $PrPt_4Ge_{12}$ structure has a roughly linear relation with the nominal Pr concentration y, strongly suggesting that the ^{141}Pr nuclei are partially filled in $[Pt_4Ge_{12}]$ cage. Since Ge and $PtGe_2$ are nonmagnetic and nonsuperconducting,[22] they have a slight influence on the study of superconducting transition and the analysis of ZF-μSR experiments. The $y = 0.5$ sample most likely has the lowest Pr filling fraction, so we choose this sample to study the effect of the insufficiently filled ^{141}Pr nuclei on superconductivity and TRS breaking in the following experiments.

The magnetization measurement indicates that the dc-susceptibility displays a strong diamagnetic signal due to the superconducting transition provided by $Pr_{1-\delta}Pt_4Ge_{12}$ in the sample at $T_c = 7.80$ K, where zero-field-cooled (ZFC) and field-cooled (FC) data deviate from each other, as shown in Fig. 2(a). The value of T_c=7.80 K derived from the midpoint of the transition at zero field, corresponding well to the result from the magnetization measurements, is nearly the same as that of $PrPt_4Ge_{12}$. The temperature dependence of the specific heat coefficients C_p/T of the sample measured at different magnetic fields are displayed in Fig. 2(b), showing the suppression of T_c by magnetic fields.

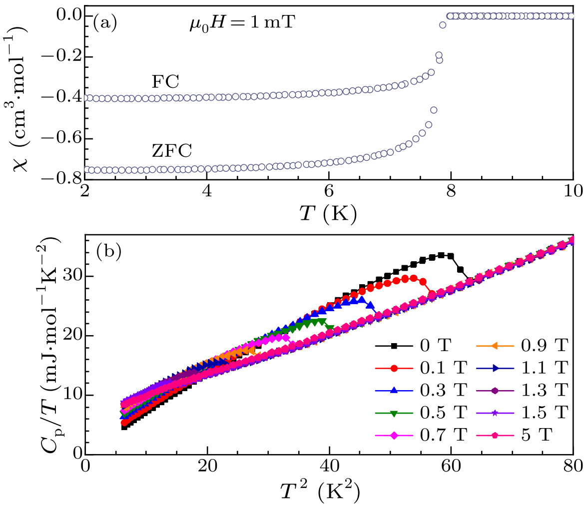

Fig. 2. Magnetic susceptibility and specific heat data of the partially filled skutterudite $Pr_{1-\delta}Pt_4Ge_{12}$. The molar mass was calculated using the mass ratio of $Pr_{1-\delta}Pt_4Ge_{12}$, Ge and $PtGe_2$. (a) Magnetic susceptibility was measured in an applied field of $\mu_0 H = 1$ mT. FC and ZFC stand for the field-cooled and zero-field-cooled measurements, respectively. (b) Specific heat data of the sample displayed as C_p/T versus T^2 in different magnetic fields.

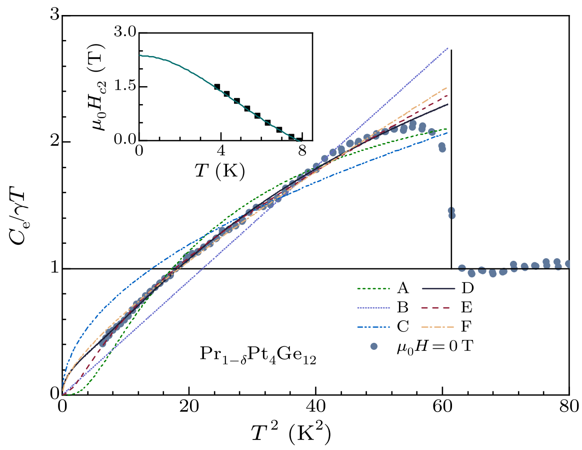

Fig. 3. Temperature dependence of the electronic specific heat coefficient of $Pr_{1-\delta}Pt_4Ge_{12}$ at zero field. The curves represent the fits using six different gap models listed in Table 1. Inset: the critical fields H_{c2} derived from the midpoints of the jump in C_p/T. The green curve is the fit of Eq. (2) to the data.

The normal-state C_p of the sample is well described by the expression $C_\mathrm{p} = \gamma T + \beta T^3$, where the first and second terms correspond to the electronic and phononic contributions, respectively. The fit in the range of 2.5–10 K gives the value of coefficients: $\gamma = 3.35\,\mathrm{mJ{\cdot}mol^{-1}{\cdot}K^{-2}}$ and β=0.28 $\mathrm{mJ{\cdot}mol^{-1}{\cdot}K^{-4}}$.

Table 1. Fitting models.

	Model	f	$\Delta/k_\mathrm{B}T_\mathrm{c}$	Correlation coefficient	$\Delta_{C_\mathrm{p}}/\gamma T_\mathrm{c}$
A	BCS	1	1.57	0.974	1.11
B	Line-node	1		0.913	1.07
C	Point-node	1		0.912	1.73
D	BCS+line-node	0.60	2.20	0.998	1.30
E	BCS+point-node	0.26	1.12	0.997	1.37
F	Line+point-node	0.51		0.993	1.44

The electronic contribution C_e is calculated by subtracting the phonon part from the total heat capacity, and is plotted as $C_\mathrm{e}/\gamma T$ versus T^2, as displayed in Fig. 3. Ge is a semiconductor and its electronic contribution can be ignored. The electronic C_p of $PtGe_2$ is extremely small compared with $Pr_{1-\delta}Pt_4Ge_{12}$ in the low temperature, thus it can be assumed that the electronic C_e with $T < 7.8\,\mathrm{K}$ is provided by $Pr_{1-\delta}Pt_4Ge_{12}$. To investigate the gap symmetry of $Pr_{1-\delta}Pt_4Ge_{12}$, the data of $C_\mathrm{e}(T)$ are fitted using the six models, as listed in Table 1. A single gap function cannot fit the data, thus we use the phenomenological two-gap α model with a weighing factor f,[23]

$$C_\mathrm{e} = fC_{\mathrm{e},1} + (1-f)C_{\mathrm{e},2}, \tag{1}$$

where $C_{\mathrm{e},x}$ ($x = 1, 2$) is the electronic contribution of one of the gaps. This model is often used to describe multi-band superconductors like MgB_2.[24] Here $C_{\mathrm{e},x} \propto e^{-\Delta/k_BT}$, $\propto T^2$, and $\propto T^3$ refer to the weakly coupled BCS gap, the point-node gap, and the line-node gap, respectively.

The data are well fitted to a combination of any two gaps (D, E, F), suggesting that $Pr_{1-\delta}Pt_4Ge_{12}$ is a multi-band superconductor. On the other hand, since the jump $\Delta_{C_\mathrm{p}}/\gamma T_\mathrm{c}$ at T_c is small, the most likely situation is E, a weakly coupled BCS gap ($\Delta/k_\mathrm{B}T_\mathrm{c} \sim 1.12$) combined with a strongly coupled gap with point nodes. However, an exact expression of the multi-band function cannot be determined due to the simple form of the two-gap α model, the one-gap symmetry can be ruled out because of the poor fit to C_p. It is noted that the multi-band feature is also observed in iso-structural Pr-based superconductors, including $PrOs_4Sb_{12}$, $PrRu_4As_{12}$, and $PrRu_4Sb_{12}$.[25,26] Considering the similarity in the structures of $PrPt_4Ge_{12}$ and $Pr_{1-\delta}Pt_4Ge_{12}$, $PrPt_4Ge_{12}$ is presumably also a multi-band superconductor. This may provide an explanation for the discrepancy of different experimental results in $PrPt_4Ge_{12}$: point-like nodes in the gap by μSR and specific heat experiments while weakly coupled BCS superconductivity by the ^{73}Ge-NQR study.[12,14] It is possible that the smaller gap is rather subtle and can be easily destroyed by external effects, e.g., a magnetic field, and then the other gap is predominant.[22]

The inset of Fig. 3 shows the temperature dependence of the upper critical field $\mu_0 H_{\mathrm{c2}}$, which is determined from the midpoints of the jumps in C_p/T in different fields. Data are best fitted by the Ginzburg–Landau (GL) two-band equation[27]

$$\mu_0 H_{\mathrm{c2}}(T) = \mu_0 H_{\mathrm{c2}}(0)\frac{1-t^2}{1+t^2}, \tag{2}$$

where $t = T/T_\mathrm{c}$, giving $\mu_0 H_{\mathrm{c2}}(0) = 2.91\,\mathrm{T}$. The coherence length ξ_0 estimated from $H_{\mathrm{c2}}(0)$ is about 11 nm. The reported value of the electron mean free path l estimated from different samples is controversial, i.e., 10–14 nm for polycrystalline $PrPt_4Ge_{12}$, and 103 nm for single crystalline $PrPt_4Ge_{12}$.[15,22] To give a heuristic estimation, we use the Wethamer–Helfand–Hohenberg (WHH) formula in the clean limit,[28] $H_{\mathrm{c2}}(0) = -0.73T_\mathrm{c}(dH_{\mathrm{c2}}/dT)_{T=T_\mathrm{c}}$, and derive $\mu_0 H_{\mathrm{c2}}(0) = 2.14\,\mathrm{T}$.

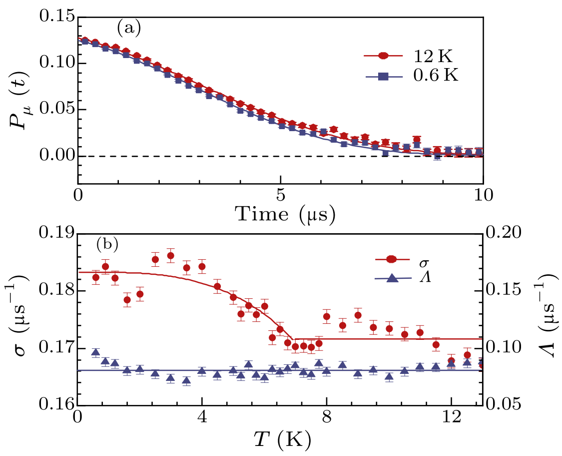

Fig. 4. (a) Zero-field μSR time spectra at 12 K (red circles) and 0.6 K (blue squares) for $Pr_{1-\delta}Pt_4Ge_{12}$. A background signal has been subtracted from the data. The corresponding solid lines are the fits according to Eq. (3), where λ is fixed at $0\,\mu\mathrm{s}^{-1}$. (b) Temperature dependence of the muon spin relaxation rates σ (red circles) and Λ (blue triangles), where σ is derived from the fitting of Eq. (3) with Λ fixed at $0.08\,\mu\mathrm{s}^{-1}$. The red curve is the fit of Eq. (5). The blue line denotes the average of Λ data from 0 to 13 K.

Further investigation of the superconducting order parameter in $Pr_{1-\delta}Pt_4Ge_{12}$ was performed by ZF-μSR experiments. Figure 4(a) shows the time evolution of the decay positron count asymmetry, which is proportional to the muon spin polarization, at temperatures above and below T_c in $Pr_{1-\delta}Pt_4Ge_{12}$. A constant background contribution, which originates from muons that stop in the silver sampler holder and nonmagnetic impurities, has been subtracted from the data. The data was initially fitted with the Voigtian function[29]

$$P_\mu(t) = G_z^{\rm KT}(\sigma, \lambda, t)\exp(-\Lambda t). \quad (3)$$

The term

$$G_z^{\rm KT}(\sigma,\lambda,t) = \frac{1}{3} + \frac{2}{3}(1-\sigma^2t^2-\lambda t) \cdot \exp\Big(-\frac{1}{2}\sigma^2t^2-\lambda t\Big) \quad (4)$$

describes a muon spin relaxation by randomly oriented static muon local fields, with Cartesian components that vary according to a convolution of Gaussian and Lorentzian distributions with distribution widths $\delta B_{\rm G}{=}\sigma/\gamma_\mu$ and $\delta B_{\rm L}{=}\lambda/\gamma_\mu$, where σ and λ are relaxation rates and $\gamma_\mu = 2\pi \times 135.53$ MHz/T is the muon gyromagnetic ratio.[8] The value of λ is extremely small and could be fixed at zero without changing the results. The value of λ is also found to be extremely small thus fixed at zero for $Pr_{1-x}Ce_xPt_4Ge_{12}$, $Pr(Os,Ru)_4Sb_{12}$, and $(Pr,La)Os_4Sb_{12}$.[30,31] The term $\exp(-\Lambda t)$ indicates an additional fluctuating relaxation process, where Λ is the damping rate. The value of Λ has a very weak temperature dependence and thus is fixed at its temperature average value of 0.08 μs^{-1}, as shown in Fig. 4(b). The small dynamic contribution Λ is presumably due to additional spin-lattice relaxation mechanisms, probably mediated by the Korringa relation of the local fluctuations from the hyperfine-enhanced ^{141}Pr nuclear dipolar field or the conduction-electron hyperfine interactions.[30] The value of $\sigma(T)$ is derived after Λ is fixed at 0.08 μs^{-1}. An obvious increase of $\sigma(T)$ is observed below $T_{\rm c}$, which signalizes the onset of a spontaneous internal field $B_{\rm s}$, indicating that TRS is broken in partially filled $Pr_{1-\delta}Pt_4Ge_{12}$.

The contributions to $\sigma(T)$ from nuclear dipolar and electrons in the superconducting state are uncorrelated in most skutterudite alloys[7,30] and added in quadrature,

$$\sigma(T) = \begin{cases} \sigma_n, & T > T_{\rm c} \\ [\sigma_n^2 + \sigma_{\rm e}(T)^2]^{1/2}, & T < T_{\rm c} \end{cases}, \quad (5)$$

where σ_n/γ_μ is the width of the nuclear dipolar field distribution, and $\sigma_{\rm e}(T)/\gamma_\mu$ is the width of the spontaneous field distribution from broken TRS. Provided that $\sigma_{\rm e}$ follows the temperature dependence of the BCS order parameter, the data are fitted with an empirical expression,[30]

$$\sigma_{\rm e}(T) = \sigma_{\rm e}(0)\tanh\Big(b\sqrt{\frac{T_{\rm m}}{T}-1}\Big), \quad (6)$$

where b is a dimensionless coefficient, $b = 1.74$ for BCS order parameter in the weak-coupling limit,[32] and $T_{\rm m}$ is the transition temperature determined by ZF-μSR experiments. The fitting results are listed in Table 2.

Table 2. Parameters from the fit of Eq. (6).

$\sigma_{\rm e}(0)$ (μs^{-1})	$\sigma_{\rm e}(0)/\gamma_\mu$ (mT)	σ_n (μs^{-1})	b	$T_{\rm m}$ (K)
0.065(5)	0.077(4)	0.171(0)	1.79(3)	6.9(2)

The increase of $\sigma(T)$ was not observed in the spin-singlet superconductor $LaPt_4Ge_{12}$,[8] suggesting that the dominant origin of broken TRS is the existence of ^{141}Pr nuclei. A previous study on $Pr_{1-x}Ce_xPt_4Ge_{12}$ reported that $\sigma_{\rm e}(0)/\gamma_\mu$ has a linear relation with ^{141}Pr nuclei concentration, indicating that Pr–Pr intersite interactions are responsible for broken TRS.[30] The value of $\sigma_{\rm e}(0)/\gamma_\mu$ in $Pr_{1-\delta}Pt_4Ge_{12}$ is 0.077(4) mT, nearly half of that (0.141 mT) in $PrPt_4Ge_{12}$.[30] Thus we speculate that the broken TRS in $PrPt_4Ge_{12}$ originates from either the ^{141}Pr nuclei or the Pr–Pr intersite interactions.

Intriguingly, similar to the case of the parent compound $PrPt_4Ge_{12}$ and Pr-related alloys including $Pr_{1-x}Ce_xPt_4Ge_{12}$,[8,30] $T_{\rm m}$ = 6.9 K is smaller than $T_{\rm c}$ = 7.8 K in $Pr_{1-\delta}Pt_4Ge_{12}$, indicating the possibility of a second phase, which could be either a distinct magnetic phase coexisting with superconductivity, or a subdominant superconducting phase with a magnetic (time-reversal violating) ground state, such as the case of $U_{1-x}Th_xBe_{13}$.[5] However, for $Pr_{1-\delta}Pt_4Ge_{12}$, the possibility of a distinct magnetic phase is excluded from the magnetization and the specific heat experiments because there is no anomaly around $T_{\rm m}$. ZF-μSR experiments also found no long-range order expected from a magnetic phase.

TRS breaking usually occurs in the triplet state with a degenerate representation,[33] including UPt_3 and Sr_2RuO_4.[34,35] A study on the superfluid density of $PrPt_4Ge_{12}$ also suggests a chiral p-wave gap function,[12] while this speculation lacks further evidence in other experiments. On the other hand, spin-singlet pairing is also plausible. In this case, broken TRS will require additional phase transitions admixing other pairing channels with the superconducting phase, e.g., the $d+is$ state.[36] Thus the difference between $T_{\rm m}$ and $T_{\rm c}$, as well as the multi-band features in $H_{\rm c2}$ and $C_{\rm p}(T)$, could be attributed to the appearance of a subdominant fully gapped component in the superconducting order parameter. It then leads to the occurrence of an intrinsic consecutive phase.[36,37] Such a proposal is not against the absence of multiple superconducting $C_{\rm p}$ jumps. A possible spin-singlet scenario has been proposed for $PrOs_4Sb_{12}$ considering broken TRS in the second phase and point nodes in the gap.[38] This scenario is compatible with our results on $Pr_{1-\delta}Pt_4Ge_{12}$. In such a state, the supercurrents are induced around nonmagnetic imperfections and produce the TRS breaking magnetic field.[36]

In summary, partially filled skutterudite $Pr_{1-\delta}Pt_4Ge_{12}$ samples have been successfully synthesized, and a study has been carried out by magnetization, specific heat, and ZF-μSR experiments.

The $[Pt_4Ge_{12}]$ cage-forming structure survives and superconductivity is observed below $T_c = 7.80\,K$. The temperature dependence of H_{c2} and the electronic specific heat are well described by the two-band model. Intriguingly, the onset of broken TRS is observed at $T_m < T_c$, possibly due to the appearance of a second phase, while no obvious specific jump is observed around T_m. The value of $\sigma_e(0)/\gamma_\mu$ in $Pr_{1-\delta}Pt_4Ge_{12}$ is half of that in $PrPt_4Ge_{12}$, indicating that the ^{141}Pr nuclei or Pr–Pr intersite interactions are responsible for broken TRS. These results suggest that $Pr_{1-\delta}Pt_4Ge_{12}$ holds a complicated superconductivity order parameter and is a unique playground for the study of unconventional superconductivity.

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