Simultaneous Nodal Superconductivity and Time-Reversal Symmetry Breaking in the Noncentrosymmetric Superconductor CaPtAs

T. Shang,1,2,* M. Smidman,3 A. Wang,3 L.-J. Chang,4 C. Baines,5 M. K. Lee,2 Z. Y. Nie,3 G. M. Pang,3 W. Xie,3 W. B. Jiang,3 M. Shi,6 M. Medarde,1 T. Shiroka,5,7 and H. Q. Yuan1,3,8,9

1Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, Villigen CH-5232, Switzerland
2Physik-Institut, Universität Zürich, Winterthurerstrasse 190, Zürich CH-8057, Switzerland
3Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China
4Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan
5Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, Villigen PSI CH-5232, Switzerland
6Swiss Light Source, Paul Scherrer Institut, Villigen CH-5232, Switzerland
7Laboratorium für Festkörperphysik, ETH Zürich, Zürich CH-8093, Switzerland
8Collaborative Innovation Center of Advanced Microstructures, Nanjing Univeristy, Nanjing 210093, China

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By employing a series of experimental techniques, we provide clear evidence that CaPtAs represents a rare example of a noncentrosymmetric superconductor which simultaneously exhibits nodes in the superconducting gap and broken time-reversal symmetry (TRS) in its superconducting state (below $T_c \approx 1.5$ K). Unlike in fully gapped superconductors, the magnetic penetration depth $\lambda(T)$ does not saturate at low temperatures, but instead it shows a $T^2$ dependence, characteristic of gap nodes. Both the superfluid density and the electronic specific heat are best described by a two-gap model comprising of a nodeless gap and a gap with nodes, rather than by single-band models. At the same time, zero-field muon-spin relaxation spectra exhibit increased relaxation rates below the onset of superconductivity, implying that TRS is broken in the superconducting state of CaPtAs, hence indicating its unconventional nature. Our observations suggest CaPtAs to be a new remarkable material that links two apparently disparate classes, that of TRS-breaking correlated magnetic superconductors with nodal gaps and the weakly correlated noncentrosymmetric superconductors with broken TRS, normally exhibiting only a fully gapped behavior.

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When entering the superconducting state, the breaking of extra symmetries in addition to U(1) gauge symmetry is normally an indication of unconventional superconductivity (SC) [1,2]. In a growing number of superconductors, time-reversal symmetry (TRS) breaking has been proved via the detection of spontaneous magnetic fields below the onset of superconductivity by means of zero-field muon-spin relaxation measurements. Notable examples include Sr$_2$RuO$_4$ [3], UPt$_3$ [4], PrOs$_4$Sb$_4$ [5], LaNiGa$_2$ [6], LaNiC$_2$, $\alpha$-Fe$_2$Si, and ReT ($T$ = transition metal) superconductors [7–13]. The first two are well-known examples of strongly correlated superconductors with unconventional pairing mechanisms [14,15], while the latter three are examples of noncentrosymmetric superconductors (NCSCs), where the lack of inversion symmetry gives rise to an antisymmetric spin-orbit coupling (ASOC) leading to spin-split Fermi surfaces. Consequently, their pairing states are not constrained to be purely singlet or triplet, and mixed-parity pairing may occur [16–18]. Owing to such mixed pairing and/or the influence of ASOC, NCSCs may exhibit significantly different properties from their conventional counterparts, e.g., superconducting gaps with nodes [19–23], upper critical fields exceeding the Pauli limit [11,24–27] or, as recently proposed, even topological superconductivity [28–32].

In general, the relationship between the breaking of TRS and a lack of inversion symmetry in the crystal structure is unclear. In many NCSCs such as Mo$_3$Al$_2$C, La$7$Si$_3$, Mg$_{10}$Ir$_{16}$B$_{16}$, or Mo$_3$P [33–38], no spontaneous magnetic fields have been observed and thus TRS is preserved in the superconducting state. A notable feature of most of the weakly correlated NCSCs with broken TRS is the presence of fully opened superconducting gaps. In the case of LaNiC$_2$, inconsistent results, including both fully open and nodal gap structures, have been found from measurements of the order parameter [39–44]. The nodeless superconductivity of weakly correlated NCSCs is not only in contrast to the general expectations for strong singlet-triplet mixing, but also sets these systems apart from the strongly correlated superconductors Sr$_2$RuO$_4$ and UPt$_3$ [3,4], where the presence of unconventional pairing mechanisms is more unambiguously determined.

In LaNiC$_2$, as well as in centrosymmetric LaNiGa$_2$, the observed TRS breaking has been accounted for by non-unitary triplet pairing [6,7,45]. This was reconciled with nodeless multigap SC by the proposal of even-parity triplet...
pairing, between electrons on different orbitals [46]. On the other hand, the ReT superconductors, which have a relatively large ASOC compared to LaNiC$_2$, appear to exhibit single fully opened gaps, more consistent with a predominantly singlet pairing. The recent observation of TRS breaking in centrosymmetric elemental Re strongly suggests that the local electronic structure of Re is crucial for understanding the TRS breaking in the ReT family [12]. The broken TRS in weakly correlated systems, which otherwise appear to behave as conventional superconductors, has led to proposals to account for this behavior with a conventional pairing mechanism [47], such as the loop-Josephson-current state, to account for this behavior with a conventional pairing mechanism [47], such as the loop-Josephson-current state.

To date, there are scarcely any examples of NCSC which clearly exhibit broken TRS and nodal-gap SC. In this Letter, we show that CaPtAs, a newly discovered NCSC [49], is a rare candidate to display both such unconventional features. Our key observations of a nodal-gap and of spontaneous magnetic fields (concomitant with the onset of SC) indicate that CaPtAs represents a new remarkable example of weakly correlated NCSC encompassing both broken TRS and nodal SC.

Polycrystalline CaPtAs was synthesized via a solid-state reaction method [49]. Magnetic susceptibility, electrical resistivity, and specific-heat measurements were performed on a Quantum Design MPMS and PPMS, respectively. The muon-spin relaxation and rotation ($\mu$SR) measurements were carried out on the low-temperature facility (LTF) spectrometer of the $\pi$M3 beam line at the Paul Scherrer Institut, Villigen, Switzerland. The temperature-dependent shift of the magnetic penetration depth, which is proportional to the frequency shift, i.e., $\Delta \lambda = G \Delta f$ (with $G$ a geometry related constant), was measured by using a tunnel-diode oscillator (TDO)-based technique at an operating frequency of 7 MHz [22,27,40].

CaPtAs crystallizes in a tetragonal noncentrosymmetric structure with space group $I4_1md$ (No. 109) [49]. The SC of CaPtAs was characterized by magnetic susceptibility, measured using both field-cooling (FC) and zero-field-cooling (ZFC) protocols. As shown in Fig. 1(a), the ZFC susceptibility (after accounting for the demagnetization factor) indicates SC below $T_c = 1.5$ K, where the electrical resistivity (right axis) drops to zero, both being consistent with the specific-heat data [50]. The lower critical field, estimated from the field-dependent magnetization, is $\mu_0 H_{c1} = 4.8(1)$ mT [see Fig. 1(b)].

Figure 2 shows the temperature dependent magnetic penetration depth $\lambda(T)$ measured by the TDO method and the corresponding exponential- and power-law fits. The TDO data over the full temperature range (see inset) illustrate the superconducting transition near $T_c = 1.5$ K. Clearly, $\lambda(T)$ follows a quadratic temperature dependence [$\lambda(T) \sim T^2$], as expected for superconductors with point nodes. In contrast, a power-law with a larger exponent [$\lambda(T) \sim T^3$] or an exponential temperature dependence [$\lambda(T) \sim e^{-\Delta \lambda(0)/T}$], the latter indicating fully gapped behavior, both deviate significantly from the experimental data. Figure 3(a) shows two typical transverse-field (TF) $\mu$SR spectra collected at temperatures above and below $T_c$, at
Here, \( H_{app} / H_{c2} \) is the reduced magnetic field.

Figures 3(b)–3(c) show the superfluid density \( (\rho_{sc} \propto \lambda^2) \) measured by TDO and \( \mu_{SR} \) vs the reduced temperature \( T/T_c \), respectively. The superfluid density clearly varies with temperature down to the lowest \( T \), i.e., well below \( T/T_c = 0.3 \). This nonconstant behavior again indicates the presence of low energy excitations and, hence, of nodes in the superconducting gap. To get further insight into the pairing symmetry, the temperature-dependent superfluid density was analyzed using different models. Considering a superconducting gap \( \Delta_f \), the superfluid density \( \rho_{sc}(T) \) can be calculated as:

\[
\rho_{sc} = 1 + 2 \left\langle \int_{\Delta_f} \frac{E}{\sqrt{E^2 - \Delta_f^2}} \frac{\partial f}{\partial E} dE \right\rangle_{FS},
\]

where \( f = (1 + e^{E/k_B T})^{-1} \) is the Fermi function and \( \left\langle \right\rangle_{FS} \) represents an average over the Fermi surface. The gap function can be written as \( \Delta_f(T) = \Delta_0(T) g_\lambda \), where \( \Delta_0 \) is the maximum gap value and \( g_\lambda \) is the angular dependence of the gap (see details in Table SI) [50]. The temperature dependence of the gap was assumed to follow \( \Delta_0(T) = \Delta_0(0) \tanh\left\{ 1.82 [0.108 (Tc/T - 1)]^{0.5} \right\} \), where \( \Delta_0(0) \) is the gap value in the zero-temperature limit.

Five different models, single-gap \( s \), \( p \), \( d \), and two-gap \( s + p \) and \( s + d \) wave, were used to analyze the superfluid density. The marked temperature dependence of the superfluid density at low-\( T \) clearly rules out a fully gapped \( s \)-wave model [see yellow lines in Figs. 3(b)–3(c)]. Also in the case of a pure \( p \) wave, we find a poor agreement with the low-\( T \) data (blue lines). A \( d \)-wave model with line nodes, can reproduce reasonably well the TF-\( \muSR \) data, but it fails to follow the low-\( T \) \( \lambda^2 \) \( (T) \) data obtained via TDO [see black lines in Figs. 3(b)–3(c)]. The slight difference between the TDO and TF-\( \muSR \) data below \( T/T_c \sim 0.5 \) is most likely due to the applied external field (8 mT) during the TF-\( \muSR \) measurements, which is not negligible compared to the small \( H_{c2} \) value of CaPtAs.

Conversely, the superfluid density is best fitted by a two-component \( (s + p) \)- or \( (s + d) \)-wave model [red and green muons in the sample and sample holder, \( \phi \) is the shared initial phase, and \( \sigma \) is the Gaussian relaxation rate. \( \sigma \) includes contributions from both the flux-line lattice (\( \sigma_n \)) and a temperature-invariant relaxation due to nuclear moments (\( \sigma_n \)). By subtracting the nuclear contribution in quadrature, one can extract \( \sigma_{sc} \), i.e., \( \sigma_{sc} = \sqrt{\sigma^2 - \sigma_n^2} \). The upper critical field of CaPtAs is relatively small compared to the field applied during the TF-\( \muSR \) measurements \( (H_{c2}/H_{appl} \sim 4.3) \) [50–52]. Hence, the effective penetration depth \( \lambda_{eff} \) had to be calculated from \( \sigma_{sc} \) by considering the overlap of the vortex cores [53]:

\[
\sigma_{sc}(h) = 0.172 \frac{\gamma_{\mu} \Phi_0}{2 \pi} (1 - h)[1 + 1.21(1 - \sqrt{h})^2] \lambda_{eff}^{-2}. \tag{2}
\]

\( \gamma_{\mu} \) is the muon gyromagnetic ratio, \( B \) is the external field, \( \Phi_0 \) is the magnetic flux quantum, and \( h \) is the relative nuclear field. The inset shows the enlarged plot of the TDO low-\( T \) region. The inset shows 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{(a) Time-domain TF-\( \muSR \) spectra in the superconducting (0.02 K) and normal (1.4 K) states of CaPtAs. Superfluid density as estimated from (b) The TDO-based method and (c) TF-\( \muSR \) vs the reduced temperature \( T/T_c \). The inset shows the enlarged plot of the TDO low-\( T \) region. (d) Zero-field electronic specific heat vs \( T/T_c \). The different lines represent fits to the various models (see text for details). The fit parameters are listed in Table SI [50].}
\end{figure}
lines in Figs. 3(b)–3(c). The good agreement with data of these models indicates the presence of multiple gaps, of which at least one has nodes on the Fermi surface. Although both models fit the superfluid density satisfactorily well across the full temperature range \((T < T_c)\), the \((s+p)\)-wave model agrees better with the \(s^\ast(T)\) data measured using the TDO method [see inset of Fig. 3(b)]. This is also strongly evidenced by both its smaller deviation from the data (see Table SI) and the quadratic low-\(T\) dependence of \(s^\ast(T)\) [50].

To further validate the above conclusions, the zero-field electronic specific heat \(C_e/T\) was also analyzed using the above models [51,54,55]. \(C_e/T\) was obtained by subtracting the phonon- and nuclear contributions from the measured data (see Fig. S2) [50] and it is shown in Fig. 3(d) as \(C_e/\gamma_n T\), with \(\gamma_n\) the normal-state electronic specific-heat coefficient. Again, the single-gap \(s\)-, \(p\)-, and \(d\)-wave models deviate significantly from the data. Conversely, both multigap models exhibit a good agreement with the experimental data across the full temperature range, with the \((s+p)\)-wave model showing the smallest deviation [50], hence providing further evidence for nodal-gap SC in CaPtAs. The fit of the \((s+p)\)-wave model to the superfluid density and the electronic specific heat [including the \(s\)-(\(\sim15\%\)) and \(p\)-wave (\(\sim85\%\)) components] are shown in Fig. S3 [50].

To search for spontaneous fields below \(T_c\), signaling possible TRS breaking in CaPtAs, we performed zero field (ZF) \(\mu SR\) measurements. The clear increase in relaxation rate in the superconducting state [see Fig. 4(a)] hints at the breaking of TRS. For nonmagnetic materials, the depolarization is generally described by a Gaussian Kubo-Toyabe relaxation function [56,57]. For CaPtAs, the ZF-\(\mu SR\) spectra were fitted by considering an additional Lorentzian relaxation component, with \(A_s\) and \(A_{bg}\) being the same as in the TF-\(\mu SR\) case:

\[
A_{ZF} = A_s \left( 1 + \frac{2}{3} \left( 1 - \frac{\sigma_{ZF}^2}{\sigma_{ZF}^2} \right) e^{-\left( \frac{\sigma_{ZF}^2}{\sigma_{ZF}^2} \right)} \right) e^{-\lambda_{ZF} t} + A_{bg}. \tag{4}
\]

Fits using the above model yield an almost temperature-independent Gaussian relaxation rate \(\sigma_{ZF}\) across the measured temperature range [see Fig. S4(b)] [50]. Hence, the Lorentzian relaxation rate \(\Lambda_{ZF}\) was estimated by fixing \(\sigma_{ZF}\) to its average value \((\sigma_{ZF}^\text{avg} = 0.13 \, \text{\mu s}^{-1})\). As shown in Fig. 4(b), a small yet measurable increase of \(\Lambda_{ZF}\) below \(T_c\) and a temperature-independent relaxation above \(T_c\) reflect the onset of spontaneous magnetic fields. This can be considered as the signature of TRS breaking in the superconducting state of CaPtAs, with similarly enhanced \(\Lambda_{ZF}\) having also been found in other TRS breaking NCSCs [7,8]. Both free- and fixed-\(\sigma_{ZF}\) analyses show a robust increase in \(\Lambda_{ZF}(T)\) below \(T_c\), demonstrating that the signal of spontaneous magnetic fields is an intrinsic effect, rather than an artifact of correlated fit parameters. This is further confirmed in Fig. S5, where we show the cross correlations between the different fit parameters [50]. Finally, longitudinal-field (LF) \(\mu SR\) measurements were performed at base temperature \((0.02 \, \text{K})\) to rule out additional extrinsic effects such as defect or impurity induced relaxation. As shown in Fig. 4(a), a small field of 10 mT is sufficient to fully decouple the muon spins from the weak spontaneous magnetic fields, indicating that the fields are static on the timescale of the muon lifetime.

To date, most NCSCs with broken TRS exhibit nodeless superconductivity, indicating that the spin-singlet channel dominates the pairing. These include the \(\alpha\)-Mn-type \(\text{Re}T\) [10–13] and \(\text{Th}_7\text{Fe}_3\)-type \(\text{La}_7T_3\) [8,9]. As for CeNiC\(_2\)-type NCSCs, the recently discovered \(\text{ThCoC}_2\) exhibits nodal SC, but no evidence of broken TRS has been found [58]. In \(\text{LaNiC}_2\), the low symmetry of its orthorhombic crystal structure means that the breaking of TRS at \(T_c\) necessarily implies nonunitary triplet pairing, and rules out the mixed singlet-triplet state described below [7,45]. However, measurements of the gap symmetry have yielded inconsistent results, where both fully-opened and nodal gap structures have been reported [39,40,40–43]. Compared to the above cases, CaPtAs represents a new remarkable NCSC, which accommodates both broken TRS and nodal SC.

One possibility is that the observed multigap superconductivity corresponds to different gaps on distinct
multigap nodal superconductivity and sizeable band splitting due to ASOC makes CaPtAs a good candidate for hosting mixed singlet and triplet pairing. While further theoretical calculations and measurements are necessary to determine the nature of the order parameter and pairing mechanism, this system may offer new insights for bridging the gap between different classes of TRS-breaking superconductors, namely strongly correlated superconductors with magnetically mediated pairing and nodal gaps (such as Sr$_3$RuO$_4$ and UPt$_3$) and the more recently discovered weakly correlated NCSCs.

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 Corresponding authors.
tian.shang@psi.ch
hqyuan@zju.edu.cn


