Spontaneous magnetization in unitary superconductors with time reversal symmetry breaking

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We report the study of spontaneous magnetization (i.e., spin polarization) for time-reversal-symmetry-breaking (TRS-breaking) superconductors with unitary pairing potentials, in the absence of external magnetic fields or Zeeman fields. Spin-singlet (Δ_s) and spin-triplet (Δ_t) pairings can coexist in superconductors whose crystal structures lack inversion symmetry. The TRS can be spontaneously broken once a relative phase of $\pm\pi/2$ is developed, forming a TRS-breaking unitary pairing state ($\Delta_s \pm i\Delta_t$). We demonstrate that such unitary pairing could give rise to spontaneous spin polarization with the help of spin-orbit coupling. Our result provides an alternative explanation for the TRS breaking, beyond the current understanding of such phenomena in the noncentrosymmetric superconductors. The experimental results of Zr_3Ir and CaPtAs are also discussed in view of our theory.

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Introduction. In condensed matter physics, superconductivity and magnetism are generally antagonistic to each other [1–3], and the interplay between them brings us intriguing phenomena. One of them is the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [4,5] in which superconducting Cooper pairs carry a finite momentum induced by an external Zeeman field. Recent theoretical efforts have been made to realize chiral Majorana modes in the topological Fulde-Ferrell (FF) phase [6,7] and the Majorana mode chain in the topological Larkin-Ovchinnikov (LO) phase [8]. Another fascinating phenomenon is the spontaneous magnetization or spin polarization (SP) in a time-reversal-symmetry-breaking (TRS-breaking) superconductor (SC) [9–11], which continuously promotes extensive experimental and theoretical research [12,13]. The TRS-breaking candidate SCs include Sr_2RuO_4 [14–16], ReT (T = transition metal) [17–22], UPt_3 [23–25], UGe_2 [26,27], URhGe [28], UCoGe [29,30], $PrOs_4Sb_{12}$ [31], URu_2Si_2 [32,33], SrPtAs [34], Ru_7B_3 [35,36], $LaNiC_2$ [37], $LaNiGa_2$ [38,39], Bi/Ni bilayers [40], CaPtAs [41], Zr_3Ir [42], and others summarized in a recent paper [13]. More recently, iron-based SCs also exhibit TRS-breaking signatures [43,44]. These exciting experimental discoveries arouse considerable attention, and a great deal of theoretical progress has recently been made on TRS-breaking SCs with mixed pairing states [45–55], nonunitary pairing states [56–67], and a Bogoliubov Fermi surfaces [68–71].

There are mainly two direct ways to probe spontaneously TRS-breaking pairing states: zero-field muon-spin relaxation (μSR) [72–74] and the polar Kerr effect (PKE) [75,76]. Firstly, μSR is especially very sensitive to a small change in internal fields (with a resolution down to 10 μT) [77]. The enhancement of the zero-field muon-spin depolarization rate in the superconducting state provides direct evidence for TRS-breaking pairing states. Besides, the PKE measures the optical phase difference between two opposite circularly polarized lights reflected on a sample surface; thus it gives information about the TRS of a system. A finite PKE unambiguously points to TRS-breaking states. Theoretically, nonunitary spin-triplet pairing potentials, such as the A_1 phase in He^3 superfluid characterized by spin-triplet $\vec{d}_s(\mathbf{k}) = k_z(1, -i, 0)$ [78], could spontaneously induce SP in a homogeneous SC, thus naturally explaining experimental observations by μSR and the PKE [1,2]. However, one may still wonder whether there is any mechanism other than the nonunitary spin-triplet pairing states to induce the SP in the TRS-breaking superconductors.

In this paper, we report the discovery of SP in TRS-breaking unitary SCs. The spin-singlet pairing (Δ_s) coexists with the spin-triplet pairing (Δ_t) in both noncentrosymmetric SCs and superconducting thin films. Once a relative phase of $\pm\pi/2$ is developed ($\Delta_s \pm i\Delta_t$), TRS is spontaneously broken. By combining the symmetry analysis and the Ginzburg-Landau (GL) theory, we find that the interplay between spin-orbit coupling (SOC) and the $\Delta_s \pm i\Delta_t$ unitary pairing potential could give rise to SP in a homogeneous SC. The direction of the induced SP is perpendicular to both the SOC $\vec{g}$ vector and the spin-triplet $\vec{d}$ vector, even though both $\vec{g}$ and $\vec{d}$ are real vectors. Our result provides an alternative explanation for the TRS-breaking phenomenon. The potential applications of our theory to recently discovered noncentrosymmetric SCs (e.g., Zr_3Ir and CaPtAs) are also discussed.

TRS-breaking unitary pairings. In the absence of external magnetic fields or Zeeman fields, the nonvanishing magnetism or SP in the superconducting states generally causes the spontaneous breaking of TRS. The SP can be generated

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by nonunitary pairing states with a complex spin-triplet $\vec{d}$ vector, whose direction is parallel to $\vec{d} \times \vec{d}^*$. Alternatively, in this paper, we explore the spontaneous SP induced by TRS-breaking unitary pairing states in SCs whose crystal structure lacks inversion symmetry. For this purpose, we start with a single-band model Hamiltonian [79],

$$\mathcal{H}_0 = \xi_k \sigma_0 + \alpha \vec{g} \cdot \vec{\sigma}, \quad (1)$$

where $\xi_k = k^2/2m - \mu$ is the electron band energy measured from the Fermi energy μ, $\vec{\sigma}$ denotes the Pauli matrices of electron spin, and α is the strength of SOC. The inversion symmetry is broken due to $\vec{g}(\mathbf{k}) = -\vec{g}(-\mathbf{k})$. In this paper, we mainly focus on the Rashba-type SOC which is given by $\vec{g} = (-k_y, k_x)$, allowed by the C_{4v} point group. There are two Fermi surfaces with opposite chirality, the two bands are $\epsilon_{k,\pm} = \xi_k \pm \alpha|\vec{g}|$, and the Fermi momentum is $k_F = \sqrt{2m\mu}$ for $\alpha \to 0$.

Then we consider the superconducting pairing Hamiltonian with attractive interactions,

$$\mathcal{H}_{\text{int}} = \sum_{\mathbf{k},\mathbf{k}'} \sum_{s_1,s_2} V_{\mathbf{k},\mathbf{k}'} c^\dagger_{\mathbf{k},s_1} c^\dagger_{-\mathbf{k},s_2} c_{-\mathbf{k}',s_2} c_{\mathbf{k}',s_1}, \quad (2)$$

where $s_{1,2}$ are spin indices. Applying the mean-field decompositions, we define the gap functions as $\Delta_{s_1,s_2}(\mathbf{k}) = \sum_{\mathbf{k}'} V_{\mathbf{k},\mathbf{k}'} \langle c_{-\mathbf{k}',s_2} c_{\mathbf{k}',s_1} \rangle$. Here, $\langle \cdots \rangle$ represents averaging over the thermal equilibrium states. After ignoring fluctuations, the mean-field pairing Hamiltonian becomes

$$\mathcal{H}_\Delta = \sum_{\mathbf{k}} \sum_{s_1,s_2} \Delta_{s_1,s_2}(\mathbf{k}) c^\dagger_{\mathbf{k},s_1} c^\dagger_{-\mathbf{k},s_2} + \text{H.c.} \quad (3)$$

Due to the breaking of inversion symmetry, the even-parity pairing coexists with the odd-parity pairing [79]. The pairing potential is generally given by $\hat{\Delta}(\mathbf{k}) = [\Delta_s \psi(\mathbf{k}) + \Delta_t \vec{d}(\mathbf{k}) \cdot \vec{\sigma}] i\sigma_y$, with $\psi(\mathbf{k}) = \psi(-\mathbf{k})$ and the real spin-triplet $\vec{d}$ vector $\vec{d}(\mathbf{k}) = -\vec{d}(-\mathbf{k})$ required by the Fermi statistic. The pairing strengths $\Delta_{s(t)} = |\Delta_{s(t)}| \exp(i\theta_{s(t)})$ are generally complex for the spin-singlet (spin-triplet) pairing states. To break TRS $\mathcal{T} = i\sigma_y \mathcal{K}$ ($\mathcal{K}$ is a complex conjugate), the relative phase $\theta_{ts} = \theta_t - \theta_s$ should be nonzero. Typically, θ_{ts} is pinned to $\pm\pi/2$, leading to the TRS-breaking unitary pairing $\Delta_s \pm i\Delta_t$, because of $\hat{\Delta}(\mathbf{k})^\dagger \hat{\Delta}(\mathbf{k}) = |\Delta_s \psi(\mathbf{k})|^2 + |\Delta_t|^2 \vec{d}(\mathbf{k}) \cdot \vec{d}(\mathbf{k})$. Here, the angular form factors for spin-singlet pairing could be either s wave ($\psi_s(\mathbf{k}) \sim \{1, \cos k_x + \cos k_y, \cos k_x \cos k_y\}$) or d wave ($\psi_d(\mathbf{k}) \sim \cos k_x - \cos k_y$). As for p-wave pairing symmetries, we focus on in-plane $\vec{d}$ vectors for simplicity, and there are four possibilities,

$$\vec{d}_{A_1}(\mathbf{k}) = (-\sin k_y, \sin k_x), \quad \vec{d}_{A_2}(\mathbf{k}) = (\sin k_x, \sin k_y),$$
$$\vec{d}_{B_1}(\mathbf{k}) = (\sin k_y, \sin k_x), \quad \vec{d}_{B_2}(\mathbf{k}) = (\sin k_x, -\sin k_y). \quad (4)$$

They belong to different one-dimensional (1D) irreducible representations of the C_{4v} point group, shown in Fig. 1(a). Note that all the spin-triplet $\vec{d}$ vectors in Eq. (4) have odd parity and are real, so that $|\vec{d}^* \times \vec{d}|^2$ vanishes. A relatively small SOC αk_F in units of $k_B T_c$ is assumed so that the spin-triplet $\vec{d}$ vectors that are not parallel with the SOC $\vec{g}$ vector could still be stabilized [80,81].

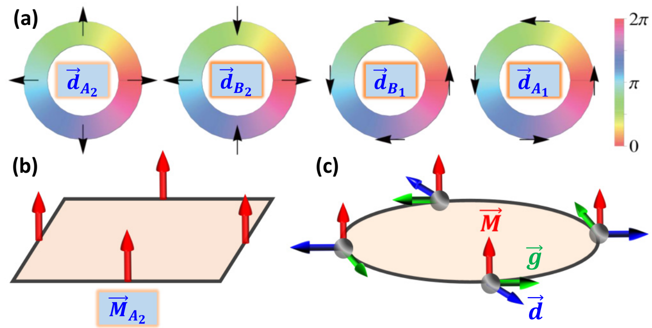

FIG. 1. Illustrations of the p-wave pairings and the boundary SP. (a) The four p-wave pairing symmetries with in-plane $\vec{d}$ vectors, labeled by the black arrows. (b) The real-space viewpoint of the boundary SP of a two-dimensional rectangular sample, marked by the red arrows. (c) The momentum space viewpoint of the $\vec{M}_{A_2}$-type SP that is parallel to $\vec{g} \times \vec{d}$, because of the product rule of the point group: $A_2 = A_2 \times A_1 (B_1 \times B_2)$.

Spontaneous spin polarization. Next, we use the GL theory to address the SP induced by the $\Delta_s \pm i\Delta_t$ unitary pairing potential in the absence of external magnetic fields or Zeeman fields. The symmetry-allowed free energy of a homogeneous SC reads

$$\mathcal{F} = F_2 + F_4 + \gamma_1 (\Delta_s^* \Delta_t)^2 + (\vec{\gamma}_2 \cdot \vec{M}) \Delta_s^* \Delta_t + \text{c.c.}, \quad (5)$$

where $F_2 = \alpha_s(T)|\Delta_s|^2 + \alpha_t(T)|\Delta_t|^2 + \alpha_M |\vec{M}|^2$ and $F_4 = \beta_s |\Delta_s|^4 + \beta_t |\Delta_t|^4 + \beta_{st} |\Delta_s|^2 |\Delta_t|^2$. Here, $\gamma_1 \neq 0$ indicates that the pairing breaks TRS since the relative phase difference between singlet and triplet pairings is developed as $\pm\pi/2$ [52]. The bilinear coupling term $\Delta_s^* \Delta_t$ pins the phase difference to an arbitrary nonzero value [82] at low temperature. Hereafter, we consider both Δ_s and Δ_t as belonging to different representations of the lattice symmetry group, and thus bilinear coupling is forbidden. Here, $\alpha_M > 0$ indicates the lack of intrinsic ferromagnetic ordering, and the γ_2 terms couple the SP $\vec{M}$ with the TRS-breaking unitary pairing $\Delta_s \pm i\Delta_t$, which satisfy both the global U(1) symmetry ($\theta_{s,t} \to \theta_{s,t} + \delta\theta$) and TRS. Once $\vec{\gamma}_2 \neq 0$, $\vec{M}$ is spontaneously induced by unitary $\Delta_s \pm i\Delta_t$. By minimizing $\mathcal{F}$, we find

$$\vec{M} = -\frac{1}{\alpha_M} \text{Im}[\vec{\gamma}_2 \Delta_s^* \Delta_t], \quad (6)$$

which will not alter the relative phase difference θ_{ts} between Δ_s and Δ_t (see Sec. A of the Supplemental Material [83]). This indicates that the unitary pairing states $\Delta_s \pm i\Delta_t$ coexist with the induced SP $\vec{M}$. The bulk magnetization vanishes in a purely clean system due to two reasons: the translational symmetry and the Meissner effect [84,85]. Nevertheless, the boundary SP [see Fig. 1(b)] persists as well as the SP around impurities in the bulk, both of which can be detected by the μSR and the PKE.

Below we first use symmetry analysis to classify the $\vec{\gamma}_2$ vector. The free energy in Eq. (5) preserves all the crystalline symmetries, which imposes strict constraints on the direction of the SP $\vec{M}$. We take the C_{4v} point group as an example to identify the ferromagnetic-type SP induced by the TRS-breaking unitary pairing potential. The character table is shown in Sec. B of the Supplemental Material [83]. A full classification for the $\vec{\gamma}_2$ terms by different symmetry groups is left for future work. The C_{4v} point group is generated by three independent symmetry operators (σ_v, σ_d, and R_{4z}): σ_v are the vertical reflection planes along x and y; σ_d are the diagonal reflection planes along the $x \pm y$ lines; and R_{4z} is the fourfold rotation along the z axis. To break both σ_d and σ_v simultaneously, only the z component of $\vec{\gamma}_2$ is nonzero, namely, $\vec{\gamma}_2 = (0, 0, \gamma_2^z)$, illustrated in Fig. 1(b). It belongs to the A_2 representation of C_{4v}, shown in Table S1 of the Supplemental Material [83]. According to the product rule of the point group, we conclude that the SP could be induced by the interplay of the s-wave (d-wave) singlet pairing and the $\vec{d}_{A_2}(\mathbf{k})$ [$\vec{d}_{B_2}(\mathbf{k})$] triplet pairing,

$$\hat{\Delta}_{s+ip} = (\Delta_s \Psi_s(\mathbf{k}) + i\Delta_t \vec{d}_{A_2}(\mathbf{k}) \cdot \vec{\sigma}) i\sigma_y,$$

$$\hat{\Delta}_{d+ip} = (\Delta_s \Psi_d(\mathbf{k}) + i\Delta_t \vec{d}_{B_2}(\mathbf{k}) \cdot \vec{\sigma}) i\sigma_y. \quad (7)$$

Both the $s + ip$ and $d + ip$ pairing states are fully gapped in 2D SCs, while gap nodes can exist in 3D SCs.

Next, we investigate the important role of Rashba SOC for the establishment of the $\vec{\gamma}_2$ term in Eq. (5). In this paper, we study a single-band Hamiltonian with SOC in Eq. (1), and the results could also be generalized to multiband systems. The coupling coefficients of $\vec{\gamma}_2$ are calculated for the Hamiltonian $\mathcal{H}_0 + \mathcal{H}_\Delta$,

$$\gamma_2^i = \frac{1}{\beta} \sum_{\mathbf{k},\omega_n} \mathrm{Tr}[G_h(\vec{d} \cdot \vec{\sigma}) G_e \sigma_i G_e \sigma_0], \quad (8)$$

with $i = \{x, y, z\}$ and $\beta = 1/(k_B T)$ the inverse of temperature. The Matsubara Green's function is $G_e(\mathbf{k}, i\omega_n) = [i\omega_n - \mathcal{H}_0(\mathbf{k})]^{-1}$ with $\omega_n = (2n + 1)\pi/\beta$ and $G_h(\mathbf{k}, i\omega_n) = G_e^*(-\mathbf{k}, -i\omega_n)$. We find that the direction of $\vec{M}$ is perpendicular to both the $\vec{d}$ vector and the SOC $\vec{g}$ vector, namely,

$$\vec{\gamma}_2 \propto i \sum_{\mathbf{k}} \langle (\vec{g}(\mathbf{k}) \times \vec{d}(\mathbf{k})) \cdot \psi_s(\mathbf{k}) \rangle_{\mathrm{FS}}, \quad (9)$$

where $\langle \cdots \rangle_{\mathrm{FS}}$ denotes the average over all the Fermi surfaces. Here, we take the $\Delta_s + i\Delta_t$ with s-wave pairing and $\vec{d}_{A_2}(\mathbf{k})$ as an example [see Fig. 1(c)], where $\vec{g} \times \vec{d}_{A_2} \approx \vec{e}_z(\sin^2 k_x + \sin^2 k_y)$. Moreover, we find the nonzero z component of $\vec{\gamma}_2$ to the leading order of $\alpha k_F / k_B T_c$ as

$$\gamma_2^z = \frac{7\zeta(3)}{8\pi^3} \frac{\alpha k_F}{k_B T_c}, \quad (10)$$

where $\zeta(z)$ is the Riemann zeta function. The crucial role of SOC in the SP is manifest in Eq. (10), representing the key result of this work. Only when $\alpha \neq 0$ can we have $\gamma_2^z \neq 0$ as well as $\tilde{M}_z \neq 0$. Therefore SOC is indispensable to induce SP by a TRS-breaking unitary pairing $\Delta_s + i\Delta_t$. Moreover, the sign of the SP is determined by $\mathrm{sgn}(M_z) = \mathrm{sgn}(\alpha\Delta_t\Delta_s)$.

To be more explicit, we perform a numerical calculation for the averaged SP based on the solution of the Bogoliubov–de Gennes (BdG) Hamiltonian,

$$\mathcal{H}_{\mathrm{BdG}} = \begin{pmatrix} \mathcal{H}_0(\mathbf{k}) & \mathcal{H}_\Delta \\ \mathcal{H}_\Delta^\dagger & -\mathcal{H}_0^*(-\mathbf{k}) \end{pmatrix}, \quad (11)$$

where the Nambu basis $(c_{\mathbf{k},\uparrow}^\dagger, c_{\mathbf{k},\downarrow}^\dagger, c_{-\mathbf{k},\uparrow}, c_{-\mathbf{k},\downarrow})^T$ is used. Here, $\mathcal{H}_0(\mathbf{k})$ is given by Eq. (1) and $\mathcal{H}_\Delta$ in Eq. (3). The averaged boundary SP is defined as

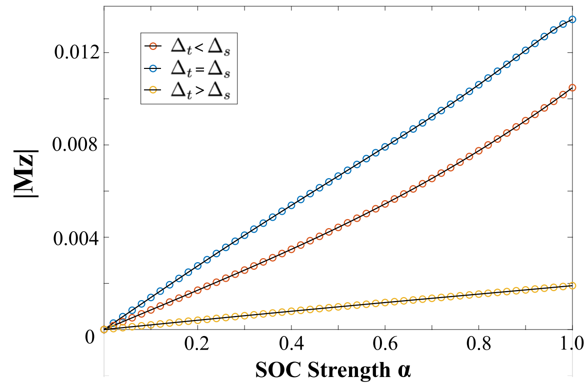

FIG. 2. The spontaneous SP induced by the $d + ip$ unitary pairing potential given by Eq. (7). The averaged SP on the boundary is calculated as a function of SOC strength for three cases: $\Delta_t < \Delta_s$ (red circles), $\Delta_t = \Delta_s$ (blue circles), and $\Delta_t > \Delta_s$ (yellow circles). Parameters $m_0 = 1$, $\mu = 1$, and $(\Delta_t, \Delta_s) = \{(1, 2), (1, 1), (2, 1)\}$ are used for the three cases.

$$\tilde{M}_z = \frac{1}{N_l} \sum_{\vec{l}} \sum_{E_n} \langle E_n(\vec{l}) | \hat{P}_e^\dagger \sigma_z(\vec{l}) \hat{P}_e | E_n(\vec{l}) \rangle_{\mathrm{BdG}}, \quad (12)$$

where $\vec{l}$ is the "edge coordinate" on a $N_x \times N_y$ rectangular lattice and $\vec{l} \in \{(1, i_y), (i_x, N_y), (N_x, i_y), (i_x, 1)\}$ with total sites $N_l = 2N_x + 2N_y - 4$, $\hat{P}_e$ is the projection operator into the particle subspace, and $|E_n\rangle$ is the solution of the BdG equation $\mathcal{H}_{\mathrm{BdG}}|E_n\rangle = E_n|E_n\rangle$.

Next, we take the $d + ip$ pairing states in Eq. (7) for an example. The numerical result is shown in Fig. 2. It confirms that the averaged spontaneous SP $\tilde{M}_z = 0$ corresponds to SOC strength $\alpha = 0$ and it increases with increasing α, consistent with the analytical analysis for γ_2^z in Eq. (10). Moreover, similar results are found in three different cases: $\Delta_t < \Delta_s$, $\Delta_t = \Delta_s$, and $\Delta_t > \Delta_s$. From this tendency, one may roughly estimate the induced SP $\tilde{M}_z \sim 0.02$ meV for Zr_3Ir, where the band splitting near the Fermi level due to SOC is about $\alpha k_F \sim 100$ meV, $T_c \approx 2.3$ K, and $\Delta_s \approx \Delta_t \sim 0.2$ meV [42]. Hence we argue that the SP induced by TRS-breaking unitary pairing is large enough to be detected by μSR measurement in Zr_3Ir [42].

Theoretical applications to noncentrosymmetric SCs. Now, we discuss the compatibility of the above superconducting pairings with the real materials. Here, we consider two different noncentrosymmetric SCs, Zr_3Ir [42] and CaPtAs [41], both exhibiting a breaking of TRS in their superconducting states. In general, the admixture of singlet and triplet pairings is mostly determined by the strength of SOC. The energy scale of band splitting caused by SOC ($\alpha k_F / k_B T_c$) is expected to be much larger in CaPtAs than in Zr_3Ir. Therefore the Zr_3Ir exhibits a fully gapped SC, while gap nodes were observed in CaPtAs, suggesting a large triplet component in the latter case as the SOC increases.

We first discuss the weak-SOC case, i.e., Zr_3Ir. The mixed pairings in Eq. (7) give rise to nine gap functions by considering three limits: $\Delta_s \ll \Delta_t$, $\Delta_s \sim \Delta_t$, and $\Delta_s \gg \Delta_t$ (see Sec.

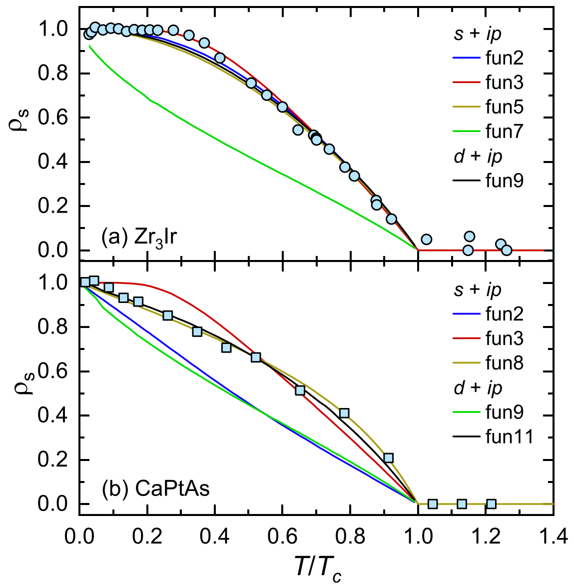

FIG. 3. The superfluid density ρ_s vs the reduced temperature T/T_c for the noncentrosymmetric SCs. (a) Zr_3Ir with a weak SOC and (b) CaPtAs with a strong SOC. The experimental data determined by the transverse-field muon-spin rotation measurements were taken from Refs. [41,42]. The solid lines represent the ρ_s fitted by different pairing functions. For CaPtAs, it might be also fitted by pairing fun 5, fun 7, fun 10, and fun 12 (see Fig. S1 of the Supplemental Material [83]).

C of the Supplemental Material [83]). If $\Delta_s \gg \Delta_t$, the gap functions become singlet pairing, inconsistent with the broken TRS in Zr_3Ir. Therefore we focus on the gap functions with $\Delta_s \ll \Delta_t$ or $\Delta_s \sim \Delta_t$. For $\Delta_s \ll \Delta_t$, triplet pairing is dominant, and the pairing function $\Delta_{s+ip} = \Delta_{d+ip} \sim \Delta_0|\sin\theta|$ exhibits gap nodes, Δ_0 being the superconducting gap at zero temperature whose value is also related to the magnitude of Δ_t. Indeed, as shown by function (fun) 2 in Fig. 3(a), the calculated superfluid density ρ_s shows a clear temperature dependence at low temperatures (see details of the calculations in Ref. [86]). For $\Delta_s \sim \Delta_t$, as shown in Fig. 3(a), fun 5 and fun 7 for $s+ip$ and fun 9 for $d+ip$ exhibit temperature-dependent superfluid density, similar to the case of fun 2. As for fun 3 ($\Delta_{s+ip} \sim \Delta_0\sqrt{1+\sin^2\theta}$), the calculated ρ_s is temperature independent at low T, an indication of fully gapped SC, and shows remarkably good agreement with the experimental data. Therefore the $s+ip$ pairing with $\Delta_s \sim \Delta_t$ might be applied to the noncentrosymmetric Zr_3Ir SC with weak SOC.

For the strong-SOC case (i.e., CaPtAs), the mixed pairings in Eq. (7) lead to 12 gap functions in total for the three different limits ($\Delta_s \ll \Delta_t$, $\Delta_s \sim \Delta_t$, and $\Delta_s \gg \Delta_t$) (see Sec. C of the Supplemental Material [83]). Considering the presence of both broken TRS and superconducting gap nodes in CaPtAs, we exclude the pairing functions with $\Delta_s \gg \Delta_t$. In the case of $\Delta_s \sim \Delta_t$, for $s+ip$ pairing, fun 3, fun 5, and fun 7 show a poor agreement with the experimental data (see Fig. S1 of the Supplemental Material [83]). Then, we focus on the gap functions with $\Delta_s \ll \Delta_t$. Both fun 2 [see Fig. 3(b) for $s+ip$] and fun 10 (see Fig. S1 for $d+ip$) exhibit a strongly temperature-dependent superfluid density and deviate significantly from the experimental data. However, for fun 8 ($\Delta_{s+ip} \sim \Delta_0|\cos\varphi\sin\varphi\sin\theta|$), the calculated ρ_s shows a good agreement with the experimental data over the entire temperature range. Furthermore, the ρ_s calculated from fun 11 and fun 12 for $d+ip$ are also highly consistent with the experimental data, and the fitting result of fun 11 ($\Delta_{d+ip} \sim \Delta_0|\cos\varphi\sin^2\theta - \sin\theta + \frac{\sin\theta}{|\sin\theta|}|$) is illustrated in Fig. 3(b). Therefore both $s+ip$ and $d+ip$ pairings with $\Delta_s \ll \Delta_t$ might be applied to the noncentrosymmetric CaPtAs SC with strong SOC. By comparing with the experimental data, we demonstrate that our theory might be practicable for both nodal and nodeless superconductivity with broken TRS in the noncentrosymmetric SCs.

Conclusion and discussion. We briefly discuss the effects of the boundary SP on first-order (second-order) 2D topological SCs, which host topological Majorana edge (corner) states (see Sec. D of the Supplemental Material [83]). A purely helical p-wave SC supports a pair of helical Majorana edge modes protected by TRS [87–89], which become fully gapped on each boundary for the $s+ip$ pairing states. Furthermore, a second-order topological SC is achieved [90–109] for the $d+ip$ case, which supports topological Majorana corner states (MCSs). They are a kind of Jackiw-Rebbi zero mode [110] sitting on each corner, protected by the combined $\sigma_d\mathcal{T}$ symmetry. Interestingly, we find that the boundary SP enlarges the edge gap to protect the MCSs.

In sum, we find that the TRS-breaking unitary pairing states could induce the spontaneous SP with the help of SOC, in the absence of external magnetic fields or Zeeman fields. We propose that both $s+ip$ and $d+ip$ spontaneously break TRS and give rise to SP, which is induced to be perpendicular to both the real spin-triplet $\vec{d}$ vector and the SOC $\vec{g}$ vector. The averaged boundary SP is also estimated to be ~0.02 meV for the noncentrosymmetric SC Zr_3Ir, which should be able to be detected in experiments. Moreover, our theory can quantitatively describe the superfluid density of Zr_3Ir and CaPtAs noncentrosymmetric SCs. Our result provides an alternative explanation to the TRS breaking, beyond the current understanding of such phenomena in the noncentrosymmetric superconductors. We also notice a recent theoretical work demonstrating that the pairing symmetry might be $d+ip$ for Sr_2RuO_4 [111]. Our theory may be also valid near an interface where spin-orbit coupling appears to explain the observations of broken TRS [14,15].

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