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# Time-reversal symmetry breaking in the new noncentrosymmetric superconductor $Zr_3Ir$

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We report the discovery of  $Zr_3Ir$  as a new type of unconventional noncentrosymmetric superconductor (with  $T_c = 2.3$  K), here investigated mostly via muon-spin rotation/relaxation ( $\mu$ SR) techniques. Its superconductivity was characterized using magnetic susceptibility, electrical resistivity, and heat capacity measurements. The low-temperature superfluid density, determined via transverse-field  $\mu$ SR and electronic specific heat, suggests a fully-gapped superconducting state. The spontaneous magnetic fields, revealed by zero-field  $\mu$ SR below  $T_c$ , indicate the breaking of time-reversal symmetry in  $Zr_3Ir$  and, hence, the unconventional nature of its superconductivity. By using symmetry arguments and electronic-structure calculations we obtain a superconducting order parameter that is fully compatible with the experimental observations. Hence, our results clearly suggest that  $Zr_3Ir$  represents a new member of noncentrosymmetric superconductors with broken time-reversal symmetry.

Unconventional superconductors, in addition to  $U(1)$  gauge symmetry, also break other types of symmetry [1, 2]. Among them, the breaking of time-reversal symmetry (TRS) below  $T_c$  has been widely studied, in particular by means of zero-field muon-spin relaxation (ZF- $\mu$ SR). As a very sensitive technique,  $\mu$ SR is able to detect the tiny spontaneous magnetic fields appearing below the onset of superconductivity (SC). Unconventional superconductors known to exhibit TRS breaking include, e.g.,  $Sr_2RuO_4$  [3],  $PrOs_4Sb_4$  [4],  $UPt_3$  [5],  $LaNiGa_2$  [6],  $LaNiC_2$ ,  $La_7T_3$ , and  $ReT$  ( $T =$  transition metal) [7–14]. The latter three also represent typical examples of noncentrosymmetric superconductors (NCSCs). In this case, the lack of space-inversion symmetry leads to an electric field gradient and, hence, to an antisymmetric spin-orbit coupling (ASOC), which splits the Fermi surface with opposite spin configurations. Often the strength of ASOC exceeds the superconducting energy gap, and the pairing of electrons belonging to different spin-split bands results in a mixture of singlet and triplet states. Due to such mixed pairing, NCSCs can exhibit significantly different properties from their conventional counterparts, e.g. a nodal superconducting gap [15–19], upper critical fields exceeding the Pauli limit [9, 20, 21] or, as recently proposed, topological superconductivity [22–24]. In turn, the structure and/or symmetry may be important in determining the effects of ASOC on the superconducting properties [25].

In general, the breaking of time-reversal and spatial-inversion symmetries are not necessarily correlated. Indeed, many NCSCs, such as  $Mo_3Al_2C$  [26],  $Mo_3Rh_2N$  [27],  $LaTSi_3$  [25, 28, 29], and  $Mg_{10}Ir_{19}B_{16}$  [30] do not exhibit spontaneous magnetic fields in the superconducting state and hence TRS is preserved. TRS breaking in NCSCs is supposed to arise mostly from unconventional pairing mechanisms. For example,  $LaNiC_2$  is

proposed to be a pure nonunitary triplet SC [7, 31] with pairing between same spins in two different orbitals [32].

Despite numerous examples of NCSCs, to date only a few of them are known to break TRS in their superconducting state. The causes of such selectivity remain largely unknown. Therefore, the availability of a new NCSC with broken TRS, such as  $Zr_3Ir$  reported here, would improve our understanding of the interplay between the different types of symmetry. In this Letter, we report systematic studies of  $Zr_3Ir$  by means of magnetization, transport, thermodynamic and muon-spin relaxation ( $\mu$ SR) measurements. The key observation of spontaneous magnetic fields, revealed by zero-field (ZF)  $\mu$ SR, indicates that  $Zr_3Ir$  represents a *new member* of the NCSC family, making it a benchmark for the current theories of TRS breaking and unconventional SC in NCSCs.

Polycrystalline  $Zr_3Ir$  samples were prepared by arc melting method [33]. The crystal structure and the sample purity were checked via x-ray powder diffraction using a Bruker D8 diffractometer. Consistent with previous results [34],  $Zr_3Ir$  crystallizes in a tetragonal  $\alpha$ - $V_3S$ -type noncentrosymmetric structure with space group  $I\bar{4}2m$  (121) [33]. The magnetic susceptibility, electrical resistivity, and specific heat measurements were performed on a Quantum Design magnetic and physical property measurement system. The  $\mu$ SR measurements were carried out on the GPS and LTF spectrometers of the  $\pi$ M3 beam line at the Paul Scherrer Institut (PSI), Villigen, Switzerland.

As shown in Fig. 1(a), the magnetic susceptibility indicates the SC onset at 2.7 K, consistent with electrical resistivity data [33]. The splitting of FC- and ZFC susceptibilities is typical of type-II superconductors. To determine  $H_{c1}$ , the field-dependent magnetization  $M(H)$

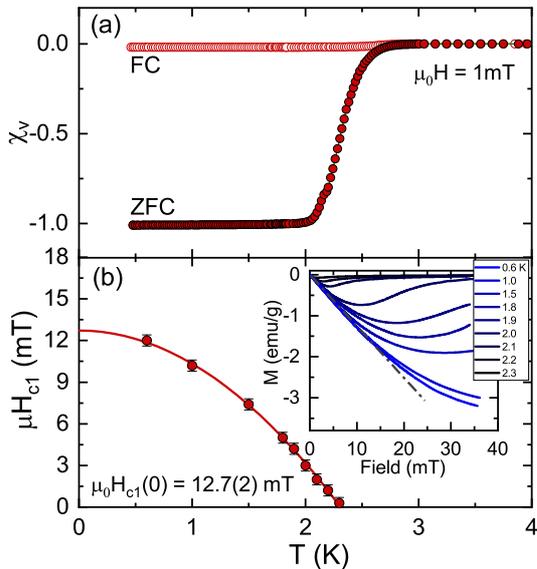


FIG. 1. (a) Temperature-dependent zero-field cooled (ZFC) and field-cooled (FC) magnetic susceptibilities, measured in an applied field of 1 mT for  $\text{Zr}_3\text{Ir}$ . (b) Estimated  $\mu_0 H_{c1}$  values vs. temperature; the solid line represents a fit to  $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)[1 - (T/T_c)^2]$ . The inset shows the field-dependent magnetization  $M(H)$  recorded at various temperatures.  $\mu_0 H_{c1}$  was identified with the deviation of  $M(H)$  from linearity (dashed-dotted line).

was measured at various temperatures, as shown in the inset of Fig. 1(b). The solid line in Fig. 1(b) is a fit to  $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)[1 - (T/T_c)^2]$ , which provides a lower critical field 12.7(1) mT and  $T_c = 2.3$  K. The bulk SC of  $\text{Zr}_3\text{Ir}$  was further confirmed by specific-heat measurements [33].

To explore the SC of  $\text{Zr}_3\text{Ir}$  at a microscopic level, we resort to transverse field (TF)  $\mu\text{SR}$  measurements. Here, a FC-protocol is used to induce a flux-line lattice (FLL) in the mixed superconducting state. The optimal field value for such experiments was determined via preliminary field-dependent  $\mu\text{SR}$  measurements [33]. Figure 2(a) shows typical TF- $\mu\text{SR}$  spectra, collected above and below  $T_c$  at 30 mT. The asymmetry of TF- $\mu\text{SR}$  spectra is described by:

$$A_{\text{TF}} = A_s e^{-\sigma^2 t^2/2} \cos(\gamma_\mu B_s t + \phi) + A_{\text{bg}} \cos(\gamma_\mu B_{\text{bg}} t + \phi). \quad (1)$$

Here  $A_s$  (88%) and  $A_{\text{bg}}$  (12%) are the sample and background asymmetries, with the latter not undergoing any depolarization.  $\gamma_\mu/2\pi = 135.53$  MHz/T is the muon gyromagnetic ratio,  $B_s$  and  $B_{\text{bg}}$  are the local fields sensed by implanted muons in the sample and the background (e.g., sample holder),  $\phi$  is a shared initial phase, and  $\sigma$  is a Gaussian relaxation rate reflecting the field-distribution inside the sample.

In the superconducting state,  $\sigma$  includes contributions from both the FLL ( $\sigma_{\text{sc}}$ ) and a smaller, temperature-independent relaxation, due to nuclear moments ( $\sigma_n$ ). The former can be extracted by subtracting the nuclear contribution in quadrature, i.e.,  $\sigma_{\text{sc}} = \sqrt{\sigma^2 - \sigma_n^2}$ . Since the upper critical field  $\mu H_{c2}$  of  $\text{Zr}_3\text{Ir}$  is relatively modest (0.62 T) [33], to extract the magnetic penetration depth  $\lambda_{\text{eff}}$  from the measured  $\sigma_{\text{sc}}$  we had to consider the expres-

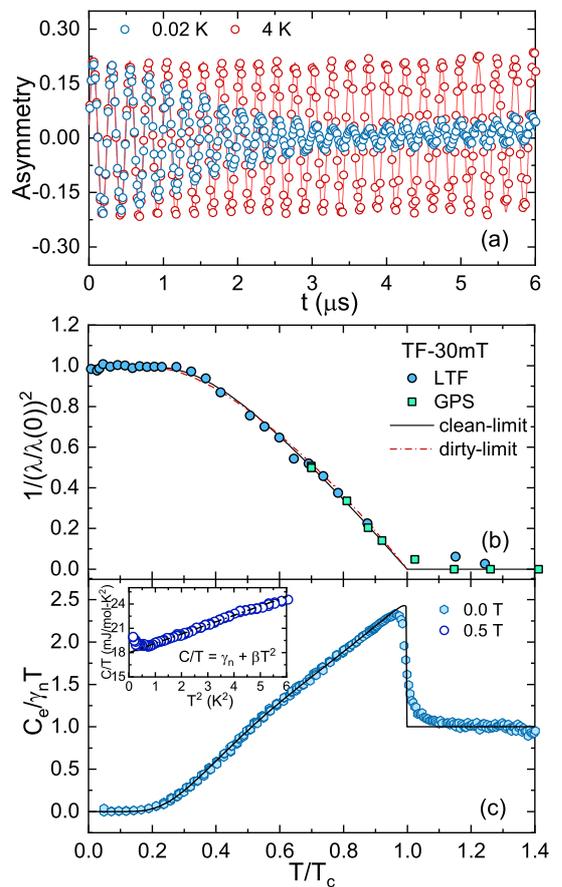


FIG. 2. (a) Time-domain TF- $\mu\text{SR}$  spectra in the superconducting (0.02 K) and the normal (4 K) phase of  $\text{Zr}_3\text{Ir}$  measured in a field of  $H_{\text{appl}} = 30$  mT. Normalized superfluid density (b) and zero-field electronic specific heat (c) vs. the reduced temperature ( $T/T_c$ ). The  $\mu\text{SR}$ -datasets collected on GPS and LTF spectrometers are highly consistent. The inset in (c) shows the raw  $C/T$  data measured in a 0.5-T applied field as a function of  $T^2$ . The dashed-line is a fit to  $C/T = \gamma_n + \beta T^2$ , from which the phonon contribution was evaluated. The solid black lines in (b) and (c) represent fits using a fully-gapped  $s$ -wave model, while the red dash-dotted line in (b) is a fit to a dirty-limit model.

sion [35, 36]:

$$\sigma_{\text{sc}}(h) = 0.172 \frac{\gamma_\mu \Phi_0}{2\pi} (1-h) [1 + 1.21(1 - \sqrt{h})^3] \lambda_{\text{eff}}^{-2}, \quad (2)$$

valid for intermediate values of the reduced magnetic field,  $h = H_{\text{appl}}/H_{c2}$ . Figure 2(b) shows the normalized superfluid density ( $\rho_{\text{sc}} \propto 1/\lambda^2$ ) versus the reduced temperature  $T/T_c$  for  $\text{Zr}_3\text{Ir}$ . For  $T < 0.3 T_c$ , the superfluid density is nearly temperature independent, indicating the absence of residual low- $T$  excitations and, hence, a fully-gapped superconducting state. The temperature-dependent superfluid density was fitted by using a fully-gapped  $s$ -wave model with a single superconducting gap, which provides  $\Delta(0) = 0.30(1)$  meV and  $\lambda(0) = 294(2)$  nm. The coherence length  $\xi_0$  is slightly larger than the electronic mean free path  $l_e$  (see Table SIII), implying that  $\text{Zr}_3\text{Ir}$  is in the dirty limit. Thus, similar to other NCSCs [37], the temperature dependence of its superfluid density was also analyzed by a dirty-limit model, which yields a gap value of 0.23(1) meV, slightly smaller than the clean-limit value, but consistent with previous studies [38].

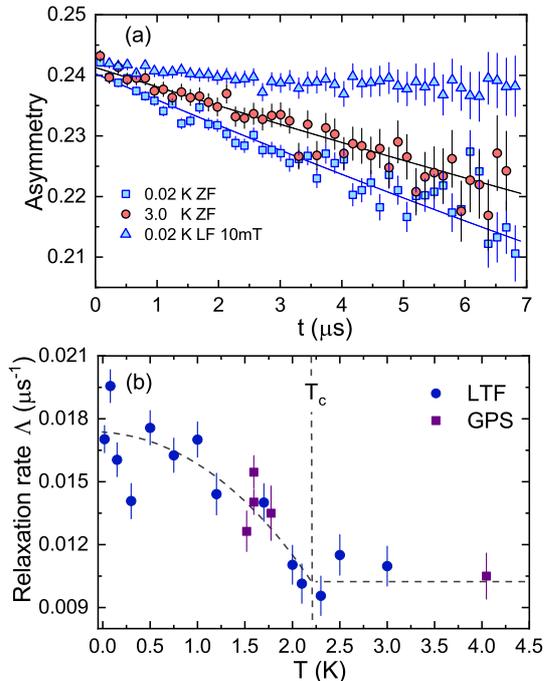


FIG. 3. Representative zero-field  $\mu$ SR spectra in the superconducting (0.02 K) and the normal (3 K) phase of  $\text{Zr}_3\text{Ir}$ , together with longitudinal field data, collected at 0.02 K and 10 mT. The solid lines are fits to Eq. (3). (b) Derived relaxation rate  $\Lambda$  vs. temperature. The dashed lines are guides to the eye. The datasets collected on GPS and LTF spectrometers are highly consistent.

The zero-field specific-heat data after subtracting the phonon  $\beta T^2$  contribution [see inset in Fig. 2(c)] are shown in Fig. 2(c). The fit (solid-line) yields a Sommerfeld coefficient  $\gamma_n = 17.9 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and a single isotropic gap,  $\Delta(0) = 0.32(1) \text{ meV}$ . Thus, both specific-heat and TF- $\mu$ SR results are compatible with a *fully-gapped* superconducting state.

ZF- $\mu$ SR measurements were used to establish the onset of TRS breaking in the superconducting state through its key signature, the appearance of spontaneous magnetic fields below  $T_c$ . Representative ZF- $\mu$ SR spectra, shown in Fig. 3(a), indicate a clear change in the muon-spin relaxation between 3 K and 0.02 K. For nonmagnetic materials, in the absence of applied fields, the depolarization of muon spins is mainly determined by the randomly oriented nuclear moments. This behavior is normally described by a Gaussian Kubo-Toyabe relaxation function [39, 40], as in the case of Re-based NCSCs [9–13]. For  $\text{Zr}_3\text{Ir}$ , the depolarization shown in Fig. 3 is more consistent with a Lorentzian decay. Indeed, attempts to analyze the data with a combined Gaussian and Lorentzian Kubo-Toyabe function, as in Refs. 9 and 10, systematically exclude the Gaussian component. This suggests that the fields sensed by the implanted muons arise from the diluted (and tiny) nuclear moments present in  $\text{Zr}_3\text{Ir}$ . Therefore, the solid lines in Fig. 3(a) are fits to a Lorentzian Kubo-Toyabe relaxation function:

$$A_{\text{ZF}} = A_s \left\{ \frac{1}{3} + \frac{2}{3} (1 - \Lambda t) e^{-\Lambda t} \right\} + A_{\text{bg}}. \quad (3)$$

Here  $A_s$  and  $A_{\text{bg}}$  are the same as in the TF- $\mu$ SR case (see Eq. 1). The derived muon-spin relaxation rate  $\Lambda$

vs. temperature is summarized in Fig. 3(b). Its relative change is comparable to that in other NCSCs with broken TRS [7–14], and  $\Lambda(T)$  shows a distinct increase below  $T_c$ , while being almost temperature independent above  $T_c$ . Such increase in the muon-spin relaxation rate below  $T_c$  was also found in other compounds, e.g.,  $\text{La}_7\text{Ir}_3$ ,  $\text{LaNiC}_2$ , and  $\text{Sr}_2\text{RuO}_4$  [3, 7, 8]. This provides unambiguous evidence that TRS is also broken in the superconducting state of  $\text{Zr}_3\text{Ir}$ . We note that, due to insufficient time resolution, a previous study reported standard deviations in  $\Lambda(T)$  of  $\sim 0.01 \mu\text{s}^{-1}$  [38]. Consequently, it could not capture the small yet systematic increase in  $\Lambda(T)$ , less than  $\sim 0.008 \mu\text{s}^{-1}$ , shown in Fig. 3(b) [33].

To rule out the possibility of extrinsic effects related to a defect/impurity-induced relaxation at low temperatures, we also carried out auxiliary longitudinal-field  $\mu$ SR measurements at base temperature (0.02 K). As shown in Fig. 3(a), a small 10 mT field is sufficient to lock the muon spins and, hence, to fully decouple them from the weak spontaneous magnetic fields. This further supports the intrinsic nature of TRS breaking in the superconducting state of  $\text{Zr}_3\text{Ir}$ .

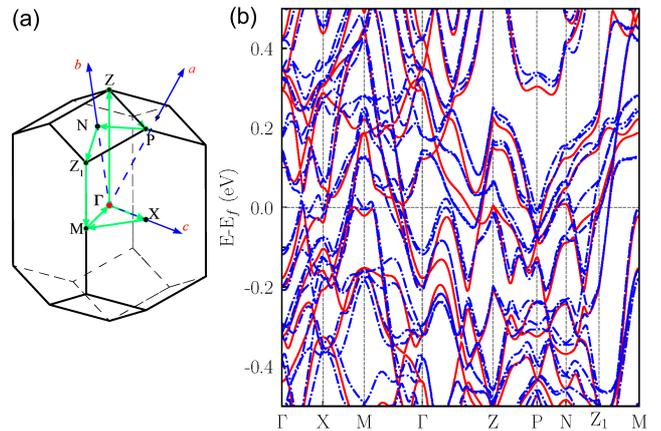


FIG. 4. (a) High-symmetry points of the  $\text{Zr}_3\text{Ir}$  unit cell. (b) Electronic band structure with- (dotted blue lines) and without SOC (solid red lines), within  $\pm 0.5 \text{ eV}$  from the Fermi energy.

To date, TRS breaking has been encountered only in three structurally different NCSCs: the  $\text{CeNiC}_2$ -type  $\text{LaNiC}_2$  [7], the  $\alpha$ -Mn-type  $\text{ReT}$  [9–13], and the  $\text{Th}_7\text{Fe}_3$ -type  $\text{La}_7\text{T}_3$  [8, 14]. With the  $\alpha$ -V<sub>3</sub>S-type  $\text{Zr}_3\text{Ir}$  reported here, we show the TRS breaking to occur in a new *structurally different* NCSC class. However, we point out that while crystal structure might influence TRS breaking in NCSCs, its role is not well known. Thus, many NCSCs, e.g.,  $\text{Mo}_3\text{Al}_2\text{C}$ ,  $\text{Mo}_3\text{Rh}_2\text{N}$ ,  $\text{LaT}_3\text{Si}_3$ ,  $\text{Mg}_{10}\text{Ir}_{19}\text{B}_{16}$ , and  $\text{Nb}_{0.5}\text{Os}_{0.5}$  [25–27, 29, 30, 41] preserve TRS although the last two share the same  $\alpha$ -Mn-type structure with other TRS-breaking  $\text{ReT}$  NCSCs. Moreover, the triplet pairing component appears to have a negligible effect in the properties of these NCSCs. Finally, in some of NCSCs, such as  $\text{Re}_3\text{W}$  [10, 42], changes in muon-spin relaxation below  $T_c$  may be below the resolution of the  $\mu$ SR technique.

To gain insight into the structure of the superconducting order parameter in  $\text{Zr}_3\text{Ir}$ , we performed electronic band-structure calculations and symmetry analysis of the

Ginzburg-Landau (GL) free energy [1, 43]. The band structures, both with and without SOC, were calculated by means of density-functional theory (DFT) within the generalized gradient approximation (GGA) [33, 44–48] and are shown in Fig. 4. The estimated band splitting near the Fermi level due to the ASOC, which plays an important role in determining the superconducting properties, is about 100 meV. While it is comparable to that of NCSCs, such as PdBiSe ( $\sim 109$  meV) [49] and  $\text{K}_2\text{Cr}_3\text{As}_3$  ( $\sim 60$  meV) [50], it is much smaller than that of  $\text{CePt}_3\text{Si}$  ( $\sim 200$  meV) [51] and  $\text{Li}_2\text{Pt}_3\text{B}$  ( $\sim 200$  meV) [52]. The band structure shown in Fig. 4(b) also reveals multiple dispersive bands crossing the Fermi energy. In particular, the electron pockets centered around the  $\Gamma$  point are much larger than the hole pockets centered around the  $Z$  point.

The space group of  $\text{Zr}_3\text{Ir}$ ,  $I\bar{4}2m$ , is symmorphic (direct product of the corresponding point group  $D_{2d}$  and the group of crystalline translations). Hence, the uniform superconducting instabilities of  $\text{Zr}_3\text{Ir}$  are fully determined by the normal-state symmetry group  $\mathcal{G} = G \otimes U(1) \otimes \mathcal{T}$ , where  $G$  is the group of point-symmetries and spin rotations, and  $\mathcal{T}$  is the group of TRS. The GL free energy of the system must be invariant under  $\mathcal{G}$ , which has the same spatial symmetry as  $D_{2d}$  having four 1D and one 2D irreducible representations (irreps). The presence of the 2D irrep allows for a two-component superconducting order parameter in  $\text{Zr}_3\text{Ir}$ , while a non-trivial phase difference between them may lead to TRS breaking. Note that SC in this channel requires additional crystalline symmetry breaking and, hence, the pairing mechanism is necessarily *unconventional* (i.e., not phonon-mediated).

SOC has dramatic consequences on the pairing symmetry of  $\text{Zr}_3\text{Ir}$  due to noncentrosymmetry and its relatively large band splitting (see Fig. 4). When SOC cannot be neglected the superconducting state is, in general, a mixture of singlets and triplets. The only possible order parameter breaking TRS in this case is  $\hat{\Delta}(\mathbf{k}) = [\Delta_0(\mathbf{k}) + \mathbf{d}(\mathbf{k}) \cdot \boldsymbol{\sigma}] i\sigma_y$  where  $\Delta_0(\mathbf{k}) = A_1(k_x + ik_y)k_z$  is the singlet component and  $\mathbf{d}(\mathbf{k}) = [A_2k_z, iA_2k_z, B_2(k_x + ik_y)]$  is the triplet component (the full derivation is given in the Supplemental Material). Here  $\boldsymbol{\sigma} = \{\sigma_x, \sigma_y, \sigma_z\}$  are the Pauli matrices and,  $A_1$ ,  $A_2$  and  $B_2$  are constants independent of  $\mathbf{k}$ . When  $|A_2|, |B_2| \ll |A_1|$  the limit of weak SOC is recovered.

Now, we discuss the compatibility of the above order parameter with the fully-gapped SC observed in  $\text{Zr}_3\text{Ir}$ . First, we consider the cases of a singlet- or triplet-dominated order parameter. A singlet-dominated TRS breaking order parameter ( $A_2, B_2 \approx 0$ ) leads to an energy gap  $|A_1||k_z|\sqrt{k_x^2 + k_y^2}$ . It has a line node at the “equator” for  $k_z = 0$  and two point nodes at the “north” and “south” poles. Similarly, a triplet-dominated TRS breaking order parameter ( $A_1 \approx 0$ ) corresponds to an energy gap  $[g(k_x, k_y) + 2A_2^2k_z^2 - 2|A_2||k_z|\sqrt{g(k_x, k_y) + A_2^2k_z^2}]^{1/2}$ , where  $g(k_x, k_y) = B_2^2(k_x^2 + k_y^2)$ . This instability also has two point nodes at the two poles, but no line nodes (see the respective gap plots in the Supplementary Material). In the general case, where both singlet- and triplet components are significant, we compute the excitation spectrum numerically, by using the Bogoliubov-de

Genes formalism [1]. We use the simplest form of normal-state band structure and ASOC-coupling constant compatible with the crystal symmetry [33]. As soon as a triplet component is present, the line node at the “equator” is gapped out. In contrast, the “north” and “south” point nodes are present throughout the phase diagram.

The above results are based only on symmetry arguments considering a generic Fermi surface. To adapt them to  $\text{Zr}_3\text{Ir}$ , we consider its Fermi surfaces which contribute the most to the density of states at the Fermi level (computed using DFT [33]). They are *open* at the two poles [33], implying fully-gapped behavior is expected for TRS-breaking order parameters with a non-negligible triplet component. Note that an equatorial line node for a singlet-dominated SC order parameter, necessarily gives rise to a gapless spectrum for the given Fermi-surface topology. Therefore, to reproduce the fully-gapped spectrum of  $\text{Zr}_3\text{Ir}$ , a triplet component (possibly small) induced by SOC is essential.

The specific-heat jump at  $T_c$  ( $\Delta C/\gamma T_c \sim 1.32$ ) and the gap to critical-temperature ratio ( $2\Delta/k_B T_c \sim 3.24$ ) of  $\text{Zr}_3\text{Ir}$  shown in Fig. 2 seem to suggest a singlet, phonon-mediated SC. This raises the question of how such a conventional mechanism may lead to a state with broken TRS, corresponding to a non-trivial irrep of the crystal point group. Recently, it was proposed that in multi-band systems, whose bands derive from distinct but symmetry-related sites within the unit cell, this may be achieved by a loop super-current state [53]. Interestingly, such conditions are satisfied in  $\text{Zr}_3\text{Ir}$ . In this picture, the  $k$ -dependent order parameter comes from a real-space pairing potential:  $|\Delta\rangle = |1\rangle + i|2\rangle$  where  $|1\rangle = (0, 0, -1, 1)$  and  $|2\rangle = (-1, 1, 0, 0)$  are real-space basis functions giving the on-site, singlet pairing strength in each of the four symmetry-related sites within the unit cell [33]. This ground state has finite currents within a unit cell spontaneously breaking TRS at  $T_c$  [53]. Note that the energy of this superconducting instability is driven by singlet pairing, while the additional triplet contribution is induced by SOC.

Finally, for weak SOC,  $G = D_{2d} \otimes SO(3)$ , with  $D_{2d}$  and  $SO(3)$  acting independently. Hence,  $G$  can have 1, 2, 3, and 6-dimensional irreps. As a result, additional TRS-breaking SC states may appear, including those arising from a pure  $SO(3)$ -pairing, as proposed for  $\text{LaNiC}_2$  and  $\text{LaNiGa}_2$  [6, 7, 31].

In conclusion, we have discovered a new structurally different member of the NCSC class,  $\text{Zr}_3\text{Ir}$ , which breaks time-reversal symmetry at the superconducting transition. The spontaneous magnetic fields appearing below  $T_c$  were detected by ZF- $\mu$ SR, while its electronic properties were investigated by means of magnetization, transport, thermodynamic, and  $\mu$ SR measurements. Both the zero-field specific-heat and superfluid density (from TF- $\mu$ SR) reveal a single-, fully-gapped superconducting state in  $\text{Zr}_3\text{Ir}$ . Theoretically, we obtain a superconducting order parameter fully compatible with the observations. Considering its different structure from the known NCSCs,  $\text{Zr}_3\text{Ir}$  is expected to stimulate further studies on the interplay of space-, time-, and gauge symmetries in

establishing the unique properties of NCSCs.

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