Fully-gapped superconducting state in interstitial-carbon-doped Zr₅Pt₃

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We report a comprehensive study of the Zr₅Pt₃Cₓ superconductors, with interstitial carbon comprised between 0 and 0.3. At a macroscopic level, their superconductivity, with Tc ranging from 4.5 to 6.3 K, was investigated via electrical-resistivity-, magnetic-susceptibility-, and specific-heat measurements. The upper critical fields µHc₂ ~ 7 T were determined mostly from measurements of the electrical resistivity in applied magnetic fields. The microscopic electronic properties were investigated by means of muon-spin rotation and relaxation (µSR) and nuclear magnetic resonance (NMR) techniques. In the normal state, NMR relaxation data indicate an almost ideal metallic behavior, confirmed by band-structure calculations, which suggest a relatively high electronic density of states at the Fermi level. The microscopic properties below the onset of superconductivity, as determined from zero-field µSR measurements, confirm a preserved time-reversal symmetry in the superconducting state of Zr₅Pt₃Cₓ. In contrast to a previous study, our µSR and NMR results suggest a conventional superconductivity in the Zr₅Pt₃Cₓ family, independent of the C content.

I. INTRODUCTION

The T₅Mₓ family, where T is a d-transition or rare-earth metal and M a (post-)transition metal or a metalloid element, features three distinct structural symmetries: orthorhombic YbSb₃-type (Pnma, No. 62), tetragonal CrB₃-type (I4/mcm, No. 140), and hexagonal Mn₃Si₃-type (P6₃/mcm, No. 193). The CrB₃-type structure is adopted by a broad range of binary and ternary compounds, e.g., the layered ternary compounds of transition metals with boron and silicon, with a TₓXB₃ stoichiometry (X = P or Si), known to exhibit many interesting properties. For T = 3d-Mn or Fe, both TₓSiB₂ and TₓPB₂ are ferromagnets with Curie temperatures above 480 and 600 K, respectively. Hence, currently they are being considered for room-temperature magnetocaloric applications or as rare-earth-free permanent magnets [1-4]. For T = 4d-Nb, Mo, or 5d-Ta, W metals, all TₓSiB₂ are superconductors, with transition temperatures in the 5 to 8 K range [5-8]. Furthermore, the recently synthesized tetragonal Mo₉PB₂ was shown to exhibit midgap superconductivity (SC) with a critical temperature Tc = 9.2 K [9, 10], the highest Tc recorded in a CrB₃-type compound.

The hexagonal Mn₃Si₃-type structure possesses an interstitial 2b site, well suited for the intercalation of light elements, such as oxygen, boron, or carbon, employed to engineer the band topology and, ultimately, the electronic properties. Superconductivity has been reported in several families of materials, including Nb₁Ir₂O₅ [11], (Nb,Zr)₂Pt₃O [12, 13], Nb₂Ge₃Cₓ [14, 15], or Zr₅Pt₃Cₓ [16], with the highest superconducting transition temperature T_c reaching ~15 K. Upon intercalation of oxygen [11], the T_c of Nb₁Ir₂ increases up to 10.5 K, while upon Pt doping, a crossover from multiple-to single-gap SC occurs in Nb₁Ir₂₋ₓPtₓO [17, 18]. Contrary to the Nb₁Ir₂O₅ case, in Zr₅Pt₃ or Zr₅Sb₃, the addition of oxygen reduces the T_c value [13, 19].

In carbon-intercalated Zr₅Pt₃Cₓ, the T_c value depends monotonically on x, first increasing up to 7 K for x = 0.3, then decreasing to ~4 K, as the amount of intercalated C is further increased [16, 20]. The first electronic specific-heat and magnetic penetration-depth studies suggested that Zr₅Pt₃ and Zr₅Pt₃C₀.3 are nodal superconductors, implying their unconventional SC character [16]. However, recent muon-spin rotation and relaxation (µSR) results are consistent with a conventional s-wave pairing in Zr₅Pt₃C₀.5 [20]. More intriguingly, the theoretical calculations predict Zr₅Pt₃Cₓ to be Dirac nodal-line semimetals and, as such, good candidates for realizing topological SC [20]. Although the superconductivity of Zr₅Pt₃Cₓ compounds has been investigated by magnetic- and transport measurements, complemented by electronic band-structure calculations, the microscopic nature of their SC is still not well established. Moreover, the lack of a shared doping makes the conclusions of the previous studies regarding the superconducting pairing in Zr₅Pt₃Cₓ inconsistent and hardly comparable [16, 20]. To clarify these issues, we synthesized a series of Zr₅Pt₃Cₓ (x = 0–0.3) samples, and systematically studied their superconducting properties by means of electrical resistivity, magnetization, and heat-capacity measurements, complemented by µSR and nuclear magnetic resonance (NMR) methods. We find that Zr₅Pt₃Cₓ exhibits a fully-gapped superconducting state with a preserved time-reversal symmetry. Our detailed local-probe results suggest a conventional s-wave SC in the Zr₅Pt₃Cₓ family, essentially independent of the C content.

II. EXPERIMENTAL DETAILS

Polycrystalline Zr₅Pt₃Cₓ (x = 0–0.3) samples were prepared by arc melting the Zr and C powders and Pt wires with different stoichiometric ratios in a high-purity argon atmosphere. Zr and C powders were firstly mixed and pressed into
pellets. The ZrC-pellets and Pt wires were then arc melted. To improve the homogeneity, the samples were flipped and remelted several times and were then annealed under vacuum conditions at 800°C over 4 days. Room-temperature x-ray powder diffraction (XRD) measurements were used to check the crystal structure and phase purity of the Zr$_5$Pt$_3$C$_x$ samples, by employing a Shimadzu (XRD-7000) diffractometer. The magnetic-susceptibility-, electrical-resistivity-, and heat-capacity measurements were performed using a Quantum Design MPMS and PPMS system. The bulk µSR measurements were carried out at the multipurpose surface-muon spectrometer (Dolly) of the Swiss muon source at the Paul Scherrer Institut in Villigen, Switzerland. Both transverse-field (TF) and zero-field (ZF) µSR measurements were performed. As to the former, they allowed us to determine the temperature evolution of the superfluid density. As to the latter, we aimed at searching for a possible breaking of time-reversal symmetry in the superconducting state of Zr$_5$Pt$_3$C$_x$. To exclude the possibility of stray magnetic fields during the measurements, we cover the 2 to 300 K temperature range. Spin-lattice relaxation times $T_1$ were measured via the inversion-recovery method, using a π–π/2–π pulse sequence with phase cycling for minimizing possible artefacts. The powder samples were used for the x-ray diffraction, magnetization, µSR, and NMR measurements, while the electrical-resistivity and heat capacity measurements were performed on the cut slabs.

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure and the purity of Zr$_5$Pt$_3$C$_x$ ($x = 0$–0.3) polycrystalline samples was checked via XRD at room temperature. The XRD patterns shown in Fig. 1(a) confirm that all of them share the same hexagonal Mn$_5$Si$_3$-type structure, with no discernible traces of foreign phases (see details in Fig. S1 in the Supplemental Material (SM) [23]). As an example, the crystal structure of Zr$_5$Pt$_3$C$_0.1$ is shown in the inset of Fig. 1(b). When $x < 1$, the occupation of the 2b sites is less than 1. We note that, for $x > 0.5$, sizeable amounts of secondary phases (mostly ZrPt) appear [16, 20]. Thus, here we investigate Zr$_5$Pt$_3$C$_x$ samples with $x \leq 0.3$. The lattice parameters of each sample were obtained by the least-squares method and the results are summarized in Fig 1(b). Upon increasing the C-content, $a$ decreases slightly, from 8.182(3) Å (for $x = 0$) to 8.167(4) Å (for $x = 0.3$), while $c$ increases from 5.384(2) Å (for $x = 0$) to 5.390(3) Å (for $x = 0.3$). In the Zr$_5$Pt$_3$ parent compound, we obtain lattice parameters consistent with previous reports [13, 16].

B. Superconducting temperature and lower critical field $H_{c1}$

The temperature dependence of the electrical resistivity $\rho(T)$, collected in zero magnetic field, reveals the metallic character of Zr$_5$Pt$_3$C$_x$ ($x = 0$–0.3). The electrical resistivity in the low-$T$ region (below 10 K) is shown in Fig. 2(a). For Zr$_5$Pt$_3$, the superconducting transition, with $T_{c}^{\text{onset}} = 7.2$ K, $T_{c}^{\text{mid}} = 6.8$ K, and $T_{c}^{\text{zero}} = 6.1$ K is clearly visible and the $T_c$s are consistent with previous results [16]. Here $T_{c}^{\text{mid}}$ indicates the temperature at the middle of superconducting transition. When intercalating carbon into the Zr$_5$Pt$_3$ structure, $T_c$ is reduced, with $T_{c}^{\text{onset}} = 5.2$ K, $T_{c}^{\text{mid}} = 4.9$ K, and $T_{c}^{\text{zero}} = 4.4$ K in Zr$_5$Pt$_3$C$_{0.3}$. The slightly different $T_c$ values between the current and the previous work are most likely attributed to a different actual carbon content [16, 20]. Since our intercalated samples exhibit almost identical $T_c$ values with varying C content, our µSR and NMR measurements focused on Zr$_5$Pt$_3$C$_x$ with $x = 0$ and 0.3.
The superconductivity of Zr$_5$Pt$_3$C$_x$ was further characterized by magnetic susceptibility measurements, using both field-cooled (FC) and zero-field-cooled (ZFC) protocols in an applied field of 1 mT. As shown in Fig. 2(b), a clear diamagnetic signal appears below the superconducting transition at $T_c = 6.3$ and 4.5 K for Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$, respectively, in agreement with the values determined from electrical resistivity in Fig. 2(a). After accounting for the demagnetization factor, the superconducting shielding fraction of Zr$_5$Pt$_3$C$_x$ samples is almost 100%, indicative of bulk SC. To determine the lower critical field $H_{c1}$, essential for performing μSR measurements on type-II superconductors, the field-dependent magnetization $M(H)$ was collected at various temperatures up to $T_c$. As an example, some representative $M(H)$ curves are shown in Fig. 3(a) for Zr$_5$Pt$_3$. The C-intercalated samples exhibit very similar features. The resulting $H_{c1}$ values as a function of temperature are summarized in Fig. 3(b) for Zr$_5$Pt$_3$C$_x$. As shown by solid lines, the estimated zero-temperature $H_{c1}$ values are $\mu_0H_{c1}(0) = 5.5(1), 3.8(1), 4.4(1)$, and 4.4(1) mT for $x = 0, 0.05, 0.15$, and 0.3, respectively. The different $H_{c1}$ values of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ are consistent with the magnetic penetration depth determined from TF-μSR measurements (see below).

C. Upper critical field $H_{c2}$

The upper critical fields $H_{c2}$ of Zr$_5$Pt$_3$C$_x$ were determined from measurements of the electrical resistivity $\rho(T, H)$ in various applied magnetic fields. As an example, the $\rho(T, H)$ curves of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ are shown in Figs. 4(a) and 4(b), respectively. In an applied field, the superconducting transition shifts toward lower temperatures and broadens. For Zr$_5$Pt$_3$C$_{0.3}$, as shown in the inset of Fig. 4(b), also specific-heat measurements in various magnetic fields were performed. Since, for $x = 0.3$, the $T_c$ values determined from the specific heat $C(T, H)/T$ coincide with $T_c^{\text{zero}}$ determined from the electrical-resistivity measurements [see Fig. 5(d)], we used the $T_c^{\text{zero}}$ values as a criterion to determine $H_{c2}(0)$ for all the Zr$_5$Pt$_3$C$_x$ samples. The $H_{c2}(T)$ vs $T_c(T)/T(0)$ data [here, $T_c(0)$ is the transition temperature in zero field] are summarized in Fig. 5. Each $H_{c2}(T)$ curve was analyzed by means of Ginzburg–Landau (GL), $H_{c2} = H_{c2}(0)(1 - t^2)/(1 + t^2)$, and Werthamer–Helfand–Hohenberg (WHH) models [25]. As shown by the dash-dotted lines, the WHH model can describe the $H_{c2}(T)$ data reasonably well up to 2 T. However, at higher magnetic fields, this model deviates significantly from the experimental data and provides underestimated $H_{c2}$ values. By contrast, as shown by the solid lines in Fig. 5, the GL model agrees remarkably well with the experimental data and provides $\mu_0H_{c2}(0) = 7.21(5), 6.26(4), 6.42(9)$, and 6.97(6) T for $x = 0, 0.05, 0.15$, and 0.3, respectively.
In the GL theory of superconductivity, the magnetic penetration depth $\lambda$ is related to the coherence length $\xi$, and the lower critical field via $\mu_0 H_{c1} = (\Phi_0/4\pi\lambda^2)\ln(\alpha(\kappa))$, where $\Phi_0 = 2.07 \times 10^{-3}$ T $\mu$m$^2$ is the quantum of magnetic flux, $\kappa = \xi/\lambda$ is the GL parameter, and $\alpha(\kappa)$ is a parameter which converges to 0.497 for $\kappa \gg 1$ [26]. By using $\mu_0 H_{c1}$ and $\xi$ values calculated from $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi(0)^2$, the resulting $\lambda_{c0} = 366(4)$ and 415(6) for Zr$_5$Pt$_3$, and Zr$_5$Pt$_3$C$_0.3$ are compatible with the experimental value determined from $\mu$SR data. All the superconducting parameters are summarized in Table I. A GL parameter $\kappa \gg 1$ confirms again that Zr$_5$Pt$_3$C$_x$ are type-II superconductors.

**D. $\mu$SR study**

1. **Transverse-field $\mu$SR**

To investigate Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ at a microscopic level, we carried out systematic TF-$\mu$SR measurements in an applied field of 30 mT, i.e., more than twice their $H_{c1}$ values [see Fig. 3(b)]. Representative TF-$\mu$SR spectra collected in the superconducting and normal states of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ are shown in Figs. 6(a) and 6(b), respectively. For both compounds, the normal-state spectra show essentially no damping, thus reflecting the uniform field distribution, as well as the lack of magnetic impurities. In the superconducting state (below $T_c$), instead, the significantly enhanced damping reflects the inhomogeneous field distribution due to the development of a flux-line lattice (FLL) [27–30]. The broadening of the field distribution is clearly visible in Figs. 6(c) and 6(d), where the fast-Fourier transform (FFT) spectra of the corresponding TF-$\mu$SR data of Zr$_5$Pt$_3$ are presented. To describe the asymmetric field distribution [e.g., see FFT at 0.3 K in Fig. 6(c)], the TF-$\mu$SR spectra were modeled using

$$A_{\mu}(t) = \sum_{i=1}^{n} A_i \cos(\gamma B_i t + \phi) e^{-\sigma_t^2 t^2/2} + A_{bg} \cos(\gamma B_{bg} t + \phi).$$

(1)

Here $A_1$, $A_{bg}$ and $B_1$, $B_{bg}$ are the initial asymmetries and local fields sensed by implanted muons in the sample and sample holder (copper, which normally shows zero muon-spin depolarization), $\gamma B/2\pi = 135.53$ MHz/T is the muon gyromagnetic ratio, $\phi$ is a shared initial phase, and $\sigma_t$ is the Gaussian relaxation rate of the ith component. Generally, the field distribution in the superconducting state is material dependent: the more asymmetric it is, the more components are required to describe it. Here, we find that, while two oscillations (i.e., $n = 2$) are required to properly describe the TF-$\mu$SR spectra of Zr$_5$Pt$_3$, a single oscillation is sufficient for Zr$_5$Pt$_3$C$_{0.3}$. For Zr$_5$Pt$_3$, the dash-dotted lines in Fig. 6(c) represent the two components at 0.3 K ($A_1$ and $A_2$) and the background signal ($A_{bg}$). Above $T_c$, the muon-spin relaxation rate is small and temperature-independent, but below $T_c$ it starts to increase due to the onset of FLL and the increased superfluid density. At the same time, a diamagnetic field shift, $\Delta B(T) = \langle B \rangle - B_{app}$, appears below $T_c$, with $\langle B \rangle = (A_1 B_1 + A_2 B_2)/A_{tot}$, $A_{tot} = A_1 + A_2$, and $B_{app} = 30$ mT (see insets in Fig. 7). The effective Gaussian relaxation rate can be calculated from $\sigma_{c}^2/\gamma^2 = \sum_{i=1}^{n} A_i^2 / \langle \sigma_t^2 \rangle^2$. Then, the superconducting Gaussian relaxation rate $\sigma_{sc}$ can be extracted by subtracting the nuclear contribution according to $\sigma_{sc} = \sqrt{\sigma_{c}^2 - \sigma_{sc}^2}$. Here, $\sigma_n$ is the nuclear relaxation rate, almost constant in the covered temperature range and extremely small for Zr$_5$Pt$_3$, as confirmed also by ZF-$\mu$SR data (see Fig. 8). At low magnetic fields ($H_{app}/H_{c2} \approx 0.04 < 1$), the effective magnetic penetration depth $\lambda_{eff}$ and, thus, the superfluid density $\rho_{sc}(\propto \lambda^{-2})$, can be calculated using $\sigma_{c}^2(T)/\gamma^2 = 0.00371 \Phi_0^2 / \lambda_{eff}^4(T)$ [26, 31].

The superfluid density $\rho_{sc}$ of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ vs the reduced temperature $T/T_c$ is shown in Figs. 7(a) and 7(b), respectively. In both cases, the temperature-invariant superfluid density below $T_c/3$ suggests the absence of low-energy

**FIG. 5.** Upper critical field $H_{c2}$ vs the reduced transition temperature $T_c/T_c(0)$ for Zr$_5$Pt$_3$ (a), Zr$_5$Pt$_3$C$_{0.05}$ (b), Zr$_5$Pt$_3$C$_{0.15}$ (c), and Zr$_5$Pt$_3$C$_{0.3}$ (d). The $T_c$ values were determined from measurements shown in Fig. 4. For Zr$_5$Pt$_3$C$_{0.3}$, the $T_c$ values determined from $C(T,H)/T$ (open symbols) are consistent with the values determined from $\rho(T,H)$ (closed symbols). The solid and dash-dotted lines represent fits to the GL- and WHH-models.

**FIG. 6.** TF-$\mu$SR spectra collected in the normal and superconducting states in an applied magnetic field of 30 mT for Zr$_5$Pt$_3$ (a) and Zr$_5$Pt$_3$C$_{0.3}$ (b). Fast Fourier transforms of the TF-$\mu$SR data shown in (a) at 0.3 K (c) and at 7 K (d). For Zr$_5$Pt$_3$, solid lines are fits to Eq. (1) using two oscillations, which are also shown separately as dash-dotted lines in (c), together with a background contribution. For Zr$_5$Pt$_3$C$_{0.3}$, solid lines are fits to Eq. (1) with a single oscillation. Note the clear field-distribution broadening due to FLL below $T_c$. The superfluid density $\rho_{sc}$ of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ vs the reduced temperature $T/T_c$ is shown in Figs. 7(a) and 7(b), respectively. In both cases, the temperature-invariant superfluid density below $T_c/3$ suggests the absence of low-energy
excitations and, hence, a fully-gapped superconducting state. Consequently, the \( \rho_s(T) \) was analyzed by means of a fully-gapped s-wave model:

\[
\rho_s(T) = \frac{\lambda_0^2(T)}{\lambda_0^2} = 1 + 2 \int_{\Delta(T)}^{\infty} \frac{\partial f}{\partial E} \frac{E dE}{\sqrt{E^2 - \Delta^2(T)}}.
\]  

(2)

Here, \( f = (1 + e^{E/k_BT})^{-1} \) is the Fermi function; \( \Delta(T) \) is the superconducting gap function, assumed to follow \( \Delta(T) = \Delta_0 \tanh \{ \Delta_0 \tanh \{ 1.82(1.018(T_c/1 - 1))^{0.51} \} \} [32, 33]; \Delta_0 \) and \( \Delta_0 \) are the magnetic penetration depth and the superconducting gap at 0 K, respectively. As shown by the solid lines in Fig. 7, the s-wave model describes \( \rho_s(T) \) very well across the entire temperature range with the fit parameters: \( \Delta_0 = 1.20(2) \) and \( 0.60(2) \) meV, and \( \Delta_0 = 333(3) \) and \( 493(2) \) nm for Zr\(_3\)Pt\(_3\) and Zr\(_5\)Pt\(_3\)C\(_3\), respectively. The gap value and the magnetic penetration depth of Zr\(_3\)Pt\(_3\)C\(_3\) are close to those of Zr\(_3\)Pt\(_3\)C\(_{0.5}\) [20]. We considered also the dirty-limit model [32], which turned out to describe fairly well the \( \rho_s(T) \) of Zr\(_3\)Pt\(_3\) and Zr\(_5\)Pt\(_3\)C\(_3\), yielding slightly lower superconducting gap values (see details in Table I).

2. Zero-field \( \mu \)SR

To verify the possible breaking of time-reversal symmetry in Zr\(_3\)Pt\(_3\)C\(_{0.3}\), we also performed ZF-\( \mu \)SR measurements in both its normal- and superconducting states. As shown in Fig. 8, neither coherent oscillations nor fast decays could be identified in the spectra collected above (10 K) and below \( T_c \) (2 K and 0.3 K), hence implying the lack of any magnetic order or fluctuations. The weak muon-spin relaxation in absence of an external magnetic field is mainly due to the randomly oriented nuclear moments, which can be modeled by a Gaussian Kubo-Toyabe relaxation function, \( G_{KT} = \frac{1}{2} + \frac{1}{3}(1 - \sigma_{2\mu}^2e^{-\sigma_{2\mu}^2T^2/2}) \) [27, 34]. Here, \( \sigma_{2\mu} \) is the zero-field Gaussian relaxation rate. The solid lines in Fig. 8 represent fits to the data by considering also an additional zero-field Lorentzian relaxation \( \lambda_{\Sigma} \), i.e., \( \lambda_{\Sigma}(T) = \lambda_{\Sigma} c e^{-\lambda_{\Sigma} e^{-t/2}} + \lambda_{bg} \). The relaxation rates in the normal- and the superconducting states are almost identical, as confirmed by the practically overlapping ZF-\( \mu \)SR spectra above and below \( T_c \). The resulting relaxations at 0.3 K are listed in Table I. This lack of evidence for an additional \( \mu \)SR relaxation below \( T_c \) excludes a possible time-reversal symmetry breaking in the superconducting state of Zr\(_5\)Pt\(_3\)C\(_{0.3}\).

E. \( ^{195}\text{Pt-NMR study} \)

Zr\(_5\)Pt\(_3\)C\(_x\) samples contain three NMR-active nuclei, i.e., \( ^{123}\text{C} \), \( ^{89}\text{Zr} \), and \( ^{195}\text{Pt} \). However, the 1.1% isotopic abundance of \( ^{123}\text{C} \) mixture with the low carbon content of the samples and its omnipresence in the probehead, made it difficult to use the \( ^{13}\text{C} \) NMR signal of Zr\(_5\)Pt\(_3\)C\(_x\). The low-frequency, low-abundance \( ^{195}\text{Zr} \), associated with its quadrupole effects (I = 5/2) made it unsuitable, too. Consequently, in the current work, we focus on the \( ^{195}\text{Pt} \) NMR results. A representative full-frequency scan is shown in Fig. S2, while the frequency ranges covered at low-\( T \) are listed in Table S1 of SM [23].

1. Static electronic properties: Knight shift

The \( ^{195}\text{Pt} \) NMR line shapes (see Fig. S3 in SM [23]) were recorded by a standard spin-echo sequence and successively fitted with the Dmfit software [35]. By assuming a purely Gaussian profile for the spin-1/2 nuclei, we determined the precise peak positions and line widths. The Pt atoms reside in 6g sites [16] and are bonded in a 9-coordinate geometry to Zr atoms. Since the latter occupy two inequivalent sites (6g and 4d), of which the first with a 9% spread in Pt-Zr distances, relatively wide \( ^{195}\text{Pt} \) NMR lines are expected. Due to the large width of the lines, the shifts appear as small (see Fig. S3 [23]). Yet, numerical fits provide shift values typical of metallic compounds (i.e., a fraction of percent). As shown in Fig. 9, in the normal state, both Zr\(_3\)Pt\(_3\) and Zr\(_5\)Pt\(_3\)C\(_3\) exhibit a temperature-independent frequency shift (known as Knight shift, \( K \)) and linewidth (full width at half maximum, \( FWHM \)). In Zr\(_5\)Pt\(_3\) (red symbols), we find \( K = 0.195\% \) and
In the normal state, both parameters are constant with temperature. Below $T_c$, we observe an increase in shift (see text for details). The arrows mark the $T_c$ values.

$$I_{\text{FWHM}} = 150 \text{kHz}, \text{ while in Zr}_5\text{Pt}_3\text{C}_{0.3} (\text{blue symbols}) these values are 10% and 5% lower, respectively.}

Similar features (i.e., wide lines, small and/or positive shifts, and no temperature dependence) have been reported also in NiPtP metallic glasses [36] or in Pt-Mo alloys [37]. These are to be compared with the $-3.5\%$ $^{195}\text{Pt}$ shift in elemental metallic Pt, whose large negative value is known to arise from a dominant core-polarization contribution [38]. In Mott’s two-band $(s + d)$ model, the density of states of the narrow $d$-band is much greater than that of the much wider $s$-band. Hence, any property which depends on the electronic density of states will, in general, be dominated by the unfilled $d$-band. In our case, the resulting positive increase in $^{195}\text{Pt}$ Knight shift provides evidence that the Pt $d$-states are filled, consistent with a charge transfer from Zr to the transition-metal atoms (we recall that Pt is twice as electronegative as Zr on the Pauling scale). In addition, the wide $^{195}\text{Pt}$ NMR linewidths, besides a distribution of atomic environments, suggest also a distribution in the degree of hybridization effects [39, 40].

The orbital Knight shift, here preponderant and temperature independent, not only justifies our normal-state results, but also explains why the change in shift in the superconducting phase is so small. The increase in shift with decreasing temperature, we observe below $T_c$, is surprising. A possible reason for this might be the locally higher magnetic field at the SC vortex cores (see further). A similar behavior has been reported, e.g., in $\text{V}_3\text{Ga}$ [41], where it was attributed to a significant reduction of the spin susceptibility. Independently of sign, a change in $K$ across $T_c$ represents a clear fingerprint of a fully-gapped conventional SC in $\text{Zr}_5\text{Pt}_3\text{C}_2$.

2. Dynamic electronic properties: Relaxation rates

In the superconducting state, the spin-lattice relaxation rates $T_1^{-1}$ follow a thermally-activated behavior (see Fig. 10), whereas at temperatures above $T_c$, both samples exhibit an almost linearly dependent $T_1^{-1}(T)$ (see inset in Fig. 11). Since both samples exhibit almost identical relaxation rates across the whole temperature range, this implies that carbon doping does not significantly affect the relaxation mechanisms, here dominated by electronic fluctuations related to the Pt and Zr atoms. Note that the absence of a clear anomaly in $T_1^{-1}(T)$ curves near the onset of SC for both compounds is most likely attributed to their broad superconducting transition. In the normal state, the temperature-dependent spin-lattice relaxation rates $T_1^{-1}(T)$ provide useful insights into the dynamics of conduction electrons and their degree of correlations. Above $T_c$, $T_1^{-1}(T)$ deviates from a purely linear temperature dependence, clearly highlighted by the $(T_1 T)^{-1}$ vs $T$ plot in Fig. 10, an indication of weak- to moderate electron correlations. In a first approximation, the estimated value of $(T_1 T)^{-1}$ at low temperature is about $4.72 \text{s}^{-1}\text{K}$. By a comparison to diborides, such as, MgB$_2$, AlB$_2$, and ZrB$_2$ (also binary superconductors [42]), this value indicates a relatively high electron density of states at the Fermi level (here dominated by the Zr and Pt $d$ bands).

Now we discuss the NMR relaxation rates in the superconducting state. In an $s$-wave superconductor, the opening of an electronic energy gap below $T_c$ implies an exponential decay of the NMR relaxation rate $T_1^{-1}$ [43]:

$$T_1^{-1} \propto \exp\left(\frac{-\Delta_0}{k_B T}\right).$$

Here, $\Delta_0$ is the same as in Eq. (2). In the superconducting state, after a slight initial enhancement, most likely due to the relaxation of nuclei inside the vortex cores [44], $T_1^{-1}$ decreases exponentially and is described very well by Eq. (3) for both Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$. It is worth noting that, at 0 K, it converges towards zero (see inset in Fig. 10), thus suggesting that the electronic spin fluctuations represent the dominant relaxation channel (reflecting the exponential decrease of unpaired electrons in superconducting phase). This result also indicates the high quality of the samples (i.e., a negligible concentration of impurities and a 100% SC...
volume fraction). At the same time, spin fluctuations might account for the drop in signal intensity (wipeout effect [45]) we observe below $T_c$ (see Fig. S6 in SM).

The superconducting gaps $\Delta_0$ derived from Eq. (3) are listed in Table I. The gap sizes are slightly different from the TF-µSR results, most likely related to the limited temperature range we can cover with our NMR setup. Although a coherence (Hebel-Slichter, HS) peak [46] just below $T_c$ is a fingerprint of s-wave superconductivity, its absence not necessarily rules it out. Many factors may account for the suppression of the HS peak (as discussed in more detail in Ref. 47), but here we attribute it to the relevant contribution of d orbitals at the Fermi level.

Finally, we consider the degree of electron correlation in the normal state which, in an ideal-metal case, can be deduced from the Korringa relation [48]:

$$ S = T_1 T K_s^2 = a S_0, \quad \text{with} \quad S_0 = \frac{\gamma_e^2}{\gamma_n^2} \frac{\hbar}{4 \pi k_B}, \quad (4) $$

where $S$ is the Korringa constant, $\gamma_e$ is the gyromagnetic ratio of free electrons, and $\gamma_n$ that of the probe nucleus. We recall that, the total Knight shift $K$ comprises both a spin- $K_s$ and a (constant) orbital part $K_{\text{orb}}$. In case of a dominant $K_s$, arising from the Fermi-contact (i.e., momentum-independent) interaction associated with the Pauli susceptibility $\chi_p$, the Korringa relation implies an $a$ close to 1. As shown in Fig. 11, apart from a weak temperature dependence due to $T_1(T)$, both compounds exhibit Korringa constants lower than $S_0$ (note that, in Fig. 11, we report $S_0/S$ on the y-axis). Clearly, the assumption of an s-type Fermi-contact interaction, required for the validity of the Korringa relation, is not fulfilled in our case. By accounting for the Pines corrections [49] to Eq. (4) (which include the terms $1/\rho^2(E_F)$ and $\chi_p^2$, reflecting the real density of states and spin susceptibility), we infer that the real $\rho(E_F)$ due to s electrons is less than expected. This suggests that the relaxation has a substantial orbital character, proportional to the density of d-states at the Fermi level, but otherwise the correlation is low. Therefore, we expect Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_{0.3}$ to be weakly correlated metals, despite a seemingly small $S$ value.

### IV. DISCUSSION

First, we discuss why our Zr$_5$Pt$_3$C$_x$ samples show a different evolution of $T_c$ with C-content compared to a previous study, where the $T_c$ values first increase from 6 K (for $x = 0$) to 7 K (for $x = 0.3$). Then, upon further increasing the C-content, $T_c$ decreases continuously to 3.5 K (for $x = 0.7$) [16]. In our case, conversely, $T_c$ decreases to 4.5 K already upon a 5% C intercalation (i.e., $x = 0.05$). Then, upon further increasing the C-content, $T_c$ remains almost constant with $x$. Such a different evolution of $T_c$ might be due to a carbon content differing from the nominal one, implying slightly different modifications of the crystal structure. In the previous study, upon C intercalation, the lattice was found to expand in the ab-plane, but to compress along the c-axis, resulting in a progressive decrease of the $c/a$ ratio. This is also the case of the Nb$_5$Ir$_{3-x}$Pt$_x$O family, where a smaller $c/a$ ratio leads to a higher $T_c$ value [17].

Our Zr$_5$Pt$_3$C$_x$ samples, instead, show an opposite behavior, with the $c/a$ ratio increasing with C-content [see Fig. 1(b)].

Why our Zr$_5$Pt$_3$C$_x$ samples show a different lattice evolution compared to the previous work is not yet clear and requires further investigation.

Second, in the previous study, the temperature-dependent electronic specific heat and magnetic penetration depth (calculated from the lower critical field $H_{c1}$) suggest a nodal superconducting gap in Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_0.3$ and possibly unconventional SC [16]. However, both measurements were limited to $\sim 2$ K, i.e., only down to 1/3$T_c$. To reliably reveal the superconducting pairing, measurements at temperatures far below the onset of SC (i.e., at $T < 1/3T_c$) are crucial, which is also one of the motivations of our study. Therefore, the original conclusion about unconventional SC in Zr$_5$Pt$_3$C$_0.3$ is not solid. This is clearly demonstrated in Fig. S7 of SM [23], where we show the magnetic penetration depth $\lambda$ vs the reduced temperature $T/T_c$ for Zr$_5$Pt$_3$C$_0.3$, both for our sample and for that reported in Ref. 16. As can be clearly seen, the $\lambda(T)$ determined from TF-µSR shows an exponential temperature dependence below 1/3$T_c$. For an isotropic single-gap superconductor, the magnetic penetration depth at $T \ll T_c$ follows $\lambda(T) - \lambda_0 = \lambda_0 \sqrt{T/T_c} e^{-\Delta_0/2T_c}$ [50], where $\lambda_0$ and $\Delta_0$ are the same as in Eq. (2). The solid line in Fig. S7 [23] is a fit to the above equation, yielding a similar superconducting gap size as that determined from superfluid density $\rho_s(T)$ in Fig. 7. The inset in Fig. S7 [23] replots the $\lambda$ vs. $(T/T_c)^2$. As indicated by the dash-dotted lines, both data sets exhibit a $T^2$ dependence down to $T/T_c \sim 0.3$, while below it, $\lambda(T)$ deviates significantly from the $T^2$ dependence, decreasing exponentially with temperature, consistent with a fully-gapped SC state. We expect also the electronic specific heat to exhibit a similar exponential behavior, although currently the relevant low-temperature data are not yet available. To conclude, the limited temperature range of the previous experimental data might lead to an incorrect conclusion about the nature of SC [16]. By contrast, our TF-µSR measurements, performed down to 0.3 K, i.e., well inside the SC state, combined with NMR results, prove beyond reasonable doubt the conventional character of Zr$_5$Pt$_3$C$_{0.3}$ superconductivity.

Third, the µSR and NMR data of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$C$_0.3$ presented here, together with the previous study on Zr$_5$Pt$_3$C$_{0.5}$, suggest that the conventional SC of Zr$_5$Pt$_3$C$_{0.3}$ is independent of carbon content. Unlike the Nb$_5$Ir$_{3-x}$Pt$_x$O family, where a crossover from multiple- to single-gap SC is observed upon
Table I. Normal- and superconducting-state properties of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$Co$_x$, as determined from electrical-resistivity-, magnetization-, heat-capacity-, NMR-, and µSR measurements. The data for Zr$_5$Pt$_3$Co$_{0.3}$ were taken from Ref. 20.

| Property | Unit | Zr$_5$Pt$_3$ | Zr$_5$Pt$_3$Co$_{0.3}$ | Zr$_5$Pt$_3$Co$_{0.5}$ |
|----------|------|-------------|----------------------|----------------------|
| $\rho_0$ | mΩcm | 0.095       | 0.155                | —                    |
| $T^p_\sigma$ | K | 6.1 | 4.4 | 3.8 |
| $T^p_\tau$ | K | 6.3 | 4.5 | 3.8 |
| $T^p_\pi$ | K | — | 4.1 | 3.9 |
| $T^p_{\text{SR}}$ | K | 6.2 | 3.9 | 3.7 |
| $\mu_0H_{c1(0)}$ | mT | 5.5(1) | 4.4(1) | 5.9 |
| $\mu_0H_{c2(0)}$ | mT | 6.5(1) | 3.2(1) | 3.4 |
| $\Delta_{\text{SR}}^{\text{E}}$ | meV | 7.21(5) | 6.97(6) | 5.4 |
| $\Delta_{\text{SR}}^{\text{C}}$ | meV | 1.20(2) | 0.60(2) | 0.59 |
| $\Delta_{\text{NMR}}^{\text{E}}$ | meV | 1.17(2) | 0.47(2) | — |
| $\Delta_{\text{NMR}}^{\text{C}}$ | meV | 0.98(8) | 1.08(8) | — |
| $E(0)$ | nm | 6.10(3) | 6.25(2) | 7.81 |
| $k_0$ | — | 61 | 67 | 60 |
| $\lambda_0$ | nm | 333(3) | 493(2) | 469 |
| $\lambda_{\text{c}}(0)$ | nm | 366(4) | 415(6) | — |
| $\lambda_{2\sigma}(0.3 \text{ K})$ | $\mu s^{-1}$ | 0.018(2) | — |
| $\sigma_{2\sigma}(0.3 \text{ K})$ | $\mu s^{-1}$ | 0.048(8) | — |
| $\lambda_{2\sigma}(10 \text{ K})$ | $\mu s^{-1}$ | 0.015(4) | — |
| $\sigma_{2\sigma}(10 \text{ K})$ | $\mu s^{-1}$ | 0.048(8) | — |

a Calculated by $\mu_0H_{c1} = (\Phi_0/4\pi\lambda^2)[\ln(x) + 0.497]$.
b Derived from clean-limit model.
c Derived from dirty-limit model.

Pt doping [17, 18], here, the single-gap SC in Zr$_5$Pt$_3$Co$_x$ is robust against the intercalation of interstitial carbon atoms. This is most likely attributed to their similar electronic band structures. According to DFT calculations, up to six bands cross the Fermi level [20]. The density of states (DOS) is dominated by Zr d-orbitals (up to 68% of the total DOS, the rest being due to Pt), while the contribution of C p-orbitals is negligible. Moreover, the change in DOS is only about 10%, even when increasing the C-content up to $x = 1$.

V. CONCLUSION

To summarize, we investigated the normal- and superconducting properties of Zr$_5$Pt$_3$Co$_x$ ($x = 0-0.3$) family of compounds by means of electrical resistivity-, magnetization-, heat-capacity-, µSR, and NMR measurements. The Zr$_5$Pt$_3$Co$_x$ exhibit bulk SC with $T_c$ between 4.5 K and 6.3 K. The electrical-resistivity measurements under applied magnetic field reveal a zero-temperature upper critical field of $7$ T. The temperature dependence of the superfluid density reveals a nodeless SC in Zr$_5$Pt$_3$Co$_x$, well described by an isotropic $s$-wave model. The conventional nature of Zr$_5$Pt$_3$Co$_x$ superconductivity is also supported by the exponential temperature-dependent NMR relation rate and the change of Knight shift below $T_c$. Finally, the lack of spontaneous magnetic fields below $T_c$ indicates that the time-reversal symmetry is preserved in the Zr$_5$Pt$_3$Co$_x$ superconductors.

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