Nodeless superconductivity and time-reversal symmetry breaking in the noncentrosymmetric superconductor $\text{Re}_{24}\text{Ti}_5$


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The noncentrosymmetric superconductor Re$_{24}$Ti$_5$, a time-reversal symmetry- (TRS-) breaking candidate with $T_c = 6$ K, was studied by means of muon-spin rotation/relaxation (μSR) and tunnel-diode oscillator techniques. At the macroscopic level, its bulk superconductivity was investigated via electrical resistivity, magnetic susceptibility, and heat-capacity measurements. The low-temperature penetration depth, superfluid density, and electronic heat capacity all evidence an $s$-wave coupling with an enhanced superconducting gap. The spontaneous magnetic fields revealed by zero-field μSR below $T_c$ indicate a time-reversal symmetry breaking and thus the unconventional nature of superconductivity in $\text{Re}_{24}\text{Ti}_5$. The concomitant occurrence of TRS breaking also in the isostructural $\text{Re}_6(\text{Zr},\text{Hf})$ compounds hints at its common origin in this superconducting family and that an enhanced spin-orbital coupling does not affect pairing symmetry.

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Superconductors with inversion centers can host either even-parity spin-singlet or odd-parity spin-triplet states. These strict symmetry-imposed requirements, however, are relaxed in noncentrosymmetric superconductors (NCSCs) where parity-mixed superconducting states are also allowed. In these materials the lack of an inversion symmetry often induces an antisymmetric spin-orbit coupling (ASOC), which can lift the degeneracy of conduction-band electrons. Since the extent of parity mixing is determined by the strength of the SOC, formally similar compounds, but with different spin-orbit couplings, can exhibit different degrees of parity mixing.

The recent interest in NCSCs is related to the complex nature of their superconducting properties [1,2]. Because of the mixed pairing, noncentrosymmetric superconductors can display significantly different properties compared to their conventional counterparts. Some NCSCs, such as CePt$_3$Si [3], CeIrSi$_3$ [4], Li$_2$Pt$_3$B [5,6], and Mo$_3$Al$_2$C [7] exhibit line nodes, whereas others, such as LaNiC$_2$ [8] and (La,Y)$_2$C$_3$ [9] show multiple superconducting gaps. Furthermore, because of the spin-triplet pairing, the upper critical field often exceeds the Pauli limit as has been found, e.g., in CePt$_3$Si [10] and Ce(Rh,Ir)Si$_3$ [11,12]. Finally, some NCSCs, as e.g., LaNiC$_2$ [13], Re$_6$(Zr,Hf) [14,15], and La-Ir$_3$ [16] are known to break the time-reversal symmetry (TRS).

The binary alloy Re$_{24}$Ti$_5$ is a NCSC with superconducting temperature $T_c = 6$ K as reported already in the 1960s [17], but its macroscopic physical properties were studied in detail only recently [18]. In this Rapid Communication we explore in details the microscopic nature of its superconductivity (SC). Similar to Re$_{24}$Zr$_5$ and Re$_{24}$Nb$_5$, Re$_{24}$Ti$_5$ also adopts an (α-Mn)-type crystal structure with space-group $I-43m$. However, although the former compounds have been widely studied by means of macro- and microscopic techniques [19,20], much less is known about Re$_{24}$Ti$_5$. A simple analogy, based on structural similarity, can lead to the wrong conclusions since a SOC-dependent parity mixing can bring about rather different superconducting properties. Since its sister compounds Re$_6$(Zr,Hf) are known to break the TRS in the superconducting state [14,15], Re$_{24}$Ti$_5$ represents an ideal opportunity to search for TRS breaking and unconventional SC in a material with a modified SOC value. Moreover, the study of additional NCSCs can bring new insight into the nature of unconventional superconductivity in general.

Considering the key role played by muon-spin-relaxation and rotation (μSR) techniques in unraveling the presence of TRS breaking in unconventional superconductors [21], in this Rapid Communication, we report on the systematic magnetization, transport, thermodynamic, tunnel-diode oscillator (TDO), and μSR studies of Re$_{24}$Ti$_5$, with particular focus on the latter. We find that below $T_c$ spontaneous magnetic fields appear, implying a superconducting state which breaks TRS and has an unconventional nature. The low-temperature...
penetration depth, superfluid density, and electronic specific heat all suggest a nodeless $s$-wave pairing mechanism.

Polycrystalline $\text{Re}_2\text{Ti}_3$ samples were prepared by arc melting $\text{Re}$ and $\text{Ti}$ metals under argon atmosphere and then annealed at 900°C for two weeks. The x-ray powder diffraction, measured on a Bruker D8 diffractometer, confirmed the $\alpha$-$\text{Mn}$ structure of $\text{Re}_2\text{Ti}_3$. Magnetic susceptibility, electrical resistivity, and specific-heat measurements in different applied magnetic fields were performed on a 7-T Quantum Design property measurement system and a 14-T physical property measurement system. The $\mu$SR measurements were carried out using the general-purpose instrument located at the $\pi$M3 beamline of the Swiss Muon Source of the Paul Scherrer Institut in Villigen, Switzerland. The temperature-dependent shift of magnetic-penetration depth was measured by using a TDO technique in a He$^3$ cryostat at an operating frequency of 7 MHz.

The magnetic susceptibility, measured at 1 mT using field-cooling (FC) and zero-field-cooling (ZFC) procedures, is shown in Fig. 1(a). The splitting of the two curves is typical of type-II superconductors, and the ZFC susceptibility indicates bulk superconductivity with $T_c = 6$ K. The electrical resistivity drops at the onset of superconductivity at 6.8 K, becoming zero at 6 K [see Fig. 2(a)]. The bulk nature of SC is further confirmed by specific-heat data [see Fig. 2(b)].

In transverse-field- (TF-) $\mu$SR measurements of superconductors, the applied magnetic field should exceed the lower $\mu_0H_{c1}$ critical value so that the additional field-distribution broadening due to the flux-line lattice (FLL) can be quantified from the muon decay rate. To determine $\mu_0H_{c1}$, the field-dependent magnetization was preliminarily measured at various temperatures below $T_c$ as shown in Fig. 1(b). The derived $\mu_0H_{c1}$ values are plotted in Fig. 1(c) as a function of temperature. The solid line is a fit to $\mu_0H_{c1}(T) = \mu_0H_{c1}(0)[1 - (T/T_c)^2]$, determining $\mu_0H_{c1}(0) = 8.3(1)$ mT.

![FIG. 1. (a) Temperature dependence of magnetic susceptibility $\chi(T)$ for $\text{Re}_2\text{Ti}_3$. (b) Magnetization versus applied magnetic field recorded at different temperatures up to $T_c$. For each temperature, $\mu_0H_{c1}$ was determined as the value where $M(H)$ deviates from linearity. (c) $\mu_0H_{c1}$ versus temperature: the solid line, a fit to $\mu_0H_{c1}(T) = \mu_0H_{c1}(0)[1 - (T/T_c)^2]$, determines $\mu_0H_{c1}(0) = 8.3(1)$ mT.](image)

![FIG. 2. (a) Temperature-dependent electrical resistivity and (b) specific heat at different applied magnetic fields up to 12 T. From (c) the suppression of $T_c$ with an increasing field we determine an upper critical field $\mu_0H_{c2}(0) = 11.2(1)$ T. The dashed line represents a fit to the Werthamer-Helfand-Hohenberg (WHH) model without spin-orbit scattering, whereas the dashed-dotted line is a fit to the Ginzburg-Landau model (see the text).](image)
possibility of a singlet-triplet-mixing state. For completeness, we estimated the upper critical field also by means of the Ginzburg-Landau model \( \mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)(1 - T^2)/(1 + T^2) \), where \( T = T/T_c \) is again the normalized temperature. As shown in Fig. 2(c) by a dashed-dotted line, at low fields, the fit is quite good. However, at higher applied fields, the fit deviates significantly from the data, providing an overestimated critical field value of \( \mu_0 H_{c2}^{\text{eff}}(0) = 13.6(2) \) T. The remarkable agreement of the more elaborate WHH model with experimental data is clearly seen in Fig. 2(c).

To investigate the superconducting properties of \( \text{Re}_2\text{Tis} \) on the microscopic level, we carried out TF-\( \mu \)SR measurements in an applied field of 20 mT. The optimal field value for such experiments was determined via a preliminary field-dependent \( \mu \)SR depolarization-rate measurement at 1.5 K. To avoid flux-pinning issues, the magnetic field (up to 750 mT) was applied in the normal state, and then the sample was cooled down to 1.5 K. As shown in Fig. 3(a), the resulting Gaussian relaxation rate \( \sigma_{sc} \) versus the applied magnetic field exhibits a maximum near the lower critical field [see Fig. 1(c)]. By considering the decrease in intervortex distance with field and vortex-core effects, a field of 20 mT (shown with an arrow), almost twice the \( \mu_0 H_{c1}(0) \) value, was chosen for the temperature-dependent study.

Figure 3(b) shows two representative TF-\( \mu \)SR spectra collected above and below \( T_c \). Below \( T_c \), the fast decay of muon-spin polarization reflects the inhomogeneous field distribution due to the FLL in the mixed superconducting state. The time-domain spectra were fitted by means of the following model with a Gaussian decay:

\[
A_T = A_s \cos(\gamma \mu B t + \phi) e^{-\sigma t^2/2} + A_{bg} \cos(\gamma \mu B_{bg} t + \phi).
\]  

(1)

Here \( A_s \) and \( A_{bg} \) are the initial muon-spin asymmetries for muons implanted in the sample and sample holder, respectively, with the latter not undergoing any depolarization. \( \gamma \mu = 2\pi \times 135.53 \) MHz/T is the muon gyromagnetic ratio, \( B_t \) and \( B_{bg} \) are the local fields sensed by implanted muons in the sample and sample holder, \( \phi \) is the (common) initial precession phase, and \( \sigma \) is a Gaussian-relaxation rate. Given the nonmagnetic nature of the sample holder, \( B_{bg} \) practically coincides with the applied magnetic field and was used as an intrinsic reference.

In the superconducting state, the Gaussian-relaxation rate includes contributions from both the FLL (\( \sigma_{sc} \)) and the nuclear magnetic moments (\( \sigma_n \)). Since \( \sigma_n \) is expected to be temperature independent in the considered temperature range, the FLL-related relaxation rate can be derived by subtracting the nuclear contribution from the measured Gaussian relaxation, i.e., \( \sigma_{sc} = \sqrt{\sigma^2 - \sigma_n^2} \). Since \( \sigma_{sc} \) is directly related to the superfluid density \( (\sigma_{sc} \propto 1/\lambda^2) \), the superconducting gap value and its symmetry can be determined from the temperature-dependent relaxation rate \( \sigma_{sc}(T) \). For small applied magnetic fields [in comparison with the upper critical field, i.e., \( H_{appl}/H_{c2} \ll 1 \)], the effective penetration depth \( \lambda_{eff} \) can be calculated from \([25,26]\)

\[
\frac{\sigma_{sc}^2(T)}{\gamma \mu^2} = 0.00371 \frac{\Phi_0}{\lambda_{eff}^4(T)}.
\]  

(2)
In a polycrystalline sample, the effective penetration depth $\lambda_{\text{eff}}$ is usually determined by the shortest penetration depth $\lambda_{ab}$, the two being related via $\lambda_{ab} = 3^{1/2} \lambda_{ab}$ [27]. Figure 3(c) shows the normalized superfluid density ($\rho_{sc} \propto \lambda_{ab}^{-2}$) as a function of temperature for Re24Ti5. The $\lambda_{ab}$ data calculated from $\mu$SR data and those from TDO measurements are also plotted, both clearly consistent with the $\mu$SR results. The temperature-dependent behavior of $\lambda_{ab}$ is well described by an $s$-wave model with a single SC gap of about 1.08 meV and a $\lambda(0)$ of 298 nm. Such a superconducting gap is similar to that of other Re-based intermetallic superconductors, e.g., Re$_6$Zr (1.21 meV) [14,28], Re$_6$Hf (0.94 meV) [22,29], and Re$_{24}$Nb$_5$ (0.89 meV) [19]. Also the $2\Delta/k_B T_c$ values of these compounds [e.g., 4.2(1) for Re$_24$Ti$_5$] are higher than 3.53, the value expected for a weakly coupled BCS superconductor, thus indicating moderately strong electron-phonon couplings in these materials. Moreover, the low-temperature penetration depth, shown in the inset of Fig. 3(c), exhibits an exponential behavior $\Delta(0) = 1.9(1)k_B T_c$. It reproduces very well the experimental data while being consistent with the TF-$\mu$SR and TDO results [see Fig. 3(e)]. The ratio $\Delta C/\gamma T_c$ was found to be 1.4, consistent with previous data [18] and in good agreement with the BCS-theory value of 1.43.

To address the key question of the occurrence of time-reversal symmetry breaking in Re$_{24}$Ti$_5$, we made use of ZF-$\mu$SR. The large muon gyromagnetic ratio, combined with the availability of 100% spin-polarized muon beams, make ZF-$\mu$SR a very powerful technique to detect the spontaneous fields as shown by its successful use in previous studies of Re$_6$(Zr,Hf) [14,15], La$_2$Ir$_3$ [16], Sr$_2$RuO$_4$ [21], and PrOs$_4$Sb$_{12}$ [30]. Normally, in the absence of external fields, the onset of the superconducting phase does not imply changes in the ZF muon-spin-relaxation rate. However, in the case of TRS breaking, the onset of tiny spontaneous currents gives rise to associated (weak) magnetic fields, promptly detected by ZF-$\mu$SR as an increase in the muon-spin-relaxation rate. Given the tiny size of such effects, we measured carefully the muon-spin-relaxation rate both well above $T_c$ and well inside the superconducting phase. As shown in Fig. 4(a), two representative ZF-$\mu$SR spectra collected above (8 K) and below (1.5 K) $T_c$ show clear differences, especially at long times. To exclude the possibility of stray magnetic fields (which in any case would affect uniformly all data sets), the magnets were quenched before the measurements, and we made use of an active field-nulling facility. Without an external field, the relaxation is determined mostly by the nuclear magnetic moments, normally described by a Gaussian Kubo-Toyabe relaxation function [31,32]. A possible spontaneous field contribution is accounted for by an additional exponential decay term. Consequently, the ZF-$\mu$SR spectra could be fitted by means of a combined Lorentzian and Gaussian Kubo-Toyabe relaxation function,

$$A_{\text{CKT}} = A_s \left\{ \frac{1}{3} + \frac{2}{3}(1 - \sigma^2t^2 - \Delta t) \right\} + A_{\text{bg}},$$

Fig. 4. (a) Representative zero-field $\mu$SR spectra for Re$_{24}$Ti$_5$ at 1.5 and 8 K and relevant fits by means of Eq. (3). A typical longitudinal-field (LF) LF-$\mu$SR data set, collected at 1.5 K in a 30-mT longitudinal field, is also shown. (b) Temperature dependence of the nuclear relaxation rate $\sigma$, and (c) electronic relaxation rate $\Lambda$. Although $\sigma$ is almost temperature independent, $\Lambda$ shows a distinct increase below $T_c$.

Here $A_s$ is the initial sample-related muon-spin asymmetry, whereas $A_{\text{bg}}$ represents a time- and temperature-independent background. As already shown in the TF-$\mu$SR case (see Fig. 3), both the background and the nuclear contributions to the decay are independent of temperature. This is clearly the case also with ZF-$\mu$SR [see Fig. 4(b)], where $\sigma(T)$ remains constant (within the experimental error) in the studied temperature range. On the other hand, the exponential component, related to the presence of spontaneous magnetic fields, shows a small yet distinct increase as the temperature is lowered below $T_c$ [see Fig. 4(c)].

Such an increase in $\Lambda(T)$, similar to that found also in Re$_6$(Zr,Hf) [14,15], represents the signature of spontaneously occurring magnetic fields and of TRS breaking in the Re$_{24}$Ti$_5$ noncentrosymmetric superconductor. Given the small size of the considered effect, to rule out the possibility of an impurity-induced relaxation (typically relevant at low temperatures), we performed auxiliary LF-$\mu$SR measurements at 1.5 K. As shown in Fig. 4(a), a field of 30 mT only is sufficient to lock the muon spins and to completely decouple them from the weak spontaneous magnetic fields, thus removing any relaxation traces related to them.

Up to now, several NCSCs, including LaNiC$_2$ [13], Re$_6$(Zr,Hf) [14,15], and La$_2$Ir$_3$ [16] have been found to exhibit a TRS breaking in the superconducting state. Yet, in many others, as, e.g., Mo$_3$Al$_2$C [7], Mg$_{10}$Ir$_9$B$_{16}$ [33], Re$_3$W [34], and PbTaSe$_2$ [35], the TRS is preserved. The Re$_{24}$Ti$_5$...
NODELESS SUPERCONDUCTIVITY AND TIME-REVERSAL … PHYSICAL REVIEW B 97, 020502(R) (2018)

considered here, a sister compound to Re₆(Zr,Hf), is a new member of the TRS-breaking NCSCs, despite a relatively reduced ASOC. This strongly suggests that, although the presence of an ASOC seems essential to induce a TRS breaking in NCSCs, its strength is not a crucial condition. Indeed, although LaNiC₂ [13] has a much weaker ASOC compared to La₇Ir₃ [16], the respective changes in zero-field muon-relaxation rates are comparable (ΔΛ ≳ 0.01 μs⁻¹). In our case, too, the replacement of the 3d Ti by the 3d Ti reduces remarkably the ASOC, yet the effects on TRS breaking remain comparable. Hence, we believe that TRS breaking in NCSCs is mostly related to the crystal-structure symmetry and, to test such a hypothesis, La₇Ti₃ compounds (T = transition metal, e.g., Ni, Pd, Rh, and Pt) represent good candidates since all of them exhibit a Th₃Fe₃-type crystal structure with the 3d to 5d transition metals covering a wide ASOC range.

The spin-triplet states can give rise to spontaneous fields in the superconducting state, which break the TRS. Most of these TRS-broken phases exhibit nodes in the superconducting state, which break the TRS. Most transition metals covering a wide ASOC range.

To summarize, we investigated the noncentrosymmetric superconductor Re₂₄Ti₅ by means of μSR and TDO techniques. Bulk superconductivity with Tc = 6 K was characterized by magnetization, transport, and specific-heat measurements. The low-temperature penetration depth, superfluid density, and the zero-field specific-heat data reveal a nodeless superconductivity in Re₂₄Ti₅, well described by an isotropic s-wave model with a single gap. The spontaneous fields, which appear below Tc and increase with decreasing temperature, provide strong evidence that the superconducting state of noncentrosymmetric Re₂₄Ti₅ breaks TRS and has an unconventional nature.

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