Original citation:
Singh, D., K. P., Sajilesh, Barker, Joel, Paul, Don McK., Hillier, A. D. and Singh, R. P. (2018) *Time-reversal symmetry breaking in the noncentrosymmetric superconductor Re6Ti*. Physical Review B, 97 (10). 100505(R). doi:10.1103/PhysRevB.97.100505

Permanent WRAP URL:
http://wrap.warwick.ac.uk/101305

Copyright and reuse:
The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions. Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher statement:
© 2018 American Physical Society

A note on versions:
The version presented here may differ from the published version or, version of record, if you wish to cite this item you are advised to consult the publisher’s version. Please see the ‘permanent WRAP URL’ above for details on accessing the published version and note that access may require a subscription.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk
Time-reversal symmetry breaking in the noncentrosymmetric superconductor Re₆Ti

D. Singh,1 Sajilesh K. P.,1 J. A. T. Barker,2 D. McK. Paul,2 A. D. Hillier,3 and R. P. Singh1,*
1Indian Institute of Science Education and Research Bhopal, Bhopal 462066, India
2Physics Department, University of Warwick, Coventry CV4 7AL, United Kingdom
3ISIS facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Oxfordshire OX11 0QX, United Kingdom

(Received 6 January 2018; published 12 March 2018)

We have investigated the superconducting state of the noncentrosymmetric superconductor Re₆Ti (Tc = 6.0 K) using a muon-spin rotation/relaxation technique. The non-zero-field muon experiment shows the presence of spontaneous magnetic fields in the superconducting state, indicating time-reversal symmetry breaking (TRSB). However, the low-temperature transverse-field muon measurements suggest nodeless s-wave superconductivity. Similar results were also observed for Re₆X (X = Zr, Hf) family of compounds which indicates that the pairing symmetry does not depend on the spin-orbital coupling. Altogether, these studies suggest an unconventional nature (TRSB) of superconductivity is intrinsic to the Re₆X family of compounds and paves the way for further studies of this family of materials.

DOI: 10.1103/PhysRevB.97.100505

Superconductors with a noncentrosymmetric crystal structure are of considerable interest due to their possible realization of unconventional superconductivity [1,2]. The lack of inversion symmetry in the lattices of these materials has significant implications on the symmetry of their superconducting state. The direct consequence of the broken inversion symmetry was first recognized in the noncentrosymmetric superconductor (NCS) CePt₃Si [3]. It shows upper critical field exceeding Pauli limiting field, indicating unconventional behavior [3–5]. In an NCS, the lack of inversion symmetry introduces a Rashba-type antisymmetric spin-orbit coupling (ASOC) [6,7], which results in the splitting of spin-up and spin-down conduction electron energy bands. This allows the mixing of orbital and spin parts of the Cooper wave function, which leads to parity mixed superconductivity. The extent of the parity mixing extent is determined by the strength of the ASOC.

Recently, rigorous experimental and theoretical investigations on NCSs have been carried out to understand their complex superconductivity properties. Indeed, unconventional superconductivity was found in several noncentrosymmetric superconductors. The examples are Li₂(Pd, Pt)B [8–11], Mo₃Al₂C [12], Re₃W [13], Nb₀.₁₈Re₀.₈₂ [14,15], Y₃C₃ [16], etc.

Recently, time-reversal symmetry breaking (a rarely observed phenomenon) has been observed in a few unconventional superconductors [17–23]. Due to parity mixed superconductivity, NCSs are prime candidates to exhibit this rarely observed phenomenon. To date, it has been reported to be observed only in a few NCS materials: LaNiC₂ [24], Re₆X (X = Zr, Hf) [25,26], Re₂₂Ti₁₅ [27], locally noncentrosymmetric SrPtAs [28], and La₇Ir₃ [29]. On the other hand, it found to be preserved in several other NCSs [12–14,16,30–32].

Our recent work primarily focused on the role of ASOC in controlling the parity mixing in NCS materials. The systems containing heavier transition-metal elements are of particular interest since there, the larger spin-orbit coupling may enhance the strength of the spin-triplet component in the pairing mixing ratio. In this regard, we systematically began the investigation on Re-based compounds with an α-Mn structure. The unconventional superconductivity was observed in a few members of the Re₆X family, e.g., Re₆Zr and Re₆Hf, which provides the evidence of time-reversal symmetry breaking (TRSB) in the superconducting ground state [25,26]. The relaxation rates associated with the TRSB signal in both the compounds were similar. This indicates that the strength of the ASOC does not play a major role in the pairing mechanism in these two materials. At the same time, contradictory results were also reported in the nuclear quadrupole resonance studies of the Re-Zr system, displaying the exponential decrease of 1/T₁ Hebel-Slichter peaks below Tc [33]. Hence, the relation between the breaking of inversion symmetry and time-reversal symmetry is not yet resolved.

Following this line of investigation, we have performed a microscopic study of Re₆Ti, which is another member of this family. Similar to its sister compounds Re₆Zr and Re₆Hf, Re₆Ti also crystallizes into an α-Mn structure with superconducting transition temperature Tc = 6.0 K. Since Ti atoms are smaller than Zr or Hf atoms, it is expected that the strength of SOC will be relatively modified, which may decrease the contribution of the spin-triplet component in the pairing mixing ratio. The effects of such changes can be relatively easily measured by muon-spin rotation (μSR) measurements which is extremely sensitive to such tiny changes in internal magnetic fields (0.1 G).

Furthermore, electronic structure calculations on the Re₆X(Zr, Hf) [34,35] family of compounds has shown that the density of states at the Fermi level is dominated by Re-5d orbitals. We have also performed zero-field μSR measurements on the isostructural NCS compound Re₂₂Ti₁₅ to examine the correlation effect of the modified Re composition on its superconducting state.
In this Rapid Communication, we show that the time-reversal symmetry is broken in the superconducting state of the binary transition-metal compound $\text{Re}_6\text{Ti}$. The TRSB signal in $\text{Re}_6\text{Ti}$ is very similar to the signal observed in other compounds ($\text{Re}_6\text{Zr}/\text{Hf}$) of this family. The low-temperature penetration depth measurements through transverse-field muon measurements suggest $s$-wave superconductivity. All these results indicate that the superconducting ground state in this family of materials is not affected by the enhanced spin-orbit coupling.

Polycrystalline samples of $\text{Re}_6\text{Ti}$ were prepared by melting stoichiometric amounts of $\text{Re}$ (99.95%; Alfa Aesar) and Ti (99.95%; Alfa Aesar) in an arc-melting furnace under ultrapure argon gas atmosphere on a water-cooled copper hearth. The samples were inverted and remelted several times to ensure homogeneous mixing of constituent elements. The resulting sample was then sealed inside an evacuated quartz tube and annealed at 850 °C for 1 wk to remove any thermal stresses. The powder x-ray diffraction pattern for $\text{Re}_6\text{Ti}$ was collected at room temperature using Cu $\text{K}\alpha$ radiation. Rietveld refined calculated pattern for the cubic noncentrosymmetric $\alpha$-$\text{Mn}$ (217) structure shown by a solid black line.

The powder x-ray diffraction pattern for $\text{Re}_6\text{Ti}$ was collected with the lattice cell parameter $a = 9.58(2)$ Å. The samples were characterized using magnetization and specific-heat measurements. The appearance of a strong diamagnetic signal at $T_c = 6.0 \pm 0.2$ K [Fig. 2(a)] confirms a superconducting transition in magnetization measurement. The low-temperature specific-heat measurement also confirms bulk superconductivity at $T_c$, where the normalized specific-heat jump $\Delta C/\gamma\text{C}_p T_c = 1.58 \pm 0.02$ (BCS value $= 1.43$). The specific-heat data in the superconducting state fits perfectly well for a single-gap $s$-wave superconductor [Fig. 2(b)], for $\Delta(0)/k_B T_c = 1.86$. This value is higher than the value for a BCS superconductor ($1.764$), suggesting moderately enhanced electron-phonon coupling. $\text{Re}_2\text{Ti}_5$ polycrystalline samples are also prepared by the same method as $\text{Re}_6\text{Ti}$, and its lattice and superconducting parameters are the same as reported by Lue et al. [36].

To probe the superconducting ground state of $\text{Re}_6\text{Ti}$, $\mu$SR measurements were carried out in the MuSR instrument at the ISIS pulsed muon and neutron spallation source. A detailed account of the $\mu$SR technique may be found in Ref. [37]. Stray fields at the sample position due to neighboring instruments and the Earth’s magnetic field are canceled to within $\sim 1.0 \mu$T using three sets of orthogonal coils and an active compensation system. The powdered $\text{Re}_6\text{Ti}$ sample was mounted on a silver holder and placed in a sorption cryostat, which operated in the temperature range 0.3–10 K. Firstly, we performed transverse-field muon spin rotation (TF-$\mu$SR) measurements to directly measure the field distribution associated with the mixed state of a type-II superconductor to gain knowledge about the symmetry of the pairing state. The sample was field cooled in an applied field of 30 mT, well above the lower critical field ($H_{c1}(0) = 5.8$ mT) in order to develop a well-ordered flux line lattice (FLL). Asymmetry spectra were recorded above (10 K) and below (0.3 K) the transition temperature $T_c$ as displayed in Fig. 3(a). In the normal state, the field distribution is homogeneous throughout the sample, which is depicted from the spectra taken at 10 K. The weak depolarization is attributed to the Gaussian relaxation that is due to the random nuclear dipolar field. The depolarization rate in the superconducting state becomes more prominent, due to the formation of an inhomogeneous field distribution in the FLL state.

Time evolution of the asymmetry is best described by the sinusoidal oscillatory function damped with a Gaussian relaxation and an oscillatory background term arising from the muons implanted directly into the silver sample holder that does not depolarize,

$$
G_{\text{TF}}(t) = A_1 \exp\left(-\frac{\sigma^2 t^2}{2}\right) \cos(w_1 t + \phi) + A_2 \cos(w_2 t + \phi).
$$

(1)
The temperature dependence of the gap in BCS approximation is given by the expression $\delta(T/T_c) = \tanh(1.82 \times 0.018(10)(T_c - T)^{0.55})$. The dirty-limit model was used since the Re6X family crystallizes in the $\alpha$-Mn structure, which is already known to have an intrinsic disorder with high residual resistivity. This yields a very low free path compared to the BCS coherence length [25,26,38,39].

We obtain good fits to the $\sigma_{S\text{FLL}}(T)$ data using the model discussed above [see Fig. 3(b)]. The fitted value for the transition temperature $T_c = 5.98(2)$ K is in good agreement with the value obtained ($T_c = 6$ K) from bulk measurements. The energy gap has a maximum magnitude of $\Delta(0) = 0.95(2)$ meV, which yields the value $\Delta(0)/k_B T_c = 1.84(2)$ which is larger than the BCS expectation (1.764), indicating enhanced electron-phonon coupling strength. This behavior is in good agreement with our heat-capacity measurements and common to the earlier studies on Re6Hf and Re6Zr where a similar strong-coupling limit was observed.

The zero-temperature effective magnetic penetration depth $\lambda(0)$ can be directly calculated from the $\sigma_{S\text{FLL}}(0)$ [0.4401(4) $\mu$s$^{-1}$] from the relation [40,41]

$$\frac{\sigma_{S\text{FLL}}^2(0)}{\gamma^2_\mu} = 0.00371 \frac{\Phi_0^3}{\lambda^4(0)},$$

where $\gamma_\mu/2\pi = 135.53$ MHz/T is the muon gyromagnetic ratio and $\Phi_0$ is the magnetic flux quantum. The magnetic penetration depth at $T = 0$ K was thus found to be $\lambda(0) = (4937 \pm 11)$ Å.

It is important to note that the polycrystalline samples with dirty-limit superconductivity are not the ideal candidates to extract the actual temperature dependence of the superfluid density. Previous studies on dirty-limit superconductors have shown that the large scattering from defects or impurities often masks the true nature of pairing symmetry in TF-$\mu$SR measurements. As briefly described by Frandsen et al. in CaIrSi [42], most of the superconductors with unconventional pairing symmetry are particularly single crystals or polycrystalline samples with a low residual resistivity (RR). In contrast, dirty-limit superconductors with a high RR have largely shown conventional $s$-wave gap symmetry. Hence, TF-$\mu$SR measurements on dirty-limit superconductors may not be sensitive to the underlying pairing state and could miss out on any signatures of an unconventional pairing state. Thus, it is highly desirable to do the penetration depth measurements on high-quality single crystals of Re6Ti in order to know the true behavior of superfluid density.

Zero-field muon spin relaxation (ZF-$\mu$SR) measurements are carried out to detect the tiny spontaneous magnetic fields associated with the broken time-reversal symmetry (TRS) in the superconducting state. The relaxation spectra was collected below ($T = 0.3$ K) and above the transition temperature ($T_c = 10$ K), as displayed in Fig. 4(a). There was no hint for an oscillatory component in the data, which suggests the absence of an ordered magnetic structure. Interestingly, the spectra trace a different relaxation channel below the transition temperature, which indicates the presence of the spontaneous internal magnetic field. In the absence of atomic moments, the relaxation is due to randomly oriented nuclear moments, which can be modeled by the Gaussian Kubo-Toyabe (KT)
To the formation of spontaneous magnetic fields below $T_c$, the temperature dependence of fit parameters $\sigma_{ZF}$ and $\Delta$ as shown in Figs. 4(b) and 4(c). The sample and background asymmetries have approximately temperature-independent values $A_0$ and $\Delta_{BG}$ at the temperature $T = 5.98 \pm 0.2$ K [see Fig. 4(b)], which is close to the superconducting transition temperature. Such a systematic increase in $\sigma_{ZF}$ below $T_c$ was also identified in other members of the Re6$X$ family [25,26] by $\mu$SR measurements. This particular behavior was attributed to the formation of spontaneous magnetic fields below $T_c$, which in turn confirmed time-reversal symmetry breaking in the spin-triplet channel in this family of compounds. These observations clearly suggest that TRS is also broken in the superconducting state of Re6$X$ family. It suggests that reduced Re composition may not have any major effect on the superconducting state. However, a generic comment cannot be made regarding its effect on the superconducting state of these compounds solely based on interpretation done using the muon data. In order to fully understand the contribution of Re bands, detailed calculations of the electronic band structure for each compound is needed.

In conclusion, we have determined that the superconducting ground state in Re6$X$ breaks time-reversal symmetry, which gives the internal field strength $|B_{int}| = 0.14$ G. According to theoretical predictions, ASOC plays a pivotal role in the mixing of spin-triplet/spin-singlet pairing. Since spin-orbit coupling varies as $Z^4$, it is expected that its strength would be weaker in Ti as compared to Hf and Zr. If this is the case, then it should reduce the spin-singlet/spin-triplet mixing ratio whose direct consequence must be visible in ZF-$\mu$SR. In contrast, we observed similar results where the TRSB signal observed in Re6$X$ is remarkably identical in magnitude to that seen in other members of the Re6$X$ family.

### Table I. Comparison of the mode of the internal field calculated for Re6$X$ ($X = Zr, Hf, Ti$).

| Compound | Internal Field |
|----------|----------------|
| Re6Hf    | 0.085          |
| Re6Zr    | 0.11           |
| Re6Ti    | 0.14           |
| Re6Ti3   | 0.13           |
is in addition to other members of the $\text{Re}_6X$ ($X = \text{Hf}, \text{Zr}$) family which shows these phenomena. The TF data suggest that the superconducting order parameter is described well by an isotropic gap with $s$-wave pairing symmetry with enhanced electron-phonon coupling, similar to that of $\text{Re}_6\text{Hf}$ and $\text{Re}_6\text{Zr}$. The emergence of similar results suggests that the strength of spin-orbit coupling does not affect the pairing symmetry in the $\text{Re}_6X$ family of compounds. Further theoretical and experimental work required one to understand the origin of the unconventional superconductivity in the $\text{Re}_6X$ family of compounds.

R.P.S. acknowledges Science and Engineering Research Board, Government of India for the Young Scientist Grant No. YSS/2015/001799 and a Ramanujan Fellowship through Grant No. SR/S2/RJN-83/2012. We thank ISIS, STFC, UK for the muon beamtime and Newton funding to conduct the $\mu$SR experiments.

[1] M. Smidman, M. B. Salamon, H. Q. Yuan, and D. F. Agterberg, Rep. Prog. Phys. 80, 036501 (2017).
[2] M. S. Scheurer, Phys. Rev. B 93, 174509 (2016).
[3] E. Bauer, G. Hilscher, H. Michor, Ch. Paul, E. W. Scheidt, A. Gribanov, Y. Seropegin, H. Noel, M. Sigrist, and P. Rogl, Phys. Rev. Lett. 92, 027003 (2004).
[4] E. Bauer and M. Sigrist, Non-Centrosymmetric Superconductors: Introduction and Overview (Springer, Berlin, 2012).
[5] E. Bauer, H. Kaldarar, A. Prokofiev, E. Royanian, A. Amato, J. Sereni, W. Brämer-Escamilla, and I. Bonalde, J. Phys. Soc. Jpn. 76, 051009 (2007).
[6] E. I. Rashba, Sov. Phys. Solid State 2, 1109 (1960).
[7] L. P. Gorkov and E. I. Rashba, Phys. Rev. Lett. 87, 037004 (2001).
[8] H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica, D. Vandervelde, K. Togano, M. Sigrist, and M. B. Salamon, Phys. Rev. Lett. 97, 017006 (2006).
[9] M. Nishiyama, Y. Inada, and G. Q. Zheng, Phys. Rev. Lett. 98, 047002 (2007).
[10] H. Takeya, M. ElMassalami, S. Kasahara, and K. Hirata, Phys. Rev. B 76, 104506 (2007).
[11] S. Harada, J. J. Zhou, Y. G. Yao, Y. Inada, and G. Q. Zheng, Phys. Rev. B 86, 220502 (2012).
[12] A. B. Karki, Y. M. Xiong, I. Vekhter, D. Browne, P. W. Adams, D. P. Young, K. R. Thomas, J. Y. Chan, H. Kim, and R. Prozorov, Phys. Rev. B 82, 064512 (2010).
[13] P. K. Biswas, M. R. Lees, A. D. Hillier, R. I. Smith, W. G. Marshall, and D. M. Paul, Phys. Rev. B 84, 184529 (2011).
[14] A. B. Karki, Y. M. Xiong, N. Haldolaarachchige, S. Stadler, I. Vekhter, P. W. Adams, D. P. Young, W. A. Phelan, and J. Y. Chan, Phys. Rev. B 83, 144525 (2011).
[15] C. S. Lue, T. H. Su, H. F. Liu, and B. L. Young, Phys. Rev. B 84, 052509 (2011).
[16] J. Chen, M. B. Salamon, S. Akutagawa, J. Akimitsu, J. Singleton, J. L. Zhang, L. Jiao, and H. Q. Yuan, Phys. Rev. B 83, 144529 (2011).
[17] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori et al., Nature (London) 394, 558 (1998).
[18] J. Xia, Y. Maeno, P. T. Beyersdorf, M. M. Fejer, and A. Kapitulnik, Phys. Rev. Lett. 97, 167002 (2006).
[19] G. M. Luke, A. Keren, L. P. Le, W. D. Wu, Y. J. Uemura, D. A. Bonn, L. Taillefer, and J. D. Garrett, Phys. Rev. Lett. 71, 1466 (1993).
[36] C. S. Lue, H. F. Liu, C. N. Kuo, P. S. Shih, J. Y. Lin, Y. K. Kuo, M. W. Chu, T. L. Hung, and Y. Y. Chen, Supercond. Sci. Technol. 26, 055011 (2013).

[37] S. L. Lee, S. H. Kilcoyne, and R. Cywinski, Muon Science: Muons in Physics, Chemistry and Materials (SUSSP Publications and IOP Publishing, Bristol, 1999).

[38] D. A. Mayoh, J. A. T. Barker, R. P. Singh, G. Balakrishnan, D. McK. Paul, and M. R. Lees, Phys. Rev. B 96, 064521 (2017).

[39] D. Singh, A. D. Hillier, A. Thamizhavel, and R. P. Singh, Phys. Rev. B 94, 054515 (2016).

[40] J. E. Sonier, J. H. Brewer, and R. F. Kiefl, Rev. Mod. Phys. 72, 769 (2000).

[41] E. H. Brandt, Phys. Rev. B 37, 2349 (1988).

[42] B. A. Frandsen, S. C. Cheung, T. Goko, L. Liu, T. Medina, T. S. J. Munsie, G. M. Luke, P. J. Baker, M. P. Jimenez S., G. Eguchi et al., Phys. Rev. B 91, 014511 (2015).

[43] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Phys. Rev. B 20, 850 (1979).