Time-reversal symmetry breaking in the noncentrosymmetric superconductor Re₆Ti

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We have investigated the superconducting state of the noncentrosymmetric superconductor Re₆Ti (Tc = 6.0 K) using a muon-spin rotation/relaxation technique. The 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 materials 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.

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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, 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)₂B [8–11], Mo₃Al₂C [12], Re₃W [13], Nb₀.1₈Re₀.₈₂ [14,15], Y₁C₃ [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], Re₄₀Ti₅ [27], locally noncentrosymmetric SrPtAs [28], and La₃Ir₃ [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 Re₄₀Ti₅ to examine the correclar 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 Re₆Ti. The TRSB signal in Re₆Ti is very similar to the signal observed in other compounds (Re₆Zr/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 Re₆Ti were prepared by melting stoichiometric amounts of Re (99.95%; Alfa Aesar) and Ti (99.95%; Alfa Aesar) in an arc-melting furnace under ultrapure argon 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 Re₆Ti was collected at room temperature. As observed from Fig. 1, the Re₆Ti sample has no impurity phase. It can be indexed by a cubic noncentrosymmetric α-Mn (217) structure shown by a solid black line.

![Intensity (counts) vs 2θ (°)](image)

FIG. 1. Powder x-ray diffraction pattern for the Re₆Ti sample recorded at room temperature using Cu Kα radiation. Rietveld refined calculated pattern for the cubic noncentrosymmetric α-Mn (217) structure shown by a solid black line.

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 \( \Delta C_p/T_c \) is \( 1.58 \pm 0.02 \) (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 \( \Delta(0)/k_BT_c = 1.86 \). This value is higher than the value for a BCS superconductor (1.764), suggesting moderately enhanced electron-phonon coupling. Re₂₄Ti₅ polycrystalline samples are also prepared by the same method as Re₆Ti, and its lattice and superconducting parameters are the same as reported by Lue et al. [36].

To probe the superconducting ground state of Re₆Ti, \( \mu \)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 \( \sim 1.0 \) μT using three sets of orthogonal coils and an active compensation system. The powdered Re₆Ti 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 directly to 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,

\[
G_{TF}(t) = A_1 \exp\left(\frac{-\sigma^2 t^2}{2}\right) \cos(w_1 t + \phi) + A_2 \cos(w_2 t + \phi). \tag{1}
\]
The depolarization rate in the superconducting state in the dirty limit for an applied field of 30 mT was following the single-gap s-wave model.

The temperature dependence of the London magnetic penetration depth $\lambda$ and thus to the superfluid density $n_s$ is given by the equation

$$\sigma_{\text{FLL}}(T) = \frac{\lambda^{-2}(T)}{\lambda^{-2}(0)}.$$

For a single-gap $s$-wave superconductor in the dirty limit, the temperature dependence of the London magnetic penetration depth within the London approximation is given by

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = \frac{\Delta(T)}{\Delta(0)} \tanh \left[ \frac{\Delta(T)}{2k_B T} \right].$$

where $\Delta(T) = \Delta_0 \delta(T/T_c)$. The temperature dependence of the gap in BCS approximation is given by the expression $\delta(T/T_c) = \tanh(\pi.82[1.018[(T_c/T) - 1]^{0.51})$. The dirty-limit model was used since the Re$_6$X 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 $\sigma_{\text{FLL}}(T)$ 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 Re$_6$Hf and Re$_6$Zr where a similar strong-coupling limit was observed.

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

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

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 is 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$_3$ [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 Re$_6$Ti 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)
function \[43\]

\[
G_{KT}(t) = \frac{1}{3} + \frac{2}{3}(1 - \sigma_{ZF}^2 t^2) \exp\left(-\frac{\sigma_{ZF}^2 t^2}{2}\right),
\]

where \(\sigma_{ZF}\) accounts for the relaxation due to static, randomly oriented nuclear dipolar local fields at the muon site. The zero-field asymmetry spectra are well described by the function

\[
A(t) = A_1 G_{KT}(t) \exp(-\Lambda t) + A_{BG},
\]

where \(A_1\) is the initial asymmetry, \(\Lambda\) is the electronic relaxation rate, and \(A_{BG}\) is the time-independent background contribution from the muons stopped in the sample holder. The above function was fitted to the ZF asymmetry spectra collected at various temperatures above and below \(T_c\), which yields the temperature dependence of fit parameters \(\sigma_{ZF}\) and \(\Lambda\) as shown in Figs. 4(b) and 4(c). The sample and background asymmetries have approximately temperature-independent values \(A_1 = 0.1732(4)\) and \(A_{BG} = 0.1158(4)\). Interestingly, the Gaussian relaxation rate parameter \(\sigma_{ZF}\) shows a clear increase below 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 Re\(_6\)X \((X = \text{Hf}, \text{Zr})\) [25,26] family 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 this compound. These observations clearly suggest that TRS is also broken in the superconducting state of Re\(_6\)Ti and Re\(_6\)X is a unique family where all the members until now have shown this exotic phenomena.

To eliminate the possibility that the above signal is due to extrinsic effects such as impurities, we applied a 15 mT longitudinal field. As depicted by the blue markers in Fig. 4(a), this was sufficient to fully decouple the muons from the internal field, which appear as flat asymmetry spectra. This indicates that the associated magnetic fields are in fact static or quasistatic on the time scale of the muon precession. The magnitude of internal field can be calculated by

\[
|B_{int}| = \sqrt{2 \frac{\sigma_{ZF}}{\gamma_\mu}},
\]

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 pairing mixing ratio whose direct consequence must be visible in ZF-\(\mu\)SR. In contrast, we observed similar results where the TRSB signal observed in Re\(_6\)Ti is remarkably identical in magnitude to that seen in other members of the Re\(_6\)X family.

In addition, the value of the calculated internal field is also comparable to the values obtained for Re\(_6\)Hf and Re\(_6\)Zr as shown in Table I. This suggests that the effect of spin-orbit coupling does not lead to an increase in the strength of the spin-triplet channel in this family of compounds. At the same time, the isostructural NCS compound Re\(_{24}\)Ti\(_5\) (ratio of 4:8:1) [36] provides a unique opportunity to study the effect of Re composition on the superconducting ground state of a Re\(_6\)X family of compounds. Interestingly, the ZF-\(\mu\)SR in this compound also shows TRSB, with a similar nature and magnitude of the temperature dependence of Gaussian relaxation rate \(\sigma_{ZF}\) [see inset of Fig. 4(b)]. Also, the internal field \(|B_{int}|\) has approximately the same magnitude as seen for other Re\(_6\)X compounds. 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 Re\(_6\)Ti breaks time-reversal symmetry, which

TABLE I. Comparison of the mode of the internal field calculated for Re\(_6\)X \((X = \text{Zr, Hf, Ti})\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Internal Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(_6)Hf</td>
<td>0.085</td>
</tr>
<tr>
<td>Re(_6)Zr</td>
<td>0.11</td>
</tr>
<tr>
<td>Re(_6)Ti</td>
<td>0.14</td>
</tr>
<tr>
<td>Re(_{24})Ti(_5)</td>
<td>0.13</td>
</tr>
</tbody>
</table>
is in addition to other members of the Re$_6$X ($X = \text{Hf, Zr}$) 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 Re$_6$Hf and Re$_6$Zr. The emergence of similar results suggests that the strength of spin-orbit coupling does not affect the pairing symmetry in the Re$_6$X family of compounds. Further theoretical and experimental work required one to understand the origin of the unconventional superconductivity in the Re$_6$X family of compounds.

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