

Detection of Time-Reversal Symmetry Breaking in the Noncentrosymmetric Superconductor Re_6Zr Using Muon-Spin Spectroscopy

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We have investigated the superconducting state of the noncentrosymmetric compound Re_6Zr using magnetization, heat capacity, and muon-spin relaxation or rotation (μSR) measurements. Re_6Zr has a superconducting transition temperature, $T_c = 6.75 \pm 0.05$ K. Transverse-field μSR experiments, used to probe the superfluid density, suggest an s -wave character for the superconducting gap. However, zero and longitudinal-field μSR data reveal the presence of spontaneous static magnetic fields below T_c indicating that time-reversal symmetry is broken in the superconducting state and an unconventional pairing mechanism. An analysis of the pairing symmetries identifies the ground states compatible with time-reversal symmetry breaking.

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The symmetry of a material plays a fundamental role in determining its physical properties. Symmetry breaking can modify the physics of a system and produce new and unusual behavior. Superconductivity is one of the best examples of a symmetry breaking phenomenon. In conventional superconductors gauge symmetry is broken, while in unconventional superconductors other symmetries may also be broken.

There has recently been a great deal of interest in noncentrosymmetric superconductors (NCS) due to the complex nature of their superconducting properties [1]. The lack of inversion symmetry in these materials induces an antisymmetric spin-orbit coupling (SOC) [2,3] which can lift the degeneracy of the conduction band electrons and may cause the superconducting pair wave function to contain mixed singlet-triplet spin states. This mixed pairing can lead noncentrosymmetric superconductors to display significantly different properties from conventional superconducting systems, e.g., nodes in the superconducting gap and upper critical fields exceeding the Pauli limiting field [1]. In addition, some of these systems display time-reversal symmetry (TRS) breaking.

One of the most direct ways of confirming the presence of an unconventional superconducting state is muon spectroscopy [4–6]. In a muon spectroscopy experiment,

100% spin-polarized positive muons are implanted one at a time into a sample. After coming to rest, the muon spin precesses in the local magnetic environment. The muons decay with a half-life of 2.2 μs , emitting a positron preferentially in the direction of the muon spin at the time of decay. The number of positrons are recorded as a function of time in forward $N_F(t)$ and backward $N_B(t)$ detectors. The time evolution of the muon polarization can be obtained by examining the normalized difference of these two functions via the asymmetry function $A(t) = (N_B(t) - N_F(t))/(N_B(t) + N_F(t))$. This technique can accurately determine the magnetic penetration depth and hence the temperature dependence of the superfluid density, yielding information on the symmetry of the superconducting gap. Muon spectroscopy can also be used to unambiguously establish the onset of time-reversal symmetry breaking in superconductors. The magnetic moments associated with the Cooper pairs are nonzero in such superconductors and a local alignment of these moments produces spontaneous, but extremely small, internal magnetic fields [7]. Muon-spin relaxation or rotation (μSR) is especially sensitive to small changes in internal fields and can easily measure fields of ~ 10 μT which correspond to moments that are just a few hundredths of a μ_B .

Time-reversal symmetry breaking is rare and has only been observed directly in a few unconventional superconductors, e.g., Sr_2RuO_4 [8,9], UPt_3 and $(\text{U}, \text{Th})\text{Be}_{13}$ [10–13], $(\text{Pr}, \text{La})(\text{Os}, \text{Ru})_4\text{Sb}_{12}$ [14,15], $\text{PrPt}_4\text{Ge}_{12}$ [16], and LaNiGa_2 [17]. The possibility of singlet-triplet pairing in noncentrosymmetric superconductors makes them prime

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candidates to exhibit TRS breaking. To date, however, the only NCS reported to show TRS breaking is LaNiC_2 [18,19]. In this material, symmetry analysis implies that the superconducting instability is of the nonunitary triplet type, with a spin-orbit coupling that is comparatively weak and with mixing of singlet and triplet pairing being forbidden by symmetry [20].

Several other noncentrosymmetric superconductors including $\text{Nb}_{0.18}\text{Re}_{0.82}$ [21], $\text{Mo}_3\text{Al}_2\text{C}$ [22], $\text{Li}_2(\text{Pd}, \text{Pt})_3\text{B}$ [23–26], $\text{Ca}(\text{Ir}, \text{Pt})\text{Si}_3$ [27], LaRhSi_3 [28], $\text{Mg}_{10}\text{Ir}_{19}\text{B}_{16}$ [29], and Re_3W [30] have been studied by magnetization, transport, and heat capacity measurements and some have been shown to exhibit unconventional superconducting behavior including triplet pairing [24] and upper critical fields close to the Pauli limit [22].

Studies using μSR have also been performed on the last four of these compounds [28,31–33]. However, no spontaneous fields were observed in the superconducting state of any of these materials indicating that the breaking of TRS is either absent or undetectable in these materials. The failure to detect TRS breaking in a number of NCS containing heavy transition metals in which SOC is normally expected to be strong and in which mixed spin-singlet spin-triplet pairing may be allowed, raises the possibility that TRS breaking may be absent in this particular class of superconductors. In order to address this question we have begun a systematic investigation of the superconducting properties of a number of noncentrosymmetric materials with the body-centered cubic $\alpha\text{-Mn}$ structure [34,35], containing the heavy transition-metal Re. In this Letter, we report the results of μSR measurements on one of these materials, Re_6Zr [34–36]. Zero and longitudinal-field μSR reveal that spontaneous magnetic fields develop at the superconducting transition temperature, confirming the presence of TRS breaking in the superconducting state of Re_6Zr . Transverse-field μSR data and a theoretical analysis of the possible pairing states in Re_6Zr demonstrate that there is a mixing of spin-singlet and spin-triplet pairing in this noncentrosymmetric superconducting compound.

Polycrystalline samples of Re_6Zr were prepared by arc melting stoichiometric quantities of high purity (5N) Zr and Re in a tetra-arc furnace (Cyberstar, Grenoble, France) under an argon (5N) atmosphere on a water-cooled copper hearth. The sample buttons were melted and flipped several times to ensure phase homogeneity. The observed weight loss during the melting was negligible. Powder x-ray diffraction data confirmed the sample has the $\alpha\text{-Mn}$ crystal structure (space group $I\bar{4}3m$, No. 217). Powder x-ray diffraction and energy dispersive x-ray spectroscopy showed that no other phases, including oxides and carbides, are present in the sample to within the limits of these analysis techniques.

The materials were characterized using magnetization M and heat capacity C measurements. These measurements indicate that Re_6Zr is a bulk superconductor with a superconducting transition temperature T_c of 6.75 ± 0.05 K [Fig. 1(a)]. This is less than the 7.4 K reported

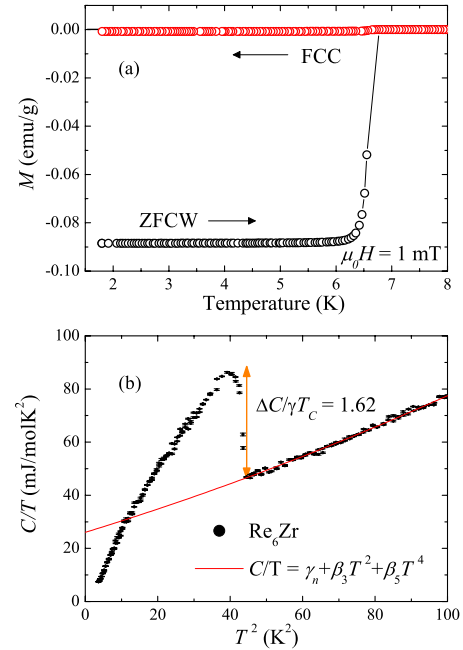


FIG. 1 (color online). (a) Temperature dependence of the magnetization collected in zero-field-cooled warming (ZFCW) and field-cooled cooling (FCC) modes in an applied field $\mu_0H = 1.0$ mT. (b) C/T versus T^2 for Re_6Zr . The line is a fit to the data using $C/T = \gamma_n + \beta_3T^2 + \beta_5T^4$ where γ_nT and $\beta_3T^3 + \beta_5T^5$ are the normal state electronic and lattice contributions to the specific heat, respectively. $\gamma_n = 26 \pm 2 \times \text{mJ mol}^{-1} \text{K}^{-2}$ and the Debye temperature calculated from β_3 is 319 ± 9 K.

previously [34]. $\Delta C/\gamma_nT_c = 1.62 \pm 0.09$ is larger than the 1.43 expected for a conventional BCS superconductor [Fig. 1(b)]. This suggests the presence of an enhanced electron-phonon coupling compared with a BCS superconductor [37]. Using the Werthamer-Helfand-Hohenberg expression [38], $H_{c2}(0) = 0.693T_c(dH_{c2}/dT)_{T_c}$, we estimate $\mu_0H_{c2}(0) = 12.20 \pm 0.06$ T which is close to the value of the Pauli paramagnetic limiting field, $\mu_0H_{\text{Pauli}} = 1.83T_c$ (in tesla) of 12.35 ± 0.09 T.

Zero-field, longitudinal-field, and transverse-field μSR experiments were carried out using the MuSR spectrometer at the ISIS pulsed muon facility. A detailed description of the different instrumental geometries can be found in Ref. [5]. A powdered sample of Re_6Zr was mounted on a sample plate made of 99.995% silver. The sample holder and sample were placed in a helium-3 cryostat with a temperature range of 0.3–10 K. The stray fields at the sample position were canceled to a level of 1 μT by an active compensation system.

Transverse-field μSR (TF- μSR) experiments were performed in the superconducting mixed state in applied fields between 40 and 60 mT, well above the $\mu_0H_{c1}(0) = 8 \pm 1$ mT of this material [37]. In this geometry, the 64 detectors in the MuSR spectrometer are combined in software to provide two orthogonal virtual detectors, each with a phase offset φ . Data were collected in the

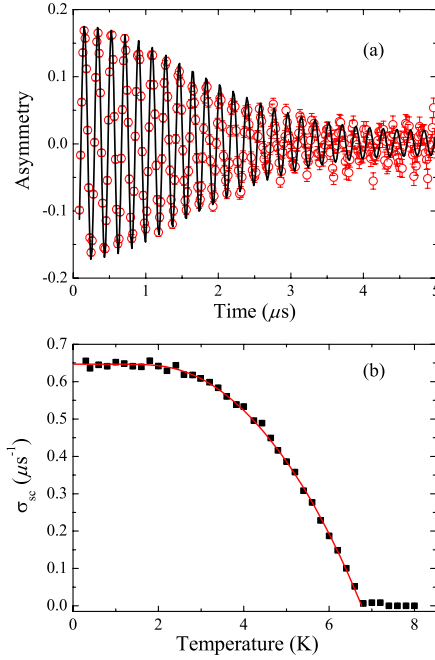


FIG. 2 (color online). (a) Transverse-field muon time spectra for Re_6Zr at $T = 0.3$ K in a magnetic field 40 mT. The solid line shows a fit to the data using Eq. (1). For clarity, only the data from one of the two virtual detectors are shown. (b) Temperature dependence of the superconducting muon-spin depolarization rate σ_{sc} collected in an applied magnetic field $\mu_0 H = 40$ mT. The solid line shows a fit to an isotropic s -wave gap.

field-cooled mode where the magnetic field was applied above the superconducting transition and the sample was then cooled to base temperature.

Figure 2(a) shows a typical TF- μ SR precession signal for Re_6Zr with an applied field of 40 mT at 300 mK. The signal decays with time because of the inhomogeneous field distribution of the flux-line lattice. The TF spectra were fitted using a sinusoidal oscillating function with a Gaussian relaxation, and an oscillatory background term arising from the muons implanted directly into the silver sample holder that do not depolarize.

$$G(t) = A_1 \exp\left(-\frac{\sigma_{sc}^2 t^2}{2}\right) \cos(2\pi\nu_1 t + \varphi_1) + A_2 \cos(2\pi\nu_2 t + \varphi_2). \quad (1)$$

σ_{sc} exhibits no field dependence between 40 and 60 mT, as expected for a material with a $\mu_0 H_{c2}(0)$ of 12.2 T. Figure 2(b) shows the T dependence of the muon depolarization rate which can be directly related to the superfluid density [5,39,40]. From this, the nature of the superconducting gap can be determined. The data can be well modeled by a single isotropic s -wave gap of 1.21 ± 0.08 meV. This gives a gap of $2\Delta/k_B T_c = 4.2 \pm 0.3$, which is higher than the 3.53 expected for BCS superconductors. This is a further indication of the enhanced electron-phonon coupling in the superconducting state.

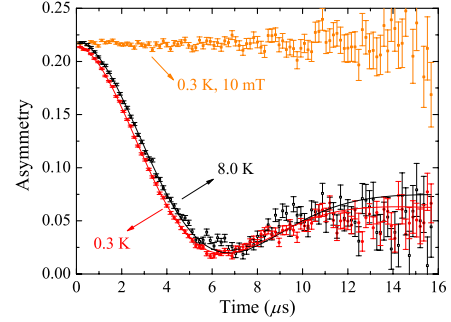


FIG. 3 (color online). Zero-field μ SR time spectra for Re_6Zr collected at 0.3 (closed symbols) and 8.0 K (open symbols) are shown together with lines that are least squares fits to the data using Eq. (3). These spectra collected below and above T_c are representative of the data collected. A LF- μ SR time spectrum taken in an applied field of 10 mT at 0.3 K is also shown.

Zero-field relaxation data were collected at several temperatures between 0.3 and 10 K. Figure 3 shows the spectra collected at 8 and 0.3 K, i.e., above and below T_c , respectively. In these relaxation experiments, any muons stopped in the silver sample holder give a time independent background. There is no indication of a precessional signal over the entire temperature range studied, ruling out the possibility of a large internal field and hence long-range magnetic order in Re_6Zr . In the absence of atomic moments, the only possibility is that the muon-spin relaxation is due to static, randomly oriented local fields associated with the nuclear moments at the muon site. This depolarization can be described by the Kubo-Toyabe (KT) function

$$G^{\text{KT}}(t) = \left[\frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2) \exp\left(-\frac{\sigma^2 t^2}{2}\right) \right] \quad (2)$$

and our spectra for Re_6Zr are well described by the function

$$G(t) = A_0 G^{\text{KT}}(t) \exp(-\Lambda t) + A_{\text{bckgrd}}, \quad (3)$$

where A_0 is the initial asymmetry, A_{bckgrd} is the background, and Λ is the electronic relaxation rate.

The parameters A_0 , Λ , and A_{bckgrd} are found to be temperature independent. Only the depolarization rate σ shows any temperature dependence increasing with decreasing temperature below T_c (see Fig. 4). Such behavior is unusual. To date, such a change in σ has only been observed in superconducting $\text{PrOs}_4\text{Sb}_{12}$ and $\text{PrPt}_4\text{Ge}_{12}$ [14,16], and more recently in LaNiGa_2 [17], none of which are NCS. The temperature dependence of σ agrees with a BCS order parameter. This increase in σ can be explained in terms of a signature of a coherent internal field with a very low frequency as discussed by Aoki *et al.* [14] for $\text{PrOs}_4\text{Sb}_{12}$. They suggest that the field distribution is Gaussian in nature compared to Sr_2RuO_4 , where Λ exhibits a spontaneous increase below T_c due to a Lorentzian-type field distribution. In order to rule out

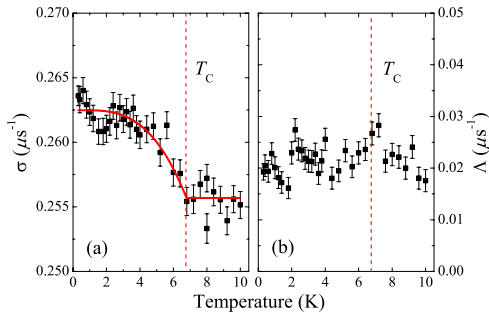


FIG. 4 (color online). (a) Temperature dependence of σ for Re_6Zr in zero field which clearly shows the spontaneous fields appearing at $T_c = 6.78$ K. The solid line is a fit to the data (reduced $\chi^2 = 1.02$) using an approximation [41] to the BCS order parameter for σ . (b) The electronic relaxation rate Λ versus temperature in zero field shows no temperature dependence.

the possibility that the increased relaxation in the superconducting state is due to extrinsic effects such as impurities, measurements were performed in weak longitudinal fields (Fig. 3). A longitudinal magnetic field of just 10 mT removes any relaxation due to the spontaneous fields and is sufficient to fully decouple the muons from this relaxation channel. This in turn shows that the associated magnetic fields are in fact static or quasistatic on the time scale of the muon precession. These observations confirm time-reversal symmetry breaking in Re_6Zr in the superconducting state.

In noncentrosymmetric superconductors, spin-orbit coupling can lead to mixed singlet-triplet pairing [3],

$$\hat{\Delta}(\mathbf{k}) = i[\Delta(\mathbf{k}) + \mathbf{d}(\mathbf{k}) \cdot \hat{\mathbf{c}}]\hat{\sigma}_y. \quad (4)$$

This in itself, however, does not suffice to yield broken time-reversal symmetry. Take, for instance, the case of $\text{Li}_2\text{Pd}_{3-x}\text{Pt}_x\text{B}$ ($0 \leq x \leq 3$). In this system, SOC induces a triplet component, $i\mathbf{d}(\mathbf{k}) \cdot \hat{\mathbf{c}}\hat{\sigma}_y$, that can be as small as $\sim 25\%$ or as large as $\sim 167\%$ of the total gap energy for $x = 0$ and 3, respectively [23–26]. The pairing mechanism in this family is believed to be conventional for all values of x and pairing is thus thought to preserve all the lattice symmetries including TRS. In contrast, the breaking of time-reversal symmetry necessitates a superconducting instability in a higher-dimensional irreducible representation of the crystal's point group. Such a state breaks additional lattice symmetries in addition to TRS. This rules out any conventional pairing mechanism, as it would necessarily lead to an order parameter in the most symmetric irreducible representation of the crystal point group, A_1 .

The results presented here make Re_6Zr only the second NCS where broken TRS has been observed directly. Moreover the other known example, LaNiC_2 [18], has a crystal point group C_{2v} whose irreducible representations are all one dimensional. It has thus been argued that for LaNiC_2 the orbital and spin degrees of freedom must be approximately decoupled at the instability, so that pairing

takes place in an almost purely triplet channel, rather than a mixed singlet-triplet one [20]. This scenario has been supported by the observation of broken TRS in centrosymmetric LaNiGa_2 [17].

In comparison to the elements in LaNiC_2 , Re has a much higher atomic number and we expect Re_6Zr to feature strong singlet-triplet mixing. The relevant point group, T_d , features one two-dimensional irreducible representation (E) and two three-dimensional irreducible representations (F_1 and F_2) [42]. Minimization of generic Landau free energies for superconducting instabilities in the E channel [43] reveals three possible ground states for this two-dimensional irreducible representation.

Of those, only one ground state breaks time-reversal symmetry. Its gap matrix has the form of Eq. (4) with the scalar $\Delta(\mathbf{k})$ and vector $\mathbf{d}(\mathbf{k})$ given, respectively, by

$$\Delta(\mathbf{k}) = 2Z^2 - X^2 - Y^2 + i(X^2 - Y^2), \quad (5)$$

$$\mathbf{d}(\mathbf{k}) = [X(Y^2 - Z^2), Y(X^2 - Z^2), Z(X^2 - Y^2)] \\ \times [2Z^2 - X^2 - Y^2 + i(X^2 - Y^2)]. \quad (6)$$

The F_1 and F_2 channels each have more ground states that break TRS, of which we give here two examples:

$$\Delta(\mathbf{k}) = (YZ + iXZ)(X^2 - Y^2)(Y^2 - Z^2)(Z^2 - X^2), \quad (7)$$

$$\mathbf{d}(\mathbf{k}) = (1, i, 0)XYZ, \quad (8)$$

for the F_1 irreducible representation; and

$$\Delta(\mathbf{k}) = (Y + iX)Z, \quad (9)$$

$$\mathbf{d}(\mathbf{k}) = (1, i, 0)XYZ(X^2 - Y^2)(Y^2 - Z^2)(Z^2 - X^2), \quad (10)$$

for F_2 . Here, as usual, $X = X(\mathbf{k})$, $Y = Y(\mathbf{k})$, and $Z = Z(\mathbf{k})$ denote three real functions that transform in the same way as the three components of the wave vector \mathbf{k} under the symmetry operations of the point group.

In summary, we have studied the noncentrosymmetric superconducting compound Re_6Zr using μSR . TF data reveal that the temperature dependence of the muon depolarization rate can be described using an s -wave model. The presence of spontaneous fields below T_c , however, provide convincing evidence for time-reversal symmetry breaking in this material and an unconventional pairing mechanism. As a result of the presence of Re, strong singlet-triplet mixing is expected in this material. Ground states consistent with the crystallographic symmetry and the observation of TRS breaking are discussed.

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