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Unconventional superconductivity in La$_7$Ir$_3$ revealed by muon spin relaxation: Introducing a new family of noncentrosymmetric superconductor that breaks time-reversal symmetry


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The superconductivity of the noncentrosymmetric compound La$_7$Ir$_3$ has been investigated using muon spin rotation and relaxation ($\mu$SR). Zero-field measurements reveal the presence of spontaneous static or quasi-static magnetic fields below the superconducting transition temperature $T_c = 2.25$ K - a clear indication that the superconducting state breaks time-reversal symmetry. Furthermore, transverse-field rotation measurements suggest that the superconducting gap is isotropic, and that the pairing symmetry of the superconducting electrons is predominantly $s$-wave with an enhanced binding strength. The results indicate that the superconductivity in La$_7$Ir$_3$ may be unconventional, and paves the way for further studies of this family of materials.

To this day, the microscopic theory of superconductivity presented by Bardeen, Cooper and Schrieffer forms the basis to the theoretical and experimental understanding of the phenomenon of superconductivity [1]. The conventional superconducting state is formed of electrons bound in spin-singlet Cooper pairs, with the attractive force mediated by the electron-phonon interaction. The Pauli principle requires that the total Cooper pair wavefunction is antisymmetric - thus a spin-singlet state has even parity, and a spin-triplet pair has odd parity [2]. In centrosymmetric materials parity is a good quantum number and no mixing of pair states is allowed. Systems lacking a centre of inversion exhibit a non-uniform lattice potential, which gives rise to an antisymmetric spin-orbit coupling [3, 4]. This leads to a splitting of the Fermi surface into spin-up and spin-down contributions [5]. Consequently, Cooper pairs may form where the composite electrons belong to different parts of this split Fermi surface - a completely different situation from the conventional case, which leads to rich and interesting new physics. This includes the potential for a ground-state that is an admixture of spin-singlet and spin-triplet superconducting channels [6], upper critical fields exceeding the Pauli limit [7], and non-trivial line or point nodes in the order parameter [2].

One of the best methods of detecting an unconventional ground-state is muon spin rotation and relaxation ($\mu$SR) [8–10]. The flux line lattice (FLL) that is established in the mixed state of a type-II superconductor leads to a distinctive field distribution in the sample. The positive muon can be employed as an extremely sensitive probe of local magnetic environments, and directly measures the distribution of fields associated with the FLL. In this way, $\mu$SR is used to calculate the temperature evolution of the magnetic penetration depth $\lambda$, and thus can determine the presence of nodes in the superconducting order parameter. The technique is also sensitive to the very small magnetic moments associated with the formation of spin-triplet electron pairs, and measurements in zero-field provide one of the most unambiguous methods of detecting this broken time-reversal symmetry [11]. Time-reversal symmetry breaking (TRSb) is an extremely rare phenomenon, which has only been reported for a handful of unconventional superconductors: the candidate chiral $p$-wave superconductor Sr$_2$RuO$_4$ [12, 13], the heavy fermion superconductors UPt$_3$ and (U,Th)Be$_{13}$ [14–17], the filled skutterudites (Pr,La)(Ru,Os)$_4$Sb$_{12}$ [18, 19], PrPt$_4$Ge$_{12}$ [20] and centrosymmetric LaNiGa$_2$ [21], and recently the caged type superconductor Lu$_3$Rh$_6$Sn$_{18}$ [22]. $\mu$SR studies have been carried out on many other noncentrosymmetric superconductors (NCS), including Ca(Ir,Pt)Si$_3$ [23], La(Rh,Pt,Pd,Ir)Si$_3$ [24–26], Mg$_{10}$Ir$_{19}$B$_{16}$ [27] and Re$_5$W [28]. No spontaneous magnetization has been observed in these materials, implying that the superconductivity in these systems occurs predominantly in a spin-singlet channel.

To date, the only non-centrosymmetric superconductors reported to break TRS are LaNiC$_2$ [29], Re$_5$Zr [30], and the locally non-centrosymmetric SrPtAs [31]. It is clearly important to search for new noncentrosymmetric structures that exhibit TRSB. Binary transition metal compounds with the Th$_7$Fe$_3$ structure have been found to play host to a large number of superconducting combinations [32, 33]. These materials crystallize in a hexagonal structure with space-group $P6_3mmc$. In this letter, evidence for TRSB in a member of this family, La$_7$Ir$_3$ is
presented; a development that introduces a new system of potential materials in which to investigate the phenomenon of spin-triplet superconductivity.

A polycrystalline sample of La$_7$Ir$_3$ was prepared by arc-melting stoichiometric quantities of La (99.9%, Alfa-Aesar) and Ir (99.99%, Alfa-Aesar) on a water-cooled copper hearth in a high-purity Ar atmosphere. Part of the sample was powdered and characteized on a PANalytical powder X-ray diffractometer. $\mu$SR measurements were carried out on the MuSR instrument at the ISIS pulsed muon and neutron spallation source. MuSR receives 40 pulses of 100% spin-polarized muons per second; these ensembles of muons are implanted into the sample and rapidly thermalise, sitting at interstitial positions in the crystal lattice. The muon spin precesses at the Larmor precession frequency, before decaying with a lifetime of 2.2 $\mu$s. The decay positron is emitted preferentially along the direction of the muon spin vector, and the emitted positrons are recorded by scintillation detectors positioned in circular arrays around the sample. The MuSR spectrometer can be rotated through $90^\circ$ in order to change the geometry of the experiment - a full description of the two detector geometries is given in Ref. [10].

Stray fields at the sample position due to the Earth and neighbouring instruments are cancelled to within 1 $\mu$T; these ensembles of muons are implanted into the sample and rapidly thermalise, sitting at interstitial positions in the crystal lattice. The muon spin precesses at the Larmor precession frequency, before decaying with a lifetime of 2.2 $\mu$s. The decay positron is emitted preferentially along the direction of the muon spin vector, and the emitted positrons are recorded by scintillation detectors positioned in circular arrays around the sample. The MuSR spectrometer can be rotated through $90^\circ$ in order to change the geometry of the experiment - a full description of the two detector geometries is given in Ref. [10].

Stray fields at the sample position due to the Earth and neighbouring instruments are cancelled to within 1 $\mu$T using three sets of orthogonal coils and an active compensation system. The powdered La$_7$Ir$_3$ was mounted on a silver holder and placed in a dilution fridge, which was used as it gives a non-depolarizing background that can be easily accounted for during data analysis.

The powder X-ray diffraction (XRD) data showed that the sample had crystallized into the Th$_2$Fe$_3$ non-centrosymmetric structure with space-group $P6_3mc$ and lattice parameters $a = 10.2376(3) \text{ Å}$ and $c = 6.4692(3) \text{ Å}$. No impurity phases were detected in the sample to within the sensitivity of the XRD technique. The sample was ground to a fine powder for the $\mu$SR experiments in a high purity Ar atmosphere, and transported in a sealed, evacuated quartz tube in order to reduce the effect of oxidation. The superconducting transition temperature, $T_c$, was determined to be 2.25 K by magnetization measurements in agreement with a previous report [32].

Transverse field $\mu$SR (TF-$\mu$SR) was performed in the field range $10 \leq \mu_0 H \leq 50$ mT. The field was applied above $T_c$ before cooling through the superconducting transition to a temperature of 100 mK, in order to stabilize a well-ordered flux line lattice in the mixed state of the superconductor. Asymmetry signals collected above and below $T_c$ are shown in Fig. 1. The time evolution of the asymmetry is described by a sinusoidal function damped with Gaussian relaxation, plus a non-decaying oscillation that originates from muons stopping in the silver:

$$G_{TF}(t) = A_1 \exp \left( -\frac{\sigma_1^2 t^2}{2} \right) \cos(\gamma_\mu B_1 t + \phi) + A_2 \cos(\gamma_\mu B_2 t + \phi).$$  

(1)

Here $A_1$ and $A_2$ are the sample and background asymmetries, $B_1$ and $B_2$ are the average fields in the superconductor and silver, $\phi$ is a shared phase offset and $\gamma_\mu/2\pi = 135.5$ MHz T$^{-1}$ is the muon gyromagnetic ratio. The depolarization rate, $\sigma$, is related to the variance of the magnetic field distribution in the superconductor. The $\sigma$ values determined by fitting the data to Eq. (1) are displayed in Fig. 2(a). The field distribution of the flux line lattice is broadened by the presence of randomly oriented nuclear magnetic moments in the sample. The depolarization due to this nuclear dipolar field $\sigma_N$ is assumed to be temperature independent, and adds in quadrature to the contribution from the flux line lattice $\sigma_{FLL}$. $\sigma_F$ is the reduced field and $\Phi_0$ is the magnetic flux quantum.

$$\sigma^2 = \sigma_{FLL}^2 + \sigma_N^2. \quad (2)$$

A background term was included to account for the nuclear contribution in our analysis, with the approximately field independent value $\sigma_N = 0.116 \pm 0.003 \mu$s$^{-1}$.

The depolarization dataset was transposed to show $\sigma$ as a function of field in Fig. 2(b). Brandt has derived a useful relation describing this field dependence [34], which is valid over the field range examined in this experiment:

$$\sigma_{FLL}^2 = 7.5 \times 10^{-4}(1-h)^2[1 + 3.9(1-h)^2]\Phi_0^2 \lambda^{-4}, \quad (3)$$

where $h = H/H_{C2}$ is the reduced field and $\Phi_0$ is the magnetic flux quantum. Fitting the data collected at a given
temperature to Eq. (3) yields the values of $\lambda$ and $\mu_B H_{C2}$. Assuming London local electrodynamics, the temperature dependence of the corrected penetration depth can be calculated for an isotropic s-wave superconductor in the clean limit using the following expression:

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = 1 + 2 \int_{\Delta(0)}^{\infty} \left( \frac{\partial f}{\partial E} \right) \frac{E \, dE}{E^2 - \Delta^2(T)}.$$  

(4)

where $f = [1 + \exp(E/\mu_B T)]^{-1}$ is the Fermi function and $\Delta(T) = \Delta(0) \tanh \{ 1.82 [1.018(T_c/T - 1)]^{0.51} \}$ is the BCS approximation for the temperature dependence of the energy gap. The full temperature dependence of the corrected inverse-squared penetration depth is displayed in Fig. 2(c) with a fit to the data using this model. The resultant value for the energy gap $\Delta_0 = 0.369 \pm 0.007$ meV yields a BCS parameter $2\Delta_0/\mu_B T_c = 3.81 \pm 0.01$. This is larger than the 3.5 expected from the BCS theory in the weak coupling limit, implying that the strength of the superconducting pairing mechanism is slightly enhanced.

The magnetic penetration depth is directly related to $(m^*/n_s)$, where $m^*$ is the effective mass of charge carrying electrons (in units of the electron rest mass $m_e$) and $n_s$ the superconducting charge carrier density. Following the procedure described in Ref. [35], our experimentally determined value of $\lambda(0) = 482 \pm 2$ nm can be coupled with a heat capacity measurement of the Sommerfeld constant $\gamma = 47 \pm 1$ mJ mol$^{-1}$ K$^{-2}$ to yield $m^*/m_e = 13.9 \pm 0.2$ and $n_s = 0.169 \pm 0.003 \times 10^{28}$ m$^{-3}$. Consequently an effective Fermi temperature $T_F = 432 \pm 8$ K may be calculated. Uemura et al. have described a method of classifying superconductors based on the ratio of the critical temperature to this effective Fermi temperature, which for this system is $T_c/T_F = 1/192$ [36–38]. This places La$_2$Ir$_3$ in the vicinity of the heavy fermion superconductors, which is reflected in the relatively large value of $m^*$.

We now consider the results from the zero-field (ZF) and longitudinal-field (LF) experiments. Figure 3(a) shows the relaxation spectra collected above and below the superconducting transition temperature in ZF. There is a clear change in the relaxation behaviour on either side of the transition. The increased relaxation below $T_c$ has been verified with the MuSR instrument in both longitudinal and transverse geometries, which requires a physical rotation of the zero-field coils by 90°. There is no hint of an oscillatory component in the spectra, which would otherwise suggest the presence of an ordered magnetic structure.

In the absence of atomic moments, the depolarization of the muon ensemble is due to the presence of static, randomly oriented nuclear moments. This behaviour is modeled by the Gaussian Kubo-Toyabe equation [39]

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

(5)

where $\sigma_{ZF}$ measures the width of the nuclear dipolar field experienced by the muons. The spectra are well described by the function

$$G(t) = A_0 G_{KT}(t) \exp(-\Delta t) + A_{bg},$$  

(6)

where $A_0$ and $A_{bg}$ are the sample and background asymmetries, respectively, and $\Delta$ measures the electronic relaxation rate.

The parameters $A_0$ and $A_{bg}$ are found to be approximately temperature independent. The nuclear depolarization rate $\sigma_{ZF}$ remains approximately flat, except as $T \to 0$ K where a slight increase is observed. The electronic relaxation rate $\Delta$ shows a systematic increase below the superconducting transition temperature (see Fig. 3, (a) and (b)). An exponential relaxation process is generally attributed to the field distribution arising from electronic spins fluctuating quickly enough to motionally

FIG. 2. (Color online) (a) TF-$\mu$SR depolarization rate collected in a range of fields between 10 and 50 mT. (b) Field dependence of the depolarization rate for a range of different temperatures. The solid lines are the results of fitting the data with Eq. (3) via Eq. (2). (c) Extracted temperature dependence of the inverse magnetic penetration depth squared. The solid line is the result of a fit using Eq. (4).
narrow the effective depolarization of the muons. However, a weak magnetic field of only 5 mT is enough to fully decouple the muon from this exponential relaxation channel. This implies that the relaxation mechanism is actually static or quasi-static with respect to the muon lifetime. Furthermore, spin fluctuations associated with the proximity to a quantum critical point would be expected to exhibit a Curie-Weiss-like temperature dependence, as opposed to the onset at $T_c$ observed [40].

Thus it is likely that the source of the ZF signals observed below $T_c$ is unique to the La$_7$Ir$_3$, and corresponds to the onset of a superconducting channel that breaks time-reversal symmetry. Aoki et al. have discussed the probable sources of the spontaneous field in superconductors with TRSB [18]. In systems where the Cooper pairs have non-zero spin and orbital moments, regions in the sample where the order parameter becomes spatially inhomogeneous, such as grain boundaries, surfaces, and impurity sites, act as field sources due to the undamped supercurrents that arise there [41]. Alternatively, if the Cooper pairs have only non-zero spin moments, a hyperfine field may be generated at the interstitial $\mu^+$ sites.

The TRSB signals are observed in the $\Lambda$ relaxation channel, akin to the NCS LaNiC$_2$ and Sr$_2$RuO$_4$ [12]. This implies that the sources of field are dilute, producing a Lorentzian field distribution that is randomly sampled by the muons. If the field sources are caused by inhomogeneities in the order parameter, one would expect the Cooper pairs to possess a non-zero orbital momentum. However, the temperature dependence of the magnetic penetration depth is well described by an isotropic s-wave model. A further complication for NCS is that the ground state may be an admixture of spin-singlet and spin-triplet superconductivity. If the Cooper pairs associated with the spin-triplet channel do indeed have an orbital momentum, the greater relative strength of the singlet to triplet channels have made its detection difficult given the sensitivity of the current experiment.

In conclusion, TF- and ZF-$\mu$SR measurements have been carried out on the noncentrosymmetric superconductor La$_7$Ir$_3$. A spontaneous magnetization is clearly observed at the superconducting transition temperature, confirming that time-reversal symmetry is broken in the superconducting state. However, the superconducting order parameter is described well by an isotropic gap with s-wave pairing symmetry and enhanced electron-phonon coupling. The results imply that La$_7$Ir$_3$ has a superconducting ground-state that features a dominant s-wave component, with the exact nature of the triplet component undetermined. In order to determine if the superconductivity is nonunitary, further experimental work on high quality single crystals is vital, coupled with group theory calculations to determine the allowed pairing symmetries. This work paves the way for further studies of the large number of superconductors in the Th$_7$Fe$_3$ family in the hunt for unconventional behaviour.

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