Unconventional Superconductivity in La₇Ir₃ 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 La₇Ir₃ is investigated using muon spin rotation and relaxation. Zero-field measurements reveal the presence of spontaneous static or quasistatic 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 La₇Ir₃ may be unconventional and paves the way for further studies of this family of materials.

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To this day, the microscopic theory of superconductivity presented by Bardeen et al. [1] forms the basis to the theoretical and experimental understanding of the phenomenon of superconductivity. 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 wave function 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 center of inversion exhibit a good quantum number, and no mixing of pair states is allowed. Systèmes lacking a centrosymmetric 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 wave function 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 center of inversion exhibit a good quantum number, and no mixing of pair states is allowed. 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 $\text{Sr}_2\text{RuO}_4$ [12,13], the heavy fermion superconductors $\text{UPt}_3$ and $(\text{U, Th})\text{Be}_3$ [14–17], the filled skutterudites $(\text{Pr, La})(\text{Ru, Os})_2\text{Sb}_12$ [18,19], $\text{PrPt}_3\text{Ge}_12$ [20] and centrosymmetric $\text{LaNiGa}_2$ [21], and recently the caged-type superconductor $\text{La}_3\text{Rh}_6\text{Sn}_{18}$ [22]. $\mu$SR studies have been carried out on many other noncentrosymmetric superconductors (NCSs), including $\text{Ca}(\text{Ir, Pt})\text{Si}_3$ [23], $\text{La}(\text{Rh, Pr, Pd, Ir})\text{Si}_3$ [24–26], $\text{Mg}_{10}\text{Ir}_{19}\text{B}_{16}$ [27], and $\text{Re}_2\text{Zr}$ [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 noncentrosymmetric superconductors reported to break TRS are $\text{LaNiC}_2$ [29], $\text{Re}_2\text{Zr}$ [30], and the locally noncentrosymmetric $\text{SrPtAs}$ [31]. It is clearly important to search for new noncentrosymmetric structures that exhibit TRSB. Binary transition metal compounds with...
the Th$_3$Fe$_3$ structure have been found to host a large number of superconducting combinations [32,33]. These materials crystallize in a hexagonal structure with space group $P6_3mc$. In this Letter, evidence for TRSB in a member of this family La$_3$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$_3$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 characterized on a PANalytical powder x-ray diffractometer. μSR 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 thermalize, sitting at interstitial positions in the crystal lattice. The muon spin precesses at the Larmor precession frequency, sitting at interstitial positions in the crystal lattice. The superconducting transition temperature $T_c$, the depolarization due to this nuclear dipolar field that originates from muons stopping in the silver:

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

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 temperature dependence of the muon depolarization rate $\sigma(T)$ extracted from fits to Eq. (1) is displayed in Fig. 2(a).

Isothermal cuts perpendicular to the $T$ axis of the $\sigma(T)$ data sets were used to determine the field dependence of the depolarization rate $\sigma(H)$ displayed in Fig. 2(b). Brandt [34] has derived a useful relation describing this field dependence, which is valid over the field range examined in this experiment:

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

FIG. 1 (color online). Representative TF μSR signals collected at (a) 100 mK and (b) 3.0 K in an applied magnetic field of 30 mT. The solid lines are fits using Eq. (1). The effect of the flux line lattice can be seen in the top panel as the strong Gaussian decay envelope of the oscillatory function. Above $T_c$, the depolarization is reduced and is due to the randomly oriented array of nuclear magnetic moments.
where $h = H / H_C^2$ is the reduced field, and $\Phi_0$ is the magnetic flux quantum. Inserting Eq. (3) into Eq. (2) yields a model that can be applied to the data in Fig. 2(b). A global fit was implemented in order to determine the temperature dependence of the inverse-squared penetration depth $\lambda^{-2}$ with the background depolarization rate shared between all temperatures. The resulting fits to the $\sigma(B)$ data are displayed as solid lines in Fig. 2(b), with the fit at 3.0 K representative of the shared background depolarization rate, $\sigma_N = (0.116 \pm 0.003) \ \mu s^{-1}$. The temperature dependence of $\lambda^{-2}$ is presented in Fig. 2(c), where $\lambda^{-2}$ has been fixed to zero above $T_c$. Assuming London local electrodynamics, the temperature dependence of the superfluid density can be calculated for an isotropic $s$-wave superconductor in the clean limit using the following expression:

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = 1 + 2 \int_{\Delta(T)}^{\infty} \frac{E \, dE}{\sqrt{E^2 - \Delta^2(T)}},$$

(4)

where $f = [1 + \exp(E/k_B T)]^{-1}$ 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 result of a fit to this model for the measured values of $\lambda^{-2}(T)$ is displayed as the solid line in Fig. 2(c). The fitted value for the energy gap $\Delta_0 = (0.369 \pm 0.007) \ \text{meV}$ yields the BCS parameter $2\Delta_0/k_B T_c = 3.81 \pm 0.01$. This is larger than the value of 3.5 expected from the BCS theory in the weak coupling limit, implying that the strength of the superconducting pairing mechanism is enhanced in this system.

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 $\lambda(0) = (482 \pm 2) \ \text{nm}$ can be coupled with a heat capacity measurement of the Sommerfeld constant $\gamma = (47 \pm 1) \ \text{mJ mol}^{-1} \ \text{K}^{-2}$ to yield $m^*/m_e = 13.9 \pm 0.2$ and $n_s = (0.169 \pm 0.003) \times 10^{28} \ \text{m}^{-3}$. Consequently, an effective Fermi temperature $T_F = (432 \pm 8) \ \text{K}$ is calculated. Uemura et al. [36–38] 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 $T_c/T_F = 1/192$. This result implies that the superconductivity in La$_3$Ir$_4$ is unconventional and places this system in the vicinity of the heavy fermion superconductors under the Uemura classification scheme.

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 behavior 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°. This is significant, as any stray field that may erroneously be interpreted as a TRSB signal will be applied in orthogonal geometries and would appear differently in the relaxation spectra. There is no hint of an oscillatory component in the data, 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 behavior 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.
The superconducting order parameter has been described to the onset of a superconducting channel that breaks time-reversal symmetry. This marks the discovery of the first hexagonal NCS to exhibit broken time-reversal symmetry. The superconducting order parameter has been described well by an isotropic s-wave model. A further implication 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, possess an orbital moment, 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 has been clearly observed at the superconducting transition temperature, confirming that time-reversal symmetry is broken in the superconducting state. This marks the discovery of the first hexagonal NCS to exhibit broken time-reversal symmetry. The superconducting order parameter has been described well by an isotropic gap with $s$-wave pairing symmetry and enhanced electron-phonon coupling. The results have implied that La$_7$Ir$_3$ has an unconventional 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$_2$Fe$_3$ family in the hunt for unconventional behavior.

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