Evidence for superconductivity with broken time-reversal symmetry in locally noncentrosymmetric SrPtAs

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We report the magnetic and superconducting properties of locally noncentrosymmetric SrPtAs obtained by muon-spin-rotation/relaxation (μSR) measurements. Zero-field μSR reveals the occurrence of small spontaneous static magnetic fields with the onset of superconductivity. This finding suggests that the superconducting state of SrPtAs breaks time-reversal symmetry. The superfluid density as determined by transverse field μSR is nearly flat approaching $T = 0$ K proving the absence of extended nodes in the gap function. By symmetry, several superconducting states supporting time-reversal-symmetry breaking in SrPtAs are allowed. Out of these, a dominantly $d + id$ (chiral d-wave) order parameter is most consistent with our experimental data.

Transition metal pnictides have attracted considerable scientific interest as they present the second largest family of superconductors after the cuprates.[1] All superconductors of this family share one common structural feature: Superconductivity takes place in a square lattice formed by the transition metal elements. Very recently superconductivity with a T_c of 2.4 K has been discovered in SrPtAs,[2] which has a unique and attractive structural feature: It crystallizes in a hexagonal structure with weakly coupled PtAs layers forming a honeycomb lattice. SrPtAs supports three pairs of split Fermi surfaces, two of which are hole-like and centered around the Γ point with a cylindrical shape extended along the k_z direction and together host only about 30% of the density of states. The remaining 70% of the density of states are hosted by the third pair of split Fermi surfaces that is electron-like, centered around the K and K' and consisting of a cylindrical and a cigar-like sheet.[3,4] One unit cell of SrPtAs contains two PtAs layers each of which lacks a center of inversion symmetry even though the system has a global inversion center.[3] Locally broken inversion symmetry in SrPtAs together with a strong spin-orbit coupling might cause dramatic effects on the superconducting properties of this system that are otherwise found in noncentrosymmetric materials only.[5] Indeed, theoretical calculations focusing on a spin-singlet order parameter for SrPtAs predict a significant enhancement of the Pauli limiting field and the zero-temperature spin susceptibility.[3] In addition, a comprehensive symmetry analysis reveals that some unconventional states are possible, such as the A_{2u} state with a dominant f-wave component and the E_g state with a dominant chiral d-wave part, which breaks time-reversal symmetry (TRS).[6]

In this Rapid Communication, we report on muon spin-rotation/relaxation (μSR) measurements to determine the magnetic and superconducting properties of SrPtAs. We find small spontaneous internal magnetic fields below T_c showing that the superconducting state breaks TRS. Low-temperature superfluid density measurements indicate the absence of extended nodes in the gap function of SrPtAs. These experimental findings are discussed in light of the different superconducting states allowed by symmetry. From these states, the E_g (chiral d-wave) order parameter is the most likely pairing state in SrPtAs. We also discuss some other possible scenarios.

Two batches of polycrystalline samples (A and B) of SrPtAs were prepared via a solid state reaction method as described in Ref. 2. Sample A is a disk-shaped pellet ($\approx$12 mm diameter and 1 mm thickness), while sample B is a powder of polycrystalline SrPtAs. Both samples were glued to a Ag sample holder. Low-temperature μSR measurements on sample A were carried out down to 0.019 K using the low-temperature facility (LTF) muon instrument located on the πM3 beamline of the Swiss Muon Source at the Paul Scherrer Institute, Villigen, Switzerland. Analogous measurements were carried out on sample B using the MuSR spectrometer at the ISIS pulsed muon facility, Oxford, United Kingdom. Data were collected with zero (ZF), longitudinal (LF), and transverse magnetic fields (TF). The magnetic field was applied above the superconducting transition temperature and the sample subsequently cooled down to base temperature. The μSR data were analyzed using the free software package MUSRFIT.[7]
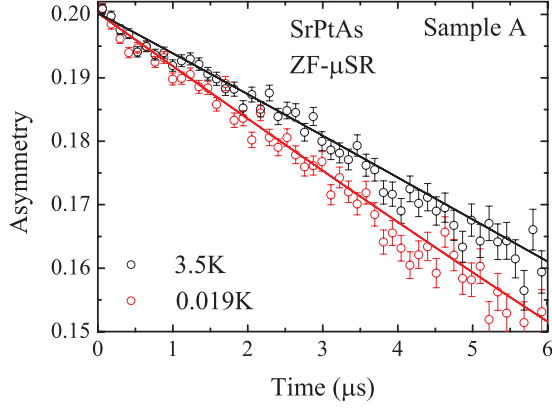
FIG. 1. (Color online) ZF-μSR time spectra for SrPtAs at 3.5 K (above T_c; open circles) and 0.019 K (below T_c; closed circles). The solid lines are the fits to the data using Eq. (1).

Figure 1 shows ZF-μSR time spectra for SrPtAs. Open circles indicate data collected at 3.5 K (above T_c) and closed circles data collected at 0.019 K (below T_c). Data taken below T_c show a greater relaxation than above T_c. The small relaxation above T_c arises from randomly oriented nuclear magnetic dipole moments that are static on the time scale of μSR. The additional relaxation of the muon spin polarization $P(t)$ below T_c is caused by spontaneous magnetic moments which may be either quasistatic or dynamic. To distinguish between these two possibilities, we have performed LF-μSR in a weak magnetic field of 9 mT. We find that this field is sufficient to decouple the muon spin polarization (see the lower panel of Fig. 2) which proves that the additional spontaneous magnetic relaxation appearing below T_c in the ZF-μSR data is due to quasistatic moments.[8] To quantitatively evaluate the ZF-μSR spectra, we fitted a combination of a static Lorentzian
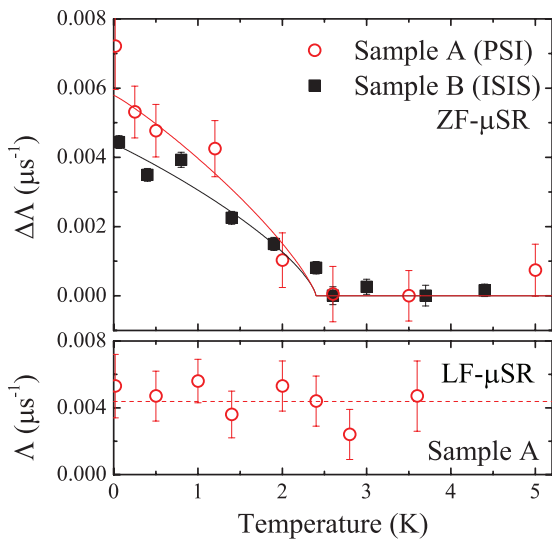

FIG. 2. (Color online) Upper panel: Temperature-dependent part of the electronic relaxation rate $\Delta\Lambda$ for two different samples of SrPtAs measured at two different μSR facilities. Lower panel: Temperature dependence of Λ (open circles) in a weak LF of 9 mT. Solid curves are guides to the eye.
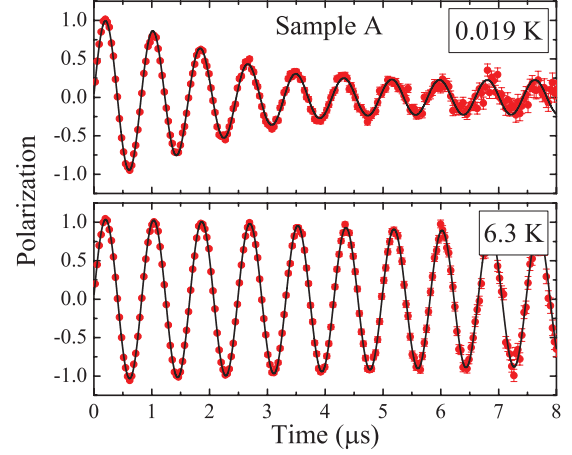

FIG. 3. (Color online) TF-μSR time spectra of SrPtAs collected at 0.019 and 6.3 K. Solid lines are fits to the data using Eq. (2).

and Gaussian Kubo-Toyabe relaxation function[9–12] to the data:

$$P(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta_{nm}^2 t^2 - \Lambda t)\exp\left(-\frac{\Delta_{nm}^2 t^2}{2} - \Lambda t\right).$$
(1)

Here Δ_{nm} and Λ are the temperature-independent Gaussian and the temperature-dependent exponential muon relaxation rates due to the presence of nuclear and electronic moments, respectively. The solid lines in Fig. 1 are fits to the data using this equation.

Both samples of SrPtAs measured at two different μSR facilities show very similar spectra. In both cases a small increase of the relaxation rate is observed below the superconducting T_c. Figure 2 shows the temperature-dependent part of the relaxation rate $\Delta\Lambda = \Lambda(T) - \Lambda(T \approx 5\,\text{K})$ for both samples. The increase of the relaxation indicates the appearance of a spontaneous magnetic field in the superconducting state of SrPtAs. The existence of such a spontaneous field in SrPtAs and its correlation with the superconducting T_c provides evidence for a superconducting state that breaks TRS. A similar behavior has been observed by μSR in the spin-triplet TRS-breaking superconductor Sr$_2$RuO$_4$.[13] Possible origins for the occurrence of TRS breaking in SrPtAs will be discussed below, but we first turn to the experimental characterization of the superconducting properties of SrPtAs.

To reveal information on the pairing symmetry in the presence of TRS breaking, we have also performed TF-μSR measurements in a field of 9 mT, which is larger than the first critical field of ≈ 4 mT that we determined by low-temperature magnetization measurements. Figure 3 shows TF-μSR precession signals of sample A of SrPtAs above and below T_c. In the normal state, the oscillation only shows very small relaxation. Below T_c, the relaxation rate increases due to the broad field distribution produced by the presence of the vortex lattice. Solid lines are fits to the data using a sinusoidally oscillating function with a Gaussian decay component:

$$P(t) = P_s \exp(-\sigma^2 t^2/2)\cos(\gamma_\mu B_{int} t + \phi)$$
$$+ P_{bgd}\cos\left(\gamma_\mu B_{bgd} t + \phi\right),$$
(2)

where P_s and P_{bgd} are the relative fractions of muons hitting the sample and the Ag sample holder, respectively, the latter

giving a practically undamped background signal. $\gamma_\mu/2\pi = 135.5$ MHz/T is the muon gyromagnetic ratio,[14] B_{int} and B_{bgd} are the internal and background magnetic field at the muon sites, $\phi = -\pi/2$ is the phase of the initial muon spin polarization with respect to the positron detector, and σ is the Gaussian muon spin relaxation rate. σ can be written as $\sigma = (\sigma_{sc}^2 + \sigma_{nm}^2)^{1/2}$, where σ_{sc} is the superconducting contribution to the relaxation rate due to the field variation across the flux line lattice, and σ_{nm} is the nuclear magnetic dipolar contribution which is assumed to be constant over the temperature range of the study.

Figure 4(a) shows the temperature dependence of σ for SrPtAs for sample A. Qualitatively similar data are obtained for sample B. In a superconductor with an ideal Ginzburg-Landau vortex lattice, σ_{sc} is related to the penetration depth λ via Brandt's equation[15]

$$\sigma_{sc} = 4.83 \times 10^4 (1-b)[1 + 1.21(1-\sqrt{b})^3]\lambda^{-2}, \quad (3)$$

where $b = H/H_{c2}$ is the ratio of the applied field to the upper critical field. The temperature dependence of λ^{-2} is shown in Fig. 4(b) for which we used the data of Ref. 2 to estimate the temperature dependence of H_{c2}. The slope of the temperature dependence of the superconducting order parameter tends to zero as the temperature approaches zero, indicating the absence of low-lying excitations. This is corroborated by a reasonable fit of the data with a one-band BCS s-wave model. In contrast, a one-band model with line nodes is unable to reproduce the data.[25] However, we emphasize that in SrPtAs multiple electronic bands cross the Fermi level and that SrPtAs lacks locally an inversion symmetry center. Hence, unconventional order parameter symmetries and multiband superconductivity can be expected. Therefore, such a simple model description of the superfluid density is not likely to reveal the true underlying pairing symmetry. However, with the present statistical accuracy we are at least confident that SrPtAs has no extended nodes in the gap function. This conclusion holds for both samples even though the measured low-temperature magnetic penetration depth is about 30% smaller for sample B [$\lambda = 239(4)$ nm] than for sample A [$\lambda = 339(6)$ nm]. The reason for this discrepancy is not known at the moment.

Interestingly, the internal magnetic field B_{int} clearly increases by about 0.15 mT below T_c as shown for sample A in the inset of Fig. 4. This behavior is unexpected since typically one observes a diamagnetic shift in spin-singlet superconductors or a constant field in spin-triplet superconductors. More detailed studies, especially on single crystals, for which demagnetization effects can be properly taken into account are required to understand this phenomenon in detail, but we suggest that this positive internal field shift might be related to the occurrence of TRS breaking in SrPtAs.

In summary, we found experimental evidence for (i) weak breaking of TRS that sets in at the same temperature as the superconducting order and (ii) no extended nodes in the order parameter. In the following, we will discuss possible origins of TRS breaking for different order parameter symmetries in the light of these experimental observations.[26]

(i) *Chiral bulk and surface states*. The most straightforward explanation for bulk TRS breaking is a superconducting order parameter of dominantly $d + id$ symmetry,
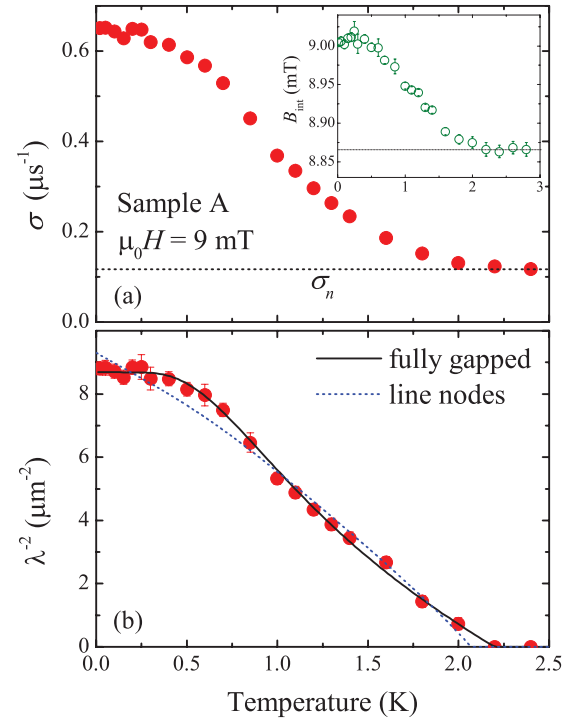

FIG. 4. (Color online) (a) Temperature dependence of σ_{sc} of SrPtAs. The inset is the temperature dependence of the internal field. (b) Temperature dependence of λ^{-2} of SrPtAs which is proportional to the superfluid density n_s/m^*. Solid and dashed lines are the fits to the data using a fully gapped model and a one-band model with line nodes, respectively.

the so-called chiral E_g state.[6] This state can be stabilized in a scenario where superconductivity is driven by the Van Hove singularities located around the M points; see Fig. 5. Intuitively, this can be explained using the following parallel to the cuprates: On the square lattice, repulsive scattering between the *two* Van Hove singularities favors the $d_{x^2-y^2}$ order parameter symmetry with *sign change*. On a lattice with threefold rotational symmetry, repulsive scattering between the *three* Van Hove singularities is frustrated. The phases of the superconducting order parameter near the Van Hove points, ϕ_i, $i = 1,2,3$, then spontaneously choose one of the TRS breaking *chiral* configurations $\phi_1 - \phi_2 = \phi_2 - \phi_3 = \pm 2\pi/3$ [see Fig. 5(a)].[16,17] The E_g state supports topologically protected chiral modes at the surface and at defects, such as the implanted muon itself.

(ii) *Frustrated interband Cooper pair scattering*. An alternative scenario for bulk TRS breaking is based on frustrated Cooper pair scattering between multiple disconnected Fermi pockets[18] located at the K and K' points. Starting from a nodeless s-wave superconducting order parameter (A_{1g} symmetry), this interpocket scattering leads to a similar chiral phase structure as in scenario (i), however, with constant phases ϕ_i, $i = 1,2,3$, on each pair of pockets [see Fig. 5(b)]. Here, the TRS breaking is a secondary transition out of a conventional s-wave superconductor.

(iii) *TRS breaking at the surface*. In view of the granularity of our samples, we comment on the possibility of spontaneous TRS breaking at the boundary, while the bulk remains in a TRS
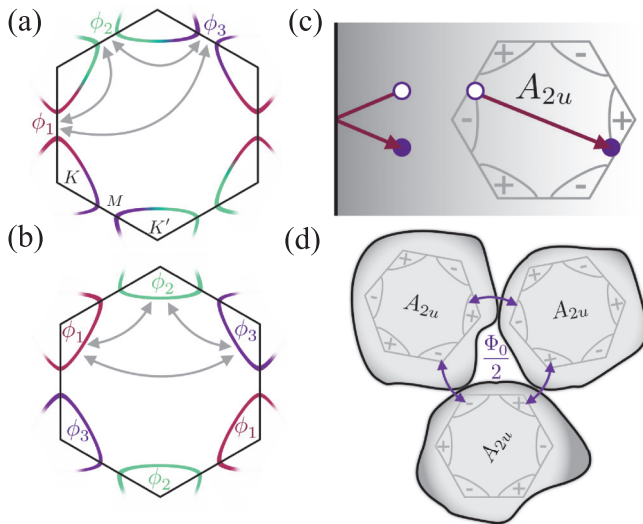
FIG. 5. (Color online) Illustration of possible mechanisms for TRS breaking in SrPtAs. (a) Frustrated inter-Fermi-surface Cooper pair scattering. (b) Stabilizing the chiral E_g state with Cooper pair scattering. (c) Andreev scattering with π phase shift in the A_{2u} state. (d) Frustrated current loops.

superconducting state. Such surface effects can be expected for a dominantly f-wave superconductor (A_{2u} state), with a gap function that changes sign under a $\pi/3$ rotation around the z axis [see Fig. 5(c)]. On the one hand, this sign change influences the Andreev scattering on the sample surface, if the surface normal has a nonvanishing component in the plane defined by the layers [see Fig. 5(c)]. Energetically, the destructively interfering scattering process leads to a suppression of the A_{2u} state close to the surface. Topologically, it equips the surface with a dispersionless 2D band structure with a degeneracy protected by TRS. Residual interactions in this surface flat band generically lift its degeneracy, thereby breaking spontaneously the TRS by nucleation of a $\Delta_{A_{2u}} + i\Delta_{A_{1g}}$ order parameter locally at the surface. On the other hand, due to the granularity of the sample, three or more crystallites can form a loop around a void within the sample, while remaining in a phase coherent superconducting state. Due to the sign change of the gap function in the A_{2u} state, the order parameter might acquire a phase shift of π around the loop.[19] To account for this phase shift, half of a superconducting flux quantum $\phi_0/2 = h/(4e)$ is trapped in the loop [see Fig. 5(d)]. The associated TRS breaking supercurrent would then cause an increase in muon depolarization rate of the muons that stop close to the loop. At low fields these frustrated current loops are expected to give rise to an unusual positive field shift, an effect that has also been observed in granular samples of high-T_c cuprates.[19,20] This granularity scenario would be consistent with the positive field shift below T_c of the sample (see inset of Fig. 4).

Notably, none of the above scenarios is compatible with an s-wave order parameter symmetry. Furthermore, in the absence of fine tuning, TRS breaking in scenarios (ii) and (iii) is expected to occur as a secondary transition, i.e., at a temperature lower than $T_c = 2.4$ K, which is in contradiction with our measurements. Hence, the chiral E_g state is the most likely explanation for TRS breaking in SrPtAs. This state is also favored by the second experimental finding that the gap function of SrPtAs possesses no extended nodes since it has only a point node on one out of six bands contributing to superconductivity, while the other pairing symmetry allowing for TRS breaking, namely A_{2u}, possesses line nodes on four of these bands.

In conclusion, we have found small static magnetic fields in two different samples of SrPtAs measured at two different μSR facilities. These internal magnetic fields set in at the superconducting T_c and grow with decreasing temperature. This provides strong evidence that the superconducting state of locally noncentrosymmetric SrPtAs breaks TRS. In addition, we observed a nearly flat temperature dependence of the superfluid density approaching $T = 0$ K proving the absence of extended nodes in the superconducting gap function. Furthermore we proposed several scenarios which can lead to TRS breaking in SrPtAs on the basis of the superconducting states allowed by symmetry. While the other states cannot be completely excluded, our experimental observations are most consistent with an E_g symmetry of the superconducting order parameter which is dominated by a spin-singlet $d + id$ (chiral d-wave) state.

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[25] For the displayed fit with line nodes, we use a one-band d-wave model. Details of models are discussed in Refs. 21,22 and also in our previous work (Refs. 23,24).

[26] A microscopic analysis of time-reversal-symmetry breaking is presented elsewhere: M. H. Fischer *et al.* (unpublished).