Spin-singlet superconductivity with a full gap in locally non-centrosymmetric SrPtAs

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Abstract

We report $^{195}$Pt-NMR and $^{75}$As-NQR measurements for the locally non-centrosymmetric superconductor SrPtAs where the As-Pt layer breaks inversion symmetry while globally the compound is centrosymmetric. The nuclear spin lattice relaxation rate $1/T_1$ shows a well-defined coherence peak below $T_c$ and decreases exponentially at low temperatures. The spin susceptibility measured by the Knight shift also decreases below $T_c$ down to $T < T_c/6$. These data together with the penetration depth obtained from the NMR spectra can be consistently explained by assuming a spin-singlet superconducting state with a full gap. Our results suggest that the spin-orbit coupling due to the local inversion-breaking is not large enough to bring about an exotic superconducting state, or the inter-layer hopping interaction is larger than the spin-orbit coupling.
In non-centrosymmetric superconductors, an antisymmetric spin-orbit coupling (ASOC) interaction is induced. As a result, a parity mixed superconducting state is allowed and the mixing extent is determined by the strength of an ASOC.\textsuperscript{1–3} Indeed, some unconventional superconductors such as spin-triplet, nodal-gap superconductivity have been reported. For example, a nodal-gap and spin-triplet superconducting state has been reported in Li\textsubscript{2}Pt\textsubscript{3}B.\textsuperscript{4,5} However, Li\textsubscript{2}Pt\textsubscript{3}B is the only example that shows unconventional superconductivity and other superconductors containing heavy elements are conventional.\textsuperscript{6–10} The difference was explained by the peculiar crystal structure distortion as to increase the extent of inversion-symmetry breaking in Li\textsubscript{2}Pt\textsubscript{3}B.\textsuperscript{11}

Recently, “locally” non-centrosymmetric systems have also attracted attention.\textsuperscript{12,13} In these systems, the whole structure remains centrosymmetric, but inversion symmetry is broken locally in some parts within the unit cell. In such systems, a possible exotic superconducting state is suggested.\textsuperscript{12,13} However, these proposals have not been tested because of lack of samples. SrPtAs ($T_c \sim 2.4$ K) is one of such candidates.\textsuperscript{14}

SrPtAs has a honeycomb layered structure and consists of Sr and Pt-As layers. SrPtAs has an inversion symmetry in the whole unit cell, but the Pt-As layer lacks an inversion center. According to the theoretical calculation, a sizable ASOC is expected.\textsuperscript{15} When the interlayer hopping is smaller than the ASOC, an exotic state, such as a chiral $d$-wave or $f$-wave state can be expected.\textsuperscript{15–17} In this paper, we report the $^{195}$Pt nuclear magnetic resonance (NMR) and $^{75}$As nuclear quadrupole resonance (NQR) measurements in the superconducting and the normal states. The spin-lattice relaxation rate, $1/T_1$, shows a clear coherence peak just below $T_c$ and decays exponentially with decreasing $T$, indicating a fully opened superconducting gap on the whole Fermi surface. The Knight shift decreases below $T_c$, indicating a spin-singlet pairing. Our results suggest that the inter-layer hopping interaction is larger than the spin-orbit coupling due to the local inversion-breaking or the spin-orbit coupling is not large enough to bring about an exotic superconducting state, as opposed to the theoretical proposals.

The polycrystalline sample of SrPtAs was synthesized by a solid-state reaction. The PtAs\textsubscript{2} precursor was first synthesized by heating Pt powder and As grains at 700 °C in an evacuated quartz tube. Then, Sr, Pt, and PtAs\textsubscript{2} powders of stoichiometric amounts were mixed and ground. The resulting powder was placed in an alumina crucible and sealed in an evacuated quartz tube. The ampule was heated at 700 °C for 3 h and then at 1000 °C for
24 h. After furnace cooling, the sample was ground, pelletized, wrapped with Ta foil, and heated at 950 °C for 2 h in an evacuated quartz tube. The pellet was crushed into powders for NMR/NQR measurements. The $T_c$ at zero and a finite magnetic field $H$ was determined by measuring the ac susceptibility using the in situ NMR/NQR coil. The $T_c$ is 2.40 K at zero field and 1.43 K at 0.0842 T. A standard phase-coherent pulsed NMR spectrometer was used to collect data. NMR/NQR measurements were performed using the spin echo method. The nuclear spin-lattice relaxation rate was measured by using a single saturation pulse. Measurements below 1.4 K were carried out in a $^3$He-$^4$He dilution refrigerator.

**FIG. 1.** $^{75}$As-NQR spectrum of SrPtAs measured at $T = 4.2$ K.

Figure 1 shows the $^{75}$As ($I = 3/2$) NQR spectrum at $T = 4.2$ K. The sharp peak centered at $f = 27.5$ MHz. The full width at the half maximum (FWHM) of the NQR spectrum is 0.54 MHz.

Figure 2 shows the temperature dependence of $1/T_1$ measured at the peak of the NQR spectrum at zero magnetic field. The nuclear magnetization curve was fitted by a single exponential function:

$$\frac{M_0 - M(t)}{M_0} = \exp\left(-\frac{3t}{T_1}\right),$$

where $M_0$ and $M(t)$ are the nuclear magnetization in the thermal equilibrium and at a time $t$ after the saturating pulse, respectively. Figure 3 shows the enlarged part of $1/T_1$ around $T_c$. As seen in the figure, $1/T_1$ varies in proportion to the temperature ($T$) above $T_c$, as expected for conventional metals, indicating no electron-electron interaction. Below $T_c$, $1/T_1$ shows a coherence peak (Hebel-Slichter peak). The $1/T_{1S}$ in the superconducting state is
FIG. 2. (color online) Temperature dependence of the $^{75}$As spin-lattice relaxation rate, $1/T_1$ measured by NQR. The straight line above $T_c$ represents the $T_1 T = \text{const}$ relation. The solid curve below $T_c$ is a calculation assuming the BCS function. The dotted curve is a calculation for a chiral $d$-wave state (see text for detail).

expressed as

$$
\frac{T_{1N}}{T_{1S}} = \frac{2}{k_B T} \int \int \left( 1 + \frac{\Delta^2}{EE'} \right) N_S(E)N_S(E') \times f(E) [1 - f(E')] \delta(E - E') dEdE',
$$

(2)

where $1/T_{1N}$ is the relaxation rate in the normal state, $N_S(E)$ is the superconducting density of states (DOS), $f(E)$ is the Fermi distribution function and $C = 1 + \frac{\Delta^2}{EE}$ is the coherence factor. To perform the calculation of eq. (2), we follow Hebel to convolute $N_S(E)$ with a broadening function $B(E)$, which is approximated with a rectangular function centered at $E$ with a height of $1/2\delta$. The solid curve below $T_c$ shown in Fig. 2 is a calculation with $2\Delta = 3.85k_BT_c$, $r \equiv \Delta(0)/\delta = 4$. It fits the experimental data reasonably well.
The parameter $2\Delta$ is close to the BCS value of $3.5k_B T_c$. This result indicates an isotropic superconducting gap in this compound.

Theoretically, a chiral $d$-wave superconducting state was proposed.\textsuperscript{16,19} In the case of $d$-wave superconductor, the coherence factor is much suppressed because of the sign change of the order parameter. In principle, a tiny coherence peak could be present for a $d$-wave state, but practically it is usually smeared out as seen in high-$T_c$ cuprates.\textsuperscript{20,21} The dotted curve of Fig. 2 and Fig. 3 is a calculation assuming the chiral $d$-wave with same parameter used in the $s$-wave fitting, $2\Delta = 3.85k_B T_c$, $r = 4$. In our experiment, the coherence peak was clearly observed, which is hard to be explained by the chiral $d$-wave superconducting state. The other report proposed a $f$-wave superconducting state.\textsuperscript{17} In such case, $1/T_1$ should show a power law $T$ dependence due to nodes in the gap function. So a $f$-wave superconducting state is not supported by our data.

Figure 4 shows the $^{195}$Pt-NMR spectra for temperature above and below $T_c(H) = 1.43$ K, respectively. The spectra can be fitted by a single Gaussian function and the FWHM of the NMR line at 1.43 K is 5.1 kHz. The very sharp transition indicates the high quality of the sample. The temperature dependence of the FWHM is shown in Fig. 5(a). Above $T_c$, the FWHM is temperature independent within the error bar. However, the FWHM is enlarged below $T_c(H)$. Below $T_c$, a vortex state produces a distribution of the magnetic field in a superconductor. As a result, an NMR spectrum is broadened.\textsuperscript{22} The difference of the FWHM between temperatures below and above $T_c$ is related to the penetration depth.
FIG. 4. (color online) $^{195}$Pt-NMR spectrum measured at a magnetic field of $H = 0.0842$ T above and below $T_c(H)$, respectively.

FIG. 5. (color online) (a) The temperature dependence of the full width at the half maximum ($FWMH$) for the $^{195}$Pt-NMR spectrum. (b) The temperature dependence of the penetration depth $\lambda$. The solid curve is a calculation by assuming a conventional $s$-wave superconducting state (see text for detail).
FIG. 6. (color online) The temperature dependence of the Knight shift for SrPtAs measured in $H = 0.0842\, T$. The solid curve below $T_c$ is a calculation assuming a spin-singlet pairing (see text for detail).

as the following,$^{23}$

$$\sqrt{\text{FWHM}(T=0)^2 - \text{FWHM}(T \geq T_c)^2} = 0.0609 \gamma_n \frac{\phi_0}{\lambda^2}$$  \hspace{1cm} (3)

Here, $\gamma_n$ is the gyromagnetic ratio for a nucleus, $\phi_0 = 2h/e = 2.07 \times 10^{-7}\, \text{Oe/cm}^2$ is the quantized magnetic flux, and $\lambda$ is London penetration depth. For a fully gapped superconductor, the temperature dependence of $\lambda$ for $T/T_c < 0.5$ is described as following,$^{24}$

$$\lambda(T) = \lambda(0) \left[1 + \sqrt{\frac{\pi \Delta}{2k_B T}} \exp \left(-\frac{\Delta}{k_B T}\right)\right]$$  \hspace{1cm} (4)

The solid line below $T_c$ in Fig. 5(b) is the calculation by assuming a fully gapped superconducting state with $\Delta(T = 0)$ obtained from the $T_1$ result and $\lambda(0)$ is calculated to be 460 nm. This value is close to a previous $\mu$SR report of $\lambda(0) = 339\, \text{nm}$.\textsuperscript{19} In a superconductor with a line-node gap, the penetration depth is proportional to $T$ at low temperatures. Our result shows that the penetration depth is $T$-independent below $0.5\, T_c$, which also excludes the possibility of $f$-wave state.

Figure 6 shows the Knight shift, $K$, as a function of temperature. The Knight shift was calculated by the nuclear gyromagnetic ratio $\gamma_N = 9.094\, \text{MHz/T}$ for $^{195}\text{Pt}$. Above $T_c$, the shift is $T$ independent, while it decreases below $T_c$. Generally, the Knight shift is expressed
as,

\[ K = K_{\text{orb}} + K_s \]  
\[ K_s = A_{hf} \chi_s \]  
\[ \chi_s = -4 \mu_B^2 \int N_S(E) \frac{\partial f(E)}{\partial E} dE, \]

where \( K_{\text{orb}} \) is the contribution due to orbital susceptibility which is \( T \)-independent, \( A_{hf} \) is the hyperfine coupling constant and \( \chi_s \) is the spin susceptibility. In the present case, \( K_{\text{orb}} \) is unknown. The solid curve below \( T_c \) in Fig. 6 is a calculation by assuming a spin-singlet state with the same gap parameter obtained from \( 1/T_1 \) fitting, and attributing the shift at the lowest temperature to be \( K_{\text{orb}} \). As can be seen in the figure, the result can also be well fitted by an \( s \)-wave state.

In conclusion, we have performed the \(^{195}\text{Pt-NMR} \) and \(^{75}\text{As-NQR} \) measurements on the locally non-centrosymmetric superconductor SrPtAs. We find that the spin-lattice relaxation rate \( 1/T_1 \) shows a coherence peak just below \( T_c \) and decreases exponentially at lower temperatures. The spin susceptibility measured by the Knight shift decreases below \( T_c \). These data together with the penetration depth obtained from the NMR data indicate that the Cooper pairs are in a singlet state with an isotropic gap. The conventional superconducting state suggests that the inter-layer hopping is large or the ASOC is weak in SrPtAs as opposed to previous theoretical proposals.

Note added: After completing this work, we became aware of a \( 1/T_1 \) measurement using NQR by Brückner et al.\(^{25} \) However, in their sample the coherence peak is much suppressed compared to ours. The \( T_c \) of Brückner et al. is lower than ours and the FWHM of NQR spectrum is broader than our sample,\(^{14} \) which may explain the suppressed coherence peak.

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