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Muon spin rotation study of the topological superconductor Sr$_x$Bi$_2$Se$_3$

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We report transverse-field (TF) muon spin rotation experiments on single crystals of the topological superconductor Sr$_x$Bi$_2$Se$_3$, with nominal concentrations $x \approx 0.15$ and $0.18$ ($T_c \sim 3$ K). The TF spectra ($B = 10$ mT), measured after cooling to below $T_c$, did not show any additional damping of the muon precession signal due to the flux line lattice within the experimental uncertainty. This puts a lower bound on the magnetic penetration depth $\lambda \geq 2.3 \mu$m. However, when we induce disorder in the vortex lattice by changing the magnetic field below $T_c$, a sizable damping rate is obtained for $T \to 0$. The data provide microscopic evidence for a superconducting volume fraction of $\sim 70\%$ in the $x = 0.18$ crystal and thus bulk superconductivity.

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I. INTRODUCTION

Sr$_x$Bi$_2$Se$_3$ belongs to the new family of Bi$_2$Se$_3$-based superconductors, which is reported to exhibit unconventional superconducting properties. The parent compound Bi$_2$Se$_3$ is a well-documented, archetypal topological insulator [1–3]. Recently, it was demonstrated that by doping Cu [4], Sr [5], Nb [6], or Tl [7] atoms, Bi$_2$Se$_3$ can be transformed into a superconductor with $T_c \sim 3$ K. Theory predicts the superconducting state to have a topological character, which is based on the close correspondence of the Bogoliubov–de Gennes Hamiltonian for the quasiparticles of the superconductor and the Bloch Hamiltonian for the insulator (for recent reviews on topological superconductivity, see Refs. [8,9]). In a topological superconductor, the condensate is expected to consist of Cooper pairs with odd-parity symmetry, while at the surface of the material, gapless Andreev bound states form that host Majorana zero modes. This provides an excellent motivation to thoroughly examine the family of Bi$_2$Se$_3$-based superconductors. These centrosymmetric compounds (D$_{3d}$ point group, $R\overline{3m}$ space group) belong to the symmetry class DIII [10]. Calculations within a two-orbital model show that odd-parity pairing, favored by strong spin-orbit coupling, can be realized [11]. In the case of Cu$_x$Bi$_2$Se$_3$, specific heat [12], upper critical field [13], and soft-point contact experiments [14] lend support to an odd-parity superconducting state. However, scanning tunneling microscopy (STM) measurements were interpreted to be consistent with s-wave pairing symmetry [15]. Clearly, further studies are required to solve this issue.

Superconductivity in Sr$_x$Bi$_2$Se$_3$ was discovered by Liu et al. [5]. Transport and magnetic measurements on Sr$_x$Bi$_2$Se$_3$ single crystals with $x = 0.06$ show $T_c = 2.5$ K. The resistivity is metallic with a low carrier concentration $n \approx 2 \times 10^{25}$ m$^{-3}$. Evidence for topological surface states was extracted from Shubnikov–de Haas oscillations observed in large magnetic fields [5]. The persistence of topological surface states upon Sr doping was confirmed by angle-resolved photoemission experiment (ARPES) measurements, which showed a topological surface state well separated from the bulk conduction band [16,17]. The superconducting state was further characterized by Shruti et al. [18], who reported $T_c = 2.9$ K for $x = 0.10$ and a large Ginzburg-Landau parameter, $\kappa \approx 120$, pointing to extreme type II superconducting behavior. A surprising discovery was made by Pan et al. [19] by performing magnetotransport measurements on crystals with nominal concentrations $x = 0.10$ and 0.15: the angular variation of the upper critical field, $B_{c2}(\theta)$, shows a pronounced twofold anisotropy for field directions in the basal plane, i.e., the rotational symmetry is broken. Magnetotransport measurements under high pressures show that the twofold anisotropy is robust up to at least $p = 2.2$ GPa [20].

Most interestingly, rotational symmetry breaking appears to be a common feature of the Bi$_2$Se$_3$-based superconductors when the dopant atoms are intercalated. In Cu$_x$Bi$_2$Se$_3$, it appears in the spin-system below $T_c$, as was established by the angular variation of the Knight shift measured by nuclear magnetic resonance (NMR) [21]. Moreover, specific-heat measurements show the basal-plane anisotropy in $B_{c2}$ is a thermodynamic bulk feature [22]. In Nb$_x$Bi$_2$Se$_3$, rotational symmetry breaking was demonstrated by torque magnetometry that probes the magnetization of the vortex lattice [23]. These recent experiments put important constraints on the superconducting order parameter. Notably, it restricts the order parameter to an odd-parity two-dimensional representation, $E_{\Delta}$, with $\Delta_3$ pairing [24–26]. Moreover, the superconducting state involves a nematic director that breaks the rotational symmetry when pinned to the crystal lattice, hence the label “nematic superconductivity.” The odd-parity Cooper pair state implies that these Bi$_2$Se$_3$-derived superconductors are topological superconductors.

Here we report a muon spin rotation study on Sr$_x$Bi$_2$Se$_3$. Muon spin rotation is an outstanding technique to determine the temperature variation of $\lambda$, as well as its absolute value, via the Gaussian damping rate, $\sigma_T$, of the $\mu^+$ precession signal in...
II. EXPERIMENT

Single-crystalline samples Sr$_x$Bi$_2$Se$_3$ with nominal values $x = 0.15$ and 0.18 were synthesized by melting high-purity elements at 850 °C in sealed evacuated quartz tubes. The crystals were formed by slowly cooling to 650 °C. The measurements show, however, that the increase of $\sigma_{TF}$ is smaller than the experimental uncertainty in field-cooling experiments, which tell us $\lambda$ is very large ($\approx 2.3$ $\mu$m for $T \to 0$). On the other hand, when we induce disorder in the vortex lattice by changing the magnetic field below $T_c$, a sizable damping rate $\sigma_{SC} \approx 0.36$ $\mu$s$^{-1}$ ($T \to 0$) is obtained. These results provide microscopic evidence for a superconducting volume fraction of $\approx 70\%$ in the crystal with nominal Sr content $x = 0.18$ and thus bulk superconductivity.

A first set of experiments was carried out for $x = 0.15$. The crystal with $T_c = 2.8$ K was slowly cooled in a TF of 10 mT ($B \parallel a$) to $T = 0.25$ K, after which $\mu$SR spectra were recorded at fixed temperatures, during stepwise increasing the temperature up to 3.0 K. The measured spectra at 0.25 and 3.0 K are shown Fig. 1, where we have plotted the decay asymmetry as a function of time. The initial asymmetry $A(0) = 0.24$ is the full experimental asymmetry ($A_{Tot}$). As can be noticed, the spectra at 0.25 and 3.0 K are very similar. We have fitted the spectra with the muon depolarization function,

$$A(t) = A_{Tot} \exp \left(-\frac{1}{2} \sigma_{TF}^2\right) \cos(2\pi vt + \phi). \tag{1}$$

Here $\sigma_{TF}$ is the Gaussian damping rate, $v = \gamma_{\mu} B_\mu / 2\pi$ is the muon precession frequency, $B_\mu$ is the average field sensed by the muon ensemble, and $\phi$ is a phase factor. The resulting temperature variation $\sigma_{TF}(T)$ is shown in Fig. 2. In the normal phase, $\sigma_{TF} = 0.089 \pm 0.002 \mu$s$^{-1}$, which we attribute to the field distribution due to nuclear moments considered.

The field is applied along the beam, and the positrons are collected in the left and right detectors. The crystals were glued with General Electric (GE) varnish to a thin copper foil that was attached to the cold finger of a helium-3 refrigerator (HELIOX, Oxford Instruments). $\mu$SR spectra were taken in the temperature interval $T = 0.25-10$ K. The $\mu$SR time spectra were analyzed with the software packages WIMDA [29] and MUSRFIT [30].

III. RESULTS AND ANALYSIS

A. Field-cooled spectra

![FIG. 1. $\mu$SR spectra for Sr$_{0.15}$Bi$_2$Se$_3$ measured in a transverse field of 10 mT ($B \parallel a$) at $T = 3.0$ K (upper panel) and $T = 0.25$ K (lower panel). The red lines are fits using the muon depolarization function Eq. (1). The spectra are taken after field cooling in 10 mT.](image-url)
static within the μSR time window. No additional damping is observed below $T_c$, within the experimental resolution, and we conclude $\sigma_{SC}$ is very small. An upper bound for $\sigma_{SC}$ can be derived with help of the equation [31]

$$\sigma_{SC} = \left(\sigma_{TF,T\rightarrow 0}^2 - \sigma_{TF,T\rightarrow T_c}^2\right)^{1/2}.$$  (2)

With the experimental uncertainty in $\sigma_{FL}$ of ±0.002 μs⁻¹, we obtain $\sigma_{SC} \leq 0.02$ μs⁻¹. This allows us to determine a lower bound for the London penetration depth. In the vortex state of an extreme type II superconductor with a trigonal flux line lattice, $\lambda$ can be estimated from the second moment of the field distribution for $B > B_{c1}$ via the relation $\left<(\Delta B)^2\right> = 0.003706\times\Phi_0^2/\lambda^4$, where $\Phi_0$ is the flux quantum [32], or

$$\lambda = (0.0609\gamma_a F_0/\sigma_{SC})^{1/2}.$$  (3)

With $\sigma_{SC} = 0.02$ μs⁻¹ we calculate $\lambda \geq 2.3$ μm for $T \rightarrow 0$.

In the experimental configuration used to measure the data in Fig. 2 ($B \parallel a$), we probe the penetration depths orthogonal to the field direction, or rather the product $\lambda_\parallel \lambda_\perp$. We have also carried out field-cooled (10 mT) measurements for $B \parallel c$ (muon spin rotated mode; here $\lambda_{u\parallel} = 0.19$) to probe the product $\lambda_\parallel \lambda_u \lambda_\perp$. The extracted $\sigma_{TF}$ values at 0.25 and 3.0 K are slightly larger than those for $B \parallel a$, but they are equal within the experimental resolution, as shown in Fig. 2. Finally, we have measured field-cooled μSR spectra on the $x = 0.18$ crystal for $B \parallel a$ at 0.25 and 3.0 K. The analysis shows $\sigma_{TF} = 0.126 \pm 0.002$ μs⁻¹ and, again, no significant temperature variation in $\sigma_{TF}$ is observed, as shown in Fig. 2. We conclude that for both crystals the London penetration is very large and a conservative lower bound is $\lambda = 2.3$ μm.

**B. Vortex lattice with disorder**

The standard procedure, used above, to extract $\lambda$ from the μSR spectra for a type II superconductor relies on cooling the crystal in a small magnetic field $> B_{c1}$, which tends to produce a well-ordered flux line lattice. Equation (3) can then be used to calculate $\lambda$ once $\sigma_{SC}$ is determined [32]. It is well known that inducing disorder in the vortex lattice increases the distribution of the internal magnetic fields, and hence $\sigma_{SC}$ [33–35]. In this case, $\lambda$ can no longer be calculated with the help of Eq. (3), because the calculation of $\lambda$ from the field distribution has become an intricate problem [33–35]. Inducing disorder in the vortex lattice provides, however, an appealing route to probe the superconducting volume fraction of our crystals.

A standard procedure to induce disorder in the flux line lattice is to cool the sample to below $T_c$ in zero field and then sweep the field to the desired TF value (ZFC mode). Examples in the literature that show a pronounced increase of $\sigma_{SC}$ due to disorder can be found in Refs. [31,36]. Here we followed a different procedure and cooled the $x = 0.18$ crystal in a strong magnetic field ($B \parallel c$) of 0.4 T to $T = 0.25$ K, after which the field was reduced to 10 mT. Decreasing the applied field causes the flux lines to move. Pinning of flux lines at crystalline defects and inhomogeneities generates magnetic disorder. We remark that for an applied field of 0.4 T, the lattice parameter of the trigonal vortex lattice is $a_\Delta = (4/3)^{1/2} (\Phi_0/B)^{1/2} = 0.08$ μm. After decreasing the field to 10 μT, $a_\Delta = 0.49$ μm. Next, $TF = 10$ μT μSR spectra were taken in the temperature range 0.25–5 K by stepwise increasing the temperature. In Fig. 3 we show the data taken at 0.25 and 3.0 K. As expected, a pronounced damping now appears in the superconducting state. We first fitted the spectrum at 0.25 K to Eq. (1), but it appeared a better fit can be made with the two-component
the sample in 10 mT to 0.25 K, next reduced the field to zero, and subsequently increased it to 14.5 mT. TF spectra ($B \parallel a$) taken after this field history showed $\sigma_{TF} = 0.20 \mu s^{-1}$ at 0.25 K, which indicates a much weaker degree of disorder in the vortex lattice. The temperature variation of the fit parameters $\sigma_{SC}$, $f_{SC}$, and $f_N$ obtained by using Eq. (4) for this second run are shown in Fig. 4.

The fitting procedure with a two-component muon depolarization function [Eq. (4)] is a standard and frequently used method to determine the superconducting volume fraction. Another method is to directly compare the frequencies in the normal and superconducting phases and the corresponding amplitudes of the fast Fourier transform (FFT). Frequency shifts of the asymmetry spectra for our data are reported in the supplemental material file [37]. Clear frequency shifts are detected in the superconducting phase. However, the shifts are small (<1.1%) and the FFTs of the asymmetry spectra relatively broad. This hampers the determination of the superconducting volume fraction from the FFTs.

**IV. DISCUSSION**

An important conclusion that can be drawn from the TF $\mu$SR spectra taken in the disordered vortex lattice case is that $\text{Sr}_x\text{Bi}_2\text{Se}_3$ for $x = 0.18$ is a bulk superconductor. We remark that specific-heat experiments around $T_c$, which provide a thermodynamic way to demonstrate bulk superconductivity, have not been reported in the literature so far. The superconducting volume fraction of 70% obtained by $\mu$SR agrees nicely with the superconducting screening fraction determined by ac-susceptibility measurements.

In the field-cooled case (ordered vortex lattice), we could not detect the damping of the $\mu^+\mu^-\text{pp}$ precession signal due to superconductivity. This puts a lower bound on the penetration depth $\lambda$ of 2.3 $\mu$m. Within the London model, $\lambda$ is related to the superfluid density $n_s$ via the relation

$$\lambda = \left(\frac{m^*}{\mu_0 n_s e^2}\right)^{1/2}.$$  

(5)

where $m^*$ is the effective mass of the charge carriers, $\mu_0$ is the permeability of the vacuum, and $e$ is the elementary charge. Assuming $m^* = m_e$, $\lambda = 2.3$ $\mu$m translates to an extremely small value $n_s \sim 0.05 \times 10^{26}$ $\text{m}^{-3}$. This is difficult to reconcile with the carrier density $n = 1.2 \times 10^{26}$ $\text{m}^{-3}$ that we measured by the Hall effect on a crystal from the same batch at 4.2 K. In the literature, however, significant lower values for $n$ have been reported: 0.27 $\times 10^{26}$ $\text{m}^{-3}$ (Ref. [5]) and 0.19 $\times 10^{26}$ $\text{m}^{-3}$ (Ref. [18]), which results in $\lambda$ values of 1.0 and 1.2 $\mu$m, respectively, using Eq. (5). A possible solution is that $m^* > m_e$, but this is not in accordance with quantum oscillation studies. For low-carrier-density samples of Bi$_2$Se$_3$, Shubnikov–de Haas data ($B \parallel c$) show $m^* = 0.124m_e$ [38]. Doping may result in a slightly larger value of $m^*$. For instance, for Cu-doped Bi$_2$Se$_3$, $m^* = 0.2 - 0.3m_e$ [39]. On the other hand, from specific-heat experiments on Cu-doped Bi$_2$Se$_3$, a quasiparticle mass of 2.6$m_e$ has been deduced [12]. Values for the effective mass of Sr$_x$Bi$_2$Se$_3$ have not been reported so far.

Very recently, TF muon spin rotation experiments on Cu$_x$Bi$_2$Se$_3$ crystals have been reported for a field of 10 mT...
applied along the c axis [40]. Interestingly, the authors do find a small increase of $\sigma_{TF}$ below $T_c$. In the normal state, $\sigma_{TF} = 0.105 \pm 0.001 \mu S^{-1}$, a value comparable to those for the Sr-doped case reported in Fig. 2. In the superconducting phase, a small but clear increase of $\sigma_{TF}$ is observed to a value of 0.113 $\pm 0.001 \mu S^{-1}$ for $T \rightarrow 0$. By analyzing the data with the help of Eq. (2), the authors calculate $\sigma_{SC} = 0.04 \mu S^{-1}$ and $\lambda = 1.6 \mu m$. We remark that the total increase in $\sigma_{TF}$ below $T_c$ is only 0.008 $\mu S^{-1}$, which is only slightly larger than the scatter in our values of $\sigma_{TF}$ (see Fig. 2). The higher precision in these experiments is partly due to very long counting times resulting in better statistics. The $\mu$SR experiments on Cu- and Sr-doped Bi$_2$Se$_3$ agree in the sense that for both $n^*=n_e$, a superfluid density $n_s = 0.11 \times 10^{26}$ m$^{-3}$, which is also at variance with the measured carrier concentration [12,39] ($n_s$ is a factor 10 smaller). The recurring result that $n_s \ll n$ seems to indicate that only part of the conduction electrons participate in the superconducting condensate. A possible explanation is substantial electronic phase inhomogeneities, where the superconducting phase (volume fraction 70% for Sr$_{0.18}$Bi$_2$Se$_3$ and 40–60% for Cu$_x$Bi$_2$Se$_3$ [12,40]) has effectively a lower carrier concentration than the normal phase. On the other hand, a similar mismatch between $n_s$ and $n$ has recently been reported for the Nb-doped low-carrier-density superconductor SrTiO$_3$ notably in the over-doped, dirty regime, which is relevant in the context of high-$T_c$ cuprates as well [41]. We remark that the discrepancy between $n_s$ and $n$ does not show up in the standard analysis of the Ginzburg–Landau parameter $\kappa = \lambda/\xi$, where $\xi$ is the superconducting coherence length. The large value of $\kappa \sim 100$ and the small coherence length $\xi \sim 15 \mu m$ extracted from transport and magnetic measurements [12,18] result in a substantial value $\lambda \sim 1.5 \mu m$. Here we have neglected for the purpose of simplicity the crystalline anisotropy of about a factor 1.5 in these parameters.

The $\mu$SR spectra for the $x = 0.18$ crystal, taken after cooling in 0.4 T and subsequently reducing the field to 10 mT, show a sizable depolarization due to disorder in the vortex lattice. If we assume a random distribution of flux lines, $\lambda$ can be calculated using the expression $(\langle \Delta B \rangle^2) = \Phi_0 \lambda / 4 \pi \lambda^2$ (see Refs. [34,35]). With $\sigma_{SC} = 0.36 \mu S^{-1}$ [see Fig. 4(a)] we calculate $\lambda = 3.0 \mu m$, a value in line with the lower bound 2.3 $\mu m$ estimated from the field-cooled experiments. It is not surprising that substantial disorder in the vortex lattice can be created. In the Cu, Sr, and Nb case, experimental evidence has been presented that the dopant atoms are intercalated in the van der Waals gaps between the quintuple layers of the Bi$_2$Se$_3$ structure [4–6]. However, partial substitution on the Bi lattice cannot be ruled out. A detailed refinement of the crystal structure after intercalation has not been reported for these compounds so far. For Cu, Bi$_2$Se$_3$ it has been inferred by analogy to related selenides that the intercalant atoms reside in the 3\$ site (Wyckoff notation) [4]. Moreover, structural investigations report considerable disorder on various length scales [42,43]. Thus the Bi-based superconductors are prone to various types of structural disorder, which in turn may provide different sources of flux pinning.

V. SUMMARY AND CONCLUSIONS

We have performed transverse field muon spin rotation experiments on single-crystalline samples of Sr$_x$Bi$_2$Se$_3$ with the aim to determine the London penetration depth, $\lambda$. Field-cooled $\mu$SR spectra measured for the ordered flux line lattice reveal, however, no additional damping of the $\mu^+\gamma$ precession signal in the superconducting phase. From the data, we infer a lower bound for 0.3 $\mu m$. By changing the applied magnetic field in the superconducting phase, we are able to induce disorder in the vortex lattice. This results in a sizable value $\sigma_{SC} = 0.36 \mu S^{-1}$ for $T \rightarrow 0$. By analyzing the $\mu$SR time spectra with a two-component function, we obtain a superconducting volume fraction of 70%. This provides solid evidence for bulk superconductivity in Sr$_x$Bi$_2$Se$_3$. We signal a discrepancy between the superfluid density, $n_s$, calculated from $\lambda$ within the London model, and the measured carrier concentration. Finally, we recall that the reported [19,21–23] breaking of rotational symmetry in the small family of Bi$_2$Se$_3$-based superconductors deserves close examination, notably because it offers an excellent opportunity to study unconventional superconductivity with a two-component order parameter.

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