Observability of superconductivity in Sr-doped Bi$_2$Se$_3$ at the surface using scanning tunneling microscope

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The superconducting materials family of doped Bi$_2$Se$_3$ remains intensively studied in the field of condensed matter physics due to strong experimental evidence for topologically non-trivial superconductivity in the bulk. However, at the surface of these materials, even the observation of superconductivity itself is still controversial. We use scanning tunneling microscopy (STM) down to 0.4 K to show that on the surface of bulk superconducting Sr$_x$Bi$_2$Se$_3$, no gap in the density of states is observed around the Fermi energy as long as clean metallic probe tips are used. Nevertheless, using scanning electron microscopy and energy-dispersive X-ray analysis, we find that micron-sized flakes of Sr$_x$Bi$_2$Se$_3$ are easily transferred from the sample onto the STM probe tip and that such flakes consistently show a superconducting gap in the density of states. We argue that the superconductivity in Sr$_x$Bi$_2$Se$_3$ crystals does not extend to the surface when the topological surface state (TSS) is intact, but in micro-flakes the TSS has been destroyed due to strain and allows the superconductivity to extend to the surface. To understand this phenomenon, we propose that the local electric field, always found in electron doped Bi$_2$Se$_3$ in the presence of the TSS due to an intrinsic upward band bending, works against superconductivity at the surface.

I. INTRODUCTION

Shortly after the discovery of superconductivity in Cu-doped Bi$_2$Se$_3$ crystals [1], Fu and Berg [2] proposed that any electron-doped Bi$_2$Se$_3$ is a viable candidate for hosting topological superconductivity with spin-triplet-like pairing. The spin-triplet-like nature of the pairing was successively confirmed by temperature-dependent nuclear magnetic resonance Knight shift ($K_s$) experiments [3], which found no change in $K_s$ below $T_c$ for magnetic fields applied parallel to the $c$-axis. Moreover, the same experiments found that the three-fold-symmetric Bi$_2$Se$_3$ lattice showed a two-fold anisotropy of $K_s$ when the magnetic field was rotated in the $ab$ plane. This indicates a spontaneous rotational symmetry breaking of the superconducting state. The two-fold symmetry of the superconducting state was also observed in specific heat [4], which indicates that this symmetry breaking is due to an anisotropy in the superconducting gap amplitude and points to nematic superconductivity [5]. A recent high-resolution x-ray diffraction (XRD) experiment clarified [6] that a tiny (~0.02%) lattice distortion dictates the nematic axis. Theoretically, this nematic superconductivity is expected in doped Bi$_2$Se$_3$ superconductors for the superconducting gap function having $E_u$ symmetry [2, 7, 8], which is topologically non-trivial.

Concurrently with the bulk characterization, surface sensitive techniques, in particular scanning tunneling microscopy (STM) and spectroscopy (STS), were used to study the superconducting properties at the surface of doped Bi$_2$Se$_3$ crystals. Already in 2013 Levy et al. [9] reported the observation of both normal-conducting and superconducting (SC) domains at the surface of Cu-doped Bi$_2$Se$_3$. These SC domains showed a fully gapped local density of states (LDOS) at the Fermi level that could be well-described within the Bardeen–Cooper–Schrieffer (BCS) theory. The observed gap width was $\Delta = 0.4$ meV at the surface and bulk resistance vs. temperature measurements showed a superconducting transition at around 3.65 K. Moreover, vortices with a diameter of about 30 nm were observed at the surface under an applied out-of-plane magnetic field of more than 0.5 T, and the upper critical field was determined to be $\mu_0H_{c2} \approx 1.65$ T. Interestingly, no zero bias conductance peaks were observed in the vortex core by Levy et al. [9] while a more recent STM study of Cu-doped Bi$_2$Se$_3$ by Tao et al. [10] resolved an Abrikosov lattice consisting of elliptically-shaped vortices on the surface, which also hosted a zero bias conductance peak. However, Tao et al. [10] also documented two different SC domains with largely different gap sizes of 0.46 meV and 0.77 meV, and 96% of the surface areas they studied did not show any superconductivity.

Such differences in the superconducting properties observed at the surface of Cu-doped Bi$_2$Se$_3$ may be related to the comparatively poor superconducting volume fraction of only about 40 – 50% [11] and associated inhomogeneity of the superconducting phase throughout the sample. In this regard, Sr$_x$Bi$_2$Se$_3$ is better suited to STM studies since the superconducting volume fraction reaches more than 90% [12] and thus one expects to avoid the ambiguity between local probe and bulk measurements that arises due to inhomogeneity.

However, at the surface of a Sr$_x$Bi$_2$Se$_3$ crystal with a bulk $T_c$ of 2.4 K, Han et al. [13] observed a superconducting gap which only dropped to 75% of the normal state conductance at the Fermi energy despite a gap size of $\Delta \approx 0.5$ meV. The authors attributed their observation to their relatively high measurement temperature of 1 K. In 2017, Du et al. [14] observed on the surface...
of a Sr₂Bi₂Se₃ crystal with a bulk $T_c$ of 3 K. SC domains with the gap size of $\Delta \approx 0.42 - 1.15$ meV. Moreover, for a domain with $\Delta \approx 0.8$ meV at $T_c = 5$ K and $\mu_0H_c2 \approx 5$ T was reported. Note that in the bulk of Sr₂Bi₂Se₃, $\mu_0H_c2$ amounts to about 1.5 T [15]. A recent work by Kumar et al. [16] reported a superconducting gap of $\Delta \approx 0.19 - 0.31$ meV on the surface of a Sr₂Bi₂Se₃ crystal with the bulk $T_c = 2.9$ K.

With regards to such inconsistencies, Wilfert et al. [17] recently showed that for Tl-doped Bi₂Te₃ and Nb-doped Bi₂Se₃, the superconducting gaps on the surface were exclusively observed due to the nominally normal conducting probe tips becoming unintentionally superconducting during the experiments. Similar experimental pitfalls were also reported for Cu-doped Bi₂Se₃ by Levy et al. [9]. Interestingly, Wilfert et al. [17] concluded that for Tl-doped Bi₂Te₃ and Nb-doped Bi₂Se₃, superconductivity does not extend to the surface where the topological surface state resides.

Here, to clarify this complicated situation, we use transport measurements to characterize the bulk $T_c$ and the carrier concentration of high-quality single crystals of Sr₂Bi₂Se₃ and subsequently perform high-resolution studies of STM and STS on the surface of crystals which are cleaved under ultra high vacuum conditions (UHV). Our base temperature is 0.4 K.

II. EXPERIMENTAL METHODS

Crystal growth. Single crystals of Sr₂Bi₂Se₃ (nominal $x = 0.06$) are grown from high-purity elemental Sr chunk (99.99%), Bi shots (99.9999%), and Se shots (99.9999%) by a conventional melt-growth method. The raw materials with a total weight of 4.0 g are mixed and sealed in an evacuated quartz tube. The tube is heated to 850°C for 48 h. It is then slowly cooled from 850°C to 600°C within 80 h and finally quenched into water at room temperature.

Transport measurements. Resistivity and Hall measurements on the samples are performed in a Quantum Design Physical Properties Measurement System (PPMS) in the standard four-terminal configuration using a low-frequency ac lock-in technique.

STM measurements. STM experiments are carried out under UHV conditions with a commercial system (Unisoku USM1300) operating at 0.4 K. Data are acquired at 0.4 K unless mentioned otherwise. Topograph and $dI/dU$ maps are recorded in the constant-current mode. Point spectroscopy data is obtained by first stabilizing for a given set-point condition and then disabling the feedback loop. $dI/dU$ curves are then recorded by means of a lock-in amplifier by adding a small modulation voltage $U_{mod}$ to the sample bias voltage $U$. High resolution $dI/dU$ spectra of superconducting gaps were normalized by fitting a second degree polynomial to the data outside the SC gap and dividing by the fitted polynomial. We have used both PtIr and W probe tips. All PtIr tips used are commercially obtained from Unisoku. The W tips are made in-house. Both types are electrochemically etched. The PtIr tips are either fresh new tips or they have been prepared by Ar ion sputtering (at an argon pressure of $3 \times 10^{-6}$ mbar and a voltage of 1 kV), followed by repeated heating by electron bombardment ($\sim 15$ W) for 20 s. Further tip forming is done by scanning on the Cu(111) surface until a clean signature of the surface state is obtained in spectroscopy. The absence of a superconducting gap on Cu(111) is also verified prior to measurements on Sr₂Bi₂Se₃. For STM measurements, Sr₂Bi₂Se₃ crystals are cleaved at room temperature and under UHV conditions. The crystal is cleaved by breaking off a 10 mm sized pole glued on the sample. The two-component epoxy glue (EPO-TEK H21D) is hardened by heating to 373 K under high vacuum conditions. STM data are processed using the WSxM software [18] and Igor Pro 9.0.

SEM and EDX analysis. Scanning electron microscope (SEM) image of the tip is obtained using the Raith Pioneer II system and the Jeol JSM-6510 SEM. Elemental chemical analysis of the material on the tip apex is done by energy-dispersive X-ray (EDX) analysis, performed using an Oxford Instruments AztecOne system with a xact Silicon Drift Detector that is combined with the Jeol SEM.

III. RESULTS AND DISCUSSION

A. Bulk properties

We have characterized the bulk properties of our Sr₂Bi₂Se₃ single crystals using resistivity ($\rho_{xx}$) and Hall resistivity ($\rho_{yx}$) measurements. An optical image of a typical sample (5 mm × 4 mm × 0.7 mm) including the electrical contacts is shown in the inset of Fig. 1(b). The temperature dependence of the resistivity is metallic [Fig. 1(a)] with the onset of superconductivity and zero-resistivity occurring at 2.90 and 2.65 K, respectively [in-
Reference | nominal Sr doping | carrier density \( n \) (\( 10^{19} \text{cm}^{-3} \))
--- | --- | ---
Liu 2015 [12] | 0.062 | 2.65
Shruti 2015 [15] | 0.1 | 1.85
Huang 2017 [19] | 0.066 | 2.75
Kuntsevich 2019 [20] | 0.064, 0.068 | 2.2, 2.1
Li 2018 [21] | 0.05 | 5.7–10
Li 2018 [21] | 0.08 | 6.8–9.2
this work | 0.06 | 3.4–6.2

TABLE I. Summary of bulk carrier density \( n \) reported for \( \text{Sr}_x\text{Bi}_2\text{Se}_3 \).

set of Fig. 1(a)]. The superconducting transition temperature \( T_c \), defined by the mid-point of the resistive transition, is 2.8 K. The residual resistivity of 0.56 m\( \Omega \)cm, which points to a high scattering rate that is always present in doped \( \text{Bi}_2\text{Se}_3 \) superconductors, is unusually large for an unconventional non-s-wave superconductor; nevertheless, it has been elucidated that in doped \( \text{Bi}_2\text{Se}_3 \) superconductors where the orbital degrees of freedom play an important role, the generalized Anderson’s theorem protects the unconventional pairing from disorder [22, 23].

The carrier density in our samples is determined from \( \rho_{yx} \) measured at 10 K as a function of perpendicular magnetic field \( B \) [Fig. 1(b)]. The \( \rho_{yx}(B) \) behavior is strictly linear in \( B \) and can be described by a single band, yielding a carrier density of \( n \approx 3 \times 10^{19} \text{cm}^{-3} \), which is extremely low for a superconductor with \( T_c \) of the order a few Kelvin. Table I gives an overview of the carrier density of \( \text{Sr}_x\text{Bi}_2\text{Se}_3 \) samples (varying nominal doping) as reported in literature along with the values observed for our samples. From Shubnikov-de Haas investigations by Köhler et al. [24] it is known that a carrier density of \( n \approx 4 \times 10^{19} \text{cm}^{-3} \) in \( \text{Bi}_2\text{Se}_3 \) corresponds to a Fermi energy of \( E_F \approx 160 \text{meV} \), which we use as a lower bound for the Fermi energy in the bulk of our \( \text{Sr}_x\text{Bi}_2\text{Se}_3 \) crystals. As an upper bound one can assume a simple parabolic dispersion for the bulk conduction band (BCB). Here, a carrier density of \( n \approx 4 \times 10^{19} \text{cm}^{-3} \) corresponds to \( E_F \approx 270 \text{meV} \) for an effective mass of \( m_{\text{eff}} = 0.15m_e \) [24, 25], with \( m_e \) the free electron mass.

The shielding fraction of our samples estimated from the zero-field-cooled magnetization measurement lies between 75% to 100% [26]. The actual data of one of the samples measured here, which showed the shielding fraction of 76%, were previously shown in Ref. [26].

B. Surface properties

A typical topograph of the cleaved \( \text{Sr}_x\text{Bi}_2\text{Se}_3 \) surface is shown in Fig. 2(a). The surface is atomically flat with some characteristic native defects, which we have previously discussed in detail [26]. A representative \( (dI/dU)/(I/U) \) spectrum, which is proportional to the local density of states (LDOS), is shown in Fig. 2(b). The minimum of the LDOS is at \( -310 \text{mV} \) and corresponds to the Dirac point (DP). Based on the band structure of \( \text{Bi}_2\text{Se}_3 \), which is well-known from ARPES
the condition \( q \) related to the wavevector \( k \) through \( q = 2k \). However, the condition \( q = 2k \) corresponds to 180° backscatter-

ing, which is strongly suppressed for a TSS with spin-momentum locking. Therefore, the dominant scattering vectors of the TSS will be smaller \([31–33]\). Even for Bi\(_2\)Se\(_3\), it has been predicted that the hexagonal warping of the TSS \([34]\) will open new scattering channels at energies sufficiently above the DP \([32]\). Since the strength of the warping term in Sr\(_x\)Bi\(_2\)Se\(_3\) is unknown, we simply use \( q \approx 1.5k \) (which is known for the more strongly warped TSS of Bi\(_2\)Te\(_3\) \([33]\)) as a lower bound for the expected scattering vector length and \( q = 2k \) as the upper bound. These two \( q \)-vectors are indicated by semicircles in the Fourier transform (FT) of the \( dI/dU \) maps \([\text{insets of Figs. 3(a) and 3(b)}]\) by taking \( |k| \) at the relevant energy from the TSS dispersion depicted in Fig. 2(c).

We only observe clear QPI at bias voltages \( \geq 100 \text{ mV} \), \( i.e. \) more than 400 mV above the DP. At this energy the iso-energy surface of the TSS of Bi\(_2\)Se\(_3\) has a hexagonal shape \([32]\) and the TSS acquires a significant out-of-plane spin-polarization, enabling scattering vectors connecting opposite sides of the iso-energy surface mainly through the vertical spin component \([31, 34]\). For the hexagonal iso-energy surface the expected \( q \) vector is still close to \( 2k \), which is in agreement with the substantial intensity in the FT of Fig. 3(a) near \( q = 2k \). Extrapolating the iso-energy surface to 700 meV above the DP by considering the simple warping term \([34]\) extracted from the data for Bi\(_2\)Se\(_3\) \([32]\), one expects a snowflake-like shape which is better known for Bi\(_2\)Te\(_3\) \([31, 33, 34]\). The scattering vector \( q \approx 1.5k \) would dominate in such an iso-energy surface, which is in agreement with the FT of Fig. 3(b). However, we note that at these high energies above the DP hybridization of the TSS with bulk bands certainly needs to be considered explicitly and will lead to modification of the dispersion relation of the TSS that go beyond what is captured by a simple warping term. Moreover, since at these energies the iso-energy surfaces not only have contributions from the TSS but also from the BCB \([32]\), scattering of bulk electrons and interband scattering between TSS and BCB may also contribute to the observed QPI.

Given these difficulties in interpreting the observed QPI, we have also examined the response of the LDOS to an external magnetic field of more than 8 T applied along the surface normal. Under these conditions, electrons are quantized into Landau levels. In the case of Dirac electrons of the TSS, the energy \( E_N \) of the \( N \)th LL is to first approximation given as

\[
E_N = E_D + \text{sgn} (N) v_F \sqrt{2eBh|N|},
\]

where \( N \) is the Landau level index, \( v_F \) is the Fermi velocity, \( B \) is the magnetic field and \( E_D \) is the Dirac point energy.

In Fig. 3(c), a set of Landau levels is visible in the LDOS in a range of \( -25 \text{ meV} \) to \( +25 \text{ meV} \) around the Fermi energy. In order to extract the energy positions of the peaks, we subtracted the background from the STS curves using a cubic spline fit for the background (in violet), and each peak was fitted using a single Gaussian

experiments \([13, 25, 27, 28]\) and schematically depicted in Fig. 2(c), we assign the increase in slope at around \(-400 \text{ mV} \) and below to the onset of the bulk valence band (BVB), and the increase at \(-100 \text{ mV} \) and above to the BCB, respectively. Therefore, at the surface of this sample, the Fermi energy lies about 100 meV above the bottom of the BCB, which is much lower than the estimate of \( E_F \approx 160 - 270 \text{ meV} \) based on transport measurements. However, this apparent disagreement is straightforwardly reconciled if we consider band bending to be present at the surface of electron-doped Bi\(_2\)Se\(_3\).

Band bending occurs due to charge transfer caused by the equilibration of the Fermi level at an interface. The charge transfer creates an electric field and the associated potential shifts the bands in the vicinity. In the case of a topological insulator, the existence of the TSS causes the charge distribution to be different near the surface compared to the bulk. When the TSS is electron-doped, the electrons in the TSS can be viewed as a negative surface charge \( \sigma_s \). This surface charge is related to the surface potential \( V_0 = V(z = 0) \propto -\sigma_s \) through Poisson’s equation and the condition of overall charge neutrality. Hence, the surface charge in the TSS causes a positive potential leading to upward band bending of the BCB when going from the bulk to the surface. In other words, at the surface, charge equilibration causes fewer electrons in the BCB than in the bulk. For highly doped semiconductors, the decay of the potential into the bulk may be estimated within the Thomas-Fermi screening model as \( V(z) = V_0 \exp(-z/r_{TF}) \), where \( r_{TF} \approx \sqrt{(\epsilon_0 \pi^2 \hbar^2)/(k_F m_{\text{eff}} e^2)} \approx 0.6 \text{ nm} \) is the Thomas-Fermi screening length and \( k_F \approx 0.7 \text{ Å}^{-1} \). Interestingly, calculations within the density functional theory (DFT) in Refs. \([29, 30]\) show that even for pristine Bi\(_2\)Se\(_3\) an intrinsic upward band bending of the BCB of the order of \( \sim 100 \text{ meV} \) takes place due to charge equilibration between bulk-like states and the TSS when the Fermi energy lies above the DP. In these calculations, the BCB has recovered its bulk value at 2 or 3 nm below the surface.

To further validate our assignment of the spectral features in our \( (dI/dU)/(I/U) \) data, we have performed additional spectroscopic characterization of the surface electronic structure by mapping the spatial variations of the LDOS. Typical \( dI/dU \) maps taken at the indicated bias voltages are shown in Figs. 3(a) and (b). The spatial modulation of the LDOS due to quasiparticle interference (QPI), as opposed to structural effects, is evident due to the decrease of the wavelength of the QPI patterns as the bias voltage is increased. Based on the band structure depicted in Fig. 2(c), the QPI at the indicated bias voltages can be due to scattering of carriers in the BCB or TSS. While contributions of scattering bulk carriers can not be ruled out, we will show in the following that the dominant contribution is due to the TSS.

For the TSS, the largest possible scattering vector \( q \) is related to the wavevector \( k \) through \( q = 2k \). However, the condition \( q = 2k \) corresponds to 180° backscatter-
We identified the positions of six LLs and plotted their energy positions as a function of $\sqrt{NB}$ (in the range of 8.0 to 8.7 T) in Fig. 3(d). By assigning the LL index of 28 to the highest peak, we can fit all the peak positions to Eq. (1) with reasonable values of $E_D$ (−306 mV) and $v_F$ ($5.8 \times 10^5$ m/s). The close-up of the fit near the data points is shown in the inset of Fig. 3(d); although the data points are very linear in this plot of $E$ vs $\sqrt{N}$, one cannot definitely tell from the data alone if the dependence on $N$ is linear (which is expected for BCB) or $\sqrt{N}$ (expected for TSS). Nevertheless, the constraint of the DP energy and $v_F$ allows us to elucidate that the $\sqrt{N}$ dependence gives a more consistent analysis (see Appendix B). Therefore, we conclude that the observed LLs confirm that the spectral features at these energies are dominated by the TSS.

C. Superconductivity of the surface

With our understanding of the electronic structure at the surface of Sr$_x$Bi$_2$Se$_3$ established in the previous subsection, we now turn to the superconducting properties. All spectroscopy experiments to this end were done at a nominal system temperature of about 0.4 K and spectra were acquired on defect-free parts of the surface such as the one depicted in Fig. 4(a).

Surprisingly, high resolution spectroscopy taken around the Fermi energy shows substantial variations. Representative spectra are gathered in Fig. 4(b) while others show a superconducting gap but with various gap sizes [black, blue, violet and green traces in Fig. 4(b)]. We have quantified the superconducting gap by fitting the spectra using the Dynes formula [35]. The differential conductance is given by:

$$G_N \frac{\partial}{\partial N} \int_{-\infty}^{\infty} N_S(E) [f(E, T_{eff}) - f(E - eV, T_{eff})] dE,$$

with $G_N$ the normal-state conductance, $f(E, T_{eff})$ the Fermi function, and $N_S(E)$ the density of states in the BCS theory given as

$$N_S(E) = \text{Re} \left( \frac{(E - i\Gamma)}{\sqrt{(E - i\Gamma)^2 - \Delta^2}} \right),$$

where $\Gamma$ is an effective broadening parameter and $\Delta$ is the superconducting gap. The effective temperature $T_{eff}$ is determined independently (see Appendix A). We have used a total of 10 different new or freshly prepared PtIr tips and one W tip. Across all tips, the minimum and maximum $\Delta$ values observed were 0.19 and 0.73 meV, respectively. Our best fits yield $\Gamma$ values that are always below our energy resolution of about 100 $\mu$eV.
FIG. 4. (a) Atomic-resolution image on the topmost Se layer. (b) Representative high resolution spectra (solid circles) taken with different tips at different positions on the surface: Substantial variations ranging from a flat LDOS at the Fermi level (red curve) to a full gap (blue curve) were observed. Spectra are offset vertically for clarity. Fitting of the data to the Dynes formula [35] yields the superconducting gap $\Delta$ of 0.39 meV (black), 0.54 meV (blue), 0.26 meV (violet), and 0.72 meV (green). Scan/stabilization parameters: (a) $U = -900$ mV, $I = 200$ pA; (b) $U = 5$ mV (red, black, green, and violet), $U = 3$ mV (blue), $I = 200$ pA (red), $I = 300$ pA (black), $I = 500$ pA (blue), $I = 100$ pA (violet), $I = 25$ nA (green), $U_{\text{mod}} = 50 \mu$V. Except for the green curve taken at 1.7 K, all the spectra were taken at 0.4 K. The effective temperature $T_{\text{eff}}$ in the fit for the black, blue, and violet fit is 0.7 K, while that for the green curve is 2 K. The $\Gamma$ value for the fits are 0.02, 0.0001, 0.05, and 0.0003 meV for black, blue, violet, and green curves, respectively.

The large scatter in the superconducting gap size at the surface is unexpected for a sample with a sharp bulk superconducting transition. Indeed, the sharp transition observed in the bulk suggest homogeneity in the sample and therefore a more or less uniform gap size of $\Delta \approx 1.76k_B T_c \approx 0.4$ meV is expected. As already mentioned in the introduction, a similar discrepancy between the superconducting gaps measured by STM and that expected from the superconducting transition temperature of the bulk has been reported in several publications on doped Bi$_2$Se$_3$ compounds, a summary is shown in Table II.

To make sure that superconducting gaps measured at the surface with STM are related to the superconducting state of the bulk, we applied an external magnetic field. Since Sr$_x$Bi$_2$Se$_3$ is known to be a type-II superconductor [15], vortices are expected to be generated in applied fields greater than the lower critical field $\mu_0 H_{c1}$. In the inset of Fig. 5 we show a 200 nm by 200 nm topography overlaid with a mapping of normalized differential conductance at zero bias taken in an applied field of 0.3 T. One can infer that the LDOS is completely uniform in this area, i.e. no vortex is observed in the entire field of view.

The absence of any vortex formation strongly suggests that the superconducting state probed by STM differs from the one in the bulk of Sr$_x$Bi$_2$Se$_3$. Before addressing the origin of this difference, we first need to establish whether the superconducting gaps observed by STM are an intrinsic property of the surface or an artifact due to the probe tip. For this purpose, we have first taken a high resolution spectrum on Sr$_x$Bi$_2$Se$_3$ (red trace in Fig. 5), and thereafter exchanged the sample against a non-superconducting copper sample and repeated the measurement with the same tip on the Cu(111) surface (black trace in Fig. 5). It is evident that the superconducting gap observed with this tip is essentially identical for both Sr$_x$Bi$_2$Se$_3$ and Cu(111) surfaces, thereby establishing unambiguously that the superconducting gap originates not from the sample surface but from the probe tip.

Having clarified that the superconducting gaps repro-
ducibly observed on Sr$_x$Bi$_2$Se$_3$ are due to superconducting probe tips and not due to superconductivity of the Sr$_x$Bi$_2$Se$_3$ surface itself, we now address the mechanism by which the tips made out of non-superconducting PtIr (or W) turn superconducting.

To this end, we have characterized a probe tip which showed a superconducting gap during STM experiments in more detail: Figure 6(a) shows an SEM image of the PtIr tip apex that is found to be covered with micron-sized flakes. The EDX spectrum [Fig. 6(b)] taken on a micro-flake marked by a dashed green circle shows prominent Bi and Se peaks, thus establishing that materials from the Sr$_x$Bi$_2$Se$_3$ crystal have been transferred onto the tip. Combined with the observation that a superconducting energy gap was measured with this probe tip prior to SEM characterization, one may conclude that the micron-sized Sr$_x$Bi$_2$Se$_3$ flakes found on the PtIr tip are superconducting.

To further support this conclusion, we have performed additional STM experiments in which we attempted to redeposit a flake onto the sample surface. Although no reproducible procedure could be established to this end, we found that mild tip-sample interactions sometimes lead to an accidental redeposition of a flake as shown in Fig. 6(c). This flake has an apparent height of ∼25 nm and it extends by about one micron. High-resolution imaging on a flat area of the flake [red square in Fig. 6(c)] clearly shows atomic resolution. The resolved hexagonal lattice locally has a lattice constant of about 0.4 Å in agreement with the Se layer of Sr$_x$Bi$_2$Se$_3$. However, one may also recognize nano-scale modifications of the surface height. We have thus compared the average in-plane atom densities of the flat part of the flake [Fig. 6(f)] with the Sr$_x$Bi$_2$Se$_3$ surface prior to redeposition of the flake [Fig. 6(g)]. Specifically, we have counted 613 atoms/100 nm$^2$ in Fig. 6(f) and 627 atoms/100 nm$^2$ in Fig. 6(g). This yields a reduction of about 2%. Note that the observed difference in average in-plane packing density only demonstrates that there must be some strain in the flake and it does not mean a homogenous tensile strain of 2%. Indeed, a detailed analysis of grain boundaries in Bi$_2$Se$_3$ given in Ref. [36] showed variations in the magnitude of in-plane strain ranging from 20% to −20% occurring on nanometer length scales. Extracting similar quantitative values of the strain-tensor of the flake requires additional data and theoretical modeling, which is beyond the scope of this work.

The $dI/dU$ spectra taken prior to the redeposition of the flake, an example of which is shown in black in Fig. 6(d), clearly presents a superconducting gap; we observed similar spectra everywhere on the Sr$_x$Bi$_2$Se$_3$ surface. However, after the redeposition of the flake, the situation changed: While the spectrum shown in red in Fig. 6(d), which was taken on the redeposited flake [in the area marked by the red square in Fig. 6(c)], presents a superconducting gap similar to that observed prior to redeposition, the spectrum shown in blue, which was taken outside of the flake [in the region marked by the blue circle], does not present a fully-developed gap. These spectroscopic observations are consistent with the interpretation that a flake formed the tip-apex prior to redeposition and it is superconducting both before and after the redeposition.

IV. DISCUSSION

As already mentioned, the Hall resistivity data of our Sr$_x$Bi$_2$Se$_3$ crystal points to the electron density of ∼4 × 10$^{19}$ cm$^{-3}$ corresponding to the Fermi energy of 160 to 270 meV measured from the conduction band bottom, whereas the STS data on the same crystal shows that at the surface, the Fermi energy is only ∼100 meV from the conduction band bottom. This difference indicates unambiguously that there is an upward band bending of the BCB present at the surface. This upward band bending is partly due to the an intrinsic effect always present in Bi$_2$Se$_3$ due to charge equilibration between bulk-like states and the TSS [29, 30], which can also be viewed as a result of many-body Coulomb interactions between the bulk and surface electrons [37]. Note that band bending at the surface can also reflect additional factors [38], such as the contact potential due to the interface with the STM tip [39] or by adsorbates. In Cu-doped Bi$_2$Se$_3$, the Coulomb interactions between bulk and surface electrons was claimed to cause an upward band bending of the BCB by about 200 meV at the surface within the length scale of about 1 nm [37].

The contact potential can be roughly estimated from the difference in work function of the metallic tip $\phi_m$ and that of Bi$_2$Se$_3$. Importantly, the latter is large $\phi_{Bi2Se3} \approx$ 5.6 eV [40] so that $\phi_{Bi2Se3} > \phi_m$ is generally fulfilled. Hence, the contact potential would only lead to the bulk bands bending down at the surface and it cannot be the cause of the observed upward band bending.

Intuitively, band bending due to adsorbates will lead to upward or downward band bending for adsorption of acceptor or donor molecules, respectively. In this context, in particular photoemission experiments suffer from photoexcited adsorbate layers [41], that act as electron donors and, similar to the adsorption of alkali metals [42], inevitably cause downward band bending. However, the experimental conditions of our STM measurements ensure an adsorbate-free surface and more generally, downward band bending is incompatible with the experimental observations.

Importantly, while the details regarding the origin of the observed band bending can be complex, there is agreement that the experimentally measured surface potential of ∼ 100 meV will be screened over a typical length scale of ∼ 1 nm [29, 30, 37]; in other words, near the surface, the bulk electrons experience an electric field of the order of 10$^8$ V/m.

The puzzling fact is that the bulk of our Sr$_x$Bi$_2$Se$_3$ crystals show robust superconductivity with $T_c = 2.8$ K and a high shielding fraction [26], while the STS measure-
FIG. 6. (a) SEM image of the apex of a PtIr tip after scanning on the sample. The apex is found to be covered with several micron-sized flakes. The dashed green circle marks the flake on which the EDX measurement shown in (b) was performed. (b) Result of the EDX analysis of the flake showing the Se peak at 1.379 keV and the Bi double peaks at 2.423 keV and 2.526 keV. (c) 3D-rendered STM image of a flake deposited on the flat Se layer by a very mild collision between the tip and sample. The deposited material has an apparent height of 23 nm and covers an area of roughly 0.2 µm². The red box marks the area where the atomic-resolution image (e) of the flake was obtained. Scan parameter: $U = -3$ V, $I = 10$ pA for (c); $U = -900$ mV, $I = 100$ pA for (e). The dashed white square in (e) encloses the area where the current image (f) was taken. (d) Black curve shows the superconducting gap measured prior to the deposition of the flake; the area where the spectrum was taken [shown in the image (g)] presents unstrained Se lattice. After the deposition of the flake, the point STS (blue curve) taken on the area of the Se layer marked by blue circle in (c) shows only a weak proximity-induced gap, indicating that the tip LDOS is not gapped under the apex configuration after the flake has left. Nevertheless, the same tip apex measures a superconducting gap (red curve) on the deposited flake in the area marked by the red box in (c). Stabilization parameter for (d): $U = 5$ mV, $I = 100$ pA, $U_{\text{mod}} = 50 \mu$V. Scan parameters for the current images: $U = -900$ mV, $I = 100$ pA for (f); $U = 5$ mV, $I = 100$ pA for (g).

Measurements found no superconducting gap anywhere on the surface down to a temperature of 0.4 K, when clean and non-superconducting probe tips are used. This absence of superconductivity on the surface has been a problem in many STM experiments performed on doped Bi$_2$Se$_3$ superconductors, but the present study found that during the prolonged scanning of the tip on the Sr$_x$Bi$_2$Se$_3$ surface, the tip will always accumulate micro-flakes of Sr$_x$Bi$_2$Se$_3$ which show superconductivity. This finding helps to clarify some discrepancies in the observed SC gaps in earlier STM studies [13, 14, 16], which were inconsistent with the bulk $T_c$. Note that our experimental observation is essentially consistent with those on superconducting TI-doped Bi$_2$Te$_3$ and Nb-doped Bi$_2$Se$_3$ reported by Wilfert et al. [17], who concluded that superconductivity does not extend to the surface in these superconductors.

Since recent experimental [43] and theoretical [44] works found a suppression of superconductivity under a strong electric field of the order of $10^8$ V/m in conventional superconductors, we speculate that the local electric field associated with the experimentally observed band bending has a similar effect on superconductivity in Sr$_x$Bi$_2$Se$_3$. Indeed, since the upward band bending is a consequence of the existence of the TSS, one would expect the electric field to disappear (and the superconductivity to extend to the surface) when the TSS is destroyed. In this regard, there have been interesting reports that the strain on the surface can destroy the TSS in Bi$_2$Se$_3$ [36, 45]. Motivated by these observations, we speculate that during the transfer of the Sr$_x$Bi$_2$Se$_3$ flakes onto the tip, the flakes experience mechanical strain and the TSS is destroyed, allowing the superconductivity to extend to the surface of the flake. Although a detailed analysis of the strain in the flakes on our STM tips is beyond the scope of this work, we note that the atomic-resolution imaging on the flat parts of a flake [Fig. 6(c)] shows dislocation features and a reduced atomic packing...
density, indicative of a strain in the flake.

Since the surface potential is an intrinsic effect linked inherently to the presence of the TSS in doped Bi$_2$Se$_3$ and hence should be a general phenomena in the family of doped Bi$_2$Se$_3$ superconductors, our speculation, that the appearance of superconductivity on the surface is related to the loss of TSS due to strain, gives a clue to understand earlier STM studies that are listed in Table II.

It is prudent to mention that the pioneering STM work by Levy et al. [9] gave persuasive evidence for superconductivity extending to the surface of Cu-doped Bi$_2$Se$_3$ crystals (i.e. appearance of vortices in an applied magnetic field and the observation of a domain boundary between superconducting and non-superconducting regions); nevertheless, the topographic images of the superconducting domains in Ref. [9] showed many structural defects such as step bunching and grain boundaries that are consistent with strains in their samples. Moreover, no evidence was shown for the TSS to remain intact on these surfaces. Another STM study [10] of Cu-doped Bi$_2$Se$_3$ likewise showed experimental proof (vortex lattice in an applied magnetic field) that superconductivity can extend to the sample surface; however, less then 4% of the studied surface area exhibited superconductivity and the remaining 96% of the surface showed no superconducting gap. Interestingly, the topographic images in Ref. [10] showed lots of structural defects, such as non-quintuple-layer step heights, in particular for the superconducting regions.

Han et al. [13] used ARPES to demonstrate that the TSS of their Sr$_x$Bi$_2$Se$_3$ samples was intact and the STS data showed a superconducting gap, but their data are also fully compatible with a superconducting flake having been transferred to the tip. The superconductivity observed on the surface of Sr$_x$Bi$_2$Se$_3$ by STM in the works by Kumar et al. [16] and Du et al. [14] showed values of $\Delta$, $T_c$, and $\mu_0H_{c2}$ that are incompatible with the bulk values; this problem can be straightforwardly reconciled if a superconducting flake was present on the tip. Interestingly, Kumar et al. [16] also performed hard point-contact spectroscopy and found an increase in $T_c$ with increasing pressure. It would be instructive to clarify if the strain due to the pressure from the tip leads to a destruction of the TSS.

V. CONCLUSION

While our Sr$_x$Bi$_2$Se$_3$ crystals present robust bulk superconductivity with $T_c = 2.8$ K, our STM measurements at 0.4 K with a fresh tip found no superconducting gap on the surface. This result is similar to many previous STM experiments on doped Bi$_2$Se$_3$ superconductors. To understand this discrepancy, we propose that the upward band bending of 60 to 170 meV, which we elucidated at the surface, is playing a key role: Because recent DFT calculations found [29, 30] that this upward band bending is an inevitable consequence of the existence of the TSS and hence is intrinsic to the electron doped Bi$_2$Se$_3$-family of materials, we argue that the electric field suppresses the superconductivity at the surface in doped Bi$_2$Se$_3$ superconductors. In this regard it was found both experimentally [43] and theoretically [44] that a strong electric field can kill superconductivity in conventional superconductors.

Intriguingly, after prolonged scanning on the Sr$_x$Bi$_2$Se$_3$ surface, the STS data taken with all probe tips eventually showed a superconducting gap whose origin can be assigned to the probe tip itself, and the ex-situ SEM/EDX analysis of the tip establishes that micron-sized flakes of Sr$_x$Bi$_2$Se$_3$ are transferred onto the tip apex during the scanning of the surface. Furthermore, we were able to redeposit a Sr$_x$Bi$_2$Se$_3$ flake back onto the Sr$_x$Bi$_2$Se$_3$ surface inside the STM and confirmed that the flakes which

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### TABLE II. Overview of surface studies on superconducting doped Bi$_2$Se$_3$ materials.

| X$_x$Bi$_2$Se$_3$ | Tip | Bulk $T_c$ (K) | $\Delta$ (meV) | Surface SC confirmed$^a$ | SC material on tip | TSS confirmed |
|------------------|-----|----------------|----------------|--------------------------|-------------------|--------------|
| Cu$_{0.2}$[9]$^*$ | Ir  | 3.65           | 0.4 / 0.6$^b$  | Yes / -                  | No / Yes          | No           |
| Cu$_{0.31}$[10]$^*$ | PtIr| 3              | 0.46 / 0.77    | Yes / No                | No / -            | No           |
| Nb$_{0.25}$[46]$^*$ | -   | 3.5            | 0.24 - 0.76$^c$| No                       | -                 | No           |
| Nb$_{0.7}$[17]$^*$ | W   | -              | 0.79           | No                       | Yes               | Yes          |
| Nb$_{0.25}$[47]$^*$ | -   | 3.4            | -             | -                        | -                 | Yes          |
| Ti$_{0.06}$Bi$_2$Te$_3$[17]$^*$ | W   | 2.3            | 1              | No                       | Yes               | Yes          |
| Sr$_{0.06}$[13]$^*$ | -   | 2.4            | 0.52           | No                       | -                 | Yes          |
| Sr$_{0.2}$[14]$^*$ | -   | 3              | 0.42 - 1.15$^c$| No                       | -                 | Yes          |
| Sr$_{0.1}$[16]$^*$ | -   | 2.9            | 0.19 - 0.31$^c$| No                       | -                 | No           |
| Sr$_{0.06}$$^d$ | PtIr | 2.8            | 0.19 - 0.73    | No                       | Yes               | Yes          |
| Sr$_{0.06}$$^d$ | W   | 2.8            | 0.26 - 0.37    | No                       | Yes               | Yes          |

**Experimental technique:** *STM, **STM and ARPES

$^a$ Observation of a vortex lattice along with identification of NSC/SC boundary with the same tip apex.

$^b$ The gap of 0.6 meV was attributed to a superconducting tip.

$^c$ All SC gaps presented are taken into consideration.

$^d$ this work.
FIG. 7. STS taken with a Nb-tip on the Au(111) surface at $T = 400$ mK. The superconducting gap of the Nb-tip (blue trace) and can be fitted using the BCS theory (red trace) with $T_{\text{eff}} = 700$ mK. Stabilization parameter: $U = 4$ mV, $I = 500$ pA, $U_{\text{mod}} = 50$ $\mu$V.$p$.

were transferred onto the tip are indeed superconducting. Since recent works reported that the TSS can be destroyed by strain [36, 45] and we actually observed lattice distortions on the redeposited flakes, we speculate that the strain in the flakes picked up by the tips destroys the TSS and allows the superconductivity to extend to the surface of the flake. This speculation that strain allows the superconductivity to extend to the surface can explain many of the puzzles in the past STM experiments [9, 10, 13, 14, 16, 17].

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Appendix A: Effective temperature

At milli-Kelvin temperatures the nominal sample temperature differs from the effective electron temperature of the tunneling junction due to experimental broadening. This (generally unknown) experimental broadening has a similar effect in high resolution spectroscopy of SC gaps as the thermal broadening, hence one defines an effective temperature $T_{\text{eff}}$ which is calibrated by fitting the $dI/dU$ spectrum of a well-known superconductor. For this purpose we fit the superconducting gap of a Nb-tip made of a high purity Nb wire measured on a non-superconducting Au(111) surface at a nominal temperature of 400 mK. We use the Dynes equation from the main text, but fix $\Gamma$ close to zero leaving only the effective temperature $T_{\text{eff}}$ and the superconducting gap $\Delta$ as fit parameters. The best fit to the experimental data is shown in Fig. 7. The fit yields $T_{\text{eff}} = 0.7$ K.

Appendix B: Analyses of the Landau level spectrum

In the main text we argued that the peaks observed in the $dI/dU$ data shown in Fig. 3 are due to Landau quantization of the TSS and not the BCB. Here, we compare the two scenarios in more detail. First, we recall that the reciprocal-space area $A(k)$ enclosed by a cyclotron orbit under the Landau quantization should satisfy the generalized Onsager relation

$$A_N(k) = 2\pi \frac{eB}{\hbar} (N + \lambda),$$

where $N$ is an integer, $e$ is the elementary charge, $B$ is the magnetic field, and $\lambda = 1/2 - \gamma/(2\pi)$ with $\gamma$ the Berry phase.

For a circular orbit, Eq. (B1) becomes

$$\pi k_N^2 = 2\pi \frac{eB}{\hbar} (N + \lambda).$$

By using this $k_N^2$ in the parabolic dispersion relation $E = \left(\hbar k^2\right)/(2m_{\text{eff}})$ for the BCB, the quantized energy levels for Schrödinger electrons are given by

$$E_N = E_{\text{BCB}} + \hbar\omega_c \left(N + 1/2 - \frac{\gamma}{2\pi}\right),$$

where $E_{\text{BCB}}$ is the energy of the bottom of the BCB. Since $\gamma = 0$ for Schrödinger electrons, one obtains

$$E_N = E_{\text{BCB}} + \hbar\omega_c (N + 1/2).$$

On the other hand, for the linear dispersion relation $E = E_D + v_F \hbar k$ of the Dirac electrons in the TSS, an analogous consideration yields

$$E_N = E_D + v_F \sqrt{2eB\hbar \left|N + 1/2 - \frac{\gamma}{2\pi}\right|},$$

Since $\gamma = \pi$ for Dirac electrons, one obtains

$$E_N = E_D + \text{sgn}(N) v_F \sqrt{2eB\hbar |N|},$$

which is already shown in the main text as Eq. (1).

Therefore, by extracting $E_N$ of the Landau levels, one can in principle distinguish between electrons stemming from the BCB (proportional to $N$) and those from the
to Eq. (B4) shown with the green straight line in Fig. 8(b) is considerably worse than for the analysis presented in the main text, which assumed the highest LL index of 28 and used Eq. (1), shown in Fig. 8(b) with the red curve. We highlight the unsatisfactory agreement between the experimental data and the fit for the BCB scenario by plotting their deviations in Fig. 8(c).

It is prudent to note that the dispersion of the actual TSS in Bi$_2$Se$_3$ deviates from a simple linear function [48]. This deviation can be approximated by considering a quadratic term in the dispersion relation. Therefore, for completeness, we have also performed an analysis based on the dispersion relation

\[ E = E_D + v_F \hbar k + \frac{\hbar^2}{2m_{\text{eff}}}k^2. \]  

(B7)

Using this dispersion and including the Zeeman energy, the following expression for the eigen-energies of the LLs is obtained for the electron branch of the curved Dirac cone [48]:

\[ E_N = E_D + \hbar \omega_c N + \sqrt{2\hbar v_F^2 eBN + \left(\frac{\hbar \omega_c N}{2} - \frac{g_s \mu_B B}{2}\right)^2}. \]  

(B8)

In the case of Bi$_2$Se$_3$, the \( g \)-factor of \( g_s = 55 \), the effective mass of \( m_{\text{eff}} = 0.25m_e \) and the Fermi velocity of \( v_F = 3 \times 10^5 \text{ m/s} \) are established to accurately describe Shubnikov-de Haas oscillations [48]. We found that the LL spectrum observed in Sr$_x$Bi$_2$Se$_3$ can be well explained [grey curve in Fig. 8(a)] by assuming a reduced Fermi velocity of \( v_F = 2.13 \times 10^5 \text{ m/s} \) and the highest LL index of 31. The reduction in the Fermi velocity is in line with the case of superconducting Cu$_x$Bi$_2$Se$_3$, where a reduction of up to 30\% was observed [37].

It should be remarked that in this analysis based on Eq. (B7), we have to assume a Dirac-point energy of \( E_D = -230 \text{ meV} \). While this is in apparent disagreement with the DP energy of about \(-310 \text{ meV}\) deduced from the minimum in the LDOS shown in Fig. 2, it can be straightforwardly reconciled by considering a tip-induced band bending that causes a shift in the DP energy; namely, as the bias voltage is increased, the electric field between the tip and the surface becomes stronger, causing the DP to shift in energy. Such a shift of about \(-80 \text{ meV}\) was deduced previously for Bi$_2$Se$_3$ by comparing STS and ARPES measurements [49]. Hence, our experimental LL spectrum is well described by both models of the TSS, i.e. Eq. (1) and Eq. (B8). Due to the ambiguity in the assignment of the LL index, a more rigorous distinction is difficult. Nevertheless, regardless of the model for the TSS, the observed LL spectrum supports the existence of upward band bending near the surface.
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