Experimental investigation of potential topological and p-wave superconductors
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Chapter 4

Possible p-wave superconductivity in the doped topological insulator \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \)

In this chapter, we report magnetic and transport measurements carried out on the candidate topological superconductor (TSC) \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \). The study mainly focuses on the response of superconductivity to a magnetic field and high pressures up to 2.3 GPa. Upon increasing the pressure, superconductivity is smoothly depressed and vanishes at \( p_c \sim 6.3 \) GPa. At the same time, the metallic behaviour is gradually lost. These features are explained by a simple model for a low electron carrier density superconductor. The analysis of the upper critical field shows that the \( B_{c2}(T) \) data collapse onto a universal curve, which clearly differs from the standard curve for a weak coupling, orbital limited, spin-singlet SC. Although an anisotropic spin-singlet state cannot be discarded completely, the absence of Pauli limiting and the similarity of \( B_{c2}(T) \) to a polar-state function point to spin-triplet SC. This observation is in accordance with theoretical predictions for TSCs.

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4.1 Introduction

Topological insulators (TIs) have sparked wide research interest because they offer a new playground for the realization of novel states of quantum matter [1,2]. In 3D TIs the bulk is insulating, but the 2D surface states - protected by a nontrivial $Z_2$ topology - are conducting due to their topological nature. More interestingly, the concept of TIs can also be applied to superconductors (SCs), due to the direct analogy between topological band theory and superconductivity [3,4]. Topological SCs in 1D, 2D and 3D are predicted to be nontrivial SCs with mixed even and odd-parity Cooper pair states [5,6]. Of major interest in the field of topological SCs is the realization of Majorana zero modes [1,2], that are predicted to exist as protected bound states on the edge of the 1D, 2D or 3D superconductor. Majorana zero modes are of great potential interest for topological quantum computation [1,2]. Recently, signatures of Majorana states have been observed for the first time experimentally in a semiconducting nanowire coupled to an ordinary s-wave superconductor [7]. This opens up the possibility to explore and fabricate a new type of quantum computation devices. Topological SCs are rather scarce. The B phase of $^3$He has recently been identified as an odd-parity time-reversal invariant topological superfluid [8], whereas the correlated metal Sr$_2$RuO$_4$ is a time-reversal symmetry breaking chiral 2D $p$-wave SC [3]. Other candidate topological superconductors can be found among the half-Heusler equiatomic platinum bismuthides LaPtBi, YPtBi, LuPtBi [9–12] and the doped semiconductor Sn$_{1-x}$In$_x$Te [13].

In 2010, Hor and co-workers initiated a new route to fabricate topological superconductors, namely, by reacting the 3D TIs Bi$_2$Se$_3$ and Bi$_2$Te$_3$ with Cu or Pd [14,15]. By intercalating Cu$^{+1}$ into the van der Waals gaps between the Bi$_2$Se$_3$ quintuple layers, SC occurs with a transition temperature $T_c = 3.8$ K in Cu$_x$Bi$_2$Se$_3$ for $0.12 \leq x \leq 0.15$. However, the reported SC shielding fractions were rather small and the resistance never attained a zero value below $T_c$, which casted some doubt on the bulk nature of SC. As regards Cu$_x$Bi$_2$Se$_3$, this concern was taken away by Kriener et al. [16,17], who showed that Bi$_2$Se$_3$ single crystals electrochemically intercalated by Cu have a SC volume fraction of about 60% (for $x = 0.29$) as evidenced by the significant jump in the electronic specific heat at $T_c$. SC was found to be robust and present for $0.1 \leq x \leq 0.6$. Photoemission experiments conducted to study the bulk and surface electron dynamics reveal that the topological character is preserved in Cu$_x$Bi$_2$Se$_3$ [18] as demonstrated in Fig. 4.1. Based on the topological invariants of the Fermi surface, Cu$_x$Bi$_2$Se$_3$ is expected to be a time-reversal invariant, fully gapped, odd parity, topological SC [5,6]. A recent study of the Cooper pairing symmetry within a two-orbital model led to the proposal that such a state can be favored by strong-spin orbit coupling [19]. Indeed several
experiments have revealed properties in line with topological SC. The magnetization in the SC state has an unusual field variation and shows curious relaxation phenomena, pointing to a spin triplet vortex phase [20]. Point contact measurements reveal a zero-bias conductance peak in the spectra, which possibly provides evidence for Majorana zero modes [21]. These signatures of topological SC make the experimental determination of the basic SC behavior of CuₓBi₂Se₃ highly relevant.

![Graphical representation of CuₓBi₂Se₃](image)

*Figure 4.1* Topological surface state of CuₓBi₂Se₃ from ARPES measurements at 4 K. The Dirac point is located at ~ -0.38 eV. The data are kindly provided by Dr. E. van Heumen (QEM group, private communication).

## 4.2 Sample preparation

A series of single crystalline samples CuₓBi₂Se₃ was prepared at the WZI by Dr. Y.K. Huang with x ranging from 0.12 to 0.3. The high purity elements Cu, Bi, and Se were molten together at 850 °C in quartz tubes sealed under high vacuum. Subsequently, the tubes were slowly cooled till 500-600 °C in order to grow the crystals. After growth the crystals were annealed for 60-100 hours.

More than thirty samples were measured in a standard bath cryostat to check for SC. All samples showed metallic behavior. Many samples revealed some traces of SC below 2-3 K. However, only very few samples showed zero resistance below the superconducting transition temperature Tₑ = 3.8 K. It appears, therefore, that SC is very fragile and sensitively depends on the sample preparation process. It was also tried to synthesize the material with the electro-chemical method, by which ideally Cu¹⁺ acts as a donor, but in contrast to Refs. [16,17] a full SC transition (R = 0) was never obtained by this route. In the remainder of
this chapter we focus on the best samples fabricated by the melting method with a nominal Cu content \( x \sim 0.3 \), a nominal Bi content \( \sim 2.1 \), and rapid quenched after annealing.

\( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) belongs to the space group \( \overline{R}3m \) and possesses a layered crystal structure with lattice parameters \( a = 4.138 \, \text{Å} \) and \( c = 28.736 \, \text{Å} \) as shown in Fig. 4.2. The pristine compound \( \text{Bi}_2\text{Se}_3 \) is constructed from double layers of \( \text{BiSe}_6 \) octahedra resulting in a Se-Bi-Se-Bi-Se five layer sandwich. The dopant Cu atoms either substitute at Bi sites or intercalate at the octahedrally coordinated \((0, 0, 1/2)\) sites (Wyckoff notation 3b site) in the Van der Waals gaps between the \( \text{Bi}_2\text{Se}_3 \) quintuple layers. SC is associated with intercalation rather than substitution [14].

\[ \text{Figure 4.2} \text{ Layered structure of } \text{Cu}_x\text{Bi}_2\text{Se}_3. \text{ The small pinkish dots depict copper atoms intercalated in the Van der Waals gaps between the quintuple layers. Picture taken from Ref. [14].} \]

4.3 Ac-susceptibility

In order to determine the superconducting shielding fraction of our samples, ac-susceptibility (\( \chi_{ac} \)) measurements have been performed at the Institute Néel by Dr. C. Paulsen in a dedicated SQUID magnetometer. Fig. 4.3 shows the low-temperature susceptibility data of two \( \text{Cu}_{0.3}\text{Bi}_{2.1}\text{Se}_3 \) samples (sample \( S||, \, m = 0.5 \, \text{g} \), sample \( S\perp, \, m = 0.25 \, \text{g} \)). The SC shielding fractions amount to \( 13\% \) and \( 16\% \), respectively. The data have been corrected for demagnetization effects. In both samples the SC transition sets in at \( T_{c-onset} = 3.1 \, \text{K} \). The signals are rather sluggish upon lowering temperature being indicative of sample inhomogeneities.
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These SC volume fractions are lower than those (up to 60 %) reported in Ref. 18 for samples prepared by electro-chemical intercalation.

![Figure 4.3](image)

Figure 4.3 Temperature dependence of the real part of the ac-susceptibility of two plate-like Cu$_{0.3}$Bi$_{2.1}$Se$_3$ crystals. Left panel: sample S∥ with the driving field in the ab-plane. Right panel: sample S⊥ with the driving field perpendicular to the ab-plane. The driving frequency is 2.1 Hz. The amplitude of the driving field is 0.25 Oe and 0.5 Oe, respectively. The driving fields are well below $H_{c1} = 5$ Oe, Ref. 22.

4.4 Electrical resistivity

![Figure 4.4](image)

Figure 4.4 Temperature dependence of the resistivity of Cu$_{0.3}$Bi$_{2.1}$Se$_3$ (sample #1) at ambient pressure. Inset: superconducting transition.

Many batches of Cu$_{x}$Bi$_2$Se$_3$ were initially tested after growth using a He bath cryostat in which the temperature can be lowered down to 1.5 K by directly decreasing the vapour pressure of liquid helium. Fig. 4.4 shows a representative resistivity curve in the temperature
range from room temperature till below $T_c$ at ambient pressure. The sample is metallic in the whole temperature range. The inset presents the resistivity around the superconducting transition. SC sets in at $T_c = 3.4$ K with initially a rather sharp drop. There is a tail below 3.2 K and the resistance reaches zero for $T < 2.8$ K. Overall, the $T_{c\text{-onset}}$ measured by transport is in agreement with the transition in $\chi_{ac}$. The tail is presumably related to sample inhomogeneities as inferred from the ac-susceptibility data as well, see Fig. 4.3. Nevertheless, the data are in good agreement with previous reports [14,16].

4.5 Upper critical field $B_{c2}$ at ambient pressure

Fig 4.5 shows the superconducting transition of a Cu$_{0.3}$Bi$_2$Se$_3$ single crystal at ambient pressure in magnetic fields applied in the hexagonal plane ($B \parallel ab$) and out of plane ($B \parallel c$). In field some additional structures appear on the curves, and these become more pronounced with increasing field. However, in essence, SC is gradually suppressed. We have determined the upper critical field $B_{c2}$, $B \parallel ab$ ($B_{c2}^{ab}$) and $B \parallel c$ ($B_{c2}^c$), by means of the midpoints of the major steps in the superconducting transition and the results are plotted in Fig 4.6.

![Figure 4.5](image)

Figure 4.5 Temperature dependence of the resistance of a Cu$_{0.3}$Bi$_2$Se$_3$ single crystal in fixed magnetic fields. Left panel: applied field parallel to the $ab$-plane, from right to left: 0 to 5.5 T in steps of 0.5 T. Right panel: field parallel to the $c$-axis, from right to left: 0 to 2.4 T in steps of 0.2 T.

For a layered compound, the upper-critical field shows a moderate anisotropy with $B_{c2}^{ab}(T \rightarrow 0) = 5.6$ T and $B_{c2}^c(T \rightarrow 0) = 1.9$ T. The anisotropy parameter is $\gamma^{an} = \frac{B_{c2}^{ab}}{B_{c2}^c} = 2.9$.

Other microscopic parameters are calculated as follows. Using the relations
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\[ B_{c2}^c = \frac{\Phi_0}{2\pi \xi_{ab}^2} \quad \text{and} \quad B_{c2}^{ab} = \frac{\Phi_0}{2\pi \xi_{ab}^c}, \]  

(4.1)

where \( \Phi_0 \) is the flux quantum, we obtain the SC coherence lengths \( \xi_{ab} = 13 \text{ nm} \) and \( \xi_c = 4 \text{ nm} \). These values are in good agreement with those reported previously [14,16].

Furthermore, it is important to distinguish whether our samples are in the clean or dirty limit, or in between. This is relevant because a sufficiently clean sample, i.e. with an electron mean free path \( \ell \) larger than \( \xi \), is a prerequisite for SC triplet pairing [22]. An estimate for \( \ell \) can be obtained from the relation

\[ \ell = \frac{\hbar k_F}{\rho_0 n e^2}, \]  

(4.2)

which assumes a spherical Fermi surface \( S_F = 4\pi k_F^2 \) with Fermi wave vector

\[ k_F = \left( 3\pi^2 n \right)^{\frac{1}{3}} \]  

(4.3)

Here \( n \) is the carrier density and \( \rho_0 \) is the residual resistivity. Using the experimental value for \( n \) derived from Hall measurements \( n = 1.2 \times 10^{26} \text{ m}^{-3} \) and \( \rho_0 = 1.5 \times 10^{-6} \Omega\text{m} \) we obtain \( k_F = 1.5 \times 10^9 \text{m}^{-1} \) and \( \ell = 34 \text{ nm} \), which ensures \( l > \xi \).

A more detailed analysis can be made by employing the slope of the upper-critical field \( dB_c/dT \) at \( T_c \) [23]. In the dirty limit case the initial slope is given by

\[ \left| \frac{dB_{c2}}{dT} \right|_{T_c} = 4480\gamma \rho_0, \]  

(4.4)

where \( \gamma \) is the Sommerfeld coefficient of the electronic specific heat per unit volume. With \( \gamma = 22.9 \text{ J/m}^3\text{K}^2 \) [16] we calculate \( |dB_{c2}/dT|_{T_c} = 0.15 \text{ T/K} \). This value is much lower than the measured values 2.0 T/K (\( B \parallel ab \)) and 0.6 T/K (\( B \parallel c \)), which confirms our samples are not in the dirty limit. By adding the clean limit term

\[ \left| \frac{dB_{c2}}{dT} \right|_{T_c} = 1.38 \times 10^{38} \gamma^2 T_c / S_F^2 \]  

(4.5)

in the model [20], estimates for \( l \) and \( \xi \) can be calculated from the experimental values of \( |dB_{c2}/dT|_{T_c} \). For \( B \parallel ab(c) \) we obtain \( l \sim 90(45) \text{ nm} \) and \( \xi \sim 9(19) \text{ nm} \). Note that in this analysis we used the normal-state \( \gamma \) value as an input parameter. If we take into account that not the whole bulk of the sample becomes superconducting (due to the incomplete shielding fraction), a reduced \( \gamma \) value [16] should be used. This will affect the absolute values of the deduced parameters, but not our conclusion that \( l > \xi \). Consequently, we argue our samples are sufficiently pure to allow for odd-parity SC.
In Fig. 4.6, we compare the experimental data of $B_c^2(T)$ with the model calculations for an $s$-wave spin singlet superconductor and a polar $p$-wave state. Obviously, the polar $p$-wave state model provides a better match. This will be further discussed in section 4.7.

![Figure 4.6](image)

*Figure 4.6* Temperature variation of the upper critical field, $B_c^2(T)$, of Cu$_{0.3}$Bi$_{2.1}$Se$_3$ (sample #1) for $B \parallel ab$ and $B \parallel c$. The blue and black solid lines indicate the model functions for an $s$-wave and polar-state superconductor, respectively (see text).

### 4.6 Superconducting transition under pressure

For two samples the pressure variation of $\rho(T)$ was measured under pressure up to 2.3 GPa. The samples were mounted in the pressure cell such that the field could be applied parallel (sample #11) and perpendicular (sample #12) to the $ab$-plane. Here, we first describe the results at zero applied magnetic field.

In Fig. 4.7 we show the pressure dependence of $\rho(T)$ around $T_c$ for sample #11. The superconducting transition becomes sharper under pressure. The overall good sample quality is attested to by the relatively small width of $\Delta T_c$ (as measured between 10% and 90% of $\rho(4 \text{ K})$), which ranges from 0.25 K at $p = 0$ to 0.06 K at $p = 2.31$ GPa. Nevertheless, a tail towards low temperatures associated with $\sim 10\%$ of the resistance path is present. For sample #12 the resistance does not reach $R = 0$, but remains finite at the level of 10% of $\rho(4 \text{ K})$, a value comparable to that reported previously by the Princeton group [14].
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Under pressure, the metallic behaviour is gradually lost as indicated by the large increase of the normal state resistivity at 4 K reported in Fig. 4.7. In Fig 4.8, we have traced the pressure variation of \(R(4 \text{K})\) and \(R(293 \text{K})\) for two samples after normalizing to the ambient pressure room temperature value \(R(239 \text{K}, p = 0)\). \(R_N(4 \text{K})\) and \(R_N(293 \text{K})\) both increase, approach each other and even cross for sample #12. This analysis also shows the metallic behaviour to be lost under pressure.

The variation of \(T_c\) with pressure determined by the midpoint of the transition is shown in Fig. 4.9 for sample #11 and #12. The results almost coincide for both samples. The solid line (see caption) suggests that \(T_c\) might be suppressed at a critical pressure \(p_c\) as high as \(\sim 6.3 \text{ GPa}\).

The depression of \(T_c\) can be understood qualitatively in a simple model for a low carrier density superconductor where

\[
T_c \sim \Theta_D \exp \left( -\frac{1}{N(0)V_0} \right),
\]

with \(\Theta_D\) the Debye temperature, \(N(0) \sim m^* n^{\frac{3}{2}}\) the density of state (with \(m^*\) the effective mass), and \(V_0\) the effective interaction parameter [24]. The increase of \(R(4\text{K})\) under pressure by a factor > 5 indicates a decrease of the carrier concentration \(n\), which in turn leads to a reduction of \(N(0)\) and \(T_c\). The reduction of \(n\) is also apparent in the temperature variation \(R(T)\) which gradually loses its metallic behavior as mentioned previously (see Fig. 4.8).
Figure 4.9 Superconducting transition temperature as a function of pressure for Cu$_{0.3}$Bi$_{2.1}$Se$_3$, sample #11 (circles) and sample #12 (triangles) as indicated. The solid line depicts a polynomial fit with linear and quadratic terms which serves to extrapolate the data. A critical pressure $p_c = 6.3$ GPa is estimated.

Hall effect experiments on a third sample (#3) confirm the gradual loss of metallic behaviour inferred from the resistivity data. The result presented in the inset of Fig 4.7 at 4 K shows that the electron carrier density $n \approx 1.2 \times 10^{26}$ m$^{-3}$ at $p = 0$ (we referred earlier from the resistivity data) drops to $n \approx 0.7 \times 10^{26}$ m$^{-3}$ at $p = 1.7$ GPa. In addition, the Hall measurements also indicate that the increase of $n$ with pressure is temperature independent.

4.7 Upper critical field $B_{c2}$ under pressure

To further elucidate the nature of superconductivity in the candidate topological superconductor Cu$_x$Bi$_2$Se$_3$, we now focus on its magnetic field response under pressure. Figs. 4.10 and 4.11 show the temperature dependence of the resistance under pressure in two particular cases: the applied field parallel (sample #11) and perpendicular (sample #12) to the $ab$-plane.

For the pressure experiment a large sized sample (sample #1) that was first measured at ambient pressure was cut into several smaller pieces. Subsequently, two of these smaller samples were mounted in the pressure cell. As mentioned previously (section 4.2), sample homogeneity is one of the central issues for experimental work at the current stage of research. These inhomogeneities show up as structures and steps in both samples in the $R(T)$ curves around the SC transition. In the following, however, we argue they do not effect the physical picture.
Possible $p$-wave superconductivity in the doped topological insulator $\text{Cu}_x\text{Bi}_2\text{Se}_3$

In order to analyze the upper-critical field $B_{c2}(T)$, it is essential to determine accurately and systematically the superconducting transition temperature at a given magnetic field. However, there is in principle no standard routine to implement this, and the problem becomes more intricate when the transitions exhibit structure. To this purpose we use the first order derivative of the $R(T)$ curves, which allows us to locate the main $R(T)$ drops in the transitions as quantitatively illustrated in Fig. 4.12 for a particular case (see caption).

By applying this method, we obtain $B_{c2}(T)$ data for the whole pressure range for the two sample configurations, which are presented in Fig. 4.13. Under pressure $B_{c2}(T)$ gradually decreases and the anisotropy parameter reduces from $\gamma_{an} = 2.9$ at $p = 0$ to 2.1 at the highest pressure $p = 2.31$ GPa. The coherence lengths increase to $\xi_{ab} = 15$ nm and $\xi_c = 7$ nm. As mentioned above, the increase of $\rho_0$ and the gradual loss of metallic behavior under pressure can for the major part be attributed mostly to a corresponding decrease of $n$, which tells us the ratio $l > \xi$ is satisfied in the entire pressure range.
Figure 4.11 Temperature variation of the resistance of Cu\textsubscript{0.3}Bi\textsubscript{2.1}Se\textsubscript{3} measured in fixed magnetic fields, $B \perp ab$-plane, ranging from 0 T (right) to 2.8 T (left) in steps of 0.2 T. (a) Sample #1 at ambient pressure; (b)-(f) sample #12 at pressures of 0.26, 0.67, 1.42, 2.02 and 2.31 GPa.

Figure 4.12 The first order derivative of the resistance versus temperature. For this case $B \parallel ab$, $p = 0.26$ GPa and $B = 4$ T. The $dR/dT$ is then smoothed to locate $T_c$. 
The functional behavior of $B_{c2}$ does not change with pressure, as demonstrated in Fig. 4.14. All the $B_{c2}(T)$ curves collapse on one single universal function $b^*(t)$, with

$$b^* = \left( B_{c2} / T_c \right) \left| dB_{c2} / dT \right|_{T_c}$$

(4.7)

and $t = T/T_c$ the reduced temperature. This holds for $B \parallel ab$, as well as for $B \parallel c$. In order to analyze the data further we have traced in Fig. 4.14 also the universal curve for a clean spin-singlet SC with the orbital limited upper-critical field

$$B_{c2}^{orb}(0) = 0.72 \times T_c \left| dB_{c2} / dT \right|_{T_c}$$

(4.8)

[Werthamer-Helfand-Hohenberg (WHH) model [25]], noting that for a dirty limit system the prefactor would reduce to 0.69. Clearly, the data deviate from the standard spin-singlet behavior. Next, we consider the suppression of the spin-singlet state by paramagnetic limiting [26,27]. The Pauli limiting field in the case of weak coupling is given by $B_P(0) = 1.86 \times T_c$. For Cu$_{0.3}$Bi$_{2.1}$Se$_3$ $B_P(0) = 6.2$ T at ambient pressure. When both orbital and spin limiting fields are present, the resulting critical field is

$$B_{c2}(0) = \frac{B_{c2}^{orb}(0)}{\sqrt{1 + \alpha^2}}$$

(4.9)

with the Maki parameter [25,28]

$$\alpha = \frac{\sqrt{2} B_{c2}^{orb}(0)}{B_P(0)}$$

(4.10)
Figure 4.14 Upper-critical field $B_{c2}(T)$ divided by $T_c$ and normalized by the initial slope $|dB_{c2}/dT|_{T_c}$ as a function of the reduced temperature $T/T_c$ at pressures of 0, 0.26, 0.67, 1.42, 2.02 and 2.31 GPa for $B \parallel ab$ (closed symbols) and $B \parallel c$ (open symbols). The lower and upper lines present model calculations for an $s$- and $p$-wave superconductor. The middle curve matches the data closely and depicts the polar-state model function scaled by a factor 0.95, which would result from a 5% larger initial slope in the model.

For $B \parallel ab(c)$ we calculate $\alpha = 1.1(0.34)$ and $B_{c2}(0) = 3.3(1.4)$ T. These values of $B_{c2}(0)$ are much lower than the experimental values (see Fig. 4.13) and we conclude the effect of Pauli limiting is absent. In general, by including the effect of paramagnetic limiting the overall critical field is reduced to below the universal spin singlet values [23,25]. Thus, the fact that our $B_{c2}$ data are well above even these universal values points to an absence of Pauli limiting, and is a strong argument in favor of spin triplet SC. The Pauli paramagnetic effect suppresses spin-singlet Cooper pairing, as well as the $L_z = 0$ triplet component $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$, while the equal-spin pairing (ESP) states $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ with $L_z = 1$ and $L_z = -1$ respectively, are stabilized in a high magnetic field. Exemplary SCs where Pauli limiting is absent are the spin-triplet SC ferromagnets URhGe [29] and UCoGe [30].

Next we consider the role of anisotropy of the crystal structure. Calculations show that for layered SCs, for $B$ parallel to the layers, $B_{c2}^{ab}$ is reduced and the critical field can exceed the values of the WHH model [31]. Cu$_x$Bi$_2$Se$_3$ is a layered compound [14] with a moderate anisotropy $\gamma^{an} = 2.9$. In this respect it is interesting to compare to other layered SCs, like alkali intercalates of the semiconductor MoS$_2$ [32], which have $\gamma^{an}$ values in the range 3.2-6.7. A striking experimental property of these layered SCs is a pronounced upward curvature of $B_{c2}(T)$ for $B$ parallel to the layers for $T < T_c$ due to dimensional crossover, which
is also a salient feature of model calculations [31]. However, an upward curvature is not observed in Cu$_x$Bi$_2$Se$_3$. In more detailed theoretical work the anisotropy of both the Fermi surface and the superconducting pairing interaction has been incorporated [33]. Under certain conditions this can give rise to deviations above the WHH curve as seen in Fig. 4.14. The bulk conduction band Fermi surface of the parent material $n$-type Bi$_2$Se$_3$ is an ellipsoid of revolution along the $k_c$ axis with trigonal warping [34]. Cu$_x$Bi$_2$Se$_3$ has a similarly shaped Fermi surface observed by Shubnikov-de Haas oscillations and ARPES measurements [35], The Fermi surface anisotropy would result in a different functional dependence of $B_{c2}(T)$ for $B \parallel ab$ and $B \parallel c$. On the qualitative level this is at variance with the universal $b^*(t)$ reported in Fig. 4.14.

Finally, we compare the $B_{c2}(T)$ data with upper-critical field calculations for a $p$-wave SC [36]. For an isotropic $p$-wave interaction the polar state (which applies for a linear combination of both ESP components) has the highest critical field for all directions of the magnetic field. In Fig. 4.14 we compare the $B_{c2}(T)$ data with the polar-state model function. This time the data lie below the model curve, but most importantly, the temperature variation itself is in agreement with the model, as illustrated by the solid black curve in Fig. 4.14. We have also considered a scaled WHH curve, but it fits the data much less well: increasing $b^*(0)$ by, e.g. 10% to match the experimental value, results in an overall curvature of $b^*(t)$ for a scaled WHH trace in disaccord with the data.

### 4.8 Discussion

In general, topological SC has been theoretically predicted to involve all three components of the triplet state with a full gap in zero field [5,6]. Recently, scanning tunneling microscopy/spectroscopy (STM/S) [37] and Andreev reflection spectroscopy [38] measurements have been performed on Cu$_x$Bi$_2$Se$_3$ samples with a low Cu content to determine the superconducting gap structure as well as the nature of the superconducting state. In this context, the simplest way to explain the observed zero field $U$-shaped scanning tunneling spectroscopy data would be based on standard BCS $s$-wave pairing for Cu intercalated Bi$_2$Se$_3$ [37]. In the reflection spectroscopy measurements, zero bias conduction peaks (ZBCPs) possibly indicative of Majorana modes can be obtained or not depending on the strength of the normal metal/superconductor barrier [38]. The Fermi surface shape evolution upon doping Bi$_2$Se$_3$ with Cu obtained from Shubnikov-de Haas oscillations and ARPES shows that upon increasing the carrier concentration the Fermi surface changes from a closed ellipsoid to an open cylinder-type; and most importantly, the Fermi surface encloses
two (or an even number) TRS points (Γ and Z), which is at variance with the theoretical prediction of the criteria for the realization of TSC in this material [19,35]. However, point contact experiments signify the existence of ZBCPs even at very low temperature (0.35 K) and in magnetic fields up to 0.45 T, which provides a strong evidence for the emergence of unconventional Andreev bound states associated with Majorana zero modes [21]. On the other hand, a fully gapped tunneling spectrum such as that seen in STS can also be understood by a more complex pairing at the surface [39]. Within this theoretical consideration, if the superconducting state is induced by a trivial s-wave pairing, the pair potential at the surface would result in an additional coherence peak within the induced energy gap in the spectroscopy. But such an extra peak was not observed in the STS spectra nor in the Andreev reflection spectroscopy [37,38]. Furthermore, model calculations indicate triplet pairing is possibly favorable for the \( L_z = 0 \) component [19]. In an applied magnetic field we expect a phase transition or crossover to a polar state to occur. It is at present not possible to explain all the experimental data in a single interpretative framework, as regards the superconducting pairing in \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \). Clearly, more theoretical work is desirable on topological superconductors in a magnetic field to settle the issue of \( B_{c2} \), and thus helps unravel the pairing mechanism of the superconducting phase.

4.9 Conclusion

By means of transport measurements we have investigated the pressure variation of the superconducting phase induced by Cu intercalation of the topological insulator \( \text{Bi}_2\text{Se}_3 \). Superconductivity is a robust phenomenon in these samples and by extrapolating \( T_c(p) \), superconductivity appears to vanish at the high critical pressure of \( p_c = 6.3 \) GPa. The metallic behavior of the system is gradually lost under pressure. The upper-critical field \( B_{c2} \) data under pressure collapse onto a single universal curve, which differs from the standard curve of a weak coupling, orbital-limited, spin-singlet superconductor. The absence of Pauli limiting, the sufficiently large mean free path, and the polar-state temperature variation of the \( B_{c2} \) data, point to \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) as a \( p \)-wave superconductor. In spite of some doubt as regards the unconventional superconducting nature in this material from recent tunneling experiments, our observations are in line with theoretical proposals that \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) is a promising candidate topological superconductor. More experimental work to unravel the superconducting state, by \( e.g. \) \( \mu \text{SR} \) or NMR experiments, is desired to further settle these issues.
Possible p-wave superconductivity in the doped topological insulator Cu$_x$Bi$_2$Se$_3$

References