Pressure-Induced Unconventional Superconducting Phase in the Topological Insulator Bi$_2$Se$_3$

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Simultaneous low-temperature electrical resistivity and Hall effect measurements were performed on single-crystalline Bi$_2$Se$_3$ under applied pressures up to 50 GPa. As a function of pressure, superconductivity is observed to onset above 11 GPa with a transition temperature $T_c$ and upper critical field $H_{c2}$ that both increase with pressure up to 30 GPa, where they reach maximum values of 7 K and 4 T, respectively. Upon further pressure increase, $T_c$ remains anomalously constant up to the highest achieved pressure. Conversely, the carrier concentration increases continuously with pressure, including a tenfold increase over the pressure range where $T_c$ remains constant. Together with a quasilinear temperature dependence of $H_{c2}$ that exceeds the orbital and Pauli limits, the anomalously stagnant pressure dependence of $T_c$ points to an unconventional pressure-induced pairing state in Bi$_2$Se$_3$ that is unique among the superconducting topological insulators.

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The interplay between superconductivity and topological insulator (TI) surface states has recently received enormous attention due to the observation of the long sought Majorana quasiparticle in InSb nanowires [1] and the promise of realizing topologically protected quantum computation [2]. Characterized by a nontrivial Z2 band topology with a bulk insulating energy gap that leads to a chiral metallic surface state with spin-momentum locking, TI surface states are analogous to the quantum Hall edge state and arise at the surface of a TI material due to the topological nature of the crossover between a nontrivial bulk insulating gap and the trivial insulating gap of the vacuum [3]. The use of the proximity effect [4–7] to induce superconductivity in Bi$_2$Se$_3$, the most well studied TI material to date, has had success in coupling these two states but suffers from the presence of bulk conducting states which require gating to realize true TI supercurrents [8].

Theoretically, nontrivial surface Andreev bound states can be directly realized by opening a superconducting energy gap in a bulk conductor [9], which is why the quest for the topological superconductor is one of the most active areas in condensed-matter physics. Recently, superconductivity has been found in materials with topologically nontrivial band structures, such as in Cu$_x$Bi$_2$Se$_3$ [10–13] and YPtBi [14,15], providing not only intrinsic systems with which to study the interplay between superconductivity and TI states, but also the potential to realize a new class of odd-parity, unconventional superconductivity [9].

The application of pressure has also uncovered superconductivity in several related materials, such as elemental Bi [16], Bi$_2$Te$_3$ [17], and Bi$_x$Te$_3$ [18], offering another route to realizing topological superconductivity. In this study, we measure transport properties of Bi$_2$Se$_3$ over an extended pressure range to investigate the ground state at ultrahigh pressures by using a designer diamond anvil cell capable of measuring both longitudinal and transverse resistivities up to 50 GPa. We observe the onset of a superconducting phase above 11 GPa that achieves a maximum transition temperature $T_c = 7$ K above 30 GPa that maintains its value up to the highest pressures achieved in this study. We discuss the implications of an anomalously constant $T_c$ that does not change with pressure, as well as an upper critical field that surpasses both orbital and Pauli limits, in terms of an unconventional superconducting state.

High-quality single crystals of Bi$_2$Se$_3$ were grown in excess selenium using the modified Bridgman technique described in detail elsewhere [19]. Single-crystal samples—with estimated thickness ($12.5 \pm 2.5$ $\mu$m) and measured carrier concentration $\sim 10^{17}$ cm$^{-3}$—were placed in contact with the electrical microprobes of an eight-probe designer diamond anvil cell [20] configured to allow combinations of both longitudinal and transverse four-wire resistance measurements [21]. Pressures were determined from the shift of the ruby fluorescence line [22]. Electronic transport measurements were performed at pressures between 4.1 and 50.1 GPa using the standard four-probe technique in both a dilution refrigerator and a pumped $^4$He cryostat, in magnetic fields up to 15 T directed parallel to the $c$ axis of the unpressurized (R-3m) crystal structure of Bi$_2$Se$_3$. Preliminary x-ray diffraction experiments are described.
Figure 1 presents a summary of the longitudinal ($\rho_{xx}$) resistivities as a function of both temperature $T$ and magnetic field $H$ measured at pressures above 13 GPa. (Resistivity data measured at lower pressures is presented elsewhere [23].) As shown previously, electrical transport measurements indicate a metallization of Bi$_2$Se$_3$ beginning above 8 GPa as revealed by the following: a tenfold decrease in the value of $\rho(300 \text{ K})$, a change in the temperature dependence of $\rho(T)$ from semiconducting to metallic conduction, the loss of curvature and development of a linear Hall resistivity $\rho_{H}(H)$, and the appearance of magnetoresistance that varies with $H^2$ [23]. Just above this pressure, traces of superconductivity appear in the form of partial resistive transitions, onsetting below 300 mK at 11.9 GPa (not shown) and gradually growing with increasing pressure. Interestingly, the value of carrier density where superconductivity first appears ($\sim 10^{20} \text{ cm}^{-3}$) is close to the carrier concentration where superconductivity is seen in Cu$_2$Bi$_2$Se$_3$ which may indicate that increased carrier concentrations are necessary for superconductivity in Bi$_2$Se$_3$ [12]. As shown in Fig. 1(a), a nearly complete resistive transition appears at 13.6 GPa with midpoint transition $T_c = 0.5 \text{ K}$ that gradually increases with increasing pressures up to $\sim 30 \text{ GPa}$. Likewise, as presented in Fig. 1(b), the upper critical field $H_{c2}$ (defined as the midpoint of the resistive transition in field) also grows with pressure, with a magnetic field dependence very similar in form to the temperature dependence presented in Fig. 1(a), which does not rule out filamentary superconductivity [21] but does suggest bulk phase transitions. Also, similar to the pressure evolution of $T_c$, $H_{c2}$ increases monotonically up to 30 GPa, above which both quantities abruptly stop growing and $T_c$ remains strikingly constant at 7 K up to 50.1 GPa.

A transition temperature that is constant over such a large pressure range is highly anomalous. In conventional phonon-mediated superconductors—like elemental Bi [16] and the two-band superconductor MgB$_2$ [24]—$T_c$ typically decreases with increasing pressure due to phonon stiffening. However, when the electronic bandwidth is sensitive to volume change, such as in transition metals, an increase in $T_c$ with pressure is also possible [25]. These two contrasting pressure-dependent evolutions of $T_c$ are engendered by the implicit dependence of $T_c$ on volume through the phonon cutoff frequency ($\Theta_D$ or $\langle \omega_c \rangle$) and the electronic density of states [$N(E_F)$], as given by the BCS relationship or the McMillan strong-coupling formalism [26,27]. Thus, for Bi$_2$Se$_3$, it is possible that these two mechanisms may be balanced so as to produce a pressure-invariant $T_c$ over a wide range of pressure.

As shown in Fig. 2, a strong sensitivity of the transverse Hall resistance $R_{xy}$ to pressure suggests that the electronic structure of Bi$_2$Se$_3$ indeed undergoes a dramatic change with pressure. A one-band Drude approximation, motivated by the linear field dependence of $R_{xy}$, yields an estimated electron carrier density $n_H$ that increases strongly with increasing pressure, consistent with the increasing metallicity observed in $\rho_{xx}$. As summarized in Fig. 3, this carrier density increases by over four orders of magnitude over the entire pressure range, suggesting significant changes in the band structure. More surprising, $n_H$ increases by a factor of ten between 30 and 50 GPa, the same range over which $T_c$ remains constant. The increasing carrier density with applied pressure suggests an increasing $N(E_F)$, which, by itself, would tend to promote an increasing $T_c$. If one assumes a typical pressure-induced phonon stiffening, then the Hall data are at least amenable to a scenario where balanced electronic and phonon contributions lead to the observed pressure invariance of $T_c$. However, in either the BCS or the strong-coupling

**FIG. 1** (color online). Longitudinal resistivity of Bi$_2$Se$_3$ for various applied pressures as a function of (a) temperature and (b) magnetic field oriented parallel to the crystallographic $c$ axis of the ambient pressure phase, at a fixed temperature of 0.5 K. (Data at 20.8 GPa were obtained with a different lead configuration resulting in larger measurement uncertainty, and are, therefore, scaled by a factor of 2.5 to match the overall trend reported previously [23].)
mediated superconductivity, the strikingly pressure-dependence of \( T_c \) would necessarily require a fine balance of parameters and an unconventional electronic contribution [21].

Moreover, the arrested evolution of \( T_c \) in Bi$_2$Se$_3$ is in contrast to that observed in two other closely related compounds where \( T_c \) is strongly suppressed with pressure, as found in Bi$_4$Te$_3$ [18] and the closely related TI material Bi$_2$Te$_3$ [17]. Interestingly, Bi$_2$Se$_3$ is known to undergo at least two structural transitions under pressure, from the ambient-pressure rhombohedral (R-3m) structure to a lower-symmetry monoclinic (C2/m) structure near 10 GPa, and then to an unknown phase above 28 GPa as measured by Raman spectroscopy [28]. In both Bi$_2$Te$_3$ and Bi$_2$Se$_3$, superconductivity appears in the monoclinic phase and abruptly strengthens upon crossing a second structural transition into a cubic phase at higher pressures [18,28–30].

Our preliminary x-ray diffraction experiments on Bi$_2$Se$_3$ yield similar results, including a structural transition to a sevenfold (C2/m) structure near 10 GPa followed by another transition to a bcc-like (C2/m) structure above 28 GPa [21]. As shown in Fig. 3, the onset of superconductivity in Bi$_2$Se$_3$ and its sharp increase to 7 K both coincide with these structural transitions in a manner similar to the other systems, suggesting a close correlation among all of these high-pressure phases. However, with \( T_c \) in Bi$_2$Te$_3$ and Bi$_2$Se$_3$ both exhibiting a notable suppression \( dT_c/dP \sim -0.13 \) K/GPa after reaching their maximum values, it is clear that the behavior in Bi$_2$Se$_3$ is anomalous.

The unique pressure evolution of \( T_c \) in Bi$_2$Se$_3$ suggests the presence of a very unconventional superconducting state. This is further evidenced by an anomalous temperature dependence of the upper critical field \( H_{c2}(T) \). To compare the data to known models, it is useful to calculate the reduced critical field, \( h^*(T) = [H_{c2}(T)/T_c]/[dH_{c2}(T)/dT]|_{T-T_c} \), and compare it to models for orbitally limited s-wave [31] and spin-triplet p-wave [32,33] superconductors. As shown in Figs. 4(b) and 4(c) for 34.4 and 50.1 GPa, respectively, \( h^*(T) \) deviates significantly from the expected orbital-limited behavior predicted by the Werthamer-Helfand-Hohenberg (WHH) theory for an s-wave superconductor, \( H_{c2}^{\text{orb}} \approx 0.7 T_c \times dH_{c2}/dT|_{T-T_c} \) (or \( h^*(0) \approx 0.7 \) [31]. This is true through the entire pressure range under study, and is immediately apparent in the observed near-linear temperature dependencies of \( H_{c2} \) shown in Fig. 4(a). The quasilinear \( h^*(T) \) curves in Fig. 4 are closer in form to that of a p-wave superconductor like the heavy-fermion compound UBe$_{13}$ [34]. However, the measured \( h^*(0) \) values in Bi$_2$Se$_3$ still slightly exceed the maximum value of \( h^*(0) = 0.8 \) expected for a polar p-wave state [32,33], further hinting at the unconventional nature of the high-pressure superconducting state of Bi$_2$Se$_3$.

To determine the influence of Pauli limiting, we calculate \( H_{c2} \) assuming that both orbital and paramagnetic pair breaking mechanisms are active. The Pauli limiting field \( H_P \) is determined by the Zeeman energy required to break...
superconductor KO$_3$O$_6$ [40], although such effects cannot arise from ellipticity alone [41]. Strong electron-phonon coupling can also slightly enhance the orbital limit [42,43], although an excessive coupling constant of $\lambda \approx 4$ would be required to explain the observed $h^*(t) \approx 0.9$. Strong spin-orbit coupling was shown early on to greatly reduce the effects of Pauli paramagnetic pair breaking [31], although a dramatic enhancement is only expected in the limit of infinite scattering strength. Finally, multiband superconductivity can also manifest deviations from WHH, as shown for Lu$_2$Fe$_{1-x}$Si$_x$ [44], and calculated for MgB$_2$ [45] and elemental Bi under pressure [46]. While such a case cannot be ruled out for Bi$_2$Se$_3$, the lack of evidence for multiband behavior in the normal-state transport, as evidenced by the linear $R_{xy}$ data in field for the two high-pressure phases, suggests otherwise.

The anomalously large upper critical field that exceeds orbital and Pauli limits and the surprising insensitivity of $T_c$ to pressure point to a unique and unconventional superconducting state in Bi$_2$Se$_3$. The possibility of this state being topological in nature is an enticing consideration, but requires several as yet unknown criteria to be satisfied. For instance, if band inversion symmetry is present, as well as a Fermi surface that is centered at time-reversal-invariant momenta such that a Dirac-type Hamiltonian describes the band structure, topological superconductivity is indeed probable given a fully gapped pairing symmetry that is odd under spatial inversion [9]. Determination of both crystallographic and electronic structures in the high-pressure phase [21] are required to understand the implications for the pairing state and its relation to the ambient pressure topological insulator state. Finally, recent evidence of $s$-wave superconductivity in Cu$_x$Bi$_2$Se$_3$ [47] must be considered in this context.

In conclusion, the metallization of Bi$_2$Se$_3$ at high pressures stabilizes a superconducting ground state above 11 GPa that appears to be optimized after a second structural phase transition above 28 GPa. The resulting phase diagram exhibits many similarities to those of other pressure-induced superconducting systems with strong spin-orbit coupling, including the role of structural transitions and the presence of an upper critical field that greatly exceeds the universal predictions for orbital and Pauli pair-breaking. The anomalously large critical fields and the pressure-invariant $T_s$ are incompatible with the expectations of archetypal, phonon-mediated, $s$-wave superconductors, suggesting the distinct possibility of an unconventional superconducting state in Bi$_2$Se$_3$.

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FIG. 4 (color online). (a) Upper critical field $H_{c2}$ of Bi$_2$Se$_3$ for various pressures up to 50 GPa, with fields applied parallel to the ambient-pressure crystallographic $c$ axis (values determined from 50% resistive transition, with error bars indicating 10%–90% values). Solid lines are guides, but all have the same functional dependence as $H_{c2}(T)$ for 34.4 GPa data. Error bars for 24.7 GPa (not shown for clarity) are $\pm 1$ T. Panels (b) and (c) present the reduced upper critical field, $h^*(t)$ with reduced temperature $t = T/T_c$, for applied pressures of 34.4 and 50.1 GPa, respectively. Solid and dashed lines indicate the calculated $h^*(t)$ dependence for orbital limited $s$-wave superconductors [31] and for a polar $p$-wave state [32,33], respectively (see text).

Cooper pairs and equates to the gap energy $\Delta$ (e.g., $H_F = 1.84T_c$ for a BCS superconductor) [35]. In the presence of both orbital and Pauli limiting, the expected upper critical field is modified to $H_{c2}^{\alpha} = H_{c2}^{orb}/\sqrt{1 + \alpha^2}$, and determined by the Maki parameter $\alpha = \sqrt{2H_{c2}^{orb}/H_F}$ [36]. At 34.4 GPa, the calculated values $H_{c2}^{orb} = 3.15$ T and $H_F = 12.9$ T yield $\alpha = 0.346$ and an expected modified value $H_{c2}^{\alpha} = 2.80$ T, notably lower than the measured value of 4 T and indicative of an absence of Pauli pair breaking. A similar case was presented for $H_{c2}$ measurements of the related superconductors YPtBi [14,37] and Cu$_x$Bi$_2$Se$_3$ [38], which also both exhibit quasilinear $H_{c2}(T)$ behavior with zero-temperature values exceeding these universal limits. In addition, Bi$_x$Te$_3$ under pressure also exhibits a linear $H_{c2}(T)$ [18], presenting an intriguing set of strong spin-orbit-coupled superconducting materials with very similar anomalous features.

While exceeding the WHH limit can be considered a sign of unconventional superconductivity [33,35], other mechanisms should also be considered. For instance, Fermi surface topology can enhance the expected WHH limit [39] as shown in the case of the pyrochlore
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