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 metallic surface state with spin-momentum locking 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 ± 2.5) µm and measured carrier concentration ~ 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 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.

Theoretical calculations predict that both orbital and Pauli limits, in terms of an unconventional superconducting state. 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.

Figure 1 presents a summary of the longitudinal ($\rho_{xx}$) resistivities as a function of both temperature $T$ and mag-
FIG. 1: 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].)

Netic 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 ($\sim 10^{20}$ 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 $T_c = 0.5$ K that gradually increases with increasing pressures up to $\sim 30$ 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 [10] and the two-band superconductor MgB$_2$ [8]—$T_c$ 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 [1]. 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 $< \omega_c >$) and the electronic density of states ($N(E_F)$), as given by the BCS relationship or the McMillan strong-coupling formalism [7, 26]. 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.

FIG. 2: Transverse Hall resistance of Bi$_2$Se$_3$ as a function of applied pressure, showing linear behavior with a negative slope indicative of a single, electronlike band. The slope decreases with applied pressure until 46.7 GPa, implying an increasing carrier concentration with pressure; 50.1 GPa presents a larger slope and concordantly smaller carrier concentration (see text for details).
The increasing carrier density with applied 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. 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$_2$Te$_3$ [18] and the closely related TI material Bi$_2$Te$_3$ [19]. 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 [1]. In both Bi$_2$Te$_3$ and Bi$_2$Te$_3$, superconductivity appears in the monoclinic phase and abruptly strengthens upon crossing a second structural transition into a cubic phase at higher pressures [1, 18, 29, 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$_2$Te$_3$ 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$_4$Te$_3$ 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, $h^\ast(T) = H_{c2}(T)/4T_c(0)$, and compare it to models for orbitally limited s-wave [31] and spin-triplet p-wave [33, 34] superconductors. As shown in Figs. 4b) and c) for 34.4 and 50.1 GPa, respectively, $h^\ast(T)$ deviates significantly from the expected orbital-limited behavior predicted by the Werthamer-Helfand-Hohenberg (WHH) theory for an s-wave superconductor, $H_{c2}^{sb} \simeq 0.7T_c \times dH_{c2}/dT|_{T=T_c}$ (or $h^\ast(0) \simeq 0.7$ [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. 4a). The quasilinear $h^\ast(T)$ curves in Fig. 4 are closer in form to that of a p-wave superconductor like the heavy-fermion compound UBe$_{13}$ [32]. However, the measured $h^\ast(0)$ values in Bi$_2$Se$_3$ still slightly exceed the maximum value of $h^\ast(0) \simeq 0.8$ expected for a polar p-wave state [33, 34], 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 Cooper pairs and equates to the gap energy $\Delta$ \( (e.g., \, H_P = 1.84T_c \, \text{for a BCS superconductor}) \) [33]. In the presence of both orbital and Pauli limiting, the expected...
FIG. 4: (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 ±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 [33, 34], respectively (see text).

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 criterial 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\(_3\) [17] 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 \( T_c \) 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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Note added.—After submission of this manuscript, we became aware of a similar study by Kong, et al.[5].

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The Designer Diamond Anvil Cell

The designer diamond anvil cell (DAC) for these experiments was composed of an 8-probe designer diamond anvil and a standard diamond anvil, both with culets of approximately 300 μm in diameter. The microprobes of the designer diamond anvil were tungsten, and they were lithographically deposited to be equally spaced on a 44-μm diameter circle at the center of the designer anvil culet. The MP35N gasket was pre-indented down to a thickness of 45 μm, and the 120-μm sample chamber was drilled into the pre-indent gasket using an electric discharge machine. Steatite powder was packed into the sample chamber along with a ruby sphere, to be used as a pressure marker. The sample, approximately 10 μm thick, was placed in contact with the microprobes of the designer anvil, and pressed into the steatite medium upon assembly of the cell.

Electrical contact is provided by the force of the cell, which physically presses the sample against the electrical contacts (microprobes of the designer anvil). Because of this, each microprobe can make electrical contact with the sample at different pressures, and some microprobes never provide adequate electrical contact. As such, and for these experiments, it was not possible to provide an adequate Hall geometry until P ≥ 29.8 GPa. Because diamond, owing to the depletion of phonons, becomes a poor thermal conductor at low temperatures, we added a “thermal strap” to the DAC in an attempt to mitigate effects associated with poor thermal contact (e.g., Joule heating). The thermal strap was a thin metal foil that was thermally (but not electrically) connected between the metal gasket and the outside cell body of the DAC.

Figure 5[A] is an optical image (taken through a red filter) of the loaded cell looking through the designer diamond. The electrical microprobes, the sample, the ruby pressure marker, the steatite pressure-transmitting medium, and the MP35N gasket material are labeled.

Magnetotransport

The lead configuration for high-pressure measurements is shown in Fig. 5[B], where the field direction H is out of the plane of the page. For both the longitudinal, ρ_xx, and transverse, R_xy, resistance measurements, the current was applied along two opposing leads. ρ_xx was measured with the leads labeled V_xx and R_xy was measured with the leads labeled V_yy. R_xy was measured for positive and negative fields and the results were symmetrized (i.e., [R(+H) – R(−H)]/2) to obtain the final value of R_xy shown in the main text. At low pressures below about 6 GPa—as shown by Hamlin, et al. [1]—the R_xy of Bi₂Se₃ shows some curvature at higher fields. However, above about 30 GPa (Fig. 2 in main text), R_xy appears to be very linear in field. As such, we conservatively use a single-band picture, rather than a compensated multi-band model [2], to extract carrier density from the R_xy data.

X-ray Diffraction

Room-temperature, angle-dispersive diffraction patterns were acquired at HPCAT (16 BM-D) of the Advanced Photon Source of Argonne National Laboratory. Conventional DACs were used for these measurements. A neon pressure-transmitting medium was used, and Cu powder was used as the pressure marker. A 10x10 μm, 32.9 keV (λ_m=0.3771 Å) incident x-ray beam, calibrated with CeO₂, was used. 2D diffraction patterns were detected with a Mar345 image plate; exposure times ranged from 60-600 seconds. 2D diffraction patterns were collapsed to 1D intensity versus 2Θ plots using the program FIT2D [3].

Example x-ray diffraction patterns are shown in Fig. [4]. The patterns show clear, unambiguous changes with applied pressure. The diffraction patterns were indexed and refined using the software program MDI Jade. The results of refinements indicate the following space groups: Bi₂Se₃-I — R3m; Bi₂Se₃-II — C2/m, 7-fold coordinated; and Bi₂Se₃-III — C2/m, bcc-like coordinated. Phase-II is similar to that reported by Vilaplana, et al [4]. Our phase-III, however, differs from recent low-temperature results of Kong, et al., where C2/c and bcc phases are proposed for pressures above 20 and 29 GPa, respectively.
lent starting point to examine the pressure dependence of superconductivity under pressure. The pressures and space groups are labeled below each diffraction pattern.

In our work, the phase transition from Bi$_2$Se$_3$-I to Bi$_2$Se$_3$-II begins near 9.5 GPa and extends just above 10 GPa. The phase transition from Bi$_2$Se$_3$-II to Bi$_2$Se$_3$-III begins near 26.5 GPa and extends just above 30.5 GPa. As the diffraction data was acquired with a high hydrostatic pressure medium, we expect that the structural transitions may exhibit wider transition ranges in the electrical transport study (above), which used steatite as a solid, pressure-transmitting medium. More details of this structural determination will be included in a forthcoming article.

**Pressure Dependence of $T_c$**

The pressure dependence of $T_c$ can be examined within the scope of a phonon-mediated pairing mechanism. The McMillan strong-coupling formalism provides an excellent starting point to examine the pressure dependence of $T_c$ [5, 8], which is given by

$$T_c \approx \frac{< \omega >}{1.2} \exp \left[ \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right],$$

where $< \omega >$ is a characteristic phonon cutoff frequency, $\lambda$ is the electron-phonon coupling strength, and $\mu^*$ is the Coulomb repulsion, which is generally considered to be pressure independent. The pressure-dependent behavior of $T_c$ can be examined by taking the derivative of Eq. (1) with respect to volume $V$. This is often done logarithmically, to yield:

$$\frac{d\ln T_c}{d\ln V} = \frac{B}{T_c} \frac{dT_c}{dP} \approx \gamma_G + \Delta \left[ \frac{d\ln n}{d\ln V} + 2\gamma_G \right].$$

where $B$ is the bulk modulus, $\gamma_G$ is the Grüneisen coefficient, $\Delta = 1.04\lambda[1 + 0.38\mu^*/(\lambda - \mu^*(1 + 0.62\mu^*)]]$, and $\eta$ is the Hopfield parameter [9]. The Hopfield parameter itself can be formalized as $\eta = N(E_F) < I^2 >$, where $N(E_F)$ is the density of states and $< I^2 >$ is an electron-ion matrix element [10]. For $s$- or $p$-electron systems, the volume-dependent derivative of the Hopfield parameter is generally estimated to be about -1 [8].

Using the bulk modulus ($B=70$ GPa, from x-ray diffraction measurements) of Bi$_2$Se$_3$-III at high pressures, we can examine the values of $\gamma_G$ and $\lambda$ that could, in principle, produce a pressure-invariant $T_c$ as we observe. Setting $\lambda=1.5$ to its highest allowable value for the McMillan formula, we can estimate a $\gamma_G=1$, which is somewhat low as compared to other materials. Weaker coupling strengths require even smaller values of $\gamma_G$, which are probably physically unrealistic. It should be noted, however, that we do not have any measurements of $\gamma_G$ at high pressures. This would require a measurement of phonons under pressure or measurements of specific heat and thermal expansion at high pressures.

If one uses the $d$-electron expectations for the pressure-variation of the Hopfield parameter $d\ln \eta/d\ln V = -3.5$, then it is possible to find values of $\lambda$ and $\gamma_G$ that fall into “reasonable” ranges for these parameters. However, there is, as yet, no justification for expecting a large volume dependence on the Hopfield parameter outside of the realm of usual $p$-electron systems. A quantitative evaluation of the volume dependence of the Hopfield parameter would require electronic structure calculations to accurately correlate the observed changes in the carrier density with changes in the density of states and to compute the electron-ion matrix element. This analysis points to the unconventional nature of the superconducting state of Bi$_2$Se$_3$ under pressure: for phonon-mediated superconductivity to exist, Bi$_2$Se$_3$ must have an unprecedented pressure dependence of its electronic component of superconductivity.

**Filamentary vs. Bulk Superconductivity**

A common concern in electrical transport measurements is the difficulty in determining filamentary versus bulk superconductivity. The high-pressure measurements reported in the main body of this manuscript are performed only with electrical transport, and there is no complimentary “bulk” measurement. Nonetheless, the pressure- and field-dependent behavior of $T_c$ in Bi$_2$Se$_3$ suggest that the superconducting state is bulk rather than filamentary.

At the extreme pressure achieved in this experiment, some pressure inhomogeneities are expected in the sample chamber of the DAC. Typically, pressure gradients result in broadening of the superconducting transitions (in our case, at high pressure we have transitions approx...
imately 0.5 K wide) as opposed to a “shorting out” of a portion of the sample. However, if the sample were composed of only a few individual, small filaments heterogeneously distributed through the sample, then one might expect to see multiple transitions, where each transition would occur at the local pressure that it experienced. The data (Fig. 1 of main text) are clearly not in favor of distinct, separate superconducting transitions.

At some concentration of filaments, however, it would be difficult to tell the difference (due to the small sample size over which gradients exist) between multiple transitions and a single, broad transition. If the superconducting state was conventional, or if it behaved similar to the Bi-Te analogues, then reproducing the nearly flat pressure dependence of $T_c$ in $\text{Bi}_2\text{Se}_3$ with filamentary superconductivity would require a very special configuration of pressure gradients. From 30-50 GPa, the pressure gradients would have to mimic an identical average pressure without significant broadening of the transition. Furthermore, given that we do not observe multiple transitions in the electrical resistivity, the gradients would have to access various pressures that all lie within about 0.5 K of one another. From this, it would seem that the small pressure dependence of $T_c$ from 30-50 GPa is unlikely to be due to filamentary superconductivity. Furthermore, the relatively large upper critical fields also suggest that the experiments are not probing small filaments of superconductivity. Of course the bulk nature of the superconducting state cannot be irrefutably examined with electrical resistivity alone.

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