

Pressure-Induced Unconventional Superconducting Phase in the Topological Insulator Bi_2Se_3

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Simultaneous low-temperature electrical resistivity and Hall effect measurements were performed on single-crystalline Bi_2Se_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_2Se_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 Z_2 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_2Se_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 $\text{Cu}_x\text{Bi}_2\text{Se}_3$ [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_2Te_3 [17], and Bi_4Te_3 [18], offering another

route to realizing topological superconductivity. In this study, we measure transport properties of Bi_2Se_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_2Se_3 were grown in excess selenium using the modified Bridgman technique described in detail elsewhere [19]. Single-crystal samples—with estimated thickness $(12.5 \pm 2.5) \mu\text{m}$ and measured carrier concentration $\sim 10^{17} \text{ cm}^{-3}$ —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 ^4He cryostat, in magnetic fields up to 15 T directed parallel to the c axis of the unpressurized ($R\text{-}3m$) crystal structure of Bi_2Se_3 . Preliminary x-ray diffraction experiments are described.

Figure 1 presents a summary of the longitudinal (ρ_{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_2Se_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, onseting 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 $\text{Cu}_x\text{Bi}_2\text{Se}_3$ which may indicate that increased carrier concentrations are necessary for superconductivity in Bi_2Se_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 (Θ_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_2Se_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_2Se_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 ρ_{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

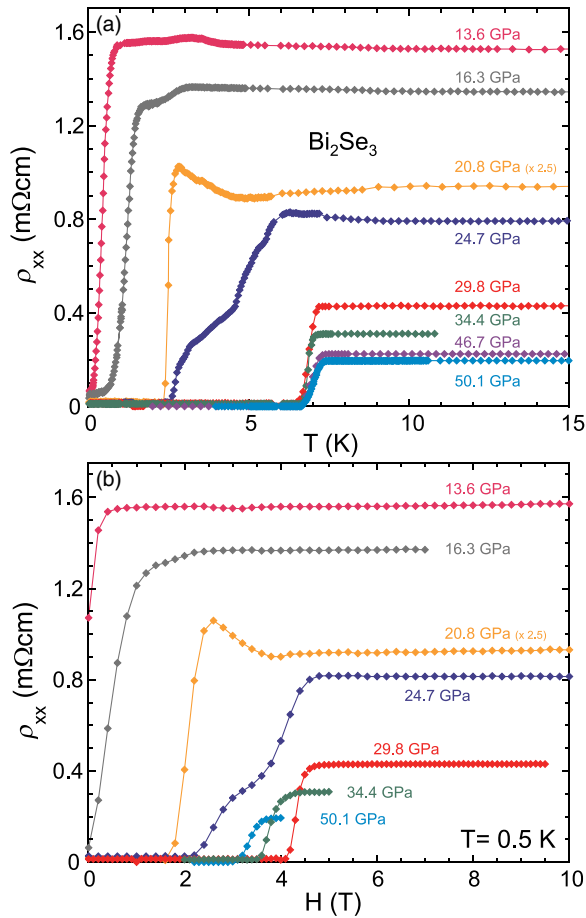


FIG. 1 (color online). Longitudinal resistivity of Bi_2Se_3 for various applied pressures as a function of (a) temperature and (b) magnetic field oriented parallel to the crystallographic c axis of the ambient pressure phase, at a fixed temperature of 0.5 K. (Data at 20.8 GPa were obtained with a different 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].)

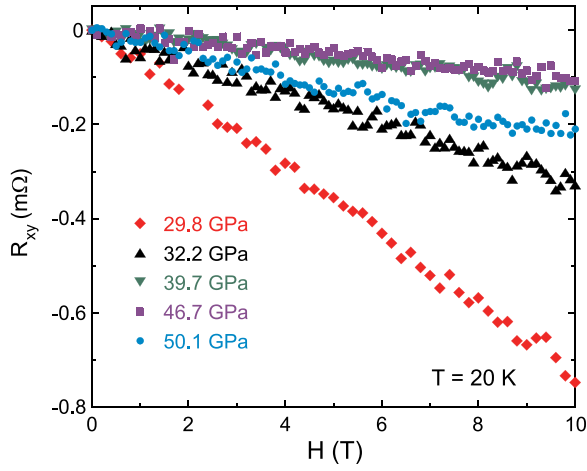


FIG. 2 (color online). Transverse Hall resistance of Bi_2Se_3 as a function of applied pressure, showing linear behavior with a negative slope indicative of a single, electronlike band. The slope decreases with applied pressure until 46.7 GPa, implying an increasing carrier concentration with pressure; 50.1 GPa presents a larger slope and concordantly smaller carrier concentration (see text for details).

theories, there are other parameters that affect the pressure dependence of T_c [24–27]. In the context of phonon-mediated superconductivity, the strikingly pressure-independent value of T_c would necessarily require a fine

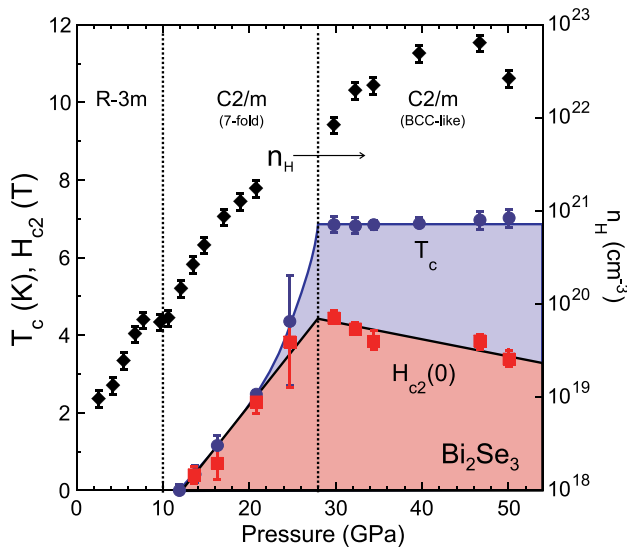


FIG. 3 (color online). Phase diagram of Bi_2Se_3 showing the evolution of carrier concentration n_H (diamonds), superconducting transition temperature T_c (circles), and upper critical field H_{c2} at zero temperature (squares) as a function of pressure for fields orientation along the crystallographic c axis of the ambient-pressure structure; n_H data below 21 GPa are from Ref. [23]. Dotted vertical lines correspond to known structural phase transitions between rhombohedral ($R-3m$) and monoclinic ($C2/m$) structures near 10 GPa, and a transition to a bcc-like ($C2/m$) structure near 28 GPa, respectively [21,23,28].

balance of parameters and an unconventional electronic contribution [21].

Moreover, the arrested evolution of T_c in Bi_2Se_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_4Te_3 [18] and the closely related TI material Bi_2Te_3 [17]. Interestingly, Bi_2Se_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_2Te_3 and Bi_4Te_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_2Se_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_2Se_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_2Te_3 and Bi_4Te_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_2Se_3 is anomalous.

The unique pressure evolution of T_c in Bi_2Se_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, $H_{c2}^{\text{orb}} \approx 0.7T_c \times dH_{c2}/dT|_{T=T_c}$ (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_2Se_3 still slightly exceed the maximum value of $h^*(0) \approx 0.8$ expected for a polar p -wave state [32,33], further hinting at the unconventional nature of the high-pressure superconducting state of Bi_2Se_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

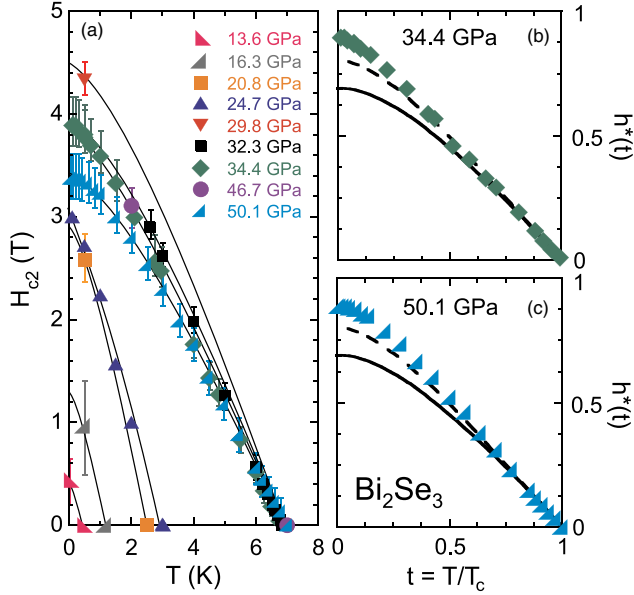


FIG. 4 (color online). (a) Upper critical field H_{c2} of Bi_2Se_3 for various pressures up to 50 GPa, with fields applied parallel to the ambient-pressure crystallographic c axis (values determined from 50% resistive transition, with error bars indicating 10%–90% values). Solid lines are guides, but 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 [32,33], respectively (see text).

Cooper pairs and equates to the gap energy Δ (e.g., $H_p = 1.84T_c$ for a BCS superconductor) [35]. In the presence of both orbital and Pauli limiting, the expected upper critical field is modified to $H_{c2}^\alpha = H_{c2}^{\text{orb}}/\sqrt{1 + \alpha^2}$, and determined by the Maki parameter $\alpha \equiv \sqrt{2}H_{c2}^{\text{orb}}/H_p$ [36]. At 34.4 GPa, the calculated values $H_{c2}^{\text{orb}} = 3.15$ T and $H_p = 12.9$ 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 $\text{Cu}_x\text{Bi}_2\text{Se}_3$ [38], which also both exhibit quasilinear $H_{c2}(T)$ behavior with zero-temperature values exceeding these universal limits. In addition, Bi_4Te_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

superconductor KOs_2O_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 $h^*(0) \approx 0.9$. Strong spin-orbit scattering 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 $\text{Lu}_2\text{Fe}_3\text{Si}_5$ [44], and calculated for MgB_2 [45] and elemental Bi under pressure [46]. While such a case cannot be ruled out for Bi_2Se_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_2Se_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 $\text{Cu}_x\text{Bi}_2\text{Se}_3$ [47] must be considered in this context.

In conclusion, the metallization of Bi_2Se_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_2Se_3 .

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Note added.—After submission of this manuscript, we became aware of a similar study by Kong *et al.* [48].

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SUPPLEMENTAL MATERIALS: Pressure-induced unconventional superconductivity in topological insulator Bi_2Se_3

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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 $300\ \mu\text{m}$ in diameter. The microprobes of the designer diamond anvil were tungsten, and they were lithographically deposited to be equally spaced on a $44\text{-}\mu\text{m}$ diameter circle at the center of the designer anvil culet. The MP35N gasket was pre-indented down to a thickness of $45\ \mu\text{m}$, and the $120\text{-}\mu\text{m}$ sample chamber was drilled into the pre-indented 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 $10\ \mu\text{m}$ 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 $P \geq 29.8\ \text{GPa}$. 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 1B 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. 1A, 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 mea-

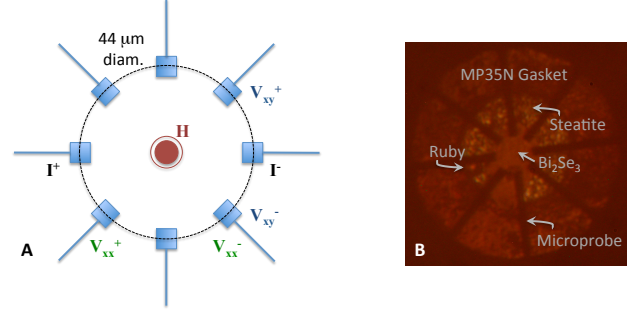


FIG. 1: (A) A sketch of the electrical contacts on the culet of the designer diamond. The current and voltage leads used for the longitudinal and transverse electrical transport measurements are labeled. (B) An image of the sample chamber of the assembled designer diamond anvil cell as seen through a red filter looking through the designer diamond.

sured with the leads labeled V_{xx} and R_{xy} was measured with the leads labeled V_{xy} . 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 $6\ \text{GPa}$ —as shown by Hamlin, *et al.*[1]—the R_{xy} of Bi_2Se_3 shows some curvature at higher fields. However, above about $30\ \text{GPa}$ (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 $10 \times 10\ \mu\text{m}$, $32.9\ \text{keV}$ ($\lambda_{inc} = 0.3771\ \text{\AA}$) incident x-ray beam, calibrated with CeO_2 , 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. 2.

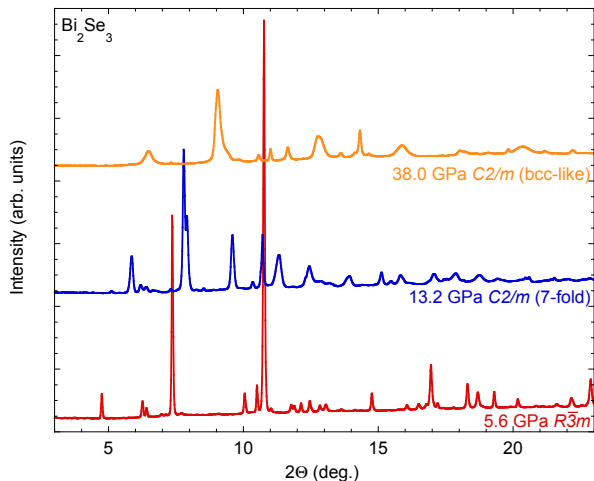


FIG. 2: Representative, room-temperature x-ray diffraction patterns for the three different structural variants of Bi_2Se_3 under pressure. The pressures and space groups are labeled below each diffraction pattern.

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: Bi_2Se_3 -I — $R\bar{3}m$; Bi_2Se_3 -II — $C2/m$, 7-fold coordinated; and Bi_2Se_3 -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 [5]. In our work, the phase transition from Bi_2Se_3 -I to Bi_2Se_3 -II begins near 9.5 GPa and extends just above 10 GPa. The phase transition from Bi_2Se_3 -II to Bi_2Se_3 -III begins near 26.5 GPa and extends just above 30.5 GPa. As the diffraction data was acquired with a highly 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 [6].

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 [7, 8], which is given by

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

where $\langle \omega \rangle$ is a characteristic phonon cutoff frequency, λ is the electron-phonon coupling strength, and μ^* 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:

$$\frac{d \ln T_c}{d \ln V} = \frac{B}{T_c} \frac{dT_c}{dP} \approx \gamma_G + \Delta \left[\frac{d \ln \eta}{d \ln V} + 2\gamma_G \right], \quad (2)$$

where B is the bulk modulus, γ_G is the Grüneisen coefficient, $\Delta \equiv 1.04\lambda[1 + 0.38\mu^*]/[\lambda - \mu^*(1 + 0.62\mu^*)]$, and η is the Hopfield parameter [9]. The Hopfield parameter itself can be formalized as $\eta = N(E_F) \langle I^2 \rangle$, where $N(E_F)$ is the density of states and $\langle I^2 \rangle$ 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_2Se_3 -III at high pressures, we can examine the values of γ_G and λ 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 γ_G , which are probably physically unrealistic. It should be noted, however, that we do not have any measurements of γ_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 λ and γ_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_2Se_3 under pressure: for phonon-mediated superconductivity to exist, Bi_2Se_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 measure-

ments 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_2Se_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 approximately 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 Bi_2Se_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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