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Realization of insulating state and superconductivity in the Rashba semiconductor BiTeCl

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Measurements of the resistivity, Hall coefficient, and Raman spectroscopy are performed on a Rashba semiconductor BiTeCl single crystal at high pressures up to 50 GPa. We find that applying pressure first induces a theoretically predicted insulating state, followed by a superconducting phase with an insulating normal state. Upon heavy compression, another different superconducting phase is entered into with a metallic normal state. A domelike evolution of the superconducting transition temperature with pressure is obtained with a crossover from the electron to hole carriers across the boundary of the two superconducting phases. These findings imply the possible realization of a topological state of the insulating and superconducting phases in this material.

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Topological insulators represent a newly discovered phase of matter with an insulating bulk state but a topologically protected metallic surface state due to time-reversal symmetry and strong spin-orbital interactions [1–4]. The experimental discovery of the three-dimensional topological insulating phase [5] opened a new era in fundamental topological physics. Superconductivity has been found in some topological insulators, mainly in compressed V_2VI_3 binary compounds such as Bi_2Te_3 [6–9], Bi_2Se_3 [10], Sb_2Te_3 [11], and intercalated $Cu_xBi_2Se_3$ [12]. However, the identification of their topological superconductivity is still a hard task and under debate [13]. In most cases, pressure is needed to drive the topological insulator to a superconductor. Superconductivity is usually accompanied by an electronic topological transition and/or structural transition [7,10]. It remains unclear whether such a transition is essential to induce superconductivity in topological insulators.

The search for topological superconductivity is being driven by the exploration of fundamental physics and for potential applications in topological quantum computation [1,2]. Layered noncentrosymmetric bismuth tellurohalides (BiTeX with X = Cl, Br, I) with large Rashba-type splittings in the bulk bands [14–16] are being examined as inversion asymmetric topological insulators [17,18]. These materials are potential candidates for building spintronic devices. Unlike previously discovered three-dimensional topological insulators with inversion symmetry, the inversion symmetry is naturally broken by the crystal structure in asymmetric topological insulators. It is highly possible to realize topological magnetoelectric effects and topological superconductivity [18–20]. The experimental realization and identification of these interesting effects are thus desired.

A pressure-induced topological insulating state was theoretically predicted for the Rashba semiconductor BiTeI [17]. However, controversial conclusions were drawn from experiments on this material [21,22]. Recently, BiTeCl was discovered to be the first example of an inversion asymmetric topological insulator from angle-resolved photoemission spectroscopy experiments [18]. This was supported by transport measurements [23]. However, quantum oscillation measurements failed to detect a Dirac surface state in BiTeCl single crystals [24,25]. Such a contradiction may come from the strong surface polarity which would generate a large effective pressure along the c axis. The applied pressure could drive several surface layers into a topological insulator, as the case in BiTeI [17,18]. Therefore, pressure is highly required to examine whether topological phase transitions could happen in these kinds of materials and whether topological superconductivity would be induced. Meanwhile, pressure-induced superconductivity from topological insulators was limited in V_2VI_3-type compounds. Finding a new superconducting family from topological insulators would add a new opportunity for exploring topological superconductivity. In this Rapid Communication we choose BiTeCl to address these issues.

High-quality single crystals of BiTeCl were grown by a self-flux method [16]. Pressure was applied at room temperature using a miniature diamond anvil cell [26]. A sample chamber of diameter 130 μm was drilled in the c-BN gasket situated in two diamond anvils with a 300 μm culet. A BiTeCl single crystal was cut with dimensions of $65 \times 65 \times 15$ μm^3. Four Pt wires were adhered to the sample using silver epoxy. Daphne oil 7373 was used as a pressure transmitting medium. Pressure was calibrated by using the ruby fluorescence shift at room temperature. Resistivity and the Hall coefficient were measured using a Quantum Design physical property measurement system (PPMS). A diamond anvil cell with a 300 μm culet was used for high-pressure Raman measurements with an incident laser wavelength of 488 nm. Neon was loaded as the pressure transmitting medium.

Figure 1 shows the temperature dependence of the resistivity for BiTeCl at various pressures up to 50.8 GPa.

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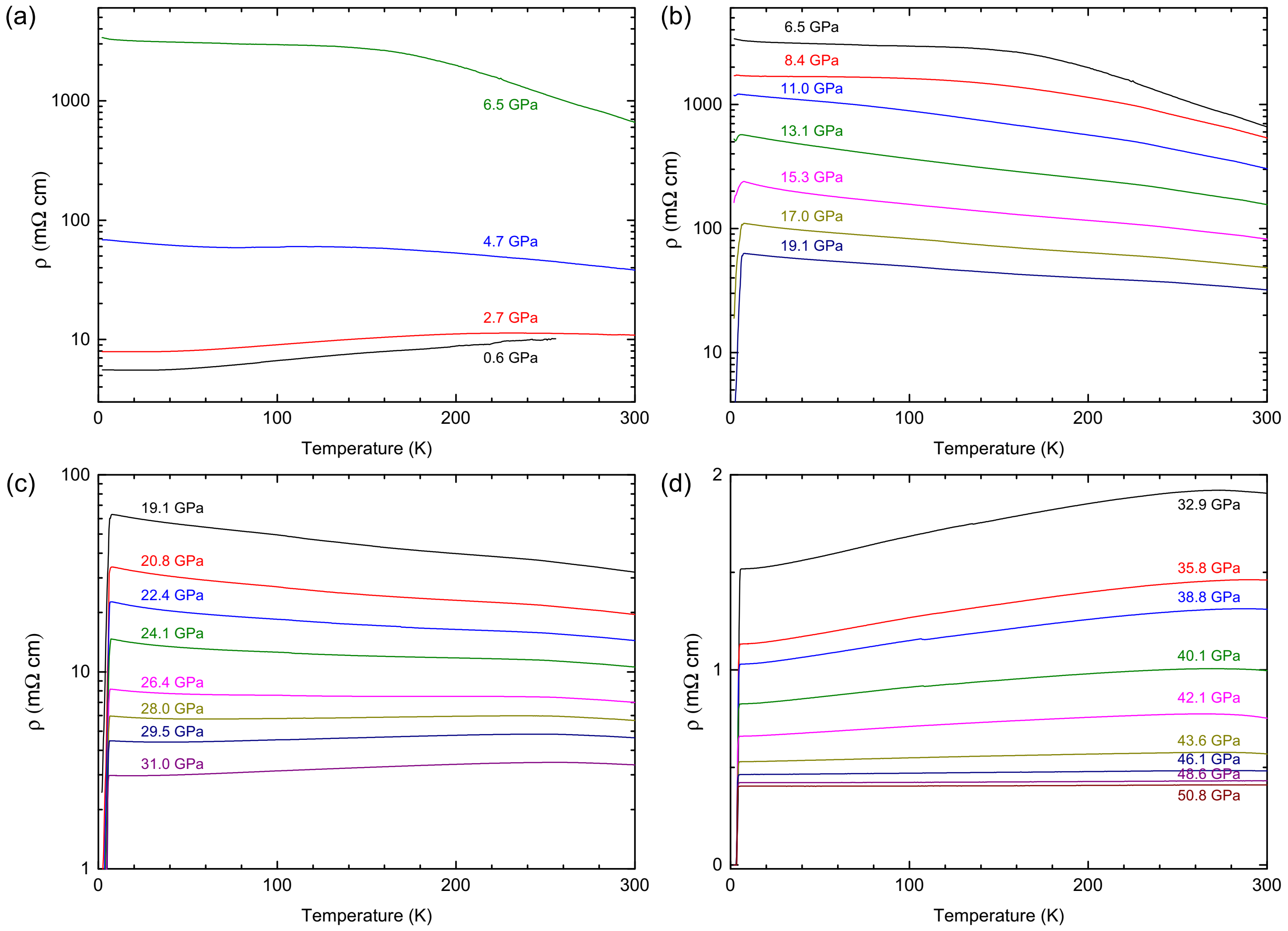

FIG. 1. Temperature dependence of the resistivity of BiTeCl at various pressures. (a) The sudden change in resistivity behavior indicates a phase transition from a Rashba semiconductor to an insulator at around 5 GPa. (b) The resistivity was gradually suppressed with increasing pressure and superconductivity emerges at above 13 GPa. The normal state behaves as an insulator (c) and a metal (d) upon heavy compression.

At low pressures below 4 GPa, the resistivity shows a metallic behavior similar to that at ambient pressure, as reported before [27,28], though this material was thought to be a Rashba semiconductor. This is probably due to the off-stoichiometry which is mostly caused by a slight Cl atom deficiency. When pressure is increased to 5 GPa, the resistivity suddenly increases almost three magnitudes of order, exhibiting an insulating behavior with a resistivity maximum at around 150 K [Fig. 1(a)]. This indicates a phase transition from a Rashba semiconductor to an insulator at around 5 GPa in BiTeCl. The realization of a topological insulator from such a kind of Rashba semiconductor by applied pressure has been theoretically predicted [17] but has not been observed experimentally. The current work may provide experimental evidence for a topological insulating state in compressed bismuth tellurohalides. With further increasing pressure, the resistivity is gradually reduced and the resistivity maximum shifts downwards to lower temperatures. Although the origin of such a maximum remains unclear, some competing orders such as charge density wave may occur in these low-dimensional electronic systems [29]. Interestingly, superconductivity emerges when the resistivity maximum is completely suppressed at around 13 GPa. However, its normal state still exhibits an insulating behavior. This behavior is different from the other superconducting phases obtained from topological insulators under pressure [7,10], classifying BiTeCl as a different type of superconductor. If a topological insulator is actually realized at high pressures, this superconductor may possess topological superconductivity. The unique spin-orbit interaction of a Rashba system contributes its superconductivity with a mixing of the singlet and triplet pair states and Majorana channels [30]. With further increasing pressure, the normal state behaves as a metal above 28 GPa. Superconductivity persists up to the highest pressure of 50.8 GPa studied. The discovery of superconductivity with interesting normal-state properties in BiTeCl adds insight into the physics in Rashba systems with strong spin-orbital coupling.

The obtained superconductivity in BiTeCl was further supported by the evolution of the resistivity-temperature curve with the applied magnetic fields (Fig. 2). The curve gradually shifts towards the lower temperatures with increasing magnetic field. The magnetic field was applied along the crystallographic c axis. It seems likely that 5 T is sufficient to suppress superconductivity at 50.8 GPa. However, a much higher field is needed to suppress superconductivity at 24.1 GPa. These two

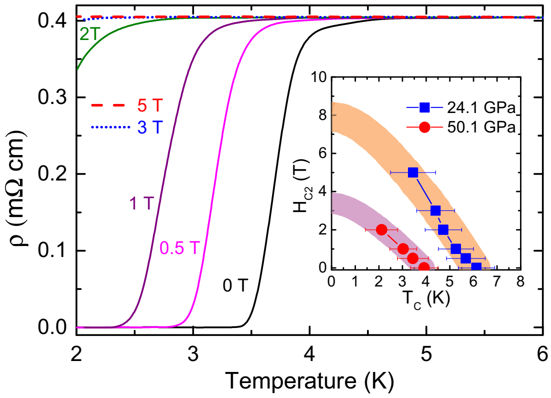

FIG. 2. Temperature dependence of the resistivity of BiTeCl at a pressure of 50.8 GPa with applied magnetic fields. Inset: Upper critical field H_{c2} for pressures of 24.1 and 50.8 GPa, respectively. T_c was determined from the 90% resistivity transition. The color area represents the calculated H_{c2} from the Werthamer-Helfand-Hohenberg equation.

pressures yield different normal-state behaviors—metallic for the former but insulating for the latter (Fig. 1). The different behaviors of the upper critical field H_{c2} also reflect the different physical properties of the two superconducting phases.

Within the weak-coupling BCS theory, an upper critical field at $T = 0$ K can be determined by the Werthamer-Helfand-Hohenberg equation [31] $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$. The colorful areas shown in the inset of Fig. 2 are the temperature dependence of H_{c2} calculated based on this equation for superconductivity at 24.1 and 50.8 GPa, respectively. The $H_{c2}(0)$ at 50.8 GPa is about 3.5 T. This value is comparable with that of the superconducting Bi_2Se_3 phase [10]. The calculated $H_{c2}(0)$ of almost 8 T at 24.1 GPa is twice larger than that at 50.8 GPa. The large difference of $H_{c2}(0)$ at 24.1 and 50.8 GPa indicates the different origins of superconductivity of those two high-pressure phases. Differing from V_2VI_3-type topological materials, the normal state of superconducting BiTeCl shows both insulating and metallic behaviors with different values of $H_{c2}(0)$. Our results indicate that the first superconducting phase with an insulating normal state is followed a Rashba semiconductor-insulator transition, but it develops into the second one with a metallic normal state upon heavy compression. The large upper critical field in the first superconducting phase results from a strong spin-orbit interaction in the Rashba system. The similarity in the normal state together with the comparable $H_{c2}(0)$ value between the second superconducting phase and V_2VI_3 compounds classifies them as conventional superconductors. A pressure-induced insulating behavior, together with the following superconductivity with an insulating normal state, is the central discovery of this work. If the obtained insulating state is exactly the same as the theoretically predicted one [17], it should possess topological order. The following superconductivity could have topological features as well. Topological superconductivity could have been realized in BiTeCl, though identification from both the experimental and theoretical sides is highly desired.

Raman spectroscopy is a powerful tool to probe the changes in the lattice and thus can provide valuable information on the structural evolution and phase transition. Figure 3 shows the Raman spectra of BiTeCl at various pressures up to 39.4 GPa. At ambient pressure, BiTeCl crystallizes in a trigonal layer structure with a space group of $P6_3mc$. This phase has seven Raman active modes ($2A_1 + 2E_1 + 3E_2$). Both E-type modes belong to the in-plane vibration of the Bi, Te, and Cl layers, while the lower E mode has a large contribution from the Cl atom vibration. The two out-of-plane A_1 modes include the vibration with higher frequencies. Our Raman measurements reproduced all these modes below 5 GPa. The obtained modes marked by the arrows are also similar to those reported previously at ambient pressure [28,32]. The two E modes with the lowest (16 cm^{-1}) and highest (120 cm^{-1}) frequencies and one A_1 mode with the highest frequency (153 cm^{-1}) have strong intensities. Applying pressure shifts the lowest frequency E mode and the highest A_1 mode to the high frequencies, while the highest E_1 mode first softens and then hardens. The E mode at around 100 cm^{-1} and the A_1 mode at around 140 cm^{-1} behave in a similar way as the highest frequency E_1 mode. The softening of these intermediate modes may contribute to the strong electron-phonon coupling favoring superconductivity.

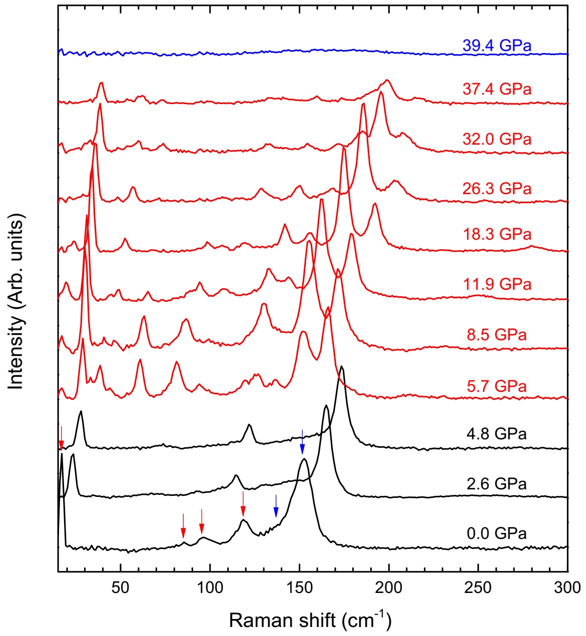

FIG. 3. Raman spectra of BiTeCl at various pressures up to 39.4 GPa. The vibrational modes in the initial Rashba semiconductor are marked by arrows. The different spectra above 5 GPa and the absence of Raman peaks above 39 GPa are consistent with the different normal-state behaviors of the two superconducting phases.

Above 5 GPa, the spectra suddenly change, indicating the appearance of a new high-pressure phase. A phase transition similar to an orthorhombic $Pnma$ structure with a semiconducting feature has been reported in the sister system, BiTeI [33]. The $Pnma$ phase has more Raman vibrational modes ($6A_g + 3B_{1g} + 6B_{2g} + 3B_{3g}$). Above 39 GPa, no Raman modes were detected, suggesting a phase transition to a highly symmetric structure with a possible cubic unit cell. This is consistent with the obtained metallic normal state of this high-pressure phase from the resistivity measurements

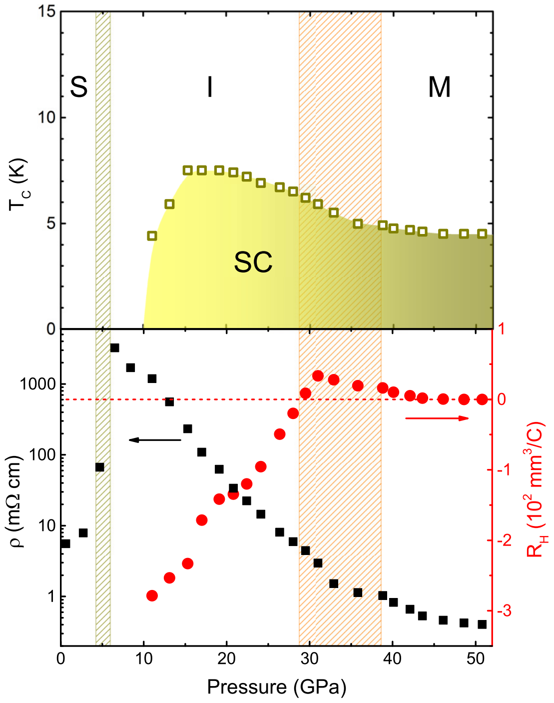

FIG. 4. Phase diagram of BiTeCl at high pressures. The lower panel shows the pressure dependence of the resistivity and Hall coefficient measured at 10 K. The dashed regions represent the phase borders of a semiconductor (S), insulator (I), and metal (M). Two high-pressure superconducting phases with insulating and metallic normal states. The dashed area represents the coexistence of two phases.

[Fig. 1(d)]. Previously, an orthorhombic $P4/nmm$ structure was suggested for dense BiTeI from combined x-ray diffraction (XRD) measurements and calculations [33]. This $P4/nmm$ phase corresponds to richer Raman active modes with nine E_g modes besides A_{1g}, B_{1g}, and B_{2g}. Our Raman data do not support the existence of the $P4/nmm$ BiTeCl. The metallic phase of BiTeCl is possibly a substitutional alloy similar to the Bi_2Te_3 system [34]. The Raman spectra also reveal the different physical properties of BiTeCl.

Combining the resistivity and Raman measurements, we can map out the phase diagram of BiTeCl (Fig. 4). Below 5 GPa, BiTeCl keeps its initial phase as a Rashba semiconductor (S) but behaves in reality as a metal or semimetal [Fig. 1(a)] [27,28]. Above that, it evolves to a superconductor with an insulating (I) normal state up to the phase boundary starting at 28 GPa. Above 39 GPa, superconductivity remains unchanged with pressure but the material possesses a metallic (M) normal state. T_c first exhibits a domelike shape with pressure and then becomes almost constant upon heavy compression. Meanwhile, the sign of the measured Hall coefficient at 10 K gradually changes from negative to positive above 28 GPa (lower panel of Fig. 4). This provides the dominant electron and hole carrier character for the two superconducting phases. The electron doping agrees with the negative thermopower [35]. The large hole carrier density in the latter is consistent with the character of the substitutional alloy that is indicated from Raman measurements. The relatively weak pressure dependence of the carrier density provides a natural explanation for the almost constant T_c and the conventional character of superconductivity of this phase.

The temperature dependence of the resistivity of BiTeCl shown in Fig. 1(b) exhibits a more complicated feature. There is a maximum around 150 K for a pressure of 6.5 GPa. Applying pressure shifts it down to lower temperatures. However, the maximum feature is gradually suppressed and superconductivity appears spontaneously. The emergence of superconductivity and the destruction of the resistivity maximum at the same pressure indicate a close connection between them. The resistivity maximum is the common feature for materials with a charge density wave. It is possible for this superconducting phase to appear after the suppression of the charge density wave. It possesses an insulating normal state [Figs. 1(b) and 1(c)]. This dramatic change in the electrical transport with pressure is also reflected by the resistivity value. The lower panel of Fig. 4 also summarizes the resistivities measured at various pressures and at 10 K. An anomaly is clearly observed across the phase boundary of the phase S and I. The crossover of the carrier character suggests a change in their different Fermi surfaces. The Rashba semiconducting phase at ambient pressure can be tuned into an insulating phase above 5 GPa. The huge enhancement of the resistivity with three magnitudes of order indicates the possible realization of a topological insulator upon compression, as suggested previously [17]. Although the estimated pressure of the surface polarity along the c axis for BiTeCl is only about 1 GPa in the angle-resolved photoemission spectroscopy measurement [18], our measurements were performed at the quasihydrostatic pressure condition, which is quite different from the nonhydrostatic environment in the angle-resolved photoemission spectroscopy experiment. A pressure-induced topological phase transition at 4–5 GPa has also been observed in its sister system, BiTeI [33,36]. These results together contribute to BiTeCl the possible topological features in its insulating state and even in its superconducting state.

In conclusion, we have carried out high-pressure resistivity, Hall coefficient, and Raman spectroscopy measurements on a Rashba semiconductor BiTeCl up to 50 GPa. We have succeeded in detecting an insulating state followed by two superconducting phases with insulating and metallic normal states, respectively. These findings enrich the superconducting family from bismuth tellurohalides. The results also highlight the possible realization of the topological state of both the insulating and superconducting phases from these Rashba semiconductors with strong spin-orbital coupling.

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