



# Pressure-induced phase transitions and superconductivity in a quasi-1-dimensional topological crystalline insulator $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub>

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Great progress has been achieved in the research field of topological states of matter during the past decade. Recently, a quasi-1-dimensional bismuth bromide, Bi<sub>4</sub>Br<sub>4</sub>, has been predicted to be a rotational symmetry-protected topological crystalline insulator; it would also exhibit more exotic topological properties under pressure. Here, we report a thorough study of phase transitions and superconductivity in a quasihydrostatically pressurized  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> crystal by performing detailed measurements of electrical resistance, alternating current magnetic susceptibility, and in situ high-pressure single-crystal X-ray diffraction together with first principles calculations. We find a pressure-induced insulator–metal transition between  $\sim$ 3.0 and 3.8 GPa where valence and conduction bands cross the Fermi level to form a set of small pockets of holes and electrons. With further increase of pressure, 2 superconductive transitions emerge. One shows a sharp resistance drop to 0 near 6.8 K at 3.8 GPa; the transition temperature gradually lowers with increasing pressure and completely vanishes above 12.0 GPa. Another transition sets in around 9.0 K at 5.5 GPa and persists up to the highest pressure of 45.0 GPa studied in this work. Intriguingly, we find that the first superconducting phase might coexist with a nontrivial rotational symmetry-protected topology in the pressure range of  $\sim$ 3.8 to 4.3 GPa; the second one is associated with a structural phase transition from monoclinic *C2/m* to triclinic *P-1* symmetry.

topological materials | superconductivity | high pressure | quasi-1-dimensional bismuth bromide

Symmetry-protected topological materials have attracted considerable attention ever since the discovery of *Z*<sub>2</sub>-type topological insulators (1–4). Among them, topological crystalline insulators (TCIs) and topological superconductors are mostly known in 2-dimensional (2D) and 3-dimensional topological phases (5–8). The search for topological superconductivity in TCIs is currently an active research endeavor in condensed matter physics (9–11). Recent theoretical works have proposed that quasi-1-dimensional (quasi-1D)  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> (Fig. 1A) could provide an example of a rotation symmetry-protected TCI having a quite large band gap with the coexistence of 2D gapless Dirac cone surface states and 1D hinge states (12, 13). Another quasi-1D  $\beta$ -Bi<sub>4</sub>Br<sub>4</sub> (Fig. 1B) having the same monoclinic *C2/m* symmetry but only half-block stacking along the *c* axis has been predicted to exhibit a Weyl semimetal phase between a weak topological insulator (WTI) and a strong topological insulator phase (14–16). These predictions have sparked interest in investigating their topological characters and electronic structures, which can be easily tuned by external pressure due to their weakly connected quasi-

1D structures. Providing a clean variation without introducing chemical doping complexity, pressure can dramatically alter a quasi-1D lattice so as to lead to a possibility of induced superconductivity. A question arises naturally: is it possible to achieve superconductivity in  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> or  $\beta$ -Bi<sub>4</sub>Br<sub>4</sub> under high pressure while their topological states remain intact?

In fact, pressure-induced superconductivity and topological phase transitions have been experimentally observed in the sister compound Bi<sub>4</sub>I<sub>4</sub> (17–19), which adopts an analogous structure consisting of 1D molecular chains that are coupled by weak van der Waals interactions. Two crystalline modifications,  $\alpha$ -Bi<sub>4</sub>I<sub>4</sub> and  $\beta$ -Bi<sub>4</sub>I<sub>4</sub>, are confirmed to be a normal insulator and a WTI at ambient pressure, respectively (20–22). Under high pressure, the  $\beta$ -Bi<sub>4</sub>I<sub>4</sub> phase undergoes superconductive and quantum phase transitions that originate from its structural instability (18). Different from Bi<sub>4</sub>I<sub>4</sub>, while  $\beta$ -Bi<sub>4</sub>Br<sub>4</sub> has not yet been identified

## Significance

The quasi-1-dimensional bismuth bromide,  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub>, has been predicted to be a rotational symmetry-protected topological crystalline insulator. The structural study under high pressure indicates that the  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> phase is stable up to 4.3 GPa. There is a rich phase diagram of physical properties under high pressure in the  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> phase (i.e., a pressure-induced insulator–metal transition and, most importantly, a superconductive phase near the boundary of the insulator–metal transition). These findings help to answer questions, such as whether it is possible for the symmetry-protected electrons to form Cooper pairs. The  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> undergoes a pressure-induced structural transition above 4.3 GPa to a triclinic *P-1* phase, which is another superconductive phase.

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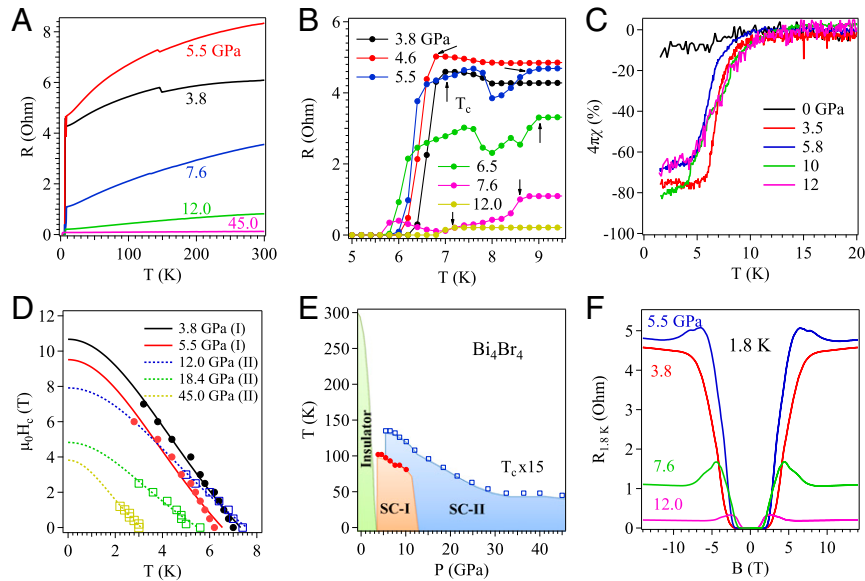
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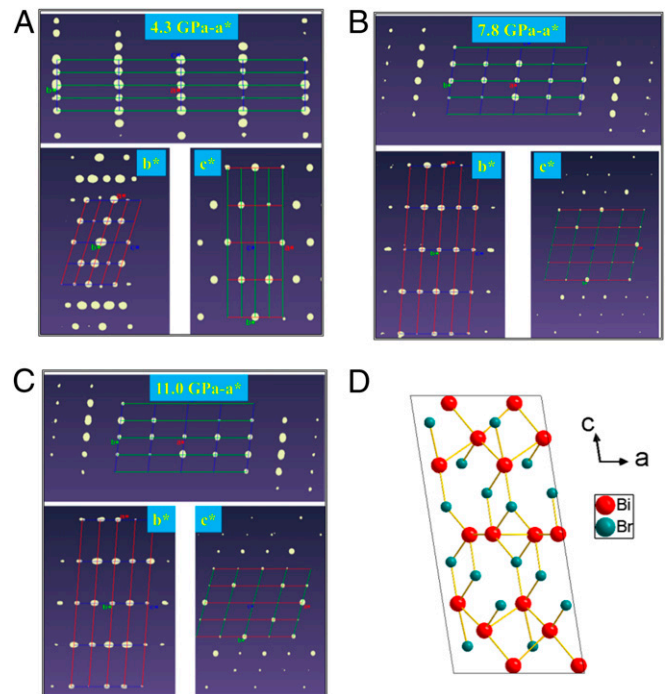


**Fig. 3.** Temperature dependence of resistance (A) at various pressures  $P \geq 3.8$  GPa and (B) around  $T_c$ . (C) Temperature dependence of AC magnetic susceptibility up to 10.0 GPa. (D) Determination of the upper critical field  $\mu_0 H_c(0)$ . (E)  $T$ - $P$  phase diagram of Bi<sub>4</sub>Br<sub>4</sub>. (F) Magnetic field dependence of resistance of a Bi<sub>4</sub>Br<sub>4</sub> crystal at different pressures.

$4\pi\chi$  of the Bi<sub>4</sub>Br<sub>4</sub> crystal at various pressures up to 12.0 GPa show clear diamagnetic responses (Fig. 3C) ( $\sim 70$  to 80%), confirming a bulk superconductivity. To determine the value of the upper critical magnetic field,  $\mu_0 H_c(0)$ , we systematically conducted the measurements near the transition temperature under external magnetic fields up to 14 T applied perpendicular to the  $ab$  plane (SI Appendix, Fig. S4). The superconducting transition temperature,  $T_c$ , is defined as the temperature where the resistance starts to deviate from the nearly temperature-independent normal-state resistance (these onset temperatures for superconducting transitions are indicated by arrows in Fig. 3B). Notably, at each pressure of  $P \geq 3.8$  GPa,  $T_c$  decreases monotonically with increasing magnetic field, and the upper critical magnetic field  $\mu_0 H_c(0)$  can be extrapolated by the Ginzburg–Landau formula  $\mu_0 H_c(T) = \mu_0 H_c(0)(1 - t^2)/(1 + t^2)$ , where  $t = T/T_c$ , as shown in Fig. 3D.

As summarized in the temperature-pressure ( $T$ - $P$ ) phase diagram shown in Fig. 3E, we find that the  $T_{c1}$  of the first superconducting (SC-I) phase decreases progressively with pressure and disappears above 12.0 GPa in our measurement, while the  $T_{c2}$  of the second superconducting (SC-II) phase appears around 5.5 GPa and manifests a monotonic decrease to the highest pressure 45.0 GPa achieved in the work. The largely different upper critical magnetic fields for the SC-I and SC-II phases indicate their distinct origins of superconductivity. Both of them are smaller than the Bardeen–Cooper–Schrieffer weak-coupling Pauli paramagnetic limit of  $1.84T_c$  ( $12.5T$  at 3.8 GPa for the SC-I phase and  $13.2T$  at 12.0 GPa for the SC-II phase). To reveal how the normal state evolves into the superconducting state, we further investigated the magnetic field dependence of magnetoresistance (MR) at various temperatures. In the low-pressure region (SI Appendix, Fig. S5), the shape of the nonsaturated positive MR curves in the normal state (e.g., 20 K) changes from a concave curve to a parabolic curve at a critical pressure of 3.8 GPa, where simultaneously, the linear MR curves and bulk superconductivity emerge. At higher pressures, the MR curves in the superconducting state exhibit a U-shaped feature with 2 cusps at a bias field  $H_{bias}$  (Fig. 3F), which gradually becomes less pronounced as pressure increases. This observation is discussed in detail below.

**Pressure-Induced Structural Transition.** To clarify whether the superconductive phase transitions are caused by pressure-induced crystal structural transitions, we first conducted an in



**Fig. 4.** (A) HP-SXRD of Bi<sub>4</sub>Br<sub>4</sub> at 4.3 GPa indexed by monoclinic  $C2/m$  structure with lattice parameters of  $a = 11.254(1)$  Å,  $b = 4.454(2)$  Å,  $c = 19.085(2)$  Å,  $\beta = 106.22(7)^\circ$ , and  $V = 918(1)$  Å<sup>3</sup>. (B) HP-SXRD of Bi<sub>4</sub>Br<sub>4</sub> at 7.8 GPa indexed by triclinic  $P-1$  structure with lattice parameters of  $a = 5.826(7)$  Å,  $b = 8.600(6)$  Å,  $c = 18.110(3)$  Å,  $\alpha = 97.60(14)^\circ$ ,  $\beta = 92.77(18)^\circ$ ,  $\gamma = 105.85(8)^\circ$ , and  $V = 862(2)$  Å<sup>3</sup>. (C) HP-SXRD of Bi<sub>4</sub>Br<sub>4</sub> at 11.0 GPa indexed by triclinic  $P-1$  structure with lattice parameters of  $a = 5.685(4)$  Å,  $b = 8.498(5)$  Å,  $c = 17.830(3)$  Å,  $\alpha = 96.92(13)^\circ$ ,  $\beta = 92.86(13)^\circ$ ,  $\gamma = 104.78(6)^\circ$ , and  $V = 824(2)$  Å<sup>3</sup>. (D) Relaxed crystal structure of Bi<sub>4</sub>Br<sub>4</sub> at 7.8 GPa.



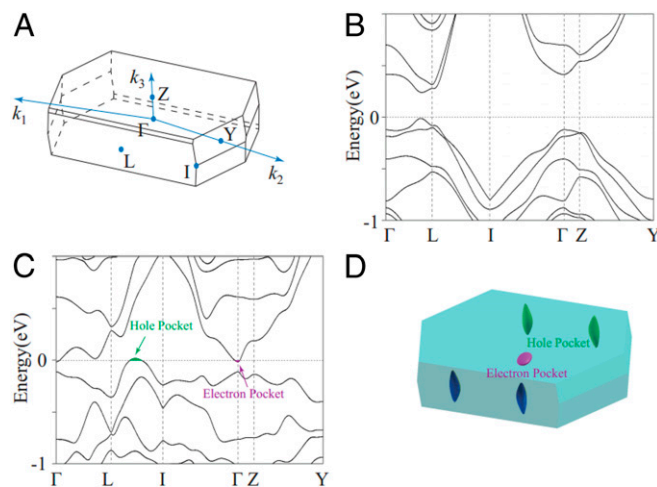
situ high-pressure single-crystal X-ray diffraction (HP-SXRD) study on an  $\alpha$ - $\text{Bi}_4\text{Br}_4$  crystal. As shown in Fig. 4A, a monoclinic  $C2/m$  structure with lattice parameters of  $a = 11.254(1)$  Å,  $b = 4.454(2)$  Å,  $c = 19.085(2)$  Å, and  $\beta = 106.22(7)^\circ$  can be well determined from the collected data at 4.3 GPa, which has the same symmetry as the ambient pressure one but a decrease in the unit cell volume. This observation indicates that the  $\alpha$ - $\text{Bi}_4\text{Br}_4$  phase is stable against pressure up to 4.3 GPa and that the origin of SC-I superconductivity is independent of a structural phase transition. At 7.8 GPa (Fig. 4B), there is a clear change in the crystal symmetry as the crystal converts from monoclinic  $C2/m$  to triclinic  $P-1$ , with a slight decrease along the  $c$  direction and a sudden collapse occurring in the  $ab$  plane (detailed atomic positions are in *SI Appendix, Table S1*). Moreover, all reflections remain quite sharp at 11.0 GPa and can be indexed by the identical  $P-1$  symmetry (Fig. 4C), revealing that the  $\alpha$ - $\text{Bi}_4\text{Br}_4$  undergoes a structural transition under hydrostatic conditions between 4.3 and 7.8 GPa, where the SC-II superconducting phase arises. Similar pressure-induced structural transitions from  $C2/m$  to  $P-1$  symmetry have been reported in a topological material  $\text{ZrTe}_5$  (25).

To confirm further the high-pressure phase, we also performed high-pressure powder X-ray diffraction (HP-PXRD) of  $\alpha$ - $\text{Bi}_4\text{Br}_4$  fine powders. On compression, however, the data quality worsens, and most reflections broaden significantly so that diffraction patterns cannot be refined. For this reason, we used pieces of crystal clusters with different orientations in the HP-PXRD experiment (*SI Appendix, Fig. S6*). The obtained reflection peaks up to 12 GPa are much sharper, although the peak intensity is not suitable for the structural refinement. A clear structural phase transition has been observed between 3.4 and 7.3 GPa, which is in agreement with the HP-SXRD results. The pattern of the high-pressure phase at 7.3 GPa matches qualitatively with the triclinic  $P-1$  lattice. More importantly, the original  $\alpha$ - $\text{Bi}_4\text{Br}_4$  phase is retrieved after releasing the pressure, ruling out the presence of any Bi as a consequence of pressure-induced phase decomposition. In addition, by performing first principles calculations based on density functional theory (DFT), we simulated the internal atomic positions for the high-pressure phase starting from those of  $\alpha$ - $\text{Bi}_4\text{Br}_4$  as displayed in Fig. 4D, which are consistent with the experimental results.

## Discussion

First, to gain more insight on the pressure-induced insulator-metal transition of  $\alpha$ - $\text{Bi}_4\text{Br}_4$ , we performed DFT calculations of the electronic band structures with and without pressure. The results, similar to those in previous reports, show  $\alpha$ - $\text{Bi}_4\text{Br}_4$  to be a TCI with a band gap  $\sim 0.2$  eV at ambient pressure (Fig. 5A and B) (12–16). The highly anisotropic features originate from its quasi-1D structure, in which the intrachain coupling is much stronger than the interchain coupling; the anisotropy not only gives rise to a weaker energy dispersion along the  $\Gamma$ -Z(L) direction in the Brillouin zone (BZ) of Fig. 5A but also, makes the band structures along the L-I direction more sensitive to pressure. On increasing pressure to 12 GPa, as shown in Fig. 5C, the highest 2 valence bands along the L-I direction approach closer to the Fermi level, and eventually, one branch of them crosses the Fermi level and forms a hole pocket. The conservation of electrons suggests that an electron pocket is found near the  $\Gamma$  point (Fig. 5C, purple). These small pockets of holes and electrons thereby make the  $\alpha$ - $\text{Bi}_4\text{Br}_4$  become a semimetal (Fig. 5C and D), which is consistent with the vanishing global band gap observed in our measurements (*SI Appendix, Fig. S7*). However, in the whole BZ, there is still a local band gap with the same topological invariants of (0, 0, 0, 2), indicating that no topological transition occurs during the insulator-metal transition.

Second, before we turn to discuss the origin of the discovered superconductivity, a critical matter is whether the superconductivity arises from a Bi impurity. Although the  $T_c$  values of the 2 superconducting transitions are very close to those of Bi under



**Fig. 5.** Electronic band structures of  $\text{Bi}_4\text{Br}_4$  with and without pressure. (A) BZ. (B) Band structure at ambient pressure. (C) Band structure at 12 GPa. (D) Small pockets of holes and electrons forming under high pressure.

pressure (e.g., 6 K at 3 GPa and 8 K at 8 GPa [26]), we have enough evidence to rule out this possibility. 1) As mentioned above, no trace of bulk Bi impurity can be found from PXRD patterns and EDX results in the crystal before loading into the high-pressure device and the crystal recovered from the high-pressure experiment, indicating that the grown crystals are highly phase pure and remain so under high pressure. 2) Both the sharp slope of the superconducting transitions and significant diamagnetic response of the AC susceptibility reveal a bulk effect, certainly not ascribed to a possible filamentary appearance of Bi impurity. 3) If the superconductivity was only stemming from the filaments or the surface, it would be readily suppressed by external magnetic fields. More importantly, the upper critical magnetic fields obtained in  $\text{Bi}_4\text{Br}_4$  ( $\mu_0 H_{c1}$  for the SC-I phase and  $\mu_0 H_{c2}$  for the SC-II phase) are much higher than the reported values of 0.1T for Bi-II phase and 3.7T for Bi-III phase (26), implying that superconductivity in  $\text{Bi}_4\text{Br}_4$  has nothing to do with any possible Bi decomposed from the sample. 4) The pressure dependence of the  $T_{c2}$  of the SC-II phase shows a more pronounced reduction than that of Bi (26). These results, therefore, support that the superconductivity observed in  $\text{Bi}_4\text{Br}_4$  is mainly intrinsic.

Furthermore, the isostructural topological compound  $\beta$ - $\text{Bi}_4\text{I}_4$  exhibits a pressure-induced superconducting transition above 15 GPa (18). Considering that the smaller Br ions in  $\text{Bi}_4\text{Br}_4$  exert a larger internal chemical pressure on sublattices, it is reasonable to expect that  $\text{Bi}_4\text{Br}_4$  would become superconducting at a much lower external pressure. Indeed, the SC-I phase with  $T_{c1} \sim 6$  K emerges fully at around 3.8 GPa. Meanwhile, our band structure calculations show that the topologically nontrivial features of  $\alpha$ - $\text{Bi}_4\text{Br}_4$  are protected by its rotational symmetry, which is experimentally identified to be robust against pressure up to 4.3 GPa. It follows that the pressure-induced superconductivity of the SC-I phase might occur in a phase with the nontrivial topology between 3.8 and 4.3 GPa. In contrast, the emergence of superconductivity of the SC-II phase is accompanied by a structural phase transition. A close look at the resistivity of Fig. 3B before entering the SC-I phase reveals an anomalous upturn with decreasing temperature, which gradually becomes broader and suppressed together with  $T_c$  on applying a magnetic field (*SI Appendix, Fig. S4*). It is also worth noting that the magnetic field dependence of resistivity  $R$  at 1.8 K (Fig. 3F) in the pressure range of  $\sim 5.5$  to 12.0 GPa exhibits a cusp-like peak. A similar resistivity upturn in the normal state on cooling and a non-monotonic behavior of MR in an SC phase have been observed

in other low-dimensional disordered superconductors (27–29). These behaviors can be elucidated in terms of phase fluctuations originating from the coexistence of SC and normal-state phases (30, 31). It is very important to note that there is no cusp in the MR at 1.8 K under 3.8 GPa and  $P > 12$  GPa. A cusp in the MR has been only observed in the pressure range  $5.5 \leq P \leq 12.0$  GPa, where the SC-I and SC-II phases coexist in the phase diagram of Fig. 3E. More intriguingly, it is possible to derive a quantum critical point from the residue resistance ratio as a function of pressure, like in black phosphorus under pressure (32) (*SI Appendix*, Fig. S8); a profound change in the electronic structures occurs at  $P \sim 19$  GPa.

## Conclusions

In conclusion, we performed theoretical calculations and detailed measurements of electrical resistance, AC magnetic susceptibility, and in situ HP-SXRD at various quasihydrostatic pressures on single crystals of  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub>. A clear insulator–metal transition has been observed between the pressures of 3.0 and 3.8 GPa where the valence and conduction bands cross the Fermi energy at different places in the BZ to form a set of electron and hole pockets. On increasing pressure further, 2 pressure-induced superconducting phases emerge. One of them, the SC-I phase, presents a sharp resistive transition with 0 resistance beginning at 3.8 GPa. Our theoretical calculation demonstrates that the nontrivial topology of  $\alpha$ -Bi<sub>4</sub>Br<sub>4</sub> persists up to even higher pressure. Consequently, it reveals the possible coexistence of superconductivity and a topologically nontrivial feature protected by the rotational crystal structure symmetry. The SC-II phase coexists

with the SC-I phase in the pressure range from 5.5 to 12.0 GPa accompanied by a structural phase transition from the ambient  $C2/m$  phase to a high-pressure  $P-1$  phase and further survives with a monotonically decreasing  $T_c$  up to 45.0 GPa achieved in this study. These results are crucial for advancing our understanding of the topological quantum phase transitions of Bi<sub>4</sub>Br<sub>4</sub>.

## Materials and Methods

Single crystals of Bi<sub>4</sub>Br<sub>4</sub> were grown by self-flux methods. Electronic transport properties of Bi<sub>4</sub>Br<sub>4</sub> were measured with a 4-probe electrical conductivity method in a diamond anvil cell (DAC) made of CuBe alloy. HP-SXRD was conducted on a Bi<sub>4</sub>Br<sub>4</sub> single crystal with a dimension of  $70 \times 40 \times 10 \mu\text{m}$  in a DAC. High-pressure AC magnetic susceptibility was measured by using the Palm cubic anvil cell, and the mutual induction method was used (33). Theoretical calculations were performed based on a DFT calculation using the projector-augmented wave method as implemented in the Vienna ab initio simulation package (34). The exchange correlation potential was treated within generalized gradient approximation of Perdew–Burke–Ernzerhof type (35). Detailed information can be found in *SI Appendix*.

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