Pressure-induced phase transitions and superconductivity in a quasi-1-dimensional topological crystalline insulator $\alpha$-Bi$_4$Br$_4$

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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$_4$Br$_4$, 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$_4$Br$_4$. The sample is stable up to 4.3 GPa. There is a rich phase diagram of physical properties under high pressure in the $\alpha$-Bi$_4$Br$_4$ 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$_4$Br$_4$ undergoes a pressure-induced structural transition above 4.3 GPa to a triclinic P-1 phase, which is another superconductive phase.

**Significance**

The quasi-1-dimensional bismuth bromide, $\alpha$-Bi$_4$Br$_4$, has been predicted to be a rotational symmetry-protected topological crystalline insulator. The structural study under high pressure indicates that the $\alpha$-Bi$_4$Br$_4$ phase is stable up to 4.3 GPa. There is a rich phase diagram of physical properties under high pressure in the $\alpha$-Bi$_4$Br$_4$ 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$_4$Br$_4$ 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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Bi$_4$Br$_4$ system. Here, we make a thorough study of Bi$_4$Br$_4$ under induce topological phases and phenomena in the promising TCI (12). Therefore, it is of interest to see whether pressure can guarantees that it is not a trivial insulator but a rotation-protected freshly cleaved α-Bi$_4$Br$_4$ crystals on the paper with millimeter grid.

Results

Pressure-Induced Insulator–Metal Transition. Needle-shaped single crystals of α-Bi$_4$Br$_4$ with dimensions up to 3 × 0.3 × 0.1 mm were grown by a self-flux method. Details can be found in SI Appendix. The sample quality was verified by powder X-ray diffraction (PXRD) (Fig. 1C and SI Appendix, Fig. S1A) and energy-dispersive X-ray spectroscopy (EDX) (SI Appendix, Fig. S1B), which show no sign of any Bi impurity. As illustrated in Fig. 1A, the quasi-1D structure of α-Bi$_4$Br$_4$ with a strong anisotropy can be easily cleaved along the ab plane. The electrical resistance of freshly cleaved α-Bi$_4$Br$_4$ crystals was measured in a standard 4-probe configuration under quasihydrostatic pressure (SI Appendix, Fig. S2).

Fig. 2A shows the electrical resistance as a function of temperature measured under 0 magnetic field in the low-pressure range up to 3.8 GPa. At ambient pressure, the resistance above 200 K shows a semiconductive temperature dependence with a thermal activation energy Δ = 45.7 meV (Fig. 2B, Inset), slightly larger than that reported for β-Bi$_4$I$_4$ (17). In the pressure range of ~2.3 to 3.0 GPa, the resistance still shows a semiconductive behavior, but the activation energy becomes smaller (SI Appendix, Fig. S3). Intriguingly, there is a steep upturn in ambient pressure resistance that signals a charge density wave (CDW) transition (24). The possible CDW transition temperature $T_{CDW}$ (Fig. 2B), which is identified from the maximum of $d(\ln R^*)/dT$, where $R^* = R(T)/R(300 \text{ K})$, gradually shifts from 23 K at ambient pressure to 6 K at 2.3 GPa and becomes difficult to observe at $P > 3.0 \text{ GPa}$. Further application of pressure gives rise to a metallic character combined with a superconductive transition at low temperatures (Fig. 3A, green). It is important to note that the cooldown and warmup resistance curves overlap perfectly below 3.0 GPa, whereas a large resistive hysteresis loop in the temperature interval between 140 and 220 K can be clearly seen at 3.0 GPa in Fig. 2A, which was confirmed in a separate run performed on another piece of crystal flake grown in a different batch, indicating a first-order transition. Since the temperature dependences of resistivity above and below the first-order transition are nearly identical, this transition does not seem to be relevant to the insulator–metal transition on crossing a critical pressure $3.0 < P_c < 3.8 \text{ GPa}$.

Pressure-Induced Superconductivity. An abrupt drop in the resistance at 3.0 GPa emerges at the onset temperature of 6.8 K (Fig. 2A, blue) and can be gradually smeared out by an external magnetic field (SI Appendix, Fig. S4), indicating filamentary superconductivity. Fig. 3A shows the temperature dependence of resistance with pressure up to 45.0 GPa. On lowering the temperature at 3.8 GPa, the 0-field resistance displays a small upturn around 6.8 K, which suggests some change in the electronic ground character, followed by a sharp drop to 0 resistance (Fig. 3B). Measurements of the alternating current (AC) susceptibility

![Fig. 1. Quasi-1D crystal structures of (A) α-Bi$_4$Br$_4$ and (B) β-Bi$_4$Br$_4$, in which quasi-1D chains run along the c axis and stack along the a axis via van der Waals interactions. (C) PXRD of α-Bi$_4$Br$_4$ flakes with the c axis coaligned normal to the sample holder under ambient condition. (Inset) A picture of α-Bi$_4$Br$_4$ crystals on the paper with millimeter grid.](Image)

![Fig. 2. (A) Temperature-dependent resistance of a Bi$_4$Br$_4$ crystal under different pressures. (B) The derivative resistance of α-Bi$_4$Br$_4$ at ambient pressure as a function of temperature. (Inset) The resistance of an α-Bi$_4$Br$_4$ crystal versus inverse temperature.](Image)
As summarized in the temperature-pressure (T–P) phase diagram shown in Fig. 3E, we find that the \( T_c \) of the first superconducting (SC-I) phase decreases progressively with pressure and disappears above 12.0 GPa in our measurement, while the \( T_c \) 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 1.84\( T_c \) (12.57 at 3.8 GPa for the SC-I phase and 13.27 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 pressures. 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 \( H_{\text{bias}} \) (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...
situ high-pressure single-crystal X-ray diffraction (HP-SXRD) study on α-Bi4Br4 crystal. As shown in Fig. 4A, a monoclinic C2/m structure with lattice parameters of \(a = 11.254(1) \, \text{Å}, b = 4.454(2) \, \text{Å}, c = 19.085(2) \, \text{Å}, \) and \(β = 106.22(7)^{\circ}\) 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 α-Bi4Br4 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 \(\alpha\)-ZrTe5 (25).

To confirm further the high-pressure phase, we also performed high-pressure powder X-ray diffraction (HP-PXRD) of α-Bi4Br4 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 α-Bi4Br4 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 preforming first principles calculations based on density functional theory (DFT), we simulated the internal atomic positions for the high-pressure phase starting from those of α-Bi4Br4 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 α-Bi4Br4, we performed DFT calculations of the electronic band structures with and without pressure. The results, similar to those in previous reports, show α-Bi4Br4 to be a TCI with a band gap ~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 Γ-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 Γ point (Fig. 5C, purple). These small pockets of holes and electrons thereby make the α-Bi4Br4 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 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 Bi4Br4 (\(\mu_0 H_{c2}\) for the SC-I phase and \(\mu_0 H_{c2}\) for the SC-II phase) are much higher than the reported values of 0.17 T for Bi-II phase and 3.77 T for Bi-III phase (26), implying that superconductivity in Bi4Br4 has nothing to do with any possible Bi decomposed from the sample. 4) The pressure dependence of the \(T_c\) of the SC-II phase shows a more pronounced reduction than that of Bi (26). These results, therefore, support that the superconductivity observed in Bi4Br4 is mainly intrinsic.

Furthermore, the isostructural topological compound β-Bi4I4 exhibits a pressure-induced superconducting transition above 15 GPa (18). Considering that the smaller Br ions in Bi4Br4 exert a larger internal chemical pressure on sublattices, it is reasonable to expect that Bi4Br4 would become superconducting at a much lower external pressure. Indeed, the SC-I phase with \(T_c \sim 6 \, \text{K}\) emerges fully at around 3.8 GPa. Meanwhile, our band structure calculations show that the topologically nontrivial features of α-Bi4Br4 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 wider 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 ~5.5 to 12.0 GPa exhibits a cusp-like peak. A similar resistivity upturn in the normal state on cooling and a non-monotonous 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 ≤ $P$ ≤ 12.0 GPa, where the SC-I and SC-II phases coexist in the phase diagram of Bi$_4$Br$_4$ (Fig. 3). 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 α-Bi$_4$Br$_4$. 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 α-Bi$_4$Br$_4$ 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 P1 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$_4$Br$_4$.

Materials and Methods

Single crystals of Bi$_4$Br$_4$ were grown by self-flux methods. Electronic transport properties of Bi$_4$Br$_4$ 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$_4$Br$_4$ single crystal with a dimension of 70 × 40 × 10 μm 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.