Pressure induced phase transitions and superconductivity in a black phosphorus single crystal

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We report a thorough study of the transport properties of the normal and superconducting states of black phosphorus BP) under magnetic field and high pressure with a large-volume apparatus that provides hydrostatic pressure to induce transitions from the layered A17 phase to the layered A7 phase and to the cubic phase of BP. Quantum oscillations can be observed at 1 GPa in both resistivity and Hall voltage, and their evolutions with pressure in the A17 phase imply a continuous enlargement of Fermi surface. A significantly large magnetoresistance MR) at low temperatures is observed in the A7 phase that becomes superconducting below a superconducting transition temperature $T_c \sim$ 6–13 K. T_c increases continuously with pressure on crossing the A7 to the cubic phase boundary. The strong MR effect can be fit by a modified Kohler s rule. A correlation between T_c and fitting parameters suggests that phonon-mediated interactions play dominant roles in driving the Cooper pairing, which is further supported by our density functional theory DFT) calculations. The change of effective carrier mobility in the A17 phase under pressure derived from the MR effect is consistent with that obtained from the temperature dependence of the quantum oscillations. In situ single-crystal diffraction under high pressure indicates a total structural reconstruction instead of simple stretching of the A17 phase layers in the A17-to-A7-phase transition. This finding helps us to interpret transport properties on crossing the phase transition under high pressure.

black phosphorus high pressure magnetoresistance Shubnikov–de Haas oscillation superconductivity

Interest in black phosphorus (BP) as an emerging 2D material has been revived after exploring graphene and transition-metal dichacolgenides (1–6). In addition to the semiconducting A17 phase with the arm-chaired layer structure, BP has another two allotropic modifications under pressure, a layered A7 phase at $5 \leq P < 10$ GPa and a cubic (C) phase at $P \geq 10$ GPa. Both high-pressure phases are superconducting. Recent high-pressure studies with a piston-cylinder cell have revealed an interesting transition from semiconductor to topological semimetal within the A17 phase at $P \sim 1$ GPa (7). However, the transitions to those high-pressure phases occur at pressures out of the pressure range of the piston-cylinder devices (8); measurements of transport properties in the A7 and the C phases have been performed so far in a diamond anvil cell (DAC) and a multianvil device with a solid pressure-transmitting medium (9, 10). The importance of the choice of pressure medium and the construction of devices in the high-pressure study is never overexaggerated. The gas phase is ideal for the pressure medium, but it suffers a huge volume collapse under pressure and is not sustained at higher pressure. Shear stress is a major concern when a liquid phase is used, which varies among common fluids used as the pressure medium (11). The nonhydrostatic component in a fluid pressure medium is significantly reduced if the high-pressure chamber is compressed from multiple directions (12). The physical properties of most 2D materials are extremely sensitive to a nonhydrostatic pressure that can alter the physical properties dramatically in some cases (13, 14). Therefore, it is highly desired to perform a thorough study of BP with a liquid-filled, large-volume multianvil device to reveal the intrinsic physical properties of the A7 phase and the C phase.

In the A17 phase of BP, arm-chaired layers are held together by the van der Waals force (15). Under ambient conditions, bulk BP has a direct band gap of about 0.3 eV at the Z point of the Brillouin zone (16). Although the volume of BP decreases dramatically under pressure, a reduction of 26 at 10 GPa (9, 17, 18), physical properties change even more remarkably under pressure. Hydrostatic pressure induces a Lifshitz-like semiconductor–semimetal transition at $P \sim 1$ GPa by closing up the direct gap (19). Increasing pressure slightly further in a narrow pressure near 1.0 GPa or applying surface charges induces a topological transition with band inversion, which results in two Dirac points near the Z point (7, 19, 20). The lack of inversion symmetry in the A17 phase converts the 2D Dirac semimetal into a Weyl semimetal (20). A negative magnetoresistance (MR) for $// \boldsymbol{I}$, consistent with the chiral anomaly characteristic of a Weyl semimetal, has indeed been reported in a high-pressure transport study (7). The Weyl semimetal phase of BP shows no sign of superconductivity down to 45 mK (21). Most previous studies were performed in the A17 phase

Significance

A high-pressure study of a black phosphorus crystal establishes a rich phase diagram, including Weyl semimetal and superconducting states, Lifshitz-type semiconductor–semimetal transitions, and two structural phase transitions. Transport properties and quantum oscillations under high pressure provide critically valuable information to understand the physics of these new phases. The pressure dependence of physical properties has been reliably measured under hydrostatic pressure and applied magnetic fields using a large-volume apparatus. Superconductivity in the A7 phase has been found to exhibit the largest magnetoresistance effect observed in its normal state so far. The Bardeen–Cooper–Schrieffer superconductivity in the A7 phase identified by the experiment can be accounted for by the phonon mechanism based on a first-principles calculation.

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PHYSICS

and report an extremely large MR effect and quantum Shubnikov–de Haas (SdH) oscillations under high pressure (7, 10, 16, 19–26). Superconductivity in BP occurring right after the A7 phase is induced at $P \geq 5$ GPa (27–29). Transport properties in the normal state of the A7 and the C phases and their relationship to superconductivity have been studied based mainly on measurements with a DAC and a multianvil device in which the solid pressure-transmitting medium used can exert a strong pressure inhomogeneity or uniaxial stress on the sample (10, 30). The most-cited high-pressure study (27) in the early days was actually made on a powder sample. It is unclear how the normal-state properties of BP are influenced by the uniaxial strains created in the devices with solid pressure media (31).

To unveil the intrinsic properties of the A7 and C phases under high pressures, we performed detailed measurements of magnetotransport properties with a large-volume cubic-anvil-cell apparatus that can maintain an excellent hydrostatic pressure condition (32–34) across the three phases of BP. In our measurements, a BP crystal grown under high pressure and temperature was cut into a rectangular bar ($0.33 \times 0.05 \times 0.50$ mm^3) with the shortest dimension along the b axis. Fig. 1, *Inset* shows a picture of our sample assembly for the resistivity measurement with four-probe leads on the a c plane crystal surface. The sample with leads is hung inside a Teflon capsule filled with glycerol as the pressure-transmitting medium. The magnetic field is applied along the b axis of the A17 phase. Detailed information about measurements with the cubic anvil cell can be found in *SI Appendix*. The sample thickness is important for measurements of transport properties in the A7 phase since the configuration can still pick up a significant contribution in the buckled layers if a layer is formed at 45° to the b–c plane of the A17 phase. In contrast, measurements on a flake sample with a DAC are dominated by the contribution normal to the layer in the A7 phase.

Results and Discussion

Resistivity Fig. 1 shows the pressure dependence of resistivity at room temperature (RT). The pressure-induced A17-to-A7-phase transitions can be clearly discerned from the abrupt drop of at 5 GPa, which is consistent with (P) data in the literature (24) and also matches the critical pressure extracted from pressure-dependent structural studies (35). In contrast, there is only a weak kink in (P) at ∼10 GPa where the A7-to-C-phase transition occurs in the structural study (17). In addition, a slope change is clearly visible at $P \sim$ 1–1.5 GPa, which is close to the reported critical pressure of 1.2 GPa for a pressure-induced Lifshitz transition obtained with a piston-cylinder cell (19).

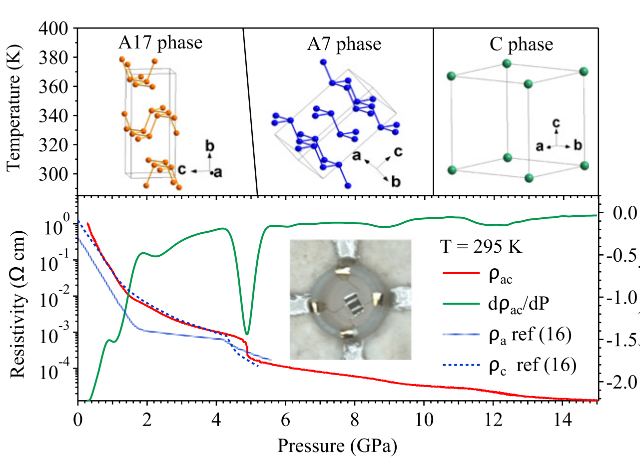

Fig. 1. Pressure dependence of structural transition and zero-field resistivity. The top illustrates BP undergoes a reversible sequence of phase transitions under pressures from an orthorhombic A17 phase to a rhombohedral A7 phase at about 5 GPa and then to a simple-cubic C phase at about 10 GPa (17). The bottom shows the pressure dependence of resistivity at RT. (*Inset*) The four-probe configuration for magnetoresistivity measurements in the cubic-anvil-cell apparatus.

Reliable resistivity data carry information that is critically important to understand the electronic states in all three phases of BP. Specifically, the magnetic field dependence of resistivity sheds light on the charge carrier density, the mobility, and the ratio of electron–electron to electron–phonon interactions. The temperature dependence of resistivity (T) under $H = 0$ and 8.5 T at various pressures is shown Fig. 2*A*. In zero field, the application of 1 GPa pressure closes up the direct band gap and results in a metallic behavior, as has also been reported previously (24). The anomalous hump around 220 K has been attributed to reduced thermal excitation of carriers during cooling at $T > 220$ K (21). This argument is not fully supported by the result of thermoelectric power measurement under the same pressure, in which no anomaly can be detected near 220 K (see the results in *SI Appendix*, Fig. S1). However, a clear anomaly does occur at 250 K in $S(T)$ at the same pressure with a magnetic field $H = 8$ T. The anomaly of (T) at 220 K disappears at $P = 3$ GPa. The resistivity at 1 GPa drops more than two orders in magnitude as the sample is cooled down from RT to 1.5 K, the largest drop ever reported for BP in the literature. The ratio $_{300K}/\ _{1.5K}$ is normally used as a measurement of a metallic sample s quality, the higher the better. In this case, hydrostatic pressure generated in the cubic anvil cell may also be a factor to differentiate our result from those in the literature. The evolution of the normal state (T) shows no sign of structural transitions at 5 GPa and 10 GPa. Like other materials showing an extremely large MR (36, 37), (T) at $H = 8.5$ T and $P = 1$ GPa increases dramatically relative to that of zero field by three orders of magnitude at low temperatures and shows a broad hump at low temperatures. This magnetic-field-induced upturn in (T) moves progressively to lower temperatures upon increasing pressure within the A17 phase ($P < 5.5$ GPa), and completely disappears as BP enters the A7 phase ($P > 5.5$ GPa). However, a significant MR effect remains at low temperatures for the A7 and even the C phases, as is shown in Fig. 2*B*.

It is important to note that the Lifshitz transition at $P \sim 1$ GPa changes the (T) from activated to metallic with a power law ($\sim T^n$) at low temperatures. A nearly temperature-independent (T) at low temperatures can be accounted for by a two-carrier model without involving any effects due to electron–electron correlations. The behavior of the (T) of BP on crossing the semiconductor–semimetal transition is in sharp contrast to that of a pressure-induced Mott insulator-to-metal transition where non-Fermi-liquid behavior with a power law exponent $n \sim$ 1–1.5 is normally observed at a quantum critical point as a long-range magnetic order is suppressed (38, 39).

Magnetoresistivity Fig. 2*B* shows the temperature dependence of the MR under different pressures. Within the A17 phase, the MR is dramatically enhanced as temperature decreases, saturating below 20 K. The MR value at 2 K and 2 GPa is similar to that at nearly the same pressure and temperature obtained with a piston-cylinder device (19). The MR remains significant even in the A7 and C phases in which superconductivity occurs at low temperatures. To our knowledge, the A7 phase of BP is the superconductor with the largest normal-state MR effect. This finding makes BP more interesting in a study of the relationship between normal-state properties and the superconducting transition. It is important to note that WTe_2 shows an extremely large MR effect only at low temperatures; at 100 K the MR effect is less than an order of magnitude (36). In contrast, the MR effect of BP at 1–2 GPa is still more than an order of magnitude at 100 K and it remains noticeable even at RT. In addition, the emergence of superconductivity in WTe_2 is accompanied by the suppression of a large MR (40).

In Boltzmann transport theory, MR in conductors arises from Lorentz-force deflection of electronic trajectories and is directly related to the electronic scattering path around the Fermi surface (FS). At a given charge carrier density n_c and single relaxation

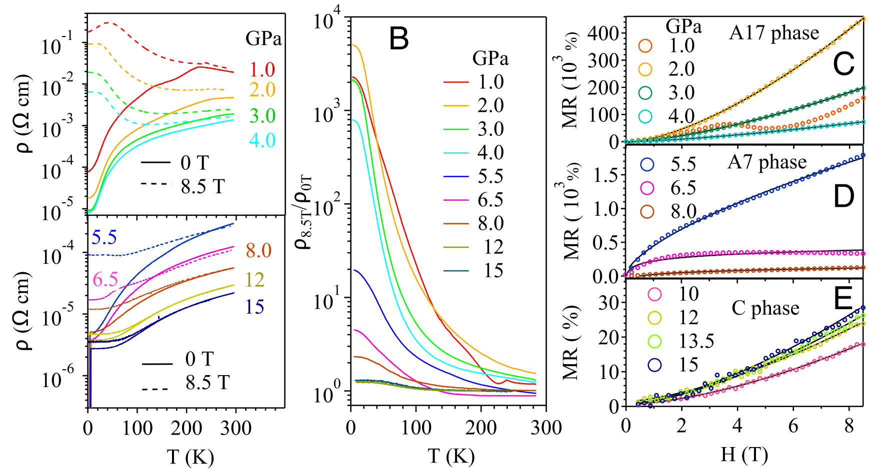

Fig. 2. Temperature dependence of resistivity (*T*) of BP (*A*) under 0 T and 8.5 T between 1 and 15 GPa and (*B*) normalized $_{8.5T}/_{0T}$. (*C*–*E*) Magnetic field dependence of MR at 1.5 K under various pressures up to 15 GPa: (*C*) A17 phase, (*D*) A7 phase, and (*E*) C phase. Open circles symbolize the experimental data and black solid lines denote the fitting curves with the modified Kohler s model.

time τ at all points on the FS, relative MR in a magnetic field $\boldsymbol{H}$ satisfies Kohler s rule (41):

$$\mathrm{MR}\equiv\frac{(H)\qquad(0)}{(0)}=F(H\tau). \qquad [\ ]$$

By assuming that the mean mobility of carriers μ_m is proportional to $e\tau\ \ m$, where e and m represent the electron charge and effective mass, respectively, and m is weakly temperature-dependent. Kohler s rule in an isotropic two-band model can be simplified to the approximate form (42)

$$\mathrm{MR}=(\mu_m H)^2, \qquad [2]$$

the same conclusion as inferred from the proposed compensative theory for the A17 phase (19). However, the isotropic assumption is apparently not applicable to highly anisotropic BP with orthorhombic symmetry (25). The anisotropic band structure near the Fermi level which is related to the effective mass and the variation of relaxation time τ with directions may result in a violation of the MR from the quadratic field dependence in Eq. **2**. To verify this consideration, we measured the field dependence of MR at 1.5 K under various pressures, as summarized in the Fig. 2 *C*–*E*. At 1 GPa, an anomalous kink was observed that can be ascribed to the Adler–Bell–Jackiw anomaly in a Weyl semimetal (7); due to the large anisotropy discussed below or to a small tilt angle relative to the original sample s position under high pressure, the chiral term $(e^3\ \ 4\pi^2\ \ ^2)\boldsymbol{E}\cdot\boldsymbol{H}$ near the Lifshitz transition (43) can acquire a dipolar component that grows rapidly as H increases so as to result in a negative contribution to the MR. At 2 GPa, the positive MR reaches about 450,000 in a magnetic field of 8.5 T without any sign of saturation. With further pressure increase, the MR decreases dramatically, but it still remains significantly large in the A7 phase before it finally drops to a moderate value in the C phase. Apparently, the MR cannot be simply described by an H^2 power law in any of the three phases. Instead, we have to fit the MR data using a modified Kohler s model (44):

$$\mathrm{MR}=(\mu_m\gamma_m H)^2=\mu_m{}^2H^{2\ \ 2}\ , \qquad [3]$$

where the H-dependent anisotropic factor $\gamma_m\propto H$ is intimately related to the field-induced changes to the FS and reflects an averaged anisotropic effect. The quality of the fit is clear in Fig. 2 *C*–*E* and the fitting parameters μ_m and as a function of pressure are plotted in Fig. 3 *A* and *B*, respectively. We have found that the mean carrier mobility μ_m is $1.3\times10^4\ \mathrm{cm}^2{\cdot}\mathrm{V}\ ^1{\cdot}\mathrm{s}\ ^1$ at 1.5 K for 2 GPa, which is the same order of magnitude as in a previous report (16). The value of μ_m rapidly decreases on crossing the A17-to-A7-phase boundary from 2 GPa to 10 GPa. μ_m again changes sharply across the boundary between the A7 and C phases and shows a slight increase with pressure in the C phase. An ≈ 0.25 in the A17 phase can be well-related to the highly anisotropic crystal structure (i.e., the arm-chaired layer and the weak coupling between layers by the van der Waals force). A similar found in the C phase cannot be attributed to the crystal structure, which is isotropic. Since the pressure-induced structural transitions among A17, A7, and C phases are reversible; no long-range atomic diffusion occurs in these phase transitions. The distribution of impurities residing in the A17 phase as the crystal is formed must follow a pattern compatible with the layered structure; the impurity distribution pattern is likely to be

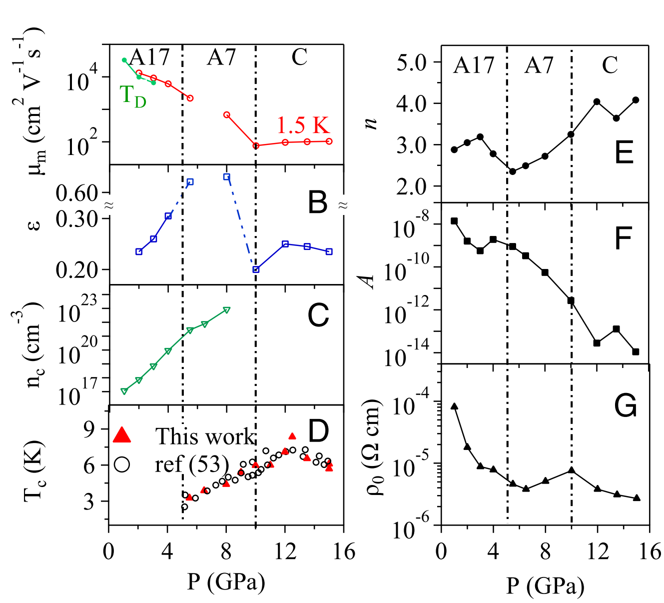

Fig. 3. (*A*–*G*) The fitting parameters from the transport properties and superconducting transition temperature as a function of pressure across A17, A7, and C phases. Error bars are smaller than symbols.

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