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

Xiang Li, Jianping Sun, Prashant Shahi, Miao Gao, Allan H. MacDonald, Yoshii Uwatoko, Tao Xiang, John B. Goodenough, Jinguang Cheng, and Jianshi Zhou

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 $p \geq 1$ 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 $T_c \approx 6-13$ 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 from semiconductor to topological semimetal within the A17 phase implies a continuous enlargement of Fermi surface. 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 superconductor in the A7 phase identified by the experiment can be accounted for by the phonon mechanism based on a first-principles calculation.

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 superconductor in the A7 phase identified by the experiment can be accounted for by the phonon mechanism based on a first-principles calculation.


To whom correspondence may be addressed. Email: jgoodenough@mail.utexas.edu, jgoodenough@mail.utexas.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1810726115/-/DCSupplemental.

Supplementary Materials

*Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712; Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; School of Physics, University of Chinese Academy of Sciences, Beijing 100049, China; Department of Physics, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur 273009, India; Department of Microelectronics Science and Engineering, Faculty of Sciences, Ningbo University, Zhejiang 315211, China; Department of Physics, The University of Texas at Austin, Austin, TX 78712; Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan; and Collaborative Innovation Centre of Quantum Matter, Beijing 100087, China.

Contributed by John B. Goodenough, August 8, 2018 (sent for review July 2, 2018; reviewed by Yuanbo Zhang and Joe D. Thompson)
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 anvils 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 $45^\circ$ 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 $\rho$ at 5 GPa, which is consistent with $\rho(P)$ 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 $\rho(P)$ 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).

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 $\rho(T)$ under $H = 0$ and 8.5 T at various pressures is shown in Fig. 2A. 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 results 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 $\rho(T)$ at the same pressure with a magnetic field $H = 8$ T. The anomaly of $\rho(T)$ 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 $\rho_{000}/\rho_{1.5K}$ 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 anvils may also be a factor to differentiate our result from those in the literature. The evolution of the normal state $\rho(T)$ shows no sign of structural transitions at 5 GPa and 10 GPa. Like other materials showing an extremely large MR (36, 37), $\rho(T)$ 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 $\rho(T)$ 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 reemerges at low temperatures for the A7 and even the C phases, as is shown in Fig. 2B.

It is important to note that the Lifshitz transition at $P \sim 1$ GPa changes the $\rho(T)$ from activated to metallic with a power law $(\rho \sim T^p)$ at low temperatures. A nearly temperature-independent $\rho(T)$ 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 $\rho(T)$ of BP on crossing the semiconductor–semimetal transition is in sharp contrast to that of pressure-induced metal–insulator-to-metal transition where non-Fermi-liquid behavior with a power law exponent $p \sim 1–1.5$ is normally observed at a quantum critical point as a long-range magnetic order is suppressed (38, 39).

**Magneto resistivity.** Fig. 2B 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 $n_e$ and single relaxation
Temperature dependence of resistivity \( \rho(T) \) of BP (A) under 0 T and 8.5 T between 1 and 15 GPa and (B) normalized \( \rho_{B}(T)/\rho(T) \) for different pressures. (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.

The mean mobility of carriers \( \mu_m \) 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)

\[
\text{MR} = \langle \mu_m H \rangle^2, 
\]

where the MR of carriers mobility \( \mu_m \) is 1.3 \( \times \) 10\(^4\) cm\(^2\) V\(^{-1}\) 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 \( \mu_m \) rapidly decreases on crossing the A17-to-A7-phase boundary from 2 GPa to 10 GPa. \( \mu_m \) 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 \( e \) 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. 2. Temperature dependence of resistivity \( \rho(T) \) of BP (A) under 0 T and 8.5 T between 1 and 15 GPa and (B) normalized \( \rho_{B}(T)/\rho(T) \) for different pressures. (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.](image-url)
transferred in the C phase. We believe it is the origin why an anisotropic parameter similar to that in the A17 phase can be obtained in the C phase. Moreover, the slight variation with pressure of the anisotropic exponent $\varepsilon$ in the A7 and C phases may be correlated to the mass renormalization effect or impurity scattering (45).

In sharp contrast, the MR in the A7 phase shows a striking deviation from the MR found in either the A17 or the C phase; fitting the data with Eq. 3 gives an abrupt increase of $\varepsilon \approx 0.70$ at 5.5 GPa and 8.0 GPa in the A7 phase. Moreover, fitting the data at 6.5 GPa to Eq. 3 failed. The MR at 6.5 GPa increases at low fields, but it decreases slightly as field further increases. This behavior is totally different from the prediction of Eq. 3, which gives a nonsaturated MR. An anomalously high $\varepsilon$ obtained from fitting the data at 5.5 GPa and 8.0 GPa to Eq. 3 and a total failure for the fitting at 6.5 GPa call our attention to the mechanism of the A17-to-A7-phase transition and the experimental setup for measuring the MR effect in the A7 phase. There are two scenarios to explain the phase transition from A17 to A7: (i) the buckled layers in the A7 phase come directly from stretching the arm-chained layers in the A17 phase (46) and (ii) P–P bonds form in some locations between the layers in the A17 phase and some bonds inside layers are broken, which give new layers of A7 phase along ~45° projected on the b–c plane in the A17 phase (47, 48).

In scenario ii, while $H$ is still normal to the current direction as shown in Fig. 1, the current is no longer carried by electrons moving within layers and the field is not normal to layers in the A7 phase. To verify the mechanism of phase transition, we have carried out a single-crystal diffraction under pressure. The detailed information about this experiment is provided in SI Appendix. Based on Bragg’s law, $2d \sin \theta = \lambda$, the X-ray diffraction pattern maps the crystal planes. Where the X-ray beam was normal to the arm-chained layers of the A17 phase we observed only a single bright spot at the 20 angle of ~25° ($d \approx 1.65$ Å), which is the (151) plane in the A17 phase. A diffraction spot at more or less the same location corresponding to the (110) plane of the A7 phase is expected (details provided in SI Appendix) if the layered structure is formed as described in scenario ii, which is indeed what we have observed. Therefore, the measurement configuration for the resistivity in Fig. 1 will pick up a combined response as the current flows within layers and between layers, whereas the field was applied along a direction about 45° normal to the buckled layers of the A7 phase. As a result, the MR effect highly depends on any subtle rotation of the sample in the cell under an assumption that the MR effect in the A7 phase is highly anisotropic. A strong angular dependence of MR has also been reported in a 3D Dirac semimetal Cd3As2, and actually an MR curve at a tilt angle of <5° is stunningly similar to that of BP at 6.5 GPa (49).

The metallic conductivity in all three phases with $H = 0$ has been fit to the power law, $\rho(T, 0) = \rho_0 + A T^n$, where $\rho_0$ is the residual resistivity. The fitting has been carried out in $\rho(T, 0)$ at different pressures below 40 K. The fitting parameters are displayed in Fig. 3 E–G. Corresponding to the dramatic change of the MR effect on crossing the three phases, parameters of fitting to the power law also show anomalies at the phase boundaries. The $n > 2$ in the power law rules out the possibility of applying the Fermi liquid mode to describe the metallic phase in the A17 phase and the normal-state resistivity in the A7 and C phases. It is at the A17-to-A7-phase boundary that a minimum $n$ close to 2 has been obtained. The residual resistivity $\rho_0$ reflects the scattering between electrons and impurities in a crystal, which normally shows a very small pressure dependence, especially in a single-crystal sample. A steeper decrease of $\rho_0$ by more than one order in magnitude in the metallic A17 phase as pressure increases is remarkable. Since $\rho_0$ is inversely proportional to the Fermi momentum $k_F$ (50), the change of $\rho_0$ is caused by a substantial enlargement (by one order) of the FS over the same pressure range derived from our SdH study below. Similar results of the FS change under pressure have also been reported in the literature (19, 21). An increase of $\rho_0$ with pressure in the A7 phase is highly unusual; it must be correlated to a change of the conducting pathway through the layer and between the layers in the A7 phase under pressure. The phase boundary at 10 GPa marks an end of this unusual pressure dependence of $\rho_0$. The initial sharp drop of $\rho_0$ with increasing pressure may be caused by a two-phase (A7 and C) coexistence.

**Hall Resistivity.** We have measured the Hall resistivity, which can probe the charge carrier density and mobility qualitatively. Fig. 4 shows the field dependence of Hall resistivity $\rho_{xy}$ at 1.5 K, which changes remarkably with increasing pressure. It should be noticed that the results presented in Fig. 4 are significantly different from those in the literature (9). A discussion about the difference between these results is given in SI Appendix. Considering the case of two carriers, the Hall resistivity $\rho_{xy}$ can be described as in ref. 21:

$$\rho_{xy} = \frac{H}{e^2} \left( \frac{n_h \mu_h^2 - n_e \mu_e^2}{n_h \mu_h + n_e \mu_e} \right) \left( \frac{1}{n_h} - \frac{1}{n_e} \right)^2 \partial^2 \rho_{xy} / \partial H^2 - \frac{H^2}{e^2} \left( \frac{n_h \mu_h^2 - n_e \mu_e^2}{n_h \mu_h + n_e \mu_e} \right) \left( \frac{1}{n_h} - \frac{1}{n_e} \right)$$

where $n_{h,e}$ and $\nu_{h,e}$ denote the carrier densities and mobilities of electron and hole, respectively. In the high-field limit ($H \gg \mu_e^{-1}$), the Hall coefficient $R_H \equiv d\rho_{xy}/dH = 1/e(n_h + n_e)$$ only depends on the difference in densities of hole and electron carriers ($n_h - n_e$), but not on their mobility. Thus, the good linearity of $\rho_{xy}$ at high fields (SI Appendix) in both the A17 and A7 phases indicates the effective carrier density $n_{eff} \equiv [1/\varepsilon(n_h - n_e) - 1]$ in the high-field region is a constant at each pressure, which justifies the assumption that the modified Kohler’s rule is applicable in our case. The calculated effective carrier density $n_{eff}$ is plotted in Fig. 3C, which shows a great enhancement with increasing pressure. $R_H$ in the A17 phase changes sign between 2 GPa and 3 GPa. The low-field behavior of $\rho_{xy}$ could be influenced by the superconductivity in the A7 phase. The sign change of $R_H$ at higher fields as a function of pressure appears not to follow a clear trend. This anomalous behavior may be related to the fact that the angle between the normal direction of layers in the A7 phase and the magnetic field direction is about 45°. In this situation, $R_H$ is highly sensitive to any tilting on the sample caused by applying pressure. As summarized in Fig. 3, our study on a BP crystal with the multianvil device gives evidence that the pressure-induced structural transitions can be well distinguished by the transport properties. The Hall resistivity versus field at low fields is not linear due to the field-dependent balance between electrons and holes. This observation does not alter the discussion and the conclusion above since they are based on the data at the high-field limit where $\rho_{xy}(H)$ approaches a linear behavior.

**SdH Oscillation.** SdH oscillations have been reported in the semimetal A17 phase at $P \geq 1$ GPa, which reflects the change of FS at different pressures (7, 19, 21). SI Appendix, Fig. S5 shows the SdH oscillations (obtained from the second derivative of
longitudinal magnetoresistivity $\rho_{xx}$ and the corresponding fast Fourier transform at different temperatures under three pressures. Our findings show that the major frequency component $\alpha$ moves substantially from $\sim-4.4$ at 1 GPa to $\sim28.0$ T at 5 GPa and to $\sim67.0$ T at 9 GPa. The increase in the major frequency component with increasing pressure implies a change in dimensions of a single cyclotron orbit of a multishelled FS. Accordingly, the cross-sectional area of FS is determined as 4.4 nm$^{-2}$ at 1 GPa, $\sim26.8$ nm$^{-2}$ at 2 GPa, and $\sim65.8$ nm$^{-2}$ at 3 GPa. SdH oscillations become indiscernible in the A17 phase for $P > 3$ GPa due to a much-enlarged FS. SI Appendix, Fig. S6, Insert displays the inverse fields corresponding to dips of oscillations as a function of the Landau index $n_L$. The intercepts at $B^2 = 0$ of the linear extrapolations of $B^2$ versus $n_L$ axis yield the SdH phase value of $\gamma + \delta$ as 0.15(1), 0.18(1), and 0.08(1) for 1, 2, and 3 GPa, respectively. Since the correction term $\delta$ varies within $\pm1/8$ in the 3D limit (51), our results indicate a phase factor $\gamma = 0$, which suggests a nontrivial Berry phase $\theta_0 = \pi$ via the relationship $\gamma = 1/2 - \theta_0/2\pi$. Our result agrees well with previous reports (7, 19). Moreover, by analyzing the temperature dependence of SdH oscillations in SI Appendix, Fig. S5, we can quantitatively obtain information about the mean mobility $\mu_m$. The amplitude of the oscillations $\Delta k$ is suppressed as temperature increases and can be described by the relation (52)

$$\Delta k \propto \frac{k T}{\sin h(k T)} \exp(-\lambda T_D),$$

where $\lambda = 2\pi k_B T_0/\hbar\omega_0 = \varepsilon B/m^*$. With Dingle temperature $T_D = h/2k_B\tau_0$. As shown in SI Appendix, Fig. S7, the best fit to Eq. 5 of our experimental data yields the effective mass $m^*$ of 0.041(1)$m_0$, 0.020(1)$m_0$, and 0.162(1)$m_0$ and a Dingle temperature $T_D$ of 15.3 K, 10.7 K, and 19.7 K for 1 GPa, 2 GPa, and 3 GPa, respectively. Such nonmonotonic changes of nonparabolic band dispersion under pressure. The corresponding effective mobility $\mu_m = e\tau/m^*$ can be calculated as $0.33 \times 10^4$ cm$^2$/V$\cdot$s$^{-1}$, 0.098 $\times 10^4$ cm$^2$/V$\cdot$s$^{-1}$, and 0.066 $\times 10^4$ cm$^2$/V$\cdot$s$^{-1}$ from 1 GPa to 3 GPa; the mobility is superimposed in Fig. 3A. The mobility derived from SdH oscillations is slightly smaller than that from the MR analysis since the former is based on data obtained at an average temperature of $\sim10$ K, whereas the latter is strictly at 1.5 K. The temperature dependence of $\mu_{m_0}$ is generally in line with that for a metal. The similar pressure dependence of $\mu_{m_0}$ from the two methods and the overall consistency in turn reinforce the validity of applying the modified Kohler’s model in analyzing the MR data.

The Lifshitz transition in BP leads to a Weyl semimetal based on an angle-resolved photoemission spectroscopy result (20). Electrons in the Weyl phase are Dirac fermions without inversion symmetry. The extremely small effective mass 0.041$m_0$ derived from the temperature dependence of SdH at 1 GPa is related to the formation of massless Dirac fermions. The Dirac fermions should also exhibit a vanishing thermoelectric power. However, this expectation has not been fulfilled in BP under pressure (see the experimental result of thermoelectric power and the discussion in SI Appendix). The effective mass increases with pressure since the state of Dirac fermions is destroyed by further increasing pressure. Although SdH disappears in the A7 phase, it is likely that the trend of small effective mass goes into the A7 phase since several parameters of transport properties change smoothly on crossing the A17-to-A7 phase boundary.

**Bardeen–Cooper–Schrieffer Superconductivity.** We now turn to discuss the pressure-induced superconductivity in BP. A zoom-in plot of $\rho(T,0)$ in Fig. 2A at low temperatures is given in Fig. 5A; the superconducting transition temperature $T_c$ versus pressure is summarized in Fig. 3D. As can be seen from Fig. 3D, superconductivity occurs right after pressure passes the A17-to-A7-phase boundary; the trend of monotonic increase of $T_c$ with pressure in the A7 phase continues on crossing the A7–C phase boundary. $T_c$ peaks out at 12.5 GPa within the C phase. These observations agree well with the results reported by Wittig et al. (53), although the pressure hydrostaticity at the sample in the latter is not clear. We have also examined the critical field $H_c$ determined from the $\rho(T)$ data under different magnetic fields; data are provided in SI Appendix, Fig. S9. The relationship of $H_c$ versus $T_c$ under different pressures is given in Fig. S5B. $H(T_c)$ follows the Ginzburg–Landau relation, $H(T_c) = H_c(1-\gamma^2)/(1+\gamma^2)$, where $\gamma = T/T_c$. It is interesting that the highest critical field does not occur in the C structure with the highest $T_c$ at 12.5 GPa but in the A7 structure at 8 GPa (see SI Appendix, Fig. S10 for the data plot). A critical field of $H_c < 0.15$ T, which is a small fraction of the Pauli limit of 1.84 T, is suppressed as $T_c$ appears to occur within the C phase. Since $H_c$ is related to the density of states $N(0)$ through the formula $H_c = 2\Delta(\pi N(0)/eF)^{1/2}$, where $\Delta$ is the gap formed in a superconducting state, the small $H_c$ observed can be accounted for by a small effective mass in the A7 phase as discussed above.

The critical pressures, $P_{c1} = 5$ GPa and $P_{c2} = 10$ GPa, for A17-to-A7- and A7-to-C-phase transitions in the literature are based on a structural study on the BP crystal grown under high pressure. Fitting parameters from transport properties of our single-crystal sample in Fig. 3 clearly indicate phase transitions at 5 GPa and 10 GPa. The peak of $T_c$ appears to occur within the C phase. As shown in Fig. 3B, the anisotropic exponent $\epsilon$ does not vanish in the isotropic C phase. More interestingly, $\epsilon$ peaks out at the pressure corresponding to a maximum $T_c$. A full understanding of the behavior of $\epsilon$ in the C phase may provide an important clue to the anomalous pressure dependence of $T_c$.

**Conclusions**

In conclusion, we have studied the transport properties of a BP crystal with a large-volume multivain apparatus filled with a liquid pressure medium. We have found that a nonsaturated, extremely large MR effect at 1.5 K in the A17 phase extends well into the A7 phase and it remains moderately large in the C phase under high pressure. Instead of the ordinary quadratic field dependence, the field dependence of the MR effect in the A17 and the C phase can be fit to a modified Kohler’s model in which an average anisotropic factor due to either anisotropic FS or scattering at impurities is introduced. The mobility obtained through the fitting is highly consistent with that derived from the temperature dependence of quantum oscillations. The anomalous field dependence of MR effect in the A7 phase can be accounted for by the structural reconstruction from the A17 to the A7 phase. Fitting the MR effect to a modified Kohler model and the normal-state resistivity to a power law give parameters that can clearly mark the phase transitions at the A17-to-A7- and A7-to-C-phase boundaries. The high-pressure study on BP leads to a rich phase diagram from the semiconductor–semimetal transition by closing up the gap between two Dirac cones, to a Weyl semimetal, and to a superconductor. To our best
knowledge, the A7 phase shows the largest MR effect in its normal state while it exhibits superconductivity below Tc. Determination of the critical field for superconductors in the A7 and the C phase helps to identify that they are BCS superconductors. By applying the McMillian–Allen–Dynes formula and the electron and phonon structure from first-principles calculations, we are able to account for superconductivity in the A7 phase and partially the pressure dependence of Tc. Although it has an isotropic crystal structure, the C phase cannot be treated as an isotropic system from fitting the MR effect. It remains to be explained why the change of anisotropy is correlated to superconductivity in the C phase.

Materials and Methods

Single-crystal samples of BP were grown in a Walker-type multianvil module (Rockland Research Co.). Single-crystal X-ray diffraction under pressure was performed on a BP crystal with a DAC mounted on a Bruker P4 diffractometer with Mo K-alpha radiation (λ = 0.71069 Å) at RT. Hydrostatic high pressure was generated by a “Palmic” cubic-anvil cell system (34). All details of these setups can be found in SI Appendix. First-principles calculation was performed within the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) formula (see SI Appendix for detailed information).

ACKNOWLEDGMENTS. This work was supported in part by the National Key R&D Program of China Grants 2018YFA0305700 and 2017YFA0302901; Natural Science Foundation of China Grants 11574377, 11744040, and 11474331; Strategic Priority Research Program and Key Research Program of Frontier Sciences of the Chinese Academy of Sciences Grant DBS07020100 and QYZDB-SSW-LH013; Zhejiang Provincial Natural Science Foundation Grant LLY17A040005; in China (Department of Defense Army Grant W911NF-16-1-0559; the NSF through the Center for Dynamics and Control of Materials, an NSF Materials Research Science and Engineering Center under Cooperative Agreement DMR-1720595; Welch Foundation Grant F-106 in USA; and Japan Society for the Promotion of Science KAKENHI Grant 15H03681 in Japan). J.S. acknowledges support from the Postdoctoral Innovative Talent Program.