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Weak antilocalization effect in exfoliated black phosphorus revealed by temperature-
and angle-dependent magnetoconductivity

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Abstract

Recently, there have been increasingly ~~heated~~ debates on whether there exists a surface resonance
state (SRS) in black phosphorus (BP), as suggested by recent angle-resolved photoemission
spectroscopy (ARPES) results. To ~~unambiguously~~ resolve this issue, we have performed
temperature- and angle-dependent magnetoconductivity measurements on exfoliated, high-quality
BP single crystals. A pronounced weak-antilocalization (WAL) effect was observed within a
narrow temperature range of 8 - 16 K, with the electrical current flowing parallel to the cleaved
ac-plane (along the *a*- or *c*-axis) and the magnetic field along the *b*-axis. The angle-dependent
magnetoconductivity and the Hikami-Larkin-Nagaoka (HLN) model-fitted results have revealed
that the observed WAL effect shows ~~obvious~~ surface-bulk coherent features, ~~which. This strongly~~
supports the existence of SRS in black phosphorus.

1. Introduction

Phosphorus is a light, pentavalent element which exists in a number of allotropic forms. As the most stable form of phosphorus under normal conditions, orthorhombic black phosphorus (BP) has a layered structure, much like graphene and transition metal dichalcogenides (TMDs), though its atoms are puckered (see Fig.1a). Extensive theoretical and experimental investigations have revealed that numerous intriguing physics can be realized in this material, such as large linear magnetoresistance (MR) [1], high in-plane anisotropy [2-4], high carrier mobility [5,6], strain-induced gap modifications [7,8], semiconductor-metal transition [9,10], and superconductivity under high pressure [11]. In addition, its unique band structure and transport properties have driven a flurry of exciting researches trying to probe the promising applications in further nanoelectronics and nanophotonics [5,6,12-14]. For example, BP has a tunable, thickness-dependent direct band gap, varying from ~ 0.3 eV (bulk) to >1.4 eV (monolayer), which is valuable for developing novel optical and other devices with functionalities based on heterostructures with two-dimensional (2D) materials [13, 14]. The field-effect transistor (FET) based on BP has been reported to exhibit superior semiconductor device performance [6,15-18]; our recent results show that BP can serve as the electrode material for all-solid-state supercapacitors [19].

Despite the numerous intriguing properties presented by BP, its electronic structures are not yet completely understood. Previous numerical work on bulk BP has shown that it has a usual narrow-gapped semiconductor with a 0.3 eV band gap at the Z point [13,14]. However, recent angle-resolved photoemission spectroscopy (ARPES) results have demonstrated that there exist surface resonance states (SRS) near the top of the valence band along the [010] direction, indicating that the current theoretical methodologies do not fully describe the important electronic properties of BP [20, 21]. In the field of nanoelectronics, surface effects like SRS and surface states (SS) have a critical role in the performance of electrical and optical devices, such as the prevention of mobility degradation and the Fermi-level pinning effect [22]. Thus, the study of SRS in relation to transport properties is not only of vital importance for understanding the relative contributions from bulk states and SRS near the Fermi level, but also crucial for the development of new electronic devices based on BP.

Similar to true surface states, surface resonance states are also localized at the surface of a

material and have no k_z dispersion. The main difference between surface states and surface resonance states is that the surface state (SS) exists only in the projected bulk band gap, whereas the surface resonance state (SRS) is a hybrid between the 2D surface state and the three-dimensional (3D) bulk state (there is a substantial spatial overlap between their wave functions), and the SRS weakly embeds in the bulk states [23, 24]. From the electronic transport point of view, SRSs allow a charge to be transferred dynamically between the surface and the bulk. Therefore, the bulk and surface transport channels can coherently couple with each other, which makes the transport exhibit both bulk and surface characteristics, as is the case in Bi thin film [25].

To observe the SRS experimentally, we must reduce the interference of the bulk states to pick out the contributions from the SS in transport, which is similar to the method used for the observation of pure surface states. For Bi, due to the semimetallic band structure in the bulk, its surface effects (SS and SRS) are usually observed in the thin film form, where the bulk-to-surface ratio has been reduced progressively [25-27]. However, as a semiconductor, bulk BP has a direct band gap of 0.2 eV, and its corresponding bulk conductivity decreases drastically at low temperatures (below 50 K) [10, 28], which allow us to observe the coherent characteristics directly on the bulk BP at low temperatures. In addition, high-resolution synchrotron-based photo-electron diffraction (HRSPD) investigations suggest that the surface of a single crystalline bulk BP can be a good approximation of an isolated single layer [29]. Following the above lines of reasoning, we have performed magnetotransport measurements on exfoliated BP single crystals, over a temperature range of 2 - 20 K in a maximum external magnetic field of 7 tesla (T), to search for the evidence of possible surface-bulk coherent transport properties. A pronounced weak-antilocalization (WAL) effect was observed in the high-quality samples within a narrow temperature range of 8 - 16 K, with the electrical current flowing parallel to the cleaved *ac*-plane (along the *a*- or *c*-axis) and a magnetic field along the *b*-axis (The notations *a*, *b*, *c* are connected with the crystallographic axis of the BP, as is shown in Fig. 1a. The *a*- and *c*-axis is along the armchair and zigzag direction, respectively. The direction *b*-axis is normal to the cleaved *ac*-plane). More intriguingly, both the angle-dependent magnetoconductivity and Hikami-Larkin-Nagaoka (HLN) fitting results show obvious surface-bulk coherent features, which is ~~a solid~~ evidence for the existence of surface resonance states [25].

2. Experiments

The BP crystals were synthesized from red phosphorous, as described in our previous work [1,19]. The as-prepared crystals were then cleaved at room temperature in an argon-filled glove box, in which the oxygen and humidity content were less than 0.1 ppm, resulting in a well-developed and shining (0/0) surface. To perform the transport measurements, a conventional Hall-bar was fabricated on the cleaved samples with a typical size of $0.6 \times 0.6 \times 0.08 \text{ mm}^3$ (see Figure 1b and c). To protect the samples from oxidation during transfer and transport measurement, we covered the surface of the samples with varnish film. The magnetotransport measurements were performed on a Quantum Design PPMS-9 with a maximum magnetic field of 7 T.

3. Results and discussions

Figure 1d shows the temperature-dependent longitudinal resistivity ρ_{xx} obtained on two representative, freshly cleaved samples (Sample A and B), from 2 K to 300 K under zero magnetic field. For both samples, ρ_{xx} increased exponentially as the temperature T decreased below 50 K, due to the freezing of impurity ionization, and did not show a trend of saturation, even at a low temperature of 2 K. For example, the more resistive Sample A exhibits an extremely large value of $952 \text{ } \Omega\text{cm}$ at 2 K, which is nearly 1,750 times larger than the resistivity at 50 K. The greatly suppression of bulk conductivity in BP provides us an opportunity to observe the SRS by using the transport measurements at low temperature.

To search for the signs of SRS, we performed magnetotransport measurements in a magnetic field up to 7 T over a temperature range of 2 K to 20 K for both the two samples. Figure 2a shows the field-dependent magnetoresistance (MR) curves (MR is defined as $[\rho(H) - \rho(0)]/\rho(0) \times 100\%$, where $\rho(H)$ and $\rho(0)$ are the resistivity at field H and zero, respectively) at different temperatures for Sample A, with the current flowing along the c -axis in the ac -plane and the magnetic field along the b -axis. Notably, the in-plane crystallographic orientations were determined by Electron back-scattered diffraction (EBSD) pattern, as shown in our previous reports [30]. The behavior of MR obtained with the current along the a -axis in the ac -plane is similar to the MR behavior with the current flowing along the c -axis, except for the value of MR [1]. It is interesting to note that the behavior of MR in Figure 2a can be divided into two regions, i.e., high-field ($> \pm 4 \text{ T}$) and low-field ($< \pm 4 \text{ T}$) regions. In the high-field region, MR increases linearly or quadratically with the increase of external magnetic field, owing to the mobility fluctuation, or Lorentz effect, as reported in our previous work [1]. In the low-field region, the MR curves display negative cusps in

the temperature range 2-8 K, which is reminiscent of the weak localization (WL) effect that results from the constructive interference of two time-reversal electron trajectories [31-35]. Usually, a WL effect occurs at low temperatures when thermal disturbance is significantly suppressed and electrons are scattered elastically with preserved phase coherence [31-35]. In the case of BP, the appearance of the WL effect can be attributed to the dominance of elastic scattering caused by impurities [36,37]. With increasing temperature, the WL effect gradually disappears; instead, a sharp positive cusp was observed in the low-field region over the temperature range 8 K to 16 K (see Fig. S1). This feature is regarded as an obvious signature of the weak-antilocalization (WAL) effect [38-41]. It should be noted here that WAL was not unique to this particular Sample A but was also observed in Sample B (as shown in Fig. S2). In contrast to WL, WAL arises in a phase-coherent conductor when destructive interference is formed between two time-reversal electron paths. It is usually observed in materials with strong spin-orbital coupling (SOC), such as Bi [25], InAs [42], and topological insulators [31, 35, 38-41]. Since phosphorus is a light element, the SOC should not be strong enough to result in WAL [8,12]. Therefore, WAL cannot be explained by the effect of SOC in BP. As is known to us, MR in the nonmagnetic materials is dominated by the orbital effects originating from the cyclotron motion of electrons due to the Lorentz force. According to the two-band model, MR can be scaled with $MR \sim (w_c \tau)^2 \sim (e\tau/m^*)B^2 \sim \mu^2 B^2$ (τ is the scattering time, m^* is the effective mass, and B is the magnetic field; $w_c (= eB/m^*)$ is the cyclotron's frequency). Thus, the behavior of MR is closely related to the band structure along the direction of magnetic field. Based on the results above, it is preliminarily supposed that the observed WAL effect is related to the special band structure along the b -axis.

To investigate the effect of band structure along c -axis on the MR, we measured the field dependence of MR at different temperatures for Sample A (see Fig. 2b), with the current flowing along the b -axis and the magnetic field applied parallel to the ac -plane (the corresponding curves are shown in Fig. S3). Since the sample along the b -axis is quite thin, we cannot use the standard 4-point configuration but the method described in the reference 42 (the electric configuration is shown in the inset of Fig. 2b). Surprisingly, no WAL was observed in this configuration; the WL effect was clearly observed, which strongly indicates that in BP, WAL is anisotropic (plane-dependent), but WL is isotropic (plane-independent). Since WL results from the elastic

scatterings of electrons at defects or imperfections in a material, it is easy to understand its isotropic feature (plane-independence). However, the WAL effect was observed only when the current was flowing along the ac -plane (either along a -axis or c -axis) with the magnetic field applied along the b -axis. This unique characteristic of WAL strongly suggests that the WAL in BP does not stem from the SOC interaction, but rather may be closely related to the special electrical band structure along the $[010]$ direction, e.g. a surface resonance state, SRS.

As mentioned above, when SRS exists in a material, the coherent coupling between the surface and bulk conduction channels leads to a transport that shows both surface (2D) transport and bulk (3D) transport characteristics [25]. Now, let us examine first whether the observed WAL effect has the 2D characteristics. We explore how the field-dependent MR varies with the tilt angle θ between H and the b -axis in magnetic fields up to 7 T for Sample A (the sketch is shown in Figure 3a). In a 2D transport system, the amplitude of MR depends only on the perpendicular component of the applied magnetic field $H\cos\theta$ to the 2D plane. The curves shown in Figure 3a represent the MR data measured at 10 K with different angles. It is evident that the value of MR decreases significantly with increasing θ over the whole magnetic field range, but particularly in the low-field region. For example, the MR obtained in 1 T at 0° is nearly 6 times larger than that at 90° (here MR is maximized at $\theta=0^\circ$). To show the relationship between MR and the perpendicular component of a magnetic field more clearly, we plotted the MR curves as a function of $H\cos\theta$ in Figure 3b. Very interestingly, all the curves obtained at different angles merge into a single curve when the perpendicular magnetic field $H\cos\theta$ is smaller than 1 T, below which the WAL effect dominates the electrical transport. This strongly suggests that the WAL in BP is 2D in nature. Moreover, as shown in Figure 3c, when the external magnetic field rotates to the angle $\theta = 90^\circ$ (H is parallel to the ac -plane and perpendicular to the current), the WAL effect disappears as surface channels are no longer present to contribute to the MR effect, which is also consistent with a 2D nature. Further, we have performed the angle-dependent transport measurements at 11 K and 2 K (see Fig. S4). It is found that the WAL observed at 11 K is also 2D in nature, whereas the WL at 2 K shows a 3D feature. Based on the results, we can ~~already~~ perceive that the WAL effect in bulk BP is dominated by the surface transport.

To gain a deeper understanding of the WAL effect in BP, we analyze the data more quantitatively by fitting the data to the Hikami-Larkin-Nagaoka (HLN) model [43]:

$$\Delta G(H) = \frac{\alpha_0 e^2}{2\pi^2 \hbar} \left[\psi\left(\frac{1}{2} + \frac{\hbar}{4eHL_\phi}\right) - \ln\left(\frac{\hbar}{4eHL_\phi}\right) \right], \quad (1)$$

where $\Delta G = G(H) - G(0)$, $G(H)$ and $G(0)$ are the respective conductivity at magnetic field H and zero, ψ is the digamma function, L_ϕ is the phase coherence length, and the coefficient α_0 is the estimated number of independent channels contributing to the interference: $\alpha_0 = -0.5$ for a single channel. In the Equation 1, we assume one dephasing rate to fit the WAL effect. However, at 8 K, the field-dependence MR curve shows a coexistence of WAL (in the low field region) and WL (in the high field region). To fit the magnetoconductance which exhibits both WAL and WL at 8 K, we assume one dephasing rate for WAL and another one for WL. Therefore, the HLN model can be modified as follow [35]:

$$\Delta G(H) = \sum_{i=0,1} \frac{\alpha_i e^2}{\pi \hbar} \left[\psi\left(\frac{1}{2} + \frac{\hbar}{4eHL_{\phi i}}\right) - \ln\left(\frac{\hbar}{4eHL_{\phi i}}\right) \right], \quad (2)$$

where the coefficients α_0 and α_1 stand for the weights of WAL and WL contributions, respectively, and $L_{\phi i}$ is the corresponding phase coherence length. In Figure 4a, we present the low-field ΔG at temperatures ranging from 8 K to 12 K. It is evident that the data of ΔG can be well described by the HLN model. The corresponding values of α_0 and L_ϕ for WAL were then obtained from the fitting as shown in Figure 4b and Figure 4c, respectively. As shown in Figure 4b, the value of L_ϕ decreases continuously with increasing temperature, indicating that WAL weakens as temperature increases. The value of L_ϕ for WAL can be expressed as: $L_\phi = \sqrt{D\tau_\phi}$, where D is the diffusion constant and τ_ϕ is the dephasing time. As shown in Figure 4b, the temperature-dependent L_ϕ is fitted well with a power law of $L_\phi \propto T^{-0.1}$. This power law leads to an effective exponent of temperature $p = 0.2$ for the dephasing time, $\tau_\phi \propto T^{-p}$; this is considerably lower than the expected value of 1 for the quasielastic Nyquist electron-electron scattering process in 2D, and indicates the existence of a weakly temperature-dependent carrier dephasing process. On the other hand, as shown in Figure 4c, a negative α_0 as large as -16.7 was obtained at 16 K, which greatly deviates from the theoretical values of -0.5 or -1. This could be attributed to the dominant contribution of the bulk at high temperatures, as observed in half-Heusler topological insulators such as ScPtBi or LuPdBi [39, 40]. As the temperature decreases, the bulk conductivity decreases dramatically, whereas the surface conducting channels play a more important role in the total conductivity leading to gradual reduction in the absolute value of α_0 . At 9 K, we can obtain an absolute value of α_0 as large as 0.58, which agrees with the theoretical value of α_0 and confirms

the 2D-dominated WAL effect.

Actually, the total measured conductance of the sample should combine both the surface and bulk contributions. As shown in Figure 3a, the non-zero MR at $\theta = 90^\circ$ strongly indicates the existence of bulk channels. Therefore, we must ask why the low-field MR curves at different angles still overlap and why the absolute value of α_0 is still close to 0.5. This question can be answered by considering the bulk-surface coherent transport, which makes the bulk and surface channels coherently couple with each other and form a single transport channel [25]. This model can also explain the deviation of the MR curve from the $H\cos\theta$ curve in the high-field regime. As shown in Figure 3b, when the magnetic field increases above 2 T, the external magnetic field breaks the time-reversal symmetry, leading to the strong suppression of the 2D-dominated WAL effect. In this scenario, due to the weakening of 2D channels, the 3D bulk channels decouple from the surface-bulk coupling. Therefore, we obtain a 3D-dominated MR in the high-field region and MR and $H\cos\theta$ curves which deviate from each other. Based on the results above, we found that both the angle-dependent magnetoconductivity and the HLN fitting results show obvious surface-bulk coherent features. This is ~~strongly~~ regarded as an ~~powerful~~ evidence for the existence of SRS in BP.

Another issue to be addressed is the extremely small absolute value of α_0 ($\alpha_0 = 0.05$) obtained at 8 K. This is closely related to competition between the WAL and WL effects. Since WL gives a positive coefficient α_1 and the WAL effect was weakened significantly by the WL effect, the deduced value of α_0 was significantly reduced [30, 34]. The crossover between the WAL and WL effects has also been observed in another 2D material, graphene, in which the transition occurs because elastic scattering weakens the chiral nature of Dirac fermions [31-33]. In this work, the WAL effect was not detected in all of the samples, though they were cleaved from the same crystal (see Fig. S5). We further found that the WAL effect in BP can only be observed in relatively high-quality samples that have fewer impurities. The WAL effect is strongly suppressed as the sample quality declines (see the Discussion Section in the Supplementary Materials). It is supposed that the origin of the suppression of WAL in BP and graphene is similar, though they possess completely different band structure. As is known to us, graphene is a semimetal and exhibits a metallic temperature dependence of the resistivity. Its band structure is completely different from that of the semiconductor BP. However, no matter graphene or BP, at the low

temperature, the impurity scattering plays an important role in their transport of electrons. In graphene, if the density of impurities reaches a certain values, the impurities scattering can make the electron obtain 2π phase, which breaks the π Berry phase of the band structure and makes quantum interference gradually change from destructive (WAL) to constructive (WL). In the case of BP, at the low temperatures, the impurity ionization dominates the transport of electrons and the obvious three-dimensional WL effect is observed below 8 K. In the temperature range of 9-16 K, the SRS dominated the transport behaviors of electrons and the possible π phase results in a WAL effect. With the decrease of temperature, the role of impurities becomes more and more important, which makes the phase of electron gradually transform from π to 2π and therefore a crossover from WAL to WL. On the other hand, in the temperature range of 9-16 K, only WAL effect is observed and we fit the field-dependent MR curves assuming one phase coherence relaxation time. In the case of 8 K, the MR curve shows a coexistence of WAL and WL and we fit it by assuming two relaxation times: one is for WL and the other one is for WAL. By using the equation 2, we can divide the relaxation time of WAL (in the low-field region) from that of WL (in the relatively high field region). Actually, we just assume only one relaxation time for WAL effect and therefore it is similar to that in graphene. Based on the results above, we supposed that the suppression of WAL in BP is ~~closely~~ related to elastic scattering (impurities, dislocations, or defects scattering) in BP, which may break the possible π Berry phase or produce an effective random magnetic field that destroys the interference, similar to the case in graphene [34].

4. Conclusions

In summary, we have observed surface-bulk coherent features by performing angle-dependent magnetotransport measurements on exfoliated in a perpendicular to the (0/0) surface within a narrow temperature range of 8 - 16 K, where the bulk conductivity decreases drastically. This result presents ~~a possible strong~~ evidence for the existence of SRS. The key to observing this feature in bulk BP is using relatively high quality samples of BP. The surface transport can be strongly suppressed by scattering caused by impurities (elastic scattering) which results in bulk transport. Our results suggest that the SRS near the Fermi Level could play a key role in electronic transport when the bulk conductivity is greatly suppressed, and therefore could pave the way for developing further BP-based nanoelectronic devices.

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FIG. 1. (a) The perspective side view of the crystal structure of bulk BP. The black arrows show the crystallographic axis of BP (b) Photograph of the devices used for transport measurements. The Hall bar configurations were pasted on the freshly cleaved (0/0) BP plane. (c) The corresponding schematic diagram of the Hall bar configurations. (d) The temperature dependence of ρ_{xx} in zero-magnetic field for two representative samples, A and B. Inset: the corresponding $\ln(\rho_{xx})$ versus $1/T$ plot. The energy gap E_g at low temperatures can be fitted by $\rho_{xx}(T) = \text{constant} \times \exp(-E_g/2k_B T)$, and the corresponding E_g of the two samples was obtained to be 20.1 meV and 16.2 meV.

FIG. 2. (a) The magnetic field dependence of MR between 2 K and 20 K with current flowing along the c -axis (in the ac -plane) and magnetic field parallel to the b -axis. Each curve is shifted vertically with equidistance to highlight the peculiar WL and WAL crossover driven by the temperature. The WAL and WL cusp was embedded on a broad parabolic or linear background. The inset presents the schematic of Hall bar configurations for measuring ρ_{xx} (the electrical configuration for measuring Hall resistivity ρ_{xy} is not presented). (b) The field-dependent MR over the temperature range of 2 - 20 K with current flowing along the b -axis (in the ab -plane) and magnetic field parallel to the c -axis. The left inset shows the schematic of measurement.

FIG. 3. (a) The magnetic field dependence of MR at 10K with magnetic field up to 7T at various angles. The left inset shows the configuration of the measurements, where θ is the angle between the magnetic field and the b -axis. (b) The curves of MR as a function of the perpendicular magnetic field component $H\cos\theta$. (c) The field-dependent MR curves at different temperatures at angle $\theta = 90^\circ$, where H is parallel to the ac -plane.

FIG.4. (a) ΔG curves at a series of temperatures (color circles). The HNL fitting lines are presented as black solid lines. (b) The temperature dependence of L_ϕ over the temperature range 8-16 K. (c) The fitted values of $|\alpha_0|$ for WAL over the temperature range 8-16 K. Inset: the values of $|\alpha|$ between 8 K and 11 K.