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Low-Energy Surface States in the Normal State of α -PdBi₂ Superconductor

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Topological superconductors as characterized by Majorana surface states have been actively searched for their significance in fundamental science and technological implication. The large spin-orbit coupling in Bi-Pd binaries has stimulated extensive investigations on the topological surface states in these superconducting compounds. Here we report a study of normal-state electronic structure in a centrosymmetric α -PdBi₂ within density functional theory calculations. By investigating the electronic structure from the bulk to slab geometries in this system, we predict for the first time that α -PdBi₂ can host orbital-dependent and asymmetric Rashba surface states near the Fermi energy. This study suggests that α -PdBi₂ will be a good candidate to explore the relationship between superconductivity and topology in condensed matter physics.

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Introduction. Recent discovery of quantum materials with gapped bulk but protected metallic surface states has sparked a revolution in condensed matter physics. Among them, although the topological insulators [1, 2] are now popular, the topological superconductors (TSCs) [3–5] are rare. Nevertheless, the TSCs are of great interest because they can host protected Majorana surface states [5–12], arising from a nontrivial topology of the bulk Bogoliubov-de-Gennes quasiparticle wavefunctions [13]. The Majorana fermions, that is, hypothetical particles originating from the field of particle physics, have been suggested [14] as a candidate for quantum bits robust against decoherence, motivating intense efforts to materialize the topological superconducting state.

It is noteworthy to mention that several theoretical proposals have been made to realize the Majorana states in the condensed matter, from the superfluid phase of cold atoms to the interface of the heterostructure with a normal metal, ferromagnetic insulator, superconductor [15–18]. The key ingredients of these systems are swave superconducting pairing, Rashba spin-orbit interaction, and ferromagnetic exchange interaction. Therefore, searching for the topological superconductivity among heavy element-based compounds is promising to realize Majorana fermion in the real material. Since the existence of the surface state, the heavy element-based compound have the strong intrinsic Rashba interaction and the superconducting pairing to drive a TSC under external magnetic field.

To date, possible topological superconductivity has been suggested in Cu- or Sr-intercalated Bi_2Se_3 [19– 25], In-doped SnTe [26], highly-pressured Bi_2Te_3 and Sb_2Te_3 [27, 28], point-contact induced pressure in Cd_3As_2 [29], and hybrid superconductor-semiconductor or -topological insulator heterostructures [30–32]. However, Pd-Bi family [33–35] of superconductors are particularly interesting because both Bi and Pd atoms intrinsically maintain strong spin-orbit coupling (SOC). The possibility of the TSC drives the incarnation of the research on Pd-Bi compounds. The noncentrosymmetric α -BiPd [36] exhibits a superconducting state at $T_c = 3.8$ K. If the TSC is realized in α -BiPd, the mixture of singlet and triplet pairings is expected due to the absence of inversion center and the strong SOC effect. However, the full gapped superconducting density of states (DOS) was revealed with the scanning tunneling spectroscopy measurement [37]. Also the angle-resolved photoemission (ARPES) experiment demonstrated that the Dirac cone was located at 700 meV below E_F [38–40]. The other member of this Pd-Bi family, PdBi₂, preserves the inversion symmetry, and it has two types of the structures, depending on the annealing temperature. Recently, β -PdBi₂ had been reported as a multi or single superconducting gap [41–44]. The Dirac point in this structure was detected 2 eV away from E_F [41]. Finally, the absence of the TSC was established by the point-contact Andreev reflection spectroscopy [45]. Although the existence of the topologically protected surface states in α -PdBi and β -PdBi₂ has been confirmed, their location of being far away from the Fermi energy negates the possibility of the topological superconducting behavior on the surfaces of these compounds, or in another word, these surface states has no effect on the bulk of the superconductor [43].

More recently, α -PdBi₂ has also been investigated by the penetration depth measurement [46]. Although the data seem to suggest that the superconducting order parameter has a similar pairing symmetry across the Pd-Bi family of superconductors, the much larger penetration depth itself as deduced for the zero-temperature limit prevents one from ruling out the existence of surface states in this material. This ambiguity suggests the need of a detailed electronic structure study even in the normal state of α -PdBi₂, which is currently not available. Here we report the electronic structure of the bulk and slab structure in α -PdBi₂ and investigate the characteristics of the surface state. We find α -PdBi₂ might be a good candidate for the TSC with the existence of low-energy surface states.

Method. We employed the density functional theory (DFT) calculation with the full-potential linearized augmented plane wave method implemented in the WIEN2k package [47]. The spin-orbit coupling was considered to describe the heavy elements of Bi and Pd. The Perdew-Burke-Ernzerhof [48] exchange-correlation functional was adopted. The experimental crystal structure was used without the structural relaxation calculation. The α -PdBi₂ has a centrosymmetric monoclinic crystal structure of space group C2/m. The experimental crystal structure has a=12.74Å, b=4.25Å, c=5.665Å, $\alpha = \gamma = 90^{\circ}$, and $\beta = 102.58^{\circ}$ [35]. The angle between *a*-axis and *c*-axis is 102.58° . *a* is two times longer than b and c. There are four formula units in the primitive unit cell to have four Pd and eight Bi atoms. Each Bi or Pd atom makes a mono-atomic single layer stacked along *a*-axis. The crystal structure was visualized in Fig. 1(b). There are two types of Bi atoms such as Bi-A and Bi-B atoms with the same local symmetry. 1-4 atoms and 5-8 atoms in Fig. 1(b) correspond Bi-A and Bi-B, respectively. The inversion symmetry is maintained in (1, 2), (3, 4), (5, 6), and (7, 8) pairs.

Results and discussions. At the first stage, we performed the DFT calculation of the bulk PdBi₂ to comprehend the underlying electronic property. The valence states of Pd are made up with $4d^8$ and $5s^2$. The valence state of Bi is expected to have $6p^3$. But, the occupancy of Pd 4d and Bi 6p states are computed to show about 8.25 and 1.15 electrons, respectively. The state of Pd 5s is almost empty. Around two electrons for each Bi and Pd ions are not included within each muffin radius. Missing electrons would be distributed in the interstitial region to indicate the covalent bond. Also, we investigated the DOS in the bulk α -PdBi₂. Figure 1(a) provides the DOS for Bi-A p, Bi-B p, and Pd d states. The DOSs of Bi-A p and Bi-B p show uniform distribution in this energy range together. Pd d states are mostly occupied to show the several manifestive peaks between -4 and -2 eV. The valence states are well delocalized to show a metallic feature. Pd d and Bi p states show strong hybridization with the similarity of peaks shown in their DOS. The strong SOC might be associated with the topological surface state through the hybridization.

We examined the surface state in the slab geometry. Since the bulk structure has the alternating stack of sin-



FIG. 1. (color online) (a) The density of states (DOS) in the α -PdBi₂ bulk . The DOS for Bi-A p (dark green), Bi-B p (green) and Pd d (red) electrons were provided between -6 and 5 eV. (b) The base-centered monoclinic crystal structure of the α -PdBi₂ bulk, drawn by VESTA package [49]. The purple and grey colors represent Bi and Pd atoms. There are two types of Bi atoms such as Bi-A (1-4) and Bi-B (5-8). The appearance of the same number is due to the periodic boundary condition. Hereafter, the energy zero in the DOS denotes the location of the Fermi energy E_F .

gle Bi and Pd layers along a axis, the bulk structure is elongated five times to become a $5 \times 1 \times 1$ unit cell. The vacuum of 40 a.u. (i.e., Bohr radius) was inserted into the $5 \times 1 \times 1$ to construct a slab structure. The slab structure is presented in Fig. 2(c). The inversion symmetry was maintained to carry out an efficient slab calculation. However, the global inversion symmetry does not affect the numerical result but is associated with computational cost. It is noteworthy that both interfaces are Bi1 layers.

We investigated how the existence of the interface would affect on the electronic structure. Figure 2(a)shows the DOS for Bi1-3 and Pd1-2 atoms as marked in Fig. 2(c). The DOS of Bi1 and Pd1 provides the additional high peak at the Fermi energy. The DOS of Bi2 does not show such a peak around E_F . Therefore, the surface state disappears drastically as going inside into the bulk. Geometrically, the distance between Bi1 and Pd1 is also shorter than that between Bi1 and Bi2. As such, the hybridization between Bi1 and Pd1 might be stronger than that between Bi1 and Bi2. The DOS of Bi3 and Pd2 located deep inside from the surface show the bulk-like DOS. We note that the DOS of Bi1-3 located around -4.5 and 3 eV shows some deviation. This difference might be attributed to modified bonding and anti-bonding states arising from the surface states. Interestingly, the DOS of the surface states is higher than that of the bulk states at E_F . When α -PdBi₂ enters the superconducting state, the surface states could affect



FIG. 2. (color online) (a) The total density of states of the selected atoms in the $5 \times 1 \times 1 \alpha$ -PdBi₂ slab. The used atoms are indicated in Fig. 2(c). (b) Schematic drawing of the surface Brillouin zone drawn by Xcrysden package [50]. High-symmetric points are marked to be used in the band structure calculation. Due to the elongation along a-axis in the slab structure, the suppression of the Brillouin zone along k_a is shown. To catch the surface states, the k-points in the $k_a=0$ plane are chosen. (c) The crystal structure of the $5 \times 1 \times 1 \alpha$ -PdBi₂ slab with 40 a.u., drawn by the VESTA package.

the superconducting pairing, which is in striking contrast to the cases of α -PdBi and β -PdBi₂, where the surface states are too far away from the Fermi energy to have any effect on the superconducting pairing.

The band structure for the $5 \times 1 \times 1$ supercell without and with the vacuum were given in Fig. 3(a) and (b), respectively. The insulating gap of around 1.4 eV at A point of the wavevector in the Brillouin zone corresponding to the $5 \times 1 \times 1$ supercell is closed due to the new surface states. Interestingly, the center of the surface bands is located in the proximity of E_F . This surface state is not associated with the global inversion symmetry of the slab structure, but with the local breakdown of the inversion symmetry at the interface between α -PdBi₂ and vacuum. This assumption is confirmed by the two slab geometries with and without the inversion symmetry to produce the same surface states. Since both interfaces of the slab structure have the same local symmetry, the surface state has a two-fold degeneracy. Besides, the red circles marked around the B and Γ points of the wavevector shows the additional clear surface effect around E_F .

To understand the SOC effect on the surface state, the slab band structure with and without SO were compared to each other. The band structure without SOC in Fig. 3(c) shows a parabolic degenerated surface state with one local minimum at the A point. The SOC drives the momentum-dependent splitting (Rashba splitting) of the degenerated surface state to induce several local minimums away from the A point. These SOC-induced Rashba surface states with their energy so close to the Fermi energy opens up a revenue for the emergence of unconventional pairing symmetry at the surface.

The characteristic of the edge state at A was analyzed with the angular-momentum-projected orbitals for each atom in the slab geometry. From the DOS shown in Fig. 2(a), the electronic states derive from Bi1 and Pd1 atoms make up with the surface states. Furthermore, the clarification of the specific angular momentum was investigated. Figure 4(a) and (b) show that the surface edge states consist of Bi1 p_y and Pd1 d_{yz}



FIG. 3. (color online) The band structure of the $5 \times 1 \times 1 \alpha$ -PdBi₂ supercell without (a) and with (b) the vacuum. The slab band structure without the spin-orbit coupling is also provided in the panel (c). The red line and dots are guided to the place we want to discuss.



FIG. 4. (color online) Angular-momentum-projected slab band structure for (a) Bi1 p_y and (b) Pd1 d_{yz} orbitals. The schematic structure with Pd1- d_{yz} and Bi1- p_y orbitals is provided in the panel (c). The other atoms except Pd1 and Bi1 are removed to show the clear relation between Bi1 and Pd1.

orbitals. Schematic real-space wavefunction distribution for these two orbitals are displayed in Fig. 4(c). Bi1 and Pd1 sites have the coordinates of (0.36388,0.61235,0.0) and (0.34137,0.6559,0.5), respectively. The x- and ycomponents of their coordinates are very close to each other. They are separated away along c-axis. The relative location between Bi1 p_y and Pd1 d_{yz} suggests the formation of π -bonding along the c-axis. This specific bonding nature might lead to the anisotropic and orbitaldependent surface states.

The detailed topology of the edge states at the A point was examined with the two-dimensional eigenvalues as a function of k_b and k_c around the A point. Figure 5 shows clearly the existence of the Dirac-cone at the A point.



FIG. 5. (color online) The formation of the Dirac cone at the A-point of the Brillouin zone. The eigenvalues of the two surface states are plotted around the A point in the k_b - k_c plane.

The energy of the Dirac point is 0.017 eV above E_F . The slight tuning of the chemical potential could enable the Dirac cone to be established at E_F . The dispersion along the k_c -direction is much steeper than that along the k_b -direction. This asymmetric Dirac cone is associated with the π bonding along the *c*-axis. The asymmetric geometry of the surface states suggests the momentum dependent effective mass of the Dirac quasiparticles. Future ARPES experiments should be able to detect this asymmetric feature of the Dirac cone in α -PdBi₂. We would like to note that although there is no theoretical formalism to directly calculate the topology nature of the bulk α -PdBi₂ metal, the fact that the contribution to the Dirac-like surface states is mainly from the Bi-*p* orbitals seems to suggest that the bulk electronic structure should be topologically nontrivial.

Fu and Kane [51] proposed that topological superconductivity could be achieved through the creation of a (p_x+ip_y) -wave superconducting pairing symmetry on the Dirac-cone type surface states inside the topological insulator band gap, when the topological insulator is in proximity to a conventional s-wave superconductor. Here the surface states are buried in the metallic bands. Therefore, whether the Cooper pairing of the surface states in α -PdBi₂ form a TSC remains an open question, for which the superconducting pair potential must be incorporated explicitly. Recently, it has been shown for both doped topological insulators [52] and iron-based superconductors [53] (both are metallic in the normal state) that the TSC with an s-wave pairing symmetry on the surface can be realized in an appropriate range of carrier doping. A similar conclusion can be drawn for α -PdBi₂.

Summary. Through a systematic analysis of electronic structure of α -PdBi₂ within the DFT framework, we have identified for the first time the existence of low-energy surface states in the proximity of E_F in this compound. The bulk DFT calculation shows the delocalized and covalent valence states. The existence of the surface geometry drives the Rashba splitting of the surface state. These split surface states meet at the A point to produce a Dirac cone in the Brillouin zone. The Dirac cone is generated by the bonding between Bi1- p_u and Pd1 d_{uz} orbitals in the interface. We have also shown the Dirac cone exhibits orbital-dependent and anisotropic momentum distribution. Since these Dirac states are close to E_F to be easily tunable, the further study of α -PdBi₂ could shed new light to the realization of the TSC. Interestingly this material will provide the ideal platform to manipulate Rashba spin-orbit coupling and s-wave superconducting pairing. When it is in contact with a ferromagnetic insulator, which provides a ferromagnetic exchange interaction, a topological superconductor which host Majorana fermions can be realized [18]. Furthermore, the high-resolution ARPES measurement in this compound will be necessary to confirm the Rashba surface states near E_F .

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