Topological Node-Line Semimetal and Dirac Semimetal State in Antiperovskite 
Cu$_3$PdN

Rui Yu$^1$, Hongming Weng$^{2,3}$†, Zhong Fang$^{2,3}$, Xi Dai$^{2,3}$, and Xiao Hu$^1$†
$^1$International Center for Materials Nanoarchitectonics (WPI-MANA)  
National Institute for Materials Science, Tsukuba 305-0044, Japan  
$^2$Beijing National Laboratory for Condensed Matter Physics,  
and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China  
$^3$Collaborative Innovation Center of Quantum Matter, Beijing 100190, China  
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Based on first-principles calculation and effective model analysis, we propose that the cubic antiperovskite material Cu$_3$PdN can host a three-dimensional (3D) topological Node-Line semimetal state when spin-orbit coupling (SOC) is ignored, which is protected by coexistence of time-reversal and inversion symmetry. There are three closed Node-Line circles in total due to the cubic symmetry. “drumhead” like surface states and flat bands are also derived. When SOC is included, each node-line evolves into a pair of stable 3D Dirac points as protected by C$_4$ rotational symmetry. This is remarkably distinguished from the Dirac semimetals known so far, such as Na$_3$Bi and Cd$_3$As$_2$, both of which have only one pair of Dirac points. Once C$_4$ symmetry is broken, the Dirac points are gapped and the system becomes a strong topological insulator with $(1;111)$ $Z_2$ indices.

I. INTRODUCTION

Band topology in condensed matters has attracted broad interests in recent years. It was prospered by the discovery of two-dimensional (2D) and three-dimensional (3D) topological insulators [16]. These materials exhibit a bulk energy gap between the valence and conduction bands, similarly to normal insulators, but with gapless boundary states that are protected by the band topology of the bulk states. Topological insulators are proposed to have potential applications in the areas of spintronics and quantum computations. Recently, the topological classification of condensed matters has been generalized from insulators to 3D metals. The topological invariant, so called Fermi Chern number, is defined on a closed 2D manifold, such as the Fermi surface, in the 3D momentum space [17,18]. This is essentially the same as Chern number defined in the whole 2D Brillouin zone (BZ) for insulators. Up to now, three types of nontrivial topological metals have been proposed. They are Weyl semimetal [9,12], Dirac semimetal [14,15] and Node-Line semimetal [14,15]. All of them have band crossing points due to band inversion [10]. For Weyl and Dirac semimetals, crossing points locate at different positions which compose Fermi surfaces. For the Node-Line semimetal (NLS), the crossing points around the Fermi level form a closed line. The breakthrough in topological semimetal research happened in material realization of Dirac semimetal state in Na$_3$Bi and Cd$_3$As$_2$, which were firstly predicted by three of the present authors and then confirmed by several experiments [17,20]. Starting from Dirac semimetal, one can obtain Weyl semimetal by breaking either time-reversal [10,11,21] or inversion symmetry [22,25]. Among them, the prediction of Weyl semimetal state in nonmagnetic and noncentrosymmetric TaAs family [26,27] have been verified by experiments [28,33].

The topological Node-Line semimetal (NLS) state is still waiting for its experimental discovery. Three of the present authors have proposed that when spin-orbit coupling (SOC) is neglected, the coexistence of time-reversal and inversion symmetry can protect Node-Line state in 3D momentum space [15]. The all-carbon Mackay-Terrenes crystal (MTC), a kind of 3D periodic network of graphene, is the first possible electronic system to realize NLS. It is heuristic that light element compound can also have nontrivial topology, which is totally different from the common wisdom that strong SOC in heavy element compounds is crucial for topological quantum states. It was also shown that in TaAs mirror symmetry can replace inversion symmetry, which, together with time-reversal symmetry, protects NLS when SOC is neglected. Possible NLS in Cu$_3$P$_2$ [34] was discussed, and it was shown that NLS state can also be realized in a well tuned photonic system [35].

In the present work, based on first-principles calculations and effective model analysis, we demonstrate that the antiperovskite material Cu$_3$PdN is a new candidate for realizing the NLS and "drumhead"-like surface flat band states, which are similar to those in Mackay-Terrenes crystal [15]. Strong SOC will drive the NLS into Dirac semimetal state with three pairs of Dirac points, leading to exotic surface Fermi arcs which can be observed in various surfaces. This is very unique since Dirac semimetals known so far, Na$_3$Bi and Cd$_3$As$_2$, have only one pair of Dirac points. When the C$_4$ symmetry in Cu$_3$PdN is broken, the Dirac points are gaped and the system becomes a strong topological insulator with $Z_2$ indices $(1;111)$. It is well known that the cooperative interactions among lattice, charge, and spin degrees of freedom make antiperovskites exhibit a wide range of interesting physical properties, such as superconductiv-
ity \cite{36}, giant magnetoresistance \cite{37}, negative thermal expansion \cite{38}, and magnetocaloric \cite{39} effect. Our prediction of 3D NLS and Dirac semimetal state in antiperovskites provides a promising platform for manipulating these exotic properties in presence of nontrivial topology.

II. CRYSTAL STRUCTURE AND METHODOLOGY

Crystal structure: The class of perovskite materials have a formula ABX$_3$, where A and B are cations and X is an anion. The antiperovskite materials parallel to perovskite ones except for switching the positions of anion and cation, namely in ABX$_3$ the X stands for an electro-positve cation, while A for an anion. As shown in Fig. 1(a), the cubic antiperovskite Cu$_3$PdN compounds crystallize in the space group of Pm$ar{3}$m of No.221 with nitrogen atom at the center of the cube surrounded by octahedrally coordinated Cu atoms and element Pd is located at the corner of the cube.

Figure 1. (Color online) (a) Crystal structure of antiperovskite compounds Cu$_3$PdN with Pm$ar{3}$m symmetry of No.221 with nitrogen atom at the center of the cube surrounded by octahedrally coordinated Cu atoms and element Pd is located at the corner of the cube. (b) Brillouin zone of bulk and the projected surface Brillouin zones of (001) (blue color) planes. The three Node-Line rings when SOC is ignored and three pairs of Dirac points (red points) when SOC included are schematically shown.

Methodology: Our calculations were performed in the framework of density functional theory, by using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation \cite{40} and the projector augmented-wave potential \cite{41}, as implemented in the Vienna \textit{ab initio} simulation package \cite{42}. The energy cutoff is set to 400 eV for the plane-wave basis. The 19 $\times$ 19 $\times$ 19 Monkhorst-Pack k points are used for bulk calculations. Structural relaxations are performed with forces converged to less than 0.001 eV/Å , and SOC is included self-consistently. To overcome the underestimation of band gap and possible overestimation of band inversion, we employed Heyd-Scuseria-Ernzerhof (HSE) screened Coulomb hybrid density functionals \cite{43} to calculate the bulk electronic structures. The surface band structures are calculated in a tight-binding scheme based on the maximally localized Wannier functions (MLWF) \cite{44}, which are projected from the bulk Bloch wave functions.

III. RESULTS AND DISCUSSIONS

A. Electronic structures

The band structure of antiperovskite Cu$_3$PdN is shown in Fig. 2. The chemical bonding between the Pd atoms and the Cu$_3$N host crystal is not understandable assuming completely filled Cu 3d$^{10}$ or Pd 4d$^{10}$ shells. The d$^{9}$s$^1$ configurations are responsible for such d$^{10}$d$^{10}$ bond. The fatted bands shown in Fig. 2 suggest that the valence and conduction bands are dominated by Pd-4d (blue) and Pd-5p (red) states, which is consistent with the d$^9$p$^1$ configurations. It is also clearly indicates the band inverted at R, where the Pd-5p is lower than Pd-4d by about 1.5 eV. To overcome possible overestimation of band inversion \cite{15}, we employed HSE screened Coulomb hybrid density functionals \cite{43} to confirm that the band inversion remains and the energy gap at R point is slightly reduced to 1.1 eV.

Without SOC, the occupied and unoccupied low energy bands are triply degenerate at R (six-fold degenerate if spin is considered). These states belong to the 3D irreducible representations $\Gamma^+_4$ and $\Gamma^+_5$ of O$_h$ group at R, respectively. We emphasize that, unlike the situation in typical TI such as the Bi$_2$Se$_3$ family compound \cite{1}, the band inversion in Cu$_3$PdN is not due to SOC. To illustrate the band inversion process in Cu$_3$PdN explicitly, we calculated energy levels of $\Gamma^+_4$ and $\Gamma^-_4$ bands at the R point for Cu$_3$PdN under different hydrostatic strains. As presented in Fig. 2(c), the band inversion happens at $a = 1.11a_0$ and the inversion energy increases as further compressing the lattice. The most interesting point of the Cu$_3$PdN bands structure without SOC is that the band crossings due to the band inversion form a closed Node-Line circle because of the coexistence of time reversal and inversion symmetry as addressed in ref. \cite{15}. Same as that in all-carbon MTC \cite{15}, there are three Node-Line circles around the R point due to the cubic symmetry as shown in Fig. 1(b).

When SOC is considered, the six-fold degenerate states are split into one four-fold and one two-fold degenerate states. As shown in Fig. 2(c), there are two four-fold degenerate states close to Fermi energy: the occupied one with $\Gamma^+_4$ symmetry and the unoccupied one with $\Gamma^-_4$ symmetry. Leaving R point to X point, the symmetry is lowered to C$_{2v}$. The four-fold degenerate states at R are split to two-fold degenerate states along R-X direction. The first-principles calculation shows that two sets of bands
with the same $\Gamma_5$ symmetry are close to the Fermi energy and a gap $\sim 0.062$ eV is opened at the intersection as shown in the inset of Fig. 2(b). In order to reduce this SOC splitting and thus achieving NLS, one can replace Pd with lighter elements, such as Ag and Ni. Along R-M direction, the symmetry property is characterized by $C_{4v}$ double group. As indicated in Fig. 2(c), two sets of bands close to Fermi energy belong to $\Gamma_7$ and $\Gamma_6$ representation, respectively. These two sets of bands are decoupled and the crossing point on R-M path is unaffected by SOC. They form a Dirac point near the Fermi energy as shown in Fig. 2(c). This Dirac point is stable because it is protected by crystal symmetry $C_4$ rotation $[47, 48]$. Once $C_4$ rotational symmetry is broken, the Dirac point will be gapped and we can calculate the parities of occupied states at eight time-reversal invariant momenta (TRIM) point. As shown in Table I, the $Z_2$ indexes of this system are $(1;111)$, indicating a strong topological insulator. The

The band structure of Cu$_3$PdN is different from that of antiperovskite Sr$_3$PbO discussed in a previous work $[47, 48]$, where the band inversion happens at $\Gamma$ point and the involved bands belong to the same irreducible presentation, which leads to anti-crossing along $\Gamma$-X direction $[47, 48]$.

Table I. Parity product of occupied states at the TRIM points. The $Z_2$ indexes are (1;111).

| TRIM points | $R$ | $\Gamma$ | $M(\times 3)$ | $X(\times 3)$ |
|-------------|-----|----------|--------------|--------------|
| parity product | +  | -       | -            | -            |

B. Effective Hamiltonian for the 3D Dirac fermion

In order to better understand the band crossing and gap opening discussed above, we derive an low energy effective Hamiltonian based on the theory of invariants in a similar way as that for Bi$_2$Se$_3$ family of materials $[17]$.

We first construct the model Hamiltonian along R-M direction. Let us set R-M along $k_z$ direction. The symmetry in this direction contains the crystalline $C_{4v}$ symmetry and inversion with time-reversal symmetry (PT). As discussed above, the wave functions of low-energy states along R-M direction are $\Gamma_6$ symmetry states with angular momentum $j_z = \pm 1/2$ and $\Gamma_7$ symmetry states with $j_z = \pm 3/2$. The model Hamiltonian respecting $C_{4v}$ symmetry and PT symmetry can be written as

\[
H_{RM} = \begin{bmatrix}
M_1 & 0 & c_2k_+ & c_3k_+^2 + c_4k_+^2 \\
M_1 & c_4k_-^2 + c_3k_-^2 & -c_2k_- \\
M_2 & 0 & M_2 \\
\dagger & & &
\end{bmatrix}
\]  

(1)

up to the second order of $k$ in basis of $|j_2 = \pm 1/2, m_2\rangle$ for $|j_2 = \pm 3/2, m_2\rangle$, where $M_1 = m_p + m_{11}k_z + m_{12}k_Z^2$, $M_2 = m_d + m_{21}k_z + m_{22}k_Z^2$, $k^2 = k_0^2 + k_0^2 + k_z^2$ and $k_\pm = k_x \pm ik_y$. The $C_4$ rotation symmetry requires the matrix element between $|j_2 = \pm 1/2\rangle$ and $|j_2 = \pm 3/2\rangle$ to take the form of $k_\pm^2$ in order to conserve the total angular moment along $z$ direction. Due to PT symmetry and mirror symmetry, all parameters in Eq. (1) can be chosen as real. Their values can be derived by fitting the dispersions to the results of first-principles calculations $[49]$. 

Along $k_z$ direction, the effective Hamiltonian is in diagonal form and the $|\pm 1/2\rangle$ sets and $|\pm 3/2\rangle$ sets are decoupled. Because the energy of $p$ and $d$ orbits are inverted at R point, namely $m_p < m_d$ and $m_{22} < 0 < m_{22}$, the $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ bands can cross at $k_z^2 = [((m_{11} - m_{21})^2 - 4(m_{12} - m_{22})(m_p - m_d))^{1/2} - (m_{11} - m_{21})]/[2(m_{12} - m_{22})]$ point.

The model Hamiltonian along R-X direction can be derived in the same way, which enjoys $C_{2v}$ symmetry and

\[
\begin{align*}
\text{Table I. Parity product of occupied states at the TRIM points. The } Z_2 \text{ indexes are (1;111).}
\end{align*}
\]
PT symmetry. From the first-principles calculations, the states near Fermi energy are characterized by $\Gamma_5$ with $j_z = |\pm 1/2\rangle$. The model Hamiltonian can be written as

$$H_{RX}(k) = \begin{pmatrix} M_1 & 0 & M_3 & c_1 k_- \\ M_1 & c_1 k_+ & -M_3 & 0 \\ M_2 & 0 & M_2 & \dagger \\ M_2 & 0 & M_2 & \dagger \end{pmatrix}$$

(2)

up to the second order of $k$ in basis $\{|j_z = \frac{1}{2}\rangle_p, |j_z = -\frac{1}{2}\rangle_d, |j_z = \frac{1}{2}\rangle_p, |j_z = -\frac{1}{2}\rangle_d\}$. Let us set $k_z$ along R-X direction. The term $M_3 = m_3 + m_31 k_z + m_32 k^2$ conserves the total angular momentum along $z$ direction. It couples the going-down $\Gamma_5$ states and going-up $\Gamma_5$ states and opens a gap at the crossing point shown in Fig. 2(c).

C. Surface states

The band inversion and the 3D Dirac cones in Cu$_3$PdN suggest the presence of topologically nontrivial surface states. In order to see this we calculate the surface electronic states based on TB Hamiltonian from MLWF [5]. We use an iterative method to obtain the surface Green’s function of the semi-infinite system. The imaginary part of the surface Green’s function is the local density of states (LDOS) at the surface. The obtained LDOS on semi-infinite (001) surfaces are presented in Fig. 3.

For the case without SOC, the bulk state is the same as MTC [15] and it is expected to see the same surface flat bands nestled inside the projected Node-Line ring on the (001) surface, namely the “drumhead” states. Figure 3(a) clearly shows the nearly flat surface bands inside the projected solid Dirac cones around $\bar{M}$. The small dispersion of this “drumhead” state comes from the fact that the Node-Line ring is not necessarily on the same energy level due to the particle-hole asymmetry. [14, 15]

Once SOC is further considered, the Node-Line ring will be gapped in general. However, there is an exception. For example, in TaAs family each ring evolves into three pairs of Weyl nodes [26]. In Cu$_3$PdN, each ring is driven into one pair of Dirac points. The (001) surface state band structure in Fig. 3(b) clearly shows the gapped bulk state along $\Gamma - \bar{M}$ direction and the existence of surface Dirac cone due to topologically nontrivial $Z_2$ indices as seen in Na$_3$Bi and Cd$_3$As$_2$. The R-X and R-M bulk band structures will overlap each other when projected onto (001) surface along the $\bar{X} - \bar{M}$ path. The bulk Dirac cones are hidden by other bulk bands. Therefore, it is difficult to identify the detailed connection of Fermi arcs in the Fermi surface plotting as shown in Fig. 4 though some eyebrow-like Fermi arcs can be clearly seen around these projected Dirac points.

IV. CONCLUSION

In summary, we propose that 3D topological Node-Line semimetal states can be obtained in a nonmagnetic and centrosymmetric system Cu$_3$PdN. The “drumhead” like surface flat bands nestled into a projected Node-Line ring have been obtained. Including SOC will drive each Node-Line ring into one pair of Dirac points to host Dirac semimetal state. The surface Dirac cone and the Fermi arcs around projected Dirac cones are observed. The existence of multiple pairs of 3D Dirac points distinguish
this system from existing Dirac semimetals with only one pair. The cubic antiperovskite structure of Cu$_2$PdN makes it a good platform for manipulating ferromagnetism, ferroelectricity and superconductivity realized in a broad class of materials with perovskite structure in presence of nontrivial topology.

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\[ m_p = -1.12 eV, \quad m_d = 0.254 eV, \quad m_{11} = -0.86, \quad m_{12} = 33.6, \quad m_{21} = -0.40, \]
\[ m_{22} = -7.1, \quad m_3 = 0.1, \quad m_{31} = 0.51, \quad m_{32} = -3.1, \]
\[ c_1 = 0.3, \quad c_2 = -0.2, \quad c_3 = 1.2 \quad \text{and} \quad c_4 = 0.95, \]
where the unit of energy is eV and the unit of length is the lattice constant.

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