Symmetry-enforced electronic nodal straight lines in CsNb$_3$SBr$_7$

Qiulin Yuan$^1$, Zhenwei Wang$^{2,*}$, Zhengxuan Wang$^1$, Xianbiao Shi$^3$ and Guangtao Wang$^{1,*}$

$^1$ College of Physics, Henan Normal University, Xinxiang, Henan 453007, People’s Republic of China
$^2$ Department of Physics, Anhui Normal University, Wuhu 241000, People’s Republic of China
$^3$ Key Laboratory of Micro-Systems and Micro-Structures Manufacturing of Ministry of Education, Harbin Institute of Technology, Harbin 150001, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: wangzhenwei@whu.edu.cn and wangtao@htu.cn

Keywords: topological materials, nodal-straight-line semimetals, nonsymorphic symmetry, Berry phase, Hofstadter’s butterfly, optical conductivity

Abstract

We propose the quaternary-compounds CsNb$_3$SBr$_7$ is a nodal-straight-line semimetal candidate based on the first-principles calculations and symmetry analyses. There are a pair of nodal straight lines locate in the $k_z = 0$ plane of Brillouin zone, which is protected by the crystal symmetry. The topological properties of nodal-straight-line state are characterized by the nontrivial Berry phase and Berry curvature. On the (001) surface of CsNb$_3$SBr$_7$, Fermi arcs form the belt-like surface state, connecting the nodal straight lines with opposite chirality. Furthermore, the Hofstadter’s butterfly and optical conductivity are investigated using a slab sample. These results not only reveal the symmetric protection mechanism of nodal straight lines, but also pave a way for exploring the electronic and optical properties of CsNb$_3$SBr$_7$ in further condensed matter physics experiments.

1. Introduction

Topological nodal line quantum states [1–13] of solid materials with unique electronic and phononic properties have triggered tremendous interest in condensed matter physics and material science [14–19]. In recent years, great efforts have been made in search of topological semimetal materials which are featured with nontrivial band degeneracy in momentum space. The novel topological phases exhibit a rich classification in geometry of gapless points, such as nodal rings [20, 21], nodal chains [22–24], and nodal net [25, 26]. They immensely enrich our knowledge of topological physics. In electronic systems, nodal line states usually are characterized by the band-touching points of conduction and valence bands near Fermi energy. Its important signature is the drum-head like surface state, which is flat in energy and filled inside the projection of the closed nodal line [7]. The intriguing drum-head like surface state provides an important platform to realize the strong electronic correlation effect and superconductivity [17–19]. Nowadays, thousands of nodal line semimetals have been predicted, and some of them are discovered in the experiment [27–31]. These works compose the topological material database [32–35] and greatly promote the studies of physical properties of topological materials.

Very recently, many phononic nodal-straight-line states have been reported in solid materials [36–38]. As is known, the existence of nodal line states is intimately associated with crystal symmetries. After investigating the conditions under which nodal straight lines occur, we found that the nodal straight lines can be classified into two types. One is the accidental degeneracy, nodal straight lines located in Brillouin zone (BZ), such as nodal straight lines in Rb$_2$Sn$_2$O$_3$ [37]. Its matrix elements of Hamiltonian vanish without physical reasons. The other is the symmetry-enforced degeneracy. Nodal straight lines locate on the high-symmetry lines of BZ, such as nodal straight lines in MgB$_2$ [36]. However, the ideal nodal straight lines have not been discovered in BZ of the realistic materials. The physical properties of nodal-straight-line...
semimetals also need to be further explored, which is important for future experimental probes and possible applications.

In this work, based on the first-principles calculations and symmetry analyses, we theoretically proposed that the quaternary-compounds CsNb$_3$SBr$_7$ is a topological nodal-straight-line semimetal candidate. Due to the protection of crystal symmetries, bands are inevitably degenerate and form two parallel nodal straight lines located in the $k_z = 0$ plane of BZ. The nodal straight lines bring nontrivial topological properties and exotic belt-like surface states on the (001) surface of CsNb$_3$SBr$_7$, which can be verified by the angle-resolved photoemission spectroscopy (ARPES) experiments. Furthermore, the Hofstadter’s butterfly and optical conductivity of CsNb$_3$SBr$_7$ are investigated using a slab sample, which is important for the further condensed matter physics experiments.

2. Crystal structure and computational methods

Quaternary-compounds CsNb$_3$SBr$_7$ crystallizes in monoclinic crystal structure with the nonsymmorphic space-group $P2_1/c$ (No. 14). Its lattice constants are $a = 10.38$ Å, $b = 7.16$ Å and $c = 19.57$ Å. The angles between crystal axes are $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 82.31^\circ$, respectively [39]. The primitive cell of CsNb$_3$SBr$_7$ including 48 atoms is shown in figure 1(a). Clusters of Nb atoms are linked by Nb–S bonds, forming an infinite chains. The adjacent chains are bridged by Cs and Br atoms. The first BZ of CsNb$_3$SBr$_7$ crystal is illustrated in figure 1(b), which is used in following discussions.

The numeral calculations are performed by Vienna *ab initio* simulation package (VASP) [40, 41] with the generalized gradient approximation of Perdew–Burke–Ernzerhof type exchange–correlation potential [42, 43]. The cut-off energy is set to 500 eV, and the maximum force is set to 0.01 eV. A $9 \times 13 \times 7$ Monkhorst–Pack $k$-point grid [44] is used for the self-consistent calculations. The nonlocal Heyd–Scuseria–Ernzerhof (HSE) hybrid functional calculations [45] are also used to check the band structure. The irreducible representations of bands are calculated using the IRVSP program in conjunction with VASP [46]. The tight-binding model is obtained by constructing maximally localized Wannier functions (MLWF) [47, 48]. Topological surface states are calculated by using iterative Green function method [49] as implemented in the WANNIERTOOLS package [50]. The Hofstadter’s butterfly and optical conductivity of CsNb$_3$SBr$_7$ were calculated using the tight-binding propagation method (TBPM) [51], which is based on the numerical solution of the time-dependent Schrödinger equation without the diagonalization of the Hamiltonian matrix.

3. Results and discussion

3.1. Electronic structure and topological properties

The band structure of CsNb$_3$SBr$_7$ without SOC is presented in figure 2(a). One observes that conduction and valence bands touch in $\Gamma$–$A$ and $\Gamma$–$B$ high-symmetry lines, indicating CsNb$_3$SBr$_7$ is a semimetal. Figure 2(b) is the enlarged view of band structure along the $\Gamma$–$A$ direction. Through calculating the irreducible representations of bands, we found that two crossing bands belong to the one-dimensional representation $\Gamma_1$ and $\Gamma_2$ of $C_1$ point group [52], respectively. According to the Schur’s lemma, the two bases belonging to two different irreducible representations are orthogonal to each other. Hence, the two bands cross without opening a gap, resulting in a crossing point band degeneracy. Figure 2(c) is the band structure of CsNb$_3$SBr$_7$ with SOC. Comparing to the result in figure 2(b), we found the crossing bands open an energy gap of 5 meV under the effect of SOC. Although SOC can induce the crossing bands to open energy gaps, the gap is too small to be measured by the ARPES experiment. Therefore, the effect of SOC can be ignored, and CsNb$_3$SBr$_7$ is viewed as a nodal-straight-line semimetal. Similar situations also arose in nodal line semimetal ZrSiS that had been experimentally confirmed [53].

Next, we calculate the three-dimensional band dispersion of CsNb$_3$SBr$_7$ in the $k_z = 0$ plane of BZ. The result is shown in figure 3(a). We find that a band crossing appears in the momentum space, which implies that gapless points form the nodal straight lines in CsNb$_3$SBr$_7$. To clearly illustrate that the nodal straight lines are straight, we plotted the distribution of energy gap between two crossing bands in $k_z = 0$ plane of BZ, as shown in figure 3(b). The red straight lines indicate the location of gapless points. Different from the nodal straight lines in Rb$_2$Sm$_2$O$_3$ [37], the gapless points accidentally form the very straight nodal lines in CsNb$_3$SBr$_7$. In order to clarify the topological property of nodal straight lines, we calculated the Berry phase...
Figure 1. (a) The crystal structure of CsNb$_3$SBr$_7$. (b) The bulk and surface BZ projected onto the $k_x$ and $k_z$ directions.

Figure 2. (a) The band structure of CsNb$_3$SBr$_7$ without SOC. There are two crossing points near Fermi energy. (b) The enlarged band structure marked by a black box in (a). The two crossing bands belong to irreducible representations $\Gamma_1$ and $\Gamma_2$, respectively. (c) The band structure of CsNb$_3$SBr$_7$ with SOC. The crossing bands open a small gap (about 5 meV) in the $\Gamma$–A high-symmetry line.

of one dimensional systems $H_{k_{l}}(k_z)$ parameterized by the in-plane momentum $k_l$, where $k_l$ is the path of $-B$–$\Gamma$–$B$. The Berry phase related to the integration path can be expressed by following equation:

$$\gamma_n = \oint A_n(k) \cdot dl,$$

where $A_n(k) = i\langle \psi_n(k) | \nabla_k | \psi_n(k) \rangle$ is the Berry connection. $\psi_n(k)$ is Bloch wave function of the occupied states. $l$ is a closed path along the $k_z$ direction due to the periodicity of BZ. In the one-dimensional parameterized systems, the Berry phase equals $\pi$ for $k_l$ inside the nodal straight lines, while it equals zero for $k_l$ outside the nodal straight lines, as shown in figure 3(c). It clearly shows that the Berry phase gets a jump of $\pi$ along the $-B$–$\Gamma$–$B$ path. Furthermore, we have calculated the Berry curvature distributions of nodal straight lines in CsNb$_3$SBr$_7$. Berry curvature is calculated by the following equation [54]:

$$\Omega(k) = \nabla_k \times A_n(k).$$
Figure 3. (a) The three-dimensional band structure of crossing bands in the \( k_z = 0 \) plane of BZ. (b) The distribution of energy gap between the crossing bands in the \( k_z = 0 \) plane of BZ. The red lines indicate the shape and position of nodal straight lines. (c) The variation of Berry phase along the –B–\( \Gamma – B \) high-symmetry line. (d) The variation of Berry curvature \( \Omega_z \) along the \( –B–\Gamma – B \) high-symmetry line.

Figure 3(d) shows the distributions of Berry curvature \( \Omega_z \) along \( –B–\Gamma – B \) high-symmetry line. One can find that the Berry curvature \( \Omega_z \) display sharp peaks in the positions of nodal straight lines, which indicates two nodal straight lines within the BZ have opposite chirality. Thus, there will be belt-like arcs connecting the nodal straight lines with opposite chirality.

3.2. Symmetry analyses of the degenerated bands

The existence of topological nodal straight lines is intimately connected with crystal symmetries, raising the following question: what is the symmetry required for the nodal straight lines appear in BZ of CsNb\(_3\)SBr\(_7\)? Beside identity \( E \), CsNb\(_3\)SBr\(_7\) only contains four symmetry operations: inversion \( P \), time-reversal \( T \) and two nonsymmorphic symmetries: a glide mirror symmetry about the \( xy \) plane, i.e., \( \tilde{M}_z = \{ M_z | 0, \frac{1}{2}, \frac{1}{2} \} \), and a twofold rotation symmetry along \( z \) axis, i.e., \( \tilde{C}_{2z} = \{ 200| 0, \frac{1}{2}, \frac{1}{2} \} \) which are the products of symmetry operators and fractional translational vectors in the unit of the lattice constant.

We first consider the \( \tilde{M}_z \) symmetry, which has the invariant subspace in the \( k_z = 0 \) plane. After applying \( \tilde{M}_z \) twice, we note that the \( x \) and \( z \) coordinates keep invariant, but \( y \) coordinate will be shifted by one lattice spacing. As a result, \( \tilde{M}_z^2 | \psi_k \rangle = e^{-i k_y b} | \psi_k \rangle \) for each Bloch state in the \( k_z = 0 \) plane. When \( k_y = \pm \pi/b \), the \( \tilde{M}_z^2 = -1 \), which generates the Kramers-like degeneracy. In other words, for any energy eigenstate \( | \psi \rangle \) with \( M_z \) eigenvalue \( g_x \), it must have a degenerate partner \( \tilde{M}_z | \psi \rangle \) with \( \tilde{M}_z \) eigenvalue \(-g_x \). Next, we turn to investigate the band-crossing points that are not isolated and form the nodal straight lines in BZ, as illustrated in figure 3(b). Because each state is double degeneracy at \( k_y = \pm \pi/b \), and the degenerate partners have opposite \( \tilde{M}_z \) eigenvalues \( \pm g_x \), which can be labeled as \((+,−)\). On the other hand, the corresponding four states are not required to be degenerate at \( \Gamma \), where the \( M_z \) eigenvalues are \((−,−,+,+)\) for the states in ascending order. Focusing on the two middle bands, they have opposite \( \tilde{M}_z \) eigenvalues, and their ordering is inverted. As a result, they must cross, forming the nodal straight lines in BZ.

Besides, the combined operation \( \tilde{C}_{2z} T \) bring in an additional band degeneracy in the \( k_z = \pm \pi/c \) plane. Due to the periodic boundary condition, the momentum in \( k_z = \pm \pi/c \) plane is invariant under \( \tilde{C}_{2z} T \) operation. After applying \( \tilde{C}_{2z} T \) twice, the \( x \) and \( y \) coordinates keep invariant and \( z \) coordinate will be...
shifted by one lattice spacing. As a result, \((\tilde{C}_2 T)^2 |\psi_k\rangle = e^{-i k_z \cdot c} |\psi_k\rangle\) for each Bloch state in \(k_z = \pm \pi/c\) plane. Consequently, \((\tilde{C}_2 T)^2 = -1\) for any \(k\) point in the \(k_z = \pm \pi/c\) plane, indicating the Kramers-like double degeneracy. These symmetry analyses agree well with the results originated first-principles calculations.

### 3.3. Topological surface states and Fermi arcs

The nontrivial topological properties of nodal straight lines are always accompanied by the exotic surface states and Fermi arcs. The momentum-resolved surface density of states (DOS) along the high-symmetry lines of (001) surface BZ is shown in figure 4(a). It is clearly visible that the bulk conductivity state and valence state touch in the high-symmetry line \(\tilde{\Gamma} \rightarrow \tilde{\Gamma}'\), and a surface state connects the projections of two nodal points. Different from conventional drum-like surface state, the nontrivial nodal straight lines own belt-like surface state [36]. To understand the belt-like surface state, we plot the isoenergy plane of surface state spectrum at the Fermi energy, as shown in figure 4(b). It can be viewed as countless broken Fermi arcs nest between the nodal straight lines with different chirality. In addition, the corresponding surface state and Fermi arcs on the (100) surface of CsNb$_3$SBr$_7$ have been shown in figures 4(c) and (d). These results can be verified by ARPES experiments.

### 3.4. Electronic and optical properties

In order to investigate the electronic and optical properties of CsNb$_3$SBr$_7$, we constructed a 20-unit-cells-thick slab sample with open boundary conditions in the \(z\) direction, containing \(500 \times 500 \times 20\) cells. The DOS is calculated by Fourier transform of the time-dependent correlation functions

\[
\rho(\varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \psi | e^{-i H t} | \psi \rangle dt,
\]

in which, the Hamiltonian is originated from the maximally localized WFs, the time evolution operator \(e^{-i H t}\) is obtained by standard Chebyshev polynomial representation, and the \(|\psi\rangle\) is a random superposition of all the basis states in real space, i.e.,

\[
|\psi\rangle = \sum_i a_i |0\rangle,
\]
Figure 5. (a) The DOS of CsNb$_3$SBr$_7$ calculated using the TBPM method without SOC. (b) The DOS of slab CsNb$_3$SBr$_7$ calculated using the TBPM method without SOC. (c) The Hofstadter’s butterflies of slab CsNb$_3$SBr$_7$ with magnetic field less than 50 T. Color bar stands for the value of DOS. (d) The optical conductivity of slab CsNb$_3$SBr$_7$.

where $a_i$ are random complex numbers normalized as $\sum_i |a_i|^2 = 1$. The bulk DOS is shown in figure 5(a). One observes that there are four Van Hove singularities at $E = -0.33$ eV, $-0.03$ eV, $0.032$ eV and $0.54$ eV, respectively. These singularities correspond to the flat band structure in figure 2(a). The surface DOS of slab CsNb$_3$SBr$_7$ is shown in figure 5(b). Comparing the bulk and surface densities of states, the significant difference is the emergence of Van Hove singularities in the vicinity of Fermi level, which is attributed to the nodal-straight-line surface state. These results can also be reproduced using the MLWF method.

Then, we extend the calculation of surface DOS under an external magnetic field which is perpendicular to the slab plane. The hopping terms $t_{ij}$ of Hamiltonian are replaced by the Peierls substitution

$$t_{ij} \rightarrow e^{-i \frac{\Phi_0}{\hbar c} \int_{R_j}^{R_i} A \cdot dl},$$

where $\Phi_0 = \hbar c/e$ is the flux quantum and $A = (-B_y, 0, 0)$ is the vector potential in the Landau gauge. The Hofstadter’s butterfly under the magnetic field less than 50 tesla (T) is shown in figure 5(c). An obvious zero-mode landau level appears at the Fermi energy, which is ascribed to the topological surface state. Meanwhile, the zero-mode landau level shows a higher DOS as the strength of magnetic field increases. In the vicinity of low energies, the energy states show quantized behavior, while the quantized phenomenon becomes unconspicuous at higher energies. This is because the highly localized DOS appears around the energy $E = \pm 0.03$ eV, which efficiently affects the properties of landau level under magnetic field. We expect that the CsNb$_3$SBr$_7$ exhibits interesting magnetoresponses which is distinct from the usual semimetal materials [55].

Then, we investigated the optical properties of CsNb$_3$SBr$_7$. The Drude contribution is ignored at $\varepsilon = 0$ and the energy-dependent optical conductivity at 300 K is calculated by using the Kubo formula

$$\text{Re} \sigma_{\alpha\beta}(\omega) = \lim_{\varepsilon \to 0^+} \frac{e^{-\beta \omega}}{\hbar \omega \Omega} \int_0^\infty e^{-\varepsilon t} \sin \omega t \times 2 \text{Im} \langle \psi | f(H) J_\alpha(t) [1 - f(H)] J_\beta | \psi \rangle dt,$$

where $\beta = 1/k_B T$ is the inverse temperature, $\Omega$ is the sample area, $f(H) = (e^{\beta (H - \mu)} + 1)^{-1}$ is the Fermi–Dirac distribution operator, $J_\alpha(t) = e^{iHt} J_\alpha e^{-iHt}$ is the time-dependent current operator in the $\alpha$ direction. The time evolution operator $e^{-iHt}$ and the Fermi–Dirac distribution operator $f(H)$ are obtained by the standard Chebyshev polynomial representation.

The optical conductivity of CsNb$_3$SBr$_7$ is shown in figure 5(d). It is well known that the optical conductivity is closely related to the DOS of occupied and unoccupied states. Through comparing the numerical results of optical conductivity and DOS of CsNb$_3$SBr$_7$, we identified the one-to-one correspondence of peaks in optical spectrum and DOS, which involved the particle–hole excitation between valence and conduction bands. In the high-energy part of optical spectrum, a peak is noticeable at energy $E = 0.87$ eV, which is associated with optical transitions between the Van Hove singularities of DOS at energies $E = -0.33$ eV and $E = 0.54$ eV. Besides, an additional peak appears in the low-energy area, which
is associated with optical transitions between the Van Hove singularities of DOS at energies $E = -0.03$ eV and $E = 0.032$ eV. These characteristics are similar to the graphene in low energy [56], which can be measured in the future optical experiments.

4. Summary

In summary, we theoretically propose that the quaternary-compounds CsNb$_3$SBr$_7$ is a nodal-straight-line semimetal candidate through the first-principles calculations and symmetry analyses. Due to the protection of glide symmetry $\tilde{M}_z$, two parallel nodal straight lines locate in the $k_z = 0$ plane of BZ. The topological properties of nodal straight lines are characterized by the nontrivial Berry phase and Berry curvature. On the (001) surface of CsNb$_3$SBr$_7$, Fermi arcs form the belt-like surface states, connecting the nodal straight lines with opposite chirality. Furthermore, the Hofstadter’s butterfly and optical conductivity of CsNb$_3$SBr$_7$ are investigated by using a slab sample. We find that nodal-straight-line state brings a highly localized surface DOS at Fermi level. Under the effect of perpendicular magnetic fields, the energy states show quantized behavior at low energies. The sharp peak of optical conductivity mainly originated from the optical transitions between the Van Hove singularities of bulk DOS in CsNb$_3$SBr$_7$. These results are important for future theoretical and experimental studies on nodal-straight-line semimetal materials.

Acknowledgments

The authors thank Jian-Ping Lv for helpful discussions. This work is supported by the Foundation Key Scientific Research Project of Universities in Henan Province (No. 19zx008) and Natural Science Foundation of China (No. 12204011). Numerical calculations were performed on the High Performance Computing Center of Henan Normal University.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Density of states of the CsNb$_3$SBr$_7$

The calculated projected DOS of the CsNb$_3$SBr$_7$ are shown in figure A1. Around Fermi energy, the DOS is dominated by 3d orbitals of Nb atoms, revealing a metallic behavior of the electronic states. It also provides evidences for us to construct WFs of CsNb$_3$SBr$_7$ in the process of numerical calculation.

Appendix B. Fermi surface of the CsNb$_3$SBr$_7$

As the CsNb$_3$SBr$_7$ is topologically nodal line semimetal, we plotted its Fermi surface in figure B1. There are mainly two straight Fermi surfaces in the $k_z = 0$ plane of BZ. The positions of Fermi surface agree well with the above results in figure 3(b).

Appendix C. The band structure of CsNb$_3$SBr$_7$

The bands calculated by the MLWF tight-binding method (red lines) are shown in figure C1(a), which fits the first principles calculations (blue lines) well. The band structure calculated by HSE is shown in figure C1(b), which indicate that the band crossing points exist robustly.
Figure A1. (a) DOS of each element. (b) and (c) are the projected DOS with specific atomic orbitals of Nb atoms.

Figure B1. Fermi surface of CsNb$_3$SBr$_7$ in the first BZ.

Figure C1. (a) The bands calculated by the MLWF tight-binding method (red lines), and the bands calculated by the first principles calculations (blue lines). The green circle show the bands crossing points exist robustly. (b) The band structure calculated by the HSE method.

ORCID iDs
Xianbiao Shi https://orcid.org/0000-0003-0017-2163

References
[1] Li R, Ma H, Cheng X, Wang S, Li D, Zhang Z, Li Y and Chen X Q 2016 Phys. Rev. Lett. 117 096401
[2] Liu Z et al 2018 Phys. Rev. X 8 031044
[3] Yan Z, Bi R, Shen H, Lu L, Zhang S C and Wang Z 2017 Phys. Rev. B 96 041103
[4] Weng H, Liang Y, Xu Q, Yu R, Fang Z, Dai X and Kawazoe Y 2015 Phys. Rev. B 92 045108
[5] Wang R Y, Chen Z J, Huang Z Q, Xia B W and Xu H 2021 Phys. Rev. Mater. 5 084202
[6] Chan Y H, Chiu C K, Chou M Y and Schnyder A P 2016 Phys. Rev. B 93 205132
