Research Article

Strain-Tuned Nodal Ring in Two-Dimensional $\text{Zn}_3\text{C}_6\text{S}_6$ Monolayers

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The nodal ring material has recently attracted wide attention due to its singular properties and potential applications in spintronics. Here, two-dimensional $\text{Zn}_3\text{C}_6\text{S}_6$ is calculated and discussed by using first-principle calculations. We found that two-dimensional $\text{Zn}_3\text{C}_6\text{S}_6$ can generate a nodal ring at 10% compressive strain, and the existence of the ring is proved by a partial charge density map. And as the compressive strain increases, the nodal ring does not disappear. At the same time, the stability of the electron-orbit coupling to the nodal ring is applied. Our findings indicate that the two-dimensional $\text{Zn}_3\text{C}_6\text{S}_6$ is promising in new electronic and spintronic applications.

1. Introduction

Since the quantum spin Hall effect and topological state have been discovered, in the field of condensed matter physics, the nontrivial singular properties of topological states and potential application prospects have quickly become hot research topics [1, 2]. These peculiar topological states, such as topological insulators [3–6], topological semimetals [7, 8], and topological superconductors [9], are predicted and confirmed. Topological insulators have been extensively studied over the past decade. Topological semimetals have attracted a lot of attention in the current study of condensed matter physical states. Topological semimetal refers to a metal state in which a class of electronic structures has a band depletion point protected by crystal symmetry in the vicinity of Fermi energy. The topological semimetals can be divided into two categories according to the difference in the dimension of the band (decoupling point). The first type of topological semimetals has zero-dimensional discrete energy band intersections in the momentum space. The most famous examples are the topological Dirac [10] and Weyl semimetals [11]. In the bulk electronic structure of the topographic Dirac and Weyl semimetals, two double degenerate or nondegenerate bands intersect to form a quadruple degenerate Dirac point or a double degenerate Weyl point. Low-energy quasiparticle

excitation near the intersection can be compared to Dirac or Weyl fermions in high-energy physics. The second type of topological semimetal has a one-dimensional quadruple or double degenerate energy band intersection in the momentum space. A material having such a nodal line is called a topological pitch line semimetal. Compared with the zero-dimensional nodal point, the one-dimensional nodal line has a richer topology. For example, they can form a nodal ring, a nodal link, a nodal chain, a nodal knot, and so on. The node ring described in this paper is characterized by a semimetal of a node ring composed of one or more closed lines, which is attracting attention due to its excellent topological properties. It is worth noting that 2D plane Cu_2Si [12] has been found to have nodal ring characteristics through experiments, forming two coordinated rings centered at the Γ point. In addition to being compatible with current nanoelectronic devices, one of the most important advantages of this material is that it can directly characterize its topological state through angular-resolved light emission spectra in experiments, which provides an ideal platform for designing new nanoscale materials.

In this paper, we designed the lattice structure of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ based on the first-principle calculation. By analyzing the energy band, we found that the energy band characteristics satisfy the conditions for forming the nodal ring, and

then, the strain control of the structure is found. Under certain compressive strain, as we expected, the nodal ring was regulated near the Fermi surface. And we have analyzed and verified the appearance of the nodal ring. More notably, the nodal ring feature in the 2D Brillouin zone is superior to the Dirac material. In the “Solid Universe,” rich symmetry due to 230 spatial groups of crystals, the types of energy band intersections protected by crystal symmetry will far exceed our imagination. In the near future, we firmly believe that there will be more topological semimetals with nontraditional energy intersections found in condensed matter physics.

2. Method

All structural and electronic properties are calculated based on the Density Functional Theory (DFT) [13] of the Vienna Computational Software Package (VASP). According to the recommendations of Perdew-Burke-Ernzerhof [14] (PBE), we use generalized gradient approximations for commutation and correlation potentials. The cutoff energy of the plane wave is set to 300 eV, the energy accuracy is 10^{-7} eV, and the maximum force allowed per atom is less than $0.01 \text{ eV}\text{\AA}^{-1}$. The Brillouin area adopts $9 \times 9 \times 1$ and the Γ centered Monkhorst-Pack network. The grid style uses a $20 \text{ \AA}$ vacuum area to avoid interaction between the layers. The band diagram was also fitted by the Wannier 90 software package.

3. Result and Discussion

3.1. Structural Properties. The structure diagram of $\text{Zn}_3\text{C}_6\text{S}_6$ is shown in Figure 1. In Figure 1(a) is the crystal structure of the $\text{Zn}_3\text{C}_6\text{S}_6$ single layer. Viewed from a side view (Figure 1(b)), the structure is a planar structure. Each unit cell contains three zinc (Zn), six sulfide (S), and six carbon (C) atoms, characterized in that each Zn atom is connected to four S atoms around it, and each atom of S is connected to an atom of zinc, and on the other end to an atom of C. The structure is isotropic, and the lattice constants a and b of the structure are both $8.88 \text{ \AA}$. The part inside the black box of Figure 1(a) represents unit cell. Two metal ions are bonded by organic molecules. The kinetic properties [15] of the 2D $\text{Zn}_3\text{C}_6\text{S}_6$ monolayer were studied by phonon dispersion calculation [16], in order to detect soft phonon modes that may cause structural instability. The calculated phonon spectrum of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ is shown in Figure 2. As can be seen from the figure, there is no imaginary frequency, indicating that the structure is stable.

3.2. Electronic Properties. We calculated the energy band of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ and found it to have semiconductor properties. Figure 3 shows the PBE band structure calculated without spin-orbit coupling (SOC) [17–19], and we have found that the bottom of the conduction band is at the same high symmetry point as the top of the valence band, Γ point. The structure is nonmagnetic and its band gap is 1.18 eV .

The intrinsic band structure is a direct bandgap semiconductor. Considering external factors, some interesting phenomena may occur at the bottom of the conduction band

FIGURE 1: (a, b) Top and side views of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ with lattice vectors a_1 and a_2 in the xy plane. The rhombus shows the unit cell.

FIGURE 2: The calculated phonon spectrum of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ monolayer.

FIGURE 3: The energy band structure of the 2D $\text{Zn}_3\text{C}_6\text{S}_6$ lattice calculated by the PBE method. The Fermi level is set to zero.

and the top of the valence band. In order to further study its electronic properties, we start with the characteristics of the band structure.

Controlling the electronic properties by applying strain [20–22], considering the practical aspects, $\leq 15\%$ of the biaxial stress is applied in the article, which is achievable in current two-dimensional material experiments. Here, we apply -10% strain, as shown in Figure 4. It can be observed that the band gap decreases as the compressive strain increases from 0 to 10% . A relatively small critical strain of about -9% was found to induce a gapless state. Interestingly, as

FIGURE 4: The band structure of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ under different biaxial strains and the corresponding ε mark in each band structure diagram. The Fermi level is set to zero.

FIGURE 5: The orbital resolution band structure of the sulfur element and the zinc element under the strain strength ($\varepsilon = 0, -10\%$).

the compressive strain increases, band intersections occur near the Fermi level, as shown in Figure 4(c). Figure 4(c) shows the energy band state when the compressive strain is 10%. The conduction band intersects with the valence band to form a ring. The red portion in Figure 4(c) is an encrypted enlarged view of the ring formed near Γ , with intersections R1 and R2 along the Γ -M and Γ -K lines, respectively. When the intersection of these line performance bands is close to the Fermi level, the quasiparticle properties [23] of the material's low-energy excitation are very different from those of the conventional Schrödinger-type quasiparticle excitation,

FIGURE 6: (a) Band structure calculated by DFT (green line) and Wannier function (orange line). (b) When $\varepsilon = 10\%$, a 3D spectrum of the $\text{Zn}_3\text{C}_6\text{S}_6$ lattice in the M - Γ - K plane.

resulting in the material exhibiting novel physical properties. The conductivity of electrons will be greatly increased, and the information transmission will be low cost and efficient. When the compressive strain continues to increase, until the addition of 15%, intersections R1 and R2 still exist, as shown in Figures 4(a)–4(c). And as the compressive strain increases, the node ring becomes larger and larger, but R1 and R2 always exist.

In order to study the electronic properties of 2D $\text{Zn}_3\text{C}_6\text{S}_6$ in depth, we start with the characteristics of the band structure. Different components of different atomic orbitals are projected in different colors. In Figure 5(a), S- p_{xy} , Zn- $d_{x^2-y^2}$, and Zn-s orbitals are far apart from Fermi energy levels. When $\varepsilon = 0\%$, they contribute to the conductance band

FIGURE 7: When $\varepsilon = 10\%$, the band structure and partial charge density.

minimum (CBM) and valence band maximum (VBM), respectively. However, when the lattice compresses, the sequence of energy band components reverses. Here, VBM is mainly contributed by Zn-s and S- p_{xy} orbitals, and CBM is mainly contributed by Zn- $d_{x^2-y^2}$ and S- p_{xy} orbitals. The energy band system exceeds the critical point, the band can be closed and then crossed, the Dirac cone R1 appears along M to Γ , and the Dirac cone R2 appears along Γ to K (see Figure 4(b) when $\varepsilon = -10\%$). Moreover, the energy band sequence between R1 and R2 is reversed, and the conduction band minimum is interchanged with the valence band maximum orbital component [24].

In order to deeply understand the energy band characteristics of $\text{Zn}_3\text{C}_6\text{S}_6$ lattice in the whole BZ, it is necessary to draw a 3D energy band diagram. Figure 6(a) shows the bands calculated by the DFT and Wannier functions [25], respectively. The figure shows that the two bands coincide, so it is confirmed that the calculated 3D band is correct. In other words, there is a node ring near the Γ point. As shown in Figure 6(b), in the 3D diagram, it can be clearly seen that the conduction band minimum and the valence band maximum are three-dimensionally intersected, and the band reversal between the conduction band and the valence band forms a back gap of 0.09 eV. The electron-like conduction band originates from the S- p_{xy} and Zn- $d_{x^2-y^2}$ orbitals, and the hole-like valence band is derived from the Zn-s and S- p_{xy} orbitals, as shown in Figure 5(b). Under spatial inversion symmetry, the parity of the wave functions of the two bands

from R1 to R2 is reversed, which prevents the interaction between S- p_{xy} and Zn- $d_{x^2-y^2}$, resulting in a node ring. The possible reasons for forming a ring are explained below. This material has a horizontal mirror M parallel to the 2D lattice. When there is no SOC, the two bands forming the node ring have different M eigenvalues. Thus, the two bands intersect to form a nodal ring.

In order to provide a reasonable theoretical basis for the existence of the node loop, a partial charge density [26] distribution map near the Fermi level is also calculated. As shown in Figure 7, point 1 in the figure corresponds to graph (a) of the partial charge density map, and point 2 corresponds to graph (b), and so on. It can be seen from the overall charge density map that the charge densities of (a), (f), (g), and (d) are the same. (e), (b), (c), and (h) have the same charge density. That is to say, point 1, point 4, point 6, and point 7 are located in the same band; point 2, point 3, point 5, and point 8 are on the same band. In this way, we can easily get the conclusion that in the 2D $\text{Zn}_3\text{C}_6\text{S}_6$ material under the compressive strain of 10%, the conduction band bottom and the valence band top of the energy band are interlaced to form the node ring in the figure.

Further, it is assumed that if nodal rings do exist, it should be possible to observe more intersections throughout the BZ in terms of symmetry effects [27]. Scilicet, a complete elliptic Dirac nodal line (DNL) [28] should exist near point Γ in the Brillouin belt. In order to verify this conjecture, we take Γ as the initial point and draw a number of surrounding

FIGURE 8: (a) Schematic diagram of rays around Γ point in the Brillouin region. (b–d) Calculated band.

FIGURE 9: (a) Energy band diagram without SOC. (b) Energy band diagram with SOC.

points, as shown in Figures 8(a)–8(d). Dirac cones appear on every ray we calculate, so the appearance of the Dirac cone near point K is an inevitable event. Not only these three points, we calculated more rays, and it is clear that a Dirac node line is formed near the Γ point.

The above calculations are performed without SOC, so it is natural to ask whether this knot is immune to SOC. Here, we find that when the SOC is turned on (see Figure 9(b)), the linear dispersion of the Dirac cone is hardly affected, and only a small band gap is generated. Therefore, the structure is robust to SOC. Since the SOC effect has no significant effect on the electronic structure, it can be predicted that the struc-

ture has a long spin coherence length, and we predict that it will be an ideal spin transport material.

4. Conclusions

In summary, we report the structural and electronic properties of 2D $\text{Zn}_3\text{C}_6\text{S}_6$, especially the electronic properties under the control of compressive strain. When the compressive strain reaches 10%, a nodal ring is formed. And we confirmed the existence of the nodal ring through the 3D energy band and also calculated the partial charge density and took a map between K and M . The spin-orbit coupling calculation confirmed the stability of the nodal ring. It fully embodies that some common materials can be made to have better properties through the regulation of external conditions. However, the experimental implementation of nodal-ring semimetallic materials is difficult. Therefore, it is of great practical significance to study the new platform of nanometer node ring, which will bring new application prospects for the development of efficient spintronics and quantum information technology.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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