CaTe: a new topological node-line and Dirac semimetal

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Topological semimetals recently stimulate intense research activities. Combining first-principles calculations and effective model analysis, we predict that CaTe is topological node-line semimetal when spin-orbit coupling (SOC) is ignored. We also obtain the nearly flat surface state which has the drumhead characteristic. When SOC is included, three node lines evolve into a pair of Dirac points along the $M-R$ line. These Dirac points are robust and protected by $C_4$ rotation symmetry. Once this crystal symmetry is broken, the Dirac points will be eliminated, and the system becomes a strong topological insulator.

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INTRODUCTION

Topological insulator (TI) has attracted broad interest in recent years[1, 2]. The unique property of TI is that the bulk state has a energy gap while the surface state is gapless. The topological property also have been proposed for three dimensional (3D) semimetal[3–7]. Up to now, three kinds of topological semimetal have been discovered, i.e., 3D Dirac semimetal (DSM)[7, 10–14], Weyl semimetal (WSM)[3, 4, 8, 9] and node-line semimetal (NLS)[15–18]. The 3D DSM has four-fold degeneracy point formed by two double degeneracy linear band crossing. Combining the crystal symmetry and time reversal symmetry, 3D DSM can be robust against external perturbations. Based on band structural calculation, several materials have been proposed to be 3D DSM[7, 10–14] and some of them already been confirmed by experiments[10–22]. If one breaks time reversal symmetry[3, 8, 9, 23] or inversion symmetry[24–27], the double degeneracy bands will split, consequently the 3D DSM evolves into WSM. Very recently, the predictions about WSM in TaAs family[26, 27] had been confirmed experimentally[28–31].

Unlike DSM and WSM whose band crossing points distribute at separate $k$ points in the Brillouin zone (BZ), for the NLS, the crossing points around the Fermi level form a closed loop. Several compounds had been proposed as NLS included MTC[16], Bernal graphite[22], hyperhoneycomb lattices[32] and antiperovskite Cu$_3$PdN[17, 18] and Cu$_3$NZN[18]. When SOC is neglected, for the system with band inversion, time reversal symmetry together with inversion symmetry or mirror symmetry will guarantee node line in 3D BZ[10, 18, 26, 34, 35]. Same with TI and WSM, NLS also has a characteristic surface state, namely, drumhead like state[15, 18]. Such 2D flat band surface state may become a route to achieve high temperature superconductivity[36, 37].

In this article, based on first-principles calculations and effective model analysis, we propose that CaTe in CsCl-type structure is a NLS with drumhead like surface flat bands when SOC is ignored. As shown in Fig. 1(b), around the $M$ point, there are three node-line rings, which is perpendicular to each other. When SOC is included, these three node-line rings evolve into two Dirac points along the $M-R$ line. The Dirac points are robust and protected by the $C_4$ rotational symmetry. If the $C_4$ symmetry is broken, the system becomes a strong topological insulator with $Z_2$ indices (1:000).

FIG. 1: (color online). (a) Crystal structure of CaTe in CsCl type phase. (b) The 3D BZ and projected (001) two dimensional (2D) BZ of CaTe. Three dash circles are the scheme of the three line nodes around the $M$ point. The blue circle is parallel to $k_x = 0$ plane, red circle is parallel to $k_x = 0$ plane and the green circle is parallel to $k_y = 0$ plane.
CRYSTAL STRUCTURE AND METHOD

As one member of the alkaline-earth chalcogenides, CaTe have attracted tremendous interests because of its technological applications ranging from catalysis to luminescence [32-34]. CaTe undergoes a phase transition from NaCl-type structure at ambient conditions to CsCl-type structure at hydrostatic pressure about 33 GPa [35, 36]. The structure of CaTe in CsCl-type is shown in Fig. 1(a). The space group of this phase is Pm3m (No. 221). The electronic band structure calculations have been carried out using the full potential linearized augmented plane wave method as implemented in WIEN2K package [37]. To obtain accurate band inversion strength and band order, the modified Becke-Johnson exchange potential together with local-density approximation for the correlation potential (MBJLDA) has been applied [40]. The plane-wave cutoff parameter RMTKmax is set to 7 and a 16×16×16 mesh was used for the BZ integral. The SOC interaction is included by using the second-order variational procedure.

ELECTRONIC STRUCTURE

Firstly, we calculate the band structure of CaTe and show the result without SOC in Fig. 2(a). By checking the wave functions, we find that the valence bands and conduction bands are mainly contributed by 5pε (blue) state of Te and 3dε (red) state of Ca, respectively, as shown in Fig. 2(a). The band inversion happened at M point where the energy of Te-5pε state is higher than the energy of Ca-3dε state by about 0.75 eV. Interestingly, this kind of band inversion is not caused by the SOC, which is different from most topological materials [1, 2]. We calculate the electronic structure of CaTe by applying tensile strain to check the origin of band inversion at M point. The energy difference between Te-5pε and Ca-3dε at hydrostatic pressure about 33 GPa [38, 39]. The structure of CaTe in CsCl-type is shown in Fig. 1(b). Due to the fact that gε(k) = 0 does not equal to zero which breaks the electron-hole symmetry, consequently, the node lines have finite energy dispersion.

When SOC is considered, three node lines evolve into two Dirac points at M - R line as shown in Fig. 2(b). At M point, the two states near Fermi level belong to irreducible representation Γ_{7} of Γ_{6}, respectively. While along the M - X line, two bands have the same irreducible representation Γ_{5} as shown in Fig. 2(b), thus they can hybridize with each other and open a small gap (about 50 meV). For both Γ - M line and M - M’ line, the two bands around Fermi level are also belong to the same irreducible representation, thus there is not band crossing along Γ - M line and M - M’ line. Since the band splitting is determined by the SOC, thus one can achieve the NLS by doping the lighter atoms such as Se, S.

Along the M - R line, which reserve the C_{4} rotation symmetry, two states with Γ_{7} and Γ_{6} at M point evolve
into $\Gamma_7$ and $\Gamma_6$, thus the hybridization between these two bands is forbidden, there is a Dirac point as shown in Fig.2(b). When the $C_4$ rotational symmetry is broken, like by strain effect, the band crossing point will disappear, and this 3D DSM will become a strong TI with topological indices $Z_2$ to be (1,0,0,0).

To understand the band inversion at $M$ point and the topological property of this system, we derive a low energy effective Hamiltonian at $M$ point based on the projection-operator method. $M$ point has $D_{4h}$ symmetry and also time reversal symmetry. As discussed above, at $M$ point, $\Gamma_7$ symmetry state has angular momentum $j_z = \pm 3/2$ and $\Gamma_8^+$ symmetry state has angular momentum $j_z = \pm 1/2$. Therefore using the basis of $(|j_z = \pm 1/2\rangle_d, |j_z = \pm 3/2\rangle_d, |j_z = -\frac{3}{2}\rangle_p, |j_z = +\frac{3}{2}\rangle_p)$, the effective Hamiltonian around $M$ point can be written as (see APPENDIX for detail.):

$$H_{\text{eff}} = \begin{pmatrix}
M_1(\hat{k}) & 0 & A\hat{k}_+ + B(\hat{k}) & D(\hat{k}) \\
0 & M_1(\hat{k}) & D(\hat{k}) & -A\hat{k}_- - B^*(\hat{k}) \\
A\hat{k}_- + B^*(\hat{k}) & D^*(\hat{k}) & M_2(\hat{k}) & 0 \\
D^*(\hat{k}) & -A\hat{k}_+ - B(\hat{k}) & 0 & M_2(\hat{k})
\end{pmatrix}$$

where $M_1(\hat{k}) = M_{10} + M_{11}(k_x^2 + k_y^2) + M_{12}k_z^2$, $M_2(\hat{k}) = M_{20} + M_{21}(k_x^2 + k_y^2) + M_{22}k_z^2$, $B(\hat{k}) = B_1k_xk_y^2 + B_2(k_x^2 + ik_y^2) + iB_3k_xk_yk_z$, $D(\hat{k}) = D_1(k_x^2 - k_y^2)k_x + iD_2k_xk_yk_z$, $k_\pm = k_x \pm ik_y$. Along the $k_z$ axis (where $k_x = 0$, $k_y = 0$) the effective Hamiltonian is diagonal, and the eigenvalues are $E(\hat{k}) = M_1(\hat{k})$ and $E(\hat{k}) = M_2(\hat{k})$. As mentioned above, the Dirac point is on the $M - \Gamma$ line, thus it is interesting to discuss the effective model along this line. Since there is the band inversion between $|j_z = \pm \frac{1}{2}\rangle_d$ and $|j_z = \pm \frac{3}{2}\rangle_d$ at $M$ point, it is easy to obtain that $M_{10} < M_{20}$, $M_{22} < 0 < M_{12}$, and the Dirac points locate at $k_c = \left(\frac{\pi}{a}, \frac{\pi}{a}, k_zc = \pm \sqrt{\frac{M_{12} - M_{22}}{M_{12} + M_{22}}}\right)$. Neglecting the high-order terms, $E(k_c + \delta k)$ can be expressed as $(M_{12} + M_{22})k_z\delta k_z \pm \sqrt{(M_{12} - M_{22})^2k_z^2\delta k_z^2 + A^2(\delta k_x^2 + \delta k_y^2)}$, where $\delta k_x, \delta y, \delta z$ are small displacement from $k_c$. In the vicinity of $k_c$, the band dispersion is a linear, thus our effective Hamiltonian is nothing but 3D massless Dirac fermions.

The band inversion at $M$ point and the Dirac nodes in CaTe suggest the existence of topological nontrivial surface state. To study the surface states in CaTe we use a 200-unit-cells-thick (001) slab with top (bottom) surface terminated by Ca (Te) atoms. The surface state is then calculated by using the tight-binding method. The hopping parameters are determined from a maximally localized Wannier functions (MLWFs), which are projected from the Bloch state derived from first-principles calculations.

Fig. 3(a)/(b) shows the surface state of CaTe (001) surface without/with SOC, respectively. When SOC is ignored, the system is a NLS, and possess nearly flat surface band around the Fermi energy. As shown in Fig. 3(a), our numerical results find that the nearly flat surface “drumhead” state appears in the interiors of the projected nodal line rings on the (001) surface around the $\overline{M}$ point. Since the slab we used has two surfaces, there are
two surface states as shown in the red lines in the Fig. 3(a). The particle-hole symmetry is broken by nonzero term $g_0(k)$, thus these two surface bands are not perfect flat with about 70 meV bandwidth. This type of 2D flat bands are proposed as a novel route to achieve high temperature superconductivity [36, 37].

When the SOC is included, three node lines are gapped out and become a pair of Dirac points along the $M - R$ line, thus the NLS become a 3D DSM. There is bulk Dirac node projected on $M$ point (the red dot) as shown in Fig. 3(b). Along the $M - \overline{X}$, there is also a projected bulk Dirac node, which locate near the $\overline{X}$ point denoted by red dots. Fig. 3(b) is clearly shows that the gapped bulk states along the $\overline{T} - \overline{X}$ direction and the existence of surface Dirac cones (in the blue circle) due to the topologically nontrivial $Z_2$ indices, like the same case in Na$_3$Bi [11] and Cd$_3$As$_2$ [12].

**CONCLUSION**

In summary, based on first-principles calculations and effective model analysis, we suggest that CaTe in CsCl-type structure is a NLS when SOC is ignored. There are three node-line rings which are perpendicular to each other around the $M$ point. With band inversion at $M$ point, this NLS is protected by the time reversal symmetry and inversion symmetry. When the SOC is included, three node-line rings become a pair of Dirac points. These Dirac nodes are robust and protected by the $C_4$ crystal symmetry and the system become a DSM.

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**APPENDIX**

The conduction and valence bands of CaTe at $M$ point are mainly contributed by four states: $|j_2 = -\frac{1}{2}\rangle_d$, $|j_2 = +\frac{1}{2}\rangle_d$, $|j_2 = -\frac{3}{2}\rangle_p$ and $|j_2 = +\frac{3}{2}\rangle_p$, we thus use these states as the basis to build the effective model Hamiltonian at the $M$ point of BZ. As a $4 \times 4$ Hermitian matrix, the effective Hamiltonian can be expended as $H = \sum_{i=1}^{16} f_i(k) \Gamma_i$, where $f_i(k)$ are function of momentum $k$. $\Gamma_i$ are Dirac matrices, which can be written as the direct product of $\sigma_i$ and $\tau_j$ ($\sigma_i = 1, 2, 3, 4$, $\tau_j = 1, 2, 3, 4$ are unit matrix $\sigma_0$ and three Pauli matrices $\sigma_x$, $\sigma_y$ and $\sigma_z$).

Under the operation of crystal symmetry and time reversal symmetry, the Hamiltonian should be invariant. This requires the function $f_i(k)$ and the associated $\Gamma_i$ matrices belong to the same irreducible representation. Thus the key problem is to determine the irreducible representation for $f_i(k)$ and $\Gamma_i$ matrices, which can be done by the projection-operator method.

Because the SOC is included, we use the double space group. Under the projection-operator method, we present the irreducible representation of Dirac $\Gamma$ matrices and polynomials of $\vec{k}$, and their transformation under time reversal in Table I. With the Table I, the effective model Hamiltonian of CaTe at $M$ point can be easily expressed as: $H = f_1(k)\Gamma_1 + f_{13}(k)\Gamma_{13} + f_8(k)\Gamma_8 - f_9(k)\Gamma_9 + D_1(k_x^2 - k_y^2)\Gamma_5 - D_2 k_z \epsilon \Gamma_{15} + D_3 k_y \epsilon \Gamma_{15} + D_3 k_z \epsilon \Gamma_{15}$, where $f_1(k) = C_1 + m_1(k_x^2 + k_y^2) + n_1 k_x^2$, $f_{13}(k) = C_{13} + m_{13}(k_x^2 + k_y^2) + n_{13} k_x^2$, $f_8(k) = A k_x + B k_x k_y + B k_y k_z + B k_z k_y$, $f_9(k) = A k_y + B k_x k_y + B k_y k_z + B k_z k_y$, $\Gamma_1 = \sigma_0 \otimes \tau_0$, $\Gamma_{13} = \sigma_3 \otimes \tau_0$, $\Gamma_8 = \sigma_1 \otimes \tau_3$, $\Gamma_9 = \sigma_2 \otimes \tau_0$, $\Gamma_6 = \sigma_1 \otimes \tau_1$, $\Gamma_7 = \sigma_1 \otimes \tau_2$. Compare with the effective Hamiltonian, we have $M_{10}(M_{20}) = C_1 + C_{13}, M_{11}(M_{21}) = m_1 + m_{13}$, $M_{12}(M_{22}) = n_1 \pm n_{13}$.

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| \( \Gamma \) matrices | representation T |
|-------------------|-----------------|
| \( \Gamma_1, \Gamma_{13} \) | \( R_1 \) + |
| \( \Gamma_4, \Gamma_{10} \) | \( R_2 \) - |
| \{\( \Gamma_2, \Gamma_3 \), \{\( \Gamma_{14}, \Gamma_{15} \)\} \} | \( R_3 \) - |
| \( \Gamma_7 \) | \( R_{10} \) - |
| \( \Gamma_{11} \) | \( R_{10} \) + |
| \( \Gamma_6 \) | \( R_{11} \) - |
| \( \Gamma_{10} \) | \( R_{11} \) + |
| \{\( \Gamma_8, \Gamma_9 \)\} | \( R_{12} \) - |
| \{\( \Gamma_5, \Gamma_{12} \)\} | \( R_{12} \) + |

**Table I:** The character table of Dirac \( \Gamma \) matrices and the polynomials of the momentum \( k \) for CaTe at M point.
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