Face centered cubic SnSe as a $\mathbb{Z}_2$ trivial Dirac nodal line material

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The presence of Dirac nodal line in the time-reversal and inversion symmetric system is dictated by $\mathbb{Z}_2$ index when spin-orbit interaction is absent. With the first principles calculation, we show that the Dirac nodal line can emerge in $\mathbb{Z}_2$ trivial material by calculating the band structure of SnSe of face centered cubic lattice as an example and it becomes a topological crystalline insulator when spin-orbit interaction is taken into account. We clarify the origin of the Dirac nodal line by obtaining irreducible representations corresponding to bands and explain the triviality of $\mathbb{Z}_2$ index. We construct an effective model representing the Dirac nodal line on the basis of the $k\cdot p$ method, and discuss the Berry phase and a surface state expected from Dirac nodal line.

Electronic states protected by the combination of crystal symmetries and topology have attracted much interest in the field of material science. Dirac electron system in materials is one of such protected electronic states, and its electronic state has been studied by the first principles calculations and by many experiments. Recently, a new kind of semimetallic state called a Dirac nodal line has been focused on, in which massless Dirac points (or nodes) form a continuous line in the energy-momentum space across the Fermi energy. For example, the existence of Dirac nodal line has been suggested in Cu$_3$NPd, CaTe, and Ca$_3$P$_2$ and Ca Chemistry. Experimentally, it has been confirmed by the photoemission spectroscopy in some materials. The properties of Dirac nodal line without spin-orbit interaction are related to those with spin-orbit interaction. Therefore, understanding Dirac nodal lines without spin-orbit interaction can contribute to understand the topological properties of the systems with spin-orbit interaction.

Generally, Dirac nodal line lies on general points in the Brillouin zone (BZ). Thus, in order to find the Dirac nodal line, it is necessary to check the whole BZ in the first principles calculation. However, it costs much time. From this reason, an alternative method that uses only the information of high symmetry points is desirable. For the systems with time-reversal (TR) symmetry and inversion symmetry, a method using $\mathbb{Z}_2$ index was proposed. [This $\mathbb{Z}_2$ index is the same as that of topological insulators with TR and inversion symmetry.] In general, when the system has the TR and inversion symmetry and does not have spin-orbit interaction, the point node (or Dirac point) can not exist. However, when such a system has a non-trivial $\mathbb{Z}_2$ index, it has been shown that the Dirac nodal line exists and the system is semimetallic.

The detailed relationship between $\mathbb{Z}_2$ index and the Dirac nodal line is as follows. When spin-orbit interaction is absent, $\mathbb{Z}_2$ index $\nu_1$ is obtained by $(-1)^{\nu_1} = \exp(i\gamma_1)$, where $\gamma_1$ is the Berry phase defined on a TR invariant loop which goes through certain four time-reversal invariant momenta (TRIM). When this TR invariant loop is penetratred by a single nodal line, the Berry phase is $\pi$. In the same way, when the TR loop is penetrated by two nodal lines, Berry phase becomes $2\pi$, which results in a trivial $\mathbb{Z}_2$ index.

In this paper, we show explicit examples where the system with trivial $\mathbb{Z}_2$ index has Dirac nodal lines. Then we discuss the effect of spin-orbit interaction on it.

Here it is worth while to note the effect of spin-orbit interaction. When the spin-orbit interaction is taken into account in the above systems with Dirac nodal lines, it has not been clarified what kind of states are realized. However it will be natural to expect that $\mathbb{Z}_2$ trivial semimetal or insulator is realized. In the following, we will show that there are some examples where Dirac nodal line system becomes a $\mathbb{Z}_2$ trivial insulator, in particular, topological crystalline insulator in the presence of spin-orbit interaction. It has been known that topological crystalline insulators has a trivial $\mathbb{Z}_2$ index but with a topological non-trivial gapless surface state. Their surface states are protected by their crystal symmetries, such as mirror symmetry. One of the well known examples of the topological crystalline insulator is SnTe, which has inverted band structure and strong spin-orbit interaction. Therefore, when spin-orbit interaction is absent, SnTe is a candidate material which has Dirac nodal line. In the following we focus on SnTe and its related material SnSe. By the first principles calculation, we calculate the band dispersions of SnTe and SnSe. As a result, we show that Dirac nodal lines exist in the $\mathbb{Z}_2$ trivial face centered cubic (f.c.c.) SnSe. We also clarify that the origin of the Dirac nodal line is its $C_2$ rotational symmetry. We construct an effective model representing the Dirac nodal line on the basis of the $k\cdot p$ method, and discuss the Berry phase and a surface state expected from the Dirac nodal line.

All of the following calculations are carried out by using Quantum ESPRESSO, which uses the plane wave density functional theory. For the exchange correlation term, generalized gradient approximation (GGA) with non-relativistic Perdew-Burke-Ernzerhof parametrization is used.

Firstly, we calculate the band structure of SnTe. For the lattice constant, we use $a_0 = 6.313$ Å which was used in the pre-
vius study.\textsuperscript{15} We found that band inversion does not occur in SnTe without spin-orbit interaction. When the spin-orbit interaction is taken into account, band energies are shifted and the band inversion takes place. However, we do not study SnTe further since we focus on a system in which a band inversion occurs without spin-orbit interaction. For this purpose, f.c.c.

SnSe is a good platform.

Although Ag\textsubscript{1-}\textsubscript{x}Sn\textsubscript{1+x}Se\textsubscript{2} is attracting attention as a superconductor\textsuperscript{16–19} and as a thermoelectric material,\textsuperscript{19–22} we focus on its topological properties. From X-ray experiment,\textsuperscript{16} it is shown that the crystal structure of Ag\textsubscript{1-}\textsubscript{x}Sn\textsubscript{1+x}Se\textsubscript{2} is f.c.c. (space group \emph{Fm3m}, No.225) for $0 < x < 0.24$. The relation between the lattice constant ($a_0$) and $x$ is given by $a_0 = 5.680 + 0.290x$ [Å]. For $x > 0.24$, the f.c.c. structure is unstable. When $x = 1$, i.e., in the case of SnSe, the crystal structure is known to be TlI structure (space group \emph{Cmcm}, No.63) and different from f.c.c. structure. However, in order to focus on Dirac nodal line, we assume f.c.c. structure even for $0.24 < x < 1$.

In the following, we show the results on SnSe. The orbitals in each atom are determined by the pseudo potential. We use 4s, 4p, 3d orbitals for Se, and 5s, 5p, 4d orbitals for Sn. In our band and DOS calculations, non-equivalent 6273 \textit{k}-points in the first BZ are used. To confirm the accuracy of the calculation, we check the results with 897 \textit{k}-points and find that the difference is negligible.

Figure 1(a) shows the total density of states (DOS) without spin-orbit interaction. Figures 1(b) and (c) show the partial DOS of s-, p-, and d orbitals in Sn and in Se, respectively. Figure 1(d) shows the band dispersion of f.c.c. SnSe, in which the path of \textit{k}-point in reciprocal lattice space is shown in Fig. 2. By comparing the partial DOS of Fig. 1(b) and (c) with the band dispersion, we find that three bands between -6.0 eV and 0 eV (Fermi energy) are mainly originated from Sn 4p orbital, and three bands between 0 eV and 4.0 eV are mainly obtained from Sn 5p orbital. It is clear that there is a band crossing on the W-L line. As shown in Fig. 2, W-L lines are located on the hexagonal parts of surface of BZ. By considering the $O_\text{h}^5$ symmetry of f.c.c. lattice, six band crossings on a hexagonal surface exist.

Next, we clarify the origin of the band crossing by studying the irreducible representation of wave function for each band. Figure 3 shows the band dispersion around L-point and the irreducible representation of each band. The symbols $D_{2d}$, $C_2$, $D_{sd}$ and $C_{1h}$ on the upper side indicate the point groups of the corresponding \textit{k}-points with Schoenflies notation. The irreducible representations of bands, $\Gamma_1$ etc., are determined on the basis of these symmetries.

In general, when two bands with different irreducible representations cross, there is no hybridization between the two bands, and thus the band repulsion does not occur. This happens on the L-W line as shown in the right panel of Fig. 3. In contrast, on the L-U/K line, the irreducible representations of wave functions are the same $\Gamma_1$. Therefore, there is a small band repulsion (the right panel of Fig. 3).

Let us discuss whether the band crossing on the L-W line is a point node or a part of line node. As described in introduction, in a system with the inversion and TR symmetry and without spin-orbit interaction, the point nodes cannot exist and the band crossings must be a part of nodal line.\textsuperscript{1,9} Since f.c.c. SnSe satisfies these conditions, the band crossing on the W-L line must be a part of nodal line. Actually, we find that the Dirac nodal line exists at the Fermi level on a hexagonal surface of BZ as shown in Fig. 4. As shown in Fig. 4(c), the nodal line penetrates the surface of BZ right on the W-L line (shown by straight solid lines) and does not touch the L-U/K line (shown by straight dashed lines).

We calculate the $Z_2$ index for f.c.c. SnSe and find that $Z_2$ index is trivial, i.e., (0:000). Here, we explain the reason why the Dirac nodal line exists even with a trivial $Z_2$ index. The eight \textit{TRIM} in BZ of f.c.c. structure consist of one $\Gamma$-point, three X-points and four L-points. In SnSe, the band inversion occurs around the L-points and the nodal lines appear also around the L-points. Band inversion on L-point changes the sign of product of the inversion eigenvalues (See Table I). Note
Fig. 3. (Color Online) Band dispersion around L-point without spin-orbit interaction. The irreducible representation of each band is also shown. The characters ($D_{2d}$, $C_2$, $D_{3d}$ and $C_{1h}$) represent the point groups of the corresponding k-points. The right panel shows the expansion near the L-point.

Fig. 4. (Color Online) All axes labels are wave number $k$. (a) Boz of f.c.c. (b) The blue plane represents the hexagonal surface of BZ. Red line is the Dirac nodal line. (c) Detail of the shape of Dirac nodal line. The scale of the perpendicular to surface is 10 times expanded. It penetrates the surface of BZ right on W-L line (solid line) and does not touch the L-U/K line (dashed line).

Fig. 5. (Color Online) Time-reversal invariant loop that corresponds to $v_1$. Parallelogram X, (L) X, X, (L) X is time-reversal invariant loop. Dashed arrows in the parallelogram exist outside BZ, and equivalent path in BZ is also shown as isolated dashed arrows. Blue arrows are not time-reversal invariant. However, two blue edges are equivalent and direction is opposite, so they cancel each other and do not contribute to $Z_2$ index.

Table I. Product of inversion eigenvalue of each TRIM for without and with band inversion. "Without band inversion" means all irreducible representation of valence band originate from Se 4p orbital. "With band inversion" means valence and conduction band are inverted on L-point, as we can see in our result for SnSe.

\[
\begin{array}{c|c|c}
\text{point} & \text{inversion eigenvalue} & \text{point} \\
F & 1 & F & 1 \\
X & 1 & X & 1 \\
L & -1 & L & 1 \\
\end{array}
\]

Table II. Components of TRIM for each index. $v_0$ is written as a product of all eight TRIM. Other three $v_i$ are written as products of four TRIM, $X$, $X$, $L$, and $L$.

\[
\begin{array}{c|c}
\text{Z}_2 \text{ index} & \text{calculated TRIM} \\
v_0 & X, X, X, L, L, L, L, L \\
v_1 & X, X, L, L \\
v_2 \text{ and } v_3 & X, X, L, L \\
\end{array}
\]

that the $Z_2$ index for weak topological insulators $v_i$ ($i = 1, 2, 3$) are defined as the products of four TRIM. Those TRIM are composed of two X-points and two L-points as shown in Table II. Because each index consists of even number of L-points, i.e., 4 or 2, the sign of inversion eigenvalue of the L-point has nothing to do with the $Z_2$ index. In the case of $Z_2$ non-trivial systems, Dirac nodal lines exists around band inverted point and the band inversion changes the $Z_2$ index. However, in f.c.c. SnSe, the band inversion occurs at even points and thus the $Z_2$ index is not changed.

This trivial $Z_2$ index is also explained in terms of the time-reversal invariant loop. An example of the TR invariant loop which corresponds to $v_i$ ($i = 1, 2, 3$) is shown in Fig. 5. The TR loop goes through the two non-equivalent L-points. Here "non-equivalent" means that the two L-points are not connected by a reciprocal lattice vector and each L-point is surrounded by a nodal line. Since the loop goes through the two non-equivalent L-points, we can understand that the TR loop is penetrated by two nodal lines. Thus the Berry phase for this loop is $\pi + \pi = 2\pi$ or $\pi - \pi = 0$ and thus the $Z_2$ index is trivial.

So far we find that the TR loop is penetrated by two Dirac nodal lines and thus they cannot be characterized by $Z_2$ index. Next, we check that a single Dirac nodal line has topological properties. By using an effective model, we will calculate the
Berry phase for the loop which is penetrated by a single nodal line. First, we construct a $7 \times 7$ tight-binding model by Slater-Koster’s method with Sn 5s, 5p orbitals and Se 4p orbital. From this tight-binding model, we derive a $2 \times 2$ effective model using the $\mathbf{k} \cdot \mathbf{p}$ perturbation. As a result, we obtain an effective model to calculate the Berry phase given by

$$H_{\text{eff}} = \left\{ \epsilon + d k_2^2 + \zeta (k_1^2 + k_2^2) \right\} \sigma_0 + \left\{ \epsilon' + \lambda' k_2^2 + \zeta' (k_1^2 + k_2^2) \right\} \sigma_z + \xi k_\perp \sigma_\perp,$$

where $\sigma_0$ is an identical matrix, $k_\perp$ is the unit vector in $k$-space with the [111] direction and $k_1, k_2$ are the other two unit vectors perpendicular to $k_\perp$. The parameters are determined as $\epsilon = -0.006, \lambda = 0.105, \zeta = -0.010, \epsilon' = 0.214, \lambda' = -0.147, \zeta' = -0.126, \xi = -0.634$. For this $2 \times 2$ Hamiltonian written by the Pauli matrices, we can define d-vector as

$$H_{\text{eff}} = d_0(k) \sigma_0 + d(k) \cdot \sigma.$$  

The eigenvalues of this Hamiltonian is given by $E(k)_\pm = d_0(k) \pm |d(k)|$. The Dirac nodal line satisfies $E(k)_+ = E(k)_- \Leftrightarrow |d(k)| = 0$. By solving this equations, we can see the Dirac nodal line exists on the line satisfying $k_\perp = 0$ and $k_1^2 + k_2^2 = |\epsilon'/\zeta'|$. By using this effective Hamiltonian, the Berry phase is easily calculated as a winding number of the d-vector. We use a square loop which is shown in Fig.6(a). The radius of the Dirac nodal line (red line) is $\sqrt{|\epsilon'/\zeta'|}$. We assume that $k_1$ is larger than $\sqrt{|\epsilon'/\zeta'|}$ on BC edge in Fig.6(a). As a result, this loop is penetrated by the Dirac nodal line once. From eq. (1) $d(k)$ is calculated explicitly. Since the coexistence of TR and inversion symmetry requires $d_0(k) = 0$, d-vector is on the $d_z - d_x$ plane. Because of $\epsilon' > 0, \lambda' < 0$ and $\zeta' < 0$ as a result of $\mathbf{k} \cdot \mathbf{p}$ perturbation, a path of d-vector for the loop OABCD is shown in Fig.6(b). Then we can show that the parabolic curve BC in Fig.6(b) exists in $d_z < 0$ area. Since the d-vector path surrounds the origin of $d$-space, the winding number is 1. From this calculation, we confirm that the single nodal line gives $\pi$ Berry phase.

The effect of spin-orbit interaction is easily understood. The band symmetries around L-points is the same as that of SnTe. So when spin-orbit interaction is taken into account, the system must be topological crystalline insulator. It must have non-trivial mirror Chern number and gapless surface states protected by mirror symmetry.

By using the effective model of eq. (1), we can derive a surface state. First, we neglect the $\sigma_0$ term because it only shifts the energy eigenvalues. To discuss the surface state, we focus on the (111) surface. Then, we can replace $k_\perp$ by $-id_\perp$ and we assume that $r_\perp = +\infty$ is out of crystal. The $k_\perp^2$ term needs more complicated treatment. We replace it by a smooth function $\Delta(r_\perp)$ which satisfies following conditions. Comparing the sign of $\sigma_z$ term from the bulk Hamiltonian (1), $\Delta(r_\perp)$ is required to satisfy $\Delta(r_\perp) = 0$ for $r_\perp = -\infty$ and $\Delta(r_\perp) < -\epsilon'$ for $r_\perp = +\infty$. As a result, an effective Hamiltonian is written as

$$H_{\text{sur}} = -i\xi \partial_{r_\perp} \sigma_z + \left[ \Delta(r_\perp) + \epsilon' + \zeta' (k_1^2 + k_2^2) \right] \sigma_z.$$  

The Hamiltonian of eq. (3) is the well known as Jackiw-Rebbi problem. It is known that an eigenstate with $E = 0$ exists, which is localized around the point satisfying the condition, $\Delta(r_\perp) + \epsilon' + \zeta' (k_1^2 + k_2^2) = 0$. By definition, this point exists around the surface, and we can see that this localized state is the surface state. Since this surface state requires the existence of a point which satisfies the condition of $\Delta(r_\perp) + \epsilon' + \zeta' (k_1^2 + k_2^2) = 0$, this surface state emerges inside the nodal line (Fig.7). This kind of surface state is sometimes called "drumhead"-like surface state and is a typical surface state of the system with the Dirac nodal lines.

In conclusion, we found by the first principles calculation that a Dirac nodal line emerges in f.c.c. SnSe which has a trivial $\mathbb{Z}_2$ index in the absence of spin-orbit interaction. We clarified that the origin of the Dirac nodal line is $C_2$ rotational symmetry by investigating the irreducible representations corresponding to the bands. The trivial $\mathbb{Z}_2$ index comes from the fact that even L-points are contained in BZ. We also showed that the single nodal line gives $\pi$ Berry phase and "drumhead"-like surface state exists, as expected generally for the Dirac nodal line. The situation is similar to the emergence of topological crystalline insulator, but the relation between Mirror Chern number and nodal line in f.c.c. SnSe is not revealed in this paper. The same situation, i.e., even number of high symmetry points with the same symmetry in BZ, can give Dirac nodal line in the $\mathbb{Z}_2$ trivial system. For example, body centered tetragonal system, such as space group No.139, is one of the candidates. However, easy method to find the Dirac nodal lines in $\mathbb{Z}_2$ trivial systems and how to classify them are remained as future works.

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Fig. 7. (Color Online) Bulk states (green and blue) and surface state (red). Purple square shows reciprocal space on surface and red ring shows nodal line on it. In fact there are many bulk states, two band making nodal line directly are selected. Surface state (red) exists inside nodal line.

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