Line-Node Dirac Semimetal and Topological Insulating Phase in Noncentrosymmetric Pnictides CaAgX (X = P, As)

Ai Yamakage,¹,³ Youichi Yamakawa,²,³ Yukio Tanaka,¹ and Yoshihiko Okamoto¹,³

¹Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan
²Department of Physics, Nagoya University, Nagoya 464-8602, Japan
³Institute for Advanced Research, Nagoya University, Nagoya 464-8601, Japan

Two noncentrosymmetric ternary pnictides, CaAgP and CaAgAs, are reported as topological line-node semimetals protected solely by mirror-reflection symmetry. The band gap vanishes on a circle in momentum space, and surface states emerge within the circle. Extending this study to spin-orbit coupled systems reveals that, compared with CaAgP, a substantial band gap is induced in CaAgAs by large spin-orbit interaction. The resulting states are a topological insulator, in which the $\mathbb{Z}_2$ topological invariant is given by 1; 000. To clarify the $\mathbb{Z}_2$ topological invariants for time-reversal-invariant systems without spatial-inversion symmetry, we introduce an alternative way to calculate the invariants characterizing a line node and topological insulator for mirror-reflection-invariant systems.

Introduction.— The idea of topology has been greatly expanded in the field of condensed matter physics. The quantum Hall effect can be viewed as a topological insulating state.¹,² In the past decade, various topological insulators respecting time-reversal symmetry have been discovered and this has motivated numerous subsequent studies.³⁻⁵ However, zero-gap semiconductors (Weyl/Dirac semimetals)⁶⁻⁹ have recently been recognized as a topologically nontrivial system. The absence of a band gap and the approximately linear dispersion in the low-energy regime are the characteristic features of the Weyl/Dirac semimetals. Because the low-lying excitations are the same as those of relativistic massless fermions, i.e., Weyl/Dirac fermions, anomalous transport phenomena such as the chiral magnetic effect¹⁰ can be expected not only in high-energy physics but also in solids.¹¹,¹² Thus, exploring topological semimetals can serve as a basis for understanding novel phenomena in condensed matter physics.

In most Weyl/Dirac semimetals, conduction bands overlap with valence bands at certain momentum points. However, the band gap rarely vanishes on a momentum line.¹³⁻¹⁶ Such a dispersion structure is called a “line node,” which is analogous to that in line-node superconductors. Recently, many systems have been proposed as line-node semimetals (e.g., graphite,¹⁷⁻¹⁹ the heterostructure of topological insulators,²⁰ hyperhoneycomb lattice,²¹ transition-metal monophosphides,²² carbon allotropes,²³,²⁴ Cu$_3$N,²⁵ antiperovskites,²⁶ rare-earth monopnictides,²⁷ and perovskite iridates²⁸⁻³¹). Furthermore, several quantum phenomena are also expected to appear in line-node semimetals; these include a flat Landau level,³² long-range Coulomb interaction,³³ the Kondo effect,³⁴ and a quasi-topological electromagnetic response that induces charge polarization and orbital magnetization proportional to the length of the line node.³⁵ Experimental results on line-node semimetal materials are also being reported.³⁶⁻³⁸ Interestingly, in addition to these materials, photonic crystals³⁹ and spin liquids⁴⁰ have been shown to host line nodes. The line-node structure of energy bands is becoming a prominent topic.

In this Letter, we propose hexagonal pnictides CaAgX (X = P and As) as novel line-node Dirac semimetals. Mewis synthesized these compounds and found that they crystallize in the ZrNiAl-type structure with space group P62m.⁴¹ As depicted in Fig. 1(a), AgX$_4$ tetrahedra form a three-dimensional network by sharing their edges and corners with intervening Ca atoms, which form a kagome-triangular lattice.⁴² An important aspect of this structure in terms of the physics of topology is that the space group has D$_{3h}$ point-group symmetry, i.e., mirror-reflection symmetry is preserved while spatial-inversion symmetry is not, although almost all of the previously studied line-node semimetal materials have spatial-inversion symmetry. First-principles calculations and symmetry consideration indicate that there actually exists a line-node in CaAgX. Additionally, the $\mathbb{Z}_2$ topological invariant regarding a line node is well defined by using mirror-reflection symmetry instead of spatial-inversion symmetry. The relation between the topological invariant and surface states is also discussed. When the spin-orbit interaction is switched on, the line node disappears and the system turns into a topological insulator. We investigate the topological phase of CaAgX both from the energy dispersion on the surface and from the $\mathbb{Z}_2$ topological invariants, which is obtained to be $\nu_0; \nu_1, \nu_2, \nu_3 = 1; 000$.

Bulk electronic states.— First, we perform the first-principles calculations by using the WIEN2k code.⁴³,⁴⁴ We use the experimental structural parameters⁴¹ for the calculations. Figure 1(b) shows the calculated band structures of CaAgP without the spin-orbit interaction. The line node is observed within 10 K from the Fermi level along the $\Gamma M$ and $\Gamma K$ lines, and it forms a circle in the $k_x$-$k_y$ plane centered at the $\Gamma$ point, as illustrated in the inset of Fig. 1(b). The band dispersion at the line node is linear along both the radial and $k_z$.
directions. This line node is not protected for the spin-orbit interaction. However, as shown in Fig. 1(c), the effect of the spin-orbit interaction in CaAgP is negligible and the size of the induced gap at the line node is of the order of 10 K because of the weak spin-orbit interaction in the P atom. In stark contrast, the spin-orbit interaction has a significant effect on the band structures of CaAgAs. We show the calculated band structure of CaAgAs without and with spin-orbit interaction in Figs. 1(d) and 1(e), respectively. The line node has a large gap of \( \sim 1000 \) K, indicating that the bulk system is an insulator.

Next, we derive tight-binding models for CaAgP and CaAgAs to investigate the surface electronic states. According to first-principles calculations, the main component of the conduction band at the \( \Gamma \) point is the \( p_z \) (\( A''_1 \) in \( D_{3h} \)) orbital of P or As atoms. In contrast, the valence band around the \( \Gamma \) point mainly consists of the \( s \) orbital (\( A'_1 \) in \( D_{3h} \)) of Ag atoms in addition to the \( p_z \) and \( p_x \) orbitals (\( E' \) in \( D_{3h} \)) of P or As atoms. Therefore, we construct the 12-orbital tight-binding models by constructing the maximally localized Wannier functions for the 3\( p \) (4\( p \)) orbitals of three P (As) atoms and the 5\( x \) orbital of three Ag atoms in CaAgP (CaAgAs).\(^{45,46}\) Furthermore, we have checked that the results do not alter even if the \( d \) orbitals of Ca atoms are taken into account.\(^{47}\) Here, the spin-orbit interaction \( H_{SO} = \lambda L \cdot S \), with \( \lambda = 0.07 \text{ eV} \) for 4\( p \) electrons, is taken into account in the CaAgAs model, whereas it is neglected in the CaAgP model. In Figs. 1(b) and 1(e), we see a good agreement between the first principle band and the obtained tight-binding band.

**Topological line node and surface states in CaAgP**– Figure 2(a) shows the angle-resolved density of states, calculated from the surface Green’s function via the QZ decomposition,\(^{48,49}\) on the (0001) surface of CaAgP. Note that two types of termination, \( \text{Ca}_3\text{X} \) and \( \text{Ag}_3\text{X}_2 \), are possible on the (0001) surface of CaAgX. Hereafter, we focus only on the former type of termination.\(^{50}\) One can clearly see that a line node is located around the \( \Gamma \) point, which is projected from the bulk line node, and there exist surface states within the node.

The bulk line node is protected by mirror-reflection symmetry with respect to the horizontal plane: \( H(k_x, k_y, k_z) = M^\dagger H(k_x, k_y, -k_z)M \). The conduction and valence bands belong to \( A''_2 \) and \( A'_1 \) representations, respectively; therefore, these bands are degenerate on the mirror-reflection invariant plane of \( k_z = 0 \). Mirror-reflection symmetry allows one to introduce the \( \mathbb{Z}_2 \) topological invariant \( \nu \) to characterize the band inversion as

\[
(-1)^{\nu(k)} = \xi(k_x, k_y, 0)\xi(k_x, k_y, \pi). \tag{1}
\]

Here, \( \xi(k) \) is the product of eigenvalues of the mirror reflection for all the occupied bands at \( k \). Obviously, \( \nu(k_x, k_y) = 1 \) indicates band inversion from \( k_z = 0 \) to \( k_z = \pi \). Moreover, it is worth mentioning that \( \nu(k_x, k_y) \) is related to the Berry phase:\(^{51}\)

\[
(-1)^{\nu(k)} = \exp \left[ \int_{-\pi}^{\pi} \Im k_z \ln \text{tr} A_z(k) + \text{tr} \ln B(k_x, k_y) \right], \tag{2}
\]
where the non-Abelian Berry connection is defined by

$$[A(k)]_{mn} = -i(k, m) \frac{\partial}{\partial k} |k, n\rangle,$$

(3)

where $|k, m\rangle$ denotes an occupied eigenstate, $B(k, k_y)$ is the sewing matrix defined by

$$[B(k_x, k_y)]_{mn} = \langle (k_x, k_y, \pi), m | B_j | (k_x, k_y, \pi) - G_z, n \rangle,$$

(4)

where $B_j$ is an operator satisfying

$$H(k) = B_j H(k + G_j) B_j,$$

(5)

and $G_j = 2\pi \mathbf{x}_j$ denotes the $j$-th reciprocal lattice vector. The calculated $\nu(k_x, k_y)$ is shown in Fig. 2(b). The topological invariant is obtained to be nontrivial, $\nu(k_x, k_y) = 1$, within the line node, while trivial, $\nu(k_x, k_y) = 0$, in the outside. Since $\nu(k_x, k_y)$ is invariant for a continuous change of parameters of the Hamiltonian, the line node is a topologically stable object.

**Topological insulating phase in CaAgAs.**—The degeneracy in dihedral point-group symmetry is lifted by the spin-orbit interaction. Correspondingly, the product of the eigenvalues of mirror reflection is always unity: $\xi(k_x, k_y, 0)\xi(k_x, k_y, \pi) = 1$; namely, the $\mathbb{Z}_2$ invariant takes the trivial value $\nu(k_x, k_y) = 0$. This means that the spin-orbit interaction yields an energy gap in the line node. Furthermore, the spin-orbit interaction gives rise to a transition from a line-node semimetal to a topological insulator. Figure 3 shows the angle-resolved density of states on the (0001) and (10\(\bar{1}\)0) surfaces. In the spin-orbit gap (~0.1 eV), gapless surface states appear. The Dirac point is located at the $\Gamma$ point. On the (0001) surface [Fig. 3(a)], the gapless surface states are smoothly deformed from those in the absence of spin-orbit interaction [Fig. 2(a)]. On the (10\(\bar{1}\)0) surface, gapless surface states with approximately linear dispersion emerge in the induced band gap. The in-plane ($\bar{\Gamma}X$) velocity of the surface Dirac fermion is slower than the out-of-plane ($\bar{\Gamma}A$) one, since the lattice constant along the $c$ axis is so small ($c/\alpha \sim 0.6$) that the interlayer coupling is much stronger.

The obtained gapless surface states, shown in Fig. 3, coincide with the $\mathbb{Z}_2$ topological invariants of $\nu_1 \nu_2 \nu_3 = 1;000$. The simplified formula for the invariant derived by Fu and Kane cannot be applied to the present system owing to the lack of spatial-inversion symmetry. Instead, with the help of mirror-reflection symmetries with respect to the horizontal $H(k_x, k_y, k_z) = M_x H(k_x, k_y, k_z) M_x$ and the vertical $H(k_x, k_y, k_z) = M_y H(k_x, -k_y, k_z) M_y$ planes, the topological invariants can be easily calculated as

$$\nu_{ij} = \frac{\Phi_{\text{pair}}(k_i) + \Phi_{\text{pair}}(k_i - \pi)}{2\pi} \mod 2,$$

(6)

for $i, j, l = 1, 2, 3$ ($i \neq j \neq l \neq i$) and $\nu = 0, 1.54$. The $\mathbb{Z}_2$ topological invariants are obtained by $\nu_0 = \nu_{10} + \nu_{11}$ mod 2, $\nu_1 = \nu_{11}$. The Berry phase is given by

$$\Phi_{\text{pair}}(k_i) = \int_{-\pi}^{\pi} dk \mathrm{tr} A_j(k) |k_i=\pi\rangle \langle k_i=\pi| - i \mathrm{tr} \ln B_j(k_i),$$

(7)

where $B_{\text{pair}}(k_i)$ is the sewing matrix defined by

$$[B_{\text{pair}}(k_i)]_{mn} = \langle k, m | B_j (k - G_j, n) | k_i=\pi, k_i=\pi\rangle.$$

(8)

Formula (7) is useful because only two points $k_i = 0$ and $k_i = \pi$ are needed for the calculation, as in the case of spatial-inversion invariant systems. The calculated Berry phases are summarized in Table I. All the Berry phases on the zone boundaries $k_i = \pi$ are zero, resulting in the topological invariants of $1;000$.

**Effective model.**—We now derive effective models for CaAgP and CaAgAs. In the model of CaAgAs (CaAgP), we (do not) take into account the spin-orbit interaction.

As discussed above, the conduction and valence bands at the $\Gamma$ point of CaAgP mainly consist of the $A'_2$ and $A'_1$ states, respectively. Thus, the low-energy electronic structure is effectively described by the two-band model

$$H_{\text{CaAgP}}(k) = c(k) + m(k) \sigma_x + v k_c \sigma_y,$$

(9)

with $c(k) = c_0 + c_1 k_x^2 + c_2 (k_x^2 + k_y^2)$ and $m(k) = m_0 + m_1 k_z^2 + m_2 (k_x^2 + k_y^2)$ in the vicinity of the $\Gamma$ point. A line node appears on the $k_z = 0$ plane under the band-inversion condition of $m_0m_2 < 0$.

In CaAgAs, the four-fold degenerated valence-band states at the $\Gamma$ point without the spin-orbit interaction, which consist of $E'$ states, are split into two doublets ($E_{3/2}$ and $E_{5/2}$) by in-

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**Table I. Berry phase $\Phi_{\text{pair}}(k_i)$ and $\mathbb{Z}_2$ invariant $\nu_{ij}$ of CaAgAs.**

| $i$ | 1 | 1 | 2 | 2 | 3 | 3 |
|-----|---|---|---|---|---|---|
| $\eta$ | 0 | 1 | 0 | 1 | 0 | 1 |
| $\Phi_{\text{pair}}(k_i = 0)$ | $2\pi$ | 0 | $2\pi$ | 0 | $2\pi$ | 0 |
| $\Phi_{\text{pair}}(k_i = \pi)$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $\nu_{ij}$ | 1 | 0 | 1 | 0 | 1 | 0 |
Introducing the spin-orbit interaction. The resulting low-energy states consist of the $E_{3/2}$ doublet in the valence band and the $E_{5/2}$ doublet in the conduction band, which are described by the Hamiltonian

$$H_{\text{CaAgAs}}(k) = \begin{pmatrix} h(k) & \Lambda(k) \\ \Lambda(k) & h(-k) \end{pmatrix}.$$  \hspace{1cm} (10)

$h(k)$ is the $2 \times 2$ Hamiltonian matrix for the states in which the $z$ components of the total angular momentum are given by $j_z = 1/2$ and by $j_z = 3/2$. $h(k)$ reads

$$h(k) = c(k) + m(k)\sigma_z + Ak_z(k_x\sigma_x - k_y\sigma_y),$$  \hspace{1cm} (11)

up to the second order of $k$. $\Lambda(k)$ is the $2 \times 2$ matrix representing the spin-mixing effect induced by the spin-orbit interaction, defined by $\Lambda(k) = \Lambda_1(k) + \Lambda_2(k)$, where

$$\Lambda_1(k) = -iB_zk_z(1 - \sigma_z) - iB_y(k_x + ik_y)\sigma_y,$$
$$\Lambda_2(k) = D\sigma_y - i(k_x^2 - k_y^2) - 2k_yk_z.$$  \hspace{1cm} (12)

$\Lambda(k)$ yields a finite energy gap on the $k_z = 0$ plane, thereby turning the system into a strong topological insulator with 1,000.

These two effective Hamiltonians qualitatively describe the electronic structures of CaAgP and CaAgAs. Therefore, it is useful for a further analysis of the electromagnetic responses and transport properties of these materials. These Hamiltonians, however, do not quantitatively reproduce the low-energy electronic states, because the line node is located rather far from the $\Gamma$ point. To obtain a quantitatively good model, one has to take into account higher energy states in addition to the low-lying states.

Summary.– We have clarified the topological electronic structure of hexagonal pnictides CaAgX ($X = P$ and As). CaAgX is a line-node Dirac semimetal in the absence of spin-orbit interaction. In reality, CaAgP exhibits line-node-semimetal properties except in the very low energy and low-temperature regime owing to the tiny spin-orbit interaction (~10 K). When P atoms are replaced with heavier As atoms, the strong spin-orbit interaction widens the size of the gap considerably at the line node. CaAgAs is found to be a strong topological insulator with the $\mathbb{Z}_2$ invariant of 1,000.

It has been known that the presence of reflection symmetry and band inversion is necessary and sufficient for the existence of a line node, whereas most of the line-node Dirac semimetals proposed so far preserve spatial-inversion symmetry. Moreover, the $\mathbb{Z}_2$ topological invariant characterizing the line node was defined in previous works in terms of $PT$ symmetry.\textsuperscript{15,25} This invariant cannot be directly applied to systems lacking inversion symmetry, including CaAgX reported here. We have introduced the alternative $\mathbb{Z}_2$ invariant $\nu(k_x, k_y)$ in this study, which is applicable to systems without spatial-inversion symmetry. This implies that line-node Dirac semimetals with and without spatial-inversion symmetry might exhibit intrinsically different electromagnetic responses and transport phenomena, which are related to the topological invariants. Superconductivity of line-node semimetals is another interesting topic, as discussed in point-node Weyl\textsuperscript{16–61} and Dirac semimetals.\textsuperscript{62} These issues will be addressed in future works.

Note added.– After the submission of this paper, we became aware of a recent preprint\textsuperscript{63} in which the relation between the Berry phase and eigenvalues of mirror reflection is discussed in a form different from Eqs. (1) and (2).

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Angle-resolved density of states on the Ag$_3$X$_2$ termination for X = P (a), As (b).

Fig. S 1. Angle-resolved density of states on the (0001) surface with the Ag$_3$X$_2$ termination for X = P (a), As (b).

S 2. $\mathbb{Z}_2$ line node protected by mirror-reflection symmetry

A line node protected by mirror-reflection symmetry is simply understood as follows: conduction and valence bands have opposite parity of the reflection hence these are degenerated at the reflection invariant plane $k_z = 0$ or $k_z = \pi$. Here, we show that the topological invariant which is associated with a line node can be defined in terms of Berry phase.

S 2.1 Definition

Suppose a system preserving mirror-reflection symmetry with respect to the horizontal plane. The Hamiltonian $H(k)$ satisfies

$$H(k_x, k_y, k_z) = M^T H(k_x, k_y, -k_z) M.$$ (S14)

Mirror-reflection operator $M$, in general, depends on $k_z$ in systems with sublattice structure. In the following, we choose the gauge in which $M$ is independent of $k_z$. Instead, the Hamiltonian has a nontrivial periodicity:

$$H(k) = B^T H(k + G_z) B,$$ (S15)

where $G_z = (0, 0, 2\pi)$ denotes the reciprocal lattice vector along the $z$ axis. The $\mathbb{Z}_2$ topological invariant $\nu(k_z, k_y)$ is defined by

$$(-1)^{\nu(k_z, k_y)} = \exp \left[ i \int_{-\pi}^{\pi} dk_z \text{tr} A_z(k) + \text{tr} \ln B(k_z, k_y) \right].$$ (S16)
The non-Abelian Berry connection $A(k)$ and unitary matrix $B(k_x, k_y)$ are defined by

$$[A(k)]_{mn} = -i(k, m) \frac{\partial}{\partial k} |k, n\rangle,$$

and

$$[B(k_x, k_y)]_{mn} = \langle (k_x, k_y, \pi), m | B(k_x, k_y, -\pi), n \rangle.$$

**S 2.2 Gauge symmetry**

Next, we show that $\nu(k_x, k_y)$ mod 2 is invariant under a $U(N)$ gauge transformation $|k, m\rangle \rightarrow |k, n\rangle[g(k)]_{mn}$. $g(k) \in U(N)$, $A(k)$ and $B(k_x, k_y)$ are transformed into

$$A(k) \rightarrow g\ast(k)A(k)g(k) - ig\ast(k) \frac{\partial g(k)}{\partial k},$$

$$B(k_x, k_y) \rightarrow g\ast(k_x, k_y, \pi)B(k_x, k_y)g(k_x, k_y, -\pi).$$

From the integral

$$\int_{-\pi}^{\pi} dk \text{tr} g\ast(k) \frac{\partial g(k)}{\partial k} = \ln \frac{\det g(k_x, k_y, \pi)}{\det g(k_x, k_y, -\pi)} + i2\pi, \quad n \in \mathbb{Z},$$

one can verify that the right hand side of Eq. (S16) is invariant under the gauge transformation.

**S 2.3 $\mathbb{Z}_2$ invariant and mirror-reflection symmetry**

If the system has mirror-reflection symmetry, $\nu(k_x, k_y)$ is the $\mathbb{Z}_2$ invariant. The mirror-reflection symmetry requires the following relation;

$$H(k_x, k_y, k_z) = M^\dagger H(k_x, k_y, -k_z)M.$$  

We introduce the unitary matrix $M(k)$ in the occupied subspace;

$$[M(k_x, k_y, k_z)]_{mn} = \langle (k_x, k_y, k_z), m | M(k_x, k_y, -k_z), n \rangle.$$  

On the reflection invariant plane of $k_z = 0$, the states are simultaneously the eigenstates of $M$ hence

$$\det M(k_x, k_y, 0) = \pm 1,$$

where the phase of $M$ is fixed as $M^2 = 1$. On the other reflection invariant plane of $k_z = \pi$, the mirror-reflection operator is modified to

$$M' = MB^9.$$  

$M'$ satisfies

$$[H(k_x, k_y, \pi), M'] = 0.$$  

Unitary matrix defined by

$$[M'(k_x, k_y, \pi)]_{mn} = \langle (k_x, k_y, \pi), m | M'(k_x, k_y, \pi), n \rangle,$$

also satisfies

$$\det M'(k_x, k_y, \pi) = \pm 1.$$  

Now we prove that $\nu(k_x, k_y)$ is the $\mathbb{Z}_2$ invariant. The non-Abelian Berry connection satisfies

$$A_\nu(k_x, k_y, k_z) = -M'(k_x, k_y, -k_z)A_z(k_x, k_y, -k_z)M(k_x, k_y, -k_z) + iM'(k_x, k_y, -k_z) \frac{\partial M(k_x, k_y, -k_z)}{-\partial k_z}. $$  

Therefore, the integral of $A$ reduces to

$$\int_0^\pi dk \text{tr} A_\nu(k) = -\int_0^\pi dk \text{tr} A_z(k) + i \int_0^\pi dk \text{tr} M'(k) \frac{\partial M(k)}{\partial k_z}. $$

The second term is rewritten as

$$i \int_0^\pi dk \text{tr} M'(k) \frac{\partial M(k)}{\partial k_z} = i \ln \frac{\det M(k_x, k_y, \pi)}{\det M(k_x, k_y, 0)} + 2n\pi.$$  

Consequently, one obtains

$$i \int_0^\pi dk \text{tr} A_z(k) + \text{tr} \ln B(k_x, k_y) = -\ln \frac{\det M'(k_x, k_y, \pi)}{\det M(k_x, k_y, 0)} + i2n\pi,$$

namely

$$(-1)^{\nu(k_x, k_y)} = \frac{\det M'(k_x, k_y, \pi)}{\det M(k_x, k_y, 0)} = \pm 1,$$

which is the same as Eq. (1) in the main manuscript.

**S 2.4 Topological invariant in spinful systems**

In spinful systems, the topological invariants of spin up and down may cancel each other out; $\nu(k_x, k_y, 0) = 0$, owing to time-reversal $T$ symmetry. The mirror reflection in spinful systems involves the spin hence $T^{-1}MT = -M$, and

$$M(k)^* = -T(-k)^\dagger M(-k)T(-k),$$

where unitary skew matrix $T(k)$ is defined by

$$[T(k)]_{mn} = \langle k, m | T | -k, n \rangle.$$  

As a result, one obtains

$$\text{tr} \ln B(k_x, k_y, 0) = -\text{tr} \ln M(k_x, k_y, 0),$$

$$\text{tr} M'(k_x, k_y, \pi) = -\text{tr} M'(k_x, k_y, \pi).$$

For $(k_x, k_y, \Gamma)$, $\Gamma = 0, \pi$, which is continuously connected (without gap closing) to a time-reversal invariant momentum $\Gamma$ within the $k_z = \Gamma$ plane, the following relation holds

$$\text{tr} M(k_x, k_y, 0) = \text{tr} M'(k_x, k_y, \pi) = 0,$$

since $\text{tr} M(\Gamma) = \text{tr} M'(\Gamma) = 0$ and $\text{tr} M(k_x, k_y, \Gamma)$ is a quantized invariant. Consequently, the number of occupied states with the eigenvalue of $+i$ of mirror reflection are the same as that with the eigenvalue of $-i$. This proves that $\det M(k_x, k_y, 0) = \det M(k_x, k_y, \Gamma) = (-1)^{N/2} \nu(k_x, k_y, 0) = 0$, where $N$ denotes the number of occupied bands, and that there is no line node encircling time-reversal invariant momenta. Note that line nodes not around time-reversal invariant momenta may appear in a case that antisymmetric spin-orbit interaction is much stronger than symmetric one, nevertheless it is not the case in an actual material CaAgX.
S 3. $\mathbb{Z}_2$ invariant and mirror-reflection symmetry in the presence of spin-orbit interaction

We show that the $\mathbb{Z}_2$ invariant characterizing insulators which respect both time-reversal and mirror-reflection symmetries reduces to the one-dimensional topological invariant Eq. (1).

S 3.1 Definition

We start with the following expression

$$\nu = \frac{\Phi(0) + \Phi(\pi)}{2\pi} \mod 2, \quad (S39)$$

\(\Phi(k_x)\) is the Berry phase defined by

$$\Phi(k_x) = \int_{-\pi}^\pi dk_y \text{tr} A_s(k) - i \text{tr} \ln B(k_y), \quad (S40)$$

with

$$[B(k_y)]_{\text{lim}} = \langle (\pi, k_y), m | B (-\pi, k_y), n \rangle. \quad (S41)$$

Operator \(B\) satisfies

$$H(k_x, k_y) = B^\dagger H(k_x + 2\pi, k_y) B. \quad (S42)$$

Equations (S39) and (S40) are equivalent to the $\mathbb{Z}_2$ invariant derived in Ref. $^{65}$ This is obviously confirmed in a particular choice of gauge in which \(B\) is the identity.

S 3.2 Mirror-reflection symmetry and reduced formula

Now we prove

$$\nu = \frac{\Phi(0) + \Phi(\pi)}{2\pi} \mod 2, \quad (S43)$$

in the presence of mirror-reflection symmetry as

$$H(k_x, k_y) = M^\dagger H(-k_x, k_y) M. \quad (S44)$$

In a manner similar to Secs. S 2.3 and S 2.4, \(\Phi(k_x)\) reduces to

$$\Phi(k_x) = 2\pi n, \quad n \in \mathbb{Z}. \quad (S45)$$

\(\Phi(k_x) \mod 2\pi\) for \(k_y \neq 0, \pi\) is gauge invariant, while on the time-reversal invariant momenta \(\Phi(0) \mod 4\pi\) and \(\Phi(\pi) \mod 4\pi\) are. $^{65}$ This means that only \(\Phi(0)\) and \(\Phi(\pi)\) determines the $\mathbb{Z}_2$ invariant. Then we arrive at Eq. (S43).

S 3.3 Line node and strong topological insulator

Suppose a system hosting a line node located on the \(k_z = 0\) plane around the \(\Gamma\) point in the Brillouin zone, as in the case of CaAgX discussed in the main manuscript. Spin-orbit interaction induces an energy gap at the line node. Here we calculate the $\mathbb{Z}_2$ topological invariant. On the \(k_x = 0\) and \(k_x = \pi\) planes, the invariant is given by

$$\nu_{12} = \frac{\Phi_{321\eta}(0) + \Phi_{321\eta}(\pi)}{2\pi} \mod 2, \quad (S46)$$

where the subscript is defined in Eq. (7). Berry phase \(\Phi_{321\eta}(\Gamma)\) is given by the integral along the \(k_z\) axis on the zone center and zone boundary, where the energy gap does not vanish as one turns off the spin-orbit interaction. From this fact, the Berry phase reduces to that in the absence of spin-orbit interaction;

$$\Phi_{321\eta}(\Gamma) = \Phi_{321\eta}^\uparrow(\Gamma) + \Phi_{321\eta}^\downarrow(\Gamma) = 2\Phi_{321\eta}^\uparrow(\Gamma), \quad (S47)$$

where \(\Phi^\uparrow\) and \(\Phi^\downarrow\) denote the Berry phase in the spin-up and spin-down subspaces without spin-orbit interaction. A similar technique is found in Refs. $^{66-68}$ Furthermore, from Eqs. (S32) and (S33),

$$\Phi_{321\eta}(\Gamma) = 2\pi \nu(\eta\pi, \Gamma) \mod 4\pi. \quad (S48)$$

The $\mathbb{Z}_2$ invariant \(\nu(k_x, k_y)\) associated with a line node is obtained to be \(\nu(k_x, k_y) = 1\) \([\nu(k_x, k_y) = 0]\) within (out of) the line node. Therefore, \(\nu_{12} = 1\) when the four time-reversal invariant momenta on the \(k_z = \eta\pi\) plane are enclosed by an odd number of line nodes, otherwise \(\nu_{12} = 0\). For instance, in the case that there is a single line node around \(\Gamma\) line = \((\Gamma^x_{\text{line}}, \Gamma^y_{\text{line}}), (\pi, \Gamma)\), the topological invariants are obtained to be

$$\nu_{12} = \frac{(\Gamma^x_{\text{line}}, \Gamma^y_{\text{line}})}{\pi}, \quad \nu_0 = 1. \quad (S49)$$

For the case of CaAgX, because a single line node appears around the \(\Gamma\) point, one gets

$$\nu_{12} = (0, 0), \quad \nu_0 = 1. \quad (S50)$$

And also, one can calculate \(\nu_3\) in a similar manner since an additional mirror-reflection symmetry with respect to the \(xz\) plane is satisfied and the system has an energy gap and no integral pass along the \(k_z\) direction through the line node on the \(k_z = \pi\) plane in the absence of spin-orbit interaction. In consequence, we obtain

$$\nu_{31} = 0. \quad (S51)$$

The resultant $\mathbb{Z}_2$ invariant is given by 1,000.

S 4. 27-orbital model

Here we show bulk and surface electronic states of a tight-binding model for CaAgX which consists of the 27 orbitals, i.e., \(d\) orbitals of Ca, \(s\) orbitals of Ag, and \(p\) orbitals of X. Similarly to the 12-orbital model as discussed in the main context, spin-orbit interaction of CaAgP is neglected.

In CaAgAs, on the other hand, spin-orbit interaction only for the \(p\) orbitals of As atoms is taken into account in the form
of $H_{\text{SOI}} = \lambda \mathbf{L} \cdot \mathbf{S}$ with $\lambda = 0.07$ eV. The bulk and surface electronic states are shown in Figs. S 2 and S 3, respectively. The obtained energy bands for both CaAgP [Fig. S 2(a)] and CaAgAs [Fig. S 2(b)] well coincide with the first-principles bands not only in the low-energy regime ($E \sim 0$ eV) but also in high-energy regime ($E \sim 1$ eV). The electronic states for CaAgX on the (0001) surface with Ca$_3$X termination are shown in Fig. S 3, which are qualitatively the same as those of the 12-orbital models shown in Figs. 2(a) and 3(a). One can confirm that the model dependence of electronic states is negligibly small.