Type-I and type-II magnetic nodal lines in a hexagonal InC sheet

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Based on first-principles calculations, we design a novel two-dimensional (2D) magnetic material featuring symmetry-protected nodal lines in momentum space. We show that indium carbide InC crystallizes in a single layer of a hexagonal honeycomb lattice, which is thermodynamically and dynamically stable under the ferromagnetic ordering of spins. A peculiar feature unique to the hexagonal InC sheet is the occurrence of type-I and type-II magnetic nodal lines coexisting in energy-momentum space. As a consequence, the Fermi surface comprises the electron and hole pockets that touch at the nodal line in both the type-I and type-II cases, each of which exhibits a distinctive geometry of Fermi surface due to their different signs of band velocities. The symmetry protection of the nodal lines is explained in detail based on our symmetry analysis. Our findings suggest hexagonal InC as a new venue for 2D magnetism and the Fermi surface topology.

INTRODUCTION

The recent development of synthesis and characterization techniques for two-dimensional (2D) materials [1–8] has led to the exciting discovery of a room-temperature ferromagnet in two dimensions [9–12]. Whereas magnetism is one of the oldest phenomena observed in materials, its realization in a 2D system has remained elusive; it is only recently that convincing evidence of ferromagnetism has been observed in 2D materials, which include thin films of chromium germanium telluride Cr2Ge2Te6 [13] and chromium triiodide CrI3 [14]. The discovery of these 2D magnetic materials has motivated numerous experimental and theoretical studies [15–20], which have potential implications for future spintronic device applications [21–24] and fundamental science [25–38].

Apart from these efforts, there have been ongoing studies regarding metal-free magnetism using the localize p_z orbitals of carbon allotropes. According to Lieb’s theorem [39], the ground electronic state of a bipartite lattice is accompanied by the electron spin of \( s = \frac{N_A - N_B}{2} \), where \( N_A \) and \( N_B \) are the number of sites in the \( A \) and \( B \) sublattices, respectively. The crucial requirement for a carbon-based bipartite lattice to realize a 2D magnet is thus to unbalance the number of the \( p_z \) orbitals between the two sublattices. This condition enforces two electrons to occupy a single \( \pi \)-state near the Fermi level, paying an extra Coulomb repulsion energy \( U \), and necessitating spin polarization depending on the strength of \( U \) with respect to the hopping strength \( t \) of the electrons [39–41].

Considered as possible realizations of Lieb’s condition, diverse carbon allotropes have been investigated based on a variety of schemes [42–67]. Despite these efforts, carbon-based 2D magnetism has remained elusive, only experimentally observed in a limited set of systems [44, 45, 67].

In this paper we suggest an alternative route toward the realization of carbon-based magnetism in two dimensions. The design principle for the spin polarization dictated from Lieb’s theorem has led us to find a new 2D magnetic material – a single layer of hexagonal indium carbide (\( h\)-InC) shown in Fig. 1. We show that the atomic structure of \( h\)-InC is thermodynamically and dynamically stable under spin-polarization. The ferromagnetic ordering of spins is energetically favored in the \( h\)-InC sheet, contributed mainly from the localized \( p_z \) orbitals of the C atoms. Equipped with a 2D metallic ferromagnet, \( h\)-InC features a peculiar electronic structure characterized by symmetry-protected magnetic nodal lines occurring in momentum space. While multiple nodal lines are formed from spin-polarized electronic energy bands near the Fermi energy, distinctive types of nodal lines coexist, referred to as type-I and type-II nodal lines, respectively [68–72]. Depending on which, a contrasting pattern of the electron and hole pockets appears in the Fermi surface diagram. Our results suggest \( h\)-InC as a feasible realization of a metal-free magnet in two dimensions, providing an ideal venue for studying the Fermi surface topology.
METHODS

We have performed first-principles calculations based on density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [73]. The projector augmented-wave pseudopotentials for the C and In atoms were used to treat the core electrons [74]. The exchange-correlation energy was calculated within the Perdew-Burke-Ernzerhof-type generalized gradient approximation [75]. The $48 \times 48$ of $k$-grid were sampled from the first Brillouin zone (BZ) using the gamma-centered Monkhorst-Pack scheme [76]. The plane wave basis was constructed within the energy cutoff of 550 eV. The two-dimensional (2D) crystal structure was approximated by placing a vacuum space of 20 Å along the out-of-plane $z$ direction. The convergence thresholds for the energy and the Hellmann-Feynman force were set to $10^{-6}$ eV and 0.01 eV/Å, respectively. The phonon calculations were carried out by using the PHONOPY package [77]. The spin-orbit coupling calculations were done by using fully relativistic pseudopotential for both the In and C atoms in a non-collinear DFT scheme.

RESULTS AND DISCUSSIONS

We begin our study with delineating the crystal structure of $h$-InC. Geometry optimization leads to the planar 2D honeycomb structure shown in Fig. 1(a) with the primitive unit cell comprising one InC formula unit. The space group of $h$-InC is $P\overline{6}m2$ (# 187). The generating point group of $P\overline{6}m2$ is isomorphic to $D_{3h}$, which contains mirror symmetry $M_z$ about the 2D ($x$-$y$) plane. As shown in detail later, $M_z$ plays an important role to protect nodal lines of the electronic energy bands for $h$-InC. The lattice constant is calculated as $a = |a_1| = |a_2| = 3.79 \text{ Å}$. Note that the nearest-neighbor C atoms are separated by $3.79 \text{ Å}$, which is much larger compared to that of graphene (1.42 Å). This large separation significantly hinders electron hopping between the C $p_z$ orbitals, thereby promoting magnetism in $h$-InC.

We expect that the crystal structure of $h$-InC is thermodynamically and dynamically stable. As shown in the energy curve evaluated as a function of the unit cell volume presented in Fig. 2(a), the atomic structure minimizes the ground-state total energy of $h$-InC, which is an indicative of its thermodynamic stability. Note that spin polarization helps stabilize the system by lowering the total energy by 69 meV per unit cell. The phonon calculations of $h$-InC further support the structural stability. The left panel of Fig. 2(b) shows the phononic energy band structure of $h$-InC that exhibits no negative frequency, confirming the dynamical stability of $h$-InC. We note that, in contrast to the spin-polarized phonon calculation, the nonmagnetic phonon calculation, which is done by manually fixing spins to zero, results in negative frequency in the energy spectrum as shown in the right panel of Fig. 2(b). This result indicates that spin polarization is indispensable for the structural stability of the $h$-InC sheet.

In line with the atomic structure calculations, the electronic structure calculations result in a ferromagnetic ground state with spin moment of $\sim 0.8 \mu_B$ per unit cell. Encouragingly, this value is close to $1 \mu_B$ that we expected from Lieb’s theorem. To further verify the origin of the magnetism, we calculate the magnetization density, which demonstrates a major contribution from the localized $p_z$ orbitals of C atoms to the spin moment. Figure 2(c) illustrates the spatial distribution of the magnetization density $n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$ with the spin-up (spin-down) density $n_{\uparrow(\downarrow)}(\mathbf{r})$. For convenience hereafter we refer to the majority and minority spins as up-spin ($\uparrow$) and down-spin ($\downarrow$).
FIG. 3. Electronic structure of $h$-InC. (a) Spin-polarized electronic energy band structure. The Fermi level is set to zero. The energy bands are calculated without SOC along the high-symmetry $k$ points of the hexagonal BZ shown in Fig. 1(b). The spin-up (majority spin) and spin-down (minority spin) bands are colored by red and blue, respectively. The mirror eigenbands with $m_z = +1$ and $m_z = -1$ are depicted by solid and dashed lines, respectively. (b) Projected density of states (PDOS) of $h$-InC. (c) Magnified green region from (a). (d) Nodal lines in energy-momentum space in $|E| < 0.4$ eV. The color scheme is used to represent the energy of the nodal line.

spin ($\uparrow$), respectively. It is clear from the figure that the spin density is more localized at the C sites. Figure 2(d) shows the cross-sectional views of the magnetization density, which further reveals that the C $p_z$ is responsible for the magnetization. The cross-sectional view along the C sites features the strong $p_z$-orbital character, in stark contrast to the In sites exhibiting negligible magnetization density. These results support that the magnetization mainly stems from the C $p_z$ orbitals, in good agreement with the expectation from Lieb’s theorem. As an element in group 13 (main group 3) of the periodic table, In provides one less valence electrons than C per unit cell. Our conjecture is that the In-substitution can play a role to remove half of the $p_z$ electrons of graphene and to enforce the rest of the $p_z$ electrons to occupy the remaining C $p_z$ orbitals of the other sublattice.

Having identified a new 2D magnetic material, we now turn to the characterization of its electronic structure. It is readily noticed that $h$-InC is a spin-polarized metal from its electronic energy band structure presented in Fig. 3(a). The Fermi level ($E = 0$) intersects with the spin-polarized energy bands. Notably, the largest spin-splitting occurs between the C $p_z$ bands that correspond to the energy bands containing the two highest occupied energy levels at the $\Gamma$ point, depicted by dashed lines in Figs. 3(a) and 3(c). The PDOS in Fig. 3(b) reveal that these energy bands mainly consist of the C $p_z$ orbitals, giving rise to the strong PDOS peaks at $E = -0.430$ eV from the spin-up band and at $E = 1.161$ eV from the spin-down band. As expected, these C $p_z$ bands have relatively a narrow bandwidth within $\sim 1.8$ eV, reflecting the hindered electron hopping between the C $p_z$ orbitals due to the interstitial In atoms.

The PDOS further reveal that all the other energy bands except the C $p_z$ bands near the Fermi level consist of the $s$, $p_x$, and $p_y$ orbitals from both C and In atoms. In detail, the bonding states of the $s$ orbitals are located deep inside the occupied region of the energy bands near $E = -10$ eV, whereas the anti-bonding states of the $s$-orbitals are placed above the Fermi level near $E = 1.43$ and 1.9 eV at the $\Gamma$ point. In addition, the strong PDOS peaks appear right below the Fermi level, contributed from the $p_x$ and $p_y$ orbitals of both C and In as well as with a sizable contribution from the In and C $s$ orbitals. This indicates that sigma bonds are formed between the $sp^2$-type orbitals of In and C. Hereafter we refer to these
bands as \( sp^2 \) bands. Note that the \( sp^2 \) \((p_z)\) bands are symmetric (anti-symmetric) under the mirror operation \( M_z \), as they comprise the \( s \), \( p_x \), and \( p_y \) \((p_z)\) orbitals.

The energy bands with different mirror eigenvalues \((m_z = \pm 1)\) can cross each other without opening a band gap as shown in Figs. 3(a) and 3(c). A mirror + band \((m_z = +1, \text{solid line})\) intersects with a mirror - band \((m_z = -1, \text{dashed line})\). Similarly, the energy bands with different spin states \((s_z = \pm 1)\) can also overlap each other without opening a band gap; a spin-up band \((s_z = +1, \text{colored by red})\) crosses a spin-down band \((s_z = -1, \text{colored by blue})\). Therefore, the mirror and spin-rotational \( SU(2) \) symmetries independently protect the nodal structure of the energy bands, and all the band crossings in Fig. 3(c) are explained based on the mirror and spin eigenvalues. For example, protected by mirror symmetry \( M_z \), the band crossings at B, C, D, and E in Fig. 3(c) are formed from the energy bands with the same spin state.

Being preserved independently without spin-orbit coupling (SOC), the mirror \( M_z \) and spin-rotational \( SU(2) \) symmetries are global symmetries in momentum space in the sense that they are respected at any \( \mathbf{k} \) point of the entire BZ. Therefore, the occurrence of band crossings that we found from the band structure signals the existence of one-dimensional nodal lines in the 2D BZ. A close inspection has found multiple nodal lines, such as shown in Fig. 3(d). Notably, the nodal line that contains the band crossing A in Fig. 3(c) is of a unique type, referred to as a type-II nodal line formed from the energy bands that have the same band velocities along the nodal lines\([69, 71]\). Note that the \( p_z \) \((sp^2)\) bands have a positive (negative) band curvature at \( \Gamma \). While conventional type-I nodal lines are formed dominantly from overlapping one \( p_z \) band and one \( sp^2 \) band, a type-II nodal line coexists, formed from the overlapping two \( sp^2 \) bands in the energy range from 0.345 eV to 0.348 eV.

We find a contrasting behavior between the type-I and type-II nodal lines, featured in the Fermi surface geometry. In the type-I case, an alternating chain of electron and hole pockets appears such that the position of the nodal line is placed inside the chain; in contrast, in the type-II case, a chain of electron and hole pockets occurs avoiding the position of the nodal line. Note that in both cases, the electron and hole pockets exist and touch each other linearly at the nodal line. Figures 4(a) and 4(d) illustrate the Fermi surface diagrams at \( E = -0.238 \) eV and \( E = 0.346 \) eV, where type-I and type-II nodal lines occur, respectively. They demonstrate that the nodal
line that is represented by a dashed line in Fig. 4(b) [(e)]
is located at the interior (exterior) part of the area sur-
rounded by the Fermi surfaces that are represented by
solid contours. Note that the Fermi surfaces are warped
hexagonally around the Γ point. The hexagonal warping
is more prominent in the type-I nodal line in Fig. 4(b)
than the type-II nodal line in Fig. 4(e), which is due to
the type-II nodal line residing closer to the Γ point.

We propose the contrasting geometry of the Fermi sur-
faces as a generic feature of the type-I and type-II nodal
lines in two dimensions, originated from the hexagonal
warping and the different signs of the band velocities.
To demonstrate this, we plot the energy bands in mo-
momentum space along the Γ − A, Γ − B, and Γ − C lines in
Fig. 4(c). We first notice that the energy disperses along
the nodal line due to the hexagonal warping. The fig-
ures show that the band crossing on the Γ − A (Γ − C)
line is shifted down (up) in energy with respect to the
Fermi energy (E = −0.238), forming an electron (hole)
 pocket, whereas the band crossing point occurs at
the Fermi energy on Γ − B. Thus, from Γ − A to Γ − C through
 Γ − B, the electron pocket is reduced to the crossing point,
and evolves to the hole pocket. Meanwhile, the different
signs of the band velocity necessitate the occurrence of
the crossing points in the outer area of the two Fermi
surfaces. Similarly, from Γ − D to Γ − F through Γ − E
for the Fermi surfaces at E = 0.346 eV, where the type-
II nodal line occurs [See Fig. 4(e)], an electron pocket evolves to a hole pocket via a band crossing point. Note
that the weaker warping of the energy bands results in
a weaker energy dispersion along the type-II nodal line
with respect to the type-I nodal line. Moreover, unlike
the type-I case, in the type-II case, the same sign of the
band velocities necessitate the occurrence of the type-II
crossing points in the outer area of the two Fermi sur-
faces as illustrated in Fig. 4(f). These contrasting patterns
of the Fermi surfaces are intrinsic to the very definition
of the type-I/type-II classification, done based the band
velocities, thus characterizing the types of the nodal lines
in two dimensions. We expect that the characteristic
feature should be observable in h-InC as in the case of
topological nodal lines in three dimensions [78–84] and
type-II Weyl nodes in topological semimetals [85–87].

So far, we have safely ignored SOC as h-InC comprises
light elements. Although minor, we have witnessed no-
ticeable effects of SOC in h-InC. First, we found that
SOC helps stabilize the atomic structure as; the total
energy is lowered by 15 meV per unit cell due to SOC in
the ferromagnetic ground state. We have tested diverse
possible spin configurations under a fully relativistic non-
collinear SOC scheme, including ferromagnetic and anti-
ferromagnetic spin configurations shown in Figs. 5(a) and
(b). We found that the ferromagnetic alignment of spins
along an in-plane direction is energetically favorable over
the other spin configuration. The total energy is more or
less isotropic within the plane independent of the spin
orientation, whereas the out-of-plane spin configuration
increases the total energy up to ∼ 0.3 meV as shown in
Fig. 5(d). Regarding the nodal lines that we found with-
out SOC, we find that SOC gaps out some of the nodal
lines. Notably, when spins are ferromagnetically aligned
along the out-of-plane z direction, the nodal lines at F,
G, H, and I in Fig. 3(c) survive, while all the other nodal
lines except them are gaped out by up to 0.1 eV. Similar-
ly, when spins are all oriented along the in-plane y di-
rection, which corresponds to the ground magnetic state
of h-InC in the presence of SOC, the nodal lines contain-
ing C, B, and H are reduced to nodal points residing in
the high-symmetry k_y = 0 line, protected by the mirror
symmetry M_y. We expect that these nodal points should
carry a topological index associated with a winding num-
ber including SOC.

CONCLUSION

In summary, we have presented our first-principles cal-
culations that predict a hexagonal 2D crystal h-InC as
a novel 2D magnetic metal. h-InC is structurally stable
and the unbalanced p_z orbitals give rise to a ferromag-
netic ground state. A striking consequence of the 2D
ferromagnetic metal hosted in a perfectly planar geometry
is the occurrence of symmetry-protected nodal lines.
in momentum space. We have demonstrated that both the type-I and type-II nodal line coexist, each of which is characterized by a distinctive pattern of the Fermi surface geometry. We suggest the newly found material as a novel venue for a 2D magnetism, supporting intriguing phenomena associated with symmetry, the Fermi surface geometry, and potentially quantum oscillations associated with the topology of the Fermi surface.

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