Tunable magnetic topological insulating phases in monolayer CrI₃

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We present results indicating that Chern insulator states can be achieved in the recently synthesized pristine chromium triiodide (CrI₃) by either electron or hole doping. Our first-principles density-functional-theory calculations confirmed that monolayer CrI₃ show nontrivial Chern number C in both the valence and conduction bands. By introducing on-site Coulomb interaction or epitaxial strain, the doped CrI₃ exhibit a series of topological quantum phase transitions between multiple Chern insulator phases as well as semimetal-to-insulator transitions. We show that the covalency of Cr d-1p bands controlled by the on-site Coulomb interaction U and strain is one of the key ingredients determining the topological phase and semimetal-insulator phase boundary.

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I. INTRODUCTION

Over the past decade, magnetic topological insulators have attracted much attention from researchers due to their potential applications to low-energy consumption electronics and spintronics devices [1–3]. Chern insulators (CIs) with nonzero Chern number C [4,5], under broken time-reversal symmetry provide quantized anomalous Hall transport without an applied magnetic field and carry C dissipationless chiral edge states at the boundary [6]. There have been several attempts to realize CI states in real materials. The first successful attempt was made by doping chromium (Cr) or vanadium (V) into bismuth (Bi) or antimony (Sb)₂Te₃ thin film [7], but this required extreme conditions such as ultralow temperature. Since the magnetic atoms that induce magnetization in topological insulators initially exhibit time-reversal symmetry [8,9], the size of the induced magnetic splitting is limited by the exchange coupling of the magnetic dopants. Strong spin-orbit coupling (SOC) and magnetic instability are two key ingredients to stabilize a large gap CI. But they are in trade of relation since an element with strong SOC usually tends to be magnetically inactive. In such cases, the choice of the practically possible ratio between those degrees of freedoms puts a challenge in choosing correct transition-metal atoms.

Significant studies have been carried out to reconfigure and manipulate the boundary state in magnetic topological insulators to improve spintronics [7,10–12]. The chirality of the edge states in (Bi₁₋ₓSbx)₂Te₃ magnetic TI thin film was controlled by the magnetization direction [10]. Even the position of the chiral edge states can be manipulated via domain control by either local magnetic field or current-induced spin-orbit torque [13,14]. Thus it would be interesting to show the tunability of chiral edge states in CIs and understand the physics behind this.

Recently, there has been increasing interest and new developments related to the so-called two-dimensional (2D) van-der-Waals materials [15]. It was theoretically suggested that topologically nontrivial phases may be realized in a monolayer of La (Lu) deposited on single-layer CrSiTe₃ (CrGeTe₃) even without spin-orbit coupling [16]. And ferromagnetic trihalide monolayers MnX₃ [17] and VX₃ [18] were proposed to be Dirac half-metals. But it is not yet verified experimentally if any monolayer trihalide would maintain Ising ferromagnetic ordering down to monolayer limit. All these previous works led us to look into new interesting 2D van-der-Waals material, chromium triiodide (CrI₃) reported to be an insulating ferromagnet with a Curie temperature (Tc) of 61 K, and is suggested to be a promising material for spintronic and magnetoelectronic research [19]. A recent measurement based on magneto-optic-Kerr-effect microscopy demonstrated that monolayered CrI₃ is an Ising ferromagnet with an out-of-plane spin orientation with Tc = 45 K, slightly lower than its bulk Tc. Since the strength of SOC for the I p orbitals is known as about 0.63 eV [20], this system may be a suitable candidate for a CI with a wide band gap.

In this paper, we demonstrate that CI phase can indeed be achieved in charge-doped monolayer CrI₃. From first-principles density-functional theory, the calculated Chern numbers confirm the existence of nontrivial band topologies in both the valence and conduction bands of the pristine monolayer CrI₃. Motivated by recent experiments on electrostatic gating on this compound [21,22], we suggest that the electron- or hole-doped CrI₃ would provide the CI phase. Unlike the other proposed systems, the nontrivial topology in the monolayer CrI₃ relies on the strong SOC of the coordinating I atoms. Even though Cr atoms, which are the main source of ferromagnetic instability, have very small atomic SOC strength, the strong SOC of I p states induces a rather large gap CI with the help of strong hybridization between Cr d and I p states near the Fermi level. Further, by the epitaxial...
strain or the Coulomb interaction $U$ tuning, we can control the
localizability of the Cr $d$ state to induce a series of TQPTs,
as well as a semimetal-to-insulator transition. Changes of
chirality through TQPTs are clearly reflected in our edge
state calculations to suggest the tunability of chiral edge
states.

II. COMPUTATIONAL DETAILS

We carried out first-principles calculations based on
density-functional theory (DFT) within the framework of
the PBE-type generalized gradient approximation functional
(PBE) [23] with on-site Coulomb interaction $U$ for the Cr
$d$ orbitals, as implemented in the VASP package [24,25].
All of the calculations were performed with a plane-wave
cutoff of 600 eV on the $8 \times 8 \times 1 \Gamma$-centered Monkhorst-
Pack $k$-point mesh grid. The vacuum layer was set to be
20 Å thick to decouple neighboring layers along the $z$
direction. The full relaxation was carried out by maintaining
the threefold rotational symmetry and inversion symmetry
inherent in the space group R3 with forces smaller than 0.01
eV/Å. We also employed the OPENMX code [26] to conduct
the symmetry analysis of the band structures and plot the
molecular orbitals. The energy cutoff for OPENMX was set to
400 Ryd.

III. RESULTS

Figure 1(a) shows the crystal structure of pristine mono-
layer CrI$_3$. The fully relaxed optimized structure, as obtained
from DFT calculations, exhibits a small trigonal distortion
of the CrI$_6$ octahedron, but still preserves the space-group
symmetry of R3 with an optimized lattice constant of $a =
7.006$ Å, where the edge-shared CrI$_6$ octahedra form a hon-
eycomb lattice of Cr atoms. Figures 1(c) and 1(d) show the
band structures of monolayer CrI$_3$ near $E_F$ with and without
SOC, respectively. According to the DFT calculations based
on the Perdew-Burke-Ernzerhof (PBE) exchange-correlation
functional the ground state of monolayer CrI$_3$ was determined
to be a ferromagnetic (FM) insulator with a band gap of about
1.2 eV without SOC and slightly less than 1.0 eV with SOC.
From the comparison of the bands with and without SOC, one
can easily conclude that the presence of strong SOC in the $t$
$p$ orbitals reduces the band gap with SOC by about 0.25 eV.
Hence, we expect that the valence bands will broaden due to
the strong hybridization of the Cr $d$-$t$ $p$ orbitals.

As illustrated in Fig. 1(b), the projected density of states
(pDOS) for Cr and I atoms without SOC shows that a band gap
is formed between the valence band maximum (VBM) of the
Cr $t_{2g}$-$1$ $p$ hybridized states and the conduction band minimum
(CBM) of the Cr $e_g$-$1$ $p$ hybridized states. The separation of Cr
$t_{2g}$ and $e_g$ is about 1.7 eV, which we attributed to the ligand
field splitting arising from the CrI$_6$ octahedron. The fully
occupied Cr $t_{2g}$ orbital states, located at about 0.5 eV below
$E_F$, were identified as a source of magnetism corresponding
to $Cr^{3+} \rightarrow d^3 (t_{2g}^{3})$. The value calculated for the magnetic moment
of $\sim 3.1 \mu_B$ with a strong out-of-plane easy-axis anisotropy of
$\sim 0.65$ meV for the monolayer CrI$_3$ is also consistent with that
reported in previous studies [19,27,28].

In addition to its FM insulator ground state [29,30],
monolayer CrI$_3$ exhibits intriguing nontrivial topology in its
conduction and valence bands. The nontrivial aspects of the
conduction and valence bands are clearly manifested in the
bands without SOC, as shown in Fig. 1(c). The conduction
bands consist primarily of Cr $e_g$ orbitals hybridized with $1$ $p$
states and form an $e_g$-manifold band structure. The conduc-
tion bands in Fig. 1(c) exhibit multiple crossings along the
symmetry lines, which correspond to the multiple Dirac cones
of the $e_g$ bands in the honeycomb lattice [31]. The valence
bands also exhibit Dirac cone features, both at the symmetry
points (e.g., $\Gamma$ and $K$) and along the symmetry lines. These
Dirac-cone band structures are expected to contribute to the
nontrivial band topology with finite Chern numbers when SOC
is introduced. We employed the WANNIER90 package [32], to calculate
the maximally localized Wannier functions (MLWFs), to in
turn characterize the topology of each band, and constructed
a tight-binding Hamiltonian to fit to the DFT band structures.
From the tight-binding Hamiltonian, we calculated the Chern
numbers ($C_n$) of each individual band by integrating their
Berry curvatures ($\Omega_{n,z}(k)$) over the Brillouin zone (BZ). As a
result, the conduction and valence bands with SOC in Fig. 1(d)
are labeled with their calculated Chern numbers ($C_n$). All
of the conduction and valence bands have nontrivial band
topologies. Further, there are several bands with high Chern
numbers.
FIG. 2. Electronic structure and topological quantum phase transition (TQPT) of hole-doped single-layer CrI₃. (a) The TQPT diagram for the Hubbard $U$ versus the epitaxial strain. (b) PBE+SOC band structure at 4% epitaxial strain with total Chern number $C = −2$. (c) The band structure with quantum critical point $U_c = 0.48$ eV exhibiting gap closing at $M$. (d) The PBE+U+SOC band structure at $U > U_c$ with total Chern number $C = 1$.

The presence of conduction and valence bands with nontrivial Chern numbers across the band gap in CrI₃ provides a unique opportunity to control its transport properties, as well as to drive electronic and topological phase transitions by charge doping. A recent experimental demonstration of the electrostatic gate control of the magnetism in both monolayer and bilayer CrI₃ [21,22] suggests that this 2D material is an ideal case for the study of tunable topological properties. Indeed, electrostatic doping has become an important practical method for driving electronic phase transitions [33], and to control the magnetic [34] and optical properties [35].

A. Hole-doped monolayer

We introduced a homogeneous background charge of $\Delta n_e = −1$ to simulate the electrostatic control of hole doping in monolayer CrI₃, and carried out self-consistent DFT calculations. The self-consistent band structure for the hole-doped ($\Delta n_e = −1$) monolayer CrI₃ was found to be close to that of the rigid-band shift of $E_F$, as shown in Fig. 1(d), maintaining its half-metallic FM state, where the Fermi level crosses two separate bands with a negative indirect gap. However, in the case of the Cr $d$ electrons, the two bands that cross $E_F$ in hole-doped CrI₃ are sensitive to both the lattice strain and the on-site Coulomb interactions. Figure 2(a) shows a relatively large band gap of $\sim 38$ meV for a tensile strain of 4%, but the band gap opening starts at a much smaller strain, of $\delta = 1\%$, even without turning on the on-site Coulomb interaction $U$, as illustrated in the strain-$U$ phase diagram of Fig. 2(a).

At $U = 0$ eV, the tensile lattice strain of $\delta = 1\%$ drives the semimetal state into an insulating state with a Chern number $C = −2$. On the other hand, interesting band crossing behavior occurs when we increase $U$. As demonstrated in Figs. 2(b)–2(d), the conduction and valence bands of hole-doped CrI₃ with $\delta = 4\%$ strain undergoes a TQPT at $U_c = 0.48$ eV, where the Chern number changes from $C = −2$ to $C = 1$. Since this TQPT is not restricted to a particular value of the strain, we explored the whole range of possible strains and $U$ parameters. The results are summarized in Fig. 2(a). The phase diagram is divided into three regions: semimetal, CI with $C = −2$, and another CI with $C = 1$. As the tensile strain increases, the insulating region becomes larger, indicating that the band gap is enhanced by strain. We noted that the TQPT from $C = −2$ to $C = 1$ occurs even in the semimetal region when the indirect gap is negative. This implies that the change of $U$ is responsible for the TQPT, i.e., the band inversion at the $M$ point, while the semimetal-to-insulator transition is driven by the lattice strain [36].

B. Electron-doped monolayer

Electron doping can be achieved in several ways in addition to via electrostatic gate control, such as by intercalation or adatom deposition of alkaline atoms. Similar studies have been reported in previous works on thin films [37,38]. In this work, we present the results of using Na adatom doping to achieve one-electron doping per (CrI₃)₂ unit cell of monolayer CrI₃, as illustrated in Fig. 3(a). The Na adatom is in the hollow region of the CrI₃ cell, i.e., at the center of the honeycomb, which is energetically stable. The cohesive energy calculation and thermodynamic stability is given in support of stability of Na-doped monolayer [36]. Figure 3(b) shows the band
and the Real (Re) and imaginary (Im) parts of the corresponding MOs symmetry of the HOB and LUB are shown. The Fermi level $(E_F)$ evolution of the HOB and LUB of the Dirac crossings at all $K$ and $M$ points in the Brillouin zone (BZ) under the PBE+$U$+SOC approximation and the Real (Re) and imaginary (Im) parts of the corresponding MOs symmetry of the HOB and LUB are shown. The Fermi level $(E_F)$ is indicated by the dashed cyan colored line between the HOMO and LUMO.

Similar to the hole-doped CrI$_3$ system, the electron-doped CrI$_3$ also underwent TQPTs as we introduced the on-site $U$ to evaluate a realistic model for the Cr $d$ electrons. The band structures shown in Figs. 3(c)–3(g) were calculated by the PBE+$U$+SOC method, with the on-site $U$ for the Cr $d$ orbitals varying from $U = 0 \text{ eV}$ to $U = 2 \text{ eV}$. As $U$ increases, the electron-doped CrI$_3$ changes from a CI with $C = -2$ to another CI with $C = 1$, then to another CI with $C = -1$. Two successive gap closings occur at the Fermi level as $U$ increases, at the $M$ point with $U_{c1} = 0.58 \text{ eV}$ and at the $K$ point with $U_{c2} = 1.39 \text{ eV}$. Figure 3(b) clearly demonstrates the topological phase transitions that occur alongside the band gap evolution at the $K$ and $M$ points when $U$ increases. Considering that the optimal value of $U$ for a Cr atom is $\sim 3 \text{ eV}$, the practical SOC band gap of the electron-doped CrI$_3$ is predicted to be $\Delta_K \sim 19 \text{ meV}$, which leads to a direct gap at the $K$ point.

C. Topological quantum phase transition

We also evaluated the TQPT for the electron-doped case by investigating the symmetries of the highest occupied band (HOB) and the lowest unoccupied band (LUB) near $E_F$ in terms of the irreducible representations (IRs) of the Little groups in the highly symmetric points of the BZ. The same analysis should be equally applicable to the hole-doped case.

Figure 4 illustrates a schematic drawing of the HOB and LUB across the entire BZ, along with the associated wavefunction symmetry. The IRs at the $M$ point with point group $C_2$ have $|A_M\rangle$ and $|B_M\rangle$, which are, respectively, even and odd with respect to the twofold rotation along the $\Gamma$-$M$ line at $U < U_{c1}$. In the presence of FM ordering, there are partial mixtures of the opposite parity states in the imaginary parts of both the HOB and LUB states due to the SOC term. The wave functions go through an inversion [Fig. 4(c)] after passing through the topological phase boundary (TPB) [Fig. 4(b)] $(U = U_{c1})$. Consequently, the band inversions at the three $M$ points in the BZ contribute to a total change in the Chern number of $\Delta C = 3$, so that the TQPT across $U = U_{c1}$ occurs from a CI with $C = -2$ to another CI with $C = 1$. A similar phenomenon occurs at the $K$ point, where the point group symmetry is $D_3$. Thus, the relevant IRs at $K$ are $|A_2, K + iA_{1, K}\rangle$ and $|A_{2, K}\rangle$, which correspond to $|A_M\rangle$ and $|B_M\rangle$ at $M$, respectively. Again, crossing the TPB at $U = U_{c2}$, the HOB and LUB states touch at the $K$ point [Fig. 4(e)] and cause the Chern number to change by $\Delta C = 2$. This change arises from the fact that there are two $K$ points in the BZ, which causes the Chern number to change from $C = 1$ to $C = -1$ at $U = U_{c2}$.

D. Topological properties

Figure 5 summarizes the topological properties of Na-doped CrI$_3$. The calculated Berry curvatures, $\Omega_{n_z}(k)$, and the anomalous Hall conductivity $\sigma_z$ for $U = 0$, 1, and 2 eV are plotted in Figs. 5(b) and 5(a). The total Chern number $C$ is calculated by integrating the Berry curvature over the first BZ while tuning the Fermi level. The anomalous Hall conductivity, $\sigma_z$, in the unit of quantum conductance, $e^2/h$, is calculated as a function of the Fermi level. The steplike change of $\sigma_z$ at $E_F$ reflects the Chern numbers of $C = -2$ for $U = 0 \text{ eV}$, $C = 1$ for $U = 1 \text{ eV}$, and $C = -1$ for $U = 2 \text{ eV}$. The sign change of the Chern number is also reflected in the Berry curvature plot. This anomalous Hall conductivity
results also indicate that even only a fractional number of electron or hole doping would show large anomalous Hall conductivity. The Berry curvature at $U = 0$ eV [Fig. 5(b)] shows that the negative peaks are only at the $M$ points in the BZ, which should lead to the total Chern number being $C = -3$ instead of $-2$. However, the PBE band structure in the electron-doped case includes two linear Dirac crossings at the $\Gamma$ and along the $\Gamma$-$M$ line in the BZ. Simply including SOC under the PBE+SOC assumption induces two band inversions at the $M$ line in the BZ. By changing the intrinsic SOC for the $I_p$ orbital (which is the key factor affecting the SOC in this material) from $\lambda^{SO}_{I-I_p} = 0$ to $\lambda^I_{I-I_p} = 1$, we observe a positive Berry peak around the $\Gamma$ point at a smaller $\lambda^I_{I-I_p} = 0.2$, where the gap $\Delta_{\text{gap, } \Gamma}$ at $\Gamma$ is reasonably small. However, the peaks spread homogeneously over all of the BZ at $\lambda^I_{I-I_p} = 1$ due to the wide gap ($\Delta_{\text{gap, } \Gamma}$) at the $\Gamma$ point, while still contributing $\Delta C = 1$ to the total Chern number [36]. This additional background Berry curvature remains throughout the $U$ regime.

We confirmed the change in the value and sign of the Chern number with increasing $U$ by calculating the edge states using the edge Green’s function with the surface-projected density of states [39]. Only the left edge of the slab is shown in Fig. 5(c) for $U = 0$, 1, and 2 eV. The winding of the edge state clearly shows that the sign of the Chern number is in agreement with the calculated Wilson loop for $U = 0$, 1, and 2 eV [36].

IV. SUMMARY

In summary, we have demonstrated that the recently synthesized monolayer CrI$_3$ exhibits nontrivial band topologies in both the valence and conduction bands. We achieved a CI state by charge doping, which is equivalent to the electrostatic gating in practice. Further, we observed a tunable magnetic topological insulator phase in electron- and hole-doped monolayer CrI$_3$ by controlling the on-site Coulomb interaction for Cr $d$ electrons. The spin-momentum locking at the edges and control over the chirality of the edge states of the charge doped monolayer CrI$_3$ open up new possibilities for the electronic manipulation of spin in topological spintronic devices. In addition, the epitaxial strain was found to play a significant role in the study of the semimetal-to-CI transition in hole-doped monolayer CrI$_3$. Monolayer CrI$_3$ with charge doping, which should be practically realizable, was found to be as stable as the pristine monolayer CrI$_3$. Although no systematic study of the possible topological properties of monolayer CrI$_3$ has yet been reported, the physical properties of charge-doped monolayer CrI$_3$ will facilitate future studies on materials that potentially exhibit novel topological phenomena.

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[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.98.155148 for the origin of the semimetal-to-insulator transition in hole-doped monolayer CrI$_3$, the origin of the Chern number $C = -2$ in the electron-doped CrI$_3$, the change of the calculated Wilson loop with $U$, the thermodynamic stability and estimate of cohesive energy of Na-doped monolayer CrI$_3$ and pristine monolayer CrI$_3$, which includes Refs. [2,39–41].


