Flux States and Topological Phases from Spontaneous Time-Reversal Symmetry Breaking in CrSi(Ge)Te_{3}-Based Systems

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We study adatom-covered single layers of CrSiTe$_3$ and CrGeTe$_3$ using first-principles calculations based on hybrid functionals. We find that the insulating ground state of a monolayer of La (Lu) deposited on single-layer CrSiTe$_3$ (CrGeTe$_3$) carries spontaneously generated current loops around the Cr sites, These "flux states" induce antiferromagnetically ordered orbital moments on the Cr sites and are also associated with nontrivial topological properties. The calculated Chern numbers for these systems are predicted to be ± 1 even in the absence of spin-orbit coupling, with sizable gaps on the order of 100 meV. The flux states and the associated topological phases result from spontaneous time-reversal symmetry breaking due to the presence of nonlocal Coulomb interactions.

Spin-orbit coupling (SOC) has played an essential role in both time-reversal (TR) invariant topological insulators and TR-breaking quantum anomalous Hall (QAH) insulators [1–4]. In the former, the nontrivial band topology typically results from band inversions driven by SOC [5–9]. In the latter SOC transmits the breaking of TR symmetry from the spin sector to the orbital sector, which is indispensable to obtain nonvanishing anomalous Hall currents in insulating systems.

Recently it has been theoretically argued that topological phases may arise even in the absence of SOC, driven only by Coulomb interactions. For example, by studying tight-binding models for the LaNiO$_3$/LaAlO$_3$ heterostructures with onsite interactions, Yang *et al.* and Rüegg and Fiete independently showed that the mean-field ground states are in the QAH phase for certain parameters of the model even in the absence of SOC [10, 11]. Moreover, Raghu *et al.* demonstrated that the Hartree-Fock ground state of a tight-binding model with nonlocal Coulomb interactions on a 2D honeycomb lattice may be a QAH insulator, where TR symmetry is spontaneously broken due to the nonlocal interactions [12]. These works suggest that the exchange part of the Coulomb interaction is the key ingredient in both of the aforementioned studies. In particular, the exchange part of the nonlocal interaction may give rise to a complex bond order parameter. This acts as a complex hopping term and generates inter-site currents [12] like those that arise in the Haldane model [3].

In this work, we report a theoretical proposal for realizing a QAH phase driven by nonlocal Coulomb interactions in the absence of SOC in systems based on CrSiTe$_3$ and CrGeTe$_3$ single layers. Unlike previous studies based on simplified lattice models [10–12], we have carried out first-principles calculations using a hybrid-functional [13] extension of density-functional theory (DFT) [14, 15]. In the hybrid-functional approach, a fraction of the exchange part of the screened Coulomb interaction is treated using nonlocal Hartree-Fock exchange. Within the hybrid-functional approach, we find that the ground state of a single-monolayer film of La deposited

on single-layer CrSiTe$_3$, or Lu on single-layer CrGeTe$_3$, is a QAH insulator with an energy gap on the order of 100 meV even in the absence of SOC.

Our calculations show that the emergence of the topologically nontrivial phase is accompanied by spontaneously generated currents that flow between the Te atoms surrounding the Cr atoms. Such a state with spontaneously generated current loops is usually denoted as a "flux state" or "flux phase," and has been proposed as the ground state for various interacting models [16–19]. Its essential feature is that the spontaneous TR symmetry breaking occurs in the orbital, as opposed to the spin, sector. To the best of our knowledge, our work is the first proposal for the appearance of a flux state and associated topological phase in a realistic material system based on first-principles computational methods. Since the hybrid-functional method has been quite successful in predicting the physical properties of a variety of material systems, we speculate that the topologically nontrivial flux state may in fact be the true ground state of these systems if they can be realized in the laboratory.

Bulk CrSiTe$_3$ and CrGeTe$_3$ are ferromagnetic insulators with Curie temperatures of 32 K and 61 K respectively [20, 21]. As shown in Fig. 1(a), the systems crystallize in a rhombohedral lattice, forming a layered structure stacked along the (111) direction with a fairly large inter-layer spacing of ~ 3.3 Å. Each layer consists of a 2D honeycomb array of Cr atoms in edge-sharing Te octahedra with the Si or Ge dimers inserted into the resulting octahedral vacancy sites. The Cr moments point normal to the layer, i.e., along the rhombohedral axis. The weak van der Waals (vdW) inter-layer coupling makes it easy to exfoliate thin films from bulk crystals [22].

Recently, Garrity and Vanderbilt proposed a general strategy for realizing the QAH state based on depositing a layer of heavy atoms (carrying strong SOC) on the surface of an ordinary magnetic insulator (providing TR symmetry breaking) [23]. Motivated by this proposal, we use first-principles calculations to study adatom layers on CrSiTe$_3$ and CrGeTe$_3$
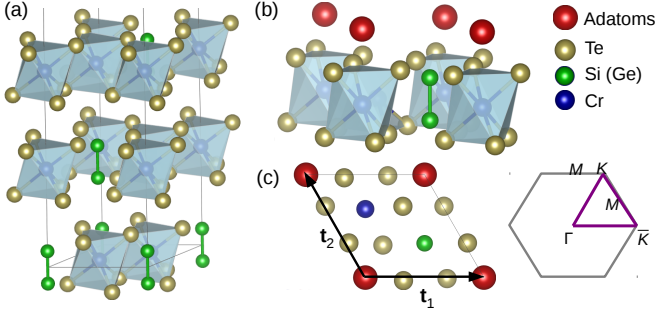
FIG. 1. (a) The lattice structures of bulk CrSiTe$_3$ and CrGeTe$_3$. (b)-(c): The structure of single-layer CrSiTe$_3$ (CrGeTe$_3$) with deposited adatoms, (b) a 3D view, and (c) a top view, with $\mathbf{t}_1$ and $\mathbf{t}_2$ denoting the 2D primitive lattice vectors, and a sketch of the hexagonal Brillouin zone.
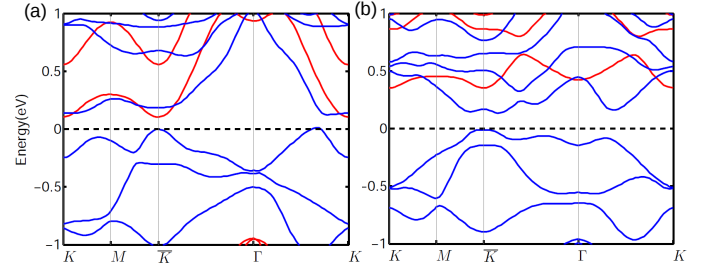

FIG. 2. The bandstructures in the absence of SOC for (a) Ge-Lu, and (b) Si-La. The red and blue curves represent the spin minority and spin majority bands respectively. The bandstructures are plotted along the high-symmetry path marked by magenta lines in the Brillouin zone shown in Fig. 1(c).

(111) single layers. As shown in Fig. 1(b) and (c), we take single-layer (SL) CrSiTe$_3$ or CrGeTe$_3$ as the substrate, and deposit one monolayer (ML) of adatoms on top of one of the two Cr sublattices so that they form a triangular lattice [24] The in-plane lattice constants of all the systems are fixed at experimental values ($a = 6.773$ Å for CrSiTe$_3$ and $a = 6.820$ Å for CrGeTe$_3$), but the internal atomic positions are fully relaxed. The structural relaxations and electronic calculations are carried out using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [13] implemented in the VASP package [25, 26] (see Supplementary Material for more computational details).

The hybrid-functional calculations identify two topological systems, namely for 1 ML La deposited on SL CrSiTe$_3$ and 1 ML Lu deposited on SL CrGeTe$_3$. Hereafter we will denote these two adatom systems as "Si-La" and "Ge-Lu" for simplicity. In the process of investigating the mechanism responsible for the band inversion and topological character in these two candidate systems, we were astonished to find that their topological character survives *even in the absence of SOC* in the hybrid-functional framework. This implies that the topological phase is unconventional in that the TR symmetry is spontaneously broken directly in the orbital sector, not by the usual SOC-mediated transmission of the TR symmetry breaking from the spin sector to the orbital sector.

To see how this comes about, consider the hybrid-functional bandstructures of Ge-Lu and Si-La computed without SOC as shown in Figs. 2 (a) and (b). Focusing on the minority-spin (red) curves, we see that the spatial wavefunctions obey TR symmetry, as expected when SOC is absent; this is visible in the "mirror symmetry" of the curves in panels K-M-$\bar{K}$ or $\bar{K}$-Γ-K, which follows from the $\mathbf{k} \to -\mathbf{k}$ symmetry that relates the two sides. For the majority-spin (blue) bands, on the other hand, this symmetry is obviously absent. This implies that the orbital TR symmetry is spontaneously broken only in the spin-majority channel. We will discuss the interesting properties of such ground states in the remainder of this paper.

In the CrSiTe$_3$ and CrGeTe$_3$ single-layer systems, the highest valence band and the lowest conduction band are mostly contributed by Te p orbitals and Cr e_g (d_{yz} and d_{xz}) orbitals respectively, all in the majority spin channel. If one ML of La or Lu is deposited on top of the layer, the adatom tends to donate two of its three valence electrons to the unoccupied Cr e_g orbitals, half-filling the four majority-spin e_g bands, while the remaining electron occupies either the $5d$ or $6s$ orbital of the adatom, also in the majority spin channel. Henceforth we ignore the minority spin states.

The above analysis assumes an ionic picture in which the hybridization between the Te p and Cr d orbitals is negligible. In reality, such hybridization is quite strong in transition-metal tellurides, as the electronegativity of Te is much weaker than that of O, and even close to that of Cr. Therefore, it is more appropriate to consider CrSiTe$_3$ and CrGeTe$_3$ as having a strongly covalent character. Most of the above arguments can be carried over to the hybridized case, except that the four otherwise e_g-like states around the Fermi level now consist of linear combinations of the Cr e_g, Te p and Cr e'_g ($d_{x^2-y^2}$ and d_{xy}) orbitals. In the absence of precise expressions for such complicated hybridized orbitals, we just denote them with some simple labels $\{\sigma_j, j = 1, 2, 3, 4\}$. The extra band from the adatom s or d orbitals lies somewhere between the two occupied and two unoccupied $\{\sigma_j\}$ bands.

Such systems with partially filled bands are expected to be metallic if Coulomb interactions are neglected. The Fermi surface of the half-filled $\{\sigma_j\}$ bands, however, may be unstable against Coulomb interactions. On the other hand, as a result of the p-d hybridizations, the inter-site matrix elements of the Coulomb interactions are expected to be substantial. Therefore, it is necessary to adopt an *ab initio* approach that takes the effects of nonlocal Coulomb interactions into account, as is the case for hybrid functionals.

Interesting physics already appears at the DFT level. The ground state in the generalized gradient approximation (GGA) turns out to be orbitally ordered in the top and bottom Te layers with spontaneous C_3 symmetry breaking. Applying local Slater-Kanamori [27] interactions (with HF treatment) to the Cr $3d$ orbitals does not open a gap, and orbital ordering in the Te layers is preserved [28].

The hybrid-functional ground states of the two systems

are found to become insulating, leading to the bandstructures shown in Fig. 2. First, as mentioned above, we note that the eigenenergies at $\mathbf{k}$ and $-\mathbf{k}$ are different for the majority spin, indicating the spontaneous breaking of TR symmetry (only) in the majority-spin channel. Such TR-breaking ground states may carry spontaneous current loops, forming flux states. Second, there are signatures of avoided crossings around K in Fig. 2(a) and Γ in Fig. 2(b), suggesting that the systems may also be topologically nontrivial (see Supplementary Material for projected energy bands).

To better understand the properties of these TR-breaking ground states, We have calculated the intersite currents between atoms based on realistic tight-binding models generated from the Wannier90 package [29, 30] (see the Supplementary Material for details). The calculated currents between first-neighbor Te atoms for the Ge-Lu system, still neglecting SOC, are shown in Fig. 3, where the currents are represented by black arrows whose thicknesses are proportional to the magnitudes of the currents. As is clear from the figure, most currents flow within the bottom Te atomic layer, forming triangular loops surrounding the Cr atoms. The two current loops centered around the two inequivalent Cr sites circulate in opposite directions, inducing antiferromagnetically ordered orbital magnetic moments on the two Cr sites as denoted by magenta arrows in Fig. 3. Without SOC, the orbital moments of the two Cr atoms are $\{-0.126\,\mu_{\mathrm{B}},\, 0.113\,\mu_{\mathrm{B}}\}$ for the Ge-Lu system, and $\{-0.066\,\mu_{\mathrm{B}},\, 0.082\,\mu_{\mathrm{B}}\}$ for the Si-La system, with the first moment referring to that of the adatom-covered Cr site. Moreover, since the highest occupied band in the Si-La system is mostly contributed by La $5d$ orbitals, there is also a relatively large orbital moment of $-0.18\mu_{\mathrm{B}}$ on the La site. For the sake of clarity, only some of the current flows are depicted in Fig. 3.

In the absence of SOC, the Hamiltonian is invariant with respect to complex conjugation of the spatial wavefunctions. We refer to this operation henceforth as "orbital TR," but we emphasize that it is only a symmetry of the fictitious SOC-free system. Because of this symmetry, each configuration reported above is only one of two equivalent configurations related by orbital TR symmetry. We refer to the one with the signs of orbital moments as reported above as the "primary" one, and the other as "secondary," although this assignment is completely arbitrary and the two are equivalent at this stage.

As discussed above, there are band-inversion characters in the spin-majority bands (see Supplementary Material), which suggest possible nontrivial band topologies in the two systems. To confirm this conjecture, we calculate the Chern numbers C using the method proposed in Ref. 31, finding $C = +1$ for the primary Ge-Lu system and $C = -1$ for the primary Si-La system. The calculated indirect gap based on the Wannier-interpolated bandstructures is ~ 70 meV for the Ge-Lu system, and is as large as ~ 130 meV for the Si-La system. Including SOC does not change the topological properties. The indirect gap with SOC included is slightly decreased for the Ge-Lu system (~ 60 meV), while it increases to ~ 160 meV for the Si-La system (see the Supplementary Material).
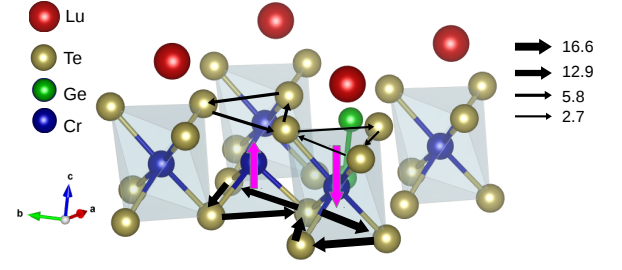

FIG. 3. Current loops flowing between the Te atoms in the majority spin channel of the SOC-free Ge-Lu system are denoted by black arrows, in units of μA. The magenta arrows denote orbital magnetic moments on the Cr sites.

The primary and secondary phases, which are energetically degenerate in the absence of SOC, are preferred by ~ 100 meV over the normal (orbital TR-symmetric) state. With SOC included, we find that the primary configuration is still preferred for the Ge-Lu system, while Si-La prefers the secondary one. Thus, both systems end up in a $C = +1$ phase. The reversal in the Si-La system implies that the Cr and La orbital moments all flip their signs in order to maximize the energy gain from SOC, changing from $\{-0.066\,\mu_{\mathrm{B}},\, 0.082\,\mu_{\mathrm{B}}\}$ to $\{0.071\,\mu_{\mathrm{B}},\, -0.080\,\mu_{\mathrm{B}}\}$ for the two Cr sites, and from $-0.18\,\mu_{\mathrm{B}}$ to $0.29\,\mu_{\mathrm{B}}$ for the La adatom. Details of the changes when SOC is turned on are provided in the Supplementary Material.

It should be emphasized that a flux state is not necessarily topologically nontrivial. As we tune the range of the screening length λ in our calculation, we find that hybridized p-d bands first drive the Si-La and Ge-Lu systems to flux states with spontaneous orbital TR symmetry breaking. Then as λ further increases, there are band inversions at the $\overline{K}$ points *within* the TR-broken flux states, leading to topologically nontrivial phases in the two systems. On the other hand, there might not be any band inversion leading to a nontrivial topology, even though TR symmetry is spontaneously broken (see the Supplementary Material).

As an additional check on the computed topological character, we have calculated the anomalous Hall conductivities σ_{yx} and the edge states in the majority spin subspace for the primary systems without SOC. As shown in Figs. 4(a) and (c), there is a single chiral edge state traversing through the bulk energy gap for each system. The chiralities are opposite, since the two systems have opposite Chern numbers in the absence of SOC. Figs. 4(b) and (d) show the anomalous Hall conductances of the two systems in the majority-spin channel as the Fermi energy is varied. (The bulk Fermi-level positions as determined by the tetrahedron method are set as the zero of energy in these plots.) There are clear signatures of plateaus quantized at $\pm e^2/h$, providing direct confirmation of the nontrivial band topology.

We now ask whether the topological phases and the flux states can survive if the Coulomb interactions are restricted to be local. As mentioned above, the Coulomb interaction in
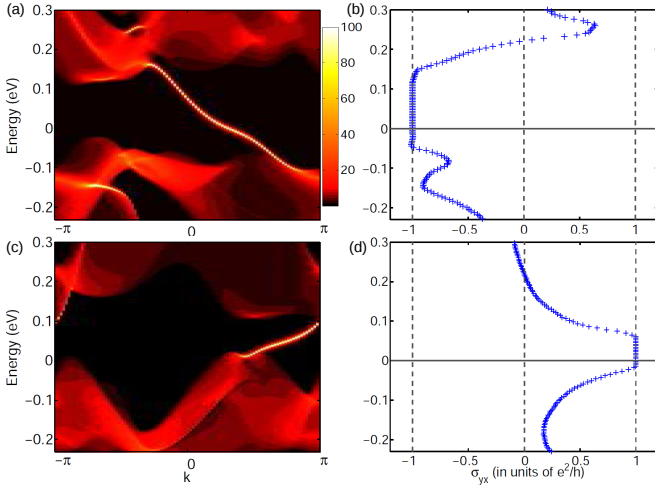
FIG. 4. Left: Edge-state spectrum in the majority spin channel for (a) Si-La and (c) Ge-Lu. Right: Dependence of majority-spin anomalous Hall conductivities as a function of Fermi-level position for (b) Si-La and (d) Ge-Lu. (All without SOC.)

the HSE hybrid functional is nonlocal, but is screened so as to have a finite range of the form $V(r) = (1 - \mathrm{erf}(r/\lambda))/r$, where "erf" denotes the error function and λ is an effective screening length [13]. We have explored the behavior of the orbital moments and Chern numbers as λ is decreased from $5\,\text{Å}$ to $1\,\text{Å}$. We characterize the staggered orbital moments by the difference ΔM_{orb} between the orbital moments on the two Cr sublattices. While the magnitude of ΔM_{orb} starts at 0.148 (0.233) μ_{B} for Ge-Lu (Si-La) at $\lambda = 5\,\text{Å}$, it falls to 0.075 (0.174) μ_{B} at $\lambda = 1.67\,\text{Å}$, and 0.016 (0.081) μ_{B} at $\lambda = 1.0\,\text{Å}$. Both systems remain topologically nontrivial down to $\lambda \sim 1.3\,\text{Å}$, and eventually become trivial when $\lambda \leq 1\,\text{Å}$. More details are presented in Supplementary Material.

The feasibility of an experimental realization of this system deserves some comment. First, our calculations suggest that two ML of adatoms may be energetically more stable than the single-ML configuration, suggesting a tendency toward segregation and island formation. Thus, low-temperature deposition of the La or Lu monolayer may be required. Alternatively, it may be possible to stabilize the adatoms in monolayer form by linking them to coordination complexes such as metallocenes [32]. On the other hand, we have argued that the topological flux states in monolayer Si-La and Ge-Lu systems originate from a Fermi-surface instability of the half-filled $\{\sigma_j\}$ (hybridized e_g-p) bands against nonlocal Coulomb interactions. Therefore it is expected that the topological phases and flux states may be present for double-layer substrates deposited with two ML adatoms in which the $\{\sigma_j\}$ bands also expect to be half-filled. Even with thicker layers of CrSiTe$_3$ or CrGeTe$_3$, it may be possible to tune the system to proper fillings using methods such as gating, codoping, and strain [33], such that the flux states are realized.

Before concluding, we make some remarks about the implications of our work for future theoretical and experimental

searches for such exchange-driven topological phases. First, the presence of extended and/or hybridized orbitals that can be acted upon by nonlocal Coulomb interactions is a common feature in a wide class of insulating materials systems. In principle there is no need to restrict the search to materials having ferromagnetic spin order, or for that matter, to systems with strong SOC. Since the scale of the gap is no longer set by the SOC strength, it may be possible to find QAH insulators with substantially larger gaps compared with those arising from conventional mechanisms [4, 23, 34]. Given the critical role played by nonlocal Coulomb interactions and p-d hybridization, some $3d$ transition-metal tellurides/selenides such as dichalcogenides and trichalcogenides, and some $4d/5d$ compounds such as iridates, may be potential candidates for such exchange-driven topological phases. Second, as the results reported in this paper are obtained from a Hartree-Fock-like approximation, it is important to inquire whether such novel ground states would survive the application of many-body techniques beyond the mean-field level.

To summarize, we have shown that hybrid-functional calculations predict the spontaneous breaking of orbital TR symmetry and the emergence of flux states and associated topological phases for a monolayer of La deposited on a single layer of CrSiTe$_3$, or similarly for Lu on CrGeTe$_3$. We attribute the appearance of these novel phases to the exchange component of the nonlocal Coulomb interaction acting in the presence of strong p-d hybridization in these transition-metal tellurides. The flux states are characterized by counterpropagating current loops between the Te atoms, which induce antiferromagnetically ordered orbital magnetic moments on the Cr sites. The associated topological phases are characterized by an anomalous Hall conductivity quantized at $\pm e^2/h$ and chiral gapless edge states even in the absence of SOC. To the best of our knowledge, our work is the first proposal for a flux state arising from spontaneous breaking of orbital TR symmetry in a condensed-matter system that is directly supported by first-principles calculations. Our work is a step forward for the understanding of topological phases in condensed matter physics, and may provide useful guidelines for future experimental and theoretical works on interaction-driven topological phases in realistic materials.

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