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.

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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 is also crucial, as it transmits the breaking of TR symmetry from the spin sector to the orbital sector, and the breaking of orbital TR symmetry 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 Slater-Kanamori type local 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 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. The exchange part of the multi-orbital on-site interaction involves the off-diagonal elements of the on-site density matrix, which are in general complex, leading to a complex combination of real atomic orbitals with spontaneously generated orbital magnetic moments [10]. On the other hand, 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, the exchange part of the screened Coulomb interaction is treated as a weighted average in which a fraction is treated using nonlocal Hartree-Fock exchange and the remainder is calculated from a conventional semilocal-density functional. 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 strat-

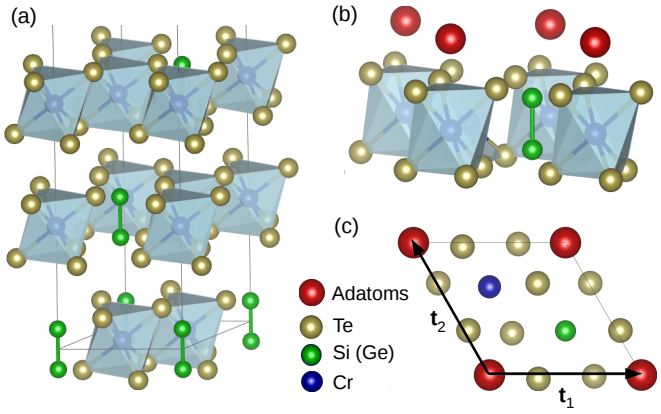

FIG. 1. (a) The lattice structures of bulk $CrSiTe_3$ and $CrGeTe_3$. (b)-(c): The structure of single-layer $CrSiTe_3$ ($CrGeTe_3$) with deposited adatoms, (b) a 3D view, and (c) a top view. $\mathbf{t}_1$ and $\mathbf{t}_2$ denote the 2D lattice vectors of the hexagonal primitive cell.

egy 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 $CrGeTe_3$ (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]

We search over a series of adatoms including Bi, Pb, Tl, Hg, Au, Ag, In, Sb, Sn, Sc, Y, La and Lu. 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.

In a first round of calculations, we adopt the "optB86b" vdW functional [25] to treat the weak coupling between the adatoms and the surface Te atoms; the local Coulomb interactions between Cr $3d$ electrons are taken into account by the rotationally invariant implementation of the "DFT+U" method [26]. In the second round we then repeat the structural relaxations and electronic calculations using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [13], which has been shown to be more successful than traditional DFT in predicting various physical properties such as energy gaps, lattice parameters and magnetic moments [27, 28]. Although the vdW corrections are no longer included, we still expect that the hybrid results are more reliable. Both the structural relaxations and electronic-structure calculations are carried out using the VASP package [29, 30]. A $6 \times 6 \times 1$ $\mathbf{k}$ mesh and a 380 eV energy cutoff are adopted, and a slab geometry is used for all the systems.

We begin by including SOC in all the calculations. According to the results computed using the vdW DFT+U functional, several of the considered systems, such as 1 ML In with -3% epitaxial strain and 1 ML Bi, possess nonzero Chern numbers. However, when we repeat the calculations for these apparently promising systems using the HSE functional, we find them restored to a trivial topological state. On the other hand, the hybrid-functional calculations identify two new 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 spatial sector, not by the usual SOC-mediated transmission of the TR symmetry breaking from the spin sector to the spatial sector. Moreover, the ground states are characterized by spontaneously generated current flows between the bottom Te atoms surrounding the two Cr sites in each primitive cell, leading to antiferromagnetically ordered orbital magnetic moments on the Cr sites.

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 TR symmetry is spontaneously broken (in the orbital sector) 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 orbital characters of the four otherwise e_g-like states around the Fermi level become much more complicated. They actually 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 bands from the adatom s or d orbitals, which also hybridize significantly with the Te p orbitals, lie somewhere between the two occupied and two unoccupied $\{\sigma_j\}$ bands.

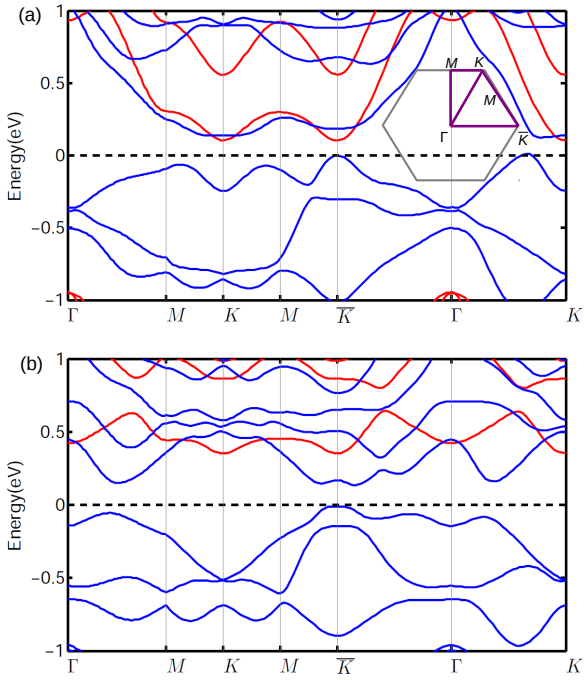

FIG. 2. The bandstructures in the absence of SOC for (a) Ge-Lu, and (b) Si-La. The red and blue curves represent the spin majority and spin minority bands respectively. The inset in (a) shows the Brillouin zone of a hexagonal lattice, and the bandstructures are plotted along the high-symmetry path marked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

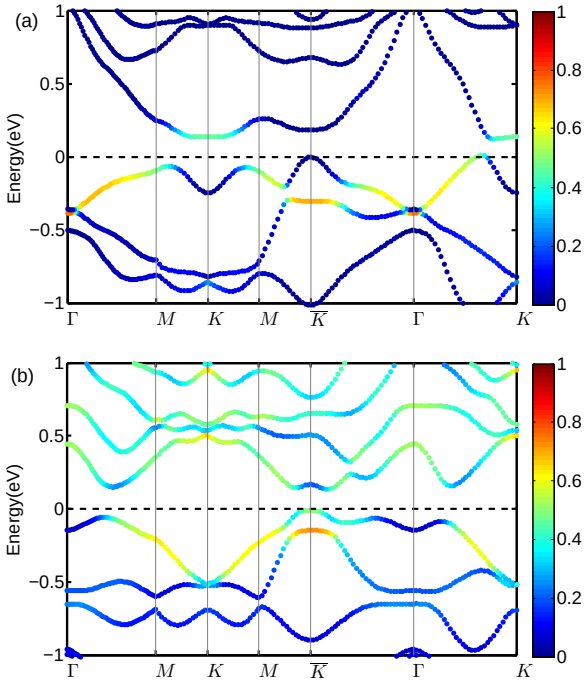

FIG. 3. Majority-spin bandstructures of (a) Ge-Lu projected onto Lu s orbitals, and (b) Si-La projected onto La d orbitals.

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. Thus, on-site interactions between Cr d electrons would be insufficient to describe the effects of the Coulomb interaction in a comprehensive manner. 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.

The hybrid-functional ground states of the two systems are found to become insulating, leading to the bandstructures shown in Fig. 2. There are a few unconventional features of the gapped bandstructures. First, as mentioned above, we note that the eigenenergies at $\mathbf{k}$ and $-\mathbf{k}$ are different for the majority spin, while they are identical for the minority spin. This indicates that TR symmetry in the orbital sector is spontaneously broken only for 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. Figs. 3(a) and (b) show the spin-majority bandstructures for the Ge-Lu and Si-La systems projected onto Lu s and La d orbitals respectively, clearly indicating a band-inversion character at Γ for Si-La and at K for Ge-Lu.

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 [31, 32] (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. 4, 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. 4. Without SOC, the orbital moments of the two Cr atoms are $\{-0.126\,\mu_{\rm B},\, 0.113\,\mu_{\rm B}\}$ for the Ge-Lu system, and $\{-0.066\,\mu_{\rm B},\, 0.082\,\mu_{\rm B}\}$ 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 $-0.18\mu_{\rm B}$ on the La site. For the sake of clarity, Fig. 4 only depicts some of the current flows; for example, there are considerable currents between the Si dimers and the Te atoms, which are required to conserve the total current on each Te site.

Note that for each system, the configuration of orbital moments and currents reported above is just one of two energetically equivalent ones, since in the absence of SOC the application of spatial-only TR (i.e., complex conjugation) will reverse all orbital moments and currents. We henceforth refer to the above-reported configurations as the "primary ones," and the reversed ones as "secondary," even though there is nothing

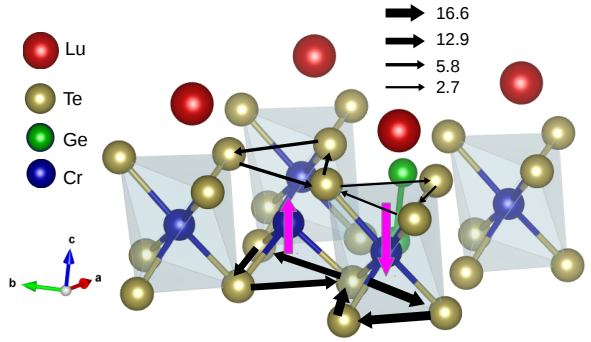

FIG. 4. Current loops flowing between the Te atoms in the majority spin channel of the SOC-free Ge-Lu system. The currents are denoted by black arrows whose thicknesses are proportional to the magnitudes of the currents. The magenta arrows denote orbital magnetic moments on the Cr sites. The currents are in units of μA.

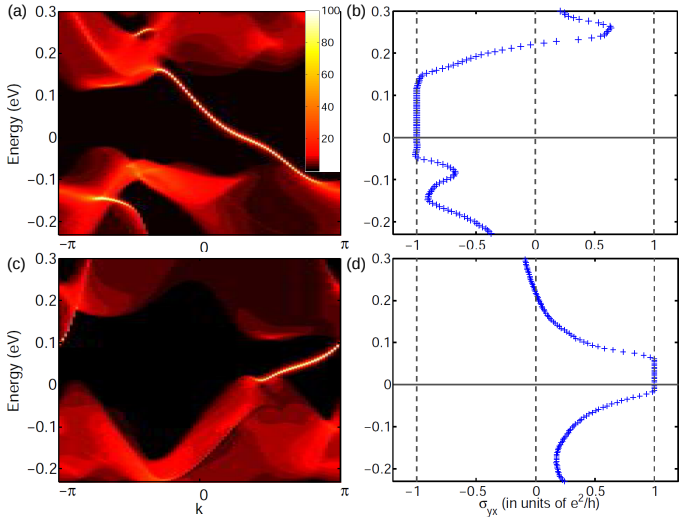

FIG. 5. Left: Edge-state spectrum in the majority spin channel for (a) Si-La and (c) Ge-Lu. Right: Dependence of majority-spin anomalous Hall conductivities as a function of Fermi-level position for (b) Si-La and (d) Ge-Lu. (All without SOC.)

at this stage to prefer one over the other.

As discussed above, the band-inversion characters shown in Fig. 3 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. 33, 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 (see the Supplementary Material) is $\sim$70 meV for the Ge-Lu system, and is as large as $\sim$130 meV for the Si-La system. Including SOC does not change the topological properties. The indirect gap with SOC included is slightly decreased for the Ge-Lu system ($\sim$60 meV), while it increases to $\sim$160 meV for the Si-La system (see the Supplementary Material).

The primary and secondary phases, which are energetically degenerate in the absence of SOC, are preferred by $\sim$100 meV over the spatial-TR-preserving 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 $\{-0.066\,\mu_B,\ 0.082\,\mu_B\}$ to $\{0.071\,\mu_B,\ -0.080\,\mu_B\}$ for the two Cr sites, and from $-0.18\,\mu_B$ to $0.29\,\mu_B$ for the La adatom. Given that the SOC strength of La is much larger than that of Cr, the system evidently selects the state with antiparallel spin and orbital moments on the La site (the spin moment on the La site is $-0.644\,\mu_B$) to maximize the energy gain from SOC. 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. That is, there might not be any band inversion leading to a nontrivial topology, even though TR symmetry is spontaneously broken. We actually find this to be the case for 1 ML Lu deposited on SL $CrSiTe_3$ and 1 ML La deposited on SL $CrGeTe_3$ in the absence of SOC, for which the bandstructures are presented in 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. 5(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. 5(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 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 Å to 1 Å. As shown in Fig. 6, the difference ΔM_{orb} between the orbital moments on the two Cr sublattices, which can be regarded as an order parameter for orbital antiferromagnetism, diminishes monotonically as the screening length is decreased. When λ =1 Å, the orbital moments almost vanish, implying that inter-site currents for such short-range Coulomb interactions are negligibly small. Both systems remain topologically nontrivial down to $\lambda \sim$1.3 Å, and eventually become trivial when $\lambda \leq$1 Å. Interestingly, the hybrid-functional bandstructures for λ=1 Å are very similar to the DFT+U bandstructures. We have also checked that one cannot obtain topologically nontrivial phases from DFT+U even if U is tuned away from the accepted value of 3.5 eV. These observations all support the conclusion that the nonlocality of the Coulomb interactions is indispensable to obtain the observed

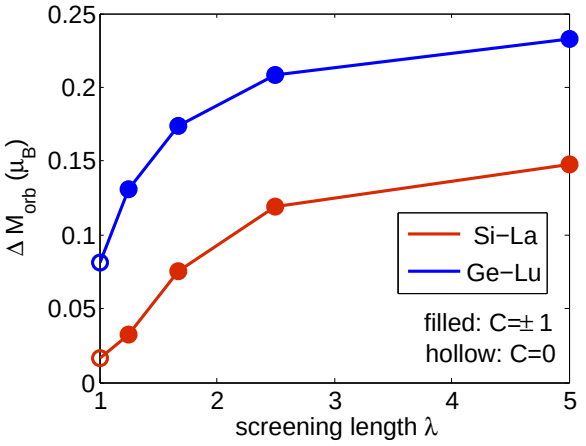

FIG. 6. The difference $\Delta M_{\rm orb}$ between the orbital magnetic moments on the two Cr sites vs. the screening length λ (in Å). Blue and red lines are for Ge-Lu and Si-La systems, and filled and hollow circles represent topologically nontrivial and trivial phases, respectively.

flux states and topological phases.

The feasibility of an experimental realization of this system deserves some comment. First, we have checked whether our results remain robust for thicker $CrSiTe_3$ or $CrGeTe_3$ layers, but unfortunately our preliminary HSE results indicate that the flux states and associated nontrivial topological phases do not survive even for double-layer substrates. This suggests that single layers of $CrSiTe_3$ or $CrGeTe_3$ would need to be prepared via exfoliation or other means, presumably on an inert substrate such as silica or boron nitride, before the adatom deposition. Even with thicker layers of $CrSiTe_3$ or $CrGeTe_3$, it may be possible to tune the system using strain [34] or chemical subsitution in such a way as to restore the flux state. Second, 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 [35].

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. In fact, 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, 36]. 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. In view of the importance of nonlocality, we expect that it will be necessary to go beyond approaches that focus on intrasite correlations, such as single-site dynamical mean-field theory. If this is not straightforward, some progress might be made in the context of model Hamiltonians.

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 the effects of Coulomb interactions in transition-metal tellurides.

ACKNOWLEDGMENTS

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