

Stability, electronic, and magnetic properties of the magnetically doped topological insulators Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3

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Magnetic interaction with the gapless surface states in a topological insulator (TI) has been predicted to give rise to a few exotic quantum phenomena. However, the effective magnetic doping of TI is still challenging in the experiment. Using first-principles calculations, the magnetic doping properties (V, Cr, Mn, and Fe) in three strong TIs (Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3) are investigated. We find that for all three TIs the cation-site substitutional doping is most energetically favorable with the anion-rich environment as the optimal growth condition. Further, our results show that under the nominal doping concentration of 4%, Cr- and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Cr-doped Sb_2Te_3 remain as insulators, while all the V- and Mn-doped TIs, and Fe-doped Sb_2Te_3 become metal. We also show that the magnetic interaction of Cr-doped Bi_2Se_3 tends to be ferromagnetic, while Fe-doped Bi_2Se_3 is likely to be antiferromagnetic. Finally, we estimate the magnetic coupling and the Curie temperature for the promising ferromagnetic insulator (Cr-doped Bi_2Se_3) by Monte Carlo simulation. These findings may provide important guidance for the magnetism incorporation in TIs experimentally.

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I. INTRODUCTION

In recent years, topological insulators characterized by insulating bulk states and gapless conducting surface states have been studied intensively both theoretically and experimentally.¹⁻⁸ Specifically, tetradymite compounds Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 were found to be three-dimensionally strong topological insulators with realistically large (a few hundred meV) bulk gap and simple surface electronic structures.^{4,5,9} On the other hand, even before the concept of the topological insulator, great efforts were made to incorporate magnetism into these systems for potential diluted magnetic semiconductors (DMS). For example, ferromagnetism was reported in Cr-doped Bi_2Se_3 (Ref. 10); Mn- and Fe-doped Bi_2Te_3 (Refs. 11-15); and V-, Cr-, and Mn-doped Sb_2Te_3 (Refs. 11,12,16-18). The ferromagnetism in the topological insulator will break the time-reversal symmetry; this intricate interplay between topological order and ferromagnetism inspired a few proposals to realize exotic quantum phenomena,¹⁹⁻²⁸ such as the magnetoelectric effect¹⁹ and quantum anomalous Hall effect (QAHE).²⁰ Experimentally the massive Dirac fermion spectrum was reported in Mn- and Fe-doped Bi_2Se_3 surface,²⁹ complex spin texture was revealed in Mn-doped Bi_2Te_3 ,³⁰ and the QAHE was recently observed in a $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{1.85}\text{Te}_3$ film under 30 mK (Ref. 31).

However, in the experiment it is still challenging to incorporate stable ferromagnetism in the TIs. For example, ferromagnetism in Fe-doped Bi_2Te_3 and Sb_2Te_3 is hardly detected even at low temperature.^{18,32,33} For Bi_2Se_3 with Mn doping a spin glass state rather than ferromagnetic state is observed.¹¹ Also both antiferromagnetism³⁴ and ferromagnetism^{10,35} were observed in Cr-doped Bi_2Se_3 . A similar controversy also exists from different groups for Fe-doped Bi_2Se_3 (Refs. 13,34,36,37). This may be related to different magnetic atoms' distribution within the host material caused by the sample preparation,

such as the temperature, flux ratio, and chemical potentials of constituent atoms.

To clarify this issue, we systematically investigate the stability, electronic, and magnetic properties of 3d transition metal (TM) elements V-, Cr-, Mn-, and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 using DFT calculations and Monte Carlo simulations. We first assess the feasibility of magnetic doping in Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 under different growth environments according to formation energy calculations.³⁸⁻⁴⁰ The preferred site for doping magnetic atoms and the optimal growth conditions are identified. Furthermore, the electronic band structure results show that Cr- and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Cr-doped Sb_2Te_3 remain as magnetic insulators with substantially reduced band gap, while all the V- and Mn-doped TIs as well as Fe-doped Sb_2Te_3 become magnetic metals. Additionally the magnetic coupling strength between magnetic atoms is studied and Curie temperature for typical concentration is estimated using Monte Carlo simulations.

This paper is organized as follows. In Sec. II we describe the method for all the calculations' proceedings. In Sec. III, we first identify the native defects of Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , which may be responsible for the intrinsic noninsulating bulk states observed in the experiment. Then we calculate the formation energies, electronic, and magnetic properties for magnetic-atom-doped TIs. We additionally show the Monte Carlo simulations for the estimation of magnetic coupling strength and Curie temperature. Finally, we conclude our paper with a brief summary of those findings.

II. METHOD

All the first-principles calculations are performed using projected augmented wave (PAW)⁴¹ potentials with Perdew-Burke-Ernzerhof-type generalized gradient approxi-

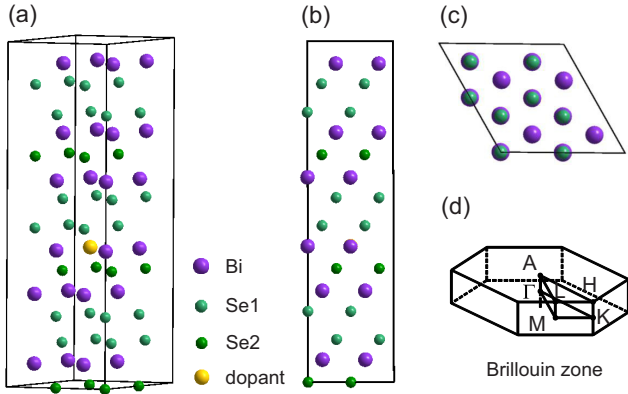


FIG. 1. (Color online) (a) Crystal structure illustration of a $2 \times 2 \times 1$ supercell for modeling a single dopant in bulk Bi_2Se_3 , with (b) for side view and (c) for top view. (d) Brillouin zone and high symmetry points of the $2 \times 2 \times 1$ supercell. There are two types of Se atoms, including Se1 involving the van der Waals bonding and the other Se2.

mation (GGA)⁴² as implemented in the Vienna *ab initio* simulation package (VASP).^{43,44} In particular, spin orbit coupling (SOC) is explicitly included due to the strong relativistic effect in Bi and Sb elements, and the significant impact on electronic structure and formation energy,⁴⁵ as also revealed by West *et al.*⁴⁶ We choose a hexagonal cell with the experimental lattice constants $a = 4.138 \text{ \AA}$, $c = 28.64 \text{ \AA}$ for Bi_2Se_3 ; $a = 4.383 \text{ \AA}$, $c = 30.487 \text{ \AA}$ for Bi_2Te_3 ; and $a = 4.250 \text{ \AA}$, $c = 30.35 \text{ \AA}$ for Sb_2Te_3 . The cutoff energy for the plane-wave expansion of electron wave function was set at 300 eV. A gamma-centered $7 \times 7 \times 2$ k mesh was adopted to sample the Brillouin zone for $2 \times 2 \times 1$ Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 supercells as illustrated in Fig. 1. For calculating the energies of charged defects or dopants, a jellium background charge is added. All atoms in each doped supercell are fully relaxed through the conjugate-gradient algorithm until the residual force on each atom is less than 0.02 eV/\AA . The numerical errors of the calculated formation energy are controlled to be less than 20 meV.

The formation energy $\Delta H_f(D, q)$ of the defect or impurity D in charge state q as a function of the Fermi energy E_F and the chemical potential μ_i^a of atom i is defined as³⁹

$$\Delta H_f(D, q) = E_{\text{tot}}(D, q) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i^a + q(E_F + E_V + \Delta V), \quad (1)$$

where $E_{\text{tot}}(D, q)$ (defect+host) is the total energy of a supercell of a host material with one defect or impurity D in a charge state q , and $E_{\text{tot}}(\text{bulk})$ (host only) is the total energy of the equivalent supercell containing only a pure host. μ_i^a denotes the chemical potential for species i (host atoms or dopants), and n_i indicates the corresponding number that has been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell. Here, it is noted that μ_i^a is given with respect to the value of a solid phase μ_i^{solid} , i.e., the absolute value of the chemical potential $\mu_i^a = \mu_i + \mu_i^{\text{solid}}$. E_F is the Fermi energy, referenced to the valence band maximum (VBM) of

the pure host crystal E_V . ΔV is a potential alignment due to different energy references in a defect containing a supercell and pure supercell in DFT calculations.

The chemical potentials depend on the experimental growth condition. The values of μ_i are determined as follows, as taking Bi_2Se_3 , for example, first, $\mu_{\text{Bi}} \leq 0$ and $\mu_{\text{Se}} \leq 0$ to avoid the precipitation of solid elements. To maintain the equilibrium growth of Bi_2Se_3 , it requires $2\mu_{\text{Bi}} + 3\mu_{\text{Se}} = \Delta H_f(\text{Bi}_2\text{Se}_3)$. Here, $\Delta H_f(\text{Bi}_2\text{Se}_3)$ is the formation energy of Bi_2Se_3 . Furthermore, $x\mu_M + y\mu_{\text{Se}} \leq \Delta H_f(M_x\text{Se}_y)$ to ensure that the competing phases $M_x\text{Se}_y$ cannot precipitate, where M is the dopant atom, i.e., V, Cr, Mn, and Fe in the paper.

$\Delta H_f(D, q)$ is a function of charge q and the Fermi energy, then we can determine the transition energy as the Fermi energy at which $\Delta H_f(D, q) = \Delta H_f(D, q')$, i.e., where the charge state of defect D spontaneously transforms from q to q' . The concentration c of defects or dopants at growth temperature T_g under thermodynamic equilibrium can be estimated from³⁹

$$c = N \exp(-\Delta H_f / k_B T_g), \quad (2)$$

where N is the number of sites that can be occupied in the lattice (per unit volume), ΔH_f is defined in Eq. (1), and k_B is the Boltzmann constant.

III. RESULTS AND DISCUSSIONS

A. Native defects

Experimentally, Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 are always dominated by conducting bulk carriers rather than being insulating even though they are all intrinsically narrow-band semiconductors. This is related to the unintentional doping induced by native defects. Bi_2Se_3 often shows n -type conductivity and is difficult to be tuned into p type via compensation doping,^{5,6,47-49} while Sb_2Te_3 shows strong p -type tendency.⁵⁰⁻⁵² For Bi_2Te_3 , it is reported to be either n type^{9,49,50,53} or p type^{18,54} depending on the growth method and environment. We then identify how the carrier type varies with the chemical potentials. The most possible native point defects including atom vacancies and antisites' defects are considered. The formation energy versus chemical potential is plotted in Fig. 2.

As shown in Fig. 2(a), donor-like defects V_{Se1} and Se_{Bi} dominate in Bi_2Se_3 in most ranges of the growth conditions according to their lowest formation energies among all the native point defects, as was also revealed by the authors of Refs. 46,55. This will lead to an intrinsic n -type doping as experimentally observed. In the extreme Bi-rich condition, the acceptor-like defect Bi_{Se1} will be preferred and the resulting doping will be p type.

For Bi_2Te_3 in Fig. 2(b), antisite defects Bi_{Te1} and Te_{Bi} are more preferred than other native point defects. We identify that acceptor-like Bi_{Te1} is likely to appear in Bi-rich condition and donor-like Te_{Bi} in Te-rich condition, leading Bi_2Te_3 to be intrinsic p type and intrinsic n type, respectively. Our result explains the experimentally reported native n - p -amphoteric-type conductivity of Bi_2Te_3 (Refs. 9,18,49,50,53,54). Our result agrees with that found in Ref. 46, while the calculation without the inclusion of SOC gives rather different values of the formation energy.⁵⁶ Experimentally, the authors of Ref. 57

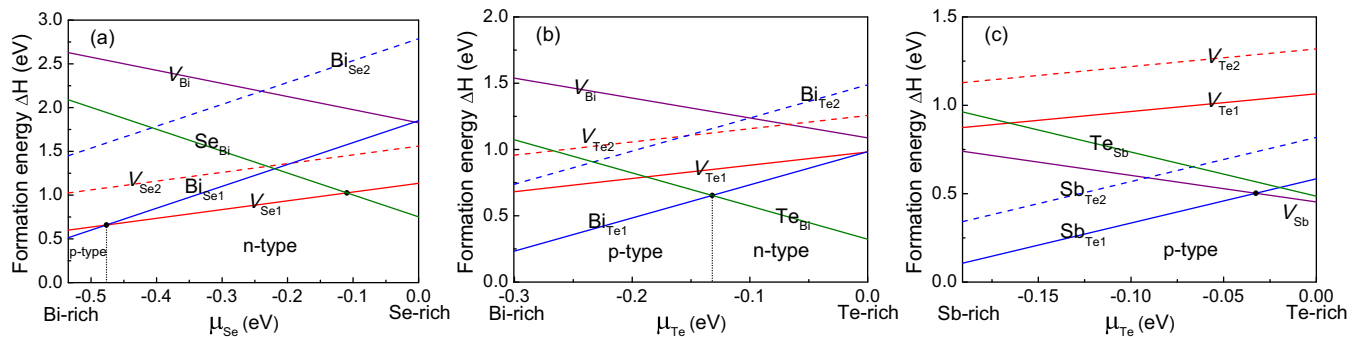


FIG. 2. (Color online) The formation energy ΔH as a function of anion chemical potential for all the possible intrinsic defects in (a) Bi_2Se_3 , (b) Bi_2Te_3 , and (c) Sb_2Te_3 . V_{Bi} , V_{Sb} , V_{Se} , and V_{Te} stand for bismuth vacancy, antimony vacancy, selenium vacancy, and tellurium vacancy, respectively, while $\text{Bi}_{\text{Se}2}$, $\text{Bi}_{\text{Te}2}$, $\text{Sb}_{\text{Te}2}$, Se_{Bi} , and Te_{Bi} are antisites' defects. 1 and 2 are labeled to distinguish Se (Te) in different layers. X rich (X for Bi, Sb, Se, or Te) indicates the extreme growth condition with μ_X taking the maximum value in Eq. (1). Vertically dotted lines highlight the boundary of carrier types.

reported the coexistence of the Te_{Bi} antisite and $\text{Bi}_{\text{Te}1}$ antisite, rendering Bi_2Te_3 to be either an n -type tendency or p -type tendency. This result further confirms our prediction.

For Sb_2Te_3 in Fig. 2(c), we find that the antisite defect $\text{Sb}_{\text{Te}1}$ is dominant with the lowest formation energy in most ranges of the growth conditions, especially in the Sb-rich condition. This can be explained qualitatively by the similar atomic sizes of the Sb atom and Te atom. As the growth atmosphere evolves to be extremely Te rich, the antimony vacancy V_{Sb} becomes the most energetically stable. Note that both $\text{Sb}_{\text{Te}1}$ and V_{Sb} are acceptor-like defects, Sb_2Te_3 is thus always intrinsic p type.^{46,51,52} Our results provide an important guide to carrier tuning in Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 as well as intrinsic carrier environments for magnetic doping. Meanwhile, these findings also provide a clear explanation to experimental reports, as listed in Table I.

B. Formation energies of magnetic doping in Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3

In this section, we will calculate the formation energies for the incorporation of TM atoms into the three TIs. First, the site preference of the TM atom (substitutional or interstitial site) is studied. Notice that the intercalated and interstitial sites were reported to be preferred for Cu in Bi_2Se_3 (Ref. 58). We have considered all the possible interstitial sites in bulk Bi_2Se_3 , including interstitial sites between different layers (intercalated sites) and interstitial sites on the same layer. Relaxed structures

indicate that all the interstitial atoms are relaxed to the three main sites, as shown in Fig. 3(a). Formation energies for both the substitution and interstitial cases are shown in Fig. 3(b). We find that the Bi substitutional site is strongly preferred⁵⁹ regardless of the changes of growing condition, as compared to all the possible interstitial sites. Our results are well in line with recent experimental findings.^{59,60} In the following we will mainly focus on cation substitutional doping.

The formation energy of TM doping as a function of chemical potential is shown in Fig. 4. Similar to TM doping in Bi_2Se_3 (Ref. 61), the formation energies exhibit the same size effect in Bi_2Te_3 and Sb_2Te_3 , that is, the formation energy is lowest for V atom doping while highest for Fe atom doping. It is attributed to the closest atom radius of the V atom to the substituted Bi or Sb atom than other dopants. Also we find that V and Cr have negative formation energies in Bi_2Se_3 and Sb_2Te_3 for the whole range of chemical potential, indicating the doping of them can occur spontaneously. Recently, heavy Cr doping of Bi_2Se_3 with the concentration up to 23% was reported⁶² and the atomic force microscopy measurement indicated Cr atoms of 20% doping concentration were uniformly distributed.³⁵ For Sb_2Te_3 , even in $\text{Sb}_{1.41}\text{Cr}_{0.59}\text{Te}_3$, Cr atoms can homogeneously distribute without clustering.¹⁸ However, in Bi_2Te_3 , only V can be spontaneously doped. Also it is rather different that the formation energies of Mn and Fe doping are positive values in all three TIs, suggesting the doping of them is not spontaneous except Mn in Bi_2Se_3 at an extremely Se-rich atmosphere. Indeed, Hor *et al.* showed that 9% Mn can

TABLE I. A list of theoretical and experimental reports of carrier-type tendency in pure Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 .

| | n -type tendency | | p -type tendency | |
|--------------------------|-------------------------------|---------------------|-------------------------------|----------------|
| | Theory | Experiment | Theory | Experiment |
| Bi_2Se_3 | Our, ^a Refs. 46,55 | Refs. 5,6,47–49 | Our, ^b Refs. 55 | |
| Bi_2Te_3 | Our, ^c Refs. 46,56 | Refs. 9,49,50,53,57 | Our, ^d Refs. 46,56 | Refs. 18,54,57 |
| Sb_2Te_3 | | | Our, Refs. 46 | Refs. 50–52 |

^aMost growth conditions.

^bExtremely Bi-rich condition.

^cTe-rich condition.

^dBi-rich condition.

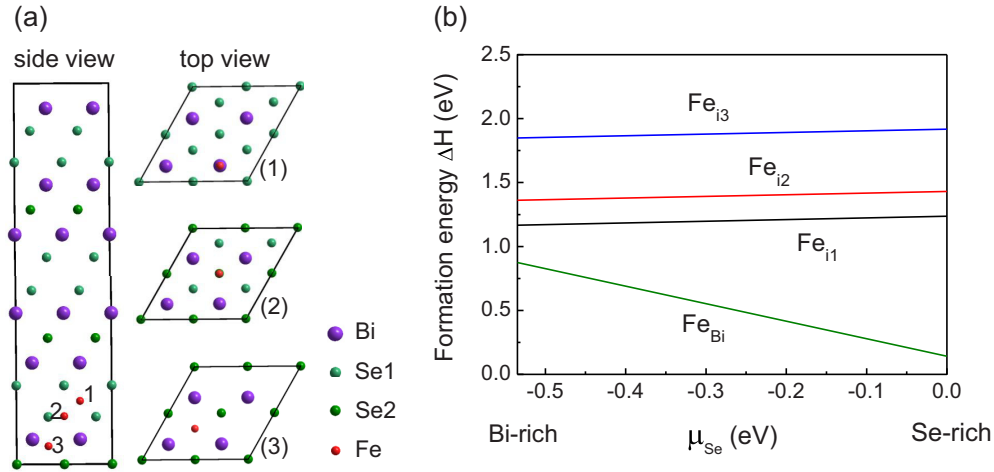


FIG. 3. (Color online) (a) Possible interstitial sites for Fe in Bi₂Se₃ after relaxation. (b) The formation energy ΔH as a function of anion chemical potential (μ_{Se}) for interstitial Fe and Fe substitutional for Bi in Bi₂Se₃. Fe_{i1} , Fe_{i2} , and Fe_{i3} stand for different sites for interstitial Fe in (a), while Fe_{Bi} denotes that the Bi atom is doped by the Fe atom.

substitute for Bi atoms with randomly distribution in Bi₂Te₃ (Ref. 14). Fe is confirmed to be even more difficult to be doped in Bi₂Se₃ with the effective doping concentration less than 2%.⁶³ Notice that Bi₂Te₃ has entirely higher formation energies for all these dopants than that in Bi₂Se₃ and Sb₂Te₃, suggesting it is relatively more difficult to dope those atoms in Bi₂Te₃.

From Sec. III A, we have known that the native defects are responsible for the various intrinsic carriers' doping. Such a carrier environment is expected to affect the formation energy of a magnetic dopant with nonzero charge state according to Eq. (1). Then we study the possible charge states by calculating the formation energy as a function of Fermi energy, as shown in Fig. 5. SOC band gaps of Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃ are calculated to be 0.32, 0.15, and 0.12 eV, respectively. Usually, band gaps originating from a charge transfer like GaAs may be underestimated by the local density approximation (LDA) or GGA method, necessary corrections are needed.⁴⁰ While for SOC opened band gaps, the GGA method can well deal with. Our values are consistent with experimental studies^{9,29} and existing calculations,^{4,20,26,46,64} and agree well with that from GW calculations for Bi₂Se₃ (Refs. 65,66) and Bi₂Te₃ (Refs. 65,67,68), although GW methods are more accurate to calculate band gaps.

(i) For Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃, anion-rich growth conditions (Se rich or Te rich) with lower formation energies are revealed to be better than cation-rich conditions (Bi rich or Sb rich) for magnetic atoms' doping, which is consistent with experimental reports.^{18,69}

(ii) For Bi₂Se₃, we find that as the Fermi energy E_F ranges from VBM at 0.0 (left edge of the shaded area) to CBM at E_g (right edge of the shaded area), V, Cr, Mn, and Fe atoms are almost stable with a charge state of +3, i.e., a neutral substitute for Bi atoms, which indicates that dopants do not introduce free carriers to the host materials. This result agrees with theoretical study from Larson *et al.*⁷⁰ and has been experimentally confirmed in Cr-doped Bi₂Se₃ (Ref. 35). Although, as E_F shifts very close to CBM, i.e., under an extremely *n*-type condition, dopants tend to act as acceptors with valency+2, especially Mn and Fe. Experimentally, Mn was indeed found to show a hole doping effect in Bi₂Se₃ (Ref. 29).

(iii) For Bi₂Te₃, the formation energies of TMs are larger than those in Bi₂Se₃ or Sb₂Te₃ both at Bi-rich and Te-rich conditions. Mn and Fe can be neutral doped in very *p*-type conditions. Mostly, Mn tends to act as an acceptor (Mn_{Bi}^-) with valence state Mn^{2+} in Bi₂Te₃. This agrees well with the experimental result from Hor *et al.*¹⁴

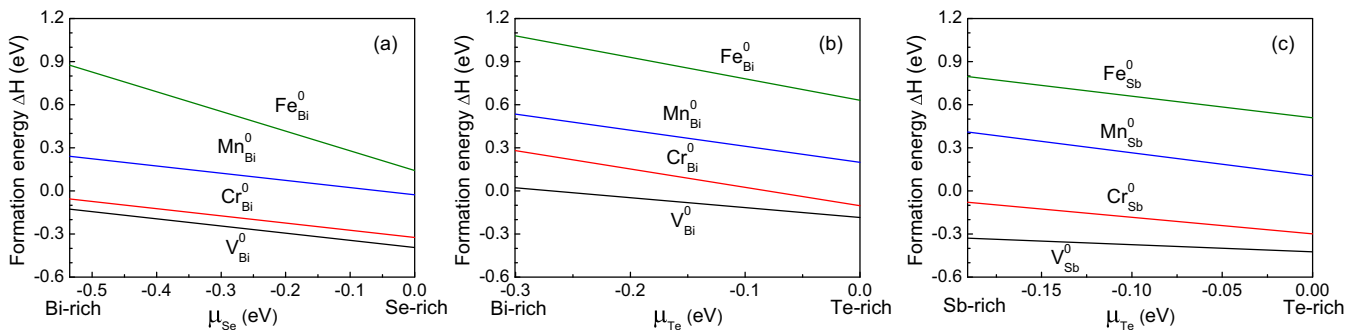


FIG. 4. (Color online) Calculated formation energies of the most stable configurations of single V, Cr, Mn, and Fe impurities doped (a) Bi₂Se₃, (b) Bi₂Te₃, and (c) Sb₂Te₃ as a function of the host element chemical potentials.

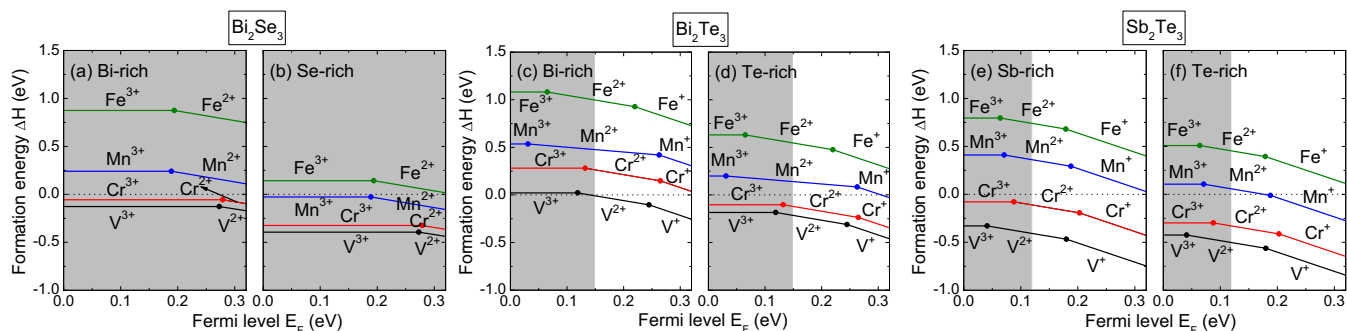


FIG. 5. (Color online) Calculated defect formation energy ΔH as a function of Fermi energy E_F for magnetically doped Bi_2Se_3 under (a) Bi-rich condition and (b) Se-rich condition; Bi_2Te_3 under (c) Bi-rich condition and (d) Te-rich condition and Sb_2Te_3 under (e) Sb-rich condition and (f) Te-rich condition. Here, E_F is referenced to the valence-band maximum (E_V) in the bulk. The shaded areas highlight band gaps, where E_F can range, as we mainly focus, from VBM ($E_F = 0$) to CBM ($E_F = E_g$). Calculated values of band gaps with SOC for Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 are 0.32, 0.15, and 0.12 eV, respectively. Solid dots denote the defect transition energies between different charge states.

(iv) For Sb_2Te_3 , a similar size effect among V, Cr, Mn, and Fe dopants is observed. V and Cr with negative formation energies can be spontaneously incorporated under a Te-rich atmosphere. Cr can be neutrally doped (Cr_{Sb}^0) (Refs. 17,18) in most ranges of the Fermi level.

From Fig. 5 we can easily determine the thermodynamic transition level from one charge state to another for different dopants, which can be observed in deep-level transient spectroscopy (DLTS) experiments or temperature-dependent Hall measurements.³⁹ We schematically illustrate them in Fig. 6. Bi_2Se_3 is revealed above to be mostly intrinsic n

type, nevertheless, from Fig. 6(a) we can see that V, Cr, Mn, and Fe are neutral stable in most carrier environments for Bi_2Se_3 , even in n -type condition (E_F near to CBM). From Fig. 6(b) for Bi_2Te_3 , it is indicated that under the n -type condition only V and Cr can neutrally substitute for the Bi atom, while Mn and Fe are energetically stable with charge states of +2. Conversely, neutral substituting is more likely to appear by V, Cr, and Fe doping than Mn in p -type Bi_2Te_3 . From Fig. 6(c) for Sb_2Te_3 , as compared to V, Mn, and Fe, Cr_{Sb} is especially deep and more difficult to be ionized from charge state Cr^{3+} to Cr^{2+} , suggesting Cr is the best candidate atom for the realization of the QAHE in Sb_2Te_3 . Actually, Cr has already been experimentally confirmed to substitute for Sb with Cr^{3+} in Sb_2Te_3 (Refs. 17,18). According to Figs. 5 and 6, even if the band gaps of Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 had a little change due to the GGA approximation, these qualitative results would not be affected, and neutral substitutions of dopants are still available.

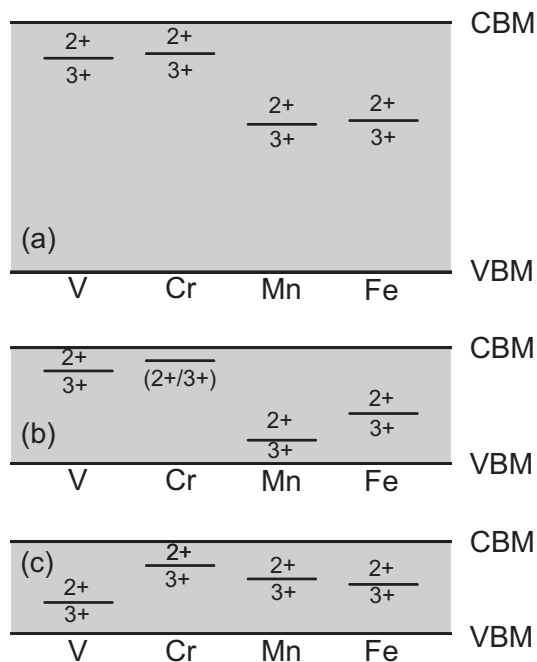


FIG. 6. Schematic representation of the thermodynamic transition levels for magnetically doped (a) Bi_2Se_3 , (b) Bi_2Te_3 , and (c) Sb_2Te_3 , which correspond to the solid dots in Fig. 5. The transition levels shown are referenced to valence-band maximum (VBM) in the bulk. The distances of $\varepsilon(3+/2+)$ to VBM, for example, indicate the thermal ionization energies of simple acceptors. The shaded areas highlight band gaps of Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , as shown in Fig. 5.

C. Electronic structure of magnetically doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3

To elaborate the electronic properties with magnetic atoms introduced in Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , we further calculate the band structures for all those magnetically doped TIs and they are shown in Fig. 7. In Fig. 7, additional states appear in the band gaps of TM-doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 and give rise to semiconducting or metallic ground states, compared to the pure host materials.^{4,61,64} The plots of TM- d orbital projected band structures show the states near the band gaps are from sizable hybridization between TM states and p states of host materials, most obvious at the Gamma point of the Brillouin zone. The results indicate that V- and Mn-doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 are metals, as shown in Figs. 7(a) to 7(c) and Figs. 7(g) to 7(i), respectively. However, Cr-doped Bi_2Se_3 exhibits an insulating magnetic state with the energy gap 0.01 eV. Compared to pure Bi_2Se_3 (Ref. 61), inverted bands are remain observed in the doped system, indicating the topological nontrivial property. Accounting to our calculations, we get similar results in Cr-doped Bi_2Te_3 with the band gap of 0.017 eV and Cr-doped Sb_2Te_3 with a larger band gap of 0.077 eV. From Figs. 7(j) to 7(l), we

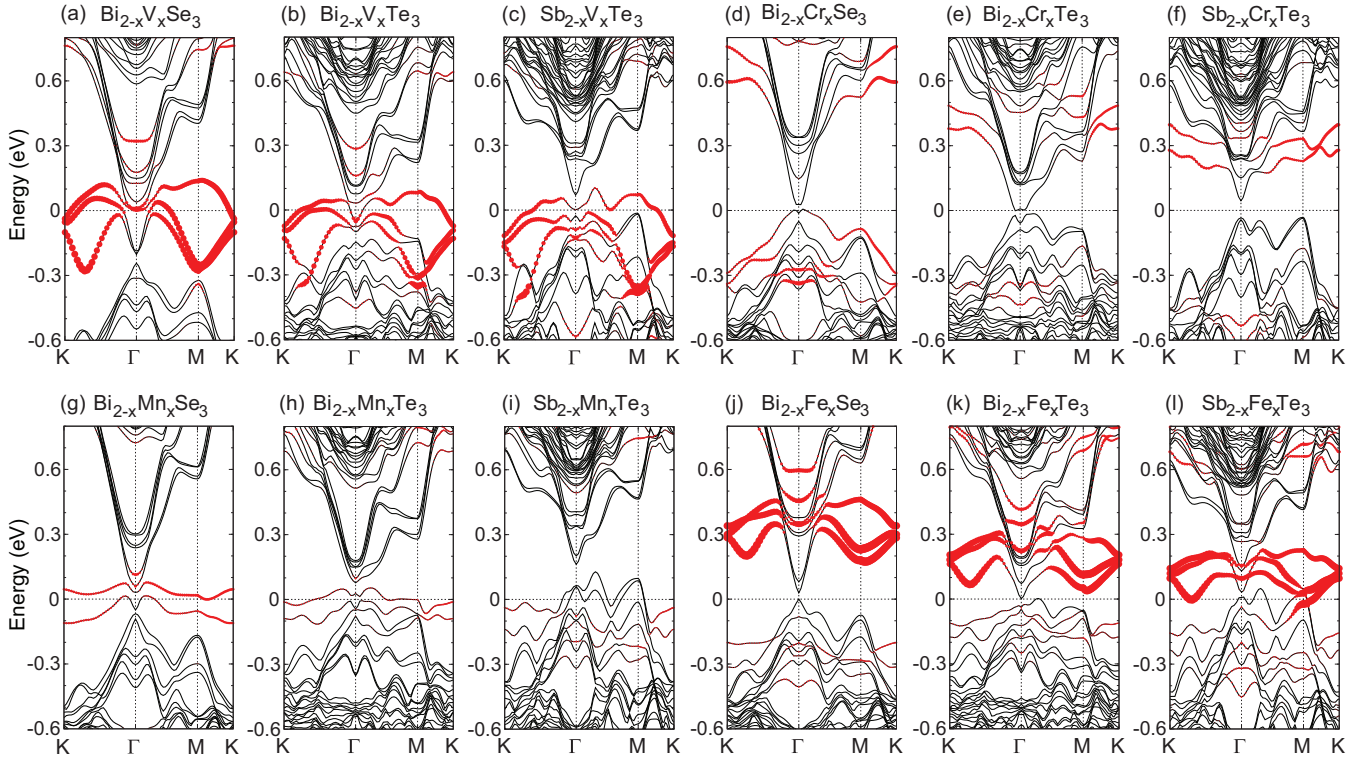


FIG. 7. (Color online) SOC band structures for relaxed V-, Cr-, Mn-, and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 with the nominal doping concentration of 4% ($x = 0.083$). The size of the red dots denotes the contribution of TM- d states.

find that Fe-doped Bi_2Se_3 manifests insulating behavior with the band gap of 0.028 eV, whereas magnetic moments of Fe-doped Bi_2Te_3 and Sb_2Te_3 are less than $5 \mu_B$, rendering Fe-doped Bi_2Te_3 to be semimetal with a narrow gap 0.0024 eV and Fe-doped Sb_2Te_3 to be gapless. The phenomenon of gap closing may lead to a topological phase transition.^{25–27} The resulting values of the band gaps and magnetic moments upon doping are listed in Table II. To investigate the effect of the electron-electron correlation on band gap and magnetic moment, we further perform GGA + U calculations with U ranging from 3 to 6 eV and $J = 0.87$ eV. We find only a slight modification of the band gaps and magnetic moments.

Notice that the band gaps are 0.32, 0.15, and 0.12 eV for Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 , respectively. However, we find the band gaps are substantially reduced to several meV upon doping. This result hints that the QAHE should be observed under low temperature in the magnetically doped Bi_2Se_3 family, which is consistent with recent experimental reports.³¹ To uncover the reason that causes this band gap

reduction, we study the effect of structural relaxation on the band gap. In Fig. 8, we show the schematic structures of doped Bi_2Se_3 before and after relaxation. The structural relaxation shows that Se atoms neighboring to dopants move inward to the dopants by sizable distances (see Table III), consistent with the findings of the authors of Ref. 70. This suggests that hybridization between the TM dopant and the neighboring Se will be strengthened and thus the impurity bands may be broadened.⁶¹ Specifically, as reported in our previous paper,⁶¹ calculated band gaps of Cr- and Fe-doped Bi_2Se_3 without relaxation are 0.28 and 0.18 eV, respectively. While after structural relaxation, the band gaps are reduced to 0.01 and 0.028 eV, respectively. GGA + U calculation for the relaxation gives essentially the same results shown in Table III as only the GGA calculation. Additional SOC relaxations for Cr- and Fe-doped Bi_2Se_3 suggest the relaxed distances change within only the order of 0.001 Å compared to non-SOC cases. We thus conclude that the band gap reduction is induced by Se-dopant hybridization.

TABLE II. Relaxed band gaps and magnetic moments (m) of Cr- and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 with SOC. The results of GGA + U with $U = 3$ eV and $J = 0.87$ eV are also listed.

| System | Cr | | | | Fe | | | |
|--------------------------|----------|--------------|--------------|--------------|-----------|--------------|--------------|--------------|
| | gap | gap (+ U) | m | m (+ U) | gap | gap (+ U) | m | m (+ U) |
| Bi_2Se_3 | 0.010 eV | 0.025 eV | $2.94 \mu_B$ | $2.99 \mu_B$ | 0.028 eV | 0.028 eV | $4.73 \mu_B$ | $4.99 \mu_B$ |
| Bi_2Te_3 | 0.017 eV | 0.019 eV | $2.93 \mu_B$ | $2.98 \mu_B$ | 0.0024 eV | 0.041 eV | $4.17 \mu_B$ | $4.09 \mu_B$ |
| Sb_2Te_3 | 0.077 eV | 0.100 eV | $3.06 \mu_B$ | $3.16 \mu_B$ | 0 | 0 | $4.17 \mu_B$ | $4.03 \mu_B$ |

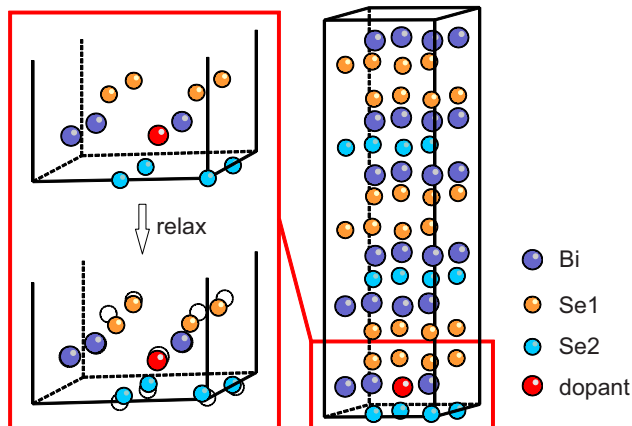


FIG. 8. (Color online) Dynamics illustration of the magnetically doped Bi_2Se_3 . Note that those Se atoms neighboring the dopants tend to be close to the dopants, while Bi atoms hardly move.

D. Magnetic properties of magnetically doped Bi_2Se_3

As proposed in Ref. 20, both an insulator and ferromagnetism are required to realize the QAHE. After possible candidates have been achieved, we then further investigate the feasibility of establishing ferromagnetism for Cr and Fe in the most promising and concerned TI Bi_2Se_3 , which has the largest band gap among all the discovered TIs. First, the magnetic ground state of single magnetic dopants in Bi_2Se_3 is identified. We have tried different initial directions of the magnetic moments. The results indicate that both Cr and Fe prefer the direction perpendicular to the Bi_2Se_3 quintuple layers (QLs) (axis 001). The magnetic moments are about $3 \mu_B$ for Cr and $5 \mu_B$ for Fe, respectively. The magnetization anisotropy energies for Cr and Fe are about 7 and 16 meV, respectively. Then, we investigate the magnetic coupling between the two TM dopants. The favored magnetic state [either ferromagnetic (FM) or anti-ferromagnetic (AFM)] is studied by calculating the total energy difference of the two configurations at the same TM-dopant separation. Our calculations indicate that weak AFM is favorable in Fe-doped Bi_2Se_3 , while the magnetism is experimentally difficult to observe^{13,36} due to the scarce effective doping concentration.⁶¹ Our previous work⁶¹ found that Cr-doped Bi_2Se_3 prefers to be in the FM state, which has been also predicted by Lu *et al.*⁷¹ and confirmed by some recent experiments.^{10,35,62} The magnetic coupling strengths $[(E_{AFM} - E_{FM})/2]$ for two Cr atoms within the same QL at

TABLE III. Amplitude of the bond length variation Δd (in \AA) from GGA and GGA + U calculations for Cr- and Fe-doped Bi_2Se_3 with all the atoms fully relaxed. Here, $\Delta d = d_{\text{relaxed}} - d_{\text{initial}}$, where the negative value means a decrease of the bond length.

| Bond length | Cr | | Fe | |
|-------------------------|------------|-----------------|------------|-----------------|
| | Δd | $\Delta d (+U)$ | Δd | $\Delta d (+U)$ |
| $d_{\text{dopant-Bi}}$ | 0.009 | 0.009 | 0.000 | 0.002 |
| $d_{\text{dopant-Se1}}$ | -0.342 | -0.305 | -0.404 | -0.360 |
| $d_{\text{dopant-Se2}}$ | -0.390 | -0.362 | -0.239 | -0.263 |

TABLE IV. Calculated magnetic coupling strength $[(E_{AFM} - E_{FM})/2]$ between two substitutional Cr atoms with different distances d for $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ ($x = 0.074$). Two Bi atoms are replaced by dopant atoms at site $i = 0$ and site j ($j = 1, 2, 3, \dots$) in a $3 \times 3 \times 1$ supercell of Bi_2Se_3 , which gives distinct configurations. The first seven nearest-neighbor configurations of Cr atoms are considered as listed. Farther neighbor configurations are ignored for their large distances of Cr atoms [d of configuration (0, 8) is already larger than 9\AA] and little contributions to the magnetic coupling strengths (less than 2 meV).

| Configuration (i, j) | d (\AA) | $(E_{AFM} - E_{FM})/2$ (meV) |
|--------------------------|----------------------|------------------------------|
| (0, 1) | 4.138 | 22.0 |
| (0, 2) | 4.456 | 13.8 |
| (0, 3) | 5.785 | 8.7 |
| (0, 4) | 6.081 | -3.8 |
| (0, 5) | 7.113 | 5.5 |
| (0, 6) | 7.167 | 2.1 |
| (0, 7) | 7.355 | -1.8 |

the first three nearest-neighboring distances are on the order of 10 meV. In our calculations, an appropriate supercell of $3 \times 3 \times 1$ Bi_2Se_3 was employed. Additional calculations from a larger supercell of $4 \times 4 \times 1$ Bi_2Se_3 indicate that magnetic coupling strengths only change within 2 meV. From the QAHE point of view, a spontaneous FM ground state is required. We therefore carried out Monte Carlo simulations^{72,73} to determine the Curie temperature (T_c) in Cr-doped Bi_2Se_3 . $L \times L \times L$ ($L = 20$) Bi_2Se_3 cells with periodic boundary conditions are used. Then the magnetic Cr atoms are randomly distributed on the Bi lattice sites of Bi_2Se_3 with the ratio of Cr:Bi to be $x : (2 - x)$, where $x = 0.074$ in the simulation. The Heisenberg Hamiltonian of the system is described as⁷²

$$E = - \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (3)$$

where J_{ij} is the exchange coupling constant between the i th and j th dopant atoms, taken from the first-principles calculations as shown in Table IV. The thermodynamic magnetization per atom can be calculated by $M(T) = \langle [(\sum_i S_i^x)^2 + (\sum_i S_i^y)^2 + (\sum_i S_i^z)^2]^{1/2} \rangle / N$, where N is the number of the magnetic dopant atoms, and $\langle \dots \rangle$ is the statistical average over different states which are generated during the Markov process.⁷² To define the Curie temperature, an accumulation of the magnetization of the fourth order U_L (Binder cumulant) is calculated by $U_L = 1 - \langle M^4 \rangle / 3 \langle M^2 \rangle^2$ (Refs. 74–76). Figure 9 shows the simulated magnetization M and U_L as a function of temperature for $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ with $x = 0.074$. We get an estimated Curie temperature T_c at about 76 K.

IV. SUMMARY

In summary, we systematically studied the stability, electronic, and magnetic properties of magnetically doped topological insulators Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 using first-principles calculations in combination with Monte Carlo simulation. Our calculations showed that cation site substitutional doping was energetically most favorable. Furthermore, we suggested a recipe of effective magnetic doping for

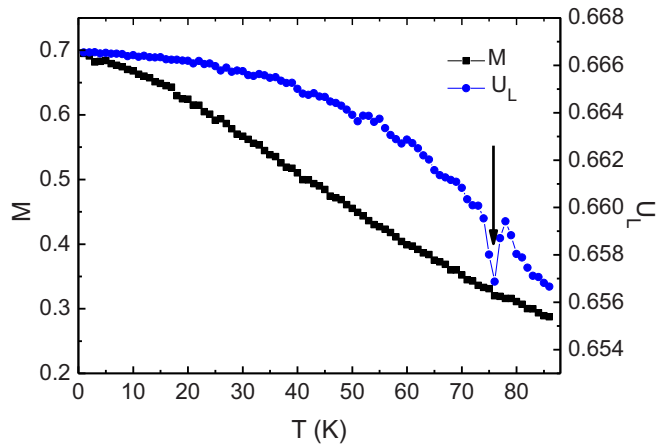


FIG. 9. (Color online) Monte Carlo simulation of $\text{Bi}_{2-x}\text{Cr}_x\text{Se}_3$ with $x = 0.074$. M is the simulated magnetization and U_L , the Binder cumulant, is the normalized fourth-order cumulant of the magnetization. The Curie temperature is estimated at about 76 K.

experimental study with the optimal growth conditions. In addition, our results indicated that under the nominal doping concentration of 4%, Cr- and Fe-doped Bi_2Se_3 , Bi_2Te_3 and Cr-doped Sb_2Te_3 remain insulators, although the band gaps were substantially reduced due to Se-dopant hybridization.

Instead, all TIs doped with V and Mn as well as Fe-doped Sb_2Te_3 became metals. Finally, we explored the magnetic coupling between dopants, suggesting FM was favorable in Cr-doped Bi_2Se_3 while AFM in the Fe-doped material. Using Monte Carlo simulation, we estimated that the Curie temperature of 7.4% Cr-doped Bi_2Se_3 was about 76 K. Our results provide important guidelines towards further experimental efforts of incorporating magnetism in TI, in particular for the realization of the QAHE based on magnetic topological insulators.

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