Stability, Electronic and Magnetic properties of magnetically doped topological insulators Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$

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Magnetic interaction with the gapless surface states in 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 experiment. Using first-principles calculations, the magnetic doping properties (V, Cr, Mn and Fe) in three strong TIs (Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$) are investigated. We find that for all three TIs the cation-site substitutional doping is most energetically favorable with 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$_2$Se$_3$, Bi$_2$Te$_3$, and Cr doped Sb$_2$Te$_3$ remain as insulator, while all TIs doped with V, Mn and Fe doped Sb$_2$Te$_3$ become metal. We also show that the magnetic interaction of Cr doped Bi$_2$Se$_3$ tends to be ferromagnetic, while Fe doped Bi$_2$Se$_3$ is likely to be antiferromagnetic. Finally, we estimate the magnetic coupling and the Curie temperature for the promising ferromagnetic insulator (Cr doped Bi$_2$Se$_3$) 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$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are found to be three-dimensional strong topological insulators with realistically large (a few hundred meV) bulk gap and simple surface electronic structure.$^{4,5,9}$ On the other hand, even before the concept of 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$_2$Se$_3$, Mn and Fe doped Bi$_2$Te$_3$, and V, Cr and Mn doped Sb$_2$Te$_3$. The ferromagnetism in topological insulator will break the time-reversal symmetry, this intricate interplay between topological order and ferromagnetism aroused a few proposals to realize exotic quantum phenomena, such as, magnetoelectric effect$^{19}$ and quantum anomalous Hall effect (QAHE).$^{20}$ Experimentally the massive Dirac fermion spectrum was reported in both Mn and Fe doped Bi$_2$Se$_3$ surface,$^{25}$ complex spin texture was revealed in Mn doped Bi$_2$Te$_3$ and QAHE was recently observed in Cr$_0$.$15$(Bi$_0$.$1$Sb$_0$.$9$)$_1$.85Te$_3$ film under 30 mK.$^{31}$ However, in experiment it is still challenging to incorporate stable ferromagnetism in the TIs aforementioned. For example, ferromagnetism in Fe doped Bi$_2$Te$_3$ and Sb$_2$Te$_3$ is hardly detected even in low temperature.$^{18,32,33}$ For Bi$_2$Se$_3$ with Mn doping a spin glass state rather than ferromagnetic state is observed.$^{11}$ Also both antiferromagnetism$^{34}$ and ferromagnetism$^{10,35}$ were observed in Cr doped Bi$_2$Se$_3$. The similar controversy also exists from different groups for Fe doped Bi$_2$Se$_3$.$^{13,34,36,37}$ This may be related to different magnetic atoms distribution within the host material caused by the sample preparation, such as, temperature, flux ratio, and chemical potentials of constituent atoms.

In order 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$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ using DFT calculations and Monte Carlo simulations. We first assess the feasibility of magnetic doping in Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ under different growth environment according to formation energy calculations.$^{38,39}$ The preferred site for the doping magnetic atoms and the optimal growth conditions are identified. Further the electronic band structure results show that Cr and Fe doped Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Cr doped Sb$_2$Te$_3$ remain as magnetic insulator with substantially reduced band gap, while all TIs doped with V and Mn as well as Fe doped Sb$_2$Te$_3$ become magnetic metal. 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 proceeding. In Sec. III, we first identify the native defects of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$, which may be responsible for the intrinsic non-insulating bulk states observed in 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) potentials with Perdew-Burke-Ernzerhof type generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP). 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, as also revealed by West et al. We choose hexagonal cell with the experimental lattice constants \(a=4.138 \text{ Å}, c=28.64 \text{ Å} \) for \(\text{Bi}_2\text{Se}_3\); \(a=4.383 \text{ Å}, c=30.487 \text{ Å} \) for \(\text{Bi}_2\text{Te}_3\) and \(a=4.250 \text{ Å}, c=30.35 \text{ Å} \) for \(\text{Sb}_2\text{Te}_3\). The cutoff energy for the plane wave expansion of electron wavefunction was set at 300 eV. A gamma-centered \(7 \times 7 \times 2\) k-mesh was adopted to sample the Brillouin zone for \(2 \times 2 \times 1\) \(\text{Bi}_2\text{Se}_3\), \(\text{Bi}_2\text{Te}_3\) and \(\text{Sb}_2\text{Te}_3\) supercells as illustrated in Fig. 1. As calculating the energies of charged defects/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/Å. The numerical errors of calculated formation energy are controlled to be less than 20 meV.

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

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

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

The chemical potentials depend on the experimental growth condition. The values of \(\mu_i\) are determined as follows, as taking \(\text{Bi}_2\text{Se}_3\) for example, first, \(\mu_{\text{Bi}} \leq 0\) and \(\mu_{\text{Se}} \leq 0\) to avoid precipitation of solid elements. To maintain equilibrium growth of \(\text{Bi}_2\text{Se}_3\), 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 \(\text{Bi}_2\text{Se}_3\). Furthermore, \(\Delta H_f(M_i\text{Se}_p)\) ensures that the competing phases \(M_i\text{Se}_p\) can not precipitate, where \(M\) is the dopant atom, i.e., \(V, \text{Cr}, \text{Mn}\) and \(\text{Fe}\) in the paper.

\(\Delta H_f(D, q)\) is a function of charge \(q\) and 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 from

\[
c = N \exp(-\Delta H_f/k_BT_g),
\]

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

III. RESULTS AND DISCUSSIONS

A. Native defects

Experimentally, \(\text{Bi}_2\text{Se}_3\), \(\text{Bi}_2\text{Te}_3\) and \(\text{Sb}_2\text{Te}_3\) 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. \(\text{Bi}_2\text{Se}_3\) often shows \(n\)-type conductivity and is difficult to be tuned into \(p\)-type via compensation doping, while \(\text{Bi}_2\text{Te}_3\) shows strong \(p\)-type tendency. For \(\text{Bi}_2\text{Te}_3\), it is reported to be either \(n\)-type or \(p\)-type 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 the most range of growth conditions according to their lowest formation energies among all the native point defects, as also revealed by Ref. 45,54. This will lead to an intrinsic \( n \)-type doping as experimentally observed. In the extreme \( Bi \)-rich condition, 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 \( Bi_2Te_3 \).\(^9,18,48,49,52,53\) Our result agrees with Ref. 45, while calculation without the inclusion of SOC gives rather different values of formation energy.\(^{55}\) Experimentally Ref. 56 reported the co-existence of \( Te_{Bi} \) antisite and \( Bi_{Te1} \) antisite, rendering \( Bi_2Te_3 \) to be either \( n \)-type tendency or \( p \)-type tendency. This result further confirms our predication.

For \( Sb_2Te_3 \) in Fig. 2(c), we find that antisite defect \( Sb_{Te1} \) is dominant with the lowest formation energy in most range of the growth conditions especially in Sb-rich condition. This can be explained qualitatively by the similar atomic sizes of Sb atom and Te atom. As the growth atmosphere evolves to be extremely Te-rich, antimony vacancy \( V_{Sb} \) becomes to be the most energetically stable. Note that both \( Sb_{Te1} \) and \( V_{Sb} \) are acceptor-like defects, \( Sb_2Te_3 \) is thus always intrinsic \( p \)-type.\(^{45,50,51}\) Our results provide an important guidance 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.

![Formation energy ∆H (eV) vs. chemical potential](image)

FIG. 2: (color online). The formation energy ∆H as a function of anion chemical potential for all the possible intrinsic defects in (a) \( Bi_2Se_3 \), (b) \( Bi_2Te_3 \) and (c) \( Sb_2Te_3 \). \( V_{Bi} \), \( V_{Si} \), \( V_{Se} \) and \( V_{Te} \) stand for bismuth vacancy, antimony vacancy, selenium vacancy and tellurium vacancy, respectively, while \( Bi_{Se} \), \( Bi_{Te} \), \( Sb_{Te} \), \( Se_{Bi} \) 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) indicate the extreme growth condition with \( \mu_X \) taking the maximum value in Eq.(1). Vertically dotted lines highlight the boundary of carrier types.

### 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\(^a\), Ref. 45,54 | Ref. 5,6,46–48        | Our\(^b\), Ref. 54    |
| \( Bi_2Te_3 \) | Our\(^c\), Ref. 45,55 | Ref. 9,48,49,52,56    | Our\(^d\), Ref. 45,55 |
| \( Sb_2Te_3 \) |                       |                       | Our, Ref. 45          |

\(^a\)most growth conditions,\(^b\)extremely Bi-rich condition,\(^c\)Te-rich condition,\(^d\)Bi-rich condition.
sites in bulk Bi₂Se₃, 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 substitution and interstitial cases are shown in Fig. 3(b). We find that Bi substitutional site is strongly preferred regardless of the changes of growing condition, as compared to all the possible interstitial sites. Our results are well in line with recently experimental findings. Then in the following we will mainly focus on cation substitutional doping.

Formation energy of TM doping as a function of chemical potential is shown in Fig. 4. Similar to TM doping in Bi₂Se₃, the formation energies exhibit the same size effect in Bi₂Te₃ and Sb₂Te₃, 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 V atom to the substituted Bi or Sb atom than other dopants. Also we find that V and Cr have negative formation energies in Bi₂Se₃ and Sb₂Te₃ for the whole range of chemical potential, indicating the doping of them can occur spontaneously. Recently, heavy Cr doping of Bi₂Se₃ with the concentration up to 23% was reported and AFM measurement indicated Cr atoms of 20% doping concentration were uniformly distributed. For Sb₂Te₃, even in Sb₁₄₋₁Cr₀₅₀Te₃, Cr atoms can homogeneously distribute without clustering. However, in Bi₂Te₃, only V can be spontaneously doped. Also it’s 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 Bi₂Se₃ at extremely Se-rich atmosphere. Indeed, Hor et al. showed that 9% Mn can substitute for Bi atoms with randomly distributing in Bi₂Te₃. Fe is confirmed even more difficult to be doped in Bi₂Se₃ with the effective doping concentration less than 2%. Notice that Bi₂Te₃ has entire 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 section III A, we have known that the native defects are responsible for the various intrinsic carriers doping. Such carrier environment is expected to affect the formation energy of 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.

(i) For Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃, anion-rich growth

FIG. 3: (color online). (a) Possible interstitial sites for Fe in Bi₂Se₃ after relaxation. (b) The formation energy ∆H as a function of anion chemical potential (µₐ) for interstitial Fe and Fe substitutional for Bi in Bi₂Se₃. Fe₁₁, Fe₁₂, and Fe₁₃ stand for different sites for interstitial Fe in (a), while FeBi denotes that Bi atom is doped by Fe atom.

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.
conditions (Se-rich or Te-rich) with lower formation energies are revealed better than cation-rich conditions (Bi-rich or Sb-rich) for magnetic atoms doping, which is consistent with experimental reports.\(^{18,63}\)

(ii) For Bi\(_2\)Se\(_3\), 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 charge state of +3, i.e., neutral substitute for Bi atoms, which indicate that dopants do not introduce free carriers to the host materials. This result agrees with theoretical study from Larson et al.\(^64\) and has been experimentally confirmed in Cr doped Bi\(_2\)Se\(_3\).\(^{35}\) Although, as \(E_F\) shifts very close to CBM, i.e., under extremely n-type condition, dopants tend to act as acceptors with valency+2, especially Mn and Fe. Experimentally, Mn was indeed found to show hole doping effect in Bi\(_2\)Se\(_3\).\(^{29}\)

(iii) For Bi\(_2\)Te\(_3\), the formation energies of TM s are larger than that in Bi\(_2\)Se\(_3\) or Sb\(_2\)Te\(_3\) 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 Bi\(_2\)Te\(_3\). This agrees well with the experimental result from Hor et al.\(^{14}\)

(iv) For Sb\(_2\)Te\(_3\), a similar size effect among V, Cr, Mn and Fe dopants is observed. V and Cr with negative formation energies can be spontaneously incorporation under Te-rich atmosphere. Cr can be neutrally doped (Cr\(_{Sb}\))\(^{17,18}\) in the most range of Fermi level.

From Fig. 5 we can easily determine the thermodynamic transition levels 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\(_2\)Se\(_3\) 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 environment for Bi\(_2\)Se\(_3\), even in n-type condition (\(E_F\) near to CBM). From Fig. 6(b) for Bi\(_2\)Te\(_3\), it is indicated that under n-type condition, only V and Cr can neutrally substitute for Bi atom, while Mn and Fe are energetically stable with charge state of +2. Conversely, neutral substituting is more likely to appear by V, Cr and Fe doping than Mn in p-type Bi\(_2\)Te\(_3\). From Fig. 6(c) for Sb\(_2\)Te\(_3\), 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 QAHE in Sb\(_2\)Te\(_3\). Actually, Cr has already been experimentally confirmed can substitute for Sb with Cr\(^{4+}\)in Sb\(_2\)Te\(_3\).\(^{17,18}\)
FIG. 7: (color online). SOC band structures for relaxed V, Cr, Mn and Fe doped Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ with the nominal doping concentration of 4% (x=0.083). The size of red dots denotes the contribution of TM- $d$ states.

TABLE II: Relaxed band gaps and magnetic moments ($m$) of Cr and Fe doped Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ 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$_2$Se$_3$    | 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$_2$Te$_3$    | 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$_2$Te$_3$    | 0.077 eV | 0.100 eV       | 3.06 $\mu_B$    | 3.16 $\mu_B$    | 0      | 0                | 4.17 $\mu_B$    | 4.03 $\mu_B$    |

C. Electronic structure of magnetically doped Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$

To elaborate the electronic properties with magnetic atoms introduced in Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$, 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$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ and give rise to semiconducting or metallic ground states, comparing to the pure host materials. 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$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are metals, as shown in Figs. 7(a)-7(c) and Figs. 7(g)-7(i), respectively. However, Cr doped Bi$_2$Se$_3$ exhibits an insulating magnetic state with the energy gap 0.01 eV. Compared to pure Bi$_2$Se$_3$, 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$_2$Te$_3$ with the band gap of 0.017 eV and Cr doped Sb$_2$Te$_3$ with a larger band gap of 0.077 eV. From Figs. 7(j)-(l), we find that Fe doped Bi$_2$Se$_3$ manifests insulating behavior with the band gap of 0.028 eV, whereas magnetic moments of Fe doped Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are less than 5 $\mu_B$, rendering Fe doped Bi$_2$Te$_3$ to be semi-metal with a narrow gap 0.0024 eV and Fe doped Sb$_2$Te$_3$ to be gapless. The phenomenon of gap closing may lead to a topological phase transition. The resulting values of band gaps and magnetic moments upon doping are listed in Table II. In order to investigate the effect of 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
FIG. 8: (color online). Dynamics illustration of the magnetically doped Bi$_2$Se$_3$. Note that those Se atoms neighboring to the dopants tend to close to the dopants, while Bi atoms hardly move.

eV. We find only slight modification of the band gaps and magnetic moments.

Notice that the band gaps are 0.32 eV, 0.15 eV and 0.12 eV for Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ respectively. However we find the band gaps are substantially reduced to several meV upon doping. This result hints that QAHE should be observed under low temperature in magnetically doped Bi$_2$Se$_3$ family, which is consistent with recent experimental reports. In order to uncover the reason which 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$_2$Se$_3$ before and after relaxation. The structural relaxation shows Se atoms neighboring to dopants move inward to the dopants by sizable distances (See Table III), as consistent with Ref. 64. This suggests that hybridization between TM dopant and the neighboring Se will be strengthened and thus the impurity bands may be broadened. Specifically as reported in our previous paper, calculated band gaps of Cr and Fe doped Bi$_2$Se$_3$ 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 GGA calculation. Additional SOC relaxations for Cr and Fe doped Bi$_2$Se$_3$ suggest the relaxed distances change within only the order of 0.001 Å comparing to non-SOC cases. We thus conclude that the band gap reduction is induced by Se-dopant hybridization.

**D. Magnetic properties of magnetically doped Bi$_2$Se$_3$**

As proposed in Ref. 20, both insulator and ferromagnetism are required to realize 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$_2$Se$_3$, which has the largest band gap among all the discovered TIs. First, the magnetic ground state of single magnetic dopants in Bi$_2$Se$_3$ is identified. We have tried different configurations (0, 8) is already larger than 9 Å and little contributions to the magnetic coupling strengths (less than 2 meV).

| Configuration (i, j) | d (Å) | (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                        |

Notice that the band gaps are 0.32 eV, 0.15 eV and 0.12 eV for Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ respectively. However we find the band gaps are substantially reduced to several meV upon doping. This result hints that QAHE should be observed under low temperature in magnetically doped Bi$_2$Se$_3$ family, which is consistent with recent experimental reports. In order to uncover the reason which 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$_2$Se$_3$ before and after relaxation. The structural relaxation shows Se atoms neighboring to dopants move inward to the dopants by sizable distances (See Table III), as consistent with Ref. 64. This suggests that hybridization between TM dopant and the neighboring Se will be strengthened and thus the impurity bands may be broadened. Specifically as reported in our previous paper, calculated band gaps of Cr and Fe doped Bi$_2$Se$_3$ 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 GGA calculation. Additional SOC relaxations for Cr and Fe doped Bi$_2$Se$_3$ suggest the relaxed distances change within only the order of 0.001 Å comparing to non-SOC cases. We thus conclude that the band gap reduction is induced by Se-dopant hybridization.

| Bond length | Cr | Fe |
|-------------|----|----|
| $d_{dopant-Bi}$ | 0.009 | 0.009 |
| $d_{dopant-Se1}$ | -0.342 | -0.305 |
| $d_{dopant-Se2}$ | -0.390 | -0.362 |

TABLE III: Amplitude of the bond length variation $\Delta d$ (in Å) from GGA and GGA+U calculations for Cr and Fe doped Bi$_2$Se$_3$ with all the atoms fully relaxed. Here, $\Delta d = d_{relaxed} - d_{initial}$, where negative value means a decrease of the bond length.

TABLE IV: Calculated magnetic coupling strength $[(E_{AFM} - E_{FM})/2]$ between two substitutional Cr atoms with different distances $d$ for Bi$_{2-x}$Cr$_x$Se$_3$ ($x = 0.074$). Two Bi atoms are replaced by dopant atoms at site $i=0$ and site $j$ ($j=1, 2, 3, \ldots$) in a $3 \times 3 \times 1$ supercell of Bi$_2$Se$_3$ which gives distinct configurations. The first seven nearest neighbor configurations of Cr atoms are considered as listed. Further neighbor configurations are ignored for their large distances of Cr atoms ($d$ of configuration (0, 8) is already larger than 9 Å) and little contributions to the magnetic coupling strengths (less than 2 meV).

An additional consideration is that the band gap reduction is induced by Se-dopant hybridization.
where \( N \) is the number of the magnetic dopant atoms, and \(<...>\) is the statistical average over different states which are generated during the Markov process. To define the Curie temperature, an accumulation of magnetization of the fourth order \( U_L \) (Binder-cumulant) are calculated by

\[
U_L = 1 - \frac{M^4}{M^2} \frac{1}{N} \quad \text{for } x = 0.074. \]

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\(_2\)Se\(_3\), Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) using first-principles calculations in combination with Monte Carlo simulation. Our calculations showed that cation site substitutional doping was energetically most favorable. Further we suggested a recipe of effective magnetic doping for 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\(_2\)Se\(_3\), Bi\(_2\)Te\(_3\), and Cr doped Sb\(_2\)Te\(_3\) were 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\(_2\)Te\(_3\) became metals. Finally, we explored the magnetic coupling between dopants, suggesting FM was favorable in Cr doped Bi\(_2\)Se\(_3\) while AFM in Fe doped material. Using Monte Carlo simulation, we estimated that the Curie temperature of 7.4\% Cr doped Bi\(_2\)Se\(_3\) was about 76 K. Our results provide important guidelines towards further experimental efforts of incorporating magnetism in TI, in particular for the realization of QAHE based on magnetic topological insulators.

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