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# Tailoring Magnetic Doping in the Topological Insulator $\text{Bi}_2\text{Se}_3$

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We theoretically investigated the possibility of establishing ferromagnetism in the topological insulator  $\text{Bi}_2\text{Se}_3$  via magnetic doping of  $3d$  transition metal elements. The formation energies, charge states, band structures, and magnetic properties of doped  $\text{Bi}_2\text{Se}_3$  are studied using first-principles calculations within density functional theory. Our results show that Bi substitutional sites are energetically more favorable than interstitial sites for single impurities. Detailed electronic structure analysis reveals that Cr and Fe doped materials are still insulating in the bulk but the intrinsic band gap of  $\text{Bi}_2\text{Se}_3$  is substantially reduced due to the strong hybridization between the  $3d$  states of the dopants and the  $p$  states of the neighboring Se atoms. The calculated magnetic coupling suggests that Cr doped  $\text{Bi}_2\text{Se}_3$  is possible to be both ferromagnetic and insulating, while Fe doped  $\text{Bi}_2\text{Se}_3$  tends to be weakly anti-ferromagnetic.

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The recent discovery of topological insulators (TIs) in narrow band gap semiconductors has generated great interest in both condensed matter physics and materials science [1–7]. The strong spin-orbit coupling (SOC) in these materials, which is responsible for the nontrivial band topology, also highlights their application potential in semiconductor spintronics [8]. In particular, the intricate interplay between topological order and ferromagnetism is expected to give rise to a variety of unconventional spintronic effects that may lead to entirely new device paradigms [9–12]. For example, a weak magnetic perturbation can open up an energy gap in the surface spectrum of a TI, resulting in the emergence of massive Dirac fermions [13]. In a TI thin film, long range magnetic order can also be established, which potentially could realize the long-sought quantum anomalous Hall state [14–16].

A natural strategy to introduce magnetism in TIs is via magnetic doping, similar to diluted magnetic semiconductors (DMS) [17]. The current research mainly focuses on the  $\text{Bi}_2\text{Se}_3$  family [13–15, 18–20]. However, existing experimental evidences have shown that the solubilities of magnetic impurities are normally very limited in  $\text{Bi}_2\text{Se}_3$  family compounds [13, 18, 21, 22], and magnetic impurities tend to form clusters instead of being individually distributed in the materials, and dopants have uncertain valency [23]. On the magnetic ordering, ferromagnetism was reported in Mn and Fe doped  $\text{Bi}_2\text{Te}_3$  [22, 24–27] and V, Cr and Mn doped  $\text{Sb}_2\text{Te}_3$  [21, 22, 25], while a spin glass state was found in Mn doped  $\text{Bi}_2\text{Se}_3$  [22]. For Cr doped  $\text{Bi}_2\text{Se}_3$ , both antiferromagnetism [28] and ferromagnetism [29] were observed, and the observations in Fe doped  $\text{Bi}_2\text{Se}_3$  were also rather controversial [24, 28, 30, 31]. From a growth point of view, it is imperative to choose proper magnetic elements and be able to precisely control the magnetic impurity distribution inside the host materials [13]. This relies on comprehensive knowledge on the kinetic and energetic behaviors of magnetic impurities

in TIs and consequently the electronic and magnetic properties. Yet, such knowledge is still lacking in the literature.

In this Letter, we investigate the feasibility of tailoring  $\text{Bi}_2\text{Se}_3$  to a ferromagnetic insulator via doping  $3d$  transition metal (TM) elements, including V, Cr, Mn, and Fe, using first-principles calculations within density functional theory (DFT). We find that Bi substitutional sites are energetically more favorable than interstitial sites for single impurities of these elements, and the optimal growth conditions for TM doping are presented. The calculated band structures reveal that only Cr and Fe doped materials are insulating in the bulk but the intrinsic band gap of  $\text{Bi}_2\text{Se}_3$  is substantially reduced due to the strong hybridization between the  $3d$  states of the dopants and the  $p$  states of the neighboring Se atoms. Further investigation on the magnetic coupling between the dopants clarifies some experimental discrepancies and suggests that Cr doped  $\text{Bi}_2\text{Se}_3$  is likely to be ferromagnetic, while Fe doped material tends to be weakly anti-ferromagnetic.

Our first-principles DFT calculations are performed using the pseudopotential plane-wave method with projected augmented wave (PAW) [32] potentials and Perdew-Burke-Ernzerhof-type generalized gradient approximation (GGA) [33] for exchange-correlation functional, as implemented in the Vienna *ab initio* simulation package (VASP) [34, 35]. A plane-wave energy cutoff energy of 300 eV is consistently used in all the calculations. Unless mentioned otherwise, SOC [36] is taken into account in all calculations. Crystalline  $\text{Bi}_2\text{Se}_3$  has a rhombohedral structure and its unit cell is composed of three weakly coupled quintuple layers (QLs). To investigate the behaviors of isolated magnetic dopants in bulk  $\text{Bi}_2\text{Se}_3$ , we employ a  $2 \times 2 \times 1$  supercell containing 24 Bi and 36 Se atoms, as shown in Fig. 1 (a). A gamma-centered  $7 \times 7 \times 2$  mesh of special  $k$  points is adopted for integrations over the Brillouin zone. In calculating the formation energies [37, 38] of charged defects, a uniform back-

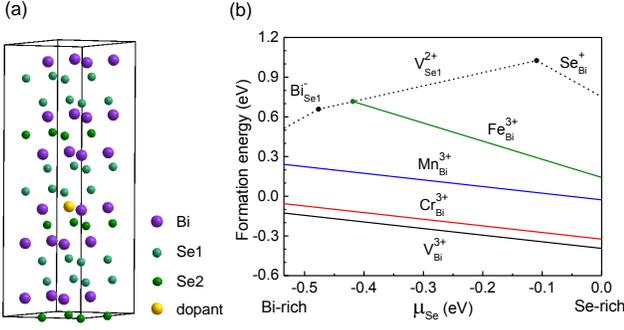


FIG. 1: (color online). (a) Illustration of a  $2 \times 2 \times 1$  supercell for modeling a single dopant in bulk  $\text{Bi}_2\text{Se}_3$ . (b) Calculated formation energies of the most stable configurations of single V, Cr, Mn, and Fe impurities doped  $\text{Bi}_2\text{Se}_3$  as a function of the host element chemical potentials. For comparison, the values of dominant intrinsic defects, selenium vacancies  $V_{\text{Se}1}$ , antisite defects  $\text{Bi}_{\text{Se}1}$  and  $\text{Se}_{\text{Bi}}$ , are shown in dashed lines.

ground charge is introduced to keep the supercell in charge neutral. With the lattice constants fixed at the experimental values of  $a=4.138 \text{ \AA}$  and  $c=28.64 \text{ \AA}$ , the internal coordinates of all the atoms are fully relaxed until the residual forces on each atom are less than  $0.02 \text{ eV/\AA}$ . All these parameters ensure the numerical errors in the calculated defect formation energies less than 20 meV.

Extensive research on the traditional DMS has indicated that their magnetic properties depend sensitively on the positions of magnetic impurities, namely, substitutional versus interstitial sites, in the host semiconductors [17]. Therefore, we first examine the site preference of a serial of single 3d TM impurities (V, Cr, Mn, and Fe) in bulk  $\text{Bi}_2\text{Se}_3$ . To this end, we place the TM impurities at all possible interstitial and substitutional sites in bulk  $\text{Bi}_2\text{Se}_3$  and compare their formation energies, which can be computed using the following expression [38]

$$\Delta H_f(TM) = E_{tot}(TM) - E_{tot}(bulk) - \sum_i n_i \mu_i, \quad (1)$$

where  $E_{tot}(TM)$  is the total energies of a supercell containing one impurity,  $E_{tot}(bulk)$  is the total energy of the equivalent supercell containing only host atoms.  $\mu_i$  denotes the chemical potential for species  $i$  (host atoms or dopants), and  $n_i$  indicates the corresponding number that have been added to or removed from the supercell. Given the host material being a binary compound, the values of  $\mu_i$  are subject to the following relations: (i)  $2\mu_{\text{Bi}} + 3\mu_{\text{Se}} = \Delta H_f(\text{Bi}_2\text{Se}_3)$ , where  $\Delta H_f(\text{Bi}_2\text{Se}_3)$  is the formation energy of bulk  $\text{Bi}_2\text{Se}_3$ , to maintain equilibrium growth of  $\text{Bi}_2\text{Se}_3$ ; (ii)  $\mu_{\text{Bi}} \leq \mu_{\text{Bi}}^0$ ,  $\mu_{\text{Se}} \leq \mu_{\text{Se}}^0$ , and  $\mu_{\text{TM}} \leq \mu_{\text{TM}}^0$  to avoid precipitation of Bi, Se, and TM elementary substances, where  $\mu_{\text{Bi}}^0$ ,  $\mu_{\text{Se}}^0$ , and  $\mu_{\text{TM}}^0$  refer to the chemical potentials of the stable Bi, Se, and TMs crystals, respectively. We chose rhombohedral Bi, hexagonal Se, nonmagnetic body-centered-cubic (bcc) V, antiferromagnetic bcc Cr, antiferromagnetic face-centered-cubic Mn, and

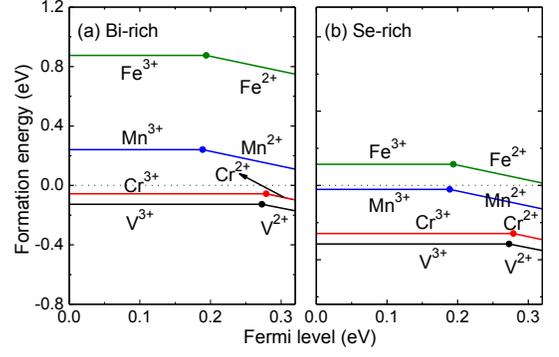


FIG. 2: (color online). Calculated formation energies of the most favorable charge states of single V, Cr, Mn, and Fe impurities doped at Bi substitutional sites in  $\text{Bi}_2\text{Se}_3$  as a function of the Fermi level under (a) Bi-rich and (b) Se-rich conditions.

ferromagnetic bcc Fe as reference to evaluate the chemical potentials of the elements; (iii)  $x\mu_{\text{TM}} + y\mu_{\text{Se}} \leq \Delta H_f(\text{TM}_x\text{Se}_y)$  to ensure that all possible competing phases  $\text{TM}_x\text{Se}_y$  can not precipitate.

Our calculated formation energies indicate that Bi substitutional sites are strongly preferred by all the TM impurities we investigated, compared to Se substitutional sites and all possible interstitial sites in bulk  $\text{Bi}_2\text{Se}_3$ . Interstitial sites in the van der Waals (vdw) gap are the most favorable interstitial sites, while their formation energies are always larger than the dopants at substitutional Bi by at least 0.29 and 1.09 eV at Bi-rich and Se-rich conditions, respectively. The reported experimental observations of interstitial dopants in the vdw gap may be due to certain kinetic constrain, that is, the growth temperatures are not high enough for the dopants to overcome the energy barriers to incorporate into the substitutional sites. Fig. 1(b) shows the formation energies of the TM impurities at Bi substitutional sites as a function of the chemical potentials of Bi and Se. The order of the formation energies,  $\Delta H_f(\text{V}) < \Delta H_f(\text{Cr}) < \Delta H_f(\text{Mn}) < \Delta H_f(\text{Fe})$ , can be attributed to the size effect of the elements; that is, the larger the atomic radius of the impurity, the closer to that of the replaced Bi atom and thus the lower the formation energy. Among the four TM elements, V and Cr possess negative formation energies in the whole range of the accessible host element chemical potentials, suggesting that these two elements can be spontaneously introduced in bulk  $\text{Bi}_2\text{Se}_3$ .

To further identify the optimal growth conditions, we investigate the competition of the TM doping with the formation of intrinsic defects. The potential intrinsic defects include bismuth vacancies  $V_{\text{Bi}}$ , selenium vacancies  $V_{\text{Se}}$ , and antisite defects  $\text{Bi}_{\text{Se}}$  and  $\text{Se}_{\text{Bi}}$  in bulk  $\text{Bi}_2\text{Se}_3$ . The most favorable intrinsic defects and their formation energies are also shown in Fig. 1(b). We find that at extremely Bi-rich growth conditions, antisite defect  $\text{Bi}_{\text{Se}1}$  is favorable, and  $\text{Bi}_2\text{Se}_3$  is expected to be intrinsic  $p$ -type. However, in the most growth region, selenium vacancies  $V_{\text{Se}1}$  and antisite defects  $\text{Se}_{\text{Bi}}$ , with both acting as donors, are dominant, rendering  $\text{Bi}_2\text{Se}_3$  intrinsic  $n$ -

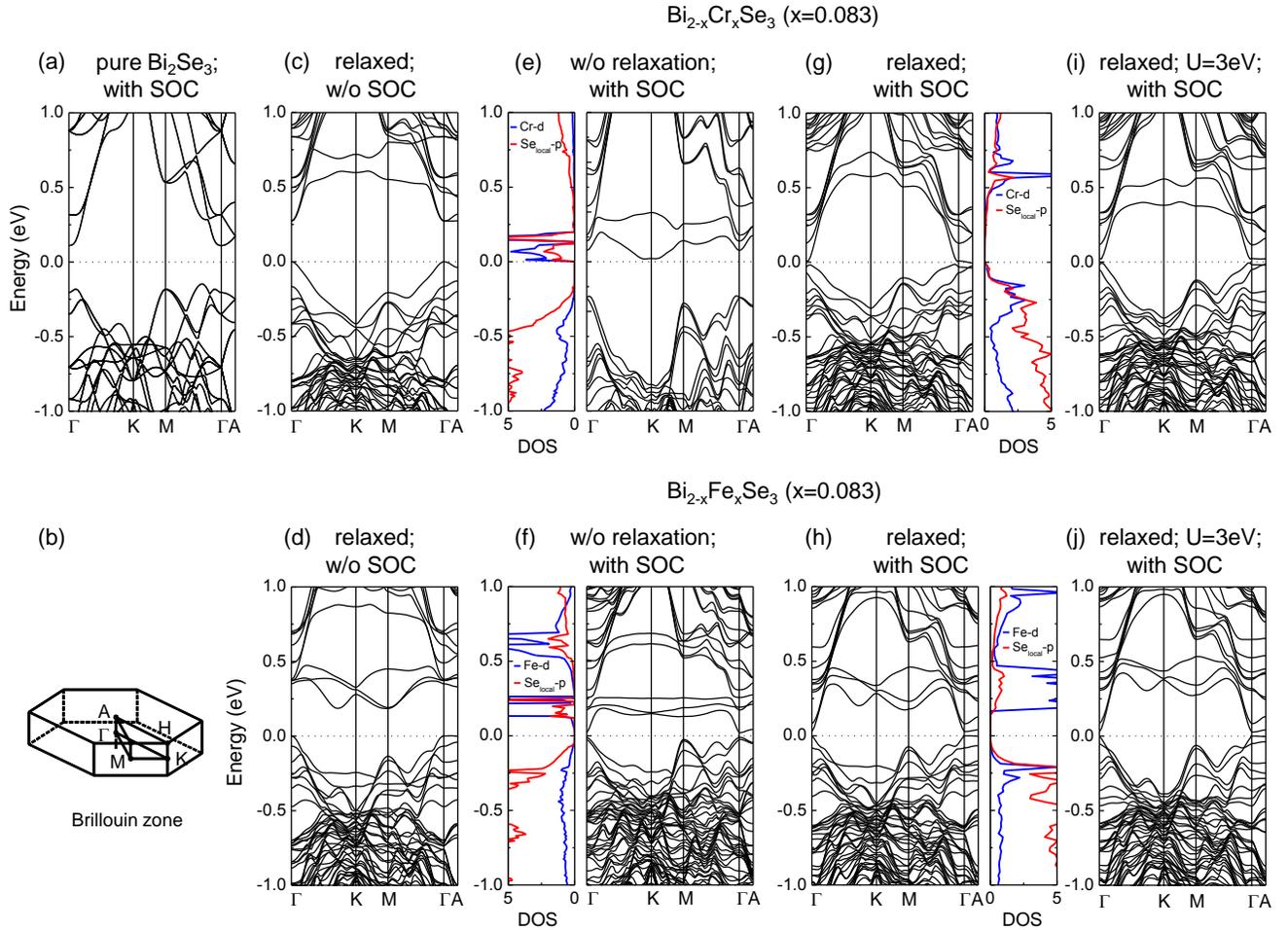


FIG. 3: (color online). (a) Band structure of  $\text{Bi}_2\text{Se}_3$  calculated for a  $2 \times 2 \times 1$  relaxed supercell with SOC. (b) Brillouin zone and high symmetry points of the  $2 \times 2 \times 1$  supercell. (c)-(j) Band structures of Cr doped and Fe doped  $\text{Bi}_2\text{Se}_3$  calculated with: (c) and (d) structural relaxation but without SOC; (e) and (f) SOC but without structural relaxation; (g) and (h) SOC and structural relaxation; (i) and (j) SOC, structural relaxation, and GGA+U ( $U=3$  eV). Structural relaxations were all performed without the inclusion of SOC. Projected partial density of states on the dopants and the neighboring Se atoms are also shown in (e)-(h).

type. This result provides a good explanation to experimental study [5, 6] and guidelines for growth control. Our results also indicate that the formation energies of V, Cr, and Mn are always lower than those of the intrinsic defects, whereas selenium vacancies ( $V_{\text{Se}1}$ ) and antisite defects ( $\text{Bi}_{\text{Se}1}$ ) are energetically more favorable at Bi-rich conditions in the case of Fe doping. Therefore, in order to effectively dope Fe in bulk  $\text{Bi}_2\text{Se}_3$ , it is required to grow the materials at Se-rich conditions. However, the thermodynamic solubility of Fe in  $\text{Bi}_2\text{Se}_3$  is expected to be limited, where the maximum doping concentration of  $\text{Bi}_{2-x}\text{Fe}_x\text{Se}_3$  is estimated to be  $x = 2.24\%$  under Se-rich condition at the melting point of  $\text{Bi}_2\text{Se}_3$  of 979 K, according to Ref. [38]. Experimentally, the effective doping concentration of Fe in  $\text{Bi}_2\text{Se}_3$  is reported to be less than 2% [18], which is consistent with our result.

In the above calculations, the whole systems are kept charge neutral, and the TM impurities therefore hold a 3+ charge state as they are introduced in Bi sites in  $\text{Bi}_2\text{Se}_3$ . Next we

study the formation energies of the doped TM impurities in various charge states. In this case, the definition of the impurity formation energy is modified as [38]

$$\Delta H_f(\text{TM}, q) = E_{\text{tot}}(\text{TM}, q) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i + q(E_F + E_V + \Delta V), \quad (2)$$

where  $E_{\text{tot}}(\text{TM}, q)$  is the total energy of a supercell containing one impurity in charge state  $q$  and  $E_F$  is the Fermi level with respect to the valence band maximum (VBM) of the intrinsic bulk  $\text{Bi}_2\text{Se}_3$  ( $E_V$ ).  $\Delta V$  is a potential alignment due to different energy reference among defect supercell and pure supercell. Fig. 2(a) and 2(b) show the calculated formation energies of the TM impurities in their favorable charge states as a function of  $E_F$  at Bi-rich and Se-rich growth conditions, respectively. The 3+ charge state of the TM impurities are preserved when  $E_F$  is smaller than 0.27, 0.28, 0.19, and 0.19 eV for V, Cr, Mn, and Fe doped cases, respectively. At ex-

tre  $n$ -type conditions, i.e.  $E_F$  approaching the conduction band minimal, the charge state of the TM impurities changes to  $2+$ , which may result in the change of carrier concentration in the materials when doping TM atoms. From Fig. 2(a) and 2(b), we obtain that Se-rich condition is more optimal than Bi-rich condition for doping TM in  $\text{Bi}_2\text{Se}_3$ . A systematic investigation of the MBE growth for  $\text{Bi}_2\text{Se}_3$  films also indicates that the optimal growth can be achieved under Se-rich atmosphere [39], which agrees with our results.

We next focus our attention on the electronic structures of the TM doped  $\text{Bi}_2\text{Se}_3$ . Structural relaxations were all performed without the inclusion of SOC. The calculated band structures do not show any noticeable difference, in comparison with the calculations with SOC included in the relaxation for Cr and Fe doped  $\text{Bi}_2\text{Se}_3$ , and the band gap differences are less than 0.01 eV. Fig. 3(a) shows the calculated band structure of pure  $\text{Bi}_2\text{Se}_3$  with SOC, which gives a band gap of 0.32 eV. In the TM doped cases, even without SOC, Cr and Fe doping results in insulating magnetic states with energy band gaps of 0.28 eV (Fig. 3(c)) and 0.18 eV (Fig. 3(d)), respectively, whereas V and Mn create impurity states in the band gap of  $\text{Bi}_2\text{Se}_3$ , which completely close the band gap and makes the materials metallic. With SOC, we obtain band gaps of 0.15 eV and 0.03 eV for Cr and Fe doped  $\text{Bi}_2\text{Se}_3$  as the dopants are fixed at the Bi sites without any structural relaxation (Fig. 3(e) and 3(f)). However, after the structural relaxation, the band gaps are further reduced, as shown in Fig. 3(g) and 3(h), to 0.010 eV and 0.028 eV for Cr and Fe doped  $\text{Bi}_2\text{Se}_3$ , respectively. This seemingly counterintuitive result can be attributed to structural relaxation induced enhancement of the electronic state hybridization between the TM dopants and their neighboring Se atoms. When all the atoms are fixed at their original crystal positions, due to the relatively small covalent radius of Cr and Fe compared with Bi, Cr and Fe states have little overlap with the neighboring Se atoms, resulting in atomic-like localized electronic states, as evidenced by the presence of the fairly flat impurity bands in the gap region shown in Fig. 3(e) and 3(f). After the structural relaxation, the distance between Cr (Fe) and the neighboring Se is decreased by about 0.4 Å (0.3 Å) and the impurity bands are substantially broadened, suggesting strong hybridization between the TM dopants and the neighboring Se atoms. A more detailed analysis on the projected partial density of states reveals that the  $d$  states of Cr and Fe hybridize the  $p$  states of Se.

We further performed GGA+U calculations with U on the TM impurities ranging from 3 to 6 eV and  $J=0.87$  eV to describe the strong electron-electron correlation in partially filled  $3d$  TM elements. The results, as shown in Fig. 3(i) and 3(j), indicate that the band gaps of Cr and Fe doped  $\text{Bi}_2\text{Se}_3$  increases to 0.025 eV and 0.028 eV for  $U=3$  eV and 0.026 eV and 0.028 eV for  $U=6$  eV, respectively. Thus electron-electron correlation could slightly enlarge the band gaps.

Finally, we discuss the magnetic properties of the TM doped  $\text{Bi}_2\text{Se}_3$ . **The magnetic ground states for single impurity doped  $\text{Bi}_2\text{Se}_3$  have been calculated with the inclusion of SOC, the results indicate that both Cr and Fe prefer the di-**

**rection perpendicular to the  $\text{Bi}_2\text{Se}_3$  QLs, with the magnetic moments close to  $3 \mu_B$  and  $5 \mu_B$ , respectively. Our results are different to the recent reports of in-plane magnetization easy axis in Ref. [40], where Fe atoms adatom on the surface of  $\text{Bi}_2\text{Se}_3(111)$  and the intergrown composite crystal of  $\text{Fe}_7\text{Se}_8$  and  $\text{Bi}_2\text{Se}_3$  [41], in which magnetic anisotropy is attributed to the intrinsic properties of ferromagnet  $\text{Fe}_7\text{Se}_8$ .** The magnetic coupling between the TM dopants is estimated by placing two TM dopants in the supercell at various separation distances and calculating the total energy difference between anti-ferromagnetic (AFM) and ferromagnetic (FM) states of the dopants at the same distance. Our preliminary results reveal that the magnetic coupling dominantly favors FM in the Cr doped  $\text{Bi}_2\text{Se}_3$  while exclusively favors weak AFM in the Fe doped case. In the Cr doped case, the coupling strength ( $(E_{AFM} - E_{FM})/2$ ) is on the order of 10 meV for the two Cr atoms within the same QL at the first three nearest neighboring distances and substantially reduced to the order of 1 meV or even less for the two Cr atoms in different QLs. Our Monte Carlo simulations based on the Heisenberg model of magnetism then show Cr doped  $\text{Bi}_2\text{Se}_3$  to be FM with the estimated Curie temperature at about 160 K. We notice that studies of the competition between weak Localization (WL) and weak antilocalization (WAL) from Lu et al [42] indicated that a ferromagnetic order can be formed in Cr doped  $\text{Bi}_2\text{Se}_3$ , which was later verified experimentally with a nominal Cr doping level of 23% [20]. More recently, ferromagnetism was reported to be observed in Cr doped  $\text{Bi}_2\text{Se}_3$  [29], which agrees well with our result.

In the Fe doped case, AFM is favorable while its coupling strength is very weak (on the order of 1 meV), even though the distance of two Fe atoms is close to 9.84 Å. Experimentally, as we previously discussed, the doping concentration of Fe in  $\text{Bi}_2\text{Se}_3$  is found to be lower than 2% [18], where the average distance between two uniformly distributed Fe atoms is about 11.79 Å. The corresponding coupling strength is predicted to be even less than 1 meV in this case. Hence, AF order in Fe doped  $\text{Bi}_2\text{Se}_3$  may not be obvious to detect, especially in the low doping concentration regime, which agrees with experimental observations of non-magnetism [24, 30]. In addition, heavily Fe doped  $\text{Bi}_2\text{Se}_3$  often exhibit FM behavior [28], since Fe often tends to form clusters or become phase separated instead of being uniformly distributed during growth.

In summary, we have studied the effects of magnetic doping of a series of  $3d$  transition metal elements in the TI  $\text{Bi}_2\text{Se}_3$  using first-principles calculations. Our calculated formation energies indicate that Bi substitutional sites are strongly preferred by all the TM impurities. By examining the energetics of the dopants in the host material and the resulting electronic structures and magnetic properties, we have found that Cr and Fe doping preserves the insulating nature of the host TI in the bulk but the intrinsic band gap is substantially reduced due to the strong hybridization between the electronic states of the dopants and the neighboring Se atoms. The further investigation on the magnetic coupling between the dopants has

suggested that Cr doped  $\text{Bi}_2\text{Se}_3$  is likely to be FM, while Fe doped material tends to be weak AFM. Only Cr doped  $\text{Bi}_2\text{Se}_3$  with both ferromagnetic and insulating properties is promising to realize the quantized anomalous Hall effect.

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