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Transition Metal Substitutions Induce Ferromagnetism in Bi_2Te_3 Lin Ju^{a*}, Tong-shuai Xu^a, Dan Hu^a, Hai-tao Cui^a, Yong-jia Zhang^b, Chang-min Shi^c*a.* School of Physics and Electric Engineering, Anyang Normal University, Anyang 455000, China*b.* Department of Physics, Taiyuan University of Technology, Taiyuan 030024, China*c.* School of Physics, State Key Laboratory for Crystal Materials, Shandong University, Jinan 250100, China

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The possibilities of magnetism induced by transition-metal atoms substitution in Bi_2Te_3 system are investigated by *ab initio* calculations. The calculated results indicate that a transition-metal atom substitution for a Bi atom produces magnetic moments, which are due to the spin-polarization of transition-metal 3d electrons. The values of magnetic moments are 0.92, 1.97, 2.97, 4.04, and 4.98 μ_B for 4% Ti-, V-, Cr-, Mn- and Fe-doped Bi_2Te_3 respectively. When substituting two transition-metal atoms, the characteristics of exchanging couple depend upon the distributions of the Bi atoms substituted. When two transition-metal atoms substituting for Bi atoms locate at the sites of Bi1 and Bi5, with the distance of 11.52 Å, the $\text{Bi}_{1.84}\text{TM}_{0.16}\text{Te}_3$ system is energetically most stable and exhibits ferromagnetic coupling.

Key words: Transition-metal atom, Substitution, Magnetic moment, First-principles calculation

I. INTRODUCTION

Recently, topological insulators with both metallic surface states and insulating bulk states have attracted enormous attention, due to their exotic physical properties and potential applications in low dissipation devices and quantum computing [1–5], particularly after the experimental confirmation of a three-dimensional topological insulator [6]. $\text{V}_2\text{-VI}_3$ compounds such as Bi_2Te_3 and Sb_2Te_3 , which are well-known conventional materials for thermoelectric applications [7–9], with unique electronic structures, exhibit a Dirac-like conducting band as the bulk topological insulators.

Bi_2Se_3 can be made into a superconductor by non-magnetic copper intercalation in the van der Waals gaps [10, 11]. The long-range magnetic order can also form in topological insulators when doped with transition metals (TM) in the bulk [12]. The introduced magnetic order can lead to the time reversal symmetry breaking, resulting in a gap opening at the Dirac point, which is the crucial criteria for the realization of many interesting phenomena, such as quantized anomalous Hall effect [13] and topological magnetoelectric effect [14].

Bi_2Te_3 and related systems with dilute dopings of transition-metal atoms (V, Cr, Mn, and Fe) have been found to be ferromagnetic at low temperatures. Dyck *et al.* found both the magnetic semiconduc-

tor $\text{Sb}_{2-x}\text{V}_x\text{Te}_3$ ($x=0.03$) and $\text{Sb}_{2-x}\text{Cr}_x\text{Te}_3$ ($x=0.095$) have a Curie temperature (T_C) around 22 and 20 K respectively [15, 16]. Hor *et al.* reported experimentally that substitution Mn into Bi_2Te_3 makes the compound magnetism and the system may be a dilute magnetic topological semiconductor. The compositions $\text{Bi}_{2-x}\text{Mn}_x\text{Te}_3$ ($x=0.04$ and 0.09) have a ferromagnetic transition with $T_C=9-12$ K. The easy axis of magnetization in the ferromagnetic phase is perpendicular to the Bi_2Te_3 basal plane [17]. In addition, the experimental research also demonstrated that a systematic Mn doping can control the dynamics of spin-Dirac fermions in Bi_2Te_3 , which results in the material potentially applications in topological device [18]. The ferromagnetic phase was also found in $p\text{-Bi}_{2-x}\text{Fe}_x\text{Te}_3$ at the temperature which increases with the Fe content x increasing to 12 K ($x=0.08$), while hole concentration decreases, *i.e.*, iron atoms exhibit donor properties. The easy-axis for magnetization is parallel to the C_3 crystallographic axis [19].

The substitutional doping with transition metals plays a very important role in tuning the electronic and magnetic properties of Bi_2Te_3 and related systems. However, the mechanisms of electronic and magnetic of TM-doped Bi_2Te_3 are still unclear. In order to address exactly these problems, we explore the electronic and magnetic properties of bulk of Bi_2Te_3 with transition metals doping via the first-principles density functional theory (DFT). The results demonstrate that for Bi_2Te_3 system, magnetic moments can be induced when one Bi atom is substituted by a TM (TM=Ti, V, Cr, Mn, and Fe) atom. We also compare the energies of ferromag-

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netic and antiferromagnetic couplings between two TM atoms substituted in Bi_2Te_3 super-cell. The type of preferential magnetic coupling of system depends upon the distributions of the Bi atoms substituted.

II. COMPUTATIONAL DETAILS

The DFT calculation is performed with the plane-wave pseudopotential method in the Vienna *ab initio* simulation package (VASP) [20, 21]. The generalized gradient approximation (GGA) [22] scheme is used to describe the exchange correlation energy. The calculated lattice constants ($a=4.386 \text{ \AA}$ and $c=30.497 \text{ \AA}$) are in good agreement with reported results [23]. We construct a $2 \times 2 \times 2$ rhombohedral Bi_2Te_3 periodic supercell containing 60 atoms, where a Bi atom is substituted by a TM atom (TM=Ti, V, Cr, Mn and Fe). Such substitution corresponds to $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$ and the doping level is 4%. An energy cutoff of 400 eV is used for the plane wave expansion of the electronic wave function. Special k points are generated with a $3 \times 3 \times 1$ grid based on Monkhorst-Pack scheme. Good convergence is obtained with these parameters. The cases of pure Bi_2Te_3 and TM atoms (TM=Ti, V, Cr, Mn and Fe) doped Bi_2Te_3 are considered. The total energy is converged to be $1.0 \times 10^{-4} \text{ eV/atom}$, while the Hellman-Feynman force is smaller than 0.01 eV/\AA in the optimized structure.

III. RESULTS AND DISCUSSION

Bulk Bi_2Te_3 has a rhombohedral crystal structure with the space group $D_{3d}^5(\text{R}\bar{3}\text{m})$ and with five atoms in a unit cell. A rhombohedral structure can be visualized as a layer structure and a hexagonal lattice cell. We plot this hexagonal cell in Fig.1. In the hexagonal cell of Bi_2Te_3 , there are five individual atomic layers in the sequence of Te-Bi-Te-Bi-Te along the trigonal axis.

The band structure of Bi_2Te_3 and related systems has been studied extensively due to their importance as room-temperature thermoelectric materials [24–30]. The density of state (DOS) for the pure system Bi_2Te_3 is given in Fig.2(a). The Te5p state formed below the Fermi level with the 5s state which is around -10 eV . The Bi6p state forms above the Fermi level. The covalent bonding leads to each Bi in a $3+$ state and each Te in a $2-$ state. In addition, the total DOS for pure Bi_2Te_3 system also shows that no spin-polarization emerges around the Fermi energy level, indicating that the pure Bi_2Te_3 is nonmagnetic, as there are no unpaired electrons.

Experimental evidence has shown that the transition-metal atoms replace the larger Bi atoms within the lattice rather than Te [19, 31]. Calculations have been performed on $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$ (TM=Ti, V, Cr, Mn, and Fe). The total DOSs of $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$ (TM=Ti, V,

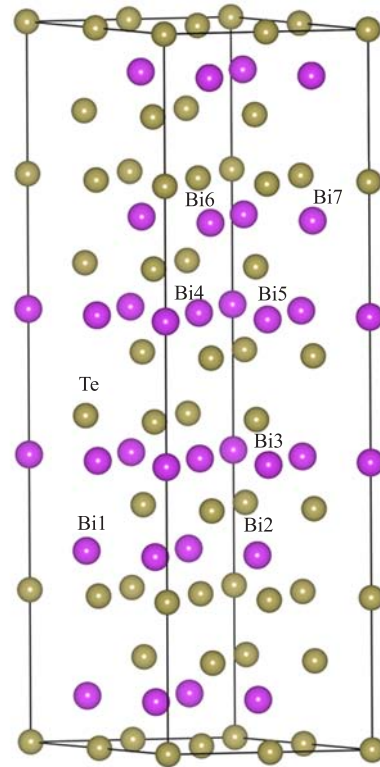


FIG. 1 The schematic crystal structure of rhombohedral Bi_2Te_3 . Sage green balls and violet balls represent Te atoms and Bi atoms, respectively.

Cr, Mn, and Fe) are shown in Fig.2 (b)–(f). An obvious spin-split in the spin-up and spin-down total DOS at/near the Fermi level can be found. Obviously, Ti-, V-, Mn-, and Fe-doped Bi_2Te_3 are all half-metals and magnetic with 100% spin polarization. The Cr-doped Bi_2Te_3 is magnetic semiconductors, because both the majority and minority spin DOSs are zero at the Fermi level and there is a clear spin polarization between the DOSs of the two spin channels around the Fermi level. According to our calculations, the value of magnetic moments are $0.92, 1.97, 2.97, 4.04,$ and $4.98 \mu_B$ for 4% Ti-, V-, Cr-, Mn- and Fe-doped Bi_2Te_3 respectively.

The total energies of the supercell with $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$ (TM=Ti, V, Cr, Mn and Fe) for spin-polarized and nonspin-polarized modes are also calculated, too. The corresponding energy difference $\Delta E_{N-M}=E_N-E_M$ between the total energies of nonmagnetic state E_N and the magnetic state E_M are $0.027, 0.63, 1.4, 0.86$ and 0.19 eV for 4% Ti, V, Cr, Mn and Fe doped Bi_2Te_3 respectively. All the results show that the magnetic state is more stable than the nonmagnetic one. Figure 3 (a)–(e) show the spin-density distribution (spin-up minus spin-down) for $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$ (TM=Ti, V, Cr, Mn and Fe). The spin density is mainly distributed on the TM atoms.

In order to understand the electronic structure further, the atom-, orbital-, and spin-projected density of

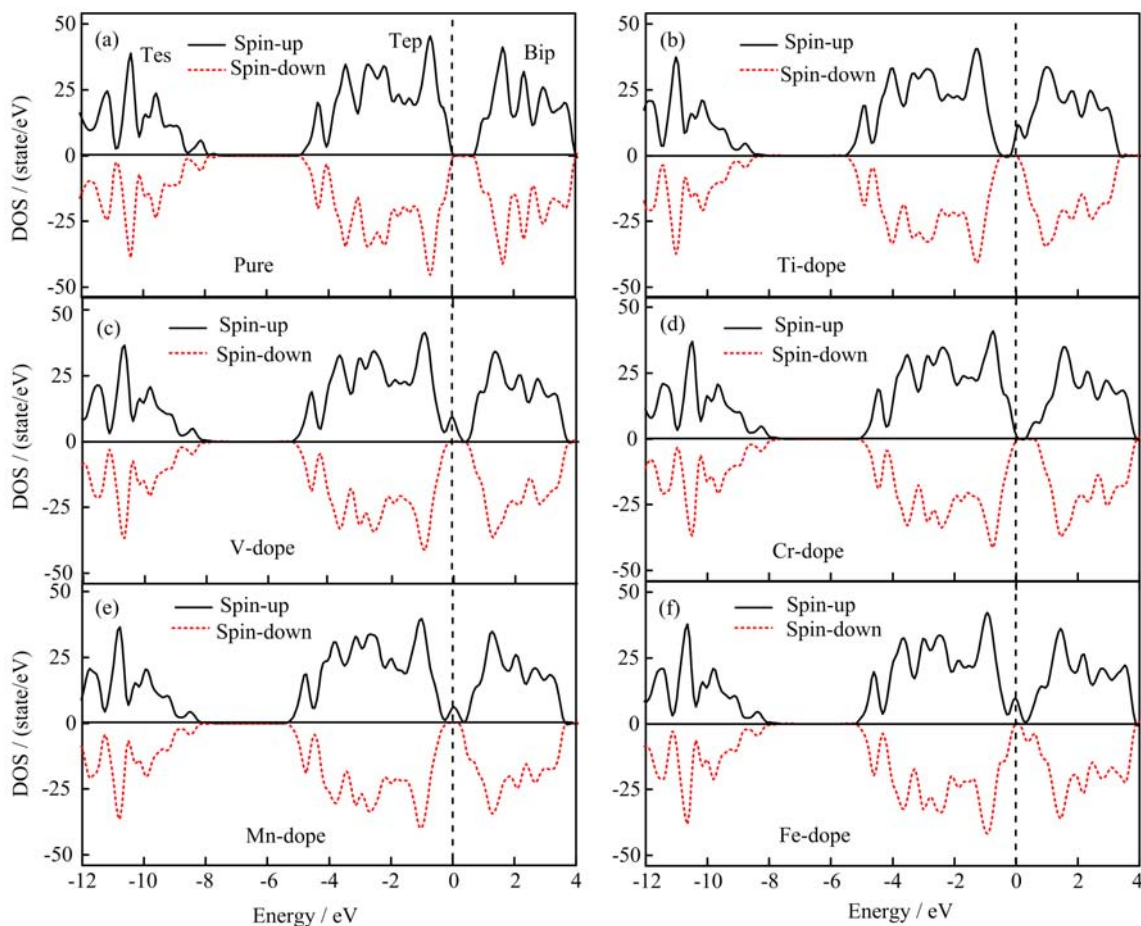


FIG. 2 Total DOS of (a) pure Bi_2Te_3 , (b) $\text{Bi}_{1.92}\text{Ti}_{0.08}\text{Te}_3$, (c) $\text{Bi}_{1.92}\text{V}_{0.08}\text{Te}_3$, (d) $\text{Bi}_{1.92}\text{Cr}_{0.08}\text{Te}_3$, (e) $\text{Bi}_{1.92}\text{Mn}_{0.08}\text{Te}_3$ and (f) $\text{Bi}_{1.92}\text{Fe}_{0.08}\text{Te}_3$, respectively. The vertical dotted line indicates the Fermi level.

the TM atom (TM=Ti, V, Mn and Fe) 3d states, Te atoms 5s and 5p states and Bi atoms 6s and 6p states are calculated and presented in Fig.4 for Ti-, V-, Mn-, and Fe-doped Bi_2Te_3 . Obviously, the TM3d DOS shows an exchange splitting between the spin-up and spin-down DOS peaks at/near the Fermi level, which results in a magnetic moment. In addition, small induced magnetic moments are also observed for the Bi and Te atoms (not shown in Fig.3), these induced magnetic moments are due to the small spin polarization of p-states of Te atoms and Bi atoms. While very small, the difference between the spin-up and spin-down DOS of Te atoms 5p states and Bi atoms 6p states can be found, which can be seen in Fig.2 (a)–(d). The Bi and Te atoms around the 3d TM atoms are polarized while other Te (or Bi) atoms are not. That is to say, the polarized electrons are decided by the distance between the Te (or Bi) atom and the TM atom. The spin-projected DOS of spin-up orbitals (or spin-down orbitals) passing through the Fermi level and spin-down orbitals (or spin-up orbitals) can exhibit the characteristics of semiconductor. Therefore, Ti-, V-, Mn-, and Fe-doped Bi_2Te_3 are the half-metal materials.

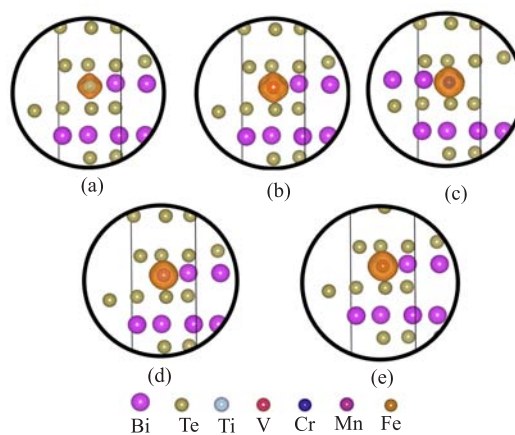


FIG. 3 Three-dimensional iso-surfaces (the iso-value is $0.01 \text{ e}/\text{\AA}^3$) of magnetization density for (a) $\text{Bi}_{1.92}\text{Ti}_{0.08}\text{Te}_3$, (b) $\text{Bi}_{1.92}\text{V}_{0.08}\text{Te}_3$, (c) $\text{Bi}_{1.92}\text{Cr}_{0.08}\text{Te}_3$, (d) $\text{Bi}_{1.92}\text{Mn}_{0.08}\text{Te}_3$, and (e) $\text{Bi}_{1.92}\text{Fe}_{0.08}\text{Te}_3$. The yellow iso-surfaces represent the spin density of spin up.

Subsequently, we perform spin polarized calculations on the Bi_2Te_3 supercell with two TM (TM=Ti, V, Cr,

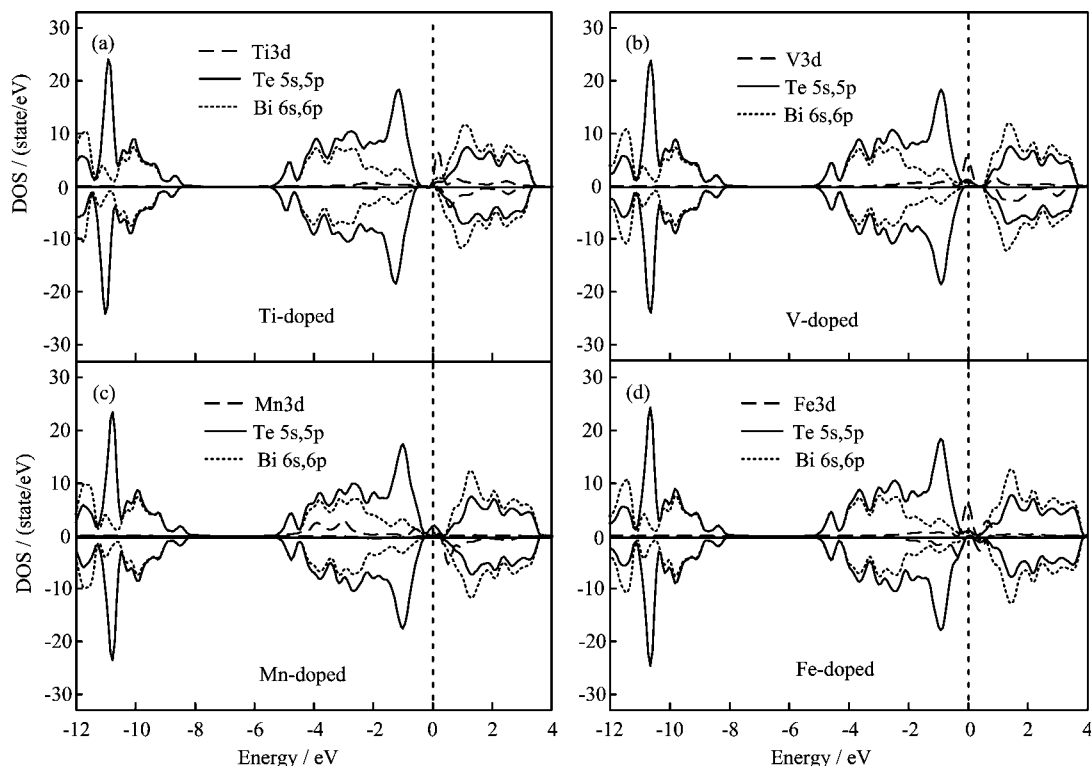


FIG. 4 Partial DOS of TM3d states, Te 5s and 5p states, and Bi 6s and 6p states for $\text{Bi}_{1.92}\text{TM}_{0.08}\text{Te}_3$. (a) Ti, (b) V, (c) Mn and (d) Fe, respectively. The vertical dotted lines indicate the Fermi level.

Mn and Fe) atoms substituting for Bi atoms in the lattice. Such substitution corresponds to $\text{Bi}_{1.84}\text{TM}_{0.16}\text{Te}_3$ and the doping level is 8%. In the supercell, we investigate six distributions of the two Bi atoms, which are replaced by TM atoms. The six cases are: (i) the two TM atoms are located at the sites of Bi1 and Bi2, and the distance is 4.45 Å; (ii) the two TM atoms are located at the sites of Bi1 and Bi3, and the distance is 6.56 Å; (iii) the two TM atoms are located at the sites of Bi1 and Bi4, and the distance is 10.63 Å; (iv) the two TM atoms are located at the sites of Bi1 and Bi5, and the distance is 11.52 Å; (v) the two TM atoms are located at the sites of Bi1 and Bi6, and the distance is 14.63 Å; (vi) the two TM atoms are located at the sites of Bi1 and Bi7, and the distance is 15.92 Å. In order to deal with the effect of the magnetic coupling between the two isolated TM atoms, we evaluate the relative energies between ferro- and antiferromagnetically ordered states by GGA calculation. Table I provides the energy differences between ferromagnetic state (FM) and antiferromagnetic state (AFM) as well as magnetic moments of two TM atoms doping. Here, $\Delta E_m = E_{\text{AFM}} - E_{\text{FM}}$ represents energy difference between antiferromagnetic state and ferromagnetic state after optimization, which enables us to estimate stable states of magnetism coupling. $\Delta E_m > 0$ indicates that the ferromagnetic state is more stable than the antiferromagnetic state, while $\Delta E_m < 0$ indicates that the antiferromagnetic state is

more stable than the ferromagnetic state. The energy differences ΔE of structures with different distance between the two TM atoms substitution for Bi atoms in Bi_2Te_3 are also listed in Table I. By comparing the total energies of the above six cases for $\text{Bi}_{1.84}\text{TM}_{0.16}\text{Te}_3$ (TM=Ti, V, Cr, Mn and Fe), we find that when the two TM atoms are located at the sites of Bi1 and Bi5, the system with ferromagnetic coupling has the lowest energy among the six cases and produces a magnetic moment of 1.91, 3.99, 6.01, 7.98, 9.46 μ_B for 8% Ti, V, Cr, Mn, and Fe doped Bi_2Te_3 . We also find that antiferromagnetic coupling is energetically favorable in the case (ii) for $\text{Bi}_{1.84}\text{Ti}_{0.16}\text{Te}_3$, case (iii) for $\text{Bi}_{1.84}\text{Cr}_{0.16}\text{Te}_3$, and case (i) for $\text{Bi}_{1.84}\text{Mn}_{0.16}\text{Te}_3$. It is evident that the type of preferential magnetic coupling of system depends upon the distributions of the TM atoms substitution for Bi atoms in Bi_2Te_3 .

IV. CONCLUSION

We explore the structural, electronic and magnetic properties of 4% TM-doped (TM=Ti, V, Cr, Mn and Fe) Bi_2Te_3 alloys via the first-principles PAW potential within DFT, employing the exchange-correlation potential provided by the GGA. The results demonstrate that, for Bi_2Te_3 system, magnetic moments can be induced when one Bi atom is substituted by a TM atom. On the electronic structures, the analyses of total

TABLE I The relative energies of states FM and AFM (ΔE_m), the total net magnetic moments (M_{tot}) and distance between the Bi Atoms substituted, values of the relative stabilities ΔE , calculated for the Bi_{1.84}TM_{0.16}Te₃.

		Atoms substituted					
		Bi1 and Bi2	Bi1 and Bi3	Bi1 and Bi4	Bi1 and Bi5	Bi1 and Bi6	Bi1 and Bi7
Distance/Å		4.45	6.56	10.63	11.52	14.63	15.92
$\Delta E_m/\text{meV}$	Bi _{1.84} Ti _{0.16} Te ₃	20.5	-18.3	10	13	14.5	77.4
	Bi _{1.84} V _{0.16} Te ₃	24.1	44.4	3	14.5	3	6.2
	Bi _{1.84} Cr _{0.16} Te ₃	12.8	3.6	-20.3	8	2.9	7.6
	Bi _{1.84} Mn _{0.16} Te ₃	-16.9	85.5	19.4	32.6	16	17.7
	Bi _{1.84} Fe _{0.16} Te ₃	49.5	7.4	5.2	17.5	12.9	9.2
M_{tot}/μ_B	Bi _{1.84} Ti _{0.16} Te ₃	2.02		1.84	1.91	1.98	1.94
	Bi _{1.84} V _{0.16} Te ₃	3.98	4.04	4.02	3.99	3.97	3.97
	Bi _{1.84} Cr _{0.16} Te ₃	6.01	6.14		6.01	5.95	5.94
	Bi _{1.84} Mn _{0.16} Te ₃		8.07	7.98	7.98	7.94	7.95
	Bi _{1.84} Fe _{0.16} Te ₃	8.45	7.17	9.65	9.46	9.28	9.68
$\Delta E/\text{meV}$	Bi _{1.84} Ti _{0.16} Te ₃	118.0	128.8	12.7	0	27	20.5
	Bi _{1.84} V _{0.16} Te ₃	157.4	110.3	8.70	0	68	59
	Bi _{1.84} Cr _{0.16} Te ₃	88.1	69.4	27.7	0	101.8	49.5
	Bi _{1.84} Mn _{0.16} Te ₃	104.0	45.1	21.9	0	181.7	157.8
	Bi _{1.84} Fe _{0.16} Te ₃	158.4	220.4	25.6	0	31.2	101.7

DOSs indicate that Ti-, V-, Mn- and Fe-doped Bi₂Te₃ alloys are all half-metals and magnetic with 100% spin polarization and seem to be good candidates for spintronic applications. It can also be found that the magnetic phase is energetically preferred to the nonmagnetic phase for all the Bi_{1.92}TM_{0.08}Te₃ (TM=Ti, V, Cr, Mn and Fe) systems. For Ti-, V-, Mn- and Fe-doped Bi₂Te₃ alloys, the results of spin-projected DOS show that the spin splitting mainly comes from TM3d states, and the peak that crosses the Fermi level consists most of the 3d state and also contains some Te5p and few Bi6p states. Small magnetic moments are also observed for the Bi and Te atoms, which are due to the small spin polarization of p-states of Te and Bi atoms. The Te and Bi atoms around the TM3d atom are polarized while other Te (or Bi) atoms are not polarized. That is to say, the polarized electrons are decided by the distance between the Te (or Bi) atom and the TM atom. We also compared the energies of ferromagnetic and antiferromagnetic couplings between two TM (TM=Ti, V, Mn and Fe) atoms substitutions in Bi₂Te₃ supercell, in which we investigate six distributions. The results show that when the two TM atoms are located at the sites of Bi1 and Bi5, the system has the lowest energy and the ferromagnetic coupling is energetically more favorable than the antiferromagnetic coupling.

V. ACKNOWLEDGMENTS

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