

## Regular article

# First-principles investigation on the magnetism of low-concentration 3d (Cr, Mn, Fe Co, Ni)-doped BeTe semiconductors



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## ABSTRACT

The structure stability, electronic structure and magnetic properties of zinc-blende  $\text{Be}_{15}\text{TMTe}_{16}$  (TM = Cr, Mn, Fe, Co and Ni) diluted magnetic semiconductors have been investigated using first-principles calculations. The  $\text{Be}_{15}\text{CrTe}_{16}$  and  $\text{Be}_{15}\text{FeTe}_{16}$  compounds are found to be half-metallic, and  $\text{Be}_{15}\text{MnTe}_{16}$  and  $\text{Be}_{15}\text{CoTe}_{16}$  compounds are found to be semiconducting, while  $\text{Be}_{15}\text{NiTe}_{16}$  is confirmed to be metallic. And the results indicate that these five compounds should be stable and may be synthesized in practice. These results suggest a possibility that  $\text{Be}_{15}\text{CrTe}_{16}$  and  $\text{Be}_{15}\text{FeTe}_{16}$  can be applied in the spintronic field.

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## 1. Introduction

In the spintronics field, in order to find more materials which are suitable to be manufacture electronic devices with low cost, small size and high speed, a large amount of research has been done. Lots of important breakthroughs on half-metallic (HM) ferromagnets, which only have one spin channel across the Fermi level [1], have arisen. From the time that NiMnSb was first predicted by Groot et al. [2], researchers have predicted theoretically and/or synthesized experimentally many HM ferromagnets, which have found wide applications in spintronics [3]. In diluted magnetic semiconductors (DMS), in which a very small amount of magnetic atoms replace some of the nonmagnetic cations in the host lattice [4,5], HM property has also been observed.

The indirect-band-gap Zinc-blende (ZB) BeTe is a typical representation of II–VI semiconductors [6–8]. Its luminous efficiency is high and absorption coefficient is low, which is only about 2.37 in the strong absorption region [9]. These special optical properties make BeTe good candidates for optoelectronic devices [7], and also facilitate the possibility to control the magnetic behavior by light irradiation in BeTe-based DMS. As it is known, there are two crystal structures for BeTe, the NiAs structure with a hexagonal lattice and the zinc-blende structure with a cubic lattice, which is the most

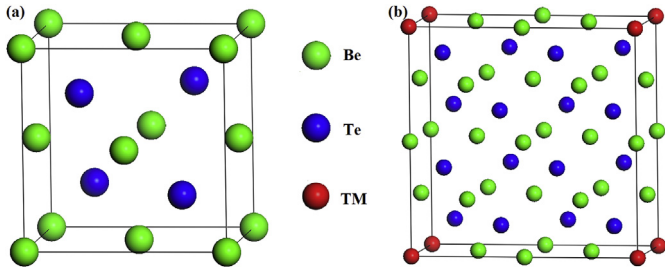
stable phase at ambient condition [10]. Much work has been done about the doping of the 3d transition metal in zinc-blende BeTe. For example, Li et al. [11] and Tanveer et al. [12] have systematically investigated the stability, electronic structure and magnetic properties of ZB  $\text{Be}_{0.75}\text{Mn}_{0.25}\text{Te}$  and  $\text{Be}_{0.75}\text{Co}_{0.25}\text{Te}$ . Noor et al. [13] have predicted that ZB  $\text{Be}_{1-x}\text{Mn}_x\text{Te}$  ( $x = 0.25, 0.5$ ) show 100% spin polarization at the Fermi level. Alay-e-Abbas et al. [14] have systematically investigated ZB  $\text{Be}_{1-x}\text{Cr}_x\text{Te}$  ( $x = 0.25, 0.5, 0.75, 1$ ) compounds and found that they are all ferromagnetic HMs. The half-metallicity of the V-doped BeTe semiconductors has also been predicted by Doumi et al. [15], Sajjad et al. [16] and Monir et al. [17]. Since the doping concentration of transition metals in semiconductors is limited and very low in experiments, the low-concentration doping must also be considered. For example, in ZB and wurtzite (WZ)  $\text{ZnX}$  ( $X = \text{S, Se and Te}$ ), a substantial amount of research on the low concentration doping of 3d transition metal (TM) atoms has been carried out [18–21]. However, there are few reports about the low concentration doping of 3d TM atoms in BeTe materials up to now. In this paper, we have investigated the structure stability, the electronic structure and the magnetism of ZB  $\text{Be}_{15}\text{TMTe}_{16}$  (TM = Cr, Mn, Fe, Co and Ni) diluted magnetic semiconductors. The calculated results reveal that potential half-metallicity can be expected in this system.

## 2. Computational details

The density functional theory (DFT) calculations were

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**Fig. 1.** The geometry configuration of (a) BeTe and (b) Be<sub>15</sub>TMTe<sub>16</sub>. The green, blue, and red balls represent Be, Te and TM atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

The lattice parameters ( $a$ , in Å), the formation energy ( $E_f$ , in eV/f.u.), the band gap (in eV), the HM gap (in eV), the total magnetic moment of Be<sub>15</sub>TMTe<sub>16</sub> ( $M_{tot}$ , in  $\mu_B$ ), and the magnetic moment of TM, Be and Te atoms ( $M_{TM}$ ,  $M_{Be}$  and  $M_{Te}$ , in  $\mu_B$ ).

Compound	$a$	$E_f$	Band gap	HM gap	$M_{tot}$	$M_{TM}$	$M_{Be}$	$M_{Te}$
BeTe	5.66	-3.87	1.99	–	0	0	0	0
Be <sub>15</sub> CrTe <sub>16</sub>	5.71	-3.79	2.02	0.87	4.00	3.24	0.02	0.03
Be <sub>15</sub> MnTe <sub>16</sub>	5.69	-3.81	0.90	–	5.00	3.86	0.02	0.06
Be <sub>15</sub> FeTe <sub>16</sub>	5.69	-3.86	1.86	0.33	4.00	3.20	0.01	0.05
Be <sub>15</sub> CoTe <sub>16</sub>	5.67	-3.86	0.32	–	3.00	2.00	0.01	0.05
Be <sub>15</sub> NiTe <sub>16</sub>	5.66	-3.84	0	–	0	0	0	0

performed using Cambridge Serial Total Energy (CASTEP) code [22]. The interaction between valence electrons and ions is treated by the ultrasoft pseudopotentials [23,24]. The Generalized Gradient Approximation [25] of Perdew, Burke and Ernzerhof [26] (GGA–PBE) is employed to treat the electronic exchange–correlation functions. For the pseudopotentials used, the electronic configurations with core level correction are Be ( $1s^22s^2$ ), Cr ( $3d^54s$ ), Mn ( $3d^54s^2$ ), Fe ( $3d^64s^2$ ), Co ( $3d^74s^2$ ), Ni ( $3d^84s^2$ ) and Te ( $5s^25p^4$ ), respectively. The plane-wave basis set are used to expand the electronic wave functions, and the cut-off energy is set as

400 eV. A  $12 \times 12 \times 12$  Monkhorst-Pack grid is employed for k-grid samplings in the irreducible Brillouin zone [27]. The convergence tolerance for the calculations is set as the difference in the total energy within  $5.0 \times 10^{-6}$  eV/atom, the maximum Hellman-Feynman force within  $10^{-2}$  eV Å<sup>-1</sup>, the maximum stress within  $2.0 \times 10^{-2}$  GPa, and the maximum displacement within  $5.0 \times 10^{-4}$  Å/atom, respectively.

### 3. Results and discussions

#### 3.1. Crystal structure

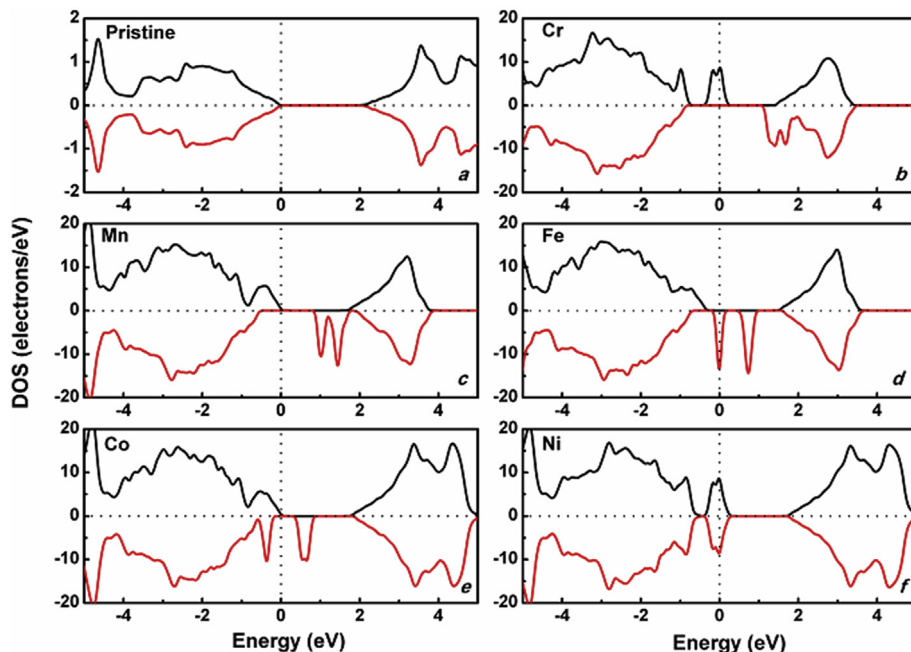
The geometry configuration of ZB BeTe is shown in Fig. 1(a). The Be atom is located at (0, 0, 0) and the Te atom is located at (1/4, 1/4, 1/4) [7] in this conventional cell with 8 atoms. To study the property of BeTe-based DMS with 3d TM doping, a super-cell with 32 atoms ( $a \times 2b \times 2c$ ) are used. As shown in Fig. 1(b), for Be<sub>15</sub>TMTe<sub>16</sub>, one TM atom is substituted for one Be atom. The equilibrium lattice constants of BeTe and Be<sub>15</sub>TMTe<sub>16</sub> are obtained by geometry optimization. The possible magnetic configurations (ferromagnetic, nonmagnetic and antiferromagnetic) are all considered. Furthermore, for the ferromagnetic and antiferromagnetic configurations, to find the stable ground state, the states with different starting magnetic moments have also been tested. The corresponding parameters are summarized in Table 1.

#### 3.2. Phase stability

Firstly, in order to investigate the phase stability of Be<sub>15</sub>TMTe<sub>16</sub>, the formation energy is calculated. The formation energy  $E_f$  is presented as following:

$$E_f = E_{total} - \sum_i n_i E_{atom}^i$$

Here,  $E_{total}$  is the total energy of the compound,  $E_{atom}^i$  is the chemical potential of the  $i$ th element and  $n_i$  is the number of the  $i$ th atom. The calculated formation energies are presented in Table 1. It



**Fig. 2.** The total DOS of Be<sub>15</sub>TMTe<sub>16</sub>.

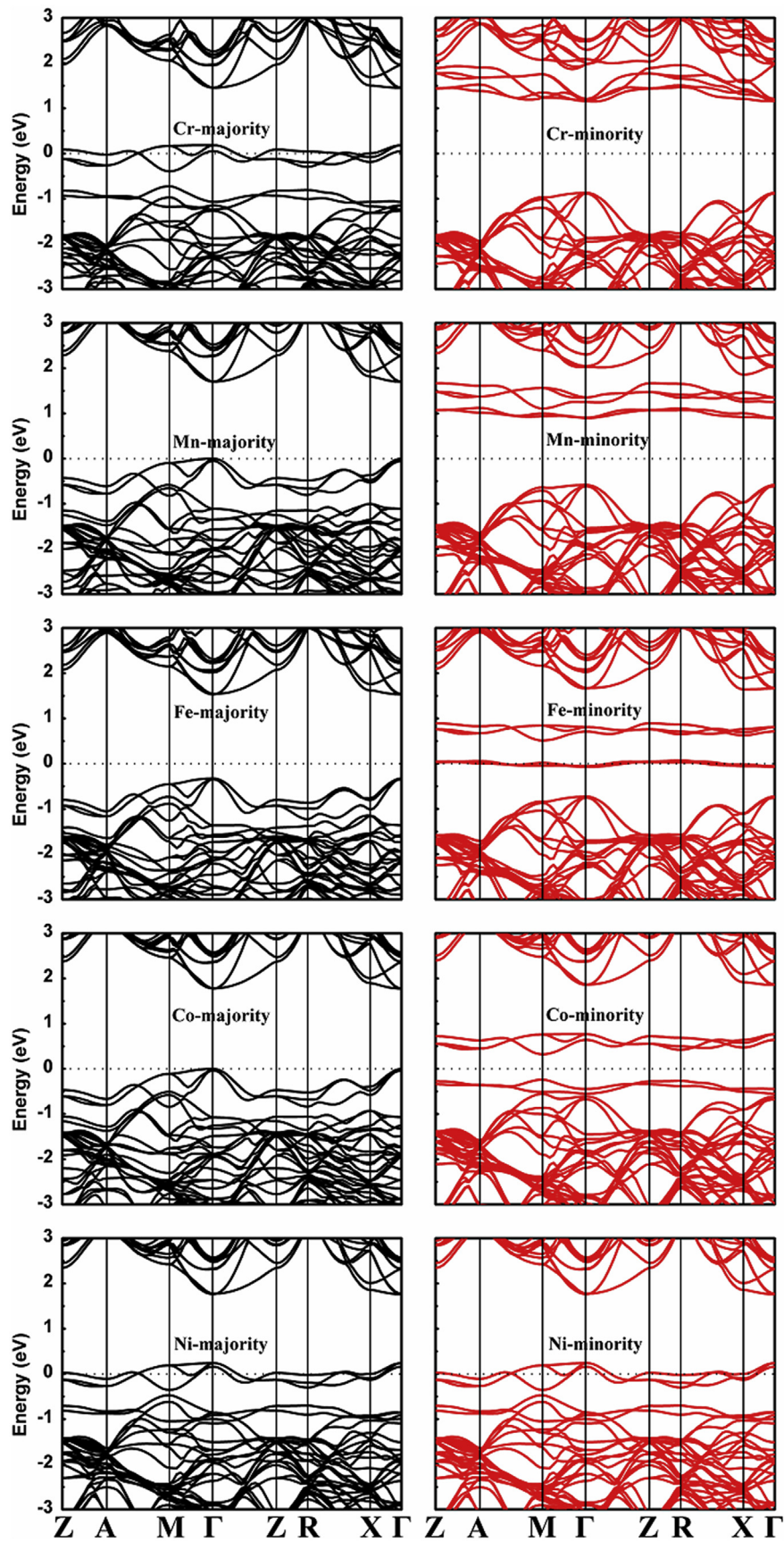


Fig. 3. The band structure of  $\text{Be}_{15}\text{TMTe}_{16}$ .

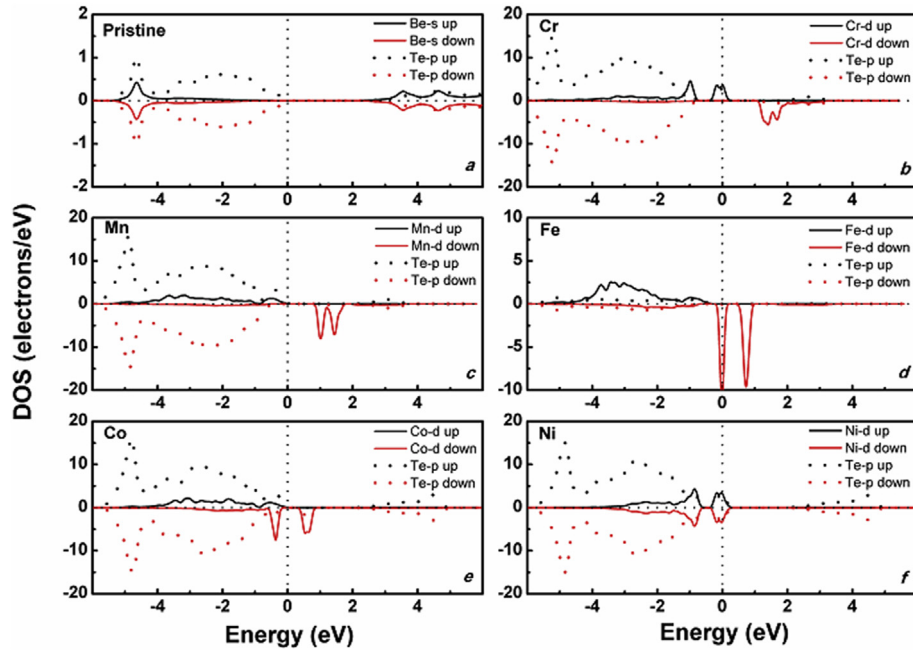


Fig. 4. The partial DOS of  $\text{Be}_{15}\text{TMTe}_{16}$ .

can be found that, for all the doped compounds, the formation energies are negative and considerable, suggesting that  $\text{Be}_{15}\text{TMTe}_{16}$  (TM = Cr, Mn, Fe, Co and Ni) compounds should be stable and may be synthesized in practice.

### 3.3. Electronic structure and magnetic properties

The total density of state (DOS) of pristine BeTe and  $\text{Be}_{15}\text{TMTe}_{16}$  are shown in Fig. 2. It can be found that, BeTe is a semiconductor with an energy gap of 1.99 eV, which is in good agreement with that obtained by Guo et al. [7]. For  $\text{Be}_{15}\text{CrTe}_{16}$ , the density of state at the Fermi level is considerable in the majority-spin state, and the density of state is zero at the Fermi level in the spin-minority state. For  $\text{Be}_{15}\text{FeTe}_{16}$ , the majority-spin state exhibits a semiconducting character, while the minority-spin state is metallic. Thus,  $\text{Be}_{15}\text{CrTe}_{16}$  and  $\text{Be}_{15}\text{FeTe}_{16}$  are HM with 100% spin polarization. The half-metallic gaps, the most proper indicator of the half-metallicity for a material, are also presented in Table 1. Here, the half-metallic gap [28,29] is defined as the minimum between the lowest energy of the majority (minority) spin conduction bands with respect to the Fermi level and the absolute values of the highest energy of the majority (minority) spin valence bands. The HM gaps are 0.33 and 0.87 eV for  $\text{Be}_{15}\text{FeTe}_{16}$  and  $\text{Be}_{15}\text{CrTe}_{16}$ , respectively. Thus, the HM property of  $\text{Be}_{15}\text{CrTe}_{16}$  should be very stable and may be suitable for the spintronic application. For  $\text{Be}_{15}\text{MnTe}_{16}$  and  $\text{Be}_{15}\text{CoTe}_{16}$ , the majority-spin and minority-spin states are not symmetrical and the energy gaps are 0.90 and 0.32 eV, respectively. So we predict that they are magnetic semiconductors. For  $\text{Be}_{15}\text{NiTe}_{16}$ , the majority-spin and minority-spin states are symmetrical and the densities of state are not zero at the Fermi level for both two states, thus  $\text{Be}_{15}\text{NiTe}_{16}$  is a nonmagnetic metal.

Fig. 3 shows the band structures of  $\text{Be}_{15}\text{TMTe}_{16}$ . It can also be found that  $\text{Be}_{15}\text{CrTe}_{16}$  and  $\text{Be}_{15}\text{FeTe}_{16}$  are HMs, and  $\text{Be}_{15}\text{MnTe}_{16}$  and  $\text{Be}_{15}\text{CoTe}_{16}$  are semiconducting, while  $\text{Be}_{15}\text{NiTe}_{16}$  is a nonmagnetic metal. Besides, the details of the band structure are different for  $\text{Be}_{15}\text{MnTe}_{16}$  and  $\text{Be}_{15}\text{CoTe}_{16}$ . For  $\text{Be}_{15}\text{MnTe}_{16}$ , both of the conduction band bottom and the valence band maximum are located at  $\Gamma$  point. It suggests that  $\text{Be}_{15}\text{MnTe}_{16}$  is a direct-band-gap magnetic

semiconductor. However, For  $\text{Be}_{15}\text{CoTe}_{16}$ , the conduction band bottom is located at M point (0.5, 0.5, 0), while the valence band maximum is located at  $\Gamma$  point, suggesting an indirect-band-gap characteristic.

The partial DOS is also calculated to investigate the magnetism of  $\text{Be}_{15}\text{TMTe}_{16}$ . Because the magnetic moment of Be is very small in  $\text{Be}_{15}\text{TMTe}_{16}$  (as shown in Table 1), the DOS of Be atoms is not shown in Fig. 4. It can be found that the strong hybridization between the 3d orbitals of the TM atoms and the host p orbitals near the Fermi level plays an important role on the formation of induced magnetism. All the 3d TM atom ions form ferromagnetic interactions between the surrounding Be and Te ions (see Table 1).

To give an insight into the magnetism in TM-doped BeTe DMS, the electronic configurations of TM ions are schematically illustrated in Fig. 5. The TM atoms occupy Be site in BeTe semiconductor, and contribute two electrons to the anionic dangling bonds. The remaining d electrons are responsible for its magnetic state. Based on the crystal field theory, we can find that the nearest neighboring Te atom form a tetrahedral crystal field, which splits the five-fold degenerate d states of the TM ion into three-fold degenerate high-lying  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ) and two-fold degenerate low-lying  $e_g$  ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) states [30,31]. And the energies of  $t_{2g}$  states are higher than  $e_g$  states because of more electrostatic interactions. The Jahn–Teller effect of some TM impurities will further change the splitting of  $t_{2g}$  and  $e_g$  states. The electron configuration of the doped TM ion is resulted from the competition between crystal field

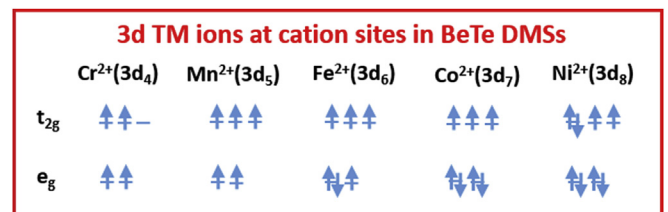


Fig. 5. The electronic configurations of  $t_{2g}$  and  $e_g$  states of 3d TM ions in BeTe DMS.

splitting energy and mean spin pairing energy (the energy required to pair up electrons in the same orbitals) [30].

Based on the above discussion, the magnetic state of TM ions in BeTe DMS can be illustrated. As shown in Fig. 5, for Mn, Fe, Co ions, the spin-up states are fully occupied, while the spin-down states are either empty or partially occupied. In this case, because of the strong hybridization between doped TM ion and its neighboring Te anions of the host semiconductor, part of the Te spin-down electrons will transfer to TM ions, thus the spin-up states of Te ions become more occupied than spin-down states and the induced magnetic moments of Te ions are parallel to that of TM (Mn, Fe, Co) ions as a result [31]. For Cr ions, we can find that the spin-up states are partially occupied. However, due to its crystal field splitting energy is larger than mean spin pairing energy, the spin-down states in Te ions will transfer to Cr ions. Thus, the spin-up states in Te is more occupied than spin-down states, and the magnetic moment of Te ions is also parallel to that of Cr ions. Since some of the spin-down states of the doped TM ion are occupied by the electrons of the host anions, the calculated magnetic moments of TM atoms in DMS are smaller than those of the corresponding free atoms. The detailed value of atomic magnetic moment can be found in Table 1.

#### 4. Conclusions

Employing the first-principles calculations, we have investigated the structure stability, electronic structure and magnetic properties of  $\text{Be}_{15}\text{TMTe}_{16}$  compounds. The conclusions can be summarized as follows:

- (1)  $\text{Be}_{15}\text{TMTe}_{16}$  (TM = Cr, Mn, Fe, Co and Ni) compounds at zero pressure can exist stably and may be synthesized in practice.
- (2)  $\text{Be}_{15}\text{CrTe}_{16}$  and  $\text{Be}_{15}\text{FeTe}_{16}$  are found to be half-metallic, and  $\text{Be}_{15}\text{MnTe}_{16}$  and  $\text{Be}_{15}\text{CoTe}_{16}$  are found to be magnetic semiconductors, while  $\text{Be}_{15}\text{NiTe}_{16}$  is confirmed to be a nonmagnetic metal.
- (3) The magnetic moments on the surrounding host ions are induced by the hybridization of 3d TM ions and the host ions, and the total magnetic moment comes mainly from the magnetic atom.

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