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Half-metallic ferromagnets based on the rock-salt IV–VI semiconductor GeTe

Yong-Hong Zhao, Wen-Hui Xie, Li-Fang Zhu and Bang-Gui Liu¹

Institute of Physics, Chinese Academy of Science, Beijing 100080, People's Republic of China
and
Beijing National Laboratory for Condensed Matter Physics, Beijing 100080,
People's Republic of China

E-mail: bgliu@aphy.iphy.ac.cn

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Abstract

Using an accurate density-functional method, we study a series of ternary transition-metal compounds based on the rock-salt IV–VI semiconductor GeTe for potential use as half-metallic ferromagnets, because some of such materials have already been fabricated and proved experimentally to be ferromagnetic. We find four half-metallic ferromagnets in ternary Cr- and V-substituted compounds and study their electronic structures and charge and spin density to clarify their bonding properties. The half-metallic ferromagnetic order is stable against possible antiferromagnetic orders. The half-metallic ferromagnetism is formed because the exchange splitting of the transition-metal d states is large enough to cause ferromagnetism and keep the minority-spin gap at the Fermi level open. These half-metallic ferromagnets could be useful in spintronics because of their relationship with the semiconductor GeTe.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The half-metallic ferromagnet has attracted considerable attention in recent years, because one of its electronic spin channels has a band gap at the Fermi energy and the other maintains a metallic behaviour [1, 2]. Since de Groot *et al* discovered the first half-metallic ferromagnet NiMnSb [3] in 1983, a number of half-metallic ferromagnets have been theoretically predicted and many of them have been confirmed experimentally [4–7]. For semiconductor spintronics, it is highly desirable to find new half-metallic materials compatible with semiconductors.

Theoretical exploration of half-metallic ferromagnets with or based on the rock-salt structure is becoming increasingly interesting because ferromagnetism has been found experimentally in the transition-metal-doped rock-salt semiconductor GeTe, although the main

¹ Author to whom any correspondence should be addressed.

attention so far has been paid to the zinc blende and wurtzite structures [8–10]. Ferromagnetic rock-salt $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ compounds have been successfully grown on BaF_2 substrates by using the ionized-cluster beam technique, with Mn concentration x ranging widely from 0.2 to 0.96 [11], and the highest observed Curie temperatures (T_c) are 140 K for $\text{Ge}_{0.49}\text{Mn}_{0.51}\text{Te}$ [11] and 167 K for $\text{Ge}_{0.5}\text{Mn}_{0.5}\text{Te}$ [12]. Ferromagnetic $\text{Ge}_{1-x}\text{Cr}_x\text{Te}$ films with Cr concentration up to $x = 0.33$ have been successfully prepared by using a sputtering method [13], and the highest T_c is approximately 50 K [13, 14]. In addition, the magnetic properties of $\text{Ge}_{1-x}\text{X}_x\text{Te}$ with rock-salt crystal structure, where X is one of the 3d transition metals and x is around 0.15, have been studied experimentally [15]. According to these experimental results, it would be of interest and feasible to theoretically explore new half-metallic ferromagnets in ternary 3d-transition-metal compounds based on IV–VI semiconductors with the rock-salt structure.

In this paper, we use an accurate full-potential density-functional method to systematically study a series of ternary compounds Ge_3XTe_4 and GeXTe_2 ($X = \text{Ti, V, Cr, Mn, Fe, Co}$ and Ni) based on the rock-salt IV–VI semiconductor GeTe in order to explore new half-metallic ferromagnets based on the rock-salt structure. The ternary compounds are obtained by partially substituting 3d transition-metal atoms for Ge atoms in the Ge fcc sublattice. Four half-metallic ferromagnets are found when substituting Cr (25% and 50%) and V (25% and 50%) for Ge in the rock-salt semiconductor GeTe . A half-metallic gap of 0.34 eV is obtained for the 50% Cr-substituted GeTe . Their electronic structures and charge and spin density distribution are studied in order to clarify their bonding property and the origin of the half-metallic ferromagnetism. Their mechanical stability is also analysed. These new half-metallic ferromagnets, based on the rock-salt IV–VI semiconductor GeTe , could be useful in spintronics.

The remaining part of this paper is organized as follows. In the next section we briefly describe the structures we use and explain our first-principle calculations in detail. In section 3 we present our main results, including the four half-metallic ferromagnets and their mechanical stability. In section 4 we explore the bonding property and the mechanism for the half-metallic ferromagnetism in these compounds. Finally, we provide some discussion and give our conclusion in section 5.

2. Computational details

The conventional unit cell of rock-salt GeTe consists of one anion fcc lattice of Te and one cation fcc lattice of Ge. In the case of 25% substitution, one transition-metal atom is substituted at one of the four sites of the Ge fcc lattice, which results in the space group $Pm\bar{3}m$ (no. 221). The 50% substitution is realized by replacing two of the four Ge atoms in the Ge fcc lattice. In this way one obtains a tetragonal structure ($P4/mmm$, no. 123). With these methods we obtain minimal primitive cells, or keep as high symmetry as possible. For every case we calculated the total energy as a function of cell volume, and thereby determined the equilibrium lattice constants. All the electronic densities of states (DOSs), bands, moments, and charge and spin density distribution are then calculated with the equilibrium lattice constants. We determine whether the magnetic structure is ferromagnetic or antiferromagnetic by comparing the total energies. In the following we use the existing definition for the half-metallic gap [10].

We make use of the Vienna package WIEN2k [16] for all our calculations. This is a full-potential (linear) augmented plane wave plus local orbitals method within the density functional theory [17]. We take the generalized gradient approximation [18] for the exchange–correlation potential. Full relativistic calculation is done for core states. For valence states, relativistic effects are taken into account within the scalar approximation. The spin–orbit coupling is proved very small and will be neglected, except in the following discussion. We use at least 3000 k -points in the first Brillouin zone. We set $R_{\text{mt}} * K_{\text{max}}$ to 8.0 and make the expansion up to

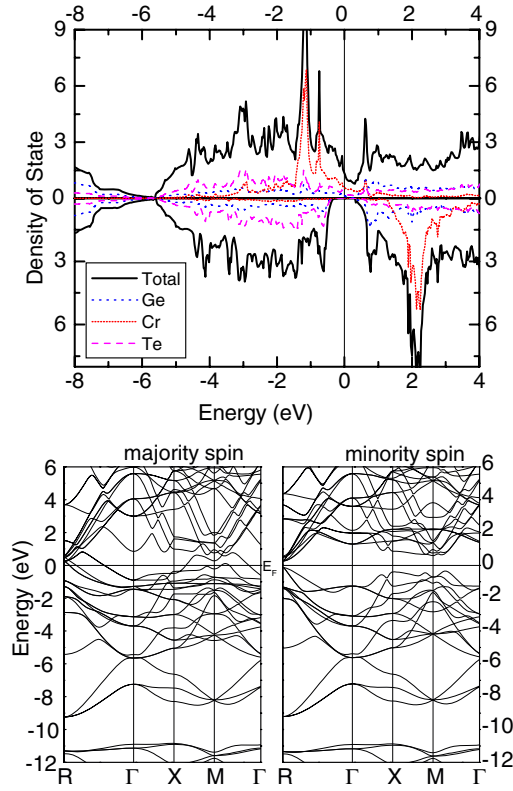


Figure 1. Spin-dependent density of states (upper part) and energy bands (lower part) of the Ge_3CrTe_4 at the equilibrium lattice constant. The solid lines show the total DOSs, the short-dotted lines the Cr partial DOS, the dotted lines the Ge partial DOS, and the dashed lines the Te partial DOS. The minority-spin band gap at the Fermi level is about 0.52 eV and the corresponding half-metallic gap is 0.19 eV.

Table 1. Equilibrium lattice constants (a or a/c in Å), magnetic moments per magnetic atom (m in units of μ_B), half-metallic gaps (g_h in eV), MIS energy gaps crossing the Fermi levels (g_\downarrow in eV), and bulk moduli (B in GPa) of the half-metals based on semiconductor GeTe.

Compound	a or a/c (Å)	m (μ_B)	g_h (eV)	g_\downarrow (eV)	B (GPa)
Ge_3CrTe_4	5.928	4	0.19	0.52	53
GeCrTe_2	4.144/5.844	4	0.34	0.88	54
Ge_3VTe_4	5.931	3	0.07	0.68	52
GeVTe_2	4.139/5.865	3	0.13	0.95	55

$l = 10$ in the muffin tins. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}| dr$, between the input charge density $[\rho_{n-1}(r)]$ and the output charge density $[\rho_n(r)]$ is less than 0.0001.

3. Main results

Among all the ternary compounds with 25% substitution, the Ge_3XTe_4 ($X = \text{V}, \text{Cr}$) are half-metallic ferromagnets at their equilibrium lattice constants. The equilibrium lattice constant a , moment m per magnetic atom, half-metallic gap g_h , minority-spin (MIS) band gap g_\downarrow , and bulk

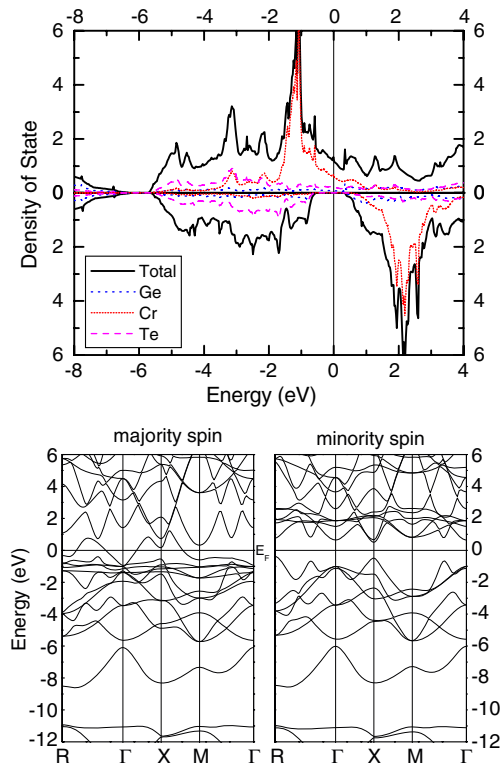


Figure 2. Spin-dependent density of states (upper part) and energy bands (lower part) of the GeCrTe_2 at the equilibrium lattice constant. The solid lines show the total DOSs, the short-dotted lines the Ge partial DOS, the dotted lines the Cr partial DOS, and the dashed lines the Te partial DOS. The minority-spin band gap at the Fermi level is about 0.88 eV and the corresponding half-metallic gap is 0.34 eV.

moduli B for the two ternary compounds are summarized in table 1. Each of the V and Cr atoms contributes a moment of 3 and 4 μ_B respectively to the total moment. The half-metallic gaps are 0.19 and 0.07 eV for Ge_3CrTe_4 and Ge_3VTe_4 , respectively. The lattice constant increases a little from Cr substitution to V substitution. The spin-dependent density of states (DOSs) and the spin-dependent energy bands of the Ge_3CrTe_4 are shown in figure 1. Ge_3VTe_4 has similar electronic structures.

For the 50% substitution of transition metals for Ge, we obtain two half-metallic ferromagnets: GeVTe_2 and GeCrTe_2 . Their equilibrium lattice constants a and c , moment m per magnetic atom, half-metallic gap g_h , MIS band gap g_l , and bulk moduli B are also summarized in table 1. Each of the Cr and V atoms contributes a moment of 4 and 3 μ_B respectively to the total moment, which is the same as in the two 25%-substituted half-metals. The DOSs and the spin-dependent energy bands of the GeCrTe_2 are shown in figure 2. Their bulk moduli are approximately the same as those of the 25%-substituted ones. Their half-metallic gaps and MIS gaps are clearly larger than those of the corresponding 25%-substituted half-metals. This means that more Cr and V substitution (up to 50%) enhances the half-metallic ferromagnetic order.

In addition, the charge densities, defined on (100), (110), and (111) planes including a magnetic atom, for the half-metallic Ge_3CrTe_4 , are calculated and shown in figure 3 (the first row of panels) to show the bonding characteristics of Cr with surrounding atoms. The spin

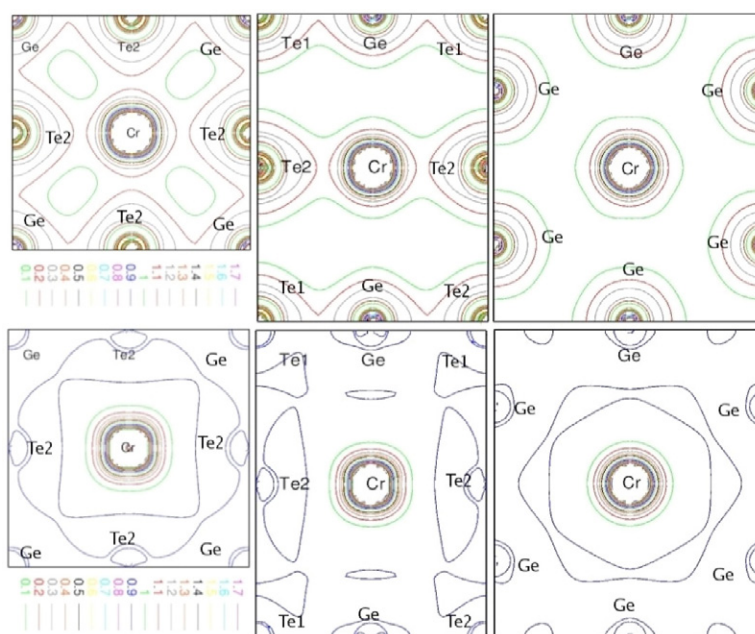


Figure 3. The charge (top row of panels) and spin (second row of panels) density distribution of Ge_3CrTe_4 at the equilibrium lattice constant. They are defined on the (100) (left), (110) (middle), and (111) (right) planes, respectively, with the Cr atom being at the centre. The positions of Ge and Te atoms are shown too.

densities defined on the same three planes are also shown in the second row of panels of figure 3. In order to investigate the mechanical stability of the half-metallic ferromagnets, we have calculated the shear modulus constants, C' and C_{44} , respectively, by computing the change in total energy of these rock-salt structures under small volume-conserving tetragonal and rhombohedral strains. The C' and C_{44} values of Ge_3CrTe_4 are 53 and 76 GPa, so Ge_3CrTe_4 is stable against tetragonal and rhombohedral deformations. We have constructed various antiferromagnetic spin configurations and compared their total energies with those of the half-metallic ferromagnets. All of the antiferromagnetic structures are at least 45 meV/f.u. higher than the ferromagnetic ones. Therefore, the four ferromagnetic half-metals are indeed stable against possible antiferromagnetic orders.

4. Bonding property and mechanism for half-metallicity

The semiconducting gap of GeTe is between the p–p bonding bands and the p–p antibonding ones. The electronic structures of all the GeTe-based half-metals have similar characteristics, so we present only those of the 25% and 50% Cr-substituted compounds and take them as the representatives to analyse the origin of the half-metallic ferromagnetism. In the case of Ge_3CrTe_4 , there is an energy gap of about 0.52 eV in its minority-spin bands, and the corresponding half-metallic gap is 0.19 eV. The energy bands between -13 and -11 eV, as shown in figure 1, originate mostly from 5s states of Te. The bands around -8 eV are mainly from 4s states of Ge. The electronic states between -6 and 4 eV originate from Ge 4p, Te 5p, and transition-metal 3d + 4s states. The spin-dependent partial DOS of Ge_3CrTe_4 is shown in figure 4. The covalent bond between Te 5p and Ge 4p yields the DOS between -6 and 0 eV

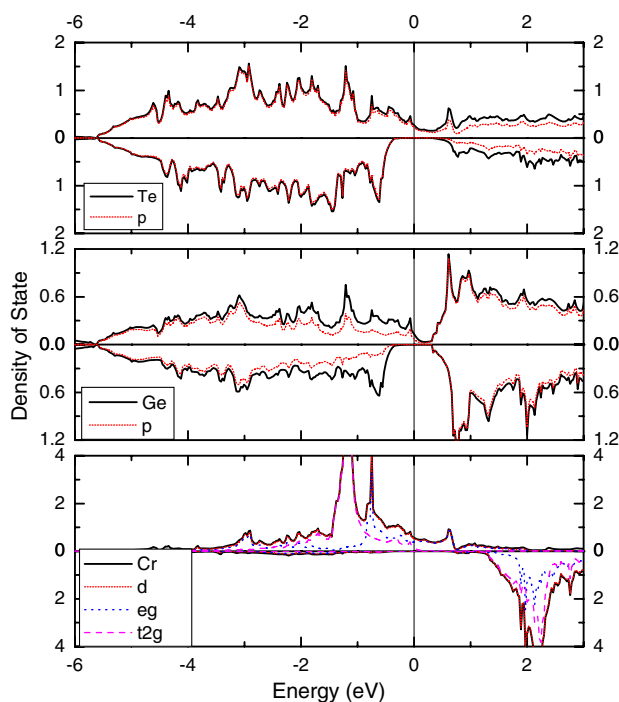


Figure 4. The spin-dependent partial DOS of the Ge_3CrTe_4 . The DOSs of Te (top) and Ge (middle) originate mainly from the Te 5p and Ge 4p states, and those of Cr (bottom) in the energy window are contributed completely by the 3d states. The d peak at 1.2 eV is from the eg state.

in the upper two panels. There are some mixing between the transition-metal 3d and 4s states. Two Cr 4s + 3d electrons move to Te, forming a bond with Te 5p. The mixing decreases from V to Ni because the energy difference between the 4s and 3d levels becomes larger from V to Ni. The ionicity of the bond of Cr with Te becomes weaker from V to Ni for the same reason. GeCrTe_2 has similar partial DOSs, as shown in figure 5. The main difference is that the d DOS peaks at -1.2 and 2.2 eV are wider than those of the Ge_3CrTe_4 . This should be caused by the fact that there is more Cr and lower crystal symmetry in GeCrTe_2 .

The basic ferromagnetism is formed because of the exchange splitting of the d bands of magnetic atoms. The exchange splitting energies, defined as the difference between the t_{2g}^{\uparrow} and t_{2g}^{\downarrow} , are about 2.5, 3.3, 4 and 2.8 eV for V, Cr, Mn, and Fe, respectively, and they follow the expected trend as a function of the number of unpaired d electrons. For the Cr case, the t_{2g}^{\uparrow} DOSs peak is at -1.1 eV and the t_{2g}^{\downarrow} peak is at 2.2 eV. For stable ferromagnetism, the t_{2g}^{\uparrow} DOSs peak should be below the Fermi level and the t_{2g}^{\downarrow} peak above the Fermi level. In all the cases from V to Fe, the crystal-field splitting energies, defined as the energy difference between the e_g and t_{2g} states, are smaller than the exchange splitting ones, so the high-spin ground states are stabilized. The effect of the spin-orbit coupling on electronic structures has been studied. In the case of the Ge_3CrTe_4 , the spin-orbit coupling changes majority-spin DOSs at the Fermi level a little, from 1.33 to 1.15/eV per state; and creates small DOSs, 0.01/eV per state, in the minority-spin gap at the Fermi level. However, the changes are very small. Therefore, it is reasonable to neglect the spin-orbit coupling in our presented figures.

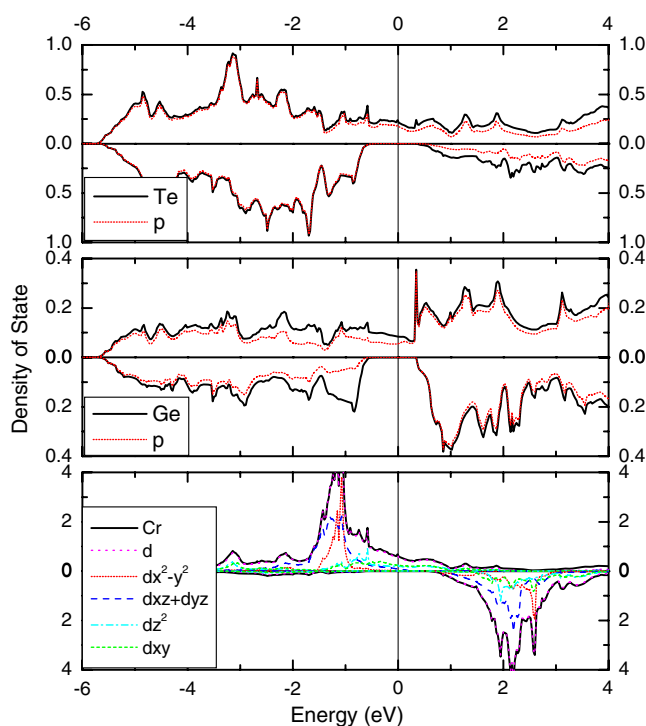


Figure 5. The spin-dependent partial DOS of the GeCrTe_2 . The DOSs of Te (top) and Ge (middle) originate mainly from the Te 5p and Ge 4p states, and those of Cr (bottom) in the energy window are contributed completely by the 3d states.

From V to Fe, the t_{2g} states are at the lower edge of the ds band manifolds. The exchange splitting pushes the minority part of the ds band manifold upwards and over the semiconducting gap of GeTe, and at the same time it pushes the majority-spin part of the ds band manifolds downwards. Some of the majority-spin ds bands move into the semiconducting gap of GeTe, but favourable DOSs distribution makes the Fermi level still stay in the minority-spin gap. As a result, the half-metallic ferromagnetism is formed. For V- and Cr-substituted GeTe, because the t_{2g} states are higher in energy than the p–p gap, they are half-metallic ferromagnets. The V-substituted half-metals have smaller half-metallic gaps because their majority-spin DOSs around the Fermi levels are a little smaller than those of the Cr-substituted ones and thus their Fermi levels must move higher. Ge_3CrTe_4 has a smaller g_h than GeCrTe_2 because it has a smaller g_\downarrow . Ge_3VTe_4 has a smaller g_h than the GeVTe_2 because its Fermi level is nearer its MIS conduction band bottom than that of GeVTe_2 is. For the Mn-substituted GeTe, there is an instability to the semiconducting state. For the Fe-substituted compound, as shown in figure 6, the Fe ds states becomes deeper, so the t_{2g} states fill the semiconducting gap of GeTe and thus we obtain an ordinary ferromagnet with a total moment $3.80 \mu_B/\text{f.u.}$

5. Discussion and conclusion

As the number of 3d valence electrons increase from Ti to Mn, the minority-spin d bands move downwards. The situation becomes less favourable when we substitute Fe, Co, and Ni for Ge in GeTe. The d electrons are more localized and lower in energy from V to Ni. The

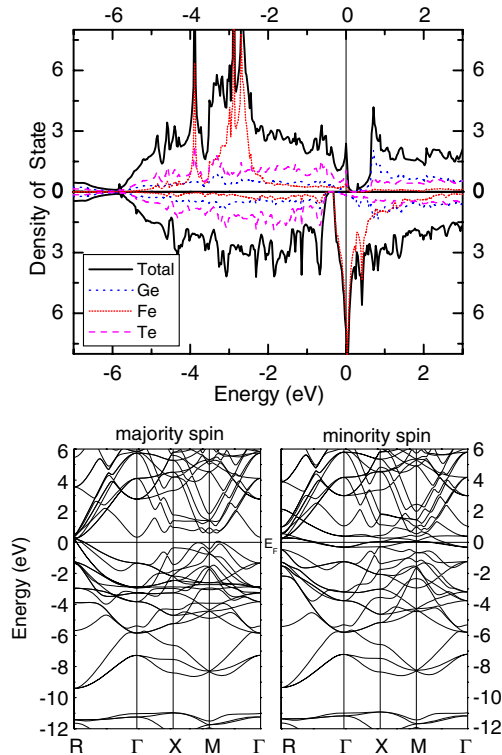


Figure 6. Spin-dependent density of states (upper part) and energy bands (lower part) of the Ge_3FeTe_4 at the equilibrium lattice constant 5.875 Å. The solid lines show the total DOSs, the short-dotted lines the Fe partial DOS, the dotted lines the Ge partial DOS, and the dashed lines the Te partial DOS.

exchange splitting increases from Ti to Mn, and then decreases from Mn to Ni. The minority-spin d bands of these Mn-, Fe-, Co- and Ni-substituted compounds are moved downwards and even below the Fermi level. Therefore, the Cr- and V-substituted GeTe compounds are half-metallic ferromagnets, while the Ti-, Fe-, Co- and Ni-substituted GeTe compounds are not. For Ge_3MnTe_4 , because of the nearly zero DOS at the Fermi level E_f , it is a semiconductor with almost zero band gap, and it is very similar to the zinc blende magnetic semiconductor MnTe [19]. With Ti substitution, we obtain an ordinary ferromagnet because the exchange spin splitting is quite small and the d states are so high that the lower majority-spin d DOS peak is in the GeTe gap. With Ni substitution, the spin exchange splitting is too small to sustain ferromagnetism in Ni-substituted GeTe, and therefore the Ni-substituted compounds are nonmagnetic.

Because it is very difficult to fabricate high-quality samples of germanium telluride with perfect stoichiometry, there have been no experimental reports of the semiconducting gap for GeTe, but DFT calculation shows that there is a Cohen–Sham gap for GeTe [20]. The real gap should be larger than the Cohen–Sham gap because of the well-known underestimation of semiconducting gaps in DFT calculations. However, the gap problem does not exist for our calculations of half-metals. Because $\text{Ge}_{1-x}\text{Cr}_x\text{Te}$ (x up to 0.33) based on GeTe has been fabricated, half-metallic Ge_3CrTe_4 can be realized by improving the sample quality of

$\text{Ge}_{0.75}\text{Cr}_{0.25}\text{Te}$, and GeCrTe_2 could be fabricated by increasing the doping level to $x = 50\%$. Since heavy Mn doping in GeTe has been realized [11] and some V has been doped in GeTe [15], we believe that the two V-substituted half-metals could be fabricated in the future.

In summary, we have used an accurate full-potential density-functional method to study a series of ternary transition-metal compounds based on the rock-salt IV–VI semiconductor GeTe. The compounds were obtained by partially substituting 3d transition metals, Ti, V, Cr, Mn, Fe, Co and Ni, for Ge in the Ge fcc sublattice of the rock-salt GeTe lattice. Two 25%-substituted half-metallic ferromagnets, Ge_3CrTe_4 , and Ge_3VTe_4 , and two 50%-substituted ones, GeCrTe_2 and GeVTe_2 , were found. They are stable against possible antiferromagnetic structures. The electronic structures, magnetic properties, and mechanical stability of the half-metallic ferromagnets were investigated. The mechanism for the half-metallicity was clarified in terms of the electronic structures. To the best of our knowledge, this is the first report on half-metallic ferromagnets in rock-salt or rock-salt-based compounds. Because of relationship with the semiconductor GeTe, they could be useful for making multilayered nanostructures for spintronics.

Acknowledgments

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