High spin polarization in ternary Ge–Mn–Te compounds based on rocksalt semiconducting

GeTe

High spin polarization in ternary Ge–Mn–Te compounds based on rocksalt semiconducting GeTe

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Abstract
We study the ternary compounds $Ge_mMn_nTe_p$ based on rocksalt semiconducting GeTe using a full-potential density-functional method. For $m + n = p$, we obtain two antiferromagnetic semiconductors in which spins are coupled with a superexchange interaction. Letting $m + n < p$, we obtain two metallic ferromagnets, $Ge_3Mn_4Te_8$ and $Ge_5Mn_2Te_8$. They have full or nearly full spin polarization at the Fermi level. Our study shows that the ferromagnetism is favorable because carriers induced by the Ge vacancies make the superexchange give way to a Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction. Our results, consistent with experiments, indicate that high spin polarization can be realized in high quality $Ge_3Mn_4Te_8$ and $Ge_5Mn_2Te_8$ samples.

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

1. Introduction

High spin polarization magnetic materials, especially half-metallic ferromagnets, are promising for spintronic applications [1]. Recently, ternary Ge–Mn–Te compounds, based on the IV–VI compound GeTe with rocksalt structure, have been synthesized on a $BaF_2(111)$ substrate with Mn composition ranging from 0.2 to 0.96 using the ionized cluster beam technique [2, 3] or radio frequency sputtering [4]. It has been shown experimentally [3, 4] that these ternary compounds are ferromagnets. A Curie temperature of 140 K was obtained in these samples [2, 5, 6]. The highest Curie temperature achieved in GeTe-based ferromagnetic (FM) semiconductors reaches 180 K [7] and is higher than the best result, 173 K, in the case of (Ga, Mn)As diluted magnetic semiconductors [8]. The magnetic order of the Ge–Mn–Te samples is determined by the competition between the FM carrier-induced Ruderman–Kittel–Kasuya–Yosida (RKKY) [9] interaction and the antiferromagnetic (AF) superexchange interaction between Mn spins. Calculated electronic structures, at least for $x = 0.25$ and 0.5, indicate that $Ge_{1-x}Mn_xTe$ should

be AF semiconductors, which is not consistent with the experimental metallic behaviors. It was shown that there exist 10% Ge vacancies in real GeTe samples [10]. More vacancies (10–20%) were believed to exist in other GeTe-based compounds such as $Ge_2Sb_{2+x}Te_5$ [11] ($0 < x < 1.0$). The experimental ferromagnetism may be correlated with the vacancies. Therefore, it is highly desirable to investigate the structural and magnetic properties of these materials in order to understand the experimental ferromagnetism of the Ge–Mn–Te samples and to search for possible better spintronics materials.

Here we use a full-potential density-functional method to study the structural and magnetic properties of ternary compounds $Ge_mMn_nTe_p$ based on rocksalt semiconductor GeTe. All structures and their internal atomic positions are fully optimized. For 25% and 50% Mn doping ($m + n = p$), we obtain two AF semiconductors: Ge_3MnTe_4 and $GeMnTe_2$. Introducing appropriate Ge vacancies, we obtain two FM metals with $m + n + 1 = p$: $Ge_3Mn_4Te_8$ and $Ge_5Mn_2Te_8$. The former has half-metallicity and the latter a nearly half-metallicity [12–14]. We investigate their electronic

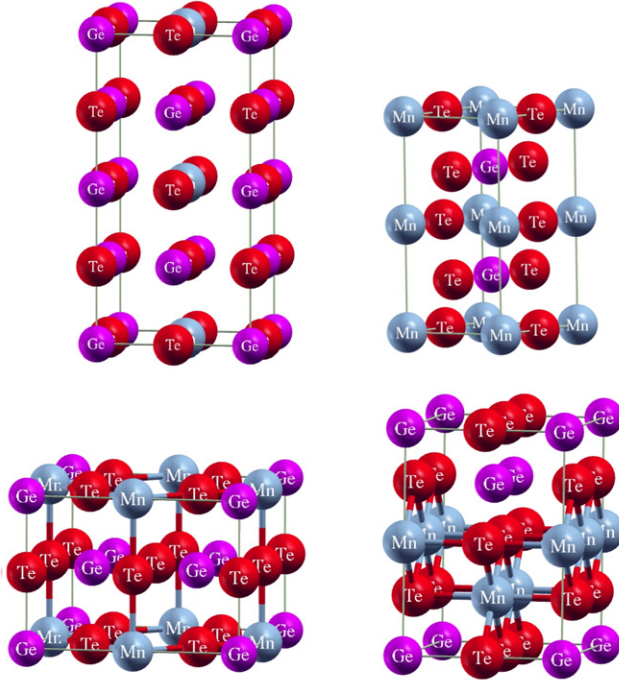**Figure 1.** The crystal structures of the AF Ge$_3$MnTe$_4$ (upper left) and GeMnTe$_2$ (upper right) and the most stable structures of Ge$_5$Mn$_2$Te$_8$ (lower left) and Ge$_3$Mn$_4$Te$_8$ (lower right).

Figure 2. Spin-dependent density of states (DOS) of the AF Ge$_3$MnTe$_4$ (upper panel) and GeMnTe$_2$ (lower panel). The thick solid lines show the total DOSs, the thin solid lines the Mn partial DOSs, the dashed lines the Ge partial DOSs, the dot lines the Te partial DOSs.

and magnetic structures to understand their magnetism. Our results show that high spin polarization can be obtained in high quality samples of these ternary compounds. These highly spin-polarized ferromagnets, although having rock-salt-based structures, could be useful in spintronics applications because they may have higher Curie temperatures than the (Ga, Mn)As diluted magnetic semiconductors.

The remaining part of this paper is organized as follows. We shall present the computational details in the next section. In section 3 we shall present our structure optimization and Ge vacancy induced ferromagnetism. In section 4 we shall present our calculated electronic structures for the two ferromagnets with high spin polarization. In section 5 we shall give our conclusion.

2. Computational details

For all our calculations we use a full-potential linearized augmented plane wave plus local orbitals method within the density-functional theory [15], as implemented in WIEN2k [16]. This full-potential method is necessary for achieving high enough calculation accuracy for our total energy comparison over different structures and magnetic orders. We take the generalized gradient approximation (GGA) [17] for the exchange–correlation potential for all presented results. This GGA is better than the local density approximation (LDA) for our magnetic systems. Full relativistic calculations are done for core states, and the scalar relativistic approximation is used for valence states. Depending on different structures, 500–3000 k-points are used in the first Brillouin zones. We set the radius of the muffin-tin
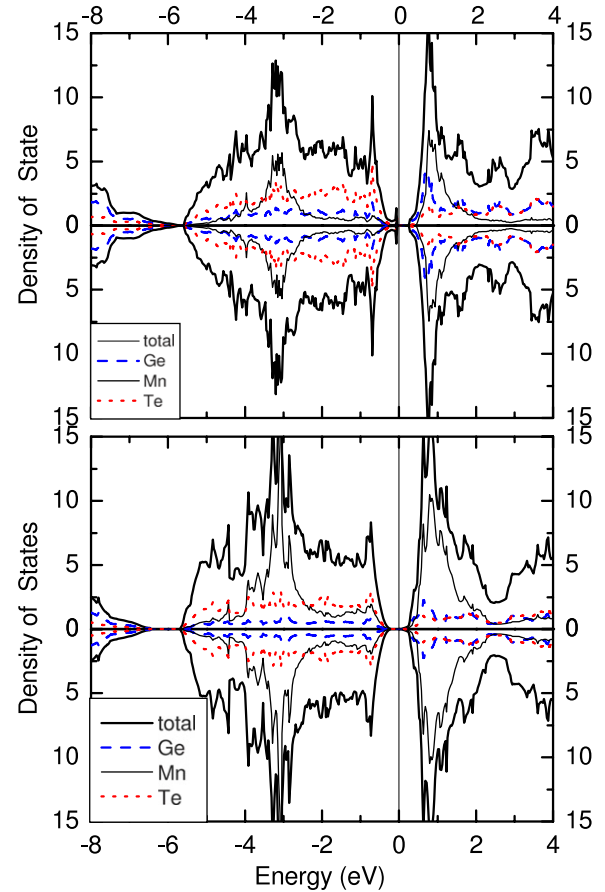
sphere (R_{mt}) to 2.5 Bohr for all atoms, let $R_{mt} * K_{max}$ equal to 9.0, and make the angular expansion up to $l_{max} = 12$ in the muffin tins. Self-consistent calculations are considered to be converged when the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}| d\mathbf{r}$, is less than 0.0001, where $\rho_{n-1}(\mathbf{r})$ and $\rho_n(\mathbf{r})$ are the input and output charge density, and the force acting on each atom is smaller than 1 mRyd/Bohr.

3. Structure optimization and Ge vacancy induced ferromagnetism

The rocksalt GeTe, having lattice constant 6.01 Å, consists of two fcc sublattices, one occupied by Te, the other by Ge [18]. We obtain 25% and 50% Mn-substituted compounds, Ge$_3$MnTe$_4$ and GeMnTe$_2$, by substituting one or two Mn atoms for Ge in the Ge sublattice. For both Ge$_3$MnTe$_4$ and GeMnTe$_2$, there is only one FM structure each. We optimize their cell volumes, geometry, and internal atomic positions, obtaining the most stable structures with space groups 221 and 123. Then we construct various AF structures from the FM structures and optimize them in the same way. Our total energy calculation indicates that both 25% and 50% Mn-substituted compounds are antiferromagnets with space groups 123 and 47 because
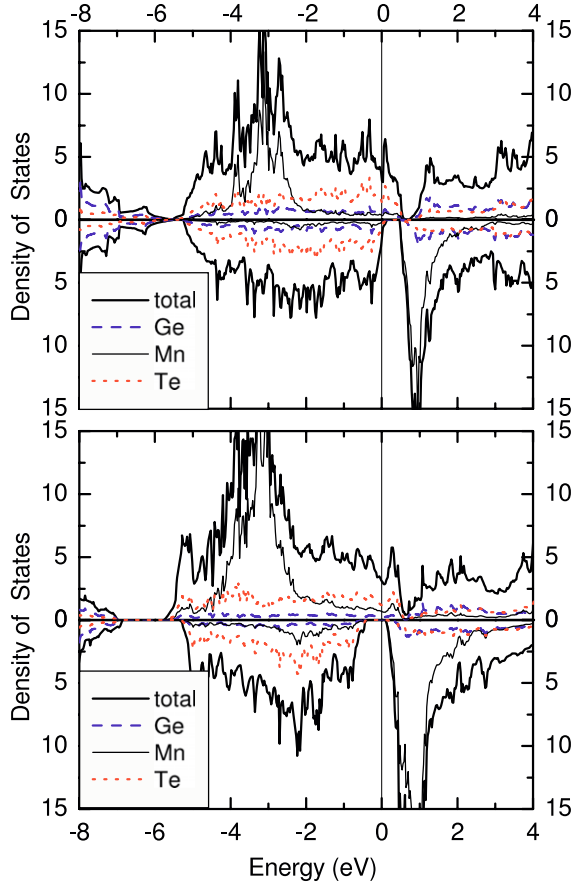
Figure 3. Spin-dependent density of states (DOS) of $Ge_5Mn_2Te_8$ (upper panel) and $Ge_3Mn_4Te_8$ (lower panel). The thick solid lines show the total DOS, the thin solid lines the Mn partial DOS, the dash lines the Ge partial DOS, the dot lines the Te partial DOS.
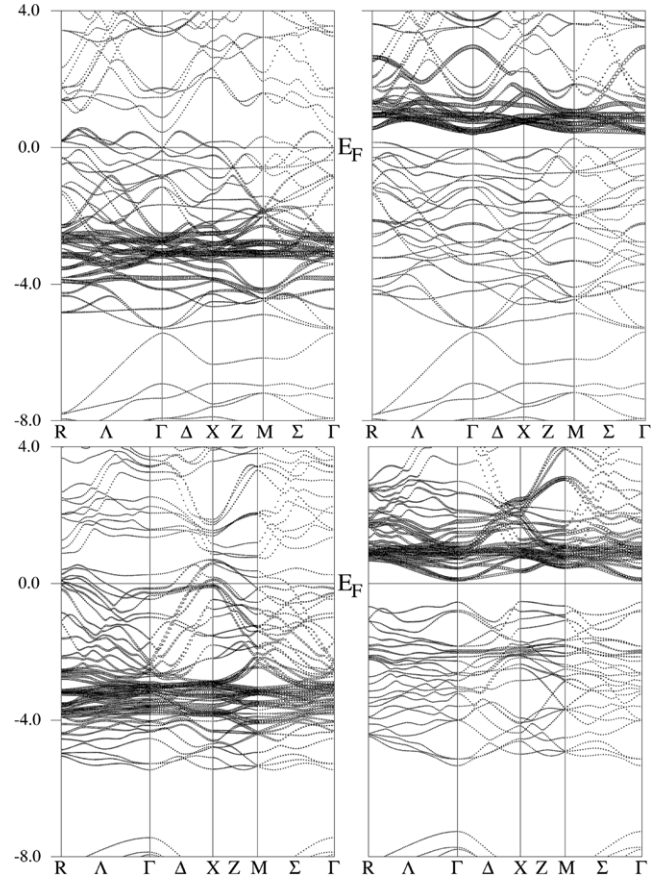

Figure 4. Spin-dependent band structures of $Ge_5Mn_2Te_8$ (upper panels) and $Ge_3Mn_4Te_8$ (lower panels). A band is plotted with circles of changing radii. The larger the circles, the more the Mn d character. The left panels show the bands of the majority-spin channel and the right panels those of the minority-spin channel.

Table 1. Magnetic orders (MO), equilibrium lattice constants (ELC, a/c or $a/b/c$), magnetic energies (ΔE), total magnetic moments (m), and bulk moduli (B) of the Ge_3MnTe_4, $GeMnTe_2$, $Ge_5Mn_2Te_8$, and $Ge_3Mn_4Te_8$.

Name	MO	ELC (Å)	ΔE (meV)	m (μ_B)	B (GPa)
Ge_3MnTe_4	AF	5.96/11.92	43	0	50.1
$GeMnTe_2$	AF	4.18/5.91/8.36	100	0	51.1
$Ge_5Mn_2Te_8$	FM	8.31/5.88	139	8.14	46.1
$Ge_3Mn_4Te_8$	FM	5.85/8.28/8.28	35	18.00	47.6

they are lower in total energy than the corresponding FM structures. Their volumes are smaller than that of GeTe by 3% and 5%. In the upper part of figure 1, we give the AF structures of the Ge_3MnTe_4 and $GeMnTe_2$. We define a magnetic energy by $\Delta E = E_{FM} - E_{AF}$. ΔE reflects the stability of the AF orders. Their equilibrium lattice constants, magnetic energies, magnetic moments, and bulk moduli are summarized in table 1. In addition, we have performed LDA calculations for these structures for confirmation. The LDA results are in agreements with the presented GGA ones. The nonmetallicity of the Mn-substituted compounds, which can be seen from the density of states in figure 2, is very different from the metallicity of V-and Cr-substituted GeTe compounds [19].

To simulate Ge vacancies we construct supercells of eight Ge and eight Te atoms in terms of the above two structures and remove one Ge atom from each of the supercells. All possible positions of Mn atom and Ge vacancies are considered. We obtain two formulae $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ including 12.5% Ge vacancies. There are three and six FM structures for them, respectively. Optimizing fully all these structures and the internal atomic positions, we obtain two lowest structures for $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$, respectively. Then we construct possible AF structures in terms of the lowest FM structures and optimize fully all the AF structures. The stable FM structures of the $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ have space groups $P4/mmm$ (123) and $Pmm2$ (25), respectively, and are shown in the lower part of figure 1. Their volumes are smaller than that of Ge_7Te_8 (space group 123 and lattice constants 8.40/5.94 Å) by 3% and 4%. In these cases the magnetic energy ΔE is defined as $E_{AF} - E_{FM}$, where E_{AF} and E_{FM} are the lowest energies among the AF and FM structures, respectively. Both $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ are ferromagnets although Ge_3MnTe_4 and $GeMnTe_2$ are antiferromagnets. The main results are summarized in table 1. For $Ge_5Mn_2Te_8$, the FM structure is lower by 139 meV per formula than the lowest AF one. For the $Ge_3Mn_4Te_8$, the total energy difference is 35 meV. This value is small but still reliable because we have used the

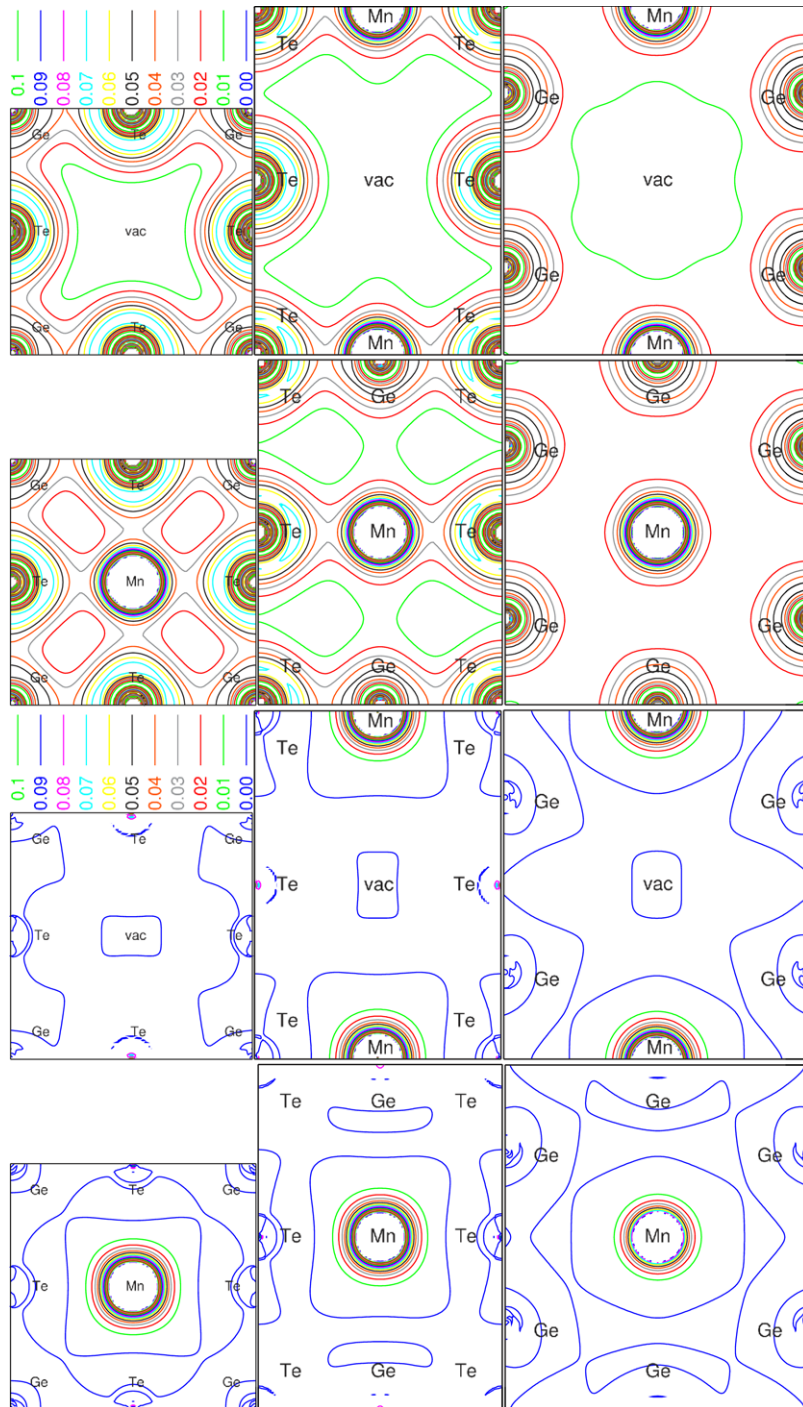**Figure 5.** The charge (first two rows) and spin (other two rows) density distributions of the $Ge_5Mn_2Te_8$ in the (100), (110), and (111) planes of the original Ge_3MnTe_4, as presented in the left, middle, and right panels. The Ge, Mn, and Te atoms are labeled and 'vac' indicates a Ge vacancy with respect to the Ge_3MnTe_4 structure.

full-potential density-functional method and set the calculation parameters to appropriate values. Therefore, the FM orders are stable against AF orders for both $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$.

4. Electronic structures and high spin polarization

The density of states of the FM $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ are presented in figure 3. It is clearly seen that the former

is a ferromagnet with nearly half-metallicity and the latter is a typical half-metallic ferromagnet [12]. Also we present the spin-dependent band structures of the $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ in figure 4. The character of the Mn d states is reflected by the radii of the circles used to plot the bands. For the $Ge_5Mn_2Te_8$, the majority-spin d states are mainly between -3.2 and -2.5 eV, and the minority-spin d states are above 0.5 eV. For the $Ge_3Mn_4Te_8$, the majority-spin d states are mainly between -3.8 and -2.8 eV, and the minority-

spin d states are above 0.15 eV. For the original compounds Ge_3MnTe_4 and $GeMnTe_2$, the Fermi energies are located in their semiconducting gaps and there are no carriers, which can be seen from figure 2. With Ge vacancies introduced in $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$, we have fewer valence electrons and the semiconducting gaps of the corresponding Ge_3MnTe_4 and $GeMnTe_2$ are partly filled. The vacancy-related carriers favor FM orders against AF ones. As a result, the $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$ become ferromagnets. They have total magnetic moments of 4.07 μ_B and 4.5 μ_B per Mn atom. The latter even has half-metallicity with a half-metallic gap of about 0.1 eV [14], being similar to half-metallic Cr- and V-substituted GeTe materials [19].

In order to explore the origin of the ferromagnetism and the half-metallicity of the FM $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$, we study their charge and spin density distributions. We present in figure 5 those of FM $Ge_5Mn_2Te_8$ in the (100), (110), and (111) planes of the original Ge_3MnTe_4. The neighborhoods of the Mn atom and Ge vacancy are included. The distributions of the $Ge_3Mn_4Te_8$ are similar, and therefore are not presented. It can be seen in the upper half of figure 5 that a vacancy, upon being formed, keeps adjacent Te atoms slightly away and absorbs adjacent Ge atoms slightly and, as a result, has a small positive effective charge. Here the electronic density distributions at and around a vacancy are self-consistently determined. That is to say, they are already most stable in terms of total energy. The lower half of figure 5 shows that the spin density is contributed mainly by Mn atoms and the Ge vacancies induce some spin density at the adjacent Te sites.

In the GeTe the Te ion assumes Te^{2-} and the Ge one Ge^{2+} and there is a semiconductor gap. The Mn doping replaces Ge^{2+} by Mn^{2+} in the Ge_3MnTe_4 and $GeMnTe_2$, but the bonding remains almost the same as that of GeTe. The spin exchange splitting makes all the Mn^{2+} d orbits half-filled, with the empty d states being high enough, so that the semiconductor gap remains open. Therefore, the Mn spins are in AF orders through a Te-mediated superexchange interaction. The Ge vacancy affects directly the nearest Te atoms. Adding one Ge vacancy means removing four valence electrons and deforming the energy band structure. Hence the Fermi level will move downward and the semiconductor gap is partly filled. As a result, carriers are yielded in the $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$, and they further induce FM RKKY interactions among the Mn spins. This RKKY spin interaction favors FM order against AF order. Therefore the two FM metals are formed out of the two AF semiconductors. The metallicity of the two compounds agrees with experiments [2, 4] and the theoretical result for dilute Mn and vacancy doping [20]. The half-metallicity of the $Ge_3Mn_4Te_8$ is attributed to the fact that the Fermi level is rightly in the minority-spin gap at the Fermi level thanks to the favorable majority-spin DOS below the Fermi level.

5. Conclusion

In summary, we use a full-potential density-functional method to study ternary Ge–Mn–Te compounds based on IV–VI rocksalt semiconducting GeTe. By substituting 25% and 50%

Mn for Ge atoms in GeTe, we get two AF semiconductors. Introducing Ge vacancies into the two AF semiconductors, we get two FM metals: $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$. The ferromagnetism is attributed to a carrier-induced RKKY interaction among Mn spins. Half-metallicity is achieved in the latter and is nearly achieved in the former, thanks to the favorable DOS below the Fermi levels.

Our results indicate that high spin polarization can be obtained in high quality samples of $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$. Because a higher Curie temperature than that for (Ga, Mn)As diluted magnetic semiconductors has been achieved in GeTe-based FM semiconductors, we believe that higher Curie temperatures can be obtained through controlling Ge vacancy and Mn dopant concentrations in some materials similar to $Ge_5Mn_2Te_8$ and $Ge_3Mn_4Te_8$. Therefore, these materials may be useful in future spintronics.

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