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First-principles study of structural, electronic, and magnetic properties of Mn_4XGe_3 (X = Fe,Co,Ni)*

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In order to search for promising candidates for spintronic applications, this paper systematically studies three ternary compounds based on Mn_5Ge_3 by using a full-potential linearized augmented plane wave method within the density functional theory. Through structure optimization and electronic structure calculations, it finds that Mn_4FeGe_3 and Mn_4CoGe_3 have much higher spin-polarization than original intermetallic compound Mn_5Ge_3, although the spin polarization of Mn_4NiGe_3 is lower than that of Mn_5Ge_3. The calculated result is in agreement with experiment in the case of Mn_4FeGe_3. Both of them can be taken as promising candidates for spintronics applications because of their high spin-polarization and compatibility with semiconductors.

Keywords: spin-polarization, spin-injection, diluted magnetic semiconductors
PACC: 6185, 7115A, 7120C, 0155

1. Introduction

High spin-polarized diluted magnetic semiconductors (DMSs)[1−3] and half-metals,[4] especially those compatible with semiconductors,[5−7] are believed to be promising candidates for the spintronic applications. Mn-doped Ge materials Mn_xGe_{1-x} (x <10%) have been reported to be excellent DMSs for information storage, but they have low Curie temperature ranging from 25 to 116 K.[8] It has been reported that intermetallic compound Mn_5Ge_3 has high spin-polarization, high Curie temperature, and compatibility with semiconductors such as Ge.[9−12] As a result, it could be used as efficient spin-injection materials along their c axis.[12,13] Recently, it was reported that after Fe is substituted for one Mn atom, the new compound Mn_4FeGe_3 has a much higher spin-polarization (about 60%) than that of Mn_5Ge_3 (about 42%). Also the new compound has higher Curie temperature (319.5 K) than that of Mn_5Ge_3 (296 K), and a crystal structure and lattice parameters similar to those of Mn_5Ge_3.[14,15] So far, there has been no theoretical study on the problem why the spin-polarization is enhanced in the Fe substituted compound Mn_4FeGe_3.

This paper systematically studies structural, electronic, and magnetic properties of three ternary compounds Mn_4XGe_3 (X = Fe, Co and Ni) by using a full-potential linearized augmented plane wave method within the density functional theory. Our calculated results indicate that the Fe-doped compound Mn_4FeGe_3 and Co-doped compound Mn_4CoGe_3 show much higher spin-polarization than original intermetallic compound Mn_5Ge_3, although the spin-polarization of Ni-doped Mn_4NiGe_3 is lower than that of Mn_5Ge_3. The calculated results in the case of Mn_4FeGe_3 are consistent with the latest experimental results. Mn_4FeGe_3 and Mn_4CoGe_3 can be taken as promising candidates for spintronic applications because of their high spin-polarization and compatibility with semiconductors.

The remaining part of this paper is organized as follows. In next section we present the computational details. The structure optimization are presented in the third section. The electronic structure and magnetic properties are discussed in the fourth section. At last we give our conclusion in the fifth section.

2. Computational details

We use the Vienna package WIEN2k[16] for all our calculations. This is a full-potential linearized augmented plane wave plus local orbitals method within

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the density functional theory.[17] For the exchange-correlation potential we take the generalized gradient approximation.[18] We do the full relativistic calculations for the core states and use the scalar relativistic approximation for the valance states. For all our calculations, we use 1000 k-points in the first Brillouin zone. The radii $R_{\rm mt}$ of transition metal muffin tins are set to 2.2 a.u, and the radius of Ge muffin tin to 2.0 a.u. We set $R_{\rm mt}K_{\rm max}$ to 9.0 and make the harmonic expansion up to $l_{\rm max} = 12$ in the muffin tins. The self-consistent calculations are considered to be converged when the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}| {\rm d}\boldsymbol{r}$, between the input density ρ_{n-1} and the output density ρ_n is less than 0.0001.

3. Structure optimization

The starting intermetallic compound Mn_5Ge_3 has a hexagonal crystal structure of $D8_8$ type (space group $P6_3/{\rm mcm}$, No. 193).[10] After replacing one Mn atom with X (X = Fe, Co, Ni), several new crystals are obtained. For the Fe-doped compound Mn_4FeGe_3 the neutron-diffraction results[19] indicated that Fe atom occupies only the 4d site and the space group of the resulting compound Mn_4FeGe_3 is $P6332$ (No. 182). Also we assume that the Co and Ni atoms occupy the same 4d positions as Fe atoms. In addition, we substitute the Mn atom in the 6g site with Fe atom and obtain a structure with space group $Cmcm$ (No. 63), but we find that this 6g-site substituted compound, after optimization, is about 0.47 eV higher in total energy than the optimized 4d-site substituted compound.

At the same time of optimizing the volume of the unit cell, we also optimize the internal parameters to make sure that the force acted on the atoms is smaller than 0.5 mRy/a.u. The resulting structural parameters are listed in Table 1. We can see that the lattice constants and internal parameters of the Mn_4XGe_3 (X = Fe, Co, Ni) differ a little from those of the starting intermetallic compound Mn_5Ge_3. All our following electronic structure calculations are done with the optimized structures.

Table 1. Equilibrium lattice constants and optimized internal parameters ($x_{\rm Mn2}$ for independent parameter of Mn at 6g sites and $x_{\rm Ge}$ for that of Ge) of the four compounds. For comparison we give experimental results in the brackets.[10,14]

compound	a/c/nm	$x_{\rm Mn2}$	$x_{\rm Ge}$
Mn_5Ge_3	0.7143/0.4958	0.2436	0.6057
	(0.7184/0.5053)	(0.2397)	(0.6030)
Mn_4FeGe_3	0.7154/0.4880	0.2397	0.6047
	(0.7169/0.4991)		
Mn_4CoGe_3	0.7127/0.4890	0.2397	0.6043
Mn_4NiGe_3	0.7066/0.5008	0.2396	0.6016

4. Electronic structure and spin polarization

The projected density of states (DOSs) of the magnetic atoms and the total DOSs of the unit cell are shown in Fig.1. It can be seen that all these

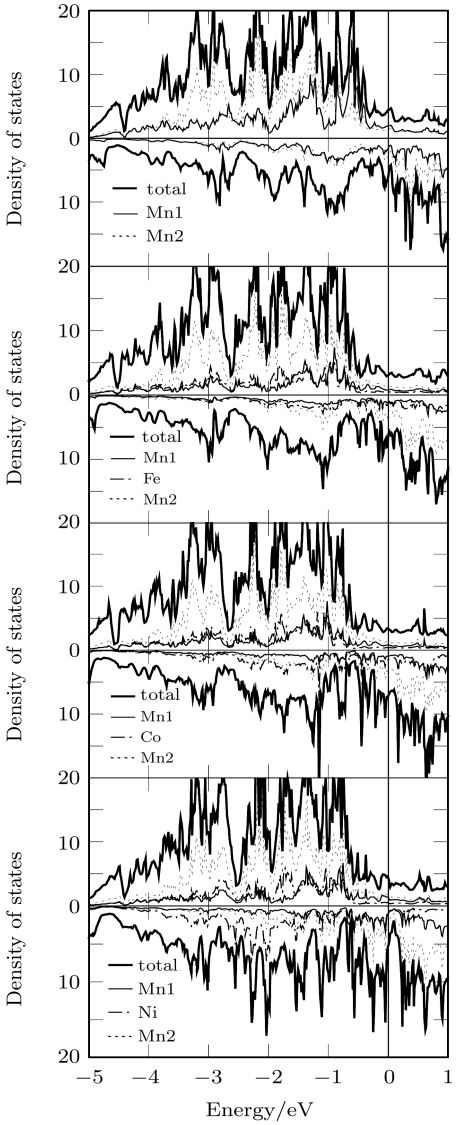


Fig.1. Spin-dependent density of states of Mn_5Ge_3, Mn_4FeGe_3, Mn_4CoGe_3 and Mn_4NiGe_3 (from top to bottom). The thick solid lines show the total DOSs, the thin solid lines the Mn1 partial DOSs, the dotted lines the Mn2 partial DOSs, and the dash-dotted lines the X (X = Fe, Co, Ni) partial DOSs.

compounds are metallic for both minority and majority spin channels. The DOSs of the four compounds at the Fermi level, $N_{\uparrow}(E_{\mathrm{F}})$ for majority spin channel and $N_{\downarrow}(E_{\mathrm{F}})$ for minority spin channel, are listed in Table 2. It should be pointed out that because our calculations are based on the optimized structural parameters, the calculated DOSs for Mn_5Ge_3 are different from those which were calculated with the experimental structural parameters.[12] From Fig.1 we can see that the 3d levels of the transition-metal elements dominate the region close to the Fermi level.

In Fig.2, we show the band structures of these compounds, where the thick lines show the 3d character of the X (X = Fe, Co, Ni) atoms. For comparison we give the band structure of Mn_5Ge_3 at the top. The left four panels of Fig.2 show the band structures of the majority spin channel and the right four panels show those of the minority spin channel. We can see from Fig.2 that the spin exchange splitting of the 3d-dominated bands of Mn1, Fe, Co, Ni decreases approximately from 3.0 eV to 2.5 eV, 1.5 eV and 0.5 eV for the Fe, Co, and Ni substitutions. It can be seen that the majority-spin DOS at the Fermi level of Mn_4FeGe_3 is smaller than that of Mn_5Ge_3, as shown in Table 2. The Mn_4CoGe_3 is similar to the Mn_4FeGe_3. For the Mn_4NiGe_3, $N_{\uparrow}(E_{\mathrm{F}}) = 4.3$ states/eV per formula unit is significantly larger than 3.04 and 3.37 states/eV per formula unit of the Mn_4FeGe_3 and Mn_4CoGe_3 because of the smaller spin exchange splitting of the Ni 3d-dominated bands.

With the increase of d-electron number, the DOSs for the minority-spin, $N_{\downarrow}(E_{\mathrm{F}})$ increase slightly from Mn_5Ge_3 to Mn_4FeGe_3 to Mn_4CoGe_3, which can be seen from Table 2. For the Ni-doped compound, the 3d-dominated bands move further downward and there appears a valley in the minority-spin DOS at the Fermi level. These result in a significantly small $N_{\downarrow}(E_{\mathrm{F}})$. The spin polarizations listed in Table 2 are defined as

$$P = [N_{\uparrow}(E_{\mathrm{F}}) - N_{\downarrow}(E_{\mathrm{F}})]/[N_{\uparrow}(E_{\mathrm{F}}) + N_{\downarrow}(E_{\mathrm{F}})]. \quad (1)$$

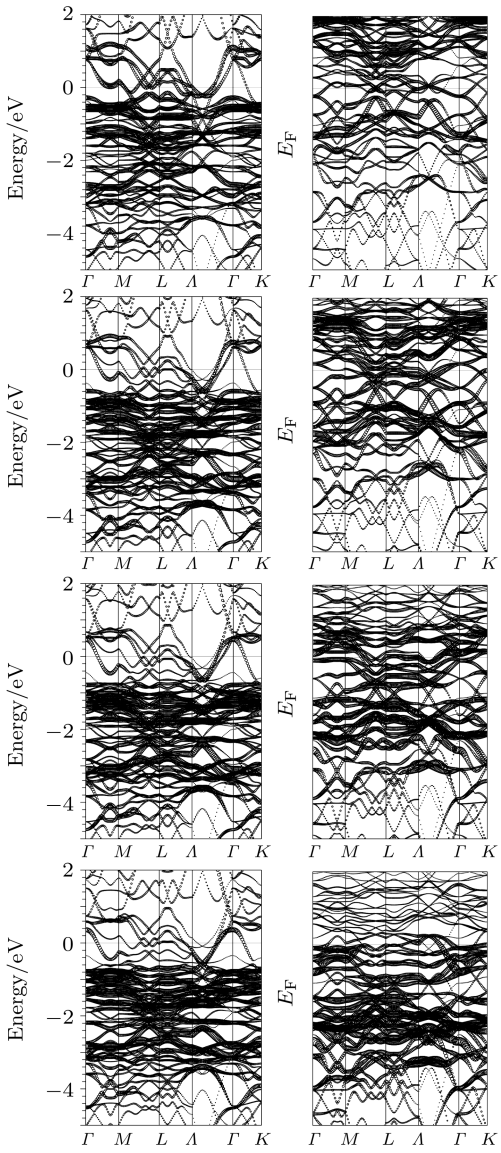


Fig.2. Spin-dependent band structure of Mn_5Ge_3, Mn_4FeGe_3, Mn_4CoGe_3 and Mn_4NiGe_3 (from top to bottom). The left panels show the majority spin bands and the right panels the minority spin ones.

Table 2. Magnetic moments within the muffin tin spheres of Mn1, Mn2, X (X = Mn1, Fe, Co, Ni), and Ge atoms and the total magnetic moment (m in μ_{B}), majority-spin and minority-spin DOSs ($N_{\uparrow}(E_{\mathrm{F}})$ and $N_{\downarrow}(E_{\mathrm{F}})$) at the Fermi level, and the spin polarization (P) of the four compounds.

compound	$(m_{\mathrm{Mn1}}\ /m_{\mathrm{Mn2}}\ /m_X\ /m_{\mathrm{Ge}}\ /m_{\mathrm{total}})/\mu_{\mathrm{B}}$	$N_{\uparrow}(E_{\mathrm{F}})$	$N_{\downarrow}(E_{\mathrm{F}})$	P/%
Mn_5Ge_3	2.18/3.06/2.18/–0.10/26.6	4.38	6.48	–19.4
Mn_4FeGe_3	2.14/3.05/1.87/–0.10/25.7	3.04	6.63	–37.5
Mn_4CoGe_3	2.20/3.03/0.97/–0.09/24.1	3.37	7.13	–35.8
Mn_4NiGe_3	1.89/3.00/0.04/–0.09/21.4	4.30	5.20	–9.50

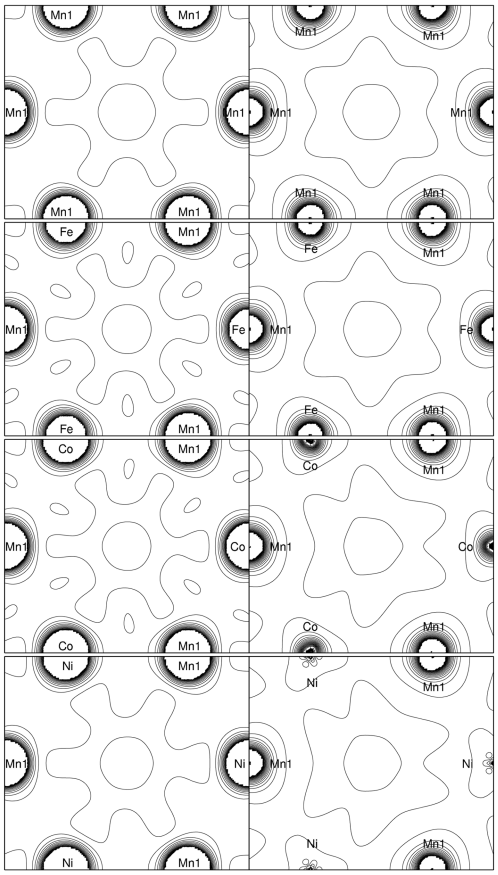


Fig.3. Charge density (left panels) and spin density (right panels) distributions in a plane perpendicular to the [0001] direction and containing X (X = Mn1, Fe, Co, Ni) atoms of the Mn_5Ge_3, Mn_4FeGe_3, Mn_4CoGe_3 and Mn_4NiGe_3 (from top to bottom).

In Fig.3, we present the charge density and spin density distributions of these compounds in a plane perpendicular to the [0001] direction and containing X (X = Mn1, Fe, Co, Ni) atoms. Also at the top of Fig.3, we give those of Mn_5Ge_3 for comparison. The left four panels show the charge density distributions and the right four panels show the spin density distributions. We can see that the spin density decreases from Mn1 to Fe, Co, and Ni. Especially for Mn_4NiGe_3, there is only little spin on the Ni sites. This is consistent with magnetic moments listed in Table 2.

5. Discussion and conclusion

We have studied three ternary compounds based on the intermetallic Mn_5Ge_3 through the first-principles calculations. We have investigated their electronic and magnetic properties in terms of their optimized structures. Their spin exchange splitting decreases from Mn_4FeGe_3 to Mn_4CoGe_3 and Mn_4NiGe_3 because of the increasing number of their d electrons. The spin-polarizations of Mn_4FeGe_3 and Mn_4CoGe_3 are much higher than that of the original compound Mn_5Ge_3. The substantial enhancement of the spin polarization of Mn_4FeGe_3 is in agreement with experimental result. Therefore, Mn_4FeGe_3 and Mn_4CoGe_3 could be used in spintronics applications because of their high spin-polarization and compatibility with semiconductors.

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