Magnetic properties of several potential rocksalt half-metallic ferromagnets based on the first-principles calculations*

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Several rocksalt Sr_4X_3N (X = O, S, Se, and Te) are predicted to be potential half-metallic ferromagnets free of transition-metal and rare-earth elements by performing the first-principles calculations. Then their magnetic properties, such as the half metallicity and the crystal-cell magnetic moments are investigated. The Sr_4X_3N possibly have higher Curie temperatures and have more stable half metallicity than the Sr_4X_3C. Their crystal-cell magnetic moments are all 1.00 μ_B. The crystal-cell magnetic moments and the half metallicity arise mainly from the N ions. The main mechanism is the strong covalent interaction leading to the sp^2 hybridized orbitals in the Sr_4X_3N. Then two Sr-5s and three N-2p electrons enter into three sp^2 hybridized orbitals. Among these five electrons, four electrons are paired and one is unpaired, so there are three spin-up electrons and two spin-down electrons in these sp^2 hybridized orbitals.

Keywords: half-metallic ferromagnets, first-principles calculations, crystal-cell magnetic moments

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1. Introduction

Half-metallic ferromagnets (HMFs) have attracted more and more research interest due to their important potential application in spintronics.[1−4] One of their two spin channels is metallic and the other is semiconducting or insulating, leading to their complete spin polarization at the Fermi level. HMFs are potentially more important magneto-resistance materials compared with traditional magnetic materials, since their spin polarization at the Fermi level is much larger than that of traditional magnetic materials.[5−7] In addition, they are considered as the most suitable magnetic electrode materials for spin semiconductors,[3,8] since their spin polarization at the Fermi level is high enough and their resistivity is close to that of semiconductors. Much attention has been paid to potential HMFs containing transition-metal or rare-earth ions, such as CrAs, CrSb and doped ZnTe, $LiPr_2O_4$, Fe_3O_4.[8−13] However, little attention was paid to potential HMFs free of transition-metal or rare-earth elements. In fact, materials free of transition-metal or rare-earth elements have many advantages compared with transition-metal and rare-earth materials. For instance, they can be prepared more easily experimentally, and the theoretical research on them is easier, since they are d and f electrons free. In this paper, the rocksalt N-doped Sr_4X_4 (X = O, S, Se, and Te) were predicted to be half-metallic. Their magnetic properties, such as the crystal-cell magnetic moments, were investigated based on the density functional theory. Furthermore, the corresponding micro-mechanism of the half metallicity and the origin of the crystal-cell magnetic moments of the N-doped Sr_4X_3N were probed.

2. Model and calculation method

Rocksalt SrX (X = O, S, Se, and Te) are typical semiconductors with crystal constants $a = b = c$. The crystal constants are determined experimentally to be 5.15 Å,[14] 6.02 Å,[15] 6.25 Å,[16] and 6.66 Å,[17] respectively. Their space group is $FM\bar{3}$-M. The geometrical structures of Sr_4X_4 crystal cells containing four Sr ions and four X ions were optimized and compared with experimental values to confirm our calculations. The

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optimized lattice constants are 5.22 Å, 6.14 Å, 6.41 Å, and 6.87 Å, respectively. The relative differences between the experimental and the optimized values are only 1.17%, 1.83%, 2.56%, and 3.15%, respectively, which shows that our optimized crystal constants are basically in accord with the experiments. The calculated band gaps of Sr_4S_4 and Sr_4Se_4 are 2.62 eV and 2.45 eV, respectively. The values are evidently larger than the corresponding band gaps of Sr_4S_4 and Sr_4Se_4 (2.54 eV and 2.27 eV) calculated based on Generalized gradient approximations (GGA) by Labidi *et al.*[18] Generally, the calculated band gaps based on GGA are much lower than experimental ones due to the underestimated correlation effect of the excitation electrons.[19] Our calculated band gaps are closer to the experimental values of 4.32 eV and 3.81 eV compared with those given by Labidi *et al.*

Then the X ion on the center of the Sr_4X_4 crystal cells was substituted by one N ion, so the N-dopant concentration is 25.0 at.%. The N-doped crystal cell is shown in Fig. 1. The chemical formula for the N-doped compound could be written as Sr_4X_3N. The optimization of geometrical structures and the calculations of magnetic properties were performed using the calculation module castep based on the density functional theory. The wave functions were expanded with the plane-wave pseudo-potentials, and the exchange correlation functions were the Perdew–Burke–Ernzerhof functional of three nonlocal gradient corrected exchange–correlation functionals. The calculation quality 'fine' was selected, corresponding to the cutoff energy of 340 eV and the k-point set of 5×5×5. The electronic structures of the corresponding isolated atoms were $4s^2 4p^6 5s^2$ for Sr, $2s^2 2p^3$ for N and $ns^2 np^4$ (n = 2, 3, 4, and 5, respectively) for X.

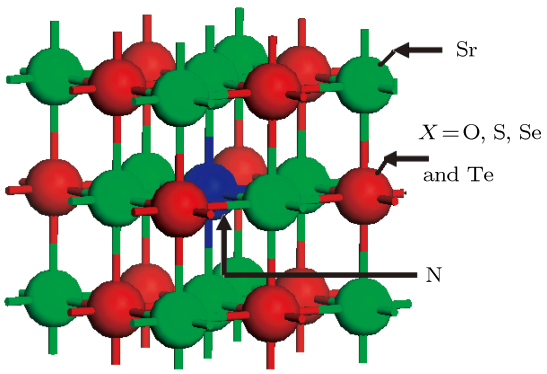


Fig. 1. (colour online) The crystal cell of Sr_4X_3N (X = O, S, Se, and Te).

Some geometrical and magnetic parameters of Sr_4X_3N (X = O, S, Se, and Te) were also calculated and are given in Table 1. From Table 1, the lattice constants of Sr_4O_3N are close to those of Sr_4O_4. While the lattice constants of other three N-doped materials are evidently lower than those of the corresponding undoped materials. The main reason is that N and O elements lie on the same period of the periodic table, so their radii are close to each other. The radii of N atoms are evidently lower than those of other X atoms (X = S, Se, and Te). Therefore, these N-doped crystal cells evidently shrink in size compared with the undoped crystal cells.

3. Results and discussion

The N-doping formation energy $E_f(N \to X)$ of Sr_4X_3N is calculated with the following formula:[12]

$$E_f(N \to X) = E_{tot}(Sr_4NX_3) + E(X) - E(N) - E_{tot}(Sr_4X_4), \quad (1)$$

where $E_{tot}(Sr_4NX_3)$ and $E_{tot}(Sr_4X_4)$ are the total energies of optimized Sr_4NX_3 and optimized Sr_4X_4 supercells, respectively. Based on our calculations, E_{tot} (Sr_4NX_3) are −4935.94 eV, −4461.67 eV, −4407.39 eV and −4292.65 eV for Sr_4NO_3, Sr_4NS_3, Sr_4NSe_3, and Sr_4NTe_3, respectively. And E_{tot} (Sr_4X_4) are −5104.64 eV, −4473.11 eV, −4400.95 eV, and −4249.42 eV for Sr_4O_4, Sr_4S_4, Sr_4Se_4, and Sr_4Te_4, respectively. The $E(N)$ and the $E(X)$ are the average energies of one N atom and one X atom obtained by the pseudo-potential method. Here, $E(N)$ = −265.93 eV and $E(X)$ are −430.83 eV, −274.02 eV, −256.42 eV, and −220.00 eV for one O, S, Se, and Te ion, respectively. Based on formula (1), $E_f(N \to X)$ are 3.80 eV, 3.35 eV, 3.00 eV, and 2.70 eV for Sr_4NO_3, Sr_4NS_3, Sr_4NSe_3, and Sr_4NTe_3, respectively. The above formation energies are all positive, showing that it is a little difficult to prepare these hypothesized materials. The formation energy decreases from Sr_4NO_3 to Sr_4NTe_3, showing that Sr_4NTe_3 is easier to prepare experimentally than Sr_4NO_3. Some N-doped strontium compounds, such as $B_3N_3O_3Sr_3$,[20] $CB_3NO_{13}Si_1Sr_7$[21] and $SrMoO_{2.49}N_{0.51}$[22] have been prepared experimentally, so we believe that it is possible to prepare these hypothesized materials in future.

The total, partial and local spin-polarized densities of states and the band structures of Sr_4X_3N near the Fermi level are shown in Fig. 2. Those densities of states and band structures with energy much smaller than the Fermi level are not plotted, since they can not influence the magnetic and the electric properties of Sr_4X_3N. Based on the total densities of states and the band structures shown in Fig. 2, the spin-polarization of Sr_4X_3N at the Fermi level is evidently

100%, since there are only spin-down sub-bands at the Fermi level. Furthermore, as shown in Table 1, the crystal cell magnetic moments defined as the sum of all ionic magnetic moments of Sr_4X_3N are all integers, i.e., $M_t = 1.00\ \mu_B$. Having integer magnetic moments is one of the most important characters of HMFs. Therefore, the four materials are potential half-metallic ferromagnets. This means that N doping may have substantial influence on the magnetic properties of rocksalt SrX.

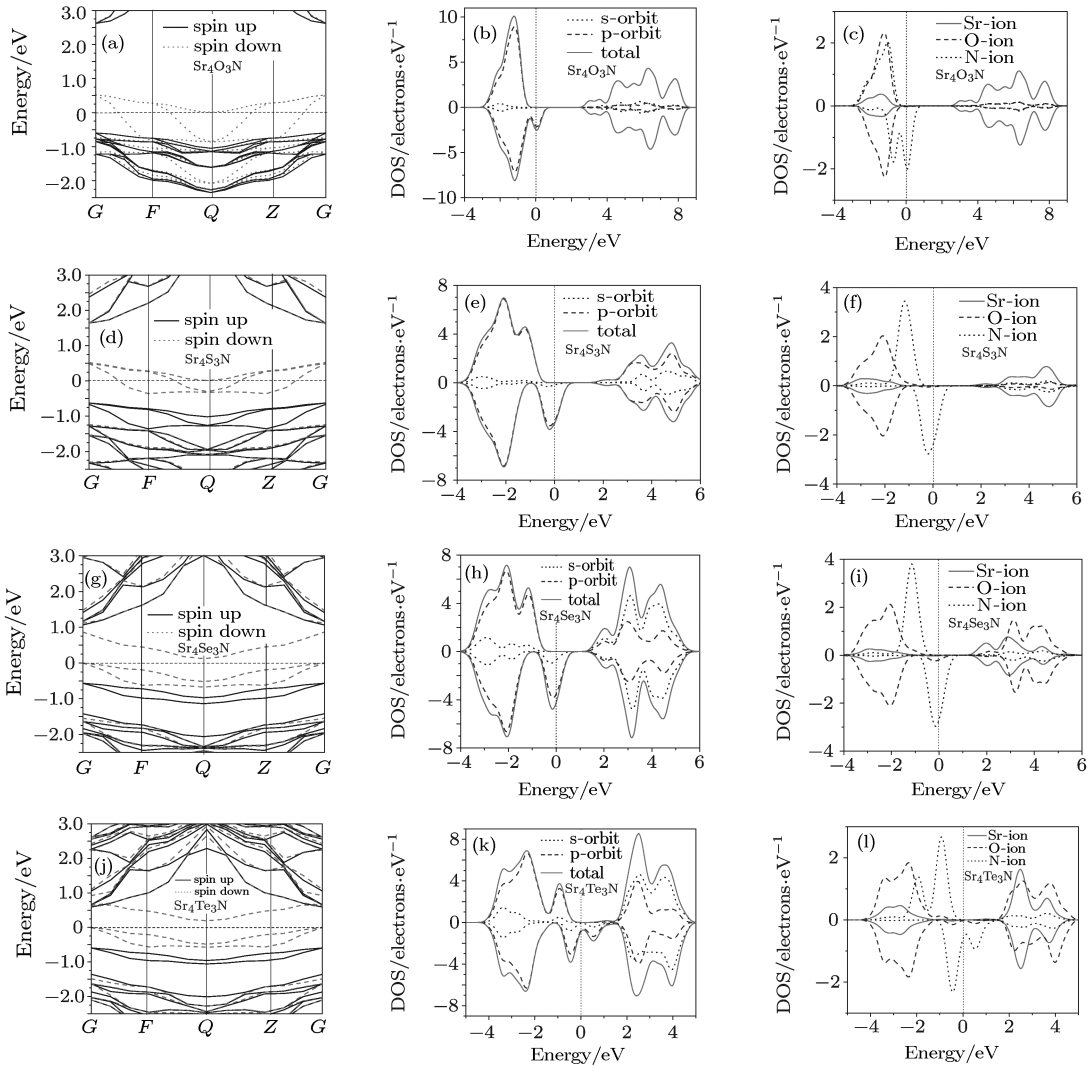


Fig. 2. Total, partial and local Spin-polarized densities of states and the band structures of Sr_4X_3N (X = O, S, Se, and Te). (a), (d), (g), and (j) show the band structures. The solid and the dashed curves are for spin-up and spin-down sub-bands, respectively. In other figures, the curves above and below the lines showing zero density of states are for spin-up and spin-down sub-bands, respectively. The solid, dotted and dashed curves in (b), (e), (h), and (k) show the total, s-partial and p-partial densities of states of Sr_4O_3N, Sr_4S_3N, Sr_4Se_3N, and Sr_4Te_3N, respectively. The solid, dotted and dashed curves in (c), (f), (i), and (l) show the local densities of states of one Sr ion , one N ion and one X ion (X = O, S, Se, and Te), corresponding to Sr_4O_3N, Sr_4S_3N, Sr_4Se_3N, and Sr_4Te_3N, respectively.

Table 1. Calculated ionic parameters of Sr_4X_3N (X = O, S, Se, and Te).

Spec.	a/Å	V/Å^3	E_0/eV	E_t/eV	E_h/eV	M_t/μ_B	M_N/μ_B	M_x/μ_B	M_{Sr}/μ_B
Sr_4O_3N	5.24	144.89	−4933.19	3.22	0.60	1.00	1.02	0.02	0.02
Sr_4S_3N	5.99	217.43	−4440.04	2.26	0.63	1.00	1.02	0.02	0.04
Sr_4Se_3N	6.23	241.46	−4392.52	1.63	0.57	1.00	1.04	0.02	0.04
Sr_4Te_3N	6.64	292.48	−4292.36	1.19	0.60	1.00	1.04	0.02	0.04

The parameters include the lattice constants (a), the volumes of crystal cells (V), the ground state energy (E_0), the total band gaps of spin-up sub-bands (E_t), the half-metallic gaps (E_h), the crystal-cell magnetic moments (M_t), the ionic magnetic moments of N ions (M_N), the maximum absolute values of ionic magnetic moments of X ions (M_X) and Sr ions (M_{Sr}).

As shown in Table 1 and Fig. 2, the total band gaps (E_ts) of spin-up sub-bands of Sr_4X_3N are 3.22 eV, 2.62 eV, 1.63 eV, and 1.19 eV, respectively. The half-metallic gaps (E_hs) of Sr_4X_3N, defined as the energy difference between the maximum energy of the semiconducting valence sub-bands and the Fermi energy of the metallic sub-bands in this paper, are 0.60 eV, 0.63 eV, 0.57 eV, and 0.60 eV, respectively. These calculated E_t and E_h by GGA are both much lower than experimental ones due to the underestimated correlation effect of the excitation electrons.[19] The experimental E_t and E_h of Sr_4X_3N may be larger than the calculated ones. The half metallicity of Sr_4X_3N may be stable, as the HMFs are usually stable if their half-metallic gaps are wide. Especially, the E_ts, 3.22 eV, and 2.26 eV of Sr_4O_3N and Sr_4S_3N are evidently larger than 2.32 eV and 1.02 eV of Sr_4O_3C and Sr_4S_3C,[23] respectively. The E_hs, 0.60 eV and 0.63 eV of Sr_4O_3N and Sr_4S_3N, are also lager than those of Sr_4O_3C and Sr_4S_3C.[23] Generally, larger half-metallic gaps mean higher Curie temperatures. Thus the N doping is more beneficial to increase the Curie temperature and to improve the half-metallic stability of rocksalt HMFs than the C doping.

As shown in Fig. 2, the spin-up and the spin-down local densities of states (LDOS) of Sr and X ions are almost symmetrical about the axial lines showing zero density of states, which indicates that there is little spin polarization in Sr and X ions. While the LDOS of N ion are evidently spin-polarized near the Fermi level. In fact, we also calculated the densities of states of un-doped rocksalt compounds and found no spin-polarization in Sr and X ions. This shows that N doping can have an important influence on the magnetic properties and on the half metallicity of Sr_4X_3N. The main reason is that the isolated N atoms have weaker electronegativity than the isolated X atoms (X = O, S, Se, and Te), since they have one less outer-shell electron than the X atoms. Therefore, the proportion of covalent bonds in Sr_4X_3N is higher than that in Sr_4X_4. The covalent interaction, i.e., the crystal field, causes the split of the energy bands of Sr_4X_3N. Furthermore, the spin polarization of N ions is much stronger than that of Sr and X ions. The half metallicity and the crystal cell magnetic moments of Sr_4X_3N mainly come from the N ions. The contributions of Sr and X ions are very weak. As shown in Table 1, the maximum absolute values of ionic magnetic moments of Sr and X ions are much smaller than those of N ions.

The total densities of states (TDOS) of Sr_4X_3N mainly come from five energy areas, i.e., the first area from −34.5 eV to −33.5 eV, the second area from −17.5 eV to −13.4 eV, the third area from −12.8 eV to −9.5 eV, the fourth area from −4.5 eV to 1.0 eV and the fifth area above 2.5 eV. The TDOS in the first area come from Sr-4s orbitals. These orbitals are localized inside Sr ions, because their energy is much lower than that of other orbitals. The TDOS in the second area mainly come from X-ns and Sr-4p orbitals. These orbitals do not hybridize with each other although their energy is close to each other, because they are shielded by their outer orbitals, i.e., X-np and Sr-5s orbitals. Therefore, they are also localized inside X and Sr ions, respectively. The TDOS in the third area come from N-2s orbitals, which are also localized inside N ions and do not hybridize with other orbitals. There is no spin polarization of the TDOS in these three energy areas, so they have no influence on the magnetic and the electric properties of Sr_4X_3N, and are not plotted in Fig. 2.

As shown in Fig. 2, the TDOS in the fourth area include both s and p orbitals coming mainly from N-2p, X-np and Sr-5s orbitals, which indicates that there are hybridized orbitals of N-2p and Sr-5s, or of X-np and Sr-5s. The N-2p orbitals are easily hybridized with the Sr-5s orbitals in the aid of the crystal field of the ligand compounds consisting of Sr and N ions, because they are both outer orbitals and their energy is close to each other. Similarly, the X-np orbitals are also easily hybridized with the Sr-5s orbitals. On the other hand, the energy of some N-2p or X-np orbitals is above the Fermi level, showing that they are not hybridized with the Sr-5s orbitals. This means that there are sp^2 hybridized orbitals of one Sr-5s and two N-2p or X-np orbitals. Generally, the energy of sp^2 hybridized orbitals is lower than that of Sr-5s, N-2p and X-np orbitals. For the N–Sr ligand compounds, there are five electrons including three N-2p and two Sr-5s electrons entering into the three sp^2 hybridized orbitals based the principle of lowest energy. This means that there are two electron-pairs and one unpaired electron, so there are three spin-up electrons and two spin-down electrons in these hybridized orbitals. For the X–Sr ligand compounds, there are six electrons including four X-2p electrons and two Sr-5s electrons entering into the three sp^2 hybridized, resulting in three electron-pairs, so there are three spin-up electrons and three spin-down electrons. From the above analysis, there is only one unpaired electrons in one Sr_4X_3N crystal cell, so the total magnetic moments are 1.00 μ_B, which is well consistent with the results shown in Table 1.

4. Conclusion

In conclusion, rocksalt Sr_4X_3N are predicted to have half metallicity by performing the first principles calculations. They possibly have higher Curie temperatures and have more stable half metallicities than Sr_4X_3C. Their crystal-cell magnetic moments are 1.00 μ_B, which is an integer. The crystal-cell magnetic moments and the half metallicity of Sr_4X_3N come mainly from the N ions. The main reason is that there are sp^2 hybridized orbitals caused by the crystal field (covalent interaction). Then three N-2p and two Sr-5s electrons form two electron pairs and one unpaired electron.

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