First-principles research on influence of C dopants on magnetic and electric properties of rocksalt MgS*

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The 2×2×1 rocksalt C-doped MgS supercells are optimized and their magnetic and electric properties, including the half-metallicity, the conductivity and the supercell magnetic moments, are calculated or analysed by the first-principles researches based on the density functional theory. Results show that the concentration of C-dopants may cause important influence on the magnetic and the electric properties of rocksalt MgS. C dopants are inclined to have a scattering distribution. $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ have evident half-metallicity. They have wide spin energy gaps, thus high Curie temperature possibly. Their supercell magnetic moments are near to integral numbers 2.0, 4.0 and 6.0 μ_B. The main reason for spin polarization and half-metallicity of C-doped MgS is that there are sp hybridized orbitals in ligand compound ML_6 caused by covalent interaction between C-ions and Mg-ions.

Keywords: half-metallicity, electric and magnetic properties, supercell magnetic moments

PACC: 7115H, 7120H, 7170C

1. Introduction

The study of spintronics, the potential second-generation electronics, focuses on the transmissions of both charges and spins of electrons. It has a more considerable application prospect than microelectronics (the first-generation electronics) that involves only charges of electrons.[1,2] There has been the increasing interest in the spintronic materials recently, including magnetic oxides such as Sr_2FeMoO_6, $La_{2/3}Sr_{1/3}MnO_3$–$SrTiO_3$ and $NiFe_2O_4$,[3–6] diluted magnetic semiconductors such as (Zn, Mn)O, (Zn, Co)O, (Ga, Mn)O, (Ga, Mn)N and (Zn, Cu)O,[3,7–11] and half-metallic materials such as Fe_3O_4, $LiPr_2O_4$, CrO_2, CrAs and CrSb.[12–19] Since their spin polarizations at the Fermi level are much higher than that of ordinary magnetic materials, the half-metallic ferromagnets (HMFs) among these spintronic materials, whose spin polarizations at the Fermi level are ±100% theoretically, possibly have a higher magnetoresistance effect than ordinary magnetic materials.[12–19] The spin polarizations of Fe, Co and Ni are only +40%, +34% and +11%, respectively.[20] Many high-quality spintronic devices based on the magnetoresistance effect of HMFs, such as magnetoresistance random access memories and read/write magnetic head of computers, may be invented in the near future. Furthermore, the realization of spin semiconductor devices requires a highly spin-polarized current to be injected from magnetic electrodes into semiconductors.[3] HMFs have 100% spin polarization, and their resistivity matches well with that of semiconductors, so they are the best magnetic electrode materials of spin semiconductors.[3] For the above reasons, HMFs have attracted much attention in the past years. Many researches on half-metallic compounds containing transition-metal elements or rare-earth elements have been carried out. Many materials such as Fe_3O_4, $LiPr_2O_4$, CrO_2, CrAs, and CrSb, are predicted to have half-metallicity based on the theoretical calculations.[3,12–19] Now some of them have been prepared and confirmed to have the half-metallicity experimentally.[3,17–19] However, there is very little work on compounds containing no transition metal or rare-earth elements. Very recently, we have predicted that C-doped alkaline-earth chalcogenides X_4CY_3 (X = Mg, Ca and Sr, Y = O and S) with the NaCl structure possess evident half-metallicity.[21] It is shown that C-dopants may cause important influence on the magnetic and the electric

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properties of semiconductor materials. In this paper, the influence of C-dopant contents on the half-metallicity and electronic structures of the semiconductor MgS with the rocksalt structure is discussed based on the first-principles calculations.

2. Technicality

In order to achieve a realistic experimental dopant concentration in a range of about 5%–30%, we used a periodic 2×2×1 rocksalt MgS supercell, which is composed of sixteen Mg ions and sixteen S ions. The MgS supercell is shown in Fig. 1, where Mg and S ions are signed by their element symbols, respectively. The space group is $Fm3m$.

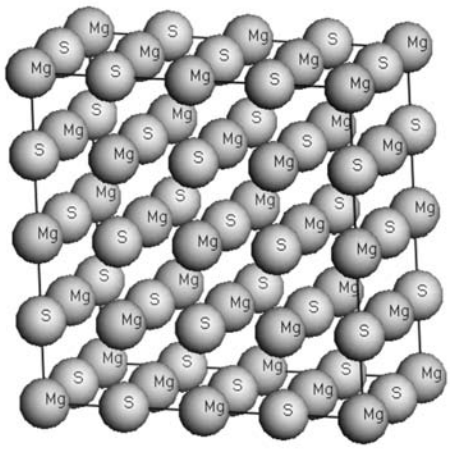


Fig. 1. The 2 × 2 × 1 rocksalt MgS supercell.

Substitution of C ions for S ions is given as follows. (i) $MgC_{0.0625}S_{0.9375}$: one S ion on the middle site of the supercell is substituted by one C ion. (ii) $^{a}MgC_{0.1250}S_{0.8750}$: two scattering S ions are substituted by two C ions. This means that the distance between these two C ions is long enough. (iii) $^{b}MgC_{0.1250}S_{0.8750}$: two neighbouring S ions around the same Mg ion are substituted by two C ions, respectively. (iv) $MgC_{0.1875}S_{0.8125}$: three scattering S ions are substituted by three C ions. The optimization of geometrical structures and the calculation of magnetic and electric properties are performed using the calculation module 'Cambridge serial total energy package (castep)' based on the density functional theory. The wave function is expanded with the plane-wave pseudo-potential, and the exchange correlation function is the Perdew–Burke–Ernzerhof functional (PBE) of three nonlocal gradient-corrected exchange-correlation functionals (GGA). The calculation quality is 'fine', corresponding to the cutoff energy 340 eV and the k-point set 5×5×5. The calculated electronic structures of isolated atoms are $2p^6 3s^2$ for Mg, $2s^2 2p^2$ for C and $3s^2 3p^4$ for S, respectively.

The geometrical structure of the MgS supercell is optimized and compared with the experimental one in order to confirm our calculations. The optimized lattice constants are $a_0 = b_0 = 10.50$ Å (1 Å = 0.1 nm) and $c_0 = 5.25$ Å, and the corresponding experimental values are $a_e = b_e = 10.40$ Å and $c_e = 5.20$ Å.[22] The relative difference between a_0 and a_e is only 0.96%, which indicates that our calculation values accord well with experimental ones.

The C-doped formation energies $E_f(C \to S)$ of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$, $^{b}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are also calculated from the following formulas:[23]

$$E_f(C \to S) = [E_{tot}(Mg_{16}C_xS_{16-x}) + xE(S) - xE(C) - E_{tot}(Mg_{16}S_{16})], \quad x = 1, 2, 3, \tag{1}$$

where $E_{tot}(Mg_{16}C_xS_{16-x})$ and $E_{tot}(Mg_{16}S_{16})$ are the total energies of the optimized $MgC_{0.0625}S_{0.9375}$ and MgS supercells, respectively. The $E_{tot}(Mg_{16}S_{16})$ is –20026.40 eV and the total energies of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$, $^{b}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are –19947.04, –19817.36, –19817.03 and –19709.02 eV, respectively. The $E(S)$ and $E(C)$ are the average energies of an S-atom and a C-atom, and they are obtained by the pseudo-potential method to be –261.44 and –155.59 eV, respectively. From formula (1), the values of E_f (C → S) for $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$, $^{b}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are calculated to be –26.49, –2.66, –2.33 and –0.17 eV, respectively. These formation energies are all negative, showing that these hypothesized materials are stable.

3. Results and discussion

3.1. Total state densities of rocksalt C-doped MgS

The spin-polarized total state densities (TDOSs) of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$, $^{b}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are shown in Figs. 2(a), 2(b), 2(c) and 2(d), respectively, where the solid and the dashed

lines represent TDOSs of up-spin and down-spin subbands, respectively. From Fig. 2, there are obvious spin polarizations for C-doped MgS near the Fermi level, while there is no spin-polarization for undoped MgS near the Fermi level. Furthermore, the down-spin subbands go through the Fermi level, which indicates that the C-doped MgS compounds are conductors, while undoped MgS compounds are evidently semiconductors, which means that C-dopants can cause substantial influence on electric and magnetic properties of MgS. There are only up-spin subbands at the Fermi level in Figs. 2(a), 2(b) and 2(d), which indicates that $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are potential half-metallic ferromagnets, whose spin-polarizations are all –100% at the Fermi level. However, there are a few up-spin state densities besides down-spin state densities in Fig. 2(c), which indicates that $^{b}MgC_{0.1250}S_{0.8750}$ is not a complete HMF, but a high spin-polarization material. Furthermore, the calculated supercell magnetic moments of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ are 1.96, 3.94 and 5.86 μ_B, respectively. These supercell magnetic moments are near to integral numbers 2.00, 4.00 and 6.00 μ_B. Having integral supercell magnetic moments is one of important characters of half-metallic materials. However, the supercell magnetic moment of $^{b}MgC_{0.1250}S_{0.8750}$ is 3.87 μ_B, which is evidently lower than that of $^{a}MgC_{0.1250}S_{0.8750}$. Therefore, scattering distribution of C dopants is beneficial to the half-metallicity. On the other hand, the calculated stable energy –19817.36 eV of $^{a}MgC_{0.1250}S_{0.8750}$ is a little lower than that of $^{b}MgC_{0.1250}S_{0.8750}$ (–19817.03 eV), which indicates that C dopants are inclined to have a scattering distribution. The main reason is that the supercell magnetic moments of C-doped MgS come mainly from C ions. The exchange interaction between neighbouring C-ions is stronger than that between scattering C ions. Stronger exchange interaction may cause supercells to obtain higher energy.

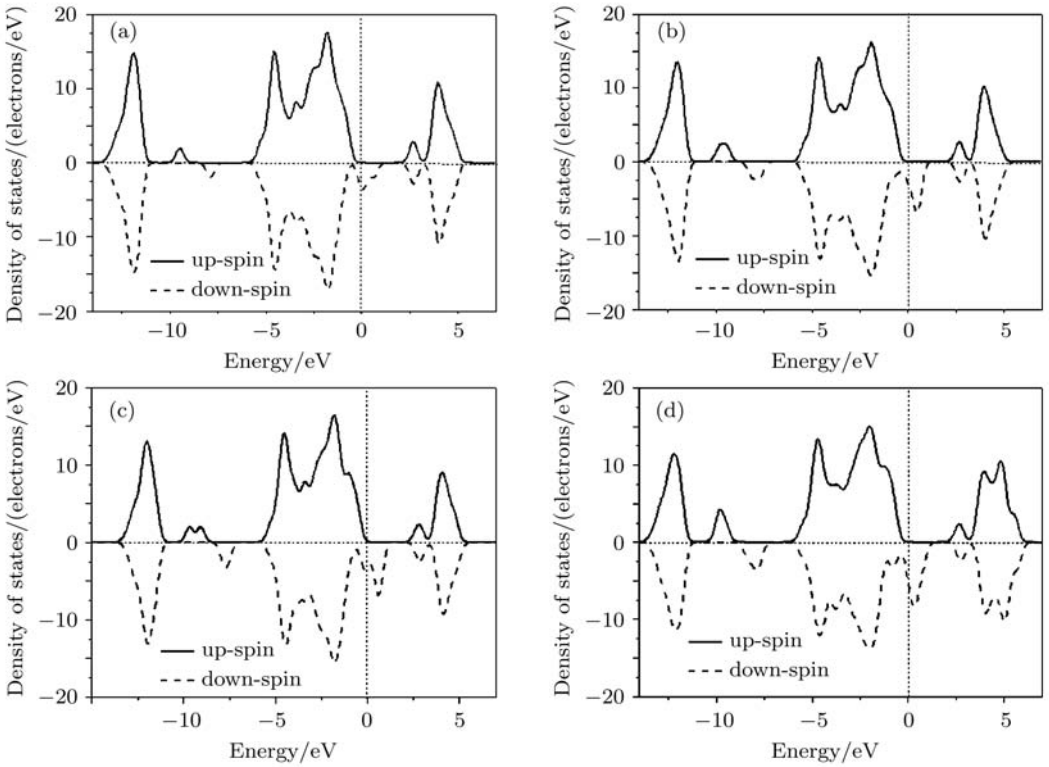


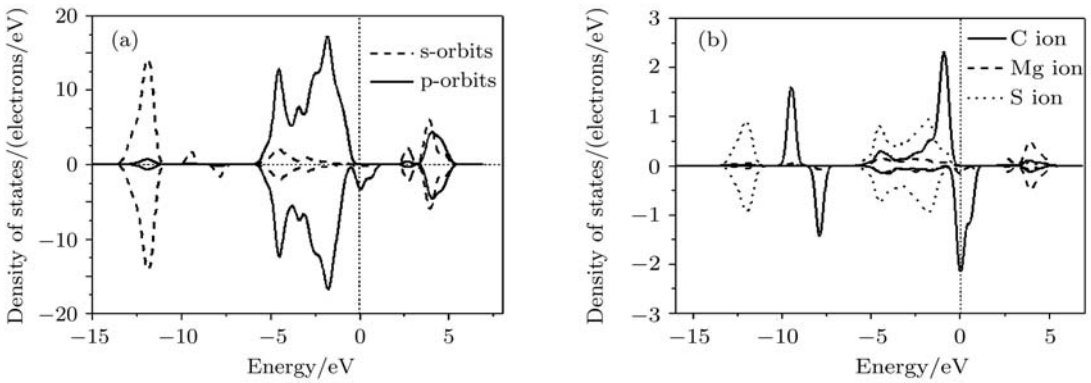
Fig. 2. Total spin-polarized state densities of $MgC_{0.0625}S_{0.9375}$ (a), $^{a}MgC_{0.1250}S_{0.8750}$ (b), $^{b}MgC_{0.1250}S_{0.8750}$ (c) and $MgC_{0.1875}S_{0.8125}$ (d).

From Figs. 2(a), 2(b) and 2(d), the values of spin gap, which are defined as the difference between the maximum energy of up-spin valence subbands and the minimum energy of the up-spin conductance subbands, are all near to 2.5 eV. The calculated spin gaps calculated from the GGA are generally less than experimental values due to the fact that the correlation effect of excitation electrons is underestimated.[24] This shows that the spin gaps of these HMFs are wide and possibly have high Curie

temperatures. This is very important for the application of magnetic materials. On the other hand, the values of the half-metallic gap or the spin-flip gap, which is defined as the difference in energy between the Fermi level of the metallic subband and the peak of the semiconducting valence subband, are 0.17, 0.08 and 0.02 eV for $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$, respectively, which are also underestimated. This shows that the C-doped half-metallic stability will decrease with the increase of C-dopant concentration.

3.2. Partial and local state densities of rocksalt C-doped MgS

In order to analyse the electronic structures of C-doped MgS deeply, the partial densities of states (PDOSs) and local densities of states (LDOSs) of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $^{b}MgC_{0.1250}S_{0.8750}$ are calculated and shown in Fig. 3, where the PDOSs of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$ and $^{b}MgC_{0.1250}S_{0.8750}$ are shown in Figs. 3(a), 3(c) and 3(e), while their LDOSs are shown in Figs. 3(b), 3(d) and 3(f), respectively. For the PDOSs, the solid and dash lines represent the PDOSs of s and p orbits, respectively. For the LDOSs, the solid, the dash and the dot lines refer to the LDOSs of C ion, Mg ion and S ion, respectively. From Figs. 3(a) and 3(b), it follows that the TDOSs of C-doped MgS are divided into five parts. The PDOSs of the first part, whose energies are in a range from –13.1 eV to –11.0 eV, decrease with the increase of C-dopant concentration. The main reason is that they come from 3s orbits of S ion (S-3s orbits for short) shown in Figs. 3(a) and 3(b), and then the concentration of S ions decreases with the increase of C ions. However, the PDOSs of the second part, whose energies vary from –10.0 eV to –7.4 eV increase with the increase of C-dopant concentration. The main reason is that they come from 2s orbits of C ion (C-2s orbits for short). These two parts are localized in S ions and C ions, respectively, because their energies are much lower than the Fermi level. They are almost axially symmetrical about the line that indicates the state density is zero, and then they can cause no influence on the electric and magnetic properties of materials. Therefore, they are not plotted in Figs. 3(c)–3(f). The PDOSs of the third part, whose energies range from –5.9 eV to 1.1 eV, come mainly from 3p orbits of S ion and 2p orbits of C ion, and partially from 3s orbits of Mg ion. This shows that there are hybridized orbits between 3p orbits of S ion and 3s orbits of Mg ion or between 3p orbits of C ion and 3s orbits of Mg ion because the energies of these orbits are close to each other. There is evident spin-polarization for the third part and its down-spin parts go through the Fermi level. This means that they make main contribution to the magnetic and the electric properties of C-doped MgS. From Fig. 3(b), the spin-polarizations of Mg and S ions are very weak, but those of C ion are very strong. Furthermore, the state densities of C ion are much larger than those of Mg ion and S ion. Therefore, C ions make a main contribution to the supercell magnetic moments and the conductivity of C-doped MgS. The fourth and fifth parts come from 2p, 3p and 3s orbits of C, S and Mg ions, respectively. Their energies are much higher than the Fermi level and they are almost axially symmetrical, so they make little contribution to the electric and the magnetic properties.



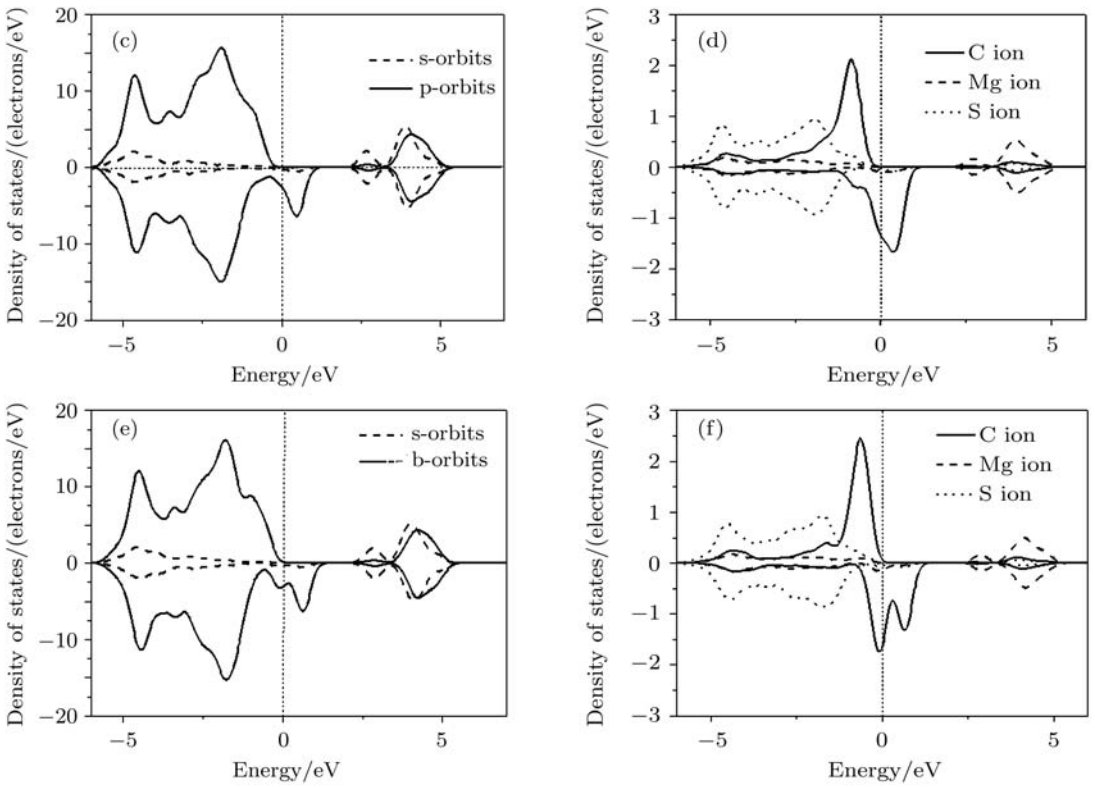


Fig. 3. Partial densities of states (PDOSs) and local densities of states (LDOSs) of $MgC_{0.0625}S_{0.9375}$ (the first row), $^{a}MgC_{0.1250}S_{0.8750}$ (the second row) and $^{b}MgC_{0.1250}S_{0.8750}$ (the third row).

From Figs. 3(c) to 3(f), it follows that the TDOSs of $^{a}MgC_{0.1250}S_{0.8750}$ and $^{b}MgC_{0.1250}S_{0.8750}$ are very similar to each other if their energies are less than –1.1 eV, but they are evidently different near the Fermi level. There is only one sharp peak for down-spin subband of $^{a}MgC_{0.1250}S_{0.8750}$, but there are two sharp peaks for down-spin subband of $^{b}MgC_{0.1250}S_{0.8750}$. On the other hand, the energy bands of $^{b}MgC_{0.1250}S_{0.8750}$, including the up-spin and down-spin subbands, shift toward high energies compared with those of $^{a}MgC_{0.1250}S_{0.8750}$. Those results show that there are a few up-spin state densities of $^{b}MgC_{0.1250}S_{0.8750}$ at the Fermi level, then $^{b}MgC_{0.1250}S_{0.8750}$ is not a real HMF. The main reason is that there is a stronger exchange interaction between two neighbouring C ions of $^{b}MgC_{0.1250}S_{0.8750}$ than that between two scattering C ions of $^{a}MgC_{0.1250}S_{0.8750}$. The stronger exchange interaction leads to the increase of supercell energy and the split of C-2p orbits.

Table 1. Some calculated electric and magnetic parameters of $MgC_{0.0625}S_{0.9375}$, $^{a}MgC_{0.1250}S_{0.8750}$, $^{b}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$.

materials	ions	E_s/e	E_p/e	E_t/e	charge/e	M/μ_B
$MgC_{0.0625}S_{0.9375}$	C	1.76	3.26	5.02	–1.02	1.54
$^{a}MgC_{0.1250}S_{0.8750}$	C_1	1.78	3.16	4.93	–0.93	1.82
	C_2	1.76	3.31	5.07	–1.07	1.44
$^{b}MgC_{0.1250}S_{0.8750}$	C_1	1.78	3.06	4.84	–0.84	1.98
	C_2	1.74	3.36	5.10	–1.10	1.22
$MgC_{0.1875}S_{0.8125}$	C_1	1.77	3.17	4.94	–0.94	1.76
	C_2	1.76	3.35	5.10	–1.10	1.40
	C_3	1.77	3.17	4.94	–0.94	1.76

Some magnetic and electric parameters of all ions of C-doped MgS are calculated in order to find the magnetic and the electric properties, but only those of C ions are given in Table 1 due to the limitation of the table length. These parameters include s, p and total electrons (E_s, E_p and E_t), charges and supercell magnetic moments (M). From Table 1, the ionic magnetic moments of C ions are close to the supercell magnetic moments of C-doped MgS and much higher than those of other ions. This shows that the supercell magnetic moments of C-doped MgS come mainly from C ions. On the other hand, the differences in absolute values of the total electrons, the charges and the ionic magnetic moments between C ions of $^{b}MgC_{0.1250}S_{0.8750}$ are evidently larger than those of $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$. Furthermore, the maximum magnetic moment of Mg-ions of $^{b}MgC_{0.1250}S_{0.8750}$ is 0.10 μ_B, which is much larger than those of $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$. This shows that the exchange interaction between neighbouring C ions in $^{b}MgC_{0.1250}S_{0.8750}$ is stronger than those between scattering C ions in $^{a}MgC_{0.1250}S_{0.8750}$ and $MgC_{0.1875}S_{0.8125}$ again.

From Fig. 1, there are eight S ions around one Mg ion, then they constitute a ligand compound, i.e. ML_6, according to the crystal field theory,[25−27] where the 'M' and 'L' denote the middle ions and their ligands, respectively. Isolated C atoms have weaker electronegativity than isolated S atoms, so there are both covalent bonds and ionic bonds between the Mg ions and the C ions, caused by the crystal field of ML_6. However, there are only ionic bonds in undoped MgS. The covalent bonds result in the sp hybridization of one 2p orbit of C ion with one 3s orbit of Mg ion since their energies are close to each other. Generally, the energy of sp hybridized orbital is lower than that of s-orbits of Mg, so two 3s electrons of Mg atom enter into two sp hybridized orbitals in parallel, respectively. These two electrons are up-spin electrons, so there is spin polarization in C-doped MgS, and the net magnetic moments of their supercells are close to 2.0, 4.0, 6.0 μ_B. On the other hand, the 1s and two 2p orbits of C ion have no contribution to the hybridized orbitals because their energies are much lower than those of outer-shell s-orbit of Mg ion. These unhybridized orbitals are controlled in their ions and there are two anti-parallel electrons in each orbit. They cause no effect on the magnetic and the electric properties of C-doped MgS.

4. Conclusions

The influence of C-doping on the magnetic and the electric properties, including the half-metallicity, the conductivity and the supercell magnetic moments of rocksalt MgS, are calculated and analysed by the first-principles researches based on the density functional theory. Results show that the concentration of C dopants may cause important influence on the magnetic and the electric properties of rocksalt MgS. C dopants are inclined to have a scattering distribution and there is half-metallicity in the C-doped MgS. It has a wide spin energy gap, then a high Curie temperature possibly. The magnetic moments of their supercell are close to integral numbers, i.e. 2.0, 4.0, and 6.0 μ_B. The main reason for spin polarization and half-metallicity of C-doped MgS is that there are sp hybridized orbitals in ligand compound ML_6, caused by the covalent interaction between C ions and Mg ions.

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