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# The structural, electronic, and magnetic properties of $SrFeO_n$ ($n = 2$ and 2.5): a GGA+$U$ study*

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Using density-functional calculations within the generalized gradient approximation (GGA)+$U$ framework, we investigate the structural, electronic, and magnetic properties of the ground states of $SrFeO_n$ ($n = 2$ and 2.5). The magnetism calculations show that the ground states of both $SrFeO_2$ and $SrFeO_{2.5}$ have G type antiferromagnetic ordering, with indirect band gaps of 0.89 and 0.79 eV, respectively. The electronic structure calculations demonstrate that Fe cations are in the high-spin state of $(d_{z^2})^2(d_{xz},d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1(S = 2)$, unlike the previous prediction of $(d_{xz},d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1(S = 2)$ for $SrFeO_2$, and in the high-spin state of $(d_{xy},d_{xz},d_{yz},d_{x^2-y^2},d_{z^2})^5(S = 5/2)$ for $SrFeO_{2.5}$.

**Keywords:** band structure, magnetic property, density functional theory

**PACC:** 7120H, 7550, 7115J

## 1. Introduction

Perovskite oxides have attracted considerable interest due to their extensive applications in a number of technologies.[1−3] The iron perovskites $SrFeO_{3-x}$ exhibit a variety of interesting fundamental aspects, ranging from charge disproportionation ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$), vacancy ordered structure, screw spin structure, giant magnetoresistance, to high-spin-to-low-spin transition.[4] In addition, they show a fast oxygen transport property observed at moderate temperatures, making them appealing for low-cost industrial applications such as gas sensors, electrodes for solid oxide fuel cells, membranes for oxygen separation, and electrocatalysis.[5] $SrFeO_{3-x}(0 \leq x \leq 0.5)$ were synthesized many years ago, however, $SrFeO_2$ ($x = 1$) was first synthesized in 2007.[6]

It is well known that the properties of perovskite oxides will change with different oxygen deficiencies. For example, stoichiometric $LaNiO_{2.5}$ has been described as an antiferromagnetic material, whereas $LaNiO_{2.6}$ has been reported to exhibit ferromagnetic ordering. $SrCoO_3$ demonstrates ferromagnetic behaviour, while $SrCoO_{2.5}$ shows antiferromagnetic ordering. Thus, it can be concluded that the magnetic properties of $LaNiO_{3-x}$ and $SrCoO_{3-x}$ are greatly dependent on the amount of the oxygen deficiency. For $SrFeO_{3-x}$, the experimental results show that $SrFeO_{3-x}$ all exhibit antiferromagnetic ordering.[6−9] However, there are three types of antiferromagnetic (AF) structures, as shown in Fig.1. The antiferromagnetic interplanar and ferromagnetic intraplanar coupling leads to the A-type, while the opposite situation (AF intraplanar and F interplanar coupling) gives the C-type. When both interactions are antiferromagnetic, it will lead to the G-type. Which type of antiferromagnetic ordering of $SrFeO_{3-x}$, and whether the magnetic property will change with different oxygen deficiencies is so far unclear. Besides, the electronic configurations of iron cations in $SrFeO_{3-x}$ are still puzzling. For instance, Tsujimoto *et al*[6] pointed out that the electronic configuration of iron cations in $SrFeO_2$ should be a twofold orbital degenerate ground state of $(d_{xz},d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$; however, it should be Jahn–Teller active, conflicting with the experimental fact that no Jahn–Teller effect exists in $SrFeO_2$.[6]

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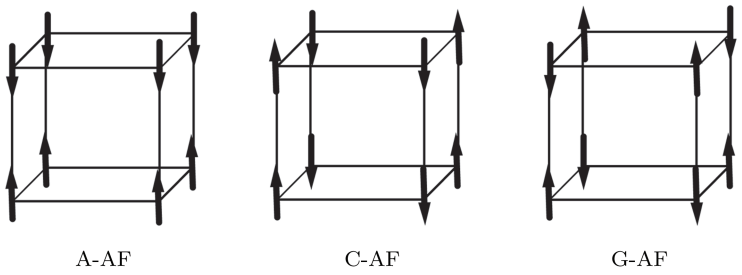



**Fig.1.** Three types of antiferromagnetic (AF) structures, A-AF, C-AF, and G-AF.

In the present work, a first-principles study of $SrFeO_x$ ($x = 2$ and 2.5) is performed to explore their structural, magnetic and electronic properties. In what follows, we will describe our computational method in Section 2 and present our results and discussions in Section 3. Finally, a summary is given in Section 4.

## 2. Computational method

In recent years, *ab initio* band-structure methods based on the local-spin-density approximation (LSDA) or spin-polarized generalized-gradient approximation (GGA) have been widely used to calculate the electronic structures of transition-metal perovskites $AMO_3$ (M, the 3d transition metal).[10−12] However, these standard approaches are not quite effective for strongly correlated systems,[11,12] especially for transition-metal oxides. Alternative approaches such as the local spin-density approximation augmented with a Hubbard $U$ (LSDA+$U$), spin-polarized generalized-gradient approximation with a Hubbard $U$ (GGA+$U$), and dynamical mean-field theory (DMFT) that include local correlations in the form of a "Hubbard $U$" are more suitable.[13−16] So in this paper, density-functional calculations are performed using GGA+$U$ and the projector augmented-wave (PAW) method as implemented in the VASP code.[17,18] In the following, we report only the best results compared with the experimental ones with $U = 4.6$ eV and $J = 0.8$ eV for Fe atoms, consistent with previous studies,[19,20] though calculations with other $U$ values between $3 \sim 6$ eV have also been performed. Convergence tests for k points and energy cutoff are performed to ensure numerical accuracy. Plane waves with kinetic energy up to 400 eV have been employed to expand the electronic wave functions. The BZ integration is carried out using a 16×16×16 Monkhorst–Pack grid in the first BZ, while a 2×2×2 supercell derivative from the $Pm\bar{3}m$ perovskite structure of $SrFeO_3$ is used for $SrFeO_2$. On the other hand, the Brillouin-zone (BZ) integration is carried out using an $8 \times 8 \times 8$ Monkhorst–Pack grid in the first BZ, while a $2\sqrt{2} \times 2\sqrt{2} \times 4$ supercell derived from the $Pm\bar{3}m$ perovskite structure of $SrFeO_3$ is used for $SrFeO_{2.5}$. To ensure high accuracy, the k-point density and the plane wave cutoff energy are increased until the change of the total energy is within $10^{-5}$ eV. The structural relaxations are performed until the Hellmann–Feynman force on each atom reduces to within 0.01 eV/Å.

## 3. Result and discussion

### 3.1. Ground states and magnetic structures of $SrFeO_n$

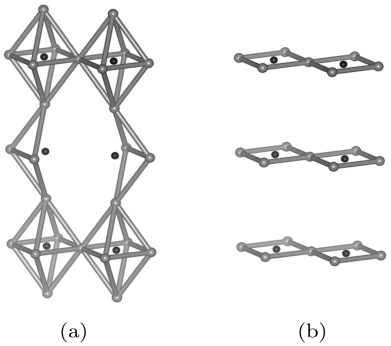
$SrFeO_{2.5}$ containing only $Fe^{+3}$ has an orthorhombic brownmillerite structure with the space group $Ibm2(Icmm)$, in which oxygen ions strung along the [110] direction of the parent perovskite are totally missing,[9,21,22] while $SrFeO_2$ containing only $Fe^{+2}$ has an unusual square-planar coordination around iron with the space group $P4/mmm$.[6] Three types of antiferromagnetic orderings are considered here. The calculated magnetic moments and total energies corresponding to the two compositions are listed in Table 1. It can be seen from the table that the G-AF states of $SrFeO_{2.5}$ and $SrFeO_2$ are at least 3.41 and 3.01 eV lower in total energy than the other two AF states, respectively. Thus, the G-AF states are the ground states of both $SrFeO_{2.5}$ and $SrFeO_2$. The magnetic moments on Fe sites of the G-AF states are 3.92 and 3.53 $\mu_B$, in good agreement with the experimental

ones of 4.0 $\mu_B$[23] and 3.6 $\mu_B$.[6] The experimental fact shows that $SrFeO_3$ has helical ordering,[7] thus, the antiferromagnetic structure of $SrFeO_n$ would vary with increasing oxygen deficiency. It is worth noting that both $SrFeO_{2.5}$ and $SrFeO_2$ showing G-AF ordering can be explained as follows. We know that $SrFeO_n$ showing antiferromagnetic ordering is mainly ascribed to the Fe–O–Fe super-exchange interaction, which is the strong antiferromagnetic coupling between two next-to-nearest neighbour cations through a non-magnetic anion. For $SrFeO_2$ and $SrFeO_{2.5}$, there are Fe cations that manage to interact with each other through non-magnetic oxygen anions between them. Because oxygen anions between the two Fe cations along the $c$ axis are totally or partly missing, the super-exchange interaction would not happen along this direction. However, it could take place between the Fe cations in $(111)_{\rm cubic}$ crystal plane. Therefore, the spin orientation of Fe cations is parallel in one $(111)_{\rm cubic}$ crystal plane, and anti-parallel in the nearest neighbouring $(111)_{\rm cubic}$ crystal planes.

**Table 1.** The total energy (TE) of a supercell in units of eV, and the magnetic moment (MM) of the Fe atom in the ground-states of $SrFeO_{2.5}$ and $SrFeO_2$ in units of $\mu_B$.

| composition | TE(A-AF) | TE(C-AF) | TE(G-AF) | MM | $MM^{expt}$ |
|---|---|---|---|---|---|
| $SrFeO_{2.5}$ | –941.84 | –941.81 | –945.25 | $3.92^{G-AF}$ | 4.0[23] |
| $SrFeO_2$ | –221.05 | –221.12 | –224.13 | $3.53^{G-AF}$ | 3.6[6] |

The optimized structures of the two compositions are described in Fig.2, while the lattice parameters corresponding to the ground states of them obtained from both this work and the experiments are listed in Table 2. It can be seen from the table that all the optimized lattice parameters are very close to the experimental ones. The cell constants of $SrFeO_n$ change a bit with different oxygen deficiencies. The values of the cell constant a of $SrFeO_2$ and $SrFeO_{2.5}$ are 3.98 and 3.89 Å, respectively, and that of $SrFeO_3$ given by Takeda *et al*[24] in experiment is 3.86 Å. It is clear that the cell constant a increases with increasing oxygen deficiency. The reason is that there is 3e transfer from Fe to O in $SrFeO_{2.5}$,[21] while there is only 2e transfer from Fe to O in $SrFeO_2$.[6] Thus the Coulomb force of attraction between the Fe cation and the O anion in $SrFeO_{2.5}$ is stronger than that of its counterpart in $SrFeO_2$.



(a) (b)

**Fig.2.** The optimized structures of $SrFeO_{2.5}$ (a), $SrFeO_2$ (b). Black and grey spheres represent iron and oxygen.

On the other hand, the cell constant $c$ of $SrFeO_{2.5}$ is 3.87 Å, larger than the value of 3.45 Å of $SrFeO_2$.

**Table 2.** The lattice parameters of $SrFeO_3$, $SrFeO_{2.5}$, and $SrFeO_2$ in units of Å.

| composition | $a$ | $c$ | $a^{expt}$ | $c^{expt}$ |
|---|---|---|---|---|
| $SrFeO_3$ | | | 3.86[24] | |
| $SrFeO_{2.5}$ | 3.89 | 3.87 | $3.91(5.53/\sqrt{2})$[25] | $3.90(15.58/4)$[25] |
| $SrFeO_2$ | 3.98 | 3.45 | 3.99[6] | 3.47[6] |

## 3.2. Electronic band structures of $SrFeO_n$

It is well known that both compositions of $SrFeO_n (n = 2, 2.5)$ show paramagnetic ordering at high temperature. The paramagnetic band structures and density of states (DOS) of $SrFeO_n$ are first calculated for comparison. During the calculation, the experimental parameters (such as space group, cell constant) are used.[6,24,25] The calculated band structures, total DOS (TDOS) and partial DOS (PDOS) are shown in Fig.3. One finds from the figure that the band structures have metallic characters with many dispersion bands crossing the Fermi level ($E_F$) (0 eV in the figure) for both $SrFeO_n$. At the region from –7 to 0 eV, there is some mixing between Fe-3d and O-2p orbitals. On the other hand, it can be seen from the Fe 3d PDOS that the peaks are all located at the vicinity of $E_F$.

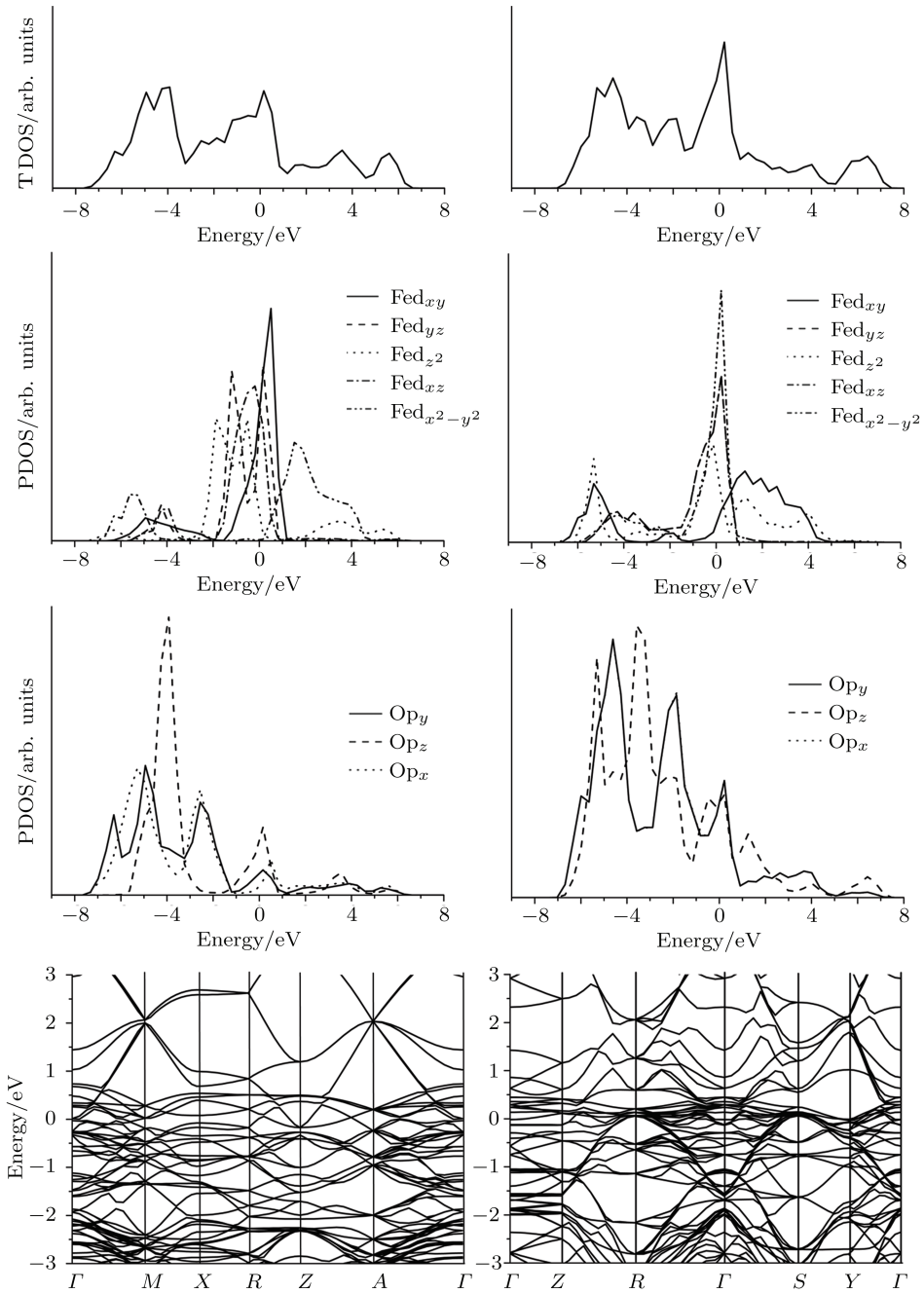



**Fig.3.** The paramagnetic band structures, total and partial density of states for $SrFeO_2$ (left) and $SrFeO_{2.5}$ (right).

Since both $SrFeO_2$ and $SrFeO_{2.5}$ experimentally exhibit antiferromagnetic ordering at low temperature,[6–9] we will discuss the electronic properties of $SrFeO_2$ and $SrFeO_{2.5}$ with antiferromagnetic ordering in the following. Figure 4 presents the antiferromagnetic band structures, TDOS and PDOS for $SrFeO_2$ and $SrFeO_{2.5}$. We can conclude from the figure that both of them, unlike their paramagnetic counterparts, exhibit the character of a indirect band gap semiconductor, in agreement with the experimental results.[6,26,27] Their conduction band minimum is at $\Gamma$, while their valence band maxima are at $M$ (or $A$) for $SrFeO_2$ and $Y$ for $SrFeO_{2.5}$. The indirect band gaps are 0.89 and 0.79 eV for $SrFeO_2$ and $SrFeO_{2.5}$, respectively.

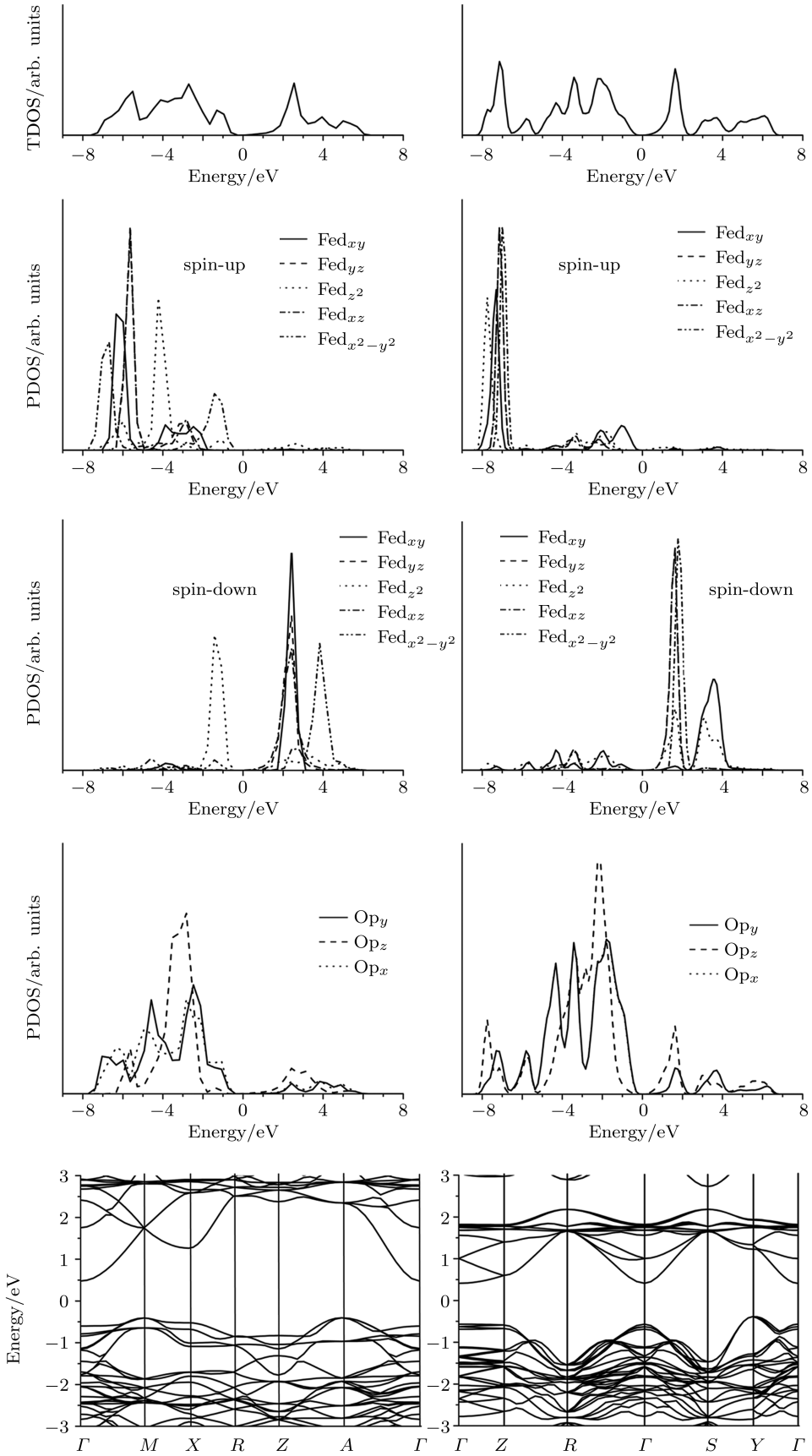



**Fig.4.** The antiferromagnetic band structures, total and partial density of states for $SrFeO_2$(left) and $SrFeO_{2.5}$(right).

On the other hand, the electronic configurations of Fe cations in $SrFeO_n$ are still open questions. From crystal field theory, the electronic configuration is mainly related to the space group of the composition. According to the space groups of $SrFeO_n$, the fivefold degenerate 3d orbitals will split. Therefore, the Fe $3d^6$ cations for $SrFeO_2$ should be in the high-spin state of $(d_{z^2})^2(d_{xz},d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1(S = 2)$, in contrast to $(d_{xz},d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1(S = 2)$ predicted by Tsujimoto *et al.*[6] This could be explained by the fact that $SrFeO_2$ has an unusual layered structure in which oxygen ions strung along the [001] direction of the parent perovskite are totally missing. Because of the oxygen deficiency, the Coloumb repulsion is deeply reduced, resulting in the energy of the $d_{z^2}$ state being significantly decreased so that it is lower than that of the doubly-degenerated ($d_{xz}$, $d_{yz}$) states. In addition, the latter one would lead to only one spin-down electron in doubly-degenerate orbitals ($d_{xz}$, $d_{yz}$), which would be Jahn–Teller active, conflicting with the experimental evidence that no Jahn–Teller effect is found in $SrFeO_2$.[6] On the other hand, the Fe $3d^5$ cations of $SrFeO_{2.5}$ should be in the high-spin state of $(d_{xy},d_{xz},d_{yz},d_{x^2-y^2},d_{z^2})^5(S = 5/2)$, in agreement with the observation of no Jahn–Teller effect. This judgement is confirmed by their densities of states. It can be seen from the spin-up PDOS that both $SrFeO_{2.5}$ and $SrFeO_2$ have the compositions of $d_{xy}$, $d_{xz}$, $d_{yz}$,$d_{\ x^2-y^2}$, and $d_{z^2}$ in their valence band, while the Fe $3d_{z^2}$ orbital of $SrFeO_{2.5}$ is located at the vicinity of –7.8 eV, much lower than that of $SrFeO_2$ located at the vicinity of –4.2 eV. Turning to the spin-down PDOS, the characters of the two compounds are quite different. The Fe $3d_{z^2}$ spin-down orbital in $SrFeO_2$ is located below the Fermi energy level, while all of the Fe 3d spin-down orbitals in $SrFeO_{2.5}$ are located above the Fermi energy level, consistent with our judgement about the electronic configurations of Fe cations for both $SrFeO_2$ and $SrFeO_{2.5}$. Finally, it can be easily seen from the figures that there are strong mixtures between Fe-3d and O-2p orbitals at the region from –7.5 to –1.0 eV for $SrFeO_2$, while there are strong mixtures between Fe-3d and O-2p orbitals existing at the region from –8.0 to –6.5 eV for $SrFeO_{2.5}$.

# 4. Summary

In summary, the structural, electronic, and magnetic properties of the ground states of $SrFeO_n$($n = 2$ and 2.5) are investigated using density-functional calculations within the generalized gradient approximation (GGA)+$U$ framework. The magnetism calculations show that $SrFeO_2$ and $SrFeO_{2.5}$ with G type antiferromagnetic orderings are the ground states, while the experimental result shows that $SrFeO_3$ has helical ordering, suggesting that the magnetic ordering would change with different amounts of vacancies of oxygen atoms. From crystal field theory, we can come to the conclusion that the Fe cations are in the high-spin states of $(d_{z^2})^2(d_{xz},d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1(S = 2)$ and $(d_{xy},d_{xz},d_{yz},d_{x^2-y^2},d_{z^2})^5(S = 5/2)$, for $SrFeO_2$ and $SrFeO_{2.5}$, respectively, consistent with the fact that no Jahn–Teller effect is observed in these two compositions. The above judgement is confirmed by their densities of states. The electronic structure calculations show that both $SrFeO_2$ and $SrFeO_{2.5}$ with antiferromagnetic phase have an indirect band gap semiconductor character with gaps of 0.89 and 0.79 eV, respectively.

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