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First principles study of the electronic and magnetic properties of the spin-ladder iron oxide $Sr_3Fe_2O_5$

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Abstract

The electronic and magnetic properties in the novel spin-ladder iron oxide $Sr_3Fe_2O_5$, containing the unusual square-planar coordination around high-spin Fe^{2+} cations, were investigated using the generalized gradient approximation plus Coulomb interaction correlation method. Our results demonstrated that the G-type antiferromagnetic configuration is the ground state, in excellent agreement with the experimental neutron powder diffraction and Mössbauer spectroscopy measurements as well as the available theoretical result in the literature, albeit the slightly larger computed magnetic moments. Moreover, the outstanding discrepancy between the two-dimensional crystal structure and the three-dimensional electronic/magnetic properties is resolved via the special localization and orientation of electronic/spin charge in real space, i.e. the dz^2 orbital ordering of the down-spin Fe 3d electron.

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Introduction

The chemistry and physics of transition-metal oxides has been full of surprises and intriguing structural, electronic and magnetic phenomena. One of the key ingredients at the origin of these effects is the availability of degenerate electronic orbitals. Whether such orbital degrees of freedom actually occur in a material depends on the nature of the atomic ions and the surrounding crystallographic structure, i.e. coordination polyhedra. Thus, the ability to tune the coordination polyhedra of transition-metal ions will offer an extra knob designing novel materials, which might possess fascinating properties and potential applications.

The coordination geometries in iron oxides have been exclusively restricted to three-dimensional polyhedra such as octahedra and tetrahedra. However, this restriction was recently circumvented by using calcium hydride as a powerful reductant at low temperature,[1] as initiated and developed by Hayward, Rosseinsky and co-workers, which provides an effective route for achieving unprecedented coordination polyhedra in transition metal oxides.[2] Applying the new synthetical

method to $SrFeO_3$, a new compound $SrFeO_2$, bearing an unusual square-planar coordination around Fe has been achieved. It has planar FeO_2 layers made up of corner-sharing FeO_4 squares with high-spin Fe^{2+} ions, separated by Sr^{2+} ions,[1,3] isostructural with the undoped high-Tc superconductor $SrCuO_2$. Compared with the low-dimensional compounds, $SrFeO_2$ exhibits interesting and apparently puzzling physical properties.[1] On the theoretical side, most of the available insight originated from the electronic structure calculations[4,5] indicated that the lone down-spin electron of the high-spin Fe^{2+} (d^6) ion located at the square-planar occupies the dz^2 orbital. This special electronic configuration demonstrated that $SrFeO_2$ is not subjected to Jahn-Teller distortion when the temperature is lowered, and is associated with three-dimensional antiferromagnetic spin order with a considerable high Néel temperature ($T_N = 473K$).

Low-temperature reaction of double-layered perovskite $Sr_3Fe_2O_7$ (space group I4/mmm) with CaH_2 gives rise to the stable novel spin-ladder iron oxide $Sr_3Fe_2O_5$.[6,7] $Sr_3Fe_2O_5$ adopts an I-centered orthorhombic space group (Immm) with a = 3.51485Å, b = 3.95271 Å and c = 20.91251 Å,[6] as shown in Fig. 1. It consists of double layers of corner-sharing FeO_2 planar interleaved by Sr^{2+} ions along the z direction, and presents the framework of ladders with two legs running along [010] and rungs along [001] direction. The neutron powder diffraction and Mössbauer spectroscopy measurements established that the presence of the long-range antiferromagnetic order, which is characterized by a magnetic propagation vector q = (1/2, 1/2, 0) and that the iron moments of $2.76\mu_B$ are aligned parallel to the z direction.[6,7] Additionally, first-principles density functional theory calculations employed the projected augmented-wave method argued the magnetic dipole-dipole interactions is essential for the three dimensional magnetic ordering in $Sr_3Fe_2O_5$.[8] Furthermore, identifying the fine details of the electronic structure, its tendency towards magnetic configuration, as well as the strength of the coupling of the magnetic ions is important for understanding the physical properties. Generally, it is well known that electronic and magnetic properties are very sensitive to the coordination polyhedra, to the best of our knowledge, a clear picture of the role of the unusual square coordination of Fe^{2+} ions in $Sr_3Fe_2O_5$ is lacking and deserves special attention. In an attempt to partly remedy this situation we have investigated the electronic and magnetic properties of $Sr_3Fe_2O_5$ using the full-potential density-functional calculations. The implications of our work in relation to recent experiments are discussed in details.

Approach

The band structure calculation is carried out within the framework of the generalized gradient approximation (GGA)+U method;[9-12] we use the highly accurate WIEN2k package,[13,14] which implements the linear augmented plane wave (LAPW) method with local orbitals.[15,16] In this method, the wavefunctions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius R_{MT} and in plane waves in the interstitial region. We adopted the experimentally determined crystal structure with space group Immm. In the calculation, we have chosen R_{MT} of 2.45, 1.95 and 1.73 bohrs for Sr, Fe and O, respectively. The Ewald cutoff radius is $R_{MT}K_{max} = 7$; the maximum l for the expansion of the wavefunctions in spherical harmonics inside the spheres was taken to be $l_{max} = 10$. The total number of k-points is 1000k in the whole Brillouin zone.[17] To take care of the strong electron correlation associated with the Fe 3d states, GGA+U calculations with an effective value $U_{eff} = 4.0$ eV were preformed, the value similar to the previous study of

$Sr_3Fe_2O_5$[8] and $SrFeO_2$[4,5,18]. To test the sensitivity of our results to the on-site effective Coulomb repulsion, somewhat larger and smaller values of U_{eff} are also used for Fe d-electrons; our conclusion still holds, given that the sizable U_{eff} is present at the Fe^{2+} sites. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit, between input charge density is less than 0.0001.

Results and discussion

In order to determine the magnetic ground state of $Sr_3Fe_2O_5$, three spin ordering configurations were explored, namely, the ferromagnetic arrangement, the A-type antiferromagnetic arrangement along the x direction, in which the ferromagnetic ordered planes of Fe sites are antiferromagnetic coupled among each planes, and the G-type antiferromagnetic arrangement, in which the antiferromagnetic ordered planes of Fe sites are antiferromagnetically coupled. Results of our calculations for these three magnetic configurations of the orthorhombic phase of $Sr_3Fe_2O_5$ are summarized in Table 1. The G-type antiferromagnetic state possesses the lowest energy, which is consistent with the experimental determinations based on the neutron powder diffraction,[6,7] irrespective of the calculated methods (GGA or GGA+U), and in fair agreement with the previous theoretical report.[8] Concerning the magnetic ground state configuration, we evaluated the value of the superexchange parameters in terms of the classic Heisenberg spin Hamiltonian:

$$H = -\sum_{i,j} J_{i,j} S_i S_j$$

Here, J>0 (J<0) represents ferromagnetic (antiferromagnetic) interactions, and S=2 is the spin of the $3d^6$ Fe^{2+} ions. On the basis of our calculations, we just consider the J_{yz} interaction within the yz planes and the J_x interaction between the yz planes along the x direction, respectively. The interaction between the perovskite building block is omitted, due to the large distances.

$$J_{yz} = \frac{1}{48S^2}(E_{G-AFM} - E_{A-AFM})$$

$$J_x = \frac{1}{32S^2}(E_{A-AFM} - E_{FM})$$

According to the GGA+U (U_{eff} = 4.0 eV) results, we obtained J_{yz} = -1.57 meV and J_x = -3.10 meV. Notice that both the interactions are negative, indicating antiferromagnetic interactions within the two-dimensional planes and between them, consolidating the G-type antiferromagnetic ground state. Owing to two-dimensional character of the structure, however, one could expect the interplane coupling strength should be small, exhibiting the two-dimensional magnetic properties. Unexpected, it is found that the robust three-dimensional G-type antiferromagnetic state within the double layers of corner-sharing FeO_2 planar is the ground state as stated above, in apparently contrast with the anticipation. This suggests that the electronic configuration of Fe^{2+} within the planar coordination plays an important role in the magnetic properties of $Sr_3Fe_2O_5$.

The calculated magnetic moment at the Fe sites varies between $3.19\mu_B$ to $3.30\mu_B$ per Fe atom depending upon the magnetic configuration considered in our calculations at the GGA level. The calculated magnetic moment at the Fe site is found to be slightly larger than the value of $2.76\mu_B$ measured from low-temperature neutron-diffraction measurements,[6,7] while it is substantially smaller than the expected value. One of the reasons for the large diminution is that the effect of quantum magnetic fluctuation enhanced inherently in the low dimensional ladder, as argued in Ref.

[6]. Alternatively, the calculated magnetic moment at the iron sites might be reduced for the expected integer value $4\mu_B$, since the Fe d electrons have the hybridization interaction with the neighboring O ions. Due to the hybridization interaction, we found that magnetic moment around $0.10\mu_B$ was induced at each O site, while the direction of the polarization depends on the magnetic arrangements. The inclusion of on-site Coulomb correlation on the Fe 3d electrons (U_{eff} = 4.0 eV) under GGA+U formulation amplifies the computed magnetic moments. The remarkable increase in the theoretical value at the Fe site is accompanied by the slightly decrease of the computed value at the O site. These observations, is expected, since GGA+U scheme tends to enhance the "localization" of Fe d states, and then diminish the hybridization interaction between the Fe d electrons and the neighboring O ions.

Since the GGA+U method delivered the similar density of states and charge density as the GGA approach, hence, the results discussed in the following are restricted within GGA scheme, unless otherwise indicated. Notice that, the ferromagnetic configuration (which is experimentally inaccessible) might provide useful references to understand the G-type antiferromagnetic configuration established. Fig. 2 uncovered the total and partial density of states corresponding to the Fe 3d electronic states of the ferromagnetic arrangement. Majority and minority spins are shown above and below the vertical axis. The plots clearly demonstrated that there is a strong hybridization interaction between the Fe 3d states and the surrounding O 2p states. Moreover, one can observe that the Fe 3d spin-up states are completely full occupied, while the spin-down states partially employed crossing the Fermi level. This reflects the large exchange splitting of the Fe 3d levels, which is responsible for the high-spin state of the Fe^{2+} ion and the computed magnetic moments. As a consequence, the GGA calculations for the ferromagnetic arrangement converged to the metallic ground state with a large density of states at the Fermi level, indicating the instability of this arrangement.

However, when one introduces the G-type antiferromagnetic ordering into the framework, the exchange interaction produces an exchange potential that effectively shifts the energy of the Fe 3d states to lower energy, giving rise to insulating behavior. The calculated band structure along the high symmetry directions of the first Brillouin zone as well as the total density of states are presented in Fig.3 and Fig.4, respectively. It is evident that the antiferromagnetic coupling leads to significant reduction in bandwidth of the energy bands and redistribution in spectral weight. A closer inspection of the site-projected density of states representations reveals that the Sr atoms have largely donated their valence electrons to the other constituents and themselves entered into nearly pure ionic states (evident from the small number of states in the valence band and a larger number of states in the conduction band). Since the Fe and O states cover the same energy range with the similar density of states curve pattern, to some extent, there maybe an appreciable hybridization, that is, a significant degree of Fe-O covalent bonding character. More important, a thorough inspection of the density of states illuminate that the electronic configuration is $(d_{z2})^2(d_{xz}d_{yz})^2(d_{xy})^1(d_{x2-y2})^1$ for the Fe^{2+} cations, where the minority spin electron exclusively occupies the d_{z2} orbital, free of the Jahn-Teller distortion. This scenario is in accord with the experimental observations[6,7] and the existing theoretical results[8,19]. Taken the Coulomb correlation effects into account, although the band gaps of $Sr_3Fe_2O_5$ for the G-type AFM arrangement increase from 0.6eV to 1.5eV, the density of states pattern remains intact. In particular, the dispersion of the energy band along all the highly symmetrical directions of the Brillouin zone is moderate and isotropic, demonstrating the strong three-dimensional behavior of the electronic

properties, which is in sharply contrast with the two-dimensional crystallographic structure of $Sr_3Fe_2O_5$.

Compared the three-dimensional electronic/magnetic properties to the two-dimensional crystallographic structure, these features poses an interesting question of how the conundrum could be reconciled. Elucidating this paradox will no doubt lead to an improvement in our understanding of diverse behavior of the transition metal oxides, because of the versatile charge, spin and orbital degrees of freedom.

To reveal the mechanism behind the interesting and puzzling physical properties of $Sr_3Fe_2O_5$, we turn our attention to the spin density distribution of the G-type antiferromagnetic arrangement of $Sr_3Fe_2O_5$, by plotting the special spin-up/down electron density for the energy window of 0.6eV just below E_F as illustrated in Fig.5. The occupied majority/minority spin state of the sixth 3d electron is predominantly of dz^2 orbital character, rather than the doubly degenerate dxz, dyz orbitals. Moreover, such a localization in the real space is accompanied by a flatness of the band levels in the Brillouin zone. Such special electronic state is originated from what is expected by crystal field splitting of D_{4h} point symmetry and molecular orbital energy[18], or the strong hybridization of iron's $3dz^2$ and 4s orbitals, as proposed by M. Takano et. al. in Ref.[5]. Hence, the three-dimensional G-type antiferromagnetic configuration could be explained on the basis of the superexchange coupling and the special localization and orientation of electronic/spin charge in real space. On one hand, according to the Goodenough-Kanamori-Anderson (GKA) rules,[20] it is well established that the spins of the Fe cations within the yz plane (Fig.1) align antiferromagnetically due to the linear Fe—O—Fe superexchange interactions. On the other hand, the obtained ferro-orbital order pattern induces the antiferromagnetic coupling along the x axis between the interplanes, which is in nice accordance with the Kugel-Khomskii Model.[21] To sum up, we address the origin of such fantastic and puzzling physical properties of $Sr_3Fe_2O_5$, and find that it might be associated with the dz^2 orbital ordering of the minority-spin 3d electron.This accounts for the modest G-type antiferromagnetic configuration, in turn, the corresponding three-dimensional electronic properties.

Conclusions

In conclusion, we have investigated the electronic and magnetic properties of $Sr_3Fe_2O_5$, an unusual square-planar coordination around the high-spin Fe^{2+} spin-ladder iron oxide. The obtained results demonstrated that the G-type antiferromagnetic configuration is the ground state, which is in excellent agreement with the experimental neutron powder diffraction and Mössbauer spectroscopy measurements and the existing theoretical reports, despite of the slightly larger calculated magnetic moments. The conundrum, the two-dimensional square lattice exhibits the modest three-dimensional electronic and magnetic properties could be understood through the dz^2 orbital ordering of the sixth minority 3d electron, on the basis of the superexchange interactions and the ferro-orbital ordering pattern. The special localization and orientation of electronic/spin charge in real space is the key factor to understand the structural stability and electronic, magnetic properties of the materials.

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Table 1. Total energies and magnetic moments of the atmoic sites calculated for the ferromagnetic, A-type antiferromagnetic and G-type antiferromagnetic configurations of $Sr_3Fe_2O_5$. The energies are given in units of eV per f.u. with respect to those of the ground state (G-type AFM). The magnetic moments are given in units of Bohr magneton (μ_B).

		FM		A-AFM		G-AFM	
Total energy	GGA(U=0.0eV)	0.095eV/a.u.		0.098eV/a.u.		0.0eV/a.u.	
	GGA+U(U=4.0eV)	0.08718eV/a.u.		0.03773eV/a.u.		0.0eV/a.u.	
Magnetic moment		Fe	O	Fe	O	Fe	O
	GGA(U=0.0eV)	3.19	0.09-0.17	±3.36	±0.11-±0.19	±3.30	±0.10
	GGA+U(U=4.0eV)	3.57	0.08-0.12	±3.55	±0.07-±0.11	±3.54	±0.07
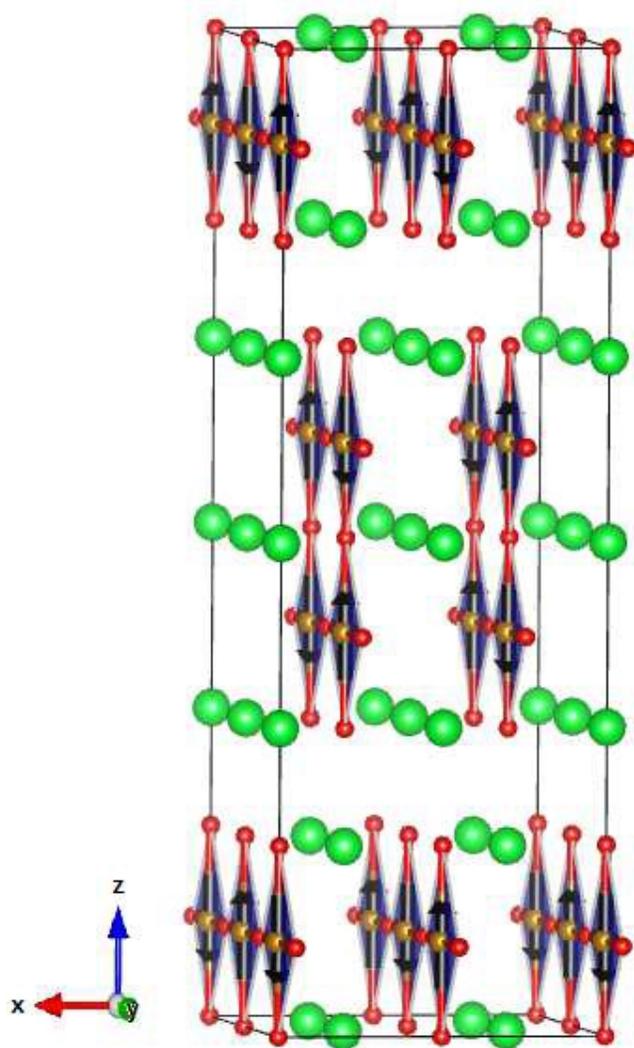
Figure 1. (Color online) The spin structure of $Sr_3Fe_2O_5$ below T_N. Green (big), red (small) spheres represent Sr and O atoms, respectively. The arrows indicate direction of the moment on the iron ions.
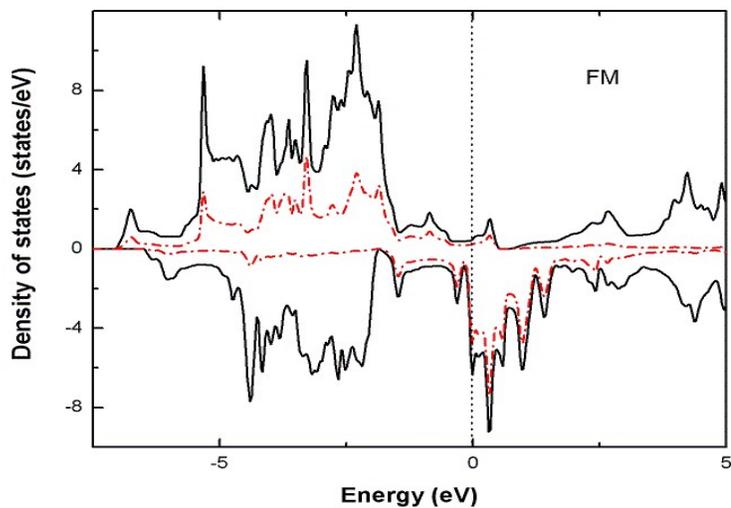
Figure 2. (Color online) The total (black solid line) and partial density of states of Fe (red dash dotted line) for ferromagnetic configuration of $Sr_3Fe_2O_5$ obtained via the GGA calculations.
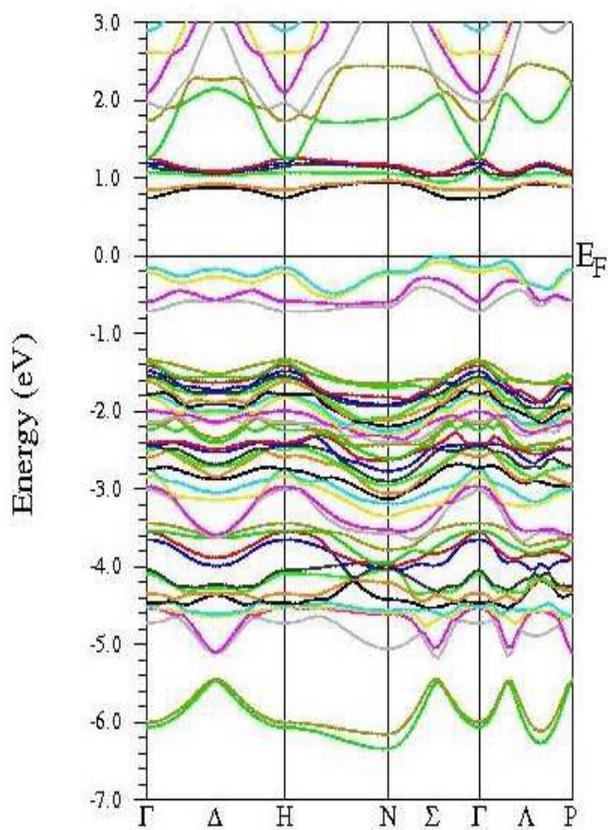
Figure 3. (Color online) The band structure for G-type antiferromagnetic configuration of $Sr_3Fe_2O_5$, obtained via the GGA calculations. The Fermi level, E_F, is set to be 0eV.
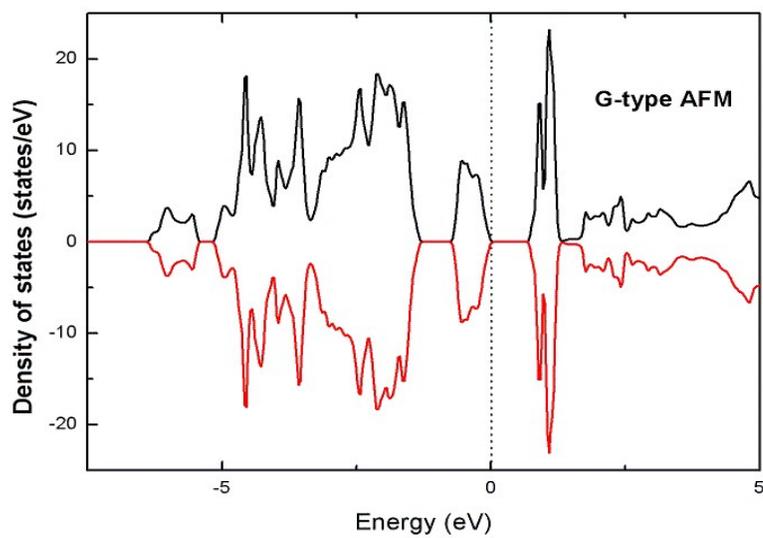
Figure 4.(Color online) The total density of states for the G-type antiferromagnetic configuration of $Sr_3Fe_2O_5$ obtained via the GGA calculations.
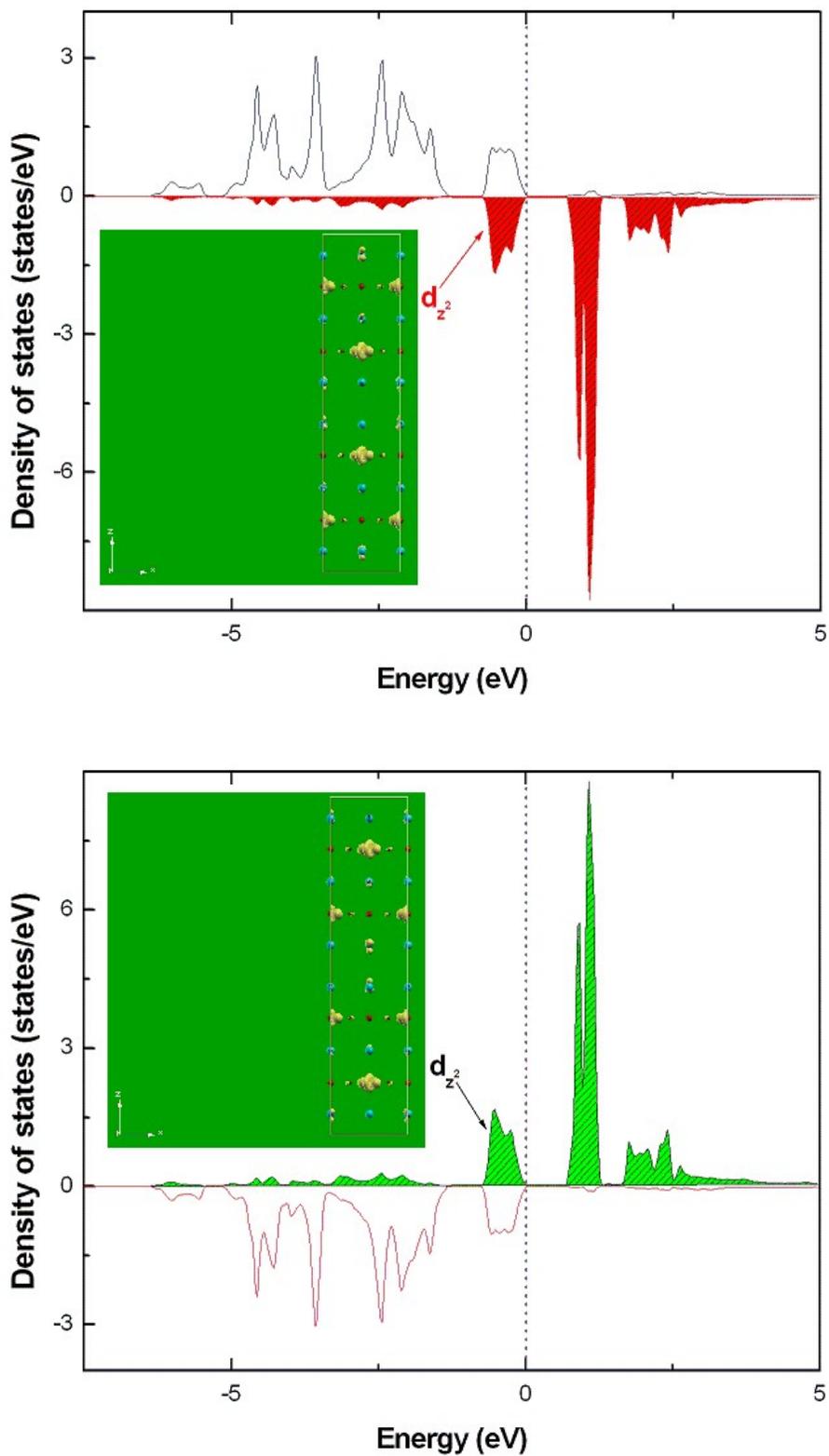
Figure 5. (Color online) The partial spin density of states for spin-up(left)/spin-down(right) Fe atom of the G-type antiferromagnetic configuration of $Sr_3Fe_2O_5$, obtained via the GGA

calculations. Isosurface of dz^2 orbital for spin-up(left)/spin-down(right) Fe d states centered at Fe site in G-type antiferromagnetic configuration $Sr_3Fe_2O_5$ (inset).