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First-principles study of electronic structure and magnetic properties of $Sr_3Fe_2O_5$ oxide*

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We investigate the electronic structure and magnetic properties of layered compound $Sr_3Fe_2O_5$ based on first-principles calculations in the framework of density functional theory with GGA+U method. Under high pressure, the ladder-type layered structure of $Sr_3Fe_2O_5$ is transformed into the infinite layered structure accompanied by a transition from G-type anti-ferromagnetic (AFM) insulator to ferromagnetic (FM) metal and a spin transition from $S = 2$ to $S = 1$. We reproduce these transformations in our calculations and give a clear physical interpretation.

Keywords: $Sr_3Fe_2O_5$, first-principles calculation, electronic structure, magnetism

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1. Introduction

In recent years, people have used some unconventional methods such as high-pressure or low-temperature topology technology to prepare some novel oxides with special structures and properties.[1–4] A typical example is Dion–Jacobson type layered perovskite oxide, such as $RbLaNb_2O_7$.[5–7] In addition, theoretically predicted oxides with a square layered crystal structure have also been synthesized, such as $CaCuO_2$[8,9] $SrCuO_2$,[10] $BaCuO_2$[11] $LaNiO_2$,[12] and $SrFeO_2$.[13] A more special one is the new oxide $SrFeO_2$ with infinite layered crystal structure prepared by Tsujimoto's team under low temperature ($\sim$ 400 K) conditions using perovskite $SrFeO_3$ and reducing substance CaH_2. The infinite layered structure is composed of two-dimensional FeO_2 layers with corner-sharing FeO_4 squares separated by Sr^{2+} ions, and this quasi-two-dimensional structure has the same crystal structure with the high-temperature superconducting matrix $SrCuO_2$.[14–16] $SrFeO_2$ shows G-type antiferromagnetic (AFM) order. Under high external pressure, it exhibits a spin transition from the high-spin state $S = 2$ to the intermediate-spin state $S = 1$, almost simultaneously accompanied by an AFM–FM transition and a insulator–metal transition.[13] Subsequently, Liis Seinberg and María Retuerto *et al.* studied the crystal structure and magnetism of the compound $SrFe_{1-x}M_xO_2$ (M = Co, Mn) by synchrotron x-ray diffraction, neutron diffraction, and Mossbaur spectrometer. $SrFe_{1-x}M_xO_2$ (M = Co, Mn) can maintain the same layered crystal structure as $SrFeO_2$ when Fe site doping is less than 30%.[17,18] Fabio Denies Romero *et al.* synthesized the compound $SrFe_{0.5}Ru_{0.5}O_2$[19] which is isostructural with $SrFeO_2$, and they found that the layered structure can be kept unchanged just for compounds with 1:1 mixture of iron and ruthenium on the B-cation site.

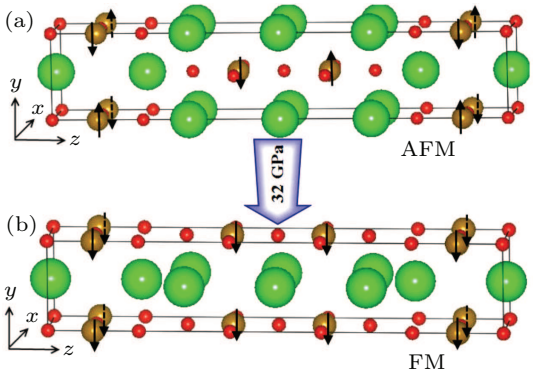


Fig. 1. (a) The structure of $Sr_3Fe_2O_5$ under ambient pressure, and (b) the structure of $Sr_3Fe_2O_5$ under high pressure, the blue balls represent Sr atoms, the red balls represent O atoms, and the brown balls represent Fe atoms. Arrows indicate the spin orientations of Fe ions.

Recently, Yamamoto *et al.* studied the special layered compound $Sr_3Fe_2O_5$,[20,21] which has a ladder-type layered structure under ambient pressure. As shown in Fig. 1(a), it has *Immm* space group symmetry (No. 71) and the lattice constants are $a = 3.51685(5)$ Å, $b = 3.95405(7)$ Å, and $c = 20.91727(36)$ Å. $Sr_3Fe_2O_5$ has an anti-ferromagnetic (AFM) structure and the Fe ion has a high spin state $S = 2$ under the ambient pressure. The ladder-type layered structure transforms to an infinite layered structure under high pressure, as shown in Fig. 1(b), and its symmetry group becomes *Ammm*. Further increasing pressure also induces a transition from antiferromagnetic (AFM) structure to ferromagnetic (FM) structure, accompanied by a spin transition from the high-spin state $S = 2$ to the intermediate-spin state of $S = 1$.[21,22] In order to better understand this compound, in this paper, we use first-principles calculations to study the electromagnetic structure

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and magnetism of $Sr_3Fe_2O_5$ under the ambient pressure and high pressure.

2. Calculation

We used the PWSCF program in the QUANTUM ESPRESSO calculation package to perform first-principles calculations.[23] Generalized gradient approximation plus Coulomb repulsive energy (GGA+U) method (super soft pseudo potential is used in the calculation)[24,25] is used in our calculation. When calculating the total energy and the density of state, we used a unit cell of 20 atoms. In the calculation, the G-type AFM (the nearest neighbor iron ions have the opposite spin direction) and the FM (the nearest neighbor iron ions have the same spin direction) structures are considered. The plane wave cut-off energy was set to be 400 eV, and a grid of 8 8 2 was taken for the Brillouin zone. These calculation parameters ensured that our calculation error is controlled within 1 meV for each atom. The U was set to be 4eV under the ambient pressure and 0 under high pressure.

3. Results and discussion

Firstly, we calculated the electronic structure and magnetic properties of $Sr_3Fe_2O_5$ under the ambient pressure. The results show that the ground state of the compound is a G-type AFM structure with a magnetic moment of $3.6\mu_B$ for Fe ion, which is consistent with the experimental result.[20,21] For GGA+U calculations, we found that the compound remained the G-type AFM state when U varied from 2 eV to 5 eV under the ambient pressure and for matching the experimental spin moment we chose the $U = 4$ eV. Figure 2 shows the total density of states for $Sr_3Fe_2O_5$, the density of states of d orbitals and sp orbitals for Fe, and the density of states of sp orbitals for O. It can be seen that the compound is an insulator under the ambient pressure. The iron 3d orbital has a larger exchange splitting, which is larger than the crystal field splitting, therefore the Fe ion has a high spin state $S = 2$, which is the same as $SrFeO_2$. The different lowest energy orbitals $d_{x^2-y^2}$ and d_{z^2} for ladder-type layered compound $Sr_3Fe_2O_5$ and infinite layered compound $SrFeO_2$ are due to different choice of z axis. The electronic structure of $Sr_3Fe_2O_5$ can also be qualitatively explained by the ionic model and the hybridization effects between the 3d orbital of Fe ion and the 2p orbital of O. The two layers in $Sr_3Fe_2O_5$ alternate in the z direction, similar to a ladder-type structure. According to crystal field theory, the degeneracy of 3d orbitals is lifted due to the ligands. The orbital splitting diagram for square-planar coordination can be derived from the octahedral diagram.[26] The electronic difference between ladder-type layered compound $Sr_3Fe_2O_5$ and the infinite layered compound $SrFeO_2$ that the lowest energy orbital in the infinite layered structure is d_{z^2}, and the lowest energy orbital in the ladder-type layered structure is $d_{x^2-y^2}$. This is because the six-coordinated Fe ion of the corresponding perovskite $SrFeO_3$ loses two oxygen atoms in the z direction to form $SrFeO_2$, which reduces the energy of the d_{z^2} orbital, while the Fe ion in $Sr_3Fe_2O_5$ has two fewer oxygen atoms in the y direction, resulting in reduction of $d_{x^2-y^2}$ orbital energy. It can be seen from Fig. 2(c) that there is a strong coupling between the 4s orbital and the $d_{x^2-y^2}$ orbital of Fe ion, which further reduces the energy of the $d_{x^2-y^2}$ orbital. In the ladder-type structure, the order of increasing energy of 3d orbitals for Fe ion is $d_{z^2} < d_{xz} < d_{xy} < d_{yz} < d_{x^2-y^2}$. According to the molecular orbital theory, the bonding state has the property of a ligand, and its energy ordering is different or completely opposite to that of the crystal field. The anti-bonding state has the properties of transition metal ions and the ordering properties of the crystal field energy levels. The density of states (Fig. 2) are obviously consistent with the results predicted by the crystal field theory and molecular orbital theory. We find that the anti-bonding state orbital appears in the range of -4 eV to 0 eV and the energy of the $d_{x^2-y^2}$ orbital is the lowest. The electronic structure is $(d_{x^2-y^2})^1(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{z^2})^1$ for the up-spin electron, and $(d_{x^2-y^2})^1(d_{yz})^0(d_{xy})^0(d_{xz})^0(d_{z^2})^0$ for the down-spin electron. It can be seen that the down-spin electrons on the d^6 orbital of the Fe ion occupy the $d_{x^2-y^2}$ orbital instead of occupying the d_{z^2} orbital like as $SrFeO_2$. Therefore, the total electronic structure of the 3d orbital of Fe ion in $Sr_3Fe_2O_5$ is $(d_{x^2-y^2})^2(d_{yz})^1(d_{xz})^1(d_{xy})^1(d_{z^2})^1$.

The G-type AFM state of $Sr_3Fe_2O_5$ under ambient pressure comes from AFM exchange interactions. According to the Fe 3d electronic configuration $(d_{x^2-y^2})^2(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{z^2})^1$, we see that the exchange interaction is due to the d_{xy}, d_{xz}, d_{yz}, d_{z^2} orbitals of two adjacent Fe ions, while the full occupied $d_{x^2-y^2}$ orbitals do not form the exchange interaction. The unpaired electrons on the two d_{xy} orbitals along the x direction form anti-ferromagnetic coupling through the Pπ bond, and the unpaired electrons on the two adjacent d_{xz}, d_{yz}, d_{z^2} orbitals along the z direction form anti-ferromagnetic coupling with the weaker π bond. If the unpaired electrons on adjacent orbitals form an anti-ferromagnetic coupling, the electrons can be delocalized over the M–O–M (or M–M) unit, thus lowering the kinetic energy. On the contrary, if a ferromagnetic coupling is formed, this delocalization is forbidden by Pauli exclusion principles, therefore, the energy is more costed. In the same way, the exchange coupling of d_{yz} and d_{xy} orbitals along the y direction is also an anti-ferromagnetic. Therefore, the system forms a G-type anti-ferromagnetic structure, which is consistent with the G-K principle.[27]

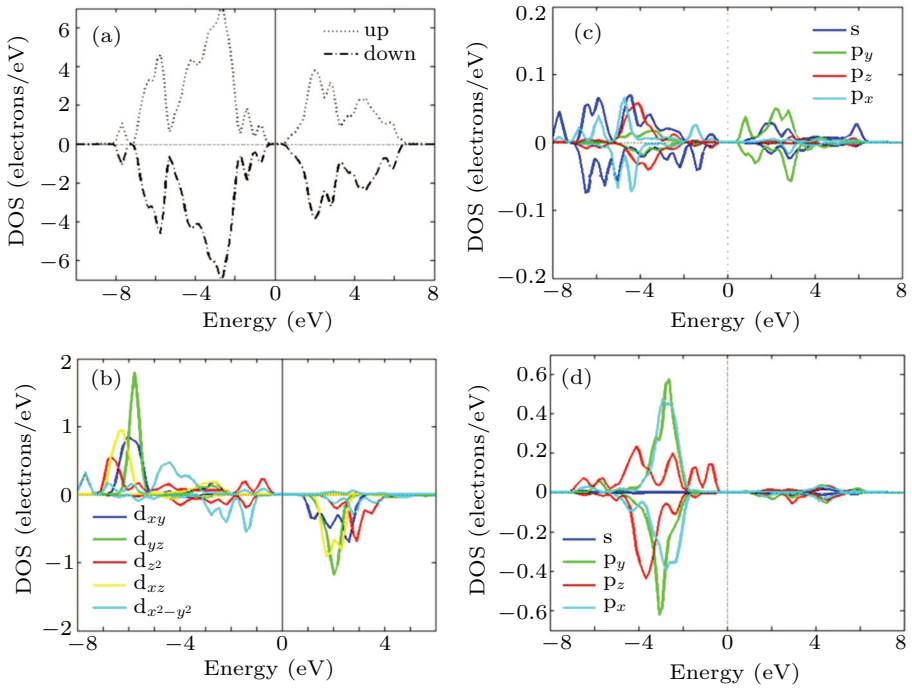


Fig. 2. (a) Total density of states (DOS), (b) density of states of d orbital for Fe^{2+}, (c) density of states of sp orbital for Fe^{2+}, and (d) density of states of sp orbital for O^{2-} under ambient pressure.

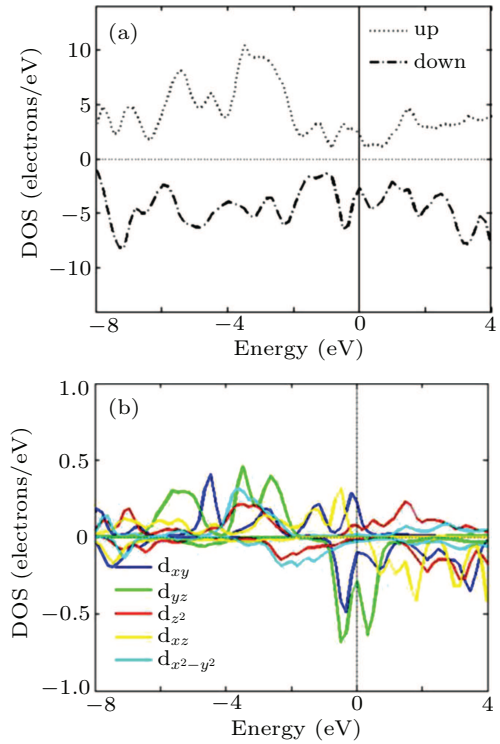


Fig. 3. (a) Total density of states (DOS) and (b) density of states of d orbital for Fe^{2+} under high pressure.

Experimental results show that the ladder-type layered structure of $Sr_3Fe_2O_5$ becomes an infinite layered structure under the external pressure around 32 GPa. A step block of the compound changes from the position (0.5 0.5 0.5) to the position (0 0.5 0.5), but still maintains the four-coordinated layered structure of Fe–O, and the corresponding space group changes from *Immm* to *Ammm*,[22] as shown in Fig. 1. We calculated the electronic structure and magnetic structure of the infinite layered compound $Sr_3Fe_2O_5$, and the results show that the ground state of the compound is a FM state, the magnetic moment of Fe ions is $2.2\mu_B$, and the density of states (Fig. 3) show that the compound is a conductor. These are consistent with the experimental results.[20,21]

It can be seen from Fig. 3(b) that the electronic structure $(d_{x^2-y^2})^2(d_{yz})^1(d_{xy})^1(d_{xz})^1(d_{z^2})^1$ under ambient pressure no longer exists. Under high pressure, the electronic structure can be approximately written as $(d_{x^2-y^2})^2(d_{yz}d_{xz})^3(d_{xy})^1(d_{z^2})^0$ (ignoring the fractional part). According to the electron occupation, the intralayer exchange effect between adjacent unoccupied d_{z^2} orbitals disappears. The interaction between adjacent d_{xy} orbitals still maintains the original anti-ferromagnetic coupling along the x and y directions. However, under high pressure, the interactions between adjacent $d_{xz}d_{yz}$ orbitals are FM in the x, y, and z directions. Along the x and y directions, the AFM interaction of the d_{xy} orbital competes with the FM interaction of the d_{xz} and d_{yz} orbitals, and the FM interaction is exceeded. Therefore, the compound exhibits a FM structure.

4. Conclusions

We performed first-principles calculations based on the generalized gradient approximation of the density functional theory plus Coulomb repulsive energy U (DFT+U), and studied the magnetic and electronic structure of the ladder-type layered compound $Sr_3Fe_2O_5$ under ambient pressure and high pressure. The electronic structure of the 3d orbital for Fe ion under ambient pressure is: $(d_{x^2-y^2})^2(d_{yz})^1(d_{xz})^1(d_{xy})^1(d_{z^2})^1$. The ladder-type layered

structure changes to an infinite layered structure when pressurized, that is, one of the stepped blocks changes from (0.5 0.5 0.5) position to (0 0.5 0.5) position, but still maintains the Fe–O four-coordinated layered structure. Further pressure changes the G-type AFM state to the FM state. We explained the magnetic state according to the G-K rule. We found the spin transition from the $S = 2$ to $S = 1$ under high pressure. These results well accounted for the experimental finding.

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