Origin of the Structural and Magnetic Anomaly of the Layered Compound SrFeO$_2$:
A Density Functional Investigation

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The structural and magnetic anomaly of the layered compound SrFeO$_2$ were examined by first principles density functional calculations and Monte Carlo simulations. The down-spin Fe 3d electron occupies the $d_z^2$ level rather than the degenerate ($d_{xz}$, $d_{yz}$) levels, which explains the absence of Jahn-Teller instability, the easy ab-plane magnetic anisotropy and the observed three-dimensional (0.5, 0.5, 0.5) antiferromagnetic order. Monte Carlo simulations show that the strong inter-layer spin exchange is essential for the high Néel temperature.

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Perovskite oxides have attracted considerable interest due to their extensive applications in a number of technological areas. Among them, SrFeO$_{3-x}$ and its related iron perovskite oxides exhibit fast oxygen transport and high electron conductivity even at low temperatures $^{[1-4]}$. It had previously been believed that the end member phases for these compounds are the orthorhombic brownmillerite SrFeO$_{2.5}$ ($x = 0.5$) and the cubic perovskite SrFeO$_3$ ($x = 0$). Very recently, the range of $x$ was extended to $x = 1$ by Tsujimoto et al., who discovered that SrFeO$_2$ has planar FeO$_2$ layers made up of corner-sharing FeO$_4$ squares with high-spin Fe$^{2+}$ ($d^6$) ions, separated by Sr$^{2+}$ ions $^{[5]}$.

SrFeO$_2$ exhibits interesting and apparently puzzling physical properties $^{[6]}$. First, if the lone down-spin electron of a high-spin Fe$^{2+}$ ($d^6$) ion at square-planar site occupies the degenerate ($d_{xz}, d_{yz}$) orbitals, as expected by the crystal field theory $^{[6]}$, SrFeO$_2$ should be subject to orbital ordering or Jahn-Teller distortion when the temperature is lowered $^{[6]}$. However, SrFeO$_2$ shows no structural instability and maintains the space group $P4/mmm$ down to 4.2 K $^{[6]}$. Second, SrFeO$_2$ displays a three-dimensional (3D) antiferromagnetic (AFM) order with a very high Néel temperature ($T_N = 473$ K) $^{[7]}$, which is even higher than that ($\sim 200$ K) of FeO with a 3D structure. Such a high 3D AFM ordering temperature in a layered system is remarkable and unexpected, because $T_N$ usually decreases drastically when the dimensionality decreases. Third, the powder neutron diffraction study shows that the magnetic moments are perpendicular to the $c$-axis (the local $z$-axis) $^{[8]}$, which is not consistent with the occupation of the ($d_{xz}, d_{yz}$) orbitals with three electrons $^{[9]}$.

To probe the causes for these apparently anomalous structural and magnetic properties in SrFeO$_2$, we examined the magnetic properties of SrFeO$_2$ by performing density functional theory (DFT) band structure and total energy calculations to evaluate its spin exchange interactions and performing Monte Carlo (MC) simulations to calculate the Néel temperature using the extracted spin exchange parameters. We show that the down-spin Fe 3d electron in SrFeO$_2$ occupies the nondegenerate $d_{z^2}$ level rather than the degenerate ($d_{xz}, d_{yz}$) levels, which explains the absence of Jahn-Teller instability, the occurrence of the easy $ab$-plane magnetic anisotropy as well as the strongly AFM coupling between the inter-layer and

\begin{table}[h]
\centering
\begin{tabular}{cccc}
\hline
 & $J_1$ & $J_2$ & $J_3$ & $J_4$ \\
\hline
SrFeO$_2$ (expt.) & 7.04 & 2.18 & 0.43 & -0.23 \\
SrFeO$_2$ (opt.) & 7.91 & 2.29 & 0.30 & -0.30 \\
CaFeO$_2$ (opt.) & 8.90 & 3.24 & 0.35 & -0.45 \\
BaFeO$_2$ (opt.) & 5.81 & 1.34 & -0.29 & -0.16 \\
\hline
\end{tabular}
\caption{Spin exchange parameters (in meV) from the LDA+U calculations. The spin exchange paths $J_1, J_2, J_3,$ and $J_4$ are defined in Fig. 1. Positive (negative) values indicate that the spin exchange interactions are AFM (FM). For SrFeO$_2$, both the experimental (expt.) $^{[6]}$ and the optimized (opt.) crystal structures were used for the calculations. For CaFeO$_2$ and BaFeO$_2$, the optimized crystal structures were used.}
\end{table}

FIG. 1: (color online) Perspective view of the tetragonal structure of SrFeO$_2$. The large, middle, and small spheres represent the Sr, Fe, and O ions, respectively. The spin exchange paths $J_1, J_2, J_3,$ and $J_4$ are also indicated.
SrFeO$_2$ adopts the P4/mmm space group with $a = 3.985$ Å and $c = 3.458$ Å at 10 K [6]. As shown in Fig. 1, the FeO$_2$ layers separated by Sr$^{2+}$ ions are stacked along the $c$ axis. As a first step to discuss the magnetic properties of SrFeO$_2$, the electronic structure of SrFeO$_2$ calculated for its ferromagnetic (FM) state [$\mathbf{q} = (0.0, 0.0, 0.0)$] is presented in Fig. 2. The band dispersion relations of Fig. 2(a) show that the FM state is metallic because the top portion of the up-spin valence bands (an O $p$ and Fe $d$ state) is above the bottom portion of the up-spin conduction bands (a Fe $p$ and Sr $d$ state) at $R$ (0.5, 0.5, 0.5) point. The plots of the density of states (DOS) and the partial DOS (PDOS) in Fig. 2(b) reveal that there is a strong hybridization between the O $2p$ and Fe $3d$ states in the valence bands. Further analysis shows that the largest coupling occur at R-point between Fe $d_{z^2}$ orbital and O $p_z$ orbitals. When the PDOS plots of the Fe and O atoms in Fig. 2(b) are compared with those of the Fe $3d$ states in Fig. 2(c), it is seen that the up-spin bands have Fe $3d$ energy levels below the O $2p$ state, whereas the down-spin Fe $3d$ bands is above. This reflects the large exchange splitting of the Fe $3d$ levels, which is responsible for the high-spin state of the Fe$^{2+}$ ion. It is important to note from Fig. 2 that the occupied down-spin state has the $d_{z^2}$ character, not the doubly-degenerate ($d_{x^2}$, $d_{y^2}$) character as expected from crystal field theory for the $D_{4h}$ point symmetry [6, 8]. This is because in the layered structure, the energy of the $d_{z^2}$ state is significantly decreased due to the reduced Coloumb repulsion. Because the $d_{z^2}$ character is non-degenerate, no Jahn-Teller type distortion is expected for SrFeO$_2$, as found experimentally [6].

To determine the magnetic ground state and discuss the magnetic properties of SrFeO$_2$, we considered four more ordered spin states besides the FM state, namely, the AF1 state with $\mathbf{q} = (0.5, 0.5, 0.5)$, the AF2 state with $\mathbf{q} = (0.0, 0.0, 0.5)$, the AF3 state with $\mathbf{q} = (0.5, 0.5, 0.0)$, and the AF4 state with $\mathbf{q} = (0.5, 0.0, 0.5)$. The experimentally observed AFM structure is AF1. Our LDA+U calculations show that all the AFM states are lower in energy than the FM state, and the AF1 state is the ground state, in good agreement with experiment [6]. These results are consistent with the facts that in the high-spin $(d^6)$ configuration, there is no partially occupied d state to stabilize the FM phase [6]. The total DOS and PDOS plots presented in Fig. 3 show that SrFeO$_2$ in the AF1 phase has a band gap as expected for this magnetic semiconductor. Comparing to the electronic band structures of the FM phase, the band structure of the AF1 phase exhibit an important difference; overall, the $d$ bands are narrower in the AF1 than in the FM state. In particular, the up-spin $d_{x^2-y^2}$ band has a significantly narrower bandwidth in the AF1 state. This observation is readily accounted for by considering a spin-1/2 square-net lattice with one magnetic orbital per site, the hopping integral $t$ between adjacent sites and the on-site repulsion $U$. For the FM arrangement of the spins, the up-spin (or down-spin) states of adjacent sites are identical in energy and
the interaction energy between them is \( t \), so the widths of the up-spin and down-spin bands are proportional to \( t \). For the AFM arrangement of spins, the up-spin (or down-spin) states of adjacent sites differ in energy by \( U \) and the interaction energy between them is \( t^2/U \), so the widths of the up-spin and down-spin bands are proportional to \( t^2/U \). Since \( t \gg t^2/U \) for usual magnetic solids, the width of the electronic energy band is much wider for the FM state than for the AFM state.

To extract the values of the four spin exchange parameters \( J_1, J_2, J_3 \) and \( J_4 \) (see Fig. 11), we map the relative energies of the five ordered spin states (i.e., FM, AF1, AF2, AF3 and AF4) obtained from the LDA+U calculations onto the corresponding energies given by the Heisenberg spin Hamiltonian made up of the four spin exchange parameters. This mapping analysis was carried out as described in ref. [17]. The obtained exchange parameters are summarized in Table I. The intra-layer NN spin exchange \( J_1 \) is quite strong, which is due to the strong 180° Fe-O-Fe superexchange between the \( d_{x^2-y^2} \) orbitals mediated by O \( p_z \) and \( p_y \) orbitals [18, 19]. The inter-layer NN spin exchange \( J_2 \) is strongly AFM and is weaker than \( J_1 \) only by a factor of \( \sim 3 \). The inter-layer spin exchange \( J_2 \) originates from the direct through-space overlap between the \( d_{xz}/d_{yz} \) orbitals of Fe.

To account for the observed anisotropic magnetic property of SrFeO\(_2\), we carried out LDA+U calculations for the FM state by including spin-orbit coupling (SOC) interactions. These LDA+U+SOC calculations show that the state with the spin moments parallel to the \( ab \)-plane is more stable than the state with the spin moments parallel to the \( c \)-axis by 4 meV/Fe, while the calculated orbital moment is 0.22 \( \mu_B \) for the \( \perp c \) spin arrangement, and 0.01 \( \mu_B \) for the \( || c \) spin arrangement. This easy \( ab \)-plane anisotropy, which is in accord with experiment [1], can be explained by analyzing the SOC Hamiltonian [20]. Since the up-spin and down-spin \( d \) bands are well separated due to the large exchange splitting, one can neglect interactions between the up-spin and down-spin states under the SOC. With \( \theta \) and \( \phi \) as the zenith and azimuth angles of the magnetization in the direction \( n(\theta, \phi) \), the spin-conserving term of the \( \lambda \mathbf{L} \cdot \mathbf{S} \) operator (\( \lambda < 0 \) for Fe\(^{2+} \)) is given by [20, 21]

\[
\lambda \hat{S}_n (\hat{L}_z \cos \theta + \frac{1}{2} \hat{L}_+ e^{-i\phi} \sin \theta + \frac{1}{2} \hat{L}_- e^{i\phi} \sin \theta) \tag{1}
\]

If SrFeO\(_2\) were to have one down-spin electron in the doubly-degenerate level (\( d_{xz}, d_{yz} \)), it should have uniaxial magnetic properties with the spin moments parallel to the \( c \)-axis (\( \theta = 0^\circ \)) according to the degenerate perturbation theory [10]. Our calculations show that, for the down-spin part, the highest occupied Fe 3d level is \( d_{xz} \) while the lowest unoccupied Fe 3d level is (\( d_{xz}, d_{yz} \)). When the spin lies in the \( ab \)-plane (\( \theta = 90^\circ \)), the mixing between \( d_{xz} \) and \( d_{xz}, d_{yz} \) due to the raising and lowering operators is the largest. Thus, nondegenerate perturbation theory shows that SrFeO\(_2\) has an easy \( ab \)-plane anisotropy with a relative large orbital moment.

To explain why the layered compound SrFeO\(_2\) has a very high Néel temperature (473 K), we perform MC simulations for a \( 12 \times 12 \times 12 \) supercell based on the classical spin Hamiltonian:

\[
H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i DS_{i z}^2 \tag{2}
\]

where the spin exchange parameters \( J_{ij} \) are those defined in Fig. 11 \( D = 1 \) meV (i.e., \( DS_{i z}^2 = 4D = 4 \) meV) is the spin anisotropy parameter, and \( S = 2 \). To obtain \( T_N \), we first calculate the specific heat \( C = (\langle E^2 \rangle - \langle E \rangle^2) / T^2 \).
after the system reaches equilibrium at a given temperature \((T)\). Then \(T_N\) can be obtained by locating the peak position in the \(C(T)\) vs. \(T\) plot, shown in Fig. 3. For SrFeO\(_2\) the calculated \(T_N\) is 354 K, which is in reasonable agreement with the experimental value of 473 K. We should note that a smaller \(U\) value leads to larger exchange parameters \(J_1\) since \(J_1 \propto \rho^2/U\), and \(J_2\) changes a little, thus \(T_N\) will be higher. For instance, if \(U = 4.0\), then \(J_1 = 8.68\,\text{meV}\) and \(J_2 = 2.23\,\text{meV}\), resulting in \(T_N = 453\,\text{K}\).

It was shown that large magnetic anisotropy energy can stabilize long-range magnetic order in a one-dimensional (1D) monatomic Co chains [22]. To determine how \(T_N\) is affected by the different spin-exchange parameters and the spin anisotropy, we performed three additional simulations; one with the spin anisotropy \(D\) neglected, one with the inter-layer exchange parameters \((J_d\) and \(J_1)\) neglected, and one with both the inter-layer spin-exchange parameters \((J_d\) and \(J_1)\) and the spin anisotropy \(D\) neglected. The resulting \(C(T)\) vs. \(T\) plots are presented in Fig. 4. As can be seen, when \(D\) is disregarded, \(T_N\) is only slightly lower (347 K). If only the inter-layer exchange parameters are neglected, the \(C(T)\) vs. \(T\) plot shows a broad peak at 220 K. A broad peak occurs at 208 K if both the inter-layer exchange parameters and the spin anisotropy are neglected. At any nonzero temperature, a 1D or 2D isotropic Heisenberg model with finite-range exchange interaction can be neither FM nor AFM [23]. Thus, the broad peak in the \(C(T)\) vs. \(T\) plot, obtained when the inter-layer exchange interactions are neglected, indicates the presence of short-range order. Our MC simulations indicate that the inter-layer interactions are primarily responsible for the high \(T_N\) of SrFeO\(_2\).

It should be noted that CaFeO\(_{3-x}\) and BaFeO\(_{3-x}\) have structures and properties similar to those of SrFeO\(_{3-x}\). Thus, it is of interest to consider the structural and magnetic properties of hypothetical CaFeO\(_2\) and BaFeO\(_2\) assuming that they are isostructural with SrFeO\(_2\). For this purpose, the structures of MFeO\(_2\) (\(M = \text{Sr, Ca, Ba}\)) were optimized by performing LDA+U calculations for the AF1 state. The optimized lattice constants \(a\) and \(c\) for SrFeO\(_2\) are 3.92 Å and 3.40 Å, respectively, which are in good agreement with experiment. The calculated lattice constants are \(a = 3.86\,\text{Å}\) and \(c = 3.12\,\text{Å}\) for CaFeO\(_2\), and \(a = 3.98\,\text{Å}\) and \(c = 3.79\,\text{Å}\) for BaFeO\(_2\). The trend in the lattice constants is consistent with the ionic radii of Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\). The exchange parameters calculated for the optimized MFeO\(_2\) (\(M = \text{Sr, Ca, Ba}\)) structures are listed in Table 4. All these compounds should have the AF1 state as the ground state since the spin exchange interactions are dominated by AFM \(J_1\) and \(J_2\).

Among MFeO\(_2\) (\(M = \text{Ca, Sr, Ba}\)), CaFeO\(_2\) has the largest \(J_1\) and \(J_2\) values, while BaFeO\(_2\) has the smallest \(J_1\) and \(J_2\) values. This trend reflects the fact that the strengths of these interactions increase with decreasing the lattice constants. Thus, CaFeO\(_2\) is predicted to have a higher \(T_N\) than does SrFeO\(_2\).

In summary, SrFeO\(_2\) has no Jahn-Teller instability because the occupied down-spin d-level is \(d_z^2\). The Néel temperature of SrFeO\(_2\) is high because the intra-layer NN spin exchange is strong while the inter-layer NN spin exchange is substantial. The in-plane magnetic anisotropy of SrFeO\(_2\) arises from the SOC-induced interaction between the \(d_{xz}\) and \((d_{yz}, d_{yz})\) states.

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