Understanding the Unique Structural and Electronic Properties of SrFeO$_2$

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We report a first-principles study of SrFeO$_2$, an infinite-layer oxide with Fe atoms in a perfect square-planar coordination down to essentially 0 K. Our results reveal this striking behavior relies on the double occupation of the 3$d_{z^2}$ orbitals of high-spin Fe$^{2+}$. Such an electronic state results from the hybridization of iron’s 3$d_{z^2}$ and 4$s$ orbitals, which enables a large reduction of the intra-atomic exchange splitting of the $z^2$ electrons. The generality of the phenomenon is discussed.

Tsujimoto et al. have recently reported on SrFeO$_2$, a novel material that exhibits a wealth of surprising properties. Most interestingly, SrFeO$_2$ presents Fe$^{2+}$ ions in a square-planar coordination, forming unprecedented infinite FeO$_2$ layers that remain undistorted down to at least 4.2 K (see Fig. 1). In addition, it undergoes a transition to an anti-ferromagnetic (AFM) state at $T_N=473$ K, a surprisingly high temperature given the seemingly two-dimensional nature of the compound. The physical origin of these features, which also appear in similar compounds studied more recently, remains unknown. Here we report a first-principles study, based on the “LDA+U” approach to Density Functional Theory (DFT), that confirms the peculiar behavior of SrFeO$_2$ and reveals its electronic origin.

**Basic properties.**—We begin by showing that our DFT methods, described in $^4$, reproduce the main results reported in Ref. $^1$. To investigate the stability of the highly-symmetric phase of SrFeO$_2$, we first determined the structural parameters that minimize the energy of the crystal under the constraints that the P4/mmm space group is preserved and the magnetic order is the AFM group is preserved and the magnetic order is the AFM ground state. Further, the Fe$^{2+}$ ions are in a high-spin configuration with a magnetic moment of about 3.6 $\mu_B$, in agreement with experiment. We also computed the exchange parameters of a model Hamiltonian $H = 1/2 \sum_{ij} J_{ij} S_i S_j$, with $|S|=2$; the results are given in Table I following the notation defined in Fig. 1. We found that the in-plane interactions are considerably stronger than those along the c direction; yet, the material is far from being two-dimensional from the magnetic point of view. Indeed, a simple (admittedly rough) mean field estimate based on our computed $J$’s renders a Néel temperature above 1000 K, and the energy scale for the magnetic couplings between FeO$_2$ planes, which we can estimate as $S^2(2J_1 - 8J_3)$, is found to be around 260 K.

![FIG. 1: (color online) 16-atom SrFeO$_2$ cell considered in most of our calculations. The ground-state magnetic structure is sketched; the lattice and exchange constants are defined.](image)

**TABLE I: Computed properties of the P4/mmm phase of SrFeO$_2$ (measured lattice parameters in parenthesis).**

| Structure: $a=b=4.01$ Å (3.99 Å); $c=3.42$ Å (3.47 Å) |
| Elastic constants (GPa): |
| $B=125$, $C_{11}=C_{22}=317$, $C_{33}=164$, $C_{12}=78$, $C_{13}=C_{23}=51$, $C_{44}=C_{55}=95$, $C_{66}=125$ |

Infra-red active modes (cm$^{-1}$): 159 and 276 ($A_{2g}$); 183, 301, and 531 ($E_u$)

Magnetic couplings (meV): $J_1=1.75$, $J_2=6.58$, $J_3=-0.26$
Thus, our results confirm the three-dimensional character of magnetism in SrFeO$_2$, and are compatible with the relatively high $T_N$ observed. We checked that values of the $U$ parameter within the 3–6 eV range, which is typical for Fe compounds, do not affect this conclusion.

Electronic structure.— Based on their $^{57}$Fe Mössbauer spectroscopy results showing a temperature-independent quadrupole splitting of about 1 mm/s, and in accordance with the usual picture from crystal-field theory, the authors of Ref. 1 assumed the $(xz, yz)^3(xy)^1(z^2)^1(x^2 − y^2)^1$ electronic configuration for the 3$d$ electrons of Fe$^{2+}$. However, in such conditions a Jahn-Teller distortion is expected to lift the degeneracy associated to the $(xz, yz)$ orbitals, at odds with the experimental results. Our calculations readily clarify this question. As shown in Fig. 2, the DFT electronic structure of SrFeO$_2$ does not agree with the one proposed in Ref. 1. We found that the sixth 3$d$ electron of high-spin Fe$^{2+}$ goes to the $z^2$ minority-spin orbital. At variance with the $(xz, yz)$ 3$d$ orbitals of Fe, the $z^2$ state is not degenerate with any other and, thus, its occupancy cannot cause any symmetry-lowering distortion that reduces the energy. Hence, this electronic configuration is compatible with the stability of the P4/mmm phase. Further, we also checked the calculation results are compatible with the Mössbauer data. We address this point below, after having discussed the electronic structure of SrFeO$_2$ in more detail.

Discussion.— Our DFT calculations provide us with a coherent picture of SrFeO$_2$, accounting for the structural and magnetic properties of the material. Yet, that picture relies on a result, the double occupation of the $z^2$ orbitals of Fe$^{2+}$, which may seem counterintuitive based on the common knowledge in molecular and solid-state chemistry. We will thus focus on this key issue: Why are the $z^2$ orbitals of Fe$^{2+}$ doubly occupied in SrFeO$_2$?

Let us start with a word of caution: Many apparently satisfying answers to the above question do not resist a rigorous analysis. For example, it may be tempting to postulate that the double occupation of the $z^2$ orbitals is determined by the fact that, as compared with the other 3$d$'s, they suffer from negligible Coulomb repulsion because they find no O$^{2−}$ ions along the direction perpendicular to the FeO$_2$ plane. This kind of argument has been invoked in several occasions and is supported by extended Hückel calculations we have performed. However, it is severely flawed: It implies that the $z^2$ orbitals should be the lowest-lying ones for both the majority- and minority-spin electrons of high-spin Fe$^{2+}$, which is in evident disagreement with the results in Fig. 2. Ultimately, the failure of this argument suggests that an independent-electron picture is not adequate to explain the electronic structure of SrFeO$_2$.

To address the above question, we proceeded by eliminating possibilities in a systematic way. Our key observations are the following. As already discussed, our calculations show SrFeO$_2$ should be regarded as a 3D crystal, and one can thus conjecture that interactions along the $c$ direction, particularly between neighboring Fe atoms, might play a role in stabilizing the doubly-occupied $z^2$ orbital. In order to investigate this possibility, we considered the limit case in which such interactions are totally suppressed. More precisely, we studied an idealized system composed of an isolated FeO$_2$ layer, fixing the number of electrons in the calculation so as to keep the Fe and O atoms in the ionization states they have in SrFeO$_2$. We denote this virtual 2D crystal as “Fe$^{2+}(O^{2−})_2 + bg”$, where “bg” refers to the homogeneous charge-compensating background introduced by the Sr atoms in the SrFeO$_2$ layer.

FIG. 2: (color online) Panel (a): Computed electronic structure of SrFeO$_2$ around the Fermi energy, which is set to 0 eV. The partial Density of States (pDOS) corresponding to the 3$d$ and 4$s$ orbitals of a particular Fe atom is indicated. The dashed line depicts the total DOS divided by a factor of four. Panels (b) and (c): Representative Γ-point eigenstates with dominating $z^2$ character, indicated with arrows in the band structure of panel (a). The plotted isosurfaces correspond to the indicated values of the squared modulus of the wave function.
to stabilize the material. Interestingly, the partial Density of States (pDOS) obtained for "Fe$^{2+}(O^{2-})_2 + bg" is essentially identical to the result for SrFeO$_2$ in Fig. 2, indicating that out-of-plane interactions play no role in determining the electronic structure of SrFeO$_2$. Recognizing that the significance of the results with a charge background may be questionable, we also run calculations for SrFeO$_2$ with a significantly increased $c$ lattice constant and ratified this conclusion.

Next, we turned our attention to the interactions within the FeO$_2$ planes. We ran calculations for slightly increased and decreased values of the $a=b$ lattice constants, and found that the most significant changes in the electronic structure pertain to the $x^2-y^2$ electrons of iron. This is not surprising, as these are the electrons forming $\sigma$ bonds with the oxygen atoms. In what regards the $z^2$ electrons, we observed no effect worth noting, which clearly indicates that the Fe–O interactions are not the key to understand the double occupation of the $z^2$ orbitals. In particular, these results rule out the possibility that $\pi$-donor interactions with the oxo ligands, which would destabilize the $xz$ and $yz$ orbitals, are at the origin of the double occupation of $z^2$. These conclusions are ratified by a standard Fe–O overlap population analysis. We also checked that the electronic structure of SrFeO$_2$ is essentially independent of the spin arrangement, and we can thus neglect inter-atomic exchange effects in this discussion.

We are thus led to conclude the double occupation of the $z^2$ orbitals must be determined by some sort of intra-atomic mechanism associated to the iron atoms. Indeed, this is the correct perspective to understand the electronic structure of SrFeO$_2$. Let us note a well-known effect that appears to be critically important in this compound: As a result of the tetragonal point symmetry at the Fe site, the $z^2$ orbital is fully symmetric and can hybridize with the formally-empty Fe-4$s$ state. In fact, the pDOS of Fig. 1 clearly shows such a hybridization occurs, being particularly important for the majority spin. As illustrated in panels (b) and (c) of Fig. 1 the majority-spin wave functions with a significant $4s$–$3d_{2z}$ mixing are characterized by (i) a shrinking of the $z^2$-like central ring, and (ii) a deformation, and greater relative weight, of the lobes extending out-of-plane. In contrast, the minority-spin electrons display a nearly pure $z^2$ character. Note also that the very different structure of the $z^2$ pDOS for the majority (roughly, triple-peaked) and minority (single-peaked) spins is consistent with this different mixing with the $4s$ orbitals. Of course, this peculiar behaviour reflects a mechanism by which the crystal minimizes its energy: Having different spin-up and spin-down $z^2$-like electrons results in a reduction of their Coulomb repulsion and, accordingly, of the corresponding intra-atomic exchange splitting $\Delta$. Indeed, the relatively small $\Delta$ associated to the $z^2$ electrons is obvious from Fig. 2. For a given orbital type, $\Delta$ can be estimated as the difference between the centers of mass of the spin-up and spin-down bands; our calculations indicate that $\Delta$ is about 2.9 eV for the $z^2$ orbitals, while the other 3$d$'s present $\Delta$'s of more than 6 eV.

We have thus identified the mechanism that allows SrFeO$_2$ to reduce its energy by adopting an electronic configuration with doubly-occupied $z^2$ orbitals. Interestingly, for this mechanism to be active we only need to have the appropriate local symmetry at the Fe site, which implies that the newly discovered effect might be quite general. To check this, we performed the following computational experiment: We considered the 3D crystal "Fe$^{2+}(O^{2-})_3 + bg" sketched in Fig. 3 fixing the number of electrons in order to retain the Fe-3$d^6$ configuration. For simplicity, we assumed a ferromagnetic order, which we checked has no effect on the electronic configuration of Fe. We fixed the in-plane lattice constant at the SrFeO$_2$ value, and monitored the evolution of different electronic solutions as the cubic crystal (d$_{FeO'}$=2 Å) undergoes a tetragonal distortion. As shown in Fig. 3 only one electronic solution is found in the cubic case: the minority-spin 3$d$ electron occupies a combination of $t_{2g}$ orbitals (from which the $xy$ orbital is selected as soon as the tetragonal distortion occurs), closing the gap of the crystal. In contrast, for the largest values of d$_{FeO'}$ considered, several solutions occur, the ground state corresponding to doubly-occupied $z^2$ orbitals. Interestingly, the solution with doubly-occupied $z^2$ already exists at d$_{FeO'}$=2.14 Å; yet, the "$xy$-to-$z^2$" crossover only occurs at d$_{FeO'}$=2.50 Å. These results show a mere symmetry breaking will not cause the double occupation of the $z^2$ orbitals; rather, a relatively large tetragonal distortion, which results in both a more anisotropic environment for the Fe atom and a reduction of the Coulomb repulsion for the $z^2$ orbitals, is required. Finally, we also checked
that changes in the in-plane lattice constant have a minor effect in the \(xy\)-to-\(z^2\) crossover.

It is not easy to estimate the universality of this mechanism for the double occupation of the \(z^2\) orbitals. It may seem surprising, for example, that such an electronic solution is not found in molecules with Fe\(^{2+}\) centers. However, after reviewing the literature for some well-known cases \(^{11}\), we have the impression that the electronic structure of iron is often conditioned by the nature of the ligands or by a reduced atomic symmetry that precedes any electronic effect associated to the metal atom itself. This suggests such systems may not be appropriate to look for effects like the one discussed here. As for crystalline materials, we only know of one candidate to present this kind of effect: the mineral gillespite (BaFeSi\(_2\)O\(_{10}\)), which contains Fe\(^{3+}\) ions in a square-planar coordination and displaying a high-spin configuration with doubly-occupied \(z^2\) orbitals.\(^{3}\) An appealing possibility, though, would be to synthesize other compounds of the SrFeO\(_2\) family. Indeed, we found that crystals like RbCoO\(_2\) and YFeO\(_2\) would present a similar pattern of electronic levels with doubly-occupied \(z^2\) orbitals. More precisely, our calculations predict RbCoO\(_2\) and YFeO\(_2\) to display a Co-3\(d^9\) high-spin configuration with a doubly-occupied \(z^2\); thus, this material might remain in the high-symmetry P4/mmm phase down to 0 K, exactly as SrFeO\(_2\). On the other hand, YFeO\(_2\) exhibits a Fe-3\(d^7\) high-spin configuration where, in addition to having a doubly-occupied \(z^2\), the last 3\(d\) electron goes to a \((xz, yz)\) state that closes the band gap; hence, this crystal should undergo a Jahn-Teller distortion.

Finally, let us discuss the compatibility between the value of the quadrupole splitting (QS) obtained from \(^{57}\)Fe Mössbauer spectroscopy, which is about 1 mm/s, and the double-occupation of the \(z^2\) orbitals, which is expected to result in QS values of 2–3 mm/s. We should begin by noting that SrFeO\(_2\) is not the only compound exhibiting this seemingly contradictory behaviour. Indeed, the Fe\(^{2+}\) atoms in the above mentioned gillespite have been reported to display QS values below 0.6 mm/s in the 80–650 K temperature range \(^{12}\). As for SrFeO\(_2\), we computed the electric field gradient at the Fe site and the corresponding QS, obtaining a value of about 0.8 mm/s. We also checked that varying \(U\) between 0 and 6 eV renders QS results in the 0.6–0.9 mm/s range, the greater values corresponding to the smaller \(U\)’s. This clearly shows that having an electronic structure with doubly occupied \(z^2\) orbitals is not incompatible with the relatively small QS values measured. As to the mechanism that causes such a reduction of the observed QS with respect to its expected value, two possibilities can be mentioned: (i) that the lattice contribution to the QS is comparable to the one coming from the 3\(d\) electrons of iron \(^{12}\), which would lead to a cancelation as their signs are known to be opposite, or (ii) that the splittings associated to iron’s 3\(d\) electrons are unusual in SrFeO\(_2\). Interestingly, our results seem to support the latter possibility: The spread in energy of the majority-spin \(z^2\) and \(x^2−y^2\) electrons (see Fig. \(^2\)) will imply a relatively large spacial spread of the corresponding Wannier functions \(^{13}\), which might result in unusually small quadrupole splittings. However, a detailed analysis of this issue is not trivial and goes beyond the scope of this paper.

**Summary.—** We have used first-principles methods to show that SrFeO\(_2\), an unusual high-spin Fe\(^{2+}\) layered phase recently reported, is free from structural instabilities and exhibits strong magnetic interactions. We find that the hybridization of iron’s 3\(d\) and 4\(s\) orbitals, which results in a large reduction of the intra-atomic exchange splitting associated to the \(z^2\) electrons, is the key feature to understand the structural stability of the material.

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