

Structural and electronic properties of SrFeO₂ from first principles

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We report on a first-principles study of SrFeO₂, an infinite-layer oxide with Fe atoms in a perfect square-planar coordination down to essentially 0 K. Our results reveal that this striking behavior relies on the double occupation of the 3d_{z²} orbitals of high-spin Fe²⁺. Such an electronic state results from electrostatic and hybridization effects, the latter enabling a large reduction in the intra-atomic exchange splitting of the z² electrons.

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I. INTRODUCTION

Tsujimoto *et al.*¹ recently reported on SrFeO₂, an unusual infinite-layer oxide with iron in square-planar coordination. This compound exhibits a number of puzzling structural and physical properties that remain unexplained and are, in fact, apparently incompatible with each other. An illustrative example of the open questions pertaining to SrFeO₂ is the absence of any structural instability in the material down to the lowest temperatures (~ 4.2 K). This behavior is most unexpected since the physical measurements reported by Tsujimoto *et al.* (i.e., their Mössbauer data) suggest that Fe²⁺ is in a high-spin state of the type $(xz, yz)^3(xy)^1(z^2)^1(x^2 - y^2)^1$, which should lead to a Jahn-Teller structural distortion to remove the (xz, yz) degeneracy. Another striking observation pertains to the Néel temperature for the antiferromagnetic phase transition of SrFeO₂, which is remarkably high (473 K) for what seems to be a magnetically two-dimensional (2D) crystal. Taking into account the fundamental interest and the variety of possible applications of SrFeO₂ and related materials displaying similar features,² there is clearly a pressing need for an independent confirmation and physical explanation of all such intriguing properties.

Recently, a first-principles study of SrFeO₂ by Xiang *et al.*³ confirmed the peculiar magnetic properties of the compound and suggested that its surprising behavior may be related to an unusual electronic structure with doubly occupied 3d_{z²} orbitals. In this paper, we go beyond the work of Ref. 3 and fully exploit the first-principles approach to present a comprehensive study of SrFeO₂. Here, in addition to the magnetic properties, we confirm the structural stability of the observed infinite-layer phase of SrFeO₂ down to essentially 0 K. We also resolve the apparent incompatibility between the measured Mössbauer spectrum and the structural and (computed) electronic properties of the compound. Finally, we also report on a systematic study that allows us to identify the physical origin of the peculiar electronic structure of the compound, with doubly occupied 3d_{z²} orbitals of high-spin Fe²⁺, and highlights the importance of intra-atomic exchange effects.

II. METHODOLOGY

We used a spin-polarized generalized gradient approximation⁴ (GGA) to density functional theory (DFT)

as implemented in the code VASP (Ref. 5) and employed the “LDA+*U*” correction of Dudarev *et al.*⁷ for the Fe-3d electrons (we used $U=4$ eV and checked that our qualitative results are already obtained at the GGA level). We employed the projector augmented wave (PAW) method⁶ to represent the ionic cores, solving explicitly for the following electrons: 4s, 4p, and 5s of Sr; 3p, 3d, and 4s of Fe; and 2s and 2p of O. The electronic wave functions were described with a plane-wave basis truncated at 400 eV. Typically, we worked with the 16-atom cell depicted in Fig. 1, which is highly symmetric and compatible with the magnetic ground state of the system, and used a $4 \times 4 \times 4$ grid for Brillouin-zone integrations. These calculation conditions were checked to render accurate results. We also used PWSCF (Ref. 8) and ABINIT,⁹ two different DFT codes, for some of the electronic structure analysis and the electric-field-gradient calculations, respectively. The LDA+*U* schemes implemented in PWSCF (Ref. 10) and ABINIT (Ref. 11) differ in some details from that of Dudarev *et al.*; we have checked that our results do not depend significantly on the specific LDA+*U* used. Wavefunction figures were prepared using the visualization software XCRYSDEN.¹²

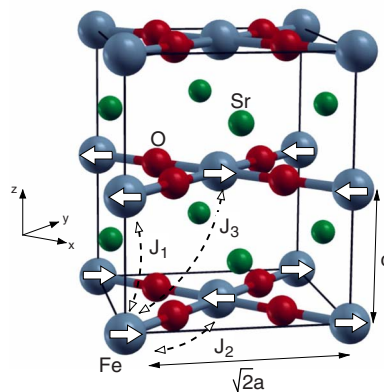


FIG. 1. (Color online) 16-atom SrFeO₂ cell considered in most of our calculations. The ground-state magnetic structure is sketched; the lattice and exchange constants are defined.

TABLE I. Computed properties of the P4/mmm phase of SrFeO₂ (measured lattice parameters in parentheses).

Structure: $a=b=4.01$ Å(3.99 Å); $c=3.42$ Å(3.47 Å)
Elastic constants (GPa):
$B=125$, $C_{11}=C_{22}=317$, $C_{33}=164$, $C_{12}=78$,
$C_{13}=C_{23}=51$, $C_{44}=C_{55}=95$, $C_{66}=125$
Infrared active modes (cm ⁻¹):
159 and 276 (A_{2u}); 183, 301, and 531 (E_u)
Magnetic couplings (meV): $J_1=1.75$, $J_2=6.58$, $J_3=-0.26$

III. BASIC RESULTS

A. Structural stability and magnetic interactions

We begin by showing that our DFT methods reproduce the main results reported in Ref. 1. To investigate the stability of the highly symmetric phase of SrFeO₂, 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 antiferromagnetic (AFM) one found experimentally. Our results, shown in Table I, are in good agreement with the measurements. We then computed the elastic constants and the phonons that are compatible with the cell of Fig. 1. The results, summarized in Table I, indicate that the P4/mmm phase of SrFeO₂ is stable upon symmetry-lowering structural distortions, thus confirming it as the ground state of the material at 0 K. It is worth noting that, while obviously anisotropic, the computed elastic constants and phonon frequencies present values that are acceptable for a three-dimensional (3D) crystal (for SrFeO₃ we obtained $C_{11}=300$ GPa and $C_{12}=140$ GPa), which suggests this infinite-layer phase is robustly (meta-)stable.

We then studied the magnetic interactions in SrFeO₂. We considered all the spin arrangements compatible with the cell in Fig. 1 and confirmed that the experimentally observed AFM pattern (sketched in the figure) is the magnetic ground state. Further, the Fe²⁺ 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 $H=1/2\sum_{ij}J_{ij}S_iS_j$, 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 FeO₂ planes, which we can estimate as $S^2(2J_1-8J_3)$, is found to be around 260 K. Thus, our results confirm the three-dimensional character of magnetism in SrFeO₂ 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.

B. Electronic structure

Based on their ⁵⁷Fe Mössbauer spectroscopy results showing a temperature-independent quadrupole splitting

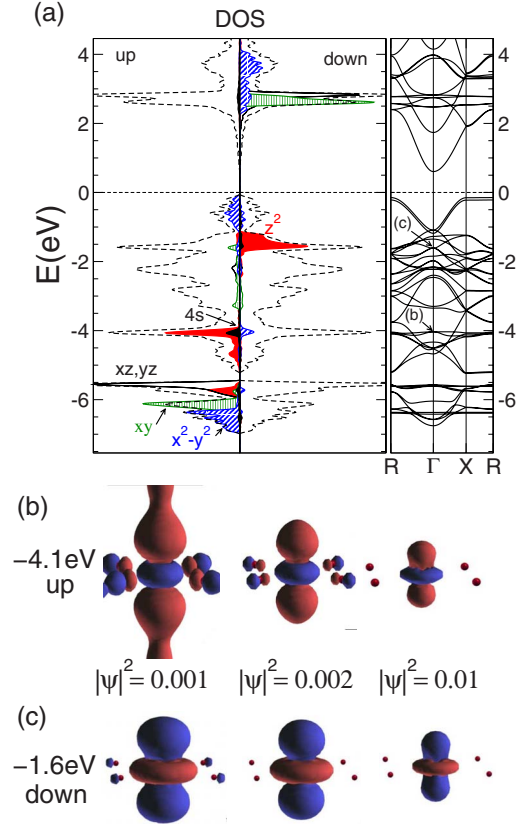


FIG. 2. (Color online) Panel (a): computed electronic structure of SrFeO₂ around the Fermi energy, which is set to 0 eV. The partial density of states corresponding to the 3d and 4s orbitals of a particular Fe atom is indicated. The dashed line depicts the total DOS divided by a factor of four. Panels (b) and (c): representative Γ -point eigenstates with dominating z^2 character indicated by arrows in the band structure of panel (a). The plotted isosurfaces correspond to the indicated values of the squared modulus of the wave function.

(QS) 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 3d electrons of Fe²⁺. However, in such conditions a Jahn-Teller distortion is expected to lift the degeneracy associated with 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 SrFeO₂ does not agree with the one proposed in Ref. 1. We found that the sixth 3d electron of high-spin Fe²⁺ goes to the z^2 minority-spin orbital. At variance with the (xz,yz) 3d 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 that the calculation results are compatible with the Mössbauer data. We address this point below after having discussed the electronic structure of SrFeO₂ in more detail.

IV. DISCUSSION

Our DFT calculations provide us with a coherent picture of SrFeO₂, accounting for the structural and magnetic prop-

erties 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 $3d$'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^{3,13} and is supported by extended Hückel calculations we have performed. However, it is not consistent with our DFT electronic structure: 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 independent-electron effects cannot fully 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 “ $\text{Fe}^{2+}(\text{O}^{2-})_2+\text{bg}$ ”, where “bg” refers to the homogeneous charge-compensating background introduced to stabilize the material. Interestingly, the partial density of states (pDOS) obtained for $\text{Fe}^{2+}(\text{O}^{2-})_2+\text{bg}$ 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 ran 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 $a=b$ lattice constants increased and decreased up to $\pm 10\%$ of their equilibrium values 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 σ bonds with the oxygen atoms. With regard to 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 π -donor interactions with the *oxo ligands*, which would destabilize the xy , 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 interatomic exchange effects in this discussion.

We are thus led to conclude that the double occupation of the z^2 orbitals must involve some sort of *intra-atomic* mechanism associated with 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- $4s$ state. In fact, the pDOS of Fig. 2 clearly shows such a hybridization occurs, being particularly important for the majority spin. As illustrated in panels (b) and (c) of Fig. 2, the majority-spin-wave functions with a significant $4s-3d_{z^2}$ mixing are characterized by (i) a shrinking of the z^2 -like central ring, and (ii) a deformation, as well as 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. Of course, this peculiar behavior 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 in their Coulomb repulsion and, accordingly, in the corresponding intra-atomic exchange splitting Δ . Indeed, the relatively small Δ associated with the z^2 electrons is obvious from Fig. 2. For a given orbital type, Δ can be estimated as the difference between the centers of mass of the spin-up and spin-down bands; our calculations indicate that Δ is about 2.9 eV for the z^2 orbitals, while the other $3d$'s present Δ 's of more than 6 eV.

We have thus identified a mechanism that allows SrFeO_2 to reduce its energy by adopting an electronic configuration with doubly occupied z^2 orbitals. Now we ask ourselves whether this mechanism, which only relies on having the appropriate local symmetry at the Fe site, is sufficient to explain the computed electronic structure. To check this, we performed the following computational experiment: We considered the 3D crystal “ $\text{Fe}^{2+}(\text{O}^{2-})_3+\text{bg}$ ” sketched in Fig. 3, fixing the number of electrons in order to retain the Fe- $3d^6$ 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 in the SrFeO_2 value and monitored the evolution of different electronic solutions¹⁴ as the cubic crystal ($d_{\text{FeO}'}=2 \text{ \AA}$) undergoes a tetragonal distortion. As shown in Fig. 3, only one electronic solution is found in the cubic case: The minority-spin $3d$ 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 $d_{\text{FeO}'}$ 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 $d_{\text{FeO}'}=2.14 \text{ \AA}$; yet, the “ xy -to- z^2 ” crossover only occurs at $d_{\text{FeO}'}=2.50 \text{ \AA}$. These results show a mere symmetry breaking, and the possibility of having $4s-3d_{z^2}$ mixing will not cause the double occupation of the z^2 orbitals. Rather, a relatively large tetragonal distortion, which re-

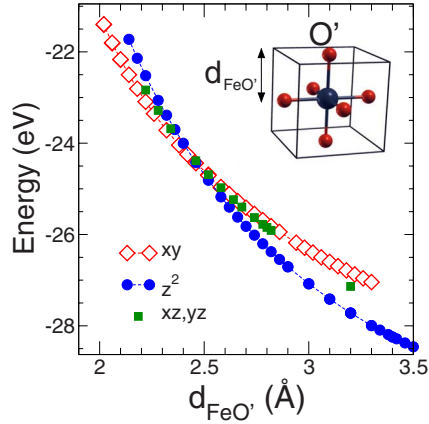


FIG. 3. (Color online) Computed energy of various electronic solutions of the $\text{Fe}^{2+}(\text{O}^{2-})_3+\text{bg}$ virtual system (see text) as a function of the distance $d_{\text{FeO}'}$ between the central Fe atom and the apical oxygens O' .

sults in both a more anisotropic environment for the Fe atom and a reduction in 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 on the xy -to- z^2 crossover.

It is not easy to estimate the universality of these effects. 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,¹⁵ 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 with the metal atom itself. This suggests that such systems may not be appropriate to look for effects such as the one discussed here. As for crystalline materials, we only know of one candidate to present this kind of effect: the mineral gillespite ($\text{BaFeSi}_4\text{O}_{10}$), which contains Fe^{2+} ions in a square-planar coordination and displaying a high-spin configuration with doubly occupied z^2 orbitals.¹³ An appealing possibility, though, would be to synthesize other compounds of the SrFeO_2 family. Indeed, we found that crystals such as RbCoO_2 and YFeO_2 present a similar pattern of electronic levels with doubly occupied z^2 orbitals. More precisely, our calculations predict that RbCoO_2 displays a $\text{Co-}3d^6$ 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 $\text{Fe-}3d^7$ high-spin configuration where, in addition to having a doubly occupied z^2 , the last $3d$ 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 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 behavior. 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.¹⁶ 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, with 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 in 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 $3d$ electrons of iron,¹⁶ which would lead to a cancellation as their signs are known to be opposite or (ii) that the splittings associated with iron's $3d$ 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(a)] will imply a relatively large spatial spread of the corresponding Wannier functions,¹⁷ 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.

V. 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. Our results reveal that this striking behavior relies on the double occupation of the $3d_{z^2}$ orbitals of high-spin Fe^{2+} . Such an electronic state results from electrostatic and hybridization effects, the latter enabling a large reduction in the intra-atomic exchange splitting of the z^2 electrons. Our simulation results also account for a concomitant decrease in the quadrupole splitting that is observed in the Mössbauer spectrum, solving apparent contradictions in the experimental results.

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