

Orbital physics in transition-metal oxides from first-principles



Hua Wu*

Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, China
Collaborative Innovation Center of Advanced Microstructures, Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 2 July 2015

Accepted 7 September 2015

Available online 23 October 2015

Keywords:

Transition-metal oxides

Orbital physics

Magnetism

First principles

ABSTRACT

Transition-metal oxides often possess charge, spin, and orbital degrees of freedom, and they are a platform for many functional materials. It is the interplay among those degrees of freedom which gives rise to the diverse properties, typically associated with the orbital physics. In this article, we will provide an overview of our first-principles studies on the orbital physics in transition-metal oxides, which include (1) orbital ordering in the layered manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ due to an anisotropic crystal field, (2) orbital ordering in the ferromagnetic insulator Cs_2AgF_4 , (3) spin–orbital state transition and varying electronic and magnetic properties in the cobaltate series $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$, and (4) spin–orbit coupling and Ising magnetism in $\text{Ca}_3\text{Co}_2\text{O}_6$, $\text{Ca}_3\text{CoMnO}_6$, and $\text{Sr}_3\text{NiIrO}_6$. Apparently, orbital physics spans 3d–4d–5d transition-metal oxides.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Transition-metal oxides (TMOs) are a great platform for functional materials, and they are a strongly correlated electron system. The charge, spin and orbital states of the TM atoms are often coupled to one another due to their multiple degrees of freedom and the electron correlation. These states are closely related to diverse material properties and functionalities, e.g., charge ordering, orbital ordering, spin-state and magnetic transitions, metal–insulator transition, superconductivity, colossal magnetoresistance, and multiferroicity. It is therefore very important to study those charge–spin–orbital states and their fascinating coupling for modeling and understanding of the abundant properties. This has formed a research stream in condensed matter physics over past decades, and orbital physics has been termed [1,2].

Orbital physics has been extensively studied for 3d TMOs and some 4d ones like ruthenates. For example, LaTiO_3 was studied for its spin dynamics and possible orbital liquid state [3–5]. VO_2 was proposed to be an orbital-assisted metal–insulator transition system where electron correlation and spin–Peierls distortion are both effective [6]. LaMnO_3 is a model system of the e_g orbital ordering. The Verwey transition of Fe_3O_4 (insulator-to-metal transition) is associated with melting of a complex charge–orbital order. LaCoO_3 has a thermally excited spin–orbital state transition,

which may be a low-spin to high-spin type [7]. $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ is an orbitally selective insulator–metal transition system [8,9]. Very recently, research interest has been extended to 5d TMOs, which probably possess a significant spin–orbit coupling and provide an avenue to novel magnetic and electronic properties due to an entangled spin–orbital state [10,11].

In this paper, we will summarize our first-principles studies on the orbital physics. We will address (1) the type of orbital order in the layered manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ and its origin, (2) orbital ordering in the ferromagnetic (FM) insulator Cs_2AgF_4 , (3) spin–orbital state transitions and exotic electronic/magnetic properties of $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$, and (4) spin–orbit coupling and significant Ising magnetism in $\text{Ca}_3\text{Co}_2\text{O}_6$, $\text{Ca}_3\text{CoMnO}_6$, and $\text{Sr}_3\text{NiIrO}_6$. Apparently, orbital physics spans the 3d–4d–5d TMOs and it is quite common.

2. Results and discussion

2.1. Orbital ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

Manganites are well known for their colossal magnetoresistance effect, which arises from a competition between a FM metallic state due to a double exchange, and an antiferromagnetic (AF) insulating state associated with charge–orbital ordering. Layered manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is one of the prototype charge–orbital ordered systems, and the pattern of its orbital ordering was subject to a debate: either the cross-type $x^2 - z^2/y^2 - z^2$ or the rod-like $3x^2 - r^2/3y^2 - r^2$ orbital ordering was proposed. An orbital ordering can have an electronic origin, e.g., via a superexchange interaction of Kugel–Khomskii model [12], or its occurrence is due to a

* Address: Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, China.

E-mail address: wuh@fudan.edu.cn

common Jahn–Teller (JT) distortion, namely, an electron–phonon coupling [13]. Even if an orbital ordering is of an electronic origin, a local lattice distortion (JT like) would always follow. Then, it is not a straightforward task to identify the origin of an orbital order.

Fortunately, normally there is a one-to-one correspondence between the orbital ordering pattern and the local distortion. Taking a transition metal with a half-filled e_g orbital in a TMO_6 octahedron as example (such as Mn^{3+}), the rod-like $3x^2 - r^2$ orbital is stabilized (destabilized) if the octahedron is uniaxially elongated (compressed). Therefore, it seems reasonable that $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ has a cross-type $x^2 - z^2/y^2 - z^2$ orbital order as the manganite has compressed Mn–O bonds which alternate in the MnO_6 octahedra along the y and x directions [14], see Fig. 1(a).

However, it was a surprise that recently we have identified the orbital order to be the rod-like $3x^2 - r^2/3y^2 - r^2$ [15], in sharp contrast to the prediction based on the local lattice distortions. Using the most recent neutron diffraction data [14], our first-principles calculations find that while the $x^2 - z^2$ is not at all an occupied eigen orbital for the nominal Mn^{3+} ion, the $3x^2 - r^2$ is an occupied eigen orbital instead and it has a lower crystal-field level than the $x^2 - z^2$ by 90 meV, see Fig. 1(b). This finding is contrary to the common view that the crystal-field level sequence and orbital state can be determined by the local distortions. Our finding is rationalized by taking into account the fact that a crystal field is a long range effect and in a layered (or chain like) material, anisotropic long-range part of the crystal field (beyond the local Jahn–Teller effect) could play a leading role in determining the level sequence. By referring to the experimental structural data [14], we find that the further neighbors of the Mn^{3+} ion are very different between

the in-plane and the out-of-plane. It is the stronger in-plane attractive interactions [higher valence states ($4+$ vs $2.25+$) and shorter distances ($3.8 \text{ \AA}$ vs $4.4 \text{ \AA}$)], in addition to the local JT effect, which stabilizes the $3x^2 - r^2/3y^2 - r^2$ orbital order, see Fig. 2. This orbital order naturally explains, via the Goodenough–Kanamori–Anderson (GKA) superexchange rules, the experimental AF structure of the CE type. The present orbital order pattern had been confirmed by an X-ray adsorption linear dichroism study [15].

Therefore, this work has demonstrated that the standard way—finding the orbital occupation of JT ions using the local distortion data—can be incorrect. For the layered materials (or more generally, for anisotropic ones), the usually ignored long-range crystal field effect and anisotropic hopping integrals could become crucial in determining the orbital occupation and the orbital order. Indeed, this anisotropic long-range crystal field effect has also been highlighted in other layered or chain-like materials [16], for understanding their intriguing orbital physics.

2.2. Orbital ordering in the ferromagnetic insulator Cs_2AgF_4

It is quite often that 3d TMOs with orbital degeneracy display an orbital ordering associated with lattice distortions (of the Jahn–Teller type). In contrast, 4d or 5d TMOs rarely show this, mainly due to the delocalized character of their 4d or 5d valence electrons. It is therefore a surprise when 4d or 5d TMOs show an orbital order. In this respect, the layered silver fluoride Cs_2AgF_4 was of concern [17]. It has the same K_2NiF_4 structure as the cuprate La_2CuO_4 . While La_2CuO_4 is a well known AF Mott insulator, Cs_2AgF_4 is a FM insulator.

As an itinerant magnetism of the Ag 4d electrons is not the case for this insulator, what is the origin of the FM order? By referring to the orthorhombic structure of Cs_2AgF_4 with the in-plane Ag–F bonds alternately elongated along the x and y axes, one could infer a $y^2 - z^2/x^2 - z^2$ orbital order for the single holes on the Ag^{2+} ions ($4d^9$), simply using the crystal field level diagram. The experimentally observed lattice distortion of the AgF_6 octahedra (here defined as the Ag–F bond length difference of $0.33 \text{ \AA}$) was well reproduced by our density functional calculations [18] (giving the value of $0.30 \text{ \AA}$) within the generalized gradient approximation. This big distortion yields an e_g crystal-field splitting of about 1 eV. The lower $3x^2 - r^2$ orbital is doubly occupied, and the higher $y^2 - z^2$ orbital is singly occupied and its exchange splitting of about 0.5 eV opens an insulating gap. The spin density is plotted in Fig. 3, and the $y^2 - z^2/x^2 - z^2$ orbital order is apparent. As the

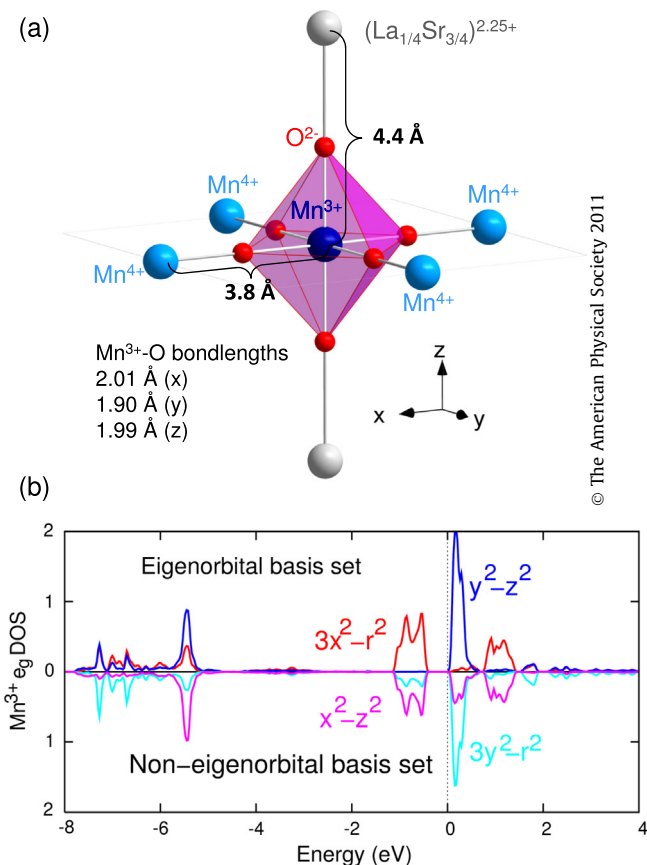


Fig. 1. (a) Local structure of the nominal Mn^{3+} ion in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, and (b) density of states (DOS) of the Mn^{3+} e_g orbitals projected onto the $(3x^2 - r^2, y^2 - z^2)$ basis set or onto $(x^2 - z^2, 3y^2 - r^2)$. Fermi level is set at zero. [Reproduced from Ref. [15]].

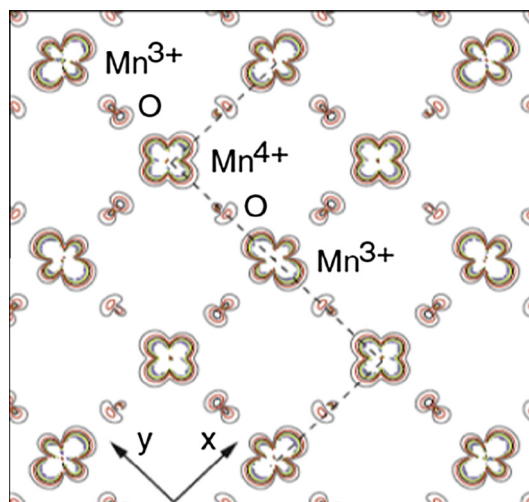
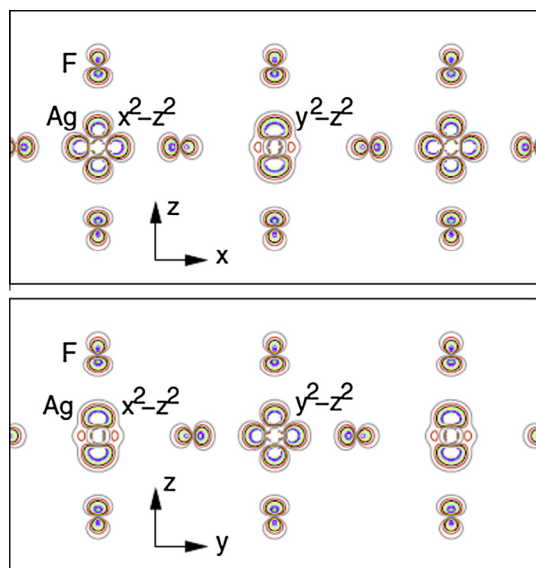


Fig. 2. In-plane orbital ordering pattern in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$.



© The American Physical Society 2007

Fig. 3. The ab -planar $x^2 - y^2/y^2 - z^2$ orbital order in Cs_2AgF_4 viewed from b or a axis. [Reproduced from Ref. [18]].

$y^2 - z^2$ and $x^2 - z^2$ orbitals on two neighboring Ag^{2+} sites are orthogonal, they would mediate a FM superexchange according to the GKA rules. Our calculations find the FM state to be more stable than an AF state by 34 meV/fu. Moreover, we have also tested the tetragonal structure of Cs_2AgF_4 . It would be nearly half metallic in our calculations. However, it turns out to be less stable than the orthorhombic structure by 27 meV/fu, which implies a stability of the orthorhombic phase (and the orbital ordering) above room temperature [17,18].

In a word, Cs_2AgF_4 is stabilized into an insulating orthorhombic phase rather than in a metallic tetragonal structure. The intrinsic lattice distortion in the former is accompanied by the $y^2 - z^2/x^2 - z^2$ orbital order. It is the orbital order which is responsible for the observed FM [17–21]. Therefore, Cs_2AgF_4 is one of the 4d-orbital ordered systems which seem not so common. Some ruthenates are another examples, which display an orbital selective metal–insulator transition in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [8,9] and PbRuO_3 [22], and orbitally driven spin singlet dimerization in two-dimensional spin = 1 $\text{La}_4\text{Ru}_2\text{O}_{10}$ [23–25].

2.3. Spin–orbital state transition in the cobaltate series $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$

The K_2NiF_4 type cobaltate La_2CoO_4 is a Mott insulator, and its AF can readily be understood via the GKA magnetic exchange of the high-spin (HS) Co^{2+} ions ($3d^7$, $t_{2g}^5e_g^2$, $S = 3/2$). The t_{2g} triplet splits into a lower xz/yz doublet and higher xy singlet, mainly due to the elongated out-of-plane Co–O bonds associated with the strain effect in this layered material.

The other ending material in this series, Sr_2CoO_4 , is a FM metal [26], and it may even be a half metal [27,28]. The constituent Co^{4+} ion is in an unusual high valence state, and then its enhanced nuclear attractive interaction lowers the on-site 3d electron level (or its chemical potential) and reduces its ionic size. As a result, there is a strong Co–O covalence effect, and the real ground state of Sr_2CoO_4 is rather $\text{Co}^{3+}\bar{L}$ than Co^{4+} [29], where $\bar{L}$ stands for a 2p hole on the ligand oxygens. It has been found, both experimentally [26] and theoretically [27–29], that the formal Co^{4+} ion is in an intermediate-spin (IS) state ($t_{2g}^4e_g^1$, $S = 3/2$), or equivalently, a HS ($t_{2g}^4e_g^2$, $S = 2$) Co^{3+} plus an antiparallel ($S = -1/2$) ligand hole. Then the itinerant O 2p holes establish the FM metallic state via the p–d exchange [26–29].

Actually, upon hole doping via a partial Sr substitution for La, $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ display abundant properties, see below. Here we study $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, LaSrCoO_4 , and $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$, using first-principles calculations, focusing on identification of their spin–orbital states and on understanding of their varying electronic and magnetic properties.

2.3.1. HS Co^{2+} /LS Co^{3+} and spin blockade in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$

In comparison with the Sr-doped layered manganite and nickelate, $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is highly insulating with an in-plane resistivity being higher than the manganite and nickelate by three orders of magnitude. Moreover, $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ has a high charge ordering temperature of about 750 K but a pretty low spin ordering temperature of about 30 K [30]. With a half doping in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, Co^{3+} ions are introduced. In contrast to the Co^{2+} ions which are normally in a HS state ($t_{2g}^5e_g^2$, $S = 3/2$), Co^{3+} ions ($3d^6$) can be in different spin states: a low-spin state (LS, t_{2g}^6 , $S = 0$), a high-spin state (HS, $t_{2g}^4e_g^2$, $S = 2$), or even an intermediate-spin state (IS, $t_{2g}^5e_g^1$, $S = 1$) [7,31,32]. The different spin states arise mainly from a competition between the Hund exchange and the crystal field, and atomic multiplet, p–d covalency, and band formation are also involved in determining the spin states. Normally, a strong crystal field favors a LS state, a weak crystal field stabilizes a HS state of the Hund rules, and strong p–d covalency and band formation could induce an IS state. Actually, the spin states and/or a spin-state transition are a subtle issue, and they could readily be affected or tuned by doping, pressure, and temperature. As different spin states have different magnetic moments and orbital occupations, their exchange couplings vary and correspondingly the electronic structures are also remarkably different. Therefore, cobaltates often display abundant magnetic and electronic properties.

We have studied $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ in different combinations of the $\text{Co}^{2+}/\text{Co}^{3+}$ spin states, using constrained local-density approximation plus Hubbard U (LDA + U) calculations [33,34]. We initialize the corresponding occupation matrix and the orbitally polarized potential for each spin state, then run constrained LDA + U calculations, in a self-consistent way and including a full electronic relaxation, to achieve each object solution. This approach allows us to obtain several multiplet solutions in a same framework, and hence it is useful to determine the ground-state solution. Based on those calculations, we have found that $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ has the HS Co^{2+} and LS Co^{3+} ground state, see Fig. 4. The HS Co^{2+} has occupied e_g antibonding orbitals and thus a long Co^{2+} –O bond. In contrast, for the LS Co^{3+} , the e_g antibonding orbitals are formally unoccupied, and thus the Co^{3+} –O bond becomes short. As a result, the long Co–O bonds for the HS Co^{2+} ions and short ones for the LS Co^{3+} ions (or equivalently, large radius of HS Co^{2+} and small one of LS Co^{3+}) apparently release the lattice strain, if they arrange into a checkerboard pattern. Then this qualitatively accounts for the high $\text{Co}^{2+}/\text{Co}^{3+}$ charge ordering temperature. However, the introduction of the nonmagnetic LS Co^{3+} ions dilutes the magnetic Co^{2+} lattice, and the superexchange coupling between the HS Co^{2+} ions becomes much weaker with the long Co^{2+} – Co^{2+} distance of about 8 Å via the intermediate –O– Co^{3+} –O– bonds. It is therefore not surprising that $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ has a low spin ordering temperature. Moreover, in the presence of HS Co^{2+} and LS Co^{3+} , the charge fluctuation seems to have no involvement of Hubbard U, as the initial state and the final state have the same $\text{Co}^{2+}/\text{Co}^{3+}$ charge state. But note that considering an e_g electron hopping from HS Co^{2+} to LS Co^{3+} , the final state would be a combination of IS Co^{3+} and IS Co^{2+} . Then an energy cost associated with the change of the spin states is estimated to be the Hund exchange J_H . This would suppress the electron hopping, causing a so-called spin blockade [35]. This spin blockade and the charge ordering both bring about the electron localization, and therefore the resistivity of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is extremely high.

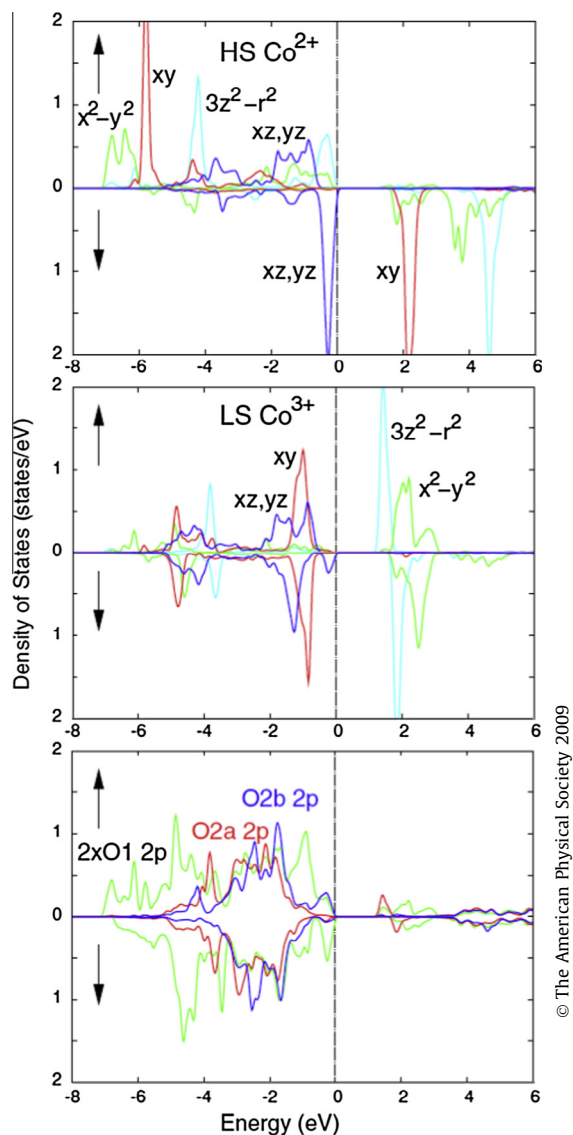


Fig. 4. DOS of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ in the HS Co^{2+} /LS- Co^{3+} ground state. [Reproduced from Ref. [32]].

Apparently, it is the HS Co^{2+} /LS- Co^{3+} charge–spin–orbital ordering which consistently explains the exotic electronic and magnetic properties of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$. Our finding confirms the X-ray absorption spectroscopic study by Chang et al. [31].

2.3.2. Mixed HS–LS Co^{3+} state in LaSrCoO_4

Now we turn to LaSrCoO_4 , which have Co^{3+} ions. The distorted CoO_6 octahedron therein has a large elongation along the c -axis due to the strain effect in this layered system. Then the large e_g crystal-field splitting and strong in-plane $\text{pd}\sigma$ hybridization could stabilize an IS state ($t_{2g}^5e_g^1$, $S = 1$). In our constrained LDA + U calculations, we indeed find this solution. This IS state is FM half-metallic with the fully spin-polarized $x^2 - y^2$ conduction band [36], see Fig. 5. However, experimentally, LaSrCoO_4 is found to be a paramagnetic insulator [37,38]. Therefore, the possible IS state is questionable.

Then we test different spin states and their possible combinations, using the constrained LDA + U calculations. With the converged results for those spin–orbital multiplets, we can sort out the ground state, which turns out to be the HS–LS mixed state [36,39], see Fig. 6. Hubbard U is involved for a charge fluctuation

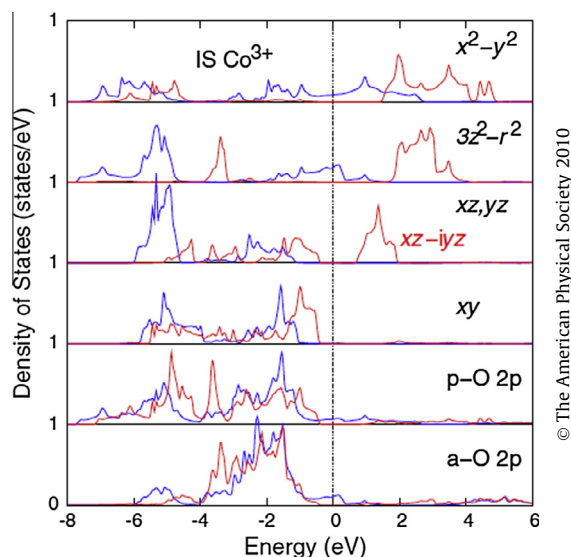


Fig. 5. Metastable half metallic solution of the IS LaSrCoO_4 . [Reproduced from Ref. [36]].

on the Co^{3+} sublattice, which gives rise to a Mott insulating behavior. Although the HS Co^{3+} ions are magnetic, they are well separated by the ligand oxygens and the nonmagnetic LS Co^{3+} . As a result, those magnetic Co^{3+} ions are only weakly coupled. Moreover, the common +3 charge state of the Co ions, albeit in different spin states, would disfavor a long-range ordering of the HS Co^{3+} and LS Co^{3+} ions. Hence their disorder would further inhibit the magnetism. This could well be the reason why a HS–LS ordered Co^{3+} sublattice has not been observed experimentally, and instead a homogeneous Co^{3+} sublattice has been assumed.

In summary, LaSrCoO_4 is not in an expected IS (FM half-metallic) state associated with the large tetragonal distortion, but in a HS–LS mixed state. This HS–LS mixing is responsible for the paramagnetic insulating behavior of LaSrCoO_4 , and it also well explains the experimentally observed effective magnetic moments and the optical spectral features [36,38].

2.3.3. Spin-state tuning metal–insulator transition in $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$

With further Sr doping, we arrive at $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$. This cobaltate has half Co^{3+} and half Co^{4+} . As seen above, the ending material Sr_2CoO_4 has the IS Co^{4+} ions and it is a FM metal with $T_C \sim 250$ K [26]. We could also understand $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$ as a half electron doping into Sr_2CoO_4 via a partial La substitution for Sr. An interesting experimental finding [37,38] was that $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$ is also FM, with a slight lower T_C than Sr_2CoO_4 , but it is insulating, with its resistivity being several orders of magnitude higher than Sr_2CoO_4 . Then a funny question arises—why $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$ is FM but insulating, or why $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ ($x = 2-1.5$) has a metal–insulator transition but sustains the FM order.

It is quite common that a FM material is metallic but an AF one is insulating. Therefore, either a FM insulator or an AF metal seems to be an exception and would be of interest. Starting from the IS Sr_2CoO_4 , the half electron doping via $\text{La} \rightarrow \text{Sr}$ substitution introduces Co^{3+} . As Co^{3+} has a bigger ionic size than Co^{4+} , the longer Co^{3+} –O bonds yield a weaker crystal field at the Co^{3+} sites. Then the Co^{3+} shall be in a higher spin state than the IS Co^{4+} , that is, a possible HS Co^{3+} state, see Fig. 7. If $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_4$ is now in a HS Co^{3+} /IS- Co^{4+} state, it would be exactly a double exchange model system—one e_g electron hops from HS Co^{3+} to IS Co^{4+} , and the initial and the final states are the same, see Fig. 7(a) and (b). The kinetic energy gain stabilizes a FM coupling between the formal

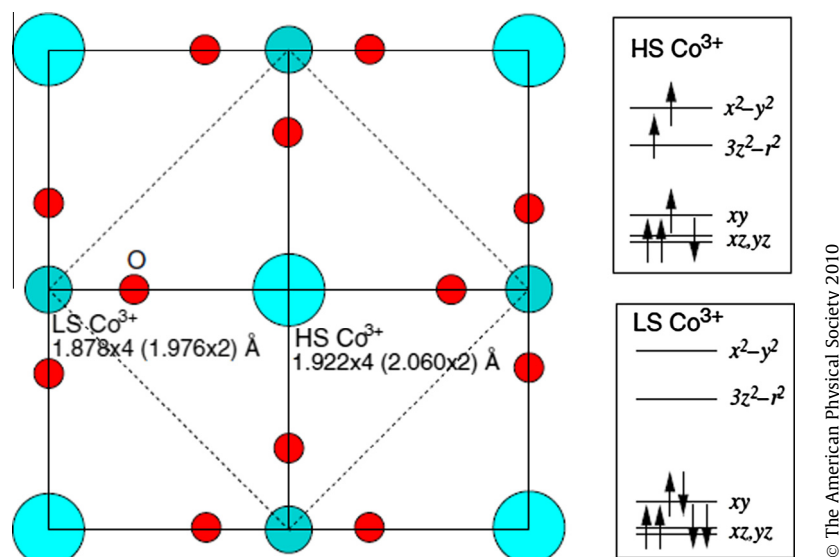


Fig. 6. A possible short-range HS-LS spin order in LaSrCoO₄. [Reproduced from Ref. [36]].

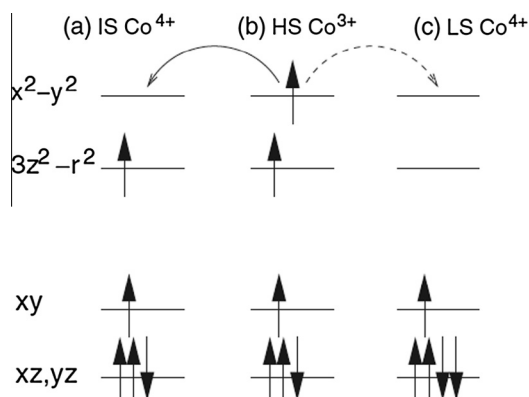


Fig. 7. Schematic level diagrams of (a) IS Co⁴⁺, (b) HS Co³⁺, and (c) LS Co⁴⁺. (a) and (b) would yield a FM half-metallic state for La_{0.5}Sr_{1.5}CoO₄. (b) and (c) would give a FM insulating solution. [Reproduced from Ref. [28]].

HS Co³⁺ and IS Co⁴⁺, and the resulting half-metallic solution would bring about a charge homogeneity and a uniform spin state [28]. While this HS-Co³⁺/IS-Co⁴⁺ solution could explain the FM of La_{0.5}Sr_{1.5}CoO₄, the predicted metallicity contradicts the observed insulating behavior.

Then we think of a possible spin-state transition. As the introduced higher spin state Co³⁺ ions have a larger ionic size than the Co⁴⁺ ions, they could bring about a chemical pressure on the Co⁴⁺ ions. As a result, the Co⁴⁺-O bonds would shrink and the enhanced crystal field would force the Co⁴⁺ ions to transit into a smaller size LS state, see Fig. 7(c). First, the HS Co³⁺/LS Co⁴⁺ help to release the lattice strain and favor their ordered arrangement. Second, an electron hopping from HS Co³⁺ to the LS Co⁴⁺ is suppressed via the spin-blockade mechanism [31,35], as the final state has different spin states than the initial state. The energy cost of Hund exchange, albeit no Hubbard U involved, and the Co³⁺/Co⁴⁺ charge ordering both inhibit the charge transfer, thus giving rise to the insulating behavior of La_{0.5}Sr_{1.5}CoO₄. Third, as the formal LS Co⁴⁺ ion has a spin = 1/2 and is still magnetic, the superexchange mechanism, via a virtual e_g electron hopping forth and back in the HS-Co³⁺/O/LS-Co⁴⁺ channel, results in a FM coupling between the HS Co³⁺ and LS Co⁴⁺ [28], see Fig. 7(b) and (c).

Indeed, we have found the HS Co³⁺/LS Co⁴⁺ ground-state solution for La_{0.5}Sr_{1.5}CoO₄, through a set of constrained LDA + U

calculations. Moreover, this ground-state solution turns out to be FM and insulating in our calculations, exactly in line with the above analyses. Then we can see that upon the half electron doping in Sr₂CoO₄ via La substitution for Sr, the HS Co³⁺ ions are introduced, and simultaneously, the otherwise IS Co⁴⁺ ions transit into the LS state. It is the IS-LS transition of the Co⁴⁺ ions which is responsible for the observed metal-insulator transition from Sr₂CoO₄ to La_{0.5}Sr_{1.5}CoO₄, and meanwhile their FM order surprisingly persists. Here it is evidenced that the funny FM insulating state is readily understood by the spin-orbital physics [28].

Apparently, in this section, the exotic electronic and magnetic properties of the cobaltate series La_{2-x}Sr_xCoO₄ (x = 0–2) are consistently explained by the varying charge-spin-orbital states of the Co ions. Therefore, one could make use of the charge-spin-orbital states to tune and functionalize the material properties of the cobaltates, e.g., via chemical doping, pressure, strain, and interface effects.

2.4. Spin-orbit coupling and Ising magnetism in Ca₃Co₂O₆, Ca₃CoMnO₆, and Sr₃NiIrO₆

In many 3d TMOs, degenerate orbital states often yield an orbital ordering via a Jahn-Teller distortion. The corresponding crystal field splitting dominates over the relativistic spin-orbit coupling (SOC), which is about few tens of meV in strength for 3d TMs. Then an orbital moment is quenched, leaving the spin magnetic moment only for most 3d TMOs. However, a series of quasi one-dimensional spin-chain compounds A₃MM'O₆ (A = Ca, Sr; M, M' = 3d, 4d, 5d TMs) possess a huge orbital moment and display a significant Ising magnetism [40,41]. Actually, this class of materials has drawn a lot of attention since 1996, and they display a stair-like magnetization, thermoelectricity, and multiferroicity as well [42–46]. As seen in Fig. 8, these materials have quasi one-dimensional (1D) spin chains extending along the c-axis. In the ab plane, those chains arrange into a hexagonal structure and they are separated by the Ca/Sr cations. A weak inter-chain AF coupling brings about a magnetic frustration, which is related to the stair-like magnetization. Here we concentrate on the stronger intra-chain magnetic coupling, and will address the nature and origin of the intra-chain magnetic structures.

Along the spin chain direction, the M and M' cations alternate, and they have different coordinations. The 3d TMs occupying the

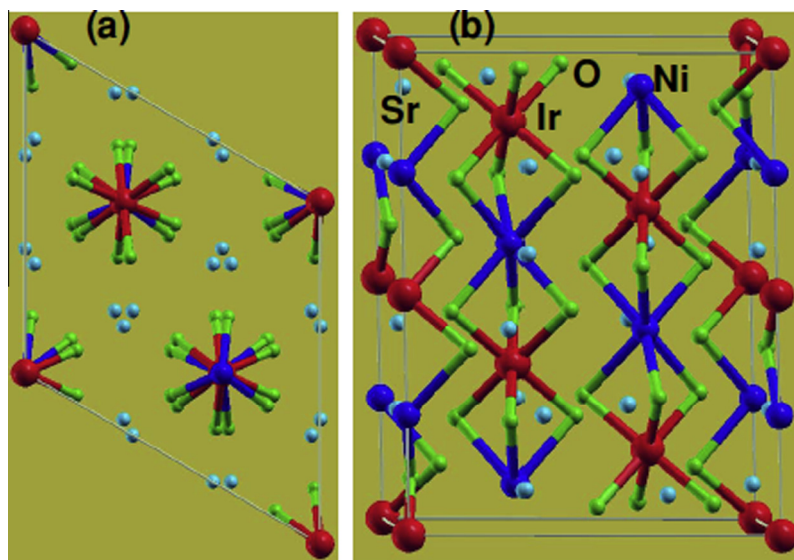


Fig. 8. (a) Top view and (b) side view of the $A_3MM'O_6$ compounds here with $A = \text{Sr}$, $M = \text{Ni}$, and $M' = \text{Ir}$. [Reproduced from Ref. [50]].

M sites have each a MO_6 trigonal prismatic coordination. In contrast, the M' sites can be occupied by 3d, 4d, or 5d TMs, and they have each a $M'O_6$ octahedral coordination. Both the trigonal prism and the octahedron have the 3-fold rotational symmetry along the c -axis. Therefore, the $M'O_6$ octahedra have also a trigonal crystal field splitting. As seen below, the d-level sequence and occupation of the M and M' ions are crucial in determining the intra-chain magnetic structures.

2.4.1. SOC and Ising magnetism in $\text{Ca}_3\text{Co}_2\text{O}_6$

We first have a look at the prototype material $\text{Ca}_3\text{Co}_2\text{O}_6$. As found both theoretically [47] and experimentally [48], it consists of the high-spin trigonal Co^{3+} and low-spin octahedral Co^{3+} . It is not surprising that the former has a higher spin state than the later, as the former feels a weaker crystal field in its more open trigonal prismatic coordinations. For the LS octahedral Co^{3+} , it has a closed t_{2g}^6 shell (albeit a small trigonal $a_{1g}-e_g'$ splitting) and is thus formally nonmagnetic. However, the HS trigonal Co^{3+} has the lower $3z^2 - r^2$ singlet and $x^2 - y^2/xy$ doublet, and the higher doublet xz/yz , see Fig. 9. The singlet $3z^2 - r^2$ and the doublet $x^2 - y^2/xy$ are almost degenerate in the crystal field levels, with the singlet being higher than the doublet by only about 30 meV as indicated by our LDA calculations [47]. As this quasi 1D cobaltate is a narrow band system and its strong correlation effect is significant, we have carried out LDA + U calculations to study its electronic structure and magnetism. Our LDA + U results show that $\text{Ca}_3\text{Co}_2\text{O}_6$ would be either an insulator with the minority-spin $3z^2 - r^2$ orbital

occupation (the majority-spin 3d orbitals are fully occupied in the HS trigonal Co^{3+} ions ($3d^6$)), or a FM half-metal with the half-filled minority-spin $x^2 - y^2/xy$ doublet of the HS trigonal Co^{3+} ions [47]. Apparently, the metallic solution contradicts the experiments. While the insulating solution seems right, the $3z^2 - r^2$ orbital occupation makes the HS trigonal Co^{3+} ions to be in an orbital singlet. Thus $\text{Ca}_3\text{Co}_2\text{O}_6$ would then be a spin-only system, which also disagrees with the observed significant Ising magnetism of $\text{Ca}_3\text{Co}_2\text{O}_6$ [40].

So far, the LDA + U calculations have failed to find a correct solution. Then we were motivated to study the SOC effect. As the $3z^2 - r^2$ and $x^2 - y^2/xy$ are almost degenerate, and they are separated from the higher-lying xz/yz doublet by about 1 eV, the SOC Hamiltonian can be simplified as $\xi L_z S_z$. The SOC mixing terms are almost ineffective, since it cannot mix up $3z^2 - r^2$ (Y_{20} or d_0) and $x^2 - y^2/xy$ ($Y_{2\pm 2}$ or $d_{\pm 2}$). Moreover, the mixing between $x^2 - y^2/xy$ ($Y_{2\pm 2}$, $d_{\pm 2}$) and xz/yz ($Y_{2\pm 1}$ or $d_{\pm 1}$) is tiny as ξ (about 70 meV) is one order of magnitude weaker than the crystal field splitting of about 1 eV. With these analyses in mind, we will see that the $x^2 - y^2/xy$ doublet simply splits into d_2 and d_{-2} in the presence of the SOC, see Fig. 9. Then the single minority-spin 3d electron of the HS trigonal Co^{3+} will occupy the d_2 orbital, giving rise to a huge orbital moment, in addition to the HS $S = 2$ spin moment.

Our LDA + U + SOC calculations indeed find a huge orbital moment of $1.66 \mu_B$ along the c -axis in the ground state solution [47]. Using constrained LDA + U + SOC calculations and assuming the d_{-2} orbital occupation, the increasing total energy allows us to estimate the SOC strength ξ to be about 70 meV. Moreover, owing to the SOC, the spin moment is also firmly fixed along the c -axis spin chain, and the magnetocrystalline anisotropy energy is calculated to be 50–70 meV. Apparently, the minority-spin d_2 occupation of the HS trigonal Co^{3+} well accounts for the observed giant orbital moment and the significant Ising magnetism [40].

2.4.2. Ising magnetism in $\text{Ca}_3\text{CoMnO}_6$

$\text{Ca}_3\text{CoMnO}_6$ is another example of the $A_3MM'O_6$ series, and it was recently found to be a multiferroic material due to an exchange striction [44]. Using constrained LDA + U + SOC calculations, we have studied the site order of Co and Mn cations on the trigonal prismatic and octahedral sites, the charge order, and the spin–orbital states [49]. We find that Co and Mn prefer the trigonal prismatic and octahedral sites, respectively. The Co ions are in +2

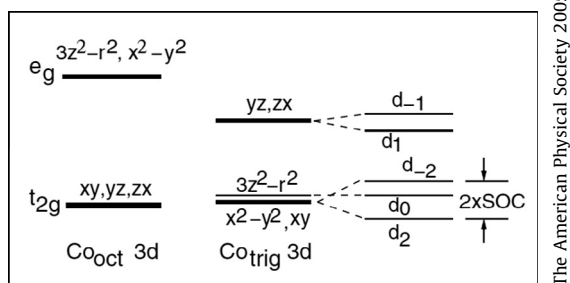


Fig. 9. Schematic level diagram of the LS octahedral Co^{3+} and the HS trigonal Co^{3+} in $\text{Ca}_3\text{Co}_2\text{O}_6$. SOC is active in the trigonal Co^{3+} . [Reproduced from Ref. [47]].

charge state, and the Mn ions +4 state. The octahedral Mn^{4+} has a closed t_{2g} shell and has a local $S = 3/2$. The Co^{2+} ($3d^7$) is in a HS state and has two electrons on the minority-spin 3d orbitals. In the trigonal prismatic crystal field seen by the Co^{2+} ions, the $x^2 - y^2/xy$ doublet is almost degenerate with the $3z^2 - r^2$ singlet, and they are well separated from the xz/yz doublet. The double occupation of $x^2 - y^2/xy$ (in terms of the single electron picture) seems to fulfill the closed-shell insulating behavior of $\text{Ca}_3\text{CoMnO}_6$. However, it turns out to be unstable in our calculations due to the strong inter-orbital Coulomb repulsion (both $x^2 - y^2$ and xy are in-plane orbitals and their orientations differ by a 45° rotation around the z -axis).

In order to reduce the repulsive interaction, the minority-spin $3z^2 - r^2$ would be occupied, and the $x^2 - y^2/xy$ doublet half-filled. As the spin-chain system $\text{Ca}_3\text{CoMnO}_6$ has an open crystal structure in the ab plane, a possible planar $x^2 - y^2/xy$ orbital order is not much helpful for energy gain along the c -axis spin chain. A more efficient way to gain energy is then the SOC, which would split the $x^2 - y^2/xy$ doublet and gain the SOC energy of about 70 meV with the minority-spin d_z occupation. Using LDA + U + SOC calculations [49], we indeed have achieved this ground-state solution. It has a giant orbital moment of $1.7 \mu_B$ at the HS trigonal Co^{2+} site, and the SOC firmly fixes both the orbital and spin moments along the spin-chain direction, thus accounting for the Ising magnetism of $\text{Ca}_3\text{CoMnO}_6$. Then a collinear up-up-down-down magnetic order along the spin chains and the $\text{Co}^{2+}/\text{Mn}^{4+}$ charge order, would produce a ferroelectric polarization due to the exchange striction, although the ferroelectric distortion could be too small to be detected [44,49].

2.4.3. SOC tuning magnetic structure in $\text{Sr}_3\text{NiIrO}_6$

Finally, we come to the 3d–5d TM hybrid $\text{Sr}_3\text{NiIrO}_6$, which is again a quasi 1D spin chain system of $\text{A}_3\text{MM}'\text{O}_6$ type. This material is recently subject to a debate on its intra-chain magnetism [41]: either a FM or an AF structure was proposed in the literature, and no consensus had been reached. This material is also of current interest due to the constituent Ir ions. An iridium ion in an octahedral coordination normally has a large t_{2g} – e_g crystal-field splitting and is thus in a low-spin state. A partially filled t_{2g} triplet orbital, e.g., t_{2g} of an Ir^{4+} ion, behaves like an effective p orbital (with an effective orbital momentum $l = 1$). Owing to a strong SOC of the heavy Ir ion, the t_{2g} splits into a lower-energy $j = 3/2$ quartet and a higher $j = 1/2$ doublet. Then a moderate electron correlation would open an energy gap within the $j = 1/2$ doublet of the Ir^{4+} ion. This yields a novel $j = 1/2$ Mott insulating state, e.g., for the widely studied layered iridate Sr_2IrO_4 [10,11]. Moreover, such spin-orbit integrated narrow band systems, having the $j = 1/2$ quantum ‘spin’, would form a new class of materials, and they are expected to bring about novel electronic and magnetic behaviors.

$\text{Sr}_3\text{NiIrO}_6$ has the trigonal Ni^{2+} and octahedral Ir^{4+} . The Ni^{2+} ($3d^8$) is in the $S = 1$ state and has two holes on the highest crystal field level doublet xz/yz , see Fig. 10(b). The LS Ir^{4+} ($5d^5$) has one hole on the t_{2g} shell. Actually, under a global trigonal crystal field, the formal t_{2g} splits into a_{1g} singlet and e'_g doublet. The a_{1g} has a large $dd\sigma$ hybridization with the Ni $3z^2 - r^2$, the e'_g has a medium $dd\pi$ hybridization with Ni xz/yz and a weak $dd\delta$ one with the Ni $x^2 - y^2/xy$. Mainly due to the elongation of the IrO_6 octahedra along the local $[111]$ direction (i.e., the crystallographic c -axis), a_{1g} lies higher than the e'_g by 210 meV as indicated by our LDA calculations [50], see Fig. 10(a). Then the single t_{2g} hole would reside on the a_{1g} orbital, in terms of the crystal-field level diagram. When we include the static electron correlation, the LDA + U calculations give a FM insulating solution. The small gap is opened by the moderate Hubbard U of the Ir 5d electrons, and the FM order is associated with the virtual hopping of the Ni^{2+} $3z^2 - r^2$ electron

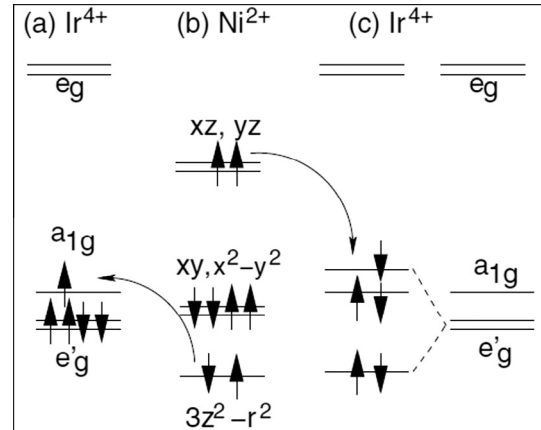


Fig. 10. Schematic level diagrams of (a) the Ir^{4+} and (b) Ni^{2+} ions in $\text{Sr}_3\text{NiIrO}_6$. (c) SOC changes the level sequence in Ir^{4+} . Different exchange paths give a FM coupling between (a) and (b), but AF between (b) and (c). [Reproduced from Ref. [50]].

to the a_{1g} hole state of Ir^{4+} [50], see Fig. 10(a) and (b). So far, this FM insulating solution seems fine, with the correct crystal-field levels and the observed insulating behavior.

Note that a strong SOC effect is typical of iridates, and the SOC strength is about 0.5 eV [10,11,51]. If now we take the SOC into account, the e'_g doublet would split into $l_z = \pm 1$ states with the energy splitting of just the SOC value, see Fig. 10(c). For the up-spin Ir 5d orbitals, $l_z = -1$ is the lower branch, and the higher branch $l_z = 1$ could even be higher than the a_{1g} singlet ($l_z = 0$). Then the crystal field level sequence is changed upon an inclusion of the SOC, and the single t_{2g} hole could reside on the upper branch of the e'_g doublet split by the SOC. Our LDA + U + SOC calculations have confirmed this orbital state, see Fig. 10(c). The Ni^{2+} has a spin moment of $1.69 \mu_B$ (close to the $S = 1$) and a small orbital moment of $0.21 \mu_B$. The Ir^{4+} has a reduced spin moment of $-0.44 \mu_B$ due to a strong Ir–O covalency, and it also has a sizeable orbital moment of $-0.51 \mu_B$ along the c -axis spin chain [50]. The orbital moment is even bigger than the spin moment (showing the importance of the SOC) and both add up to $-0.95 \mu_B$. The AF coupling between the Ni^{2+} and Ir^{4+} is now due to the virtual hopping of the Ni^{2+} xz/yz electrons to the Ir^{4+} e'_g hole state via the medium $dd\pi$ hybridization (the Ni^{2+} $3z^2 - r^2$ orbital is orthogonal to the e'_g orbital and thus no electron hopping can occur in between them). Indeed, our LDA + U + SOC calculations find that the intra-chain AF state is more stable than the FM by about 60 meV/fu [50].

In summary, the spin-chain system $\text{Sr}_3\text{NiIrO}_6$ has $S = 1$ Ni^{2+} and LS ($S = 1/2$) Ir^{4+} ions. The Ir^{4+} ($5d^5$) has a single t_{2g} hole. According to the crystal field level diagram, the single hole resides on the a_{1g} ($3z^2 - r^2$) orbital. Then the $dd\sigma$ hybridization favors a FM coupling and the system would be a pure spin system. However, as the SOC is remarkable at the Ir^{4+} sites, its inclusion will change the crystal-field level sequence and thus alter the hole state. As a result, the Ir^{4+} ions possess a sizeable orbital moment and display an Ising like magnetism. Moreover, the exchange pathway is modified and an intra-chain AF ground state is stabilized. This work [50] highlights the impact of SOC on the magnetism of $\text{Sr}_3\text{NiIrO}_6$, and it clarifies the nature and origin of the intra-chain AF and well accounts for the most recent experiments [41].

3. Conclusion

To conclude this paper, orbital physics is an important branch of the electron correlation and is widespread in transition metal oxides. Degenerate orbital states often couple to the charge, spin and lattice degrees of freedom, thus giving rise to abundant electronic

and magnetic properties and diverse functionalities. Exploring orbital physics is of current interest—tuning the properties and designing materials via manipulating the orbital states. Oxide interfaces and heterostructures have long been a platform to achieve new functionalities, and they are now subject to extensive studies also for orbital physics, which is associated with the surface polarization, charge transfer, strain effects and lattice dimensionality. It is a hope to achieve orbital engineering by making use of orbital physics.

Acknowledgements

The author thanks D.I. Khomskii, L.H. Tjeng, M. Braden, Z. Hu, T. Burnus, C.F. Chang, and X.D. Ou for valuable discussions. The author acknowledges financial supports from NSF of China (Grant Nos. 11274070 and 11474059), MOE Grant No. 20120071110006, and ShuGuang Program of Shanghai (Grant No. 12SG06).

References

- [1] Y. Tokura, N. Nagaosa, *Science* 288 (2000) 462.
- [2] E. Dagotto, *Science* 309 (2005) 257–262.
- [3] B. Keimer, D. Casa, A. Ivanov, J.W. Lynn, M.V. Zimmermann, J.P. Hill, D. Gibbs, Y. Taguchi, Y. Tokura, *Phys. Rev. Lett.* 85 (2000) 3946.
- [4] G. Khaliullin, S. Maekawa, *Phys. Rev. Lett.* 85 (2000) 3950.
- [5] M.W. Haverkort, Z. Hu, A. Tanaka, G. Ghiringhelli, H. Roth, M. Cwik, T. Lorenz, C. Schüßler-Langeheine, S.V. Streltsov, A.S. Mylnikova, V.I. Anisimov, C. de Nadai, N.B. Brookes, H.H. Hsieh, H.-J. Lin, C.T. Chen, T. Mizokawa, Y. Taguchi, Y. Tokura, D.I. Khomskii, L.H. Tjeng, *Phys. Rev. Lett.* 94 (2005) 056401.
- [6] M.W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S.V. Streltsov, M.A. Korotin, V.I. Anisimov, H.H. Hsieh, H.-J. Lin, C.T. Chen, D.I. Khomskii, L.H. Tjeng, *Phys. Rev. Lett.* 95 (2005) 196404.
- [7] M.W. Haverkort, Z. Hu, J.C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N.B. Brookes, H.H. Hsieh, H.-J. Lin, C.T. Chen, L.H. Tjeng, *Phys. Rev. Lett.* 97 (2006) 176405.
- [8] Luca de' Medici, S.R. Hassan, Massimo Capone, Xi Dai, *Phys. Rev. Lett.* 102 (2009) 126401.
- [9] M. Neupane, P. Richard, Z.-H. Pan, Y.-M. Xu, R. Jin, D. Mandrus, X. Dai, Z. Fang, Z. Wang, H. Ding, *Phys. Rev. Lett.* 103 (2009) 097001.
- [10] B.J. Kim, H. Jin, S.J. Moon, J.-Y. Kim, B.-G. Park, C.S. Leem, J. Yu, T.W. Noh, K. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, E. Rotenberg, *Phys. Rev. Lett.* 101 (2008) 076402.
- [11] B.J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, T. Arima, *Science* 323 (2009) 1329.
- [12] K.I. Kugel, D.I. Khomskii, *Zh. Eksp. Teor. Fiz.* 64 (1973) 1429 (*Sov. Phys. JETP* 37 (1973) 725); D.I. Khomskii, K.I. Kugel, *Solid State Commun.* 13 (1973) 763.
- [13] Eva Pavarini, Erik Koch, *Phys. Rev. Lett.* 104 (2010) 086402.
- [14] O. Schumann, Ph.D. thesis, University of Cologne, 2010.
- [15] H. Wu, C.F. Chang, O. Schumann, Z. Hu, J.C. Cezar, T. Burnus, N. Hollmann, N.B. Brookes, A. Tanaka, M. Braden, L.H. Tjeng, D.I. Khomskii, *Phys. Rev. B* 84 (2011) 155126.
- [16] L. Hozoi, H. Gretarsson, J.P. Clancy, B.-G. Jeon, B. Lee, K.H. Kim, V. Yushankhai, Peter Fulde, D. Casa, T. Gog, Jungho Kim, A.H. Said, M.H. Upton, Young-June Kim, Jeroen van den Brink, *Phys. Rev. B* 89 (2014) 115111.
- [17] S.E. McLain, M.R. Dolgos, D.A. Tennant, J.F.C. Turner, T. Barnes, T. Proffen, B.C. Sales, R.I. Bewley, *Nat. Mater.* 5 (2006) 561.
- [18] H. Wu, D.I. Khomskii, *Phys. Rev. B* 76 (2007) 155115.
- [19] E.-J. Kan, L.-F. Yuan, J. Yang, J.G. Hou, *Phys. Rev. B* 76 (2007) 024417.
- [20] X. Hao, Y. Xu, Z. Wu, D. Zhou, X. Liu, J. Meng, *Phys. Rev. B* 76 (2007) 054426.
- [21] Deepa Kasinathan, Klaus Koepnick, Ulrike Nitzsche, Helge Rosner, *Phys. Rev. Lett.* 99 (2007) 247210.
- [22] S.A.J. Kimber, J.A. Rodgers, H. Wu, C.A. Murray, D.N. Argyriou, A.N. Fitch, D.I. Khomskii, J.P. Attfield, *Phys. Rev. Lett.* 102 (2009) 046409.
- [23] P. Khalifah, R. Osborn, Q. Huang, H.W. Zandbergen, R. Jin, Y. Liu, D. Mandrus, R. J. Cava, *Science* 297 (2002) 2237.
- [24] H. Wu, Z. Hu, T. Burnus, J.D. Denlinger, P.G. Khalifah, D.G. Mandrus, L.-Y. Jang, H.H. Hsieh, A. Tanaka, K.S. Liang, J.W. Allen, R.J. Cava, D.I. Khomskii, L.H. Tjeng, *Phys. Rev. Lett.* 96 (2006) 256402.
- [25] S.J. Moon, W.S. Choi, S.J. Kim, Y.S. Lee, P.G. Khalifah, D. Mandrus, T.W. Noh, *Phys. Rev. Lett.* 100 (2008) 116404.
- [26] J. Matsuno, Y. Okimoto, Z. Fang, X.Z. Yu, Y. Matsui, N. Nagaosa, M. Kawasaki, Y. Tokura, *Phys. Rev. Lett.* 93 (2004) 167202.
- [27] S.K. Pandey, *Phys. Rev. B* 81 (2010) 035114.
- [28] H. Wu, *Phys. Rev. B* 86 (2012) 075120.
- [29] R.H. Potze, G.A. Sawatzky, M. Abbate, *Phys. Rev. B* 51 (1995) 11501.
- [30] I.A. Zaliznyak, J.P. Hill, J.M. Tranquada, R. Erwin, Y. Moritomo, *Phys. Rev. Lett.* 85 (2000) 4353.
- [31] C.F. Chang, Z. Hu, Hua Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H.H. Hsieh, C.T. Chen, L.H. Tjeng, *Phys. Rev. Lett.* 102 (2009) 116401.
- [32] H. Wu, T. Burnus, *Phys. Rev. B* 80 (2009) 081105(R).
- [33] V.I. Anisimov, I.V. Solov'yev, M.A. Korotin, M.T. Czyzyk, G.A. Sawatzky, *Phys. Rev. B* 48 (1993) 16929.
- [34] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, WIEN2k code, 2001, ISBN 3-9501031-1-2.
- [35] A. Maignan, V. Caignaut, B. Raveau, D. Khomskii, G. Sawatzky, *Phys. Rev. Lett.* 93 (2004) 026401.
- [36] H. Wu, *Phys. Rev. B* 81 (2010) 115127.
- [37] Y. Shimada, S. Miyasaka, R. Kumai, Y. Tokura, *Phys. Rev. B* 73 (2006) 134424.
- [38] A.V. Chichev, M. Dlouhá, S. Vratislav, K. Knížek, J. Hejtmánek, M. Maryško, M. Veverka, Z. Jiráček, N.O. Golosova, D.P. Kozlenko, B.N. Savenko, *Phys. Rev. B* 74 (2006) 134414.
- [39] J. Wang, W. Zhang, D.Y. Xing, *Phys. Rev. B* 62 (2000) 14140; J. Wang, Y.C. Tao, W. Zhang, D.Y. Xing, *J. Phys.: Condens. Matter* 12 (2000) 7425.
- [40] A. Maignan, V. Hardy, S. Hébert, M. Drillon, M.R. Lees, O. Petrenko, D. Mc, K. Paul, D. Khomskii, *J. Mater. Chem.* 14 (2004) 1231.
- [41] D. Mikhailova, B. Schwarz, A. Senyshyn, A.M.T. Bell, Y. Skourski, H. Ehrenberg, A.A. Tsirlin, S. Agrestini, M. Rotter, P. Reiche, J.M. Chen, Z. Hu, Z.M. Li, Z.F. Li, L. H. Tjeng, *Phys. Rev. B* 86 (2012) 134409.
- [42] H. Fjellvåg, E. Gulbrandsen, S. Aasland, A. Olsen, B. Hauback, *J. Solid State Chem.* 124 (1996) 190.
- [43] S. Niitaka, K. Yoshimura, K. Kosuge, M. Nishi, K. Kakurai, *Phys. Rev. Lett.* 87 (2001) 177202.
- [44] Y.J. Choi, H.T. Yi, S. Lee, Q. Huang, V. Kiryukhin, S.-W. Cheong, *Phys. Rev. Lett.* 100 (2008) 047601.
- [45] S. Agrestini, C.L. Fleck, L.C. Chapon, C. Mazzoli, A. Bombardi, M.R. Lees, O.A. Petrenko, *Phys. Rev. Lett.* 106 (2011) 197204.
- [46] Y. Kamiya, C.D. Batista, *Phys. Rev. Lett.* 109 (2012) 067204.
- [47] H. Wu, M.W. Haverkort, Z. Hu, D.I. Khomskii, L.H. Tjeng, *Phys. Rev. Lett.* 95 (2005) 186401.
- [48] T. Burnus, Z. Hu, M.W. Haverkort, J.C. Cezar, D. Flahaut, V. Hardy, A. Maignan, N.B. Brookes, A. Tanaka, H.H. Hsieh, H.-J. Lin, C.T. Chen, H. Tjeng, *Phys. Rev. B* 74 (2006) 245111.
- [49] H. Wu, T. Burnus, Z. Hu, C. Martin, A. Maignan, J.C. Cezar, A. Tanaka, N.B. Brookes, D.I. Khomskii, L.H. Tjeng, *Phys. Rev. Lett.* 102 (2009) 026404.
- [50] X.D. Ou, H. Wu, *Sci. Rep.* 4 (2014) 4609.
- [51] X.D. Ou, H. Wu, *Phys. Rev. B* 89 (2014) 035138.