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Impact of spin-orbit coupling on the magnetism of Sr_3MIrO_6 ($M = \text{Ni}, \text{Co}$)

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Iridates are of current great interest for their entangled spin-orbital state and possibly exotic properties. In this work, using density functional calculations, we have demonstrated that the hexagonal spin-chain materials Sr_3MIrO_6 ($M = \text{Ni}, \text{Co}$) are an iridate system in which the spin-orbit coupling (SOC) tunes the magnetic and electronic properties. The significant SOC alters the orbital state, the exchange pathway, and thus the magnetic structure. This work clarifies the nature and the origin of the intra-chain antiferromagnetism of Sr_3MIrO_6 and well accounts for the most recent experiments.

Charge, spin and orbital states are often coupled in 3d transition-metal oxides due to their multiple degrees of freedom and electron correlation. These states are closely related to diverse material properties and functionalities, e.g., charge ordering, orbital ordering, spin-state and magnetic transition, 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, see e.g., a short review by Dagotto¹. Very recently, research interest has been extended to 5d transition-metal oxides, 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.

In this respect, iridates are a representative example^{2–17}. An octahedrally coordinated iridium ion normally has a large t_{2g} - e_g crystal-field splitting due to the delocalized character of its 5d electrons. The resultant low-spin state with only a t_{2g} occupation makes an open shell Ir^{n+} ion (e.g., t_{2g}^5 for $n = 4$) behave effectively like p electrons (with an effective orbital momentum $\tilde{l} = 1$). As a result, an intrinsic strong spin-orbit coupling (SOC) splits the t_{2g} levels into a lower $\tilde{j} = 3/2$ quartet and a higher $\tilde{j} = 1/2$ doublet. Then, for an Ir^{4+} constituent oxide, the half-filled $\tilde{j} = 1/2$ doublet may form, due to a moderate electron correlation, a novel $\tilde{j} = 1/2$ Mott insulating state^{2,3}. It has been proposed that such a spin-orbital entangled state can bring about exotic properties, e.g., correlated topological insulator^{4,5}, superconductivity⁶, Kitaev model^{7,8}, Weyl semimetal⁹, and unusual magnetism¹⁰.

In this Report, we have studied the 3d–5d transition-metal hybrid material Sr_3MIrO_6 ($M = \text{Ni}, \text{Co}$), and find that the SOC has a significant impact on its magnetism by tuning its spin-orbital states and the Ir-M inter-orbital interactions. This system has a general chemical formula $A_3\text{MM}'\text{O}_6$ ($A = \text{Ca}, \text{Sr}$; $M = 3\text{d transition metal}$, $M' = 3\text{d}, 4\text{d}, 5\text{d transition metal}$) and displays an in-plane hexagonal structure and out-of-plane spin chains, see Fig. 1. Those quasi one-dimensional spin chains each consist of alternating face-sharing MO_6 trigonal prisms and $\text{M}'\text{O}_6$ octahedra. This system drew a lot of attention in the past decade^{18–27}, because of its intriguing step-wise magnetization, significant Ising-like magnetism, thermoelectricity, and multiferroicity. $\text{Sr}_3\text{NiIrO}_6$ and $\text{Sr}_3\text{CoIrO}_6$ also possess fascinating magnetism^{28–31}. Owing to their complex temperature-dependent magnetic transitions, a standing issue is the nature of their dominant intrachain magnetism: either an intrachain ferromagnetic (FM) exchange^{28,29} or an antiferromagnetic (AF) coupling^{30,31} was proposed in previous studies. Moreover, the origin of the magnetism remains elusive. Therefore, $\text{Sr}_3\text{NiIrO}_6$ and $\text{Sr}_3\text{CoIrO}_6$ call for a prompt study to clarify the nature and origin of their intriguing intrachain magnetism. As seen below, we make a comparative study for $\text{Sr}_3\text{NiIrO}_6$ and $\text{Sr}_3\text{CoIrO}_6$, by carrying out a systematic set of electronic structure calculations. Our results consistently explain the experimental observations and settle the standing issue. In particular, we find that the SOC of the Ir^{4+} ion plays an essential role in determining the intrachain AF structure of Sr_3MIrO_6 ($M = \text{Ni}, \text{Co}$) by tuning the crystal-field level sequence and altering the Ir-M inter-orbital interactions. Therefore, Sr_3MIrO_6 is added to the iridate category which highlights the significance of the SOC.

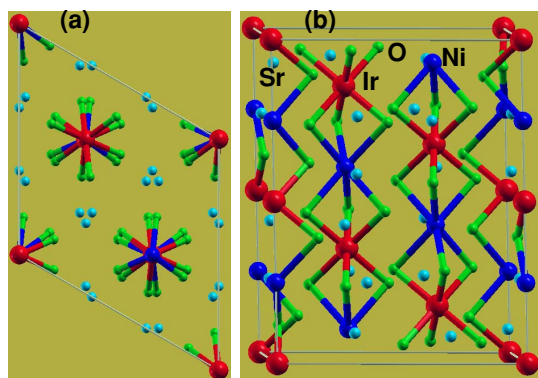


Figure 1 | Crystal structure plot of $\text{Sr}_3\text{MlIrO}_6$ (a) projected onto the ab plane and (b) in a perspective view. It has a hexagonal ab plane and quasi one-dimensional MlIrO_6 spin chains extending along the c-axis, in which the IrO_6 octahedra and MO_6 trigonal prisms are alternating.

Results

Crystal-field levels. We first carry out spin-restricted LDA calculations to estimate the crystal field splitting. The calculated DOS (density of states) results for $\text{Sr}_3\text{NiIrO}_6$ are shown in Fig. 2. The O 2p valence bands lie in between -7 and -2 eV. They have a significant covalency with the delocalized Ir 5d orbital and bring about the Ir 5d bonding state around -6 eV. A relatively weak Ni-O hybridization yields the Ni 3d bonding state in between -2 and -4 eV. Both the Ir 5d and Ni 3d antibonding states lie above -2 eV. For the Ir ion, its local octahedral coordination but a trigonal crystal field in the global coordinate system split the otherwise t_{2g} triplet into the e'_g doublet and the a_{1g} singlet both of the concern. The e_g doublet is far above them by 3 eV and is out of the concern. The a_{1g} singlet can be written as $3z^2 - r^2$, as the z-axis of the hexagonal lattice is

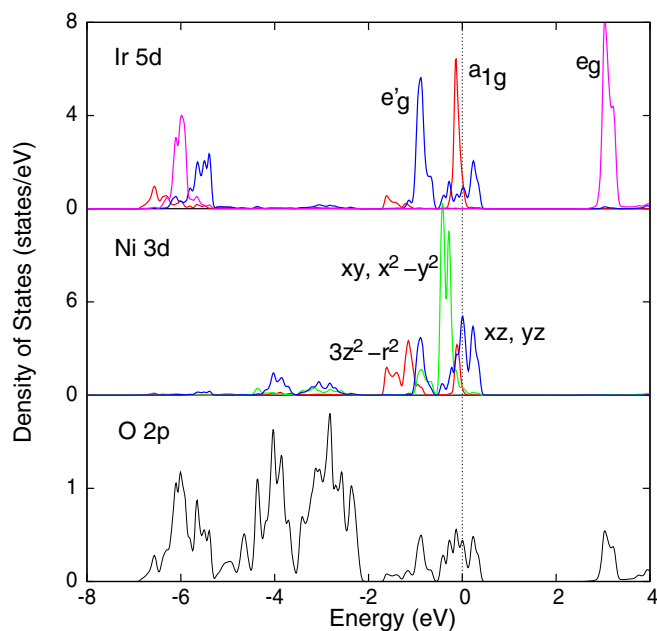


Figure 2 | Partial density of states (DOS) of $\text{Sr}_3\text{NiIrO}_6$ in the nonmagnetic state calculated by LDA. The octahedral Ir ion has a common large $t_{2g} - e_g$ crystal field splitting of more than 3 eV; and in a trigonal crystal field (elongation of the IrO_6 octahedron along the local [111] direction, i.e., the z-axis of the hexagonal lattice), the t_{2g} splits further into a lower e'_g doublet and a higher a_{1g} singlet. The trigonal prismatic coordination produces the Ni 3d crystal-field level sequence (from low to high) as $3z^2 - r^2/xy, x^2 - y^2/xz, yz$.

along the [111] direction of the local IrO_6 octahedra. Moreover, the e'_g doublet can be expressed as $\sqrt{2/3}xy + \sqrt{1/3}yz$ and $\sqrt{2/3}(x^2 - y^2) - \sqrt{1/3}xz$, when the y-axis is set along the $[\bar{1}10]$ direction of the local IrO_6 octahedra (then the x-axis is uniquely defined and the xy is in the hexagonal ab plane). By integrating the DOS and determining the center of gravity for each eigen orbital within the antibonding energy range, we find that the e'_g doublet is lower than the a_{1g} singlet by 0.21 eV. Actually, the $a_{1g}-e'_g$ level splitting is an important issue. The trigonal distortion of the IrO_6 octahedron¹⁹, e'_g-e_g mixing³², and long-ranged crystal field due to the lattice anisotropy³³ all contribute to the splitting. All these effects are properly included in the LDA calculation. Although the contribution of the lattice anisotropy is often quite complicate³³, the $a_{1g}-e'_g$ level ordering can be understood, as the elongation of the IrO_6 octahedron along the [111] direction (the resultant O-Ir-O bond angle deviating from the ideal 90° by 5.4° ²⁸) raises a_{1g} with respect to e'_g , and the e'_g-e_g mixing pushes e'_g downwards³². For the Ni ion, its trigonal prismatic coordination produces the crystal-field level sequence of the Ni 3d electrons as $3z^2 - r^2/xy, x^2 - y^2/xz, yz$ (0/0.57/0.76 eV). Furthermore, there are inter-site interactions between the Ir 5d and Ni 3d orbitals, see Fig. 2. The Ir $a_{1g} 3z^2 - r^2$ and Ni $3z^2 - r^2$ electrons have a lobe pointing to each other and have a $dd\sigma$ hybridization. The Ir e'_g orbital has, via its xz or yz component, a $dd\pi$ hybridization with the Ni xz/yz; and via its xy or $x^2 - y^2$ component, a weak $dd\delta$ hybridization with the Ni xy/ $x^2 - y^2$. Note that those crystal-field level sequences and the Ir-Ni inter-orbital hybridizations are crucial for understanding of the spin-orbital state and the intrachain magnetism in $\text{Sr}_3\text{MlIrO}_6$, as seen below.

Spin polarization and electron correlation. Then we perform spin-polarized LSDA calculations. We start with a FM or an AF state with the Ni^{2+} spin = 1 and Ir^{4+} spin = 1/2, but both calculations converge to a same FM metallic solution (not shown here). It has a total spin moment of $2.82 \mu_B/\text{fu}$, consisting of the local spin moments of $1.46 \mu_B/\text{Ni}^{2+}$, $0.54 \mu_B/\text{Ir}^{4+}$, and $0.11 \mu_B/\text{O}$. The Ni^{2+} ion has the electronic configuration $(3z^2 - r^2)^2(xy, x^2 - y^2)^4(xz, yz)^2$, and the Ir^{4+} has a single t_{2g} hole mostly on the a_{1g} orbital [i.e., $(e'_g)^4 a_{1g}^1$]. The Ir-O and Ni-O covalencies bring about an appreciable spin moment of $0.11 \mu_B$ on each oxygen. As the a_{1g} orbital is a higher crystal-field level than the e'_g , the a_{1g} hole state allows a direct a_{1g} electron hopping from Ni^{2+} to Ir^{4+} , and this prompts the FM metallic solution.

The above LSDA metallic solution contradicts the experimental insulating behavior. In order to probe the electron correlation effect, we now carry out LSDA + U calculations. The electron correlation stabilizes the Ni^{2+} S = 1 state and the calculated spin moment of Ni^{2+} is enhanced to $1.68 \mu_B$. As seen in Fig. 3(a), the single Ir^{4+} t_{2g} hole now fully occupies the down-spin a_{1g} orbital. The Ir^{4+} spin moment is also increased to $0.64 \mu_B$. Owing to the correlation driven d-electron localization, the induced 2p spin moment on oxygen via the Ir-O and Ni-O hybridizations is reduced to $0.08 \mu_B$. Apparently, electron correlations make the Ir 5d and Ni 3d spin-orbital states fully polarized, thus giving an insulating solution. The tiny band gap is within the Ir t_{2g} shell, and it is due to a relatively weak electron correlation of delocalized 5d electrons. As Ir^{4+} has the single t_{2g} hole on the down-spin $a_{1g} (3z^2 - r^2)$ orbital, the down-spin $3z^2 - r^2$ electron of Ni^{2+} can hop forth and back. In order to maximize the local Hund exchange on the virtual Ni^{3+} ion in the excited intermediate state, the hopping $3z^2 - r^2$ electron should be in the minority-spin channel, see Fig. 4 (b). Then this exchange mechanism gives the FM coupling between Ir^{4+} S = 1/2 and Ni^{2+} S = 1. Indeed, our LSDA + U calculation gives a total maximal spin moment of $3 \mu_B/\text{fu}$ for this FM insulating state. Here we note that the Ir^{4+} $a_{1g} (3z^2 - r^2)$ orbital is orthogonal to the Ni^{2+} xz/yz and xy/ $x^2 - y^2$ orbitals, and hence there is no hopping between them to account for the magnetism. Moreover, the Ir^{4+} e_g

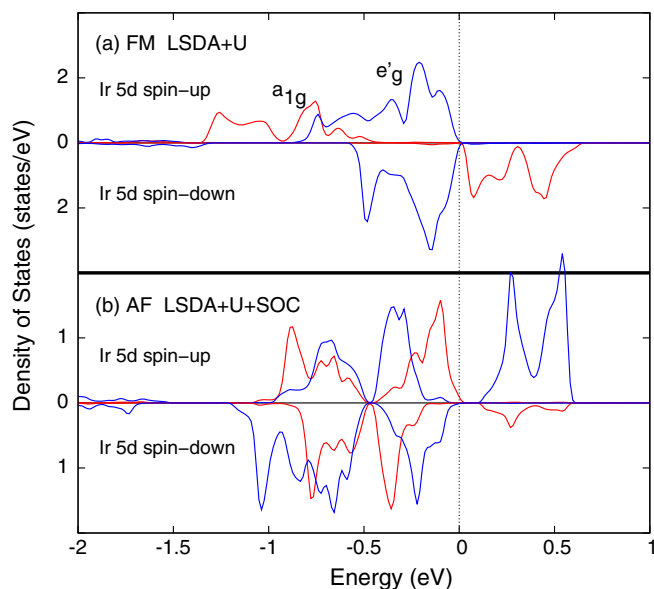


Figure 3 | The partial DOS of the Ir-5d a_{1g} and e'_g orbitals in $\text{Sr}_3\text{NiIrO}_6$ in (a) the FM state calculated by LSDA + U and in (b) the AF state by LSDA + U + SOC. Taking the Ni^{2+} $S = 1$ as a reference, the Ir^{4+} ion has a down-spin a_{1g} empty state in (a) but an up-spin e'_g empty state (i.e., a complex orbital with $l_z = 1$) in (b).

empty bands are too high (see Fig. 2) to be relevant for the magnetic coupling. Therefore, with the crystal-field level diagrams depicted in Figs. 4(a) and 4(b), the electron correlation and inter-orbital hybridization give rise to the FM insulating solution.

Spin-orbit coupling. As 5d transition metals have an intrinsic strong SOC and particularly iridates are a representative example in this respect, now we are motivated to study the SOC effect by doing LSDA + U + SOC calculations. It is interesting to note that now we get an AF insulating solution with a small band gap of 0.15 eV, see Fig. 3(b). Particularly, this solution has the Ir^{4+} single t_{2g} hole on the e'_g orbital, in sharp contrast to the a_{1g} hole state in the above LSDA + U FM insulating solution. The Ni^{2+} retains its configuration state and has a spin moment of $1.69 \mu_B$. Owing to the small crystal-field splitting of 0.19 eV between $(xy, x^2 - y^2)$ and (xz, yz) , a finite mixing between them due to the Ni SOC gives also a small orbital moment of $0.21 \mu_B$ on Ni^{2+} . The Ir^{4+} ion has now a spin moment of $-0.44 \mu_B$. Moreover, the e'_g doublet can form a complex orbital with $l_z = \pm 1$.

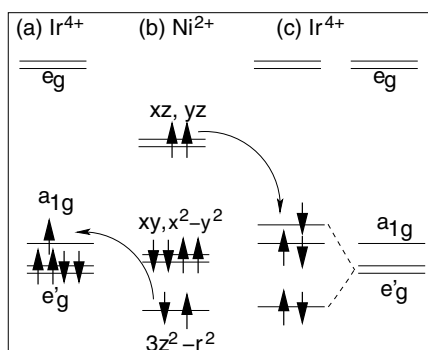


Figure 4 | Schematic level diagrams of the Ir^{4+} 5d and Ni^{2+} 3d orbitals. The down-spin $3z^2 - r^2$ electron mediates a FM coupling via a $dd\sigma$ hybridization [(a) and (b)]. The up-spin xz/yz electrons mediate an AF coupling via a $dd\pi$ hybridization [(b) and (c)], in which the SOC splits the e'_g doublet.

Then in the up-spin channel, the SOC lowers $l_z = -1$ state, and the $l_z = 1$ state is pushed above the Fermi level by SOC and moderate electron correlation, determining the modest band gap and giving an orbital moment of $-0.51 \mu_B$ on Ir^{4+} . Owing to the significant Ir-O covalency, both the spin and orbital moments are reduced from their respective ideal unit value. In the AF state of Ni^{2+} $S = 1$ and Ir^{4+} $S = -1/2$, the induced magnetic moment on oxygen gets tiny (only about $0.01 \mu_B$).

Discussion

The above results indicate an interesting evolution of the intrachain magnetic structure, from the LSDA + U FM state to the LSDA + U + SOC AF state. It is ascribed to the SOC tuning orbital state of the Ir^{4+} ion. Although the a_{1g} is a higher crystal-field level than the e'_g by 0.21 eV, the significant SOC of the Ir^{4+} ion (being about 0.5 eV) can well split the e'_g doublet and eventually places the upper branch above the a_{1g} (Fig. 4(c)). As a result, the single t_{2g} hole of the Ir^{4+} ion lies in the e'_g state. Then, the up-spin xz/yz electrons of the Ni^{2+} ion can hop, forth and back, to the up-spin e'_g empty state (i.e., the up-spin $l_z = 1$ branch), giving rise to the AF coupling via the $dd\pi$ hybridization (Figs. 4(b) and 4(c)). Actually, using the orbital states depicted in Figs. 4(b) and 4(c), we also calculated the FM state. Our LSDA + U + SOC calculations find that the FM state is indeed less stable than the AF ground state by 67 meV/fu. Corresponding LSDA + U + SOC calculations, with Hund exchange parameter $J = 0.9$ eV for Ni 3d and $J = 0.4$ eV for Ir 5d, find that the AF ground state is more stable than the FM state by 63 meV/fu. In addition, the spin (orbital) magnetic moment changes within 0.1 (0.05) μ_B . Therefore, here the J parameter has an insignificant influence on the calculated results. As the SOC is intrinsic in iridates, the AF ground state is deemed reliable from the LSDA + U + SOC calculations, but the FM state seems fictitious from the LSDA + U calculations without inclusion of the SOC. Indeed, the AF ground state agrees with the most recent experiment³⁰. Therefore, we can conclude that it is the significant SOC of the Ir^{4+} ion which tunes the spin-orbital states and Ir-Ni inter-orbital interactions and hence determines the AF structure of $\text{Sr}_3\text{NiIrO}_6$.

Now we turn to $\text{Sr}_3\text{CoIrO}_6$. As this material has practically the same crystal structure as $\text{Sr}_3\text{NiIrO}_6$ ^{28,30}, both systems have many common features in the electronic and magnetic structures. The a_{1g} singlet of the Ir^{4+} ion is higher than the e'_g doublet in the crystal-field level diagram. Moreover, the high-spin Co^{2+} ion has the same crystal-field level sequence as Ni^{2+} , but it now has one hole on the $xy/x^2 - y^2$ doublet (compared with Ni^{2+} , see Fig. 4(b)). Our LSDA + U calculations give a FM metallic solution due to the $3z^2 - r^2$ electron hopping and the $3/4$ filled $xy/x^2 - y^2$ bands. Apparently, this solution contradicts the experimental AF insulating behavior³⁰.

However, when we include SOC by doing LSDA + U + SOC calculations, we have obtained the correct AF insulating solution (see Fig. 5) in good agreement with the experiment³⁰. The high-spin Co^{2+} ion ($S = 3/2$) has a spin moment of $2.66 \mu_B$. In its down-spin channel, the $xy/x^2 - y^2$ doublet form the complex orbitals $(x^2 - y^2) \pm ixy$ with $l_z = \pm 2$, and the Co^{2+} SOC lowers the $l_z = 2$ state but lifts the $l_z = -2$ state. The electron correlation places the former at -1.5 eV and the latter at 2 eV. As a result, the Co^{2+} ion has also a huge orbital moment of $1.71 \mu_B$. In total, the Co^{2+} ion has the magnetic moment of $4.37 \mu_B$ and it is firmly aligned, due to the SOC, along the hexagonal c -axis (i.e., a significant Ising-like spin system). Moreover, the Ir 5d states are almost the same as in $\text{Sr}_3\text{NiIrO}_6$: the Ir^{4+} SOC places the single t_{2g} hole on the e'_g doublet; the SOC and moderate electron correlation determine the small insulating gap within the Ir^{4+} t_{2g} shell, see Fig. 5. The Ir^{4+} ion has the spin (orbital) moment of -0.39 (-0.47) μ_B and in total $-0.86 \mu_B$. Using these spin-orbital states, our LSDA + U + SOC calculations find that the AF ground state is more stable than the FM state by 122 meV/fu, which changes

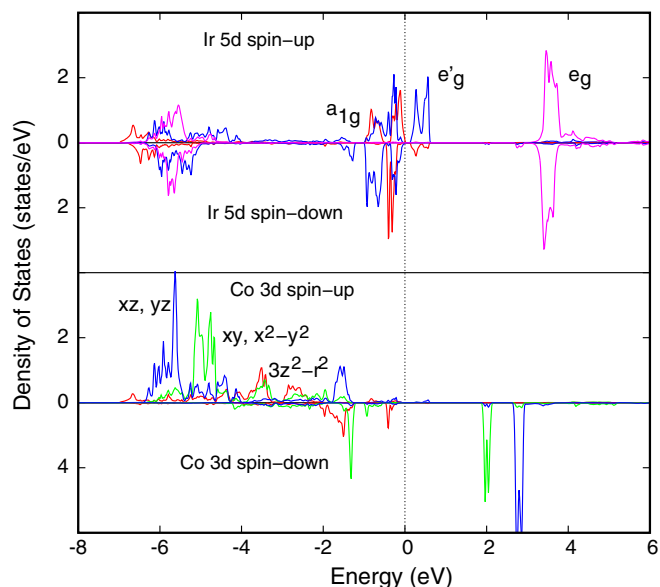


Figure 5 | The partial DOS of the Ir 5d and Co 3d eigen orbitals in AF $\text{Sr}_3\text{CoIrO}_6$ calculated by LSDA + U + SOC. The high-spin Co^{2+} ion ($S = 3/2$) has the orbitals $3z^2 - r^2$ (red curve) and $[(x^2 - y^2) + ixy]/\sqrt{2}$ ($l_z = 2$) occupied (green curve) in its down-spin channel. The Ir^{4+} ($S = -1/2$) has the e'_g $l_z = 1$ empty state (blue curve) in its up-spin channel.

little to 130 meV/fu when including Hund exchange $J = 0.9$ eV for Co 3d and $J = 0.4$ eV for Ir 5d.

By looking at Figs. 4(b) and 4(c), and now having also one hole on the down-spin $xy/x^2 - y^2$ doublet for Co^{2+} , we find that the net spin = 1 from xz/yz and the net spin = 1/2 from $xy/x^2 - y^2$ both contribute to the AF exchange with the net Ir spin = -1/2 from the e'_g . The former is via a $dd\pi$ hybridization as in $\text{Sr}_3\text{NiIrO}_6$, and the latter a weaker $dd\delta$ one (which is missing in $\text{Sr}_3\text{NiIrO}_6$). This, together with the spin values (Co^{2+} $S = 3/2$ vs Ni^{2+} $S = 1$), qualitatively accounts for a higher stability of the AF ground state over the FM state in $\text{Sr}_3\text{CoIrO}_6$ than in $\text{Sr}_3\text{NiIrO}_6$, i.e., 122 vs 67 meV/fu. In addition, the $dd\delta$ hybridization results in the smaller spin and orbital moments of the Ir^{4+} ion in $\text{Sr}_3\text{CoIrO}_6$ ($0.39 + 0.47 \mu_B$) than in $\text{Sr}_3\text{NiIrO}_6$ ($0.44 + 0.51 \mu_B$). Note that all these results qualitatively explain the (slightly) higher intrachain AF transition temperature of 90 K in $\text{Sr}_3\text{CoIrO}_6$ than 85 K in $\text{Sr}_3\text{NiIrO}_6$ ³⁰. Moreover, the calculated magnetic moments of the significant Ising type, $4.37 \mu_B/\text{Co}^{2+}$ and $-0.86 \mu_B/\text{Ir}^{4+}$, also agree reasonably well with the experimental ones of 3.6 and $-0.6 \mu_B$ in $\text{Sr}_3\text{CoIrO}_6$ ³⁰.

In summary, using density functional calculations including spin-orbit coupling (SOC) and electron correlation, we have demonstrated that the SOC of the Ir^{4+} ion plays an essential role in determining the antiferromagnetism of the hexagonal spin-chain system Sr_3MIrO_6 ($M = \text{Ni}, \text{Co}$) by tuning the crystal-field level sequence and altering the Ir-M inter-orbital interactions. The SOC splits the e'_g doublet of the octahedral Ir^{4+} ion (t_{2g}^5) in a trigonal crystal field, and the single t_{2g} hole resides on the e'_g upper branch and gives rise to the antiferromagnetic superexchange. In absence of the SOC, however, the single t_{2g} hole would occupy the a_{1g} singlet instead, which would mediate an unreal ferromagnetic exchange due to a direct a_{1g} hopping along the Ir-M chain. We also find that the Ni^{2+} and Co^{2+} ions are both in a high-spin state and moreover the Co^{2+} ion carries a huge orbital moment. This work well accounts for the most recent experiments and magnifies again the significance of the SOC in iridates.

Methods

We have carried out density functional calculations, using the full-potential augmented plane wave plus local orbital code (Wien2k)³⁴. We use the structural data of $\text{Sr}_3\text{NiIrO}_6$ measured by neutron diffraction at 10 K²⁸ and of $\text{Sr}_3\text{CoIrO}_6$ at 4 K³⁰. They have practically the same crystal structure: the Ir-O bondlength of 2.01 Å, the M-O 2.18 Å, and the M-Ir 2.78 Å for $M = \text{Ni}$ and Co ; the small deviation of the O-Ir-O bond angle (from the ideal 90°) due to a small elongated trigonal distortion of the IrO_6 octahedron, being 5.4° for $M = \text{Ni}$ and 5.2° for $M = \text{Co}$. The muffin-tin sphere radii are chosen to be 2.8, 2.2, 2.2 and 1.5 Bohr for Sr, Ni/Co, and Ir and O atoms, respectively. The plane-wave cut-off energy of 16 Ry is set for the interstitial wave functions, and $5 \times 5 \times 5$ k mesh for integration over the rhombohedral Brillouin zone. Using $7 \times 7 \times 7$ k mesh (more than a doubling) gives practically the same results, with the total energy converging within 2 meV/fu. We employ the local spin density approximation³⁵ plus Hubbard U (LSDA + U) method³⁶ to describe the electron correlation of the M 3d and Ir 5d electrons, with the LSDA + U double counting correction made in a fully atomic limit³⁶. The typical values, effective $U = 2, 4$ and 5 eV ($U_{\text{eff}} = U - J$ with Hund exchange parameter J being set at zero) are used for the Ir 5d, Co 3d, and Ni 3d states, respectively. Note that our key results – the coupled spin-orbital state and the magnetic ground state – are independent of the tested U values (1–3 eV for Ir 5d and 3–7 eV for Co/Ni 3d). To account for (near) degeneracy of the Ir 5d orbitals (and of M 3d orbitals as well), the SOC is included by the second-variational method with scalar relativistic wave functions. In order to probe diverse possible spin-orbital states and magnetic structures, we excess them in our calculations by setting their respective occupation number matrix and thus orbitally dependent potentials, and then do self-consistent calculations including a full electronic relaxation. (Otherwise, some states of the concern or even the ground state cannot be achieved.) An advantage of this procedure is such that we can reliably determine the magnetic ground state by a direct comparison of the different states^{19,21}.

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Author contributions

H.W. conceived the idea and designed the research. X.O. and H.W. performed the calculations. H.W. and X.O. prepared the manuscript.

Additional information

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