Long-range magnetic interaction and frustration in double perovskites Sr$_2$NilrO$_6$ and Sr$_2$ZnIrO$_6$

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One often counts the nearest neighbouring (NN) exchange interactions for understanding of a magnetic insulator. Here we present first-principles calculations for the newly synthesized double perovskites Sr$_2$NilrO$_6$ and Sr$_2$ZnIrO$_6$, and we find that the 2NN Ir-Ir antiferromagnetic coupling is even stronger than the 1NN Ni-Ir ferromagnetic one. Thus, the leading antiferromagnetic interactions in the fcc Ir sublattice give rise to a magnetic frustration. Sr$_2$NilrO$_6$ and Sr$_2$ZnIrO$_6$ hence appear very similarly as a distorted low-temperature antiferromagnet (probably, of type III). This work highlights the long-range magnetic interactions of the delocalized 5d electrons, and it also addresses why the spin-orbit coupling is ineffective here.

In the insulating transition-metal (TM) oxides, superexchange (SE) coupling of neighbouring magnetic ions via intermediate oxygen, according to the Goodenough-Kanamori-Anderson rules, commonly plays a leading role in their magnetic order. One simple but useful rule is that for a linear M-O-M' exchange path, the SE would be antiferromagnetic (AF) [ferromagnetic (FM)] when the active orbitals of M and M' are same [different]. Fig. 1 (a) shows two d$^1$ ions each having two orthogonal A–B levels and the same A-level occupation. Taking into account an effective hopping t between two ions associated with the charge fluctuation (d$^1$ + d$^1$ → d$^0$ + d$^2$) where the electron correlation Hubbard U is involved, an energy gain of an AF order (relative to a FM one) is proportional to $t^2/U$ in a strong correlation limit ($U \gg t$). Fig. 1 (b) shows two different d$^1$ level occupations, and a FM stability against AF is proportional to $t_{JH}^2/U^2$ where $t_{JH}$ is a Hund exchange. This is the reason why a FM Mott insulator is often associated with orbital physics (e.g., an orbital ordering) and its $T_C$ is much lower (due to the factor $t_{JH}^2/U^2 \sim 1/5$) than the $T_N$ of many AF Mott insulators.

In practice, it is often sufficient to consider the SE between the nearest neighbouring (NN) magnetic ions only. This approach applies with much success to numerous insulating 3d TM oxides, where the 3d electrons are quite localized due to the strong correlation effect. In recent years, 5d TM oxides have received considerable attention because of their significant spin-orbit coupling (SOC) effect and possibly exotic properties. The hybrid 3d–5d TM oxides have received considerable attention because of their significant spin-orbit coupling (SOC) effect and possibly exotic properties. Among them, the double perovskites A$_2$BB'O$_6$ (A = alkaline earth metal, B = 3d TM, and B' = 5d TM) are an important material platform. Sr$_2$FeReO$_6$ is an above room temperature (RT) ferromagnetic half metal, and Sr$_2$GrOsO$_4$ is a ferrimagnetic insulator with a seemingly highest $T_C$ in the perovskite oxides, etc. As 5d electrons are moderately or weakly correlated and their orbitals are much delocalized, their magnetic coupling could well be a long-range interaction.

In this work, we study the electronic structure and magnetism of the newly synthesized double perovskite Sr$_2$NilrO$_6$, using density functional calculations. This material crystallizes in the monoclinic space group P21/n at RT (see Fig. 2) and undergoes two structural phase transitions (P21/n → I4/m → Fm-3m) upon heating. Magnetic susceptibility measurements suggest the establishment of AF interactions at $T_N = 58$ K. This oxide has the Ni$^{3+}$ (t$_2g^3$)-Ir$^{5+}$ (t$_{2g}^5$) charge state as seen below. Taking into account a charge fluctuation into the common Ni$^{3+}$–Ir$^{5+}$ state (a reverse Ni$^{2+}$–Ir$^{6+}$ is quite unusual), both the Ni up-spin $e_g$ and down-spin t$_{2g}$ electron hopping (the Ni up-spin t$_{2g}$ levels lie lowest due to the crystal field splitting and Hund exchange) would give a FM SE between the Ni$^{3+}$ and Ir$^{5+}$ ions, see Figs. 1(c) and 1(d). As the $e_g$ and t$_{2g}$ levels are orthogonal, the $e_g$ (t$_{2g}$) electron hopping follows the simple SE mechanism plotted in Fig. 1(b) [Fig. 1(a)]. Apparently, this expected FM order contradicts the observed AF in Sr$_2$NilrO$_6$, and thus consideration of only NN Ni$^{2+}$–Ir$^{6+}$ coupling would be a
mistake here. Then, a possibly long-ranged Ir–Ir coupling within the fcc sublattice should be invoked, which would be AF due to the half-filled \(t_{2g}\) shells [Figs. 1(d) and 1(e)]. As we calculate below, there is indeed a long-range AF interaction in the fcc Ir\(^{6+}\) sublattice, and the second NN Ir–Ir AF coupling energy is even bigger than the first NN Ni–Ir FM one, thus giving rise to a magnetic frustration. As a result, \(\text{Sr}_2\text{NiIrO}_6\) behaves as a distorted low-temperature antiferromagnet (probably, of type III). Naturally, the frustrated AF couplings in the fcc Ir\(^{6+}\) sublattice explain a very similar magnetic property in the isostructural \(\text{Sr}_2\text{ZnIrO}_6\). Note that one could take care of long-range magnetic interaction of the delocalized 5d electrons.

**Results**

We first study the electronic structure of \(\text{Sr}_2\text{NiIrO}_6\) and the Ni–Ir coupling. Fig. 3 shows the orbitally resolved density of states (DOS) calculated by LSDA for the FM state. The delocalized Ir 5d electrons have a strong covalency with the ligand oxygens, giving rise to a large bonding-antibonding splitting. The \(p_d\) splitting of the Ir \(e_g\) electrons is up to 9 eV, and the \(p_d\) splitting of the Ir \(t_{2g}\) electrons is about 6 eV. The Ir 5d electrons have a \(t_{2g}-e_g\) crystal-field splitting of more than 3 eV. Besides the occupied bonding states (around \(-6\) eV) ascribed to the lower-lying \(O 2p\) bands, only the up-spin Ir \(t_{2g}\) state is occupied, giving a formal Ir\(^{6+}\) charge state with a \(t_{2g}^6e_g^0\) \((S = 3/2)\) configuration. In contrast, the Ni 3d electrons are confined and have a smaller \(p_d\sigma (p_d\pi)\) bonding-antibonding splitting of 4 eV.

![Figure 1](https://www.nature.com/scientificreports/) (a) AF and (b) FM SE between two two-level d\(^{1}\) ions. (c) and (d): \(\text{Sr}_2\text{NiIrO}_6\) would be FM, according to the SE between the NN Ni\(^{2+}\) and Ir\(^{6+}\) ions. (d) and (e): AF SE in the fcc Ir\(^{6+}\) sublattice.

![Figure 2](https://www.nature.com/scientificreports/) Double perovskite structure of \(\text{Sr}_2\text{NiIrO}_6\). The Ni and Ir ions form their respective fcc sublattices.

![Figure 3](https://www.nature.com/scientificreports/) Ir 5d and Ni 3d DOS of \(\text{Sr}_2\text{NiIrO}_6\) calculated by LSDA for the FM state. The solid red (thin blue) curves stand for the up (down) spin channel. Fermi level is set at zero energy. \(\text{Sr}_2\text{NiIrO}_6\) has the Ni\(^{2+}\) \((t_{2g}^6e_g^0)\)-Ir\(^{6+}\) \((t_{2g}^6)\) charge state.

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particularly those associated with the delocalized Ir 5d electrons. To do so, we use two artificial systems with either Ir$^{4+}$ or Ni$^{2+}$ magnetic sublattice only, Sr$_2$ZnIrO$_6$ [i.e., Sr$_2$Zn(Ni)IrO$_6$ in Table 1] and La$_2$NiSiO$_6$ both in the Sr$_2$NiIrO$_6$ structure, to calculate the 2NN Ir$^{4+}$-Ir$^{4+}$ and Ni$^{2+}$-Ni$^{2+}$ exchange parameters ($J'_{\text{Ir-Ir}}$ and $J'_{\text{Ni-Ni}}$ with a reference to the 1NN J$_{\text{Ni-Ir}}$). This approach avoids choices of complicate magnetic structures in bigger supercells, and allows to estimate the two parameters separately. For Sr$_2$Zn(Ni)IrO$_6$, the layered AF state (FM ab planes alternate along the c axis, see also Fig. 2) is more stable than the FM state by 0.42 eV/f.u. The corresponding energy difference of 19 meV/f.u for La$_2$NiSiO$_6$ gives AF J$_{\text{Ni-Ni}}$ = 19/8 ≈ 2.4 meV, see Table 1.

As the magnetic Ir$^{4+}$ and Ni$^{2+}$ ions have closed subshells, the SE interactions naturally explain the AF $J'_{\text{Ir-Ir}}$ and $J'_{\text{Ni-Ni}}$. Note that the Ni$^{2+}$ 3d electrons are confined but the Ir$^{4+}$ 5d electrons are delocalized, it is therefore not surprising that $J'_{\text{Ir-Ir}}$ is about four times as big as J$_{\text{Ni-Ni}}$. However, it is a bit surprising that the 2NN AF $J'_{\text{Ir-Ir}}$ is even bigger than the 1NN FM J$_{\text{Ni-Ni}}$ thus giving rise to a magnetic frustration in Sr$_2$NiIrO$_6$. This vital role of the strong 2NN AF Ir-Ir coupling is also manifested in the real double perovskite Sr$_2$ZnIrO$_6$, see below.

Sr$_2$ZnIrO$_6$ has a very similar crystal structure and magnetic property to Sr$_2$NiIrO$_6$, and it has AF interactions at $T_N = 46$ K$^{17}$. We have also calculated different magnetic states of Sr$_2$ZnIrO$_6$ and find the 2NN AF $J_{\text{Ir-Ir}}$ = 75/8 ≈ 9.4 meV (see Table I), being close to J$_{\text{Ir-Ir}}$ = 10.5 meV in Sr$_2$NiIrO$_6$. As the delocalized Ir 5d electrons produce a long-range magnetic interaction, we also estimate the 3NN AF $J'_{\text{Ir-Ir}}$ (the exchange path along the linear Ir-O-Ni-O-Ir bonds with the Ir-Ir distance of 7.8 Å) by calculating the bilayered AF state of Sr$_2$ZnIrO$_6$. The bilayered AF state has FM ab planes but AF alternation every bilayer along the c axis, and it is more stable than the FM state by 42 meV/f.u. The exchange energy per formula unit can be expressed as $6J_{\text{Ir-Ir}} + 3J'_{\text{Ir-Ir}}$ for the FM state and $2J_{\text{Ir-Ir}} + J'_{\text{Ir-Ir}}$ for the bilayered AF state. Therefore, the AF $J'_{\text{Ir-Ir}}$ is estimated to be $(42 - 4 \times 9.4)/2 = 2.2$ meV.

**Discussion**

As seen from the above results, apparently the Ir-Ir magnetic interactions are long-ranged and have a non-negligible strength even at a distance of about 8 Å. It is the long-range AF interactions of the Ir$^{4+}$ sublattice which make Sr$_2$ZnIrO$_6$ magnetically frustrated. As both $J_{\text{Ir-Ir}} = 9.4$ meV and $J'_{\text{Ir-Ir}} = 2.2$ meV (see Table I) are AF, and $J_{\text{Ir-Ir}}$ versus $J'_{\text{Ir-Ir}} < 1/2$, Sr$_2$ZnIrO$_6$ is most probably a type-III antiferromagnet $^{19}$ . Moreover, while the strongest 2NN AF $J_{\text{Ir-Ir}}$ overwhelms the 1NN FM J$_{\text{Ni-Ir}}$ and also makes Sr$_2$NiIrO$_6$ magnetically frustrated, the FM J$_{\text{Ni-Ni}}$ could lift (or at least, partially) the frustration and select one state out of the degenerate manifold of fcc AF. In a word, the long-range magnetic interactions and frustration would make the cubic double perovskites Sr$_2$NiIrO$_6$ and Sr$_2$ZnIrO$_6$ distorted, and this would partially relieve the magnetic frustration and eventually stabilize them into a similar low-temperature antiferromagnet $^{20}$ which is worth a further experimental study.

Finally, we check if the SOC is important or not in the present materials. Normally, SOC is important in heavy 5d TMs, and particularly, iridates recently receive great interest $^{10}$ . Owing to a large crystal-field splitting, iridates are in a low-spin state with only the $t_{2g}$ occupation (e.g., in a cubic crystal field). Then the SOC splits the $t_{2g}$ triplet (with also 2-fold spin degeneracy) into the lower J = 3/2 quartet and the higher J = 1/2 doublet $^{11}$ . We have used this SOC basis set to project the Ir$^{4+}$ $t_{2g}$ DOS of Sr$_2$ZnIrO$_6$ calculated by LDA + SOC, but we find that the J = 3/2 and the J = 1/2 states are completely mixed, see Fig. 5(a). Therefore, the J = 3/2 and the J = 1/2 states are not at all eigen orbitals in Sr$_2$ZnIrO$_6$ (and in Sr$_2$NiIrO$_6$ with the same fcc Ir$^{4+}$ sublattice). This is because the delocalized Ir 5d electrons form, with the intersite electron hoppings in the fcc sublattice (the high coordination of twelve), a 'broad' band with its bandwidth being more than 1 eV. Then the SOC effect is 'killed'.

| System       | Magn.   | $\Delta E$ (meV/f.u) | $M_{\text{Ni}-\text{Ir}}$ (µB) |
|--------------|---------|---------------------|-------------------------------|
| Sr$_2$NiIrO$_6$ | FM      | 0                   | 1.76/1.46                     |
| Sr$_2$Zn[Ni]IrO$_6$ | G-AF   | 89                  | 1.64/1.28                     |
| La$_2$NiSiO$_6$ | FM      | 0                   | 1/1.39                        |
| Sr$_2$ZnIrO$_6$ | Layered AF | -84              | 1/1.31                        |
| J$_{\text{Ir-Ir}}$ | 9.4, 10.5 | 2.4               | 1/1.34                        |

**Table 1** Relative total energies $\Delta E$ (meV/f.u) and spin moments $M$ (in unit of $\mu_B$) calculated by LDA + U for different systems in different magnetic states. The Ir-Ir magnetic interactions are estimated for Sr$_2$ZnIrO$_6$ either in Sr$_2$NiIrO$_6$ structure (Zn substitution for Ni) or in its real structure $^{17}$. The Ni-Ni exchange coupling is estimated using the artificial La$_2$NiSiO$_6$ in Sr$_2$NiIrO$_6$ structure. The derived exchange energy parameters (meV) for the 1NN Ni-Ir, 2NN Ir-Ir and Ni-Ni, and 3NN Ir-Ir pairs are listed in the last two rows.
In contrast, if the Ir-Ir coordination number is reduced as in the low-dimensional iridates, the SOC effect would be manifested. To check this, we also calculate the artificial system Sr$_2$GaIr$_{0.5}$Si$_{0.5}$O$_6$ (in Sr$_2$ZnIrO$_6$ structure) with alternating GaIr and SiIr planes. The Ga$^{3+}$ and Ir$^{4+}$ ions have well comparable ionic sizes, and they make charge balanced and the Ir$^{4+}$-Ir$^{4+}$ ions only four-coordinated. In this case, the SOC splitting of about 0.5 eV between the J = 3/2 and the J = 1/2 states is well restored as seen in Fig. 5(b), and thus the J = 3/2 and the J = 1/2 states would serve as eigen orbitals in a good approximation.

The above results show that in Sr$_2$ZnIrO$_6$ and Sr$_2$NiIrO$_6$ the delocalized Ir$^{4+}$ 5d electrons have an insignificant SOC effect due to the band formation in the fcc sublattice. Moreover, the half-filled t$_{2g}$ subsHELL of the high-valence Ir$^{4+}$ ion has an intrinsic exchange splitting of about 1 eV, see Fig. 3. Both the band effect and the exchange splitting are stronger than the SOC strength, making the SOC ineffective in Sr$_2$NiIrO$_6$ and Sr$_2$ZnIrO$_6$. Our LSDA + U + SOC test calculations indeed show that the Ir$^{4+}$ ion has only a small orbital moment of 0.07 $\mu_B$, being antiparallel to the spin moment of about 1.3 $\mu_B$ reduced from the formal S = 3/2. Therefore, both Sr$_2$ZnIrO$_6$ and Sr$_2$NiIrO$_6$ can be described as an Ir$^{4+}$ S = 3/2 fcc frustrated system, although Sr$_2$NiIrO$_6$ itself has an appreciable Ni$^{3+}$-Ir$^{4+}$ FM coupling.

In summary, using density functional calculations, we find that the newly synthesized isostuctural double perovskites Sr$_2$NiIrO$_6$ and Sr$_2$ZnIrO$_6$ are insulating and have the formal Ir$^{4+}$ S = 3/2 fcc sublattice, in addition to the Ni$^{3+}$ S = 1 sublattice in the former. The delocalized Ir 5d electrons produce long-range magnetic interactions, and the 2NN Ir-ir AF interaction turns out to be even stronger than the 1NN Ni-Ir FM interaction. Therefore, the leading AF interactions in the fcc Ir sublattice give rise to a magnetic frustration in both Sr$_2$NiIrO$_6$ and Sr$_2$ZnIrO$_6$. As a result, both the cubic compounds appear as a distorted low-temperature antiferromagnet (probably, of type III). Note that the band formation in the high-coordination Ir 1r sublattice and the exchange splitting of the high-valence Ir$^{4+}$ ion both make the SOC ineffective, and the long-range interactions of the delocalized 5d electrons (band formation and magnetic coupling) would be taken care of.

![Figure 5](https://www.nature.com/scientificreports/images/07542-fig5.png)

**Figure 5** The LDA + SOC calculated Ir$^{4+}$ t$_{2g}$ DOS projected onto the SOC basis set, the J = 3/2 quartet (solid red curves) and the J = 1/2 doublet (dashed blue curves). (a) In Sr$_2$ZnIrO$_6$, the overall mixing of the J = 3/2 and J = 1/2 states is due to the band formation of the delocalized Ir 5d electrons in the fcc Ir sublattice with twelve Ir-Ir coordination. (b) The SOC splitting of about 0.5 eV between the J = 3/2 and the J = 1/2 states is restored upon the reduction of the Ir-Ir coordination to four, which is modeled in the artificial system Sr$_2$GaIr$_{0.5}$Si$_{0.5}$O$_6$ (in Sr$_2$ZnIrO$_6$ structure) with alternating GaIr and SiIr planes.

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**Methods**

Our calculations were performed using the full-potential augmented plane waves plus local orbitals method (WIEN2k code)\cite{23}. We took the structure data of Sr$_2$NiO$_6$, measured by neutron diffraction at RT\cite{24}. The muffin-tin sphere radii are chosen to be 2.8, 2.1, and 1.5 Bohr for Sr, Ni, Ir, and O atoms, respectively. The cutoff energy of 16 Ry is used for plane wave expansion of interstitial wave functions, and 6 × 6 × 4 k mesh for integration over the Brillouin zone, both of which ensure a sufficient numerical accuracy. SOC is included by the second-variational method with scalar relativistic wave functions. We employ the local spin density approximation plus Hubbard U (LSDA + U) method\cite{25} and use the typical values, U = 6 eV and J$_{HF}$ = 0.9 eV (U = 2 eV and J$_{HF}$ = 0.4 eV), to describe electron correlation of the Ni 3d (Ir 5d) electrons. The calculated Mott insulating state of Sr$_2$NiIrO$_6$ remains unchanged within a reasonable range of the U values (U = −4 eV for Ni 3d and U = −1–3 eV for Ir 5d), and the corresponding variation of 1–2 meV for the exchange energy parameters does not affect our discussion and conclusion about the frustrated magnetism.
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Author contributions

H.W. conceived the idea and designed the research. X.O. performed the calculations, with helps of Z.L., F.F. and H.W. H.W. and X.O. prepared the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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In the original version of the Article, the first affiliation ‘Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, and Department of Physics, Fudan University, Shanghai 200433, China’ was omitted for author Hua Wu. This has now been corrected in both the HTML and PDF versions of the Article.