Revisiting Goodenough-Kanamori rules in a new series of double perovskites LaSr$_{1-x}$Ca$_x$NiReO$_6$

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The magnetic ground states in highly ordered double perovskites LaSr$_{1-x}$Ca$_x$NiReO$_6$ ($x = 0.0, 0.5, 1.0$) are studied in view of the Goodenough-Kanamori rules of superexchange interactions in this paper. In LaSrNiReO$_6$, Ni and Re sublattices are found to exhibit curious magnetic states separately, but no long range magnetic ordering is achieved. The magnetic transition at ~255 K is identified with the independent Re sublattice magnetic ordering. Interestingly, the sublattice interactions are tuned by modifying the Ni-O-Re bond angles through Ca doping. Upon Ca doping, the Ni and Re sublattices start to display a ferrimagnetically ordered state at low temperature. The neutron powder diffraction data reveals long range ferrimagnetic ordering of the Ni and Re magnetic sublattices along the crystallographic b-axis. The transition temperature of the ferrimagnetic phase increases monotonically with increasing Ca concentration.

Double perovskites (DP; $A_{x}BB'$O$_6$)$^{1-11}$ belong to a class of materials which exhibit many interesting properties and rich physics. Understandably, the choice of the transition metal ions at the $B$ and $B'$ sites with different electron occupancies decide the material properties of the DPs. When both $B$ and $B'$ are magnetic ions, the magnetic and electronic properties of the system are governed by $B$-$O$-$B'$ interaction within a rock salt type structural definition as shown in Fig. 1(a). For example, the high temperature ferromagnetic (FM) order ($T_C > 400$ K) of the DP compounds, Sr$_2$FeMoO$_6$ and Sr$_2$FeReO$_6$ is explained by a generalized double exchange mechanism through electronic band filling of the (Mo/Re)$_{t_{2g}}$-O-$t_{2g}$ conduction band$^4$. However, if the $B$-site ion is non-magnetic, the magnetic ground state would be defined by the edge-shared network of tetrahedra comprising the $B'$ magnetic ions (Fig. 1(b)). Such systems often exhibit geometric frustration in presence of antiferromagnetic nearest-neighbor correlations. Recently, detailed theoretical investigations have been carried out on similar DPs with the magnetic $B'$ ions, having nd$^2$ and nd$^5$ ($n = 4, 5$) electronic configurations and significant spin orbit coupling (SOC)$^{12,13}$. Here, the nearest neighbor distance between the tetrahedrally arranged 4d/5d magnetic ions naturally becomes much larger compared to the cases when both $B$ and $B'$ sites are filled up with the magnetic ions. This reduces the inter-atomic exchange between the magnetic ions which helps to protect the SOC driven states. This situation opens up many options, and consequently many double perovskites with $d^1$ (e.g., Ba$_2$YMoO$_6$, Sr$_2$CaReO$_6$, Sr$_2$MgReO$_6$, Ba$_2$NaOsO$_6$ etc.) as well as $d^2$ electronic configurations (e.g., Ba$_2$CaOsO$_6$, Ba$_2$YReO$_6$, La$_2$LiReO$_6$ etc.) have been studied, where numerous unusual magnetic ground states are revealed$^{14-19}$.

Another interesting possibility appears in DPs, when both $B$ and $B'$ ions are magnetic, but the valence electrons of $B$ ion lack the orbital symmetry of the same of $B'$ ion for effective $B$-$O$-$B'$ super-exchange interaction. Such a

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situation will give rise to two noninteracting or weakly interacting magnetic sublattices. It will be interesting to gradually manipulate the extent of B-O-B’ interaction by carefully changing the B-O-B’ angle, and consequently follow the evolution of two sublattices getting engaged in single magnetic lattice (Fig. 1(b) → Fig. 1(a)), following the famous Goodenough-Kanamori rule. Accordingly, we have designed a series of DPs, LaSr₁₋ₓCaₓNiReO₆, having a combination of 3d and 5d transition metals Ni^{2+} (3d⁹, t₂g⁳e₈g) and Re^{5+} (5d⁵, t₂g²) at the B and B’ sites, respectively. Due to large crystal field splitting, the empty eg manifold and do not contribute in any interatomic exchange interaction. The filled t₂g orbital of Ni as well has less involvement in the exchange interaction. The only possible exchange interaction that can be active between the e₈ of Ni^{2+} and the t₂g of Re^{5+}, will be very weak if the B-O-B’ angle is strictly 180°, as the overlap integral between the e₈ and the t₂g becomes zero. However, finite overlap between these orbitals can be introduced by tuning the bond angles and lattice parameters as a consequence of the doping of Sr³⁺ ions by smaller sized Ca²⁺ ions.

In our design criteria of the ordered LaSr₁₋ₓCaₓNiReO₆ series, B, B’ cations are also selected in such a way that there are large differences in their charge and ionic radii, in order to achieve complete B-O-B’ angle. Due to large crystal field splitting, the empty eg manifold and do not contribute in any interatomic exchange interaction. The filled t₂g orbital of Ni as well has less involvement in the exchange interaction. The only possible exchange interaction that can be active between the e₈ of Ni^{2+} and the t₂g of Re^{5+}, will be very weak if the B-O-B’ angle is strictly 180°, as the overlap integral between the e₈ and the t₂g becomes zero. However, finite overlap between these orbitals can be introduced by tuning the bond angles and lattice parameters as a consequence of the doping of Sr³⁺ ions by smaller sized Ca²⁺ ions.

**Results**

All the samples appeared to be single phased as no impurity peak is detected in the whole 2θ range in the powder XRD data, collected at room temperature for LaSr₁₋ₓCaₓNiReO₆ (LSCNRO) series (see Fig. 2(a,b)). The observed (circle), calculated (line through the data) and the difference (blue dashed line) diffraction data are shown in Fig. 2 for x = 0.0 and 1.0 compositions respectively, which could be fitted with the P2₁/n space group. The system shows increase in monoclinic distortion (see the insets to Fig. 2(a,b)) with increasing Ca concentration (see Fig. S1 in SI to compare the XRD patterns for all the three compositions collected at a synchrotron X-ray source). The system undergoes multiple magnetic transitions, indicated by a divergence between ZFC and FC at ~255 K, typical for Ni-O-Re (ZNBO) bond angles from 180°. This deviation enables substantial superexchange interaction between the Ni e₈ and Re t₂g orbitals, resulting to an overall ferrimagnetic order between two individual ferromagnetic sublattices.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Crystal structure: (a) The crystal structure of the B-site ordered double perovskite, AᵥBB’O₆. (b) The geometrically frustrated face-centered cubic lattice of edge-shared tetrahedra formed by the B’ sites.
is much more intense relative to the higher energy one, while both the peaks have similar intensities in case of NdNiO$_3$, PrNiO$_3$ and LaNiO$_3$, containing Ni$^{3+}$ ions$^{18}$. Also, the spectral feature of the L$_{2,3}$ edge of all the three compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ for all compositions, clearly resemble to that of NiO. Hence it can be inferred that Ni is in 2$^{+}$ charge state for all the LSCNRO compositions.

The resistivity data were fitted using an activated transport model as well as using variable range hopping model. Both the data were nonlinear on a $T^{-1}$ scale and was found to be linear on a $T^{-1/4}$ scale (see inset to Fig. 4(a,b)), in accordance with a three-dimensional variable range hopping transport model$^{19}$. The insulating nature of the compounds can be explained by the fact that Ni$^{2+}$; 3$d^8$ effectively provides electrons of $e_g$ symmetry at the valence band as the $t_{2g}$ bands are completely filled up, while Re$^{5+}$; 5$f^8$ has partially filled $t_{2g}$ bands, thus from the symmetry consideration the electron hopping is prohibited (see the inset of Fig. 4(a)). However, a nonzero hopping probability is realized if the bond angles deviate sufficiently from 180°, thereby enabling Ni$^{2+}$-Re$^{5+}$ hybridization via oxygen (compare the inset to Fig. 4(b)). Replacing Sr$^{2+}$ by the smaller Ca$^{2+}$ ion, we anticipate a larger octahedral distortion that can provide a route for hybridization between the Ni$^{2+}$ and Re$^{5+}$. Indeed, a larger amount of distortion is achieved as understood from the crystal structure of LaCaNiReO$_6$ and consequently a clear decrease in the resistivity is also observed, although the temperature dependence still suggests that the material is best described as an insulator/semiconductor.

Next, we have looked into the magnetic properties details. The zero field cooled (ZFC) and field cooled (FC) data recorded with an applied field of 200 Oe for the three compositions of LSCNRO are shown in Fig. 5(a–c). The magnetization versus field ($M(H)$) curves, collected at room temperature: The observed (black circle), calculated (red line) and the difference (blue dashed line) in LSCNRO compositions. In order to maintain charge neutrality, the charge state of Re should then be 5$^{+}$ as Sr$^{2+}$, La$^{3+}$ and O$^{2-}$ are expected to be very stable at their respective ionic states.

The coercivity of all the samples are very high in general, which arises as a result of large spin-orbit coupling and Re$^{5+}$ contribution of both Ni$^{2+}$ and Re$^{5+}$ and this reduction in magnitude can attributed to the spin-orbit coupling in Re$^{4,20}$. For $x = 0.5$ (Fig. 5(b)) a ferro/ferrimagnetic (FM) like transition is observed at 45 K, along with the high temperature FC-ZFC bifurcated curves. This FM like transition gradually shifts to higher temperatures with increasing $x$ ( ~110 K for $x = 1.0$; Fig. 5(c)). Also as $x$ increases, the FM like transition becomes stronger to obscure the high temperature FC-ZFC splitting. The effective magnetic moment obtained from Curie-Weiss fit for $x = 1.0$ (see Fig. S2(b)) is 3.59 $\mu_B$.

The magnetization versus field ($M(H)$) data, collected at 5 K for the three compositions are plotted in Fig. 5(d). The coercivity of all the samples is very high in general, which arises as a result of large spin-orbit coupling driven anisotropy, commonly observed for Re based DPs$^{4,20}$. However, the overall nature of the $M(H)$ curves varies drastically with $x$. The remnant magnetization increases continuously with clear signatures of magnetic saturation as a function of Ca-doping. This observation clearly suggests significant changes in magnetic interactions with increasing monoclinic distortions and decreasing $B$-$O$-$B'$ angle.

Figure 2. Combined Rietveld refinement of the X-ray diffraction pattern and the neutron diffraction pattern collected at room temperature: The observed (black circle), calculated (red line) and the difference (blue dashed line) diffraction data for (a,c) $x = 0.0$, (b,d) $x = 1.0$ compositions are shown. Insets of (a,b) show the magnified view of the peaks around $2\theta \sim 32^\circ$, emphasizing the monoclinic distortion in case of $x = 1.0$ sample.
Table 1. Refinement parameters of the $x = 0.0$ and $1.0$ compositions obtained from combination of the XRD and NPD data collected at 300 K and NPD data at 2 K. The $x$, $y$, $z$ coordinates for Ni1/Re1 and Re2/Ni2 are 1/2,0,1/2 and 1/2,0,0 respectively.

| Space group | $x = 0.0$ | $x = 1.0$ |
|-------------|-----------|-----------|
|              | 300 K     | 2 K       | 300 K     | 2 K       |
|              | $P2_1/n$  | $P2_1/n$  | $P2_1/n$  | $P2_1/n$  |
| $a$ (Å)     | 5.5980 (1) | 5.5862 (1) | 5.49735 (5) | 5.48136 (8) |
| $b$ (Å)     | 5.5748 (1) | 5.5693 (1) | 5.58551 (4) | 5.59108 (8) |
| $c$ (Å)     | 7.8947 (2) | 7.8846 (1) | 7.80465 (7) | 7.78287 (9) |
| $\beta$     | 90.021 (8) | 90.045 (2) | 89.8729 (9) | 89.924 (4)  |
| Cell Vol. (Å$^3$) | 246.38 (1) | 245.30 (1) | 239.638 (3) | 238.517 (6) |
| $R_{wp}$    | 5.21       | 4.58       | 4.39       | 6.81       |
| $\chi^2$    | 2.17       | 4.98       | 6.37       | 1.99       |

| La/(Sr/Ca)  | $x = 0.0$ | $x = 1.0$ |
|-------------|-----------|-----------|
|             | 0.4896 (3) | 0.4977 (7) |
| $y$         | 0.294 (1)  | 0.291 (1)  |
| $z$         | 0.034 (1)  | 0.035 (1)  |
| $B$ (Å$^2$) | 0.72 (4)   | 0.89 (5)   |

| Ni1/Re1     | occupancy | 96.0/0.04 | 99.9/0.01 |
|-------------|-----------|-----------|-----------|
| $B$ (Å$^2$) | 0.42 (1)  | 0.48 (1)  | 0.45 (4)  |

| Re2/Ni2     | occupancy | 96.0/0.04 | 99.9/0.01 |
|-------------|-----------|-----------|-----------|
| $B$ (Å$^2$) | 0.42 (1)  | 0.48 (1)  | 0.45 (4)  |

| O1          | $x$       | 0.294 (1)  | 0.291 (1)  |
|-------------|-----------|-----------|-----------|
| $y$         | 0.289 (1)  | 0.287 (1)  |
| $z$         | 0.034 (1)  | 0.0472 (9) |
| $B$ (Å$^2$) | 0.72 (4)   | 0.89 (5)   |

| O2          | $x$       | 0.237 (1)  | 0.228 (1)  |
|-------------|-----------|-----------|-----------|
| $y$         | 0.769 (1)  | 0.7937 (9) |
| $z$         | 0.024 (1)  | 0.0349 (9) |
| $B$ (Å$^2$) | 0.73 (5)   | 0.79 (9)   |

| O3          | $x$       | 0.573 (1)  | 0.571 (1)  |
|-------------|-----------|-----------|-----------|
| $y$         | −0.0014 (9)| −0.0015 (9)| −0.0217 (6)| −0.0220 (4)|
| $z$         | 0.247 (2)  | 0.248 (1)  | 0.2413 (9) |
| $B$ (Å$^2$) | 0.68 (2)   | 0.80 (5)   | 0.78 (1)   |

Table 2. (Ni,Re)-O bond distances and Ni-O-Re bond angles extracted from the data of Table 1.
In order to have more insight about the observed magnetic transitions, neutron powder diffraction (NPD) were carried out for the end compositions at 2 K. The changes in the lattice parameters, bond lengths and bond angles with temperature have been listed in Tables 1 and 2. For $x=0.0$, there is a contraction of the lattice parameters with decrease in temperature with no signature of long range magnetic ordering (see Fig. 6(a)), which suggests that the observed magnetic transitions in the magnetization curves are of short range type. Our observation is in accordance with the NPD measurements of SrLaNiReO$_6$ reported in ref. 21 which also lacked evidence of long-range magnetic ordering.

The neutron diffraction patterns of $x=1.0$ recorded at 2 K and 300 K are shown in Fig. 7(a). From Table 1 it is evident that there is an elongation in the lattice parameter along $b$ axis with the decrease in temperature. Contrary to $x=0.0$, it is observed that the nuclear peak profile in the vicinity of 24° comprising(011), (101), and (−101) nuclear Bragg peaks clearly gets enhanced in intensity at 2 K. Since no extra magnetic reflections with significant intensity are observed, the magnetic structure can be assumed to coincide with the crystal structure.
and propagation vector \( k = (000) \) may be used to model the structure. Thus, using the formalism of propagation vectors in conjunction with the irreducible representation analysis as described in ref. \(^{22}\), the magnetic reducible representation for the magnetic atoms can be decomposed as a direct sum of irreducible representations. For the refinement of the magnetic structure, the symmetry elements and basis vectors of the irreducible representations (\( \Gamma \)) for magnetic Ni (Re) atom were obtained using \( \text{BasIre} \) program available within the FullProf suite, using the \( k = (000) \) propagation vector. It is observed that the magnetic representation of Ni (Re) ion comprises two irreducible representations \( \Gamma' = \Gamma_1 + \Gamma_3 \). The two \( \Gamma \) values were tested sequentially with the measured pattern at 2 K and we could refine the magnetic structure satisfactorily using the basis vectors of \( \Gamma_1 \). Although using this same representation, a collection of peaks at around \( 2\theta = 47^\circ \) shows magnetic contributions, the magnetic structure factor turns out to be less than 1\% of the nuclear intensity with magnetic form factor for Ni\(^{2+}\) being around 0.7 at this Q-value, which hinders the accurate estimation of the magnetic structure from this peak. Thus the most probable magnetic structure can be estimated from the peak near \( 24^\circ \) using the basis vectors of \( \Gamma_1 \). It was found that the Ni (Re) moments lie predominantly along negative (positive) \( b \) direction with a very small canting, which could not be resolved within the measuring capability. Hence, the moments were constrained along \( b \) direction and refined. The obtained moments on Ni and Re are \(-2.0 (4) \mu_B\) and \(1.0 (4) \mu_B\) (Table 3, Fig. 8), respectively, resulting in a net magnetic moment of \(-1.0 \mu_B\) per formula unit along the negative \( b \) direction.

Figure 5. Magnetic measurements: (a–c) ZFC FC, \( M(T) \) data of LaSr\(_{1-x}\)Ca\(_x\)NiReO\(_6\) with \( x = 0.0, 0.5 \) and 1.0 measured with \( H = 200 \text{ Oe} \). Inset of (a) shows the temperature dependence of magnetic susceptibility of \( x = 0.0 \) composition in an applied field of 5000 Oe. (d) \( M(H) \) curves for \( x = 0.0, 0.5 \) and 1.0 compositions. Inset shows variation of \( H_C \) with doping.
Discussions

In a highly ordered B-site double perovskite with magnetic ions at B and B′ sites the long range magnetic order is always determined by the type of active exchange interaction that mediates through the B-O-B′ connectivity. For localized electrons (i.e. the d electrons), the magnetic interaction between two transition metal B and B′ cations is often described by the Goodenough-Kanamori rules of superexchange interaction23,24. According to this rule, when the orbitals of two magnetic ions have a significant overlap integral, the superexchange is antiferromagnetic.

Figure 6. Neutron diffraction measurements for x = 0.0 composition: (a) Neutron diffraction pattern for x = 0.0, recorded at 2 K and 300 K. No magnetic Bragg peaks are observed. (b) Rietveld refinement of NPD data at 2 K. The solid line through the experimental points is the Rietveld refinement profile calculated for the space group P2₁/n structural model. The vertical bars indicate the Bragg positions. The lowermost curve represents the difference between the experimental data and the calculated results.

Figure 7. Neutron diffraction measurements for x = 1.0 composition: (a) Neutron diffraction pattern for x = 1.0 recorded at 2 K and 300 K. Inset shows the enhanced intensity of the nuclear Bragg peak at 24° at 2 K. Rietveld refinement of NPD data for x = 1.0 at (b) T = 2 K (considering magnetic structure). The solid line through the experimental points is the Rietveld refinement profile calculated for the space group P2₁/n structural model. The vertical bars indicate the Bragg positions. The lowermost curve represents the difference between the experimental data and calculated results.
Table 3. Results obtained from NPD data collected at 2 K for $x = 1.0$ sample. $M_t$ is refined and the net magnetic moment is listed above.

| Atom type | $M_{tot}$ (μB) |
|-----------|----------------|
| Ni        | -2.0 (4)       |
| Re        | 1.0 (4)        |

Figure 8. Magnetic structure for $x = 1.0$ at $T = 2$ K. Arrows indicate the direction of the Ni (blue sphere) and Re (orange sphere) moments. The La/Ca, and O atoms are not shown for clarity. The average value of the ordered magnetic moment is estimated as $\sim 1.0$ μB/f.u.

$(\angle e_x(B')-O-e_y(B') = 180^\circ, \angle t_{g_2}(B')-O-t_{g_1}(B') = 180^\circ, \angle t_{g_2}(B')-O-t_{g_1}(B') = 90^\circ)$. However, when the orbitals are arranged in such a way that they are expected to be in contact but to have no/weak overlap integral - most notably $t_{g_2}$ and $e_y$ in $180^\circ$ position, where the overlap is zero by symmetry, the rules predict ferromagnetic interaction, which is usually very weak in strength. In case of highly ordered LaSr1-xCaNiReO6 compounds, Ni 3d and Re 5d orbitals are connected via oxygen 2p orbitals. From refinement of XRD and NPD, the average Ni-O-Re bond angle ($\angle NOR$) comes about $160^\circ$ for $x = 0.0$ sample and $\sim 152^\circ$ for $x = 1.0$ sample. Therefore in case of $x = 0.0$ sample, when $\angle NOR$ is closer to $180^\circ$, the superexchange interaction between half filled $t_{g_2}$ orbitals of Ni$^{2+}$ and partially filled $t_{g_1}$ orbitals of Re$^{5+}$ is a weak ferromagnetic interaction. Of course, there could be magnetic signals appearing from independent Ni and Re sublattices as well. However, as the $\angle NOR$ start deviating noticeably from $180^\circ$ (e.g. $x = 1.0$), a sizeable overlap between the $e_y$ and $t_{g_2}$ orbitals starts to favor antiferromagnetic (AFM) interaction between the partially filled Ni $e_y$ and Re $t_{g_2}$ orbitals following the Goodenough-Kanamori rule. Further, we have noticed that the smaller volume of the $x = 1.0$ sample compared to $x = 0.0$ sample has no significant effect in the Ni/Re-O bond lengths. The reduction of the lattice parameters is compensated by the smaller $\angle NOR$ angles.

We conclude that the low temperature magnetic feature observed in $x = 0.0$ compound could very well be a reminiscence of the weak ferromagnetism predicted by Goodenough-Kanamori rule, but could also be an independent Ni sublattice feature as is seen in other Ni analog samples, such as, SrNiWO3, SrNiTeO3 with nonmagnetic W4+ (Xe[4f10]) and Te6+ ([Kr] 4d10) at the $B'$ site, where the antiferromagnetic transition occurs at 35 K and 54 K, respectively25. This low temperature transition has been identified as the onset of a spin glass behavior in $x = 0.0$ compound25. On the other hand, the observed bifurcation between ZFC and FC curves at higher temperatures in $x = 0.0$ compound is clearly very similar to what is commonly observed when Re-ion sits in the geometrically frustrated fcc lattice (the $B'$-site) within the double perovskite structure, but having nonmagnetic $B$-site ions, e.g., Sr$_2$CaReO$_6$, Sr$_2$InReO$_6$.26.

For $x = 1.0$ sample, further deviation of $\angle NOR$ from $180^\circ$ compared to that of $x = 0.0$ enables an antiferromagnetic interaction between Ni$^{2+}$ and Re$^{5+}$ ions. In an ordered structure, this will result the moment of the individual sublattice to order along the same direction. Strong spin-orbit interaction may result magneto-crystalline anisotropy in case of the Re 5d spins, while the Ni spins, residing in more isotropic 3d orbitals, will orient antiparallel to Re spins following the super-exchange interaction. Therefore, the final magnetic structure is resulted in an ferrimagnetic arrangement between the two sublattices along the crystallographic $b$-axis. In LSCNRO, both Ni$^{2+}$ and Re$^{5+}$ ions have two unpaired electrons. However, the strong spin-orbit coupling in 5d orbitals (relative to 3d orbitals) usually results in a reduced total moment in Re ions compared to its spin only value27–29, which is clearly observed from the NPD analysis. The net magnetic moment of $\sim 1.0$ μB/f.u. obtained from NPD is in good agreement with the observed moment in $M$ vs $H$ data at the highest applied field $\sim 0.75$ μT.
In conclusion, a series of double perovskites, \( \text{La}_{2-x}\text{Ca}_x\text{NiReO}_6 \) \((x = 0.0, 0.5, 1.0)\) is realized with partially filled orbitals of \( e_g \) and \( t_{2g} \) symmetries (local) at highly ordered \( B \) and \( B' \)-sites respectively. All the compositions adopt a monoclinic structure. In La\( \text{Sr}_{1.6}\text{NiReO}_6 \) \((x = 0.0)\), an unusual divergence between the ZFC and FC curves is identified with the magnetic state that arises from Re \( t_{2g} \) ions sitting in a geometrically frustrated fcc sublattice in DP host. At low temperature \((-27 K)\), the system undergoes another magnetic transition, where weak ferromagnetism predicted by Goodenough-Kanamori rule could be identified. As lattice parameter decreases with Ca doping, the reduced Ni-O- Re bond angle introduces nonzero overlap integral between Ni \( e_g \) and Re \( t_{2g} \) orbitals, which favors a ferrimagnetic alignment between Ni and Re sublattices along the \( b \)-axis. The neutron powder diffraction measurement conducted at room temperature and low temperature \((2K)\) revealed that the \( x = 0.0 \) sample possesses a disordered/short-range magnetic state at low temperature, while for Ca sample, the Ni and Re sublattices aligned ferrimagnetically to give a long range magnetic order evidenced from the magnetic Bragg peak corresponding to the double perovskite superlattice peak.

**Methods**

Four samples of \( \text{La}_{2-x}\text{Ca}_x\text{NiReO}_6 \) \((LSCNRO) \)(\(x = 0.0, 0.5, 1.0)\) were synthesized by solid state synthesis route. Highly pure \( \text{La}_2\text{O}_3, \text{SrCO}_3, \text{CaCO}_3, \text{NiO}, \text{Re}_2\text{O}_7 \) and Re metal were used as the starting materials. The synthesis was done in two steps. In the first step, \( \text{La}_2\text{NiO}_4 \) was made by heating a mixture of stoichiometric \( \text{La}_2\text{O}_3 \) and \( \text{NiO} \) at \(1250°C\) in an inert atmosphere. Next, stoichiometric amount of \( \text{La}_2\text{NiO}_4, \text{SrCO}_3, \text{CaCO}_3, \text{NiO}, \text{Re}_2\text{O}_7 \) and Re metal were mixed inside a glovebox and the resultant mixture was sealed after heating them at \(1000°C\) for 12 hours in an inert atmosphere. Next, stoichiometric amount of \( \text{La}_2\text{NiO}_4, \text{SrCO}_3, \text{CaCO}_3, \text{NiO}, \text{Re}_2\text{O}_7 \) and Re metal were sealed inside a quartz tube, which was then annealed at \(1200°C\) for the final product.

The phase purity of the three samples \((x = 0.0, 0.5, 1.0)\) were checked by x-ray diffraction (XRD) Bruker AXS: D8 Advance x-ray diffractometer \((Cu K\alpha, \lambda = 1.54059 Å)\) as well as at MCX beamline of the Elettra Synchrotron Centre, Italy using wavelength of 0.751 Å. The XRD data were analyzed via Rietveld refinement using the FullProf\textsuperscript{30} program. La, Ca, Sr, Ni, Re quantitative analysis were performed in Inductively Coupled Plasma Optical Emission Spectroscopy \((ICP-OES) \) (Perkin-Elmer USA, Optima 2100 DV) instrument following standard protocol of sample analysis. d.c. magnetic measurements were carried out in a Quantum Design SQUID magnetometer. Resistivity measurements were performed in a home made four probe setup. Soft x-ray absorption spectroscopy \((XAS)\) was performed at 11011 beamlines of the Swedish synchrotron facility MAX-lab, Lund. All the XAS spectra were measured by recording the total electron yield. Neutron powder diffraction \((NPD)\) measurements were performed using the HRPT\textsuperscript{31} diffractometer at the Paul Scherrer Institut, SINQ (Switzerland). The neutron wavelength was set to \(\lambda = 1.89 Å\) and about 1 g of \(x = 0.0\) and \(x = 1.0 \) samples were used. Magnetic structure refinements were performed using the FullProf suite\textsuperscript{32}.

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**References**

1. Anderson, M. T., Greenwood, K. B., Taylor, G. A. & Poeppelmeier, K. R. B-cation arrangements in double perovskites. Prog. Solid State Chem. 22, 197–233 (1993).
2. Knapp, M. C. & Woodward, P. M. A-Site Cation Ordering in AA\_BB'O\_8 Perovskites. J. Solid State Chem. 179, 1076–1085 (2006).
3. Vasala, S. & Karpinnen, M. A BB'O\_8 perovskites: A review. Prog. Solid State Chem. 43, 1–36 (2015).
4. Serrate, D., De. Teresa, J. M. & Ibarra, M. R. Double perovskites with ferromagnetism above room temperature. Phys. Rev. Lett. 104, 177202 (2010).
5. Chen, G. & Balents, L. Spin-orbit coupling in d\_2 ordered double perovskites. Phys. Rev. B 84, 094420 (2011).
6. Aharen, T. et al. Structure and magnetic properties of the S = 1 geometrically frustrated double perovskites \( \text{La}_2\text{ReO}_6 \) and \( \text{Ba}_2\text{ReO}_6 \). Phys. Rev. B 81, 046436 (2010).
7. Vries, M. A., de, Mclaughlin, A. C. & Bos, J. W. G. Valence Bond Glass on an fcc Lattice in the Double Perovskite \( \text{Ba}_2\text{YMoO}_6 \). Phys. Rev. Lett. 104, 177202 (2010).
8. Aharen, T. et al. Magnetic properties of the geometrically frustrated S = 1/2 antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 224409 (2010).
9. Yana, T. et al. Ferromagnetism in the Mott Insulator \( \text{Ba}_2\text{NiO}_3 \). Phys. Rev. Lett. 104, 227202 (2010).
10. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
11. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
12. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
13. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
14. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
15. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
16. Yana, T. et al. Magnetic properties of the geometrically frustrated \( S = 1/2 \) antiferromagnets, \( \text{La}_2\text{MnO}_6 \), \( \text{La}_2\text{NiO}_6 \), and \( \text{Ba}_2\text{MnO}_6 \), with the B-site ordered double perovskite structure: Evidence for a collective spin-singlet ground state. Phys. Rev. B 81, 046436 (2010).
23. Goodenough, J. B. Theory of the Role of Covalence in the Perovskite-Type Manganites [La,M(II)MnO3]. Phys. Rev 100, 564 (1955).
24. Kanamori, J. Superexchange interaction and symmetry properties of electron orbitals. J. Phys. Chem. Solids 10, 87–98 (1959).
25. Iwanaga, D., Inaguma, Y. & Itoh, M. Structure and magnetic properties of Sr2NiO4 (A = W, Te). Mater. Res. Bull. 35, 449–457 (2000).
26. Gao, H. et al. Structure-property relations in the distorted ordered double perovskite Sr2InReO6. Phys. Rev. B 83, 134406 (2011).
27. Sikora, M. et al. Evidence of unquenched Re orbital magnetic moment in AA’FeReO6 double perovskites. Appl. Phys. Lett. 89, 062509 (2006).
28. Michalik, J. M. et al. High-field magnetization measurements in Sr2CrReO6 double perovskite: Evidence for orbital contribution to the magnetization. Eur. Phys. Lett. 78, 17006 (2007).
29. Jeon, B. C. et al. Electronic structure of double perovskite A2FeReO6 (A = Ba and Ca): interplay between spin-orbit interaction, electron correlation, and lattice distortion. J. Phys.: Condens. Matter 22, 345602 (2010).
30. Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. Physica B 192, 55–69 (1993).
31. Fischer, P. et al. High-resolution powder diffractometer HRPT for thermal neutrons at SINQ. Physica B 276–278, 146–147 (2000).

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Author contributions

S.J. and P.A. contributed equally. S.J. designed the project and the method of synthesis. S.J. and P.A. have synthesized and characterized the compounds. S.J. and P.A. have performed the XAS and R vs T measurements and analysis. The magnetic measurements and analysis are performed by S.J., P.A., P.A.K. and P.S., while O.K.F., E.N., V.P., M.M. and Y.S. have performed the NPD measurements. O.K. has helped in performing x-ray absorption spectroscopy and contributed in discussion. V.S. has done the NPD analysis and the combined NPD and XRD refinement. S.J., P.A. and S.R. wrote the main body of the manuscript, while all the authors contributed in writing and reviewing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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