Coupled Nd and B′ spin ordering in the double perovskites Nd₂NaB'O₆ (B′ = Ru, Os)

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We present a neutron powder diffraction study of the monoclinic double perovskite systems Nd₂NaB'O₆ (B′ = Ru, Os), with magnetic atoms occupying both the A and B′ sites. Our measurements reveal coupled spin ordering between the Nd and B′ atoms with magnetic transition temperatures of 14 K for Nd₂NaRuO₆ and 16 K for Nd₂NaOsO₆. There is a Type I antiferromagnetic structure associated with the Ru and Os sublattices, with the ferromagnetic planes stacked along the c-axis and [110] direction respectively, while the Nd sublattices exhibit complex, canted antiferromagnetism with different spin arrangements in each system.

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Double perovskites with the formula A₂BB′O₆ have attracted considerable interest recently from both applied and fundamental physics perspectives. The excitement from the applied physics community has largely centered around the observation of room-temperature colossal magnetoresistance coupled with half-metallic behaviour in Sr₂FeMoO₆.¹ These unique properties ensure a high degree of spin polarization of the charge carriers in a useful temperature regime applicable to potential spintronics devices.²

On the fundamental side, double perovskite systems provide excellent opportunities to study geometric frustration on the B′-site face-centered cubic (FCC) sublattice while tuning both the spin quantum number S and spin-orbit coupling. Past efforts have found several exotic magnetic ground states, mostly in systems characterized by quantum spins of S = 1/2 or 1. The diverse magnetism includes a collective singlet state coexisting with paramagnetism in Ba₂YMoO₆,³ ⁴, a collective singlet state in La₂LiReO₆,⁵ spin freezing without long-range order in Ba₂YReO₆,⁵, Sr₂MgReO₆,⁶ and Sr₂CaReO₆,⁷ short-range order in La₂LiMoO₆,⁸ and a ferromagnetic (FM) Mott insulating state in Ba₂NaOsO₆.⁹,¹⁰. Theoretical studies have also indicated that a wealth of other magnetic ground states are possible in these 4d and 5d double perovskite quantum spin systems.¹¹ ¹²

Some of the most interesting physical and magnetic properties observed in the double perovskite family can be attributed to the interactions between different types of magnetic atoms on the B and B′ sites. For example, the colossal magnetoresistance and half-metallic behaviour of Sr₂FeMoO₆ and related systems¹² arises from an antiferromagnetic coupling between the delocalized 4d or 5d electrons and the localized 3d electrons. Moreover, the systems Bi₂FeCrO₆,¹³ ¹⁵ and Bi₂NiMnO₆¹⁶ are rare examples of multiferroics with both large spontaneous magnetization and polarization. Bi₂NiMnO₆ exhibits ferromagnetic properties, resulting from distributing two types of transition metal ions with and without ε₉ electrons in a rock-salt configuration, while Bi₂FeCrO₆ is a ferrimagnet.

In contrast to the extensive studies performed on the sub-set of double perovskites with magnetic B and B′ sites, systems with magnetic ions on both the A and B′ sites remain largely unexplored territory. Exploratory synthesis via solid state reactions and hydroxide flux methods¹⁸ have produced a series of these materials, including R₂NaRuO₆,¹⁹, R₂NaOsO₆,²⁰, R₂LiOsO₆²¹ and R₂MgIrO₆²² (R = rare earth), but the magnetic properties have generally only been investigated with bulk probes such as magnetic susceptibility.

FIG. 1: Double perovskite structure, with the large blue octahedra representing NaO₆, the small green octahedra depicting B′O₆, and the isolated gray spheres corresponding to Nd atoms. The small ionic radius of Nd leads to a large tilting of the NaO₆ and B′O₆ octahedra in Nd₂NaRuO₆ and Nd₂NaOsO₆.
One exception is the recent work of Ref. [23], where neutron diffraction was used to investigate magnetic ordering in the systems $R_2LiRuO_6$ ($R = \text{Nd, Tb, Pr}$). The authors found that all compositions showed evidence for long-range magnetic order except for the Gd system, with the Ru sublattice exhibiting common Type I antiferromagnetic (AF) order and the spins of the rare earth atoms forming a canted arrangement. It is also interesting to note that the magnetic transitions involved coupled spin ordering of the two magnetic sublattices with $T_1's > 10$ K, while in several double perovskite systems with only an A-site rare earth magnetic sublattice, no magnetic ordering has been observed in susceptibility measurements down to 2 K [24, 25]. These observations indicate that the magnetic behaviour of the rare earth ions in these systems is very sensitive to the presence of other types of magnetic atoms.

The syntheses, crystal structures (shown in Fig. 1) and magnetic susceptibilities of the monoclinic double perovskites $\text{Nd}_2\text{NaRuO}_6$ and $\text{Nd}_2\text{NaOsO}_6$ were recently reported [13, 20]. These materials combine a small A site cation with a relatively large ionic radii difference between the B and B' sites, and therefore exhibit very large, room-temperature structural distortions relative to most other double perovskites. Comparing the $\text{Nd}_2\text{NaRuO}_6$ and $\text{Nd}_2\text{NaOsO}_6$ magnetization and magnetic susceptibility results to $\text{La}_2\text{NaRuO}_6$ and $\text{La}_2\text{NaOsO}_6$ clearly shows that the addition of the magnetic rare earth sublattice dramatically alters the magnetic properties of these materials. For example, the small deviation from the Curie-Weiss law with decreasing temperature in the susceptibility of $\text{La}_2\text{NaRuO}_6$ is replaced by a large ferromagnetic-like increase in the susceptibility for $\text{Nd}_2\text{NaRuO}_6$, and significant magnetic hysteresis is observed in the M vs. H curve for the Nd system that is absent in the La case. Furthermore, a ferromagnetic-like increase with decreasing temperature in the susceptibility of $\text{La}_2\text{NaOsO}_6$ gives way to complicated magnetic behaviour for $\text{Nd}_2\text{NaOsO}_6$, likely indicative of a spin-flop transition for an applied field of 1.7 T at $T = 2$ K.

In this work, neutron powder diffraction (NPD) measurements have been performed on the double perovskites $\text{Nd}_2\text{NaRuO}_6$ and $\text{Nd}_2\text{NaOsO}_6$. These specific materials were chosen in an effort to better understand how the unconventional magnetism in $\text{La}_2\text{NaRuO}_6$ and $\text{La}_2\text{NaOsO}_6$ [26] evolves when an exchange path between the A and B' sites is added to these materials. To produce a large enough yield of both materials for the diffraction experiments, solid state synthesis methods were required. For polycrystalline $\text{Nd}_2\text{NaRuO}_6$, $\text{Nd}_2\text{O}_3$ (Alfa Aesar, 99.99%) was first activated by heating in air at 1000°C for 12 h, $\text{Na}_2\text{CO}_3$ (Mallinckrodt, 99.95%) was dried overnight at 150°C, and $\text{RuO}_2$ was prepared by heating $\text{Ru}$ (Engelhard, 99.95%) in air at 1000°C for 24 h. The starting materials were then mixed together in a 1:0.55:1 ratio, and this included a 10% molar excess of $\text{Na}_2\text{CO}_3$ to offset the volatilization of $\text{Na}_2\text{O}$ during heating. This mixture was heated to 500°C in 1 h, held at 500°C for 8 h, heated to 900°C in 1 h, and held at 900°C for 12 h before turning off the furnace and allowing the sample to cool to room temperature. Powder X-ray diffraction showed the presence of $\text{Nd}_2\text{NaRuO}_6$, as well as $\text{Nd}_2\text{O}_3$ and $\text{Nd}_3\text{RuO}_7$ impurities. Therefore, the sample was ground together with additional $\text{Na}_2\text{CO}_3$ and $\text{RuO}_2$, and then subjected to the same heating profile. Due to remaining impurities as confirmed by powder X-ray diffraction, this process was repeated twice more. Finally, all the peaks in the powder pattern could be indexed in the monoclinic space group $P2_1/n$ with lattice parameters in good agreement with those reported for $\text{Nd}_2\text{NaRuO}_6$ [19].

For polycrystalline $\text{Nd}_2\text{NaOsO}_6$, the starting materials were nearly identical, with the only difference being that Os (J&J Materials Inc.) replaced $\text{RuO}_2$. The heat treatment was also slightly modified, as the starting mixture was heated to 700°C in 1 h and held at 700°C for 6 h, before turning off the furnace and allowing the sample to cool to room temperature. Powder X-ray diffraction showed the presence of $\text{Nd}_2\text{NaOsO}_6$, as well as $\text{Nd}_2\text{O}_3$ and $\text{Nd}_3\text{OsO}_7$ impurities. Therefore, the sample was ground together with additional $\text{Na}_2\text{CO}_3$ and Os, and then subjected to the same heating profile. Due to remaining impurities as confirmed by powder X-ray diffraction, this process was repeated four more times. Finally, all the peaks in the powder pattern could be indexed in the monoclinic space group $P2_1/n$ with lattice parameters in good agreement with those reported for $\text{Nd}_2\text{NaOsO}_6$ [20].

For the neutron powder diffraction experiment, roughly 5

FIG. 2: Neutron powder diffraction measurements with a wavelength of 1.54 Å at $T = 50$ K for both (a) $\text{Nd}_2\text{NaRuO}_6$ and (b) $\text{Nd}_2\text{NaOsO}_6$. 
g of each polycrystalline sample was loaded in a closed-cycle refrigerator and studied using the HB-2A powder diffractometer at the High Flux Isotope Reactor of Oak Ridge National Laboratory. Data from HB-2A were collected with neutron wavelengths $\lambda = 1.54$ Å and $\lambda = 2.41$ Å at temperatures of 4 - 50 K using a collimation of 12'-open-6'. The shorter wavelength gives a greater intensity and higher Q coverage that was used to investigate the crystal structures in this low temperature regime, while the longer wavelength gives lower Q coverage and greater resolution that was important for investigating the magnetic structures of these materials. The NPD data was analyzed using the Rietveld refinement program FullProf[27] and the representational analysis software SARAh[28].

Our neutron diffraction results for Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$ reveal that the Nd and B' spins order at the same temperature with very similar magnetic structures to the Nd$_2$LiRuO$_6$ analogue[23]. More specifically, the B' sublattices are characterized by Type I antiferromagnetic order with the ferromagnetic planes stacked along the c-axis and the $[110]$ direction in the Ru and Os compositions respectively, while the Nd sublattices form different canted arrangements in the two materials. The extra Nd-O-B' exchange interactions in these materials have a significant effect on the magnetism, effectively destroying the delicate balance of extended superexchange interactions that lead to the incommensurate magnetic structure of La$_2$NaRuO$_6$ and the drastically-reduced ordered moment of La$_2$NaOsO$_6$.

Figure 2 shows $\lambda = 1.54$ Å NPD data at $T = 50$ K for monoclinic Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$, while Table I shows the refinement parameters extracted from the $T = 4$ K data. Comparing these results with previous X-ray diffraction data collected on single crystals at room temperature[19, 20] reveals no evidence for a structural phase transition between 300 and 4 K in either material, and the structural distortion remains large at all temperatures as indicated by the 4 K $\beta$ values of 90.898(3)$^\circ$ and 90.870(1)$^\circ$ for the Ru and Os systems respectively. The Rietveld refinements confirm that there is essentially no site mixing between the Na and B' atomic positions, as expected for double perovskite systems with a charge difference of +4 between the B and B' sites[29]. There was also no site mixing found between the Nd and Na atomic positions.

As indicated by the $\lambda = 2.41$ Å NPD data presented in Fig. 3 at low temperatures additional scattering is observed in both the Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$ neutron diffraction patterns at commensurate positions. The peaks can be indexed on the basis of a propagation vector $\vec{k} = 0$ for the Ru system and $\vec{k} = (0.5 0.5 0)$ for the Os analogue. Fig. 3(c) shows the temperature-dependence of the normalized magnetic intensity for the Nd$_2$NaRuO$_6$ (0 1 0) magnetic reflection, revealing a magnetic transition temperature of $\sim 14$ K. A similar plot of the (0 0.5 1) magnetic reflection for Nd$_2$NaOsO$_6$, shown in Fig. 3(f), indicates a magnetic transition temperature of $\sim 16$ K. For the Os material, a series of powder diffraction patterns were collected between 4 and 20 K to investigate the potential change in the magnetic structure suggested by previous susceptibility measurements around 10 K[20]. However, only a smooth increase in the intensities of the magnetic peaks with decreasing temperature was observed.

Representational analysis allowed the possible magnetic structures for these materials to be constrained on the basis of the crystal symmetry. The diffraction data was first modeled assuming magnetic ordering of only the Ru or Nd moments at the transition, but it quickly became clear that these assumptions could not explain the data. There are only two irreducible representations consistent with coupled Nd and Ru spin ordering and the observed propagation vector for Nd$_2$NaRuO$_6$: these are $\Gamma_1$ and $\Gamma_3$ in Kovalev’s notation[30]. One of the main differences between these two magnetic structures is the spin components that are coupled ferromagnetically. More specifically, the spin components along the b-axis are ferromagnetically-coupled for both sublattices in the $\Gamma_1$ representation, while the spin components along both the a- and c-axes are ferromagnetically-coupled in the $\Gamma_3$ representation.

The neutron diffraction data shows no magnetic intensity at the (002) position, while there is significant magnetic intensity at the (200) and (002) positions. These observations are only consistent with the $\Gamma_1$ spin model, and this refinement is illustrated in Fig. 3(b) with the corresponding magnetic structure shown in Fig. 4(a). The Nd spins form a

| Atom | Site | x   | y   | z   |
|------|------|-----|-----|-----|
| Nd   | 4e   | 0.4837(8) | 0.0750(5) | 0.2534(6) |
| Na   | 2a   | 0   | 0   | 0   |
| Ru   | 2b   | 0.5 | 0.5 | 0   |
| O$_1$ | 4e   | 0.209(1) | 0.328(1) | 0.0518(7) |
| O$_2$ | 4e   | 0.614(1) | 0.4512(9) | 0.2298(7) |
| O$_3$ | 4e   | 0.331(1) | 0.781(1) | 0.0660(7) |

| Atom | Site | x   | y   | z   |
|------|------|-----|-----|-----|
| Nd   | 4e   | 0.4815(4) | 0.0698(3) | 0.2533(3) |
| Na   | 2a   | 0   | 0   | 0   |
| Os   | 2b   | 0.5 | 0.5 | 0   |
| O$_1$ | 4e   | 0.20868(5) | 0.3268(5) | 0.0504(3) |
| O$_2$ | 4e   | 0.6155(5) | 0.4498(4) | 0.2307(3) |
| O$_3$ | 4e   | 0.3380(5) | 0.7805(4) | 0.0658(3) |
There are only two magnetic models allowed by symmetry that are consistent with coupled Nd and Os spin ordering. There is no Os moment for this refinement. The data was also refined using the Ru magnetic form factors from Ref. [32] and the Ru magnetic intensity at the (0.5 0.5 1) position for Nd and Os was measured, the estimate for $B^6_{\text{Os}}$ and $B^6_{\text{Ru}}$ are shown for Nd and Os respectively at 50 K and (c) $T = 50 K$. Neutron powder diffraction data with $\lambda = 2.41 \text{ Å}$ is shown for Nd$_2$NaRuO$_6$ at (a) $T = 50 K$ and (b) $T = 4 K$. The magnetic refinement at 4 K corresponds to the $\Gamma_2 - \Gamma_4$ model, as explained in the text. (f) A plot of the normalized magnetic intensity at the (0.5 0.5 1) position for Nd$_2$NaOsO$_6$, showing an increase in intensity below the magnetic transition at $T = 16 K$. The solid curves in (c) and (f) are guides to the eye.

A similar situation was encountered for the Os sample, as no suitable magnetic models were found when assuming that only the Nd or Os spins ordered at the magnetic transition. There are also only two magnetic models allowed by symmetry that are consistent with coupled Nd and Os spin ordering and the observed propagation vector for Nd$_2$NaOsO$_6$. In Kovalev's notation[30], these two models are superpositions of the $\Gamma_2$ and $\Gamma_4$ irreducible representations and can be described as $\Gamma_2 + \Gamma_4$ and $\Gamma_2 - \Gamma_4$. The basis vectors and the refined moments for these two models are indicated in Table II. A non-zero Os moment is critical to account for the full intensity of the magnetic peak at (0.5 0.5 0) in each case. The magnetic refinements were performed using the Os$^{5+}$ magnetic form factor from Ref. [38]. The $\Gamma_2 - \Gamma_4$ model gives the best refinement, with the result illustrated in Fig 3(e) and a picture of the magnetic structure depicted in Fig 3(b).

### Table II: Magnetic models and refined magnetic moments for Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$.  

| Model | Ru $\Gamma_2$ | Os $\Gamma_2 + \Gamma_4$ | Os $\Gamma_2 - \Gamma_4$ |
|-------|--------------|-----------------|-----------------|
| $B_1$ | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] |
| $B_2$ | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] |
| Nd$_1$ | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] |
| Nd$_2$ | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] |
| Nd$_3$ | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] | [v$_1$, v$_2$, v$_3$] |
| Nd$_4$ | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] | [-v$_1$, v$_2$, -v$_3$] |

| Model | $\mu_x$ | $\mu_y$ | $\mu_z$ | $\mu$ |
|-------|---------|---------|---------|-------|
| $B_1$, $\mu_x$ | 1.29(6) | 0 | 0 | 0 |
| $\mu_y$ | 0 | 0 | 0.9(1) |
| $\mu_z$ | 1.0(1) | -0.64(9) | 0 |
| $\mu$ | 1.62(8) | 0.64(9) | 0.9(1) |

| Nd$_1$, $\mu_x$ | -1.05(4) | 0.1(1) | 0.2(2) |
| $\mu_y$ | -1.98(3) | 1.20(6) | 1.16(9) |
| $\mu_z$ | 0.56(5) | -1.18(8) | -1.1(1) |
| $\mu$ | 2.31(3) | 1.69(7) | 1.6(1) |

$K_{\text{mag}}(\%)$ | 10.8 | 18.1 | 16.8 |
Nd moment for this system is significantly reduced compared to Nd$_2$NaRuO$_6$, suggesting that the size of the ordered B' moment affects the magnitude of the rare earth moment. Unlike Nd$_2$NaRuO$_6$, the stacking of the ferromagnetic planes associated with the Type I AF order is along the [110] direction.

The B' sublattices of Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$ exhibit conventional Type I AF order for S = 3/2 B' double perovskites despite the large monoclinic structural distortions. This is in sharp contrast to the unconventional magnetism found in the highly-distorted compounds La$_2$NaRuO$_6$ and La$_2$NaOsO$_6$ [26], characterized by incommensurate magnetism and a drastically-reduced ordered moment respectively. The Nd compounds actually have even larger monoclinic structural distortions than their La counterparts, but the B' magnetic ground states are exactly what one expects for undistorted systems with dominant B'-O-O-B' AF exchange interactions. The addition of the rare earth magnetic sublattice seems to destroy the delicate balance of competing exchange interactions giving rise to the unconventional magnetism in the La systems and instead stabilizes simple, commensurate AF on the B' sublattice. The rare earth ions introduce Nd-O-B' interactions into the systems. Although these new couplings are expected to be weaker than B'-O-O-B' extended superexchange, and this is supported by the nearly identical magnetic transition temperatures between the La$_2$NaB'O$_6$ and Nd$_2$NaB'O$_6$ compounds, they are strong enough to act as a significant perturbation and alter the magnetic ground state of the B' sublattice. The resulting magnetic structures are very similar to the spin arrangements reported for R$_2$LiRuO$_6$ [23].

Both the ordered Ru and Os moments of Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$ are significantly reduced compared to the expected spin only value of 3 $\mu_B$. Due to the orbital singlet ground states of the B' atoms of these systems, spin-orbit coupling should have a negligible effect on reducing the ordered moment size. However, strong covalency effects are often associated with 4d and 5d magnetic systems and have been suggested to lead to smaller moments in these materials, particularly in iridates [39] and osmates [40, 41]. In fact, the Os atoms of Nd$_2$NaOsO$_6$ and NaOsO$_3$ [40] are found in nearly identical, slightly-distorted oxygen octahedral cages so covalency effects should be very similar in the two systems. This is consistent with the comparable Os ordered moments of the two materials: 1.0(1) $\mu_B$ for NaOsO$_3$ and 0.9(1) $\mu_B$ for Nd$_2$NaOsO$_6$. Furthermore, the difference in the B' ordered moment size for Nd$_2$NaOsO$_6$ and Nd$_2$NaRuO$_6$ can also be explained by covalency effects, as these are expected to be enhanced in the osmate, relative to the ruthenate, due to the extended nature of the Os 5d orbitals.

In conclusion, we have investigated the magnetic properties of the double perovskites Nd$_2$NaRuO$_6$ and Nd$_2$NaOsO$_6$ with neutron powder diffraction. Despite the large monoclinic structural distortions of these materials, the B' sublattices exhibit conventional Type I AF order, as observed for several S = 3/2 B' double perovskites. The Nd and B' ions are also found to order at the same magnetic transition temperature. The magnetic Nd sublattice creates Nd-O-B' couplings, effectively destroying the delicate balance of extended superexchange interactions that lead to unconventional magnetism in the highly-distorted double perovskites La$_2$NaRuO$_6$ and La$_2$NaOsO$_6$. These results indicate that A-site magnetic rare earths play an essential role in the determination of the magnetic ground state for the B' sublattice in double perovskite systems.

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