Synthesis and magnetism of extended solids containing transition-metal cations in square-planar, MO_4 coordination sites.

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ABSTRACT: With the exception of systems containing Cu^{2+} , complex metal oxides containing paramagnetic transition-metal cations in square-planar coordination are rare. However, by either introducing chalcogenide, pnictide or halide anions to form mixed-anion systems, or by utilizing low-temperature topochemical reduction via anion-deintercalation, an extensive range of phases containing square-planar MO_4 units can be prepared. The crystal chemistry of a series of transition-metal $\text{A}_2\text{MO}_2\text{X}_2$ oxyhalide and $\text{A}_2\text{MO}_2\text{B}_2\text{X}_2$ oxychalcogenide and oxypnictide phases is reviewed along with how their magnetic behavior changes as a function of transition-metal and electron count. As a contrast, these mixed-anion phases are then compared to a series of topochemically reduced, metastable transition-metal oxides which also contain square-planar coordinated transition-metals, to more fully illustrate the magnetic properties of extended frameworks of square-planar MO_4 units.

Introduction

As a class of materials, complex transition-metal oxides exhibit a rich variety of magnetic behavior. This includes relatively simple ferromagnetic, antiferromagnetic and ferrimagnetic states,¹ more complex phenomena such as metamagnetism² and spin-glass behavior³, and even properties such as magnetoresistance⁴ or magnetoelectric behavior⁵ where the magnetization of compounds is coupled to some other property such as electronic transport or electrical polarization. This wide variety of behavior can be attributed to a number of factors: i) the prevalence of transition-metals which can adopt stable oxidation states which have unpaired d-electrons when chemically bound to oxide ions ii) the variety of mechanisms which can couple these unpaired d-electrons into collective behavior and iii) the relative ease with which these interactions can be modulated and tuned via chemical and structural modification.

A feature which is decisive in determining the magnetic properties of a complex transition-metal oxide is the local electronic configuration of the transition-metal cation (the energy ordering of the d-orbitals and how these are filled with electrons) because this local configuration defines how many unpaired electrons are present, and strongly influences the mechanisms by which they can interact.⁶ This local electronic configuration is in turn defined in chemical terms by the identity of the transition metal, the transition-metal oxidation state (d-electron count) and the number of coordinating ligands and the geometry they adopt around the cation. As noted above, there are a wide variety of transition-metals which can be included in complex oxides in a variety of oxidation states. However, when it comes to the local coordination environment choices are more limited, with octahedral and tetrahedral coordination dominating, and geometries such as square-planar coordination being rare. In this forum article strategies for preparing extended solids containing transition-metals in MO_4 square-planar coordination will be outlined and the diverse magnetic properties of these compounds reviewed.

Figure 1. The d-orbital splitting of tetrahedral (T_d) and square-planar (D_{4h}) coordinated MO_4 units, illustrating the potential for enhanced electronic stability of D_{4h} coordination for a d^8 or d^9 electron count.

Thermodynamic instability of square-planar coordination in oxides. The dearth of complex oxides containing transition-metal cations in square-planar coordination can be attributed to the inherent thermodynamic unfavorability of square-planar coordination, compared to octahedral or tetrahedral coordination.⁷ This relative instability of square-planar coordination can be considered as a competition between two factors: packing efficiency and local electronic stability. In terms of solid-state packing, square-planar coordinations are disfavored because they have shorter anion-anion distances (and thus greater unfavorable anion-anion repulsion) than the corresponding tetrahedral arrangements. However, square-planar coordination can be favored on electronic grounds over tetrahedral coordination for d^8 and d^9 electron counts, as shown in Figure 1, but the relatively weak ligand field strength of the oxide ion means that the electronic stability of d^8 square-planar units can generally only overcome the unfavorable steric/packing factors under the influence of the stronger ligand-fields of the heavy 4d and 5d transition-metals. In the case of a d^8 electron count this means cations such as Pd^{2+} or Pt^{2+} , and while there are indeed many examples of complex oxides containing square-planar Pd^{2+} or Pt^{2+} , these phases are of limited interest from a magnetic perspective because the

electronic stability that favors the local square-planar coordination for these ions arises from an $S = 0$ diamagnetic state.

If we instead focus on a d^9 electron count, we find that there are also relatively few options, as copper is the only transition metal which adopts a thermodynamically stable oxidation state with a d^9 electron count (Cu^{2+}) in oxides, because the divalent oxidation states of the heavier group 12 elements, Ag^{2+} and Au^{2+} , are either unstable in oxide environments or tend to disproportionate into M^{1+} – M^{3+} combinations, as exemplified by the simple binary oxide AgO .⁸ As a consequence the only extensive ‘family’ of complex oxides to contain transition-metals in square-planar MO_4 coordination are the cuprates – a class of oxides which have been extensively studied due to the observation of high-temperature superconductivity in many complex copper oxides.⁹

There are a few exceptions to the ‘copper only’ narrative given above, for example Na_4IrO_4 contains square-planar Ir^{4+}O_4 units^{10–13} which are stable because the electron-electron repulsion is weak in 5d orbitals (Na_4CoO_4 has tetrahedral Co^{4+}O_4 units) suggesting a mechanism to stabilize square-planar configurations in analogous phases, but these are rare. So it is generally true to state that complex transition-metal oxides prepared at high temperature under thermodynamic conditions strongly disfavor local square-planar coordination. However, there are conditions where this unfavorability is weakened or reversed. Below two such situations are outlined: mixed-anion systems and the products of topochemical reduction.

Mixed Anion Phases.

A general feature of transition-metal oxyhalide and oxychalcogenide phases is, that due to large differences in size and polarizability between the oxide and halide/chalcogenide anions, these compounds tend to adopt anion-ordered structures in which the different anions are segregated into separate layers. This feature can be exploited to prepare phases containing transition-metal cations in O_4X_2 coordinations with 4 short bonds to a square of ‘equatorial’ oxide anions, and two much longer bonds to a pair of ‘axial’ X hetero-anions, as shown in Figure 2. The large difference in equatorial and axial bond lengths means these sites can be considered to be effectively square-planar, and a range of first-row transition metals can be stabilized within these apex-linked, approximately square-planar sites, to form structures in which the MO_2 sheets are stacked with either A_2X_2 ($\text{A} = \text{Sr}, \text{Ba}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) rock salt layers in the case of the halides, or $\text{A}_2\text{B}_2\text{E}_2$ ($\text{A} = \text{Sr}, \text{Ba}; \text{B} = \text{transition metal}; \text{E} = \text{chalcogenide or pnictide anion}$) layers, as shown in Figure 2. These frameworks allow the local and collective magnetic behavior of non- d^8/d^9 transition metal cations to be studied, with the chemistry and magnetism of these phases best considered based on the identity of the ‘square-planar’ transition-metal cation.

Manganese. The oxychalcogenide phase $\text{Sr}_2\text{MnO}_2\text{Cu}_{2-\delta}\text{S}_2$ ($\delta \sim 0.5$) adopts the layered structure shown in Figure 3, but in which 25% of the copper cations are missing from the Cu_2S_2 anti-fluorite sheets, resulting in a mixed-valent $\text{Mn}^{\text{II/III}}$ phase of composition $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$.^{14–15} Magnetization and neutron diffraction data show that the square-planar manganese cations adopt an antiferromagnetic structure below $T_N \sim 29$ K, in which the manganese spins align ferromagnetically within each MnO_2 sheet (consistent with a double-exchange type coupling between the $\text{Mn}^{\text{II/III}}$ centers) but antiferromagnetically between adjacent sheets, to yield an A-type antiferromagnetic

Figure 2. The crystal structures of $\text{Sr}_2\text{CoO}_2\text{Cl}_2$ and $\text{Sr}_2\text{CoO}_2\text{Cu}_2\text{S}_2$. Light blue, red, grey, green, dark blue and yellow spheres represent Co, O, Sr, Cl, Cu and S respectively.

Figure 3. The crystal structures of the $n = 1, 2, 3$ members of the $\text{Sr}_2\text{MnO}_2\text{Cu}_{2n-\delta}\text{S}_{n+1}$ homologous series. Grey, purple, red, blue and yellow spheres represent Sr, Mn, O, Cu and S respectively.

structure.¹⁴ $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{Se}_2$ and $\text{Sr}_2\text{MnO}_2\text{Ag}_{1.5}\text{Se}_2$ also adopt structures with the same type of transition-metal deficiency as the Cu-S phase,^{16–17} with magnetization data also indicating antiferromagnetic order below $T_N \sim 54$ K and ~ 65 K for the two phases respectively, and neutron diffraction data confirming that $\text{Sr}_2\text{MnO}_2\text{Ag}_{1.5}\text{Se}_2$ adopts an A-type antiferromagnetic structure analogous to $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$.¹⁶

The antiferromagnetic coupling between the MnO_2 sheets in these oxychalcogenide phases can be tuned by increasing the interlayer separation. In the Sr-Mn-O-Cu-S system this can be achieved by varying the thickness of the CuS anti-fluorite blocks in the $\text{Sr}_2\text{MnO}_2\text{Cu}_{2n-\delta}\text{S}_{n+1}$ homologous series, shown in Figure 3.¹⁴ Thus while the $n = 1$ phase $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ is an antiferromagnet at low temperature, the $n = 3$ phase $\text{Sr}_2\text{MnO}_2\text{Cu}_{5.5}\text{S}_4$ appears to adopt a ferromagnetic state, and the $n = 2$ phase $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ is metamagnetic, being antiferromagnetically ordered in small applied fields, but driven into a ferromagnetic state in applied fields greater than 1.3 T.¹⁴

By replacing the (Ag/Cu)-chalcogenide layers with Zn_2As_2 layers it is possible to prepare phases containing only Mn^{2+} within the MnO_2 sheets.^{18–19} Magnetization data show that both $\text{Sr}_2\text{MnO}_2\text{Zn}_2\text{As}_2$ and $\text{Ba}_2\text{MnO}_2\text{Zn}_2\text{As}_2$ are paramagnetic for $T > 180$ K, with susceptibilities consistent with high-spin, $S = 5/2$ Mn^{2+} centers. On cooling $\text{Ba}_2\text{MnO}_2\text{Zn}_2\text{As}_2$ adopts a short-range magnetically ordered state with a correlation length of ~ 250 Å at 4K, while low-temperature neutron diffraction data give no indication of a magnetically ordered state for $\text{Sr}_2\text{MnO}_2\text{Zn}_2\text{As}_2$, consistent with the proposal of a spin-glass ground state for this phase.^{18–19}

It is surprising that reducing the square-planar manganese cations from a mixed valent $\text{Mn}^{\text{II/III}}$ state to an all Mn^{II} state suppresses magnetic order, as it might be expected that a singly-occupied $d_{x^2-y^2}$ orbital would lead to strong in-plane antiferromagnetic coupling within the MnO_2 sheets. However it has been suggested that changes to the inter-layer coupling between the MnO_2 sheets, rather than intra-layer coupling, are responsible for the change in low-temperature magnetic behaviour.¹⁹

By utilizing high-pressure synthesis conditions (6 GPa) it is possible to prepare $\text{Sr}_2\text{MnO}_2\text{Cl}_2$, containing nominally square-planar Mn^{2+} centres.²⁰ Magnetization data collected from $\text{Sr}_2\text{MnO}_2\text{Cl}_2$ indicate paramagnetic behavior down to 16 K, however the observed susceptibility is much smaller than would be expected from $S = 5/2$ Mn^{2+} centers. This reduced moment has been attributed to a low level of anion disorder in the phase, highlighting the synthesis challenge represented by this class of materials.

Cobalt. A range of mixed-anion phases can be prepared containing Co^{2+} cations in approximately square-planar coordination in which CoO_2^{2-} sheets are stacked with either $\text{A}_2\text{B}_2\text{Ch}_2^{2+}$ ($\text{A} = \text{Sr}, \text{Ba}; \text{B} = \text{Cu}, \text{Ag}; \text{Ch} = \text{S}, \text{Se}, \text{Te}$)^{17, 21-23} transition-metal chalcogenide layers, or $\text{A}_2\text{X}_2^{2+}$ ($\text{A} = \text{Sr}; \text{X} = \text{Cl}, \text{Br}$)²⁴⁻²⁵ rock-salt layers. These phases are observed to adopt antiferromagnetically ordered states at low temperature, consistent with strong $\text{Co}(d_{x^2-y^2})^1\text{-O}(2p)\text{-Co}(d_{x^2-y^2})^1$ 180° super-exchange interactions within the CoO_2 planes. However, the ordered moments observed for these phases are much larger than values predicted by the spin-only formula, suggesting strong spin-orbit coupling. Clarke *et al.* have correlated the variation in the size of the cobalt moment with the ratio of $\text{Co-X}_{\text{axial}}/\text{Co-O}_{\text{equatorial}}$ bond lengths – i.e. how ‘square-planar’ to cobalt coordination site actually is. Using the $\text{A}_2\text{CoO}_2\text{Cu}_2\text{S}_2$ system as an example they then show how the splitting of the cobalt d-orbitals varies as a function of this bond length ratio, as shown in Figure 4, and how that this leads to the variation in local cobalt moment observed experimentally.

Similar arguments and calculations have been used by Gui *et al.*²⁶ to propose that orbital splitting case (iii) in Figure 4 also applies to the oxyhalide $\text{Sr}_2\text{CoO}_2\text{Cl}_2$, which further explains why the symmetry lowering structural phase transition (Jahn-Teller distortion) expected as a consequence of the orbital degeneracy of splitting case (iv) – the ‘true’ square-planar case – is not observed.

A further mechanism to stabilize approximately square-planar $\text{Co}^{\text{II}}\text{O}_4$ units is observed for the oxypnictide phase BaCoAsO_5 ²⁷ in which the interaction between what would be a doubly filled $\text{Co-}d_{z^2}$ orbital in an isolated CoO_4 unit, and a doubly filled E orbital (stereo-active lone pair) of an isolated AsO_3 unit, lead to a net bonding interaction via a two-orbital, three-electron stabilization. While the resulting system still retains a high degree of orbital degeneracy in the cobalt d-states, the observed paramagnetic moment of the system ($T > 50$ K) is close to the expected spin-only value for Co^{2+} indicating, that in contrast to the other oxychalcogenides and oxyhalides, strong spin-orbital coupling is not in operation in BaCoAsO_5 .

Nickel. A limited series of Ni^{II} -containing oxychlorides ($\text{Sr}_2\text{NiO}_2\text{Cl}_2$)²⁰ and oxychalcogenides ($\text{Sr}_2\text{NiO}_2\text{Cu}_2\text{S}_2$, $(\text{Ba}, \text{Sr})_2\text{NiO}_2\text{Ag}_2\text{Se}_2$)²⁸⁻³⁰ can be prepared. However, with the

Figure 4. Schematic showing the d-orbital splitting for high-spin Co^{2+} ranging from (i) strictly octahedral, to (iv) strictly square-planar via highly tetragonally elongated CoO_4X_2 coordinations (ii, iii), after ref²⁹.

exception of $\text{Sr}_2\text{NiO}_2\text{Cu}_2\text{S}_2$ these phases require high-pressure synthesis conditions. In common with the Co^{2+} -containing phases, the local magnetic moment of the Ni^{II} centers also depends sensitively on the local bonding environment as relatively small changes in the equatorial Ni-O bond length can switch between an $S = 0$ or $S = 1$ spin state – a situation which is further complicated by weak interactions with the ‘axial’ halide or chalcogenide anions.

Experimental observations show that $\text{Sr}_2\text{NiO}_2\text{Cl}_2$ adopts a high-spin $S = 1$ local configuration (in contrast to $\text{Ba}_2\text{PdO}_2\text{Cl}_2$ which adopts an $S = 0$, diamagnetic spin state) which appears to be antiferromagnetically ordered at low temperature.²⁰ Similarly $\text{Sr}_2\text{NiO}_2\text{Ag}_2\text{Se}_2$ and $\text{Ba}_2\text{NiO}_2\text{Ag}_2\text{Se}_2$ also adopt $S = 1$ spin states, with neutron diffraction data confirming an antiferromagnetic ground state for the barium phase, and the lack of low-temperature magnetic scattering for the strontium phase suggesting a spin-glass ground state for this material.³⁰

The situation for $\text{Sr}_2\text{NiO}_2\text{Cu}_2\text{S}_2$ is more complex as this material appears to lie close to the cross over point between $S = 1$ and $S = 0$ ground states.²⁹ The magnetic susceptibility of this phase is positive at 250 K, indicating an $S = 1$ state at this temperature. On cooling the phase undergoes a series of complex lattice parameter changes and a heat capacity anomaly which coincides with a sharp drop in the magnetic susceptibility. No magnetic neutron scattering is observed at low temperature and an analysis of the local Ni coordination shows that the ratio of Ni-S to Ni-O bond lengths increases at $T \sim 130$ K, consistent with a change to a ‘more square-planar’ nickel coordination environment. In combination these observations are taken as evidence for a nickel spin-state transition, although further investigation is required to make this definitive.

Chromium. The di-valent oxidation state of chromium is not typically stable in extended oxides, as illustrated by the lack of a stable CrO phase. However, when combined with ‘softer’ anions, such as the pnictogens, it is possible to not only stabilize Cr^{2+} in an oxide chemical environment, but also locate Cr^{2+} cations within square-planar coordinations. For example $\text{Sr}_2\text{CrO}_2\text{Cr}_2\text{As}_2$ adopts a structure analogous to $\text{Sr}_2\text{CoO}_2\text{Cu}_2\text{S}_2$ but with Cr^{2+} replacing both Co^{2+} and Cu^{1+} and As^{3+} replacing S^{2-} .³¹ $\text{Sr}_2\text{CrO}_2\text{Cr}_2\text{As}_2$ adopts a sequence of magnetically ordered states. In the temperature range $291 < T/\text{K} < 590$ the Cr^{2+} centers in the Cr_2As_2 anti-fluorite blocks are antiferromagnetically ordered with moments aligned along the z -axis stacking direction. On cooling below 291 K the ‘square-planar’ Cr^{2+} centres within the CrO_2 layers order anti-

ferromagnetically, with moments aligned along the z -axis, and concomitant with this ordering the moments of the chromium cations within the anti-fluorite blocks reorient to lie within the xy -plane.³² It had previously been assumed that there was little coupling between the Cr_2As_2 and CrO_2 blocks, so the interactions which lead to the spin reorientation are yet to be fully understood.

Topochemically Reduced Phases.

Topochemical reduction via anion deintercalation offers the opportunity to broaden the range of transition-metal cations which can be located in square-planar coordination environments. This approach has been widely applied to complex oxides with perovskite structures, or layered analogues, because on reduction the ‘apical’ oxide ions can be removed from the octahedral coordination environments of the transition metal to yield metastable phases containing square-planar coordinated cations.³³

Square-planar Ni(II) and Ni(I). Much of the initial work applying topochemical reduction to complex oxides focused on preparing Ni^{1+} phases to investigate their relationship to the superconducting Cu^{2+} oxides.³⁴ For example by heating the metallic Ni^{3+} phase, LaNiO_3 , either in the presence of dilute hydrogen or oxygen getters, such as Zr or Ti, topochemically reduced LaNiO_{3-x} ($0 < x < 0.5$) phases can be formed.³⁵⁻³⁷ As the concentration of oxygen vacancies increase, the LaNiO_{3-x} system changes from metallic to semiconducting behavior at $x \sim 0.3$. This is accompanied by a conversion of some of the NiO_6 octahedral units to NiO_4 square-planar units, which form chains within the perovskite framework, such that at $x = 0.5$ half of the nickel centers are located in octahedral sites and half in square-planar sites as shown in Figure 5.³⁸ Neutron diffraction data indicate that $\text{La}_2\text{Ni}_2\text{O}_5$ adopts an antiferromagnetic state at low temperature in which the octahedrally coordinated Ni^{2+} centers order with a local moment of $\sim 1.9(3)\mu_B$, while there is no evidence for an ordered moment on the square-planar sites.³⁹ This suggests that the Ni^{2+}O_4 square-planar centers in $\text{La}_2\text{Ni}_2\text{O}_5$ adopt an $S = 0$, low-spin configuration, and comparison of the Ni–O bond lengths of these units with square-planar Ni^{2+}O_4 units in other phases supports this proposal.³⁵

Further reduction of the LaNiO_{3-x} system with hydrogen is possible, but experimentally challenging.⁴⁰⁻⁴¹ However, by changing to solid hydride reducing agents such as NaH or CaH_2 ,^{33, 42} further reduction of the LaNiO_{3-x} system becomes facile, readily allowing the preparation of the infinite-layer, Ni^{1+} phase LaNiO_2 .⁴³⁻⁴⁴ Furthermore, this reduction chemistry can also be applied to other members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ homologous series of Ruddlesden-Popper phases to generate the corresponding $\text{La}_{n+1}\text{Ni}_n\text{O}_{2n+2}$ compounds which contain mixed valent $\text{Ni}^{1+/2+}$ cations within sheets of apex-linked, square-planar coordination sites separated by La_2O layers, in an analogy to the T' structure of Nd_2CuO_4 , as shown in Figure 5.⁴⁵⁻⁴⁷

The electronic properties of the members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{2n+2}$ series change as a function of the dimensionality of the structural framework.⁴⁸ The $n = \infty$ member, LaNiO_2 , can be considered to have a three-dimensional structure which electronic structure calculations predict to be metallic, although experimental measurements are less clear.⁴³ The $n = 2$ member, $\text{La}_3\text{Ni}_2\text{O}_6$ can be considered the most two-dimensional of the series and is observed to be insulating over the

Figure 5. The crystal structures of topochemically reduced nickel perovskite oxides. Blue, red and grey spheres represent Ni, O and La respectively.

temperature range 5 – 400 K, with no evidence for magnetic order in this temperature range.⁴⁹ The $n = 3$ member $\text{La}_4\text{Ni}_3\text{O}_8$ has a dimensionality which can be considered as intermediate between 2 and 3. Transport measurements exhibit a sharp increase in the resistance of $\text{La}_4\text{Ni}_3\text{O}_8$ at $T \sim 105$ K, which is accompanied by a heat capacity anomaly.⁵⁰ Single-crystal X-ray diffraction data show this anomaly arises due to the onset of stripe charge-ordering of the Ni^{1+} and Ni^{2+} centers in a manner broadly analogous to that observed for $\text{La}_{5/3}\text{Sr}_{1/3}\text{NiO}_4$.⁵¹ The praseodymium based $n = 3$ phase $\text{Pr}_4\text{Ni}_3\text{O}_8$ remains metallic down to 2 K with no indication of any ordering transition in heat capacity measurements,⁵² and it has been suggested that this large change in physical behavior is down to a chemical pressure effect arising from the decreased size of Pr^{3+} .

Square-planar Fe^{2+} . The development of hydride reducing agents has broadened the range of systems to which topochemical reduction can be applied beyond those resulting in d^8 and d^9 electron counts. One of the most striking early successes in applying these ideas to metals earlier in the transition series was the preparation of SrFeO_2 via the reduction of SrFeO_{3-x} .⁵³ SrFeO_2 adopts an infinite layer structure, analogous to LaNiO_2 ,⁴³ in which d^6 , $S = 2$, Fe^{2+} centers reside in sheets of apex-linked square-planar sites, as shown in Figure 6. Compared to the d^8 or d^9 electron counts of Ni^{2+} or Cu^{2+} the d^6 electron count of Fe^{2+} provides no obvious strong stabilization of square-planar coordination, however empirical observations indicate this configuration appears to have considerable robustness, with SrFeO_2 being thermally stable up to 500 °C in the presence of oxygen and at least 680 °C in oxygen-free conditions.⁵⁴⁻⁵⁵ This stability is also illustrated by the ease with which the $n = 1$ and $n = 2$ members of the $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$

Figure 6. The structures of SrFeO_2 , Sr_2FeO_3 , $\text{Sr}_3\text{Fe}_2\text{O}_5$ and $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$. Grey, brown, red and green spheres represent Sr, Fe, O and Cl respectively.

Ruddlesden-Popper series can be converted to Sr_2FeO_3 and $\text{Sr}_3\text{Fe}_2\text{O}_5$ respectively – phases which also contain apex-linked square-planar Fe^{2+}O_4 units (Figure 6).⁵⁶⁻⁵⁸ Similarly the oxychloride $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cl}_2$ can be converted to $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$, a phase with infinite sheets of Fe^{2+}O_4 units, as shown in Figure 6.⁵⁹

DFT calculations indicate the square-planar Fe^{2+} centers have an $S = 2$, $(d_{z^2})^2(d_{xz/yz})^2(d_{xy})^1(d_{x^2-y^2})^1$ electronic configuration.⁶⁰⁻⁶¹ Strong in-plane $\text{Fe}(d_{x^2-y^2})^1\text{O}(2p)\text{Fe}(d_{x^2-y^2})^1$ super-exchange, combined with inter-plane direct exchange between $\text{Fe}(d_{xz/yz})$ orbitals leads to antiferromagnetic ground states for all of these phases with the observed magnetic ordering temperatures correlating to the structural dimensionality of the phases: SrFeO_2 , $T_N = 473 \text{ K}$;⁵³ $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$, $T_N = 378 \text{ K}$;⁵⁹ $\text{Sr}_3\text{Fe}_2\text{O}_5$, $T_N = 296 \text{ K}$;⁵⁷ Sr_2FeO_3 , $T_N = 179 \text{ K}$.⁵⁶

The application of pressure to phases in the Sr-Fe-O system results in a dramatic change to their physical behavior. As pressure is applied to SrFeO_2 the lattice parameters of the phase contract smoothly, as measured by X-ray powder diffraction, up to a pressure of $\sim 33 \text{ GPa}$ with the $\text{Fe}-\square-\text{Fe}$ c -axis being significantly more compressible than the $\text{Fe}-\text{O}-\text{Fe}$

Figure 7. The ambient-pressure and high-pressure structures of $\text{Sr}_3\text{Fe}_2\text{O}_5$. Grey, brown and red spheres represent Sr, Fe and O respectively.

a -axis.⁶² At $P \sim 33 \text{ GPa}$ SrFeO_2 undergoes an anomalous volume contraction associated with a sharp contraction of the crystallographic a -axis.⁵⁷ ^{57}Fe Mössbauer data indicate that this volume change is associated with a change in the iron spin-state, from $S = 2$ to $S = 1$, and a change in the magnetic ordering from antiferromagnetic to ferromagnetic. The application of pressure also leads to a decline in the electrical resistivity of SrFeO_2 , with a sharp drop between 27 GPa and 37 GPa , suggesting an insulator to metal transition is associated with the spin-state change. DFT calculations indicate that the spin-state change occurs because on the application of pressure the compression of the in-plane $\text{Fe}-\text{O}$ distance raises the energy of the $d_{x^2-y^2}$ orbitals, furthermore the compression of the c -axis shortens the $\text{Fe}-\text{Fe}$ distance, enhancing the $d_{xz/yz}$ bonding interaction, lowering the energy of these orbitals and as a result the electronic configuration of each iron center effectively changes from $S = 2$, $(d_{z^2})^2(d_{xz/yz})^2(d_{xy})^1(d_{x^2-y^2})^1$ to $S = 1$, $(d_{z^2})^2(d_{xz/yz})^3(d_{xy})^1(d_{x^2-y^2})^0$.^{58, 62-63}

The high-pressure behavior of $\text{Sr}_3\text{Fe}_2\text{O}_5$ is more complex than that of SrFeO_2 because the former phase undergoes a structural phase transition at $P \sim 30 \text{ GPa}$ in which the $\text{Sr}_3\text{Fe}_2\text{O}_5$ blocks which make up the structure, change their stacking from the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ stacking of the $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ ‘parent’ phase, to a $(\frac{1}{2}, 0, \frac{1}{2})$ stacking as shown in Figure 7.⁶⁴ This is then followed by a further phase transition at $P \sim 34 \text{ GPa}$ to a ferromagnetic, $S = 1$, metallic state, analogous to that seen for SrFeO_2 .⁶⁵⁻⁶⁶

Cobalt. The preparation of phases containing square-planar Co^{1+} or Co^{2+} centers by topochemical reduction is challenging. While LaNiO_3 and $\text{SrFeO}_{3-\delta}$ can be converted into LaNiO_2 and SrFeO_2 respectively,^{43, 53} neither LaCoO_3 nor $\text{SrCoO}_{3-\delta}$ can be reduced to the corresponding ACoO_2 phases. Indeed, the substitution of cobalt into $\text{SrFeO}_{3-\delta}$ to form $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ suppresses the formation of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_2$ phases for $x > 0.3$.⁶⁷ A rare example where it is possible to form square-planar CoO_4 units via topochemical reduction of a perovskite occurs in the conversion of the cation-ordered, anion-deficient perovskite $\text{LaBaCo}_2\text{O}_5$ to $\text{LaBaCo}_2\text{O}_{4.25}$.⁶⁸ This latter phase has a complex structure in which half of the cobalt cations reside in Co^{2+}O_4

distorted tetrahedral coordination, one quarter in Co^{2+}O_5 square-based pyramids and one quarter in Co^{1+}O_4 square-planar sites. Neutron diffraction data reveal that $\text{LaBaCoO}_{4.25}$ adopts an antiferromagnetically ordered state below $T \sim 325$ K in which the d^8 square-planar Co^{1+}O_4 units are in a low-spin, $S = 0$, diamagnetic spin-state.

While the topochemical reduction of perovskite oxides to form square-planar coordinated cobalt centers is challenging, it is possible to reduce the cobalt oxychloride phase $\text{Sr}_3\text{Co}_2\text{O}_5\text{Cl}_2$, in a manner directly analogous to the reduction of $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cl}_2$ described above,⁵⁹ to yield $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$.⁶⁹ This phase contains infinite sheets of apex-linked Co^{2+}O_4 units, similar to those present in $\text{Sr}_2\text{CoO}_2\text{Cl}_2$ or $\text{Sr}_2\text{CoO}_2\text{Cu}_2\text{S}_2$, described above. However, unlike these phases $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$ undergoes a tetragonal to orthorhombic symmetry lowering phase transition on cooling below 200 K. This is consistent with a Jahn-Teller distortion which lifts the orbital degeneracy of the $(d_{z^2})^2(d_{xz/yz})^3(d_{xy})^1(d_{x^2-y^2})^1$ local cobalt electronic state as shown in Figure 8. Further cooling below 50 K results in the onset of canted antiferromagnetic order, with the ordered moment observed by neutron diffraction, $3.78\mu_B$, being significantly larger than the spin only moment expected for $S = 3/2$ Co^{2+} , again indicating that strong spin-orbit coupling is occurring in this cobalt phase.⁶⁹

The observation of a Jahn-Teller distortion at low temperature in $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$, unlike $\text{Sr}_2\text{CoO}_2\text{Cl}_2$ or $\text{Sr}_2\text{CoO}_2\text{Cu}_2\text{S}_2$,^{21, 25} indicates that the local electronic configuration of the Co^{2+} centers in the double layer phase is described by case (iv) in Figure 4. This is consistent with an extended Co-Cl bond in $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$ ($2.950(2)$ Å)⁶⁹ compared to $\text{Sr}_2\text{CoO}_2\text{Cl}$ ($2.754(2)$ Å)²⁴ and the occupation of an O_4Cl , rather than an O_4Cl_2 coordination site.

A further difference between topochemically reduced oxychlorides and oxides is that an extensive solid solution between $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$ and $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$ can be formed,⁷⁰ while there is only limited solubility of cobalt in SrFeO_2 .⁶⁷ However as $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$ (G-type) and $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$ (C-type) adopt different antiferromagnetic structures, cobalt-for-iron substitution of $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$ suppresses long-range antiferromagnetic order and $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_4\text{Cl}_2$ phases with $x > 0.6$ being spin-glasses.⁷⁰

Topochemical reduction of 4d and 5d transition-metal systems. Utilizing a mixed-anion strategy and/or topochemical reduction it is possible to extend the range of electron counts for transition-metal cations in square-planar coordination beyond the thermodynamically favored d^8 and d^9 values to include d^7 , d^6 , d^5 and even d^4 . However almost all of the phases described above exhibit antiferromagnetic ground states and most phases with electron counts of d^8 or lower are semiconducting, at least at ambient pressure. This general behavior can be attributed to two features of 3d transition metal oxides: i) the bands derived from the transition-metal 3d orbitals which form in oxides are generally narrow, resulting in a prevalence of Mott-Hubbard insulating behavior.^{1, 71} ii) the relatively weak crystal field arising from $3d\text{-O}2p$ interactions results in the occupation of the metal $d_{x^2-y^2}$ orbitals for electron counts of d^5 or greater – a configuration which almost inevitably leads to strong antiferromagnetic coupling via $(d_{x^2-y^2})^1\text{-O}(2p)^2\text{-(}d_{x^2-y^2})^1$ super-exchange.⁶

Figure 8. (top) The crystal structure of $\text{Sr}_3\text{Co}_2\text{O}_4\text{Cl}_2$ at 300 K and 5 K. Grey, blue, red and green spheres represent Sr, Co, O, and Cl respectively. (bottom) the change in d-orbital splitting associated with symmetry lowering phase transition.

The introduction of 4d and 5d transition metals would be expected to increase the diversity of physical behavior as the heavier metals would broaden the metal-based d-bands, favoring itinerant electron behavior. Furthermore the larger crystal field interactions of 4d and 5d transition-metals will favor intermediate and low-spin configurations, decreasing the likelihood of antiferromagnetic ground states.

Ruthenium. Unfortunately the direct topochemical reduction of 4d and 5d transition metal perovskite oxides is not simple. The standard M^{2+}/M reduction potential of all 4d and 5d transition metals is positive, in contrast to the 3d metals where the M^{2+}/M reduction potential is negative.⁸ Thus it is not a surprise that while the 3d transition metal system SrFeO_3 can be topochemically reduced to SrFeO_2 , the reduction of the corresponding 4d system, SrRuO_3 , yields $\text{SrO} + \text{Ru}$ in a non-topochemical process.⁷² However, it is possible to stabilize reduced 4d and 5d transition metals cations within oxide frameworks by combining them with 3d transition metals. Thus the reduction of the cation-disordered phase $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_3$ yields $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_2$, a phase with an infinite layer structure, analogous to SrFeO_2 , but containing square-planar Fe^{2+}O_4 and Ru^{2+}O_4 units, with the presence of Ru^{2+} confirmed by XANES measurements.⁷² Electronic structure calculations reveal that the Fe^{2+} centers in $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_2$ adopt the same $S = 2$ local electronic configuration as observed in SrFeO_2 , however the stronger Ru-O ligand field interaction leads to an $S = 1$, $(d_{z^2})^2(d_{xz/yz})^3(d_{xy})^1(d_{x^2-y^2})^0$ electronic

state for Ru^{2+} , analogous to that observed for the Fe^{2+} centers in the high-pressure phase of SrFeO_2 . The combination of differing electronic configuration for Fe^{2+} and Ru^{2+} and the cation disorder in $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_2$ leads to frustration in the magnetic couplings and spin-glass behavior below 60 K.

The reduction of the $n = 2$ and $n = 3$ members of the $\text{Sr}_{n+1}(\text{Fe}_{0.5}\text{Ru}_{0.5})_n\text{O}_{3n+1}$ Ruddlesden-Popper series is more complex than the corresponding reduction of $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_3$ because a lower level of reduction is observed which limits the reduced compositions to $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.35}$ and $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.68}$ respectively.⁷³ Diffraction data reveals that the products of reduction are actually 2-phase mixtures, thus $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.35}$ is a mixture of $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.25}$ and $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.44}$, while $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.68}$ is a mixture of $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.50}$ and $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.86}$. The average transition metal oxidation states of these 2-phase mixtures are +2.70 and +2.68 for $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.35}$ and $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.68}$ respectively, and XANES data show all the iron present in these phases is Fe^{3+} while the ruthenium is a mixture of Ru^{2+} and Ru^{3+} . Thus $\text{Sr}_2(\text{Fe}_{0.5}\text{Ru}_{0.5})\text{O}_{3.35}$ and $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_{5.68}$ are two rare examples of materials containing square-planar Fe^{3+} centers. In common with $\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_2$ these phases are spin-glasses at low temperature.⁷³

The cation disorder in the $\text{Sr}_{n+1}(\text{Fe}_{0.5}\text{Ru}_{0.5})_n\text{O}_{3n-x}$ phases masks the nature of the magnetic interactions between the iron and ruthenium centers and results in spin-glass ground states. However, it is possible to topochemically reduce cation-ordered double perovskite phases to yield cation ordered structures containing transition-metal cations in square-planar coordination. LaSrNiRuO_6 is a cation ordered perovskite phase in which the Ni and Ru cations adopt a ‘rock salt’ ordered arrangement.⁷⁴⁻⁷⁵ Reaction with CaH_2 converts LaSrNiRuO_6 into LaSrNiRuO_4 , a phase which adopts an infinite-layer structure consisting of square-planar Ni^{1+} and Ru^{2+} centers arranged in a manner which conserves the cation order of LaSrNiRuO_6 , as shown in Figure 9.⁷⁶

At room temperature LaSrNiRuO_4 is paramagnetic with a susceptibility which is consistent with $S = 1/2$, Ni^{1+} and $S = 1$, Ru^{2+} centers. On cooling below 250 K, LaSrNiRuO_4 enters an insulating ferromagnetic state with a saturated moment of $1\mu_B$ per formula unit at 5 K. The coupling interactions which lead to this state are uncertain as neutron powder diffraction data indicate that only Ni has an ordered moment at low temperature, yet susceptibility data show no residual paramagnetic moment for Ru. Crystallographic data show some weak signs of a local Jahn-Teller distortion of the RuO_4 units at low temperature, which could result in a diamagnetic configuration for ruthenium, however this is still to be resolved conclusively.⁷⁶⁻⁷⁷

Iridium. As noted above, it is possible to prepare complex oxides containing square-planar IrO_4 units directly, as observed for Na_4IrO_4 ,¹⁰⁻¹³ however such phases are few and far between, so topochemical reduction allows the number of examples to be increased. Topochemical reduction of the double perovskite $\text{Sr}_2\text{FeIrO}_6$ ⁷⁸⁻⁷⁹ yields $\text{Sr}_2\text{FeIrO}_4$ which has a cation-ordered infinite layer structure, analogous to LaSrNiRuO_4 , but containing square-planar Fe^{2+} and Ir^{2+} cations.⁸⁰ DFT calculations reveal the iron centers adopt the high-spin, $S = 2$ configuration observed for Fe^{2+} in SrFeO_2 , while

Figure 9. The cation-ordered crystal structures of LaSrNiRuO_6 and LaSrNiRuO_4 . Grey, blue, green and red spheres represent La/Sr, Ni, Ru and O respectively.

the iridium adopts a low-spin $S = 1/2$, $(d_{z^2})^2(d_{xz}/yz)^4(d_{xy})^1(d_{x^2-y^2})^0$ configuration, consistent with the much larger ligand-field of a 5d transition metal. On cooling below 115 K $\text{Sr}_2\text{FeIrO}_4$ adopts the antiferromagnetic state shown in Figure 10, which has the unusual feature that the Fe–Ir couplings are ferromagnetic in the x -direction and antiferromagnetic in the y -direction, even though these two directions are symmetry equivalent in the tetragonal room-temperature crystal structure. In addition, the interlayer couplings between FeIrO_4 sheets alternates between antiferromagnetic and ferromagnetic along the z -axis.

DFT calculations reveal the unusual magnetic structure arises because both the nearest-neighbor Fe–Ir (J_1) and next-nearest-neighbor Ir–Ir (J_2) couplings are antiferromagnetic and of similar strength. These two couplings cannot be simultaneously satisfied, as shown in Figure 10, so the system is frustrated. On cooling below 115 K, $\text{Sr}_2\text{FeIrO}_4$ undergoes a structural distortion which lowers the symmetry of the lattice from tetragonal to monoclinic. This breaks the 4-fold symmetry of the MO_4 ‘squares’ resulting in two distinct, mutually *trans* pairs of Fe–O and Ir–O bonds with significantly different bond lengths (Fe–O 1.999(7) Å vs. 1.970(7) Å; Ir–O 2.026(7) Å vs. 1.989(7) Å) leading to a distinct diamond-like coordination for the two ions. This differentiation of the x and y directions in the lattice lifts the magnetic frustration as it allows the J_1 coupling to split into ferromagnetic and antiferromagnetic couplings along the x and y direction respectively.⁸⁰ This strong magneto-lattice coupling can be seen to arise from the novel local electronic configurations of the square-planar coordinated transition metals.

Conclusions.

By employing a mixed-anion strategy, or by utilizing topochemical reduction, a growing variety of phases can be prepared which contain square-planar MO_4 units which are either isolated or connected via corner-sharing into 1D chains or 2D sheets. The magnetic behavior of these materials, at least those exclusively containing 3d transition-metals, is almost exclusively dominated by strong antiferromagnetic $(d_{x^2-y^2})^1\text{--O}(2p)^2\text{--}(d_{x^2-y^2})^1$ super-exchange couplings. However by introducing heavier 4d or 5d transition-metals additional coupling interactions are introduced leading to ferromagnetic ground states and more complex behavior in which the magnetic and lattice degrees of freedom are coupled. Considering the limited number of examples of 3d/4d and 3d/5d phases

Figure 10. a) The magnetic structure of $\text{Sr}_2\text{FeIrO}_4$ b) the J_1 Fe-Ir nearest-neighbor Fe-Ir coupling and c) the J_2 next-nearest-neighbor Ir-Ir coupling. Brown, blue and red spheres represent Fe, Ir and O respectively.

prepared to date compared to the number of metal combinations and arrangements that could be envisioned, it seems likely that a rich variety of new phases exhibiting novel physical and chemical behavior await discovery.

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ACKNOWLEDGMENT

I thank The Leverhulme Trust grant award RPG-2014-366 “Topochemical reduction of 4d and 5d transition metal oxides” for supporting this work.

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For Table of Contents Only. By utilizing a mixed-anion strategy, or by employing topochemical reduction, a range of extended solids can be prepared which contain transition-metal cations in square-planar, MO_4 , coordination sites, despite the thermodynamic unfavorability of this local coordination for non- d^8 electron counts.