

Strontium Vanadium Oxide–Hydrides: “Square-Planar” Two-Electron Phases**

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Abstract: A series of strontium vanadium oxide–hydride phases prepared by utilizing a low-temperature synthesis strategy in which oxide ions in $\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ ($n = \infty, 1, 2$) phases are topochemically replaced by hydride ions to form SrVO_2H , $\text{Sr}_2\text{VO}_3\text{H}$, and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$, respectively. These new phases contain sheets or chains of apex-linked V^{3+}O_4 squares stacked with SrH layers/chains, such that the $n = \infty$ member, SrVO_2H , can be considered to be analogous to “infinite-layer” phases, such as $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ (the parent phase of the high- T_c cuprate superconductors), but with a d^2 electron count. All three oxide–hydride phases exhibit strong antiferromagnetic coupling, with SrVO_2H exhibiting an antiferromagnetic ordering temperature, $T_N > 300$ K. The strong antiferromagnetic couplings are surprising given they appear to arise from π -type magnetic exchange.

Low-temperature topochemical synthesis routes offer an alternative strategy for preparing phases containing square-planar transition-metal centers. For example, the low-temperature reductive deintercalation of oxide ions from the perovskite phases LaNiO_3 and $\text{SrFeO}_{3-\delta}$, using the hydride reducing agents NaH and CaH_2 respectively, yield LaNiO_2 and SrFeO_2 .^[1] These reduced oxides consist of infinite sheets of square-planar Ni^{1+}O_4 or Fe^{2+}O_4 centers stacked with La^{3+} or Sr^{2+} cations, respectively. By applying this reductive deintercalation approach to other perovskite oxides the catalogue of transition-metal cations that can be located in planar sites can be extended to include Co^+ ($\text{LaBaCo}_2\text{O}_{4.25}$) and Ru^{2+} ($\text{SrFe}_{0.5}\text{Ru}_{0.5}\text{O}_2$).^[2] Furthermore, by utilizing layered $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ Ruddlesden–Popper oxides or $\text{A}_3\text{B}_2\text{O}_5\text{Cl}_2$ oxychlorides, additional lower dimensional structures containing isolated double sheets ($\text{Sr}_3\text{M}_2\text{O}_4\text{Cl}_2$, $\text{M} = \text{Fe}, \text{Co}$), chains (LaSrNiO_{3+x} , Sr_2FeO_3), or double chains ($\text{Sr}_3\text{Fe}_2\text{O}_5$) of apex-linked MO_4 squares can be prepared.^[3]

Despite the growing diversity of materials containing square-planar transition metal centers, a common feature of all of these phases is a relatively high d-electron count: d^6 (Fe^{2+} , Ru^{2+}), d^7 (Co^{2+}), d^8 (Co^{1+} , Ni^{2+} , Cu^{3+}), or d^9 (Ni^{1+} , Cu^{2+}). As a consequence, most of the phases prepared are Mott–Hubbard insulators, with a strong tendency for anti-ferromagnetic order owing to the occupation of σ -symmetry metal d-orbitals. To extend the study of square-planar-coordinated transition-metal systems to earlier, electron-poor transition metals, we have focused on the topochemical reduction of V^{4+} oxides.

The reaction of the perovskite phase SrVO_3 with CaH_2 at 610°C results in the formation of a new tetragonal phase ($P4/mmm$: $a = 3.93$ Å, $c = 3.66$ Å). X-ray powder diffraction data show that the cation lattice of SrVO_3 is retained in the new material; however, neutron powder diffraction data (Supporting Information, Figure S1) and chemical titrations indicate that rather than a simple oxygen deintercalation process to form SrVO_{3-x} (as has been previously observed for a wide variety of other transition metal perovskite oxides^[4]), reaction with CaH_2 results in an anion exchange reaction and the formation of the oxide–hydride phase SrVO_2H (Figure 1 a), with CaO being the other solid product (full details of the structural refinement strategy are given in the Supporting Information).

The anion exchange of oxide for hydride in an extended solid is rare but not unprecedented. Analogous reactions have

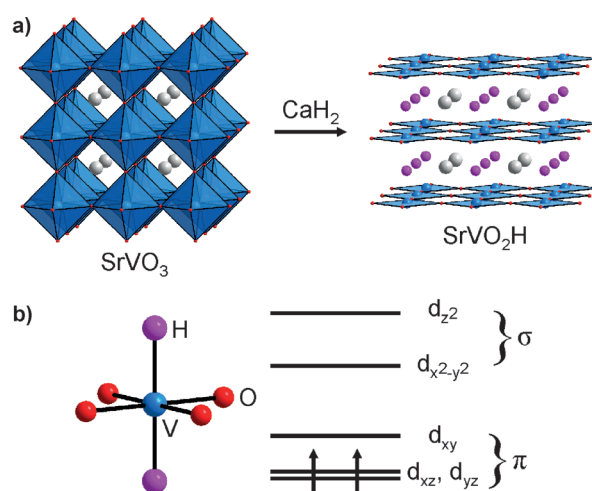


Figure 1. Crystal and local electronic structure of SrVO_2H . a) The cubic perovskite SrVO_3 is transformed topochemically into the tetragonal oxide–hydride SrVO_2H by the action of CaH_2 at 610°C . Sr gray, V blue, O red, H pink. b) The local O_4H_2 coordination of vanadium results in a $(d_{xy}, d_{xz})^2$ electronic state.

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[**] We thank R. Smith for assistance collecting the neutron powder diffraction data. Experiments at the ISIS pulsed neutron facility were supported by a beam time allocation from the STFC. Part of this work was performed at the Swiss Muon Source, and we thank H. Luetkens for technical assistance and the EPSRC for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201403536>.

been observed when the cobalt Ruddlesden–Popper phases LaSrCoO_4 and $\text{Sr}_3\text{Co}_2\text{O}_{7-x}$ react with CaH_2 to form $\text{LaSrCoO}_3\text{H}_{0.7}$ and $\text{Sr}_3\text{Co}_2\text{O}_{4.33}\text{H}_{0.84}$ respectively, and when ATiO_3 ($A = \text{Ba}, \text{Sr}, \text{Ca}$) phases react with CaH_2 to form $\text{ATiO}_{3-x}\text{H}_y$.^[5] What is different in this case, and previously unobserved, is that the anion-exchange reaction is stoichiometric (within the sensitivity of our measurements) and results in a fully anion-ordered phase. A direct 1:1 replacement of oxide with hydride converts SrVO_3 into SrVO_2H , accompanied by a concomitant reduction of V^{4+} to V^{3+} . It should be noted that samples contained small quantities of SrVO_{3-x} owing to the presence of some $\text{Sr}_{1-\delta}\text{VO}_3$ in the starting material, as discussed in detail in the Supporting Information.

The structure of SrVO_2H consists of V^{3+} cations located within square planes of oxide ions, as shown in Figure 1a. These V^{3+}O_4 units share corners to form infinite VO_2 sheets directly analogous the CuO_2 planes observed in $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$, the parent phase of the high- T_c superconducting cuprates.^[6] However, unlike $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ or other infinite layer phases such as LaNiO_2 or SrFeO_2 , the VO_2 sheets in SrVO_2H are connected by the hydride ions, which occupy the remaining two coordination sites around each V^{3+} center. Thus the structure of SrVO_2H can be described by a $\text{VO}_2\text{-SrH-VO}_2\text{-SrH}$ stacking sequence.

Despite the formal six-fold VO_4H_2 coordination of the vanadium centers in SrVO_2H , there is a direct structural and electronic analogy between this phase and the infinite-layer ABO_2 phases. This is because the 1s valence orbitals of the hydride ions have strict σ -type symmetry with respect to the vanadium cations and are thus orthogonal to the π symmetry d_{xz} , d_{yz} , and d_{xy} orbitals from which the HOMO (a degenerate $(d_{xz}, d_{yz})^2$ pair) and LUMO (the d_{xy} orbital) of the local VO_4H_2 unit are derived (after interaction with π -type symmetry oxygen 2p orbitals), as shown in Figure 1b. Thus to a first approximation the d-electrons in SrVO_2H only “see” the infinite layer V–O framework, as the σ -type vanadium d-orbitals which do interact with the H 1s orbitals are empty and energetically remote from the filled orbitals. As a result, SrVO_2H can be considered directly analogous to a d^2 infinite-layer system, such as the hypothetical phase “ KVO_2 ” in which the SrH layers are replaced by layers of potassium cations.

Analogous reactions between CaH_2 and the $n = 1$ and $n = 2$ members of the $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}$ Ruddlesden–Popper series also result in anion exchange reactions. Thus tetragonal Sr_2VO_4 and $\text{Sr}_3\text{V}_2\text{O}_7$ yield orthorhombic $\text{Sr}_2\text{VO}_3\text{H}$ ($Immm$: $a = 3.88 \text{ \AA}$, $b = 3.66 \text{ \AA}$, $c = 12.77 \text{ \AA}$) and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ ($Immm$: $a = 3.91 \text{ \AA}$, $b = 3.66 \text{ \AA}$, $c = 20.63 \text{ \AA}$) respectively as shown in Figure 2. Full details of the structural and chemical characterization of the $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ ($n = 1, 2$) phases are given in Supporting Information, Figures S2 and S3. As shown in Figure 2, $\text{Sr}_2\text{VO}_3\text{H}$ and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ are also constructed from VO_4H_2 units. However, due to the layered nature of the of the Ruddlesden–Popper “parent” phases, $\text{Sr}_2\text{VO}_3\text{H}$ and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ adopt structures containing chains or double chains of apex-linked VO_4 squares. As the local geometry at vanadium is the same in $\text{Sr}_2\text{VO}_3\text{H}$ and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ as in SrVO_2H , by the electronic arguments described above, these materials can be seen as the d^2 analogues of orthorhombic $\text{Sr}_2\text{CuO}_3/\text{Sr}_2\text{FeO}_3$ and $\text{Sr}_3\text{Fe}_2\text{O}_5$, respectively.^[3d,e,7]

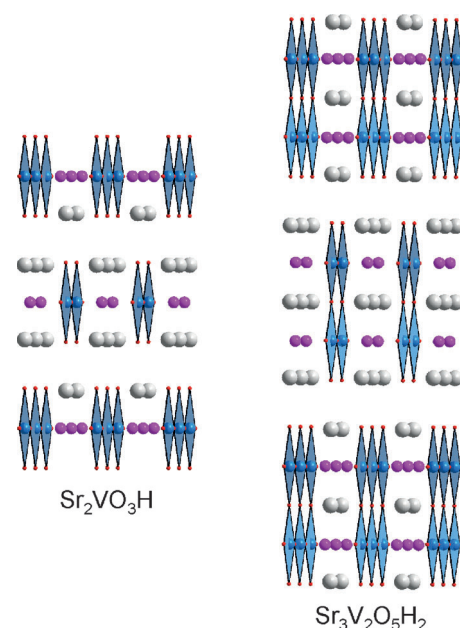


Figure 2. Reaction of Sr_2VO_4 and $\text{Sr}_3\text{V}_2\text{O}_7$ with CaH_2 , resulting in the formation of the oxide–hydrides $\text{Sr}_2\text{VO}_3\text{H}$ and $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$, respectively. Sr gray, V blue, O red, H pink.

Examining the structures of the three $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases reveals that the vanadium hydride bond lengths are almost identical in all three materials ($\text{V–H} = 1.834(1) \text{ \AA}$, $1.833(1) \text{ \AA}$, and $1.834(1) \text{ \AA}$ for $n = 1, 2$, and ∞ , respectively). These values compare well with bridging V–H bonds observed in silylamino(disilylamido) V^{3+} complexes, such as $[\{\text{V}(\text{N}^{\text{H}})_2\}_2(\mu\text{-H})_2]$ ($\text{V–H} = 1.83(3) \text{ \AA}$ and $1.85(3) \text{ \AA}$)^[8] and the metal hydride “ VH_{2-x} ” ($\text{V–H} = 1.84 \text{ \AA}$)^[9] and fall into the range of Co–H bond lengths observed in cobalt oxide hydride phases.^[5a,b]

Neutron powder diffraction data collected at 5 K (Supporting Information, Figures S1–S3) indicate that all three oxide–hydride phases adopt the antiferromagnetically ordered states shown in Figure 3, and this behavior is confirmed by the observation of large static magnetic fields within the materials by zero-field muon-spin relaxation ($\mu^+\text{SR}$) measurements (Supporting Information, Figure S6). On warming $\text{Sr}_2\text{VO}_3\text{H}$ from 5 K, the ordered magnetic moment observed by neutron powder diffraction, and the static magnetic field observed by $\mu^+\text{SR}$, decline to zero (Figure 4), consistent with an antiferromagnetic ordering temperature of $T_N \approx 170 \text{ K}$. Analogous behavior is observed for $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ (Supporting Information, Figure S4), indicating an ordering temperature of $T_N \approx 240 \text{ K}$ for this phase. Rather surprisingly, neither zero-field cooled nor field cooled magnetization data collected from either $\text{Sr}_2\text{VO}_3\text{H}$ or $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ show anomalies at these magnetic ordering temperatures (Figure 4; Supporting Information, Figure S4). Neutron diffraction data collected from SrVO_2H at 298 K indicate that antiferromagnetic order persists to room temperature (Supporting Information, Figure S1). The ordered moments at 5 K and 298 K are rather similar (5 K: $1.56(2) \mu_B$; 298 K: $1.49(1) \mu_B$), suggesting that the antiferromagnetic ordering temperature, T_N , is much greater than 300 K.

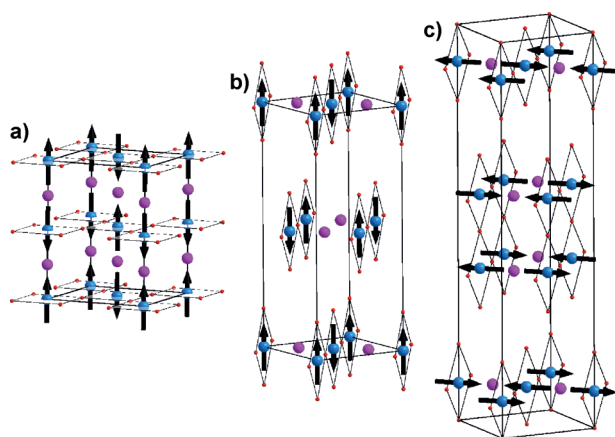


Figure 3. Refinement against neutron powder diffraction data collected at 5 K, revealing: a) SrVO_2H b) $\text{Sr}_2\text{VO}_3\text{H}$ and c) $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ adopt antiferromagnetically ordered states with ordered moments of 1.56(2), 1.54(5), and 1.35(8) μ_B per vanadium center, respectively. V blue, O red, H pink.

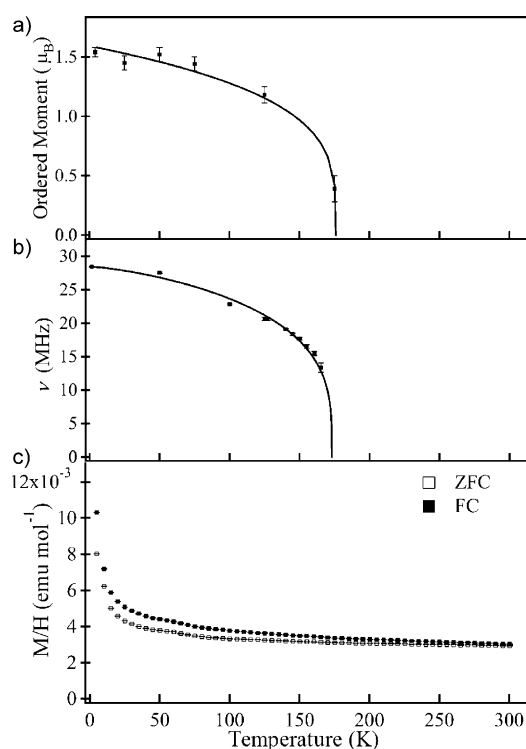


Figure 4. Magnetic data from $\text{Sr}_2\text{VO}_3\text{H}$. a) The ordered moment refined from neutron diffraction data, and b) the muon oscillation frequency plotted against temperature, indicating an antiferromagnetic ordering temperature of $T_N \approx 171$ (1) K. In contrast, c) the zero-field cooled and field cooled susceptibility data measured in a field of 100 Oe show no feature at this temperature.

The antiferromagnetic ordering temperatures of the $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases reflect the decreasing dimensionality of the vanadium-anion lattices. Similar effects are observed for the structurally analogous $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{2n+1}\text{Fe}^{2+}$ oxide phases: “three-dimensional” SrVO_2H ($T_N > 300$ K) and SrFeO_2 ($T_N = 468$ K) have higher ordering temperatures

than the “1.5-dimensional” $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ ($T_N = 240$ K), and $\text{Sr}_3\text{Fe}_2\text{O}_5$ ($T_N = 378$ K) than the “quasi one-dimensional” $\text{Sr}_2\text{VO}_3\text{H}$ ($T_N = 170$ K) and Sr_2FeO_3 ($T_N = 179$ K).^[1b,3d,e] This variation in magnetic ordering temperature with dimensionality suggests that the strengths of the magnetic couplings within the “perovskite blocks” of all three $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases are comparable, with the variation in T_N being attributable to the presence of SrO rock salt layers in the $n=1$ and $n=2$ materials. The high magnetic ordering temperatures observed for $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases are surprising given that the magnetically ordered states appear to arise exclusively from interactions between electrons in π -symmetry d-orbitals (d_{xz} and d_{yz}) rather than the much stronger σ -type superexchange between $d_{x^2-y^2}$ orbitals observed for the $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{2n+1}$ series.^[10]

An additional unexpected feature of the magnetic behavior of $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases is the lack of any signature in the magnetization data at the antiferromagnetic ordering temperatures of these materials. Powder neutron diffraction data and $\mu^+\text{SR}$ data agree on the simultaneous disappearance of a long-range antiferromagnetically ordered lattice and a static magnetic field in $\text{Sr}_2\text{VO}_3\text{H}$ at $T_N = 170$ K (Figure 4), but this event leads to no observable change in the magnetization of the material. These observations may suggest that strong dynamic magnetic correlations in $\text{Sr}_2\text{VO}_3\text{H}$ build up well above T_N so that the entropy released at the magnetic transition is suppressed, leading to minimal change in the measured susceptibility. The sudden onset of static long-range order is nevertheless clearly manifested in the diffraction and $\mu^+\text{SR}$ data. Analogous behavior also appears to be exhibited by $\text{Sr}_3\text{V}_2\text{O}_5\text{H}_2$ (Supporting Information, Figure S4). Such unusual magnetic behavior in a chemically unique set of materials clearly warrants further investigation. Furthermore, we note that the “parent” materials of a number of unconventional superconducting phases are antiferromagnetic insulators in their undoped forms, and the unusual magnetic behavior of $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases may be a prelude to similar behavior. Thus the $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ phases reported herein do not just extend the catalogue of complex oxides containing square-planar-coordinated transition-metal centers, but offer a new low electron-count regime in which to investigate the interactions between strongly interacting transition metal d-electrons.

Experimental Section

$\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ ($n = 1, 2, \infty$) phases were prepared by reduction of V^{5+} precursors under flowing hydrogen, as described previously.^[11] Reduction of the $\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ materials was achieved using CaH_2 .^[5a] Full details of the synthesis of $\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ ($n = 1, 2, \infty$) phases and their subsequent conversion into $\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n$ ($n = 1, 2, \infty$) phases is given in the Supporting Information. Neutron powder diffraction data were collected using the POLARIS diffractometer (ISIS neutron source, UK) from samples contained within vanadium cans sealed under an argon atmosphere with an indium washer. Rietveld profile refinement was performed using the GSAS suite of programs.^[12] Oxidative titrations were performed to determine the vanadium oxidation states of materials by dissolving samples in a 1:1 solution of sulfuric acid, followed by titration with KMnO_4 under inert argon atmosphere. Magnetization data were collected using

a Quantum Design MPMS SQUID magnetometer. The μ^+ SR experiments were carried out at the Swiss Muon Source, PSI, Switzerland. In a μ^+ SR experiment, spin-polarized muons were implanted in the bulk of a material and the time dependence of their polarization monitored by recording the angular distribution of the subsequent positron decay. All of the samples were analyzed by X-ray powder diffraction and oxidative TGA/titration to ensure they had not decomposed (oxidized) during the physical measurements.

Received: March 20, 2014

Revised: May 18, 2014

Published online: June 24, 2014

Keywords: oxide-hydrides · solid-state reactions · solid-state structures · topochemistry

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