Orbital Delocalization and Enhancement of Magnetic Interactions in Perovskite Oxyhydrides

Kai Liu, Yusheng Hou, Xingao Gong & Hongjun Xiang

Recent experiments showed that some perovskite oxyhydrides have surprisingly high magnetic-transition temperature. In order to unveil the origin of this interesting phenomenon, we investigate the magnetism in SrCrO$_2$H and SrVO$_2$H on the basis of first-principles calculations and Monte Carlo simulations. Our work indicates that the Cr-O-Cr superexchange interaction in SrCrO$_2$H is unexpectedly strong. Different from the previous explanation in terms of the H$^-$ ion substitution induced increase of the Cr-O-Cr bond angle, we reveal instead that this is mainly because the 3$d$ orbitals in perovskite oxyhydrides becomes more delocalized since H$^-$ ions have weaker electronegativity and less electrons than O$^{2-}$ ions. The delocalized 3$d$ orbitals result in stronger Cr-O interactions and enhance the magnetic-transition temperature. This novel mechanism is also applicable to the case of SrVO$_2$H. Furthermore, we predict that SrFeO$_2$H will have unprecedented high Neel temperature because of the extraordinarily strong Fe-H-Fe $\sigma$-type interactions. Our work suggests the anion substitution can be used to effectively manipulate the magnetic properties of perovskite compounds.

Complex transition metal oxides have been the subject of enduring interest due to the wide variety of physical properties they exhibit, to name a few, high-$T_c$ superconductivity, magnetoresistance, multiferroicity, thermoelectric response, and so on$^{1-7}$. For the past few years, scientists have found that replacing segmental O$^{2-}$ ions in transition metal oxides by N$_3^-$, F$^-$ or S$_2^-$ can result in novel materials such as pigments, water-splitting photocatalysis, dielectric and cathode material$^{8-12}$. Different from N$_3^-$, F$^-$ or S$_2^-$ which has p valence electrons, the H$^-$ anion has a filled 1$s^2$ electronic configuration that is fundamentally different from the O$^{2-}$ ion case. Therefore, it is expected that the H$^-$ ion substitution might leads to exotic behaviors in perovskite. In pioneering works, a large amount of hydrogen species were incorporated into ATiO$_3$ (A = Ba, Sr, Ca) and Sr$_2$VO$_4$ lattice through the use of CaH$_2$ reductant$^{13-16}$. The resulting oxyhydride ATiO$_3$$_x$H$_x$ exhibits high electronic conductivity and its hydride ions are exchangeable with gaseous hydrogen at elevated temperature, indicating that it can be an ideal mixed electron/hydride conductor for electrochemical applications$^{13-15}$. In oxyhydride Sr$_2$VO$_4$$_x$H$_x$, the hydride ion could act as an effective carrier dopant because the hydrogen and oxygen concentrations can be controlled$^{16}$. Interestingly, it was experimentally found that the magnetic properties of transition metal oxides may change dramatically if some oxygen anions are replaced by hydrogen anions. An antiferromagnetic-to-ferromagnetic transition in EuTiO$_3$$_x$H$_x$ induced by hydride substitution was reported, where the ferromagnetism was caused by the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between the Eu$^{^{3+}}$ spins mediated by the itinerant Ti 3$d$ electrons$^{17}$. LaSrCoO$_3$H$_{0.7}$-$^{20}$ and Sr$_2$Co$_2$O$_{4.33}$H$_{0.84}$-$^{21}$ were found to display high magnetic transition temperatures. Recently, the stoichiometric perovskite oxyhydrides SrCrO$_2$H and SrVO$_2$H have been synthesized$^{22,23}$. The average structure of SrCrO$_2$H is the cubic perovskite where the hydride ions are randomly distributed. In SrVO$_2$H, the planar VO$_2$ layers are connected by hydride ions. The experimentally observed antiferromagnetic (AFM) Neel temperature ($T_N$) of SrCrO$_2$H and SrVO$_2$H are around 380 K and higher than 300 K$^{22,23}$, respectively. It is puzzling that the Neel temperature $T_N$ of SrCrO$_2$H is higher than that (290 K)$^{24,25}$ of LaCrO$_3$. In both SrCrO$_2$H and LaCrO$_3$, the valence of Cr element is 3+ with the three 3$d$ electrons occupying the t$_{2g}$ orbitals, that...
is the G-type. Our GGA magnetic (FM), A-type AFM, C-type AFM and G-type AFM states. The experimentally observed AFM structure (NNN) super-superexchange interaction in the plane; (4) spin exchange parameters, our Monte Carlo (MC) simulations indicate that the negligible. The AFM nature of the NN interactions can result in the G-type AFM order. Based on the calculated

The computed phonon frequencies26 (see Supplementary Figure S3) indicate that the ground state structure of the experimentally observed structure of SrCrO2H. Second, we find that the magnetic properties of another SrCrO2H structure with a high ordered structure (see Fig. 1a) to investigate the magnetism in SrCrO2H for the following reasons. First, by using the cluster expansion approach, we find the ground state structure of SrCrO2H is similar to the experimentally observed SrVO2H structure. The Cr3+ cations are located within square planes of oxide ions and form CrO2 sheets. The CrO2 sheets are connected by hydride ions, which occupy the remaining two coordination sites around each Cr3+ center. Thus the ground state structure of SrCrO2H can be described by a CrO2-SrH-CrO2-SrH stacking sequence.

To examine the magnetic properties of SrCrO2H, we considered four ordered spin states, namely, the ferro magnetic (FM), A-type AFM, C-type AFM and G-type AFM states. The experimentally observed AFM structure is the G-type. Our GGA + U calculations show that all the AFM states have lower energy than the FM state, and the G-type AFM is indeed the ground state, in consistent with experimental observations22. To extract the values of the spin exchange parameters, we adopt the four-state mapping approach27,28. There are four relevant Cr-Cr spin exchange interactions (see Fig. 1a): (1) J3 is the nearest neighbor (NN) superexchange interaction for the Cr-O-Cr path; (2) J4 is the NN spin exchange interaction for the Cr-H-Cr path; (3) J1 is next nearest neighbor (NNN) super-supersuperexchange interaction in the plane; (4) J2 is the NNN out of plane super-supersuperexchange interaction. The calculated exchange parameters in the tetragonal structure of SrCrO2H are summarized in Table 1. As expected, the NN Cr-Cr path has the strongest spin exchange interaction (J3) since it is mediated by the strong π-σ hybridization between 3d and 2p orbitals. The NN spin exchange interaction J3 is weakly AFM due to the direct through-space overlap between the t2g orbitals of Cr3+ ions. The NNN exchange interactions (J4 and J1) are negligible. The AFM nature of the NN interactions can result in the G-type AFM order. Based on the calculated spin exchange parameters, our Monte Carlo (MC) simulations indicate that the TN is around 285 K. If a smaller Hubbard U is adopted, we can get higher TN according to the theory of superexchange, in better agreement with the experimentally observed TN22.

For comparison, we also studied the magnetism in LaCrO3. Experiments show the ground state structure of LaCrO3 is the GdFeO3--type distorted perovskite with Pbnm space group and its lattice constants are a = 5.478, b = 7.759, and c = 5.51629. The lattice constants of our optimized Pbnm structure are a = 5.468 Å, b = 7.758 Å,
and \( c = 5.497 \text{ Å} \), in good agreement with experiment. The obtained spin exchange parameters of the optimized LaCrO\(_3\) are summarized in Table 1. The NN interaction \( J_O \) is AFM and the NNN interactions are negligible. This is in accord with the experimentally observed G-type AFM ground state in LaCrO\(_3\). Compared with SrCrO\(_2\)H, it is clear that \( J_O \) in LaCrO\(_3\) is much weaker. Based on the calculated spin exchange parameters, our MC simulations indicate that the \( T_N \) for LaCrO\(_3\) is around 133 K. Therefore, our theoretical calculations confirm the experimental observation that SrCrO\(_2\)H has a higher \( T_N \) than LaCrO\(_3\), as shown in Fig. 3.

Now we begin to understand the difference in the magnetic properties between SrCrO\(_2\)H and LaCrO\(_3\). There are two significant differences between SrCrO\(_2\)H and LaCrO\(_3\). First, there is a structural difference. The CrO\(_6\) octahedron in LaCrO\(_3\) is tilted due to a small tolerance factor, while there is no octahedron tilt in SrCrO\(_2\)H. As a result, the Cr-O-Cr angle in SrCrO\(_2\)H is 180° while the average Cr-O-Cr angle in LaCrO\(_3\) is 167°. Second, a chemical difference exists since one third of the O\(_2^-\) ions are replaced by H\(^-\) ions. To make clear whether the structural difference or the chemical difference is responsible for the stronger Cr-O-Cr exchange in SrCrO\(_2\)H, we investigate the magnetic properties of SrCrO\(_2\)H and LaCrO\(_3\) with the same cubic perovskite crystal structure. The lattice constant is set to be the average lattice constant (3.85 Å) of experimental SrCrO\(_2\)H structure\(^{22}\). Note that the hypothetic cubic LaCrO\(_3\) phase can be regarded as a result of substituting Sr\(^{2+}\) and H\(^-\) in cubic SrCrO\(_2\)H with La\(^{3+}\) and O\(_2^-\), respectively. The computed spin exchange parameters of these two cubic structures are summarized in Table 1. Surprisingly and interestingly, the Cr-O-Cr superexchange (29.69 meV) in SrCrO\(_2\)H is almost as twice as that (14.25 meV) in LaCrO\(_3\). As expected, the Cr-O-Cr exchange in cubic LaCrO\(_3\) is stronger than that (8.88 meV) in \( Pbnm \) LaCrO\(_3\) according to the Goodenough-Kanamori rule\(^{30–32}\). Previously, it was suggested that the structural difference is solely responsible for the high \( T_N \) in SrCrO\(_2\)H\(^{22}\). However, our calculations show that the structure difference and chemical difference enhance the Cr-O-Cr exchange interaction by 5.37 meV and 15.44 meV, respectively. Therefore, the effect
and Cr₂, and LaCrO₃. The energy level and occupancy of the 3d wavefunctions. These hopping parameters are listed in Table 2. We can see that the hopping parameter is rather close to that (about 5.5 eV) in LaCrO₃. Therefore, we can regard the stronger crystal-field splitting of chemical difference on the Cr-Cr exchange interaction is much more important than that of the structural difference.

To account for why Jₓ for the Cr₁-O-Cr₂ path along the x axis, as shown in Fig. 1a. According to Anderson’s superexchange theory, the magnitude of the spin exchange can be estimated by Jₓ = t²/Δ, where t is the effective hopping between the d orbitals and Δ is the energy difference between majority-spin and minority-spin orbitals. In the cubic SrCrO₂H or LaCrO₃, the dₓₙ orbitals can only interact with the neighboring dₓₙ orbitals, and so do dₓᵧ, dᵧₓ. The magnitude of Jₓ for the Cr₁-O-Cr₂ path can be estimated as Jₓ = t²ₓₙ/Δₓ₊ + t²ₓᵧ/Δₓ₋ + t²ᵧₓ/Δᵧₓ, where t_m (m = x, y, xy) is effective hopping between the m orbitals of Cr₁ and Cr₂, and Δ_m is the energy difference between the majority-spin m orbital and minority-spin m orbital of the Cr₇⁺ ion (see Fig. 2b). The Δ_m parameters are estimated by constructing the maximally localized Wannier functions (MLWFs) based on the ferromagnetic electronic structure. It turns out that Δ_m (about 5.3 eV) in SrCrO₂H is rather close to that (about 5.9 eV) in LaCrO₃. Therefore, we can regard Δ_m as a constant. The effective hopping parameter tₓₙ between the Cr₃d orbitals is obtained by constructing the MLWFs using the spin-unpolarized Bloch wavefunctions. These hopping parameters are listed in Table 2. We can see that the hopping parameter tₓₙ between the dₓₙ orbitals of Cr₁ and Cr₂ is negligible since these two orbitals are almost parallel to each other. The π-π hopping parameter tᵧₓ in the cubic SrCrO₂H are the same as that in the cubic LaCrO₃. The striking result is that the π-π hopping parameter tᵧₓ between the dᵧₓ orbitals of Cr₁ and Cr₂ in the cubic SrCrO₂H is almost 50% stronger than that in LaCrO₃. Using these hopping parameters, we can estimate the ratio between Jₓ for the cubic SrCrO₂H and that in LaCrO₃ as:

$$\frac{J_x(SrCrO_2H)}{J_x(LaCrO_3)} = \frac{t_{x\pi}^2(SrCrO_2H)}{t_{x\pi}^2(LaCrO_3)} = 2.1.$$  

Thus, our first-principles result can be well accounted for by this simple model. This analysis clearly shows that the stronger hopping in SrCrO₂H is responsible for its high Tₘ.

Figure 2a shows the real-space distribution of the dₓₙ-like MLWFs in the cubic SrCrO₂H and LaCrO₃. It is clear that the effective dₓₙ-like MLWF not only distributes around the Cr ion, but also has tails on the neighboring O²⁻ ions due to the anti-bonding π⁻ hybridization between Cr-dₓₙ and O-2p orbitals. It is the tails on the O²⁻ ions that mediate the effective hopping between the Cr-dₓₙ orbitals. An interesting observation is that the lobes on the O²⁻ ion in the MLWF of SrCrO₂H are bigger than those in LaCrO₃. This suggests that the interaction between Cr-dₓₙ orbital and O-p orbital in SrCrO₂H is stronger than that in LaCrO₃, in agreement with our previous result that the effective hopping between the dₓₙ orbitals of Cr₁ and Cr₂ in SrCrO₂H is larger than that in LaCrO₃.

Table 2. Effective hopping between the dₓₙ, dₓᵧ, dᵧₓ, orbitals of nearest neighboring Cr ions in cubic SrCrO₂H and LaCrO₃ through the MLWF technique.

|     | tₓₙ (eV) | tₓᵧ (eV) | tᵧₓ (eV) |
|-----|---------|---------|---------|
| SrCrO₂H (cubic) | −0.385  | 0.002  | −0.213  |
| LaCrO₃ (cubic)  | −0.217  | −0.017  | −0.217  |

Figure 3. Specific heat of SrCrO₂H and LaCrO₃ calculated as a function of temperature from the MC simulations of the classical spin Hamiltonian.
We propose that the stronger interaction between Cr-$d_{xz}$ orbital and O-$p_z$ orbital in SrCrO$_2$H results from the more delocalized Cr-$d_{xz}$ orbital in SrCrO$_2$H (see Supplementary Figure S5). This is supported by a separate MLWF analysis which indicates that the spread of the atomic Cr-$d_{xz}$ orbital in the cubic SrCrO$_2$H is larger than that in the cubic LaCrO$_3$. The more delocalized Cr-$d_{xz}$ orbital in SrCrO$_2$H can be reasoned by considering the electrostatic potential exerted on the Cr 3$d$ electrons. The contour plots of the electrostatic potential on the $xz$-plane are displayed in the Fig. 4c,d. We can see that the electrostatic potential along the Cr-H direction is much weaker than that along the Cr-O direction. Thus, the $d_{xz}$ orbital in SrCrO$_2$H is more delocalized along the $z$-axis, as can also be seen from Fig. 4a. It is the weaker repulsion between the H$^-$ ion and the 3$d$ electrons that makes the $d_{xz}$ orbital in SrCrO$_2$H more delocalized. The weaker electrostatic potential along the Cr-H direction results from the fact that H$^-$ ions have the weaker electronegativity and less charge than O$^{2-}$ ions. Therefore, the replacement of O$^{2-}$ ions by H$^-$ ions will not only change the hybridization type between the transition metal and the anions, but also affect the wavefunction distribution of $d$ orbitals. Such novel mechanism revealed here for SrCrO$_2$H can be also applied to SrVO$_2$H. The only difference is that there is one $d$ electron less than that in SrCrO$_2$H, which makes the $T_N$ slightly lower (see Supplementary Material). We note that first-principles calculations were recently carried out to study the electronic and magnetic properties of SrVO$_2$H. However, the mechanism for the high Neel temperature in SrVO$_2$H was not discovered.

The mechanism that the H$^-$ ion induced delocalization of the $d$ orbitals is general and may have profound effect on the electronic and magnetic properties of other perovskite oxyhydrides. Below we will predict that SrFeO$_2$H has an extremely high $T_N$. With the cluster expansion approach, we predict that SrFeO$_2$H takes the same ground state structure as that of SrCrO$_2$H. This is reasonable since the ionic radius of the Fe$^{3+}$ ion is close to that of the Cr$^{3+}$ ion. The optimized lattice constants $a$ and $c$ for SrFeO$_2$H are 3.997 Å and 3.645 Å, respectively. The computed phonon dispersion (see Supplementary Figure S4) indicates that SrFeO$_2$H is dynamically stable. The spin exchange parameters calculated for the optimized SrFeO$_2$H structures are listed in Table 1. SrFeO$_2$H takes the G-type AFM order as the magnetic ground state since the NN AFM spin exchanges $J_{0}$ (Fe-O-Fe) and $J_{1}$ (Fe-H-Fe) are dominant. To our surprise, the spin exchange $J_{0}$ (89.26 meV) in SrFeO$_2$H is much stronger than $J_{0}$ (39.63 meV) in SrFeO$_2$H. Note that the much stronger Fe-H-Fe interaction is not mainly caused by the shorter Fe-H distance than the Fe-O distance, because similar results are also obtained in the cubic perovskite SrFeO$_2$H.

![Figure 4. Isosurface plots of the Cr-$d_{xz}$ like MLWFs for (a) cubic SrCrO$_2$H and (b) cubic LaCrO$_3$. The lobes on the O$^{2-}$ ion in the MLWF of SrCrO$_2$H are bigger than those of LaCrO$_3$, indicating that the hybridization between Cr-$d_{xz}$ orbital and O-$p_z$ is stronger in SrCrO$_2$H. Contour plots of the electrostatic potential in (c) cubic SrCrO$_2$H and (d) cubic LaCrO$_3$, projected on the $xz$-plane passing through Cr, H, and O sites. The electrostatic potential along the Cr-H direction is much weaker than that along the Cr-O direction in SrCrO$_2$H.](image-url)
structure. In fact, the much stronger Fe-H-Fe interaction is mainly because the out-of-plane Fe-\(d_{z^2-r^2}\) orbital is much delocalized than the in-plane Fe-\(d_{xy}\) and \(d_{yz}\) orbitals. Therefore, the \(\sigma\) bond between the H 1s orbital and Fe-\(d_{z^2-r^2}\) orbital is much stronger than the \(\sigma\) bond between the O-2p orbitals and the in-plane Fe \(d_{xy}\) and \(d_{yz}\) orbitals (see Supplementary Figure S6). Similar to the cases of SrCrO\(_2\)H and SrVO\(_2\)H, the weaker electrostatic potential of H\(^-\) ions exerting on the \(d\) electrons of Fe\(^{3+}\) ions leads to more delocalized Fe-\(d_{z^2-r^2}\) orbitals, which results in an anomalously strong spin exchange \(J_{SS}\). Our MC simulations indicate that the \(T_N\) of SrFeO\(_2\)H is around 826 K, which is even higher than that of BiFeO\(_3\) \((T_N = 643\) K\)\(^{15}\) and SrFeO\(_2\) with a quasi-two-dimensional structure \((T_N = 473\) K\)\(^{35}\). Our result suggests that the replacement of O\(^2-\) ions by H\(^-\) ions can enhance the magnetic interactions not only in \(t_{2g}\) \(d^3\) and \(d^2\) systems, but also in \(d^1\) systems. Our work suggests that the high magnetic transition temperature in LaSrCoO\(_3\)H\(_{0.7}\)\(^{18-20}\) and SrCO\(_3\)O\(_{3\delta}\)H\(_{0.8}\)\(^{24}\) should be also due to the H\(^-\) ion induced delocalization of the 3d \(\sigma\) orbitals.

In summary, we perform a systematic theoretical study on the magnetic properties of perovskite oxyhydrides. The high magnetic transition temperature in SrCrO\(_2\)H is revealed to be due to the delocalization of 3d orbitals in perovskite oxyhydrides. This is because H\(^-\) ions have weaker electronegativity and fewer electrons than O\(^{2-}\) ions. The more delocalized 3d orbitals in SrCrO\(_2\)H make Cr-O-Cr superexchange strong and \(T_N\) high. This novel mechanism also applies to the case of SrVO\(_2\)H. We predict that the \(\sigma\)-type Fe-H-Fe interactions in SrFeO\(_2\)H are extraordinarily strong which also result from the delocalization of the 3d orbitals. The delocalization of d orbitals in oxyhydrides discovered in this work is universal and may also have profound effects on properties other than the magnetic properties.

### Methods

Our DFT calculations are performed on the basis of the projector augmented wave method\(^{38,39}\) encoded in the Vienna ab initio simulation package\(^{40,41}\) (VASP) using the generalized–gradient approximation (GGA) of Perdew, Burke, and Ernzerhof\(^{42}\). The plane-wave cutoff energy is set to be 450 eV. To properly describe the strong electron correlation in the 3d transition-metal oxide, the GGA plus on-site repulsion \(U\) method (GGA + \(U\)) is employed\(^{43}\). \(U = 4\) eV and \(J = 1\) eV are applied to the 3d electron of Cr\(^{3+}\) ions. The maximally localized Wannier functions (MLWFs) are constructed with the Wannier90 program\(^{44,45}\). The spread functional is considered to be converged if the corresponding fractional change because two successive iterations is smaller than 10\(^{-5}\). To find the ground state structures of SrCrO\(_2\)H, SrVO\(_2\)H, and SrFeO\(_2\)H, we adopt the cluster expansion approach\(^{46}\) by using the alloy theoretic automation toolkit (ATAT)\(^{47}\).

We perform parallel tempering Monte Carlo (PTMC) simulations\(^{48,49}\) to estimate the magnetic transition temperature. In PTMC simulations, many replicas with different temperature are simultaneously simulated and a virtual process exchanging configuration of these replicas is introduced. PTMC simulations can avoid a local minimum at low temperatures and can reduce relaxation time. We adopt a 10 \(\times\) 10 \(\times\) 10 supercell to perform PTMC simulations. Our test shows that the results obtained with a 12 \(\times\) 12 \(\times\) 12 supercell are almost the same as those with the 10 \(\times\) 10 \(\times\) 10 supercell. The number of replicas is set to 120.

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