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# Local electronic and magnetic studies of an artificial $\text{La}_2\text{FeCrO}_6$ double perovskite

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Through the utilization of element-resolved polarized x-ray probes, the electronic and magnetic state of an artificial  $\text{La}_2\text{FeCrO}_6$  double perovskite were explored. Applying unit-cell level control of thin film growth on  $\text{SrTiO}_3(111)$ , the rock salt double perovskite structure can be created for this system, which does not have an ordered perovskite phase in the bulk. We find that the Fe and Cr are in the proper 3+ valence state, but, contrary to previous studies, the element-resolved magnetic studies find the moments in field are small and show no evidence of sizable magnetic moments in the remanent state. Based on our findings, we argue that the ground state is consistent with canted antiferromagnetic order. © 2010 American Institute of Physics. [doi:10.1063/1.3455323]

The double-perovskite crystal structure,  $\text{A}_2\text{BB}'\text{O}_6$  provides a rich framework for engineering materials with unrealized electronic and magnetic properties.<sup>1</sup> By rationally designing superlattices (SL), these features can be exploited to design artificial magnets. Specifically, the  $180^\circ$  superexchange between transition metal (TM) ions, which occupy the B and B' sublattices, can be governed through the choice of TM, growth direction, stacking periodicity, etc.<sup>2–4</sup>

$\text{La}_2\text{FeCrO}_6$  is a model system in theoretical discourses over the Goodenough–Kanamori rules.<sup>5</sup> However, numerous experimental attempts at conventional chemical bulk synthesis have failed to produce an ordered phase of  $\text{La}_2\text{FeCrO}_6$ .<sup>6–8</sup> Artificial structures fabricated through multitarget pulsed laser deposition are an effective means to produce these unconventional ordered phases.<sup>2–4</sup> By stacking alternating monolayers of stoichiometric  $\text{LaCrO}_3$  and  $\text{LaFeO}_3$  on a  $\text{SrTiO}_3$  (STO) substrate orientated along the (111) plane (see Fig. 1), an artificial double perovskite with rock salt B-site ordering can be fabricated.

In a previous study of this system, an average magnetization of  $3 \mu_B$  per TM ion was measured with a superconducting quantum interference device magnetometer and an undifferentiated B-site charge state [ $\text{Cr}^{3+}(3d^3), \text{Fe}^{3+}(3d^5)$ ] with ferromagnetic coupling between Cr and Fe was deduced, which agrees with the Goodenough–Kanamori rules.<sup>2,5,9</sup> However, a postpublishing technical comment showed that the actual magnetization was  $0.009 \mu_B$  per site at low field,<sup>10</sup> which raises questions concerning the nature of the ordered magnetic state.

In this letter, we report on the electronic and magnetic structure of an artificial  $\text{La}_2\text{FeCrO}_6$  double perovskite that is grown as a single unit cell  $\text{LaFeO}_3/\text{LaCrO}_3$  SL on STO (111) substrates. X-ray absorption spectroscopy (XAS) shows that both Cr and Fe are trivalent in an  $\text{O}_h$  ligand field symmetry and high spin state. At low temperatures and large magnetic fields, x-ray magnetic circular dichroism (XMCD) shows that the magnetic moments of Fe and Cr are coupled ferromagnetically. However, the moments are only a tenth of the

expected values for a saturated ferromagnetic state and the signal disappears in zero magnetic field, which are both suggestive of an antiferromagnetic state.

Using the element specific techniques of XAS and XMCD, the local electronic and magnetic properties of  $\text{LaCrO}_3$  and  $\text{LaFeO}_3$  SL were investigated. XAS/XMCD is defined as the sum/difference between the absorption spectra for left-polarized and right-polarized x-rays. The sample was mounted inside a superconducting magnet system with incidence angle of  $10^\circ$  from the sample plane ( $80^\circ$  from the growth axis). Since the beam and magnetic field are parallel, this aligns the field primarily in-plane. The polarization of the x-ray beam is switched between left-circularly and right-circularly polarized light at each energy interval in order to measure the photon helicity and magnetization parallel ( $I^+$ ) and antiparallel ( $I^-$ ). XAS ( $I^+ + I^-$ ) stems from the electronic character of a particular element in its environment, while XMCD's ( $I^+ - I^-$ ) magnetic origins probe the element specific net magnetization. Due to XMCD's monolayer sensitivity and penetration depth of several hundred angstroms, it is a prime candidate for exploring nanoscale magnetism at interfaces. In the past, this technique was used to study ultrathin

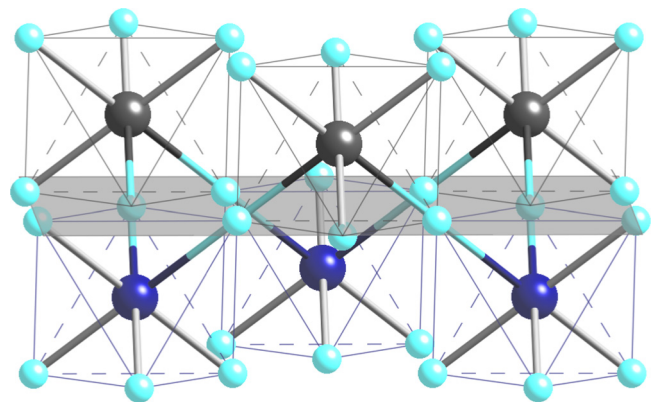
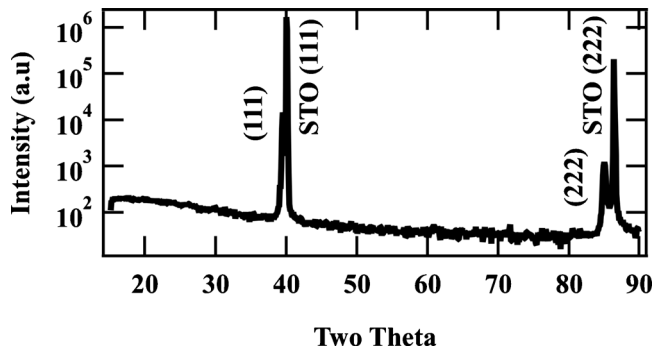


FIG. 1. (Color online) Model of interface between  $\text{LaFeO}_3$  and  $\text{LaCrO}_3$  monolayers grown in the [111] direction. Superexchange path is indicated by multicolored bonds. Layer above plane represents  $\text{LaFeO}_3$ . Layer below plane represents  $\text{LaCrO}_3$ .

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FIG. 2. XRD  $\theta$ - $2\theta$  scan of a SL.

films of manganites, cuprates, cobaltites, etc.<sup>11,12</sup>

The single unit cell  $\text{LaFeO}_3/\text{LaCrO}_3$  SL was fabricated on commercially available STO (111) substrates by pulsed laser deposition with *in situ* monitoring by high-pressure reflection-high-energy-electron-diffraction (RHEED).<sup>13</sup> In an alternating sequence, a KrF excimer laser ( $\lambda=248$  nm) ablated stoichiometric targets of  $\text{LaFeO}_3$  and  $\text{LaCrO}_3$  to produce SL with a 1/1 stacking periodicity. The alternating pattern of  $\text{LaFeO}_3$  and  $\text{LaCrO}_3$  unit cells was repeated fifty times, which gives a total thickness of  $\sim 23$  nm. During deposition, the substrate temperature was held at  $720^\circ\text{C}$  and an oxygen partial pressure of 10 mTorr was maintained inside the chamber.

The structural quality of these SL was verified by conventional x-ray diffraction (XRD). Figure 2 displays the  $\theta$ - $2\theta$  scan for the SL. As expected, the SL possess a single-phase [111] orientation, which testifies to the quality of the epitaxial growth. Calculations of the (111) lattice spacing from the XRD data give a value of  $2.284\text{ \AA}$ , which is 1% to 2% larger than in bulk  $\text{LaCrO}_3$  and  $\text{LaFeO}_3$ , respectively. The anticipated enlargement of the unit cell normal to the surface reflects the lateral compressive strain from the lattice mismatch between STO and the SL. Notice, this lattice spacing is also in agreement with previously reported results.<sup>2</sup> At the same time, the diffraction experiment failed to resolve superstructure peaks indicative of B site cation ordering. These superstructure reflections stem from the twofold doubling of the perovskite unit cell and are conventionally used to quantify the degree of ordering in rock salt type double perovskites.<sup>14</sup> Our simulations of the XRD pattern for perfect ordering show that predicted intensities of superstructure peaks are two to three orders of magnitude smaller than the principle peaks and therefore below the detection limit of our instrument.<sup>15</sup>

In order to determine the electronic and magnetic structure of the SL, XAS and XMCD experiments were carried out at the 4-ID-C beamline of the Advanced Photon Source (APS) in Argonne National Laboratory. We used circularly polarized soft x-rays at the  $L$ -absorption edges of Cr and Fe. Energy resolution was 0.1 eV across the  $L_{3,2}$  edges. Spectra were recorded in total electron yield mode on the Fe and Cr  $L$  edges at an incident angle of  $10^\circ$  out of plane. The sample temperature was held at 10 K and an external magnetic field of 0.1 and 5 T are applied.

Figure 3 compares the Cr and Fe  $L_{3,2}$  XAS spectra of the SL to that of  $\text{Cr}^{3+}(\text{Cr}_2\text{O}_3)$  and  $\text{Fe}^{3+}(\alpha\text{-Fe}_2\text{O}_3)$  standards.<sup>16,17</sup> The Cr/Fe  $L$  edge begins around 570/700 eV and extends to 590/730 eV. Consider the case of Cr. Based on the analogous

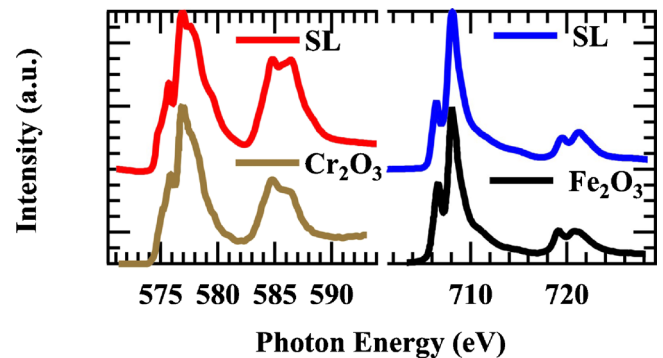


FIG. 3. (Color online) (Left) XAS at the Cr  $L$  edge on top and  $\text{Cr}_2\text{O}_3$  reference spectrum (see Ref. 16) on bottom. (Right) XAS at the Fe  $L$  edge on top and  $\text{Fe}_2\text{O}_3$  reference spectrum (see Ref. 18) on bottom.

local electronic structure (Cr in an octahedral cage of six oxygen anions) and strong resemblances in spectral features, the spectrum for the SL can be interpreted based on calculated spectra of  $\text{Cr}_2\text{O}_3$ . The ground state is high spin  $t_{2g}^3$  with a 3+ valence.  $\text{Cr}_2\text{O}_3$  has a crystal field splitting parameter  $10 Dq=2.0$  eV and a small distortion from octahedral symmetry.<sup>16</sup> In the same manner, the Fe  $L$  edges of the SL and  $\alpha\text{-Fe}_2\text{O}_3$  can be compared. Fe ions are in the high spin state  $t_{2g}^3e_g^2$  and have a valency of 3+. The crystal field splitting parameter for  $\alpha\text{-Fe}_2\text{O}_3$  is  $10 Dq=1.45$  eV, and the ligand field symmetry is  $O_h$ .<sup>18</sup>

In Fig. 4, the XMCD spectra on the Cr and Fe  $L_{3,2}$  edges at a sample temperature of 10 K and an external magnetic field of 5 T are presented. The XMCD intensities have been normalized by the XAS peaks. Comparing both the Cr and Fe  $2p$  XMCD, the agreement between the polarities of the two spectra indicates the parallel alignment of magnetic moments on Cr and Fe ions in the presence of the external magnetic field. Both Cr and Fe show a maximum asymmetry of  $\sim -2.6\%$  at the  $L_3$  edges. This is unexpected, since for a typical ferromagnet with an average magnetic moment of 3 to  $5\ \mu_B$  per TM site, the anticipated XMCD is 30%–40%. The magnitude of the magnetic moments can be estimated by weighting the size of the measured XMCD against standards of known moments with the same valence, ligand field symmetry, and spectral features.<sup>17,19</sup> Following this procedure, assignments of  $0.31\ \mu_B/\text{Cr}$  and  $0.21\ \mu_B/\text{Fe}$  are made for the SL in a magnetic field of 5 T and, when the magnetic field was turned down to 0.1 T, there was no measurable XMCD signal at either edge indicating that the moment at remanence is quite small. For perfect ferromagnetic ordering theoretical values of  $3\ \mu_B/\text{Cr}$  and  $5\ \mu_B/\text{Fe}$  were expected.

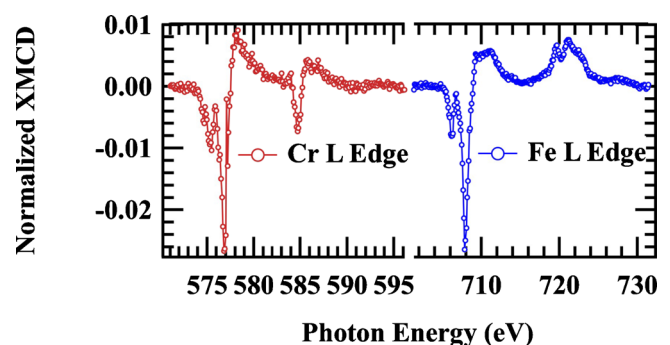


FIG. 4. (Color online) XMCD spectrum. (Right) Cr  $L$  edge. (Left) Fe  $L$  edge at  $T=10$  K and  $H=5$  T.



The moments at 5 T are an order of magnitude smaller than Ueda *et al.*,<sup>20</sup> however in thin film experiments caution is required in interpreting magnetometry data, where extrinsic factors can lead to spurious results. It was also noted that due to a conversion error actual magnetization was  $0.009 \mu_B$  per site in a measurement at 0.1 T,<sup>10</sup> which is at the level of the noise in our measurements.

There are several possible explanations for the low moment. One is that the films are disordered and not in a rock salt perovskite structure. The complementary ionic radii of trivalent Cr and Fe hinder efforts to produce an order phase leading to antisite disorder, where the perfect alternating order of Fe and Cr is broken. Then the system would consist of patches of G-type antiferromagnetic  $\text{LaFeO}_3$  and  $\text{LaCrO}_3$ , which would have no moment at zero field. However, our experience with G-type antiferromagnets is that their moments are hard to cant in this kind of ordered state. To test this we looked at a single layer  $\text{LaFeO}_3$  film and found no observable XMCD at a field of 5 T and temperature of 10 K. In addition, the difference in lattice parameters for  $\text{LaFeO}_3$  and  $\text{LaCrO}_3$  would lead to a distinctly different average c-axis lattice parameter. A second option is to look at other magnetic configurations which have local ferromagnetic (FM) coupling of Cr and Fe but an overall antiferromagnetic (AFM) state. Band-structure calculations have concluded that the ground state might be ferrimagnetic.<sup>1,21</sup> Furthermore, the Goodenough–Kanamori rule are ambiguous for a  $d^3-d^5$  superexchange. The  $pd\sigma$  hybridization between the  $e_g$  orbitals of the TM ions and the oxygen  $p\sigma$  orbital is FM, while the  $pd\pi$  hybridization with the  $t_{2g}$  is AFM.<sup>5</sup> The amount of orbital overlap is greater in the case of  $pd\sigma$  hybridization, however there are more paths in  $pd\pi$  hybridization. This competition between FM and AFM superexchange combined with nontrivial longer-range interactions or Dzyaloshinsky–Moriya type antisymmetric exchange could lead to a canted AFM state.<sup>22,23</sup> From our experimental findings, we can only conclude that the ground state is consistent with canted AFM order.

In summary, we have investigated the local electronic and magnetic environment of Cr and Fe in artificial  $\text{La}_2\text{FeCrO}_6$  perovskite by XAS and XMCD. XAS confirms that Cr and Fe are trivalent and in the high spin state. The marginal magnetic moments of Cr and Fe which only appear in large external magnetic fields are consistent with a canted AFM system.

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