Controlling spin ordering in frustrated magnets via thin film heteroepitaxy

Jodi M. Iwata-Harms,1 Franklin J. Wong,1,2 Urusa S. Alaan,1 B. J. Kirby,3 Julie A. Borchers,3 Michael F. Toney,4 Brittany B. Nelson-Cheeseman,1 Marco Liberati,5 Elke Arenholz,3 and Yuri Suzuki1,2,6

1Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA
2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
4Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
5Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
6Department of Applied Physics and Geophysics Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA

1Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA
2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
4Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
5Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

(Received 5 January 2012; revised manuscript received 5 April 2012; published 20 June 2012)

Competing exchange interactions can give rise to varying degrees of frustration that manifest itself in noncollinear magnetic moment ordering or canonical geometric frustration in magnets with large ground-state degeneracies. Relieving this frustration has the potential to stabilize ground states inaccessible in the bulk. We demonstrate that heteroepitaxial lattice distortions can modify the strength of exchange interactions in thin films of the frustrated ferrimagnet, CuCr2O4. The reduction of magnetic frustration in CuCr2O4 through lattice distortions results in greater collinear spin ordering in CuCr2O4 thin films and an enhanced magnetization. We identify heteroepitaxial lattice distortions as a method to tune spin functionality and potentially lift ground-state degeneracies more broadly in frustrated magnets.

DOI: 10.1103/PhysRevB.85.214424 PACS number(s): 75.25.—j, 75.50.Gg, 75.30.Et, 75.70.Ak

Magnets with varying degrees of frustration can give rise to noncollinear magnetic ordering or canonical geometric frustration characterized by large ground-state degeneracies. The properties of these frustrated systems are particularly susceptible to small perturbations such as electric and magnetic fields, chemical modification, and strain. With advances in thin film deposition techniques, we can use heteroepitaxy to explore new spin phase-space regions in these frustrated magnets. Of particular interest are spinel structure compounds with magnetic cations. The chromite spinels (ACr2O4) display magnetic ground states that range from highly frustrated systems like canonical geometrically frustrated magnets1 to those with reduced frustration such as noncollinear spin systems that exhibit helicoidal2–4 and triangular, canted5,6 order. Theoretical studies have focused on their spin ordering stability,7 and experimental studies have uncovered spin-lattice coupling,8 multiferroicity,9–11 and magnetism-induced anisotropic lattice dynamics.12 In heterostructures, the chromites have revealed large junction magnetoresistance and spin filtering demonstrating their potential for oxide-based spintronics.13–15 The ability to tune the physical properties of spinel chromites is the first step towards exploiting new ground states in canted and strongly geometrically frustrated magnetic oxides.

There have been numerous studies for which heteroepitaxial strain has given rise to emergent phenomena or tuned functionality in complex oxides.16,17 In many of these studies, heteroepitaxial strain induces lattice distortions that, in turn, modify the electronic structure and magnetic ordering.18 However, epitaxial strain may lift the degeneracy of the ground states of frustrated magnets through the modification of exchange interactions, thus providing a different approach for controlling spin order in oxide thin films. A model system for the study of such effects is the tetragonal, canted ferrimagnet, CuCr2O4 (CCO). CuCr2O4 exhibits noncollinear moment ordering due to the presence of closely competing exchange interactions between magnetic moments of the tetrahedrally and octahedrally coordinated cations.

In this work, we demonstrate the lifting of magnetic frustration through the modification of exchange interactions with heteroepitaxy. More specifically we demonstrate that by decreasing the tetragonality of the CCO unit cell and thus yielding greater collinear alignment between the Cr3+ moments, we heal the frustration of the magnetic moments in CCO thin films and significantly enhance the magnetization compared to that of bulk. X-ray diffraction (XRD) indicates that epitaxial strain stabilizes a more cubic unit cell compared to the bulk isostructural CCO films on MgAl2O4 (MAO) substrates. Bulk magnetometry measurements performed with a superconducting quantum interference device (SQUID) magnetometer demonstrate enhanced magnetization. Neutron reflectivity (NR) shows magnetic uniformity in the films, thus eliminating surface or interface effects as the source of enhancement. Element-specific x-ray magnetic circular dichroism (XMCD) studies suggest that the increased net moment of Cr3+ is responsible for the enhanced magnetization.

Bulk CCO is an insulating ferrimagnetic spinel oxide with a tetragonal unit cell (a = 6.03 Å, c = 7.78 Å) and c/a ratio of 1.29 (Fig. 1).5 Its body-centered tetragonal lattice is formed by Cu2+ (1μB) cations which occupy the tetrahedral sites because the Cr3+ (3μB) cations strongly prefer the octahedral sites.5,19 The edge-shared Cr3+ octahedral cages result in a geometrically frustrated lattice as the antiferromagnetic exchange interactions among nearest-neighbor Cr3+ cations cannot be simultaneously satisfied with Ising spins.1 This leads to a large macroscopic ground-state degeneracy in the presence of structural order.1 However, the tetragonal distortion induced by the presence of magnetic, Jahn-Teller active 3d9 Cu2+ in the tetrahedral sites removes this degeneracy favoring an ordered state with strong competing exchange interactions in which the exchange energy between Cu2+ and Cr3+, H_{Cu^2+Cr^{3+}}, is on the order of H_{Cr^{3+}Cr^{3+}}, using the classical Heisenberg
between nearest-neighbor (004) Cr₃⁺
cations are aligned parallel to each other in the
planes. The Cr₃⁺ moments between adjacent (004)
planes are canted relative to each other by the angle ϕbulk = 151°. This results in a low magnetic moment of 0.51 μB f.u.⁻¹ which is an order of magnitude smaller than 5 μB f.u.⁻¹ of the Néel configuration.⁵

CCO thin films were grown by pulsed laser deposition on cubic (110) spinel MAO (a = 8.08 Å) and perovskite SrTiO₃ (STO) (a = 3.905 Å) substrates. The films were grown at 500°C in 15 mTorr of O₂ with a KrF laser and fluence of approximately 1 J cm⁻². The structure of our films was characterized with four-circle XRD at 8000 eV on beamline 7-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) and by cross-sectional high-resolution transmission electron microscopy (HRTEM) using a Philips CM300FEG microscope at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory (LBNL). Element-specific cation valence information was obtained from L-edge x-ray absorption (XA) spectroscopy on beamlines 6.3.1 and 4.0.2 of the Advanced Light Source (ALS). Site-specific elemental information was obtained from resonant x-ray scattering (RXS) measurements on beamlines 7-2 and 2-1 at SSRL. Film thicknesses were determined by Rutherford backscattering spectroscopy (RBS) at the Ion Beam Analysis Facility at LBNL and confirmed by x-ray reflectivity (XRR) on a Philips Analytical X’pert MRD diffractometer.

The bulk magnetization of the CCO films was measured in a Quantum Design MPMS 5XL SQUID magnetometer. The magnetic depth profile was extracted from NR measurements performed at the NIST Center for Neutron Research on the NG-1 reflectometer. For polarized neutron reflectivity (PNR), CCO samples were field cooled at 1.5 T to 5 K and measured at 660 mT. Unpolarized NR was performed at 7 T. Both PNR and NR used the specular reflectivity geometry. Element-specific magnetic XMCD measurements were performed at 25 K in total electron yield mode at normal incidence on beamlines 6.3.1 and 4.0.2 of the ALS.

RBS confirmed the 1:2 ratio of Cu to Cr cations, to within 5% standard error of the measurement, for our CCO films. The Cr L-edge XA spectra were consistent with octahedrally coordinated Cr⁴⁺ while the Cu L-edge XA spectra were indicative of Cu²⁺. To identify the coordination of Cu, we use RXS. In general, for a cubic spinel, the structure factor of the 220 reflection is dependent only on the tetrahedral sites. For the 220 reflection of CCO (Fig. 3), we observe a strong decrease in the diffracted peak intensity due to absorption at the Cu K-edge. This indicates that the 220 planes are occupied by Cu with tetrahedral coordination. A nominal decrease in the 220 diffracted peak intensity at the Cr K-edge suggests a small amount, if any, of tetrahedral Cr consistent with bulk studies. These studies indicate that the bulk valence states and site occupancies are robust and preserved in the thin films, thereby eliminating cation inversion and changing valence states as sources of the enhanced magnetization.

We grew a series of CCO thin films ranging in thickness from 7 to 148 nm. To facilitate epitaxial growth, we selected (110) MAO and (110) STO substrates that provide a rectangular surface unit cell to tetragonal CCO. For MAO substrates, the lattice mismatch along substrate edge directions are +3.8% along [001]CCO|[001]MAO, and −5.8% along [010]CCO|[110] MAO. For STO substrates, the lattice mismatch along substrate edge directions are +0.39% along...
Substrates show isostructural growth; whereas CCO films on STO substrate zone axis for (a) MAO and (b) STO. CCO films on MAO (substrate directions are shown) recorded along the $[0\bar{1}0]$ CCO || $[1\bar{1}0]$ K with varying thickness at the (a) Cr and (b) Cu regions with defective stacking of the isostructural growth, whereas CCO films on STO exhibit and STO are shown in Fig. 4. CCO films on MAO exhibit larger for samples on STO compared to MAO, while the mismatch along the $[001]$ direction is $-0.8\%$ to $5.3\%$ with decreasing film thickness, and is greater than the compressive strain along $[010]$ CCO which ranges from about $-0.8\%$ to $-2.6\%$.

The more cubic unit cell of CCO thin films has strong implications on their magnetic properties due to the strong coupling between structure and magnetism. Using RBS to determine the thickness of two 99 nm CCO films grown simultaneously on STO and MAO, we find that the hysteresis loops of these films at 5 K in Fig. 5(a) demonstrate differences in saturation magnetization ($M_s$) when measured with SQUID magnetometry along the out-of-plane $[100]$ CCO. CCO on STO has a nearly bulk-like magnetization value which is attributed to lattice relaxation due to the large lattice mismatch along the $[010]$ CCO direction, whereas CCO on MAO exhibits a dramatically enhanced $M_s$ exceeding that of bulk. Figure 5(b) shows a general trend of higher magnetization in thinner films of CCO on MAO in which $M_s$ values up to $1.7\mu_B$ F.u.$^{-1}$ are obtained when measured along the $[010]$ CCO direction. Since CCO films have a (001) magnetically easy plane and magnetocrystalline anisotropy effects are dominant, magnetic properties measured along out-of-plane $[100]$ CCO and in-plane $[010]$ CCO are considered equivalent.

PNR was used to probe the depth profile of CCO films as it is directly sensitive to the layer magnetization and nuclear composition. In Fig. 5(c), the spin-up and spin-down non-spin-flip scattering for a 71 nm film is measured with a 660 mT field applied along $[010]$ CCO at 5 K. These spectra are sensitive only to the in-plane component of magnetization. The structure and the distinct oscillations are indicative of characteristic scattering lengths. From known isotopic scattering lengths that predict the absence of nuclear contrast and experimental verification that reveal a damped signal, we can conclude that the oscillations are due to magnetic contrast. Spin-flip scattering, which originates from a net in-plane magnetization perpendicular to the field, is absent, thus indicating a (001) magnetically easy plane. Using exact dynamical formalism, we modeled the PNR data to obtain the nuclear scattering length density (SLD) and magnetization profiles of the CCO samples. Figure 5(d) shows that the PNR data are consistent with a uniform magnetization throughout the depth of the film. The absence of any inhomogeneity in the magnetic profile indicates that the enhancement is due to neither interfacial nor surface effects.

To extract $M_s$, we performed scattering measurements at 5 K in higher fields with an unpolarized neutron beam to avoid difficulties in maintaining neutron spin orientation at high fields. As in the PNR data, any oscillation observed with unpolarized neutron reflectometry (NR) is purely magnetic in origin, thus allowing for the calculation of $M_s$ when measured in a 7 T field. A direct comparison [Fig. 5(b)] of the $M_s$ values

![FIG. 3. (Color online) RXS of the 220 reflection of CCO films with varying thickness at the (a) Cr and (b) Cu K-edge.](image1)

![FIG. 4. Cross-sectional HRTEM image and Fourier transform (substrate directions are shown) recorded along the $[010]$ CCO || $[1\bar{1}0]$ substrate zone axis for (a) MAO and (b) STO. CCO films on MAO substrates show isostructural growth; whereas CCO films on STO substrates exhibit regions with defective stacking of the $\{111\}$ planes with respect to the substrate crystal.](image2)
TABLE I. Lattice parameters of CCO films on MAO of varying thickness as determined by XRD.

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5.93</td>
<td>5.87</td>
<td>8.19</td>
<td>1.38</td>
</tr>
<tr>
<td>27</td>
<td>5.93</td>
<td>5.94</td>
<td>7.95</td>
<td>1.34</td>
</tr>
<tr>
<td>57</td>
<td>5.95</td>
<td>5.96</td>
<td>7.915</td>
<td>1.33</td>
</tr>
<tr>
<td>71</td>
<td>5.95</td>
<td>5.96</td>
<td>7.89</td>
<td>1.325</td>
</tr>
<tr>
<td>99</td>
<td>5.95</td>
<td>5.98</td>
<td>7.84</td>
<td>1.32</td>
</tr>
<tr>
<td>BULK</td>
<td>6.03</td>
<td>6.03</td>
<td>7.78</td>
<td>1.29</td>
</tr>
</tbody>
</table>

extracted from NR and SQUID magnetometry show that the magnetization is enhanced compared to that of bulk. For the 71 and 148 nm films, PNR corroborates the approximately twofold increase in $M_s$ observed by SQUID. However, for the thinner 45 nm film, SQUID magnetometry indicates that the magnetization increases to nearly 1.7 $\mu_B$ f.u.$^{-1}$ while NR finds that the magnetization decreases to 0.90 $\mu_B$ f.u.$^{-1}$. This discrepancy is attributed to error associated with our methods for extracting the magnetization of the film in SQUID magnetometry, in particular, removal of the diamagnetic contribution from the MAO substrates and imperfect sample shapes.

Finally, XMCD studies were performed to investigate element-specific magnetization. Figure 6 shows the Cu and Cr $L$-edge XMCD spectra, normalized to the incoming photon flux, for 45 and 148 nm thick CCO samples in an applied field of ±1.8 T. The antiparallel orientation of the Cu and Cr XMCD spectra is consistent with ferrimagnetic alignment in which the net Cr moment is parallel to the applied field. The XMCD peak intensities for the Cu$^{2+}$ and Cr$^{3+}$ edges of the two films inform us about the origin of the changing magnetization observed in bulk measurements. According to SQUID magnetometry, the magnetization of the 45 nm film was 80–90% higher than the 148 nm film. In Fig. 6(a), the Cu XMCD signal of the 45 and 148 nm films are essentially the same. However, in Fig. 6(b) the peak Cr$^{3+}$ dichroism signal changes approximately 30%. The discrepancy in the magnitude of the increased magnetization between the two techniques is attributed to the low 1.8 T field that is inadequate for magnetic saturation in the XMCD measurements. Thus the increased signal from the Cr$^{3+}$ cations and the net Cr moment aligned parallel to the field indicate that increased magnetization of the thinner films can be attributed
to more collinear moment alignment of Cr\(^{3+}\) between adjacent (004) planes.

In bulk CCO, the tetragonal structure and triangular ground-state moment configuration are the result of competition between the exchange and Jahn-Teller energies. The reduced symmetry results in longer intraplanar Cr-O bonds on the (004) planes and shorter interplanar Cr-O bonds orthogonal to the c axis. Kaplan has shown that the angle of canting is related to the ratio of three exchange terms in which \(\cos(\phi) = (2J_{Cu^2+Cr^3-} + J'_{Cu^2+Cr^3-})/(4J'_{Cr^3+Cr^3-} + J_{Cr^3+Cr^3-})\). As \(\phi\) is smaller in thin films than in bulk, the strength of the exchange interactions in CCO must be affected by lattice distortions induced by heteroepitaxy. The reduction in interaction strength between interplanar Cr\(^{3+}\) predominantly affects the associated exchange terms, \(J_{Cu^2+Cr^3-}\) and \(J'_{Cr^3+Cr^3-}\). Concomitant with the modified orbital overlap, we believe the decreased \(J'_{Cr^3+Cr^3-}\) has a greater effect than the decreased \(J_{Cu^2+Cr^3-}\), thus resulting in a decrease in \(\phi\) and moment canting and an increase in enhanced magnetization.

Finally, the nature of magnetism in CCO precludes the stabilization of alternative spin configurations. The magnetization in our films is too low for a Néel configuration. Long-range, coherent spiral ordering or uniform canting in one direction away from the field is also unlikely as PNR measurements find the absence of spin-flip scattering, thus indicating that there is no net [001] magnetization. Furthermore, despite lattice strains, our CCO films remain noncubic making the Yafet-Kittel canted spin configuration likely as predicted by theoretical studies.

In conclusion, we have successfully demonstrated the ability to induce greater spin alignment in canted, magnetically frustrated CCO thin films via heteroepitaxy. By stabilizing a more cubic unit cell, we observe enhanced magnetization of CCO films that can be understood in terms of reducing the frustration of the magnetic lattice of CCO and modifying the strength of competing exchange interactions.

Our results demonstrate a route for using heteroepitaxy to stabilize greater magnetic ordering in canted magnetic systems. To account for the magnetic enhancement in our epitaxial CCO films, we propose that lattice distortions induced by epitaxial strain reduce the frustration thereby allowing for the rotation of the Cr\(^{3+}\) moments towards a more collinear alignment. The degree of moment rotation for Cr\(^{3+}\), represented by \(\phi\), can be estimated from SQUID magnetometry data assuming negligible out-of-plane moment rotations. While octahedra rotations are possible, their effects are difficult to quantify with the characterization techniques used. (PNR cannot rule out the presence of tilting of the magnetization away from the field direction.) The magnetization values in Fig. 5(b) are consistent with ferrimagnetic alignment between Cr\(^{3+}\) and Cu\(^{2+}\) with \(\phi\) ranging between 121° and 142° compared to the bulk value of 151°. For tetragonal CCO, Kaplan has shown that the angle of canting is related to the ratio of three exchange terms in which \(\cos(\phi) = (2J_{Cu^2+Cr^3-} + J'_{Cu^2+Cr^3-})/(4J'_{Cr^3+Cr^3-} + J_{Cr^3+Cr^3-})\). As \(\phi\) is smaller in thin films than in bulk, the strength of the exchange interactions in CCO must be affected by lattice distortions induced by heteroepitaxy. The reduction in interaction strength between interplanar Cr\(^{3+}\) predominantly affects the associated exchange terms, \(J_{Cu^2+Cr^3-}\) and \(J'_{Cr^3+Cr^3-}\). Concomitant with the modified orbital overlap, we believe the decreased \(J'_{Cr^3+Cr^3-}\) has a greater effect than the decreased \(J_{Cu^2+Cr^3-}\), thus resulting in a decrease in \(\phi\) and moment canting and an increase in enhanced magnetization.

This work was supported by the National Science Foundation under Grants No. 0604277 and No. 1104401. U.S.A. was supported by an NSF graduate fellowship. F.J.W., the Advanced Light Source, and the National Center for Electron Microscopy are supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the US Department of Energy under Contract No. DE-AC02-05CH11231. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the US Department of Energy, Office of Basic Energy Sciences. We would like to thank K. M. Yu, R. V. Chopdekar, J. S. Bettinger, V. V. Mehta, S. Anwar, and M. A. Mayer for assistance in data collection and discussion.
30 In order to maintain beam polarization, our measurements were limited to fields below 700 mT. Hence reported PNR magnetization values are not obtained at saturation.
31 J. B. Goodenough, in Magnetism and the Chemical Bond (Krieger, New York, 1976), Chap. 3.