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Publication Date

2009-11-01

The relationship between structure and enhanced magnetism in tetragonal, magnetically-frustrated spinel thin films

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Epitaxial spinel oxide thin films enable the stabilization of ground states with magnetic and electronic properties that are enhanced compared to that of their bulk counterpart[1-4]. In particular, the enhancement of magnetization in spinel films has been explained in terms of off-stoichiometry, varying concentrations of cation valence states, cation inversion, and varying distribution of spin states. We have studied copper chromite, $CuCr_2O_4$ (CCO), thin films in which we have correlated enhanced magnetization with changes in structure. In bulk form $CuCr_2O_4$ is a normal spinel with a tetragonal unit cell and a large c/a ratio of 1.29. Unlike other chromites, large Jahn-Teller distortions, a result of $3d^9$ Cu^{2+} occupying tetrahedral interstitial sites, remove the cubic symmetry of the unit cell, thus giving rise to a frustrated triangular cation moment configuration[5,6]. This magnetic frustration reduces the overall magnetic moment to 0.5 μ_B/f.u. (T_C = 125K) as compared to a collinear moment configuration (5 μ_B/f.u.). The frustrated, triangular cation moment configuration, combined with its robust normal cation distribution, and large tetragonal distortion makes CCO a model system for exploring the magnetism-structure relationship for enhanced magnetization.

A series of CCO thin films, ranging in thickness from 7 nm to 100 nm, have been grown using pulsed laser deposition on (110) $MgAl_2O_4$ (MAO) substrates. Atomic force microscopy has shown that these films have a roughness of approximately 0.5 nm which is on the order of a unit cell. Cross-sectional transmission electron microscopy confirms isostructural growth on 110-oriented MAO substrates. Bulk magnetic measurements from CCO thin films performed with a SQUID magnetometer show moments up to 5 μ_B/f.u. at 5K which is almost ten times greater than that of its bulk counterpart as shown in Figure 1. The enhanced moment is thickness dependent which suggests that strain influences this enhancement. Similarly, Curie temperatures are also thickness dependent: thinner films exhibit a greater suppression of T_C indicative of the effect of strain on exchange interactions.

Structural studies were performed to quantify strain in the heteroepitaxial CCO films. Bulk CCO lattice parameters have an average mismatch of 4.4% from MAO. X-ray diffraction shows a slight shift of the out of plane film peaks as a function of thickness indicative of strain relaxation. In-plane X-ray diffraction measurements indicate significant tensile and compressive strain parallel to the plane compared to the smaller amount of out-of-plane compressive strain as a result of growing on (110) MAO. These studies show that the c/a ratio of the CCO unit cell gradually evolves into a more cubic-like structure as a function of decreasing film thickness.

The stabilization of a more cubic-like structure is critical for achieving the enhanced moment. In thinner films, the substrate-induced strain is large enough to overcome Jahn-Teller effects thereby relieving the magnetic frustration of the triangular moment configuration, and allowing the moments to stabilize in a more collinear configuration. This resultant configuration changes bond angles which likely affects A-A, B-B, and A-B site interactions leading to a higher overall

moment. Neutron reflectivity and X-ray reflectivity measurements will enable us to confirm this relationship between the enhanced magnetism and structure.

In our films enhanced magnetization cannot be due to cation inversion, disorder, or varying cation valences like that observed in $NiFe_2O_4$[2], $CuFe_2O_4$[3], and $ZnFe_2O_4$[4]. Bulk $CuCr_2O_4$ has a robust normal cation site distribution. This is due to the strong preference of Cr^{3+} to occupy the octahedral site of the spinel unit cell[7]. As a result, the Cu^{2+} ($3d^9$) cations are forced into the tetrahedral sites. In our films, X-ray absorption spectroscopy measurements, taken at BL4.0.2 at the Advanced Light Sources, indicate the presence of only Cr^{3+} in our CCO thin films. Resonant X-ray scattering measurements (RXS) have confirmed that there is no cation inversion as Cu^{2+} cations occupy tetrahedral sites while Cr^{3+} cations occupy the octahedral sites.

Supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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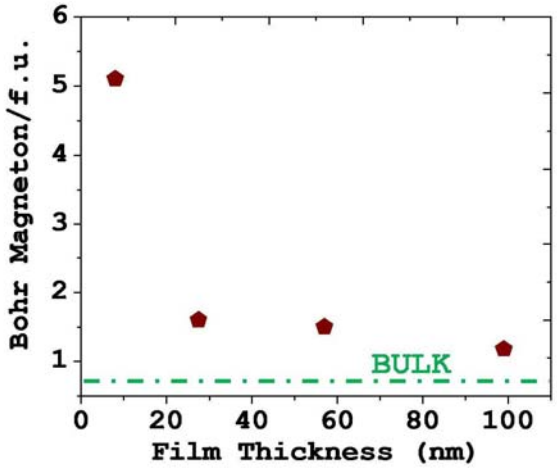

Figure 1. Magnetic moment of CCO thin films as a function of thickness at 5K.