Magnetism of $NiMn_2O_4$–Fe_3O_4 spinel interfaces

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We investigate the magnetic properties of the isostructural spinel-spinel interface of $NiMn_2O_4$(NMO)–Fe_3O_4. Although the magnetic transition temperature of the NMO film is preserved, both bulk and interface sensitive measurements demonstrate that the interface exhibits strong interfacial magnetic coupling up to room temperature. While NMO thin films have a ferrimagnetic transition temperature of 60 K, both $NiFe_2O_4$ and $MnFe_2O_4$ are ferrimagnetic at room temperature. Our experimental results suggest that these magnetic properties arise from a thin interdiffused region of $(Fe,Mn,Ni)_3O_4$ at the interface, leading to Mn and Ni magnetic properties similar to those of $MnFe_2O_4$ and $NiFe_2O_4$.

The oxide spinel Fe_3O_4 is an ideal candidate for a highly spin polarized electrode material to be used in spintronic applications. It has been theoretically predicted to be half-metallic, and is highly attractive for applications due to its high Curie temperature (T_C) of 850 K.[1] Experimental studies of Fe_3O_4 in spintronic heterostructures, however, have exhibited much lower junction magnetoresistance (JMR) values than expected from a half-metallic electrode material. Among the highest JMR values of Fe_3O_4-based heterostructures are observed in layered systems with epitaxially grown isostructural spinel barrier layers. Oxide spinels such as $CoCr_2O_4$, $MgTi_2O_4$, $FeGa_2O_4$, and $MnCr_2O_4$ have been used as barrier layers in magnetic tunnel junctions with spinel Fe_3O_4 and half-metallic perovskite electrodes,[2,3] while $CoFe_2O_4$ has been used with Fe_3O_4 in spin-filter junctions.[4,5] Recently, $NiMn_2O_4$ (NMO) has also been identified as an effective spin-filter barrier material in Fe_3O_4-based magnetic junctions with perovskite counter-electrodes.[6] Whereas perovskite and spinel layers have been shown to be magnetically uncoupled in these structures,[6] the magnetism near the isostructural spinel interfaces is a subject of interest. A more detailed investigation of the interfacial magnetic interactions between spinel structure materials is necessary in order to understand transport and magnetic interaction results attributed to these multilayers, as well as to optimize the use of these heterostructures for spintronic applications.

In this paper, we observe magnetic properties in $NiMn_2O_4$ thin film bilayers with Fe_3O_4 not observed in either film alone. Although the NMO magnetic transition at 60 K is preserved, interfacial element-specific magnetism measurements of NMO/Fe_3O_4 bilayers show strong interfacial coupling of the Fe, Mn, and Ni moments. We suggest that these magnetic results can be explained by a thin interdiffused layer at the interface.

Thin film heterostructures of NMO and Fe_3O_4 were grown by pulsed laser deposition on (110)-oriented single crystal $SrTiO_3$ (STO) substrates. The NMO was grown at 600 °C in 10 mTorr of 99% N_2/1% O_2, while the Fe_3O_4 was grown at 400 °C in vacuum. The NMO film was grown first to minimize oxidation of the Fe_3O_4 film during deposition. The films grow epitaxially on the STO substrates as confirmed by x-ray diffraction and Rutherford backscattering measurements. The single NMO thin films have a T_C of 60 K.[7] The bulk magnetism of the samples was probed by a superconducting quantum interference device (SQUID) magnetometer. The element-specific magnetic properties of the interfacial Ni, Mn, and Fe were investigated by x-ray magnetic circular dichroism (XMCD) (BL4.0.2 and BL6.3.1) in total electron yield at the Advanced Light Source. Due to the surface sensitive nature of this technique and in order to be interface specific, all samples had a 5 nm Fe_3O_4 top layer. Additionally, because the NMO films have a low saturation magnetization ($0.8\mu_B$) compared to Fe_3O_4 films ($4.1\mu_B$), two different thicknesses of NMO film in the bilayer (40 and 5 nm) were utilized to elucidate any effect of the bulk NMO film on the interface. Lastly, because these measurements are relevant to spin polarized heterostructures, where the bottom spinel layer is usually grown on a perovskite counterelectrode, such a heterostructure was also investigated. Therefore, the NMO/Fe_3O_4 interface was investigated in the following three samples: a “thick bilayer” of STO||NMO(40nm)/Fe_3O_4(5 nm), a “thin bilayer” of STO||NMO(5nm)/Fe_3O_4(5nm), and a “trilayer” of

STO||$La_{0.7}Sr_{0.3}MnO_3$(LSMO)(40nm)/NMO(5nm)/Fe_3O_4(5nm). All magnetic measurements were performed along the [100] in-plane direction.

Moment versus temperature measurements taken at 10Oe of the NMO/Fe_3O_4 bilayers are shown in Fig. 1(a). The thick bilayer sample shows a Brillouin shape for the NMO T_C of 60K; however, after reaching a minimum at 60 K, the moment begins to rise with increasing temperature [Fig. 1(a)], uncharacteristic of the magnetic behavior observed in either individual film. This behavior is largely absent in the thin bilayer sample, although a slight discontinuity may be seen at 50K [Fig. 1(b)]. Such results prompted more detailed investigation of the magnetic interactions at the interface.

XMCD spectra and hysteresis loops of the NMO/Fe_3O_4 interface were taken in all heterostructures at various temperatures. The x-ray absorption spectroscopy (XAS) and XMCD results of the thin NMO bilayer are displayed in Fig. 2. The NMO/Fe_3O_4 interface exhibits virtually identical Fe, Mn, and Ni XAS and XMCD spectra for all temperatures of 30–300 K, as seen in Fig. 2. The thick NMO bilayer and trilayer samples also demonstrate this behavior. In addition, for a given temperature, the Fe, Mn, and Ni XMCD hysteresis loops are identical to one another. Nevertheless, the *shape* of the hysteresis loops changes distinctly as a function of temperature, showing a dramatic increase in coercive field for all three elements below the NMO T_C. Similar results are seen in the temperature dependent hysteresis loops of the trilayer sample. As shown in Fig. 3, the coercive fields of the Fe are the same at 80 and 55 K, but increase at 30 and 15 K. Furthermore, at 55 K, the hysteresis loop shows a slight decrease in remanent dichroism, which is consistent with the minimum moment in the SQUID data. As the normalized Fe, Mn, and Ni hysteresis loops are identical for each given temperature, this hysteresis loop behavior is seen in the Mn and Ni as a function of temperature also, but has been omitted for clarity in Fig. 3.

One can now discuss the apparent source of the bulk moment measurements by utilizing the element and interface specific XMCD information. First, it appears that there is significant magnetic coupling at the interface, as evidenced by identical Fe, Mn, and Ni hysteresis loops. However, although they are identical for a given temperature, the magnetic nature of the hysteresis loops becomes increasingly harder as the temperature is decreased below 60 K. This evolution suggests that the species at the interface are coupled to the magnetically soft Fe_3O_4 at temperatures above the NMO T_C, but, as the NMO layer becomes ferrimagnetic, the species couple to the magnetically hard NMO as well. The decrease in remanent asymmetry observed in the trilayer around 60 K could be due to a magnetic frustration of the interfacial species as the NMO layer becomes ferrimagnetic. This can all be related to the *increase* in bulk moment observed above 60 K in Fig. 1(a) in the following way: Just above the T_C of the NMO film, the bulk hysteresis loop exhibits greater squareness than that at lower temperatures, which results in an effective *increase* in moment at small fields as the temperature is increased.

The magnetic transition of the NMO film in the presence of this strong magnetic coupling at the interface is also of interest. It is apparent from the change in hysteresis loop shape and increase in coercive field in Fig. 3 that even the thin NMO layer undergoes a

magnetic transition around 60 K. Any depressed onset of the coupling to the NMO layer could be due to the relatively low magnetization of the NMO compared to the Fe_3O_4.

Now that we have discussed how the interfacial species respond to the bulk of the NMO and Fe_3O_4 thin films, let us focus on how the magnetic species at the interface can give rise to significant Mn and Ni magnetic circular dichroism at room temperature. Two possible explanations are (1) a thin interfacial layer of the NMO thin film magnetized far above the NMO T_C by the close proximity to the Fe_3O_4 layer or (2) the presence of a mixed $(Fe,Mn,Ni)_3O_4$ spinel at the interface that is ferrimagnetic at room temperature. Such a solid solution at the interface is reasonable as the cations of the spinel structure occupy only a small fraction of the available octahedral and tetrahedral sites of the oxygen face-centered-cubic sublattice, leaving ample opportunity for cation diffusion throughout the structure.

The XAS and XMCD data support the presence of Mn and Ni in $MnFe_2O_4$ and $NiFe_2O_4$ environments at the interface, consistent with a mixed $(Fe,Mn,Ni)_3O_4$ spinel. The Ni XAS and XMCD spectra are characteristic of $NiFe_2O_4$, while the Mn XAS and XMCD spectra are characteristic of $MnFe_2O_4$.[8] Additionally, the alignment of the Ni and Mn moments with respect to the Fe moments in the XMCD is consistent with $MnFe_2O_4$ and $NiFe_2O_4$. As seen in Fig. 2, the maximum Ni dichroism is parallel to the third peak of the Fe dichroism, as in bulk $NiFe_2O_4$, and the maximum Mn dichroism is antiparallel to the third peak of the Fe dichroism, as in bulk $MnFe_2O_4$.[9] Furthermore, the lack of a change in the Mn and Ni XMCD spectra below the NMO T_C may result from probing the magnetism in an interdiffused region, which would form the bulk of the XMCD probing depth and, due to the comparatively high saturation magnetization values of $NiFe_2O_4$ and $MnFe_2O_4$ with respect to NMO, overwhelm the NMO dichroism.

In conclusion, isostructural spinel interfaces of Fe_3O_4 and $NiMn_2O_4$ exhibit strong interfacial magnetic coupling, although the NMO T_C of 60 K is preserved. Element and interface specific magnetic analysis suggests that this behavior is due to limited interdiffusion of the Fe, Mn, and Ni cations at the interface, thus creating a spinel solid solution of $(Fe,Mn,Ni)_3O_4$ that exhibits the magnetic properties of $NiFe_2O_4$ and $MnFe_2O_4$. Above the NMO T_C, this interdiffused region couples to the magnetic Fe_3O_4 layers; however, with the onset of ferrimagnetism in the NMO film, the interfacial region first becomes frustrated, and then couples to the magnetically hard NMO. This work is relevant in understanding magnetic interfacial interactions in spinel-spinel heterostructures.

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FIGURES

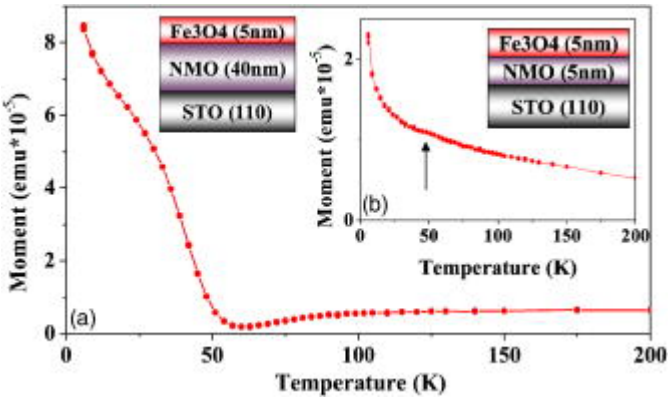

Fig. 1. Moment as a function of temperature for (a) thick (40 nm) NMO bilayer and (b) thin (5 nm) NMO bilayer.

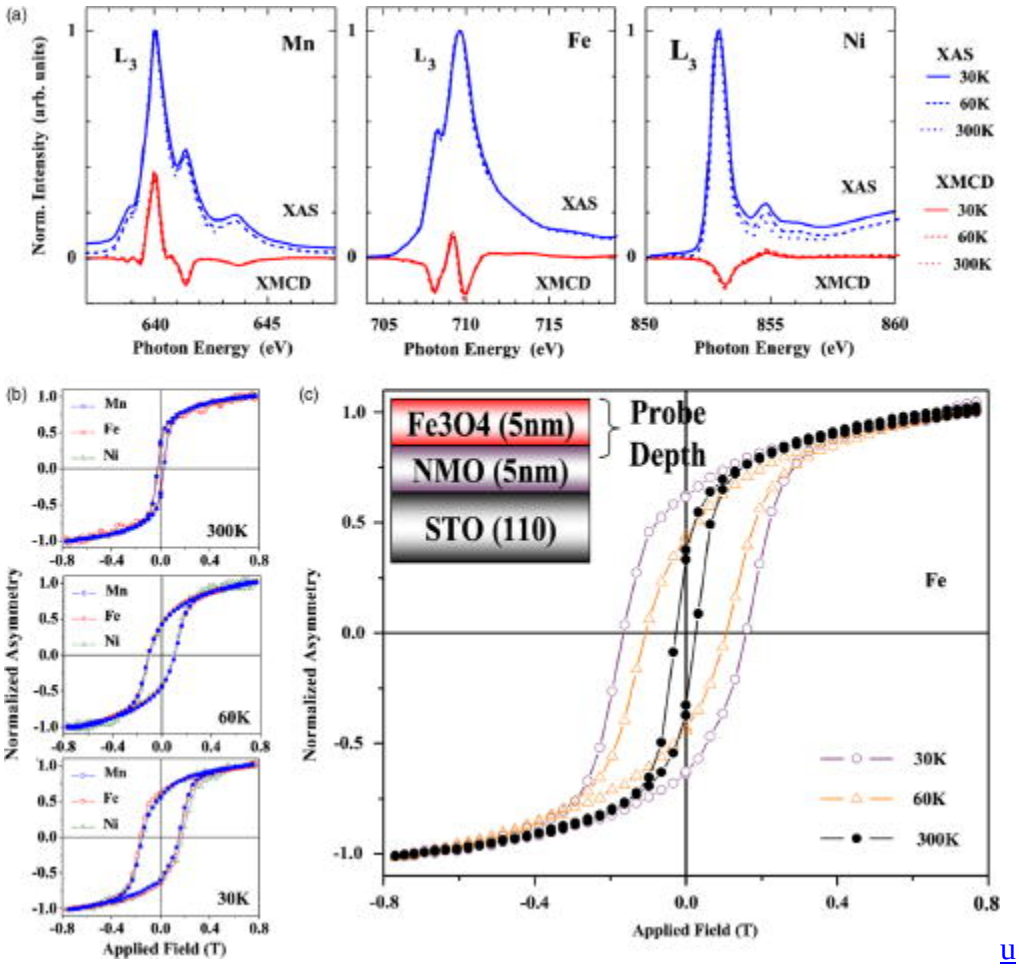

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Fig. 2. Element-specific magnetism of Fe_3O_4/NMO interface in thin NMO/Fe_3O_4 bilayer. (a) XAS and XMCD spectra for Mn, Fe, and Ni as a function of temperature. (b) Mn, Fe, and Ni normalized XMCD hystersis loops at each temperature. (c) Fe normalized XMCD hysteresis loops as a function of temperature.

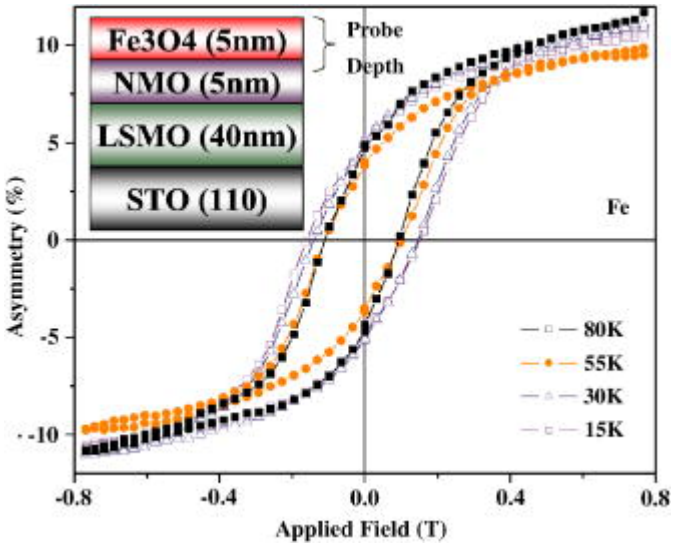

Fig. 3. Fe XMCD hysteresis loops as a function of temperature, probing top of trilayer sample with 5 nm mean probe depth.

FOOTNOTES

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