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Exchange coupling in single-crystalline spinel-structure (Mn,Zn)Fe_2O_4/$CoFe_2O_4$ bilayers

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We have observed strong exchange coupling between single-crystalline spinel-structure ferrite thin films of $CoFe_2O_4$ and magnetically soft (Mn,Zn)Fe_2O_4 at room temperature. The exchange coupling constant of the interface, A_{int}, which is estimated from exchange-biased (Mn,Zn)Fe_2O_4 loops is comparable to estimated exchange coupling constants within each individual layer, A_{MZF} and A_{CF}. This result contrasts with exchange coupling in polycrystalline $Ni_{0.8}Fe_{0.2}$/$Mn_{0.5}Fe_{0.5}$ and $Ni_{0.81}Fe_{0.19}$/$Ni_{0.53}Mn_{0.47}$ bilayers where A_{int} is at best two orders of magnitude smaller than estimates of A_{NiFe}. [S0163-1829(96)03721-6]

Exchange coupling between an antiferromagnetic and a ferromagnetic film or between two ferromagnetic films has been extensively studied since the phenomenon was discovered by Meiklejohn and Bean.[1] This short-range exchange interaction at the interface tends to keep spins in adjacent layers oriented with respect to one another. Exchange-coupled systems consisting of a magnetically soft metallic ferromagnet NiFe alloy biased by an antiferromagnet such as a MnFe alloy have been extensively studied especially in light of magnetoresistive read head applications.[2,3] However, the energy associated with the exchange offset in this and similar polycrystalline systems is two orders of magnitude weaker than the ideal exchange interaction energy available at the interface. The weak interaction has been modeled by invoking interdiffusion of atomic species at the interface and half integral height steps at the interface.

Exchange anisotropy in single-crystalline bilayers has not been previously studied, but potentially allows the investigation of exchange coupling without the ambiguity of polycrystallinity.[4] We have used magnetically hard ferromagnetic $CoFe_2O_4$ (CF) films to achieve *strong* unidirectional exchange biasing of soft ($Mn_{0.46}Zn_{0.54}$)Fe_2O_4 (MZF) films.[5] We have observed magnetic properties in our strongly exchange-coupled layers that are predicted by micromagnetic theory.

In our single-crystalline MZF/CF bilayer system, the Curie temperatures of both films are well above room temperature, thus making the system viable for technological applications. In contrast to the metallic NiFe/MnFe bilayer system, the MZF/CF bilayer system is a plausible candidate for thin-film inductor applications because of its low conductivity and thus low eddy current losses. These spinel-structure ferrites have a very small (0.4%) lattice constant mismatch so that we obtain good epitaxy in MZF/CF heterostructures. MZF has a relatively high saturation magnetization of 320 emu/cm^3 and a low bulk crystalline anisotropy of $K_1 \sim 4\times10^3$ ergs/cm^3, thus making it a good soft magnetic layer candidate. CF has a high saturation magnetization of 400 emu/cm^3 and a very high crystalline anisotropy of $K_1 \sim 3\times10^6$ ergs/cm^3. The CF films have square magnetization loops (M-H loops) with coercive fields of 3–5 kOe measured along the easy axis. Thus the CF films strongly resist demagnetization and are suitable for biasing.

To obtain high-quality single-crystalline ferrite thin films with bulk saturation magnetization properties and square loops, we have grown ferrite layers on $CoCr_2O_4$- (CCO-) buffered $SrTiO_3$ (STO) and $MgAl_2O_4$ (MAO). The CCO buffer layer also has a spinel crystal structure, but is paramagnetic at room temperature. The ferrite heterostructures and the underlying buffer layer were grown by pulsed laser deposition.[5] The ferrite films were grown at 400 °C with a KrF excimer laser at 10 Hz and an energy density of 4 J/cm^2 in a 1-mTorr O_2 atmosphere. Both the ferrite films and underlying buffer layers show excellent crystalline quality as inferred from x-ray diffraction using Cu $K\alpha$ radiation and Rutherford backscattering (RBS) analysis by using 1.8-MeV $^4He^+$ ions. The full width half maximum (FWHM) of rocking curves of the ferrite film peaks are typically $\Delta\omega \sim 0.5°$, and the RBS figure of merit of crystallinity, χ_{min}, is about 16%. Detailed structural characterization of single-layer MZF and CF films and the underlying CCO buffer layer has been presented elsewhere.[5] For the MZF/CF bilayers, we grew the MZF and CF layers sequentially on CCO-buffered (110) STO and MAO; the (110) orientation of the ferrites on the buffered substrate is especially useful as it places the easy and hard axes of the ferrite layers in the plane of the substrate. As in the single-layer ferrite films, structural analysis of the ferrite bilayers including x-ray diffraction, RBS ion channeling, atomic force microscopy, and transmission electron microscopy reveals a consistent picture of ferrite films, indicating excellent crystalline quality.[5] X-ray-diffraction analysis shows excellent crystalline quality of the ferrite bilayers with FWHM rocking curves of $\Delta\omega \sim 0.6°$. Studies of the correlation of structural and magnetic properties reveal that excellent structural properties are necessary to obtain good magnetic properties.[5] To minimize potential interdiffusion problems, we have deposited the ferrite layers at a low temperature of 400 °C. The M-H loops of single-MZF-layer films on CCO demonstrate that there is negligible interdiffusion of cobalt into the MZF layer. Therefore we expect negligible cobalt interdiffusion at the MZF/CF interface in bilayers. We report here on a series of bilayers consisting of 1600 Å of CF on which 900, 1500, and 3000 Å of MZF were grown to study the dependence of the exchange coupling phenomenon on film thickness.

M-H loops of the bilayers show bulk magnetization values for both of the layers. Figure 1 is a plot of a major loop

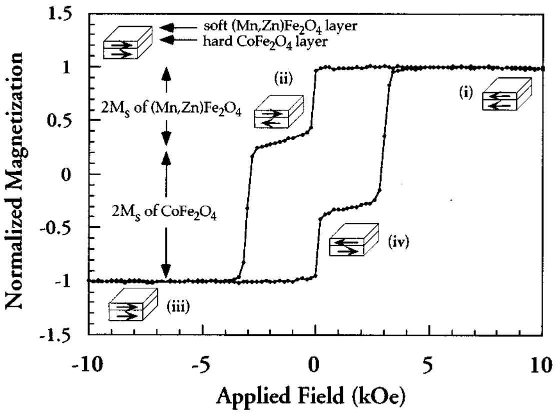

FIG. 1. Major loop of a 1500-Å (Mn,Zn)Fe$_2$O$_4$/1600-Å CoFe$_2$O$_4$ bilayer on CoCr$_2$O$_4$-buffered MgAl$_2$O$_4$. The spin directions in the hard and soft layers are schematically shown in four different sections of the loop. The magnetizations attributed to the (Mn,Zn)Fe$_2$O$_4$ and CoFe$_2$O$_4$ layers are indicated.

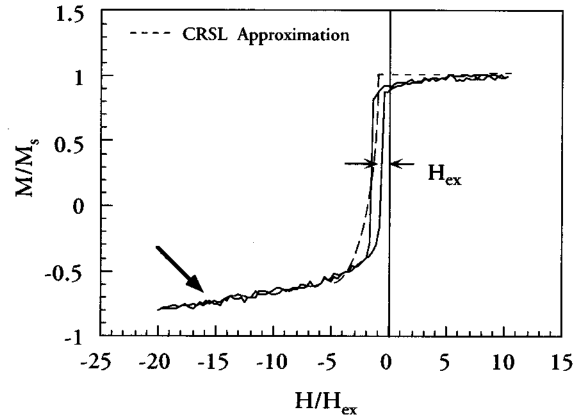

FIG. 2. Exchange-biased loop of (Mn,Zn)Fe$_2$O$_4$ of a 1500-Å (Mn,Zn)Fe$_2$O$_4$/1600-Å CoFe$_2$O$_4$ bilayer with an exchange field of 50 Oe. The (fixed) magnetization attributed to CoFe$_2$O$_4$ has been subtracted from the data. The asymmetric approach to saturation is characteristic of a coherent rotation of the moments in the soft (Mn,Zn)Fe$_2$O$_4$ layer. The heavy arrow indicates the asymptotic approach to saturation. The dotted line represents a calculation using the CRSL approximation as described in the text.

of a 1500-Å MZF/1600-Å CF bilayer on MAO when the field is applied in the plane of the bilayer along the easy [001] axis of the CF layer. The CF and MZF layers exhibit square hysteretic contributions to the major loop. The schematic diagrams of the soft and hard ferrite layers in Fig. 1 indicate the spin directions in four different regions of the loop. In regions (ii) and (iv) of the loop, an increasing fraction of the magnetic moment in MZF reorients from being parallel to antiparallel to the magnetization of the CF layer with increasing field. The spins of MZF farthest away from the MZF/CF interface reorient first, while the spins of MZF closest to the interface remain pinned by the adjacent CF layer until the coercive field of the CF layer is finally attained. When the field is applied along the hard axis of CF, the major loop reveals a reversible curve with two distinct slopes; the steeper slope near the origin is attributed to the MZF, while the smaller slope is attributed to the CF.

To isolate exchange coupled loops of the MZF layer from the CF contribution, we pole the sample in the plane of the bilayer along the easy [001] axis of the CF layer to 10 kOe, which is well above its saturation field. Then we trace a minor loop between +0.5 and −1 kOe. In this field range, the magnetization of the CF is fixed; only the spins in the MZF can reorient. The resulting exchange-biased loop of a 1500-Å MZF/1600-Å CF bilayer is shown in Fig. 2. It is important to note that although Fig. 2 represents a minor loop for the system overall, it is effectively a major loop for the MZF layer since this layer is being driven from positive to negative saturation and back. We will therefore refer to this minor loop as ''exchange biased,'' keeping in mind that in many other systems an offset *M*-*H* loop is not proof of exchange coupling.[6] The exchange coupling of the MZF layer to the adjacent CF layer is manifest clearly both in the offset, H_{ex}, and in the asymmetry of the loop.

Since exchange coupling involves the pinning of spins in a soft magnetic layer by the adjacent hard magnetic layer, the effect of exchange coupling must decrease with increasing thickness of the soft layer, everything else being the same. We find that the exchange field H_{ex} varies inversely with the MZF thickness (Fig. 3). This inverse linear dependence of H_{ex} on MZF thickness is evidence for the interfacial nature of the interaction that gives rise to the exchange-biased loop. Such a dependence is also seen in exchange-biased NiFe systems.

If the exchange coupling energy is small enough so that the magnetization is uniform within each layer, then simple energy considerations yield $H_{ex}=A_{int}/M_s t a_0$, where A_{int} is the effective exchange constant at the interface, M_s, t, and a_0 are the saturation magnetization, thickness, and lattice constant of the soft MZF layer. However, such a model is inconsistent with the asymptotic tail of the exchange-biased loop in Fig. 2 (arrow); if the magnetization of both layers were uniform, we would expect square exchange-biased loops for MZF layers as is observed in most NiFe/MnFe bilayers.[3] More realistic models include the possibility of nonuniform spin configurations in one or both layers. The introduction of a domain wall into the hard layer was examined by Hellman *et al.*, Mauri *et al.*, and others.[7] The pres-

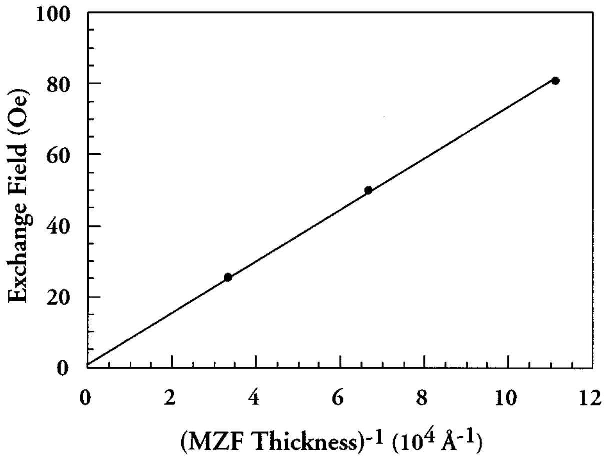

FIG. 3. Exchange bias field versus the inverse of the thickness in each of the bilayers. A least-squares fit of the above intercepts the origin which is the limit that the thickness of the (Mn,Zn)Fe$_2$O$_4$ layer goes to infinity and the exchange field vanishes.

ence of domain walls is difficult to observe directly in typical bilayer systems where the hard layer is an antiferromagnet. In our MZF/CF bilayers, however, the hard CF layer has an easily measurable magnetic moment. We can rule out the presence of domain walls since the major loop indicates that the entire moment attributable to CF switches at ±3 kOe (Fig. 1).

A model that incorporates coherent rotation of spins in the soft layer (CRSL) has been formulated by Goto *et al.* The model assumes that the soft layer is infinitely soft and the spins in the soft layer at the interface are pinned.[8] In this model, competition between the magnetostatic energy and the exchange energy of the soft layer gives rise to a rotation of the spins in the soft layer. This problem can be solved analytically. The M-H loop is asymmetric and approaches saturation asymptotically on one side as $\propto(1-M/M_s)\propto 1/\sqrt{H/H_{\mathrm{ex}}}$ (dotted line in Fig. 2). The exchange bias field takes the form $H_{\mathrm{ex}}=\pi^2 A_{\mathrm{MZF}}/2M_s t^2$, where A_{MZF} is the exchange constant for the soft MZF layer.

Goto *et al.* obtained M-H loops qualitatively similar to the prediction of the CRSL model in electroplated $\mathrm{Ni}_{0.81}\mathrm{FeO}_{.19}/\mathrm{Ni}_{0.4}\mathrm{Co}_{0.6}$ bilayers and found $H_{\mathrm{ex}}\propto t^{-2}$.[8] In typical NiFe/MnFe bilayer systems, symmetric square offset loops are observed, suggesting very weak interfacial exchange coupling.[3] Recently, Lin *et al.* have observed that thermal annealing of $\mathrm{Ni}_{0.81}\mathrm{Fe}_{0.19}/\mathrm{Ni}_{0.53}\mathrm{Mn}_{0.47}$ bilayers improves interfacial exchange coupling.[9] The NiFe exchange loops of Lin *et al.* are asymmetric with a gradual approach to $-M_s$. This suggests the relevance of the CRSL model to this system. However, the magnetization saturates at fields only 2 or 3 times H_{ex}. The saturation field is related to the energy that is required to decouple every spin in the soft layer from the spins in the hard layer, and so we estimate $A_{\mathrm{int}}\sim M_s t a_0 H_{\mathrm{sat}}$. This estimate for A_{int} is still two orders of magnitude smaller than the exchange constants estimated for NiFe or NiMn ($\sim 1\times 10^{-6}$ ergs/cm). Exchange interactions are extremely sensitive to defects and to the quality of the entire interface and are far more sensitive than any structural probe. Therefore it is not surprising that the exchange coupling across polycrystalline ferromagnet/antiferromagnet interfaces might be relatively weak.

In our MZF/CF bilayers, we see a characteristic asymmetric M-H loop for the exchange-biased loops of all the bilayers grown on both types of substrates (Fig. 2). The approach to saturation has the $\sqrt{H}$ functional form predicted by CRSL up to fields of ±3 kOe. From Figs. 1 and 2, we can obtain a lower limit for the saturation field of exchange-biased MZF loops to within the accuracy of our estimate of M_s of MZF and the switching field of CF, namely, $H_{\mathrm{sat}}>3$ kOe. This lower limit for the saturation field yields a lower limit for the exchange interaction constant $A_{\mathrm{int}}>M_s t a_0 H_{\mathrm{sat}}\sim 6\times 10^{-7}$ ergs/cm. This value is comparable to estimates of $A_{\mathrm{MZF}}\sim A_{\mathrm{CF}}\sim 7\times 10^{-7}$ ergs/cm.[10] Such close agreement is fortuitous given the crudeness of the model. However, it suggests essentially ideal interfacial contact, which reflects the high degree of structural integrity in our MZF/CF bilayers.

While the CRSL model predicts a continuous approach to saturation in the soft film, we see an initial abrupt jump with hysteresis, reminiscent of domain-wall motion in our bilayers. The model assumes negligible anisotropy in the soft layer and thus no classical domain wall. The finite crystal anisotropy of our MZF films gives rise to an equilibrium Bloch wall width of $\sim\pi\sqrt{A_{\mathrm{MZF}}/K_{\mathrm{MZF}}}\sim 1500$ Å, which is comparable to the film thickness. This may account for the abrupt change in magnetization in our bilayers. Therefore, in contrast to the simple CRSL model where the twist in the spins in the soft layer is a result of the competition between magnetostatic and exchange energies, the initial twist in the MZF layers may be a result of the competition between the anisotropy energy of the MZF and exchange energy. It turns out that while the [001] axis is an easy axis for CF, it is a hard axis for MZF. Therefore the reversal of spins in the MZF/CF bilayers is expected to be considerably more complicated than in the CRSL model. Further work on numerical simulation of a model that includes these anisotropy effects is in progress.

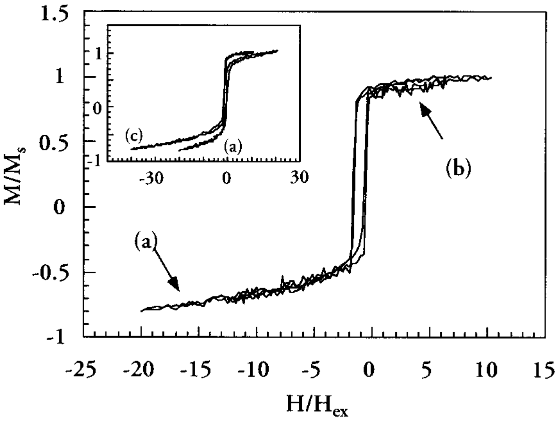

FIG. 4. Exchange-biased loops of (a) a 1500-Å (Mn,Zn)$\mathrm{Fe_2O_4}$/1600-Å $\mathrm{CoFe_2O_4}$ bilayer and (b) a 900-Å (Mn,Zn)$\mathrm{Fe_2O_4}$/1600-Å $\mathrm{CoFe_2O_4}$ bilayer scale when the field is normalized by the coercive field and the magnetization is normalized by the saturation magnetization. (c) The 3000-Å (Mn,Zn)$\mathrm{Fe_2O_4}$/1600-Å $\mathrm{CoFe_2O_4}$ bilayer exhibits a more rounded exchange loop, showing the effects of the finite anisotropy of the soft (Mn,Zn)$\mathrm{Fe_2O_4}$ layer. In all cases the (fixed) magnetization attributed to $\mathrm{CoFe_2O_4}$ has been subtracted from the data.

In our bilayer system, we do not see the t^{-2} dependence of H_{ex} predicted by the CRSL model and demonstrated by Goto *et al.* in the $\mathrm{Ni}_{0.81}\mathrm{Fe}_{0.19}/\mathrm{Ni}_{0.4}\mathrm{Co}_{0.6}$ system (Fig. 3). This is not surprising if what gives rise to H_{ex} in our MZF/CF bilayers is the competition of anisotropy energy and exchange energy and not the competition between magnetostatic and exchange energy as the CRSL model assumes.

In the exchange-biased loops of 1500-Å MZF/1600-Å CF and 900-Å MZF/1600-Å CF where the domain-wall width of the MZF $\sim\pi\sqrt{A_{\mathrm{MZF}}/K_{\mathrm{MZF}}}\sim 1500$ Å is comparable to the thickness of the soft layer, we see a slight rounding of the exchange-biased loops as the MZF layer begins to switch. Since the easy axis of the MZF layer does not coincide with the poled direction of the CF, it is energetically favorable for the spins in the MZF to point away from the poled direction of the CF and towards the easy axis of MZF. This bending of the MZF spins manifests itself in a slight rounding in the upper part of the exchange-biased loop. The exchange-biased loops of these two bilayers scale when the field is normalized by the coercive field and the magnetization is normalized by M_s (Fig. 4). The scaling of the line shape of the exchange-biased loops suggests that the competition of the anisotropy energy and the exchange energy is well characterized by H_{ex} and M_s. However, the M-H loops of the 3000-Å MZF/1600-Å CF bilayer are more rounded and do not scale with the other two loops (Fig. 4, inset). When the thickness of the MZF layer is much larger than the domain-wall width in the case of the 3000-Å MZF/1600-Å CF bilayer, the CF layer no longer effectively exchange couples to the entire MZF layer, thus resulting in a more rounded exchange loop.

When the bilayers are poled to $+10$ kOe along the easy [001] direction of the CF layer, M-H loops measured along the [110] direction (hard direction) are symmetric about the origin and have very little hysteresis. The ability to obtain the coherent rotation of moments without accompanying hysteresis, and hence losses, is crucial for high-frequency inductor applications. Details of the angular dependence of the exchange-biased loops will be discussed in a future publication.

In conclusion, we have demonstrated strong exchange coupling at room temperature in single-crystalline spinel ferrite MZF/CF bilayers that is stronger than that observed in polycrystalline NiFe/MnFe and NiFe/NiMn systems. The characteristic asymmetry of the exchange-biased MZF loops and estimates of the exchange interaction constant A_{int} indicate strong exchange coupling in the ferrite bilayers.

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[10] We estimate the exchange constant of MZF as $A_{\mathrm{MZF}} \sim 2J_{\mathrm{ex}}S^2/a_0$, where the lattice constant $a_0 = 8.4$ Å/2=4.2 Å and J_{ex} is the exchange integral. If we use the approximation $J_{\mathrm{ex}} \sim 3k_B\Theta/[2zS(S+1)]$, where Θ is the Curie temperature and z is the number of nearest neighbors so that exchange forces are effective only between nearest neighbors, we obtain $A_{\mathrm{MZF}} \sim 7\times10^{-7}$ ergs/cm^3.