Perpendicular Coupling in Exchange-Biased Fe_3O_4/CoO Superlattices

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The CoO antiferromagnetic ordering in exchange-biased (001) Fe_3O_4/CoO superlattices has been determined as a function of temperature and magnetic field using neutron diffraction methods. The Co spins preferentially align in domains in which the spins are perpendicular to the net Fe_3O_4 moment direction. This 90° orientation between the Fe_3O_4 and CoO spins is a direct consequence of the interfacial exchange coupling giving rise to exchange biasing, as is not observed in a comparable MgO/CoO superlattice. [S0031-9007(97)05088-6]

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One of the most striking discoveries in magnetism has been the observation of hysteresis loops shifted away from the zero-field axis for a variety of ferromagnetic (FM) materials in contact with antiferromagnetic (AFM) ones [1]. Presently, it is well established that this biasing of the FM magnetization loop (H_{EB}) occurs after cooling in an applied magnetic field through the AFM ordering temperature (T_N). The effect is thus attributed to the interfacial exchange interaction between the FM and AFM spins. In the earliest theory [1], the AFM spins are assumed to order in a single domain in which all of the interfacial AFM spins perfectly align in a single direction parallel to the FM spins. The net moment due to these uncompensated, interfacial AFM spins is essential for the observed biasing behavior. Recently, considerable experimental effort [2–7] has been devoted to this "exchange-biasing" phenomenon in view of its technological significance in the domain stabilization of magnetoresistive devices, e.g., spin valves [8,9]. However, these studies find biasing fields typically 2 orders of magnitude lower than those expected based on the early Meiklejohn-Bean model [1]. In addition, this model cannot explain the recent observations of biasing in systems with so-called "compensated" AFM surfaces which are expected to have no net interfacial moment [4,5].

In order to reconcile these differences, newer theories of exchange biasing have described distinct AFM spin structures responsible for biasing [10–12]. In particular, Mauri *et al.* [10] and Malozemoff [11] have discussed the role of domain walls oriented either parallel or perpendicular to the interface. Still assuming that the FM and AFM spins at the interface couple collinearly, these theories find exchange-bias field values closer to those observed experimentally. More recently, Koon has considered domain formation stemming from a 90° coupling between the AFM and FM moments for compensated AFM surfaces [12]. From the foregoing, it is clear that a detailed knowledge of the AFM spin structure in an exchange-biased system is crucial to understanding the biasing effect. However, to date, little experimental work has been done on the AFM ordering in buried FM/AFM interfaces [6], since few techniques can probe these AFM layers directly [13].

In this Letter, we report neutron diffraction results which explicitly demonstrate perpendicular coupling in exchange-biased (001) Fe_3O_4/CoO superlattices with compensated AFM surfaces. We find that upon magnetizing the ferrimagnetic Fe_3O_4 layer, the AFM CoO spins preferentially align in domains with the spins perpendicular to the net Fe_3O_4 moment. The temperature, field, and CoO thickness dependencies of this AFM spin structure track the biased magnetization behavior and differ significantly from those of a comparable unbiased MgO/CoO sample. Hence, this is the first *direct* observation of 90° exchange coupling that is strongly correlated to the exchange-biasing features.

For this study, two Fe_3O_4/CoO superlattices, $[Fe_3O_4(100\ \text{Å})/CoO(30\ \text{Å})]_{50}$ and $[Fe_3O_4(100\ \text{Å})/CoO(100\ \text{Å})]_{50}$, were grown by molecular beam epitaxy onto 1.6 cm diameter [001] MgO substrates [5,14]. Despite differences in the crystal structures of the spinel Fe_3O_4 and the rocksalt CoO, the oxygen sublattices match to within 1.5%. The single-crystalline superlattices had rocking curve widths of $\approx 0.2°$ and interfacial widths of $\approx 2\ \text{Å} \pm 1\ \text{Å}$ as determined from x-ray diffraction and reflectivity data. The magnetization response was investigated by field cooling from 350 K in a 4400 kA/m (55 kOe) field using a SQUID magnetometer. Table I lists the Fe_3O_4/CoO samples' blocking temperatures (T_B) below which exchange biasing is observed for the given field cooling conditions. Also in the table are the exchange bias (H_{EB}) and coercive (H_C) fields at 78 K. Details of these results will be provided elsewhere [15]. An additional unbiased molecular beam epitaxy superlattice with nonmagnetic MgO spacers, $[MgO(30\ \text{Å})/CoO(30\ \text{Å})]_{333}$, was also made for comparison.

Neutron diffraction experiments were conducted at the National Institute of Standards and Technology research reactor using the BT-2 and BT-9 triple-axis spectrometers as well as the SPINS triple-axis spectrometer for polarized

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TABLE I. Blocking temperatures (T_B), exchange-bias fields (H_{EB}), coercive fields (H_C), and antiferromagnetic ordering temperatures (T_N), for $[Fe_3O_4(100\ Å)/CoO(30\ Å)]_{50}$ and $[Fe_3O_4(100\ Å)/CoO(100\ Å)]_{50}$.

	CoO(30 Å)	CoO(100 Å)
T_B	240 K ± 10 K	290 K ± 10 K
H_{EB} (78 K)	550 Oe ± 50 Oe	1300 Oe ± 100 Oe
H_C (78 K)	6000 Oe ± 100 Oe	3200 Oe ± 100 Oe
T_N	450 K ± 15 K	325 K ± 15 K

beam analysis. For the data shown, the samples were oriented vertically with the [001] growth direction and the growth plane [110] axis defining the scattering plane (inset in Figs. 1 and 2). A superconducting magnet was used to apply magnetic fields from 0 to 50 kOe parallel to the vertical $[1\bar{1}0]$ growth plane direction. Because of scattering geometry constraints, magnetic field effects in the horizontal [110] direction in the growth plane were studied in remanence after saturation in 14 kOe. For the polarized beam experiments [16], the non-spin-flip and the spin-flip scattering from the sample were measured with instrumental efficiencies greater than 91%.

In order to investigate the CoO magnetic structure, we scanned the four {111} reflections (illustrated in the inset in Fig. 2) extensively [17], as these reflections have the strongest contribution from the CoO AFM order. While the Fe_3O_4 ferrimagnetic order also contributes to these reflections, its component is broadened by stacking faults at the superlattice interfaces and can thus be separated from the CoO scattering as in Ref. [13]. We note that each of the four {111} reflections samples a different {111} domain. Additional reflections were scanned to further characterize the superlattice structural and magnetic ordering as in Ref. [13]. These measurements confirm that for all three superlattices, the Co spins lie in ferromagnetic sheets that alternate antiferromagnetically along four possible ⟨111⟩ propagation directions (inset in Fig. 2), as in bulk CoO [18].

Initial zero-field diffraction characterization revealed differences in the onset of AFM ordering among the superlattices. Table I lists the effective CoO ordering temperatures extracted from the temperature dependence of the (111) integrated intensity for the two Fe_3O_4/CoO samples. We note that they are higher than that of bulk CoO ($T_N = 291$ K) and that of the MgO/CoO superlattice ($T_N = 300$ K ± 10 K). In addition, the observation of higher ordering temperatures than blocking temperatures ($T_N > T_B$) for the Fe_3O_4/CoO samples indicates that factors other than the mere presence of AFM order must govern the onset of exchange biasing. This behavior will be discussed in detail elsewhere [15].

In order to examine the AFM spin structure in the exchange-biased state, the superlattices were investigated in remanence after cooling in fields sufficient to reorient the Fe_3O_4 layers. We observe that the relative population of the four {111} CoO domains is substantially altered

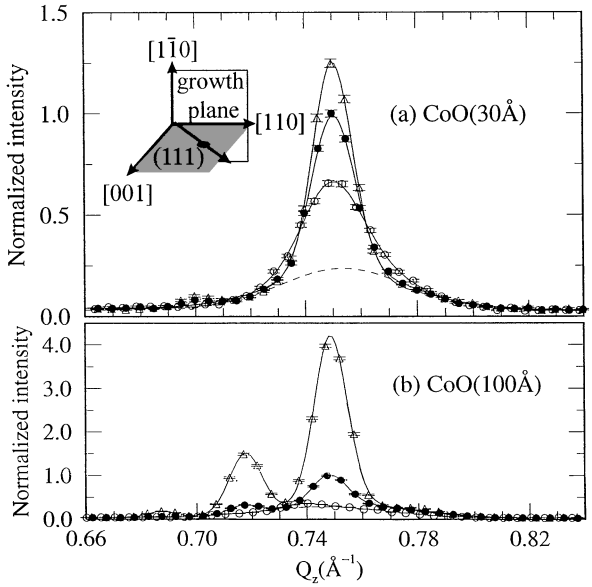

FIG. 1. Neutron diffraction scans of the (111) reflection along the [00l] growth axis direction (scattering vector Q_z) for (a) $[Fe_3O_4(100\ Å)/CoO(30\ Å)]_{50}$ and (b) $[Fe_3O_4(100\ Å)/CoO(100\ Å)]_{50}$ taken at 78 K in zero field. The •, ∘, and △ indicate data taken after zero-field cooling (initial state), field cooling ($H = 14$ kOe) from 320 K in the $[1\bar{1}0]$ direction, and field cooling ($H = 14$ kOe) from 320 K in the [110] direction, respectively. The data are normalized to initial state scans. The peaks have been fitted with Gaussians (solid line); the dashed lines indicate the broad, temperature and field independent Fe_3O_4 contribution. The inset illustrates the scattering geometry.

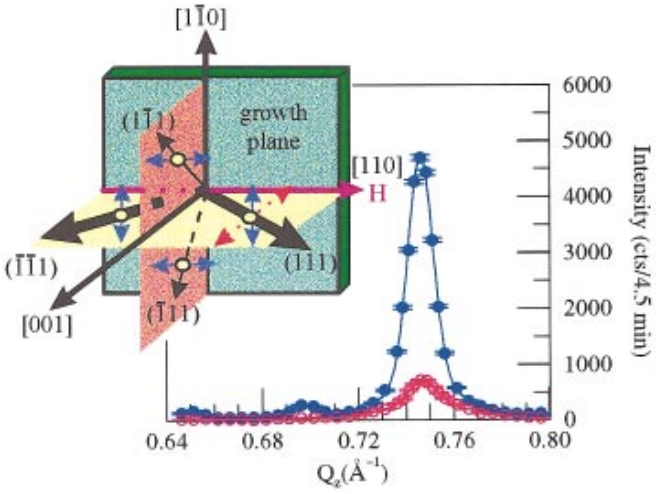

FIG. 2(color). Non-spin-flip (blue •) and spin-flip (red ∘) cross sections for the (111) reflection scanned along the [001] growth axis direction. The data are for the $[Fe_3O_4(100\ Å)/CoO(30\ Å)]_{50}$ sample taken at 78 K in zero field after field cooling ($H = 14$ kOe) in the [110] direction. Inset illustrates the Co spin direction within the four {111} domains with the more populated domains indicated by thicker lines. For the (111) domain, the projections sensed by the non-spin-flip (blue arrow along $[1\bar{1}0]$) and spin-flip (red dotted arrow along $[11\bar{2}]$) cross sections are shown.

as compared to the zero-field cooled state. Figures 1(a) and 1(b) show neutron diffraction scans through the (111) reflection for the Fe_3O_4/CoO superlattices prepared in different field conditions. For both of the Fe_3O_4/CoO samples, the (111) peak intensity *decreases* after cooling in a vertical $[1\bar{1}0]$ field and *increases* after cooling in a horizontal [110] field, relative to the zero-field cooled data. The broad Fe_3O_4 contribution to the scattering (dashed line in Fig. 1) has the same magnitude and width in each of these scans, and hence, the field-induced changes in Fig. 1 can be attributed solely to *CoO spin reorientations*. Analogous intensity changes were observed for the three other {111} reflections. Apparently, the effect of field cooling is to preferentially move the Co spins into {111} domains with corresponding ⟨111⟩ directions closer to the field and net Fe_3O_4 moment direction (inset in Fig. 2). For both samples, the coherence of the AFM order is long range along the growth axis (>300 Å), as evidenced by the narrow CoO peak widths [19]. Analogous field-induced spin reorientation effects were *not* observed in the MgO/CoO superlattice, which after cooling in a 14 kOe vertical $[1\bar{1}0]$ field, showed less than a 1% change in {111} intensity relative to the zero-field cooled intensity. Hence, the changes in {111} intensities observed in the Fe_3O_4/CoO samples appear to result from coupling to the Fe_3O_4 layers (or its effective field) rather than to the applied field directly.

Polarized beam measurements were undertaken to understand the origin of these field-induced changes in the Fe_3O_4/CoO superlattices. Figure 2 shows a typical (111) scan for the Fe_3O_4(100 Å)/CoO(30 Å) sample. In this measurement, the non-spin-flip scattering is sensitive only to the moment projection parallel to the $[1\bar{1}0]$ direction, while the spin-flip scattering is sensitive to the moment projection perpendicular to the $[1\bar{1}0]$ direction within the (111) plane (inset in Fig. 2). Note that the non-spin-flip scattering dominates the spin-flip scattering in this case. Thus, from this and related measurements, we find that to within (±2°), all of the AFM Co moments in the (111) and mirror symmetric $(\bar{1}\bar{1}1)$ domains lie in the growth plane along the $[1\bar{1}0]$ direction [20]. Similarly, the moments in the $(1\bar{1}1)$ and $(\bar{1}11)$ domains are parallel to the growth plane [110] direction (inset in Fig. 2). The same moment axes persist *independent* of temperature and field for the Fe_3O_4(100 Å)/Co(30 Å) sample as well as for the Fe_3O_4(100 Å)/Co(100 Å) and the MgO(30 Å)/CoO(30 Å) superlattices. These data suggest that the CoO spin structure in the superlattices are highly anisotropic, presumably as a consequence of epitaxial growth constraints. For each (111) domain, the alignment of the spins along a single axis in the growth plane contrasts with the behavior of bulk CoO [18], which has three easy axes canted 8° out of the (111) plane.

The presence of these constrained easy axes provides a basis for understanding the {111} field-dependent intensity changes in the Fe_3O_4/CoO samples. The lack of field response for the MgO/CoO superlattice despite similar easy axes indicates further that the CoO changes stem mostly from the coupling to the Fe_3O_4 layers and are not primarily a direct response to the applied field for thin CoO layers. From the field configuration depicted in the inset in Fig. 2, we note that the Fe_3O_4 magnetization direction ([110]) is *perpendicular* to the AFM spin direction ($[1\bar{1}0]$) in the favored (111) and $(\bar{1}\bar{1}1)$ domains. The unfavored $(1\bar{1}1)$ and $(\bar{1}11)$ domains have Co easy axes parallel to the net Fe_3O_4 moment direction. Thus, these data reveal that the Co moments couple perpendicularly to the Fe_3O_4 moments in this exchange-biased system in analogy to the classic spin-flop transition [12].

Additional experiments as a function of temperature and field demonstrate that this perpendicular coupling and its resulting spin reorientation effects are directly related to the biasing behavior. As depicted in Fig. 3 for both Fe_3O_4/CoO samples, we examined at several temperatures the (111) peak intensity as a function of field applied parallel to the vertical $[1\bar{1}0]$ direction. After cooling in zero field, the application of a large $[1\bar{1}0]$ field greatly decreases the (111) peak intensity, as this unfavored domain is characterized by Co easy axes parallel to the net Fe_3O_4 moment. For the Fe_3O_4(100 Å)/CoO(30 Å) superlattice at 260 K [$T_B < T < T_N$ (see Table I)], this intensity reduction is mostly reversible on field cycling [Fig. 3(a)]. However, at 78 K ($T < T_B$), the initial zero-field intensity is never recovered upon field cycling, though the original spin state is partially restored at ±5 kOe, a value which approximately matches the coercive fields listed in Table I. Thus, the spin reorientation induced by the 90° Fe_3O_4/CoO coupling irreversibly "freezes in" only when the sample is cooled below its blocking temperature,

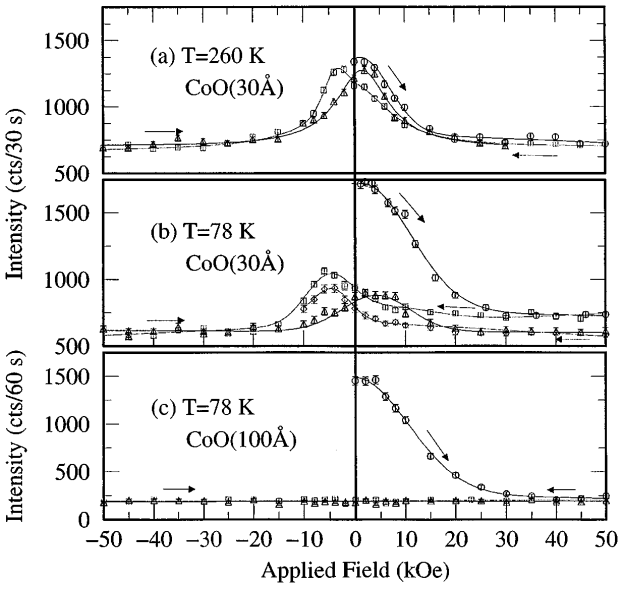

FIG. 3. (111) peak intensity vs applied field along the $[1\bar{1}0]$ direction for (a) $[Fe_3O_4(100\ Å)/CoO(30\ Å)]_{50}$ at 260 K (b) and at 78 K, and for (c) $[Fe_3O_4(100\ Å)/CoO(30\ Å)]_{50}$ at 78 K. The ∘, □, △, and ◇ symbols refer to successive field cyclings. Curves drawn are guides to the eye.

$T_B = 240$ K. For the 100 Å CoO multilayer at 78 K, the initial reduction of the intensity with increasing field is more pronounced, consistent with the larger exchange-bias field (see Table I). Upon field cycling, the spin structure does not change substantially, as the (111) intensity is essentially flat as shown in Fig. 3. We reiterate that these field-induced changes are not observed in the MgO/CoO superlattice, which after zero-field cooling to 78 K, showed less than a 5% decrease in (111) intensity in a 50 kOe field. These field-cycling data indicate that the onset and magnitude of the biased magnetization behavior is correlated to the Co spin reorientation effects induced by the perpendicular coupling.

In total, these neutron diffraction results emphasize the complex nature of the CoO AFM structure in the Fe_3O_4/CoO system as a result of the strong CoO anisotropy and exchange interactions. In these superlattices, the Co spins in each {111} domain are strongly constrained to lie along new ⟨110⟩ directions in the growth plane. Instead of changes to these spin *directions*, we have found that in response to different Fe_3O_4 magnetization conditions, the {111} domain *populations* change. The preferred domains show a 90° coupling between the antiferromagnetic and ferrimagnetic moments. These domain changes induced by the coupling are correlated to the observed biasing behavior.

These results have important implications for theories of exchange biasing. The presence of perpendicular coupling between the CoO and net Fe_3O_4 moments is consistent with the expected interaction proposed recently by Koon [12]. This 90° coupling must be included in calculations of the exchange-bias fields and may reconcile differences with observed values for this system [5,15]. However, the domain formation in this system is also complicated by the presence of multiple {111} domains in CoO [11], an effect which is not included in Koon's theory. The average domain sizes along the growth axis directions in our superlattices are quite large, as the AFM coherence extends across bilayers. In addition, the (001) Fe_3O_4/CoO interfaces themselves are complex due to the different crystal and magnetic structures of the two components [5,13]. These issues must be addressed to understand fully the exchange-biasing mechanisms for this system.

In conclusion, we have directly demonstrated for the first time irreversible {111} domain reorientation effects correlated with the magnetization behavior in exchange-biased Fe_3O_4/CoO superlattices. The effect is driven by a preferred perpendicular orientation of the antiferromagnetic spins to the ferrimagnetic moment direction. The results indicate the importance of the details of the AFM spin structure for realistic models of exchange biasing.

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