Difference between Blocking and Néel Temperatures in the Exchange Biased Fe_3O_4/CoO System

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The blocking temperature T_B has been determined as a function of the antiferromagnetic layer thickness in the Fe_3O_4/CoO exchange biased system. For CoO layers thinner than 50 Å, T_B is reduced below the Néel temperature T_N of bulk CoO (291 K), independent of crystallographic orientation or film substrate (α-Al_2O_3, $SrTiO_3$, and MgO). Neutron diffraction studies show that T_B does not track the CoO ordering temperature and, hence, that this reduction in T_B does *not* arise from finite-size scaling. Instead, the ordering temperature of the CoO layers is *enhanced* above the bulk T_N for layer thicknesses $\lesssim$100 Å due to the proximity of magnetic Fe_3O_4 layers.

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The coupling between ultrathin antiferromagnetic (AF) and ferromagnetic (F) layers has received considerable attention lately [1], as field cooling through the antiferromagnetic ordering temperature, T_N, may result in a shift of the hysteresis loop along the field axis by an amount H_{eb}. This exchange biasing effect [2] is used currently to pin the magnetization in giant magnetoresistance (GMR) spin valves and is extensively studied as many aspects of this coupling between AF and F layers are still unresolved [3–6]. Thus far most work has focused on explaining the magnitude of H_{eb} [3–6]. Limited attention has been given to the temperature dependent aspects of H_{eb}, although these are highly significant for a deeper understanding of biasing [7–9] and are also relevant for applications [10].

In the most elementary consideration [2] one can derive an expression for H_{eb} by considering that reversing the F magnetization in an AF-F exchange biased system will require twice the energy of the exchange coupled bonds across the AF-F interface. Balancing this energy with the gain in Zeeman energy leads to the following expression:

$$H_{eb} = \frac{n2J_{ex}|S_F||S_{AF}|}{a^2\mu_0 M_F t_F}, \qquad (1)$$

with a the lattice parameter, n/a^2 the number of exchange coupled bonds across the AF-F interface per unit area, J_{ex} the exchange constant, S_i the spin of either F or AF, μ_0 the vacuum permeability, M_F the magnetization of the F layer, and t_F the thickness of the F layer. From Eq. (1) one would expect the following: first, that the temperature dependence of H_{eb} is governed by the Brillouin-type temperature dependence of the AF (staggered) magnetization, since the AF layer has the lowest ordering temperature, and second, that H_{eb} vanishes at T_N of the AF material. However, in practice linear temperature dependencies are often found (which in polycrystalline AF layers may be understood on the basis of a distribution of grain sizes or exchange contributions [7–9]). Moreover, one finds at low antiferromagnetic layer thickness that the blocking temperature T_B (i.e., the temperature at which biasing vanishes) is smaller than the bulk T_N [11–15].

In this Letter we describe the effect of the variation of the antiferromagnetic layer thickness t_{AF} on T_B for the *single-crystalline* Fe_3O_4/CoO system. We have studied this system as CoO has a comparatively simple AF spin structure and has been studied extensively [16]. Moreover, high quality Fe_3O_4/CoO multilayers can be grown by molecular beam epitaxy [17]. Despite the limited CoO volume in these samples, high angle neutron diffraction is quite sensitive to the AF order because the multilayer geometry enhances and amplifies the scattering from these thin layers. Many studies have found that, for small t_{AF}, T_B is reduced below the bulk T_N of the AF material [11–15]. In addition, it has been reported that the ordering temperature of ultrathin antiferromagnetic oxide films is smaller than the bulk T_N for $t_{AF} \lesssim 100$ Å [18–20]. Hence, it is widely believed that T_B follows T_N in AF/F exchange biased systems and that the reduction of T_B for small t_{AF} arises from finite-size scaling [11,13,14]. To test this, we have performed neutron diffraction measurements of the ordering temperature for CoO layers with small t_{AF} in exchange biased samples, for which we have also determined the blocking temperature by bulk magnetization techniques. Surprisingly, we find from neutron diffraction measurements that the ordering temperature of CoO in Fe_3O_4/CoO exchange biased systems is *larger* than the bulk T_N for small t_{AF} at which T_B is *reduced*. Thus the reduction in T_B is *not* the result of finite-size scaling.

Fe_3O_4/CoO bilayers and multilayers were grown on (0001) α-Al_2O_3, (100) $SrTiO_3$, and (100) MgO substrates in an oxidic molecular beam epitaxy system, with CoO the first layer being deposited [17]. As verified by reflection high-energy electron diffraction (RHEED) and x-ray diffraction, the Fe_3O_4/CoO layers were epitaxial with a [111] orientation for the Al_2O_3 substrates and [100]

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orientation for the $SrTiO_3$ and MgO substrates. Measured rocking curve widths (FWHM) for the Al_2O_3, $SrTiO_3$, and MgO were $\approx 3°$, $\approx 1.3°$, and 0.35°, respectively. For the bilayers, the Fe_3O_4 layer thickness was held constant at 120 ± 9 Å, while for the multilayers, the Fe_3O_4 layer thickness was 100 Å and t_{CoO} was 17, 30, 40, or 100 Å. Further details about the growth are given elsewhere [17]. Magnetic measurements were performed in a SQUID magnetometer after field cooling from 350 K in a 4400 kA/m field through the T_N of bulk CoO [21]. Neutron diffraction studies were performed at the NIST Center for Neutron Research on the BT-9 and BT-2 triple-axis spectrometers using a neutron wavelength of 2.35 Å. In these studies, the Fe_3O_4/CoO multilayers were used to enhance the scattered intensity. Samples for cross-sectional high-resolution transmission electron microscopy (HRTEM) were prepared using mechanical polishing and argon-ion milling. HRTEM was done at 300 kV.

Figure 1 shows the exchange biasing field as a function of temperature T for a [111] oriented 125 Å Fe_3O_4/33 Å CoO bilayer grown on α-Al_2O_3. As reported previously for the Fe_3O_4/CoO system [12,21], the temperature dependence of H_{eb} is linear and H_{eb} vanishes at T_B, which is 220 ± 10 K in this case. From this and similar data, T_B was determined as a function of CoO layer thickness, t_{CoO}, for both [111] and [100] oriented bilayers as well as the [100] oriented multilayers. The results are shown in Fig. 2. The inset displays T_B for small t_{CoO} and shows that T_B depends linearly on t_{CoO} for $t_{CoO} < 20$ Å. For $t_{CoO} > 20$ Å the dependence of T_B on t_{CoO} is nonlinear and, at 92 Å, T_B reaches 291 K, the ordering temperature of bulk CoO. For $t_{CoO} \lesssim 50$ Å, T_B is smaller than T_N of bulk CoO, as also reported for other exchange biased systems [11,14,15,19]. In addition, we find that T_B does not depend on the substrate (Al_2O_3, $SrTiO_3$, or MgO) or on its orientation ([111] or [100]).

To test the hypothesis that the reduction of T_B at small t_{CoO} is due to a finite-size scaling and a related reduction of the ordering temperature of ultrathin CoO layers, neutron diffraction experiments were performed to measure directly the ordering temperature of CoO in Fe_3O_4/CoO multilayers. As the {111} class of reflections has the strongest contribution from the CoO AF order and the CoO (111) reflection can be very well distinguished from the broader Fe_3O_4 (111) reflection [22,23], this (111) reflection was studied as a function of temperature for four Fe_3O_4/CoO multilayers. Figure 3 shows the change in intensity of this (111) reflection as a function of T for the (100 Å Fe_3O_4/30 Å CoO)$_{\times 50}$ multilayer. Note that since the transition is smeared it is difficult to define a precise transition temperature marking the onset of the CoO antiferromagnetic order. Nevertheless, these data clearly show, when we take the temperature where the intensity I deviates from its high-temperature limiting value as the ordering temperature, that for the 30 Å CoO layer (Fig. 3b) this temperature is *increased* well above the $T_N = 291$ K of bulk CoO, to around 450 ± 15 K. Using another criterion for ordering such as the crossing point of the two lines in Fig. 3b would not change the conclusion that T_N is substantially increased above 291 K.

In principle the Fe_3O_4/CoO superlattice undergoes only one true phase transition, which occurs near the T_C of Fe_3O_4. While the Co spins near the interface are polarized by exchange coupling to the Fe moments, the Co spins in the center of the CoO layer initially remain disordered. However, with decreasing temperature AF correlations develop throughout the CoO layer, driven by the AF coupling [22]. Thus we define the effective T_N of the CoO layer as the temperature at which the Co lattice develops a measurable staggered magnetization. The neutron diffraction studies on the other multilayers show that this effective T_N

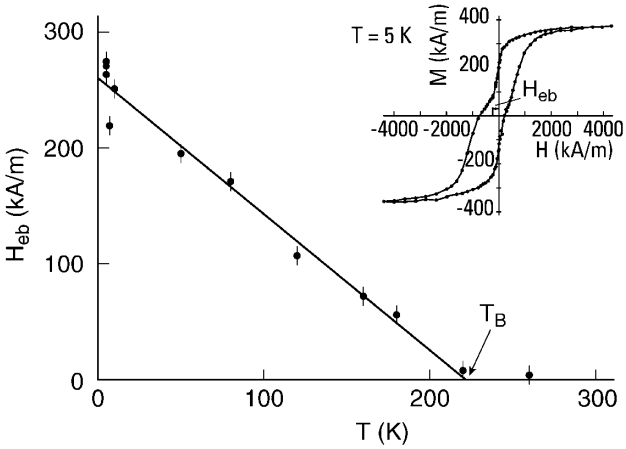

FIG. 1. The exchange biasing field H_{eb} versus temperature T for a [111] oriented 125 Å Fe_3O_4/33 Å CoO bilayer. Note the linear dependence of H_{eb} on T. The biasing vanishes at the blocking temperature $T_B = 220 \pm 10$ K. The inset shows the hysteresis loop at 5 K after cooling from 350 K in a field of 4400 kA/m.

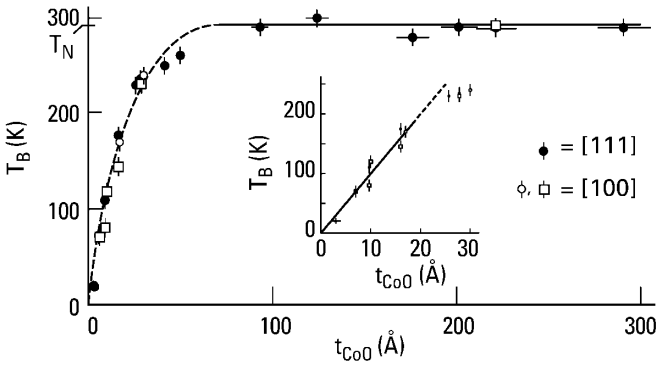

FIG. 2. Blocking temperature T_B as a function of the CoO layer thickness t_{CoO} in Fe_3O_4/CoO bilayers for two orientations. The curve is a guide to the eye. Note that there is no measurable influence of the substrate used: Al_2O_3 (•), $SrTiO_3$ (○), or MgO (□). The inset shows that the T_B data display a linear dependence on t_{CoO} for $t_{CoO} < 20$ Å.

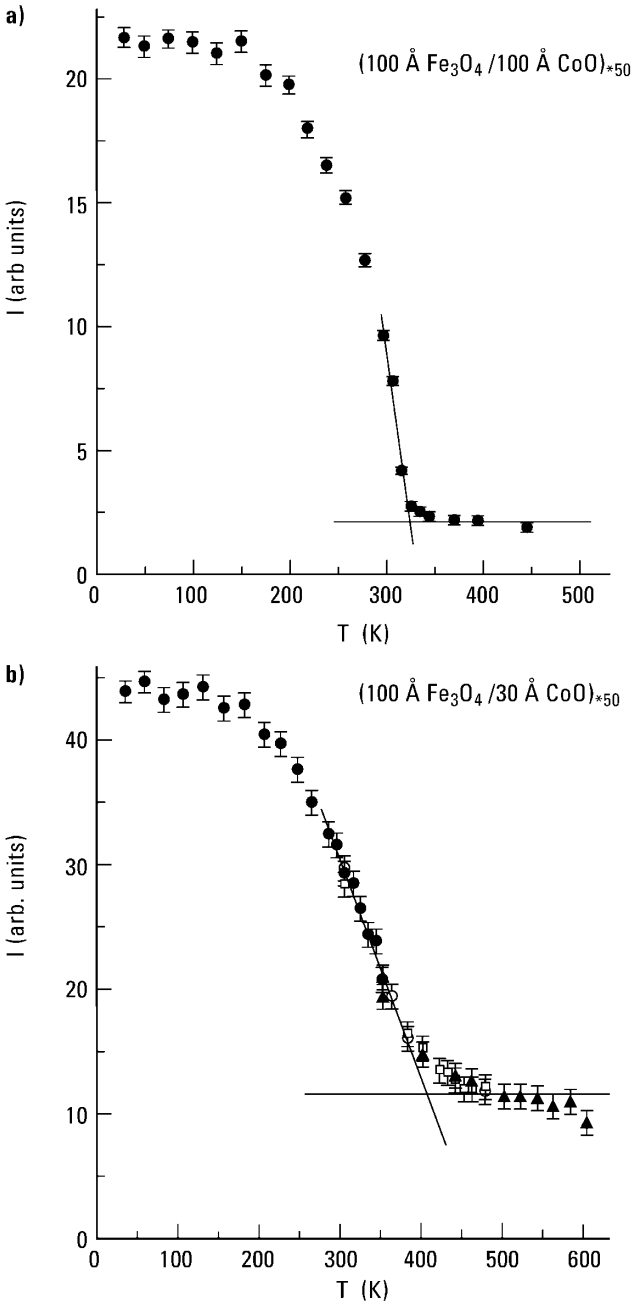

FIG. 3. The intensity I of the (111) reflection as a function of T for a (100 Å Fe_3O_4/100 Å CoO)$_{\times 50}$ (a) and a (100 Å Fe_3O_4/30 Å CoO)$_{\times 50}$ (b) multilayer. Note the drop in I around 410 K in the latter. (The various symbols denote the results from different experimental runs.)

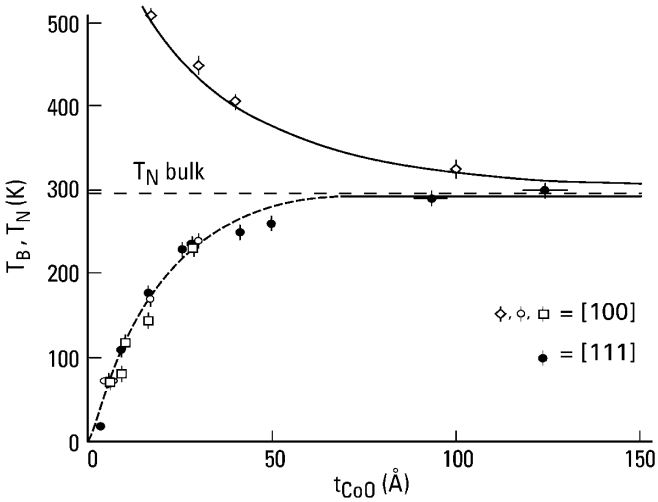

FIG. 4. Both the measured CoO ordering temperatures, T_N (◇ symbols) and blocking temperatures (●, ○, and □ symbols) are given versus the thickness of the CoO layer for the Fe_3O_4/CoO system. Note the divergence of the two curves, indicating that the measured reduction of T_B is not due to a reduction of the ordering temperature at low t_{CoO}.

exceeds 291 K for $t_{CoO} < 100$ Å, approaching the bulk value as t_{CoO} is increased. In Fig. 4 the results for T_N are given together with those for T_B plotted versus AF layer thickness, t_{CoO}. This figure clearly shows that the reduction of T_B at $t_{CoO} < 50$ Å *cannot* be due to a reduction in T_N, as T_N is *increased* in this regime. This observed increase in T_N for $t_{CoO} < 50$ Å arises from magnetic coupling and proximity to the ferrimagnetic Fe_3O_4, which in bulk orders at $T_C = 858$ K. The data can be understood within the context of a mean-field model in which the two disparate ordering temperatures approach each other as a function of the relative Fe_3O_4 and CoO layer thickness which alters the coupling experienced by the Co and Fe spins in the center of each layer [22]. As an independent experimental test, we also measured T_N for a 30 Å CoO layer in a (30 Å CoO/18 Å MgO)$_{\times 50}$ multilayer grown on (100) MgO. In this case, due to the absence of a magnetic layer, T_N was not increased but was approximately equal to the bulk value of 291 K. This is similar to the situation for ultrathin metallic magnetic films, where the ordering temperature reaches the bulk value at 5–6 monolayers [24]. Note that, at a CoO layer thickness of $\approx$30 Å, T_B of a Fe_3O_4/CoO bilayer is already substantially reduced below the bulk T_N value (Figs. 1 and 2).

Since a reduction in the CoO ordering temperature cannot be responsible for the reduction in T_B as a function of decreasing AF thickness, we have considered alternative interpretations beyond finite-size scaling. At $t_{CoO} \lesssim 50$ Å the AF layers might be composed of magnetically isolated "islands" and consequently the reduced T_B could be the temperature at which these islands become superparamagnetic. However, there is no evidence for the existence of such islands in high-resolution TEM studies for a number of samples, as illustrated by the HRTEM image in Fig. 5 for a [111] oriented 140 Å Fe_3O_4/10 Å CoO bilayer grown on α-Al_2O_3. The variation in contrast is merely due to variation in thickness of the sample after argon ion milling. Crossed lattice fringes are visible throughout the entire Fe_3O_4/CoO bilayer, evidencing its epitaxial growth. In fact, a reduction of T_B by superparamagnetism would require unrealistically small

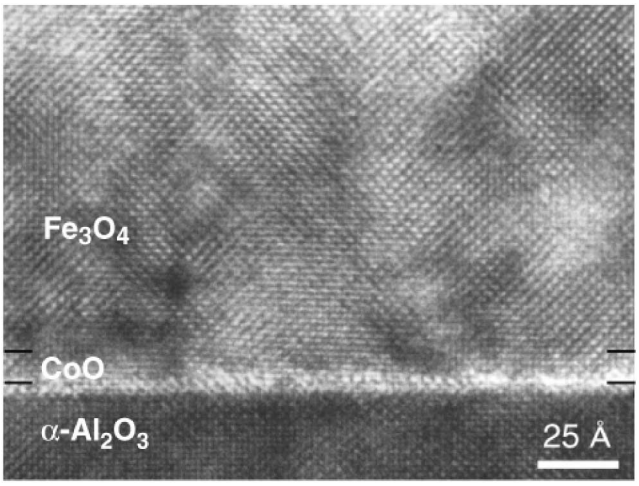

FIG. 5. High-resolution TEM image of a [111] oriented 140 Å Fe_3O_4/10 Å CoO bilayer grown on (0001) α-Al_2O_3.

islands. Superparamagnetic behavior occurs when $\tau = \tau_0 \exp(KV/k_B T)$ with τ the relaxation rate, τ_0 a constant of order 10^{-9} s, K the anisotropy constant, $V = A \times t_{AF}$, the volume of the island, where A is its surface area, and k_B Boltzmann's constant [25]. Thus one can calculate that $T_B = [KA/k_B \ln(10^9 \tau)]t_{AF}$. From the inset of Fig. 2, we find experimentally that $T_B/t_{AF} \simeq 10$ K/Å. With $K = 1.1 \times 10^7$ J/m^3 [26] and taking $\tau \approx 10^2$ s for the time scale of the measurement of T_B, we find that a match to the experimental T_B/t_{AF} requires that A be 1.6×1.6 Å^2. As this theoretical estimated size is unphysically small and as extensive TEM experiments do not show islands (e.g., up to 200 Å wide in Fig. 5), we believe that the reduction of T_B cannot be the result of superparamagnetic behavior.

It is also unlikely that the reduction of T_B stems from a reduction of the CoO anisotropy and the resulting inability of the CoO layer to sustain an AF domain wall as the temperature approaches T_N. First, in CoO the anisotropy is dominated by the Co^{2+} single ion anisotropy, which does not depend on layer thickness. Second, calculations show that at 0 K the width of an AF domain wall parallel to the interface already exceeds t_{CoO} for the CoO layers with $t_{CoO} \lesssim 30$ Å, which still exhibit biasing [27].

Although we do not have an explanation for the surprising combination of an enhanced T_N and a decreased blocking temperature T_B, it is clear that this finding must serve as a touchstone for any theory of exchange biasing. A successful theory should be able to explain not only the magnitude of H_{eb} but also its temperature dependence, including the difference between T_B and T_N.

In conclusion, we have demonstrated that T_B is not a measure of the CoO ordering temperature in this exchange biased system. Specifically, for ultrathin CoO layers in a Fe_3O_4/CoO multilayer, T_B decreases with decreasing CoO layer thickness while the effective Néel temperature increases due to magnetic proximity effects. Although observed in many systems, the reduction of T_B with decreasing t_{AF} thus does not result from finite-size scaling and remains a topic for further study.

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