Electron-Mediated Ferromagnetic Behavior in CoO/ZnO Multilayers

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Electron-mediated ferromagnetic behavior in CoO/ZnO multilayers

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Abstract

CoO/Al-doped ZnO (AZO) multilayers exhibit ferromagnetism up to ~ 300 K. The magnetic behavior oscillates with odd versus even number of Co layers in the insulating antiferromagnetic CoO and (separately) with the thickness of the AZO layers, and vanishes if AZO is replaced by intrinsic ZnO. Magnetization is due to uncompensated (111) ferromagnetic planes of insulating CoO for odd numbers of atomic planes per layer which are coupled together via RKKY exchange mediated by electron carriers in the non-magnetic AZO layers. The period of the oscillation with AZO thickness qualitatively matches the Fermi wavevector calculated from the carrier concentration measured by ordinary Hall effect. Magnetic polarization of the AZO carriers is confirmed via anomalous Hall effect which is proportional to the magnetization.

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Since the concept of the spin transistor was suggested by Datta and Das [1] in 1991, there has been great interest in spintronic devices including spin injection into a semiconductor [2, 3]. (Ga,Mn)As has been thoroughly investigated as a candidate for spin injection and has shown clear spin transference in magnetic, transport, and optical measurements [2]. However, the working temperature of these materials is less than 150 K, making it unsuitable for room temperature applications [2]. Dietl suggested that a p-type ZnO-based magnetic semiconductor would have a high Curie temperature (T_C) [4], and there have been many reports on the magnetic properties of this semiconductor with widely varying T_C's. However, the microscopic origin of magnetic properties is still controversial in ZnO-based systems [5-10] where clustering of Co is a common problem that leads to coexistent magnetic and semiconducting properties, but not a magnetic semiconductor [11].

Multilayer structures have been proposed in a number of studies in connection with spin injection including attempts at doping of ZnO using a (Co/ZnO) multilayer structure [12,13]. At room temperature, magneto-optical Kerr rotation was observed on annealed [Co/ZnO] multilayer samples but is likely due to ferromagnetic (FM) Co clusters [14]. Recently, we demonstrated ferromagnetism below 10 K via electron carriers in a (Zn,Co)O- based field-effect transistor [15] with low concentration Co uniformly distributed in ZnO. Ferromagnetism was created via gate-controlled electron concentration and measured using the anomalous Hall effect (AHE), but was limited to below 10 K.

In order to increase T_C while avoiding Co clusters, we propose a (CoO/ZnO) multilayer system. CoO is a known insulating antiferromagnet (AFM) with Néel temperature of ~300 K. The (111) planes are ferromagnetic (FM) with antiferromagnetic coupling between these planes [16]. The moments in the FM (111) planes are canted along the <11-7> directions, making an angle of 23.85º out of the (111) plane [17]. By growing epitaxial CoO (111) films with a precisely controlled number of planes, we create FM surfaces of CoO; even numbers of planes have zero net moment, while odd numbers have an uncompensated plane of FM spins. The resistivity in the ZnO layers is controlled by Al doping; 2 at.% Al in ZnO (AZO) produces conducting behavior [18]. By creating a multilayer structure of an odd number of CoO planes layered with AZO, the uncompensated FM (111) planes in each CoO layer will be exchange-coupled to each other, via an RKKY-mediated exchange coupling in the AZO layer. In this paper, we show that such a multilayer is ferromagnetic just below room temperature, with spontaneous magnetization that is modulated by both the number

of CoO layers and the AZO thickness, and vanishes for undoped ZnO. We also show an anomalous Hall effect due to polarization of the free carriers in the AZO layers, demonstrating magnetic semiconductor behavior very close to room temperature.

Epitaxial superlattices of (CoO/ AZO), with varying thicknesses of CoO (111) (from 2.0-3.2 nm) and AZO (0002) (from 1.5 - 6 nm), were deposited onto GaAs (111)B (As terminated) and Al_2O_3(0001) substrates via DC and RF-magnetron sputtering, respectively. The multilayers (MLs) consisted of 30 repetitions of the CoO/AZO bilayer with an AZO capping layer: (AZO/[(CoO/AZO)]$_{30}$/substrate). Films were grown at 300^{o}C with a base pressure below 10^{-7} Torr and an Ar^+ (20 sccm) sputtering pressure of 5 mTorr. A small amount of oxygen (1 sccm 20% O_2:Ar) was introduced at the sample during each CoO layer growth. Film structure was characterized by X-ray diffraction (XRD). Magnetic and magneto-transport properties were investigated from 10 to 300 K with a superconducting quantum interference device (SQUID) magnetometer. Films were processed into a Hall bar geometry (40 μm-width, 140 μm-length) for transport measurements using standard photolithography and wet etch techniques. 50 nm Au top electrodes (with 5 nm Cr sticking layer) were defined by a lift-off process, and indium bonding used to make current and voltage contacts.

Typical XRD measurements are presented in Figure 1: a [CoO(~100 nm)/AZO(~80 nm)]$_1$ bilayer and a [CoO (3.2 nm)/AZO(2.5 nm)]$_{30}$ multilayer on GaAs (111) show AZO (0002) and CoO (111) diffraction peaks, as well as GaAs (111) substrate peaks. The in-plane alignment of the AZO, CoO and substrate were measured by ϕ-scans, shown in Fig. 1(c). The peaks from the (101) planes of the AZO layers and the (110) planes of the CoO layers show six-fold symmetry, as expected for epitaxial films of AZO (0002) and CoO (111) orientations [19]. Multilayer films grown with ZnO in place of AZO are structurally similar, and the structural quality is similar for both GaAs and Al_2O_3 substrates. The periodic layered structure of the multilayers is reflected by the low angle superlattice diffraction peaks shown in Fig. 1(d), which are observed for AZO thickness as small as 2.4 nm. Superlattice repeat distances were calculated from the peak positions in Fig. 1(d), and are in close agreement with the intended thicknesses. The small low angle oscillations reflect the total thickness of the film, in agreement with the expected thickness. Fits to reflectivity data show roughness on the order of 1-2 nm.

Magnetization M was measured as a function of in-plane applied field H and temperature T for multilayers with various CoO layer thickness t_{CoO}, measured in units of number of CoO (111) planes n_{Co} for a fixed thickness (2.5 nm) of the AZO layer. The <11-7> directions project on the (111) plane along the <11-2> directions, which coincide with the cleavage directions of GaAs (111). The <11-2> directions are equivalent for a cubic structure. However, due to the tetragonal distortion of CoO in the antiferromagnetic phase, the symmetry is broken, and the directions are not magnetically equivalent. The plots presented here were obtained along the easy axis. For all films, raw data show a temperature-dependent paramagnetic (PM) signal and a temperature-independent diamagnetic background. The PM signal is large at low T with a saturation magnetization ~5 times larger than the FM contribution of the films exhibiting ferromagnetism. The PM signal follows a Brillouin (H/T) behavior, hence is negligible above ~20 K. In the following figures, the PM and diamagnetic contributions are subtracted in order to display the FM contribution. Figure 2(a) shows M in units of emu/layer-cm^2 *vs*. H at 100 K. These data show ferromagnetism at 100 K for all n_{Co}, but the spontaneous magnetization M_s – defined as the extrapolation to zero field of the high-field magnetization at 100 K – varies as a function of n_{Co}. Figure 2(b) shows M_s *vs.* t_{CoO} for a fixed AZO thickness of 2.5 nm. Thin films with odd n_{Co} (9, 11, 13) show a large FM signal, suggesting FM coupling between uncompensated surface Co spins in neighboring CoO layers, as shown schematically in Fig. 3(b). For even n_{Co}, M_s is significantly smaller; the remaining signal may be due to roughness of the CoO layers.

We now turn to the dependence of $M(H,T)$ on thickness of the AZO layers. Figure 3(a) shows M_s at 10 K as a function of AZO thickness for t_{CoO} = 3.2 nm. M_s alternates between zero and a peak that decreases with increasing AZO thickness. The characteristic oscillation period is approximately 1 nm, suggesting that the conducting AZO layers are mediating an RKKY-type exchange interaction between layers of uncompensated Co spins at the CoO/ZnO interfaces schematically shown in Fig. 3(b), as seen in Co/Cr and Co/Ru MLs [20]. The RKKY character of this interaction is supported by the fit to the experimental data shown in Fig. 3(a) using the model by Levy *et al.* [21] for interacting planes of spins. The range dependence follows the expected $\exp(-d/\lambda)/d^2$ function and the derived Fermi vector is k_F = 3 nm^{-1}. We note that at each minimum, several t_{AZO} give zero M_s; we suggest this is because J=0 (uncoupled layers) or J <0 (antiferromagnetically coupled layers) give

M_s~0 while only J >0 (ferromagnetically coupled layers) gives significant M_s. A magnetization increase at some field might be expected in the *M(H,T)* curves for J <0 (t_{AZO} = 3 nm) or J = 0 (t_{AZO} = 2.8 nm) but is less obvious than a ferromagnetic signal (and more masked by the PM background).

Figure 4 shows *M(H,T)* (*H* applied in plane) for the multilayer structure with maximum M_s: AZO(2.5nm)/[CoO(3.2nm)/AZO(2.5nm)]$_{30}$. *M(H)* shows a clear hysteresis loop at 10 K (Fig. 4(a)). At 300 K, the magnetization is smaller than at 10 K but still clearly present (Fig. 4(b)). At 10K, assuming all Co ions have a magnetic moment ~4 μ_B [22], ~5% of Co atoms at the interfaces contribute to the ferromagnetic signal. The rest of the interface Co moments are likely responsible for the PM contribution measured at low *T*.

To prove that the interaction between uncompensated Co spins at the surfaces of each antiferromagnetic CoO layer for n_{Co} = odd is governed by carriers in the conducting AZO, a set of films was made with AZO replaced by intrinsic ZnO, an insulator with a carrier concentration at room temperature less than 10^{16} cm^{-3}. ZnO(2.5nm)/[CoO(3.2nm)/ZnO(2.5nm)]$_{30}$ multilayer was grown on GaAs (111). No ferromagnetic signal was observed at any *T* or *H*, (an example is shown in the inset of Fig. 4(a)) confirming the crucial role of the conduction electrons in the magnetic behavior of these films.

As further magnetic characterization, two different MLs ([CoO/AZO]$_{30}$ and [CoO/ZnO(intrinsic)]$_{30}$) were cooled from 390 K to 10 K in zero field (ZFC) and in 70 kOe (FC), and measured on warming in 250 Oe (Fig. 4(c)). In the (CoO/AZO) MLs, both ZFC and FC *M(T)* are significantly larger than in the (CoO/ZnO) MLs, with very different *T* dependence. For (CoO/AZO) MLs, *M(T)* only gradually decreases with increasing *T* and abruptly drops near 300 K, the Néel temperature of CoO, while *M(T)* of (CoO/ZnO) MLs is dominated by a PM signal of uncoupled spins. Figure 4(d) shows a comparison between FC *M(T)* of [CoO(3.2nm)/AZO(2.5nm)]$_{30}$ and the normalized intensity of the (½, ½, ½) AFM Bragg peak for CoO measured by neutron scattering (NS) measurements for (CoO/MgO) MLs [23]. *M(T)* of the conducting (AZO/CoO) MLs scales with the *T*-dependence of the Bragg peak, indicating the intrinsic nature of *M* in the (CoO/AZO) MLs.

By contrast, FC *M(T)* of insulating (CoO/ZnO) is much smaller, with a field-independent plateau at moderate *T* and sharp Curie-law-like upturn at low *T* with a magnitude that depends

strongly on H; ZFC $M(T)$ of insulating (CoO/ZnO) shows only the low T upturn. This dependence is very similar to that seen in previous studies of (SiO_2/CoO) MLs [24] and (MgO/CoO) MLs [23], where it was ascribed to two distinct types of uncompensated spins. The "plateau" (between ~50-200 K) was associated with interfacial uncompensated spins that are strongly coupled to the antiferromagnetic spins in the bulk of the layer (but not to other layers), and the upturn at low T was associated with spins which are even more weakly coupled to the antiferromagnetic spins [24-25]. The blocking temperature (T_B) [24] of the present insulating (CoO/ZnO) MLs is 230 K, the same as that of the [SiO_2/CoO(3.0nm)] MLs. These data, confirm the crucial role played by the carriers in the AZO layer; without these, CoO uncompensated moments behave independently, pinned by the antiferromagnetic Néel vector, and able to be partially trapped by cooling in a field, *but not exhibiting ferromagnetism*.

To further characterize the magnetic coupling and the role of AZO, we measured the resistivity and Hall effect at 10 and 300 K. The Hall effect has two components: the ordinary and anomalous Hall effect (OHE and AHE respectively). AHE is a signature of spin-polarized carriers in electrically conductive ferromagnets: a Hall resistance proportional to magnetization can be attributed to asymmetric carrier scattering by magnetic impurities in the presence of spin-orbit interactions [15]. In this system, the CoO is insulating (confirmed experimentally for (CoO/ZnO) multilayers) so the Hall effect is completely determined by the carriers in the AZO layer. In the absence of CoO, AZO shows OHE but no AHE. Figure 5(a) shows the Hall resistance (R_H) *vs.* H for the (CoO/AZO) ML with the highest M_s (t_{AZO} = 2.5nm, t_{CoO} = 3.2nm). R_H shows a negative slope at both 10 and 300 K due to the OHE. From this, we determine the sign of the carriers (electrons) and their density, 7.1×10^{19} cm^{-3} and 1.07×10^{20} cm^{-3}, respectively, consistent with 2% Al. Based on the free electron model with carrier density 7.1 (±0.2) $\times10^{19}$ cm^{-3}, we obtain k_F = 1.28±0.02 nm^{-1} while the full fit to the experimental data gives k_F = 3.0±0.2 nm^{-1}. However, it is generally recognized that the free electron model is an oversimplification, and multiple periods can be obtained from different spanning vectors of the real Fermi surface [26]. Regardless, in this case the conducting AZO layers are clearly mediating an exchange interaction between Co spins at the CoO/ZnO interface (Fig. 3(b)). At 10 K, R_H shows a clear non-linearity in H due to an AHE. The insets of Figure 5(a) show the AHE, obtained by subtracting the linear contribution from the OHE. Since the magnetic field is applied perpendicular to the sample plane in measuring R_H, the AHE is associated with the

component of M perpendicular to the plane, $M(H_\perp)$. Figure 5(b) shows $M(H_\perp)$ at 10 K which is significantly smaller (~ 8×) than M measured in an in-plane applied field ($H_{//}$) [Figure 4(a)], due to the strong magnetic anisotropy of CoO ($K_{CoO} = 1.1\times10^7$ J/m^3) [27]. Naively, one would expect $M(H_\perp) \sim 0.4\ M(H_{//})$ due to the canting of the Co spins ~ 24º away from the (111) plane, but the tetragonal distortion of the CoO lattice in the antiferromagnetic phase and possible epitaxial strain can affect this angle. The AHE shown in Fig. 5(a) is proportional to $M(H_\perp)$ confirming that the AHE in the AZO is due to scattering from spins at the CoO/AZO interfaces.

In summary, ferromagnetic magnetization of uncompensated (111) planes of spins at CoO/AZO interfaces up to nearly 300 K was observed in epitaxial (CoO/AZO) multilayers with an odd number of CoO planes in each CoO layer. The magnetization is mediated by electrons in the AZO layer and oscillates with AZO thickness with a period that qualitatively relates to the carrier density, indicating RKKY-like coupling of the layers. This ferromagnetic state vanishes for an even number of CoO planes, when the CoO layer has zero magnetization, or the AZO layer is replaced with insulating ZnO. A low-field AHE of the AZO layer proportional to M demonstrates spin polarization. The (AZO/CoO) multilayer system thus gives a robust ZnO-based magnetic semiconductor which can be used as a spin-electronics system near room temperature. Substitution or even just small additions of NiO (which has a Néel temperature of 550 K) to CoO is likely to increase the useful temperature to above room temperature.

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Figures

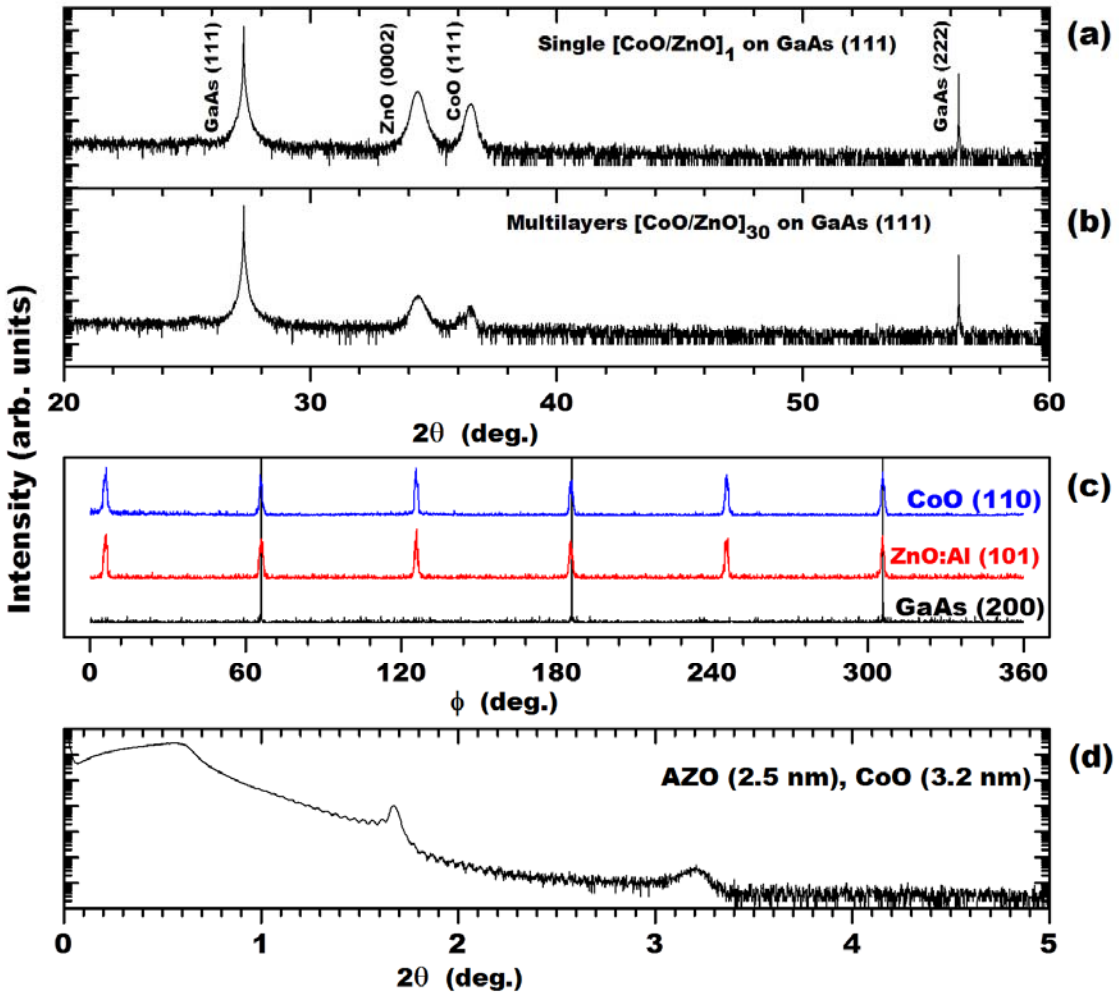

Figure 1. XRD θ-2θ scan (log scale) for (a) [CoO(~100nm)/AZO(~80nm)]$_1$ bilayer and (b) AZO/[CoO(3.2 nm)/AZO(2.5 nm)]$_{30}$ multilayer, grown on GaAs (111); ZnO (0002), CoO (111) peaks and GaAs (111) substrate peaks are observed. (c) ϕ-scans of off-axis peaks show epitaxial growth. (d) Superlattice peaks in AZO/[CoO(3.2 nm)/AZO(2.5 nm)]$_{30}$//GaAs(111) multilayer film at low angle.

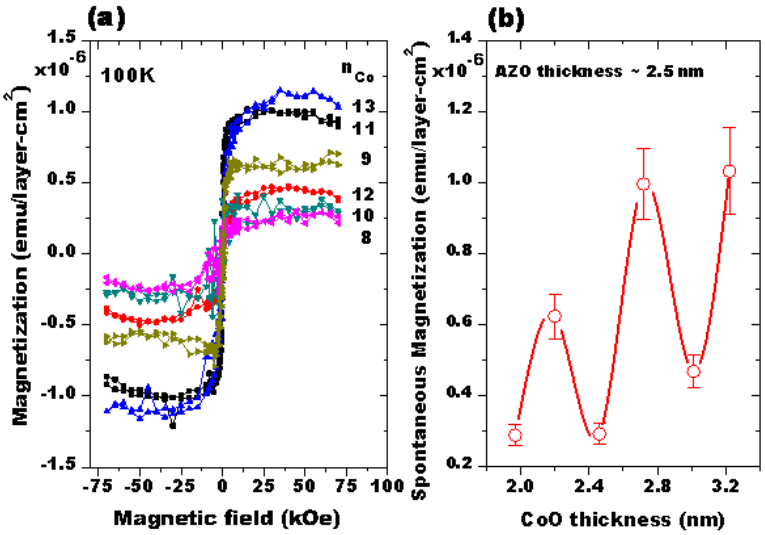

Figure 2. (a) *M* in units of emu/layer-cm^2 vs in-plane *H* at T=100 K for various AZO/[CoO(n_{Co})/AZO(2.5nm)]$_{30}$ //Al_2O_3(0001) MLs. Diamagnetic and paramagnetic contributions have been subtracted (the latter negligible at 100 K). (b) M_s *vs.* CoO thickness.

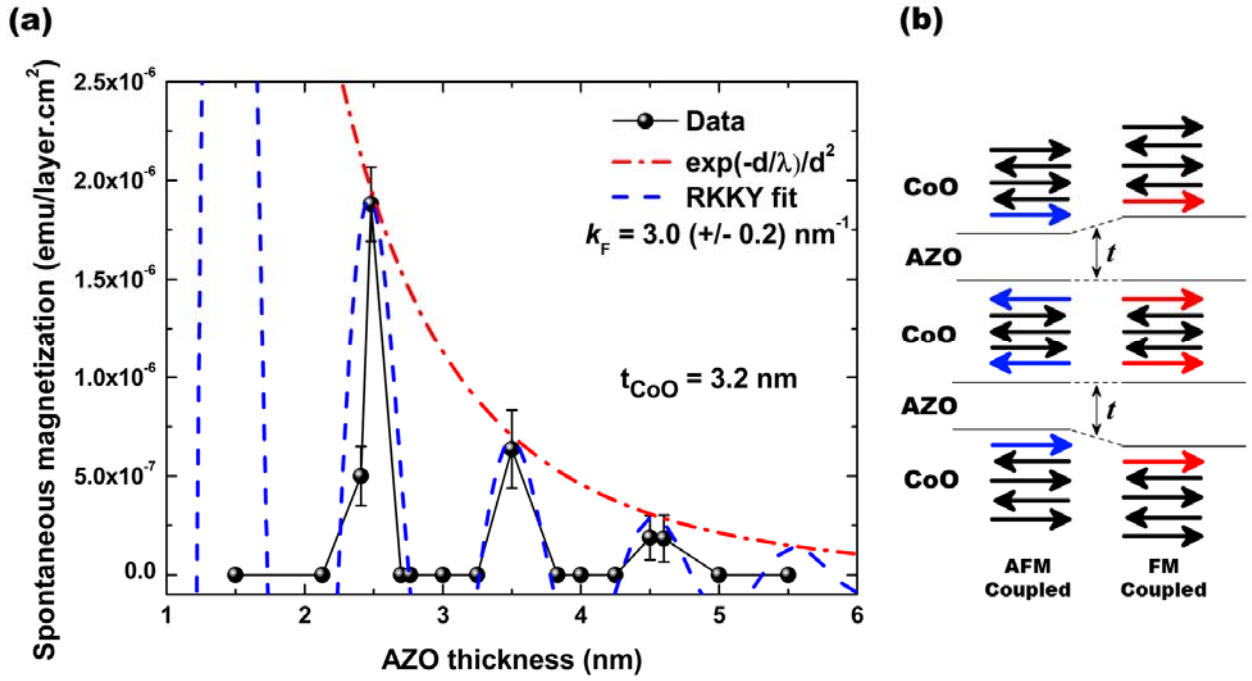

Figure 3. (a) Spontaneous magnetization *vs.* AZO thickness, from *M(H)* data at 10 K on AZO/[CoO(3.2nm)/AZO(t_{AZO})]$_{30}$ //GaAs(111) MLs. Blue dashed line shows full RKKY fit to data [21]; red the range-dependent part. (b) Schematic of CoO/AZO ML structure with n_{Co}=5 and t_{AZO} corresponding to AFM (left) or FM (right) coupling. Blue and red arrows represent uncompensated planes of (111) spins. Co spins are represented parallel to the interfaces to convey conceptual information about coupling although they actually point slightly out of the (111) plane, giving rise to a small perpendicular component of M_s. An even number of Co planes would show similar FM/AFM coupling across t_{AZO}, but no net FM moment.

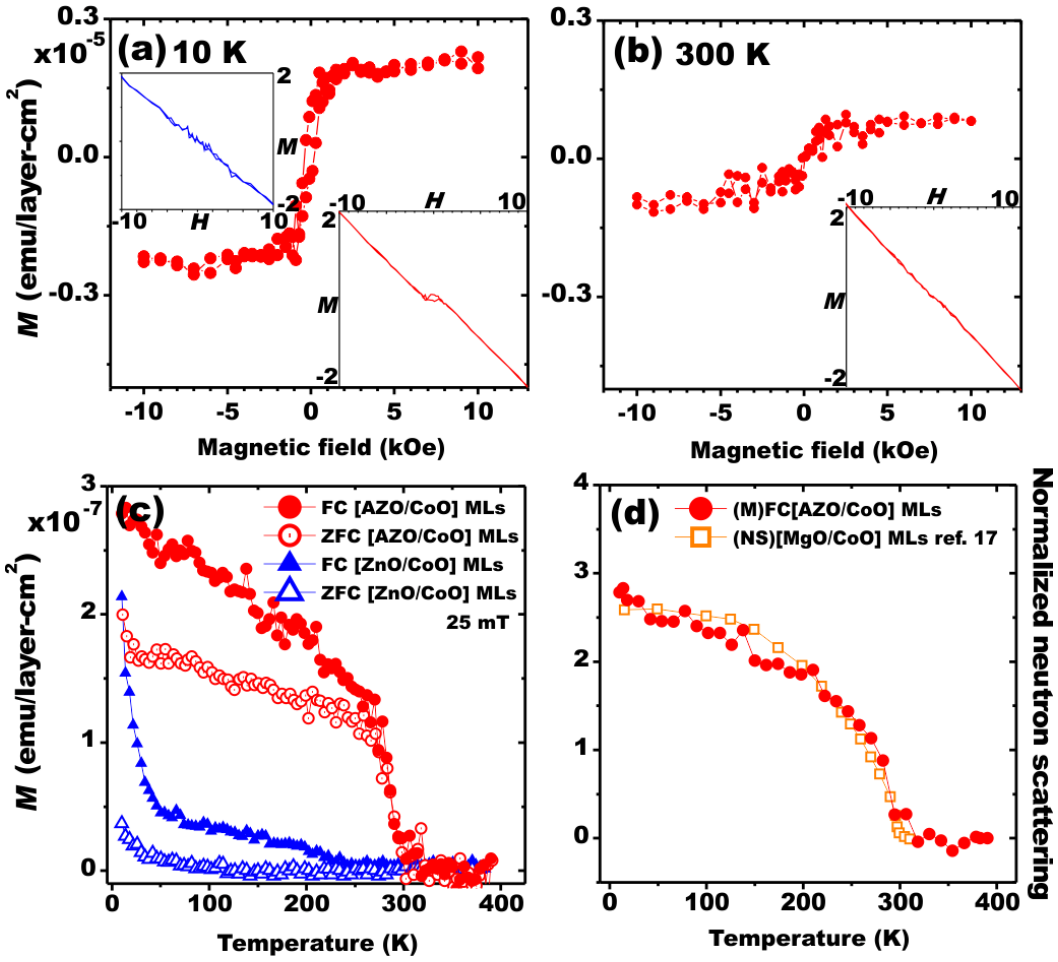

Figure 4. *M vs.* $H_{//}$ for (red) [CoO(3.2nm)/AZO(2.5nm)]$_{30}$ //GaAs(111) at (a) 10 K and (b) 300 K, (linear paramagnetic and diamagnetic backgrounds subtracted). Raw data (dominated by diamagnetic background) is shown in insets. Raw data at 10 K for (blue) [CoO(3.2nm)/ZnO(2.5nm)]$_{30}$ //GaAs(111) is also shown in inset in (a). (c) *M(T)* of conducting (AZO/CoO) and insulating (ZnO/CoO) MLs measured at 250 Oe on warming after cooling in zero field (ZFC) or 70 kOe (FC). (d) FC *M(T)* compared to neutron scattering (NS) data for (CoO/MgO) MLs of similar CoO thickness (ref. 17).

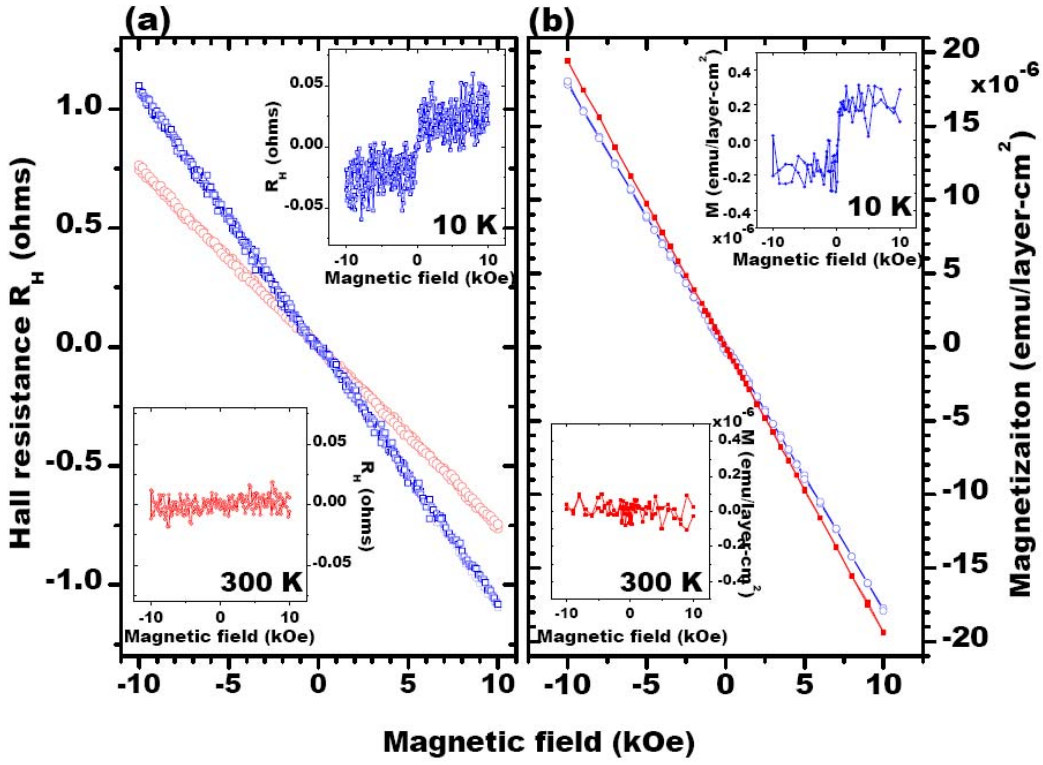

Figure 5. (a) Hall resistance and (b) M at 10K (blue) and 300K (red) *vs.* $H_{\perp}$ for [CoO(3.2nm)/AZO(2.5nm)]$_{30}$//GaAs(111). (a) Insets show AHE after subtracting linear OHE. (b) Insets show $M(H_{\perp})$ after subtracting diamagnetic and paramagnetic contributions.

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