Thickness-dependent magnetic properties of oxygen-deficient EuO

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We have studied how the magnetic properties of oxygen-deficient EuO sputtered thin films vary as a function of thickness. The magnetic moment, measured by polarized neutron reflectometry, and the Curie temperature are found to decrease with reducing thickness. Our results indicate that these surface-induced effects are caused by the reduced number of nearest neighbors, band bending, and the partial depopulation of the 4*f* states of Eu.

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I. INTRODUCTION

Electron-doped EuO is a semiconductor which undergoes a simultaneous ferromagnetic and insulating-conducting phase transition, across which the resistivity drops by 8 to 13 orders of magnitude[1,2] and the conduction electrons become nearly 100% spin polarized,[3,4] making EuO a candidate for efficient spin filtering.[5,6] Electron doping increases the Curie temperature of EuO thin films to above 200 K[7] from 70 K for undoped EuO, and also increases the magnetic moment up to 7.13 μ_B from the intrinsic value of 7 μ_B.[6] This is due to the enhanced, conduction-electron-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling between the Eu 4*f* spins.[8,9] In thin films and interfaces, these fundamental magnetic properties can also be influenced by additional factors, such as surface-induced modification of the crystalline environment and of the band structure,[10] as well as magnetic proximity effects.[11–13] These interface effects have been studied experimentally mainly in 3*d* systems, be they itinerant ferromagnets[10] or transition metal oxides,[14,15] while interfaces of the 4*f* compound EuO have only been analyzed theoretically.[16,17]

We have studied systematically the Curie temperature $T_C(d)$ and magnetic moment per Eu atom, $m(d)$, in dependence of the thickness d of layers of oxygen-deficient $EuO_{0.96}$, interfaced with Pt capping layers. In the thickness range from 2 to 6 nm, we find a systematic reduction of both $T_C(d)$ and $m(d)$ with decreasing d, while our previous investigation in the range from 7 to 12 nm for various oxygen-vacancy concentrations did not show a thickness-dependent variation of these magnetic properties. We find that band bending, the reduced number of nearest neighbors at the interface, and a spatially nonuniform spin-exchange coupling are the primary causes of the thickness dependence of $T_C(d)$ and $m(d)$, due to the increased relative importance of the interface. We are then able to estimate a spatial extension of 9 nm for the effective spin coupling in $EuO_{0.96}$.

This paper is organized as follows. In Sec. II, we describe the growth process and the experimental details of the measurement techniques. Section III discusses the experimental results, in particular the thickness-dependent measurement of the magnetic moment and $T_C(d)$ of EuO_{1-x}.

II. EXPERIMENTAL METHODS

Thin films of EuO_{1-x} with $x = 4\%$ were deposited by cosputtering of Eu_2O_3 and Eu on Si substrates with a Pt buffer and capping layer of 10 nm each, as described in Ref. 6. The samples were characterized by a superconducting quantum interference device (SQUID), x-ray reflectometry (XRR), and polarized neutron reflectometry (PNR) on the CRISP beamline at ISIS,[18] following the same analysis as carried out in Ref. 6. The accurate determination of the magnetic moment per Eu atom is achieved by fitting the PNR data to a theoretical model with the following parameters: neutron scattering length, neutron absorption, atom number density, fraction of nonmagnetic phases, film thickness, and total magnetic moment of each layer. Except for the latter two, all parameters used to model the data in the present work were found to be the same as for the thicker samples previously measured,[6] indicating a consistent growth process and enabling a direct comparison. This model is explained in detail in Ref. 6.

III. MAGNETIC MEASUREMENTS OF EuO_{1-x}

The PNR data and theoretical fits are shown in Fig. 1, where the reduction in peak spacing and the progressive separation of the spin-up and spin-down curves track the increase in thickness. The samples were polycrystalline and the interlayer roughness was estimated to be about 0.6 nm (rms amplitude).

A. Curie temperature

We analyze first the thickness-dependent T_C for $EuO_{0.96}$ in the thickness range between 2 and 40 nm, plotted in Fig. 2 and normalized to the respective bulk value T_C^∞, together with data for EuO taken from Refs. 19 and 20. The reduction of $T_C(d)$ for stoichiometric, i.e., insulating, EuO can be understood qualitatively by describing the Eu 4*f* subsystem within a spin $S = 7/2$ Heisenberg model with an effective nearest-neighbor spin-exchange coupling J.[9] In mean-field theory $T_C^{(MF)} = ZJ/4k_B$, that is proportional to the number of nearest neighbors Z, which is reduced from $Z_b = 12$ in the

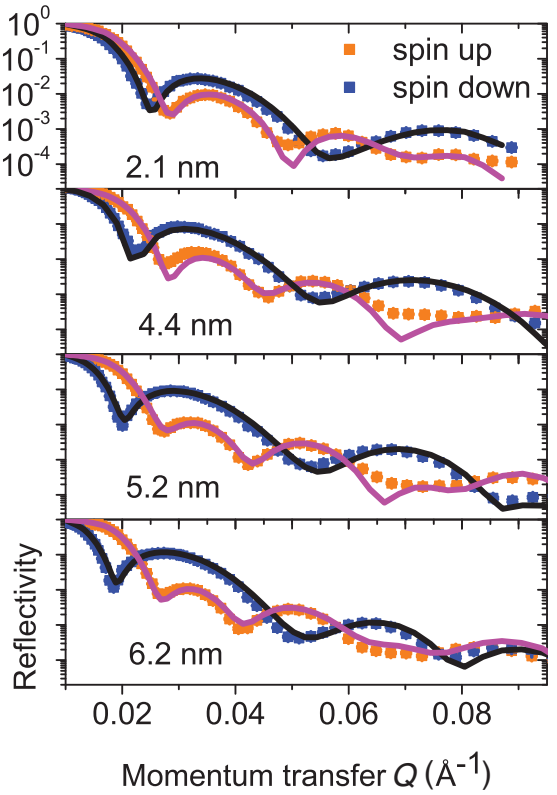

FIG. 1. (Color online) PNR data (data points) and fit (lines) for varying thickness, $d_{\mathrm{PNR}} = 2.1$, 4.4, 5.2, and 6.2 nm. Data taken at $T = 5$ K with an applied magnetic field of 3 kOe. The lateral dimensions of the data points indicate the extension of the vertical and horizontal error bars.

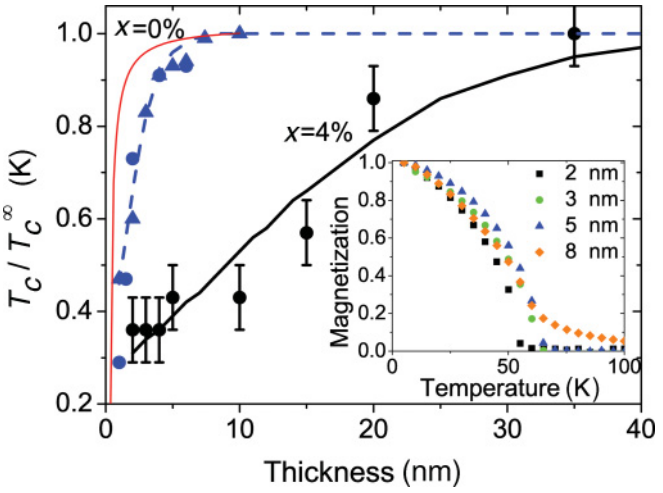

FIG. 2. (Color online) $T_C(d)/T_C^{\infty}$ of EuO_{1-x} for varying thickness, for $x = 4\%$ (black circles). The data for $x = 0\%$ (blue triangles and circles) is taken from Refs. 19 and 20. Above 40 nm, T_C for $x = 4\%$ saturates to 140 K (normalized value of unity, data points not shown). The red curve represents Eq. (1) normalized to its value for the largest experimentally considered thickness (10 nm). The black and blue fit lines are described in the text. The inset shows the $EuO_{0.96}$ magnetization as a function of temperature for increasing thickness, with a 50 Oe applied field. Each magnetization curve is normalized to its own value at 5 K.

bulk fcc lattice of EuO to $Z_i = 8$ at the interface (k_B is the Boltzmann constant). This will give an effective spin-exchange coupling, which varies spatially in the direction perpendicular to the film. However, the ferromagnetic transition must occur for the entire film at a single T_C. The T_C reduction may, thus, be estimated by averaging Z over a film with n atomic layers (a monolayer of EuO is 0.25 nm) and two interfaces:

$$T_C^{(\mathrm{MF})} = \frac{2Z_i + (n-2)Z_b}{n}\,\frac{J}{4k_B}, \quad n \geqslant 2. \tag{1}$$

This expression, after normalization to T_C^{∞} and free of adjustable parameters, is shown in Fig. 2 (red curve). We attribute the stronger experimental T_C suppression to the fact that in EuO next-nearest-neighbor couplings are not negligible[9] and that, in thin films, fluctuations not included in mean-field theory become increasingly important.

For oxygen-deficient $EuO_{0.96}$, a simple analysis in terms of a reduced number of neighbors is not sufficient due to the additional longer-range RKKY exchange interaction. While the RKKY interaction causes an increase in the absolute value of T_C relative to undoped EuO,[9] it also has the consequence of making the films more susceptible to surface effects: the reduction in T_C extends up to significantly larger thicknesses. Electrostatic considerations discussed below (in the context of the magnetic moment data) indicate band bending at the interface, which will give a spatially nonuniform band occupation and magnetization. The conduction-band occupation especially is an important factor in determining T_C: its value is doubled from 70 to 140 K for bulk-like thin films of $EuO_{0.96}$ compared to EuO.[6] Depletion of the conduction band states at the interface is then likely to be an important factor in decreasing T_C. We can extract an experimental estimate for the range ξ of the effective spin coupling by fitting the experimental data with a phenomenological Fermi-like function, $T_C/T_C^{\infty} = [\exp(1 - d/\xi) + 1]^{-1}$, which describes both the T_C saturation for large d and the approximately linear T_C suppression for small d, by a single length scale ξ. The best fits yield an effective range of $\xi \approx 1.2$ nm for $x = 0\%$ and $\xi \approx 9$ nm for $x = 4\%$ (blue and black fit lines in Fig. 2). We have attempted, but failed, to reproduce the reduction in T_C for $EuO_{0.96}$ by performing mean-field calculations for a layered Heisenberg model with an additional, RKKY-induced, effective spin-exchange coupling $J'(z) = J_0 \cos(2k_F z)/z$, cut off at the thermal length, where z is the distance between two spins perpendicular to the interface. We found a T_C reduction for films up to $d = 40$ nm (not shown) in qualitative agreement with experiment. However, it was not possible to reproduce the experimental $T_C(d)$ curve quantitatively by a spatially constant strength J_0 of the RKKY-induced interaction, likely indicating spatially nonuniform modifications in this interaction. We attribute this to substantial conduction-band bending near the interfaces, which will be discussed below.

B. Magnetic moment

We analyze now how the layer-averaged magnetic moment varies as a function of thickness. The magnetic moment per Eu atom (measured by PNR at 5 K; cf. Fig. 1) and thickness (measured by PNR and XRR) for magnetically saturated

TABLE I. Magnetic moment of $EuO_{0.96}$ with varying thickness.

d_{PNR} (nm)	d_{XRR} (nm)	$\mu(B)$ PNR ($\pm 0.09\ \mu_B$) (μ_B/Eu atom)
2.1	1.8	6.41
4.4	4.5	6.80
5.2	5.5	6.99
6.2	5.8	7.08
11.7	12.3	7.07

$EuO_{0.96}$ are indicated in Table I (the data for the 11.7 nm sample is taken from Ref. 6). The expected magnetic moment for $EuO_{0.96}$ is 7.08 μ_B/Eu atom.[6] As seen in Fig. 3, there is a marked reduction of the magnetic moment with decreasing thickness, by up to 9% for the 2.1-nm sample. We note that a decreased value for the moment of stoichiometric EuO is visible in the data reported by Santos *et al.*,[19] which we also plot in Fig. 3. (The fact that their measured moment per Eu atom of 7.3 μ_B in the 6-nm film exceeds the maximum possible value for stoichiometric EuO is attributed to an overall underestimation of the film thickness. We normalized their thickness and magnetic moment values to give the 6-nm sample a moment of 7 μ_B). The intra-atomic spin is independent of interatomic exchange interactions; therefore, the moment reduction cannot be explained in terms of surface-reduced effective-exchange couplings, in contrast to the case of the T_C suppression. However, simple electrostatic considerations indicate that band bending will occur at the interface between Pt and EuO_{1-x}, to such a degree that it will partially depopulate the $4f$ states, thus decreasing the total intra-atomic spin for the Eu atoms near the interface. The PNR measurement gives the magnetic moment per atom in the whole EuO_{1-x} layer; thus it will average the reduced moment of the atoms in the region where the bands are bent with that of the atoms in the inner monolayers. Band bending can be understood by noting the large difference between the work functions Φ of EuO_{1-x} ($\Phi_{EuO} \lesssim 1$ eV[21]) and of Pt ($\Phi_{Pt} \approx 5.6$ eV); one can thus predict a significant electron transfer from EuO_{1-x} to Pt, resulting in an interface potential $V(z)$, where z is the vertical distance from the interface. Since the difference between the work functions, $\Phi_{Pt} - \Phi_{EuO} \approx 4.6$ eV, is larger than the binding energy of the Eu $4f$ band, whose upper edge lies about 1.2 eV below the conduction band,[3,21] the charge transfer will involve not only the conduction electrons, but also the $4f$ electrons, i.e., the Eu $4f$ band will be bent upward to cross the Fermi level. Signatures of a modified surface electronic structure have been reported previously for EuO bulk crystals[22,23] and possibly thin films.[24] Supporting experimental evidence for a significant upward band bending at the Pt-EuO_{1-x} interface can, however, be seen in the temperature dependence of the magnetization shown in the inset of Fig. 2. These magnetization curves are notable for the disappearance of the secondary dome with decreasing film thickness. This dome is always present in the magnetization curves of doped EuO samples;[5,6] it constitutes a deviation from the Brillouin function of a Heisenberg lattice of localized spins,[6] and it is associated with the exchange interaction mediated by the occupied conduction band.[9] The disappearance of the secondary dome thus indicates a complete depopulation of the EuO_{1-x} conduction band, which we attribute to an upward bending above the chemical potential. This would also contribute to the reduction of T_C, which we have discussed above. From the preceding electrostatic considerations, in agreement with the inference drawn from the thickness-dependent magnetization curves, we conclude that the moment reduction below the Hund's rule moment of $m_{4f} = 7\ \mu_B$ for atomic Eu is caused by an upward bending of the conduction band as well as of the Eu $4f$ states, which are partially depopulated near the interface upon crossing the chemical potential. This explanation is in agreement with the reduced moment measured by SQUID by Santos *et al.*[19] since in their samples Cu, having a similar work function to Pt, can cause a similar upward band bending. Band bending also explains the reduced barrier height, relative to bulk EuO, found in their transport measurements. The length scale for the range of the band bending is controlled by the charge screening lengths in the EuO conduction and $4f$ bands, i.e., significantly shorter than the range of the RKKY interaction. This is consistent with our experimental finding that the bulk moment is recovered for film thickness $d \geqslant 6$ nm (Fig. 3), while the bulk T_C is obtained only for thickness $d \geqslant 40$ nm (Fig. 2). Band bending due to interface charge transfer can be calculated within a semiclassical Thomas-Fermi theory, where the local interface potential, $V(z)$, and the interface charge density distribution in that potential, $\delta\rho(z)$, are calculated self-consistently using Gauss' law and the locally shifted band-energy levels, respectively, and minimizing the total energy of the interface.[25]

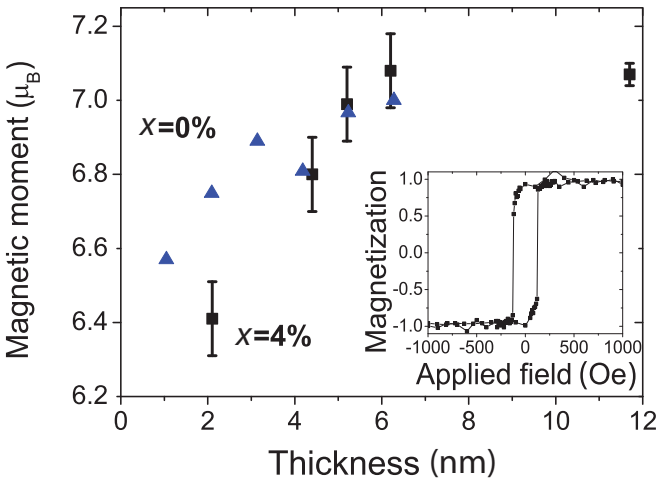

FIG. 3. (Color online) Magnetic moment of $EuO_{0.96}$ for varying thickness (black squares), $t_{PNR} = 2.1$, 4.4, 5.2, and 6.2 nm. The 11.7 nm data point is taken from Ref. 6. Data for EuO (blue triangles) is taken from Ref. 19. The inset shows a hysteresis loop taken by SQUID at 5 K for a 2-nm $EuO_{0.96}$ sample.

To support the above conclusions, we now analyze alternative explanations for the moment reduction, discussing why we can exclude them as significant factors.

Intermixing. The moment reduction could originate not from a real intra-atomic reduction, but from intermixing or alloying at the interface. Since the PNR measurement gives the average magnetic moment per atom, the higher number of

nonmagnetic atoms would artificially decrease the moment assigned to Eu. The high accuracy and sensitivity of the PNR experiment however lets us exclude such a possibility: any kind of intermixing at the interface would cause a significant variation from the expected number density and scattering length for $EuO_{0.96}$, because the values of these parameters for Pt are significantly different[6] and intermixing would be apparent in fitting the PNR data (View Fig. S1 in the Supplemental Material[26]). We can therefore attribute the magnetic moment reduction exclusively to the $EuO_{0.96}$ layer. Additionally, the data cannot be convincingly modeled by a weighted average of surface and inner layers with different magnetization (View Fig. S2 in the Supplemental Material[27]), indicating that the magnetization is continuously nonuniform in space.

Landé factor. We can exclude that the origin of the moment reduction lies in a renormalization of the Landé factor g near the interface to a value significantly below the bulk one: in saturated, thicker (bulk-like) films of $EuO_{0.96}$, the observed magnetic moment per Eu atom is $m = 7.08\ \mu_B$ (cf. Table I), i.e., equal to the combined maximum spin moment of the Eu $4f$ electrons and of the two dopant electrons per oxygen vacancy, $m = g\ (7/2 + x)\ \mu_B$, where the Landé factor assumes its vacuum value, $g = 2$. This indicates that orbital, band structure, or many-body effects do not play a significant role for the g factor. Hence we do not expect that g is modified due to orbital quenching or a change of band structure near the interface. Moreover, the Landé factor of Pt has consistently been reported to be larger than 2,[28] so that we do not expect a reduction of g in EuO_{1-x} due to proximity to Pt.

Surface pinning. A last factor to consider is that the $4f$ orbitals of EuO have been reported to be susceptible to pinning from the local crystalline environment;[29,30] this could cause a reduction of the moment by forcing part of the magnetization vector to lie in an out-of-plane direction. However, the anisotropy contribution from pinning in EuO has been reported to be weak.[30] This is in agreement with our SQUID measurements in an out-of-plane configuration (not shown), which confirm the magnetization to lie in-plane.

IV. SUMMARY

We have performed systematic measurements of the Curie temperature and layer-average magnetic moment in thin, oxygen-deficient EuO films in dependence of the film thickness. These measurements enabled us to study the influence of the film interface and to analyze the physical effects contributing to their reduction. In stoichiometric EuO, the Curie temperature is reduced for film thicknesses smaller than 10 nm, and this reduction can be understood by the reduced number of neighboring magnetic atoms at the surface of the Eu sublattice. In electron-doped $EuO_{0.96}$, there is an overall, numerical enhancement of the Curie temperature with respect to stoichiometric EuO, but the surface-induced reduction extends up to higher film thicknesses of about 40 nm. The overall absolute-value enhancement and the thickness-dependent reduction can both be understood qualitatively in terms of the long-range RKKY spin-exchange interaction.

We also observe a reduction in the moment of $EuO_{0.96}$. By considering the large difference in work functions between EuO and Pt, we expect that band bending will occur at the interface, to such an extent as to partially depopulate the $4f$ states. This is in agreement with the absence of the expected deviation from the Brillouin function in the temperature dependence of the magnetization, which indicates depletion of the conduction band. Having excluded other possible factors for the reduction in the layer-average magnetic moment, we conclude that band bending causes a nonuniform decrease in the moment of Eu, reducing the total spin per Eu atom at the interface. We conjecture that the moment may thus be controlled by the interface work functions. More detailed, spatially dependent calculations will, however, be needed to understand quantitatively the reduction of the magnetic moment as well as of the Curie temperature.

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