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Lutetium-doped EuO films grown by molecular-beam epitaxy

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The effect of lutetium doping on the structural, electronic, and magnetic properties of epitaxial EuO thin films grown by reactive molecular-beam epitaxy is experimentally investigated. The behavior of Lu-doped EuO is contrasted with doping by lanthanum and gadolinium. All three dopants are found to behave similarly despite differences in electronic configuration and ionic size. Andreev reflection measurements on Lu-doped EuO reveal a spin-polarization of 96% in the conduction band, despite non-magnetic carriers introduced by 5% lutetium doping. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4723570]

The ferromagnetic half-metal europium oxide (EuO) has potential for spin-based devices like spin-injectors based on its >90% spin-polarization[1] or optical devices based on its giant magneto-optic Kerr effect[2] and a Faraday rotation of 8.5×10^5 deg/cm in a field of 2 T.[3] Its low Curie temperature ($T_C = 69$ K),[4] however, impedes the incorporation of EuO into devices.

The T_C of EuO can be increased by doping it with electrons. The interaction between the Eu *f*-electrons and the dopant electrons enhances the ferromagnetic exchange energy[4,5] and results in an increased T_C. To date, this has been accomplished through the use of trivalent cations including iron,[6–8] lanthanum,[1,9,10] gadolinium,[11–17] and holmium.[9] Alternatively, the T_C can be increased by deliberately making oxygen-deficient EuO such that the resulting oxygen vacancies donate an electron.[6,18–22] In the cation-doped EuO films, an unknown and uncontrolled concentration of oxygen vacancies is often included, which may be responsible for the disparate results for the dependence of T_C on cation doping. For example, in films doped with gadolinium, the maximum reported T_C varies between 120 K (Ref. 15) and 170 K.[14] Films doped with lanthanum have a maximum reported T_C between 118 K (Ref. 1) and 200 K.[10] Likewise, for films doped with iron, the reported T_C varies between 88 K and 200 K.[6,7] For Gd-doped films grown in an adsorption-controlled regime, however, the Curie temperatures are consistent and similar,[15,16] conceivably due to a minimized amount of oxygen vacancies realized in this particular growth regime.[23] In this letter, we report the behavior of an unexplored dopant for EuO, lutetium, which enhances the T_C in epitaxial films grown in an adsorption-controlled regime. We contrast the magnetic and electronic properties of EuO doped with lanthanum, gadolinium, and lutetium when grown under identical adsorption-controlled growth conditions.

Doped EuO thin films were grown directly on (110) YAlO$_3$ substrates via reactive oxide molecular-beam epitaxy (Veeco 930 and GEN10) in an adsorption-controlled growth regime at a substrate temperature of 350 °C to ensure high crystalline quality and stoichiometric films.[17,23] Pure oxygen gas was introduced during growth to a background oxygen partial pressure of 1×10^{-9} Torr above the base pressure of the vacuum system. In the adsorption-controlled regime, the oxygen flux limits the EuO growth rate if the incident flux of europium metal is greater than the effective oxygen flux. The adsorption-controlled growth regime and the growth rate of EuO were determined by measuring the areal density of Eu atoms in calibration EuO samples using Rutherford backscattering spectrometry (RBS).[23] Each film was nominally 35 nm thick, but the uncertainty in the exact oxygen flux during each growth corresponds to roughly 10% variability in the EuO growth rate and therefore the thickness. Europium and the dopant were codeposited from separate effusion cells. Prior to growth, the europium flux was calibrated using a quartz crystal microbalance (QCM) to a flux of 1.1×10^{14} atoms/(cm$^2 \times$ s). This flux was 100% higher than the rate at which europium was incorporated into the EuO film. The lanthanum, gadolinium, and lutetium fluxes were calibrated by a QCM to correspond to 4% doping of the EuO for the films characterized by *in situ* x-ray photoelectron spectroscopy (XPS) measurements and 5% for the films characterized *ex situ*.

Several films were transferred under ultra-high vacuum immediately after growth into an analysis chamber for XPS characterization using Mg K_α radiation (1253.6 eV). The remaining films were capped with 20 nm of amorphous silicon to protect the films from further oxidation during their *ex situ* characterization. Structural characterization was performed using four-circle X-ray diffraction (XRD) utilizing Cu K_α radiation. The T_C was determined using superconducting quantum-interference-device (SQUID) magnetometry. The films were measured in zero field after applying a demagnetization routine at 300 K to minimize the spurious magnetic fields originating from parts of the SQUID.[16] At

this temperature the EuO is in the paramagnetic state without oriented ferromagnetic domains. Bridges were patterned into the doped EuO films using photolithography in combination with *in situ* ion etching and sputter deposition.[16] Bridges $1\,mm \times 0.1\,mm$ in size were used for four-point resistivity measurements from $4\,K$ to $300\,K$ and Hall measurements at $4\,K$, and bridges $50\,\mu m \times 250\,\mu m$ in size were used across a ramp-type junction between superconducting niobium and metallic Lu-doped EuO for differential four-point conductivity measurements for Andreev reflection from $1.8\,K$ to $12\,K$.

The effect of the three dopants on the crystallinity of the epitaxial doped EuO films was assessed by XRD. Figure 1 shows the θ-2θ XRD patterns of typical EuO films doped with 5% lanthanum, gadolinium, or lutetium. All samples exhibit only 00ℓ EuO peaks in addition to the substrate peaks. XRD rocking curves show the full width at half maximum (FWHM) of the EuO 002 peaks to be $0.16 \pm 0.01°$ for all samples. These data indicate that the doped EuO samples are structurally indistinguishable by XRD.

SQUID magnetometry reveals the T_C of the 5% doped films to be similar. La-doped EuO has $T_C = 116\,K$; Gd-doped EuO has $T_C = 122\,K$; and Lu-doped EuO has $T_C = 119\,K$ as seen in Fig. 2(a). The observed kink in the Lu-doped EuO (and to a lesser extent, the La-doped EuO) could be consistent with clustering of dopants in the film.[10] The temperature dependence of the resistivity for the same samples is shown in Fig. 2(b). Hall measurements for these samples reveal that Gd-doped EuO has the highest carrier concentration with $n = 5 \times 10^{20}\,cm^{-3}$ followed by both the La- and the Lu-doped EuO with carrier concentrations of $n = 2.1 \times 10^{20}\,cm^{-3}$ and $n = 1.8 \times 10^{20}\,cm^{-3}$, respectively. The difference in T_C and carrier concentration is within the accuracy of our doping level control, the accuracy of the film thickness, and the strong dependence of dopant activation on substrate temperature.[1]

XAS was used to verify the 3^+ oxidation state of the gadolinium in the Gd-doped EuO films[17] and XPS was used to verify the 3^+ oxidation state of the lanthanum and lutetium in the La- and Lu-doped EuO films, respectively. XAS and XPS were also used to confirm that the oxidation state of Eu is nearly completely Eu^{2+}, with a small amount
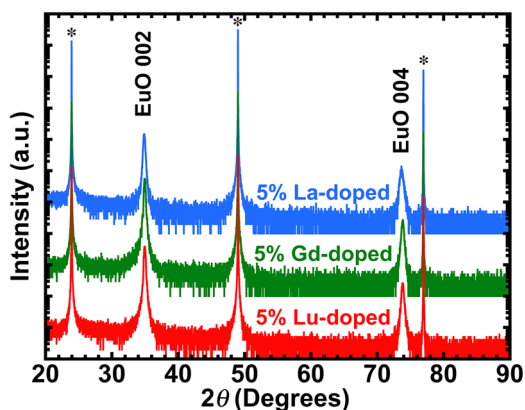
of Eu^{3+} attributed to surface oxidation in uncapped samples as documented in the supplementary information of Ref. 16. Figure 3 shows the XPS intensity of the lutetium $4\,d$ core-level multiplets for the lutetium in Lu-doped EuO, lutetium metal, and Lu_2O_3. Lutetium metal was deposited at room temperature in vacuum by MBE, and Lu_2O_3 was formed by keeping the lutetium metal in vacuum with a background pressure of 2×10^{-9} Torr for at least $1\,h$. Comparing the peak positions to the literature[16] confirmed

FIG. 2. (a) Normalized magnetization as a function of temperature of the same three samples studied in Fig. 1. All three dopants increase the T_C to approximately the same value at 5% doping concentration. (b) Resistivity as a function of temperature for the same three samples. Doped EuO exhibits reduced resistivity and a reduced metal-to-insulator transition compared to undoped EuO. The change in resistivity is comparable regardless of dopant choice.

FIG. 1. θ-2θ scans comparing epitaxial EuO films with 5% lanthanum-doping (blue), 5% gadolinium-doping (green), and 5% lutetium-doping (red). All three films are phase-pure with no indication of dopant insolubility. The curves are offset for clarity and the substrate peaks are marked with asterisks.
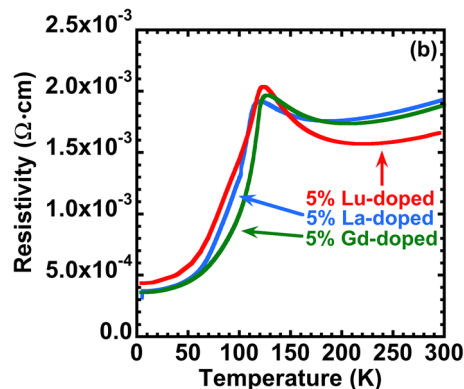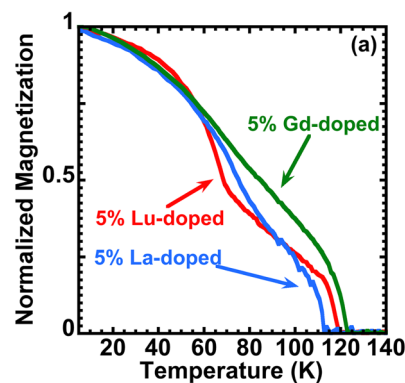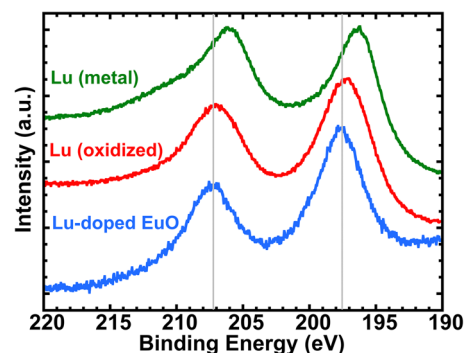
FIG. 3. Comparison of X-ray photoemission intensity of the lutetium $4\,d$ core-level multiplets between 4% Lu-doped EuO (blue), lutetium metal (green), and oxidized lutetium (red). The dashed lines are guides for the eye to highlight the similarity in peak position between the 4% Lu-doped EuO and the oxidized lutetium.
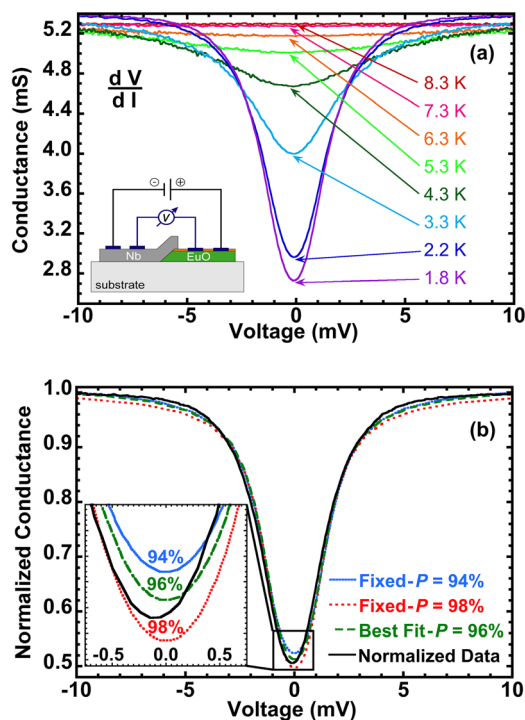
FIG. 4. Andreev reflection measurements of the contact between a niobium electrode and the same 5% Lu-doped sample studied in Figs. 1 and 2. (a) Conductance vs. voltage characteristics were measured at different temperatures. Below the superconducting gap of the niobium electrode, the conductance diminishes because Andreev reflection is forbidden for an interface between a 100% spin-polarized material and a superconductor. The inset shows a schematic of the ramp-type junction used for differential four-point conductivity measurements. (b) Fits to the 1.8 K measurement using the Blonder-Tinkham-Klapwijk model are in accordance with a spin-polarization of 96% (green). For comparison, fits are shown that fix P to 94% (blue) and to 98% (red). The inset shows the overlap of the curves near zero voltage bias to better illustrate the match of the best fit. The best fit parameters were $Z = 0.9$, $\Delta = 1.28$ meV, $R = 77$, and $P = 96\%$.

that the lutetium in the Lu-doped EuO film was indeed 3^+ as expected. A similar process was followed for identifying the oxidation state of lanthanum in the La-doped EuO. From the free carrier concentration, oxidation state, and the doping concentration, it is evident rare-earth dopant ions inject far less than one mobile electron into the EuO conduction band. The dopant activation is less than 40%, in agreement with results for Gd-doped EuO,[24] pointing to the possible ubiquity of the challenge of achieving high dopant activation in EuO. All samples have comparable resistivity curves, reduced dopant activation, and fairly similar carrier concentrations.

Differential conductance measurements were performed on 5% Lu-doped EuO and are shown in Fig. 4. Since Andreev reflection is suppressed at the interface between a material with high spin-polarization and a superconducting material, a drop in conductivity across the Lu-doped EuO/Nb interface for energies less than the superconducting gap of the niobium film at temperatures below the superconducting critical temperature is expected. By fitting the drop in conductance to the Blonder-Tinkham-Klapwijk model[25] that has been modified specifically for non-negligible series resistance in spin-polarized ferromagnetic semiconductor devices,[26–28] one can extract the spin-polarization value. The best fit is in accordance with a spin-polarization of 96%,

which is in agreement with previous reports of the near-complete spin-polarization of EuO.[1] The high spin-polarization despite 5% doping of nonmagnetic atoms is critically important, as it shows that EuO retains its high spin-polarization in the presence of a dopant which significantly boosts its T_C. This is not so surprising given that doped EuO is a half-metal due to the spin-splitting of the conduction band,[29–31] so the carriers are spin-polarized anyway despite the nature of the dopant.

In summary, we have explored the properties of Lu-doped EuO. Lutetium donates electrons to EuO in the same fashion as lanthanum and gadolinium dopants. Furthermore, EuO retains near-complete spin-polarization ($P = 96\%$) despite being heavily doped with the non-magnetic ion Lu^{3+}.

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