Soft x-ray magnetic circular dichroism study on Gd-doped EuO thin films

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We report on the growth and magnetic properties of Gd-doped EuO thin films. We prepared samples with Gd concentrations up to 11% by means of molecular beam epitaxy under distillation conditions. Using soft x-ray magnetic circular dichroism at the Eu and Gd $M_{4,5}$ edges, we found that T_C ranges from 69 K for pure stoichiometric EuO to about 170 K for films with the optimal Gd doping of around 4%. The doping dependence of T_C has been investigated and compared with available theoretical predictions. We also show that the Gd magnetic moment couples ferromagnetically to that of Eu.

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EuO is one of the rare ferromagnetic semiconductors. In the stoichiometric case it has a Curie temperature of 69 K.[1] Slightly Eu-rich EuO shows a metallic low-temperature phase and the magnetic phase transition is accompanied by a metal-to-insulator transition (MIT), where the change in resistivity can exceed ten orders of magnitude depending on the exact stoichiometry.[2,3] An applied magnetic field shifts the MIT temperature considerably which results in a colossal magnetoresistance (CMR) effect with a resistivity change of up to eight orders of magnitude.[3] The Curie temperature (T_C) can be strongly enhanced by electron doping. It has been found that several percents of Gd doping increases T_C to 125 K, whereas oxygen deficiency can further enhance T_C to 160 K.[1,4] In the ferromagnetic state the unoccupied density of states shows a splitting of about 0.6 eV between the spin-up and spin-down states leading to an almost 100% spin polarization of the charge carriers in electron doped EuO.[5] This essentially complete spin polarization makes EuO a very attractive candidate for fundamental research in the field of spintronics.

In this paper we show that Gd-doped EuO films can be prepared with good control of the Gd concentration and oxygen stoichiometry using the molecular beam epitaxy (MBE) technique under distillation condition. We used *in-situ* soft x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) in the range of the Eu and Gd $M_{4,5}$ edges ($3d \rightarrow 4f$) to characterize the chemical composition and magnetic properties of the films. The doping dependence of T_C for a wide range of Gd concentration has been investigated and we compared the results to predictions of mean-field calculations. We also address the long standing issue whether the Gd spins couple ferromagnetically or antiferromagnetically to the Eu spins, and whether this coupling depends on the Gd concentration.

The XAS and XMCD measurements were performed at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The samples were grown *in situ* in a MBE chamber with a base pressure of 2×10^{-10} mbar. The spectra were recorded using the total electron yield method. The photon energy resolution at the Eu and Gd $M_{4,5}$ edges ($h\nu \approx 1100-1250$ eV) was ≈0.6 eV, and the degree of circular polarization was ≈80%. For the XMCD measurements the angle of incidence was set to 45°. This angle is a compromise between a maximum projection of the photon spin on the sample magnetization (the in-plane easy axis requires grazing incidence) and the avoidance of saturation effects, which may occur if the photon incidence is too grazing, because then the photon penetration depth becomes comparable to the electron escape depth. The samples were placed in a magnetic field of about 0.2 T using an *ex situ* rotatable permanent magnet.

Gd-doped EuO films were grown *in situ* by means of MBE. High purity Eu and Gd metal were evaporated from effusion cells and molecular oxygen was supplied simultaneously through a leak valve. To prevent the formation of oxides higher than EuO, such as Eu_2O_3 or Eu_3O_4, as well as of Eu-metal clusters we set the Eu evaporation rate such that it is much in excess compared to the oxygen rate. At the same time, we kept the substrate temperature sufficiently high so that a distillation process occurs in which excess Eu, which has not reacted to EuO, is reevaporated into the vacuum.[6,7] Thus the growth rate is in effect determined by the oxygen dose rate. The use of the distillation conditions is essential; otherwise one is confronted with the difficult task to control very precisely the relative rates between Eu and O to obtain (quasi) stoichiometric EuO.[4] The doping with Gd has been accomplished by evaporating Gd and Eu metal simultaneously.

The Eu deposition rate was set at about 11 Å/min, and the Gd rate was varied between 0.1 and 2.7 Å/min as checked using a crystal thickness monitor. The oxygen partial pressure was set at 6×10^{-8} mbar above the base pressure as monitored by a quadrupole mass spectrometer and was kept constant within $\pm 0.2 \times 10^{-8}$ mbar. As substrates we used epi-polished single crystal of $Al_2O_3(1\bar{1}02)$ and MgO(100). Prior to growth the substrates were annealed at $T=600$ °C in the case of Al_2O_3 and $T=450$ °C for MgO in an oxygen atmosphere of 1×10^{-7} mbar in order to obtain clean and well-ordered substrate surfaces. The substrates were kept at $T=350$ °C during growth. The so prepared samples were polycrystalline with a thickness of ≈60 nm. At this thickness an eventual effect of the surface on the magnetic properties can be safely neglected.

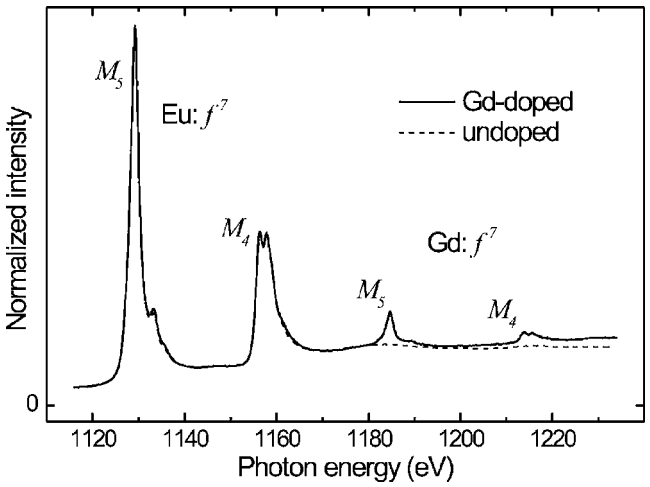

FIG. 1. Eu and Gd $M_{4,5}$ ($3d \rightarrow 4f$) XAS spectra of a stoichiometric (undoped) EuO sample and a 10% Gd-doped EuO sample.

Figure 1 shows the XAS spectra of an undoped- and a Gd-doped EuO film across the Eu and Gd $M_{4,5}$ edges. The Eu spectra of the doped and undoped cases are identical and look very similar to the theoretical spectrum calculated for a $3d^{10}4f^7 \rightarrow 3d^9 4f^8$ transition.[8] This means that the Eu ions in our films are divalent. Moreover, these experimental spectra look very different from the one calculated for a Eu^{3+} ion,[8] and have no extra peaks at higher energies which otherwise would indicate the presence of Eu^{3+} ions.[9] All this demonstrates that our EuO films are indeed free from Eu^{3+} contamination.

The Gd $M_{4,5}$ white line also shows all the characteristics of a $3d^{10}4f^7 \rightarrow 3d^9 4f^8$ transition,[8] which is consistent with the fact that Gd has always the $4f^7$ configuration. The very similar spectral line shapes and photoabsorption cross sections facilitate the determination of the Gd concentration in the doped EuO films: We can simply deduce this from the ratio of the main-peak heights of the Gd and Eu spectra after subtracting the extended x-ray absorption fine structure (EXAFS) of pure EuO in the Gd $M_{4,5}$ energy range. This is a simple and reliable procedure with the advantage that the Gd concentration can be determined *in situ*. For the particular Gd-doped film shown in Fig. 1 we find that the Gd concentration is about 10%.

The magnetic properties of the samples have been investigated by XMCD.[10] Figure 2 shows the Eu $M_{4,5}$ spectra of a 3.7% Gd-doped EuO sample recorded at a temperature of 20 K using circularly polarized x-rays with the photon spin parallel and antiparallel to the magnetic field direction. Clearly the two spectra show significant differences; the difference spectrum, i.e. the XMCD spectrum, is given by the lowest curve and it matches very nicely the theoretical spectrum for a Eu^{2+} ion.[10] The largest XMCD signals can be observed at 1129.1 eV, which is about 0.1 eV higher in energy than the maximum of the M_5 white line, and at 1157.9 eV for the M_4. The experimental XMCD effect, defined as the difference of both spectra divided by their sum, becomes 28% and −41% for the M_5 and the M_4 white line, respectively. In these numbers the angle of incidence and the degree of photonpolarization have been taken into account.

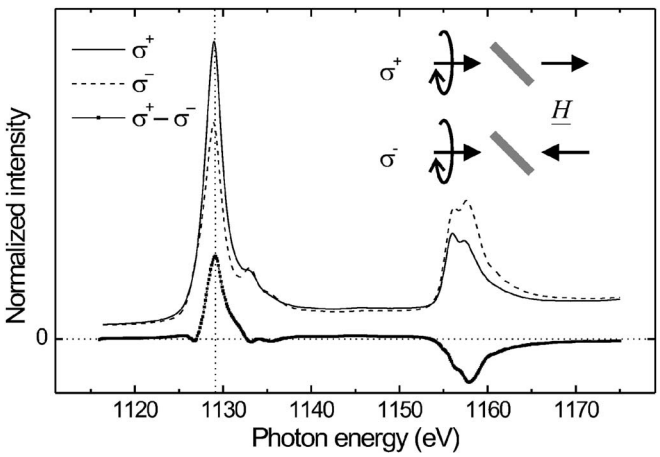

FIG. 2. Eu $M_{4,5}$ XAS spectra of a 3.7% Gd-doped EuO sample recorded at 20 K using circularly polarized x rays with the photon spin parallel (solid line) and antiparallel (dashed line) to the magnetic field direction. The lowest curve shows the difference between both, which is called the XMCD spectrum.

Since about 51% XMCD effect is expected theoretically at the M_5 white line for a fully magnetized Eu^{2+} ion,[10] we conclude that the degree of magnetization, in this measurement is about 55% due to the relatively small external magnetic field of 0.2 T.

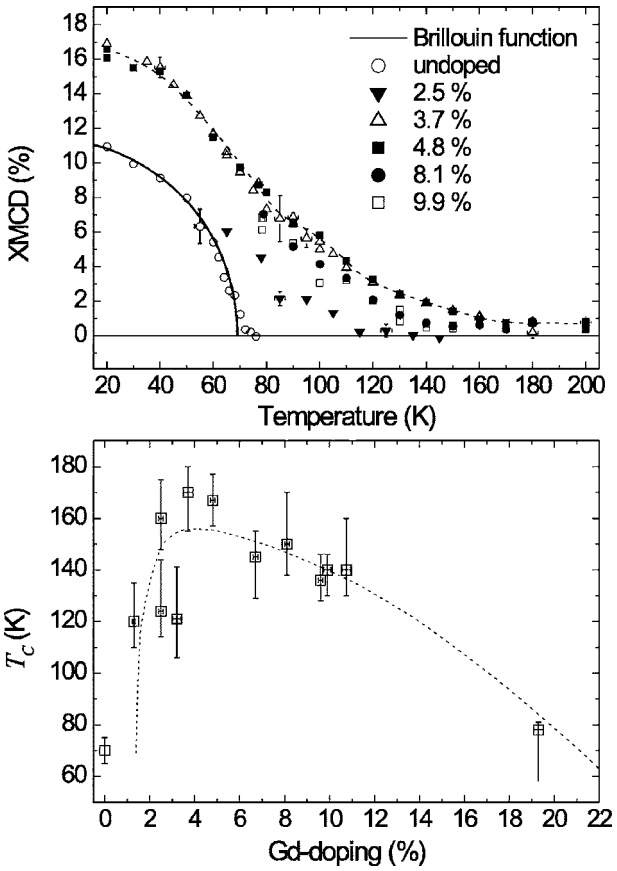

FIG. 3. Top panel: XMCD effect as a function of temperature for EuO samples with different Gd doping levels. Bottom panel: Doping dependence of the Curie temperature (T_C). The dotted line represents the result of a mean-field calculation.

The top panel of Fig. 3 depicts the XMCD effect in pure EuO and several Gd-doped EuO thin films with different doping levels as a function of temperature. The XMCD effect has been evaluated at the photon energy of 1129.1 eV. The undoped EuO sample (open circles) clearly follows a Brillouin function with a T_C of about 69 K, identical to the value for bulk EuO. This result demonstrates that this EuO film is stoichiometric, i.e., without oxygen deficiency which otherwise would have influenced the magnetic properties. This in turn proves once again that the growth recipe based on the distillation process is successful.

Upon doping with Gd the magnetization increases, the shape of the temperature dependence of the XMCD effect deviates strongly from the Brillouin function, and T_C is enhanced considerably. Here we took as T_C the temperature above which the XMCD signal is constant. The bottom panel of Fig. 3 shows T_C as a function of the Gd doping concentration. Starting from around 69 K for undoped EuO, T_C increases rapidly upon Gd doping and reaches a maximum of about 170 K at a doping concentration of about 4%. To our knowledge, this is the highest T_C reported so far for a EuO system under ambient pressures. For higher Gd concentrations T_C slowly decreases again.

The deviation of the magnetization curves from the Brillouin function in case of the doped samples is qualitatively in agreement with magnetization curves reported earlier for bulk samples of Gd-doped EuO. Mauger explains this by the temperature dependence of the effective magnetic coupling due to the successive population of the spin-up and spin-down conduction subband which enters the exchange coupling constant.[11] The doping dependence of T_C has also been calculated by Mauger[11] using a mean-field approximation, the results of which are depicted in the bottom panel of Fig. 3. The calculation assumes a critical Gd concentration of about 1%; below this concentration it is energetically favorable for the "extra" electrons to remain localized around the Gd impurities, forming a bound magnetic polaron. Consequently there is no indirect exchange mediated via free carriers, and T_C is not enhanced with respect to undoped EuO. Above the critical Gd concentration, free carriers are available and T_C increases accordingly. There is a maximum in T_C which according to the model is due to the instability of the ferromagnetic configuration with respect to a spiral configuration along the [111] direction if the concentration is too high.[11] The agreement between experiment and theory appears to be satisfactory.

An open question so far is whether the Gd spins in Gd-doped EuO are coupled to the Eu spins, and if so, whether they are parallel or antiparallel aligned. Until now little has been reported on this subject in literature. From the few studies carried out in the past it was suggested that the Gd spins may be aligned antiparallel to the Eu spins in Gd-doped EuS films[12] and single crystals.[13] Now, with the XMCD technique, the issue of spin alignment can be addressed in a straightforward manner.

In panel (a) of Fig. 4 we present the Eu and Gd $M_{4,5}$ spectra of a 3.7% Gd-doped EuO film taken at 20 K using circularly polarized light. The XMCD effect in the Eu $M_{4,5}$ edges can be clearly seen, with the M_5 peak having larger intensity for σ^+ polarized x rays (solid line) than for

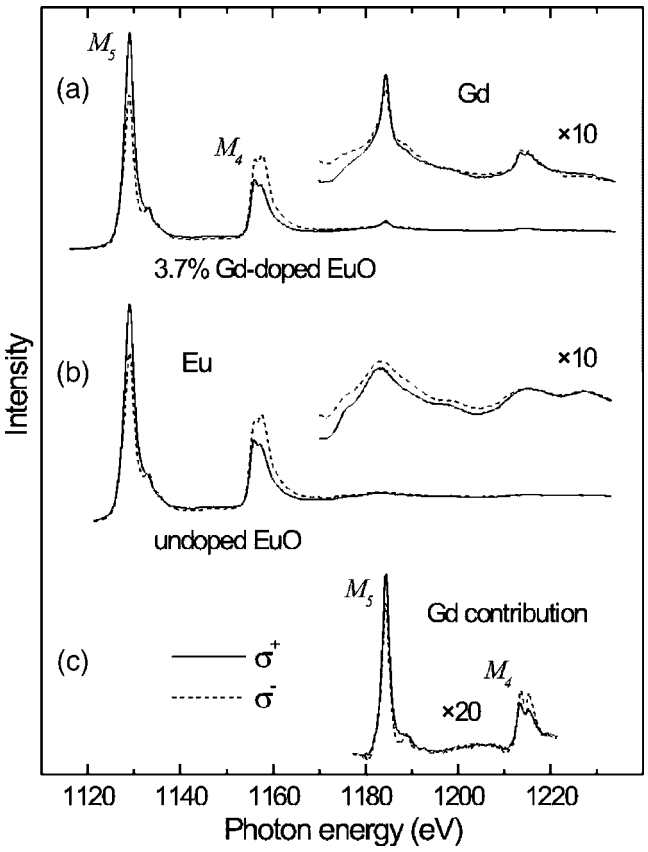

FIG. 4. Eu and Gd $M_{4,5}$ XAS spectra of (a) a 3.7% Gd-doped EuO sample and (b) an undoped EuO sample, recorded at 20 K using circularly polarized x rays with the photon spin parallel and antiparallel to the magnetic field direction. (c) The net Gd $M_{4,5}$ contribution, obtained by subtracting the EuO spectra from those of the 3.7% Gd-doped EuO.

σ^-polarization (dashed line). Since the intensity of the Gd contribution is relatively weak, we have magnified the Gd part of the spectra by a factor of ten. The XMCD effect for the Gd edges is now clearly visible, but we also observe that the background changes with the polarization of the light. We attribute this to the presence of the EXAFS of the Eu edges, which is superimposed on the Gd spectra. As can be seen in panel (b) of Fig. 4, the Eu EXAFS of undoped EuO indeed carries an XMCD effect in the photon energy region of the Gd edge. To solve this background problem, we subtract the spectrum of the undoped EuO from that of the Gd-doped EuO. The resulting net Gd contribution to the spectra is shown in panel (c) of Fig. 4, and the similarity of the Gd spectra with those of Eu is striking. In particular, the Gd M_5 peak with σ^+ light lies above that with σ^-, i.e., identical to the Eu case. This directly means that the Gd and Eu $4f$ spins are aligned parallel. We have investigated the Gd $4f$ spin alignment for various doping levels up to 11%, and found in all cases that it is parallel to the Eu spins, in agreement with the calculation of Mauger.[11]

In conclusion, we have successfully prepared Gd-doped EuO films with Gd concentrations up to 11% with controlled stoichiometry by means of molecular beam epitaxy. The magnetic ordering temperature is enhanced upon Gd doping

and a record high $T_C \approx 170$ K has been achieved for an optimal Gd concentration of around 4%. The doping dependence of T_C has been investigated and found to be in reasonable agreement with the mean-field results by Mauger. We also revealed that the Gd magnetic moments couple ferromagnetically to the magnetic moments of Eu.

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