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

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We report on the growth and characterization of ferromagnetic Gd-doped EuO thin films. We prepared samples with Gd concentrations up to 11% by means of molecular beam epitaxy under distillation conditions, which allows a very precise control of the doping concentration and oxygen stoichiometry. Using soft x-ray magnetic circular dichroism at the Eu and Gd $M_{4,5}$ edges, we found that the Curie temperature ranged from 69 K for pure stoichiometric EuO to about 170 K for the film with the optimal Gd doping of around 4%. 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 and it has a Curie temperature of 69 K.¹ In slightly Eurich EuO the low-temperature phase is metallic and the magnetic phase transition is accompanied by a metalto-insulator transition (MIT), where the change in resistivity can exceed 10 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 8 orders of magnitude.³ The Curie temperature T_C can be strongly enhanced by electron doping. It has been found that several percent of Gd doping enhances T_C to 125 K, whereas oxygen deficiency can further increase 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 spindown 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 conditions. We investigated the doping dependence of the ferromagnetic ordering temperature for a wide range of Gd concentration. 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 results are compared to predictions from 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 NSRRC in Taiwan using *in-situ* MBE grown samples. The spectra were recorded using the total electron yield method in a chamber with a base pressure of 2×10^{-10} mbar. The photon energy resolution at the Eu and Gd $M_{4,5}$ edges ($h\nu \approx 1100-1250 \text{ eV}$) was set at 0.6 eV, and the degree of circular polarization was $\approx 80\%$. For the XMCD measurements the angle of x-ray 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 angle of 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 MBE. High purity Eu and Gd metal was evaporated from effusion cells and molecular oxygen gas was supplied simultaneously through a leak valve. The formation of oxides higher than EuO, such as Eu_2O_3 or Eu_3O_4 , as well as of Eu metal clusters has to be prevented. This requires to set the Eu evaporation rate higher relative to the oxygen dosing, such that the Eu is much in excess. At the same time, the substrate temperature is kept at a sufficiently high temperature so that a distillation process occurs in which excess Eu which has not reacted to EuO is re-evaporated into the vacuum.^{6,7} 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. The evaporation rate was checked with a crystal thickness monitor. The oxygen partial pressure was set at 6×10^{-8} mbar above the base pressure as monitored with a quadrupole mass spectrometer and kept constant within $\pm 0.2 \times 10^{-8}$ mbar. As substrates we used epi-polished single crystal of Al₂O₃(1102) and MgO(100). Prior to growth the substrates were annealed at $T = 600^{\circ}$ C in the case of Al₂O₃ and $T = 450^{\circ}$ C for MgO in an oxygen atmosphere of 1×10^{-7} mbar in order to obtain a clean



FIG. 1: Eu and Gd $M_{4,5}$ $(3d \rightarrow 4f)$ XAS spectra of a stoichiometric (undoped) EuO sample and a 9.9% Gd-doped EuO sample.

and well-ordered substrate surfaces. The substrates were kept at $T = 350^{\circ}$ C during growth.

Fig. 1 shows the XAS spectra of an undoped and a Gddoped EuO film across the Eu and Gd $M_{4,5}$ edges. The Eu spectra of the doped and undoped case are identical and look very similar to the theoretical spectrum calculated for a $3d^{10}4f^7 \rightarrow 3d^94f^8$ 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 Eu³⁺ ion,⁸ and also have no extra peaks at higher energies which otherwise would indicate the presence of Eu³⁺ ions.⁹ All this demonstrates that our EuO films are indeed free from Eu³⁺ contamination.

The Gd spectrum in Fig. 1 has also all the characteristics of a $3d^{10}4f^7 \rightarrow 3d^94f^8$ transition.⁸ This is consistent with the fact that Gd has always the $4f^7$ configuration. The fact that Eu and Gd have the identical 4fconfiguration and very similar spectral line shapes facilitates 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 9.9%.

The magnetic properties of the samples have been investigated by XMCD.¹⁰ Fig. 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. 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



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.

line, and at 1157.9 eV for the M_4 . This XMCD spectrum matches very nicely the theoretical spectrum for a Eu²⁺ ion.¹⁰ The experimental XMCD effect, defined as the difference divided by the 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 photon polarization have been taken into account. Since about 51% XMCD effect is expected theoretically at the M_5 white line for a fully magnetized Eu²⁺ ion,¹⁰ we conclude that the degree of magnetization in this measurement is about 55%.

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. However, 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 from the Brillouin function of the temperature dependence of the XMCD effect 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-



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.

up and spin-down conduction subband which enters the exchange coupling constant.¹¹ The doping dependence of T_C has also been modelled by Mauger.¹¹ The bottom panel of Fig. 3 shows the reproduced curve calculated using a mean-field approximation. 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 when 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



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.

suggested that the Gd spins may be aligned antiparallel to the Eu spins in Gd-doped EuS films¹² and single crystals.¹³ Now, with the XMCD technique being developed into maturity over the last 15 years, 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 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 extended x-ray absorption fine structure (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 resolve 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 analysis 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

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upon Gd doping and a record high $T_C \approx 170$ K has been achieved for an optimal Gd concentration of around 4%. We also revealed that the Gd magnetic moments couple ferromagnetically to the magnetic moments of Eu.

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