Spin splitting of the conduction band of the ferromagnetic semiconductor EuO

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EuO is a semiconductor with a band gap of about 1.2 eV and is one of the very rare ferromagnetic oxides [1]. Its Curie temperature (T_c) is around 69 K and the crystal structure is rocksalt (fcc) with a lattice constant of 5.144 Å. EuO becomes metallic below T_c and the metal-insulator transition (MIT) is very spectacular: the resistivity drops by as much as 8 orders of magnitude [2]. Moreover, an applied magnetic field shifts the MIT temperature, resulting in colossal magnetoresistance (CMR) with changes in resistivity of up to 6 orders of magnitude [2]. This CMR behavior in EuO is in fact much more extreme than in the well-known $La_{1-x}Sr_xMnO_3$ materials. Upon doping with Gd for example, the T_c of EuO can be raised to about 145 K [3].

The basic electronic structure of EuO consists of a filled O $2p$ band, a half-filled Eu $4f$ shell ($4f^7$) and an (almost) empty Eu $5d$-$6s$ like conduction band. The interesting properties of EuO are probably caused by the interplay of the (doping dependent) charge carriers in the conduction band with the electrons in the Eu $4f$ shell. Local exchange interactions favor a ferromagnetic spin alignment of these Eu $5d$-$6s$ charge carriers with the high-spin (S=7/2) Eu $4f$ ions. It is believed that a ferromagnetic ordering of the Eu ions results in an enormous increase of the hopping integrals for spin-parallel conduction electrons. Optical measurements have shown that the absorption edge is then reduced by as much as 0.25 eV [4]. Early spin-resolved photo-emission and field emission studies (more than 20 years ago), reveal high degrees of spin-polarization of the Eu $4f$ states [5,6].

In this study we focus on the energetics and spin character of the Eu $5d$-$6s$ like conduction band states (e.g. exchange splitting, band width) and how they change in going through the magnetic ordering and metal-insulator transition temperatures. Of great interest is to investigate the spin-polarization of the conduction band states closest to the Fermi level as function of temperature since it is expected that it is here where the charge carriers will move upon electron doping of the EuO.

We have carried out spin-resolved photoemission and resonant-Auger experiments as well as x-ray absorption (XAS) experiments on EuO thin films, using both linearly and circularly polarized soft-x-rays. The availability of EuO in thin film form is crucial for the measurement of spin-polarized electron spectroscopies because the remanent magnetic field created by the tiny amount of material involved is negligibly small, and thus a perturbation of the trajectories of the emitted photoelectrons can be avoided. The thin films are made *in-situ* using a simultanious co-evaporation and distillation process. We are able to obtain EuO with good control of the stoichiometry as is demonstrated earlier by x-ray and ultraviolet electron spectroscopic (XPS, UPS) measurements in our Groningen laboratory.

We have measured the spin-resolved valence band photoemission of EuO at about 40 K and we found a spin-polarization of about 50% for the Eu $4f$ peak, indicating the degree of remanence of our films at this temperature. This is confirmed by magnetic circular dichoism measurements at the Eu $M_{4,5}$ ($3d\rightarrow4f$) photoabsorption edges. We have also detected the small (1% effect) but clear magnetic circular dichroism signal in the O K ($1s\rightarrow2p$) absorption edge, and this maybe taken as an indication for the amount of orbital moment that is transferred from the Eu $5d$ to the O $2p$ [7].

In varying the temperature across T_c, we have observed large changes over a wide energy range in the line shape of the O K XAS, as shown in Fig.1. We ascribe these changes to the appearence and disapperance of the exchange splitting in the Eu $5d$-$6s$ conduction band that is strongly hybridized with the O $2p$ band. The behavior of this unoccupied band can be characterized as itinerant, which makes EuO an interesting material since it also contains localized moments given by the Eu $4f$ orbitals. Both double-exchange and superexchange type of mechanisms may therefore be at work in EuO.

To determine the spin-polarized unoccupied density of states and the magnitude of the exchange splitting, we have applied a new combination of spectroscopic techniques, namely the spin-resolved resonant-Auger O K XAS. The underlying concept of this type of constant-final-state (CFS) experiment is as follows. The ground state consists mainly of the $O(2p^6)Eu(4f^75d^0)$ configuration. Strong overlap between the O $2p$ and the Eu $5d$ results in the occupation of also the $O(2p^5)Eu(4f^75d^1)$ configuration. The measurement of the O K XAS spectrum with $O(1s^12p^6)Eu(4f^75d^1)$ like final states therefore provides information about the unoccupied Eu $5d$ density of states. We notice that if the unoccupied Eu $5d$ band is spin-polarized, so will be the O $2p$ hole in the ground state and thus also the O $1s$ hole in the XAS final state. The subsequent Auger decay of the XAS state leads to $O(2p^4)$ like final states [8], and the outgoing Auger electron will also be spin-polarized with an equally high degree since the O two-hole final states are of pure singlet (^1S and ^1D) symmetry (^3P transitions

are forbidden) [9]. Thus, the measurement of the spin of the O-1$s2p2p$ Auger across the O K edge will reveal the spin-polarization of the unoccupied Eu $5d$ band. We note that this type of spin-resolved O K XAS is different from an O K magnetic circular dichroism (MCD) experiment. In the latter the helicity of the circulary-polarized light is varied and the dichroic signal contains a more convoluted information about the spin and the orbital moments transferred from the cations [7].

The results of the spin-resolved O K XAS measurements are shown in the top panel of Fig.2. The spin-up and spin-down conduction bands can be clearly distinguished, and we observe that the exchange splitting is about 0.5 eV. These results are nicely in agreement with the spin-resolved unoccupied O $2p$ partial density of states from LDA+U calculations as depicted in the bottom panel of Fig.2. Very important is the experimental observation that the bottom of the conduction band consists only of the spin-up states. This means that upon electron doping, the charge carriers will be moving in a 100% spin-polarized band, an aspect that is extremely interesting for applications in the field of spintronics.

We now arrive at the following picture for the metal-insulator transition in EuO. Above T_c, impurities or dopants have their energy levels located slightly below the bottom of the conduction band, and the material behaves like a semiconductor: the resistivity decreases with increasing temperatures as a result of a thermal activation of the electrons from the impurity states into the conduction band. Below T_c, the conduction band becomes broader due to the exchange splitting, and the impurity states now fall into the conduction band. The electrons of these impurities can then propagate in the conduction band without needing any activation energy, and the system behaves like a metal. Moreover, these charge carriers are 100% spin-polarized.

To conclude, our experiments have revealed large changes in the unoccupied density of states of EuO if the temperature is varied accross T_c. Spin-resolved measurements have shown that this is caused by the appearence or disappearence of an exchange splitting between the spin-up and spin-down density of states. The exchange splitting is appreciable, about 0.5 eV. We have also found out that electron doped EuO in the ferromagnetic state will have charge carriers with a 100% spin-polarization.

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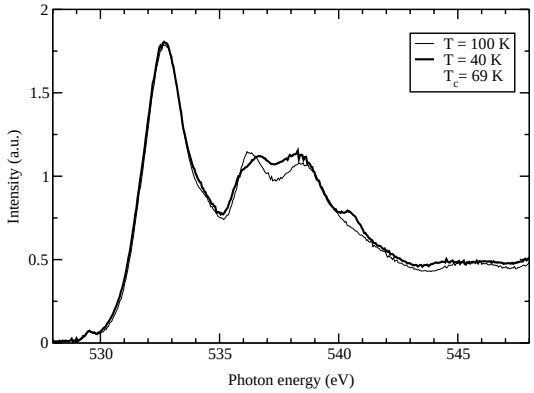

FIG. 1. O K x-ray absorption spectrum of EuO, above (thin solid line) and below (thick solid line) the Curie temperature (T_c = 69 K).

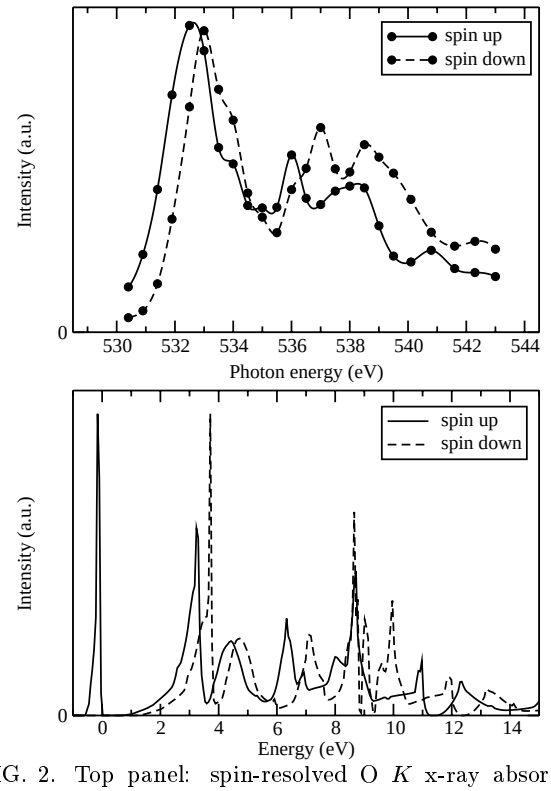

FIG. 2. Top panel: spin-resolved O K x-ray absorption spectrum of EuO. Bottom panel: spin-resolved unoccupied O 2p partial density of states from LDA+U calculations.