

Exchange Splitting and Charge Carrier Spin Polarization in EuO

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High quality thin films of the ferromagnetic semiconductor EuO have been prepared and were studied using a new form of spin-resolved spectroscopy. We observed large changes in the electronic structure across the Curie and metal-insulator transition temperature. We found that these are caused by the exchange splitting of the conduction band in the ferromagnetic state, which is as large as 0.6 eV. We also present strong evidence that the bottom of the conduction band consists mainly of majority spins. This implies that doped charge carriers in EuO are practically fully spin polarized.

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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 [1,2]. Its Curie temperature (T_c) is around 69 K and the crystal structure is rocksalt (fcc) with a lattice constant of 5.144 Å. Eu-rich EuO becomes metallic below T_c and the metal-insulator transition (MIT) is spectacular: the resistivity drops by as much as 8 orders of magnitude [3,4]. Moreover, an applied magnetic field shifts the MIT temperature considerably, resulting in a colossal magnetoresistance (CMR) with changes in resistivity of up to 6 orders of magnitude [4]. This CMR behavior in EuO is in fact more extreme than in the now much investigated $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ materials [5,6]. Much of what is known about the basic electronic structure of EuO dates back to about 30 years ago and is based mainly on optical measurements [7–9] and band structure calculations [10]. With the properties being so spectacular, it is surprising that very little has been done so far to determine the electronic structure of EuO using more modern and direct methods such as electron spectroscopies.

Here we introduce spin-resolved x-ray absorption spectroscopy, a new type of spin-resolved electron spectroscopy technique to study directly the conduction band of EuO where most of the effects related to the MIT and CMR are expected to show up. Spin-resolved measurements of the conduction band could previously be obtained only by spin-polarized inverse photoemission spectroscopy. Spin-resolved x-ray absorption spectroscopy is an alternative technique which is especially well suited to the study of ferromagnetic oxides, a currently interesting broad class of materials. Using this technique we observed large changes in the conduction band across T_c and we were able to show experimentally that these are caused by an exchange splitting of the conduction band below T_c . Moreover, we found that this splitting is as large as 0.6 eV and show that the states close to the bottom of the conduction band are almost fully spin

polarized, which is very interesting for basic research in the field of spintronics.

The experiments were performed using the helical undulator [11] based beam line ID12B [12] at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Photoemission and Auger spectra were recorded using a 140 mm mean radius hemispherical analyzer coupled to a mini-Mott 25 kV spin polarimeter [13]. The spin detector had an efficiency (Sherman function) of 17%, and the energy resolution of the electron analyzer was 0.7 eV. The photon energy resolution was set at 0.2 eV. The measurements were carried out at normal emission with respect to the sample surface and at an angle of incidence of the x rays of 60°. The sample was magnetized remanently in-plane using a pulsed magnetic coil, the magnetization direction was alternated to eliminate the effect of instrumental asymmetries [14]. The pressure of the spectrometer chamber was better than 1×10^{-10} mbar.

EuO samples with a film thickness of ≈ 200 Å were grown *in situ* by evaporating Eu metal from a Knudsen cell at a rate of ≈ 3 Å per minute in an oxygen atmosphere of 1×10^{-8} mbar on top of a Cr covered, chemically polished Al_2O_3 substrate kept at 280 °C. In a separate experiment in the Groningen laboratory, we have verified that this recipe provides us with high quality polycrystalline EuO films. Valence band and core level x-ray photoemission spectroscopy (XPS) show no detectable presence of Eu^{3+} ions, and ultraviolet photoemission experiments reveal that there is no detectable density of states at the Fermi level, demonstrating that we have indeed obtained nearly stoichiometric semiconducting EuO without detectable traces of Eu_2O_3 , Eu_3O_4 , or Eu metal. The left panel of Fig. 1 displays the magneto-optical Kerr rotation as a function of temperature on our films using a He-Ne laser ($h\nu = 1.96$ eV) and shows that these films have indeed the correct T_c of 69 K. The right panel of Fig. 1 depicts the resistivity of the films as a function of

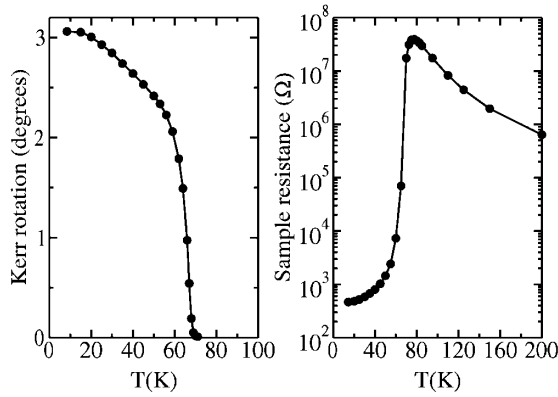


FIG. 1. Left panel: Remanent longitudinal Kerr-rotation of a 50 nm EuO thin film as a function of temperature using p -polarized light at $h\nu = 1.96$ eV and $\theta_{in} = 45^\circ$. Right panel: metal-insulator transition in the temperature dependent resistivity of a EuO film.

temperature, and it demonstrates clearly the presence of a metal-insulator transition at T_c . The very large change in resistivity, namely 5 orders in magnitude, indicates that the carrier concentration due to oxygen defects, i.e., the off-stoichiometry, is of the order of 0.3% or less [4].

To study the conduction band of EuO, we use O K -edge x-ray absorption spectroscopy (XAS). This technique probes the O $2p$ character of the conduction band, which is present because of the covalent mixing between the O $2p$ and Eu $5d-6s$ orbitals. Figure 2 displays the O K XAS spectra, recorded by collecting the total electron yield (sample current) as a function of photon energy. Large changes over a wide energy range can be clearly seen between the spectra taken above and below T_c . The low temperature spectrum contains more structures and is generally also broader. We note that the spectra also show a very small feature at 529.7 eV photon energy, with a spectral weight of not more than 0.1% relative to the entire spectrum. Since the intensity of this feature is extremely sensitive to additional treatments of the sample

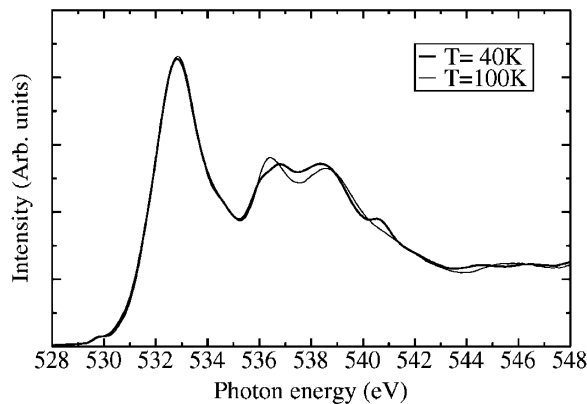


FIG. 2. O K x-ray absorption spectrum of EuO, above (thin solid line) and below (thick solid line) the Curie temperature ($T_c = 69$ K).

surface it is probably related to surface states [15] or imperfections at the surface.

It is evident that the spectral changes across T_c cannot be explained by a phonon mechanism, since the changes involve more than a simple broadening, and above all, since the spectrum becomes broader upon temperature lowering. Because there are also no changes in the crystal structure across T_c , we attribute the spectral changes to the appearance of a spin-splitting in the Eu $5d$ like conduction band below T_c . To prove this, we have to determine the spin-polarized unoccupied density of states. To this end, we measured the O K XAS spectrum no longer in the total electron yield mode, but in a partial electron yield mode in which we monitor the O $KL_{23}L_{23}$ Auger peaks that emerge at a constant kinetic energy from the XAS process. By measuring the spin-polarization of this Auger signal while scanning the photon energy across the O K edge, we can obtain the *spin-resolved* O K XAS spectrum.

The underlying concept of this new type of experiment is illustrated in Fig. 3. This figure shows the O $1s$ core level, the occupied O $2p$ valence band, and the unoccupied Eu $5d-6s$ conduction band. Quotation marks indicate that due to covalent mixing the conduction band also has some O $2p$ character and the valence band some Eu $5d-6s$ character. This mixing allows an x ray to excite an O $1s$ electron to the conduction band, leaving a spin-polarized core hole if the conduction band is spin polarized (middle panel Fig. 3). The subsequent $KL_{23}L_{23}$ Auger decay of the XAS state leads to O($2p^4$) like final states [16], and the outgoing Auger electron will now also be spin-polarized (right panel Fig. 3). Unique to a $KL_{23}L_{23}$ Auger decay is that the entire two-hole final states are of pure singlet (1S and 1D) symmetry since the triplet 3P transitions are forbidden by Auger selection rules [17,18]. This implies that the O $KL_{23}L_{23}$ Auger electrons will have a degree of spin polarization which is equal to that of the conduction band, but which has an opposite sign due to the singlet character of the Auger transition. Thus, the measurement of the spin

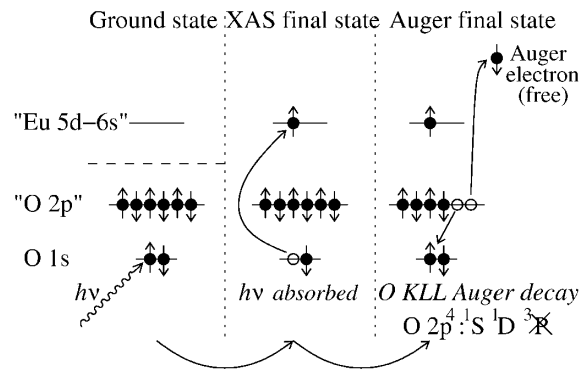


FIG. 3. Mechanism of spin-resolved x-ray absorption spectroscopy. The spin of the outgoing O $KL_{23}L_{23}$ Auger electron is opposite to the spin of the electron that is excited in the x-ray absorption process. This scheme illustrates the observation of a spin-up conduction band state.

of the O $KL_{23}L_{23}$ Auger electrons across the O K edge will reflect the spin polarization of the unoccupied conduction band states. We note that spin-resolved XAS is different from a magnetic circular dichroism (MCD) experiment. In the latter the helicity of the circularly polarized light is varied and the dichroic signal contains a more convoluted information about the spin and the orbital moments of the unoccupied states [19]. We also note that 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 very small amount of material involved is negligibly small, and thus a perturbation of the trajectories of the emitted electrons can be avoided.

As an illustration, we show in Fig. 4 a small selection of the photoelectron spectra which we have taken from the EuO valence band and the O $KL_{23}L_{23}$ Auger as a function of photon energy at $T = 20$ K. The left panel displays the unpolarized spectra, while the right panel gives the difference spectra between the spin-up and spin-down channels (the spin-up direction is parallel to the magnetization direction). We can clearly distinguish the narrow Eu $4f^7 \rightarrow 4f^6$ photoemission (PES) peak in the valence band spectrum [20,21], and observe that its spin polarization is about 50%, indicating that the remanent magnetization of the EuO films at this temperature is only half of the saturation magnetization. This remanence is confirmed by analyzing the magnetic circular dichroism measurements at the Eu M_{45} ($3d \rightarrow 4f$) photoabsorption edges and is comparable to magnetization measurements on EuO films [22].

It is interesting to see the strong photon energy dependence of the magnitude and spin-difference of the O $KL_{23}L_{23}$ Auger. By measuring these spin-resolved O $KL_{23}L_{23}$ Auger spectra across the entire O K edge region with closely spaced photon energy intervals, we can construct an accurate spin-resolved O K XAS spectrum of EuO. The results are shown in the top panel of Fig. 5.

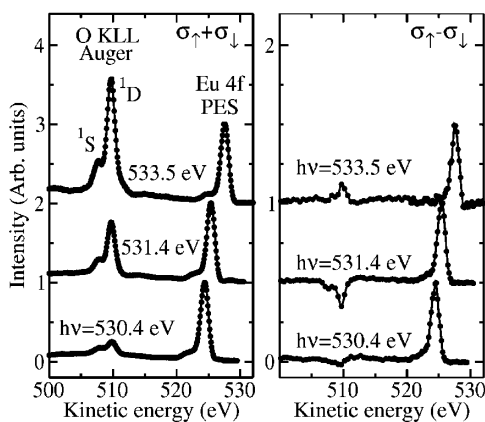


FIG. 4. Left panel: spin-integrated valence band photoemission and O $KL_{23}L_{23}$ Auger spectra of EuO. Right panel: difference spectra between the spin-up and spin-down channels for the valence band and O $KL_{23}L_{23}$ Auger.

Here a normalization for full sample magnetization has been made using the measured spin polarization of the Eu $4f$. We observe an almost rigid splitting between the spin-up and spin-down peaks near the bottom of the conduction band, which is as large as 0.6 eV. Extrapolation of the data strongly suggests a very high spin polarization at the bottom of the band. It is also interesting to note that the spin-polarized features at 536.0 and 536.8 eV correspond with features in the low temperature XAS scan of Fig. 2, and that above T_c these peaks seem to merge into one feature at 536.4 eV, indicating that the changes in the density of states below T_c can indeed largely be attributed to a spin-splitting, which is a shift of the spin-up band to lower energy and the spin-down band to higher energy. However, at higher energies the spin behavior seems to be less simple: the spin-up feature at 540.7 eV, for example, does not seem to have a spin-down counterpart, possibly due to the near presence of the $4f^7 \rightarrow 4f^8$ electron addition peak in the conduction band. To strengthen our understanding of the experimental findings, we have also carried out band structure calculations in the local spin density approximation including the on site Hubbard U (LSDA + U) [23]

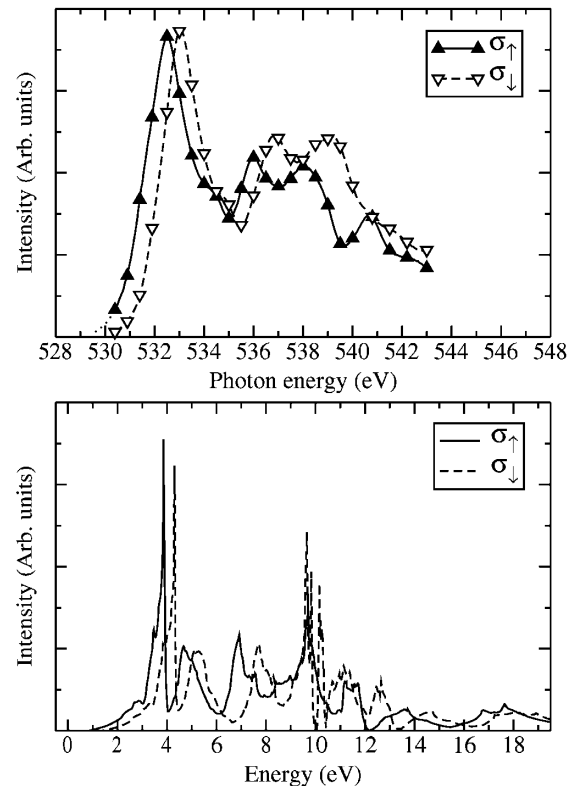


FIG. 5. Top panel: spin-resolved O K x-ray absorption spectrum of EuO taken at 20 K. Bottom panel: spin-resolved unoccupied O $2p$ partial density of states from LSDA + U calculations ($U = 7.0$ eV). The zero of energy corresponds to the top of the valence band. For comparison: the difference between the O $1s$ XPS onset and the valence band onset is 528.5 ± 0.5 eV. The O $1s$ XPS onset is taken as being 1 eV below the peak value.

for EuO in the ferromagnetic state. The bottom panel of Fig. 5 displays the results for the spin-resolved unoccupied O $2p$ partial density of states. The agreement between this mean-field theory and the experiment is remarkable: the approximate position and spin-splitting of most peaks is well reproduced, including the more intricate features that arise at about 10 eV above the Fermi level which are associated with the unoccupied $4f$ states. Recently we have become aware of calculations that obtain results similar to ours [24,25]. When comparing XAS with band structure calculations it should be noted that the interaction between the core hole and the conduction band electron can in principle lead to excitonic effects in the XAS spectra. However these effects generally lead to sharp white lines which we do not observe here. Moreover, because the core hole is on the oxygen atom while the conduction band consists of Eu orbitals, the interaction with an O $1s$ core hole is so small as compared to the $5d$ bandwidth that its effect will be negligible. This conclusion is also based on a vast amount of data on the O K edge XAS of transition metal oxides.

These experimental results clearly demonstrate that the large changes observed in the conduction band structure below T_c in Fig. 2 are caused by a spin-splitting. We attribute this splitting to the direct exchange interaction between the localized $4f$ moments and the delocalized $5d$ - $6s$ conduction band states. We note that these measurements suggest that the redshift of the optical absorption edge is also due to this spin-splitting rather than to a broadening of the conduction band. These results support the following picture for the metal-insulator transition in Eu-rich EuO [3]. Above T_c , defect or impurity states 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 defect states into the conduction band. Below T_c , the conduction band splits due to the exchange interactions, and the defect states now fall into the conduction band. The electrons of these defects can then propagate in the spin-polarized bottom of the conduction band without needing any activation energy, and the system behaves like a metal. As we estimate the depolarization of the conduction band due to spin-orbit coupling ($\xi_{5d} = 0.067$ eV) to be small (less than 5%), we expect the doped charge carriers in ferromagnetic EuO to be almost fully spin polarized, an observation that is very interesting for fundamental research projects in the field of spintronics.

To conclude, our experiments have revealed large changes in the conduction band states of EuO if the temperature is varied across T_c . Using new spin-resolved measurements we have shown that these changes are caused by a splitting between the spin-up and spin-down unoccupied density of states. This exchange splitting is appreciable, about 0.6 eV. From this we conclude that electron doped EuO in the ferromagnetic state will have charge carriers with an almost 100% spin polarization.

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