Magnetic circular dichroism in the $2p4d$ x-ray emission of EuO

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Magnetic circular dichroism is observed for ferromagnetic EuO ($T_C = 69$ K) in the $\beta_{2,15}$ fluorescence at incident photon energies resonant with the $2p_{3/2}$ excitation. The dichroism is dominated by exchange interaction between the localized $4f$ electrons and the final state $4d$ core hole. The spectral shapes obtained by atomic multiplet calculations for the $2p4d$ emission show good agreement with the experimental data.

I. INTRODUCTION

Due to the advantages of intense synchrotron radiation sources and the possibility of generating circularly polarized x rays with modern insertion devices, techniques like resonant inelastic x-ray scattering (RIXS) have become an important tool to study the electronic and magnetic structure of ferromagnetic and ferrimagnetic materials. Experimental work has been done in this field for Fe ($L_{2,3}$ fluorescence),[1,2] Fe, Co, and Ni ($L_{2,3}$ x-ray emission),[3] and for the rare earth element gadolinium ($L\alpha$ and $L\beta$ x-ray emission).[4] It is well known that the elements of the rare earth group show strange behavior in magnetic circular dichroism[5] (MCD) caused by the strong exchange interactions between the $4f$ electrons and the investigated final state of the electron system. Due to the strong spin polarization of the half-filled $4f$ shell it is possible to use these electrons as an internal spin reference. This reference is utilized to probe the spin polarization of unoccupied states in the following way. Knowing the spin orientation of the $4d^9$ multiplets with respect to the $4f$ spin reference, one can get information about the spin orientation of the unoccupied $5d$ band, when a $2p_{3/2} \rightarrow 5d^1$ transition is excited resonantly and the $4d^{10} \rightarrow 2p_{3/2}$ reemission is investigated. In this report we show first that RIXS combined with the use of circular polarized x rays allows one to get the desired information about the spin polarization of the $4d$ core level electrons. This creates an alternative to circularly excited x-ray photoemission spectroscopy (XPS), where experiments have been performed on Gd $4d$ and $4f$ photoemission.[5,6]

Theoretical models/calculations of RIXS spectra for rare earth systems have to take into account that resonant x-ray emission is a two-photon process, implying an initial, an intermediate, and a final state with different transition probabilities and selection rules for the absorption and the emission process.[7] This results in emission lines that are often split into huge multiplet families (for XPS spectra also).[8] Therefore, the use of atomic multiplet calculations for x-ray core emission spectra is a suitable method to describe the observed features of the experimental spectra.[9–11] We want to present another example of the strong circular dichroism in the x-ray emission of rare earth systems and the power of theoretical multiplet calculation for the interpretation of these emission spectra, as already shown for gadolinium metal[11] and the trivalent Nd^{3+}, Gd^{3+}, and Dy^{3+}.[12]

II. EXPERIMENT

In our experiment we studied magnetically aligned EuO below its Curie temperature. The electron configuration of Eu^{2+} is $[Xe]4f^7$. Excitations from the $2p^6 4d^{10} 4f^7$ ground state to the $2p^5 4d^{10} 4f^7 \varepsilon_d$ intermediate state were produced by setting the incident x-ray energy well above the L_{III} absorption edge (6978 eV). The observed deexcitation was the $L\beta_{2,15}$ emission, which results in a $2p^6 4d^9 4f^7 \varepsilon_d$ final state.

The experiment was performed on the beamline G 3 at the Hamburger Synchrotronstrahlungslabor HASYLAB using the off-plane emission of a bending magnet to obtain partially circularly polarized x rays. Monte Carlo simulations estimate a degree of circular polarization of 0.7 for the parameters used: 2 mm beam height and 2 mm vertical offset to the orbital plane of the storage ring.[13,14] The x rays were monochromatized by a germanium (311) double crystal, and the Bragg angle for the required energy degrades the degree of circular polarization by an additional factor of 0.4 due to the semiempirical relation

$$P_{deg} = \frac{4\cos^2 2\theta}{(1+\cos 2\theta)^2}. \tag{1}$$

The scattering angle was 90° and the incident angle between beam and sample surface 35°, to get the best compromise between self-absorption effects and usable sample size. The incident angle attenuates the coupling between the magnetic moments of the sample and the photon spin by a factor of 0.84, so that finally the effective degree of circular polarization was about 23%. The scattered radiation was analyzed in the horizontal plane by a Rowland circle spectrometer,[16] equipped with a spherically bent silicon analyzer crystal with bending radius $R = 1$ m and using an asymmetric (531) reflection of the (111) wafer surface. The achieved overall resolution was about 1.4 eV. The required magnetic field was aligned parallel to the sample surface and created by a permanent magnet structure with a homogeneous field of 0.9 T in the center of its bore hole. A continuous flow cryostat cooled the sample down to a temperature of 30 K. The speci-

men had an area of 7×4 mm^2 and was a 2 mm thick slice of polycrystalline EuO, which was prepared by a melting process according to the chemical reaction $Eu_2O_3 + Eu \rightarrow 3\,EuO$. Our specimen was characterized by x-ray diffraction and by magnetization measurements. $M(H)$ scans resulted in a saturation magnetization of 22 kOe, which is near the value of 24.1 kOe reported in the literature.[15] $M(T)$ curves showed a Curie temperature of 69.5 K. The application of a position sensitive proportional gas counter as detector and the beam width of 5 mm make it possible to analyze an energy range of about 7 eV (projected on the Rowland circle) simultaneously, so that the scanning steps of the spectrometer could be increased and the recording time of one single spectrum decreased to a typical time of 7 min. To exclude artifacts and spurious effects, the magnetic field orientation was reversed after every scanning step of the spectrometer and the photon helicity was changed after every scan.

III. CALCULATIONS

The theoretical calculations made for the $2p4d$ emission are based on an atomic model, which only includes the seven unpaired $4f$ electrons in their ground state ^8S.[17]

The $2p$ photoemission process can be described as $4f^7(^8S)\rightarrow 2p^5 4f^7(^8S)\varepsilon_d$. More than 99.9% of the intensity goes to the intermediate states that have their $4f$ electrons still in the ^8S symmetry. Because of this, there is no possibility for interference effects in the intermediate state. This also implies that a two-step formalism can be used and the calculated signal is given by the product of x-ray absorption and x-ray emission intensities. The $2p_{3/2}4d$ x-ray emission spectral shape can be calculated from the dipole transitions of $2p^5 4f^7$ to $4d^9 4f^7$. Whereas in the intermediate state the $4f$ electrons keep their ^8S symmetry, in the final state the strong interactions with the $4d$ states completely mix the ''pure'' $4f$ symmetries.

The $2p4d$ x-ray emission spectra reflect the large $4f4f$ interactions (F^2_{ff} is equal to 11.4 eV) and the large $4d4f$ exchange interactions (G^1_{df} is equal to 15.1 eV). The $4d$ spin-orbit interaction (2.00 eV) and the $4f$ spin-orbit interaction (0.18 eV) are much smaller. The $2p_{3/2}4d$ spectrum of Fig. 1(b) shows six ^8S-related sticks between 6840 and 6845 eV, split by the $4d$ spin-orbit coupling. The MCD theoretical signal is obtained by adding the four intermediate states of the $2p_{3/2}$ state according to their spin polarization.[11] This automatically implies that the integral of the MCD over the $2p_{3/2}4d$ edge is exactly zero (because the $2p_{3/2}$ core level is not spin polarized). Note that we are closer to LS coupling than to jj coupling and it is more appropriate to speak about $4d$ spin down and $4d$ spin up (instead of $4d_{5/2}$ and $4d_{3/2}$) for the main peak and the satellite. Due to the definition of the positive quantization axis as parallel to the magnetic moments, spin down is assigned to a spin orientation parallel to the spin of the $4f$ electrons (majority spin orientation). In Fig. 2(a) it can be seen that the latter contains mostly negative sticks, but at the low energy side some positive sticks are visible. In other words the satellite is not 100% spin polarized. The spectrum is convoluted with the lifetime broadening of the $2p$ core hole [5 eV full width at half maximum (FWHM)] and the experimental resolution of a Gaussian (1.5 eV FWHM). It is noted that the calculation is in complete analogy with the Gd metal $2p4d$ emission data,[11] with only the values of the atomic parameters being different.

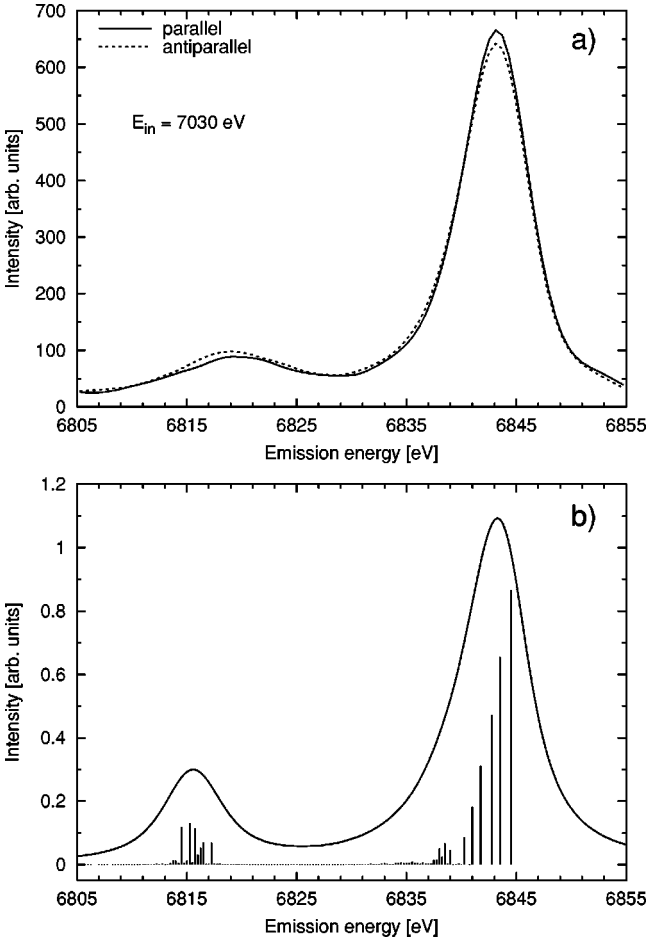

FIG. 1. Experimental (a) and calculated (b) resonant inelastic x-ray scattering spectra of EuO. The two experimental curves were recorded at an excitation energy of 7030 eV with parallel orientation (solid line) between the photon helicity and sample magnetization, and antiparallel orientation (dashed line), respectively. Both spectra were normalized to the incident photon intensity and smoothed by cubic splines. The calculated $2p_{3/2}4d$ x-ray emission spectral shape (b) is obtained by convolution of the transition probabilities (sticks) with a Gaussian (1.5 eV FWHM) and a Lorentzian (5.0 eV FWHM).

IV. DISCUSSION

The measured emission spectra [Fig. 1(a)] show two main features, namely, a peak at the position of the well known $\beta_{2,15}$ fluorescence at 6843.2 eV and a broader satellite 23 eV below the main peak, in analogy to the observations made for the Gd $L\beta_{2,15}$ emission.[4]

The experimental dichroic signal is obtained by adding spectra with the orientation of photon helicity parallel to the sample magnetization and then subtracting the spectra obtained with the orientation of helicity antiparallel to the sample magnetization (parallel minus antiparallel). The experimental MCD is rescaled to the calculated values at the

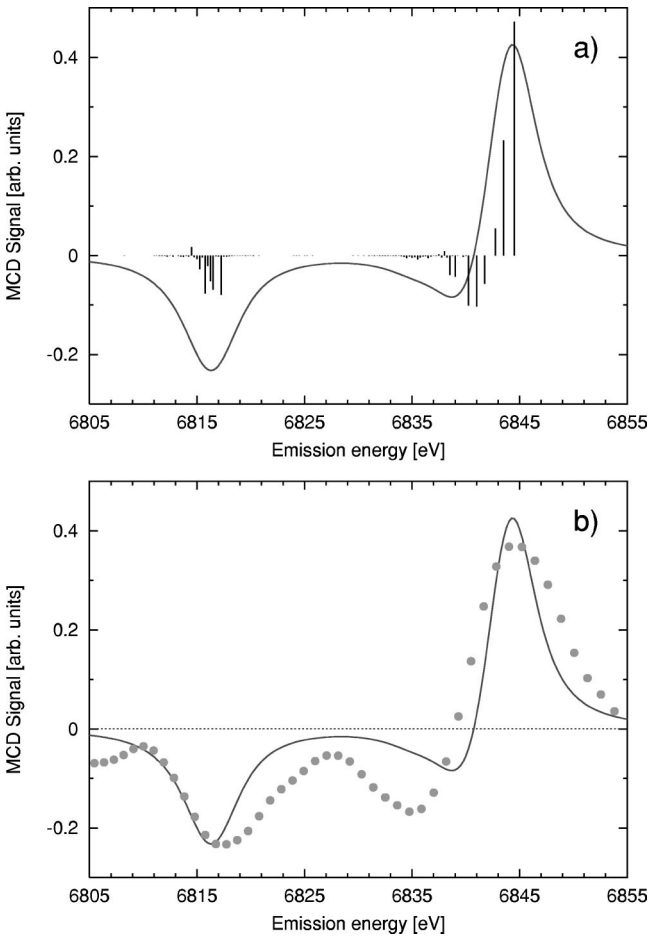

FIG. 2. (a) Corresponding MCD of the $2p_{3/2}4d$ x-ray emission of Fig. 1(b). (b) Comparison of the calculated dichroic signal (solid line and sticks) and the experimental results (dots). The experimental curve is the difference of the two spectra in Fig. 1(a) (parallel minus antiparallel orientation), smoothed by cubic splines and normalized to the calculated MCD signal.

peak position of the main line and smoothed by fitting with cubic spline functions, finally. Figure 2(b) shows the experimental results compared to the calculated MCD signal.

From the analysis given above, we conclude that configurations of the $4d$ electrons with spin orientation mostly parallel to the spin of the $4f$ electrons (majority spin orientation) lead to the line at 6843.2 eV and configurations of the $4d$ electrons with spin orientation antiparallel to the $4f$ (minority spin orientation) result in the line at 6820 eV. Since the spin orientation of the excited photoelectron from the $2p_{3/2}$ level is directly related to the spin of the $4d$ electron in the emission process, provided that no spin flip occurs, the intensity of the emission line with dominantly spin-down character at 6843.2 eV (spin-up character at 6820 eV) depends on the transition probability of the $2p_{3/2}$ electron into unoccupied states for different spin orientations. Due to this fact, modifications in the dichroic signal are expected when the $2p$ core electron is excited resonantly into unoccupied $5d$ states due to the influence of the spin character of the corresponding $5d$ band.[18,19] Those features are observed in the Gd case.[4] Here only measurements with excitations of the $2p_{3/2}$ photoelectron far above the $5d$ density of states were made. It is expected that resonant excitation of the EuO $2p_{3/2}$ level will yield a larger change of the spectral shape than in the case of Gd, because of the stronger white line in the absorption edge.[20]

The difference between the energy position of the satellite in experiment and in theory (which can be slightly seen in Fig. 1) is explained in the following way. The distance between the main peak and the satellite is essentially given by the $4d4f$ exchange splitting. This exchange splitting is described with the G^1, G^3, and G^5 Slater integrals. It can be observed that the exchange splitting is approximately 27 eV in the calculations and about 23 eV in experiment. This implies that the $4d4f$ Slater integrals are only some 85% of their atomic values. As noted above, the atomic Slater integrals are approximated as 80% of the theoretical Hartree-Fock values. This implies that instead of an 80% reduction, a 67% reduction must be used to move the satellite to the correct position. This result is in line with the result for Gd and also with the photoemission results for several rare earths.[8] An additional effect is that the satellite is much broader than the main line. This is a well known effect and is caused by the additional lifetime broadening of the satellite structure due to extra Auger decay channels.[8]

V. CONCLUSION

In conclusion, we have shown that a strong dichroism in the EuO $L\beta_{2,15}$ emission is visible, even observable with a poor degree of circularly polarized photon beam, of which the main features are very similar to the observations made for the rare earth element Gd, due to its electron configuration $[\mathrm{Xe}]4f^7 5d^1 6s^2$ which is related to Eu^{2+}. Atomic multiplet calculations were confirmed as a suitable tool to describe the RIXS processes and the theoretical results obtained for the EuO case show good agreement with the experimental data.

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