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Sulphur K-edge x-ray absorption fine-structure studies of EuS and GdS

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Abstract. High-resolution sulphur K-edge x-ray absorption near-edge structure spectra have been recorded for europium and gadolinium monosulphides. A comparison of the experimental spectra with the element-projected partial density of unoccupied states calculated using a spin-polarized linear muffin-tin orbital method revealed a rather good agreement. Our analysis suggests that there is a strong hybridization of the 4f and 5d orbitals of the rare earths with the p orbitals of the sulphur which also contribute to the conduction band. The strong d–p and f–p interactions result in a large sulphur p-band polarization which has been confirmed experimentally by the detection of a strong x-ray magnetic circular dichroism signal at the S K edge in EuS.

1. Introduction

The europium and gadolinium monosulphides (EuS and GdS) are well-known model compounds as regards studying magnetism in solids [1]. Despite the fact that the two chalcogenides crystallize in the same fcc rock-salt structure and the rare-earth ions have identical $4f^7$ configurations, their magnetic and electronic properties are surprisingly different. EuS is a ferromagnetic semiconductor with $T_C = 16.57$ K [2], whereas GdS is metallic and exhibits antiferromagnetic order of the second kind below $T_N = 57$ K [3]. Their magnetism is caused by spin-only 4f magnetic moments ($7\mu_B$) which are strongly localized on the rare-earth ions. The magnetic properties of these compounds are usually considered to result from a competition between two types of interaction: an indirect ferromagnetic exchange via 5d conduction bands and an antiferromagnetic cation–anion–cation superexchange [4]. The following picture emerges: superexchange strongly dominates in GdS and gives rise to antiferromagnetic ordering, while indirect exchange via 5d states is a driving force of the ferromagnetism in EuS. Since the superexchange mechanism assumes some hybridization of the 5d (4f) states of the rare earth with the 3p states of the sulphur, one would expect in GdS more extensive admixture of the rare-earth states into the valence band as well as admixture of the sulphur p states into the conduction band. Such an increase of the interatomic overlap would not be surprising since the lattice constant of GdS (5.56 Å) is smaller than that of EuS (5.96 Å). To investigate the changes in the electronic structure of unoccupied states projected on the sulphur site we tried to compare the x-ray absorption near-edge structure (XANES) spectra of EuS and GdS at the S K edge. According to the electric dipole selection rule, these spectra directly probe the unoccupied density of states with p symmetry. Even though the S

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K-edge XANES spectra have already been measured for a series of rare-earth monosulphides [5], poor instrumental resolution prevented the authors from drawing any reliable conclusions. On the other hand, the sulphur p states in the conduction band have a fairly delocalized nature and therefore the one-electron energy band model is in principle valid. This encouraged us to calculate the element-projected conduction band density of states using a spin-polarized LMTO method and to compare the results with our experimental XANES spectra.

There is an additional point which deserves more attention. Recent spin-polarized extended x-ray absorption fine-structure (EXAFS) experiments [6] gave us a very strong indication that the sulphur anion should carry a magnetic moment in ferromagnetic EuS. Later, similar conclusions but reached in a more indirect way were also drawn from neutron diffraction studies under high pressure [7]. These results suggest that the anion valent p electrons are involved in the ferromagnetic interaction in EuS via a polarization exchange mechanism as predicted a long time ago [8]. Unfortunately, this mechanism has never been confirmed experimentally, although it is often cited to explain the magnetic properties of semiconductor spin glasses [9] and semimagnetic semiconductors [10]. We will show below that x-ray magnetic circular dichroism (XMCD) spectra recorded for the first time at the sulphur K edge confirm the strong spin polarization of the anion p band in EuS.

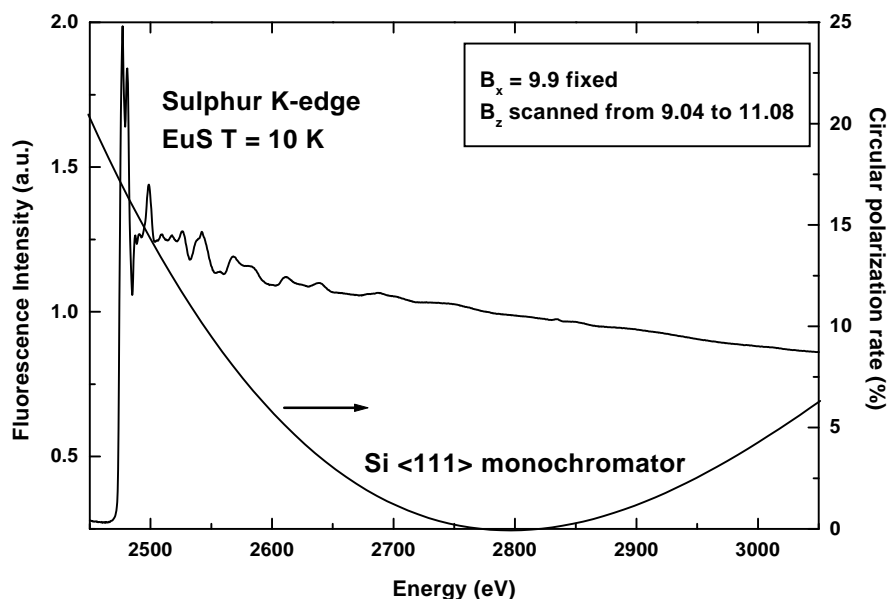


Figure 1. The polarization transfer function of the Si(111) monochromator and the sulphur K-edge EXAFS spectrum of EuS recorded using the undulator gap-scan technique.

2. Experimental procedure

The experiments were performed at the ESRF beamline ID12A [11]. Elliptically polarized x-rays were generated with a helical undulator, Helios-II, that makes it possible to flip the photon helicity. The double-crystal fixed-exit monochromator was equipped with a pair of Si(111) crystals cooled down to -140 °C. Given the ultra-low emittance of the source, we checked that the energy resolution was close to the theoretical limit: 0.35 eV at the sulphur

K edge. Higher-order harmonics were very efficiently cut off by two SiC mirrors operated at an angle of incidence of 8 mrad. Since the mirrors are located upstream with respect to the monochromator, the heat load on the first crystal is strongly reduced and this improves the stability of our experiments. This is of crucial importance for XMCD experiments at the sulphur K edge since the expected signal is very small because the circular polarization rate of the x-ray beam does not exceed 18% due to the poor polarization transfer function of the monochromator for a Bragg angle of $\simeq 52^\circ$. The calculated circular polarization transfer function of the Si(111) monochromator is shown in figure 1 together with a sulphur K-edge EXAFS spectrum of EuS recorded using the recently developed undulator gap-scan technique [12].

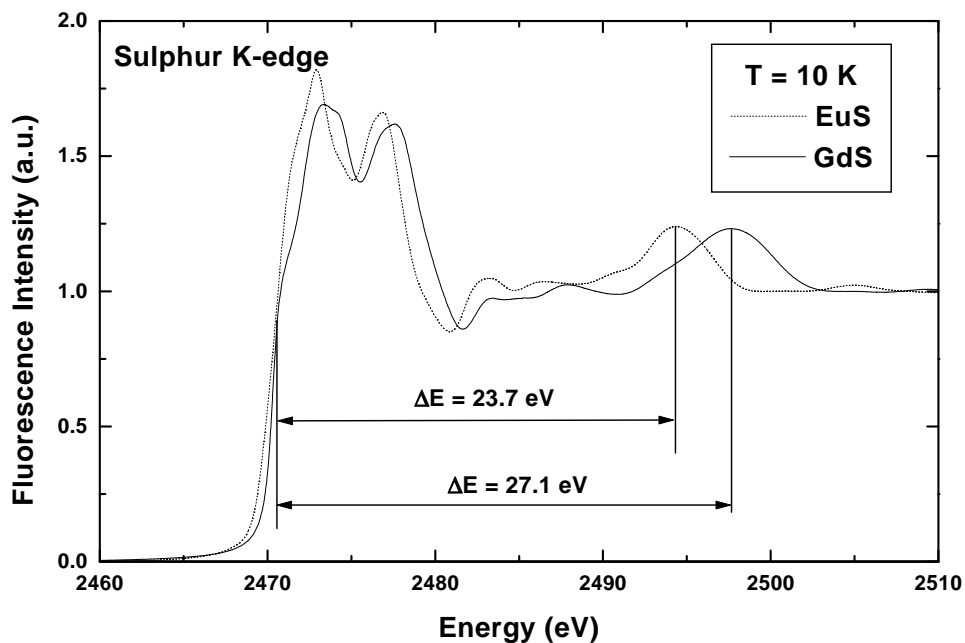


Figure 2. Normalized sulphur K-edge XANES spectra of polycrystalline EuS and GdS single crystals recorded at 10 K.

Polycrystalline EuS powder (purity grade: 99.9%) was purchased from Cerac Incorporated. Fine particles were mixed with boron nitride powder in order to increase the thermal conductivity and were pressed into pellets. We used a GdS single crystal with a cubic shape, $5 \times 5 \times 5 \text{ mm}^3$. The samples were mounted on the cold finger of the helium cryostat located in the bore of a superconducting electromagnet. All of the measurements were performed at $T = 10 \text{ K}$. During the XMCD experiments, a magnetic field of 1.5 T was applied parallel to the direction of the x-ray beam propagation to align the magnetic moments.

The spectra were recorded in the total-fluorescence-yield mode. The detector was a Si photodiode located inside the radiation shield of the magnet at 90° with respect to the incident beam. Since the x-ray beam was chopped at $f_0 \sim 67 \text{ Hz}$, a digital lock-in allowed us to get rid of low-frequency drifts. The experimental XANES spectra were systematically corrected for self-absorption using a homographic transform described elsewhere [13]. The XMCD spectra displayed below are differences between consecutive scans run with opposite photon helicity. Of course, in order to check that our spectra were free of artefacts, XMCD spectra were also recorded with the opposite direction of the magnetic field.

3. Results and discussion

We have compared in figure 2 the sulphur K-edge XANES spectra of EuS and GdS recorded at 10 K and corrected for self-absorption. Since the spectra were collected consecutively, there is no ambiguity as regards the energy scale. For the sake of comparison, the XANES spectra were systematically renormalized with respect to the edge jump. As illustrated by figure 2, there is a striking similarity between the sulphur K-edge XANES spectra of EuS and GdS, but with small relative energy shifts of the maxima. Keeping in mind that the two compounds have different lattice parameters, we tried to correlate the relative positions of the shape resonance according to Natoli's rule: $\Delta E \times R^2 = \text{constant}$ [14], where ΔE is the energy position of the shape resonance peak and R is the radius of the first-neighbour shell. Typically, shape resonance peaks were found for EuS and GdS at $\Delta E_{\text{EuS}} = 23.7$ eV and $\Delta E_{\text{GdS}} = 27.1$ eV above the absorption edge, respectively. Note that the ratio $(\Delta E \times R^2)_{\text{EuS}}/(\Delta E \times R^2)_{\text{GdS}}$ is within 0.5% equal to unity.

The sulphur K-edge XANES spectra are dominated by a quite intense white line which exhibits a well-resolved double-peak structure for both EuS and GdS. The splittings of the white line are nearly the same for the two compounds (3.8 eV). A very similar structure has been also reported for a $\text{Sm}_{0.82}\text{Gd}_{0.18}\text{S}$ solid solution [15]. The presence of a white line indicates that there is a large density of sulphur p states at the bottom of the conduction band. The fact that the intensities of the white lines are about the same for the two compounds suggests that there is very little change in the density of sulphur p states in the conduction band between EuS and GdS. This is exactly opposite to what one would expect from the classical description of magnetic interactions in these compounds. The only noticeable difference between the S K XANES spectra of the two compounds is a much sharper absorption edge for GdS and a more prominent shoulder at the edge. This result led us to the conclusion that the change of conductivity between EuS and GdS does not affect the electronic structure at the sulphur anion and is entirely correlated with the change of population of the 5d states of the rare earth. Photoemission data [16] and optical reflectivity studies [17] have shown that in EuS 4f electrons form a quite narrow band which is located just at the top of the valence band, and one observes a pronounced crystal-field splitting of the empty 5d conduction band (~ 2.2 eV), whereas in GdS the occupied 4f states are of the order of 10 eV below the Fermi level where there is a maximum of the 5d density of states. The conduction electrons are thus screening the crystal-field splitting of the 5d band.

In order to elucidate the origin of the white line and its well-resolved structure in the XANES spectra, we have performed spin-polarized band-structure calculations for the ferromagnetic EuS by means of the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation. We used the TB-LMTO code developed by Andersen and Jepsen [18]. Since the crystal structure of EuS ($Fm\bar{3}m$, $a = 5.96$ Å) is relatively open, we had to introduce two empty spheres in the unit cell to obtain a good convergence in the calculations. In order to get an accurate density of states, 897 k -points in the irreducible part of the Brillouin zone have been used. The results of our band-structure calculations were found to agree qualitatively with those obtained previously using a spin-polarized augmented-plane-wave (APW) method [19]. We have reproduced in figure 3 the local density of unoccupied states (the DOS per unit cell and per eV) of the projected d and f symmetries in the Eu and p symmetry in the S Wigner-Seitz spheres. Note that the sulphur 3p density of states is multiplied by a factor 20. The Fermi level was chosen to be located in the low-energy tail of the XANES spectrum (at $E = 2469.3$ eV).

The structure of the sulphur 3p density of states reproduces nicely the features observed in the XANES spectrum. The double-peak structure and the shoulder at the edge are clearly

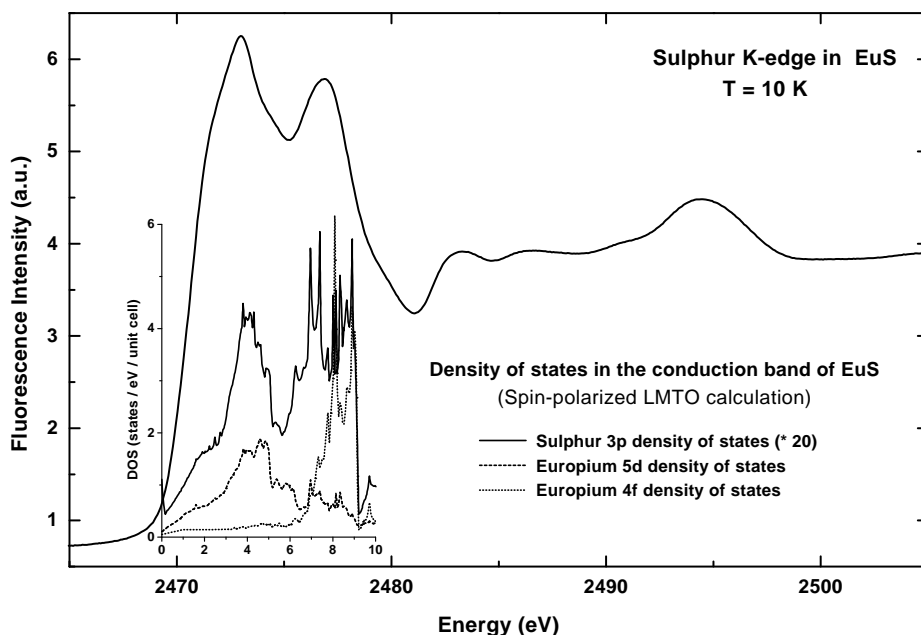


Figure 3. The density of electronic states above the Fermi level and the sulphur K-edge XANES spectrum of ferromagnetic EuS.

present in the p-projected density of states. Moreover, the total width of the white line exactly coincides with the overall width of the sulphur p states in the conduction band which is mainly formed by the 5d and 4f states of Eu. The most significant result as regards the conduction band is a strong hybridization of the 3p states of sulphur with the 5d states of Eu (the first peak of the white line and the shoulder) and with the 4f empty states of Eu (the second peak of the white line). Thus, there are strong cation–anion 4f–3p and 5d–3p interactions in EuS.

We expect these interactions to induce a spin polarization of the S p band and to promote a polarization exchange coupling between the Eu moments via the polarized shells of anions. This is fully supported by sulphur K-edge XMCD experiments on ferromagnetic EuS. Such experiments were challenging because the circular polarization rate of the incident x-ray beam was very poor. Nevertheless, the measured XMCD signal, with a peak amplitude of less than 0.2%, is not ambiguous, as reflected by the nearly perfect inversion of the signal when the direction of the magnetic field is reversed (figure 4). If one takes into account the polarization transfer function of the monochromator, the corrected amplitude of the XMCD signal becomes huge: about 1% compared to any other XMCD results at the K edges. Unfortunately, a quantitative interpretation of K-edge XMCD spectra is not yet possible, since there is no reliable theory; nevertheless, the observed signal is to be ascribed to a strong spin–orbit coupling in the sulphur 3p final state in EuS. These results give a very strong indication of the spin polarization of the 3p states of sulphur in ferromagnetic EuS, as a consequence of the cation–anion 4f–3p and 5d–3p interactions predicted by our band-structure calculations.

Given the fact that the sulphur K-edge XANES spectra are very similar for the two compounds, one would expect the sulphur 3p states to also be polarized in GdS. Unfortunately, the antiferromagnetic ordering in GdS makes XMCD measurements impossible and, hence, the use of another technique (e.g. x-ray magnetic linear dichroism) has to be envisaged in order to study the polarization of the valence electrons in such an antiferromagnet.

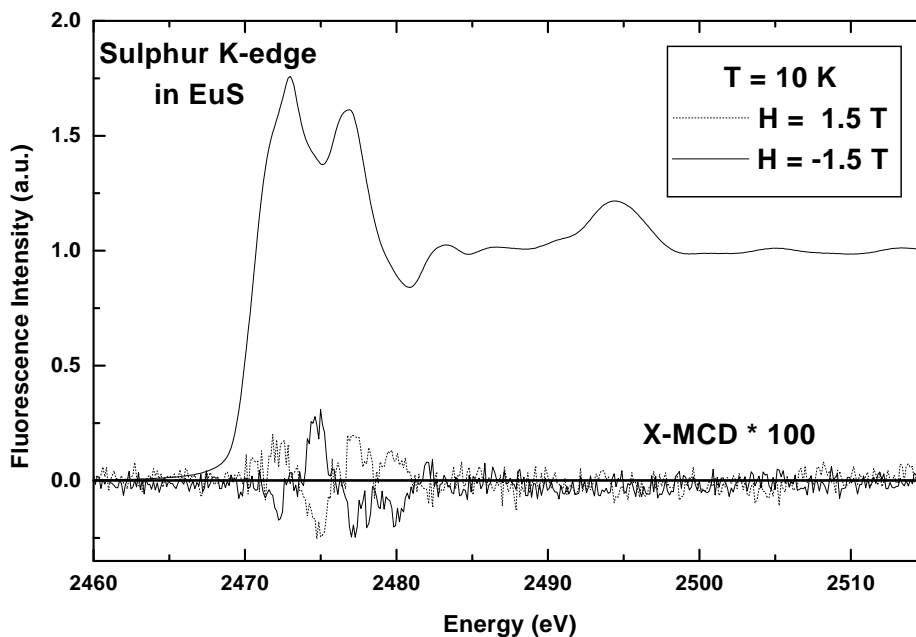


Figure 4. XMCD spectra of EuS recorded for two opposite orientations of the magnetic field.

4. Conclusions

We have performed a comparative study of the XANES spectra recorded at the sulphur K edge for EuS and GdS. The presence of the strong white line is clearly indicative of a large density of unoccupied p states for the S anion. The comparison with spin-polarized band-structure calculations for EuS suggests that the splitting of the white line at the sulphur K edge is related to the anion–cation 3p–5d and 3p–4f hybridizations. These hybridizations result in a strong spin polarization of the sulphur 3p band, which is confirmed by XMCD spectra recorded for the first time at the sulphur K edge.

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