

Full multiple scattering analysis of X-ray absorption near edge structure at the Eu L₃-edge in EuO

Alexei Kuzmin^{a,*}, J. Purans^{a,b}, G. Moreau^c

^a Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063 Riga, Latvia

^b Dipartimento di Fisica, dell'Università di Trento, I-38050 Povo (Trento), Italy

^c Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

Abstract

X-ray absorption near edge structure (XANES) at the Eu L₃-edge in crystalline EuO is interpreted within full multiple scattering (FMS) formalism. Our theoretical results, based on the ab initio self-consistent (SC) potential calculations, are in good agreement with experimental data. The main features in the experimental signal are reproduced taking into account a cluster of about five coordination shells, centred at the europium atom and having EuO structure. An addition of more distant coordination shells makes features only better resolved. The relatively high intensity of the peak, located just above the Eu L₃-edge, indicates that 5d states are well localised. Comparative analysis with the O K-edge XANES suggests that Eu 5d states are strongly mixed with O 2p states.
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1. Introduction

Europium oxide EuO is a ferromagnetic semiconductor with the Curie temperature $T_C = 69.15$ K [1]. It has the rock-salt-type (fcc) crystal structure with a lattice parameter $a_0 = 5.1439$ Å [2]. According to the augmented-plane-wave (APW) theoretical calculations [3], the empty Eu 5d conduction band in EuO is separated from the filled O 2p states by about 3.1 eV. The top of the valence band is formed by the localized half-filled 4f states, located in the band gap at 1.14 eV below the 5d band bottom. The Eu 5d band is split by the crystal field into t_{2g} and e_g sub-bands separated by $10Dq \sim 2.50$ eV [3].

The magnetic ordering in EuO is determined by the nearest-neighbour (NN) and next-nearest-neighbour (NNN) superexchange $\text{Eu}^{2+}-\text{O}^{2-}-\text{Eu}^{2+}$ interactions [4], which strongly affect the 4f–5d gap and are responsible for the 0.27 eV red shift of the optical absorption edge occurring below T_C [5]. The exchange coupling of itinerant electrons to localized magnetic moments is currently described within the so-called s–f exchange model [6]. While the

purely magnetic properties of EuO are due to the localized 4f-electrons, the conductivity properties are determined by the quasi-free electrons in rather broad (5d, 6s) conduction bands. In particular, EuO has an insulator-to-metal transition below 50 K, resulting in a 13 orders-of-magnitude increase in the conductivity [7]. The electronic structure of EuO also shows remarkable size [8], thickness [9] and pressure [10] dependence.

X-ray absorption spectroscopy (XAS) is well suitable tool to study the local atomic and empty-states electronic structure of europium oxide [11–14]. The big advantage of XAS is possibility to probe the electronic-states with required angular momentum by the appropriate choice of an absorption edge. In [11] the width of the first main peak in the Eu L₃-edge absorption spectrum was analysed in a number of solid solutions, and it was concluded that Eu 5d states remain atomic-like and do not form a delocalised band. More recent works on EuO, related to the high-pressure XAS studies at the Eu L₃-edge [12] and to the X-ray magnetic circular dichroism [13] and spin-resolved X-ray absorption [14] measurements at the O K-edge, provided mostly with qualitative interpretation of X-ray absorption near edge structure (XANES).

In this work we present results of a study of unoccupied-states above the Fermi level in EuO by XAS and provide with

* Corresponding author. Fax: +371-7132778.

E-mail address: a.kuzmin@cfi.lu.lv (A. Kuzmin).

quantitative interpretation, based on ab initio full multiple scattering (FMS) approach.

2. Experimental and data analysis

The crystalline sample EuO was finely ground and mechanically mixed with cellulose powder under nitrogen atmosphere to give pressed pellets with thickness chosen to obtain an absorption jump value close to one. To avoid oxidation of Eu^{2+} ions all manipulations were performed under nitrogen atmosphere.

X-ray absorption spectrum of EuO was recorded at the Eu L_3 -edge using synchrotron radiation from the LURE DCI storage ring. A standard transmission scheme at the D21 (XAS-2) beam-line, with a Si(3 1 1) double-crystal monochromator and two ion chambers containing N_2 gas, was used. The experiment was performed at room temperature with an energy resolution of about 2 eV.

The Eu L_3 -edge XANES signals were analysed by a comparison of experimental data with theoretical spectra, calculated by the ab initio relativistic FEFF8 code [15] within the FMS approach. The FEFF8 code [15] implements the one-electron theory, based on a self-consistent (SC) real-space Green's-function formalism and final-state potentials taking into account a screened core-hole. The excitation threshold in the FEFF8 is the Fermi energy E_F , determined from the SC cluster potential by requiring a fixed number of electrons in occupied-states below E_F [15]. The detailed description of the FEFF8 code can be found in [15,16].

The FMS calculations of the Eu L_3 -edge XANES were performed for several cluster sizes, having the structure of crystalline EuO with the lattice parameter $a_0 = 5.1439 \text{ \AA}$ [2]. In Table 1, we present structural parameters (type of atoms, number of atoms, shell radii) for the first eight coordination shells used in the FMS calculations. The scattering cluster potential was approximated by the 11% overlapped muffin-tin (MT) spherical potentials ($R_{\text{MT}}(\text{Eu}) = 1.73 \text{ \AA}$ and $R_{\text{MT}}(\text{O}) = 1.10 \text{ \AA}$) determined following the Norman prescription [15]. The self-consistency was achieved

Table 1
Structure of the eight coordination shells cluster for EuO, based on the lattice parameter $a_0 = 5.1439 \text{ \AA}$ [2]

Coordination shell number	Neighbouring atom	Number of atoms in the coordination shell	Coordination shell radius (\AA)
1	O (Eu)	6	2.572
2	Eu (O)	12	3.637
3	O (Eu)	8	4.455
4	Eu (O)	6	5.144
5	O (Eu)	24	5.751
6	Eu (O)	24	6.300
7	Eu (O)	12	7.275
8	O (Eu)	30	7.716

Atom types without brackets are for the central europium atom; in the brackets, for the central oxygen atom.

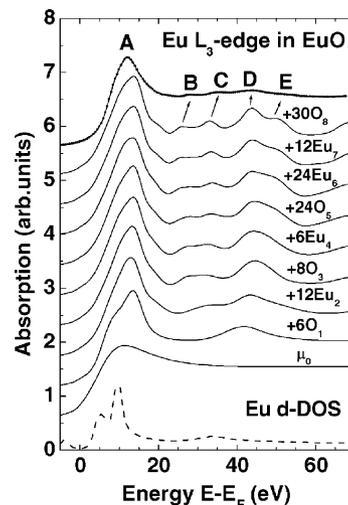


Fig. 1. Comparison of experimental (upper curve) and theoretical XANES of EuO at the Eu L_3 -edge. The theoretical signals were calculated within FMS formalism. The lower dashed curve is the Eu d-projected DOS. The energy scale is relative to the Fermi level E_F . Main features are labelled by letters from A to E.

for the cluster size of 5.5 \AA . The exchange interactions were described by the real energy-dependent Dirac–Hara potential [17]: it does not account for inelastic losses but allows for the better reproduction of the XANES energy scale. The Eu L_3 -edge XANES broadening due to the finite lifetime was accounted through the core-hole level width set to 3.73 eV [18]. The results of the calculations are shown in Fig. 1. Note that due to the final-state in the X-ray absorption process is fully relaxed with a core-hole [15], the partial density of states (DOS) probed by XAS differs from the one in the ground-state band structure calculations [3].

The O K-edge XANES signals were also calculated for comparison using the same approach. The O K-edge core-hole level width was set to 0.16 eV [18]. The position of the Fermi level was placed at 3 eV above the one, predicted from the SC procedure, to get best agreement with the experimental data from [13]. Comparison between our theoretical results and the experimental O K-edge XANES, measured at 10 K in [13], is shown in Fig. 2.

Note that our calculations at both Eu L_3 - and O K-edges do not take into account the thermal disorder and magnetic interaction effects. We expect that possible contribution from both effects is below the accuracy of our FMS calculations. However, temperature dependent studies have to be done in the future to answer this point.

3. Results and discussion

Europium and oxygen absorption edges provide with complementary information. The O K-edge XANES extends up to 25 eV above the Fermi level, thus covering a small part of the energy range available at the Eu L_3 -edge,

which goes up to 70 eV. However, the energy resolution at the O K-edge is significantly better due to much smaller natural core-hole level width. Besides, the two XANES signals allow to probe unoccupied-states with different orbital momentum.

The experimental Eu L₃-edge XANES is shown in Fig. 1 (upper curve). According to the dipole selection rule $\Delta l = \pm 1$ (Δl is the change of the angular momentum of the photoelectron), it is due to transitions from atomic-like Eu 2p_{3/2} state to unoccupied-states with d-character above the Fermi level. Here we neglect transitions to the states with s-character since their contribution is expected to be negligible [19]. Note that the final-state is relaxed in the presence of the Eu 2p core-hole positive charge. Pure atomic absorption, i.e. in the absence of neighbouring atoms, denoted by μ_0 in Fig. 1, is structureless except for the peak A, located just above the edge.

The origin of the peak A is attributed to the quasi-bound final-state with Eu 5d-character, which is split by the octahedral crystal field of oxygen atoms. Although the splitting is not present in the experimental spectrum due to the natural broadening at the Eu L₃-edge, it is well visible in the calculated Eu d-projected DOS (lower dashed curve in Fig. 1), and its amount is about 5 eV. The peak A intensity increases strongly upon an addition of six oxygen atoms O₁, located in the first coordination shell, however, it changes insignificantly upon further increase of the cluster size. Some variation of the peak A profile is due to the interference between many scattering signals, whose number increases upon an increase of the cluster size. The relatively high intensity of the peak A is due to well localized character of europium 5d states [20] and hybridisation between 5d(Eu)- and 2p(O) states. This conclusion is fully supported by the analysis of the O K-edge. Here, the dipole-allowed transitions are from

O 1s core state to unoccupied-states with p-character above the Fermi level. Also in this case, the final-state is relaxed in the presence of the O 1s core-hole, however, the amount of the relaxation is expected to be smaller than for the Eu-edge. In the case of purely ionic Eu²⁺–O²⁻ bonding, the 2p(O) states must be occupied, and the transition 1s → 2p should not be observed. However, this transition is well visible in the experimental [13,14] and calculated O K-edge XANES as the first peak a in Fig. 2. As follows from the FMS calculations, the intensity of the peak a is saturated after addition of two coordination shells, composed of six europium (Eu₁) and 12 oxygen (O₂) atoms.

The origin of the next four peaks B–E in the Eu L₃-edge XANES is more complex. The smallest cluster size, within which the photoelectron scattering is able to reproduce these peaks, is about five coordination shells around absorbing europium atom (Fig. 1). This size corresponds to a sphere of 6 Å radius that is roughly comparable to the mean free path of the photoelectron, which varies between 3 and 7 Å as was estimated from the FEFF8 calculation with the complex Hedin–Lundqvist exchange-correlation potential [15,17]. Further increase of the cluster size till eight shells does not result in any new features, but slightly improves the visibility of the four peaks. The peaks B–E are attributed to the interference effects between different multiple-scattering (MS) signals, and represent the beginning of extended X-ray absorption fine structure (EXAFS) region. In Fig. 3, several EXAFS signals χ_n , calculated within MS formalism up to the n -order are compared with the experimental XANES. Here, χ_2 corresponds to the sum of all single-scattering (SS) signals, χ_3 denotes the sum of all SS and double-scattering (DS) signals, χ_4 denotes the sum of all SS + DS plus triple-scattering signals, etc. It is clear that the SS model χ_2 fails to reproduce all peaks

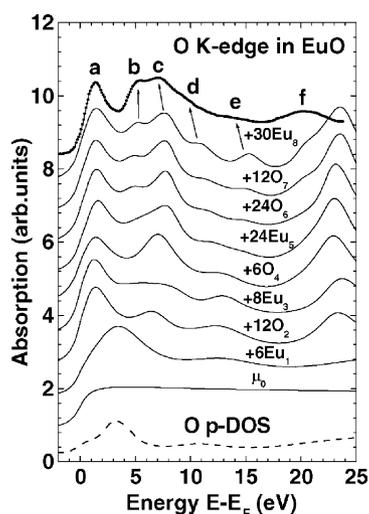


Fig. 2. Comparison of experimental (upper curve) and calculated XANES of EuO at the O K-edge. The experimental data are taken from [13]. The lower dashed curve is the O p-projected DOS. The energy scale is relative to the Fermi level E_F . Main features are labelled by letters from a to f.

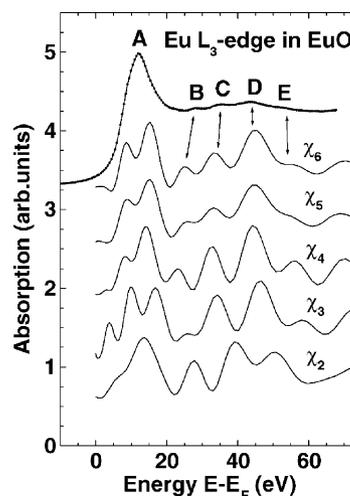


Fig. 3. Comparison of experimental (upper curve) XANES and theoretical EXAFS of EuO at the Eu L₃-edge. The theoretical EXAFS signals χ_n were calculated for the eight shells cluster within multiple-scattering formalism up to the n -order. The energy scale is relative to the Fermi level E_F . Main features are labelled by letters from A to E.

except the peak A, and the scattering processes not less than the fifth order ($n \geq 5$) must be taken into account to describe peaks B–E.

The O K-edge XANES in EuO (Fig. 2) has the typical shape for a compound with the rock-salt structure [21]. Note that starting from the peak c, there is a progressive mismatch in the energy position of the peaks in the calculated and experimental XANES signals presumably due to an inaccuracy of the exchange potential, used in the calculations. The origin of the peaks b–f in the O K-edge XANES is due to the photoelectron scattering at the neighbouring atoms, located within the first six–seven coordination shells (Fig. 2). The smallest size of the cluster, which gives XANES signal able to reproduce all main peaks, is about five coordination shells around absorbing oxygen atom. Among these, the first four shells, composed of the nearest-neighbours along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic directions, produce the main contribution. Thus, both Eu L_3 -edge and O K-edge XANES are determined mainly by the local environment around absorbing atoms.

4. Conclusions

The interpretation of X-ray absorption near edge structure at the Eu L_3 -edge and O K-edge in crystalline EuO is given within ab initio FMS formalism. Our theoretical results show rather good agreement with the experimental data. However, some difference in the energy position of peaks in the experimental and theoretical spectra is present, especially for the O K-edge. We attribute it to the inaccuracies of the exchange potential calculation.

We found that main peaks in the XANES signals at both edges can be explained taking into account rather small clusters of about five coordination shells. The high intensity of the peak, located just above the Eu L_3 -edge, indicates that Eu 5d states have localized character. Besides, comparative analysis with the O K-edge XANES suggests that Eu 5d- and O 2p states are strongly mixed.

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