ESRF	**Experiment title:** *Electronic properties and local structure of Eu2+-doped KBr with pressure in phases B1 and B2: correlations between photoluminescence and structure.*	**Experiment number**: HC-3913
Beamline: BM23	**Date of experiment**: from: 17/10/2018 to: 23/10/2018	**Date of report**: "relevant report"
Shifts: 18	**Local contact(s)**: Angelika Rosa	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Fernando Rodríguez*, Universidad de Cantabria

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Report:

This beamtime has generated two published works and one to be submitted.

First work:

Abstract

An advanced experimental and theoretical model to explain the correlation between the electronic and local structure of Eu^{2+} in two different environments within a same compound, EuS, is presented. EuX monochalcogenides (X: O, S, Se, Te) exhibit anomalies in all their properties around 14 GPa with a semiconductor to metal transition. Although it is known that these changes are related to the $4f^7 5d^0 \rightarrow 4f^6 5d^1$ electronic transition, no consistent model of the pressure-induced modifications of the electronic structure currently exists. We show, by optical and x-ray absorption spectroscopy, and by ab initio calculations up to 35 GPa, that the pressure evolution of the crystal field plays a major role in triggering the observed electronic transitions from semiconductor to the half-metal and finally to the metallic state.

Full reference detail:

Virginia Monteseguro, Jose A. Barreda-Argüeso, Javier Ruiz-Fuertes, Angelika D. Rosa, Holger L. Meyerheim, Tetsuo Irifune, and Fernando Rodriguez. *Crystal-field mediated electronic transitions of EuS up to 35 GPa*. **Scientific Reports**,12, 1217 (2022).

Second work:

This work has been published as a Comment in Physical Review Letters. Our Comment corrects a wrong interpretation of the physical theory behind the x-ray absorption near edge structure (XANES).

Full reference detail:

Virginia Monteseguro, Javier Ruiz-Fuertes, Jose A. Barreda-Argüeso, Holger L. Meyerheim, Angelika D. Rosa, and Fernando Rodriguez. *Comment on "Mechanisms for Pressure-InducedIsostructural Phase Transitions in EuO"*. **Physical Review Letters** 128, 099701 (2022).

Third work:

This work will be submitted to Physical Review B.

Abstract:

Europium is a fundamental element for lighting and sensing in optical materials either as an impurity or as a part of the composition. In the former case, the knowledge of the europium valence state is necessary for an adequate material characterization regarding its luminescent properties. This knowledge is crucial when the europium impurity replaces a monovalent ion since charge compensation can led to different Eu-related phases or structures inside the host material. Here we investigate $EuBr_2$-doped KBr as a function of the nominal europium concentration by means of x-ray absorption spectroscopy (XAS). Although Eu^{2+} governs the absorption and luminescence properties of the material, the XAS analysis carried out in different doped KBr samples ranging from 70 to 700 ppm reveal that both Eu^{2+} and Eu^{3+} are formed in Czohralski as-grown single crystals. In particular, we demonstrate that $EuBr_2$ doping with concentrations greater than about 200 ppm (0.02 mol%) does not contribute to increase the Eu^{2+} concentration but Eu^{3+} instead. The relative concentrations of Eu^{2+}/Eu^{3+} were obtained by analysing the intensities of the L_3-edge obtained from XAS in fluorescence mode, which identifies the two major valence states of europium: E_{L3} = 6973.5 eV for Eu^{2+}, and E_{L3} = 6981.5 eV for Eu^{3+}.

Experimental setup:

The X-ray absorption near edge spectroscopy (XANES) spectra at the Eu–L_3 edge were measured at BM23 in fluorescence mode, using a Silicon Drift Detector Vortex for the fluorescence signal, and a double crystal Si(111) monochromator. The microXAS station built with KB mirrors with a Pt coating was used to focus the x-ray beam to a spot of 5×5 μm^2 in size. The x-ray incidence angle onto the mirrors was fixed to 6.5 mrad to eliminate higher harmonics. The XANES profiles were fitted by the sum of an arctangent and two Gaussian functions in order to obtain the integrated intensities and the energy position of white light (WL) associated to the Eu^{2+} (6973 eV) and Eu^{3+} (6981 eV) edges as a function of the europium concentration. The modification of the relative Eu^{2+} to Eu^{3+} concentration ratio was derived by fitting the relative changes of the spectral weights (A1 and A2) of the Eu^{2+} ($4f^7$) and Eu^{3+} ($4f^6$) contribution of the XANES. Their relative abundance is then estimated by using the formula A2 /(A1 + A2) where A1 and A2 are the areas of the Gaussian peaks in the curve fitting of the WL and the first oscillation, respectively.

Results:

The XANES analysis carried out in different doped KBr samples ranging from 70 to 700 ppm reveal that both Eu^{2+} and Eu^{3+} are formed in Czohralski as-grown single crystals (Fig. 1). In particular, we demonstrate that $EuBr_2$ doping with concentrations greater than about 200 ppm (0.02 mol%) does not contribute to increase the Eu^{2+} concentration but Eu^{3+} instead. The relative concentrations of Eu^{2+}/Eu^{3+} were obtained by analysing the intensities of the L_3-edge obtained from XAS in fluorescence mode, which identifies the two major valence states of europium: E_{L3} = 6973.5 eV for Eu^{2+}, and E_{L3} = 6981.5 eV for Eu^{3+}.

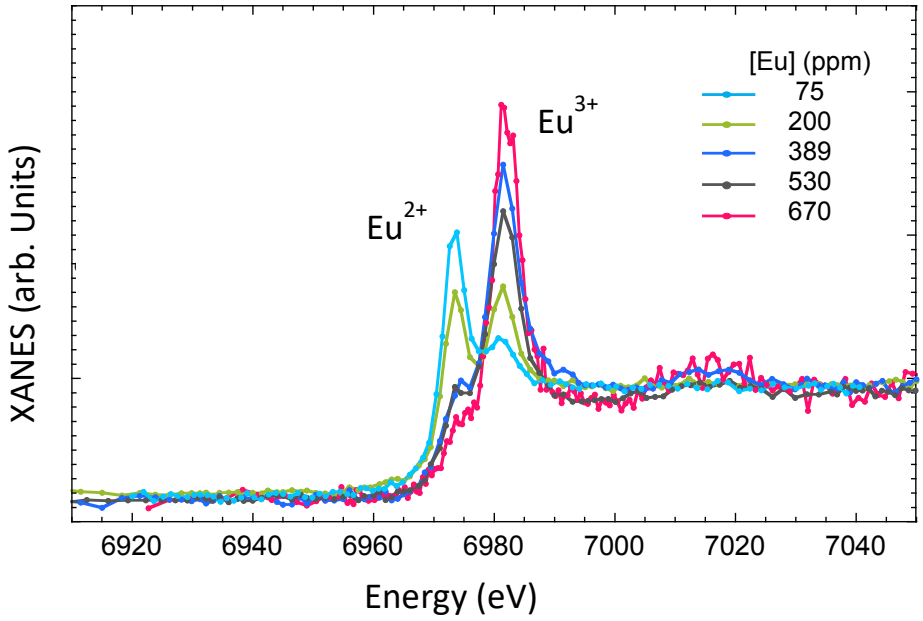

Figure 1. X-ray absorption measurements in fluorescence mode at Eu L_3-edge of $EuBr_2$-doped KBr samples with nominal europium concentrations of 75, 200, 389, 530, and 670 ppm.