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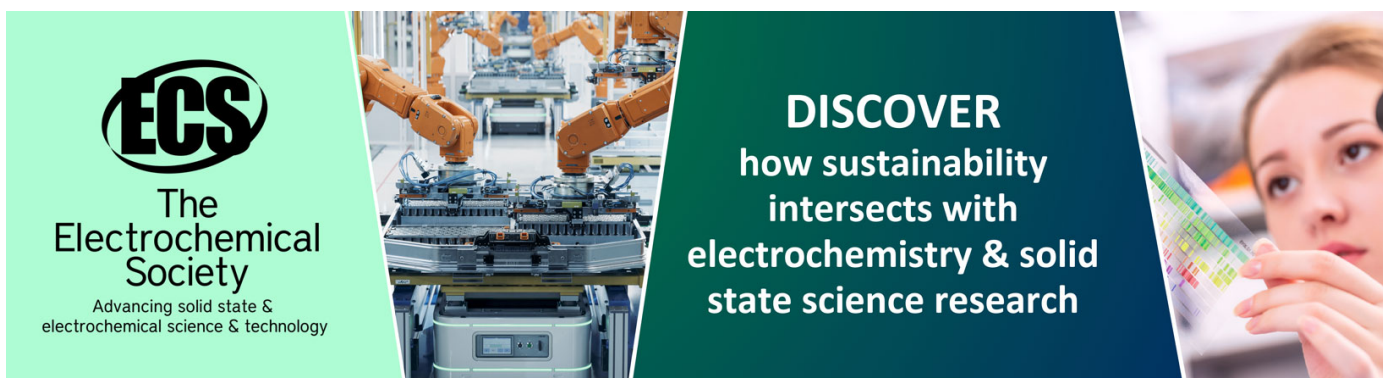
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Valence-selective XAFS spectroscopy using EuL_{γ_4} emission

H Hayashi¹, N Kawamura², M Mizumaki², T Takabatake³, H Imura⁴, K Okamoto⁵, and T Akai⁴

¹Japan Women's University, 2-8-1, Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan

²JASRI/SPRING-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

³Graduate School of Advanced Science of Matter, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8530, Japan

⁴Mitsubishi Chemical Group, Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

⁵Mitsubishi Chemical Group, Science and Technology Research Center, Inc., 8-3-1, Chu-o, Ami, Inashiki, Ibaraki 300-0332, Japan

hayashih@fc.jwu.ac.jp

Abstract. EuL_{γ_4} emission spectra show a large chemical shift (~ 5 eV), depending on the valence state of a compound. The applicability of this emission to valence-selective X-ray absorption fine structure spectroscopy was demonstrated by performing partial fluorescence yield measurements using a 1:1 mixture of EuS and Eu_2O_3 and using valence-fluctuating compounds, such as $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$.

1. Introduction

Lanthanide compounds often exhibit remarkable optical, electrical, and magnetic properties. Mixed valence and changes in the valence play a crucial role in determining their properties. The valence states of lanthanide compounds strongly depend on their chemical environments. Therefore, the information on local electronic and magnetic structures around the ions of interest is important for exploring the various applications of lanthanide materials. X-ray absorption fine structure (XAFS) spectroscopy can be used to probe the local structures, and the XAFS spectra of many lanthanide systems have been measured in previous studies [1–4]. In most of the previous XAFS studies, the “white line” observed in the L_3 -XAFS spectra of lanthanides was used to determine the relative weights of different configurations of a compound. The high-energy part of XAFS, including the extended XAFS (EXAFS), provides more detailed information on the atomic and electronic structures of the species of lanthanides being studied. However, the high-energy part has not been used extensively for studying mixed-valence compounds. This is because conventional XAFS spectra average over all species of an element in a sample. Thus, many features that are specific to certain species cannot be deduced from these spectra. Therefore, it is desirable to use a method that can selectively probe different forms of the same element.

In the past, a selective technique based on the chemical effects on hard X-ray emissions has already been proposed [5–8], and this technique has been effectively used to measure selective XAFS spectra of several fourth row elements [9–11]. In this technique, selective XAFS spectra are generally deduced from partial fluorescence yield (PFY) spectra [5–7,12,13]. The PFY spectra are obtained by measuring the excitation-energy dependence of the components of X-ray emissions that exhibit chemical effects. Using suitable emissions, it may be possible to selectively measure the XAFS spectra of just the metal ions that have a particular oxidation state, a particular spin, or both [5,6,8]. Although the usefulness of this method has been well recognized, it has not been established thus far. To the best of our knowledge, the practical application of this method to lanthanide compounds had not been reported until 2009 [14]. This is because the chemical effects of these compounds, particularly those caused by inner-shell→core emissions, are small. In contrast, outer-shell→core emissions, even those occurring in lanthanides, can show relatively large chemical effects [14,15], but unfortunately, their intensities are intrinsically low. The current developments in multicrystal spectrometers that are used with synchrotron X-ray sources, have helped overcome this problem of low-intensity emissions [8,16,17]. In a very recent study, we investigated the chemical effects on the $\text{EuL}\gamma_4$ ($\text{Eu}5\text{p}\rightarrow\text{Eu}2\text{s}$) emission line and its possible use as a probe for carrying out selective XAFS spectroscopy [14]. Modern X-ray studies have not focused on this emission line (as well as other similar weak lines of lanthanides).

In this paper, we present the $\text{EuL}\gamma_4$ -PFY L_1 -XAFS spectra of several Eu samples, and demonstrate the applicability of this method to practically important materials.

2. Experimental

The experimental details have been described elsewhere [14]. The experiments were performed using a multicrystal, multidetector spectrometer [8,18] at the beamline BL39XU of SPring-8. The spectrometer comprises five pairs of a spherically bent Si(444) crystal and a scintillation counter (seven pairs of the Si crystal and a Si-PIN detector were employed for performing $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ measurements). $\text{EuL}\gamma_4$ spectra were measured by rotating the crystals and moving the detectors simultaneously along a linear path. PFY spectra were measured using the same setup, and the incident energy of the X-rays (E_1) was scanned at constant emission energy (E_2). The overall energy resolution was found to be approximately 0.9 eV at an energy of $E_1 = E_2 = 8$ keV.

Commercially available EuS (Eu^{2+}), EuF_3 (Eu^{3+}), and Eu_2O_3 (Eu^{3+}) with 3-N purity were used without further purification. $\text{Eu}_3\text{Pd}_{20}\text{Ge}_6$ (Eu^{2+} and Eu^{3+}) was prepared by the arc-melting method [19]. $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ (Eu^{2+} and Eu^{3+}) was annealed in air to oxidize doped Eu^{2+} [20]. All the measurements were performed at room temperature.

3. Results and discussions

Figure 1 shows the $\text{EuL}\gamma_4$ spectra of EuS , Eu_2O_3 , and EuF_3 . The spectra were all measured at $E_1 = 8.150$ keV, which is well above the EuL_1 -absorption edge energy (~ 8.06 keV). The spectra of the Eu^{3+} compounds did not differ significantly and were within the experimental error of this study. The EuS (Eu^{2+}) profile, on the other hand, exhibited a considerably large chemical shift of approximately 5 eV (estimated as the difference between the centers of the Eu^{2+} and Eu^{3+} bands). This large shift was attributed to the combination of the screening effect, band-structure effects, charge transfer effects, and exchange interactions [14].

Because of the large chemical shift, $\text{EuL}\gamma_4$ emission is suitable for measuring valence-selective XAFS. PFY EuL_1 -XAFS spectra of 1:1 mixture of EuS and Eu_2O_3 are shown in Figure 2. For comparison, conventional EuL_1 -XAFS spectra of this mixture (dotted line), EuS (chain line), and Eu_2O_3 (solid line) are also shown in the figure. The two PFY spectra were measured at $E_2 = 8.020$ keV and 8.030 keV, respectively (see inset of Figure 2). These would hereafter be referred as “PFY 8.020keV” and “PFY 8.030keV,” respectively. As seen in the figure, the PFY spectra were significantly different; for example, the edge energy of PFY 8.020keV (Eu^{2+} selective) was lower than that of PFY 8.030keV (Eu^{3+} selective). The PFY 8.030keV spectrum agreed fairly well with the

conventional XAFS spectrum of Eu_2O_3 , indicating that it is a good approximation of the Eu^{3+} selective XAFS spectrum. A EuL_{γ_4} profile analysis of the mixture [14] showed that contributions of the Eu^{2+} component in the PFY 8.020keV and those of the Eu^{3+} component in the PFY 8.030keV were 58% and 77%, respectively. It is possible to deduce “genuine” Eu^{2+} and Eu^{3+} selective XAFS spectra on the basis of the component analysis. As expected, the Eu^{3+} spectrum thus deduced almost overlapped with the EuL_1 -XAFS spectrum of Eu_2O_3 , and the Eu^{2+} spectrum roughly coincided with the EuL_1 -XAFS spectrum of EuS [14]. The minor differences between the Eu^{2+} spectrum and the conventional EuS spectrum could probably be attributed to the spin-selective property of the EuL_{γ_4} of EuS (owing to the interactions between 4f electron and 5p hole in the final state) [14]. In addition, it should be noted that the background emission in the EuL_{γ_4} spectra (see Figure 1) was too large to accurately determine the relatively weaker Eu^{2+} components [14]. The reduction or a more accurate estimation of the background is considered as an important future task. However, even at this stage, EuL_{γ_4} PFY spectroscopy can be a useful method for measuring a Eu^{3+} -selective XAFS spectrum.

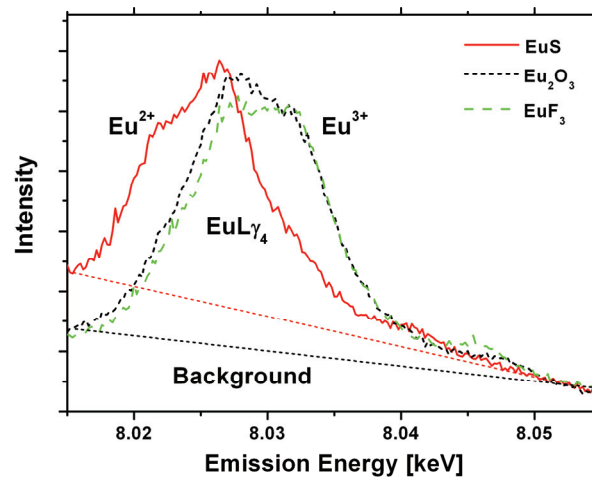


Figure 1. EuL_{γ_4} spectra of EuS , Eu_2O_3 , and EuF_3 . The “background” (dotted lines) linearly decreases with the emission energy.

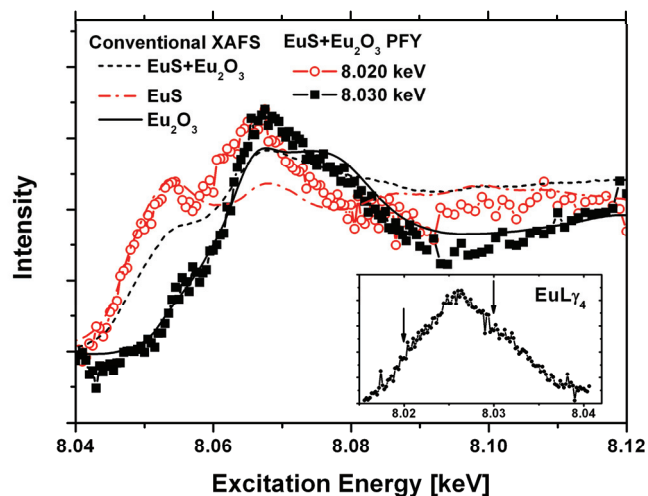


Figure 2. PFY EuL_1 -XAFS spectra and conventional EuL_1 -XAFS spectrum of 1:1 mixture of EuS and Eu_2O_3 . The conventional spectra of EuS and Eu_2O_3 are also shown. The inset shows the

EuL γ_4 spectrum of the mixture; the arrows indicate the emission energies (E_2) corresponding to the PFY measurements.

In order to examine the applicability of this method to materials of practical importance, PFY spectra of a valence-fluctuating material, Eu₃Pd₂₀Ge₆ (Eu²⁺:Eu³⁺ = 1:3; Eu 15 wt%) [19], and a phosphor, BaMgAl₁₀O₁₇:Eu (Eu²⁺:Eu³⁺ = 13:7; Eu 2 wt%) [20], were measured.

Figure 3 shows the observed PFY spectra of Eu₃Pd₂₀Ge₆ [14]. As was the case with the 1:1 mixture, clear spectral differences between the two PFY spectra were observed, particularly around the EuL₁ edge. Taking into account the fact that the relative concentration of Eu³⁺ in Eu₃Pd₂₀Ge₆ (Eu³⁺/Eu²⁺ = 3) is higher than that in the 1:1 mixture (Eu³⁺/Eu²⁺ = 1), we can consider the PFY 8.030keV spectrum to be an approximation of the Eu³⁺-selective XAFS spectrum. The PFY 8.030keV spectrum was characterized by a distinct hump at E_1 = 8.055 keV, which was not clearly observed in the conventional XAFS spectrum. Further investigations of this hump are required. The results of these investigations might provide an insight into the electronic and atomic structures of Eu₃Pd₂₀Ge₆.

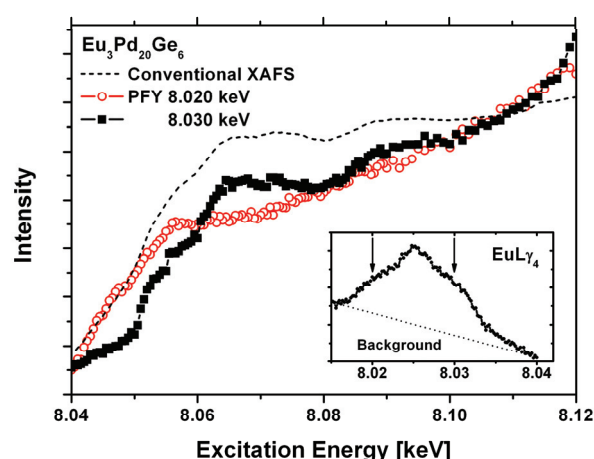


Figure 3. PFY EuL₁-XAFS spectra and conventional EuL₁-XAFS spectrum of Eu₃Pd₂₀Ge₆. The inset shows the EuL γ_4 spectrum; the arrows indicate the emission energies (E_2) corresponding to the PFY measurements.

Figure 4 shows PFY EuL₁-XAFS spectra of BaMgAl₁₀O₁₇:Eu. Graded spectral changes observed from E_2 = 8.020 keV to E_2 = 8.030 keV suggest that, even for diluted materials with a Eu concentration of ~2 wt%, it is (at least potentially) possible to perform valence-selective XAFS measurements by the present method.

In conclusion, we demonstrated that a multicrystal spectrometer is capable of efficiently measuring the hitherto neglected X-ray emission line of EuL γ_4 with high accuracy. We observed that the EuL γ_4 spectra are sensitive to the valence states of the Eu compounds, and we demonstrated the applicability of this emission line as a probe to selective XAFS spectroscopy. It is interesting to determine whether the state sensitivity of the L γ_4 emission line is characteristic of only Eu or whether it is a property of all lanthanides. Further theoretical and experimental studies on the L γ_4 emission lines of lanthanides are currently in progress.

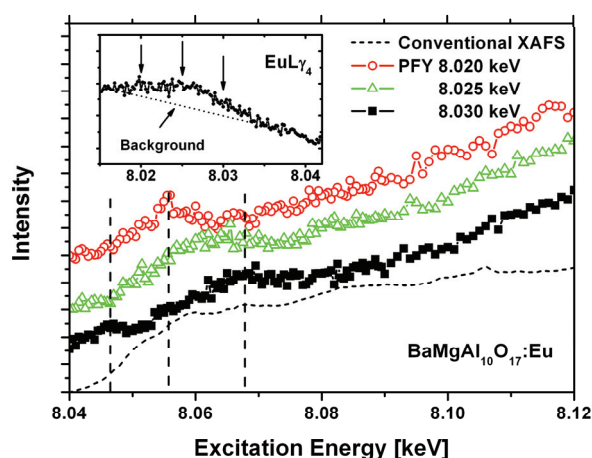


Figure 4. PFY EuL_1 -XAFS spectra and conventional EuL_1 -XAFS spectrum of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$. The broken lines serve as a guide to the eye. The inset shows the EuL_4 spectrum; the arrows indicate the excitation energy (E_2) corresponding to the PFY measurements.

4. Acknowledgements

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