Valence-selective XAFS spectroscopy using EuLγ4 emission

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Abstract. EuLγ4 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 Eu2O3 and using valence-fluctuating compounds, such as Eu3Pd20Ge6 and BaMgAl10O17: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 Lγ-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 EuLγ4 (Eu5p→Eu2s) 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 EuLγ4-PFY L1-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 BaMgAl10O17:Eu measurements). EuLγ4 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 (E1) was scanned at constant emission energy (E2). The overall energy resolution was found to be approximately 0.9 eV at an energy of E1 = E2 = 8 keV.

Commercially available EuS (Eu2+), EuF3 (Eu3+), and Eu2O3 (Eu3+) with 3-N purity were used without further purification. Eu5Pd20Ge6 (Eu2+ and Eu3+) was prepared by the arc-melting method [19]. BaMgAl10O17:Eu (Eu2+ and Eu3+) was annealed in air to oxidized doped Eu2+ [20]. All the measurements were performed at room temperature.

3. Results and discussions

Figure 1 shows the EuLγ4 spectra of EuS, Eu2O3, and EuF3. The spectra were all measured at E1 = 8.150 keV, which is well above the EuL1-absorption edge energy (~8.06 keV). The spectra of the Eu3+ compounds did not differ significantly and were within the experimental error of this study. The EuS (Eu3+) profile, on the other hand, exhibited a considerably large chemical shift of approximately 5 eV (estimated as the difference between the centers of the Eu2+ and Eu3+ 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, EuLγ4 emission is suitable for measuring valence-selective XAFS. PFY EuL1-XAFS spectra of 1:1 mixture of EuS and Eu2O3 are shown in Figure 2. For comparison, conventional EuL1-XAFS spectra of this mixture (dotted line), EuS (chain line), and Eu2O3 (solid line) are also shown in the figure. The two PFY spectra were measured at E2 = 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 (Eu2+ selective) was lower than that of PFY 8.030keV (Eu3+ selective). The PFY 8.030keV spectrum agreed fairly well with the
conventional XAFS spectrum of Eu₂O₃, indicating that it is a good approximation of the Eu³⁺ selective XAFS spectrum. A EuL₄ profile analysis of the mixture [14] showed that contributions of the Eu²⁺ component in the PFY 8.020keV and those of the Eu³⁺ component in the PFY 8.030keV were 58% and 77%, respectively. It is possible to deduce “genuine” Eu²⁺ and Eu³⁺ selective XAFS spectra on the basis of the component analysis. As expected, the Eu³⁺ spectrum thus deduced almost overlapped with the EuL₁-XAFS spectrum of Eu₂O₃, and the Eu²⁺ spectrum roughly coincided with the EuL₁-XAFS spectrum of EuS [14]. The minor differences between the Eu²⁺ spectrum and the conventional EuS spectrum could probably be attributed to the spin-selective property of the EuL₄ 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 EuL₄ spectra (see Figure 1) was too large to accurately determine the relatively weaker Eu²⁺ components [14]. The reduction or a more accurate estimation of the background is considered as an important future task. However, even at this stage, EuL₄ PFY spectroscopy can be a useful method for measuring a Eu³⁺-selective XAFS spectrum.

Figure 1. EuL₄ spectra of EuS, Eu₂O₃, and EuF₃. The “background” (dotted lines) linearly decreases with the emission energy.

Figure 2. PFY EuL₁-XAFS spectra and conventional EuL₁-XAFS spectrum of 1:1 mixture of EuS and Eu₂O₃. The conventional spectra of EuS and Eu₂O₃ are also shown. The inset shows the
EuLγ4 spectrum of the mixture; the arrows indicate the emission energies (E2) 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 E1 = 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 EuLγ4 spectrum; the arrows indicate the emission energies (E2) corresponding to the PFY measurements.

Figure 4 shows PFY EuL1-XAFS spectra of BaMgAl10O17:Eu. Graded spectral changes observed from E2 = 8.020 keV to E2 = 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 EuLγ4 with high accuracy. We observed that the EuLγ4 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 Lγ4 emission line is characteristic of only Eu or whether it is a property of all lanthanides. Further theoretical and experimental studies on the Lγ4 emission lines of lanthanides are currently in progress.
Figure 4. PFY EuL_{\gamma4}-XAFS spectra and conventional EuL_{\gamma4}-XAFS spectrum of BaMgAl_{10}O_{17}:Eu. The broken lines serve as a guide to the eye. The inset shows the EuL_{\gamma4} spectrum; the arrows indicate the excitation energy (E_2) corresponding to the PFY measurements.

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