Eu K-XAFS of europium dioxymono-cyanamide with the conversion He+ ion yield method

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Conversion He+ ion yield (HIY) XAFS measurement, in which He+ ion is collected using the conversion electron yield (CEY) cell under atmospheric He gas environment, has been attempted at Eu K-absorption edge (48.5keV) for europium dioxymonocyanamide. The shape of Eu K-XAFS spectrum measured by the HIY method was similar to that measured by the conventional transmission method, while the signal-to-background ratio decreased with an increase in absorption edge energy, owing to low Auger electron emission probability. The evidences suggest that the HIY method is still applicable to the XAFS measurement for materials which could not be pulverized at such higher energy region.

Keywords: **conversion electron yield, conversion He+ ion yield, europium dioxymonocyanamide.**

1. Introduction

As an alternative of the conventional transmission method, such various yield techniques as fluorescence yield (FLY), electron yield, photoelectron or Auger electron yield, optical photon yield and so on, have been employed in XAFS measurements. As for conversion electron yield (CEY) method, which is one of a total electron yield technique and is analogous technique used in conversion electron Mössbauer spectroscopy, a specimen current is measured in a gas environment (Kordesch & Hoffman, 1984).

It is well known that the CEY-XAFS is a powerful tool for analyzing local structure of near surface for not only thin films but also bulk materials (Kordesch & Hoffman, 1984; Guo & L.DenBoer, 1985; Bouldin, et al,

1987; Elam, et al, 1988; Elam, et al, 1989; Tourillon, et al, 1989; Galen, et al, 1990; Jiang & Crozier, 1990; Jacuer, et al, 1990; Kemner, et al, 1992; Choi, et al, 1992; Mimault, et al, 1994; Schroeder, et al, 1995; Stern, et al, 1995; Takahashi, et al. 1995; Regnard, et al, 1996; Takahashi, et al, 1997; Naftel, et al, 1998; Takahashi, et al, 1998). The complementarity is found between the CEY-XAFS and the FLY-XAFS, another widely used technique as the yield technique; the latter leads a bulk information if a grazing incident technique is not applied and concerns the radiative decay of the core hole while the Auger electron, ejected in the non-radiative decay process, is detected in the former. On measuring the XAFS spectra for a concentrated material, the CEY-XAFS generally has the advantage of the FLY-XAFS. By contraries, the FLY-XAFS might be favorable at higher energy region, since the Auger electron emission probability decreases with increasing the atomic number. By applying negative bias to the collecting electrode and collecting He+ ion, the conversion He+ ion yield (HIY) spectrum is measurable with the CEY cell (Takahashi, et al, 1995, 1997). Both CEY and HIY spectra resemble to the transmission spectrum and analyses of the yield spectra lead to the same EXAFS parameters as those obtained by the transmission spectrum (Takahashi, et al, 1995).

In the present study, the feasibility of the HIY-XAFS measurement at rather higher energy region was examined by comparing the HIY-XAFS spectrum with corresponding transmission XAFS spectrum. And the signal-to-background ratio S_B at Eu K-absorption edge has been compared with that at K-absorption edge of lighter elements such as Ti, Fe, Mo and In. A sample supplied to the measurement at higher energy region was europium dioxymonocyanamide, $Eu_2O_2CN_2$, one of a series of newly synthesized layer compounds (Hashimoto, et al, 1994, 1995; Hashimoto, 1995). The compound is well-characterized and is highly stable to both the air and water, meaning that the sample is suitable to a test specimen for surveying the near surface sensitive HIY technique.

2. Experimental

$Eu_2O_2CN_2$ was prepared by heating Eu_2O_3 in a graphite boat at 1223K for 12hr under flowing ammonia gas. The crystal structure and chemical composition for the product were confirmed by the powder X-ray diffraction analysis and both CHN analysis and weight change on oxidizing the product to Eu_2O_3. Both foils and sheets of Ti, Fe and Mo and In_2O_3 powder used were commercial products.

XAFS measurements at both Eu and In K-absorption edge were carried out at BL01B1 of SPring-8 using the inclined fixed-exit double-crystal monochromator. The higher harmonics were rejected by Rh-coated mirrors. As for measuring the HIY spectra, the current from the sample, put on the specimen electrode with a conductive adhesive tape, was measured under a He gas flow. Applied voltage for collecting He+ ion was set to -1kV. XAFS measurements at Ti, Fe and Mo K-absorption edge were executed at BL12C of the Photon Factory, High Energy Accelerator Research Organization (KEK).

The monochromator used was Si(111) double-crystal monochromator and quartz mirrors rejected the higher harmonics. The HIY spectra were measured by the same cell as that used on Eu and In K-XAFS measurements. All the measurements were executed at room temperature. The usual XAFS analysis was carried out using the program package, XANADU (Sakane, et al, 1993; Takahashi & Sakane, 1997).

3. Results and Discussion

Eu K-XANES for $Eu_2O_2CN_2$ measured using the HIY and the conventional transmission methods are compared in Fig. 1a. Solid and broken lines display the transmission and the HIY XANES, respectively. The spectra are normalized by the amount of the edge jump. The rising of XANES spectra is rater dull and is spread to a energy range as large as about 100eV, which seems to concern with the life time of the core hole. Distinct difference between both spectra cannot be found.

Figure 1b is comparison of EXAFS and shows that HIY-EXAFS is noisier, especially at larger k value. The Fourier transforms of k^3-weighed HIY-EXAFS was also

somewhat noisy one, but two peaks, corresponding to the first neighboring oxygen and the second neighboring nitrogen atoms, were observed in the imaginary part of Fourier transforms for both the HIY and the transmission EXAFS. Moreover, the curve-fitting analysis of Fourier-filtered EXAFS function leads to distance between Eu and O of 0.227 and distance between Eu and N of 0.260nm, which are consistent with those determined by the powder X-ray diffraction study (Hashimoto, 1995). The shape of the HIY-EXAFS around 4.5• $^{-1}$, which is different from the transmission EXAFS, splits into two maxima and such splitting is also found at larger k value, ie., at 6.5 and 8.5 • $^{-1}$. The evidence will be investigated further after getting spectrum with better signal-to-noise ratio S_N.

The signal-to-background ratio S_B (Stöhr, 1992), defined as,

$$S_B = I_s / I_b,$$

was tabulated for the present HIY-XAFS spectra (Table 1). S_B decreases monotonously with an increase in the absorption edge energy, ie, a decrease in the Auger electron emission probability, but for La L_{III}-edge of $La_2O_2CN_2$. S_B of the Ar^+ ion yield XAFS for $Eu_2O_2CN_2$, which is measured by the same CEY cell under flowing Ar gas instead of He gas, is almost half of S_B of the HIY-XAFS for $Eu_2O_2CN_2$. The evidence appears to owe to an increase of the background current because the absorption cross-section of Ar is larger than that of He at these energy region.

In conclusion, both no sign of dullness in the XANES and no amplitude reduction in EXAFS function, measured by the HIY(CEY) method at Eu K-edge compared with the transmission XAFS appears that the CEY method is still applicable to the XAFS measurement for materials, which could not be pulverized, at such higher energy region, in spite of low Auger electron emission probability.
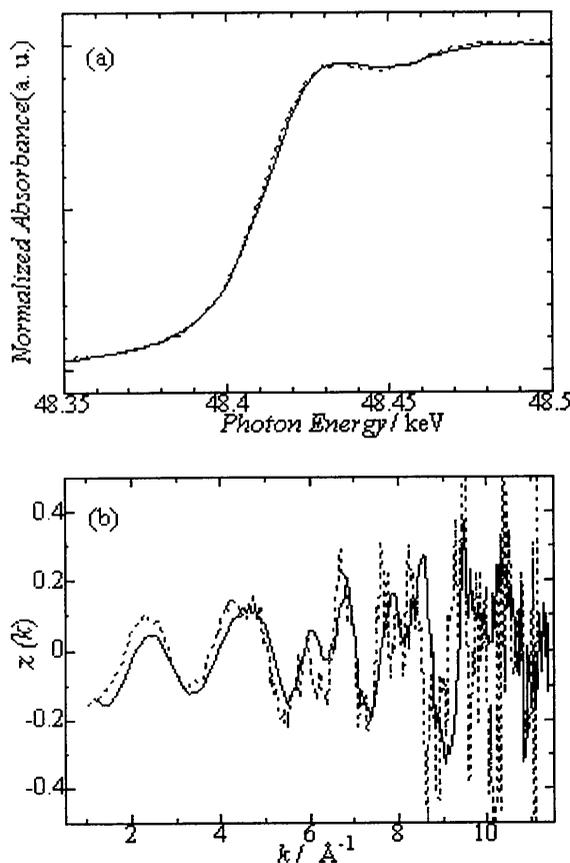
Figure 1
Comparison of Eu K-XAFS spectra for $Eu_2O_2CN_2$ measured by the conventional transmission and the HIY method. (a)Normalized XANES spectra and (b)EXAFS function. Solid and broken lines denote the transmission and the HIY method, respectively.

Table 1
Comparison of signal-to-background ratio S_B for the present HIY spectra with Auger electron emission probability, ω at corresponding absorption edge.

Specimen	Absorption Edge	Energy / keV	ω^* / %	S_B
Ti	Ti-K	4.965	0.80	3.66
Fe	Fe-K	7.111	0.68	2.39
Mo	Mo-K	20.004	0.25	1.41
In_2O_3	In-K	27.942	0.16	0.87
$Eu_2O_2CN_2$	Eu-K	48.520	0.08	0.55
$Eu_2O_2CN_2$**	Eu-K	48.520	0.08	0.30
$La_2O_2CN_2$	La-L_{III}	5.484	0.87	0.48

*Auger electron emission probability was calculated by the equation appeared in "Principle and Practice of X-ray Spectrometric Analysis"(Bertin, 1975).
**Spectra were measured using the Ar^+ ion yield method. See text.

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