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EXAFS Studies of Some Neptunium Compounds

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Introduction

Actinide compounds are characterized by the existence of 5f electrons which alters their states between itinerant and localized ones with changing environment. Therefore, it is very important to clarify the structure of 5f electrons in the compounds for predict the behavior of the actinides in a complex environment.

The application of synchrotron radiation gives a unique chance to extract the accurate information on the behavior. At the 27B beam station, the handling of some α-emitting nuclides such as ^{237}Np, ^{243}Am, ^{241}Am, ^{244}Cm etc. can be made in a sealed container.

The EXAFS have been extensively studied on uranium, and the correlation between the formal valence and the edge position has been found. However, studies on neptunium and plutonium are very limited. The objectives of this study are to provide the means for structural analyses of highly reactive sample, and to clarify the 5f structure of the neptunium in the compounds by examining the XANES features. Also, it should be noted that the XAFS measurement of solid Np compounds in this study is the first one in Japan.

Experimental Procedures

Neptunium(IV) dioxide, $^{237}NpO_2$, amorphous neptunyl(V) hydroxide, $^{237}NpO_2(OH)$, and crystalline neptunyl(VI) hydroxide, $^{237}NpO_2(OH)_2$, were used in the EXAFS measurement. Several mg of the Np compounds and graphite powders were pressed into small discs of 7 mm in diameter, and then sealed in a special container by a resin material, shown in Fig.1.

Fig.1: Np sample disc sealed in a container, where the sample was triple sealed by two resin and Capton foil.

XAFS measurements were conducted at the PF on the BL27B endstation. All the XAFS spectra were collected at the Np L_{III}-edge in transmission mode at room temperature using a Si(111) double crystal monochrometer, where a special closed container containing the three samples, in which exchanging the sample can be done without opening it, was used.

Results and discussion

Fig.2 shows the EXAFS spectra of Np samples, where pure zirconium metal foil was used as an internal standard of energy. Strong absorption and white line are observed for NpO_2 sample, compared with those of two neptunyl compounds. A detailed comparison of the Np L_{III} near edge features in Np samples is presented in Fig.3. The white line position of hexavalent $NpO_2(OH)_2$ is obviously shifted by about 2eV, with respect to pentavalent $NpO_2(OH)$ or tetravalent NpO_2. It is also noted that there is a small shoulder above the white line maximum in the spectra of the neptunyl samples, which is very similar to mixed valence features in the rare-earth compounds.

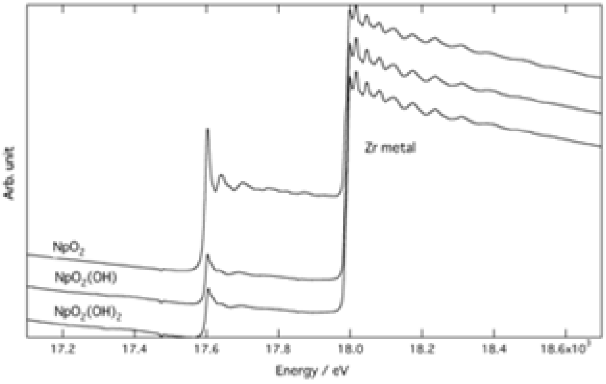

Fig.2: XAFS spectra at the Np LIII edges of Np samples with Zr internal standard.

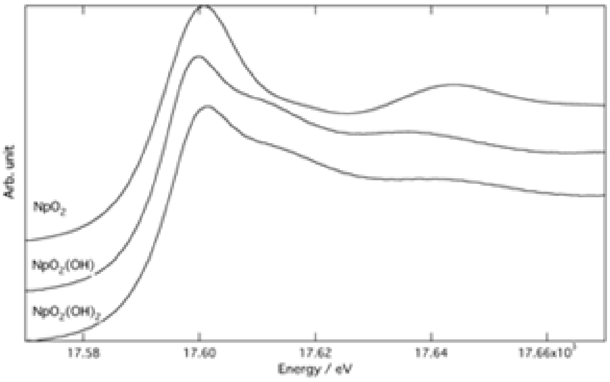

Fig.3 : XANES spectra at the Np LIII edges of Np compounds.

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