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Ce K-EDGE EXAFS SPECTRUM OF CeO$_2$

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The Ce K-edge (40 keV) EXAFS of CeO$_2$ was successfully measured by using Si(553) double crystal monochromator and the synchrotron radiation emitted from the Photon Factory wiggler. The energy resolution was estimated to be about 17 eV from the width of the Ce K-edge absorption edge. The distances of Ce-O and Ce-Ce were determined to be 2.28(3) Å and 3.38(5) Å by using theoretically derived phase shifts. We demonstrated the possibility of elucidating structural parameters from K-edge EXAFS spectra of the atoms with the medium Z values (50<Z<60).

INTRODUCTION

EXAFS spectroscopy has proved to be a powerful tool for the determination of the local structure around a specified atom in polyatomic system. The heavy elements with Z > 50 have usually been investigated with the EXAFS above L$_3$-edge instead of K-edge for the following reasons.

1. The reflectivity of crystals as well as the intensities of X-ray sources decreases at high photon energies.
2. The lifetime broadening of K-edge becomes appreciable for the heavy atoms.

For the elements with medium atomic numbers (50<Z<60), however, the energy separation of L$_3$ and L$_2$ edges is considerably small (less than 600 eV, i.e. k<12 Å$^{-1}$) and thus EXAFS oscillation can not be obtained over the sufficient data range. This shorter data range limits the precision of EXAFS. Hence the K-edge EXAFS measurements are desirable but seldom has been carried out on these elements for the above-mentioned reasons. However the lifetime broadening of those elements is less than 15 eV$^2$ and it is possible to measure their K-edge EXAFS spectra considering the energy resolution necessary for EXAFS measurement to be 10-20 eV. The difficulty exists in a technical problem. In this work we shall show that it is possible to measure the Ce K-edge EXAFS spectrum of CeO$_2$ (40 keV) with a good S/N ratio by using wiggler radiation and Si(553) double crystal monochromator.

EXPERIMENTAL

Ce K-edge EXAFS spectrum was measured at the wiggler beam line 14A of Photon Factory (KEK-PF). The critical wavelength of the radiation is 0.6 Å at 5 T wiggler operation. The X-ray was monochromatized by Si(553) double crystal monochromator, which covers
the energy range 23 keV-85 keV. The details of the instrument are described elsewhere\textsuperscript{4,5). The parallelism of two crystals and the translation of the second crystal were finely adjusted at each data point to keep the beam from going away. The $I_0$ and $I$ were monitored by Xe- or Kr-filled ionization chambers.

The EXAFS spectra above $L_1$-, $L_2$- and $L_3$-edges were recorded at BL-10B of Photon Factory\textsuperscript{6).}

RESULTS AND DISCUSSION

The $K$-edge absorption spectrum of CeO$_2$ is shown in Fig.1. The fine structure extends 500 eV above the edge. Figures 2-4 show the $L_1$-, $L_2$- and $L_3$-edges EXAFS spectra. The fine structures in the pre-edge region of $L_1$- and $L_2$-edge absorption spectra are the $L_2$- and $L_3$-edge EXAFS oscillations which extend over the $L_1$-edge and $L_2$-edge, respectively. The $L_3$-edge EXAFS oscillation is truncated by $L_2$-edge at 6160 keV and the $L_2$-edge EXAFS oscillation is in turn truncated by $L_1$-edge at 6550 eV. Thus the three $L$-edges were interfered with each other.

Comparing $K$-edge absorption spectrum with the $L_1$-edge one as shown in Fig.2, the first edge peak of $K$-edge absorption is diminished to some degree due to the lifetime broadening of the core hole. The energy resolution estimated from the width of the absorption edge\textsuperscript{2) is 17 eV which is in good agreement with the theoretically-calculated lifetime broadening\textsuperscript{2). Figure 5 shows the $k^2$-weighted $K$-edge EXAFS oscillation together with $L$-edges EXAFS oscillations. Figure 6 shows the Fourier transforms of the EXAFS oscillations of Fig.5. The first peak is corresponding to the Ce-O and the second one is to the Ce-Ce.
By correcting the phase shifts by using the theoretically-derived ones\(^1\), the distances of the Ce-O and Ce-Ce bondings are 2.28(3) Å and 3.88(5) Å, respectively. The distances of Ce-O and Ce-Ce determined from crystallographical data are 2.32 Å and 3.82 Å, respectively. Thus we conclude that it is possible to elucidate the structural parameters from Ce K-edge EXAFS. The core hole lifetime broadening diminished the amplitudes of the peaks appearing in the Fourier transformation of the Ce K-edge EXAFS compared to those of L\(_1\)-edge one.

The merits of the K-edge EXAFS measurement for the atoms with medium atomic numbers are summarized as follows.

1. The K-edge spectrum is not interfered with by the other absorption edges and the long data range is available for the data reduction.

2. The absorption of the other elements are very low because the photon energy is higher than 30 keV and the investigation of the dilute system is possible in a transmission mode.

3. EXAFS is described by the simple formalism because the only one transition to the p-state is allowed.

References

Fig. 6 Fourier transforms of K-edge (a), $L_1$-edge (b), $L_2$-edge (c), and $L_3$-edge (d).

5) Y. Satow et al., to be published.