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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 reasons¹⁾.

- (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. $k < 12 \text{ Å}^{-1}$) 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 eV²⁾ 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 operation³⁾. The X-ray was monochromatized by Si(553) double crystal monochromator, which covers

Fig.1 Ce K-edge EXAFS spectrum

Fig.2 Ce L_1 -edge EXAFS spectrum Fig.3 Ce L_2 -edge EXAFS spectrum Fig.4 Ce L_3 -edge EXAFS spectrum

the energy range 23 keV-85 keV. The details of the instrument are described elsewhere⁴⁾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 Factory⁶⁾.

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 edge²⁾ is 17 eV which is in good agreement with the theoretically-calculated lifetime broadening²⁾. Figure 5 shows the k^3 -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.

Fig.5 $K^3 \chi(k)$ of K-edge(a), L_1 -edge(b), L_2 -edge(c), and L_3 -edge of CeO_2

By correcting the phase shifts by using the theoretically-derived ones⁷⁾, 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

- 1) P.Rabe, G.Tolkehn and A.Werner, J.Phys.C **12**, 899(1979).
- 2) B.K.Agarwal, "X-ray Spectroscopy", Springer-Verlag, Heiderberg, (1979).
- 3) T.Yamakawa et al., Nucl. Instr. and Meth., A246, 32(1986).
- 4) M.Ando, Y.Satow, H.Kawata, P.Spieker, and S.Suzuki, Nuclear Instr. and Meth., A246, 144(1986).

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.

6) H.Oyanagi, T.Matsushita, M.Ito, and H.Kuroda, KEK Report, 1984,83-30.

7) B.K.Teo and P.A.Lee, J.Am.Chem.Soc., 100, 2815(1979).