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XAFS spectra in the high-energy region measured at SPring-8

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XAFS spectra near K absorption edges of Pt (78.4 keV) and Pb (88.0 keV) were measured in transmission mode with Si (511) planes of an adjustable inclined double-crystal monochromator at bending-magnet beamline BL01B1 at SPring-8. The energy resolution was estimated as good as 7 eV at Pt K-edge, benefitted from the high brilliant x-rays from the SPring-8 storage ring. Blunt edge jumps and reduction of EXAFS amplitude were observed owing to the finite lifetime of the core hole as predicted theoretically. Local structure parameters have been successfully evaluated from EXAFS signal above the K edge.

Keywords: XAFS, high energy, finite lifetime effect of core hole

1. Introduction

We have sufficient photon density even at 100 keV from a bending magnet at SPring-8 storage ring so as to observe qualitative XAFS (X-ray Absorption Fine Structure) spectra near K absorption edges for almost all heavy elements. Since an EXAFS (Extended X-ray Absorption Fine Structure) signal above an L_{III} absorption edge is followed by the L_{II} absorption edge, the energy range is limited for the analysis. Therefore, EXAFS spectra with K absorption edge are anticipated in order to improve the accuracy of local structure parameters for elements, e.g. lanthanoids. However, it is theoretically pointed out that the finite lifetime of a core hole smears out EXAFS oscillation, and that this effect becomes more serious for K absorption edges of heavier elements (Stearns, 1984).

XAFS spectra were measured near K absorption edges of Ce (40.5 keV), Dy (53.8 keV), Ta (67.4 keV) and Pt (78.4 keV), which were observed preliminary at the Photon Factory in the National Laboratory of High Energy Physics (KEK-PF) (Nishihata et al., 1998). Although the measurement was carried out with rather poor energy resolution, it was successfully shown that the local structure parameters can be evaluated on the spectrum in the high energy region and the effect of the finite lifetime of the core hole can be effectively taken together into the mean-free-path term in the EXAFS function using the data at high-k region. The high-brilliance x-rays of third generation synchrotron radiation source enable us to measure XAFS spectra with better energy resolution than before. Here we show the first XAFS spectra near Pt and Pb (88.0 keV) K edges observed at SPring-8.

2. Experimental and analysis

X-ray absorption spectra near K edges of Pt (foil) and Pb ($PbTiO_3$) were measured at bending-magnet beamline BL01B1 at SPring-8. The adjustable inclined double-crystal monochromator, which is the standard monochromator at SPring-8, can provide a wide energy range from 4.5 to 110 keV by inclining a single pair of crystals and choosing (111), (311) and (511) reflections (Uruga et al., 1995). Measurements were carried out at room temperature in transmission mode with Si (511) planes of the monochromator with an encoder to monitor the correct Bragg angle. The incident and transmitted x-ray intensities, I_0 and I, were monitored with a flowing Kr gas ionization chambers 17 cm long and 31 cm long, respectively. It took 5 s to monitor the x-ray intensities for each data point. Counting of higher-order harmonics was estimated to be less than 1 % in comparison with that of the K edge energy, by considering both of photon flux of the source and efficiency of the detector. Although the cross section of the Compton scattering increases in the high energy region, it is almost independent of energy within the energy range for standard XAFS measurement. A slit in front of the ionization chamber

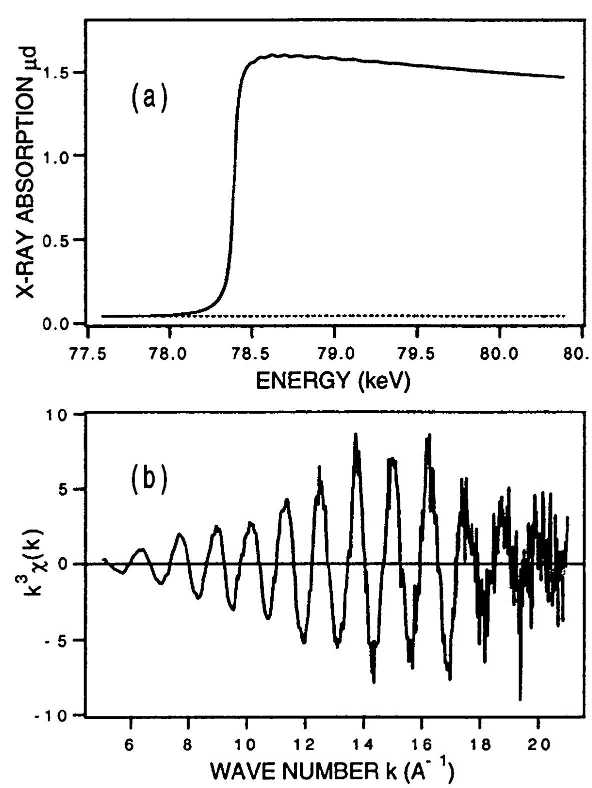

Figure 1
(a) XAFS spectrum near the Pt K edge of Pt foil at room temperature.
(b) EXAFS function above the Pt K edge.

prevented the detector from counting the component of the Compton scattering. The energy resolution of Pt and Pb K edges were estimated to be 7 and 8 eV, respectively, from the vertical size of the x-ray source (0.1 mm) and the width of the vertical slit at 47 m from the source (0.2 mm). Such energy resolutions allow us to discuss EXAFS function even at low-k region. Since the width of the rocking curve of the monochromator crystal is sharp, the first crystal holder is equipped with a piezo actuator for keeping the crystals in parallel during the scan.

The programmes XAFS93 and MBF93 (Maeda, 1987) were employed for the data analysis to determine local strcture parameters. We used an EXAFS formula for the harmonic model based on single-scattering theory and expressed by the cumulant expansion (Ishii, 1992). The mean-free-path, λ, of the photoelectron was assumed to be proportional to the wavenumber k: $\lambda = k / \eta$, where η is a constant. The threshold energy E_0 was assigned to an inflection point of the absorption edge: 78.395 keV and 88.005 keV for Pt and Pb K edges, respectively. EXAFS oscillation are normalized adequately using McMaster's coefficients. A Fourier-filtered EXAFS function concerning the first nearest neighbour atom was compared with a theoretical one which was calculated with the theoretical table by McKale et al. (1988). In the parameter fitting, the theoretical EXAFS function was filtered in the same way as the observed one in order to eliminate truncation effects through the Fourier transformation of the data. We used a non-linear least-squares fitting method to determine the local structure parameters.

3. Results and discussion

Figure 1 (a) shows the x-ray absorption spectrum near the Pt K edge of Pt foil. The width of the edge jump is as wide as about 100 eV and dependent on the width of the initial state of the K level, Γ_K. The blunt edge jump makes it difficult to extract the EXAFS signal at low-k values, while the EXAFS signal is defined well up to 20 A^{-1}, as shown in Fig. 1 (b). The near-edge-structure is unusual in an ordinary sense. The energy, where the absorption saturates on average, is converted to the wavenumber k = 6 A^{-1}: the photoelectron has enough kinetic energy to transit between the central and neighbouring atoms. The effect originated from the finite lifetime of the core hole

Table 1
Local structure parameters of Pt-foil estimated from EXAFS spectra of K and L_{III} edges.

Edge	N	R(A)	ΔR (A)	$\sigma^{(2)}$ (A^2)	η (A^{-2})
K	12	2.767(2)	-0.007	0.0046(1)	4.01(10)
L_{III}	12	2.765(1)	-0.009	0.0053(1)	0.99(2)

causes not only the EXAFS amplitude reduction, but also the change in the x-ray absorption in the vicinity of the edge. Moreover, EXAFS oscillation of outer shells seems to smear out. This suggests that the local structure in the different distance range would be evaluated separately by comparing K edge XAFS with L_I edge XAFS, where the symmetry of the photoelectron is the same.

An EXAFS signal was theoretically shown to be reduced owing to the short lifetime of a K hole (Stearns, 1984). This smearing effect mainly behaves in a similar manner to the mean-free-path term. Since the mean-free-path is assumed to depend on the wavenumber, the constant η can be taken for rough estimation of the finite lifetime of the core hole as follows;

$$\lambda' = k/[\eta + (m\Gamma_K/2\hbar)] \\ = k/\eta',$$

where m and $\hbar$ are the mass of an electron and Planck's constant, respectively. The Fourier-filtered EXAFS function of the Pt K edge concerning the first nearest neighbour is compared with that of the Pt L_{III} edge in Fig. 2. The amplitude of the EXAFS function of K edge reduces much at low-k values. The phase cannot be compared exactly in the figure, because it depends on the origin of the energy of the photoelectron. Local structure parameters of Pt are given in Table 1. Here, R is the interatomic distance and ΔR is the difference in the interatomic distance obtained by EXAFS and x-ray diffraction. The coordination number N was fixed to be 12. The interatomic distance R and the Debye-Waller factor $\sigma^{(2)}$ obatined for K edge are in good agreement with those obtained for L_{III} edge, which are taken from the previous report (Nishihata et al., 1998). The large value of η for K edge means a short mean-free-path of the photoelectron. The difference of η between η_K and η_{LIII}, which could be related to

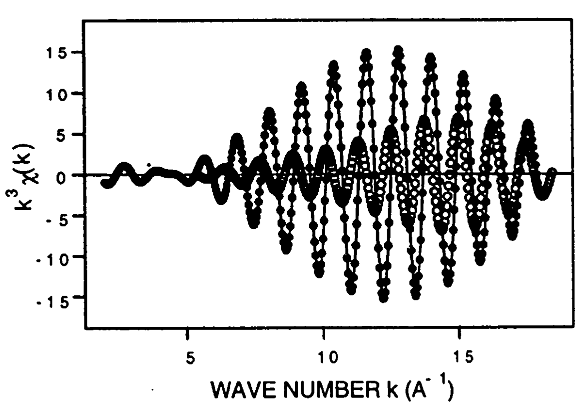

Figure 2
The Fourier-filtered EXAFS function concerning the first nearest neighbour of the Pt K edge (open circles) is compared with that of the Pt L_{III} edge (closed circles).

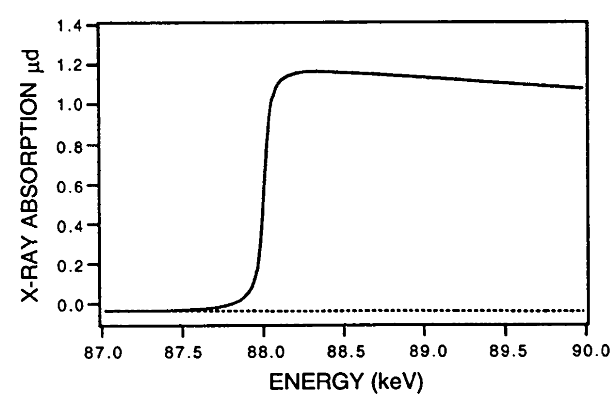

Figure 3
XAFS spectrum near the Pb K edge of $PbTiO_3$ powder sample at room temperature.

the increase of the finite lifetime effect due to the K hole, is consistent with the semi-empirical values by Krause & Oliver (1979).

Figure 3 shows the XAFS spectrum near the Pb K edge of $PbTiO_3$ powder. Any EXAFS oscillation was not observed at the least at room temperature, suggesting that the finite lifetime of the core hole is too short to make it, and that it is senvitive to Debye-Waller factor at high-k values.

4. Conclusion

XAFS spectra near K absorption edges of Pt and Pb enough to discuss EXAFS oscillation at low-k values were measured with good energy resolution at SPring-8. Although the amplitude of the EXAFS signal above the Pt K edge considerably reduces especially at low-k values owing to the finite lifetime of the core hole, it has been shown that there is utility to K edge XAFS measurement at high energies. On the other hand, any EXAFS oscillation was not observed above the Pb K edge at the least at room temperature, suggesting large effect of the finite lifetime of the core hole and the Debye-Waller factor.

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