

Experimental technique for radiative-process-resolved X-ray absorption spectroscopy at the inner-shell excitation thresholds

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Partial-fluorescence-yield (PFY) x-ray absorption measurements, using the optimized window widths of position sensitive detectors in wave-length dispersive x-ray spectrometers, have been applied for radiative-process-resolved (RPR) x-ray absorption spectroscopy. We have measured PFY-absorption spectra of graphite and diamond at the C K threshold and of *h*-BN and *c*-BN at the B K threshold. Resonant elastic x-ray scattering was observed in graphite and *h*-BN on their PFY-absorption spectra, and excitonic x-ray scattering was observed in diamond and *c*-BN. These results show that PFY-absorption measurements for RPR x-ray absorption spectroscopy can provide the information about the electronic structures and the radiative-decay process in inner-shell excitation.

Keywords: x-ray absorption, x-ray emission process, graphite, diamond, boron nitride

Introduction

X-ray absorption spectroscopy (XAS) at the inner-shell excitation thresholds provides a lot of information about electronic structure and chemical-bonding-states of molecules/materials. Especially, recent availability of high-energy-resolution and high-flux soft x-rays using synchrotron radiation has contributed to the development of many novel x-ray absorption experiments in wide range of research fields. In the x-ray absorption experiments, x-ray absorption spectra have usually been measured by monitoring electron yield (for example photoelectron Auger electrons, and sample photocurrent) and fluorescence yield (FY) (Stohr, 1992). In the FY-absorption measurements, the measured x-rays are usually the ordinary fluorescent x-rays resulted from the transition of valence electrons to inner core holes. However, the monitored x-rays may often include not only the ordinary fluorescent x-rays but also the x-rays emitted from other radiative processes such as resonant elastic/inelastic x-ray scattering at thresholds (Ederer & McGuire, 1996), specular reflection of x-rays, and diffuse scattering by surface irregularities. Therefore, we can obtain more detailed information about x-ray absorption followed by radiative-decays in inner-shell excitation, if we could measure the x-ray absorption spectra resolved for the individual radiative processes.

One of the simple methods for radiative-process-resolved (RPR) x-ray absorption spectral measurements is to selectively measure the photon energy of emitted x-rays by optimizing window widths of position-sensitive detectors (PSD) in wavelength-dispersive x-ray spectrometers. By using this technique, we have successfully separated the resonant elastic x-ray scattering (REXS) from FY-absorption spectra of graphite at C K threshold (Muramatsu *et al.*, 2000) and have demonstrated that the RPR-XAS could be a useful tool for analyzing the electronic structure of materials.

In this paper, we will demonstrate the experimental details for

PRP-XAS and PRP x-ray absorption measurements of the graphite/diamond and *h*-BN/*c*-BN systems to further investigate REXS in these systems.

Experiment

RPR x-ray absorption spectra can especially be obtained from the partial-fluorescence-yield (PFY) x-ray absorption measurements using a wavelength-dispersive x-ray spectrometer with PSD. For the PFY-absorption measurements, we can selectively extract x-ray emission signals from specified radiation processes by optimizing the window width on the PSD. In this study, the PFY-absorption measurements were carried out by using a grating x-ray spectrometer installed in beamline (BL) 8.0 (Jia *et al.*, 1995) at the Advanced Light Source (ALS). Figure 1 shows the top view of the optical arrangement for the measurements. Monochromatized undulator beams irradiate a sample, and fluorescent x-rays and other scattered x-rays emitted from the sample are monochromatized by a spherical grating and detected by the PSD. The entrance slit and the grating of the grating x-ray spectrometer are aligned perpendicularly to the incident undulator beams in the horizontal E-vector plane. In this arrangement, the high-energy and low-energy window widths on the PSD can be varied by adjustments of the high- and low-energy masks. To measure the PFY-absorption spectra, we scanned the incident beam energy monitoring the x-ray intensities detected on the PSD whose window widths were optimized by its high- and low-energy masks. The energy resolution of the PFY-absorption measurements in the C K region was estimated to be less than 0.5 eV for a 100- μ m exit slit and a 380-line/mm grating with a 70-m radius in the beamline monochromator.

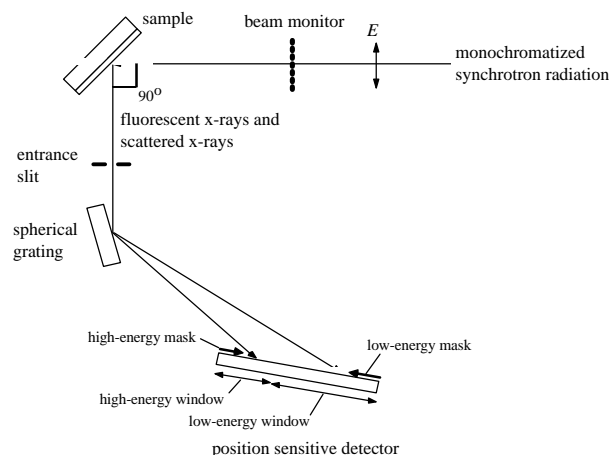


Figure 1

Top view of the optical arrangement for the PFY-absorption measurements in BL-8.0.

Powder samples were used in these measurements and the angle of incident beam onto the samples was optimized to minimize the detection of elastic scattering and reflected light. Commercially obtained powder samples of graphite, diamond, *h*-BN and *c*-BN were used to observe the REXS. Average particle size of these powder samples were 50 – 250 μ m. These powder samples were pressed on indium sheets which covered with sample holders. Total-electron-yield (TEY) x-ray absorption spectra of these samples were also measured as references by monitoring the sample photocurrent in BL-6.3.2 (Underwood *et al.*, 1996). The energy resolution of the TEY-absorption measurements in the C K region was estimated to

be 0.07 eV for 20- μm exit slit and a 600-line/mm grating. Samples were in a 10^{-8} -Torr vacuum during the PFY- and TEY-absorption measurements.

Results and Discussion

Figure 2 shows the C K x-ray emission spectra, which were obtained using 320-eV x-ray excitation, and PFY- and TEY-absorption spectra of (a) graphite powder and (b) diamond. For graphite, the PSD was positioned to detect x-rays from 263 to 298 eV as shown in the C K x-ray emission spectrum. In the x-ray emission spectrum, elastic x-ray scattering can be expected in the energy region above 284 eV and resonant inelastic x-ray scattering (RIXS) or fluorescent x-ray emission can be expected below 284 eV. In this PSD setup, the width of the wide window (denoted by A in the figure) was tuned from 263 to 298 eV, that of the low-energy window (B) was from 263 to 284 eV, and that of the high-energy window (C) was from 284 to 298 eV, as illustrated in the x-ray emission spectrum. The lower panel shows the PFY-absorption spectra taken with (A) the wide, (B) low-energy, and (C) high-energy windows, as well as the spectra obtained after subtracting (B) from (A) and the TEY-absorption spectra of graphite. These PFY-absorption spectra can be obtained by monitoring I/I_0 , where I is the x-ray intensity measured by the PSD and I_0 is the incident-beam photocurrent intensity measured by a gold-mesh beam monitor in front of the samples. In these measurements, the shape of the I/I_0 spectra may not precisely reflect the C K absorption structure of the samples because of carbon contamination of the beamline optics in BL-8.0. Therefore, the I/I_0 spectra of (A) and (B) are not agree with the previously published x-ray absorption spectra of graphite.

We detected RIXS in the low-energy window (B), elastic x-ray scattering in the high-energy window (C), and both RIXS and elastic x-ray scattering in the wide window (A). Therefore, energy-dependent spectra of elastic x-ray scattering can be obtained from the PFY-absorption spectra of (C) or the spectra obtained after subtracting (B) from (A). In the high-energy-window PFY-absorption spectrum of the graphite (C), a sharp peak was observed near 285 eV, followed by a slight plateau in the energy region from 285 to 292 eV. These spectral features of (C) were approximately reproduced in the spectrum obtained after subtracting (B) from (A). Comparing these energy-dependent spectra of elastic x-ray scattering with the TEY-absorption spectrum which is in good agreement with the published spectrum (Skytt *et al.*, 1994) measured with the normal incidence irradiation onto the sample surface, we found that the sharp 285-eV scattering peak corresponds to the π^* -absorption peak and that the broad portion in the range from 285 to 292 eV corresponds to the region between the π^* - and σ^* -absorption peaks. No scattering structure was observed above the σ^* -peak region. This elastic x-ray scattering in graphite thus corresponds to the threshold unoccupied electronic structure, and it can be identified as *participator* REXS via π^* orbitals; *participator* REXS is caused by the radiative transition of \hat{O} participator \hat{O} electrons, excited in the threshold localized states, to the inner core-holes. The spectral height at 285 eV in the low-energy-window spectrum shows the probability of *spectator* RIXS occurring; *spectator* RIXS is caused by the interaction of \hat{O} spectator \hat{O} electrons, excited in threshold localized states, with valence electrons. In comparison, the peak height at 285 eV in the wide-window spectrum includes both *spectator* RIXS and *participator* REXS. Consequently, we can quantitatively determine the transition-probability ratio of the *spectator* RIXS and *participator* REXS by comparing these peak heights; the probabilities of transition to *participator* REXS or to *spectator* RIXS in the π^* -resonant radiative-decay process of graphite powder were determined to be approximately 47% and 53%, respectively. For diamond, shown in Fig. 2(b), a peak at 289

eV and a small peak at 284 eV were observed in the high-energy-window PFY-absorption spectrum (C) and the spectrum obtained after subtracting (B) from (A). In comparison to the I_0 spectral shape, the 284-eV peaks in the I/I_0 spectra of (A), (B), and (C), and in the spectrum obtained after subtracting (B) from (A) are the result of carbon contamination of the beamline optics. The peak at 289 eV, however, corresponds to the threshold peak caused by an exciton in the TEY-absorption which is in good agreement with the published spectrum (Ma *et al.*, 1992). Therefore, the 289-eV peak may also be elastic x-ray scattering via exciton states. This resonant phenomenon in exciton states was discovered and explained by Ma *et al.* (Ma, 1993) as resulting from the vibronic coupling effects of core excitons. Except for this excitonic x-ray scattering, no significant scattering structure was observed for diamond.

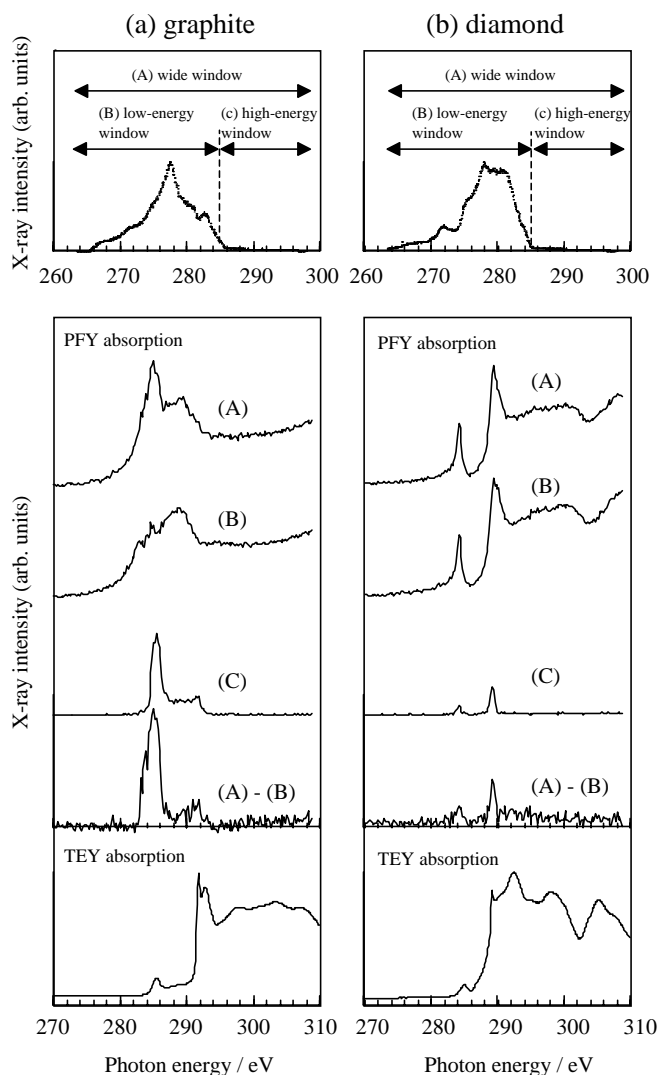


Figure 2 C K x-ray emission spectra (upper panels) and PFY- and TEY-absorption spectra (lower panels) of (a) graphite powder and (b) diamond. The x-ray emission spectra were obtained using 320-eV excitation. The PFY-absorption spectra were taken by monitoring the x-ray intensity measured by the PSD with (A) wide, (B) low-energy, and (C) high-energy windows. Spectra obtained after subtracting (B) from (A), denoted by (A) - (B), are also shown.

Figure 3 shows the B K x-ray emission spectra, which were obtained using 210-eV x-ray excitation, and PFY- and TEY-absorption spectra of (a) *h*-BN and (b) *c*-BN. In the x-ray emission spectra, elastic x-ray scattering can be expected in the energy region above 189 eV and RIXS or fluorescent x-ray emission can be expected below 189 eV. In this PSD setup, the width of the wide window (A) was tuned from 168 to 200 eV, that of the low-energy window (B) was from 168 to 189 eV, and that of the high-energy window (C) was from 189 to 200 eV. The lower panels show the PFY-absorption spectra taken with (A) the wide, (B) low-energy, and (C) high-energy windows, as well as the spectra obtained after subtracting (B) from (A) and the TEY-absorption spectra.

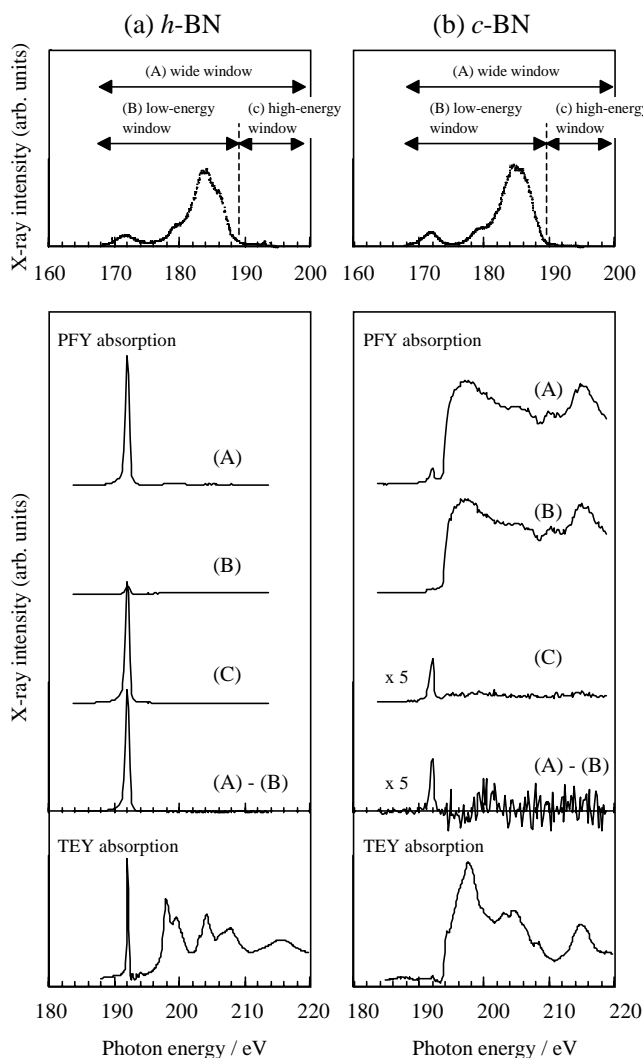


Figure 3
B K x-ray emission spectra (upper panels) and PFY- and TEY-absorption spectra (lower panels) of (a) *h*-BN and (b) *c*-BN. The x-ray emission spectra were obtained using 210-eV excitation. The PFY absorption spectra were taken by monitoring the x-ray intensity measured by the PSD with (A) wide, (B) low-energy, and (C) high-energy windows. Spectra obtained after subtracting (B) from (A), denoted by (A) - (B), are also shown.

In the PFY-absorption spectra of *h*-BN, an intense peak was observed at 192 eV in the wide-window (A) and in the high-energy-window (C) spectra. Although the weak peak was observed at 192 eV in the low-energy-window (B) spectrum, the intense peak

structure of the high-energy window spectrum (C) was also observed in the spectrum obtained after subtracting (B) from (A). Comparing these energy-dependent spectra of elastic x-ray scattering with the TEY-absorption spectrum which is in good agreement with the published spectrum (Jia *et al.*, 1996), we found that the intense 192-eV scattering peak corresponds to the π^* -absorption peak. This elastic x-ray scattering in *h*-BN can therefore be identified as *participator* REXS via π^* -orbitals. From the comparison of the peak height at 192 eV in the wide-window spectrum (A) with the low-energy-window spectrum (B), the probabilities of transition to *participator* REXS or to *spectator* RIXS in the π^* -resonant radiative-decay process of *h*-BN were determined to be approximately 94% and 6%, respectively. For *c*-BN, shown in Fig. 3(b), a weak peak near 192 eV was observed in the high-energy-window spectrum (C) and the spectrum obtained after subtracting (B) from (A). The peak near 192 eV, however, corresponds to the threshold small peak caused by an exciton in the TEY-absorption which is in agreement with the published spectrum of *c*-BN crystal (Shin *et al.*, 1995) without the intensity of the excitonic peak near 192 eV. Because the *c*-BN powder sample was used in this study, its excitonic peak intensity may be weaker than one of *c*-BN crystal. Therefore, the weak 192-eV peak may also be elastic x-ray scattering via exciton states. The *participator* REXS of *h*-BN and the excitonic scattering of *c*-BN are as same as the above mentioned *participator* REXS of graphite taking hexagonal structure and excitonic scattering of diamond taking cubic structure, respectively.

Conclusion

To demonstrate the RPR-XAS, we have measured PFY-absorption spectra of graphite and diamond at the C K threshold and those of *h*-BN and *c*-BN at the B K threshold, using the different PSD window widths optimized by the high- and low-energy masks of the PSD. From these PFY x-ray absorption measurements, we observed *participator* REXSs in graphite and *h*-BN. In diamond and *c*-BN, however, no REXS was observed, except for a small amount of excitonic x-ray scattering. These results show that the PFY-absorption measurements for RPR-XAS can provide the information about the electronic structures and the radiative-decay process.

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