

Resonant X-Ray Raman Scattering in B $K\alpha$ Emission Spectra of Boron Oxide (B_2O_3) Excited by Undulator Radiation

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The satellite structure for the B $K\alpha$ emission spectrum of boron oxide has been elucidated by threshold experiments carried out by varying the excitation energy of the incident undulator beam from below the B K absorption edge to several tens of eV above the absorption edge. Prominent emission of the satellite peak was observed when the excitation energy was tuned to the narrow pre-edge peak in the absorption spectrum, corresponding to the transition from B($1s$) to an unoccupied antibonding $p\pi^*$ orbital. It is concluded that the satellite peak originates from resonant x-ray Raman scattering due to a B($1s$)- $p\pi^*$ -B($1s^{-1}$) transition.

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Recently, several x-ray emission threshold studies have been investigated especially with respect to satellite structures associated with x-ray emission spectra using monochromatized synchrotron radiation [1-4]. Resonant Raman scattering was first observed by Sparks [5] from various metallic elements. Resonant emission has also been observed in the L regions of transition metals and their oxide compounds [6,7]. However, only a few attempts [8] have so far been made at the K region of low atomic number elements such as boron, carbon, and nitrogen, because of their low fluorescent yields and lack of the suitable excitation x rays in the VUV/soft-x-ray region.

The B $K\alpha$ emission spectra for boron and its related compounds have been investigated by many researchers with the use of high resolution x-ray emission spectroscopy [9-13]. Most of these spectra were obtained by either electron excitation or x-ray excitation using conventional x-ray sources. In the B $K\alpha$ emission spectra of boron oxide (B_2O_3) and boron nitride (BN), satellite peaks are evident at both high- and low-energy sides of the main emission peak due to the B($2p$)-B($1s^{-1}$) transition. The nature of the low-energy satellites has recently been clarified and assigned to the transition from the molecular orbital with B($2p$) and O($2s$) or N($2s$) character to B($1s^{-1}$) core hole [14]. After the submission of this paper, O'Brien *et al.* [15] reported the excitation energy dependence of B $K\alpha$ emission spectra of B_2O_3 and BN using monochromatized synchrotron radiation. They found that the main emission peaks and the low-energy satellites are shifted to lower energy when exciting into the core exciton states. For the high-energy satellites, Luck and Urch [16] observed that the high-energy satellite intensity of several boron oxide compounds correlates with the coordination number of boron. However, the nature of the high-energy satellites has not yet been clearly elucidated.

The aim of this study is to investigate the satellite structures in the B $K\alpha$ emission spectra of boron com-

pounds using highly brilliant undulator radiation as an excitation source. In this paper, the origin of the high-energy satellite in the B $K\alpha$ emission spectrum of B_2O_3 is described, which was elucidated by measuring selectively excited B $K\alpha$ emission spectra using a quasimonochromatic or monochromatic undulator beam.

Spectroscopic measurements of B_2O_3 were carried out with a fluorescent x-ray spectrometer (FXS) of a novel design [17] installed on an undulator beam line (BL-16U) at the Photon Factory [18]. The purity of the commercially obtained solid B_2O_3 sample exceeds 99.9%. The FXS utilizes a variable-spacing grating with an average groove density of 2400 lines/mm and entrance-slitless optics. Undulator radiation emitted from the 26-period undulator is monochromatized by a 2-m grazing incidence monochromator (2-m GIM) [19,20] on the beam line. By varying the magnetic gap of the undulator from 91 to 105 mm, the photon energy of the undulator first harmonic was tuned from 185 to 271 eV, covering from below the B K absorption edge to the continuum. The quasimonochromatic undulator first harmonic beam obtained through the 2-m GIM as the zeroth order diffraction or monochromatic beam is normally incident to the sample and is used for B K excitation. The detection angle of fluorescent x rays is 35° from the sample normal axis. Both B $K\alpha$ emission spectra and x-ray absorption near edge structure (XANES) spectra with fluorescent x-ray detection can be obtained by combining the FXS with the 2-m GIM. The optical design and performance of this system are described in detail elsewhere [14].

Figure 1 shows a typical B $K\alpha$ emission spectrum excited by a quasimonochromatic undulator first harmonic beam and fluorescence XANES spectrum of B_2O_3 . The theoretical spectrum generated from the discrete variational (DV)- $X\alpha$ molecular orbital calculation [21,22] is also shown in this figure. The peak energy of the quasimonochromatic undulator first harmonic beam was tuned to 215 eV on the continuum with an energy width (FWHM) of about 20 eV to maximize B K excitation. In

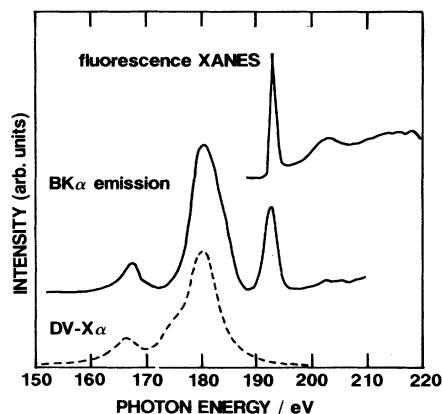


FIG. 1. A typical B $K\alpha$ emission spectrum excited by a quasimonochromatic undulator beam and a fluorescence XANES spectrum of solid B_2O_3 . A calculated DV- $X\alpha$ emission spectrum (broken line) [14] is superimposed on these experimental spectra.

the measured emission spectrum, the main emission peak due to a $B(2p)-B(1s^{-1})$ transition was observed at 180 eV. With the aid of the calculated DV- $X\alpha$ spectrum, the low-energy satellite peak observed at 165 eV can be attributed to a transition from a molecular orbital consisting of $B(2p)$ and $O(2s)$ character to a $B(1s^{-1})$ core hole. However, the high-energy satellite observed at 193 eV is not revealed in the calculated spectrum. Therefore, the origin of the high-energy satellite is not explained by the ordinary fluorescence process from an occupied valence orbital to an inner core hole. It must be noted also that the peak energy of the observed high-energy satellite nearly corresponds to the narrow pre-edge absorption peak assigned to a $B(1s)$ (antibonding $p\pi^*$ orbital) transition in the XANES spectrum.

Taking advantage of the quasimonochromatic character of the undulator radiation, dependence of the B $K\alpha$ emission spectra on excitation energy was surveyed by varying the magnetic gap of the undulator. Figure 2 shows the B $K\alpha$ emission spectra excited by the quasimonochromatic undulator first harmonic. The magnetic gap was varied from 91 to 105 mm, corresponding to the peak energy of the first harmonic from 185 to 271 eV. Individual spectral distributions of the incident undulator beam are also included in the figure. An increase in the high-energy satellite peak intensity was clearly observed as the magnetic gap was reduced from 105 to 92 mm. The intensity of the high-energy satellite was maximized when the magnetic gap was tuned to 92 mm and the peak energy of the undulator first harmonic nearly corresponds to the high-energy satellite. However, the peak intensity drastically decreased when the gap was reduced to 91 mm. Therefore, it is experimentally confirmed that the prominent emission of the high-energy satellite is not due to the ordinary first order optical process (fluorescence process). On the other hand, the peak intensity of the

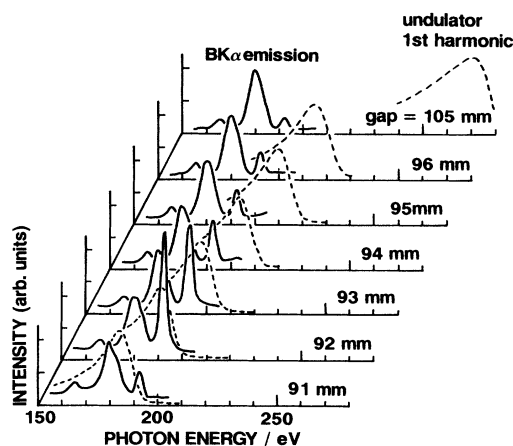


FIG. 2. The B $K\alpha$ emission spectra excited by a quasimonochromatic undulator beam are plotted for different magnetic gaps varying from 91 to 105 mm. Spectral distribution of the undulator first harmonic (broken line) is also shown in the figure.

low-energy satellite remained constant despite varying the magnetic gap from 91 to 105 mm. This seems reasonable, since the low-energy satellite is due to the ordinary fluorescence process as mentioned above.

To further investigate the unique behavior of the high-energy satellite, the scattered radiation spectrum was measured with a monochromatized incident beam. The energy width of the incident beam was tuned to about 2 eV. Figure 3 shows the result of this measurement (a) and the fluorescence XANES spectrum (b). The intensity of the scattering drastically increased at 193 eV, and slightly increased at about 200 eV. The prominent scattering peak at 193 eV corresponds to the high-energy satellite peak in the B $K\alpha$ emission spectra. Therefore, it is obvious that the high-energy satellite is revealed when the photon energy of the incident beam is tuned to coincide with the energy of the satellite peak. By comparison with the XANES spectrum, these scattering peaks correspond to absorption peaks. A peak shift between the

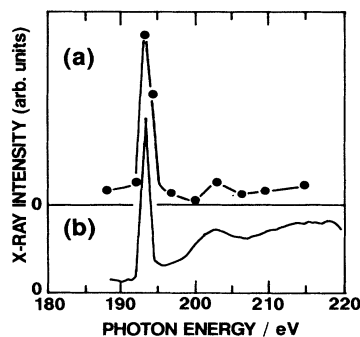


FIG. 3. Spectral distribution of the scattered radiation (a) and the fluorescence XANES spectrum (b) is plotted.

scattering and absorption peaks was not observed within the 2-eV resolution of the incident beam. Similarity of the spectral shape between the scattering and the absorption spectra can be explained by x-ray Raman scattering [23] that is the inelastic scattering of x rays by inner-shell electrons. For light elements, the spectral profiles of the x-ray Raman scattering should be similar to the x-ray absorption spectra, because the dynamic structure factor that reflects the property of the x-ray Raman scattering is directly proportional to the x-ray absorption cross section [24]. Therefore, the origin of the high-energy satellite observed at 193 eV is shown to be the resonant x-ray Raman scattering. This resonant x-ray Raman scattering process is described as follows. The first step involves the excitation of an electron from $B(1s)$ to a localized $p\pi^*$ orbital at 193 eV. This is followed by the direct transition of the excited electron from $p\pi^*$ to the $B(1s^{-1})$ core hole.

Figure 4 shows the B $K\alpha$ emission spectra excited by a monochromatized beam from 193.0 eV on the $p\pi^*$ resonance to 214.8 eV on the continuum. No high-energy satellite was observed in the spectra excited at 196.8, 203.1, and 214.8 eV. In these spectra, the peak width (FWHM) of the main emission peaks observed at 180 eV was measured about 7.5 eV. Scattering peaks of the incident beam were revealed in the 196.8- and 203.1-eV spectra. On the other hand, the resonant x-ray Raman scattering at 193 eV was revealed about 6 times higher than that of the main peak in the 193.0-eV spectrum. The main emission peak was observed at 178 eV, and its FWHM was measured about 6.5 eV. The main peak energy shift of 2 eV between the on resonance and the on continuum agrees with the previous data [15]. This energy shift is interpreted by O'Brien [15] as a result of phonon relaxation and differences in initial- and final-state electronic screening by a spectator electron excited electron in the localized $p\pi^*$ orbital. A similar energy shift has been observed in the Cl $K\beta$ emission spectra of $CFCl_3$ excited below and above the Cl K absorption edge [4]. The narrowing of the main emission peak features may be attributed to lifetime broadening of an inner-shell vacancy. This effect has been observed also in the $K\beta$ emission of argon gas excited on the subthreshold resonance [3,25]. The energy shift and the narrowing effect have been recognized as characteristic of resonant x-ray Raman scattering. Therefore, the observed energy shift and narrowing in the B $K\alpha$ emission spectrum of B_2O_3 excited at 193 eV provide further evidence that the high-energy satellite is due to the resonant x-ray Raman scattering.

We also observed the resonant phenomena in the B $K\alpha$ emission spectrum of BN, which will be reported in detail elsewhere [26]. The coordination number for boron in B_2O_3 and BN is 3, with boron taking a trigonal planar structure. Therefore, resonant x-ray Raman scattering is expected in other trigonally coordinated compounds in which localized antibonding $p\pi^*$ orbitals are generated.

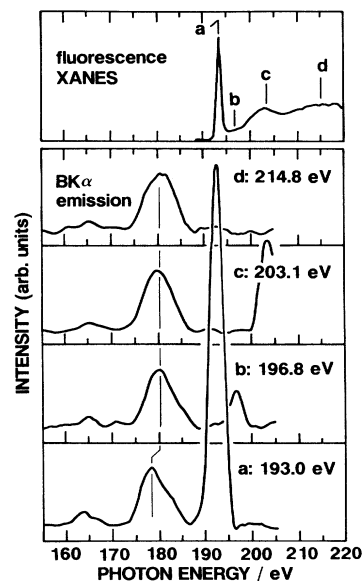


FIG. 4. The B $K\alpha$ emission spectra excited by a monochromatized undulator beam at 193.0 (a), 196.8 (b), 203.1 (c), and 214.8 eV (d). These spectra were slightly smoothed. Excitation energies were indicated in the fluorescence XANES spectrum on the upper panel.

Studies on the resonant x-ray Raman scattering and corresponding strong absorption may provide information about the localization of unoccupied antibonding orbitals.

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- [1] P. L. Cowan, *Phys. Scr.* **T31**, 112 (1990).
- [2] N. Wassdahl, P. Bleckert, G. Bray, P. Glans, N. Martensson, J. Nordgren, J. E. Rubensson, R. Nyholm, and S. Cramm, in *Proceedings of the Fifteenth International Conference on X-Ray and Inner-Shell Processes*, AIP Conf. Proc. No. 215 (AIP, New York, 1990), p. 451.
- [3] R. D. Deslattes, R. E. LaVilla, P. L. Cowan, and A. Henins, *Phys. Rev. A* **27**, 923 (1983).
- [4] R. C. C. Perera, R. E. LaVilla, P. L. Cowan, T. Jach, and B. Karlin, *Phys. Scr.* **36**, 132 (1987).
- [5] C. J. Sparks, Jr., *Phys. Rev. Lett.* **33**, 262 (1974).
- [6] N. Wassdahl, J. E. Rubensson, G. Bray, P. Glans, P. Bleckert, R. Nyholm, S. Cramm, N. Martensson, and J. Nordgren, *Phys. Rev. Lett.* **64**, 2807 (1990).
- [7] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J. E. Rubensson, and N. Wassdahl, *Rev. Sci. Instrum.* **60**, 1690 (1989).

- [8] Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J-E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan, *Phys. Rev. Lett.* **69**, 2598 (1992).
- [9] J. E. Holiday, *Adv. X-Ray Anal.* **9**, 365 (1965).
- [10] D. W. Fischer and W. L. Baun, *J. Appl. Phys.* **37**, 768 (1966).
- [11] Y. Hayashi, *Science Report of the Tohoku University* **11**, 43 (1968).
- [12] V. A. Fomichev, T. M. Zimkina, and I. I. Lyakhovskaya, *Fiz. Tverd. Tela* **12**, 156 (1970) [*Sov. Phys. Solid State* **12**, 123 (1970)].
- [13] I. I. Lyakhovskaya, T. M. Zimkina, and V. A. Fomichev, *Fiz. Tverd. Tela* **12**, 174 (1970) [*Sov. Phys. Solid State* **12**, 138 (1970)].
- [14] Y. Muramatsu, M. Oshima, J. Kawai, and H. Kato, *Nucl. Instrum. Methods Phys. Res., Sect. B* **75**, 559 (1993).
- [15] W. L. O'Brien, J. Jia, Q-Y. Dong, T. A. Callcott, K. E. Miyano, D. L. Ederer, D. R. Mueller, and C-C. Kao, *Phys. Rev. Lett.* **70**, 238 (1993).
- [16] S. Luck and D. S. Urch, *Phys. Scr.* **41**, 970 (1990).
- [17] Y. Muramatsu, M. Oshima, T. Shoji, and H. Kato, *Rev. Sci. Instrum.* **63**, 5597 (1992).
- [18] T. Matsushita, H. Maezawa, T. Ishikawa, M. Nomura, A. Nakagawa, A. Mikuni, Y. Muramatsu, Y. Satow, T. Kosuge, S. Sato, T. Koide, N. Kanaya, S. Asaoka, and I. Nagakura, *Rev. Sci. Instrum.* **60**, 1874 (1989).
- [19] Y. Muramatsu and H. Maezawa, *Rev. Sci. Instrum.* **60**, 2078 (1989).
- [20] Y. Muramatsu, H. Kato, H. Maezawa, and T. Harada, *Rev. Sci. Instrum.* **63**, 1305 (1992).
- [21] C. Satoko, M. Tsukada, and H. Adachi, *J. Phys. Soc. Jpn.* **45**, 1333 (1978).
- [22] J. Kawai, K. Maeda, I. Higashi, M. Takami, Y. Hayashi, and M. Uda, *Phys. Rev. B* **42**, 5693 (1990).
- [23] Y. Mizuno and Y. Ohura, *J. Phys. Soc. Jpn.* **22**, 445 (1967).
- [24] H. Nagasawa, S. Mourikis, and W. Schulke, *J. Phys. Soc. Jpn.* **58**, 710 (1989).
- [25] T. Tulkki and T. Aberg, *J. Phys. B* **15**, L435 (1982).
- [26] Y. Muramatsu, J. Kawai, T. Scimeca, M. Oshima, and H. Kato (to be published).