

Enhanced Resonant X-Ray Emissions of Mechanically Milled Hexagonal Boron Nitride in Boron K-Shell Excitation

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(Received 20 October 1995)

Enhanced resonant x-ray emissions were observed from mechanically milled hexagonal boron nitride nanoclusters in boron *K*-shell excitation using quasimonochromatic undulator radiation. The resonant x-ray emission intensity increases with decrease in size of the milled clusters. Comparison of the measured x-ray emission spectra with the calculated spectra using the discrete-variational $X\alpha$ methods showed enhanced resonant x-ray emissions originate from the $B 1s-n^*-B 1s^{-1}$ electron transition, with n^* an unoccupied nonbonding orbital of twofold-coordination boron atoms with dangling bonds. X-ray emissions excited to n^* orbitals may be possible for detecting dangling bonds in nanoclusters. [S0031-9007(96)00198-6]

PACS numbers: 78.70.En

Soft x-ray emission spectroscopy has recently been studied using synchrotron radiation to investigate the electronic characteristics of various materials. In particular, resonant x-ray emissions occurring when the excitation energy is tuned to a specific level provide new information on the excitation dynamics in the interaction process of photons and electrons. The satellite structure in fluorescent x-ray emission spectra has recently been investigated by measuring selectively excited x-ray emission spectra [1–4]. We have demonstrated that the high-energy satellites in the B *K* x-ray emission spectra of boron oxide and boron nitride originate from resonant x-ray emissions due to an electron transition between boron $1s$ and unoccupied antibonding orbitals [5,6]. Prominent resonant x-ray emissions are observed in molecules with strongly localized unoccupied antibonding π^* orbitals, such as in boron atoms with threefold coordination. Kashiwai, Kouzuki, and Motoyama [7] also found that the spectral profile of the B *K* x-ray emissions of hexagonal boron nitride (*h*-BN) powder, taken with high-energy electron beam excitation, depends slightly on the mechanical milling time of the powder. To further investigate this phenomenon, we measured selectively excited B *K* x-ray emission spectra of mechanically milled *h*-BN clusters by using quasimonochromatic undulator radiation, focusing on resonant x-ray emissions. In this Letter, we describe how resonant x-ray emissions depend on disorder in the layered

hexagonal structure of BN clusters created by mechanical milling, by comparing the measured x-ray emission spectra with calculated discrete-variational (DV) $X\alpha$ spectra.

We used commercial *h*-BN powder samples whose purity was more than 99.99%. The samples were mechanically milled for 0.5, 1.0, 5.0, and 10.0 h in an argon atmosphere to prevent oxidation. The hexagonal crystal structure of the individual samples were identified from the spectrum profiles of the x-ray diffraction: Their particle size was estimated from the peak width in the x-ray diffraction spectra. The average size L of the particles was estimated from the full width at half maximum (FWHM) of the x-ray diffraction peak $\Delta(2\theta)$ by using the Scherrer equation [8] $\Delta(2\theta) = \lambda/L \cos\theta_0$, where λ is the diffraction wavelength and θ_0 is the Bragg angle. The estimated average particle size was 1000, 140, 50, 20, and less than 20 Å for the 0-, 0.5-, 1-, 5-, and 10-h milled samples, respectively.

The B *K* x-ray emission spectra and the absorption spectra were obtained using a grating x-ray spectrometer in the BL-16 undulator beam line at the Photon Factory (PF) [9–11]. The grating was a 2-m variable-spaced grating with a groove density of 2400 lines/mm: Its incident angle was fixed at 87°. A gas-flow-type proportional counter was used for x-ray detection. For the x-ray emission measurements, the quasimonochromatic undulator first harmonic beam was incident on the sample, and

x-ray emission spectra were taken with an energy resolution of about 2 eV. The peak energy of the incident undulator first harmonics was varied from 180 to 230 eV, which covered from below the boron K -shell threshold to continuum, by adjusting the magnetic gap of the undulator. The energy width of the first harmonics was about 12 eV. For the absorption measurements, a monochromatized undulator beam with an energy resolution of 0.8 eV was incident on the sample, and the B K x-ray emissions were detected. The incident beam was scanned from 188 to 208 eV. Each measurement time was about 30 min for both the emission and absorption measurements. Decomposition of the samples was not observed during these measurements with 300 mA beam current in the PF-synchrotron ring. Details of the spectroscopic measurements are described elsewhere [12,13].

The B K x-ray emission spectra of the unmilled sample with a particle size of 1000 Å are shown in Fig. 1. The peak energy of the incident beam was tuned from about 180 to 230 eV by varying the magnetic gap of the undulator from 92 to 100 mm. In the spectrum measured with the highest energy excitation with a magnetic gap of 100 mm, the main B K x-ray emission peak due to a $B 2p-B 1s^{-1}$ transition was observed at 181.5 eV and the low-energy satellite due to a $N 2s-B 1s^{-1}$ transition was observed at 170 eV. This spectral profile agrees with previous data obtained with high-energy electron beam

excitation [14,15]. No high-energy satellite was observed in 92- and 100-mm gap spectra, but high-energy satellites were observed at 192 and 197 eV in other gap spectra. The high-energy satellite intensity obviously increases when the photon energy of the incident beam coincides with the satellite energies. The origin of the high-energy satellites was identified as resonant x-ray emissions due to a $B 1s-\pi^*-B 1s^{-1}$ transition, where π^* means the π portion of the unoccupied boron $2p$ orbitals [6].

Figure 2 shows that the B K x-ray emission spectra of mechanically milled h -BN samples, excited by quasi-monochromatic undulator first harmonics tuned to the π^* -orbital excitation with a 94 mm magnetic gap. It is clear that the resonant x-ray emission of the high-energy satellite at 192 eV greatly increased as the mechanical milling time was increased; however, the peak intensities of the main B K x-ray emission peak at 181.5 eV and the low-energy satellite at 170 eV were almost constant and independent of the mechanical milling time. The high-energy satellite at 197 eV was also barely enhanced by the milling. The peak intensity ratio of the enhanced resonant x-ray emission to the main B K x-ray emission was 0.35 for the unmilled sample, but the ratio increased to more than 5.0 for the 5- and 10-h milled samples. The FWHM of the enhanced peak is about 3 eV, and the spectral shape has a slight tail at the higher energy side. The dependence of the resonant x-ray emission intensity on the average particle size of the milled samples is shown in

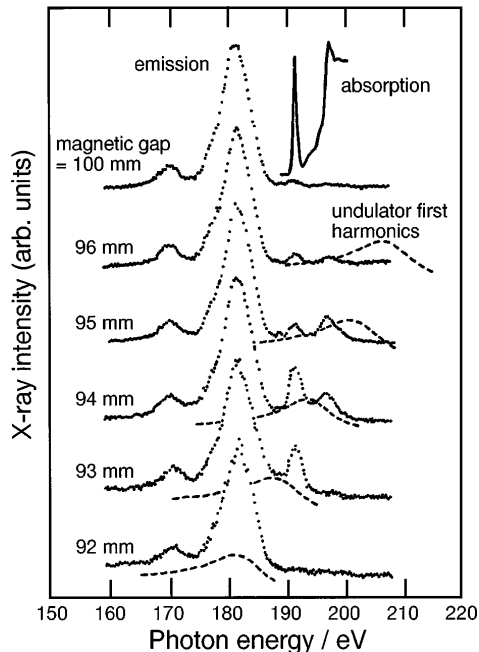


FIG. 1. B K x-ray emission spectra of unmilled h -BN, excited by quasimonochromatic undulator first harmonics (dotted line). The absorption spectrum (solid line) and the spectral profiles of the incident first harmonics (dashed line) are also shown. Peak energies of the first harmonics were tuned from below the boron K -shell threshold to continuum by varying the magnetic gap of the undulator from 92 to 100 mm.

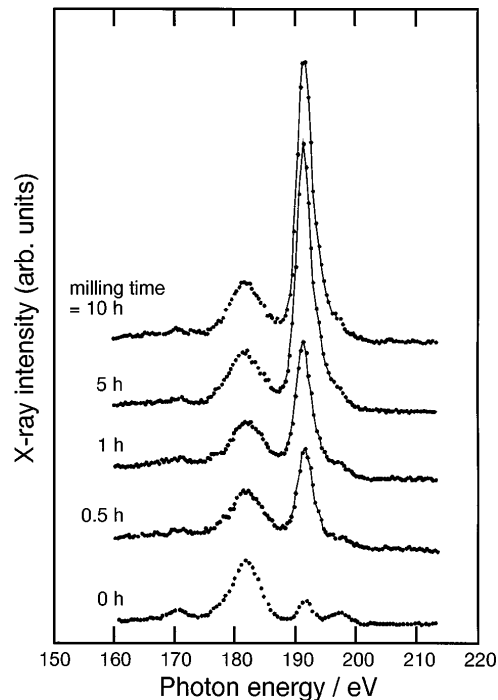


FIG. 2. B K x-ray emission spectra of unmilled and milled h -BN. The peak energy of the incident beam was tuned to 193 eV with a magnetic gap of 94 mm. Milling time is also shown.

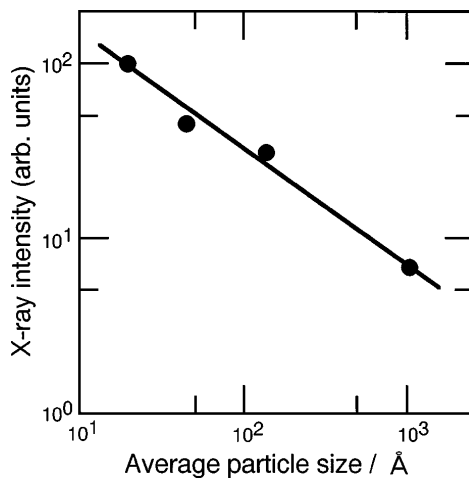


FIG. 3. Dependence of resonant x-ray emission peak intensity on average particle size of milled *h*-BN clusters.

Fig. 3. The emission intensity is inversely proportional to the average particle size, showing that the state of the unoccupied orbitals near π^* is directly affected by the fine structure of the milled BN clusters.

We think that the enhancement of resonant x-ray emissions originates from dangling bond formation in BN clusters. Fine cluster formation due to mechanical milling destroys the threefold B-N bonds in a layered hexagonal structure, causing the twofold B-N bonds with dangling bonds in the BN clusters. Kawai *et al.* [16] calculated the boron $2p$ density of states (DOS) of the hexagonal B_8N_8 model cluster shown in Fig. 4 by using the discrete-variational (DV) $X\alpha$ methods [17]. The length of a B-N bond is 1.45 Å. Five boron atoms located on the edge of the model cluster are twofold atoms with dangling bonds, and the inner three boron atoms are threefold atoms. Figure 5 shows the calculated boron $2p$ DOS of the occupied and unoccupied orbitals of (a) threefold and (b) twofold boron atoms. The major components of the lower unoccupied orbitals, shown as the four portions of a_i ($i = 1-4$) in the figure, are π^* in threefold boron and n^* in twofold boron. n^* denotes an unoccupied nonbonding orbital due to a dangling bond. The energy position of the four a_i components in n^* is apparently the same as that in π^* in threefold boron atoms: 0.7, 3.5, 6.8, and 8.7 eV above the Fermi energy level. Compared with the measured x-ray emission spectra in Fig. 2, the enhanced resonant x-ray emission of the high-energy satellite at 192 eV corresponds to a_1 and a_2 components, although the fine spectral structure based on a_1 and a_2 was barely distinguishable because of insufficient energy resolution in the measurements. The high-energy satellite at 197 eV also corresponds to a_3 and a_4 components. The main difference in the components between π^* and n^* is the peak intensity of a_1 : The a_1 peak intensity per boron atom in n^* is about 8 times larger than that in π^* . This shows that the cross section of the resonant

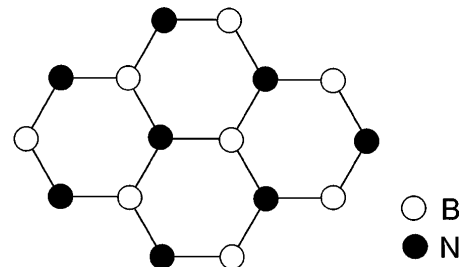


FIG. 4. Model cluster of *h*-BN for the DV- $X\alpha$ calculations [16].

x-ray emissions due to an n^* resonance ($B 1s-n^*-B 1s^{-1}$ transition) through the a_1 component is larger than that of a π^* resonance. On the other hand, the peak intensity of the a_3 and a_4 components in n^* is smaller than that in π^* : This agrees with the nonenhancement of the high-energy satellite at 197 eV. Therefore, we think that the enhanced resonant x-ray emission at 192 eV of the milled BN clusters originates in the n^* resonance through the a_1 component.

In a plane rhombic model cluster of B_xN_x ($x = n^2 + 4n + 3$) composed of $(n + 1)^2$ pieces of hexagonal B_3N_3 units, the number of twofold boron atoms is $2n + 3$, and that of threefold atoms is $n^2 + 2n$. (For example, the B_8N_8 cluster shown in Fig. 4 can be expressed as $n = 1$.) The average particle size of the model cluster can be expressed as $(Lx^2 + Ly^2)^{1/2}$, where Lx is the length of the longer diagonal ($= 4.4n + 2.9$ Å) and Ly is the shorter diagonal ($= 2.5n + 2.5$ Å) of the rhombic model.

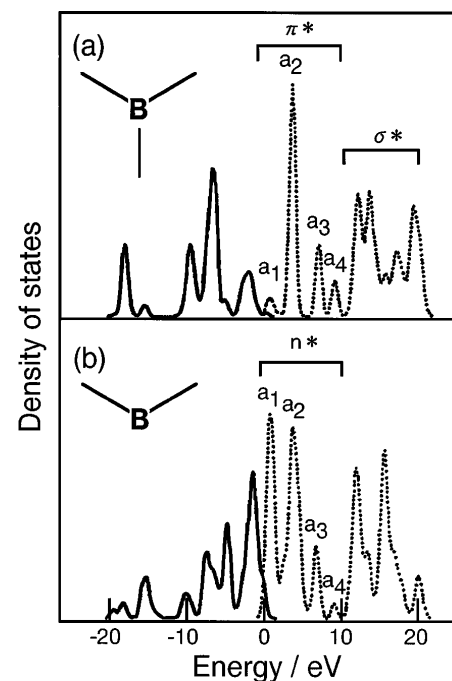


FIG. 5. Calculated boron $2p$ density of states of (a) threefold and (b) twofold coordination boron atoms: occupied (solid line), unoccupied (dotted line) [16].

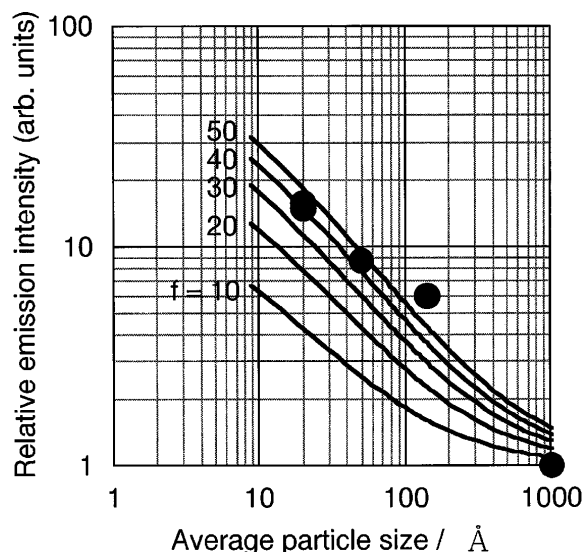


FIG. 6. Calculated relative resonant x-ray emission intensity of plane rhombic model clusters of B_xN_x (solid line) and the experimental data (black circles).

Since resonant x-ray emissions are considered to be the sum of the n^* resonance from the twofold boron atoms and the π^* resonance from threefold boron atoms, the relative intensity of the resonant x-ray emissions (I_{rel}) of this model cluster can be expressed as follows:

$$I_{rel} = [(n^2 + 2n) + f(2n + 3)] / (n^2 + 4n + 3),$$

where f is the relative cross section of the n^* resonance. Figure 6 shows the calculated resonant x-ray emission intensity of the model cluster with f as a parameter from 10 to 50, and the measured intensity normalized by the resonant x-ray emission intensity of the unmilled sample. The experimental data agree with the calculated line for $f = 40$. Although this f value seems to be slightly large compared with the above-mentioned DOS ratio of n^* to π^* , this calculation accounts approximately for the relationship between the measured resonant x-ray emission intensity and the average particle size. Mechanically milled samples should contain not only the ideal plane clusters but also layered clusters and defects. When we use various layered cluster models with defects, our simulation results actually give smaller f values which agree well with the experimental data.

In conclusion, the enhanced resonant x-ray emission peak due to mechanical milling is explained by the increased portion of n^* instead of π^* in the unoccupied boron $2p$ orbitals, caused by the formation of dangling

bonds in BN nanoclusters. Furthermore, it may be possible to use these resonant x-ray emissions to detect dangling bonds in nanoclusters.

We would like to thank Professor Tadashi Matsushita and Professor Hideki Maezawa of the Photon Factory for stimulating discussions.

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