

# Nonresonant X-ray Raman Scattering from Cubic BN

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## Introduction

Since its first synthesis in 1957 [1], cubic BN (c-BN) has attracted both experimental and theoretical interest [2, 3]. Past experimental works include almost all different spectroscopy methods, such as infrared and ultraviolet [4], vacuum ultraviolet [5], optical Raman [6], x-ray absorption spectroscopy [7, 8], resonant photoemission [9], and electron energy loss spectroscopy [10]. Most recently, the plasmon-Compton profile has been studied by using nonresonant inelastic x-ray scattering (NRIXS) from the valence electrons and quantitative density functional theory (DFT) calculations [11].

Here, we report on the first measurement of NRIXS from the core-shell electrons of both boron (B) and nitrogen (N) in c-BN. NRIXS from core-shell electrons is commonly called nonresonant x-ray Raman scattering (XRS) [12], and it has been investigated by several groups as a complementary probe to soft x-ray absorption fine structure (XAFS) [12]. The present measurements were part of the commissioning study of a new IXS analyzer installed onto a six-circle diffractometer in the PNC-CAT beamline 20-ID-C. As we report elsewhere [13], this study also serves as the basis for a critical comparison of two competing *ab initio* theoretical treatments of transition matrix elements for core-shell photoelectron processes.

XRS is a weak-scattering technique that can be treated by the lowest-order Born approximation. The cross section does not depend on the incoming and outgoing states of the x-rays but only on the transferred momentum and energy. In the vertical plane of horizontally polarized and incident synchrotron radiation, the transition probability is proportional to:

$$w(\vec{q}, \omega) \sim \sum_f \langle 0 | \rho^+(\vec{q}) | f \rangle \langle f | \rho(\vec{q}) | 0 \rangle \delta(\omega - E_f + E_0),$$

where  $\rho(q)$  is the electron density in momentum space [12]. For a powder sample in the dipole approximation, one finds:

$$w(\vec{q}, \omega) \sim \vec{q} \cdot \sum_f |\langle 0 | \vec{r} | f \rangle|^2 \delta(\omega - E_f + E_0) \cdot \vec{q} = \vec{q} \cdot \mathbf{T}(\omega) \cdot \vec{q}.$$

The transition probability has the same matrix element as that found in XAFS.

## Methods, Materials, and Results

All measurements were carried out at sector 20-ID of the PNC-CAT beamline at the APS. After passing a Si (1,1,1) monochromator, the beam was focused by a toroidal mirror to a size of 300  $\mu\text{m}$  (width)  $\times$  100  $\mu\text{m}$  (height) at the sample position. The IXS analyzer consists of a 11.4-cm-diameter, spherically bent, Si (1,1,1) crystal analyzer with 1-m radius of curvature, which is mounted on the detector arm of a six-circle Huber diffractometer. A Bragg backscattering geometry of 87.7° angle is employed with an object-to-image demagnification ratio of about 1.2. In this geometry, the (5,5,5) Si reflection occurs at the *de facto* elastic energy of 9892.7 eV. The profile of the elastic peak fit well to a Gaussian and gave an energy resolution of 1.6 eV [i.e., comparable to the energy resolution of the incident beam from the Si (1,1,1) monochromator].

A sample of micrometer-sized c-BN powder (Alfa Aesar) was packed in a 3-mm-thick disk and mounted on a Huber 1003a goniometer head working in the Laue geometry (transmission mode). The scattering angle is 35°, which corresponds to a momentum transfer  $q$  of 3.02  $\text{\AA}^{-1}$ . The core electron orbital radii are estimated to be  $a_0 = 0.11 \text{ \AA}$  for B and 0.08  $\text{\AA}$  for N. Since  $a_0 q$  is  $< 1$ , the dipole condition was met for both species. The detector is an Amptek XR-100CR Si-PIN diode with a Be window, combined with a 2-mm-diameter front pinhole. Data from all scans are regroupped and binned. Every final data point has an average measurement duration of 32 s in a roughly 0.5-eV step. The total counts in each binned point for the top of first peaks are about 8200 for B and 2600 for N. The total measurement time for each of the B and N XRS edges is 4.5 h.

We present our experimental results in Fig. 1. The absolute energy shifts for both edges are 195.0 eV for B and 403.6 eV for N. Pre-edge data were used as background estimation for an exponential decay of the Compton tail. The errors were from counting statistics and from the smooth background subtraction. Measurement at a 20° scattering angle was also carried out for B, and the results were unchanged in every detail, which serves to verify that the measurements at 35°, where the scattering intensity is larger, are, in fact, in the dipole limit.

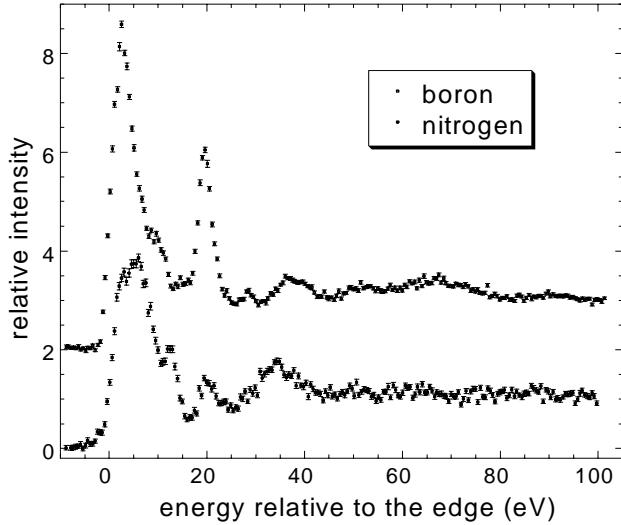


FIG. 1. Background-free nonresonant x-ray Raman spectra for B (top) and N (bottom) from c-BN powder sample. The B curve is displaced.

## Discussion

The B and N XRS spectra display similar profiles and match peak positions very well in the first 40-eV region from the edge. This can be explained by the real-space full multiple scattering picture. When photoelectrons come out of both types of atoms, their scattering paths are exactly the same because of the total interchangeability of the crystalline positions for B and N. The only differences are a result of the phase shifts from backscattering. Given the similar atomic numbers for B and N, the pseudo-potentials for both sites should be quite similar. An examination of the path contributions [13] reveals that the first peak is due to the nearest neighbor (B-N) scattering, which is equivalent to the  $sp^3$  hybridization in the bond

picture. We defer further discussion of these results to a longer manuscript in preparation [13].

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## References

- [1] R. H. Wentorf, J. Chem. Phys. **26**, 956 (1957).
- [2] R. M. Wentzcovich et al., Phys. Rev. B **34**, 1071 (1986); M. P. Surh et al., Phys. Rev. B **43**, 9126 (1991).
- [3] E. L. Shirley, J. Electron Spectrosc. Relat. Phenom. **110-111**, 305 (2001).
- [4] P. J. Gielisse et al., Phys. Rev. **155**, 1039 (1967); R. M. Chrenko, Solid State Commun. **14**, 511 (1974).
- [5] N. Miyata et al., Phys. Rev. B **40**, 12028 (1989).
- [6] A. D. Alvarenga et al., J. Appl. Phys. **72**, 1955 (1992).
- [7] V. A. Fomichev and M. A. Rumsh, J. Phys. Chem. Solids **29**, 1015 (1968).
- [8] A. Chaiken et al., Appl. Phys. Lett. **63**, 2112 (1993); I. Jimenez et al., Phys. Rev. B **55**, 12035 (1997).
- [9] A. Agui et al., Phys. Rev. B **55**, 2073 (1997); S. Shin et al., PRB **52**, 11853 (1995).
- [10] M. Jaouen et al., Micro. Microanal. Microstruct. **6**, 127 (1995); D. N. Jayawardane et al., Phys. Rev. B **64**, 115107 (2001).
- [11] S. Galambosi et al., Phys. Rev. B **64**, 024102 (2001).
- [12] Y. Mizuno et al., J. Phys. Soc. Jpn. **22**, 445 (1967).
- [13] Y. Feng et al., Phys. Rev. B (in preparation).