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High-resolution inelastic x-ray scattering study of the boron K absorption edge

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Inelastic scattering of 6.5-keV x rays has been used to study the near-edge structure of the β-rhombohedral boron K absorption edge. High resolution (better than 1 eV) combined with bright, intense synchrotron radiation makes it possible to probe the fine structure of the density of unoccupied electron states and compare results with the few existing band-structure calculations for solid boron.

In spite of its low atomic number, few attempts have been made to determine the electronic structure of boron. This is due to its complicated crystal structure; even the simplest form (α-rhombohedral) contains 12 atoms per unit cell, whereas the unit cell of the more stable structure (β-rhombohedral) contains 105 atoms. Perrot[1] applied a muffin-tin-orbitals method to calculate the band structure of α-boron. The resulting nonmetallic behavior with an indirect band gap of 2.9 eV was in qualitative agreement with the observed properties but the width of the valence band and the size of the gap did not agree with the experimental data. Bullett[2,3] used atomic $2s$ and $2p$ orbitals as a basis set to calculate the electron states in the B_{12} cluster which is a common feature of most forms of boron and boron compounds. The charge configuration of each atom in this cluster turned out to be close to s^1p^2 instead of s^2p^1 in atomic boron. The electrons which were not involved in bonds in this cluster were then allowed to make bonds with neighboring clusters. Exchange and correlation effects were included in the local-density-functional scheme. The calculated band gap, 1.7 eV, and the width of the valence band, 20 eV, were close to the experimental estimates. Due to the complex structure of β-boron, the k-space sampling was done using fewer points and the resulting band gap, 2.7 eV, does not necessarily give the minimum gap. The experimental values, obtained using thermal, optical, and Hall effect techniques, are close to 1.5 eV.[4] The calculated valence-band width, 20 eV, was the same as in α-boron. Zdetsis and Papademitriou[5] used an unrestricted Hartree-Fock method to calculate the density of states in the B_{12} cluster but they did not take into account the effect of neighboring clusters.

X-ray-absorption near-edge structure (XANES) is a well-established technique for obtaining information about the band structure in solids. In the case of light elements conventional absorption measurements are difficult because the edge energies correspond to the ultraviolet or soft-x-ray region of the electromagnetic spectrum and therefore very thin samples and clean surfaces are required. An effective way to overcome these difficulties is to use inelastic x-ray scattering. The mean energy of the scattered spectrum in the inelastic-scattering process can be calculated from the well-known energy relation in Compton scattering

$$E_2 = \frac{E_1}{1 + \frac{E_1}{mc^2}(1 - \cos\phi)} \ , \tag{1}$$

where E_1 and E_2 are the incident and scattered photon energies, respectively, mc^2 the electron rest energy and ϕ the scattering angle. For example, when $E_1 = 6.5$ keV and $\phi = 90°$, the center of the inelastic spectrum occurs at about 6.4 keV and binding edges of the order of 100 eV can be easily studied (the edge position is $E_1 - E_{\text{bind}}$). However, because of the low scattering cross section an intense radiation source is required in order to obtain quantitative information about the structural properties. Schülke et al.[6] studied the XANES region of graphite and Tohji and Udagawa[7] the extended x-ray absorption-edge structure (EXAFS) of graphite and diamond with this technique using synchrotron radiation.

The K-shell contribution to the inelastically scattered spectrum from solid boron was first studied by Suzuki and Nagasawa[8] using a conventional x-ray tube and a crystal analyzer. They were, however, more interested in the scattering cross section than the observed line shape. The XANES region of boron was measured using Cu $K\beta$ x rays from a rotating anode tube by Zdetsis and Papademitriou.[5] Because of their relatively low resolution (10 eV) and the use of nonmonochromatic radiation (an incident beam monochromator was not used), no fine structure of the edge was found, but a noticeable increase in scattering almost 100 eV above the edge was observed. This was interpreted as a transition from boron $1s$ states to d-type unoccupied states, thus violating the dipole selection rules. This observation was supported by their density of states calculation. It was later argued by Manninen, Eteläniemi, and Suortti[9] that this anomalous structure was due to the zinc fluorescence excited by

the continuous spectrum of x rays. In a similar experiment with monochromatic Cu $K\alpha_1$ radiation Manninen, Eteläniemi, and Suortti found no trace of the anomalous peaks but the counting rate was too low to make a definite statement. In this work we present high-resolution synchrotron radiation data of the near-edge structure of rhombohedral α-boron, keeping in mind the controversial results of the previous experiments. The near-edge structure is compared with the existing theoretical data.

The experiment was carried out on the X25 hybrid wiggler beam line at the National Synchrotron Light Source, at the Brookhaven Laboratory. A double focusing mirror and a two-crystal Si(220) monochromator were used to provide an incident beam having a size less than 1 mm^2, a measured energy resolution of 0.7 eV at 6.5 keV and a flux of about 2×10^{11} photons/s. The sample was pressed boron powder (purity of 99 %) manufactured by Koch & Light. The absorption half thickness of boron for 6.5-keV radiation is about 1 mm which guarantees bulk electronic information in this experiment. The scattered radiation was measured using a spherically bent Si(440) crystal close to backscattering, having an energy resolution of 0.3 eV, and a position sensitive detector, both on the same Rowland circle with the sample.[10] The scattered spectrum was measured by scanning the incident energy and keeping the scattered energy constant. Because of the complicated crystal structure of boron, several Bragg reflections were found when the scattering angle ϕ [see Eq. (1)] was optimized. Although the effect of these reflections in the energy range of interest is negligible, scattering angles corresponding to Bragg reflections were avoided. The total-energy resolution, measured using the elastic line, was 0.8 eV.

The 1s binding energy of boron is 188 eV. To optimize the scattering angle for K-edge region studies, the overlap with the valence electron contribution should be minimized. This can be done by decreasing the scattering angle ϕ [see Eq. (1)] and thus shifting the center of the inelastic spectrum towards the elastic line. Because this also means a reduction in the scattering from the K shell (the inelastic-scattering factor decreases as function of sin $\phi/2$), a compromise, using angles of 80° and 90°, was made.

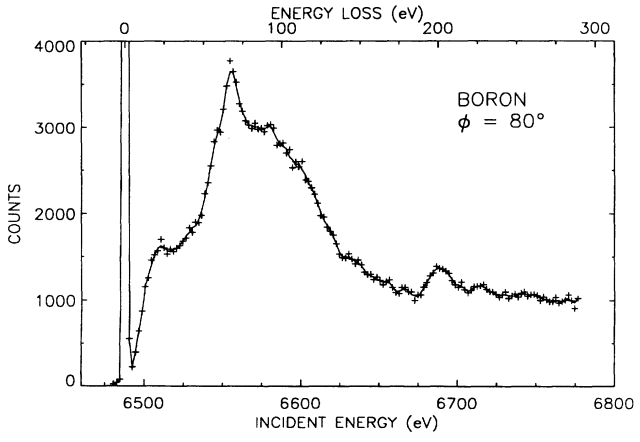

FIG. 1. Measured inelastically scattered spectrum from boron sample. The step size is 2 eV and the measuring time 120 s/step. The boron K edge is at 6676 eV.

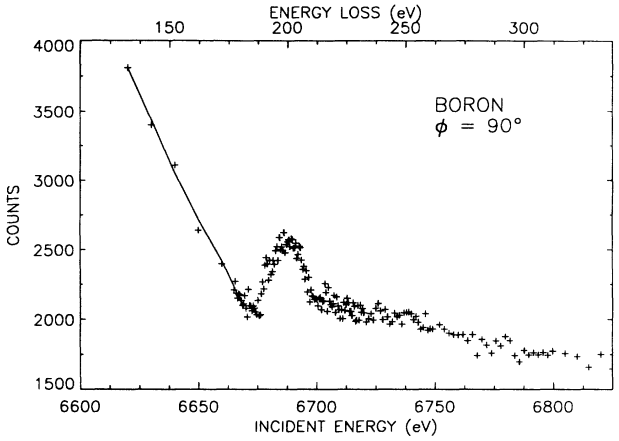

FIG. 2. K-edge region of the spectrum in Fig. 1. Finer steps (1 eV) has been used close to the edge. Measuring time is 160 s/step.

A long-range energy scan including the elastic line, contribution of the valence electrons, and the K edge is shown in Fig. 1, taken at a scattering angle of 80°. Although the measuring time was only 120 s/step with a step interval of 2 eV, the main features of the scattered spectrum can easily be seen. The valence electron contribution includes two edges corresponding to the hybridized s and p electrons, the XANES structure above those edges and the momentum broadened continuum centered at 70 eV below the elastic line according to Eq. (1). Because of the selection rules (the s- and p-edge structures probe different type of final states) the peak at about 70 eV seems to be a dominant feature. A detailed analysis of this part of the spectrum would also give important information about the scattering system, as shown in the case of Li by Schülke *et al.*[11]

The K-edge region, measured with finer steps is shown in Fig. 2. Although the main interest of this work was the XANES structure above the K edge, it is easily seen that no anomalous peaks exist below 300 eV. This confirms the earlier argument[9] and is clearly contrary to the prediction and observation by Zdetsis and Pademitriou[5]. The resolution in the present experiment is one order of magnitude better and monochromatic incident radiation is used.

The XANES region, around 200 eV in Fig. 2, was measured with 0.5-eV steps at the scattering angles of 90° and 80°. The total measuring times were 310 s/step and 900 s/step, respectively. The valence electron contribution overlaps with the energy range of interest, as seen in Figs. 1 and 2, but it has a smooth shape and does not affect the conclusions concerning the XANES structure. The absorption correction in this narrow energy range is very small. Multiple scattering also adds only a smooth background.

The experimental XANES spectra are given in Fig. 3.

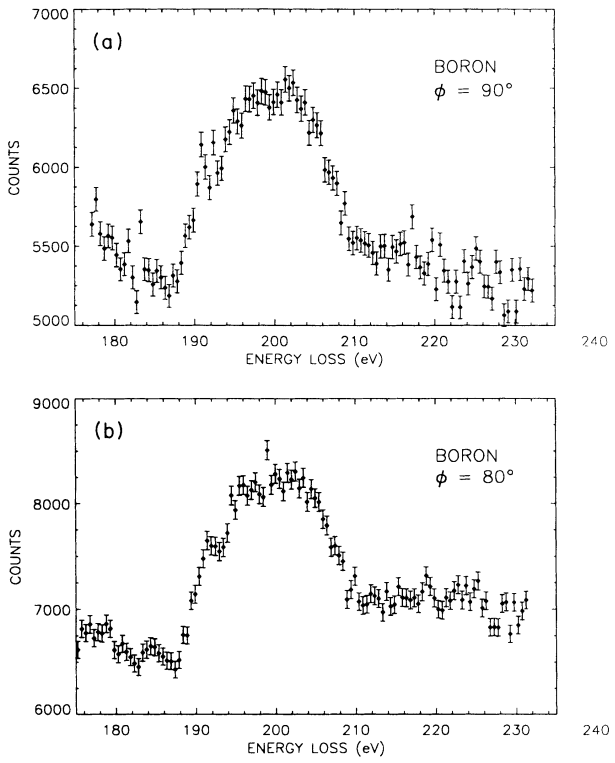

FIG. 3. XANES region of the boron K edge, measured using the scattering angles of (a) 90° and (b) 80°. The step size is 0.5 eV and the total measuring time 310 s/step and 900 s/step, respectively. The error bars shown represent statistical error.

Within the statistical error they look identical, both showing a peak at about 192 eV and a broad band with a full width at half maximum (FWHM) of about 17 eV. Interpreted in terms of the band-structure calculations, the peak at 192 eV can be clearly seen in the calculated density of states.[2,3] It also exists in the other crystalline forms of boron and boron compounds having similar icosahedron geometry, like B_4C, for example.[2] The size of the peak depends, however, on the crystal structure. On the other hand, such a peak has not been found in amorphous boron.[12,13] Interpreted in terms of the electronic structure,[2,3] this peak is due to the antibonding πp states in the B_{12} cluster; electronic transitions from K shell to these states are allowed within the dipole approximation. In order to have more information about the origin of this peak, measurements on a boron single crystal would be very interesting. By rotating the crystal with respect to the scattering vector, the symmetry properties of the final p states could be probed. Due to the high melting point of boron, growing of such a crystal is a difficult task. This kind of soft x-ray-absorption study at the boron K edge has been done on BN single crystal.[14] A conclusion based on mostly πp-like final states was also drawn in that work.

The only calculation giving the density of the unoccupied states over the whole range of interest[5] agrees qualitatively with the present XANES data except for the strong peak close to 210 eV, which is not seen in Fig. 3. This can be due to the fact that the calculation includes both s- and p-like states and it is not resolved into partial densities of unoccupied states. Unfortunately the calculation of Bullett,[2,3] which seems to predict quite correctly the band-gap and valence-band width, only gives the bottom part of the conduction-band density of states extending 5 eV above the occupied states. In order to make more quantitative conclusions, partial densities of unoccupied states should be known because K-edge XANES probes mainly p-like final states. Hopefully this experiment will encourage such calculations.

This work shows the usefulness of inelastic x-ray scattering spectroscopy in the case of light elements. By increasing the analyzer crystal size and using vacuum throughout the beam path, one order of magnitude could easily be gained in the scattered intensity and would additionally improve the signal-to-background ratio at the binding edge. In the present experiment there is a small air scattering contribution which adds additional smooth background. These improvements would allow measurements of XANES and EXAFS of light elements and their compounds in reasonable measuring time. Combined with an experiment probing the density of occupied states, photoelectron spectroscopy for example, a comprehensive picture about their electronic properties could be obtained.

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