Effect of x-ray polarization at the boron K edge in hexagonal BN

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High-resolution absorption measurements were made at the K edge of boron in hexagonal boron nitride using polarized synchrotron radiation and different orientations of the crystal axis. The work made use of the highly focused beam at the exit slit of a new grazing-incidence ultrahigh-vacuum monochromator at the Stanford Synchrotron Radiation Project. An isolated exciton line was observed at threshold (192 eV) which did not increase as the electric vector became parallel to the c axis. On the other hand, a second shoulder or line at 195 eV increased rapidly when the crystal was rotated in the beam. The results can be understood in terms of excitons formed from particular regions of the Brillouin zone with selection rules appropriate to the layer crystal.

The absorption of x rays in the K-edge region of boron (~190 eV) has been reported for polyatomic molecules such as BF_3,[1,2] and a number of gaseous and solid boron compounds.[3] In general, these spectra have been taken with high resolution, but no results have appeared using polarized radiation. Here, with polarized x rays, we show how core excitations are influenced by crystalline anisotropy.

The boron K spectrum of BF_3 gas begins with a strong line at 195.62 eV whose full width at half-height is about 0.6 eV. The BF_3 molecule is planar (point group D_{3h}) and the observed line is due to excitation of a $1s$ (A_1') core electron to an antibonding molecular orbital of type A_2'' whose parentage is mainly $2p_z$ wave functions centered on the boron. Although these p_z-like orbitals are perpendicular to the plane of the molecule no polarization effects are expected in absorption, since random orientation occurs in the gas phase. On the other hand, each boron atom in hexagonal BN is surrounded by three nitrogen atoms in a plane characteristic of a simple layer compound. As in the BF_3 molecule, the point-group symmetry at the boron is D_{3h}. Strong anisotropy for the electric vector oriented perpendicular ($\vec{E}\perp\vec{c}$) or parallel ($\vec{E}\parallel\vec{c}$) to the crystal axis is expected.

In the present work, transmission measurements were made on compression-annealed pyrolytic boron nitride[4] which is highly oriented in layers (mosaic spread ~2°). Samples were thinned by cleaving using Cellotape followed by ion milling. A small sample mounted over an aperture about 1 mm in diameter was mounted close to the exit slit of the new grazing-incidence monochromator[5] at the Stanford Synchrotron Radiation Project. The sample was arranged so that it could be rotated about a vertical axis from $\theta=0$ ($\vec{E}\perp\vec{c}$) to a value of θ of about 23°, as shown in Fig. 1. The synchrotron radiation is polarized in the horizontal plane so that this rotation brings a component of electric field parallel to the crystal axis $\vec{E}\parallel\vec{c}$.

The results of transmission runs with the sample at $\theta=0$ and $\theta=23°$ are shown in Fig. 2. Here we plot optical density in arbitrary units versus photon energy in eV. The background due to the source and the spectrometer is smoothly rising in this part of the spectrum and has been subtracted. Notice that there is little or no change in the line at 192 eV (feature a in Fig. 2) but that a line at 194.5 eV (feature b) rises rapidly with increasing angle θ.

The spectrum at $\theta=0$ ($\vec{E}\perp\vec{c}$) agrees with the published data of Fomichev[1] on hexagonal BN, except that we observe line a at 192.0 instead of 191.8 eV, within experimental error. We find that the full width at half maximum of this line appears to be about 0.65 eV, which is very close to that observed for the first intense band in BF_3.[2] This width is primarily the intrinsic linewidth. In both cases grazing-incidence spectrometers with about 0.1-Å bandpass were used. At 190 eV this corresponds to an energy bandwidth of 0.3 eV; therefore from the observed line shape it appears that the boron K width in these compounds is about 0.58 eV or less. A substantial shift appears in the boron K threshold from elemental boron to BF_3 as shown in Table I. Even in BN there appears to be considerable charge transfer

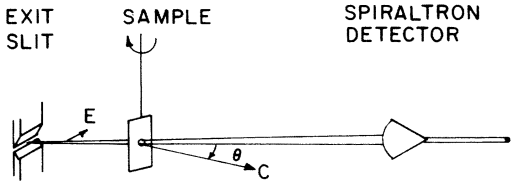

FIG. 1. Arrangement of the sample close to the exit slit of the grazing-incidence monochromator. All components are within an ultrahigh-vacuum system not shown.

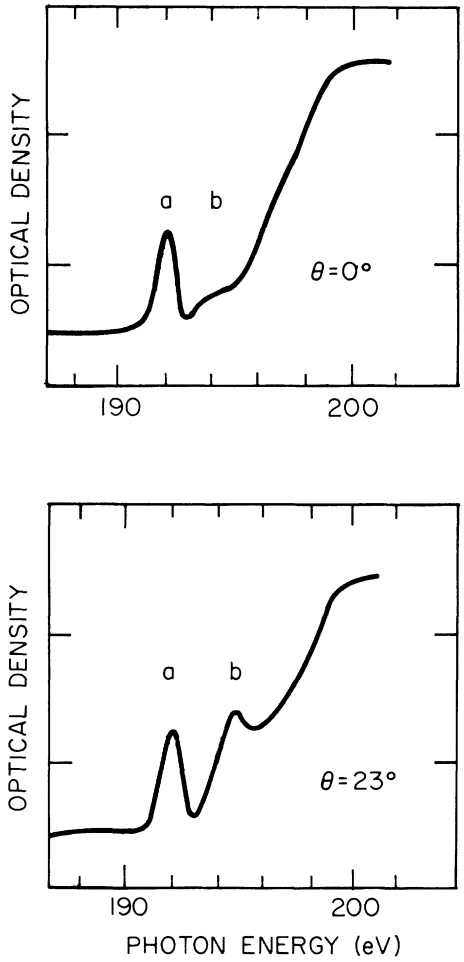

FIG. 2. Optical density in arbitrary units vs photon energy in eV for a thin sample of hexagonal BN. Line *a* is at the beginning of the *K* threshold. The upper curve was taken for $\vec{E} \perp \vec{c}$, whereas the lower curve, $\theta = 23°$, had a substantial component of $\vec{E} \parallel \vec{c}$.

from boron to the surrounding electronegative ions.

Boron nitride of the type studied here is an insulator with a strong direct bandgap at about 5.7 eV and a weaker (indirect?) gap at about 4.3 eV.[6] Considering the general behavior of the response of insulating crystals in the extreme ultraviolet,[7] bands *a* and *b* can be ascribed to core excitons or excitation states of boron in BN. Coulomb interaction between core hole and excited electron is important and probably lowers the energy a few electron volts. This can be estimated by comparing ESCA (electron spectroscopy for chemical analysis) data with the photoabsorption threshold.[8] For example, x-ray photoemission data on BN (Ref. 9) show that the difference between the boron *K*-shell energy and the top of the valence band is 188.6 eV. Adding the direct band-gap energy (5.7 eV) to this gives 193.3 eV, which is one or two electron volts larger than the position of line

TABLE I. Position in eV of the boron *K* threshold in elemental boron, and the first *K*-absorption line observed in hexagonal BN and in the molecular gases BCl_3 and BF_3, with data from the present work and Ref. 2.

B	BN	BCl_3	BF_3
187	192.0	192.44	195.62

a shown in Fig. 2.

The excited state of the BN crystal, although local in nature, can be constructed from band theory, at least in principle. Assuming an *s* exciton envelope function the selection rules for these strong transitions can be obtained from the symmetry properties of the band states involved. Figure 3 shows the band structure of BN calculated by Doni and Pastori-Paravicini[10] in a two-dimensional approximation. Two dimensions are adequate for general features, although the

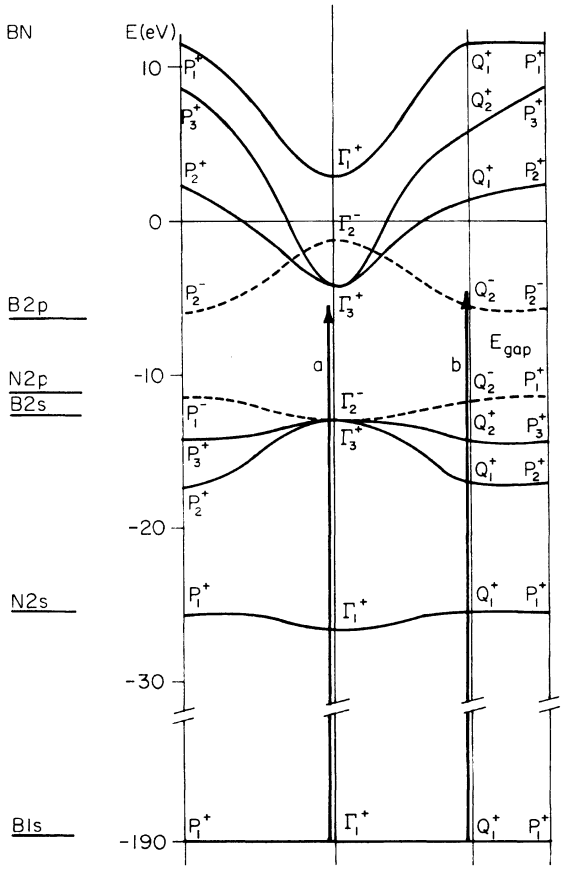

FIG. 3. Band diagram for two-dimensional BN from the work of Doni and Pastori-Paravicini (Ref. 11). The π bands are shown by dotted lines, and an approximate position of the boron *K* shell is indicated. Suggested transitions from peaks *a* and *b* in Fig. 2 are shown by arrows.

π orbitals (dashed lines in Fig. 3) are modified by the more complete calculation. Notice that the bandgap at Q (or P) is closely associated with the difference in the boron and nitrogen atomic levels.

In Fig. 3 we have indicated the flat boron K band at about -190 eV with a break in scale. Principal points in these bands are labeled in conventional notation, including the indices + and − which indicate that states must be even or odd upon reflection in a layer plane. Strict selection rules apply for optical transitions due to this reflection symmetry. When light is polarized perpendicular to c ($\vec{E}\perp\vec{c}$) the transitions are − to − or + to +. For $\vec{E}\parallel\vec{c}$ transitions + to − or − to + become possible. The s core state on the boron is even in reflection; therefore transitions to the π (or p_z-like) conduction-band minimum near Q_2^- are not allowed when $\vec{E}\perp\vec{c}$. Thus line a in Fig. 2 most likely involves states near the Γ_3^+ conduction-band minimum which can be represented by combinations of p_x and p_y. The transition Γ_1^+ to Γ_3^+ is allowed at normal incidence and would behave as line a with increasing θ. On the other hand, line b probably is associated with π states Q_2^- or P_2^- which transform as p_z. These transitions are unallowed for $\vec{E}\perp\vec{c}$ but a 2° mosaic spread would permit a small residue, as seen in the $\theta = 0$ curve of Fig. 2. Peak b is strong at $\theta = 23°$ because of an appreciable component $\vec{E}\parallel\vec{c}$ and even-to-odd transitions such as Q_1^+ to Q_2^-. The relative positions of the Γ_3^+ and Q_2^- conduction-band states are probably not known well enough from the band calculation for perfect agreement. Here we should turn to the three-dimensional results where the conduction bands are split and displaced upwards.[10] In any case, corrections for the Coulomb interactions between electrons and holes have not been accurately estimated. It would be most interesting to have a correct theoretical treatment of these compact core excitation states.

It is interesting to compare the soft-x-ray response of BN with the ultraviolet optical constants deduced from electron-energy loss.[11] Again the lowest-energy band in ϵ_2 occurs for $\vec{E}\perp\vec{c}$ at 6.5 eV and a second band at 9.4 eV is allowed only for $\vec{E}\parallel\vec{c}$. Furthermore, we would like to suggest that here in the uv these absorption lines are due to excitons. The conduction-band states involved may be the same as those discussed above since the valence bands are relatively flat. It would be worthwhile to have optical-constant measurements for polarized light from the region of the bandgap to beyond 20 eV where the nitrogen 2s shell can be excited.

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