PHOTOEMISSION INVESTIGATION OF HEXAGONAL BN: BAND STRUCTURE

AND ATOMIC EFFECTS

by

J. Barth and C. Kunz

II. Institut für Experimentalphysik, Universität Hamburg

and

Deutsches Elektronen-Synchrotron DESY, Hamburg

and

T.M. Zimkina

Institute of Physics, A.A.Zhdanov State University, Leningrad, USSR

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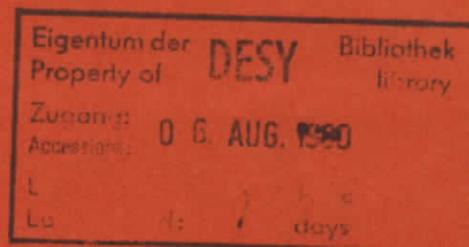
II. Institut für Experimentalphysik, Universität Hamburg,

D-2000 Hamburg 50, and Deutsches Elektronen-Synchrotron DESY,

D-2000 Hamburg 52, Germany

and

T.M. Zimkina

Institute of Physics, A.A. Zhdanov State University, Leningrad, USSR

Abstract

Photoemission valence band spectra and the polarization dependent
photoyield at the B K-edge are compared to calculated densities
of states. Excitonic effects at the edge are discussed. For the
decay of exciton and ionized core the influence of atomic effects is
shown.

The electronic structure of hexagonal BN has been the subject of
numerous investigations because band structure calculations profit
from the special symmetries of the lattice, while the anisotropies
of this layered crystal makes experimental work very attractive.
Nevertheless, the results give no consistent picture. In 1971, Nakhmanson
and Smirnov noted a rough agreement between their band structure calculation[1]
and X ray emission and absorption data of Fomichev and Rumsh[2]. But a
more critical comparison by Tegeler et al.[3] between band structure calculat-
ions and angular dependent X-ray emission spectra showed severe discrepancies
in many details. Nevertheless, the work of Nakhmanson and Smirnov gave
the best results among all calculations considered. As to the conduction
bands, two later absorption[4] and energy loss[5] measurements at the B K-edge
both making use of anisotropic effects revealed contradictory energy
positions for the B 1s $\rightarrow$ π^{*} excitation.

In order to clarify these inconsistencies it appeared to be promising to
try photoemission measurements on hexagonal BN. Energy distribution curves
(EDC's) of the valence electrons can be compared with calculated densities
of states, and polarization dependent yield spectra of the B K-edge may clari-
fy the location of the B 1s $\rightarrow$ π^{*} excitation.

For our investigations we took advantage of the highly polarized synchrotron
radiation monochromatized by the FLIPPER monochromator[6] at the storage ring
DORIS in Hamburg. The geometry in the sample chamber allows measurements
with complete s-polarization $(\vec{E} \perp \vec{c})$ and a mixture of s- and p-polarization
without changing the collection geometry of the electron analyzer (double
pass CMA)[7]. Here we chose an angle of 45° between the electric vector and
the c-axis of the crystal. The samples of sintered BN were cleaved in the
system which had a pressure of $5 \cdot 10^{-10}$ Torr. Charging was prevented by use
of a flood gun, in addition the samples were heated up to 350° C to increase
an ionic conductivity.

Figure 1 shows two EDC's of the valence band taken at different photon energies.
For these EDC's a polarization dependence was not observed. The low binding
energy part of the spectra consists of a broad maximum at 5 eV and two shoulders
at 2.5 eV and 10 eV binding energy followed by another maximum at 18 eV which
originates from the N 2s level. As was demonstrated on graphite, excitation
energies around 60 eV yield a maximum contribution of p-symmetric states while

at higher energies excitations of s-symmetric states are dominant[8]. The same must hold for BN because of the similar electronic structure. Thus the comparison of the two EDC's leads to a rough separation of the valence band into the predominantly s-symmetric part below and p-symmetric part above 7 eV binding energy.

The calculated density of states by Nakhmanson and Smirnov[1] is shown in the bottom part of figure 1 as modified by Tegeler et al.[3] on the basis of their X-ray emission and XPS data by shifting the subbands closer together. A reasonable agreement between the calculation and the experimental data was achieved that way[3] and so it is achieved in the present work. The symmetries of the subbands are given as p-like for the π-band, s-p mixed for the σ bands and for the s band mainly s-like[1] with an admixture of p-like states localized at the B atom[9].

It should be mentioned that as an effect of the modification procedure the top of the σ subbands extends to above the π band which must not be taken seriously. In fact, the π electrons situated between the crystal layers are the most weakly bound ones and thus the partly ionic character of the bonding (25%[10]) leads to a division of the π charge between B and N with the ratio of 0.5 : 1.5[3]. Consequently, we expect the empty π states to be the lowest unoccupied states localized mainly at the B atom.

Photoyield spectra could only be obtained by measuring the partial yield in order to keep the electrons of the flood gun out of the analyzer. No differences were observed for final energies of 10 eV (0.12 eV bandpass) and 70 eV (1.2 eV bandpass). The photoyield spectrum of the B K-edge taken at 70 eV final energy is displayed in the upper part of figure 2. It shows a prominent maximum at 192.0 eV, a double hump at 198.3 eV and 199.5 eV and a broad structure around 204.5 eV. The origin of these maxima may be structures of the density of conduction band states or variations of the matrix element. Since the excitation starts from an s level, only p-symmetric final states are allowed. In a first step we assume a structureless matrix element to compare the yield spectrum with the density of empty states which was qualitatively estimated by Nakhmanson and Smirnov for their calculated band structure[1] (bottom part of figure 2). Again the symmetries of the subbands are given as p-like for the π band, s-p mixed for the σ band and mainly s-like for the s band which therefore should not contribute to the B 1s absorption. The structures of the yield spectrum and the density of empty states were aligned by

multiplying the energy scale of the band structure calculation with a factor of 0.6 (see Fig. 2).

Brown et al. discussed in detail that for the transitions from the core level into the empty π band, a polarization dependent selection rule is valid even if they are influenced by exciton interaction[4]: these transitions are forbidden for s-polarized light, i.e. if the electric vector is perpendicular to the c axis. Therefore, we have measured yield spectra for different polarizations and we find a dependence of the yield at the maximum at 192 eV and at the weak structure at approximately 194.5 eV which agrees reasonably well with the π band from the density of states[1] scaled by the factor of 0.6 (see Fig. 2). The structures in this energy range do not vanish completely for s-polarized excitation which may be explained by an imperfect orientation of the crystal layers. For a sample of pyrolytic BN we found a much stronger polarization dependence (see insert of Fig. 2). Obviously, the crystal orientation of the pyrolytic BN sample is much better, but this sample could not be cleaved in situ.

Our results are in agreement with those of recent energy loss measurements[5] which similarly show three maxima at the B K-edge at 192 eV, 199 eV and 204.5 eV. From the angular distribution of the electrons, it was concluded that the first peak originated from excitations into π^* states and the others into σ^* states. Our results disagree with the polarization dependent absorption spectra of Brown et al.[4] who find a polarization dependence only for a peak at 194.5 eV. While our yield spectrum for p-polarized excitation also shows a peak at 194.5 eV, it remains unclear why the polarization dependence of the 192 eV maximum, where the effect is of equal strength, was not detected in ref. 4.

Considering the detailed shape of these structures we note the sharpness of the strong 192 eV maximum at the onset. After correcting for the experimental resolution we find 0.4 eV for the FWHM. This finding is to be seen in contrast to the FWHM of the B 1s photoemission line which we measured to be 1.5 eV (experimental resolution deconvoluted) at 250 eV photon energy. Because of the partly ionic character of BN the photoemission line width should mainly be determined by phonons coupled to the photoionization process[11]. We take the much lower width of the excitation at 192 eV as an argument for its correspondence to an exciton excitation.

The exciton binding energy can be estimated from the B 1s binding energy for which we find (188.5 ± 0.5) eV with respect to the top of the valence band, and the optical band gap of (5.7 ± 0.2) eV[12], yielding (2.2 ± 0.6) eV exciton binding energy for the 192 eV maximum. Of course, excitonic interaction may modify also the transitions to the other conduction bands. A satisfactory understanding of the detailed structures at the B K-edge may require a more accurate band structure calculation. A comparison with the N K-absorption may be helpful instead. This spectrum as measured by Fomichev and Rumsh with only poor resolution (2.8 eV) shows three maxima at 402.1 eV, 409.0 eV and 416.6 eV[2]. Subtraction of the N 1s binding energy of 396 eV[13] locates these peaks relative to the top of the valence band. The first two maxima are then found to lie at about 2.5 eV higher energy above the top of the valence band than the first maximum and the double hump of the B K-absorption. This indicates an absence of strong exciton effects for the N K excitations and can be interpreted by noting that a N 1s hole is shielded much more efficiently than a B 2s hole, because the loosely bound π-electrons are strongly localized at the N atoms (compare Ref. 14).

We now turn to the investigation of the decay of the B 1s exciton at 192 eV which evidently is located below the conduction band edge. The EDC for 192 eV resonance excitation is shown in Figure 3a (solid curve). An EDC taken just below the onset of B K-excitation is displayed for comparison (broken curve), the intensities of both EDC's are normalized to equal photon flux. For experimental reasons the EDC's are taken in s-polarization ($\vec{E} \perp \vec{c}$). A striking result is the 5-fold higher intensity in the valence band maximum for resonance excitation which we explain by electron emission via a direct recombination decay of the exciton. If relaxation is negligible, such a decay process transfers the full excitation energy to the emitted electron which in the case of BN can only be a valence electron. Thus we get an intensity gain in the valence band region. A similar effect has been observed in rare earth compounds[15], where the emission from the rare earth derived states was enhanced when the 4d core electrons could be excited into quasi bound states. Since the resonance EDC of BN also displays an Auger edge, the KVV Auger decay of the 192 eV excitation takes place in addition. From a serie of EDC's the intensities of the valence band and KVV Auger emission have been extracted and normalized to the yield curve. Thus we are able to determine the ratio of the two competing decay processes of direct recombination and KVV Auger transition at the 192 eV excitation as 1 : 2.

We note that our proof of the direct recombination for the 192 excitation unambiguously clarifies the origin of a peak that was found near this energy in electron excited X-ray emission spectra and has been a matter of discussion (see, e.g. Ref. 2, 16). The emission of X-ray fluorescence is a competing decay process which, compared with the Auger transition, occurs with only 10^{-4} fold probability in this energy range. Recombination processes of quasibound states excited by electron impact have been observed in either X-ray emission[17] and Auger spectra[18] of rare earths. For BN, we explain the shift of 0.5 eV towards lower energy in the emission spectrum[2] as originating from relaxation due to phonon coupling in combination with self absorption in the exciton line.

Comparing the shape of the valence band emission in both EDC's strong differences are found. Obviously, the direct recombination does not involve the whole valence band with equal probability. Since the matrix element for this process is a special case of an Auger matrix element only states localized at the B atom should contribute strongly. Furthermore, it has recently been shown that for s-p band materials Auger distributions involving the valence band are dominated by the p-symmetric part of the valence states due to matrix element effects[19,20].

We want to test this assumption considering the resonance EDC of Figure 3a. Subtraction of the EDC taken below the B K-edge accounts for directly excited photoelectrons. Thus, the difference spectrum (Fig. 3b, solid curve) contains only electrons excited by the exciton decay and the corresponding background of scattered electrons. The valence band region, i.e. the electrons from the direct recombination, which should reflect the p-symmetric valence states localized at the B atom must therefore be comparable with a B K X-ray emission spectrum which contains exactly the transitions from these states. In fact, the comparison with the X-ray emission spectrum taken from Reference 3 shows an excellent agreement (see Fig. 3b). In order to optimize the agreement the energy scale of the X-ray emission spectrum was located such that the top of the photoemission valence band corresponds to 187 eV which is 1.5 eV less than the B 1s binding energy. This shift is in the order of the energy difference between the 192 eV exciton absorption and reemission lines and may equally be explained by phonon coupling.

Further, the distribution of the KVV Auger electrons must be comparable
with the selfconvolution of the X-ray emission spectrum since two
valence electrons take part. For this comparison the emission spectrum
of Figure 3b was subtracted as well as the estimated background of in-
elastically scattered electrons (dotted line). This procedure leaves us
with the distribution of KVV Auger electrons (Fig. 3c, solid curve) which
is in good agreement with the selfconvolution of the X-ray emission
spectrum from Reference 3. Small deviations in the details can be ex-
plained as due to the neglected contribution of s-symmetric states. Plasmon
losses may play an additional role. We observe a weak structure 9 eV
below the B 1s photoemission line excited with 250 eV photons which agrees
with the π-plasmon loss determined from XPS spectra[21].

In conclusion, we have presented EDC's of the BN valence band that can
be compared with band structure calculations. Polarization dependent photo-
yield spectra at the B K-edge led to an identification of the B 1s $\rightarrow$ π^{*}
excitation for which experimental results were contradictory. The influence
of exciton interaction at the edge was found to be considerable. For the
prominent exciton at the onset of the edge we studied the decay processes
in detail. In either the direct recombination or the Auger decay predominantly
the p-symmetric local density of valence states at the B atom takes part.

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Figure Captions

Fig. 1: Energy distribution of the valence electrons at 65.6 eV
(solid curve, resolution 0.5 eV) and at 190.6 eV photon
energy (broken curve, resolution 1 eV). In the lower part,
the density of states calculated by Nakhmanson and Smirnov[1]
as modified by Tegeler et al.[3] is displayed.

Fig. 2: Polarization dependent photoyield at the B K-edge (resolution
0.4 eV) for sintered and pyrolytic (insert) BN samples. The
lower part shows the density of conduction band states given by
Nakhmanson and Smirnov[1]. In order to align the structures with
the maxima of the yield spectrum, the energy scale of the
calculation has been multiplied with 0.6.

Fig. 3: a) EDC at the 192 eV resonance (solid curve, resolution 0.8 eV)
compared with an EDC taken at a photon energy below the B K-onset
(broken curve, see also Fig. 1).
b) Difference spectrum of the two curves in part a) (solid
curve). This should contain only electrons excited by the decay
of the 192 eV exciton. The valence band region is compared with
the B K emission spectrum from Ref. 3. The estimated background
of the Auger electrons is indicated by the dotted line.
c) Difference spectrum of the two curves in part b) (solid curve).
This should contain only the KVV Auger electrons of the 192 eV
exciton decay. Their energy distribution is compared with the
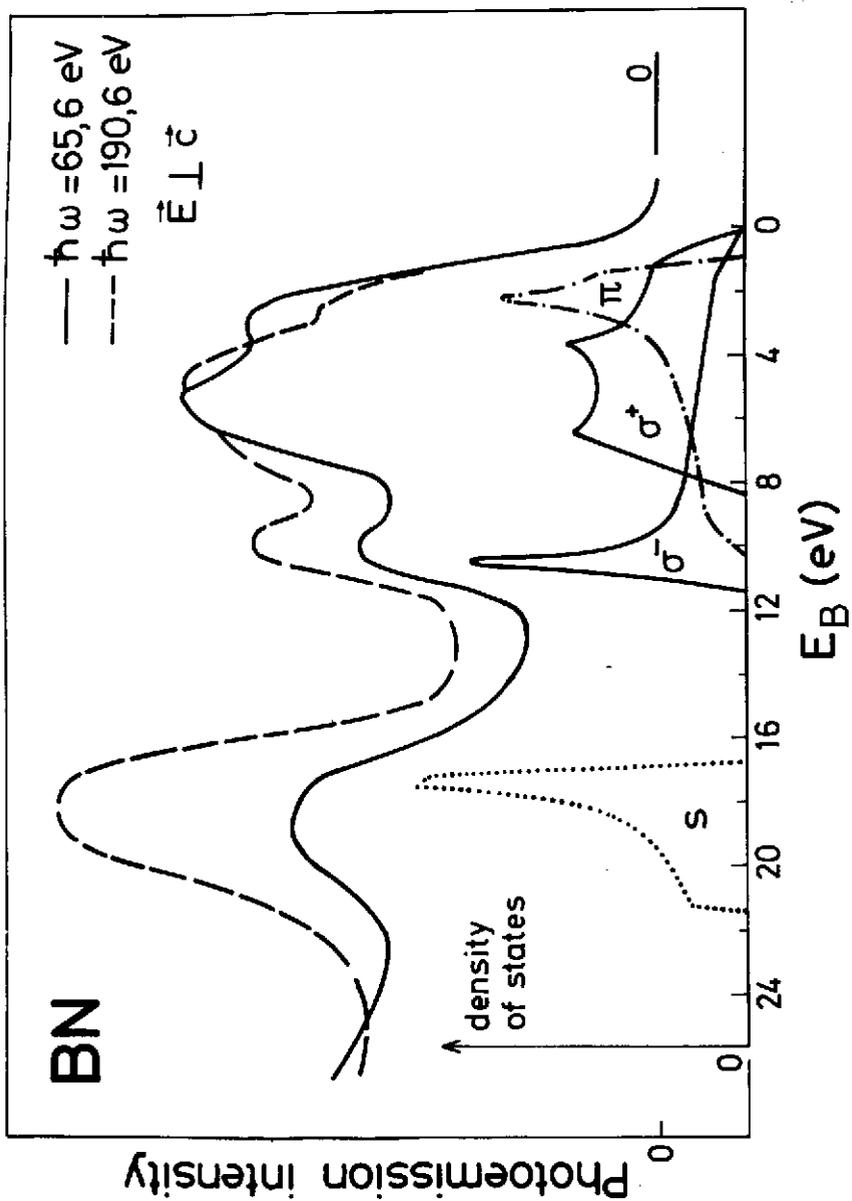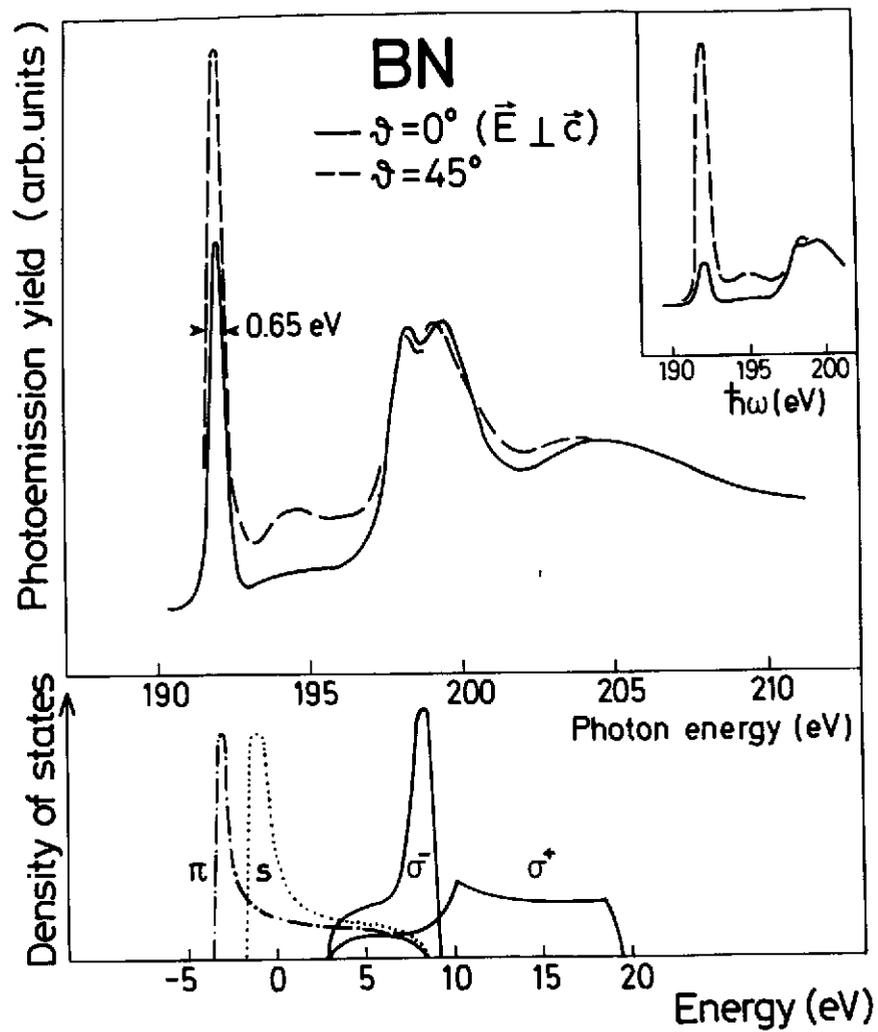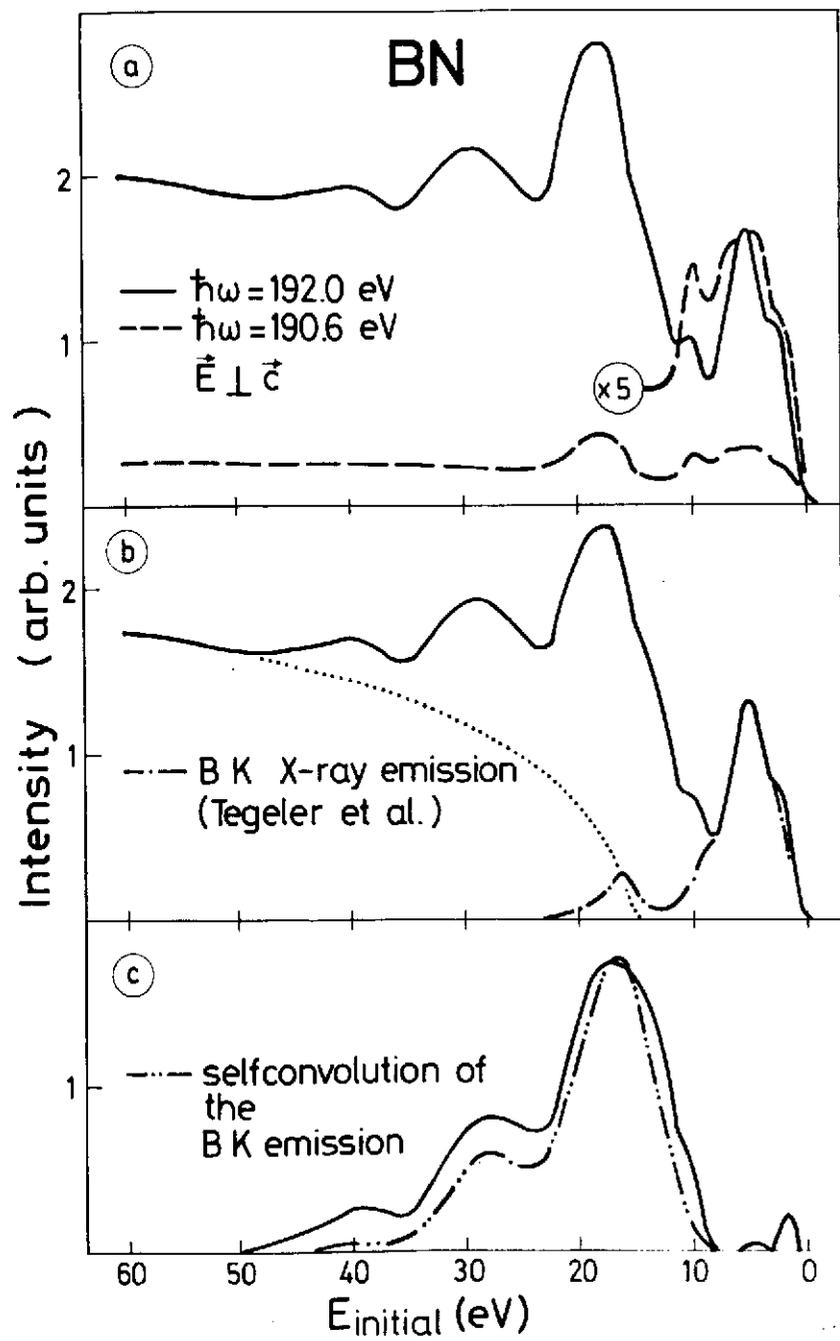selfconvolution of the B K emission spectrum from Ref. 3.

Fig. 1

Fig. 2

Fig. 3