DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-78/05
May 1978

ON THE ELECTRONIC STRUCTURE OF HEXAGONAL BORON NITRIDE

by

E. Tegeler, N. Kosuch, G. Wiech, and A. Faessler
Sektion Physik der Universität München

NOTKESTRASSE 85 · 2 HAMBURG 52

ON THE ELECTRONIC STRUCTURE OF HEXAGONAL BORON NITRIDE

E. Tegeler, N. Kosuch, G. Wiech, and A. Faessler

Sektion Physik der Universität München

The anisotropic emission of the K x-radiation of boron and nitrogen in hexagonal boron nitride BN permits the determination of the π- and σ-subbands of the two x-ray spectra. Together with the x-ray photoelectron spectrum a consistent picture of the valence band of BN is obtained. Position and width of the s-, σ-, and π-bands are determined. None of the band structure and density of states calculations known so far is in satisfactory agreement with the experimental observations.

Die anisotrope Emission der K-Röntgenstrahlung von Bor und Stickstoff in hexagonalem Bornitrid BN erlaubt die Bestimmung der π- und σ-Teilbanden der beiden Röntgenspektren. Zusammen mit dem Röntgen-Photoelektronenspektrum ergibt sich daraus ein konsistentes Bild des Valenzbandes von BN. Breite und Lage der s-, σ- und π-Bande werden bestimmt. Keine der vorliegenden Bandstruktur- und Zustandsdichteberechnungen zeigt eine zufriedenstellende Übereinstimmung mit den experimentellen Beobachtungen.

I. Introduction

In recent years the electronic structure of hexagonal boron nitride BN has been the subject of several theoretical calculations (1-5). In some cases not only the band structure $E(\vec{k})$ but also the density of states N(E) has been calculated (2-4). The results of these calculations agree with regard to the gross features of the electronic structure of BN, but there is considerable disagreement concerning the width of the energy bands and the amount of their overlap.

A suitable method for the experimental investigation of the valence band structure of BN is x-ray spectroscopy in combination with x-ray photoelectron spectroscopy. Both techniques permit a study of the whole energy range of the valence band. In the case of light elements x-ray and photoelectron spectra are to some extent complementary. The intensity of x-ray emission spectra is determined mainly by the dipole matrix element; the XP-spectrum depends on the photoelectric cross sections. So x-ray K-spectra provide information about p-like states of the valence band, whereas XP-spectra reflect the s-density of states, since for light elements the cross section ratio $\sigma_s/\sigma_p \gg 1$.

In the case of layer crystals the emission of the characteristic x-radiation is anisotropic. By measuring the intensity distribution of a spectrum of a single crystal, as a function of the take-off angle (e.g. the angle between the emitted radiation and the sample surface), information is obtained which considerably exceeds that obtained from polycrystalline samples without texture. Recently this technique has been successfully applied to graphite (6-8) for separating the π- and σ-bands and for a detailed comparison with theoretical calculations of the valence band structure. It may also be applied to the study of the electronic structure of hexagonal boron nitride which has a crystal structure very similar to that of graphite.

Experimental data which can be compared with band calculations covering the whole energy range of the valence band were until recently the x-ray K emission spectra of both components of BN measured by Fomichev and Rumsh (11), who, however, used only one take-off angle, and the XP-spectrum observed by Hamrin et al. (9). A comparison of band calculations with these experimental observations was carried out by Fomichev (10). The present paper deals with a detailed comparison of band calculations with experimental results obtained by the investigation of the x-ray K-emission spectra of boron and nitrogen as a function of the take-off angle. These measurements were published in two previous papers (7,12). Additionally the x-ray photoelectron spectrum of BN was remeasured. It will be seen that the x-ray spectroscopic data together with the XP-spectrum give a consistent picture of the electronic structure of boron nitride.

II. The spectroscopic data

1. The x-ray emission spectra

The K-emission bands of boron and nitrogen in BN for three different take-off angles are shown in Fig. 1. The resolution is 0.2 eV for the boron spectrum and 0.7 eV for the nitrogen spectrum. Experimental details are described in the above mentioned papers (7,12).

A separation of either emission band into a π- and a σ-component is possible on account of the different polarization of the two subbands. From the atomic point of view the π-band corresponds to transitions with $\Delta m = 0$ (linearly polarized with the E-vector parallel to the c-axis of the crystal); the σ-band corresponds to transitions with $\Delta m = \pm 1$ (polarized perpendicular to the c-axis), m being the magnetic quantum number. It should be mentioned that the separation

into the two subbands is also feasible using a polycrystalline sample with partially orientated crystallites, if, as in the case of BN, single crystals are not available (12). Self-absorption of the radiation in the sample and different reflectivities of the grating for the different polarized subbands are without noticeable influence on the results of the separation (12).

The shape of the subbands does not depend upon the take-off angle, their contribution to the intensity of the total band is, however, a function of this angle. Thus for any take-off angle the intensity distribution of the emission band can be represented as a superposition of the two subbands.

The subbands obtained are shown as dashed lines in Fig. 1. The sum of the subbands (full curve) is in agreement with the measured emission band, and this is also true for the other spectra not shown in Fig. 1. So the separation into the π- and σ-bands is consistent (12).

As can be seen in Fig. 1 the dependence of the shape of the N K-emission band upon the take-off angle is very pronounced. The effect is less marked in the case of the B K-emission band, because the intensity of the π-band relative to that of the σ-band is smaller for boron than for nitrogen.

2. The x-ray photoelectron spectrum

The x-ray photoelectron spectrum of BN was measured by Hamrin et al. (9) who used the non-monochromatic Mg Kα-radiation for excitation. The statistical error of this measurement is comparatively large, and it is difficult to estimate the influence of the $K\alpha_{3,4}$ satellites. So the x-ray photoelectron spectrum was remeasured using Al Kα-radiation, with a VG ESCA III spectrometer+).

+) We are greatly indepted to Dr. D.S. Urch, Queen Mary College, London, for the possibility to measure the photoelectron spectrum in his laboratory.

Spectra were obtained using an x-ray power of 10 kV, 20 mA and at a pressure of about 10^{-8} Torr.

According to the geometry of the instrument the sample was irradiated under an angle of 45°, and the take-off angle of the photoelectron beam was also 45°. Because of the large angle of acceptance of the spectrometer the shape of the photoelectron spectrum seems to be independent of either angle. The resolution was 1.6 eV.

The spectra were obtained in the step-scanning mode, counting for 50 s at each step. The counting rate in the main maximum was about 45 c/s. The result of four scans is shown in Fig. 2. For the calibration of the energy scale the Au $f_{7/2}$-level with a binding energy of -83.6 eV was used. Corrections were made for the background of the Al $K\alpha_{3,4}$-satellites. The corrected spectrum is shown at the bottom of Fig. 3. It agrees well with the spectrum obtained by Hamrin et al. (9) except for the feature at a binding energy of -3.5 eV observed only by these authors. It may be caused by the Mg Kα-satellites and be associated with the peak at a binding energy of -11.5 eV. Since the Al Kα-satellites have a greater distance from the main line, no structure is observed at -3.5 eV in this case.

The binding energy of the 1s-level of boron and nitrogen was also measured. For N 1s the binding energy is -379.9 ± 0.2 eV, and for B 1s it is -190.4 ± 0.2 eV. These results agree within the limits of error with those determined by Hamrin et al..

3. Interpretation of the coordinated spectra

In Fig. 3 the x-ray spectra and the XP-spectrum are aligned in such a way that features corresponding to transitions of electrons with the same binding energy appear below each other. A K x-ray transition of energy E is coordinated to the binding energy E_v of the corresponding electron in the valence band by the relation $E = E_v - E_c$, E_c being the binding energy of an electron in the 1s level as determined by the XP-measurement. To improve the positioning of corresponding features the N K-spectrum was shifted by 0.5 eV towards the top of the valence band, while the B K-spectrum was shifted by 0.2 eV in the opposite direction. These shifts are within the limits of error given by the determination of the energy values of the 1s levels and by the calibration of the N K-emission band. The intensity ratios of the π- and σ-subbands in Fig. 3 correspond to those found for a polycrystal with isotropically distributed crystallites.

The different spectra reflect electrons with different symmetries. The s-like electrons, reflected in the XP-spectrum, are concentrated mainly in the lower part of the valence band, while p-like electrons showing up in the x-ray spectra are concentrated in the upper part of the valence band.

The experimental results shown in Fig. 3 represent a consistent view with regard to position and width of the different energy bands. Three regions can be distinguished: the π-band at low binding energies overlapping with the σ-band, which is separated by an energy gap from the so-called s-band. The π-band extends from -2.3 ± 0.5 eV to -10.2 ± 0.5 eV, and the σ-band from -2.7 ± 0.5 eV to -14.0 ± 0.5 eV. The values for the s-band are -17.2 ± 0.5 eV to -23.0 ± 1.0 eV; these values, however, do not reflect the real width of the s-band, since this band is strongly broadened by Auger-transitions. The real width of the s-band may be smaller by up to about 3 eV than the experimental value.

The s-band exhibits no structures. Besides the dominating s-components indicated in the XP-spectrum the s-band has also a B 2p component, but N 2p is almost completely absent. The most pronounced structures are observed in the σ-band, which according to band structure calculations, consists of two overlapping bands. The x-ray spectra show three distinct structures, which are also indicated in the XP-spectrum; their positions agree in all three spectra with the exception of the middle structure. - The σ-band includes a considerable amount of s-character at its bottom while the top part is mainly of p-character.

The π-band consists exclusively of p-states and therefore scarcely contributes to the XP-spectrum. There is no similarity between the π-band of boron and that of nitrogen. In the π-band of nitrogen the intensity is concentrated in the high energy part of the band, in the π-band of boron the intensity distribution is more symmetric. The same is true for the σ-band; again a higher percentage of the total intensity of the nitrogen spectrum is located in the upper part of the valence band. This shows that the weakly bound electrons are localized mainly near the nitrogen atom, which means that they hardly contribute to the chemical bonding.

III. Comparison of the spectroscopic data with theoretical results

In this section the spectroscopic data are compared with theoretical results. Band structure calculations of the layer crystal BN based on a two-dimensional unit cell (1,4) (containing one boron and one nitrogen atom) show four valence bands, the three lowest having σ-character, the uppermost having π-charakter. If a three-dimensional unit cell is used (with two boron and two nitrogen atoms), these energy bands split into eight bands. This splitting is small in the case of the σ-bands. For the π-bands the maximum distance between the two bands is about 1.6 eV (2,3); this leads to an increased width of the π-band.

The lowest σ-band is generally denoted as s-band. For the two higher σ-bands the upper limits of the bands coincide at the Γ point in all calculations; the band width, however, is different for the two bands. Since an experimental separation of these two σ-energy bands is not possible, the emission resulting from both bands is denoted in the following as the σ-band.

The width of the various bands and their energetic position relative to each other as determined from band structure calculations of the different authors are listed in table 1 together with the experimental values. The theoretical values were mostly taken from band structure curves and therefore may differ slightly from the calculated values.

It is evident that the calculated widths of all bands are too small, except those of Nakhmanson and Smirnov (2). The three different results obtained by Zunger et al. (4) were calculated using different methods of approximation. It is remarkable, that the extended Hückel method (EXH) provides results which are in better agreement with the experimental values than those obtained by the simple iterative extended Hückel method (SIEXH) and hardly worse than those of the modified iterated Hückel method (MIEXH).

Of all theoretical calculations only those of Nakhamson and Smirnov (2) agree reasonably with the spectroscopic results. The calculated widths of the σ- and the s-band agree within the limits of error with the experimental values, but the value for the width of the π-band is somewhat too large. Also, the overlap of the π- and σ-band and the gap between the σ- and s-band are much too large, when compared with the experimental observations.

In the following section the spectra are discussed in the light of density-of-states calculations. Such a calculation has been performed by Nakhmanson and Smirnov (2) based on the band structure calculation discussed above. Two further calculations of the density of states are not very suitable for a comparison with the spectroscopic data; in one case the energy steps in the histogram are too large (3), in the other case the π- and σ-densities have not been calculated separately (4).

For a comparison of the experimental results with the π- and σ-density of states calculated by Nakhmanson and Smirnov the peak of the theoretical π-band was aligned with the sharp peak of the π-band of the nitrogen spectrum. To get reasonable agreement between the experimental data and the corresponding structures in the calculated σ- and s-bands, the theoretical bands had to be shifted by 4.5 eV and 7.2 eV, respectively, towards the top of the valence band. The result of this procedure is shown in Fig. 3. The top of the valence band was arbitrarily chosen as zero-point of the energy scale.

An analogous procedure was applied to the density-of-states calculation of graphite, the π- and σ-subbands of which can be calculated separately and therefore may be shifted relative to each other (13,6). Semochkin and Borovskii (16) argue that in the case of BN the π- and σ-bands also can be calculated separately. As has been shown above the widths of the calculated bands agree reasonably with the experimental data, but their energy separation does not; so an independent choice of the zero-point of the energy scale seems to be justified. In this way a reasonable agreement between the spectroscopic data and the denstiy-of-states calculation is obtained.

IV. Discussion of the π-, σ-, and s-subband

a. π-band

The B K- and the N K-emission band are closely related to the local partial p-density of states in the environment of the B and N atoms, respectively. Assuming the transition probability of the corresponding x-ray transitions to be constant, the x-ray emission bands will be directly proportional to the local partial density of states. Since the π-band contains only p_z-electrons (i.e. no electrons with s-like symmetry) the superposition of the π-bands of the two x-ray spectra should be proportional to the π-density. For this one has to know the ratio in which the intensities of the N K- and B K-emission bands have to be summed up, in other words, one has to know the ratio of the local boron and nitrogen π-charges. This question cannot be answered on the basis of present x-ray data.

In his calculations of the electronic structure of BN molecular clusters Zunger (5) determined the number of π-electrons in the B and N sphere. According to this calculations 0.5 electrons of the two electrons of the π-energy band are located at the boron atom, and 1.5 electrons at the nitrogen atom. This result is supported by NMR-measurements of Silver and Bray (14), who obtained a π-charge at the B atoms of 0.45 ± 0.015 electrons.

We have therefore added the integral intensities of the π-emission bands of boron ($I_{\pi,B}$) and nitrogen ($I_{\pi,N}$) in the ratio $I_{\pi,B} : I_{\pi,N} = 0.5 : 1.5$. In Fig. 4 the sum curve is compared with the above mentioned π-density of states, both curves having been normalized to equal areas.

The shape of the calculated density of states curve in the upper part of the π-band is, on the whole, reflected correctly by the sum curve. The lower limit of the calculated π-density of states, however, has binding energies which are too large, and the density-of-states curve rises too steeply in this region. If the influence of the matrix element is neglected this means that the π-energy band near point Γ should lie at smaller binding energies and, that it should rise more quickly.

b. σ-band

From the separation of the x-ray emission bands into π- and σ-subbands the ratios of the integral intensities $I_{\pi,B} : I_{\sigma,B}$ and $I_{\pi,N} : I_{\sigma,N}$ are known. Using the ratio $I_{\pi,B} : I_{\pi,N} = 0.5 : 1.5$, also the ratio $I_{\sigma,B} : I_{\sigma,N} = 2.3 : 3.4$ can be determined, and so the sum curve of the x-ray σ-bands of boron and nitrogen can be obtained. A comparison of the sum of the σ-emission bands and the calculated density of states is shown in the left part of Fig. 4 (see also III d). Unlike the π-density, the σ-density of states contains s-like states, which should be concentrated mainly at the bottom of the σ-band. Therefore one should expect agreement between the σ-density of states and the sum-curve in the upper part of the band, while in the lower part the sum curve should be below the density-of-states curve.

Regarding the position and the width of the structural features there is good agreement between theory and experiment. In the middle of the band both curves agree satisfactorily. In the top part of the σ-band, however, the calculated density of states is considerably larger than the sum of the emission bands. For the bottom part the calculated distribution is too spike-shaped and seems to be too narrow in width, even if the s-like part (XP-spectrum, Fig. 3) has been taken into account. At the top of the σ-band and at the bottom of the π-band the theoretical density of states is too high, which possibly may be connected with the fact that the overlap of these bands is too small.

c. s-band

Because of pronounced Auger-broadening of the spectra a comparison between theory and experiment for the s-band hardly is possible. Both theory and experiment exhibit only a lineshaped maximum which is asymmetrically broadened to the bottom of the band.

d. The relative intensities of the π- and σ-bands

If the transition probability is identical for the different subbands, the integral intensities of the emission bands are proportional to the number of electrons in the unit cell having corresponding symmetry. With this assumption and using the emission spectra of a polycristalline sample with isotropically distributed crystallites one would obtain for the two dimensional unit cell 2.3 boron pσ- and 3.4 nitrogen pσ-electrons in addition to the two pπ-electrons; only 0.3 out of eight electrons with s-like symmetry would be left. This obviously is an unreasonable result. So we have to assume that the transition probability for the pσ-electrons is greater than for pπ-electrons. If it is assumed that the transition probability for pσ-electrons is twice as high as for pπ-electrons, one obtains 3.1 electrons with s-like symmetry. A similar value was obtained in the case of graphite (15).

Since the positions of the structures in the density-of-states calculations agree quite well with those of the sum of the two x-ray emission spectra, it may be concluded that the energy dependence of the matrix element behaves in such a way, that it does not lead to additional structures. We have assumed the transition probability to be constant within the subbands, but to be, for the π-band, only one half of that for the σ-band.

In Fig. 4 the areas of the calculated σ- and π-density-of-states curves are in the ratio of 2:1. The ratio of the integral intensities of the two sum curves, however, is different from that corresponding to a polycrystalline sample with isotropically distributed cristallites: to get reasonable agreement with theory the σ-band had to be attenuated by a factor of two.

A similar observation was made in the case of graphite:
the π-band in the emission spectrum is weaker than expected. Kieser (15) finds in the energy region of the π-band a relatively great discrepancy between the calculated density of states and the experimental data. For a comparison with theory Berg et al. (6) used the x-ray emission spectrum obtained from a single crystal on which the radiation was taken off at a small angle to the layer planes; in this case the π-band is overweighted.

Thus the difference of about a factor two in the transition probabilities of the π- and σ-electrons is observed as well for graphite as for BN. Because of the different spatial distribution of the π- and σ-electrons differences in the matrix element for the two symmetry types are not surprising.

A more detailed elucidation of the electronic structure of BN would be possible if calculations of the x-ray emission spectra were available. Attempts in this direction have been made by Semochkin and Borovskii (16) who calculated the B σ- and N σ-emission bands using the method of equivalent orbitals; in the calculations the matrix element was considered to be constant. A comparison with the experimental results shows that the calculation does not correctly reflect the energy position and the relative intensities of the structural details, particularly in the low energy part.

In conclusion it may be stated that improved band structure calculation are needed. Moreover calculations of the local partial density of states or rather of the intensity distribution of the x-ray π- and σ-subbands should be performed.

Acknowledgments

This work was supported by the Deutsches Elektronen-Synchrotron DESY. Financial support by the Bundesministerium für Forschung und Technologie is gratefully acknowledged. Thanks are due to Professor H. Bross and to Dr. D.S. Urch for critically reading the manuscript. G.W. gratefully acknowledges the support of NATO (Research Grant No. 1080 to Dr. D.S. Urch) enabling XP-measurements at Queen Mary College, London.

References

1. E. Doni and G. Pastori Parravicini, Nuov.Cim. B64, 117 (1969)
2. M.S. Nakhmanson and V.P. Smirnov, Sov.Phys. - Solid State 13, 2763 (1972)
3. J. Zupan, Phys.Rev. B6, 2477 (1972)
4. A. Zunger, A. Katzir, and A. Halperin, Phys.Rev. B13, 5560 (1976)
5. A. Zunger, J.Phys. C7, 76 and 96 (1974)
6. O. Berg, G. Dräger, and U. Brümmer, phys.stat.sol. (b) 74, 341 (1976)
7. C. Beyreuther, R. Hierl, and G. Wiech, Ber. Bunsenges. Phys. Chem. 79, 1081 (1975)
8. G. Wiech, in: X-Ray Photoelectron Spectroscopy, Academy of Sciences of the Ukrainian S.S.R., Institute of Metal Physics, Kiev "Naukova Dumka" 1977, p. 74
9. K. Hamrin, G. Johannson, U. Gelius, C. Nordling, and K. Siegbahn, Physica Scripta 1, 277 (1970)
10. V.A. Fomichev, Sov.Phys. - Solid State 13, 754 (1971)
11. V.A. Fomichev and M.A. Rumsh, J.Phys.Chem. Solids 29, 1015 (1968)
12. E. Tegeler, N. Kosuch, G. Wiech, and A. Faessler, phys.stat.sol. (b) 84, 561 (1977)
13. E.K. Kortela, R. Manne, J.Phys. C7, 1749 (1974)
14. A.H. Silver and P.J. Bray, J.Chem.Phys. 32, 288 (1960)
15. J. Kieser, Z. Physik B26, 1 (1977)
16. P.N. Semochkin and I.B. Borovskii, Fiz.Met. & Metalloved 39, 497 (1975) Engl. transl. in: Phys.Met. & Metallogr. 39, 41 (1975)

Figure captions

Fig. 1 X-ray K-emission spectra of boron (left) and of nitrogen (right) of hexagonal boron nitride BN at take-off angles of 10°, 30°, and 80° and separation into π- and σ-subbands.

.... observed spectrum, ------------- subbands,

———— sum of subbands

The tailing of the N K-emission band on the low energy side is shown in Fig. 3

Fig. 2 X-ray photoelectron spectrum of hexagonal boron nitride BN.

...... observed spectrum, ------- background, ——— contribution of Al Kα satellites.

Fig. 3 π- and σ-bands of the N K- and B K-emission, x-ray photoelectron spectrum, and density of states (after (4); bands shifted). σ-band: full curves, π-bands: dashed curves.

Fig. 4 Calculated density of states (dashed lines) (4) and sum of the σ-bands of B and N (left) and of the π-bands of B and N (right).

Table 1: Width of π, σ, and s bands of hexagonal BN and their relative positions (in eV)

Author	Width of π-band	Width of σ-band	Width of s-band	Overlap between π- and σ-band	Gap between σ- and s-band
Doni and Pastori Parravicini (1)	1.2	3.3	0.9	0.2	8.5
Zupan (3)	3.6	6.3	0.5	3.0	7.4
Nakhmanson and Smirnov (2)	9.3	11.2	4.7	5.8	8.0
Zunger, Katzir, and Halperin (4)					
EXH-method	2.0	5.1	4.3	2.0	8.0
SIEXH-method	2.0	2.6	1.8	0.6 eV gap	11.4
MIEXh-method	4.6	4.4	3.3	2.6	7.6
Experiment	7.9 ± 0.7	11.3 ± 0.7	5.8 ± 1.5	7.5 ± 0.4	3.2 ± 0.7

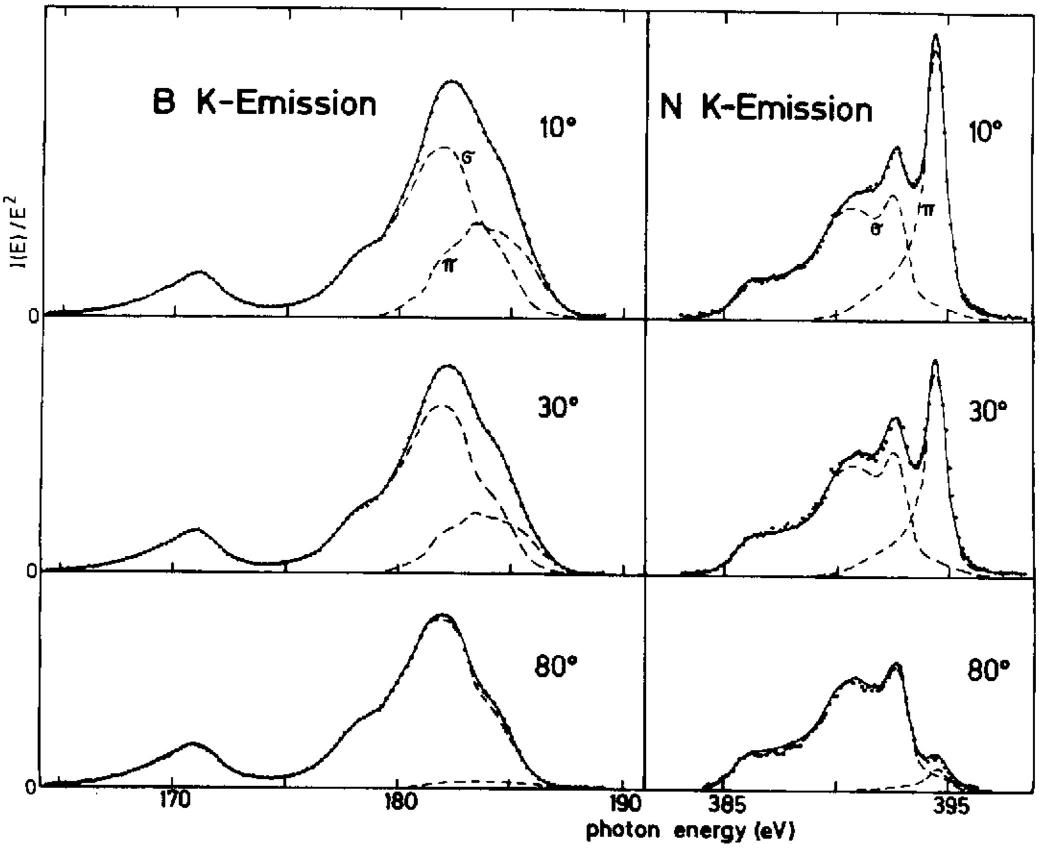

Fig. 1

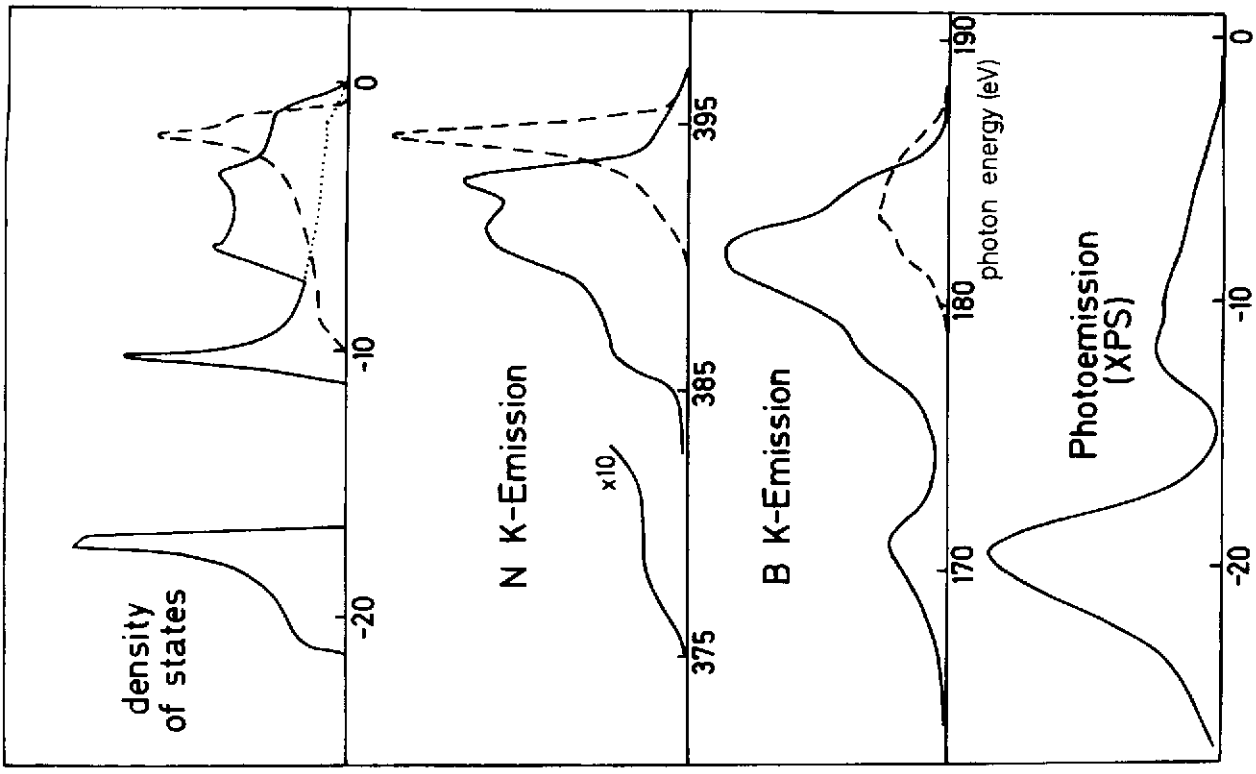
density of states
-20
-10
0
N K-Emission
x10
375
385
395
B K-Emission
170
180
190
photon energy (eV)
Photoemission (XPS)
-20
-10
0
binding energy (eV)

Fig. 3

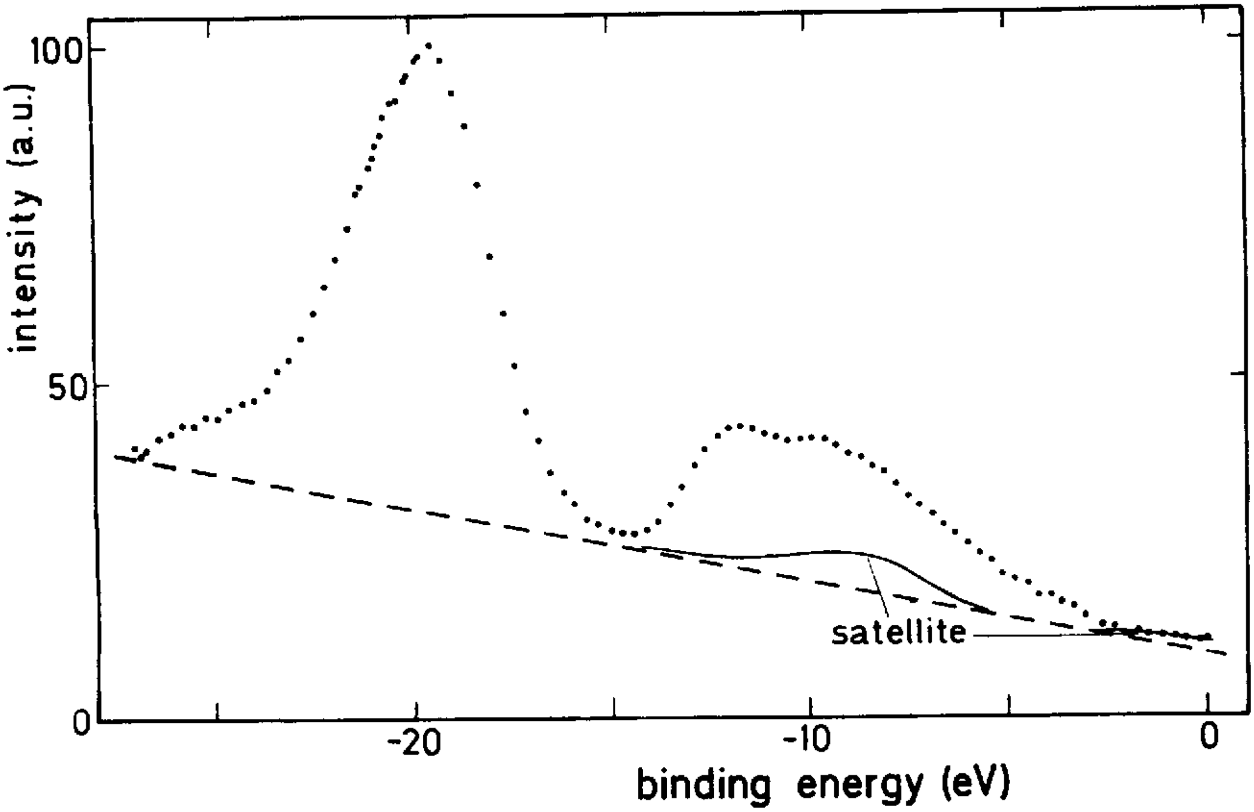
intensity (a.u.)
100
50
0
-20
-10
0
binding energy (eV)
satellite

Fig. 2

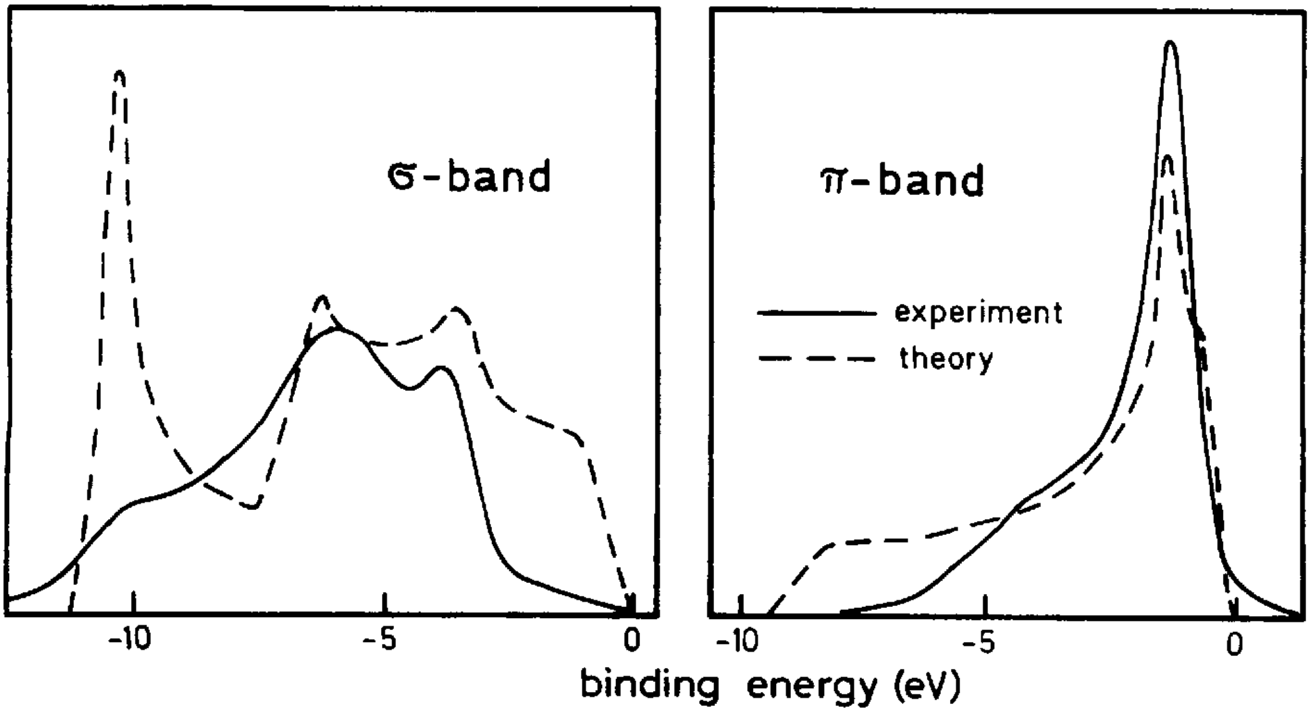

Fig. 4