DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-77/07
May 1977

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Anisotropic Emission of the X-Ray K-Emission Band of Nitrogen in Hexagonal Boron Nitride[*)]

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The intensity distribution of the N K-emission band of hexagonal boron nitride samples with partially orientated crystallites was found to be strongly dependent upon the take-off angle of the emitted radiation. The observed emission bands can be separated unambiguously into a σ- and a π-subband. On the basis of the directional characteristic of radiating dipoles within the layers (σ-bondings) and perpendicular to the layers (π-bonding) the angular dependence of the intensity of the subbands is quantitatively explained. In addition the degree of orientation of the crystallites in the sample can be determined. The intensity distributions of the emission bands to be expected for single crystals and for samples without any texture are determined; in the latter case the results are found to be in good agreement with experimental results.

Die Intensitätsverteilung der N K-Emissionsbande von Proben hexagonalen Bornitrids mit teilweise orientierten Kristalliten zeigt eine starke Abhängigkeit vom Abnahmewinkel der emittierten Strahlung. Die gemessenen Emissionsbanden können eindeutig in eine σ- und π-Teilbande zerlegt werden. Auf der Basis der Richtungscharakteristik von strahlenden Dipolen in der Schicht (σ-Bindung) und senkrecht zur Schicht (π-Bindung) wird die Winkelabhängigkeit der Intensität der Teilbanden quantitativ erklärt. Zusätzlich kann der Orientierungsgrad der Kristallite in der Probe bestimmt werden. Die Intensitätsverteilungen der Emissionsbande, wie man sie für Einkristalle und Proben ohne Textur erwartet, werden ermittelt; im letzteren Fall befinden sich die Ergebnisse in guter Übereinstimmung mit experimentellen Ergebnissen.

[*)] Work supported by Bundesminsterium für Forschung und Technology BMFT and Deutsches Elektronen-Synchrotron DESY

1. Introduction

In recent years several substances with anisotropic crystal structure were found to show an anisotropic emission of their characteristic x-rays, which means that the shape of the emission spectrum depends upon the take-off angle of the radiation.

The most pronounced effect known so far was observed for the K-emission band of graphite [1-3]. Hexagonal boron nitride BN being a layer crystal with a structure similar to that of graphite also shows an anisotropic emission of its characteristic x-rays. It was recently observed for both the K-emission band of boron [4,5] and the K-emission band of nitrogen [5]. - Obviously the anisotropic emission is the explanation for the discrepancies between the results of earlier measurements of the emission bands of graphite and boron nitride [6-11].

In the measurements of the anisotropic emission of the N K-emission band of boron nitride by Borovskii et al. [5] only two take-off angles were used, and the spectral resolution was low. So it seemed worth-while to remeasure this spectrum.

Samples of polycrystalline BN with partially orientated crystallites were used for the measurements. A quantitative interpretation of the anisotropic x-ray emission of such texture samples of BN is possible only if the spectrum is measured at several take-off angles. These measurements also permit the construction of the N K-emission band of a BN single crystal. Furthermore it is possible to determine the degree of orientation of the crystallites in the sample.

2. Experimental

Since single crystals of sufficient size are not available the measurements were performed with samples of powdered BN. The powder (purity better than 98 %) was rubbed onto a scratched plate of aluminum. Thus a smooth surface is obtained, and the hexagonal layers of the crystallites will be orientated preferably parallel to the surface of the sample (texture).

The N K-emission was excited with the synchrotron radiation of the storage ring DORIS in Hamburg and measured with a 2m concave grating spectrometer using an open photon multiplier as a detector [12]. The resolution of the instrument was about 0.7 eV for energies higher than 380 eV, and was reduced to about 2.5 eV for energies between 370 eV and 380 eV due to the very low intensities. The accuracy of the energy calibration is +0.3 eV. With a special sample holder it was possible to adjust any take-off angle between 10° and 80°. The angle between the synchrotron radiation and the emitted radiation entering the spectrometer was always about 90°. The measurements were carried out at a pressure of 10^{-8} Torr in the sample chamber.

3. Results

The N K-emission band of hexagonal boron nitride was measured for take-off angles from 10° up to 80° in steps of 10°. The results are shown in Fig. 1. In the low energy part the shape of the spectra does not change with the take-off angle. Therefore the spectra were normalized in intensity in this region; the curves obtained were identical for the whole energy range from 372 eV up to about 390 eV. Above 390 eV the intensity of the spectra changes drastically with the take-off angle. This is true especially for the peak at 394.5 eV which is the dominating feature in the 10° spectrum, but decreases to a weak structure in the 10° curve. With the spectra normalized at low energies it can be shown that due to self-absorption the intensity of the spectra in the high energy region is decreased by less than 5 % if the take-off angle is increased from 10° to 80°. In the following discussion the influence of self-absorption will therefore be neglected. As in the case of graphite the emission bands can be separated in two subbands, the π- and the σ-band. Because of the special normalization the σ-band is identical for all take-off angles, while the contribution of the π-band to the measured spectrum varies with the take-off angle.

In order to get the π- and σ-subbands, two spectra measured at different take-off angles are subtracted. The intensity distribution of the resulting curve and the π-band are equal but for a proportional factor. The shape of the σ-band results from the demand that the superposition of the constant σ-band with the π-band multiplied with an angular dependent factor has to match the measured curves for all take-off angles. In the present case this leads to an unambiguous and consistent separation of the measured spectra in a σ- and a π-subband.

In Fig. 2 the measured spectra (points) together with their π- and σ-bands obtained as described above (dashed curves) are presented for three different take-off angles. The very weak structure at about 379.5 eV, belonging to the σ-band, is not considered here. The main part of the σ-emission band extends from 385 eV up to 396 eV and exhibits four different structural features: a plateau-like region (386 - 389 eV) with slightly increasing intensity, a broad maximum at 390.8 eV, and another sharper maximum of somewhat higher intensity at 392.6 eV with a steep slope on the high energy side followed by some tailing. The π-band, the intensity of which strongly changes with the take-off angle extends from 390 eV to 397 eV. The maximum of the π-band is at 394.5 eV; there are no further structural details.

The full line is the superposition of the σ- and the π-band. As can be seen, the sum curve fits the experimental data quite well. The same is also found for the other take-off angles not shown in Fig. 2. Thus the separation into the two subbands is consistent.

4. The angular dependence of the N K-emission band

According to band structure calculations the valence band of hexagonal boron nitride consists of three σ-bands and one π-band (13,14), the electrons in the π-band having the lowest bond energies. The angular dependence of the intensity of the x-ray emission bands is caused by the different symmetries of the initial electron state, because the final 1s states has spherical symmetry. When electron transitions occur from the π-band to an empty 1s state (π-emission band) the emitted radiation has the characteristics of a classical dipole oscillating parallel to the crystallographic c-axis; the radiation generated by transitions from the σ-bands to 1s states (σ-emission band) has the characteristics of two dipoles lying within the layer planes and orientated perpendicular to each other (5). The shape of the emission bands is not dependent upon the take-off angle, their intensity, however, changes with the take-off angle. So we can write for the emission band $I(\delta,E)$, observed at a take-off angle δ

$$I(\delta,E) = f_\sigma(\delta) \cdot I^0_\sigma(E) + f_\pi(\delta) \cdot I^0_\pi(E), \qquad (1)$$

where $I^0_\sigma(E)$ and $I^0_\pi(E)$ are the maximum intensities for the σ- and π-band, and $f_\sigma(\delta)$ and $f_\pi(\delta)$ represent angular dependent intensity factors with values varying between zero and unity. In the case of a single crystal, for these intensity factors the following expressions are obtained:

$$f_\sigma(\delta) = \frac{1}{2}\left[1 + \sin^2\delta\right] \; ; \quad f_\pi(\delta) = \cos^2\delta. \qquad (2)$$

If a sample shows a texture, the distribution of the partially orientated crystallites may be described by a function $\rho(\theta,\phi)$, where θ is the polar angle, i.e. the angle between the vertical axis of the sample surface and the c-axis of the tilted crystallites, and ϕ is the azimuthal angle of the c-axis. In general the distribution function $\rho(\theta,\phi)$ of polycrystalline samples does not depend on ϕ, all angles ϕ having the same probability. On the other hand due to the special preparation of the samples the orientation may become ϕ-dependent in that the crystallites preferably are put in the direction of rubbing. Samples prepared with different directions of rubbing, however, showed identical emission spectra for the same take-off angle. Therefore the orientation of the crystallites can be described by the ϕ-independent function $\rho(\theta)$. Let this function be normalized in the following way:

$$\int \rho(\theta)\ d\Omega = 1\ ; \tag{3}$$

the integral is to take over the area of the upper half of the sphere.

The calculation of the emission band $I(\delta,E)$ of a sample with partially orientated crystallites is also based on equation (1). For the calculation of the intensity factors $f_\sigma(\delta)$ and $f_\pi(\delta)$, however, the contribution of all dipoles distributed according to the distribution function $\rho(\theta)$ must be summed up. The intensity factors then get the following form:

$$\begin{aligned} f_\sigma(\delta) &= \frac{1}{2}\left\{ \int \rho(\theta)\ \sin^2 z_{\sigma 1}\ d\Omega + \int \rho(\theta)\ \sin^2 z_{\sigma 2}\ d\Omega \right\} \\ f_\pi(\delta) &= \int \rho(\theta)\ \sin^2 z_\pi\ d\Omega\ , \end{aligned} \tag{4}$$

$z_{\sigma 1}$, $z_{\sigma 2}$, and z_π being the angles between the dipole axes of the corresponding dipoles in a crystallite and the direction of the propagation vector of the emitted radiation.

According to Borovskii et al. [5] we define a parameter α which describes the orientation of the crystallites:

$$\alpha = \int \rho(\theta)\ \cos^2\theta\ d\Omega. \tag{5}$$

From [5] we obtain for a single crystal $\alpha=1$, for a polycrystalline sample without any texture $\alpha=1/3$, and for samples with texture $1/3<\alpha<1$.

Making use of [5] and [3] we get the following expressions for the intensity factors $f_\sigma(\delta)$ and $f_\pi(\delta)$ of [4]:

$$\begin{aligned} f_\sigma(\delta) &= \frac{1}{4}\left[(3-\alpha) + (3\alpha - 1)\ \sin^2\delta\right] \\ f_\pi(\delta) &= \frac{1}{2}\left[(1+\alpha) + (1 - 3\alpha)\ \sin^2\delta\right] \end{aligned} \tag{6}$$

As can be seen the relations (2) for a single crystal follow from (6) by putting $\alpha=1$.

It is not possible to determine $f_\sigma(\delta)$ and $f_\pi(\delta)$ themselves from the experimental data, only the ratio $f_\pi(\delta)/f_\sigma(\delta)$ can be obtained. Using equation (6) we find:

$$\frac{f_\pi(\delta)}{f_\sigma(\delta)} = 2\ \frac{(1+\alpha) + (1-3\alpha)\ \sin^2\delta}{(3-\alpha) + (3\alpha-1)\ \sin^2\delta}\ . \tag{7}$$

In Fig. 3 the ratio $f_\pi(\delta)/f_\sigma(\delta)$ is shown for different values of the parameter α. It may be emphasized that for $\sin^2\delta = 1/3$ ($\delta \approx 35.3^\circ$) the ratio $f_\pi(\delta)/f_\sigma(\delta)$ does not depend on α, i.e. on the degree of orientation of the crystallites of the sample. This means that the x-ray spectrum of any polycrystalline sample and of single crystals has the same intensity distribution if measured at a take-off angle of 35.3°.

If the spectra are normalized so that the intensity of the σ-band is constant for all spectra (see Figs. 1 and 2) the intensity of the π-band is proportional to $(f_\pi(\delta)/f_\sigma(\delta))\cdot I_\pi^0(E)$. The ratio $f_\pi(\delta)/f_\sigma(\delta)$ is unity for $\delta \approx 35.3^\circ$. Therefore the spectrum measured at this take-off angle allows to determine the missing intensity normalization of $I_\pi^0(E)$ in relation to $I_\sigma^0(E)$. For convenience in all figures showing N K-emission bands the intensity scale is normalized so that the maximum intensity of the π-band is unity for a take-off angle of 35.3°.

It may be mentioned that the considerations of this chapter are valid for the K-emission spectra not only of BN but of all layer crystals in which only

π- and σ-electrons contribute to the bond.

The intensity ratios $f_\pi(\delta)/f_\sigma(\delta)$ as determined from the experimental data of Fig. 2 and from the spectra obtained for the other take-off angles are also marked in Fig. 3. As can be seen the experimental values come closest to the curve calculated for $\alpha=0.9$.

This result is surprising to some extent because the measurements were performed with different samples; for the various samples one would expect a certain scattering of the results. But the observations show that within the effective depth of the samples (which is at most 1 μ, while the thickness of the sample is >100 μ) by the process of rubbing a high - and reproduceable - degree of orientation of the microcrystallites is obtained. Other methods seem to be less effective: the samples of a piece of compact BN[a] which was supposed to be highly orientated proved to be much less anisotropic than our samples, and Borovskii et al. [5] report for their samples a value of $\alpha = 0.45$.

From the fact that in our case the parameter $\alpha=0.9$, which is not far from the value for a single crystal ($\alpha=1$), no conclusions can be drawn concerning the shape of the distribution function $\rho(\theta)$. It is, however, possible to estimate its width.

Assuming $\rho(\theta)$ to have a rectangle or triangle distribution, or to be a Gaussian, the percentage of the crystallites tilted by an angle $\leq\theta$ was calculated for $\alpha=0.9$. A rectangle or triangle distribution is rather unrealistic, because this would mean that the probability of a crystal tilted by an angle larger than $\theta=\theta_{max}$ is zero. On the other hand the results for $\alpha=0.9$ based on different distribution functions $\rho(\theta)$ are close together, and widely separated from those for $\alpha=1.0$ and $\alpha=1/3$. Thus α turns out to be a proper parameter to describe the degree of the texture of a sample. Assuming $\rho(\theta)$ to be a Gaussian it is found that 50 % of the crystallites are tilted less than about 16° for $\alpha=0.9$.

5. The N K-emission spectrum of a BN single crystal and of isotropically distributed crystallites

By the method described in the previous chapter the N K-emission band for any degree of orientation of the crystallites and for any take-off angle can be constructed. It is only necessary to use the subband $I^0_\sigma(E)$ and $I^0_\pi(E)$ obtained from the experimental curves, and to choose special values for the parameters α and δ.

In Fig. 4 the constructed N K-emission band for a single crystal of BN is shown. The full curve is that one would observe looking parallel to the layers, corresponding to a take-off angle $\delta=0^\circ$. Perpendicular to the layers (take-off angle $\delta=90^\circ$) one would observe the curve denoted as σ-curve. The comparison shows that the N K-emission band of the single crystal is very similar to the spectrum observed for the powder sample at $\delta=80^\circ$. The peak at 394.5 eV is higher by only about 15% due to the larger contribution of the π-band.

Figure 5 shows the calculated intensity distribution for isotropically distributed BN crystallites ($\alpha=1/3$; full line) together with its σ- and π-subbands (dashed lines). As already mentioned above (see also Fig. 3) the intensity distribution of this spectrum is expected to be independent on the take-off angle.

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[a] We thank Prof. H.-U. Chun, Institut für Physikalische Chemie der Universität Frankfurt, for this sample.

This could be checked experimentally. A sample without texture was obtained in the following way: BN powder whirled up in the air was gathered on a small plate spread with glue. The spectrum of this sample, obtained for a take-off angle of 10° is shown in Fig. 5. Because of the relative small amount of BN in such a sample the statistics are not as good as in the cases described above. A curve measured at 60° using the same sample is practically identical with the curve shown in Fig. 5, in agreement with the expectations. Moreover, the experimental result is in good agreement with the intensity distribution constructed according to formulas (1) and (7).

In connection with the last result it may be asked, whether the reflectivity of the grating and/or the quantum yield of the detector depend upon the different directions of polarization of the radiation, thus affecting the true intensity ratio of the π- and σ-band. It is evident that the spectrum of a sample without texture will not be affected by these effects. In the case of textured samples also good agreement was found between the calculated and measured intensity ratios of the subbands (see Fig. 3), so the influence of the above mentioned effects can be neglected.

According to the method described in this paper the intensity distributions $I^0_\pi(E)$ and $I^0_\sigma(E)$, and also the intensity ratio $f_\pi(\delta)/f_\sigma(\delta)$ of the π- and σ-band can be obtained independent on the texture of the sample and the angle of observation. The same method can also be applied to study the anisotropy of the B K-emission of boron nitride [4]. Then all experimental data will be available for a comparison with theoretical calculations of the electronic structure of the valence band of boron nitride.

Acknowledgements

We gratefully acknowledge financial support by the Bundesminsterium für Forschung und Technologie, and we would like to thank for the possibility to use the experimental facilities of the Deutsches Elektronen-Synchrotron DESY, Hamburg.

References

1. Chr. Beyreuther, G. Wiech, Physica Fennica 9, Suppl. S1, 176 (1974)
2. J. Müller, K. Feser, G. Wiech, A. Faessler, Physics Letters 44A, 263 (1973)
3. U. Berg, G. Dräger, O. Brümmer, phys.stat.sol. (b) 74, 341 (1976)
4. Chr. Beyreuther, R. Hierl, G. Wiech, Ber. Bunsenges. Phys. Chem. 79, 1082 (1975)
5. I.B. Borovskii, P.N. Semochkin, M. Rzaeva, Fiz.Met.&Metalloved. (USSR) 40, 537 (1975)
6. F. Tyren, Nova Acta Reg.Soc.Sci. Upsaliensis 12, 7 (1940)
7. H.M. O'Bryan, H.W.B. Skinner, Proc.Roy.Soc. London 176, 229 (1949)
8. J.E. Holliday, in "The Handbook of X-rays", ed. E.F. Kaelble, McGraw Hill Book Co., New York 1967, p. 38
9. D.W. Fischer, W.L. Baun, J.Chem.Phys. 43, 2075 (1965)
10. Y. Hayasi, Sci.Rep. Tohoku Univ. Ser. I 51, 43 (1968)
11. V.A. Fomichev, M.A. Rumsh, J.Phys.Chem. Solids 29, 1015 (1968)
12. W. Schnell, G. Wiech, Mikrochim. Acta (in press)
13. M.S. Nakhmanson, V.P. Smirnov, Sov.Phys. - Solid State 13, 2763 (1972)
14. A. Zunger, A. Katzir, A. Halperin, Phys.Rev. B13, 5560 (1976)

Figure captions

Fig. 1 Intensity distribution of N K-emission band of hexagonal boron nitride samples with partially orientated crystallites between 384 eV and 398 eV (above) and between 372 eV and 384 eV (below) as a function of the take-off angle; spectra normalized at 388 eV.

Fig. 2 N K-emission bands measured at take-off angles of 10°, 40° and 80° and separation in σ- and π-subbands.

Fig. 3 Intensity ratios $f_\pi(\delta)/f_\sigma(\delta)$ as a function of the take-off angle for samples with different orientation parameter α, and comparison with experimental results.

Fig. 4 Construction of the N K-emission band of a single crystal for observation parallel to the crystal layers (full curve), using the σ- and π-subbands from Fig. 2, multiplied with an intensity factor obtained from equation (7) (dashed lines).

Fig. 5 Construction of the N K-emission band of a polycrystalline sample without texture (full line), using the σ- and π-subbands from Fig. 2, multiplied with an intensity factor obtained from equation (7) (dashed lines), and spectrum measured at a take-off angle of 10° (points).

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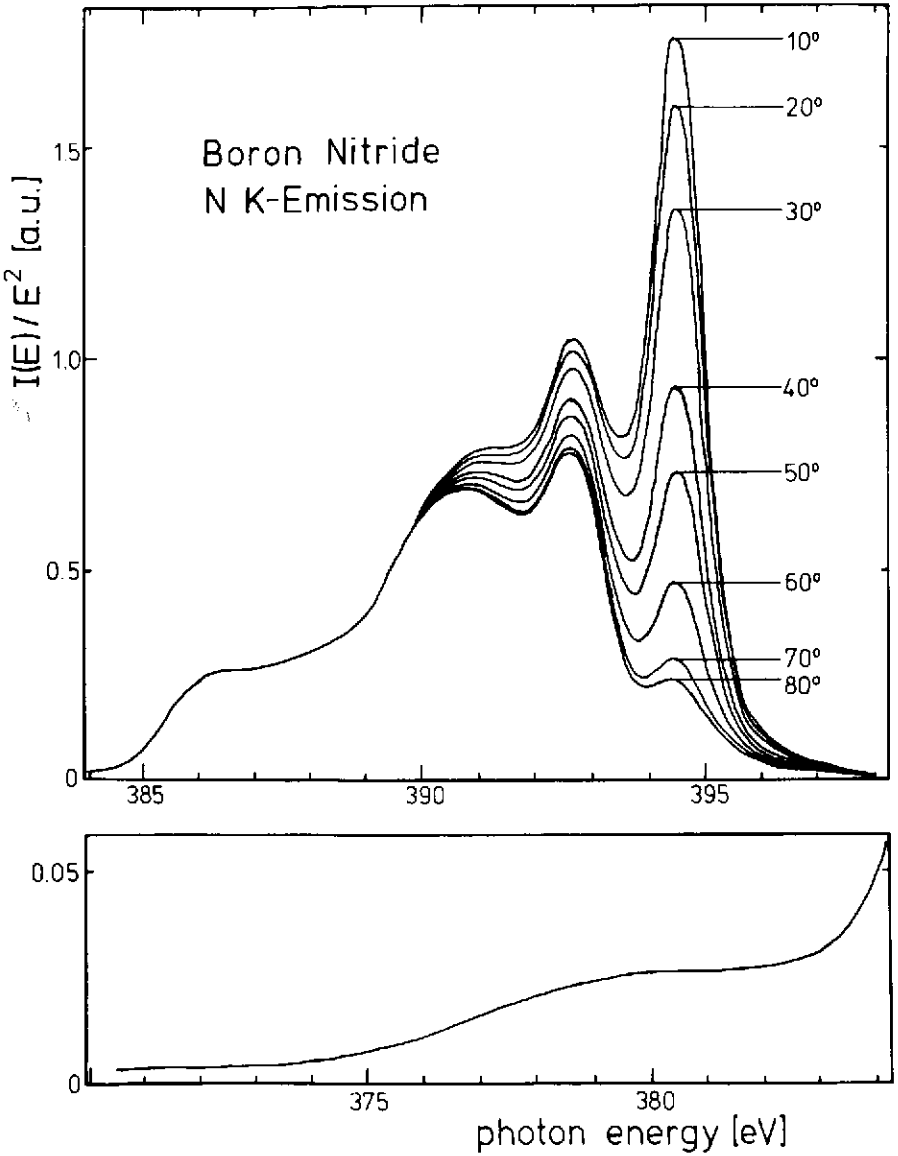

Fig. 1

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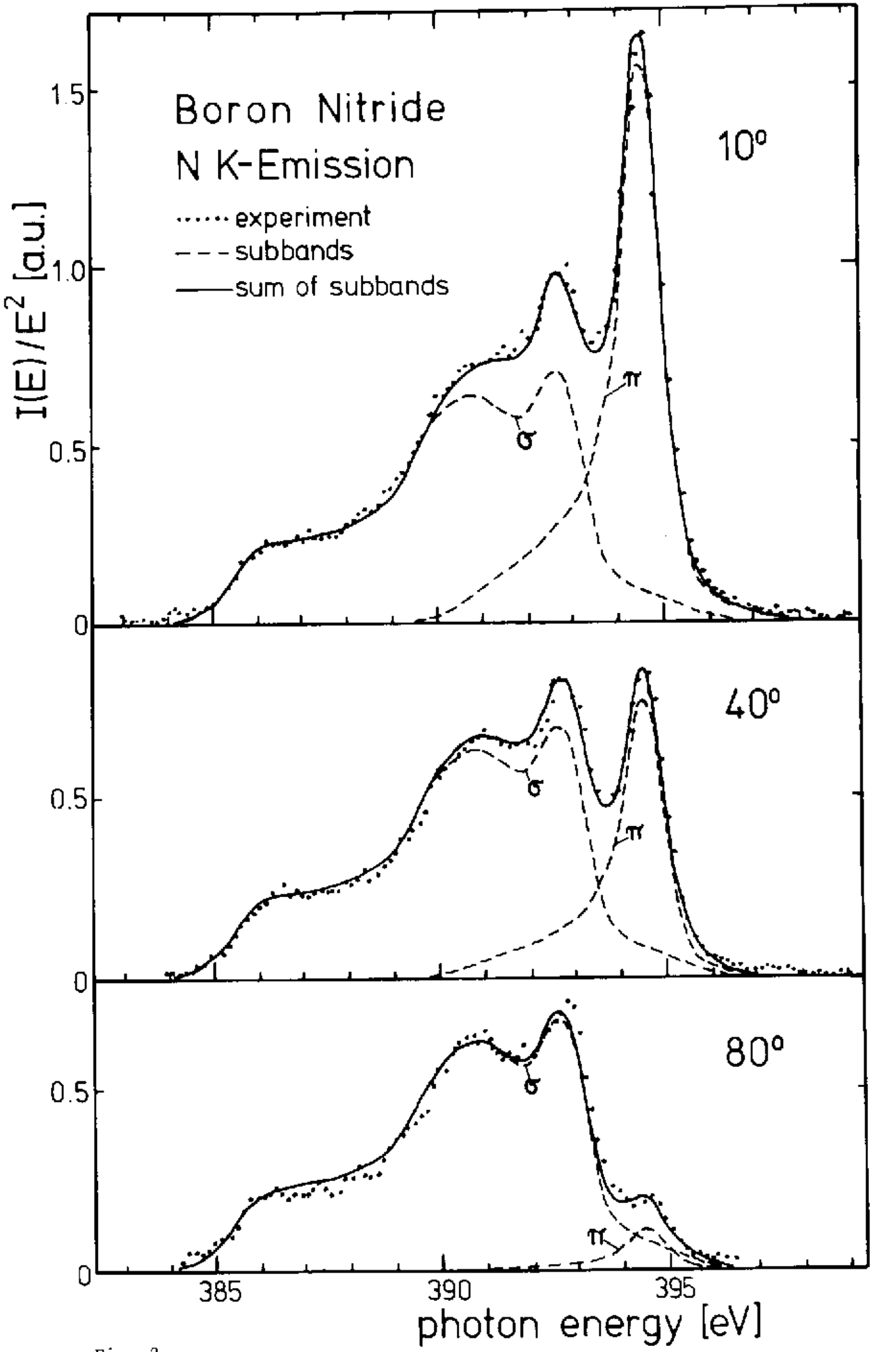

Fig. 2

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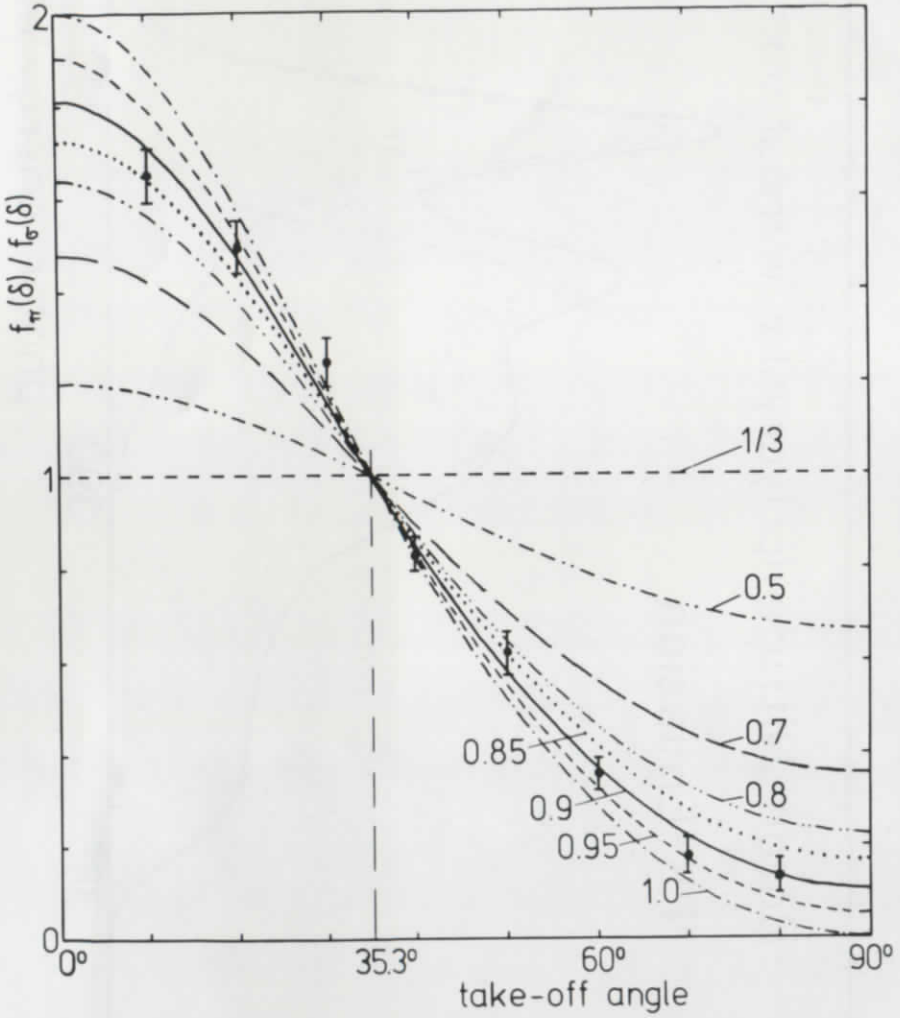

Fig. 3

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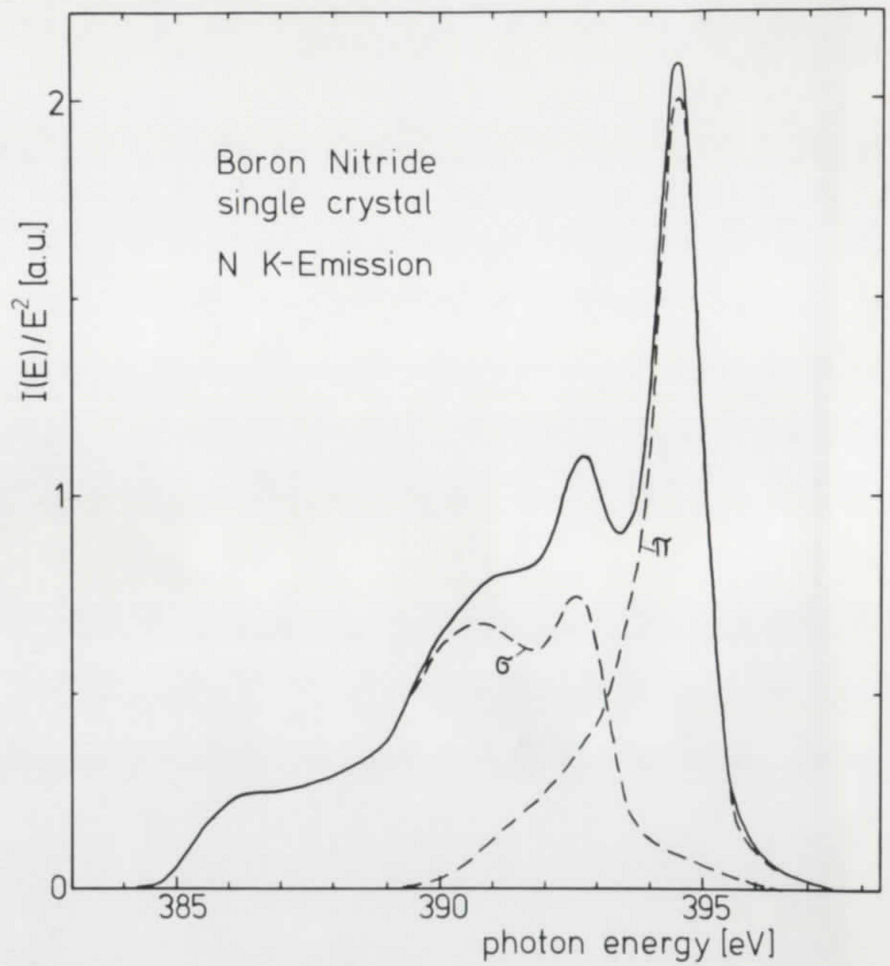

Fig. 4

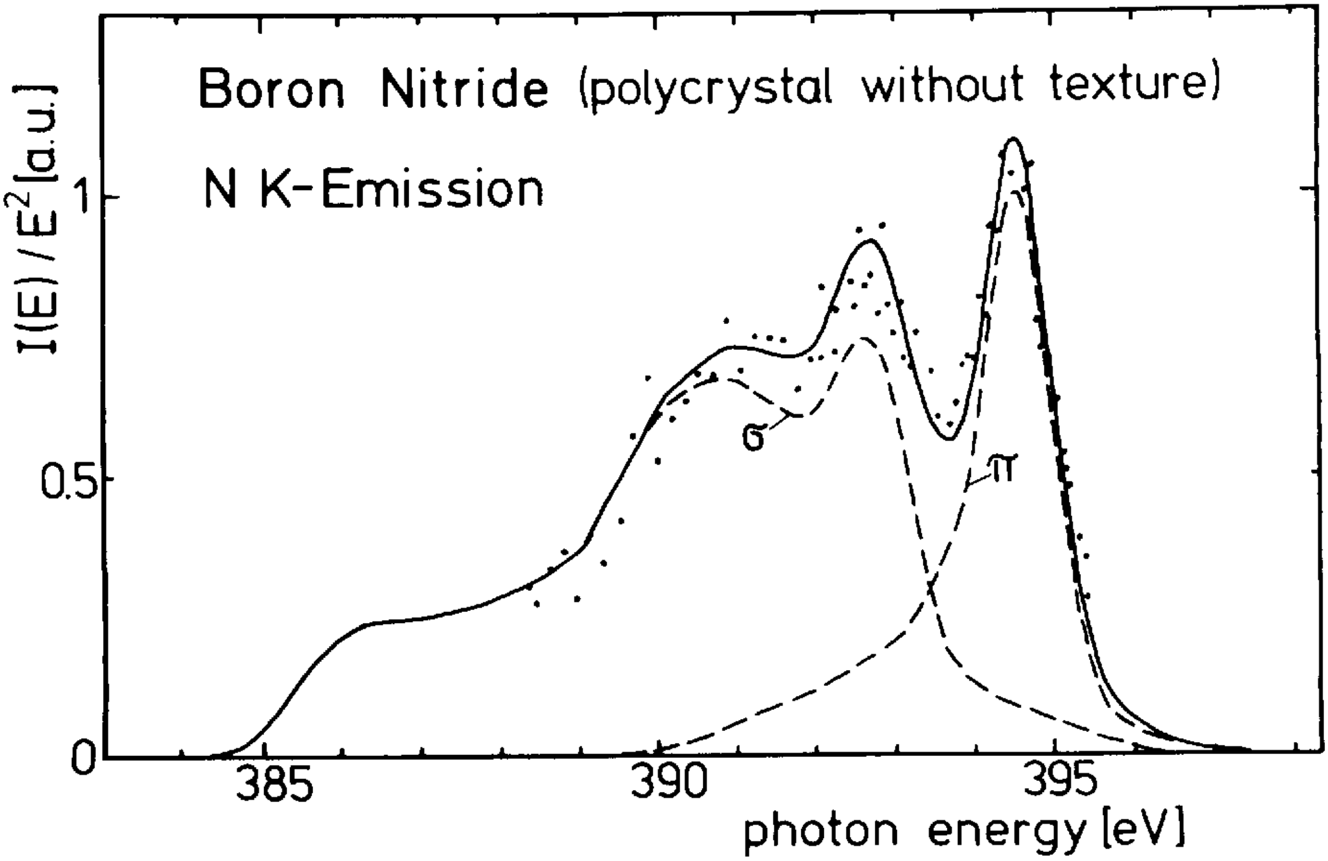
Boron Nitride (polycrystal without texture)
N K-Emission
I(E) / E² [a.u.]
1
0.5
0
385
390
395
photon energy [eV]
σ
π

Fig. 5