phys. stat. sol. **26**, 591 (1968)

Subject classification: 20.1; 13.1; 22.2

Institute of Physics, Czechoslovak Academy of Sciences, Prague

Optical Absorption Edge of AlN Single Crystals

By

J. PASTRŇÁK and L. ROSKOVCOVÁ

From measurements of the absorption coefficient of AlN single crystals the direct band gap values $E_G = (5.88 \pm 0.05)$ eV and $E_G = (5.74 \pm 0.05)$ eV for $\boldsymbol{E} \perp \boldsymbol{c}$ and $\boldsymbol{E} \parallel \boldsymbol{c}$, respectively, are determined. The slow increase in the absorption coefficient at the low-energy side of the direct gap is related to indirect transitions. The exact determination of the indirect gap is hindered by oxygen absorption bands at (4.53 ± 0.08) and (4.80 ± 0.08) eV.

Aus Messungen des Absorptionskoeffizienten von AlN-Einkristallen werden die direkten Bandabstände $E_G = (5{,}88 \pm 0.05)$ eV und $E_G = (5{,}74 \pm 0{,}05)$ eV für $\boldsymbol{E} \perp \boldsymbol{c}$ bzw. $\boldsymbol{E} \parallel \boldsymbol{c}$ bestimmt. Der schwache Anstieg des Absorptionskoeffizienten an der langwelligen Seite der direkten Bandkante wird indirekten Übergängen zugeschrieben. Die exakte Bestimmung der indirekten Kante wird durch Sauerstoff-Absorptionsbanden bei $(4{,}53 \pm 0{,}08)$ und $(4{,}80 \pm 0{,}08)$ eV verhindert.

1. Introduction

Very few data exist about the band structure of AlN. Starting from different empirical formulae some authors give E_G values ranging from 4 to 6 eV [1 to 3] without specifying the character of optical transitions. In the case of AlN belonging to $A^{III}B^{V}$ compounds with a small average atomic number an indirect gap is to be expected [4, 5]. Indirect transitions for AlN are predicted also by Wang et al. [6] with the indirect edge at 4.3 eV. Their existence seems to be confirmed by the spectral dependence of the index of refraction in the region of strong absorption [7].

The experimental results concerning the electron absorption of AlN are rather contradictory. Lagrenaudie [8] has found $E_G = 3.8$ eV, Kaner and Rabenau [9] concluded from their diffuse reflectance measurements that $E_G > 5$ eV; the same result is given by Fisher [10]. From transmission measurements on thin layers a strong absorption region beginning at ≈ 6 eV has been found by one of the authors [11]; the lower value of the absorption coefficient lying approximately at ≈ 5 eV was supposed to be probably caused by indirect transitions. These data were in agreement with diffuse reflectance measurements and the spectral dependence of photosensitivity [11]. The latest value for the band gap $E_G = (5.9 \pm 0.2)$ eV was obtained by Edwards et al. [12] and Cox et al. [13] from measurements on single crystals. Group analysis including optical selection rules for AlN was performed by Hejda [14].

Isoelectronic compounds with AlN which crystallizes in the wurtzite structure [15] are SiC and BP. For all structures of SiC as well as for BP which crystallizes only in the sphalerite structure, indirect transitions were found [16 to 20, 6]. The band structure of wurtzite crystals can be derived from that of sphalerite by application of a small crystal field perturbation [21, 22]. The indirect band gap in these materials seems therefore to yield another argument in favour of an indirect gap of AlN.

2. Experimental

Single crystals of AlN were prepared by direct reaction of aluminum vapour with nitrogen at high temperatures (1900 °C) [23]. Plate-like crystals with the c-axis perpendicular to the crystal plane, prisms parallel to the c-axis as well as crystal twins of the deltoid shape [7] with the c-axis in the crystal plane were used for measurements. In the last case only one half of the crystal was used. All crystals showed perfectly smooth natural surfaces, so that polishing was not necessary. The areas of the crystals were about 1 mm^2 or less, the thickness varied from 2 to 200 μm. The thickness of crystals was determined either directly on a microscope in bright and dark field or from the shift of interference maxima on the transmittivity curves measured at different angles of incidence [7]. The lattice parameters were checked by X-ray measurement and were in agreement with published data [15].

The transmission of the crystals in the UV region (2000 to 3600 Å) was measured on the double-beam spectrophotometer Optica Milano with a linear dispersion of 20 Å/mm. As light source a deuterium discharge lampe was used. All measurements were performed in polarized light, a set of quartz glas plates operating at the Brewster angle was used as polarizer.

Because of the high degree of parallelism of surfaces of the measured crystals interference maxima were obtained on the transmission curves for thin crystals (Fig. 1) which could be used for thickness determination as well as for the determination of the index of refraction [7]. For the determination of the absorption coefficient the mean values of transmission were used. The calculations of αd were performed with the help of tables computed by Kahan and Lipson [24]. The values of R were determined from known data of the index of refraction. The transmission of some crystals was measured in the temperature range 20 to

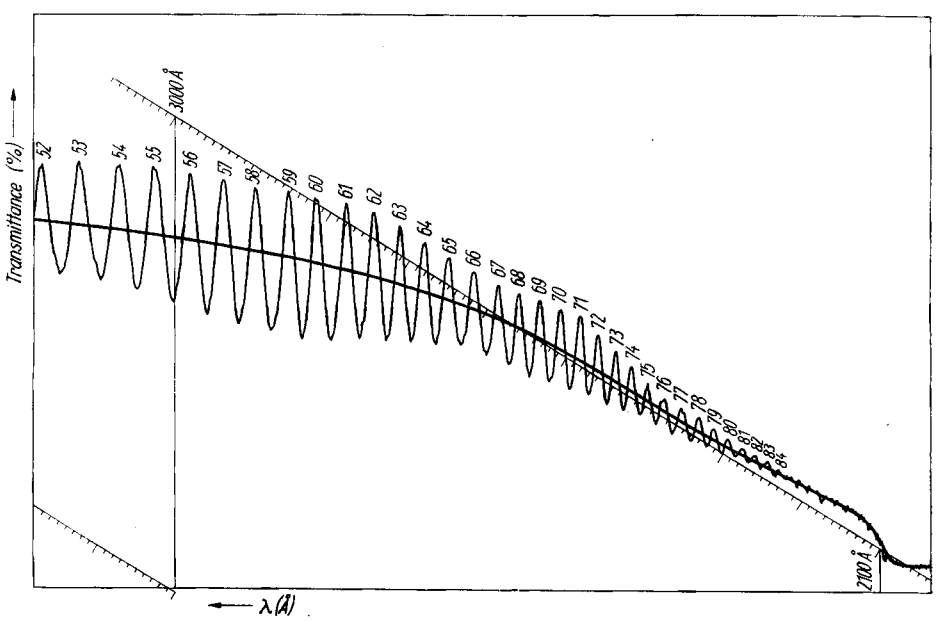

Fig. 1. Record of the transmission curve of AlN single crystals for polarized light with $E \perp c$. The sample thickness is 3.66 μm. The numbers at different maxima are the interference order

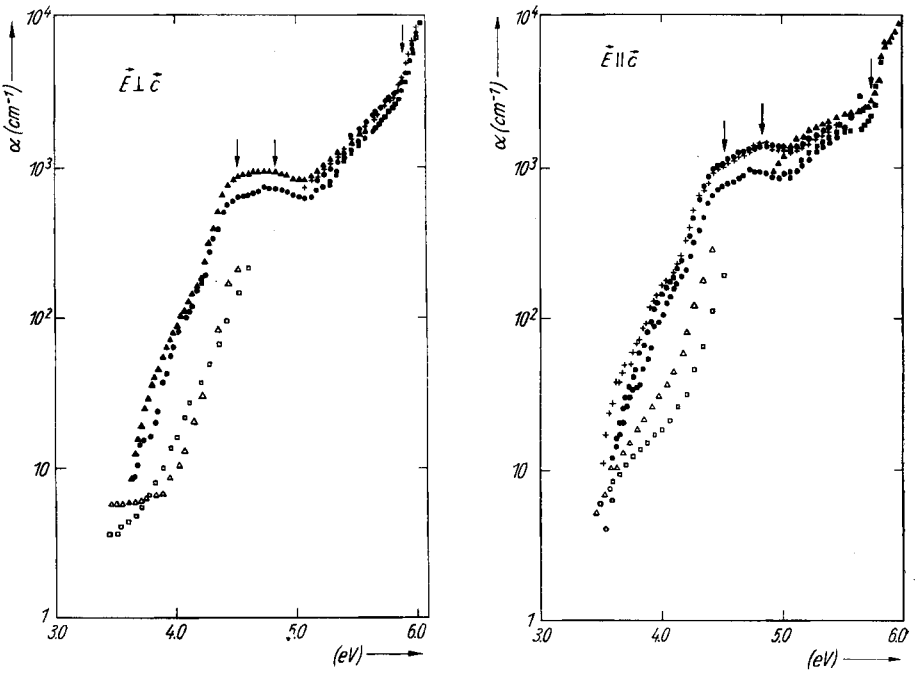

Fig. 2. Absorption coefficient for different samples. a) $\boldsymbol{E} \perp \boldsymbol{c}$, b) $\boldsymbol{E} \parallel \boldsymbol{c}$. On the abscissor $h\nu$ is plotted

800 °K, but most measurements were made at room temperature because additional windows of the temperature chamber increased the experimental errors in the case of small crystals.

Fig. 2 a and b show the values of the absorption coefficient of different samples for the polarization $\boldsymbol{E} \perp \boldsymbol{c}$ and $\boldsymbol{E} \parallel \boldsymbol{c}$ versus photon energy. On the background of the slowly monotonously rising absorption a broad absorption band can be clearly recognized in both polarizations. These maxima can be seen comparatively clearly on Fig. 3 where $\alpha^{1/2}$ is plotted against photon energy for

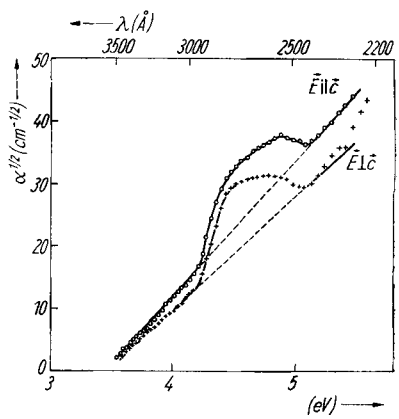

Fig. 3. Spectral dependence of $\alpha^{1/2}$ for a sample 19.63 μm thick. On the abscissor $h\nu$ is plotted

a sample with thickness of 19.63 μm. This plot allowed the continuous background to be substracted from the indirect transitions. From the shape of the band at least two maxima can be determined. The first one lying approximately at (4.53 ± 0.08) eV has for the sample in question a maximum value of the absorption coefficient of $\alpha_M \approx 600\ \mathrm{cm}^{-1}$ and a halfwidth of $\Delta \approx 0.4$ eV and is practically unpolarized. The second band lies at (4.80 ± 0.08) eV and has for $\boldsymbol{E} \perp \boldsymbol{c}$ $\alpha_\perp \approx 340\ \mathrm{cm}^{-1}$ and $\Delta_\perp \approx 0.24$ eV and for $\boldsymbol{E} \parallel \boldsymbol{c}$ $\alpha_\parallel \approx 460\ \mathrm{cm}^{-1}$ and $\Delta_\parallel \approx 0.26$ eV, i.e. it is stronger in $\boldsymbol{E} \parallel \boldsymbol{c}$ polarization, the degree of polarization being $\delta = 0.2$.

The temperature dependence of these two maxima has been measured in the region 293 to 800 °K. The halfwidth of the maxima for both polarizations is given in Table 1.

Table 1

T (°K)	$\Delta(T)$ (eV) $\boldsymbol{E} \perp \boldsymbol{c}$	$\Delta(T)$ (eV) $\boldsymbol{E} \parallel \boldsymbol{c}$
293	0.56	0.59
388	0.60	0.61
473	0.63	0.63
573	0.67	0.65
681	0.71	0.67
781	0.75	0.70

From the formulae for the halfwidth [25]

$$\Delta(T) = \Delta(0)\left[\tanh \frac{h\nu}{2kT}\right]^{-1/2}$$

the energy of phonons taking part in the electronic transitions was graphically determined. $h\nu = (91 \pm 10)$ meV was found in agreement with the data for optical phonons. From IR transmission measurements in the multiphonon region the phonon energies LO = 91.4, TO_1 = 82.5, TO_2 = 78.1, LA = 62.9, TA_1 = = 55.3, and TA_2 = 50.9 meV were determined [26]. The value (91 ± 10) meV found here seems to correspond to the longitudinal optical phonon branch.

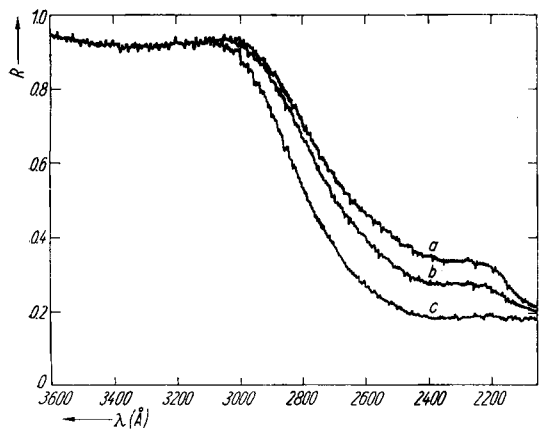

Fig. 4. Diffuse reflectance of AlN powder with different O_2 content. (a) 0.55%, (b) 0.75%, (c) 1.08%

To clarify the origin of these bands we measured the diffuse reflectance on AlN powder samples where purity could be easier controlled and checked. The grain size was 1 to 3 μm, the grains were well developed with natural crystal surfaces. In Fig. 4 the results for three samples with different oxygen contamination are given, the amount of oxygen having been determined by chemical analysis. The intensity of the absorption bands is directly proportional to the oxygen content. In the region of these oxygen bands at (4.45 ± 0.05) and (4.95 ± 0.05) eV an excitation maximum on photoluminescence curves has been observed [27].

3. Discussion

The spectral dependence of the absorption coefficient in the absorption edge region is in agreement with the assumption of an indirect gap. The fact that the maxima of oxygen impurity are overlapping the slowly rising intrinsic absorption makes the usual procedure of plotting the square root of α against photon energy to find the indirect band gap very difficult. The amount of oxygen impurity is different in different crystals and cannot be determined in individual single crystals. As we probably were not fully able to control this problem during crystal growth, the great dispersion in experimental points in the region of the oxygen maxima (Fig. 2a, b) is supposed to be caused by this fact. We can only estimate the position of the indirect band gap, it is equal or higher than 3.5 eV.

We connected the onset of direct transitions with the break on the spectral absorption curves, where the absorption rises steeply and reaches values of 10^4 to 10^5 cm^{-1}. We obtain for $\boldsymbol{E} \perp \boldsymbol{c}$ the value $E_G = (5.88 \pm 0.05)$ eV and for $\boldsymbol{E} \parallel \boldsymbol{c}$ $E_G = (5.74 \pm 0.05)$ eV. These values for the direct gap are in agreement with Ormont's estimation [1] and with the measurements reported in papers [12] and [13].

Comparing the optical absorption of AlN with that of BP and SiC we see that the values of the direct band gap are very close for all these compounds while the indirect gap for AlN is the highest one. This is in accordance with the highest ratio of ionic bonding in AlN, where the effective charges of the ions are $q = 1.2$ [26, 28].

The information regarding the band structure of AlN which can be derived from our measurements is shown in Fig. 5. According to group analysis [14, 29] the direct transitions are supposed to occur between the Γ_1, Γ_5 levels of the valence band maximum split by the crystal field and spin–orbit interaction and the Γ_1 level of the minimum of the conduction band.

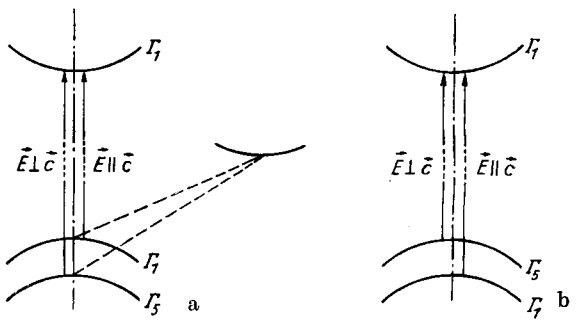

Fig. 5. Model of the band scheme in the Γ-point. a) AlN, b) ZnS (CdS)

According to Herman [30] the spin–orbit splitting of the Γ_5 level should be 0.016 eV, a value being lower than our experimental errors.

For AlN, where the direct band gap for $\boldsymbol{E} \parallel \boldsymbol{c}$ is less than for $\boldsymbol{E} \perp \boldsymbol{c}$, according to the selection rules the situation shown in Fig. 5a with $E(\Gamma_5) < E(\Gamma_1)$ fits the experimental results. With ZnS and CdS the reverse relation $E(\Gamma_1) < E(\Gamma_5)$ was found [31 to 33] (Fig. 5b). This fact seems to be in agreement with the spectral dependence of the index of refraction of these materials. In the long-wave region far enough from the absorption edge the relation $n_{\parallel} > n_{\perp}$ holds for AlN, CdS, and ZnS. In the vicinity of the absorption edge CdS as well as ZnS show inversion of birefringence [34, 37] so that near the edge $n_{\parallel} < n_{\perp}$. This behaviour is consistent with the fact that the optical transitions for the ordinary ray begin at lower energies than for the extraordinary ray. On AlN such effect was not observed [7] in agreement with the proposed scheme (Fig. 5a).

This difference may be caused by the different crystal field perturbation in AlN, where the ratio $c/a = 1.6$ is smaller than in ZnS and CdS.

As far as the location of the absolute conduction band minimum in the Brillouin zone is concerned, only speculation is possible. Wang et al. [6] suppose for AlN indirect transitions among levels which are equivalent to the $\Gamma_{15} \rightarrow X_3$ levels of sphalerite (the case of BP and α-SiC). The progress in studying the detailed shape of the absorption edge will be made only simultaneously with the progress in preparing single crystals of AlN without oxygen impurity.

Acknowledgements

We are grateful to Ing. V. Stupka and Mr. J. Veselý for the help in the preparation of AlN single crystals, to Mrs. A. Kučeravá who performed a great part of the numerical calculation, to Dr. A. T. Collins of the King's College of London for helpful and interesting correspondence, and to Dr. A. Kahan and Dr. H. G. Lipson for the tables used in the calculation. We are grateful to Ing. J. Hejduk and Dr. J. Novák CSc., for the necessary chemical analysis.

References

[1] B. F. ORMONT, Voprosy metallurgii i fiziki poluprovodnikov, Izd. Akad. Nauk SSSR, Moskva 1961 (p. 5).
[2] P. MANCA, J. Phys. Chem. Solids **20**, 268 (1961).
[3] V. A. PRESNOV, Fiz. tverd. Tela **4**, 548 (1962).
[4] C. HILSUM and A. C. ROSE-INNES, Semiconducting III–V Compounds, Chap. III/1, Pergamon Press 1961.
[5] W. PAUL, J. appl. Phys. Suppl. **32**, 2082 (1961).
[6] C. C. WANG, M. CARDONA, and A. G. FISCHER, RCA Rev. **25**, 159 (1964).
[7] J. PASTRŇÁK and L. ROSKOVCOVÁ, phys. stat. sol. **14**, K5 (1966).
[8] J. LAGRENAUDIE, J. Chim. phys. **53**, 222 (1956).
[9] E. KANER and A. RABENAU, Z. Naturf. **12a**, 942 (1957).
[10] A. G. FISCHER, Solid State Electronics **2**, 232 (1961).
[11] J. PASTRŇÁK, Acta phys. Polon. **25**, 51 (1964).
[12] J. EDWARDS, K. KAWABE, G. STEWENS, and R. H. TREDGOLD, Solid State Commun. **3**, 99 (1965).
[13] G. A. COX, D. O. CUMMINS, K. KAWABE, and R. H. TREDGOLD, J. Phys. Chem. Solids **28**, 543 (1967).
[14] B. HEJDA, Proc. Internat. Conf. Luminescence, Budapest 1966.
[15] G. A. JEFFEREY and G. S. PARRY, J. chem. Phys. **23**, 406 (1955).

[16] B. Stone and P. Hill, Phys. Rev. Letters **4**, 282 (1960).
[17] R. J. Auber, R. Y. Koyma, E. E. Loebner, and R. C. Lucas, Phys. Rev. Letters **12**, 538 (1964).
[18] W. J. Choyke and L. Patrick, Phys. Rev. **105**, 1721 (1957).
[19] H. Philipp and E. Taft, Proc. Conf. on SiC, Pergamon Press 1960 (p. 366).
[20] L. Patrick, W. J. Choyke, and D. R. Hamilton, Phys. Rev. **137**, A1515 (1965).
[21] M. Cardona, J. Phys. Chem. Solids **24**, 1543 (1963).
[22] J. L. Birman, Phys. Rev. **115**, 1493 (1959).
[23] J. Pastrňák and L. Roskovcová, phys. stat. sol. **7**, 331 (1964).
[24] A. Kahan and H. G. Lipson, AFCRL-63-325, June 1963.
[25] D. Curie, Luminescence cristalline, Chap. 2/3, Dunod, Paris 1960.
[26] A. T. Collins, E. C. Lightowlers, and P. T. Dean, Phys. Rev. **158**, 833 (1967).
[27] V. Losík, Thesis, K. U. Prague 1965.
[28] L. Roskovcová, J. Pastrňák, and R. Babušková, phys. stat. sol. **20**, K29 (1967).
[29] J. L. Birman, Phys. Rev. **114**, 1490 (1959).
[30] F. Herman, Phys. Rev. Letters **11**, 541 (1963).
[31] T. C. Collins, R. N. Euwema, and J. S. Dewitt, J. Phys. Soc. Japan **21**, Suppl., 15 (1966).
[32] T. K. Bergstresser and M. L. Cohen, Phys. Letters (Netherlands) **23**, 8 (1966).
[33] J. L. Birman, H. Samelson, and A. Lempicki, GT & E Res. Developm. J. **1**, 2 (1961).
[34] S. J. Czyzak, W. M. Baker, R. C. Crane, and J. B. Howe, J. Opt. Soc. Amer. **47**, 240 (1957).
S. J. Czyzak, R. C. Crane, and T. M. Bieniewski, J. Opt. Soc. Amer. **49**, 485 (1959).
[35] L. Roskovcová and J. Pastrňák, Czech. J. Phys. **B17**, 562 (1967).
[36] S. Pačesová, private communication.
[37] W. Wardzyński, Proc. Roy. Soc. **A260**, 370 (1961).

(Received January 3, 1968)