

## ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

# Evaluation of Physical Parameters for the Group III Nitrates: BN, AlN, GaN, and InN

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**Abstract**—Estimation of dielectric, optical, electrooptical, magnetic, elastic, photoelastic, piezoelectric, and phonon characteristics of XN (X = B, Al, Ga, In) crystals is performed by simple methods using quantum-mechanical and semiempirical approaches. The values of deformation potentials and magnetic susceptibilities are determined. The results of calculations are compared with the available experimental data and the calculations of other authors. © 2002 MAIK “Nauka/Interperiodica”.

In spite of the fact that much attention has been paid in recent years to the experimental studies of the Group III metals (III-nitrates; see, for example, Proceedings of the Conference [1] and references therein), many characteristics, even for the most commonly used polytypes, are still not available. Consequently, theoretical investigation of III-nitrates is quite a topical problem. The *ab initio* numerical methods are usually employed for the calculation of various characteristics of these nitrates [1]. However, it is obviously of interest to use a simplified Harrison’s method based on the bonding orbitals [2, 3]. This method allows one to obtain analytical expressions for a large number of physical characteristics of semiconductor crystals. We used various modifications of the bonding-orbital method in [2, 3] for the description of wide-gap semiconductors. In this study, we have applied the above method to III-nitrates, including indium nitrite, which we have not yet investigated. In contrast to [4–10], here we use the values of atomic terms taken from the tables compiled by Herman and Skillman [2]. The input parameters for calculation are given in Table 1. Note that the covalence ( $\alpha_c$ ) of the compounds in the BN  $\rightarrow$  InN series decreases, and the polarity ( $\alpha_p$ ) increases.

Table 2 presents the results of the calculation of high frequency ( $\epsilon_\infty$ ) and static ( $\epsilon_0$ ) dielectric constants performed using the formulas given in [4]. In contrast to [2, 3], the calculation of ( $\epsilon_0$ ) was made taking into account the contribution of ion cores to screening. The bracketed values are the experimental ones taken from the reference book [11]. According to the data given in [2],  $\epsilon_\infty = 4.5$  for BN, and  $\epsilon_\infty = 4.8$  for AlN. The values of  $\epsilon_\infty$  for BN and AlN given in [12, 13] are equal to 4.53 and 4.46, respectively. The agreement between the calculated and experimental data is quite satisfactory. It is notable that almost identical results are obtained by the *ab initio* calculations [14]. Thus, in accordance with the experiment, both high frequency and static dielectric

constants obtained theoretically increase in the BN  $\rightarrow$  InN series with increasing polarity of bonding  $\alpha_p$ .

Table 2 also gives the values of electronic quadratic susceptibility  $\chi_{14}^e$ , the linear electrooptical coefficient  $r_{41}$ , and photoelastic constants  $p_{ij}$  calculated for cubic

**Table 1.** Input parameters for the calculations:  $d$  is the nearest-neighbor distance in a crystal [2],  $V_2$  and  $V_3$  are the covalent and ionic energies [3],  $\alpha_c$  and  $\alpha_p$  are the covalence and polarity [3], and  $\gamma$  is the adjustable parameter in calculation of dielectric properties [2]

Quantity	BN	AlN	GaN	InN
$d, \text{\AA}$	1.57	1.89	1.94	2.15
$-V_2, \text{eV}$	9.95	6.87	6.52	5.31
$V_3, \text{eV}$	3.12	4.09	3.92	4.16
$\alpha_c$	0.95	0.86	0.86	0.80
$\alpha_p$	0.30	0.51	0.52	0.59
$\gamma$	1.25	1.50	1.50	2.00

Note: The values of atomic terms are taken from the tables of Herman and Skillman [2].

**Table 2.** Results of the calculation of high-frequency ( $\epsilon_\infty$ ) and static ( $\epsilon_0$ ) dielectric constants, electronic quadratic susceptibility ( $\chi_{14}^e$ ), linear electrooptical coefficient ( $r_{41}$ ), and photoelastic constants ( $p_{ij}$ ) for cubic crystals

Quantity	BN	AlN	GaN	InN
$\epsilon_\infty$	4.40	5.32	5.38 (5.8)	8.04(9.3)
$\epsilon_0$	4.87	8.41	10.74 (12.2)	14.86
$\chi_{14}^e \times 10^{-7}, \text{CGSE}$	0.20	0.81	0.89	2.78
$r_{41} \times 10^{-7}, \text{CGSE}$	−0.05	−0.21	−0.14	−0.29
$p_{11} \times 10^2$	−29.7	−0.86	−7.3	1.1
$p_{12} \times 10^2$	−10.4	−3.0	−2.6	0.4
$p_{44} \times 10^2$	−15.2	−4.4	−3.7	0.6

Note: Experimental data [11] are shown in brackets.

**Table 3.** Results of the calculation of quadratic susceptibility ( $\chi_{ij}$ ) and photoelastic constants ( $p_{ij}$ ) for hexagonal crystals

Quantity	BN	AlN	GaN	InN
$\chi_{33} \times 10^8$ , CGSE	0.92	5.4	3.7	17.4
$(\chi_{31} = \chi_{15}) \times 10^8$ , CGSE	-0.46	-2.7	-1.8	-8.7
$-p_{11} \times 10^2$	34.7	10.0	8.6	-1.4
$-p_{33} \times 10^2$	37.0	10.7	9.1	-1.4
$-p_{12} \times 10^2$	9.2	2.7	2.3	-0.3
$-p_{13} \times 10^2$	6.7	1.9	1.7	-0.2
$-p_{44} \times 10^2$	11.0	3.2	2.7	-0.4
$-p_{66} \times 10^2$	12.8	3.7	3.2	-0.5

**Table 4.** Dimensionless Keating's force constants ( $\alpha^*$  and  $\beta^*$ ), elastic constants for cubic ( $C_{ij}^c$ ) and hexagonal ( $C_{ij}^h$ ) crystals, and corresponding bulk moduli ( $B^c$  and  $B^h$ ) (in GPa)

Quantity	GaN	AlN	InN
$\alpha^*$	4.36	4.61	4.20
$\beta^*$	0.92	1.12	0.80
$C_{11}^c$	322	325	178
$C_{12}^c$	156	142	92
$C_{44}^c$	138	147	73
$B^c$	211	203	121
$C_{11}^h$	373(390)	369(345)	204
$C_{33}^h$	398(398)	395(395)	217
$C_{44}^h$	105(105)	96(118)	50
$C_{66}^h$	123(123)	112	60
$C_{12}^h$	130(145)	145(125)	85
$C_{13}^h$	106(106)	120(120)	72
$B^h$	203	211	120

Note: The experimental data [14] are shown in brackets.

**Table 5.** Results of the calculation of the charge of a metallic ion ( $z^*$ ), the relative internal displacement ( $\zeta$ ), piezoelectric charge ( $e_p^*$ ), and piezoelectric constant ( $e_{14}$ ) for cubic crystals

Quantity	BN	AlN	GaN	InN
$z^*$	0.20	1.04	1.06	1.76
$\zeta$	0.62	0.72	0.72	0.77
$e_p^*$	-0.25	0.65	0.67	1.46
$e_{14}$ , C/m <sup>2</sup>	-0.19	0.54	0.53	0.95

crystals by the formulas given in [4, 5]. The values of susceptibility  $\chi_{14}^e$  increase with increasing polarity  $\alpha_p$ ; the electrooptical coefficients, remaining negative, increase in magnitude in the BN  $\rightarrow$  InN series. In contrast to the original approach [2, 3], we took into account the band effects in frames of the extended method of bonding orbitals. The photoelastic constants  $p_{ij}$ , obtained from the expressions derived previously by analogy with the elastic constants, change from large-magnitude negative values for BN to small positive values for InN. Unfortunately, the corresponding experimental data are not available to us. The same is true for the values  $\chi_{33}$ ,  $\chi_{13}$ , and  $p_{ij}$  for hexagonal crystals. From the calculations, it follows that the magnitudes of the susceptibilities  $\chi_{33}$  ( $>0$ ) and  $\chi_{13}$  ( $<0$ ) increase in the BN  $\rightarrow$  InN series; the changes in  $p_{ij}$  have the same tendency as for cubic crystals.

The results of the calculations of elastic constants for cubic,  $C_{ij}^c$ , and hexagonal,  $C_{ij}^h$ , crystals and the corresponding bulk moduli ( $B^c$  and  $B^h$ ), derived by us previously in terms of the Keating–Harrison model [15, 6], are given in Table 4. In calculations, we used the experimental data on elastic properties of GaN hexagonal crystals [16] and polycrystalline AlN films [17]. It should be pointed out that the *ab initio* calculations [18] yield  $B^c = 195$  and 195 GPa,  $B^h = 195$  and 194 GPa, for GaN and AlN, respectively. The values of  $C_{ij}^h$ , which are close to those calculated by us, were obtained theoretically in [19].

Table 5 contains the results of the calculations of piezoelectric parameters performed by the method published in [7] for cubic crystals. The calculations show that the charge of a metallic ion  $z^*$ , the relative internal displacement  $\zeta$ , piezoelectric charge  $e_p^*$ , and piezoelectric constant  $e_{14}$  increase in the BN  $\rightarrow$  InN series. Unfortunately, the constant  $e_{14}$  is known only from one publication [20], which gives  $e_{14} = 0.375$  C/m<sup>2</sup> for cubic indium nitrate. This value is 2.5 times smaller than the value obtained by us. Generally speaking, such a discrepancy is not surprising (see, for example, [2]) because the calculation of  $e_{14}$  is a complicated problem. In this context, it is worth mentioning that there is a lack of theoretical studies in this field. We know only one publication [21] devoted to the calculation of the piezoelectric constant for hexagonal AlN and ZnO crystals.

The results of the calculation of phonon frequencies (in cm<sup>-1</sup>) for cubic crystals using the formulas given in [8] are listed in Table 6. According to [22], the experimental frequencies of transverse and longitudinal optical phonons are equal to  $\omega_{TO}(0) = 478$  cm<sup>-1</sup> and  $\omega_{LO}(0) = 694$  cm<sup>-1</sup>, which is in excellent agreement with our results. The *ab initio* calculations [18] yield  $\omega_{TO}(0) = 648$  and 558 cm<sup>-1</sup> for AlN and GaN, respectively, which is, on average, 1.5 times larger than our

**Table 6.** Results of the calculations of phonon frequencies (in  $\text{cm}^{-1}$ ) for cubic crystals

Quantity	AlN	GaN	InN
$\omega_{TO}(0)$	454	545	474
$\omega_{LO}(0)$	606	703	640
$\omega_{TA}(2\pi/a)$	205	246	213
$\omega_{LA}(2\pi/a)$	368	442	383

**Table 7.** Results of the calculation of deformation potential of the conduction band ( $E_{dc}$ ) and orbital diamagnetic ( $\chi_L$ ), paramagnetic ( $\chi_P$ ), core diamagnetic ( $\chi_C$ ), and total magnetic ( $\chi$ ) permittivities for cubic crystals

Quantity	BN	AlN	GaN	InN
$-E_{dc}, \text{eV}$	6.76	4.49	4.43	3.54
$\chi_L \times 10^6$	-2.43	-2.02	-1.97	-1.78
$\chi_P \times 10^6$	2.01	1.22	1.18	0.86
$\chi_C \times 10^6$	-0.01	-0.18	-0.56	-1.49
$\chi \times 10^6$	-0.43	-0.98	-1.85	-2.41

values. Similar results for the same compounds are given in [23]. The results of *ab initio* calculations [24] for GaN are also close to ours. Using the data for hexagonal GaN and AlN obtained in [25], we calculated the following frequencies at  $T = 300 \text{ K}$ :  $\omega_{TO}(0) = 532 - A_1(TO)$ ,  $599 - E_1(TO)$ ,  $\omega_{LO}(0) = 734 - A_1(LO)$ ,  $741 - E_1(LO)$  for GaN;  $\omega_{TO}(0) = 611 - A_1(TO)$ ,  $670 - E_1(TO)$ ,  $\omega_{LO}(0) = 881 - A_1(LO)$ ,  $922 - E_1(LO)$  for AlN (henceforth, all frequencies are given in  $\text{cm}^{-1}$ ). Comparison with our results obtained for cubic crystals shows that the agreement is quite satisfactory for thallium nitrate, while our values for aluminum nitrate are approximately 1.5 times smaller than the experimental ones. As for the low-frequency modes, the authors of [25] reported the following frequencies for transverse acoustic phonon  $\omega_{TA}(2\pi/a)$  ( $E_2(\text{low})$ ): 144 and 245 for GaN and AlN, respectively. These values are in excellent agreement with our results for indium nitrates and smaller by a factor of 0.7 with respect to our value obtained for aluminum nitrate. The results of *ab initio* calculations of low-frequency modes of transverse acoustic phonons  $\omega_{LA}(2\pi/a)$  ( $B_1(\text{low})$ ) in [26] differ from those obtained by us, on average, by 1.5 times. Thus, a simplified approach to the calculation of frequencies proposed in [8] yields a semiquantitative agreement with the experiment.

Table 7 contains the results of the calculation of the deformation potential ( $E_{dc}$ ) of the conduction band and the orbital diamagnetic ( $\chi_L$ ), paramagnetic ( $\chi_P$ ), core diamagnetic ( $\chi_C$ ), and total ( $\chi$ ) magnetic permittivities for cubic crystals. The calculations were performed according to the method suggested in [9, 10] for cubic crystals. One can easily see the trends in the change of

polarity  $\alpha_p$ . Unfortunately, the corresponding experimental data are not available.

In conclusion, we suggest a relationship between the covalence  $\alpha_c$ , according to Harrison, with ionicity  $f_i$ , according to Phillips (see, for example, [8]):

$$f_i = 1 - \alpha_c^3.$$

Then, in the BN  $\rightarrow$  AlN  $\rightarrow$  GaN  $\rightarrow$  InN series, we have  $f_i = 0.13, 0.36, 0.37$ , and  $0.49$ .

To summarize, we may state that the simplified method developed by us for calculating the physical characteristics of semiconductor crystals, on the basis of a modification of Harrison's bonding-orbitals method and in combination with crystallographic analogies and some semiempirical models (like Keating's model), can provide a reasonable description of properties of III-nitrates. Such an approach allows one to estimate in a simple way a required property of both pure compounds and alloys.

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