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Hydrostatic deformation potentials and the question of exciton binding energies and splittings in aluminium nitride

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By comparing a series of optical experiments performed on bulk aluminum nitride crystals and heteroepitaxial films, we determine the hydrostatic excitonic deformation potentials of AlN. The agreement between the whole available experimental data and our analysis consolidates this determination. Using the previously determined values of the valence-band deformation potentials which account for the strain-induced variation in the crystal-field splitting: $d_3=-8.19$ eV and $d_4=4.10$ eV we obtain values of −6.04 and 2.15 eV for the hydrostatic excitonic deformation potentials a_1 and a_2 in the context of the quasicubic approximation. This constitutes the first series of values coherent with the whole set of experimental data. The experimental value of 1*s*-2*s* splitting disagrees with the theory of excitons in anisotropic semiconductors. This disagreement, we attribute it to our poor knowledge of the valence-band dispersion relations of AlN and to the difficulty we face for including in the calculation plausible values for the anisotropic hole effective mass, dielectric constant.

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Aluminum nitride is a promising material for realizing light-emitting or light-detecting devices susceptible to operate in the ultraviolet energy region.[1] This material may also be useful for supplying nitride growth laboratories and companies with substrates having good thermal performances in terms of heat dissipation. Growths of the material itself, of high-quality epitaxies are tricky. Measuring the optical properties of AlN requires experimental optical spectroscopy facilities that operate at energies higher than 6 eV. Thus, much less research has been dedicated to it than it has been in case of GaN. In this paper, we investigate the experimental values of the deformation potentials at the Γ point of the Brillouin zone. To do so, we compare the optical properties of AlN bulk crystals and heteroepitaxial films with calculations of optical transitions in the context of a model which we used to solve the problem of the value of the band gap of GaN epilayers.[2–4] We propose a −218 meV value for the crystal-field splitting parameters in the valence band of bulk AlN. Taking into account the previously determined values of the valence-band deformation potentials which account for the strain-induced variation in the crystal-field splitting:[5] $d_3=-8.19$ eV and $d_4=4.10$ eV, values of −6.04 and 2.15 eV are obtained for the hydrostatic excitonic deformation potentials a_1 and a_2, respectively, in the context of the quasicubic approximation, which constitutes the first series of values coherent with the whole set of experimental data. The second part of this paper is dedicated to the splitting between the ground state (GS) and what is attributed to the first excited state (ES) of exciton. This splitting has been measured in the 36–38 meV range for bulk AlN and in case of strained layer epitaxy.[6–9] We compare this value with predictions that can be made using a mathematical calculation of excitonic binding energies in case of anisotropic masses.[10,11] This model, which was successfully applied to excitons in semiconductors such as CdS, GaSe, and MoS_2,[10] does not fit with the experiment when using the theoretical values of the parameters that describe the dispersion relations in the valence band.

The band gap of aluminum nitride was only recently measured accurately by means of high-resolution optical spectroscopy. The value of the lowest excitonic band gap sits near 6.029 eV at 6–10K in bulk AlN.[12] Built-in strain fields blueshift it up to 6.138 eV in (0001)-oriented high-quality epilayers grown on *c*-plane sapphire substrates.[9] In their 2007 paper, Ikeda *et al.*[5] reported a tenth of complementary intermediate values. It is now well established that heteroepitaxial growth generally produces strain fields that modify the band gap of the semiconductor. Correlation between values of band gaps measured by optical means and values of the lattice parameter obtained by x-ray diffraction experiments can be realized experimentally.[13–16] The AlN case will be handled here similarly with the approach we used for GaN (Refs. 2–4) and ZnO (Refs. 17 and 18) epilayers. The correlation between strain and energy shifts is made in the context of the deformation potential formalism. The conduction to valence-band transitions of strained AlN are described as the differences between the eigenvalues of Hamiltonians that are very different for these two bands.

The Hamiltonian for the *s*-type conduction band writes,[19,20]

$$H_{c\text{-}strain}=E_C^0+c_1e_{zz}+c_2(e_{xx}+e_{yy}), \tag{1}$$

where E_C^0 is the conduction-band energy in bulk AlN, c_1 and c_2 are the conduction-band deformation potentials, and the e_{ij}'s are the components of the strain, if any. The situation is much more complicated for the *p*-type valence band. In bulk AlN three parameters are needed to account for the valence-band energies that result at the Γ point from the arrangement of aluminum and nitrogen atoms leading to formation of a stable wurtzite crystal. The lifting of the sixfold degeneracy of the valence band into three Kramers doublets is quantized using a crystal-field splitting parameter Δ_1^0 and two parameters that describe the spin-orbit interaction: Δ_2 and Δ_3. The mathematical theory of invariants indicates that six deformation potentials are needed to account for the effect of the most general strain field.[20] In case of wurtzite epilayers that experience a symmetric strain field in the (0001) growth plane, the only nonvanishing components of the strain are e_{zz} and $e_{xx}=e_{yy}$, which leads to a substantial simplification of the valence-band Hamiltonian.[2] Under such strain field the average value of the valence band of bulk AlN E_v^0 is shifted by an amount $\delta_1=d_1e_{zz}+d_2(e_{xx}+e_{yy})$ and the crystal-field splitting is varied by an amount $\delta_2=d_3e_{zz}+d_4(e_{xx}+e_{yy})$. The quantities d_i's are four of the six valence-band deformation potentials. Using the standard definitions of the valence-band irreducible representations, the Hamiltonian of the valence band is written as[2,13,19,21]

$$H_{V\text{-}strain} = \begin{array}{ccc} |\Gamma_9\rangle & |\Gamma_7^1\rangle & |\Gamma_7^2\rangle \\ E_v^0+\delta_1+\Delta_1^0+\delta_2+\Delta_2 & 0 & 0 \\ 0 & E_v^0+\delta_1+\Delta_1^0+\delta_2-\Delta_2 & \sqrt{2}\Delta_3 \\ 0 & \sqrt{2}\Delta_3 & E_v^0+\delta_1 \end{array}. \tag{2}$$

Let $\Delta_1=\Delta_1^0+\delta_2$ and let $E_v=E_v^0+\delta_1$.

The eigenvalues and their corresponding eigenvectors are doubly degenerate and given by

$$E_9=E_v+\Delta_1+\Delta_2, \tag{3}$$

$$E_7^{1,2}=E_v+\frac{\Delta_1-\Delta_2}{2}\mp\left|\frac{\Delta_1-\Delta_2}{2}\right|\sqrt{1+\frac{8\Delta_3^2}{(\Delta_1-\Delta_2)^2}} \tag{4}$$

with $|\varphi\Gamma_7^{1,2}\rangle$ eigenvectors being

$$|\varphi\Gamma_7^{1,2}\rangle=a|\Gamma_7^{2,1}\rangle\mp\sqrt{1-a^2}|\Gamma_7^{1,2}\rangle. \tag{5}$$

In Eq. (5), the parameter a is given by

$$a=\frac{\sqrt{2}\Delta_3}{\sqrt{\left(\frac{\Delta_1-\Delta_2}{2}-\left|\frac{\Delta_1-\Delta_2}{2}\right|\sqrt{1+\frac{8\Delta_3^2}{(\Delta_1-\Delta_2)^2}}\right)^2+2\Delta_3^2}}. \tag{6}$$

In group III element nitrides, the spin-orbit interaction is small and $\Delta_2\approx\Delta_3\approx 6$ meV.[2,22] From the previous works on bulk AlN, or on strained AlN layers, we are aware that Δ_1^0 is negative and very large compared to values of Δ_2 and Δ_3. As a net result of this, in the context of a band-to-band description of the transition energies, the optical transition of lowest energy occurs between the conduction band and the $|\varphi\Gamma_7^2\rangle$ valence band which is essentially built from p_z-type states. This transition is almost forbidden if an optical spectroscopy experiment is performed with the Poynting vector of the photon aligned along the [0001] direction of the AlN crystal. To observe it in decent conditions, the Poynting vector of the photon has to be given an oblique orientation, or it has to be oriented along the $[10\bar{1}0]$ direction. The transition between the conduction band and the $|\Gamma_9\rangle$ valence band is strictly forbidden if the electric field of the photon is aligned along the [0001] direction of the AlN crystal, which is a good indicator for the identification of this valence-band state.

Chen *et al.*[12] early reported unambiguous selection rules and identification of the valence-band ordering in bulk AlN. They demonstrated that the transition between the conduction band and the lowest of the valence band involves the $|\Gamma_7^2\rangle$ valence band while the highest-energy transition involves the $|\Gamma_7^1\rangle$ valence band. The large value of Δ_1^0 (they proposed −230 meV) compared to values of Δ_2 and Δ_3 leads to almost total decoupling of the $|\Gamma_7\rangle$ states in Eq. (2). Silveira *et al.*[6] slightly later brought a positive validation to this proposal. More recently some very high-quality AlN strained layer epitaxies were reported, that these authors studied quite deeply.[9] The transition energies are all blueshifted with respect to the case of bulk AlN. Further defining the strain-induced variation in the band gap in terms of differences between conduction- and valence-band energies one defines a new parameter $\xi_1=(c_1-d_1)e_{zz}+(c_2-d_2)(e_{xx}+e_{yy})$, the experimental report of a ground-state transition energy which shifts from 6029 up to 6138 meV while the higher-energy transitions only shift by an amount of 35 meV which leads us to conclude that ξ_1 and δ_2 have different signs. We have analyzed these data according with the approach we earlier developed for GaN and ZnO epilayers.[2,17] The result is shown in Fig. 1 where the optical energies are plotted versus the energy of the fundamental transition. The unstrained AlN data is consistent with a crystal-field splitting value $\Delta_1^0=-218$ meV while the optical properties of the strained layer is consistent with $\Delta_1=-145$ meV. The overall data is extremely well fitted by using $\frac{\xi_1}{\delta_2}=-1.466$. We wish to outline here that our analysis includes the experimental data of Ref. 4 for which there is no other information than the plot in Fig. 1 of Ref. 4. We digitized the figure in order to get this data for our own purpose.

In terms of deformation potentials, the quasicubic approximation is generally used by experimentalists to reduce the number of parameters.[23] Recent theoretical calculation suggests that this does not really holds for AlN,[24] but the disagreement is not worse than for GaN or InN (see Table 1 of Ref. 16),

$$c_1=c_2, \tag{7}$$

$$d_1-d_2=-d_3, \tag{8}$$

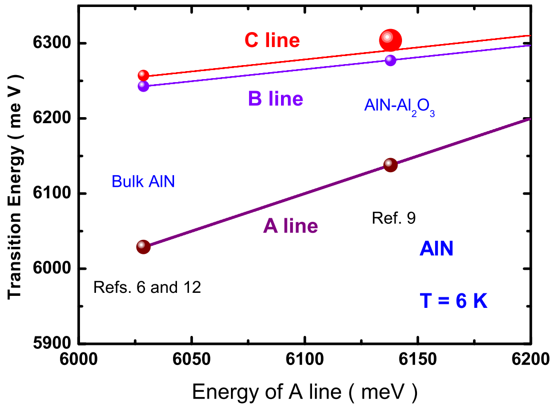

FIG. 1. (Color online) Optical properties of bulk AlN and heteroepitaxies: plot of the transition energies versus the energy of line A. The experimental data are taken from the literature and represented with dots having diameters modified according to the accuracy of the data. The data is taken from Refs. 6 and 12 for the bulk, from Ref. 9 for the heteroepitaxy.

$$d_3 = -2d_4. \tag{9}$$

After some algebra, taking into account elasticity relations and using the experimental values of the stiffness coefficients: $C_{13}=-120$ GPa and $C_{33}=395$ GPa,[5] one can correlate the values of the in-plane components of the strain e_{xx} and e_{zz} to the value of the on-axis one e_{zz},

$$e_{xx} = e_{yy} = -\frac{C_{33}}{2C_{13}} e_{zz}. \tag{10}$$

And rearranging the $\frac{\xi_1}{\delta_2}$ ratio such as that strain disappears from it, one obtains a new relation between the hydrostatic deformation potentials,

$$\frac{c_1 - d_1}{c_2 - d_2} = \frac{C_{33} - \frac{\xi_1}{\delta_2}(C_{13} + C_{33})}{C_{13} + \frac{\xi_1}{\delta_2}(C_{13} + C_{33})}. \tag{11}$$

From the work of Ikeda *et al.*,[5] we know the values of d_3 and d_4,

$$d_3 = -8.19 \text{ eV} \tag{12}$$

and

$$d_4 = 4.10 \text{ eV}. \tag{13}$$

Thus we can propose the following values:

$$a_1 = c_1 - d_1 = -6.04 \text{ eV} \tag{14}$$

and

$$a_2 = c_2 - d_2 = 2.15 \text{ eV}. \tag{15}$$

The values of whole set of these four deformation potentials result from the quasicubic approximation. Table I compares these experimental values with recent theoretical ones.[24]

At this stage one could argue that excitonic effects have been neglected, which is the case. We believe that excitonic correlation energies do not vary with strain in these AlN layers due to the valence-band configuration. The second part of this paper is dedicated to this problem in AlN.

TABLE I. Excitonic deformation potentials in AlN: comparison between recent theoretical values and experimental ones.

$c_1 - d_1$ (eV)	$c_2 - d_2$ (eV)	d_3 (eV)	d_4 (eV)	d_5 (eV)
-4.31[a]	-12.11 [a]	9.12[a]	-3.79 [a]	-3.23
		-8.19 [b]	4.10[b]	
-6.04[c]	2.15[c]	-8.19 [c]	4.10[c]	

[a] Reference 24.
[b] Reference 5.
[c] This work.

Silveira *et al.*[6] have reported reflectance structures at 6.029 and 6.065 eV at 6 K. They attributed this 36 meV splitting to 1*s*-2*s* splitting. By straightforward application of the physics of hydrogenic atoms they concluded the exciton binding energy to be 48 meV. This would locate the band gap E_g of unstrained AlN at 6.080 eV at low temperature. Considering the strained layer epitaxy and the report of Onuma *et al.*,[9] we note a 38 meV splitting after processing of their data. Still using the model of the hydrogen atom, though slightly doubting about its applicability (see row 30, first column of page 023529–6 of Ref. 9), they however report an exciton binding energy of 52 meV.

We will examine now this problem including mass anisotropy effects. AlN crystallizes in the wurtzite symmetry; therefore it is an anisotropic material. The calculation of exciton binding energies in anisotropic semiconductors is a complicated mathematical problem which started to be addressed more than 40 years ago by many researchers, using various approaches. The theoretical works published earlier than their own contribution to this topic were summarized by Baldereschi and Diaz.[10] In the case of isotropic semiconductors, the problem is "restricted" to solving analytically Leibnitz's famous second-order nonlinear differential equation. There is no longer an analytical solution to that problem when anisotropy occurs in the kinetic-energy term or in the potential-energy term of the Schrödinger equation used to describe the exciton in anisotropic media. The approach proposed by Baldereschi and Diaz (BD),[10] and hereafter referenced as the BD method consists, to describe the wave function of the anisotropic exciton, in using an expansion of the exciton wave functions into hydrogenic functions. This method is more powerful, they say it, and we believe it too, than previous approaches. They could thus predict very *general and universal trends* and their calculation was successfully used to interpret the rich series of excitonic features in case of two-dimensional semiconductors such as CdS, GaSe, and MoS_2.

We utilize this calculation in order to interpret quantitatively the excitonic fine structure splitting observed in the optical spectra of aluminum nitride. The agreement between this model and the experimental reports is again very good, it indicates the observation of optical features that are unambiguously attributed to excited state excitons and as a final message, it brings evidence that substantial improvements of the structural quality of aluminum nitride epitaxies have been realized during the last years.

We recall some general properties of excitons. In the framework of the effective-mass approximation, in the case of isotropic valence and conduction bands, the free exciton states are generally obtained as the solutions of a stationary Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m_0\mu}\nabla^2-\frac{q^2}{4\pi\varepsilon_0\varepsilon}\frac{1}{r}\right]\Phi^{\nu}(r)=(E^{\nu}_{exc}-E_g)\Phi^{\nu}(r). \tag{16}$$

In this equation, q is the elementary charge, m_0 the electron mass at rest, and ε_0 is the dielectric constant of the vacuum. Beyond the frame of the *in vacuo* hydrogen atom, and to describe the Wannier exciton in a periodic crystal, within the effective-mass approximation, one needs to further introduce the isotropic electron-hole reduced mass μ and the isotropic dielectric constant ε of the medium where electron and holes orbit with respect to each other. An experiment which probes the optical properties of the material will reveal excitonic-related features at a series of energies E^{ν}_{exc} below the energy of the material band gap E_g.[25] In Eq. (16) above, ν is used to represent the whole quantum numbers solutions of this equation. The solutions of the problem are the well-known hydrogenlike functions $\Phi^{nlm}(r)$ and the eigenvalues are given by $E^{nlm}_{exc}=E_g-\frac{R}{n^2}$, where

$$R=\frac{m_0q^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{\mu}{\varepsilon^2}=2m_0c^2\alpha^2\frac{\mu}{\varepsilon^2}. \tag{17}$$

In the equation above $\alpha=\frac{q^2}{4\pi\varepsilon_0\hbar c}\approx\frac{1}{137}$ is the fine structure constant which characterizes the strength of the electromagnetic interaction, m_0 is the electron mass at rest, and c is the *in vacuo* velocity of light. R is an effective Rydberg energy. The Hamiltonian given at the left-hand part of Eq. (16) has spherical symmetry, and therefore commutes with the square of the angular momentum operator L^2 and with the component L_z of L. The eigenstates are degenerated. This degeneracy depends on n, and it equals n^2 in the spinless description, $2n^2$ when spin is taken into account. This orbital degeneracy can be lifted if including relativistic effects or if including a mass anisotropy effect in the kinetic-energy term in Eq. (16). Relativistic effects are vanishingly small.[26]

We now consider the exciton effects in crystals which are anisotropic along a crystal axis (z axis). Let $\mu_\parallel$ and $\mu_\perp$ the reduced masses parallel and perpendicular to the direction of the z axis, and $\varepsilon_\parallel$ and $\varepsilon_\perp$ the corresponding dielectric constants. The effective-mass equation for excitons in this anisotropic crystal is,

$$\left[-\frac{\hbar^2}{2\mu_\parallel}\frac{\partial^2}{\partial z^2}-\frac{\hbar^2}{2\mu_\perp}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial x^2}\right)-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{\sqrt{[\varepsilon_\parallel\varepsilon_\perp(x^2+y^2)+\varepsilon_\perp^2z^2]}}\right]\times\Phi^{\beta}(r)=(E^{\beta}_{exc}-E_g)\Phi^{\beta}(r). \tag{18}$$

Rearranging this equation by making the following substitutions: $x'=x$, $y'=y$, and $z'=\sqrt{\frac{\mu_\parallel}{\mu\perp}}z$, one obtains

$$\left[-\frac{\hbar^2}{2\mu_\perp}\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{\partial^2}{\partial z'^2}\right)-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{\sqrt{[\varepsilon_\parallel\varepsilon_\perp(x'^2+y'^2+\gamma z'^2)]}}\right]\times\Psi^{\beta}(r')=(E^{\beta}_{exc}-E_g)\Psi^{\beta}(r'), \tag{19}$$

where

$$\gamma=\frac{\varepsilon_\perp}{\varepsilon_\parallel}\frac{\mu_\parallel}{\mu_\perp}, \tag{20}$$

γ is an anisotropy parameter.

States $|\Psi^{\beta}\rangle$ are now classified in accordance with the irreducible representations of the cylindrical group D^h_∞. Baldereschi and Diaz[10] proposed to expand the excitonic function $|\Psi^{\beta}\rangle$ along a series of hydrogenic functions $|\Phi^{nlm}\rangle$. They demonstrated that for anisotropy factors larger than 0.2, an expansion of $|\Psi^{\beta}\rangle$ along 42 hydrogenic functions was giving an extremely good convergence of the calculation for the six lowest states. In the BD model,[10] matrix elements between states $|\Phi^{nlm}\rangle$ with different $|m|$ or between states of different parities vanish for symmetry reasons, matrices between different $|m|$ and parity can be diagonalized separately. Further defining the reduced Rydberg energy: $R^*=2m_0c^2\alpha^2\frac{\mu_\perp}{\varepsilon_\parallel\varepsilon_\perp}$, they computed the reduced GS energy to vary as a function of γ. This variation we express here as follows:

$$E_{\text{GS}}=0.8279+0.95452e^{-[\gamma/0.5881]} \tag{21}$$

When $\gamma=1$ the ground state is purely the $1s$ state. For other values of γ it is a γ-dependent admixture of $1s,2s,3s,3d(m=0),4s,\ldots$ The splitting between the ground state and the first ES is

$$E_{\text{GS-ES}}=0.61274+0.7029e^{-[\gamma/0.61622]}. \tag{22}$$

When $\gamma=1$ the excited state is purely the $2s$ state. For other values of γ it is a γ-dependent admixture of $1s,2s,3s,3d(m=0),4s,\ldots$

The excellent agreement obtained by these authors for interpreting the physics of excitons in CdS, GaSe, MoS_2 motivates us for transferring this model to nitrides, which are modern anisotropic semiconductors. Our interest here is to study excitons in aluminum nitride in order to calibrate the performances of the material via study of its optical properties. The hole effective masses are obtained via a $\mathbf{k}.\mathbf{p}$ description of the valence-band dispersion relations near the Γ point.

Let us first describe the dispersion relations at $k_x=k_y=0$ and at $k_z\neq0$. Related to the valence-band states, the dispersion relations are the solutions of the 3×3 matrix below,

$$\begin{array}{ccc} |\Gamma_9\rangle & |\Gamma_7^1\rangle & |\Gamma_7^2\rangle \\ \Delta_1+\Delta_2+\frac{\hbar^2}{2m_0}(A_1+A_3)k_z^2 & 0 & 0 \\ 0 & \Delta_1-\Delta_2+\frac{\hbar^2}{2m_0}(A_1+A_3)k_z^2 & \sqrt{2}\Delta_3 \\ 0 & \sqrt{2}\Delta_3 & \frac{\hbar^2}{2m_0}A_1k_z^2 \end{array} . \quad (23)$$

The effective matrix for getting the dispersion relations when $k_z=k_y=0$ and $k_x\neq 0$ is different as shown below

$$\begin{array}{ccc} |\Gamma_9\rangle & |\Gamma_7^1\rangle & |\Gamma_7^2\rangle \\ \Delta_1+\Delta_2+\frac{\hbar^2}{2m_0}(A_2+A_4)k_z^2 & \frac{\hbar^2}{2m_0}A_5k_z^2 & 0 \\ \frac{\hbar^2}{2m_0}A_5k_z^2 & \Delta_1-\Delta_2+\frac{\hbar^2}{2m_0}(A_2+A_4)k_z^2 & \sqrt{2}\Delta_3 \\ 0 & \sqrt{2}\Delta_3 & \frac{\hbar^2}{2m_0}A_2k_z^2 \end{array} . \quad (24)$$

The fundamental valence band of AlN has Γ_7 symmetry,[12] its wave functions is mainly built from $|\Gamma_7^2\rangle$ (p_z-type Bloch waves), the hole effective mass are $\approx|\frac{1}{A_1}|$ and $\approx|\frac{1}{A_2}|$ along the [001] axis and in the orthogonal direction, respectively. In terms of excitonic masses one obtains: $\frac{1}{\mu_\parallel}\approx\frac{1}{m_{e\parallel}}+|A_1|$ and $\frac{1}{\mu_\perp}\approx\frac{1}{m_{e\perp}}+|A_2|$. Using for the aluminum nitride, the valence-band parameters recommended by Ikeda *et al.*,[5] their values for the electron masses and dielectric constants (see Table II), we calculate an anisotropy parameter $\gamma=0.469$ for the exciton built from the fundamental valence-band ($|\Gamma_7\rangle$ symmetry) state. According to BD,[10] the exciton binding energy equals in that case 1.25 times the reduced Rydberg energy (57 meV). One gets an excitonic binding energy of 72.5 meV. The GS-ES ($1s$-$2s$) splitting energy is found at 0.94 time the reduced Rydberg energy, that is to say 53.5 meV. This 53.5 meV value is some 50% larger that what is proposed experimentally. Obviously the agreement between the theory and the experiment is disastrous. After careful examination of the situation, we came to the conclusion that the discrepancy might reside at the scale of the values of the parameters of AlN, namely, A_1 and A_2 we used, which were computed by Suzuki *et al.*[27] in 1995. There is to date no debate in terms of their values, or at the scale of the values of the dielectric constants, or at both. We unfortunately cannot conclude more than this. Using the parameters of Ref. 21, we get $\gamma=0.41$, an enhancement factor of 1.3, and a reduced Rydberg energy of 70.7 meV, the exciton binding energy is then 92 meV and the GS-ES splitting is computed at 69 meV. The agreement with the experimental proposal is worse. Another possibility to explain this discrepancy could be that the high-energy transition is wrongly interpreted in terms of $1s$-$2s$ splitting. Answer to this question could be easily brought by making magneto-optical spectroscopy investigation.

The higher-energy valence band of AlN has Γ_9 symmetry the hole effective mass are $\approx|\frac{1}{A_1+A_3}|$ and $\approx|\frac{1}{A_2+A_4}|$ along the [001] axis and in the orthogonal direction, respectively. In terms of excitonic masses one has: $\frac{1}{\mu_\parallel}\approx\frac{1}{m_{e\parallel}}+|A_1+A_3|$ and $\frac{1}{\mu_\perp}\approx\frac{1}{m_{e\perp}}+|A_2+A_4|$. The dispersion relations of the third valence band of Γ_7 symmetry are very similar to the dispersion relations of the $|\Gamma_9\rangle$ valence band. We calculate an anisotropy parameter $\gamma=0.51$ for the excitons built from these valence bands and excitonic binding energies of 78 meV.

A very abstract mathematical treatment of anisotropic exciton has been recently published by Muljarov *et al.*[28,29] It scales a larger set of anisotropy parameters than the BD theory does in the one hand, and they compute the evolution of the oscillator strengths versus anisotropy more accurately also, in another hand. According to their approach, the exciton binding energy expressed in terms of the exciton binding energy at $\gamma=1$ is

TABLE II. Recent values for effective masses, dielectric constants, and valence-band parameters in aluminum nitride. The data are taken from Ref. 4.

$m_{e\parallel}$	$m_{e\perp}$	$\varepsilon_\parallel$	$\varepsilon_\perp$	A_1	A_2	A_3	A_4
0.32	0.28	8.45	7.33	−3.95	−0.27	3.68	−1.84

$$E_{\mathrm{GS}}(\gamma) = \frac{4}{(1+\gamma^{1/3})^2} E_{\mathrm{GS}} \quad (\gamma = 1). \tag{25}$$

Using this equation we compute enhancements of 1.266 and 1.236 for γ=0.469 and γ=0.510, respectively. This is fully comparable with the predictions of the BD methods. More interesting is the evolution of the oscillator strengths with γ, which indicates that one expect a ratio close to ~8 for the ratio of oscillator strength of the ground state and excited state of *A* exciton in AlN, when $\gamma \sim 0.47$. This value is quite close to the exact value 8 which is expected from the theory of hydrogenic atoms but astonishingly far from the fitted value reported by Silveira *et al.*[6] who measured 5, a value which is not possible. In summary, in AlN, neither the energy splittings nor the ratio of oscillator strengths matches to the theory of anisotropic excitons. This paves the way for interesting future investigations.

The calculation applied to the *A* exciton in GaN gives a binding energy of 27 meV and a 1*s*-2*s* splitting of 19.5 meV in remarkable agreement with the experimental data of Alemu *et al.*,[30] Kornitzer *et al.*,[31] Rodina *et al.*,[32] etc. We note that an adiabatic calculation like the one made here, which does not include complementary mixings produced by the long-range Coulomb interaction (the exciton binding energy is larger than the valence-band splitting) gives surprisingly good results.

In conclusion, experimental values of four of the six excitonic deformation potentials of AlN have now been established. Agreement exists with the whole available experimental data, which consolidates this determination. Concerning the exciton binding energy, we are blocked by the disagreement between the experimental reports and the data interpretation using a theoretical model consolidated by several fruitful comparisons in case of anisotropic materials such as CdS, GaN, GaSe, and MOS_2. At this stage going further requires both experimental and complementary theoretical investigations of the band structure of AlN. An effective magneto-photoluminescence experiment has been used to derive the effective-mass parameters for a similar anisotropy system[33] and the technique could be used for this material in the future study.

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