

Internal structure of the neutral donor-bound exciton complex in cubic zinc-blende and wurtzite semiconductors

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We calculate the fine structure splitting of the near band edge donor-bound excitons in major cubic semiconductors using an approach inspired by an earlier one that consists in replacing the Morse potential by a Kratzer one, in order to account for the repulsion between the donor and the hole. A regular trend is observed when plotting the computed results in terms of donor binding energies for all these semiconductors. Second, we extend the method to wurtzite semiconductors, namely CdS, GaN, and ZnO. The previously reported trend is found again, but enriched with the strong anisotropy of the dispersion relations in the valence band of these semiconductors. We end up in addressing a quantitative interpretation of the fine structure splitting of the donor bound exciton complex which includes the jj coupling between the valence band Bloch and the envelope nonrigid rotator hole states.

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Since the introduction of the concept of excitons by Frenkel and Peierls¹ in the thirties of the last century, an impressive amount of work has been consecrated to the importance of these analogs of atoms in solids and in other light emitting systems. Bulk and low dimensional semiconductors have been elaborated and are the *ad hoc* solid state laboratories for studying all possible forms of exciton complexes: free excitons, impurity-bound excitons, excitons localized to potential fluctuations, excitons coupled with phonons, with the electromagnetic field. All these kinds of excitons have specific spectroscopic properties which are still not understood in all details. Our present work focuses on neutral shallow donor bound excitons (D^0X). These excitons have been found to exhibit a fine structure splitting that was interpreted: first in terms of a rigid hole-donor rotator model in CdTe,^{2,3} and second in terms of a nonrigid hole-donor rotator model in GaAs,⁴ InP,^{5,6} CdS.⁷ Similar features were later observed in ZnTe,⁸ Si:Li,⁹ and ZnO.¹⁰ Regarding the technologically important semiconductor GaN, data are more recent. Neu *et al.*¹¹ and Kornitzer *et al.*¹² have first reported the clear observation of additional lines on the high energy side of the D^0X line. These lines were not correlated by these authors with the existence of different donors in the GaN film nor to the valence band splitting. Later, Neu *et al.*¹³ have published a detailed comparison of the donor bound exciton spectroscopy in both ZnSe and GaN. They have unambiguously shown the existence of similar properties for ZnSe and GaN and brought, in particular, the knowledge of the spectroscopic properties of donor bound excitons in GaN to the

degree of sophistication reached for the other materials. The purpose of this paper is to attribute these additional lines to excited states of the donor bound exciton built from a Γ_9 hole. Our aim is to further give an explanation of some puzzling features of donor bound exciton recombination in GaN: a change of the dominant two electron replica between 1.8 K and 10 K, with a ~ 1 meV blueshift,¹³ and an apparent decay time of this replica much longer than that of the D^0X ground state.¹⁴ Before going further, we wish to outline the extreme complexity of the theoretical treatment of the donor bound exciton in cubic semiconductors due to the existence of the fourfold degeneracy of the valence band at the zone center and in α -GaN and α -ZnO wurtzitic semiconductors when the donor potentials mixes Γ_9 and Γ_7 valence band states. Last, it is difficult to get rid of relativistic (spin and exchange-related) effects. In this paper, we restrict ourselves to the decoupled band situation so that we have to deal with a single band spinless Schrödinger equation rather than to introduce a many-band approach similar to the one used by Baldereschi and Lipari¹⁵ to treat acceptor states in cubic semiconductors.

We first calculate the fine structure splitting of the near band edge donor-bound excitons in major cubic semiconductors in an approach inspired from the one earlier proposed which consists in replacing the Morse potential with a Kratzer potential in order to account for the repulsion between the donor and the hole.⁶ A marked trend is computed if plotting the results in terms of effective mass donor binding energies for all these semiconductors. Second, we extend the

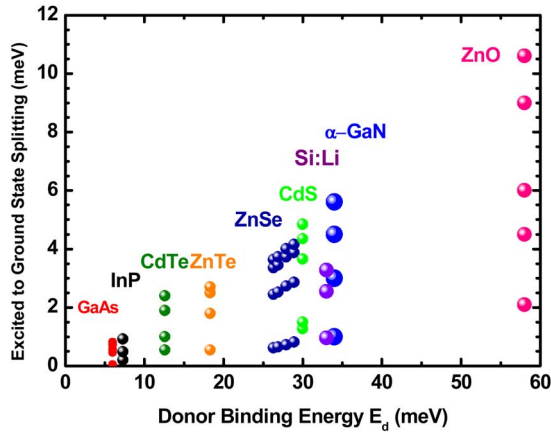


FIG. 1. (Color online) Plot of the energy of different photoluminescence lines associated with the donor bound exciton relative to the lowest fluorescent level versus effective mass donor binding energies in major semiconductors.

method to wurtzite semiconductors, namely CdS, GaN, and ZnO. A quantitative interpretation is achieved for wurtzite and for cubic semiconductors, by introducing the jj coupling between orbital angular momentum of the hole envelope function and the Bloch valence band state. The magnitude of such coupling is found to follow some kind of rough general trend and is about one thirtieth of the donor binding energy. Its value is larger in wide band gap semiconductors than it is in GaAs, which probably explains why it was never considered before, to the best of our knowledge.

The energy splittings of the D^0X bound exciton lines measured for several semiconductors relatively to the position of the lowest energy feature of the series have been plotted in Fig. 1 as a function of the effective mass donor binding energy E_d . The data has been collected from the literature.²⁻¹³ Some deviations from a general trend are found since data were taken on samples grown by different methods, giving sometimes substantial scattering. We wish to emphasize the fact that we look for general properties here. Sample purities were probably different from a material to another one and some deviations may be found in the literature if considering data measured on the same semiconductor compounds, but grown using different methods, due to chemical shift effects. Demonstration of such data scattering due to different impurities is quantitatively illustrated in the figure, in the specific case of ZnSe. For this material, a research group¹⁶ selectively incorporated several dopants in the material during the growth and then performed a careful analysis of the photoluminescence data which furnished them an unambiguous correlation of the splittings with the donor binding energy, that is to say a clear evidence of strong chemical effects.

The donor bound exciton problem is a four-particle many body problem dealing with electrostatic interactions between: (i) the static positive system that constitutes the nucleus of the donor whose electrons except one are either engaged to the chemical bound or constitute core levels, (ii) the remaining electron that circulates at typically one Bohr

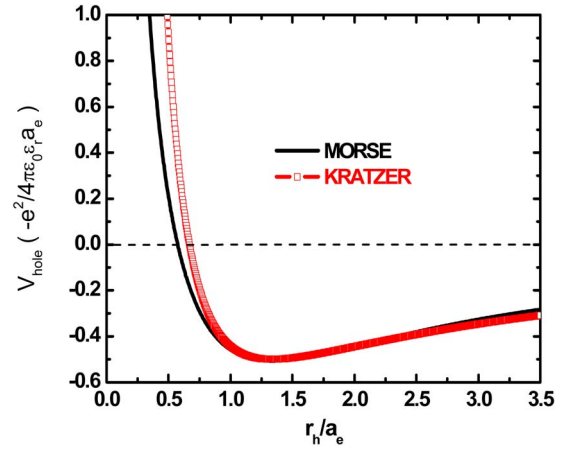


FIG. 2. (Color online) Comparison of the Morse and Kratzer potentials in dimensionless units.

radius a_e from this nucleus if in a $1S$ state, (iii) a hole arising from the trapping of a free exciton by the donor, and (iv) an electron arising from the trapping of a free exciton by the donor. The conditions for having a stable state by balancing electrostatic repulsions and attractions were elucidated by Munsch.¹⁷ The two electrons are treated as identical particles giving, as demonstrated by Lavallard and Benoit à la Guillaume,³ a low energy singlet state (antiparallel spins of the two electrons) and a Pauli forbidden triplet state degenerate with the conduction band. In the case of a frozen lattice, the spatial wave function of the D_0X bound exciton is written $\Psi(\mathbf{r}_e, \mathbf{r}'_e, \mathbf{r}_h) = \varphi_{1s}(\mathbf{r}_e) \varphi_{1s}(\mathbf{r}'_e) \chi(\mathbf{r}_h)$ as a function of the positions $\mathbf{r}_e, \mathbf{r}'_e, \mathbf{r}_h$ of the two electrons and of the hole. The hole motion is obtained as the solution of a Schrödinger equation using a Morse potential.¹⁸ This Morse potential V_M writes in terms of the reduced unit $x = r_h/a_e$ as follows:

$$V_M(x) = -\frac{e^2}{4\pi\epsilon_0\epsilon_r a_e x} [1 - 2e^{-2x}(1+x)], \quad (1)$$

which is minimized for $x = 1.337$, a_e is the electron Bohr radius in the donor bound exciton complex. Due to the extreme difficulty in handling analytical solutions of excited states in case of a Morse potential, we assimilate, as usually done, the Morse potential to a short range nonrelativistic (*spin-independent*) Kratzer potential that we write here

$$V_K(x) = -2D \left(\frac{t}{x} - \frac{t^2}{2x^2} \right) \quad (2)$$

with $D = \frac{e^2}{8\pi\epsilon_0\epsilon_r a_e}$ and $t = 1.337$. It is worthwhile remarking from the simple theory of the hydrogenic atoms that the quantity $-\frac{e^2}{4\pi\epsilon_0\epsilon_r a_e}$ is nothing but twice the average effective mass donor binding energy E_d . In the expression of the Kratzer potential above, D is then the effective mass donor binding energy.

Figure 2 illustrates the deviations between the Morse and Kratzer potentials. We note a substantial discrepancy in the

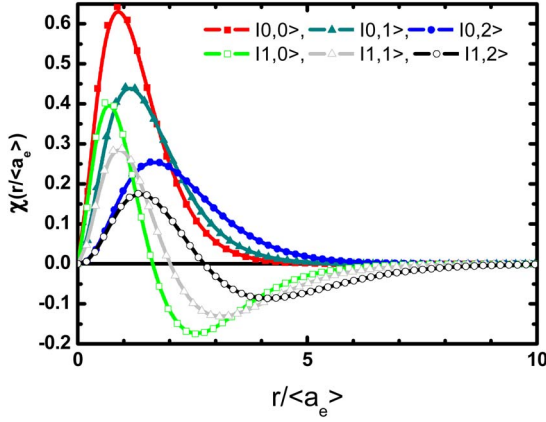


FIG. 3. (Color online) Typical rotator radial functions calculated for GaAs.

small x region and a subtle one for large x . Working in the context of isotropic valence band dispersion, the Kratzer potential problem is nothing but a Coulomb interaction problem for a particle with mass m , where the orbital terms $\frac{\ell(\ell+1)\hbar^2}{2mr_h^2}$ is rewritten as¹⁹ $\frac{\ell(\ell+1)\hbar^2 - 4mE_d a_e^2}{2mr_h^2} = \frac{\nu(\nu+1)\hbar^2}{2mr_h^2}$. ℓ is the orbital quantum number of the traditional hydrogenic problem and ν is a real number. We therefore face an analytical solution for this problem. Working similarly to Puls, Henneberger, and Voigt¹⁸ when treating the CdS case, we obtain variationally *the total energy equation of the D_0X complex*. In contrast with them, we write it

$$E(n, \ell, a_e) = 2E_g + 2E_d \left[\left(\frac{a_d}{a_e} \right)^2 - \frac{11}{8} \frac{a_d}{a_e} - \frac{t^2 m_h}{2m_e} \left[\frac{1}{n + \frac{1}{2} + \sqrt{\left(\ell + \frac{1}{2} \right)^2 + \frac{t^2 m_h a_e}{m_e a_d}} \right]^2 \right]. \quad (3)$$

In the above equation, n and ℓ are quantum numbers, a_d is the effective mass Bohr radius of the electron/donor complex and a_e is varied to minimize the energy. The principal quantum number n runs from 0 and indicates the number of nodes for the radial function. ℓ runs from 0 to any integer value, and does not need to keep being smaller than n . The radial hole wave functions are confluent hypergeometric functions of the kind $M(-n, 2\nu+1, 2\alpha x)$.^{19,20} Number ν was previously defined and $\alpha = \sqrt{\frac{2m(a_e)E(n, \ell, \langle a_e \rangle)}{\hbar^2}}$. These radial functions have $2\ell+1$ degeneracy. The total wave function of the hole is the product of the valence band Bloch state with the rotator envelope state with quantum number $n=0, 1, 2, \dots$, and usual spherical harmonic Y_ℓ^m with quantum number ℓ, m . We have plotted in Fig. 3 some typical radial parts of the hole wave functions computed for the GaAs case ($E_d=6$ meV, $m_e=0.067$, and $m_h=0.51$). We have estimated the error made by replacing the Morse potential by a Kratzer one by computing

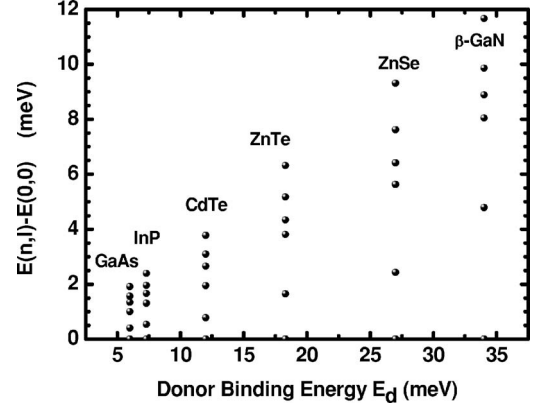


FIG. 4. Calculated splitting of rotator states versus effective mass donor binding energies in cubic semiconductors.

the expectation value of $V_M - V_K$ for the first levels. The result is a slight increase of the ground state binding energy and a slight decrease of that of the excited states. Indeed, Fig. 2 shows that V_M is less repulsive than V_K when $r_h/a_e < 1.337$ (and less attractive when $r_h/a_e > 1.337$). Looking at the relative wave functions spreading in Fig. 3 explains this result. Anyhow, the error made by replacing the Morse with a Kratzer potential is only weakly impacting the energies. We note that, in the GaAs case, the ratio between the variational parameter $\langle a_e \rangle$ that minimizes Eq. (3) and a_d are 1.16, 1.21, 1.26, 1.32, 1.28, and 1.3 concerning $|0,0\rangle$, $|0,1\rangle$, $|0,2\rangle$, $|0,3\rangle$, $|1,0\rangle$, and $|1,1\rangle$, states, respectively. However, after being minimized at $\langle a_e \rangle$ which is an increasing function of $\{n, \ell\}$, as shown above, energies $E(n, \ell, \langle a_e \rangle) \equiv E(n, \ell)$ are obtained. Figure 4 illustrates the energy differences $E(n, \ell) - E(0, 0)$ that we compute for the major cubic semiconductors when taking heavy hole masses. There is a good overall agreement between the calculation and the experiment, but a careful comparison of the experimental and computed data in Fig. 4 indicates that the calculation always overestimates by a factor ~ 2 the splitting between the two low energy levels $|0,0\rangle$, and $|0,1\rangle$. For higher quantum numbers, one reaches a situation where the variational calculation is not applicable without making excessive errors.

Let us now consider the total hole wave functions and their symmetries. *The total angular momentum of the hole state is written $J_{tot} = J + \ell$, with J being the angular momentum of the periodic Bloch wave at $k=0$ and ℓ the angular momentum of the rotator state*. The topmost valence band heavy hole Bloch state is noted $[J, m_J]$ in terms of its angular momentum J (J is $3/2$), and in terms of its projection m_J (m_J is $\pm 3/2$). For the ground state $|0,0\rangle$ of the rotator, the total hole wave function has the symmetry of the valence band, $J_{tot}=3/2$ and may be written $|\frac{3}{2}, \pm \frac{3}{2}\rangle$.

The situation is more complicated concerning excited rotator states. States resulting from coupling a valence $J=3/2$ state with a $\ell=1$ rotator state are represented as $|J_{tot}, m_{J_{tot}}\rangle$ by the value and projection of their total angular momentum J_{tot} and are written as linear combinations of $|m_J, m_\ell\rangle$ vectors where m_J and m_ℓ are the projections of the valence band hole and rotator state angular momenta, respectively

$$\begin{aligned}
\left| \frac{5}{2}, \frac{5}{2} \right\rangle &= \left| \frac{3}{2}, 1 \right\rangle \\
\left| \frac{5}{2}, \frac{3}{2} \right\rangle &= \sqrt{\frac{2}{5}} \left| \frac{3}{2}, 0 \right\rangle + \sqrt{\frac{3}{5}} \left| \frac{1}{2}, 1 \right\rangle \\
\left| \frac{5}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1}{10}} \left| \frac{3}{2}, -1 \right\rangle + \sqrt{\frac{3}{5}} \left| \frac{1}{2}, 0 \right\rangle + \sqrt{\frac{3}{10}} \left| \frac{-1}{2}, 1 \right\rangle \\
\left| \frac{5}{2}, \frac{-1}{2} \right\rangle &= \sqrt{\frac{3}{10}} \left| \frac{1}{2}, -1 \right\rangle + \sqrt{\frac{3}{5}} \left| \frac{-1}{2}, 0 \right\rangle + \sqrt{\frac{1}{10}} \left| \frac{-3}{2}, 1 \right\rangle \\
\left| \frac{5}{2}, \frac{-3}{2} \right\rangle &= \sqrt{\frac{3}{5}} \left| \frac{-1}{2}, -1 \right\rangle + \sqrt{\frac{2}{5}} \left| \frac{-3}{2}, 0 \right\rangle \\
\left| \frac{5}{2}, \frac{-5}{2} \right\rangle &= \left| \frac{-3}{2}, -1 \right\rangle \\
\left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \sqrt{\frac{3}{5}} \left| \frac{3}{2}, 0 \right\rangle - \sqrt{\frac{2}{5}} \left| \frac{1}{2}, 1 \right\rangle \\
\left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{2}{5}} \left| \frac{3}{2}, -1 \right\rangle + \sqrt{\frac{1}{15}} \left| \frac{1}{2}, 0 \right\rangle - 2\sqrt{\frac{2}{15}} \left| \frac{-1}{2}, 1 \right\rangle \\
\left| \frac{3}{2}, \frac{-1}{2} \right\rangle &= 2\sqrt{\frac{2}{15}} \left| \frac{1}{2}, -1 \right\rangle - \sqrt{\frac{1}{15}} \left| \frac{-1}{2}, 0 \right\rangle + \sqrt{\frac{2}{5}} \left| \frac{-3}{2}, 1 \right\rangle \\
\left| \frac{3}{2}, \frac{-3}{2} \right\rangle &= \sqrt{\frac{2}{5}} \left| \frac{-1}{2}, -1 \right\rangle - \sqrt{\frac{3}{5}} \left| \frac{-3}{2}, 0 \right\rangle \\
\left| \frac{1}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1}{2}} \left| \frac{3}{2}, -1 \right\rangle - \sqrt{\frac{1}{3}} \left| \frac{1}{2}, 0 \right\rangle + \sqrt{\frac{1}{6}} \left| \frac{-1}{2}, 1 \right\rangle \\
\left| \frac{1}{2}, \frac{-1}{2} \right\rangle &= \sqrt{\frac{1}{6}} \left| \frac{1}{2}, -1 \right\rangle - \sqrt{\frac{1}{3}} \left| \frac{-1}{2}, 0 \right\rangle + \sqrt{\frac{1}{2}} \left| \frac{1}{2}, -1 \right\rangle.
\end{aligned}$$

These states have even parity since both $\ell=1$ and $J=3/2$ states are odd in real space.

We now discuss the selection rules for donor bound exciton recombination from the basis of the simplest of the symmetry arguments: parity. We restrict our discussion to dipole allowed recombination mechanisms. Since the dipole matrix element has odd parity when the starting states have a given parity odd (resp. even), the final states should have even (resp. odd) parity. The ground state of the donor bound exciton complex has odd parity. When one of the electrons and the hole recombine leaving the last electron in a nS state, the final state has even parity. This recombination process is dipole allowed and efficiently couples with the electromagnetic field. The first excited state correspond to the first excited state of the hole rotator. The total wave function of the complex is even and the most probable recombination process is a complex process leaving the remaining electron in a $2p$ (or other odd) final state. Recombination from the second excited state of the hole rotator is a dipole allowed process. These selection rules predicted by using a spherical model are not so strict in a real cubic or wurtzite semiconductor. The above scheme of selection rules for two electron transitions of neutral donor bound excitons is straightforward and replaces earlier ideas, where transitions between states of the same parity was argued to dominate if the D^0X complex is regarded as an exciton bound to the donor as an entity (see, e.g., Ref. 8).

The splitting energies of rotator states are in general of the order of 1 meV in wide band gap semiconductors as it can be seen in Fig. 1. At low temperatures, only the ground state of the donor bound exciton is occupied whilst a slight increase of the temperature will enhance the occupation rate of the first excited state, improving the intensity of the two electron replica from this state. This may explain the change of two electron satellite spectrum in GaN with increasing temperature reported in Ref. 13. It could also be a possible explanation of the long decay time of this replica relative to the observed decay time of the D^0X ground state,¹⁴ if it is the excited state replica that is observed. Indeed, Neu *et al.*¹³ have shown that the lifetime of the first excited state of D^0X

is about 5 times that of the ground state, in agreement with the apparent decay time ratio.¹⁴

The effect of the temperature on the D^0X recombination is clearly revealed in Fig. 5 where the two electron satellite spectra in a bulk GaN sample grown by hydride vapor phase epitaxy (HVPE) that has about the same density of O and Si donors (about $4 \times 10^{15} \text{ cm}^{-3}$ each) is shown. A similar set of lines are observed for each donor, involving $2s$, $3s$, and $4s$ final states connecting to the bound exciton ground state, and $2p$, $3p$ states connecting with the excited D^0X states (labeled a , b , c , ...²¹ While the former dominate at low temperature, the latter are mainly involved at the higher temperatures. We conclude that the two electron satellites are extremely sensitive to the temperature of the excitons or electron bath, in other words, to the temperature at which the experiment is performed. These reasons explain why we often observe two electron transitions in wide band gap semiconductors, since: (i) the large donor binding energies are favorable, (ii) performing experiments at $T \geq 10$ – 20 K, a temperature reached when gluing the sample to a cold finger cryostat instead of immersing it in superfluid liquid helium helps also. In the advent of excessive inhomogeneous broadening, generally encountered when working on heteroepitaxial films, it may be unreasonable to expect the resolution of details of the two-electron replica features.

Wurtzite semiconductors are in essence anisotropic materials. The Hamiltonian is much more complicated, compared to cubic ones, since the kinetic energy part of the spherical symmetry $\frac{p_x^2 + p_y^2 + p_z^2}{2m}$ must be separated in and has cylindrical symmetry along the (0001) axis. The $2\ell+1$ degeneracy of the $|n, \ell\rangle$ eigenstates of the spherical case is lifted and states with similar $|m_\ell|$ values couple through the anisotropy of the kinetic energy Hamiltonian. This is a “classical” situation, typical of excitons met in anisotropic crystals, that Faulkner²² has described in the 70’s, giving the most accurate method for dealing with this problem. We have reproduced the calculation of Puls, Henneberger, and Voigt¹⁸ for the CdS case and we extended it to GaN and ZnO. Obviously the computed splittings are still higher than the experiment

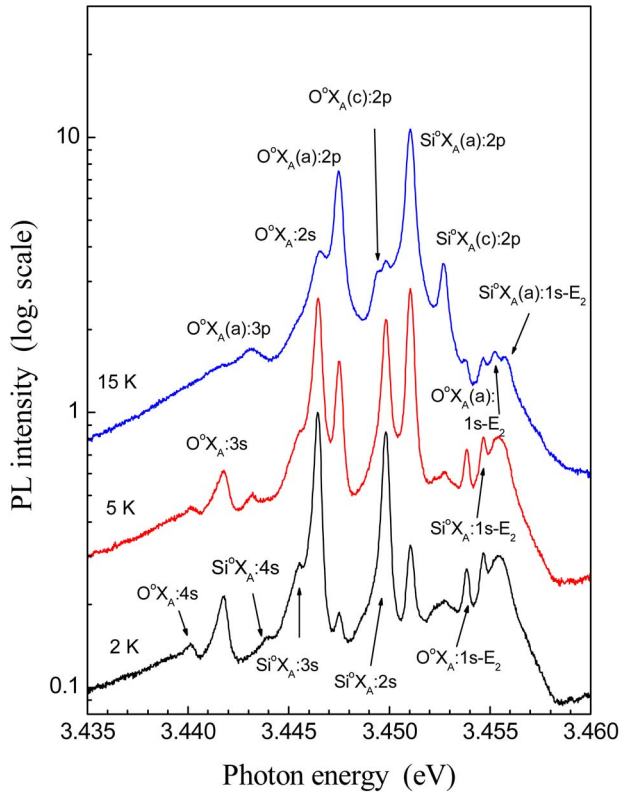


FIG. 5. (Color online) Photoluminescence spectra taken for a 1 mm thick HVPE bulk GaN sample as a function of temperature in the two electron satellite energy region. Two distinct donors are identified in the sample, namely oxygen (O) and silicon (Si). The two electron transitions spectra are shown to experience a modification of shape in favour of satellites with remaining donor electrons in nP states when temperature increases. Also note the recombination lines with energy relaxation via simultaneous photon and phonon creations (E_2 phonon) in the right hand part of the spectra.

as seen in Fig. 6. Using the GaN values we get 2 meV between $|0,0,0\rangle$, and $|0,1,0\rangle$ (we now have to label states $|n,\ell,|m_\ell\rangle$), a value to be compared with the value of 1.3 meV experimentally reported by Neu *et al.*^{11,13} and Ko-

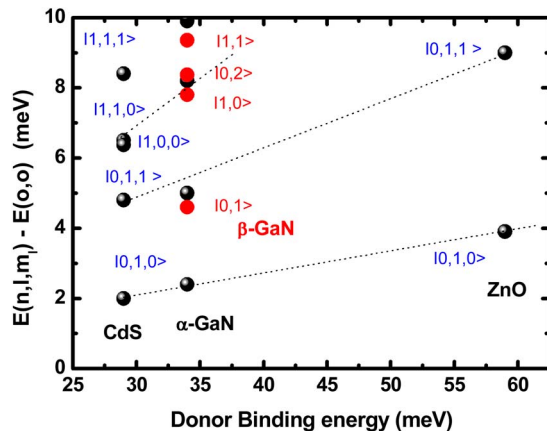


FIG. 6. (Color online) Calculated splittings of rotator states versus effective mass donor binding energies in wurtzite semiconductors. β -GaN is indicated for the sake of the comparison.

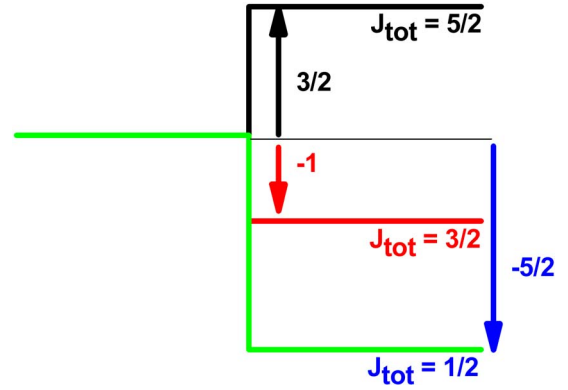


FIG. 7. (Color online) Fine structure splitting of the $|0,1\rangle$ rotator state due to jj coupling with the $J=3/2$ valence band in spherical symmetry.

ritzner *et al.*¹² Without ignoring the fact that we are dealing with some oversimplified calculation, we have computed the splitting of the donor bound exciton energies for the high energy excited states associated with quantum number $\ell=1$ of the rotator in the context of a $j-j$ coupling scheme. In the context of such model, the different levels are shifted of an amount $\Sigma \frac{j_{tot}^2 - \ell^2 - j^2}{2}$ as sketched in Fig. 7 for spherical symmetry. Such an interaction obviously decreases the total energy of the excited levels and reduces the splitting with the donor bound exciton ground state. The general disagreement between our calculation and the experimental data for all semiconductors treated here can be reasonably by-passed as shown in Fig. 8, where are plotted using vertical bars the experimental splitting between the first and second D^0X recombination lines in semiconductors and our calculation (full dots) corrected by introducing an *ad hoc* $j-j$ -coupling term Σ that is roughly connected to the effective mass donor binding energy as follows:

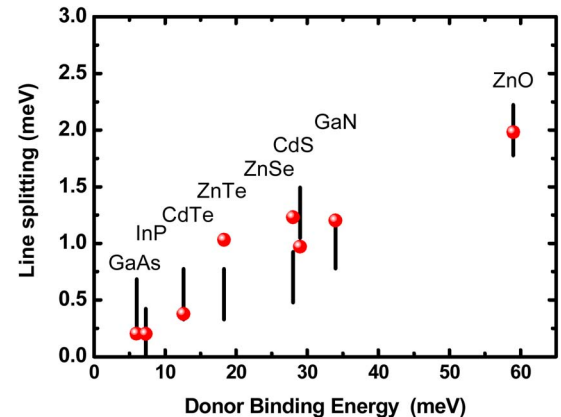


FIG. 8. (Color online) Plot of the splitting between ground states and first excited state of the donor bound excitons versus donor binding energy. Vertical bars are used to represent experimental values and their scatterings, full dots are used to represent the result of the calculation corrected by the jj coupling interaction.

$$\Sigma \sim \frac{E_d}{30}. \quad (4)$$

This equation is some kind of analog to Haynes' rule connecting the exciton binding energy to the binding energy of the effective mass donor or acceptor.²³

We estimate Σ to be about 0.5–1 meV in both CdS and GaN, a value comparable with the value of the short range spin exchange interaction for the free exciton in these materials.^{24,25} In the case of ZnO, the experimental splitting is 2 meV while the computed one is 4. This gives Σ to be about 1.5 to 2 meV in ZnO, a third of the short range exchange interaction.²⁶ At this stage, we would like to emphasise the extreme difficulty to achieve accurate calculations for several reasons: (i) the effective masses are not known with a sufficient accuracy; (ii) higher excited states having similar symmetry anti-cross leading to an intricate pattern

out of the scope of calculation; (iii) a variational treatment is valid for ground states only; (iv) a better description would of course require a full relativistic calculation out of the scope of our variational treatment, that is to say beyond the aim of the present paper.

In conclusion, we have shown that the internal structure of the donor bound exciton in GaN is understood, that it can be accounted for as in all other semiconductors in the context of a nonrigid rotator model. To describe the total and real symmetry of the wave functions of the rotator states requires taking into account of the j - j coupling between the angular momentum of the envelope function of the rotator with the angular momentum valence band Bloch states. This explains selection rules for two electron transitions and the temperature dependence of the corresponding fluorescent features.

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