# Location of lanthanide impurity levels in the III-V semiconductor GaN

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Knowledge from lanthanide spectroscopy on wide band gap (6–10 eV) inorganic compounds is used to understand and predict optical and electronic properties of the lanthanides in the III-V semiconductor GaN. For the first time the location of the $4f^n$ ground state energy of each divalent and trivalent lanthanide ion relative to the valence and conduction bands in GaN is presented. The authors will demonstrate that the quantum efficiency of luminescence from $Pr^{3+}$, $Eu^{3+}$, $Tb^{3+}$, and $Yb^{3+}$ depends on the location of the lanthanide levels. Level location also controls electron acceptor and electron donor properties of lanthanide ions. © *2006 American Institute of Physics*.
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There is strong interest in the electronic and optical properties of lanthanide doped III-V semiconductors. The wide band gaps of, for example, GaN (3.5 eV) or AlN (6.2 eV) can be combined with the luminescence of lanthanides (Ln) to develop blue, green, or red emitting thin film electroluminescent devices.[1–3] Practical applications of GaN:Ln are, however, still limited because of the low luminescence efficiency.[4,5] The luminescence performance has been studied for thin film GaN,[1] amorphous GaN,[6] bulk crystalline GaN,[7] and GaN quantum dots.[8] Lanthanide ion implantation profiles,[9] local symmetry around lanthanide ions,[2,4] energy transfer from GaN to the lanthanide,[4,10] and annealing treatments[11] have all been subject of study with the aim to improve luminescence performance. However, two basic questions are never asked in these studies: (1) What is the location of the Ln-ion energy levels relative to the conduction band (CB) and valence band (VB) of GaN? (2) How do level locations affect luminescence, charge trapping, and charge donating processes?

There has been a 40 years long research effort on lanthanide doped wide band gap (6–10 eV) compounds that has resulted in lighting and display phosphors with maximum efficiency. In that field the same two questions were asked many times, but not until the last five years answers were provided. As a result methods are available to determine and predict level locations for all the lanthanides in wide band gap inorganic compounds.[12,13] They work surprisingly well and require only few parameters that can be determined by spectroscopic techniques. The method has been applied to wide band gap inorganic compounds such as $CaF_2$ and $YPO_4$ (Ref. 12) and also to the smaller band gap compounds $CaGa_2S_4$ (Ref. 14) and $LaBr_3$.[15] $LnC_{25}H_{38}N_4S_6$ with the soft donor ligands of nitrogen and sulfur is the first organic compound where the method has been applied.[16]

In this letter we apply these methods for the first time to the III-V compound GaN. The approximate locations of the divalent and trivalent lanthanide $4f^n$ levels relative to the valence and conduction band of GaN are presented. We will relate the level positions to the luminescence and electronic properties of $GaN:Ln^{3+}$.

The binding energy of the lowest $4f^n$ state of a $Ln^{q+}$ lanthanide ion, where $n$ denotes the number of electrons in the $4f$ shell and $q+$ the ionic charge, shows always a characteristic pattern with changing $n$.[12,13] These patterns are exemplified in Fig. 1. Curve (a) connects the $4f^n$ ground state binding energies of the trivalent lanthanide ions where the zero of energy is put at the $4f^6$ ground state of $Eu^{3+}$. The binding is largest when the $4f$ shell is half ($Gd^{3+}$) or completely ($Lu^{3+}$) filled, and it is smallest when occupied by one ($Ce^{3+}$) or eight ($Tb^{3+}$) electrons. It appears that the variation with $n$ scales slightly with the band gap of the compound. In wide band gap oxides and fluorides, curve (b) appears more appropriate where the binding energy for large $n$ is slighly reduced (<0.5 eV) as compared to small band gap compounds.[13,14]

With the energy difference $\Delta E(\mathrm{Eu})$ between the $4f^6$ ground state of $Eu^{3+}$ and the $4f^7$ ground state of $Eu^{2+}$, we can express the dependence of binding energy on $q$. Also $\Delta E(\mathrm{Eu})$ scales with the band gap of the compound. It decreases from ≈6.7 eV, see curve (d), for wide band gap compounds to values ≈5.7 eV, see curve (c), for small band gap compounds such as $CaGa_2S_4$.[14,15] For the small band gap compound GaN we will assume that $\Delta E(\mathrm{Eu})=5.7\pm0.3$ eV and adopt curves (a) and (c) to represent the change in binding energy with charge and type of lanthanide.

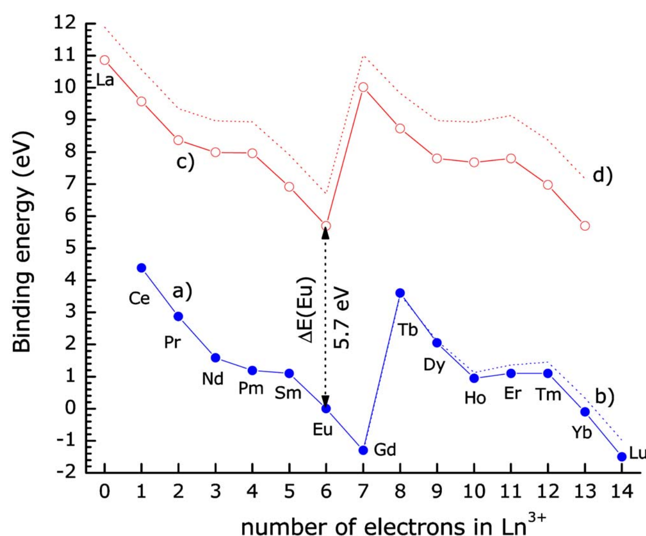


FIG. 1. (Color online) Universal behavior of $4f$-electron binding energies of (a) trivalent and (c) divalent lanthanide ions in 4–6 eV band gap compounds (sulfides and iodides) with $\Delta E(\mathrm{Eu})\approx5.7$ eV. The curves (b) and (d) pertain to 7–12 eV band gap compounds (fluorides and oxides) with $\Delta E(\mathrm{Eu}^{q+})\approx6.7$ eV.

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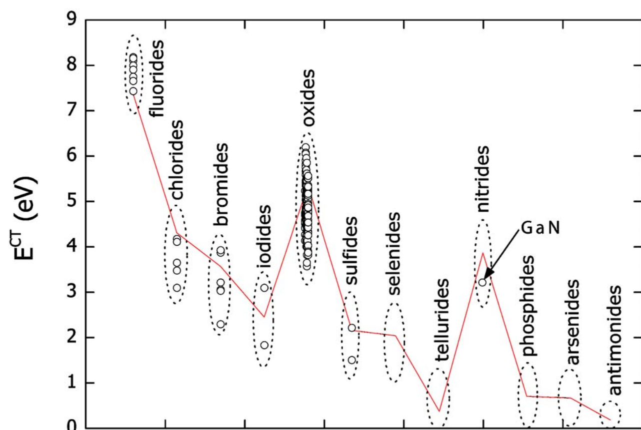


FIG. 2. (Color online) Energy $E^{CT}$ of charge transfer from the uppermost anion valence band to $Eu^{3+}$ in compounds. The solid curve is obtained from Jörgensen's relationship between $E^{CT}$ and the Pauling electronegativity of anions.

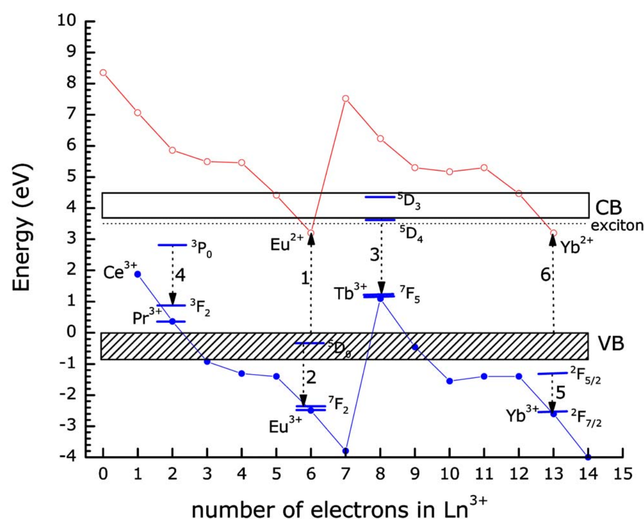


FIG. 3. (Color online) Proposed location of the lowest $4f^n$ states of divalent and trivalent lanthanides in GaN. Optical transitions (arrows) and relevant excited and ground state $4f^n$ level locations (bars) are shown. The top of the valence band is at energy zero. The GaN exciton state is at 3.48 eV and the conduction band bottom is estimated at 3.7 eV.

We only need to place the top of the GaN valence band in Fig. 1 to arrive at a complete level scheme for GaN. The required information is obtained from the excitation spectrum of 622 nm red $^5D_0 \rightarrow {}^7F_2$ emission of $Eu^{3+}$ in GaN. It reveals a 40 nm broad but clear and distinct excitation band at 388 nm.[7] Similar, but less clear excitation spectra were reported before.[2,4,17] Morishima *et al.*[17] suggest that the band is due to electron transfer from the nitrogen valence band to $Eu^{3+}$, but Nyein *et al.*[4] attribute it to an unknown defect state. To further resolve this issue we will make use of the data compiled in Fig. 2 on the energy $E^{CT}$ of charge transfer (CT) from the valence band to $Eu^{3+}$ in wide band gap compounds.[13] One observes a strong dependence of $E^{CT}$ on type of anion valence band (F, Cl, Br, I, O, and S). According to Jörgensen $E^{CT}$ is linearly related with the Pauling electronegativity $\eta$ of the anion,[13,18]

$$E^{CT} = 3.72(\eta - 2)\ \text{eV}. \tag{1}$$

Although Eq. (1) does not account for the wide variation in $E^{CT}$ within, for example, the oxide compounds, it does provide the trend with type of anion, see the solid curve in Fig. 2. It predicts where we may expect the CT band for compounds with $Se^{2-}$, $Te^{2-}$, $N^{3-}$, $P^{3-}$, $As^{3-}$, or $Sb^{3-}$ anion valence bands. Data on $E^{CT}$ in these types of compounds are not available, but Eq. (1) predicts values around 3.5 eV for the nitrides. This provides us with strong support to follow the original assignment by Morishima *et al.*[17] that the 388 nm (3.2 eV) excitation band in GaN:$Eu^{3+}$ is due to the nitride to $Eu^{3+}$ electron transfer.

$E^{CT}$=3.2 eV is a good measure for the energy difference between the top of the valence band and the ground state of $Eu^{2+}$,[12,13] and we therefore locate that ground state at 3.2±0.3 eV above the GaN valence band. The final result is shown in Fig. 3 where arrow 1 indicates the CT transition of 3.2 eV and arrow 2 the $^5D_0 \rightarrow {}^7F_2$ emission of $Eu^{3+}$. Note that the zero of energy in the scheme of Fig. 3 is placed at the top of the valence band. GaN has a direct band gap with the exciton level at 3.48 eV.[19] Assuming an exciton binding energy of ≈0.2 eV, we estimate the conduction band bottom at 3.7 eV.

Figure 3 reveals that, even considering a possible error of ±0.5 eV, the $^5D_3$ state of $Tb^{3+}$ is located well inside the conduction band. An electron in $^5D_3$ then delocalizes rapidly into the conduction band and the luminescence starting from that state is efficiently quenched. On the other hand the $^5D_4$ state of $Tb^{3+}$ is located just below the conduction band and $^5D_4 \rightarrow {}^7F_5$ emission might be possible although one may expect a low quenching temperature due to thermally excited ionization to conduction band states. Indeed most papers on GaN:$Tb^{3+}$ report green $^5D_4$ emission (see arrow 3) at low temperature that is severely quenched at room temperature.[6,10,20] These reports do not observe any emission from $^5D_3$ which agrees with the predictions from Fig. 3. Interestingly the $^5D_4$ emission of $Tb^{3+}$ is stable up to room temperature in GaN quantum dots.[8] We can explain this by confinement of the GaN conduction band states. The band gap energy increases and the $^5D_4$ state becomes more stable against thermally activated ionization. Note that the activation energy for thermal quenching of the $Tb^{3+}$ $^5D_4$ emission can be used for a more accurate positioning of the lanthanide ground states in Fig. 3.

Figure 3 shows that the $^3P_0$ state of $Pr^{3+}$ is almost 0.8 eV further below the conduction band than the $^5D_4$ state of $Tb^{3+}$. $Pr^{3+}$ $^3P_0 \rightarrow {}^3F_2$ emission (arrow 4) is therefore more stable against quenching by thermal ionization than the green $Tb^{3+}$ emission. Indeed there is no significant thermal quenching of the $Pr^{3+}$ $^3P_0 \rightarrow {}^3F_2$ emission at room temperature.[11]

Various explanations for the quenching of the red $Eu^{3+}$ $^5D_0 \rightarrow {}^7F_2$ emission in GaN, see arrow 2 in Fig. 3, were suggested, e.g., a temperature dependent energy transfer process from GaN to Eu,[4,5] quenching due to a change in excitation efficiency,[4] and quenching by excitation transfer to impurities.[5] In wide band gap inorganic compounds the most important quenching route for $Eu^{3+}$ is via energy exchange with the VB→$Eu^{3+}$ charge transfer (arrow 1).[21] For example, in $Y_2O_3$:$Eu^{3+}$ with large charge transfer energy of $E^{CT}$=5.2 eV, the emission is stable up to a temperature of 800 K.[22] However, in the inorganic europium-$\beta$-diketonate complex with small $E^{CT}$≈3 eV quenching already starts at 230 K.[23] Quenching by energy exchange with the CT state has not been considered yet for GaN:Eu but the small value of $E^{CT}$=3.2 eV suggests that it is likely to occur at room temperature.

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GaN:$Yb^{3+}$ shows 1.2 eV $^2F_{5/2} \rightarrow {}^2F_{7/2}$ narrow line emission (arrow 5 in Fig. 3) under excitation across the band gap.[24] Figure 3 predicts that one can also excite this emission by a VB$\rightarrow Yb^{3+}$ charge transfer transition at around 3.2 eV (arrow 6). It has not yet been reported, but it should reveal itself around 380 nm in the excitation spectrum of $Yb^{3+}$ emission.

Finally, Fig. 3 shows that $Eu^{2+}$ and $Yb^{2+}$ have their ground states below the conduction band, and therefore of all trivalent lanthanide ions only $Eu^{3+}$ and $Yb^{3+}$ can trap a free electron to form a stable divalent lanthanide. $Ce^{3+}$, $Pr^{3+}$, and $Tb^{3+}$ have their ground states in the forbidden gap and they can trap holes from the valence band to form a tetravalent lanthanide. Because of the close proximity of the $Pr^{3+}$ or $Tb^{3+}$ ground state to the valence band, it can be expected that $Pr^{4+}$ or $Tb^{4+}$ may act as a hole donor resulting in *p*-type GaN. Combined with *n*-type GaN:$Eu^{2+}$ we envisage that *p* -*n* junctions can be made with GaN:Ln of interest for optoelectronic device applications. The above examples and reasoning demonstrate that knowledge on level energy location as in Fig. 3 provides a tool to understand and predict properties of III-V compounds.

In summary, we have presented a scheme with the location of all lanthanide 4*f* energy states relative to the valence and conduction bands of GaN. With the scheme we demonstrated that many optical and electronic properties involving the lanthanide ions in GaN can be explained and to some extent predicted. The methods to construct the lanthanide level schemes in GaN can equally well be applied to wider band gap III-V compounds such as AlN or smaller band gap III-V compounds such as InN or GaP.


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