Rare-earth impurities in gallium nitride: The role of the Hubbard potential☆

G. Caroena [a], J.F. Justo [b,*], W.V.M. Machado [a], L.V.C. Assali [a]

[a] Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo, SP, Brazil
[b] Escola Politécnica, Universidade de São Paulo, CP 61548, CEP 05424-970, São Paulo, SP, Brazil

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ABSTRACT

We performed a first principles investigation on the electronic properties of 4f-rare earth substitutional impurities in zincblende gallium nitride (GaN:RE$_{Ga}$, with RE = Eu, Gd, Tb, Dy, Ho, Er and Tm). The calculations were performed within the all electron methodology and the density functional theory. We investigated how the introduction of the on-site Hubbard U potential ($GGA + U$) corrects the electronic properties of those impurities. We showed that a self-consistent procedure to compute the Hubbard potential provides a reliable description on the position of the 4f-related energy levels with respect of the GaN valence band top. The results were compared to available data coming from a recent phenomenological model.

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1. Introduction

Photoluminescence in rare earth (RE) doped semiconductors received great attention over the last two decades, mainly due to potential applications in optoelectronics, such as light-emitting diodes, displays, and lasers [1–3]. Rare earth atoms exhibit partially filled 4f shells, and luminescence has been associated to intra-f electronic transitions. It is well established that, for the free ions, intra-4f electric dipole transitions are forbidden and that such transition only take place when the RE ions are in a crystal field. This field splits the 4f-related energy levels, modifying the dipole selection rules, which allows the intra-f transitions.

In semiconductors, RE ions have been used to build optoelectronic devices. This would be particularly interesting for the well-established silicon technology, since pure silicon presents poor optical properties, and RE ions could bring new possibilities for integrated circuits [4,5]. However, attempts to use RE for optical applications in silicon have been hindered by the fact that the luminescence shows a strong temperature dependence, with large quenching at room temperature. On the other hand, RE ions in III-nitride semiconductors present promising applications, since the optical intensity generally has a small temperature dependence [6,7].

The RE atoms have a $4f^m5d^06s^2$ configuration. Three valence electrons ($5d^16s^2$) form the conduction band in metals, or are transferred to other ions in salts, while the remaining electrons stay essentially as 4f atomic states. The constituent RE atoms generally behave as trivalent ions with configuration $4f^{n-1}$ ($n = 2$ to 14, from Ce^{3+} to Yb^{3+}). Therefore, it is generally assumed that RE ions, introduced as impurities

in a III-nitride semiconductor matrix, stay in the 3+ oxidation state since, in substitutional III site, it donates three electrons to bind with the nitrogen neighboring atoms.

First principles modeling represents a powerful tool to investigate the properties of RE-related materials [8]. However, there are still several methodological challenges that have hindered an appropriate description of the 4f-related energy levels. It is well documented in the literature that the methods based on the density functional theory generally fail in describing the interactions of highly correlated systems, such as the 3d-related and 4f-related electronic systems. Such limitations could be overcome using a correction in the electronic interactions, with the introduction of the on-site Hubbard U potential [9–11]. Here, we show that a self-consistent procedure to compute that potential [13] provides an appropriate description of the 4f-related energy levels of RE ions. This was initially shown for the case of the metallic RE crystals, in which there are available experimental data [15] for comparison. We then used the same procedure to describe the RE (from Eu to Tm) as an impurity in gallium nitride, and compared with results from a recent phenomenological model [14].

2. Methodology

We used the all-electron spin-polarized full-potential linearized augmented plane wave (FP-LAPW) method [16], implemented in the WIEN2k package [17]. The calculations were performed within the framework of the density functional theory (DFT) and the generalized gradient approximation (GGA) [18] plus the on-site Hubbard U potential ($GGA + U$) [12,13]. Self-consistent iterations were performed until convergence in the total energy of 10^{-4} Ry was achieved. In all systems, the internal degrees of freedom were optimized, with no symmetry constraints, until the force in each atom was smaller than 10^{-3} Ry/a.u. Such convergence parameters have been shown to provide a reliable description of the electronic and

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structural properties of several semiconducting materials [19–23]. The on-site Hubbard U potential values for the 4f-states of the RE atoms were obtained self-consistently, using the methodology described by Madsen and Novák [24]. This procedure was based on the fundamental work [12] in which the U parameter is defined as the cost in Coulomb energy by placing two electrons on the same site. It was originally developed for linearized muffin tin orbital basis sets [12], in which the Hubbard correction was introduced in the hopping individual terms. Since this is not possible within the LAPW methodology, the self-consistent U value of a certain orbital is computed by constraining this orbital as a core state. The resulting U value is then used in a usual GGA + U calculation, without any constraint [24], implemented in the rotationally invariant procedure [25] including a partial correction for the self-interaction.

For the calculations of the RE in metallic phase, we considered the respective stable zero-temperature crystalline phases (BCC for Eu and HCP for Gd, Tb, Dy, Ho, Er, and Tm). Convergence criteria on total energy considered a plane-wave basis set to describe the interstitial region, limited by the wave number $9.0/R_{RE}$ (maximum length of the plane-waves). Here, $R_{RE} = 2.0$ a.u. is the RE atomic radii that prevents sphere superpositions. The Brillouin zone was sampled by a Monkhorst-Pack (MP) grid with about 5000 k-points [26].

For the calculation of the RE as an impurity in zincblende GaN, we considered a 54-atom reference FCC supercell, with the substitutional RE ion sitting in a gallium site. Convergence on the total energy was achieved using a plane-wave basis set, with the set limited by the wave number $7.0/R$, where R is the smallest radius of spheres which define the host atoms. We used $R_{Ga} = 1.8$ a.u., $R_N = 1.5$ a.u., and $R_{RE} = 1.8$ a.u. The irreducible Brillouin zone was sampled by a $(2 \times 2 \times 2)$ MP grid.

3. Results

Although the RE impurities in III–V semiconductors have been extensively studied over the last two decades, there are still several controversies in the literature [9]. For example, where do the 4f-related energy levels lie with respect to the semiconducting valence and conduction bands? What are the microscopic mechanisms that control the photoluminescence quenching? In order to address several of those points, it is important to have a good understanding on the microscopic properties of those centers.

For RE elements, the 4f levels generally play a minor role on bonding, such that they stay essentially atomic-like. Those atoms bind with their neighboring ones through their 5d and 6s atomic valence states [15]. Following such perception, earlier theoretical investigations generally considered the 4f electrons as core states with a constrained occupation [27]. Such assumption has been considered for the RE elements in either a crystalline environment or as an impurity in semiconducting hosts. The development of more modern methodologies, in which the 4f electrons could be better treated as valence states, for example within the DFT + U [12,13], suggested a more complex electronic structure for those RE impurities. However, there is still considerable controversy in the literature on what procedure should be used in order to determine the Hubbard U potential values [9,14].

While several investigations suggested that the 4f-levels of the RE impurities in GaN lie in the materials bandgap [1], others suggested that they stay as resonant levels in the materials valence and conduction bands [14]. There is still no definitive answer to those questions from either experimental or theoretical data. On the other hand, there are some experimental data that has established the positions of the 4f-related energy levels (with respect to the Fermi level) in metallic RE crystalline phases [15]. Therefore, those results in metallic phases could serve as a benchmark for theoretical modeling to describe the 4f-related levels in III-V semiconductors. They could at least help into defining a reliable procedure to obtain the Hubbard potential of those 4f levels for RE impurities in GaN hosts.

For the RE in metallic phases, the U values, obtained self-consistently, are presented in Table 1. As an example of those results, Fig. 1 shows the partial density of states (PDOS) of the Er 4f, 5d, and 6s in the metallic phase (a) without and (b) with the Hubbard U correction. Without the correction, the Fermi level lies in the 4f orbitals, contrary to the experimental data [15]. The introduction of the Hubbard (4f) U potential moves the 4f states away from the Fermi level, being now consistent with experimental observations. With the correction, we found that the highest occupied (HO) and the lowest unoccupied (LU) 4f orbitals of Er lie respectively at about 7.3 eV below and 1.7 eV above the Fermi level. Those values agree reasonably well with experimental data of 4.7 and 2.1 eV, respectively [15]. For all other RE elements investigated here (from Eu to Tm), without the U potential, the theoretical 4f-related states lie in the Fermi level, contrasting with the experimental data. Therefore, the introduction of the U potential corrects the position of those 4f-related energy states (with respect to the Fermi level) for all those metals. Table 1 shows the highest occupied and lowest unoccupied 4f-related energy eigenvalues with respect to the Fermi level, as compared to available experimental data [15]. The good agreement in the trends between the theoretical and experimental data, presented in Fig. 2, indicates that the procedure used here, to obtain the U Hubbard potential, provides an appropriate description on the electronic correlation of the 4f electrons. We should stress that our results provide the lowest unoccupied (LU) levels in excellent agreement with experimental data, while they overestimate the position of the highest occupied (HO) level. Such behavior should, in fact, be expected from the beginning. Experiments [15] obtained the position of the highest occupied 4f level by electron ejection, by x-ray photoemission spectroscopy (XPS) [15], measuring the $RE^{3+} \rightarrow RE^{4+}$ transition. On the other hand, our theoretical model provides only the eigenvalues associated with all occupied 4f states. Therefore, the theoretical model is expected to overestimate the correction in the electronic correlation. This is observed for all RE elements in Fig. 2. Additionally, experiments obtain the position of the lowest occupied 4f state with electron injection in the unoccupied 4f states, by bremsstrahlung isochromat spectroscopy (BIS) [15], measuring the $RE^{3+} \rightarrow RE^{2+}$ transition. We compared such experimental data with the lowest unoccupied (LU) 4f-related eigenvalues. Therefore, theory and experiment provide consistent results, since there is negligible differences in computing the one electron correlation.

The calculations on the RE metallic phases helped to identify the appropriate procedure to compute the Hubbard U potential. Therefore, this procedure should also provide a reliable description on the electronic properties of RE elements as impurities in semiconductors. Then, we have computed the properties of substitutional RE impurities in the cation site (GaN:RE$_{Ga}$, RE = Eu, Gd, Tb, Dy, Ho, Er, and Tm), using the same methodology and procedures described earlier. The Hubbard U potentials of RE impurities were obtained self-consistently and are presented in Table 2. According to the table, from Tb to Tm, the U potentials are around the same value (8.3 eV), while for Eu and Gd, the

Table 1
Results for the RE in respective metallic phases. The table presents the self-consistent Hubbard (U) parameter, the positions of the highest occupied, E_{4f} (HO) and the lowest unoccupied, E_{4f} (LU), energy eigenvalues with respect to the Fermi energy level. The difference between those two values is given by $\Delta E_{4f} = E_{4f}(LU) - E_{4f}(HO)$. The results are compared to experimental (exp) data [15]. All energies are given in eV.

|	Eu	Gd	Tb	Dy	Ho	Er	Tm
U	6.8	7.4	7.8	7.4	7.8	8.2	8.2
E_{4f} (HO)	−2.3	−8.8	−4.1	−5.6	−6.5	−7.3	−7.0
E_{4f}^{exp}(HO)	−1.5	−7.4	−2.2	−3.9	−4.9	−4.7	−4.6
E_{4f} (LU)	8.7	3.3	2.9	2.3	1.9	1.7	1.2
E_{4f}^{exp}(LU)	8.6	4.0	2.8	1.8	1.9	2.1	1.1
ΔE_{4f}	11.0	12.1	7.0	7.9	8.4	9.0	8.2
ΔE_{4f}^{exp}	10.1	11.4	5.0	5.7	6.8	6.9	5.7
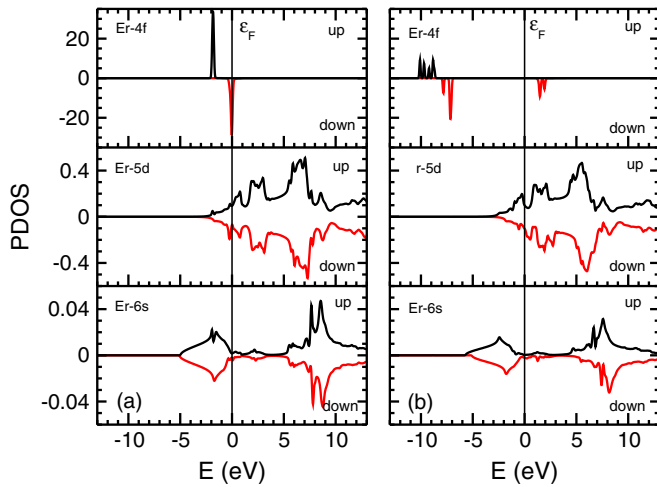
Fig. 1. The partial density of states (PDOS) of Er in a metallic phase with (a) GGA ($U=0$) and (b) GGA$+U$ ($U=8.2$ eV). ε_F represents the Fermi level of the metallic system.

Table 2
Results for the RE as substitutional impurities in GaN. The table presents the self-consistent Hubbard (U) parameter, the positions of the highest occupied, E_{4f} (HO) and the lowest unoccupied, E_{4f} (LU), energy eigenvalues with respect to the top of the valence band. The difference between those two values is given by $\Delta E_{4f}=E_{4f}(\text{LU})-E_{4f}(\text{HO})$. The results are compared to data (mod) from a phenomenological model [14]. All energies are given in eV.

	Eu	Gd	Tb	Dy	Ho	Er	Tm
U	9.4	6.8	8.3	8.3	8.3	8.4	8.4
E_{4f} (HO)	−5.2	−5.1	−1.8	−2.9	−3.7	−4.1	−4.2
E_{4f}^{mod}(HO)	−2.5	−3.8	1.1	−0.5	−1.5	−1.4	−1.4
E_{4f} (LU)	3.2	6.6	6.3	5.1	5.2	5.0	3.5
E_{4f}^{mod}(LU)	3.2	7.4	6.2	5.2	5.1	5.2	4.5
ΔE_{4f}	8.4	11.7	8.1	8.0	8.9	9.1	7.7
ΔE_{4f}^{mod}	5.7	11.2	5.1	5.7	6.6	6.6	5.9

4. Summary

In summary, we have investigated the electronic properties of substitutional RE impurities (from Eu to Tm) in zincblende gallium nitride. We find that the RE impurities stay in a 3+ oxidation state, consistent with earlier investigations. Additionally, we have shown that the self-consistent procedure to compute the values of the Hubbard U parameter provides a reliable description on the electronic properties of those impurities. This is confirmed comparing our results with available data from a recent phenomenological model [14], as well as from experiments [15] in the case of RE in metallic phase. Our theoretical model also indicates that the RE impurities introduce no energy eigenvalue levels in the GaN bandgap, which is consistent with the results of that phenomenological model.

respective U's deviate from that value. When comparing our results with the ones for RE nitrides [28], we find that our values are in good agreement for most of the RE elements. It should be pointed out that although the RE atoms in both systems have nitrogen neighbors, there are important differences on the number of neighbors and interatomic distances, reflecting different effects on screening.

The 4f-related energy eigenvalues, with respect to the GaN valence and conduction bands, for the specific case of a substitutional Er impurity is presented in Fig. 3. The figure shows the center (a) without and (b) with Hubbard U potential correction. Without the correction, there are 4f-related states inside the GaN bandgap. On the other hand, the introduction of the U correction increases the splitting between 4f-related occupied and unoccupied states, cleaning the GaN bandgap of any 4f-related level. Independent of the U correction, our results indicated that the substitutional RE atoms stayed in a 3+ oxidation state, consistent with earlier assumptions.

Fig. 4 presents the theoretical highest occupied and lowest unoccupied 4f-related RE (from Eu to Tm) eigenvalues with respect to the GaN valence band top, using the respective U corrections. The results compare well with recent data, obtained using a phenomenological model [14,29]. Our results indicated that no RE impurity introduces energy levels within the GaN bandgap, which are consistent with that model, except for the case of the Tb one. However, as pointed out before in the case of RE metals, our results provide the 4f-related energy eigenvalues. Fig. 4b shows the splitting between the highest occupied and lowest unoccupied 4f-related RE levels. The trend on energies, along the RE impurity series, is consistent with that phenomenological model [14].
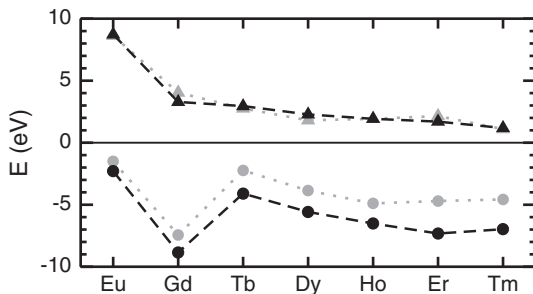
Fig. 2. The highest occupied (black circle) and lowest unoccupied (black triangle) 4f orbitals in RE metallic phases with respect to the Fermi level (at $E=0$ eV), considering the Hubbard potential correction. Black (gray) symbols represent theoretical (experimental) data. Dashed lines are only a guide to the eye.
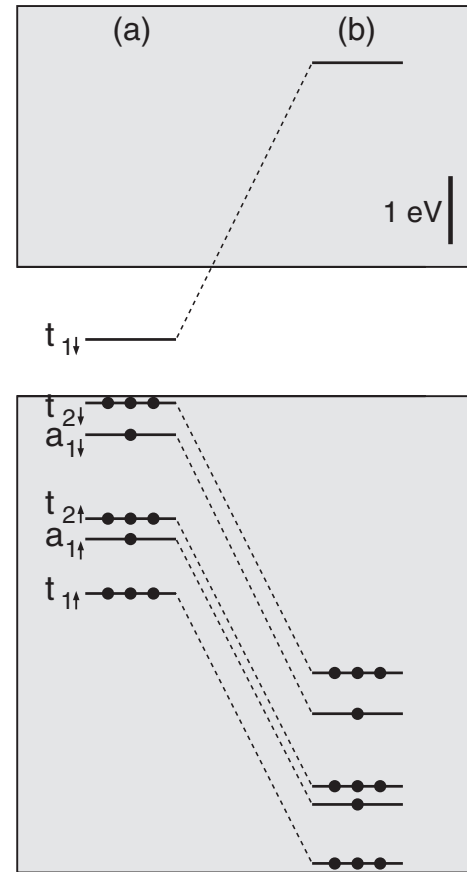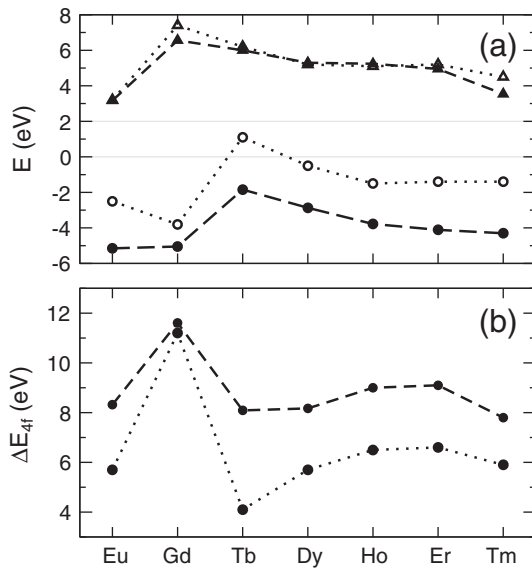

Fig. 3. The 4f-related energy eigenvalues for the Er impurity in zincblende GaN without (a) and with (b) on-site Hubbard U potential correction. The theoretical GaN bandgap was found to be 2.0 eV. The labeling of energy levels was obtained by the 4f-projected partial density of states and according to Γ-point symmetry.

Fig. 4. (a) Highest occupied (circles) and lowest unoccupied (triangle) for 4f-related energy eigenvalues with respect to GaN valence band top and conduction band bottom (grey lines) values, considering the Hubbard potential correction. The figure compares the results of our calculations (closed symbols) with the ones predicted from a phenomenological model (open symbols) [14]. (b) The separation energy between the highest occupied and lowest occupied 4f-related energy levels, as presented in panel (a).

Acknowledgments

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