Lanthanide impurities in wide bandgap semiconductors: a possible roadmap for spintronic devices

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Abstract

The electronic properties of lanthanide (from Eu to Tm) impurities in wurtzite gallium nitride and zinc oxide were investigated by first principles calculations, using an all electron methodology plus a Hubbard potential correction. The results indicated that the 4f-related energy levels remain outside the bandgap in both materials, in good agreement with a recent phenomenological model, based on experimental data. Additionally, zinc oxide doped with lanthanide impurities became an n-type material, showing a coupling between the 4f-related spin polarized states and the carriers. This coupling may generate spin polarized currents, which could lead to applications in spintronic devices.

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Wide bandgap semiconductors, doped with rare earth (RE) impurities, received great attention over the last decade, mainly due to potential applications in optoelectronic and spintronic devices. Rare earth lanthanide atoms exhibit partially filled 4f shells, and intra-4f electric dipole transitions are forbidden for the free ions. On the other hand, the respective transition probabilities increase considerably when the ions are placed in a crystal field, that splits the 4f-related energy levels, modifying the dipole selection rules and leading to luminescent centers.

Although theoretical modeling has been used to investigate the properties of RE-related materials, several methodological challenges have hindered an appropriate description of the 4f-related states in crystalline environments, such as RE impurities in semiconductors. It is well documented that the density functional theory generally fails in describing highly correlated systems, such as the interactions in 4f-related electronic states. Such limitations could in part be overcome with the introduction of an on-site Hubbard U potential correction. One of the major outcomes of this correction is a better description of the energy splitting between occupied and unoccupied 4f-related electronic levels. We have recently shown that this procedure provides a good description of the electronic structure of metallic RE crystals, when compared to available experimental data. Here, we show that the same procedure is also appropriate to describe the trends on the 4f-related energy levels of RE impurities (from Eu to Tm), with respect to the bandgap, in wurtzite gallium nitride and zinc oxide crystals. The results were discussed in the context of a recent phenomenological model to determine the energy positions of 4f-related electronic systems in crystalline environments. Our results also indicate that doping ZnO with lanthanide impurities leads to a n-type material, with a magnetic coupling between the 4f-related states and the carriers. This suggests that such systems could generate spin polarized carrier currents, allowing to envision potential applications in spintronic devices.

In RE lanthanide atoms, the 4f states play a minor role on bonding, staying in an atomic-like configuration. Therefore, those atoms bind to their neighboring ones through their outer (5d, 6s, and 6p) atomic valence states. Earlier theoretical investigations generally considered the 4f electrons as core states, with constrained occupations which were based on experimental results. State of the art methodologies, such as the one used here, now allow to treat the 4f electrons as valence states, with no constrained occupations, opening the possibility to model those systems more realistically.
Our calculations were performed using the all-electron spin-polarized full-potential linearized augmented plane wave method [14], implemented in the WIEN2k package [15], within the framework of the density functional theory. The exchange correlation potential was described by the generalized gradient approximation [16] plus the on-site Hubbard U potential, implemented in a rotationally invariant procedure [7–9]. Self-consistent iterations were performed until convergence in the total energy of $10^{-5}$ Ry was achieved. In all systems, the internal degrees of freedom were optimized, with no symmetry constraints, until the force in any atom was smaller than $10^{-3}$ Ry/a.u. We considered a 56-atom reference hexagonal supercell of GaN or ZnO, with the RE atom in a substitutional cation site. A detailed description of the simulation cell is presented elsewhere [17]. In order to check the convergence of our results with respect to the supercell size, we performed test simulations with larger supercells (up to 108 atoms) and observed that the results were essentially unchanged in comparison to those with the 56-atom supercell. The irreducible Brillouin zone was sampled by a $(2 \times 2 \times 2)$ grid. Convergence on the total energy was achieved using a plane-wave basis set, limited by the wave number $8.0/R$ (maximum length of the plane-waves), where $R = 1.5$ a.u. is the smallest atomic sphere radius. All those approximations provide a reliable description on the electronic and structural properties of several impurity centers in semiconductors [17–20].

We initially used an on-site Hubbard potential correction, computed self-consistently [8], for the 3d states of the cation atoms (Ga or Zn, respectively in GaN or ZnO) in the crystal hosts. We found self-consistent values of $U_{3d}(\text{Ga}) = 10.9$ eV and $U_{3d}(\text{Zn}) = 7.6$ eV. Such corrections provided structural and electronic properties of the respective crystalline systems in agreement with available experimental [21, 22] and theoretical [23] data. The Hubbard correction improved the description of the bandgap of GaN (ZnO), going from 1.7 (0.8) eV to 2.2 (1.6) eV. This correction still underestimates the bandgap of GaN (ZnO) as compared to the experimental value of 3.5 (3.4) eV [21, 22]. We then implemented the correction in the 4f states of the RE impurities within the same methodology, in order to get an appropriate description of the highly correlated 4f-related electronic states.

Figures (a) and (b) present the highest occupied (HO) and lowest unoccupied (LU) 4f-related RE eigenvalues with relation to the GaN and ZnO bandgaps, respectively. For GaN, shown in fig. (a), our results give trends along the RE series in excellent agreement with those of a phenomenological model based on experimental data [24, 25]. However, our
calculations provide absolute values for the HO levels which are about 2 eV lower when compared to that model. Our results also indicated that RE impurities introduce no energy levels within the materials bandgap, which is fully consistent with the phenomenological model, except for the Tb impurity. In order to clarify this point, we stress that a direct comparison of our results with experimental or phenomenological ones has its shortcomings. Our results are represented by the 4f-related Kohn-Sham eigenvalues, while the experimental data comprises the multiplet electronic configurations, measured for the electronic transitions, related to the respective ionization energies. However, our results provided a proper description on the 4f-related energy splitting (excitation) between the 3+ and 2+ oxidation charge states of all RE impurities, which is represented by the respective energy difference between the HO and the LU 4f-related states ($\Delta \varepsilon_{4f}$). These results offered an additional certification that the procedure used here, to obtain the Hubbard U values for the 4f-states, describes their electronic correlation appropriately.

Figure (1(c)) presents the Hubbard U$_{4f}$ values, obtained self-consistently, for each impurity in GaN and ZnO. For GaN, those values are very close to the respective $\Delta \varepsilon_{4f}$, all of them lying between 8 and 9 eV. The only exception is Gd, where $U_{4f}(\text{Gd}) = 6.8$ eV and $\Delta \varepsilon_{4f}(\text{Gd}) = 11.7$ eV. The Gd impurity is a particular case in the RE series, since it has a half-filled 4f state. As a result, $\Delta \varepsilon_{4f}$ is between a fully occupied spin up energy level and a fully unoccupied spin down one. For any other impurity of this series, $\Delta \varepsilon_{4f}$ is between two spin up levels (before Gd) or two spin down ones (after Gd). Therefore, the exchange-correlation interaction for Gd, and consequently the energy splitting between occupied and unoccupied states, is already reasonably well described even without a Hubbard correction. Without the correction, $\Delta \varepsilon_{4f}(\text{Gd})$ is already 5.2 eV in our calculations, fully consistent with a recent investigation [26], that found a value around 4.5 eV. For any other RE impurity, without the Hubbard correction, $\Delta \varepsilon_{4f}$ is smaller than 1 eV. As a result, the electronic structure of those systems cannot be described appropriately without the Hubbard correction. Therefore, a smaller $U_{4f}$ value for Gd, as compared to other RE impurities, is enough to provide a proper description of the respective electronic structure.

Consistent with the discussion for impurities in GaN, the trends along the RE series in ZnO are in excellent agreement with the phenomenological model [27], as shown in fig. (1(b)). Our results indicate that no RE impurity introduces energy levels within the ZnO bandgap. However, the phenomenological model suggests that the 3+ oxidation state of Tb is inside
the ZnO bandgap (about 0.8 eV higher than the top of the valence band). The trends on
the splitting between the HO and LU 4f-related RE levels are in good agreement with that
model [27]. As discussed in the previous paragraph for Gd in GaN, Gd in ZnO also has an
U value that is considerably smaller than the respective HO-LU energy splitting, as shown
in fig. 1(c). In ZnO, $U_{4f}(\text{Gd}) = 5.9 \text{ eV}$ while $\Delta \varepsilon_{4f}(\text{Gd}) = 10.6 \text{ eV}$. According to the figure,
the computed $U_{4f}$ values of the respective RE impurities are systematically smaller in ZnO
than in GaN, which reflects the role of the neighboring atoms, and even the larger ionicity
of ZnO compared to that of GaN, on the 4f-related correlation.

It is worth mentioning that we computed the valence band offset between ZnO and GaN
host materials, following the procedure described in Ref. [18]. In order to get that, we
considered an alignment of the RE 5d-related energy levels, according to the average energy
of spin up and down states. For all RE impurities, this average energy is resonant in the
conduction band, at 4.7 eV (5.9 eV) above the GaN (ZnO) valence band top, which resulted
in a band offset of 1.2 eV between those two materials. This band offset is essentially the same
with or without the Hubbard U correction in the 3d-states of the cation atoms. Such result is
in excellent agreement with the one from another investigation [28], providing an additional
certification of this methodology to describe the positions of the energy eigenvalues with
respect to the materials bandgaps.

The results of RE in ZnO showed great similarities with those of RE in GaN. Such
similarities are not fortuitous and carry important implications. First, when a RE impurity
replaces a trivalent cation atom (Ga) in GaN, it donates three electrons to bind with the
nitrogen neighboring atoms, staying in a 3+ oxidation state. As a result, all the RE centers
in the neutral charge states have their total spin associated exclusively to the 4f-related
states. Following the same reasoning, when a RE impurity replaces a divalent cation atom
(Zn) in ZnO, it would be expected that the impurity donates two electrons to bind with the
oxygen neighboring atoms, resulting in a 2+ oxidation state. Our results showed otherwise,
they indicated that all RE impurities in ZnO stay in a 3+ oxidation state, as for the RE
impurities in GaN. Such results in ZnO are fully consistent with assumptions used in the
phenomenological model [27]. For a RE in ZnO to achieve such oxidation state, it donates
two electrons to stabilize the binding with the oxygen neighboring atoms, while the third
electron populates the bottom of the ZnO conduction band. As a result, in contrast to what
occurs in GaN, a neutrally charged RE impurity in ZnO has its total spin associated to
both the 4f-related states and the delocalized spin polarized carrier in the conduction band. Therefore, doping ZnO with RE impurities leads to an n-type semiconductor.

The delocalized spin polarized carrier in the conduction band bottom opens the possibility of getting diluted magnetic semiconductors [29] using RE doped ZnO. Such possibility could be investigated by observing the partial density of states in the impurity sites. Figure 2 presents the projected s, p, d, and f density of states inside the RE atomic sphere of the ZnO:Eu and ZnO:Gd systems. For Eu, there is an unoccupied 4f-related state just over the Fermi energy, while for Gd such 4f-related state is about 4 eV above the Fermi energy. In the ZnO:Eu system, the unoccupied 4f-related level interacts with the delocalized energy level that defines the conduction band bottom, which is occupied by an almost-free carrier. This result indicates the viability of getting spin polarized carriers in ZnO:Eu, although this would be more difficult using other RE impurities. Figure 3 shows the density of the electron (carrier) in the conduction band bottom for Eu and Gd impurities in ZnO. The figure shows the localized 4f character in the Eu site in ZnO:Eu, which is much stronger than in the ZnO:Gd system. For Eu, such localization (about 7% of charge inside the Eu sphere) is enough to provide a spin polarized carrier current, within the Zener model [29].

In summary, we have investigated the electronic properties of substitutional RE impurities (from Eu to Tm) in gallium nitride and zinc oxide. We found that the RE impurities stay in a 3+ oxidation state in both materials, consistent with experimental assumptions. Additionally, we have shown that the self-consistent procedure to compute the values of the Hubbard U parameters provides a reliable description on the electronic properties of those impurity centers. This is confirmed by comparing our results with available data from a recent phenomenological model [12]. Our theoretical model also indicated that no RE impurity introduce energy levels in either GaN or ZnO bandgaps. However, in ZnO the impurities lead to an n-type material, independent of the Fermi level energy. There is strong evidence that the negative carrier could be magnetically coupled with the 4f-related states, which could generate spin polarized carrier currents. Moreover, since the 4f-related energy levels introduced by the impurities are highly localized, weakly interacting with the host atoms, the alloying of ZnO with these RE elements could lead to diluted magnetic semiconductors. For RE in GaN, our results show that the alloying of GaN with these elements could only lead to diluted magnetic semiconductors if the RE impurities are complexed with other defects, in order to generate the almost free carriers, as discussed in
Ref. [6].

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FIG. 1: Results of our calculations (closed symbols) of RE impurities in (a) GaN and (b) ZnO compared to the ones predicted from a phenomenological model (open symbols) [25, 27]. The figure presents the highest occupied (circles) and lowest unoccupied (triangles) 4f-related energy eigenvalues ($\varepsilon_{4f}$), in the respective valence and conduction bands (gray regions), considering the Hubbard potential corrections. All experimental and theoretical values are presented with respect to the GaN and ZnO valence band tops, taken as reference values. The (c) panel presents the $U_{4f}$ values, obtained self-consistently, for 4f-related states of each impurity in GaN (open diamond symbols) and ZnO (closed diamond symbols).
FIG. 2: The s, p, d, and f projected density of states (PDOS) inside the (a) Eu and (b) Gd atomic spheres ($R_{RE} = 2$ a.u.) for spin up and spin down energy levels in ZnO. The dashed lines represent the valence band top ($\varepsilon_v$) and the conduction band bottom (at the Fermi energy $\varepsilon_F$).
FIG. 3: Electron density in the [11\overline{2}0] plane for the electron in the conduction band bottom (Fermi energy level) for (a) Eu and (b) Gd in ZnO. The coloring goes from red (high density) to violet (low density), following the rainbow sequence.