An Efficient LDA+*U* Based Tight Binding Approach[†]

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The functionals usually applied in DFT calculations have deficiencies in describing systems with strongly localized electrons such as transition metals or rare earth (RE) compounds. In this work, we present the self-consistent charge density based functional tight binding (SCC-DFTB) calculation scheme including LDA+*U* like potentials and apply it for the simulation of RE-doped GaN. DFTB parameters for the simulation of GaN and a selection of rare earth ions, where the f electrons were explicitly included in the valence, have been created. The results of the simulations were tested against experimental data (where present) and against various more sophisticated but computationally more costly DFT calculations. Our approach is found to correctly reproduce the geometry and the energetic of the studied systems.

Introduction

Doping semiconductors with rare earths (RE) has attracted the attention of the scientific community in the past decade due to their almost monochromatic visible light emission. The wavelength of the RE emmisions are almost independent of host, with different RE giving rise to a choice of colors. Eu, Er, and Tm, for example, have been successfully exploited as primary colors in thin film electroluminescent (TFEL) phosphor systems.[1] The sharp intra-f optical transitions responsible for the emission spectra of RE-doped samples are shielded by the outer valence electrons and therefore quite unaffected by the host. Several studies on various Er-doped semiconductors have shown that increasing the band gap of the host material reduces the thermal quenching of the Er^{3+} emission,[2] hence using wide-gap semiconductors as a host enables a more efficient room temperature RE emission. GaN is a suitable wide band gap semiconductor to host RE dopants because it is transparent in the visible region and because the RE emission is not quenched at room temperature. Both properties contrast with other hosts such as Si and GaAs. RE-doped GaN has recently attracted attention also as a promising candidate for the realization of high T_c spintronic devices.[3,4]

Theoretical study of RE-doped GaN presents several tough challenges for the usual methods due to the size of system required for simulations, the chemical complexity of the many defects present, and the nature of the lanthanides themselves. A proper treatment of the strongly correlated 4f electrons of the RE goes beyond a classical L(S)DA approach, and computational methods that are able to address the problem in a rigorous way like the GW approximation are computationally very demanding. In attempt to improve the description of strongly correlated systems while extending the size of the studied system, an LDA+*U*[5] like approach was implemented in the spin-polarized charge self-consistent DFTB.[6,7] This gives us the possibility to treat large RE-containing systems in a proper manner and within a fast TB framework. In this work we show the results of the simulation of RE substitutionals in hexagonal GaN. We created DFTB parameters for the RE that are of interest their emission spectra (Pr, Eu, Er, Tm) and the RE that are of possible interest for spintronic devices (Eu, Gd) because of their magnetic properties.

DFTB Method

The spin-polarized, charge self-consistent, DFTB approach is based on a second-order expansion of the spin-dependent Kohn−Sham[8,9] total energy functional with respect to a given reference charge and magnetization density. The method has been extensively discussed elsewhere[7,10,11] and will not be repeated here. Despite its simplicity (a two center non-orthogonal Hamiltonian is used), the density functional based tight-binding (DFTB) method scheme has been proven to be accurate when applied to solid state,[12] molecular, and biological systems.[13] Materials like silicon,[14] SiC,[15] diamond,[16] boron and boron nitride,[17] and III−V semiconductors like GaN[18] and GaAs[19] have successfully been studied within the DFTB approach. The study of strongly correlated systems (like RE or transition metal containing compounds) goes beyond the range of the usual problems in solid-state physics because of the nature of these systems themselves. RE ions, for example, have atomic numbers of between 57 and 70; hence, relativistic effects begin to become important. Additionally, many properties of transition metal or lanthanide elements depend on the strongly correlated behavior of their d or f electrons. To study such cases requires a more sophisticated theory than simple mean-field methods. To address all of this additional complexity in treating lanthanides, the DFTB method has been substantially extended. To treat strongly correlated systems, an LDA+*U*[5,6] approach has been adopted. We would like to remark that (to our knowledge) DFTB contains the first TB implementation of LDA+*U*.

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LDA and Orbital Dependent Potentials

In the density functional theory (DFT), the many-body problem is reduced (mapped) to the problem of a non-interacting system with a one-electron exchange-correlation potential. This is then approximated, typically using the exchange-correlation present in a homogeneous electron gas (LDA). Materials with strongly correlated electrons however are examples where this mean field approach most strikingly fails. LDA is a method with an orbitally independent potential, and applying it to a system containing transition metals (TM) or rare earths (RE) with partially filled d or f shells gives results consistent with a metallic electronic structure and itinerant d or f electrons, which is definitely wrong for most lanthanide compounds and several examples of TM systems (NiO being the classic example). Other choices for the exchange correlation such as generalized gradient (GGA) can also be applied, but as with LDA, this is a mean-field correction for the non-interacting system, so it suffers from the same pathology. In the strongly correlated systems the d or f electrons are often well-localized, and there is a noticeable energy difference between occupied and unoccupied sub-bands, which are called *lower* and *upper Hubbard bands*, in analogy with the Hubbard Hamiltonian approach. There have been a number of attempts to improve the LDA and make it able to account for strong electron−electron correlation. The full self-interaction corrected (SIC) approach[20] can reproduce the localized nature of d and f electrons in TM and RE compounds as well as the total energy of these systems but is not intended to reproduce the one-electron energies, additionally SIC is known to over-correct many properties.[21] There have also been several recent attempts to approximate the effects of the SIC method with local corrections. The LDA+U approach is conceptually similar to the Hubbard Hamiltonian approach: the non-local and energy-dependent self-energy is approximated by a frequency-independent but non-local screened Coulomb potential.

LDA + U. As discussed by Anisimov et al.,[22] it is natural separate electrons into localized d or f electrons and delocalized s and p electrons. While for the latter an orbitally independent one-electron potential (as in LDA) will suffice, a local interaction better describes the former. This is of the form $1/2\Sigma_{i\neq j}n_in_j$, where n_i are the occupancies of the localized shells. If we assume that the Coulomb energy for the electron−electron interaction as a function of the total number of electrons $N = \Sigma n_i$ given by LDA is a good approximation (even if it gives wrong single-particle energies), then LDA already contains part of this energy, which must be subtracted from the total energy and instead replaced with a Hubbard model-like term.

As a result we get the functional:[23,24]

$$E = E_{\mathrm{LDA}} - \frac{1}{2}UN(N-1) + \frac{U}{2}\sum_{i\neq j} n_i n_j$$

Strictly speaking, the process of subtracting the double-counting of the electron−electron interaction of strongly correlated electrons from the LDA total energy and substituting it with a Hubbard Hamiltonian-like term is not without ambiguity. The electron−electron interactions have already been taken in account in a mean field way with LDA, while the Hubbard Hamiltonian also incorporates a large part of the total Coulomb energy of the system. One can try to identify those parts of the DFT total energy corresponding to the interactions included with the Hubbard Hamiltonian in order to subtract them. This is not trivial, because while the DFT Hamiltonian is written in terms of the total density, the Hubbard Hamiltonian is written in terms of orbital occupation numbers. A direct link between the two is not straightforward. Second, even if it would be possible to totally remove the on-site Coulombic contribution in the LDA and Hartree contributions, it would be undesirable, as the spatial variation of the Coulomb and exchange-correlation potential is important and better described in the DFT than in the Hubbard approach. It is instead better to try and identify a mean-field part of the Hubbard Hamiltonian and subtract that, leaving only a correction to the LDA solution. The fully localized limit (FLL) functional described above gives a rotationally symmetric contribution to the energy and Hamiltonian of

$$\Delta E = -\frac{1}{2}(U-J)\sum_{\sigma} \mathrm{Tr}[n^{\sigma}\cdot n^{\sigma} - n^{\sigma}]$$

$$\Delta V^{\sigma}_{\mu\nu} = -(U-J)\left(n^{\sigma}_{\mu\nu} - \frac{1}{2}\delta_{\mu\nu}\right)$$

where the occupation matrix n is usually taken to be on-site blocks for a given l shell, this expression produces the correct behavior in the FLL where $n_{m\sigma} = 0$ or 1.

LDA + U-like Approach in DFTB. While it has previously been suggested that for *empirical* tight-binding the effects of on-site correlation can be mimicked by an empirical adjustment of symmetry resolved on-site energies,[27] this is problematic, for example, for low symmetry d electron systems or for f manifolds. In the RE ions of interest here, the so-called FLL should be achieved (i.e., the orbital occupations of states localized within the 4f manifold should be either be 0 or 1[23,24]).

In the rotationally invariant form of LDA+U,[25] the correction to LDA potential is of the form

$$\Delta V^{\sigma}_{\mu\nu} = -(U-J)(n^{\sigma}_{\mu\nu} - \mathrm{DC}[n^{\sigma}_{\mu\nu}]) \qquad (1)$$

where n^{σ}_{i} is the local spin occupation number within a given atomic manifold, and $(U - J)$ is the screened and spherically averaged Coulombic electron−electron interaction. DC[n] is the double-counting term, and in this work we use the FLL limit of

$$\mathrm{DC}^{\sigma}_{\mu\nu}[n]^{\mathrm{FLL}} = \frac{1}{2}\delta_{\mu\nu} \qquad (2)$$

$(U - J)$ is usually taken to be either an adjustable parameter or from a constrained DFT calculation, as we do in this work, but it is interesting to note that $(U - J)$ is typically about half of the free atomic values. Since the DFTB energy is normally a reasonable approximation to the LDA energy, it seems sensible to adopt the form of the LDA+U energy correction unchanged for DFTB.

There is then the issue of how to choose the on-site occupation matrix[28] for a non-orthogonal basis. We present results for both the on-site and the dual basis forms of LDA+U. In the on-site case, the modification to the total energy and the DFTB Hamiltonian can be written in terms of atomic sub-blocks of the single-particle density matrix (ρ) as

$$\Delta E_{\mathrm{LDA}+U} = \frac{1}{2}\sum_{A,\sigma}\sum_{l\notin A}(U_l - J_l) \times \mathrm{Tr}(\rho - \rho\cdot\rho)_{\rho\in l} \qquad (3)$$

$$\Delta V^{\sigma}_{\mathrm{LDA}+Ul\in A} = (U_l - J_l)(\delta_{\mu\nu} - \rho^{\sigma}_{\mu\nu})_{l\in A} \qquad (4)$$

while for the dual basis case, the occupation matrix takes the form of a generalization of Mulliken charges:

$$n^{\sigma}_{\mu\in A,\nu\in A} = \frac{1}{2}\sum_{B}\sum_{\tau\notin B}(S_{\mu\tau}\rho_{\tau\nu} + \rho_{\mu\tau}S_{\tau\nu}) \quad (5)$$

where the diagonal of the occupation matrix are then basis-function resolved Mulliken charges.

Results and Discussion

After testing the parameters, we apply our calculation scheme to the RE substitutional RE_{Ga} of the selected RE in hexagonal (wurtzite) GaN. As all of the selected RE show similar characteristics. In the exposition of the results, we pay particular attention to the substitutional Er_{Ga}, which we chose as representative for this class of defects. For this substitutional we report in some detail the energetic, discussing the related band structures and density of states (DOS), stressing the differences between a classic L(S)DA and the L(S)DA+U approach. RE_{Ga} are well-suited as test systems because they are expected to be the simplest stable RE defects in GaN, because there are several theoretical studies[29−31] we can use for comparison and finally because these dopants have been already investigated experimentally to some extent. Er:GaN-based light-emitting diodes (LED)[32] have in fact stimulated many experimental attempts to understand[33] the mechanisms underlying the emission from Er-doped samples and to exploit[34−36] and improve[37,38] the emission itself. Much is known about Er ions in GaN (i.e., they prefer the Ga position,[39] occur in 3+ valence state,[32] and possess C_{3v} symmetry[40] with relatively short distances to the surrounding N-ligands[41]).

Substitutional RE_{Ga} in Wurtzite GaN. To investigate the substitutionals RE_{Ga} we used super-cells containing 256 atoms and a 4 × 4 × 4 Monkhorst-Pack[43] k-point sampling. All the data reported here were calculated with these super-cells. The geometries have been relaxed in different spin configurations to find the one which minimizes the total energy. We found all the substitutionals RE_{Ga} to have C_{3v} symmetry. The symmetry is a particularly important parameter in the investigation of the RE defects, because it can be measured experimentally and because it is known that intra-f transitions are enhanced by lowering the symmetry.[42] For example the symmetry difference between Eu and Tb substitutionals in GaN has been suggested to be the cause of the higher luminescence intensity of Eu-doped GaN than Tb-doped.[42] All the studied RE substitutionals after geometry optimization are on-site, even in the case of Eu, which was found by RBS measurements to be displaced from the Ga site of 0.2 Å.[47] Our results agree with the suggestion of Filhol et al.,[29] that the experimental data in case of Eu originate from some defect complex. The calculated geometries in the neighborhood of the substitutional for each selected RE are reported in Table 1, while in the Table 2 experimental measurements and other ab initio calculations are reported for a direct confrontation. The calculated values are in good agreement with the experimental measurements. It is interesting to observe that in all the cases the RE-N bond is shortened, in average by 15−20% as compared to the corresponding RE nitride. All the RE ions are bigger (both in the neutral and in the +3 charge state) than the Ga ion they take the place of, and the proportion of the distortion caused by the substitutionals reflects the dimension of the dopants. Apart from the relative small (in all the cases less than 16%) compressive stress in the neighborhood of the RE no other effects on the host geometry are observed: RE are thus easily incorporated in the GaN host structure as substitutional in the Ga site. We believe that the C_{3v} symmetry of the substitutionals is not an intrinsic property of the defect but is rather due to the lattice symmetry, because we found that RE_{Ga} substitutionals in zinc-blended GaN have the higher tetrahedral symmetry. At this point we notice that LDA+U does not really influence the structure, as the geometries calculated with LDA and LDA+U differ by less than 0.5%.

TABLE 1: Bond Lengths (Å) and Local Strain around the C_{3v} RE_{Ga} Substitutional in GaN, Calculated with DFTB[a]

	$RE-N_1$	$RE-N_2$	$RE-Ga_1$	$RE-Ga_2$	strain
Pr	2.179	2.187	3.368	3.393	11.4%
Eu	2.271	2.280	3.376	3.401	16.1%
Gd	2.146	2.158	3.302	3.319	9.8%
Er	2.129	2.138	3.325	3.360	8.8%
Tm	2.124	2.131	3.271	3.320	8.5%

[a] The local strain is the ratio between the RE−N Bonds and the Ga−N Bonds in the Bulk.

TABLE 2: Reference Bond Lengths (Å) and Local Strain around the C_{3v} RE_{Ga} Substitutional in GaN[a]

	$RE-N_1$	$RE-N_2$	$RE-Ga_1$	$RE-Ga_2$
Eu[44]	2.3	2.5	3.3	3.3
Gd[45]	2.23	2.23	3.31	3.31
Er[29]	2.13	2.16	3.22	3.26
Er[33]	2.17	2.17	3.26	3.26
Tm[46]	2.19	2.19	3.29	3.29
Tm[29]	2.12	2.15	3.22	3.25

[a] Mostly EXAFS measurements are reported, for more details see the individual references. The measured distances refer to RE concentration similar to the one simulated with our calculations. To our knowledge no experiments have been performed to measure the bond distances in Pr-doped GaN. Local strain is defined as before.

Let us consider now the electronic properties of the RE substitutionals. All the RE_{Ga} are found both with LDA and LDA+U to be trivalent (i.e., in neutral super-cells there is an effective 3^+ charge on the RE ion). Generally (except for Gd) two of the $6s^2$ electrons and one of the 4f are donated to the GaN lattice as compared to the free atom. In the special case of Gd, due to its half filled 4f shell, instead the three donated outer electrons are the two $6s^2$ and one 5d (i.e., the total number of f electrons does not change). A more detailed discussion of the energetic of the single RE_{Ga} will be published elsewhere,[49] instead here we concentrate on the electronic properties of the substitutional Er_{Ga} to show how LDA and LDA+U influence the description of the system. For Er_{Ga}, reference calculations were executed with the ab initio all electron code Wien2k.[48] In Figure 1, the band structures of the substitutional Er_{Ga} calculated with DFTB and DFTB+U (first row) and LDA/LDA+U using Wien2k (second row) are reported. Let us first examine the LDA case: the size of the GaN original band gap (3.44 eV for DFTB and 2.2 eV for Wien2K) is not modified by the presence of the substitutional, while in the middle of the gap appear very localized f-related levels. An LSDA analysis reveals how these levels are occupied for Er case and for the other RE: 7 up electrons and 4 down in the Er case (2 and 0 for Pr, 6−0 for Eu, 7−0 for Gd and 7−5 for Tm). The corresponding DOS, also calculated with DFTB (first row) and Wien2K (second row) are reported in Figure 2 for the Er case. The peak in the middle of the band gap is related to the f levels.

In order to examine and understand the results obtained with LDA+U, we need to understand how it influences the system. The choice of the value $U - J$ is a central point in the whole LDA+U theory. How should we choose this value? The orbital dependent potentials introduced with LDA+U are used to correctly reproduce the separation between the two Hubbard sub-bands of full and empty f states, with the parameter $U - J$ corresponding to the energy difference of the two bands. An estimate of the separation between the two Hubbard sub-bands

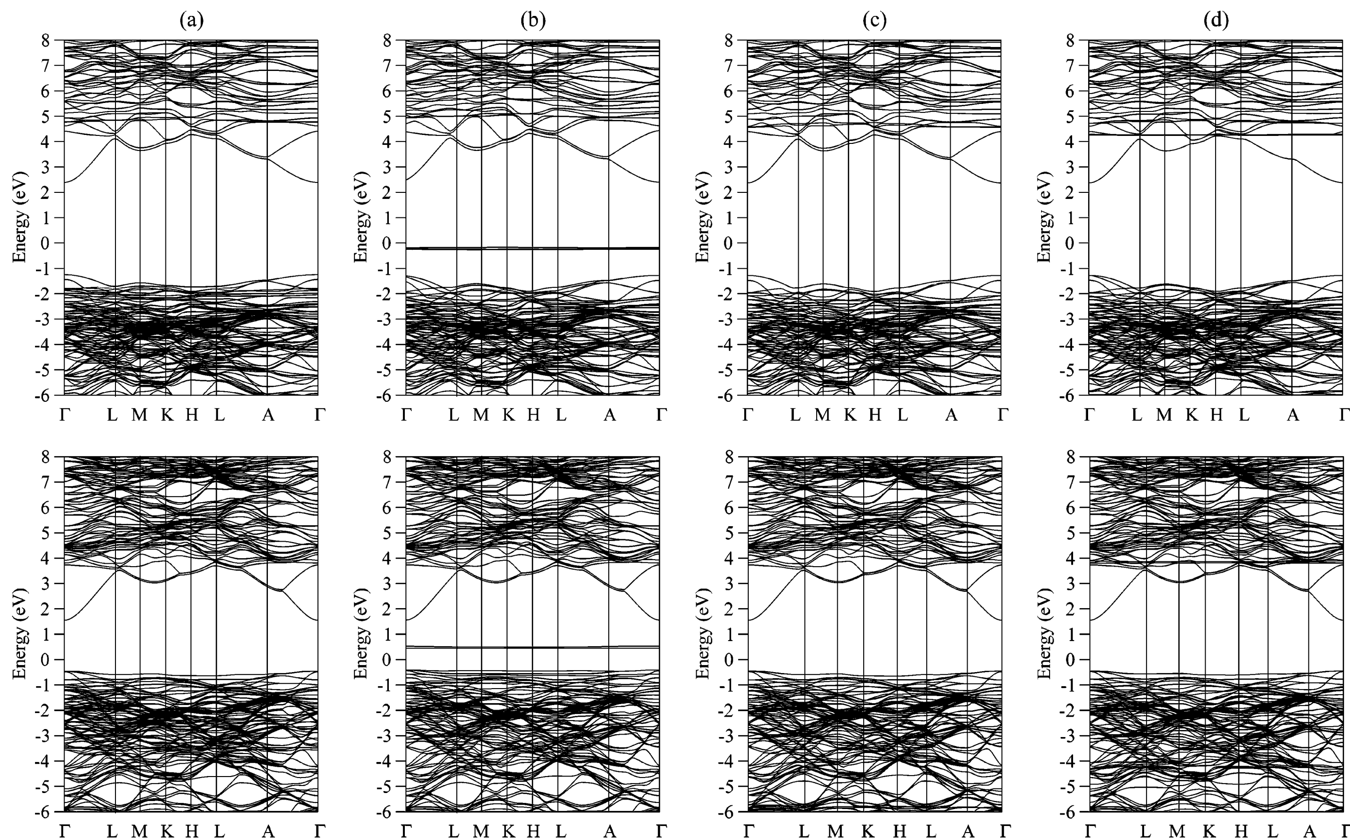

Figure 1. Substitutional Er_{Ga} in the neutral charge state in wurtzite GaN. Spin-resolved (spin up in panels a and c, spin down in panels b and d) energy band structure calculated with LDA (a and b) and LSDA+U (c and d) obtained with a value of ($U - J$) of 0.28 H. In the first row are reported the DFTB and in the second the Wien2k reference calculations.

is given by the Hubbard-U of the atomic shell giving rise to the mentioned bands, so that a first sensible choice for the $U - J$ parameter is exactly the Hubbard-U of the corresponding atomic shell. Both in DFTB and in the Wien2k reference calculations we used the value of $1/2U_f$, which was calculated for the atom using Janak's theorem, namely, 7.6 eV. This value is consistent with that used in similar simulations.[50] The $+U$ potentials are applied only to the f shells.

We would like to understand how the LDA+U representation changes the description of the system. We illustrate the effect of the $+U$ potentials on the f electrons using as example the substitutional Er_{Ga} in GaN itself. As already seen with LDA and in the DFTB approximation, all substitutional RE_{Ga} introduce localized defect levels in the GaN band gap. This is the situation reported for Er_{Ga} in the band structure in Figure 3 (first box from the left) and in the DOS of Figure 2 (upper part). When we apply the $+U$ potentials (see the boxes in Figure 3), the empty levels shift upward while filled ones move downward, almost linearly with the ($U - J$) parameter. In the Er case shown in Figure 3, all f-related levels have been ejected from the band gap for a value of ($U - J$) of about 0.26 H ,and they lie well outside the gap for the used value of 0.28 H. Examining the related density of state we notice that the peak corresponding to the f electrons in the LDA representation is split into two peaks corresponding to the filled f states and to the empty f states, which are moved from the original position respectively downward and upward. It is interesting to notice in Figure 3 that empty f states as well as occupied f states are shifted almost linearly with the value of $U - J$ even after they pass into the conduction and valence bands. This indicates that the f states do not undergo any major hybridization within the host. This behavior is quite different from systems like NiO and is most probably due to the localized nature of the f orbitals and the consequent screening effects of the outer atomic shells. The same features observed in the density of states can also be observed in the calculated band structures for the super-cell containing the Er substitutional (Figure 1): as one would expect, the occupied states are pushed downward in the valence band and the empty states are pushed upward in the conduction band, leaving the original band gap completely empty. A detailed discussion about the interpretation of this clear gap can be found in ref 51 and references therein. Both the band structures and the DOS for the studied system calculated with Wien2K and with DFTB are in very good agreement. The substitutionals RE_{Ga} of the other selected RE behave very similar, and we do not report them here in detail. Summarizing, when we examine the different RE with a classic LSDA approach we find they all introduce very localized f-related levels in the GaN band gap, whose position depends from the RE and is and deeper for heavier RE. When we investigate the substitutionals with the LSDA+U approach, as with the Er case, the gap levels are removed leaving the original GaN band gap completely clear.

The above discussion neglects the effects of spin−orbit coupling, we have also carried out provisional calculations in the case of Er using the methodology outlined in ref 53 in addition to the LDA+U-like treatment for DFTB. Using a 4f spin orbit constant of 2234 cm^{-1}, with the Er magnetic moment in the *a* plane,[54] we find that the 7-fold degenerate localized gap levels shown in Figure 1 in the gap are split into four filled and three empty non-degenerate levels that remain in the gap spanning a range of ~700 meV. Applying the FLL-LDA+U approach again ejects these states from the gap, demonstraiting that in this case correlation has a larger effect than spin−orbit coupling. The possibility of acceptor or donor states has not been investigated in this work, as all the calculations were performed on neutral super-cells.

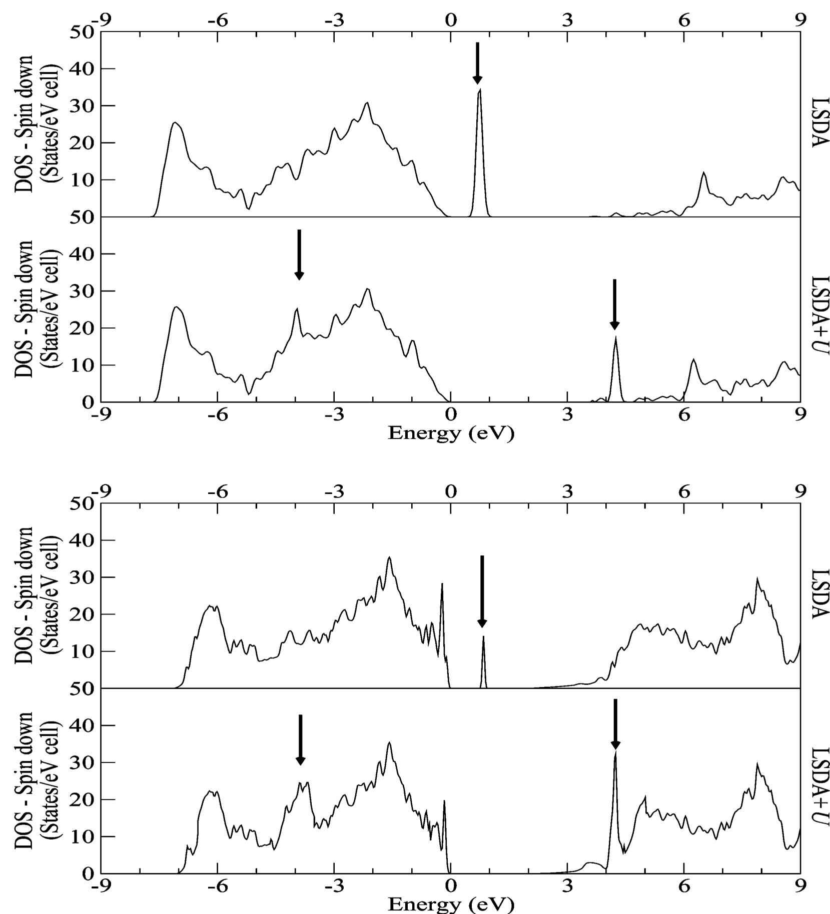

Figure 2. Spin-resolved DOS calculated with LDA and LSDA+U for the substitutional ErGa in the neutral charge state in wurtzite GaN. In the first row are reported the DFTB and in the second the Wien2K reference calculations. For the used $U - J$ values, see the text. The arrows show the position of the f-related peaks. We only show the spin down electrons, as the spin up states are fully occupied and included in the valence band. In the LDA+U calculations, the f-related peak visible in the band gap is split in two parts, the rest of the structure remains almost untouched. The valence band maximum is chosen as zero of the energy scale.

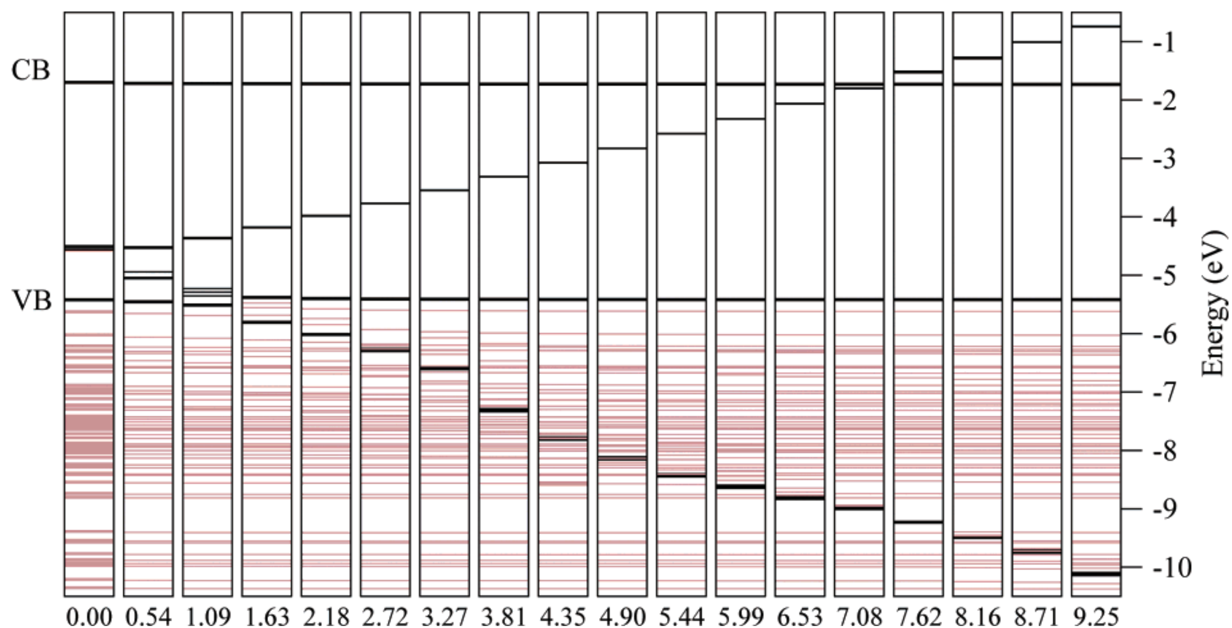

Figure 3. Substitutional Er_{Ga} in the neutral charge state in wurtzite GaN. Effect of the $+U$ potential on the induced gap levels at the Γ point, shown for different values of the parameter ($U - J$) from 0.00 to 9.25 eV. The fact that the position of the f-related levels grows almost linearly with the $+U$ potential even within the valence and conduction bands suggests that the f orbitals do not hybridize with the host orbitals.

Conclusions

We presented an efficient calculation scheme in framework of the SCC-DFTB for the simulation of strongly correlated electrons and applied it to RE defects in GaN. The capability of the method to carry on spin-polarized calculations as well as its capability to treat in a proper way strong correlated systems

with an LDA+U-like approach make DFTB a powerful tool for the simulation of RE defects and allows us a systematic study of the RE defects and defect complexes. The accuracy of the parameters (preliminary results obtained with our parameters have been also presented in ref 52), and the efficiency of this method allow the investigation of extended systems and the systematic sampling of many configurations for defect physics and chemistry. Tests simulations done on the substitutionals RE_{Ga} in GaN have been reported here. Properties like geometries, band structures, and density of states were tested against experimental measurements and DFT calculations showing a remarkable transferability and an overall good agreement between our simulations and existing data. Summarizing what we found about the RE_{Ga} substitutionals, we can affirm that they are always trivalent in their neutral state, easily incorporated in the GaN host charge state. The classical LDA and the more sophisticated LDA+U approach predict the same structure that is with the RE placed at the Ga site and tetrahedrally coordinate with C_{3v} symmetry but qualitative different band structures.

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