Simone Sanna, *Rare Earth point defects in GaN.*
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# Abstract

In this work we investigate rare earth doped GaN, by means of theoretical simulations. The optical emission from rare earth ions (RE) consists of very sharp lines (ranging from the UV to IR), whose wave length is determined by the energy of the corresponding transition within the $4f$-shell. Rare earth doped GaN has been used as phosphors in the realisation of GaN-based flat panel displays, even if the RE luminescence could not be related up to date to a singular or to a group of lanthanide defects and few is known about the mechanisms leading to the emission.
The huge unit cells necessary to model the experimental system, where dilute amount of rare earth ions are used, are handled with the charge self consistent density-functional based-tight binding (SCC-DFTB) calculational scheme. The method has been extended to include LDA+$U$ and simplified self interaction corrected (SIC)-like potentials for the simulation of systems with localised and strongly correlated electrons. This approach attempts to combine the efficiency of the tight-binding with the accuracy of more sophisticated *ab initio* methods allowing the treatment of highly correlated electrons also for very large systems.
A set of tight-binding parameters has been created to model the interaction of GaN with some dopants, including a selection of lanthanide ions interesting due to their optical or magnetic properties (Pr, Eu, Gd, Er and Tm). The *f*-electrons were treated as valence electrons. The validity of the parameters was thoroughly tested against experimental data, in particular bulk ErN in the rock-salt phase is investigated in detail and found to be a half-metal in the ferromagnetic phase.
In addition, the TB approach opens the possibility to overcome one of the most relevant problems of the density-functional theory (DFT) calculations in the local density approximation (LDA), the considerable underestimation of the band gap. A qualitatively correct description of the band gap is crucial for the simulation of rare earth doped GaN, because the luminescence intensity of the implanted samples depends on the size of the host band gap and because the rare earths could introduce charge transition levels near the conduction band. In this work these levels are calculated with the Slater-Janak (SJ) transition state model, which allows an approximate calculation of the charge transition levels by analysing the Kohn-Sham eigenvalues of the DFT. Unfortunately, the usual LDA and its gradient extensions fail in describing the Kohn-Sham eigenvalues of the lanthanides sufficiently well. We show (analytically and by means of representative examples) that the SJ-transition state becomes a powerful tool if applied self-consistently within a LDA+$U$ extension of DFT. The simulations confirmed that the lanthanide ions prefer the Ga lattice site. Isolated substitutionals $RE_{Ga}$ are very stable defects, present in the $C_{3v}$ symmetry. $RE_{Ga}$ are found to introduce only a small distortion in the host lattice and in the charge distribution of the ligands and are therefore easily incorporated in the GaN host. Rare earth interstitials are found not to be stable against the kick-out of a neighbouring Ga which is replaced by the rare earth. Complexes formed by lanthanide substitutionals and N-interstitials or anti-sites ($I_N$ and $Ga_N$ or $N_{Ga}$) are characterised by high formation and low binding energies and are unlikely to be formed under equilibrium conditions. Among the defects which can be related with the luminescence we have found the close pairs formed by $RE_{Ga}$ substitutionals and vacancies or $O_N$ substitutionals. These complexes are stable (bound) at typical annealing temperatures and introduce localised levels in the GaN band gap. On the basis of these results we conclude our work with a possible model for the mechanisms leading to the luminescence, where the nitrogen vacancies in $RE_{Ga}$ $V_N$ pairs act as assistant for the energy transfer to the $f$-shell of the lanthanides.