LDA+U calculations of Cr, Mn, Fe, and Co ions in GaN: impact of the U(N)

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The known failure of the Local Density Approximation (LDA) is the underestimation of the band gap in solids, ascribed to the oversimplified treatment of exchange-correlation effects. In the case of GaN, the LDA band gap is 1.8 eV, compared to the experimental value of 3.5 eV. A considerable improvement is obtained by adding the +U term [1] for particular atomic orbitals. The +U term was widely applied to the compact d-shell of transition metal (TM) ions. However, adding the +U term to d(Ga) does not correct the LDA gap of GaN. We showed that the correct E_{gap} is obtained by applying U(N)=4-5 eV to the p(N) orbitals. Next, we analyzed the impact U(TM) for Cr, Mn, Fe, and Co in GaN, considering U(TM) as a free parameter.

The inclusion of U(N) affects the TM-induced states in the band gap depending on their symmetry, because the t_2 triplets hybridize with the host states, while the e_2 doublets are predominantly impurity-like. Consequently, the former states are more sensitive to the changes of U(N) than the latter ones. By taking these effects into account we explain why most of the TM mid-gap states are largely independent of the change of E_{gap} of GaN induced by the U(N) correction, or, in other words, their "absolute energies" are constant. On the other hand, level energies relative to the VBT can change by 0.5 eV. Thus, the U(N) corrections affect the energies of intracenter optical transitions less than those of the ionization transitions (like $Mn^{3+} + h\nu \rightarrow Mn^{4+}$ + conduction electron). Equilibrium atomic configurations, and the dependence on the impurity charge state were analyzed. Finally, comparison with experimental data was performed. The calculations were done for 128-atom supercells using the Quantum Espresso package [2].

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[1] M. Cococcini and S. de Gironcoli, Phys. Rev. B **71**, 35105 (2005).
[2] www.pwscf.org.