# Pseudo-Jahn-Teller effect and negative-$U_{eff}$ feature induced by the +U term in LDA+U: V:Ga, Fe, and Mn in GaN

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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, and particularly drastic in transition metal (TM) oxides. A considerable improvement is obtained by adding the +U correction for particular atomic orbitals. While the impact of +U terms was extensively discussed for ideal crystals, its impact on the electronic structure of defects is less understood. We analyzed the impact of the +U term for Mn and Fe ions, and for the gallium vacancy V:Ga in GaN. The calculations were done for 128-atom supercells using the Quantum Espresso package [1]. The +U term was treated as a free parameter, and it was applied to both p(N) and d(TM) orbitals. A correct band gap of GaN is obtained with U(N)=4 eV.

The sign of the +U correction for a given defect level depends on its occupation, and shifts the occupied (empty) levels downwards (upwards) [2]. Strong dependence of the defect levels on their occupation leads to two remarkable effects. The first one is the pseudo-Jahn-Teller effect. In takes place when a degenerate multiplet is partially occupied with electrons, and the +U term drives its symmetry-lowering splitting. The effect is of purely electronic origin, and does not depend on the relaxation of atoms in the surrounding of the defect. The second one is the so-called "negative-$U_{eff}$" effect, which consists in the instability of some charge states of the defect. (In the case of DX centers, it is the neutral charge state of donor which is unstable due to the large atomic relaxations.) Again, the effect is driven by the +U corrections, and does not necessitate atomic displacements.

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