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Summary of PHD Thesis „Electronic structure of Cr, Mn, Fe, and Co ions in GaN and AlN: LDA and LDA+U calculations"

I performed a detailed analysis of the electronic structure of Cr, Mn, Fe, and Co in both GaN and AlN, and compared the results with experimental data. The exchange-correlation coupling was described within the Generalized Gradient Approximation (GGA). The known failure of the GGA is the underestimation of the band gap in solids, ascribed to the oversimplified treatment of exchange-correlation effects. In the case of GaN, the GGA 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 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. I showed that the correct E_{gap} is obtained by applying $U(N)=5$ eV to the p(N) orbitals. Next, I analyzed the impact $U(TM)$ for Cr, Mn, Fe, and Co in GaN and AlN. The magnitude of $U(TM)$ was treated as a free parameter, which assumes values between -2 and 6 eV.

In GaN and AlN, the crystal field splits the impurity d-shell into the t triplet and the e doublet, which are further split into the spin-up and spin-down states by the exchange coupling. Some of these levels are in the gap, and others are degenerate with the valence or the conduction band. Which of them are the gap states is determined by the impurity, its charge state, and the host. I find that the impact of the increasing U on the energy levels strongly depends on their symmetry, occupancy determined by the charge state, and hybridization with host states, and is much higher for e than for t. In some cases, the energy of $e\uparrow$ decreases by as much as 8 eV, while that of $e\downarrow$ rises by 5 eV, but typical changes are smaller. The t states change by 1 eV or less. The results are very similar for GaN and AlN. Those dependencies are explained by the fact that the hybridization of gap states of TM ions with the host depend on level symmetry, and is more pronounced for t than for e levels (which are predominantly impurity-like). Consequently, the former states are more sensitive to the changes of $U(N)$ than the latter ones. Furthermore, by assuming that 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, I obtain that the VBT decreases by 0.5 eV when $U(N)$ increases from 0 to 5 eV.

The comparison of the calculated electronic structures with calculations based on hybrid functionals shows that the results of both approaches are the same to within 0.2 eV for $U(TM)=U(N)=5$ eV.

The calculated energies of intra-center optical transitions, the transition levels, and ionization energies were compared with experimental data. The obtained results show that for Mn and Fe, the best overall agreement with experiment is obtained for $U(TM)\cong 0$, or even $U(TM)\cong -1$ eV. The value $U\cong 4$ eV, often used for TM impurities in III-V compounds, leads to serious disagreements with the experimental data exceeding 1 eV.

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