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Impact of Exchange-Correlations Effects ($+U$ Corrections) on the Energy Levels of Mn and Fe Impurities in GaN and AlN: A Comparison with Experiment

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Electronic structure of Mn and Fe impurities in GaN and AlN are calculated within the density functional theory in the generalized gradient approximation without and with the $+U$ corrections. The comparison with the available experimental data shows that the results obtained with $U = 0$ are in good agreement with experiment. Inclusion of $+U$ corrections makes the agreement worse.

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1. Introduction

The prospect of possible spintronic applications of III–V nitrides doped with transition metals (TMs) lead to the intensive experimental studies of these systems in the last decade. These include optical and transport measurements, used to precisely determine the energies of impurity-induced states in the band gap. This situation allows for a detailed evaluation of the accuracy of various theoretical approaches applied. In particular, from the theoretical side, the role of the exchange--correlation electron–electron coupling in systems with transition metal or rare earth ions is an object of the current discussion, and the intra-center coupling is often taken into account by the Hubbard $+U$ term [1]. This procedure is aimed to correct some of deficiencies of the popular local density approximation to the density functional theory, which leads to, e.g., the wrong character (metallic instead of insulating) of transition metal oxides.

TM impurities in III–V nitrides were previously studied theoretically by first-principles calculations [2–8], and some of them included the $+U$ corrections [5–7] or used hybrid functionals [8]. Here, we have chosen the nitrides because of their wide band gap, which allows for the presence of the impurity states in the gap, with energies determined by optical experiments [9–14]; one can note that in the most popular GaAs:Mn such states are absent.

2. Method of calculations

We performed an analysis of the electronic structure of Mn and Fe in both GaN and AlN in the wurtzite structure. Various charge states of impurities were considered. The Quantum Espresso package [15], the large unit cells with 72 atoms, and ultrasoft atomic pseudopotentials were used. The exchange-correlation coupling was described within the generalized gradient approximation [16]. The plane wave basis with the kinetic energy cutoff of 30 Ry provided a convergent description of the analyzed properties. The Brillouin zone summations were performed using the Monkhorst–Pack scheme with a $2 \times 2 \times 2$ k-point mesh. The Methfessel–Paxton smearing method with the smearing width of 0.0136 eV has been used for obtaining partial occupancies. Ionic positions were optimized until the forces acting on ions were smaller than 0.02 eV/Å. In addition, we have included the on-site electron–electron interaction within the $+U$ approach [1]. The magnitude of U was treated as a free parameter which assumes values between -2 and 6 eV.

3. Results

In GaN and AlN, the crystal field splits the TM impurity d-shell into the t_2 triplet and the e doublet, which are also split into the spin-up and spin-down states by the exchange coupling, see Fig. 1. The crystal field of the wurtzite structure further splits the triplets into singlets and doublets. However, this splitting is about 0.1 eV, and we neglect it here for the sake of clarity of the discussion. Which of the impurity states are the gap states is determined by the impurity, its charge state, and the host.

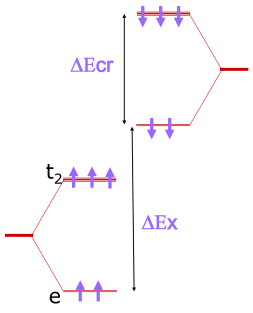

Fig. 1. Schematic splitting of the TM impurity d-shell into doublet e and triplet t_2 states by the crystal field, ΔE_{cr}, and the exchange-correlation splitting ΔE_{xc} into spin-up and spin-down states.

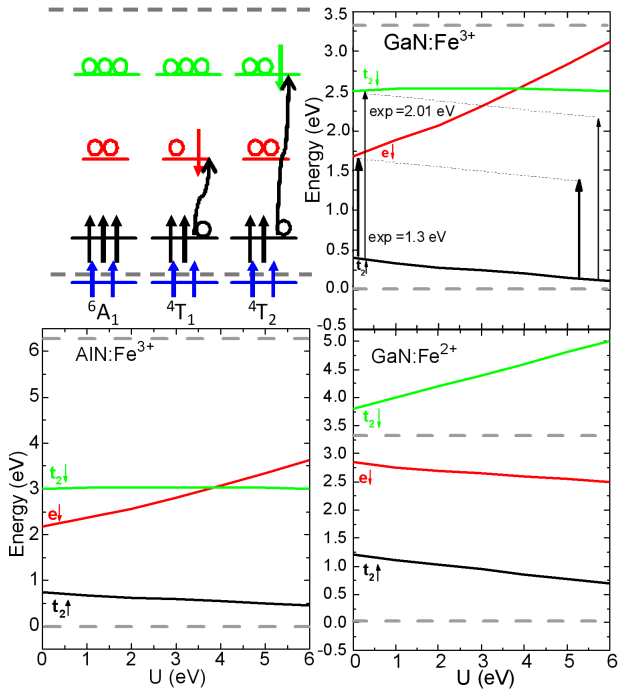

Fig. 2. The upper left part schematically shows the ground state electronic configuration of Fe^{3+} in GaN and two experimentally observed optical transitions. The upper right part shows the calculated energies of Fe^{3+} levels in GaN as a function of U. The two arrows correspond to the two transitions shown in the top left part. The energy levels of GaN:Fe^{2+} and AlN:Fe^{3+} are shown in the two bottom parts. Dashed lines indicate the top of the valence band and the bottom of the conduction band.

The considered TM impurities in an ideal III–V crystal are in the 3+ charge state. In the case of Fe ion, this corresponds to the d^5 high-spin configuration, with 5 electrons filling the $e\uparrow$ and the $t_2\uparrow$ states. The configuration of Mn is d^4. The impact of the increasing $+U$ value on the energy levels of Fe^{3+} in both GaN and AlN, and for Fe^{2+} in GaN, is shown in Fig. 2. For $U = 0$, i.e., within the GGA, $e\uparrow$ is a resonance degenerate with the valence band, while $t_2\uparrow$ is located in the gap, close to the valence band top. The empty $e_2\downarrow$ and $t_2\downarrow$ are also shown. As it follows from Fig. 2, the impact of the increasing U on the energy levels strongly depends on their symmetry, and is much higher for the e than for the t_2 states. In fact, for GaN:Fe^{3+}, the energy of $e_2\downarrow$ decreases by as much as ≈ 7 eV, while that of $e_2\uparrow$ rises by 1.5 eV. On the other hand, the energies of t_2 states change by less than 0.3 eV. These results are very similar for GaN and AlN (see Fig. 2).

The calculated energies of intra-center optical transitions, the transition levels, and ionization energies were compared with experimental data [9–14]. The obtained results show that for both Mn and Fe the best overall agreement with experiment is obtained for $U \approx 0$. In particular, the levels of Fe impurity were investigated in optical and transport measurements [9–11]. There are two characteristic intracenter transitions of Fe^{3+}, at 1.3 and 2.01 eV, respectively, observed in both GaN and AlN. They are schematically shown in the left upper part of Fig. 2, and they correspond to transitions between the $^6A_1$ ground state, and the two $^4T_1$ and $^4T_2$ configurations. The calculated transition energies for $U = 0$ (1.3 and 2.15 eV, respectively) agree very well with these data, see left upper part. The value $U = 4$ eV, often used to describe TM impurities in III–V compounds, leads to serious disagreements with the experiment, since the energy of the $^6A_1$–$^4T_1$ transition increases from 1.3 to about 2.5 eV.

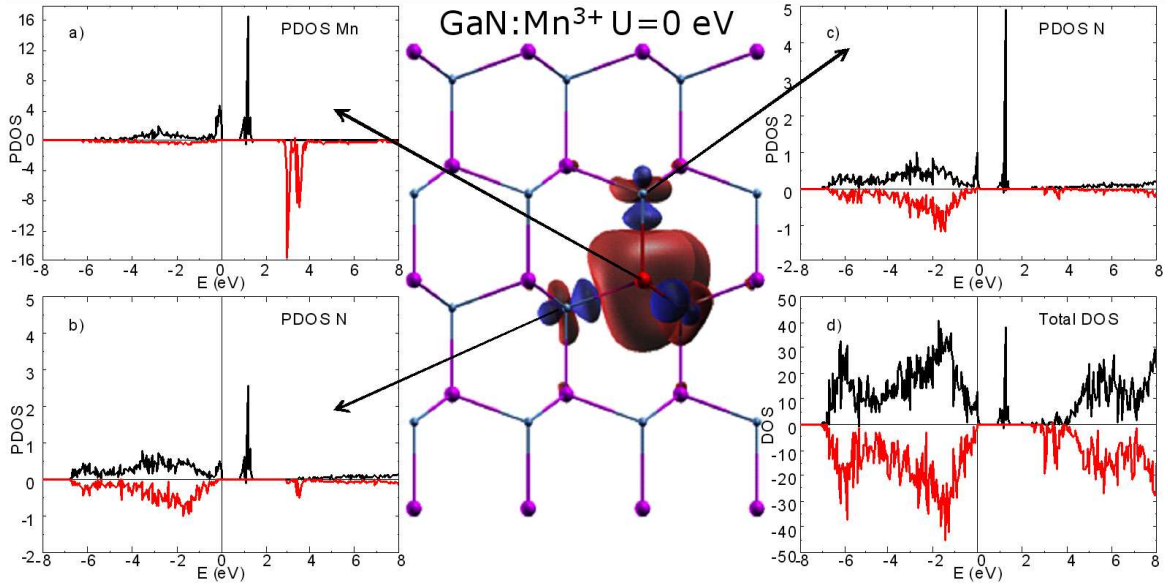

Fig. 3. Spin density of Mn in GaN (central figure), (d) total density of states (DOS) and DOS projected on Mn (a) and N states ((b) and (c)) for U(Mn) = 0 eV. The central (red), small (blue) and large (magenta) balls represent Mn, N, and Ga atoms, respectively.

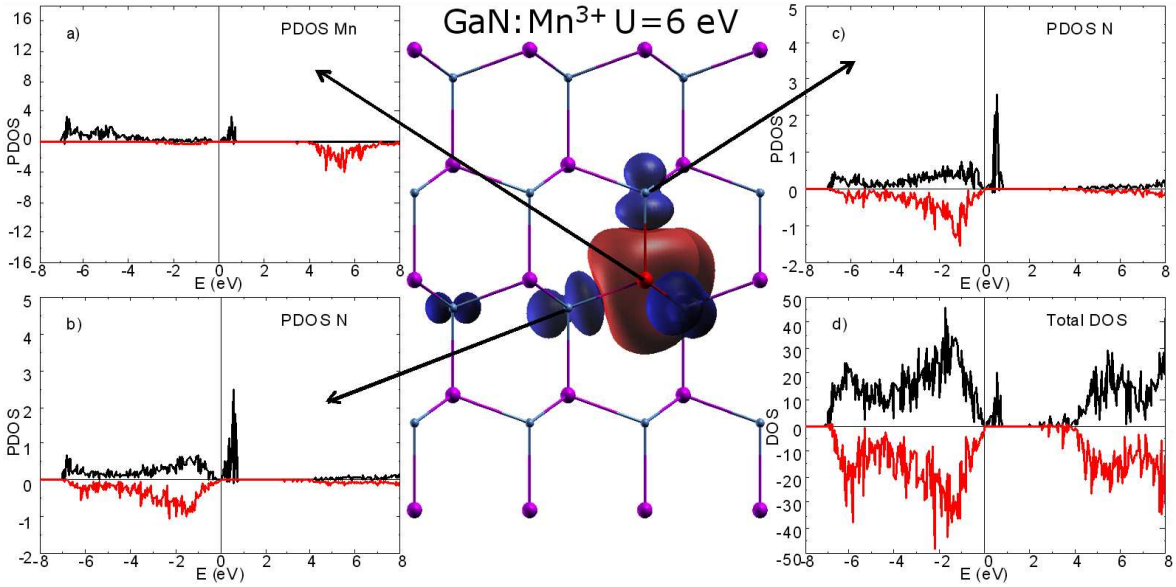

Fig. 4. Spin density of Mn in GaN (central figure), (d) total DOS, and DOS projected on Mn (a) and N states ((b) and (c)) for U(Mn) = 6 eV. The central (red), small (blue) and large (magenta) balls represent Mn, N, and Ga atoms, respectively.

The calculated spin density of Mn^{3+} in GaN is shown in Figs. 3 and 4. For $U = 0$, Fig. 3, the total density of states (DOS), together with its projection on the Mn ion and its first N neighbors, show that Mn induces a doublet $e\uparrow$ very close to the top of the valence band, and a $t_2\uparrow$ triplet in the band gap, separated by about 1.3 eV. For $U = 6$ eV, Fig. 4, the spin-up levels are lower in energy, and $e\uparrow$ is degenerate with the valence band, which is in contradiction with experiment [12]. One can also see a delocalization of the spin density, manifested in the increased contribution of the second N neighbors of Mn.

4. Summary

Electronic structure and energy levels of Fe and Mn ions in GaN and AlN were studied by first principles calculations and compared with experimental results. The GGA results without the $+U$ correction describe well experimental data on both the intracenter transitions seen in optical experiments, and the energies of the gap states relative to the valence band top. Inclusion of the $+U$ corrections strongly affects the e-levels, shifting the occupied states down and the empty states upward in energy, while the t_2 levels are much less affected. For $U = 0$, the obtained agreement with experiment is satisfactory, and it becomes worse for the non-vanishing U.

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