Trends in ferromagnetism, hole localization, and acceptor level depth for Mn substitution in GaN, GaP, GaAs, and GaSb

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We examine the intrinsic mechanism of ferromagnetism in dilute magnetic semiconductors by analyzing the trends in the electronic structure as the host is changed from GaN to GaSb, keeping the transition metal impurity fixed. In contrast with earlier interpretations which depended on the

to $t_+(pd)$. The antibonding nature is evident from the pocket of zero charge density along the Mn–X bond. Concomitant with the reduced Mn localization on the *antibonding* t_+ state at E_F, the *bonding* state at 3–4 eV below E_F exhibits (in Fig. 1) increased Mn localization along the same GaN→GaP →GaAs→GaSb series (as a result of "*pd* level anticrossing" discussed in Ref. 6).

By adding an electron to the antibonding t_+^2 level, we convert $Mn^{3+}(t^2)$ to $Mn^{2+}(t^3)$, thus creating an acceptor transition. The corresponding change $E(0/-)$ in the total energy is depicted in Fig. 3 with respect to the calculated band edges[15] of the unstrained zinc-blende solids. We see that the acceptor level is very deep in GaN:Mn in agreement with experiment[4] and it becomes progressively shallower as the anion X becomes heavier, also in agreement with experiment.[16] Thus, moving along the series GaN→GaP →GaAs→GaSb, the *antibonding*, hole-carrying t_+ orbital becomes less Mn-localized, the acceptor level becomes shallower, and the bonding orbitals located in the valence band become more localized on Mn, as observed in photoemission experiments.[17] The strong d character of the hole in Mn doped GaX semiconductors has implications on the usefulness of these materials as a source of spin-polarized carriers (

GaN:Mn shows large ferromagnetic stabilization energies for some pairs of Mn atoms parallels that of Dietl and Ohno,[2] the mechanism behind it is entirely different: Their model assumes a host-like delocalized hole for all materials on the basis of which they attributed trends in J to *volume scaling*, $J \sim V^{-1} = R^{-3}$, leading to a large J for the shortest bond-length material (here, GaN). We allow different materials to exhibit different localizations, finding large FM stabilization energies in GaN *despite* it not having host-like-hole states.

(2) The ferromagnetic stabilization energy is large, even for fourth Mn pair separations, (Fig. 4). Thus, *indirect* exchange (via the intervening anions) is at play.

(3) Certain crystallographic orientations of the Mn–Mn pair are seen to have the largest stabilization energies for the ferromagnetic state, e.g., the $\langle 110 \rangle$ orientation akin to $n=1$ and $n=4$ neighbors, whereas $\langle 001 \rangle$-oriented pairs ($n=2$) have the weakest FM. This reflects the orientational dependence of the coupling matrix elements between the two t_2 (pd) hybrids orbitals located on different Mn sites. The matrix elements and therefore the bonding is maximized when the t_2 (pd) hybrid orbitals point toward each other. On the other hand in zinc-blende symmetry e-orbitals point *in-between* the nearest neighbors, leading to vanishing matrix elements when the Mn atoms occupy $\langle 110 \rangle$ oriented lattice positions. Indeed there can be several exchange paths, between the t_2 orbitals on the two Mn atoms, the most obvious choice being one mediated via the host anion states *via $p-d$* coupling, and the other mediated by $d-d$ interaction. Our calculations help us distinguish which is the relevant exchange path. For cases where the hole is in a level with e symmetry, such as GaAs:Fe (Ref. 6), the ferromagnetic contribution from the hole is found to be small. As the coupling