nated by Ga, and exhibits a single charge state Mn^{2+} for all values of the Fermi energy. The $(0/+)$ and $(+/2+)$ donor transitions are found to lie inside the conduction band, so, isolated Mn_i produce electrons that will compensate the holes created by Mn_{Ga}.

(iii) Under *bulk* growth conditions, the formation energy per Mn of substitutional Mn is $\Delta H(Mn^0_{Ga}) = 0.91$

$\Delta H_f(\mathrm{MnAs}) = -0.74\ (-0.61)$ eV and $\Delta H_f(\mathrm{MnAs})_{epi} \sim 0$ eV. For elemental Mn we assume the nonmagnetic fcc structure,[20] while for elemental Ga, we assume the base-centered orthorhombic structure.

The charge corrected[11] Mn_{Ga} (0/-) transition as well as the difference in formation energies between Mn^0_{Ga} and Mn_i^{2+} are given in Table I for supercell sizes of 64 and 216 atoms. We see that changing the supercell size from 64 to 216 atoms lowers the acceptor energy by 30–50 meV and stabilizes Mn^0_{Ga} over Mn_i^{2+} by 50–150 meV. The charge correction increases the acceptor energy by 60–90 meV and stabilizes Mn^0_{Ga} over Mn_i^{2+} by 250–350 meV.

III. RESULTS

A. Isolated substitutional Mn on the Ga site of GaAs

Figure 1 describes the formation energy $\Delta H(\mathrm{Mn}^0_{Ga})$ of neutral substitutional Mn in GaAs as a function of the chemical potentials μ_{As} and μ_{Mn}. The shaded areas denote chemical potentials that produce unwanted products: (i) When μ_{As} becomes greater than zero (the cohesive energy of solid As) we have precipitation of elemental As as shown on the left hand side of Fig. 1. (ii) In the opposite limit, when μ_{As} takes more negative values than the formation energy $\Delta H(\mathrm{GaAs})$, we have maximally As-poor conditions and the host itself becomes unstable, as shown on the right hand side of Fig. 1. (iii) The diagonal lines in the main body of Fig. 1 denote different values of μ_{Mn}. When the chemical potential of Mn becomes greater than zero (the cohesive energy of solid Mn), metallic Mn will precipitate as shown in the bottom right

conditions, the lowest energy charge state is Mn^{0}_{Ga}, whereas for higher Fermi energy the stablest charge state is Mn^{-}_{Ga}. Table I gives the (0/-) acceptor transition energy calculated with various supercell sizes with and without charge correction. The most converged (0/-) transition energy calculated for the 216 atom cell and corrected for charge interactions is $E_v + 0.13$ eV, in good agreement with the measured value of $E_v + 0.11$ eV.[8] Fig. 2 shows that under epitaxial conditions (right y axis), the formation energy of Mn^{0}_{Ga} is lowered by 0.74 eV.

We next describe the electronic structure of Mn_{Ga}. In Figs. 3(a) and 3(b) we show the Mn d projected partial density of states (PDOS) for two charge states of substitutional Mn. The main features can be understood as arising from the hybridization between the anion dangling bonds generated by a Ga vacancy and the d levels on the Mn ion placed at the vacant site.[3] The Mn d ion levels are split by the tetrahedral crystal field into $t_2(d)$ and $e(d)$. Exchange interactions further split these levels into spin-up ($\uparrow$) and spin-down ($\downarrow$) levels. The $t_2(d)$ levels on the Mn atom hybridize with the levels with the same symmetry on the As dangling bonds, while the $e(d)$ levels have no other states available for significant coupling.[3] Because the location of the Mn ion d levels is below the dangling bond levels, after hybridization, the deeper bonding t_2 states have dominantly Mn d character

was detected by an analysis of the EPR spectrum[23] as well as by Rutherford back scattering.[5] The distinction between the two types of T_d interstitial sites (Mn-next to As vs Mn-next to Ga) is difficult to determine experimentally and involved an analysis of the experimentally measured contact interaction in terms of the covalency of the Mn-X bond. This analysis suggested that Mn_i(Ga) was more stable, while our total energy calculations suggest that Mn_i(As) is more stable.

The formation energy of various charge states of interstitial Mn is shown in Fig. 2 for $\mu_{As}=0$ and $\mu_{Mn}=\Delta H(\mathrm{MnAs})$. We see that the stable charge state is Mn_i^{2+} for the full range of Fermi level, with maximum stability at $\epsilon_F=0$. To compare the relative stability of Mn_i^{2+} at $\epsilon_F=0$ with substitutional Mn_{Ga}^{0}, we show in the upper scale of Fig. 1 the difference $\Delta H(\mathrm{Mn}_i^{2+})-\Delta H(\mathrm{Mn}_{Ga}^{0})$ between the formation energies of interstitial and substitutional Mn. We see that substitutional Ga is stabler on the left hand side of the figure, i.e., sufficiently As-rich, whereas interstitial Mn is stabler at the right hand side of the figure, i.e., sufficiently As-poor. The energy difference is

$$\Delta H(\mathrm{Mn}_i^{2+})-\Delta H(\mathrm{Mn}_{Ga}^{0})=0.38+\mu_{As}+2\epsilon_F\,.$$

For $\mu_{As}=0$, the substitutional Mn are stabler by 0.38 eV, while for moderately As-rich conditions, say $\mu_{As}=-0.4$ eV, both defects have comparable formation energies.

These results are in agreement with recent experiments using liquid phase epitaxy[9] to introduce Mn in GaAs. Experimentally a decrease in hole concentration is found as the Mn concentration is increased. Under the Ga-rich growth conditions used, As antisites are not expected to bF10 1 Tf ef 9.777 0 0 9.777 154.097the Ga-riumet32946.introduour.7(G6Tc 82.9(at7m777 154

energy E_0 has two channels of hopping present between S and I. The dominant factor in determining the configuration which has the lowest energy are the hopping matrix elements - $V_{S,I}$ between S and I and $V_{S,S}$ between the two S's. To a

to be coherent with the zinc-blende lattice, the formation energy of both substitutional and interstitial decrease. At this point, the solubility is large enough to form clusters. We find that S-I-S clusters are more stable than S-S-S clusters. S-I-S clusters are found to be strongly bound with respect to their constituents and exhibit partial or total hole compensation. While isolated Mn_i behaves like a hole killer and is expected to destroy ferromagnetism, in $(Mn_{Ga}\text{-}Mn_i\text{-}Mn_{Ga})^0$, the Mn_i is found to mediate the ferromagnetic arrangement of spins on Mn_{Ga}. The charged complex $(Mn_{Ga}\text{-}Mn_i\text{-}Mn_{Ga})^{2+}$ has a similar ferromagnetic stabilization energy on the two Mn_{Ga} sites as in a $Mn^0_{Ga}\text{-}Mn^0_{Ga}$ cluster without Mn_i *almost as if* Mn_i *did not exist*. Thus ferromagnetism in Mn doped GaAs arises from holes due to substitutional Mn_{Ga}, as well as from $Mn_{Ga}\text{-}Mn_i\text{-}Mn_{Ga}$ complexes.

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