Transition from Ferromagnetism to Antiferromagnetism in \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \)

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Using density functional theory, we study the magnetic stability of the \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \) alloy system. We show that unlike \( \text{Ga}_{1-x}\text{Mn}_y\text{As} \), which shows only ferromagnetic (FM) phase, \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \) can be stable in either FM or antiferromagnetic phases depending on the alloy concentration. The magnetic order can also be altered by applying pressure or with charge compensation. A unified model is used to explain these behaviors.

The discovery of ferromagnetism in Mn-containing III-V semiconductors has attracted significant attention in the last decade because the interesting combination of semiconductor electronics and metallic ferromagnetism creates great potential for developing functional devices that manipulate spin, as well as charge. Among the materials that have been investigated, \( \text{GaMnN} \) is one of the most interesting systems. On one hand, original theoretical predictions suggest that high \( T_c \) ferromagnetism can be achieved in the \( \text{GaMnN} \) alloy \[1\], which has resulted in an extensive experimental, as well as theoretical, study of its physical properties. On the other hand, available experimental data often contradict each other. Some reports show that high \( T_c \) ferromagnetism is achievable in this system \[2, 3, 4, 5\]; others show that the magnetic coupling of the Mn ions in \( \text{GaMnN} \) is actually antiferromagnetic (AFM) \[6\]. The exact nature of the magnetism observed in this system is also still under debate \[7, 8, 9\]. Some groups suggested that the observed ferromagnetism could be due to secondary phases generated during growth, and that \( \text{GaMnN} \) is a spin glass system \[8\]. Other groups argue that no secondary phase is observed in their single-crystal \( \text{GaMnN} \) samples that show ferromagnetism \[9\]. There are also discussions about whether the relevant Mn 3d state has \( d^4 \) or \( d^5 + h \) character, or whether the \( d \) levels are localized in the bandgap or inside the valence band \[10\].

Although many of the issues are still under intensive study, recent \textit{ab initio} band structure and total energy calculations \[11, 12, 13\] seem to agree that Mn 3d levels are located in the gap, and that the interaction between substitutional Mn ions is ferromagnetic (FM) at low Mn concentration. Because previous \textit{ab initio} studies also find that pure \begin{symbol}{MnN} \end{symbol} has an AFM ground state \[14\], an interesting question was raised about how the magnetic and electronic properties of \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \) evolve as a function of the Mn concentration \( x \). Furthermore, it is now well known that the ferromagnetism observed in Mn-containing GaAs is caused by holes in the host valence-band-derived states. It would be important to understand how the mechanism changes in Mn-containing GaN, where the holes are created in the Mn \( d \) bands.

In this paper, using \textit{ab initio} band structure and total energy methods, we study the magnetic properties of \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \) in the low and high Mn concentration regimes. We also study the effects of pressure and charge compensation on the magnetic properties of this system. We show that unlike in \( \text{GaMnAs} \), where \( p-d \) coupling induced level splitting at the valence band maximum (VBM) is the dominant effect that stabilizes the FM phase, direct Mn-Mn \( d-d \) coupling mediated by anion \( p \) states is the dominant effect in \( \text{GaMnN} \) \[15\]. We find that in \( \text{GaMnN} \): (i) The Mn 3d states are inside the band gap, in agreement with previous calculations. (ii) At low Mn concentrations, the Mn atom tends to have a higher magnetic moment and the magnetic ground state is FM. (iii) At higher concentration, the magnetic moment of Mn decreases and the ground state changes to AFM phase. (iv) When the material is compressed, the system becomes more stable in the AFM phase, even at low concentrations. (v) When Mn is negatively charged, the system turns to AFM, even at low concentrations. We show that all these results can be explained by the level crossing of Mn \( d \) spin-up and spin-down states, which varies with Mn concentration and pressure.

The calculations were performed using an \textit{ab initio} plane wave basis code \[16\], based on the density functional theory and using ultrasoft pseudopotentials \[17\]. For the exchange and correlation potential, we used the generalized gradient approximation of Perdew and Wang \[18\]. All the structural degrees of freedom (lattice parameters and atomic positions) are optimized by minimizing quantum mechanical forces and total energy. The Brillouin zone integration is performed using the Monkhost-Pack special \( k \) points scheme \[19\]. A large number of \( k \) points and high cut-off energies for the basis functions are used to ensure a convergence error within a few meV. We considered the zinc-blende alloy and assumed that the same results also hold for the alloy in a wurtzite structure. The disorder of the alloy is taken into account explicitly through the special quasirandom structure approach \[20\]. Supercells up to 64 atoms have been used. For AFM calculations involving more than two Mn atoms, the sign of the magnetic moments on each Mn site are initially distributed randomly. For the cases where the AFM configuration was higher in energy than the FM phase, several other AFM magnetic configurations are tested to make sure that the FM phase indeed has the lowest total energy.

We find that unlike \( \text{Ga}_{1-x}\text{Mn}_y\text{As} \), where the ground state is always FM, in \( \text{Ga}_{1-x}\text{Mn}_x\text{N} \), the magnetic ground
state changes with Mn concentration $x$. At low Mn concentrations, our calculations show that the FM phase of the Mn atoms is more stable, in agreement with other previous theoretical calculations [13]. However, at high Mn concentrations, the lowest energy state becomes AFM. To understand this interesting behavior, we have drawn schematically in Figs. 1 and 2 the Mn $d$ energy levels and the coupling between them in the spin-up and spin down states. Because the spin-orbit coupling is neglected in our discussion, only states with the same spin and symmetry can couple to each other. We find that when Mn atoms are added to GaN, the Mn $3d$ levels are introduced inside the band gap with a $d^4$ configuration. At each spin channel, due to the crystal field splitting, the $t_{2g}$ state is above the $e_g$ state. The crystal field splitting increases when Mn concentration increases due to the coupling between the Mn $t_{2g}$ and N $p_{z}$ states [21].

When the crystal field splitting is relatively smaller than the spin exchange splitting, the majority spin states will be filled, except for the holes in the $t_{2g}$ state, while the minority spin states are empty (Fig. 1). In the FM configuration, the majority spin state of neighboring Mn atoms couple to each other (Fig. 1a), and the level repulsion pushes one level up and one down. Because the $t_{2g}$ state is not fully occupied, the level repulsion puts the holes in the higher energy level, and can thus stabilize the FM phase [17, 22]. The energy gain in this case depends on the position of the Mn-Mn pair and increases with the hole concentration at the $t_{2g}$ level. In the AFM configuration the majority spin state of one Mn atom couples only to the minority spin states of the other Mn atom (Fig. 1b) with opposite moment. This level repulsion push the occupied levels down and the unoccupied levels up, thus can stabilize the AFM phase. The coupling increases when the spin exchange splitting between the occupied and unoccupied states decreases and when the hole concentration at the $t_{2g}$ state decreases.

At low Mn concentration, because the $p$-$d$ repulsion is weak, the exchange splitting is larger than the crystal field splitting (Fig. 1) and the FM interaction is larger than the AFM one. This explains why GaMnN has a FM ground state at low Mn concentration. When the Mn concentration increases, the crystal field splitting increases due to the larger $p$-$d$ repulsion. The dispersion of the $Mn_d$ band also increases. When part of the majority spin $t_{2g}$ levels becomes higher than the minority spin $e_g$ state, charge transfer will occur between these two states, which leads to a reduced spin exchange splitting, as shown in Fig. 2. Because reduced spin exchange splitting will enhance the AFM coupling between the Mn $d$ majority state and the minority state, the system will become increasingly stable in the AFM phase when the Mn concentration increases. It is worth noting that when the crystal field splitting increases further, only the $e_g$ states will be occupied and the system will become paramagnetic, with no magnetic moment at the Mn site.

To test the model discussed above, we plotted in Fig. 3 the total and the projected density of states (DOS) of Ga$_{1-x}$Mn$_x$N with $x = 0.25$ and $x = 0.75$, which has FM and AFM ground states, respectively. From the calculated projected density of states (PDOS), we find that at $x = 0.25$, in the FM case, the holes are created in the spin-up channel, whereas in the AFM phase, the holes are created in both spin channels. The calculated magnetic moment is $3.59 \mu_B$ for the FM phase and $3.32 \mu_B$ for the AFM phase.

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**FIG. 1:** Schematic model for the hole-mediated stabilization of ferromagnetic phase in Ga$_{1-x}$Mn$_x$N with low Mn concentration. In this case, the crystal field splitting is smaller than the exchange splitting. The $t_{2g}$ state is the hybridized state with majority Mn $t_{2g}$ character. For simplicity, the N $t_{2g}$ state is not shown.

**FIG. 2:** Schematic model for the stabilization of antiferromagnetic phase in Ga$_{1-x}$Mn$_x$N with high Mn concentrations. In this case, the crystal field splitting is comparable to the exchange splitting.
Density of States (arb. unit)

-9 -6 -3 0 3 6

Energy (eV)

FIG. 3: Total (solid) and Mn\textit{d} projected (dashed) density of states for Ga\textsubscript{1-x}Mn\textsubscript{x}N with different concentrations and magnetic configurations. FM is for ferromagnetic and AFM for antiferromagnetic. The Fermi energy is at zero energy.

The reason that the FM phase has a larger magnetic moment is because the AFM coupling shown in Fig. 1b mixes filled and empty \(d\) states, thus reducing the magnetic moment in the AFM phase. At \(x = 0.75\), the increase of the Mn concentration also increases the \(p-d\) repulsion, leading to a large overlap between the majority spin \(t_{2d}\) levels and the minority spin \(e_{d}\) levels. Due to the charge transfer between the majority spin and minority spin states, the minority \(e_{d}\) state is partially occupied and the magnetic moment is reduced. In the FM and AFM phases, the calculated magnetic moments are 1.96 and 2.40 \(\mu_B\), respectively. In this case, the FM phase has a smaller moment than the AFM phase, opposite to that at low Mn concentration. This is because at higher concentration, the charge transfer from the spin-up \(t_{2d}\) level to the spin-down \(e_{d}\) level is larger in the AFM phase. We see that the calculated results are consistent with our model.

Our discussion above shows that the change from FM to AFM in GaMnN when Mn concentration increases is due to the increased crystal field splitting and band broadening, which leads to a reduced Mn \(d-d\) spin exchange splitting. We notice that the same effect can also be simulated by applying pressure (or reducing the lattice constant). This is because under pressure, the increased \(p-d\) coupling increases the crystal field splitting.

To test this, we repeated the calculation at \(x = 0.25\), but at a lattice constant that is 10\% smaller than the equilibrium lattice constant. We find that under this compression, the system indeed becomes more stable in the AFM phase, whereas at its equilibrium lattice constant, it is more stable in the FM phase. The magnetic moment in this case is also reduced, being 2.48 \(\mu_B\) for the AFM phase and 2.41 \(\mu_B\) for the FM phase, similar to the case of high concentrations. A similar effect was previously observed in the surface of GaN, where the distance between Mn atoms is smaller.

The model we discussed above (Fig. 1) also shows that the FM phase is more stable when holes are in the Mn \(d\) bands, whereas the AFM phase will be more stable when the holes are filled. To test this, we have calculated the energy difference \(\Delta E_{FM-AFM}\) as a function of the number of electrons added per Mn atom at \(x = 0.25\). The results are plotted in Fig. 4. We find that, indeed, the system becomes more stable in the AFM phase when the added electron reaches 0.62 per Mn atom.

In summary, we have explained the magnetic behavior of GaMnN using a band structure model. We show that because the Mn \(d\) states are inside the GaN band gap, its behavior is quite different from that of GaMnAs. The stability of its magnetic phases can change from FM to AFM, depending on the Mn concentration, pressure, and charge compensation.

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