Properties of wurtzite w -MnN and of w -MnN inclusions in (Ga,Mn)N

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Mn ions in (Ga,Mn)N exhibit a tendency to form pairs, which is enhanced by ferromagnetic Mn–Mn coupling. We also find that segregation of Mn to form MnN clusters in the wurtzite structure of host GaN is energetically favorable. However, our first-principles calculations show that both w -MnN inclusions stretched to fit the lattice constant of GaN, and relaxed ones with the equilibrium lattice constant of MnN are antiferromagnetic, and thus they are not responsible for the high temperature ferromagnetism reported for (Ga,Mn)N. Incorporation of Mn on the N sites is prohibited by the high formation energy of Mn_N. © 2006 American Institute of Physics. [DOI: 10.1063/1.2180874]

Considerable effort is currently devoted to the search for semiconductors with ferromagnetism controlled by band carriers for potential spintronic applications.¹ (Ga,Mn)N attracts particular attention because the predicted Curie temperatures T_C exceed the room temperature.² Recent works have provided a satisfactory picture of the *electronic* properties of an isolated Mn atom in GaN, according to which $d(\text{Mn})$ states are located in the lower part of the band gap.^{3–5} On the other hand, a consistent picture of the *magnetic* properties of (Ga,Mn)N is lacking. The Mn–Mn coupling observed in samples with low Mn content is antiferromagnetic (AFM).⁶ In samples with the Mn content above 1 at %, ferromagnetic (FM) order was observed in n -type and/or insulating,^{7–9} as well as in p -type^{10,11} samples. In some cases, T_C exceeded 300 K. However, typically only a small fraction of about 1–10% of Mn spins participates in ferromagnetism, and ferro- and paramagnetism coexist. Several of these observations are not compatible with the assumption of FM mediated by free carriers in samples with a random distribution of Mn ions.

A possible explanation of the high-temperature FM is the presence of inclusions of magnetic phases of the GaMnN ternary system. In fact, inclusions of AFM GaMn₃N₄,⁹ and of ferrimagnetic Mn₄N and other Mn_xN_y phases,¹² have been experimentally detected, where their identification was facilitated by the perovskite crystalline structure. However, in most works, the presence of inclusions is not reported. This may trivially be due to their absence. On the other hand, another possible explanation is that the dimensions of inclusions and their volume are below the detection limit. For example, Dhar *et al.*¹³ have seen inclusions in (Ga,Mn)N by transmission electron microscope, but not by x-ray diffraction. Moreover, the crystalline structure of inclusions may depend on their size: this is the case of (Ga,Mn)As, where the structure of small pseudomorphic MnAs-rich clusters is zinc blende, but large and relaxed clusters are in their equilibrium NiAs phase.¹⁴ These results have stimulated us to analyze properties of the wurtzite w -MnN inclusions in GaN,

which are more difficult to identify experimentally than inclusions with the perovskite structure. In the last part, we analyze the case of Mn substituting for N. This may lead to formation of MnGa compound, which is a FM material with a high $T_C > 600$ K,¹⁵ or of other phases of the Mn_xGa_y alloy.

The calculations are performed using the code developed in Ref. 16 and ultrasoft pseudopotentials. Previous works have shown that the local spin density approximation (LSDA) and the generalized gradient approximation (GGA) (Ref. 17) for substitutional Mn in both GaAs and GaN give very similar results,^{18,19} and that LSDA provides an excellent description of interstitial Mn in (Ga,Mn)As.²⁰ Here, we use GGA, which is supposed to be superior for magnetic systems, such as MnN. The kinetic energy cutoff for the plane wave basis is 35 Ry. For w -MnN the Brillouin zone summations are converged with a $12 \times 12 \times 10$ Monkhorst–Pack k -point grid. The properties of (Ga,Mn)N with low Mn content are analyzed using a large unit cell with 72 atoms and a $2 \times 2 \times 2k$ -point grid in the folded Brillouin zone. The positions of all atoms in the unit cell are allowed to relax.

We begin with (Ga,Mn)N with 6% of Mn. We find that the alloy is unstable with respect to segregation of Mn. This follows from the fact that the energy of a nearest neighbor Mn_{Ga}–Mn_{Ga} pair is lower by $E_b = 0.5$ eV than that of the distant pair separated by 7.45 Å, out of which about 0.15 eV is due to an increased magnetic coupling. A similar value was found for cubic GaN.²¹ Interestingly, E_b depends on the Fermi energy and is the strongest in intrinsic (Ga,Mn)N with Mn in the $3+(d^4)$ configuration. When the Mn ions are in the Mn²⁺ (d^5) or Mn⁴⁺ (d^3) configurations in codoped samples, E_b is reduced to ~ 0.2 eV by the Coulomb repulsion between charged Mn. This is due to the fact that Mn in GaN is an electrically active impurity with $d(\text{Mn})$ levels in the band gap^{3–5} and it can assume several charge states. This effect does not occur in III–V or II–VI alloys, such as (Ga,In)As, since Ga and In atoms are isovalent. The instability toward segregation generates fluctuations in the alloy composition. In the limiting case, it may result in the formation of w -MnN inclusions, which are investigated below.

Assuming the ideal value of the c/a ratio, we find that the lattice constant of w -MnN (Ref. 22) is $a(\text{MnN}) = 3.11$ Å, which is smaller than $a(\text{GaN}) = 3.21$ Å, by 3.1%.

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FIG. 1. The calculated energy difference ΔE^{A-F} per unit cell between the AFM and FM phases of w -MnN as a function of the lattice constant. The equilibrium lattice constant of MnN is indicated by an arrow.

The calculated parameter u is very close to the ideal value 0.375. To analyze magnetic properties of MnN, we compare the two simplest magnetic orderings, i.e., the FM phase with the type-I AFM phase, in which the Mn spins in consecutive (0001) planes are antiparallel. Therefore, there is a possibility that a different AFM ordering may have a lower energy and thus the region of stability of the FM phase is more restrained than what we find. However, in CdMnTe the energy difference between AFM-I and AFM-III phases is 2 meV/Mn,²³ which does not qualitatively alter our conclusions.

According to our results, magnetic properties of w -MnN critically depend on the lattice constant. The calculated energy difference ΔE^{A-F} between AFM and FM phases and the magnetic moment per Mn atom are shown in Figs. 1 and 2, respectively. Beginning with the small values of the lattice constant (i.e., high compressive strains) we see that w -MnN with $a < 2.82$ Å is nonmagnetic due to the vanishing magnetic moment of Mn. Next, in the range between ~ 2.82 Å and 3.05 Å, the stable phase is FM. With the increase in the lattice constant, the equilibrium order changes from FM to AFM for $a > 3.05$ Å. In particular, w -MnN at the theoretical equilibrium $a = 3.11$ Å is AFM, the energy of the FM phase is higher by 40 meV/Mn, and the magnetic moment per Mn ion is $3.05 \mu_B$. Finally, from Fig. 2, it follows that the magnetic moment in the stable phase is larger than that in the unstable phase, adding to the phase stability.

The results of Figs. 1 and 2 show that inclusions of w -MnN in GaN are AFM, independent of their size (i.e., both small inclusions stretched to fit the lattice constant of GaN and inclusions that are sufficiently large to have the equilibrium lattice constant of MnN). Similarly, we expect the MnN inclusions both in AlN with $a(\text{AlN}) = 3.12$ Å and in InN to be AFM as well.

FIG. 2. (Color online) The calculated magnetic moment per Mn of the FM (black dots) and AFM (open dots) phases as a function of the lattice constant. The equilibrium lattice constants of MnN and GaN are indicated by arrows. The vertical dashed line shows the crossover from AFM to FM phase.

FIG. 3. (Color online) Density of states of w -MnN. The dashed line shows E_F . Spin up and spin down states are displayed with different signs.

An important consequence of the segregation of Mn described in the first part of this letter is its impact on the magnetic coupling. In intrinsic (Ga,Mn)N, Mn–Mn pairs are coupled ferromagnetically.^{5,21} However, the coupling strength strongly depends on the local chemical composition. It even changes sign from FM to AFM already for a relatively small cluster of four neighboring Mn_{Ga} atoms.²¹ The results of Fig. 1 explain this change as being due to the onset of AFM coupling that is present in stretched MnN with the lattice constant of GaN. Thus, the tendency toward segregation is expected to reduce the T_C . Moreover, these results show that a straightforward application of the Ruderman-Kittel-Kasuya-Yoshida-type models of magnetic coupling does not hold in (Ga,Mn)N.

The dependence of the magnetic moment of Mn on the lattice constant may be understood by analyzing the electronic structure of MnN. The $d(\text{Mn})$ states are split by two effects. First, the crystal field splits the $d(\text{Mn})$ orbital quintet into a doublet e and a triplet t_2 . Second, the exchange interaction splits the $d(\text{Mn})$ into spin-up and spin-down states. Both splittings are seen in Fig. 3, which shows the total density of states for $a = 3.13$ Å. The spin-up bands, which extend from 10 to 15 eV, are built up from the $d(\text{Mn})$ orbitals; the exchange-split spin-down bands have energies from 12 to 17 eV. The $p(\text{N})$ -derived bands are positioned below the $d(\text{Mn})$ -derived bands: the spin-up bands with energies from 6 to 9 eV are combinations of $\sim 60\%$ of $p(\text{N})$ hybridized with $\sim 40\%$ of $d(\text{Mn})$. With a decreasing lattice constant the crystal-field splitting increases, while the exchange splitting decreases, and vanishes for $a = 2.8$ Å, when the densities of spin-up and down states are equal. Finally, we mention that the properties of the zinc-blende phase of MnN, relevant in the case of cubic GaN, were considered by Janotti *et al.*²⁴ They find that the lattice constant of MnN is somewhat smaller than that of cubic GaN, and that the magnetic moment per Mn ion is about $1.9 \mu_B$, which is similar to our results for the hexagonal structure.

Finally, we should discuss the possibility of inclusions involving substitution on the anion sublattice. The formation energy E_{form} of, e.g., Mn_N , is given by

$$E_{\text{form}} = [E_{\text{tot}}(\text{Mn}_\text{N}) + \mu(\text{N})] - [E_{\text{tot}}(\text{GaN}) + \mu(\text{Mn})],$$

where E_{tot} is the total energy of the unit cell with or without the defect, and $\mu(\text{N})$ and $\mu(\text{Mn})$ are the chemical potentials of the sources of N and Mn.²⁵ We stress that the quantity of interest is the difference between formation energies of Mn_{Ga} and Mn_N , which does not depend on the value of $\mu(\text{Mn})$. For this reason, we estimate E_{form} assuming elemental sources of

atoms (i.e., bulk Ga and Mn, and the N_2 molecule), and the experimental values of their cohesive energies. We find that $E_{\text{form}}(\text{Mn}_N)=8$ eV in spite of large displacements of the Mn neighbors. Such a high value is typical for antisite defects in III nitrides, due to the large strain energy caused by the large difference between the atomic radii of Mn and N, as well as by the high stiffness of these materials.²⁶ In particular, $E_{\text{form}}(\text{Mn}_N)$ is higher than $E_{\text{form}}(\text{Mn}_{\text{Ga}})=0.7$ eV by as much as 7.3 eV. This indicates that the substitution of N atom by Mn, corresponding to an antisitelike acceptor, is very unlikely, and that the concentration of Mn_{Ga} should be about 6 orders of magnitude higher than that of Mn_N .

The solubility of dopants may be increased by the formation of dopant pairs, if they have a significant binding energy. This tendency may result in segregation effects discussed above. The binding energy for the $\text{Mn}_N\text{--Mn}_N$ pair, about 3 eV, is much larger than that of a $\text{Mn}_{\text{Ga}}\text{--Mn}_{\text{Ga}}$ pair (0.5 eV), but it does not compensate for the high value of E_{form} . Interestingly, we find that the $\text{Mn}_N\text{--Mn}_N$ pair is coupled ferromagnetically with $\Delta E^{\text{A-F}}=0.15$ eV. However, these results indicate that GaMn nanoclusters should not form in bulk (Ga,Mn)N, especially after the growth. They may possibly form at the surface during growth in N-deficient conditions.

In summary, we investigated the possible formation and properties of w -MnN and MnGa inclusions in (Ga,Mn)N using first principles calculations. We find that the formation of MnN inclusions is favorable because of the instability of (Ga,Mn)N with respect to segregation. However, at both the GaN and the MnN equilibrium lattice constants, antiferromagnetic ordering is predicted. The formation of MnGa clusters is not expected due to the very high value of $E_{\text{form}}(\text{Ga}_N)$.

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