

Antiferromagnetic coupling driven by bond length contraction near $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ film surface

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Abstract

Using first principles calculations based on gradient corrected density functional theory we show that Mn atoms, which couple ferromagnetically in bulk $\text{Ga}_{1-x}\text{Mn}_x\text{N}$, couple antiferromagnetically on its surface. This change in magnetic behavior is brought about by a contraction of the Mn-Mn and Mn-N bond lengths which is significantly greater on the surface than in the bulk. The present study provides new insight for explaining the numerous conflicting experimental observations in Mn doped GaN systems.

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Spintronics which exploits electron's spin degree of freedom to store and carry information has the potential to revolutionize the electronics industry. To this end the dilute magnetic semiconductors (DMS) are considered to be an important class of materials. Following the discovery of ferromagnetism in (Ga,Mn)As [1] and the subsequent theoretical prediction [2] that Mn doped GaN could be ferromagnetic at or above room temperature, numerous attempts have been made to synthesize this promising DMS material [3-19]. However, the results have been rather confusing. Not only the reported Curie temperatures [3-14] vary over a wide range (10K-945K), but also it is uncertain whether the ground state of (Ga,Mn)N is ferromagnetic (FM) or antiferromagnetic (AF) [15-21]. It has been found that at low temperature (<10K) the magnetic behavior of the (Ga,Mn)N layers prepared by reactive molecular beam epitaxy show antiferromagnetic characteristics with a spin-glass transition [17]. Magnetic measurement at T=2K using superconducting quantum interference device (SQUID) magnetometer also shows antiferromagnetic coupling between Mn ions in (Ga,Mn)N sample [18]. An understanding of the controversy between FM and AF is both important and challenging [20, 21].

To understand the origin of magnetism in Mn doped GaN, several theoretical studies have recently been performed. However, all the reported calculations predicted ferromagnetism for $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ [22-28], and no study has been reported to explain the antiferromagnetic coupling observed in experiments. We should note that these theoretical calculations correspond to bulk $\text{Ga}_{1-x}\text{Mn}_x\text{N}$

system while the AF ordering seen experimentally corresponds to thin films synthesized using molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD). In addition, previous theoretical studies used either tight binding method or conventional pseudo-potentials and did not fully relax the geometry following Mn substitution. In some studies, the antiferromagnetic configurations were not even considered.

In this letter, we have studied the magnetic properties of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ in both bulk and thin film forms by allowing full structural relaxation. Using density functional theory and generalized gradient approximation for exchange and correlation, we have calculated the total energies, electronic structure, and magnetic coupling for FM and AF coupling in bulk and (11 $\bar{2}$ 0) film in the wurtzite structure. Calculations have also been performed on the (110) film in zinc blende structure, but these results will be published elsewhere. We show that bulk $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ is ferromagnetic with or without structural relaxation. On the contrary, the un-relaxed thin film is ferromagnetic which becomes antiferromagnetic after relaxation.

Calculations of the total energies and forces, and optimizations of geometry were carried out using a plane-wave basis set with the projector augmented plane wave (PAW) method [29] as implemented in the Vienna *Ab initio* Simulation Package (VASP) [30]. The particular advantage of the PAW method over the conventional pseudo-potentials and ultra soft pseudo-potentials is that it can improve the accuracy especially for magnetic systems and for materials including early d-electron or f-electron elements. The energy cutoff was set to 330 eV and the

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convergence in energy and force were 10^{-4} eV and 3×10^{-3} eV/Å, respectively.

We begin the calculations with bulk wurtzite structure. Using a supercell of $\text{Ga}_{14}\text{Mn}_2\text{N}_{16}$ with the experimental lattice constants ($a=b=3.189$, $c=5.185$ Å) and $(6 \times 6 \times 6)$ Monkhorst-Pack [31] k-point mesh we found that without the structure optimization the coupling between these two Mn atoms is ferromagnetic as predicted by previous studies [22-28]. The FM state lies 0.053 eV lower in energy than the AF state. When the structure is fully relaxed without symmetry constraint, Mn-N bond length is found to be 1.99 Å, which is in good agreement with the experimental value of 2.01 ± 0.03 Å [32]. The ground state of the system remained ferromagnetic although the energy difference between AF and FM states is 0.077 eV. Therefore, the structure optimization in bulk did not change the ferromagnetic coupling characteristic. This is due to the fact that the changes in structure for substitutional doping of Mn are minor in bulk.

We now discuss our results on thin film. We have modeled the thin film having $(11\bar{2}0)$ orientation and wurtzite structure by a slab of 9 layers. The corresponding supercell contains 72 atoms (36 Ga and 36 N atoms). To preserve symmetry, the top and bottom layers of the slab were taken to be identical, and each slab was separated from the other by a vacuum region of 10 Å. The central three layers were held fixed at their bulk configuration while the three surface layers on either side of the slab were allowed to relax without any symmetry constraint. K-point convergence was achieved with $(6 \times 4 \times 1)$ grid, and tests with up to $(8 \times 6 \times 2)$ mesh were made. Tests were also made on slabs containing 11 and 13 layers (88 and 104 atoms/supercell respectively). We found that the slab with 9 layers is adequate to mimic the thin film.

In Fig. 1 we show the supercell corresponding to the thin film. The darker numbered atoms are Ga, and the lighter atoms are N. To study the site preference of a *single* Mn atom, we replaced one Ga atom by Mn on the surface layer, the second layer and the third layer and computed the total energies. Note that to preserve symmetry corresponding Ga atom on the lower half of the slab was also replaced by Mn. We find that Mn atom prefers to reside on the surface site which lies 1.37 eV and 1.54 eV below that of the second and third layer, respectively. This is consistent with experiment where Mn atoms doped in GaN migrated to the surface site upon annealing [33].

To study the magnetic coupling between Mn atoms, it is necessary to replace at least *two* Ga atoms in the top half of the supercell by *two* Mn atoms. To preserve symmetry corresponding Ga atoms from the lower half of the slab were also replaced by Mn atoms. This amounts to a super cell consisting of $\text{Ga}_{32}\text{Mn}_4\text{N}_{36}$ (11% Mn concentration). There

are many ways in which this substitution can be achieved. We have considered five different configurations. In Table 1, we show which of the Ga atoms in Fig. 1 were replaced by Mn atoms for each of the five configurations. The relative energies of the ferromagnetic (FM) and antiferromagnetic (AF) states for each of the configuration are listed in Table 1. Note that the energies are measured with respect to the ground state which we find to be antiferromagnetic with Mn atoms residing at nearest neighbor positions around nitrogen atom on the surface layer. The corresponding ferromagnetic state lies 0.40 eV higher in energy. In configurations of II, III, and IV, the energy difference between FM and AF is small, but these configurations are much higher in energy relative to configuration I.

The total densities of states (DOS) for un-relaxed and fully relaxed $\text{Ga}_{34}\text{Mn}_4\text{N}_{36}$ thin film are shown in Figure 2 (a) and (b) respectively. For the un-relaxed surface, the coupling is ferromagnetic and the DOS shows half-metallic behavior similar to that in (Ga,Mn)N bulk. When the surface is fully relaxed, the coupling becomes antiferromagnetic and the spin up and spin down DOS are identical as the total moment of the system is zero. The magnetic moment at each of the Mn site is found to be $3.0 \mu_B$ with opposite spin orientation, which is reduced as compared to the un-relaxed situation ($3.80 \mu_B$). The main contribution to this moment comes from the Mn 3d electrons as can be seen from the partial DOS for one Mn atom in Fig. 2(c). The hybridization between N 2p and Mn 3d reduces the magnetic moment as compared to that of a free Mn atom.

As discussed above, the magnetic coupling between Mn atoms in the bulk is not affected by the relaxation of the structure. However, the situation is different for the surface case. If the surface is not relaxed, the coupling is ferromagnetic, which becomes antiferromagnetic upon optimization. To understand the physics involved, we checked the changes in bond lengths. Due to relaxation, the bond lengths near the film surface are contracted. For example, in the ground state the bond length of Mn-N (1.82 Å) and Mn-Mn (2.98 Å) in the first surface layer is significantly shorter than the corresponding bulk values (1.99 and 3.23 Å, respectively). It has been established that the magnetic couplings between Mn atoms are sensitive to the Mn-Mn distance [34-36]. For example, in orthorhombic and monoclinic-layered LiMnO_2 , the coupling between two Mn atoms change from ferromagnetic phase to antiferromagnetic phase when the Mn-Mn distance changes from 2.82 to 2.79 Å [34]. In a recent report, Hobbs and his co-workers studied the distance dependence of the pairwise exchange interactions in a Heisenberg-like model for bulk Mn and found antiferromagnetic coupling for short interatomic distances which switches to ferromagnetic coupling at larger distances. It is this sensitivity of magnetic

coupling to the atomic distance that makes Mn-based materials display very complicated magnetic structures ranging from nonmagnetic, to anti-ferromagnetic, low spin ferrimagnetic, and high spin ferromagnetic phases [35, 36].

When going from the surface to the interior of the film, the bond length contraction vanishes gradually. Therefore, we can expect an evolution from antiferro- to ferro- magnetic coupling as one penetrates into sub-surface layers. This is exactly what happens. Table 2 lists the changes in magnetic state and Mn-Mn bond length in going from the surface down to the inside of the bulk. Because in the ground state Mn atoms prefer to cluster around a nitrogen atom, we checked the possibility of such clustering for the first three layers. They correspond to the substituted Ga sites identified by (1, 3), (5, 6) and (10, 11) respectively on one side of the slab in Fig. 1. We found that the bond length contraction mainly occurs in the first two layers, and the magnetic couplings are antiferromagnetic. In the third layer, the bond length is close to the bulk, and the coupling switches to being ferromagnetic.

It is important to discuss the effect of supercell construction on the preferred magnetic coupling between Mn atoms in bulk and surface since the limited supercell sizes in both bulk and surface can allow the mirror images of Mn atoms from neighboring supercells to interfere. To clarify these points we have performed additional bulk and surface calculations with larger supercells. In the bulk $\text{Ga}_{14}\text{Mn}_2\text{N}_{16}$ supercell the two Ga atoms on the (0001) plane were replaced by Mn. This gives rise to a continuous line of Mn atoms separated by lines of Ga atoms. We, therefore, used a different (3x3x2) supercell of $\text{Ga}_{34}\text{Mn}_2\text{N}_{36}$ to model the bulk case where the Ga atoms belonging to two adjacent planes linked by a N atom were replaced by Mn. The minimum distance between Mn-N-Mn and its image is 8.0 Å. Using a (5x5x5) Monkhorst-Pack grid we found the results to be nearly same as that given earlier for the smaller supercell, namely, the ground state in the bulk is FM and lies 0.08eV lower in energy than the AF state. The Mn-N bond length is 1.98 Å.

It is also legitimate to wonder if the regular distribution of Mn on the surface layer could also be responsible for the AF coupling. For example, in the ground state configuration in Fig. 1 the Mn atoms form infinite chains along [0001] direction. To examine if the AF coupling in the surface could be due to this chain formation, we repeated the bulk calculations by using a 3x3x1 supercell of $\text{Ga}_{16}\text{Mn}_2\text{N}_{18}$ where Mn atoms also form an infinite chain in the bulk with the same [0001] orientation and the same 11% concentration as in the surface case. The minimum distance between the chain and its image in this bulk case is 8.44 Å. The calculation was performed with 4x4x8 k-point mesh. The ground state was found to be ferromagnetic with the

FM state being 0.07eV lower in energy than the AF state. We found the Mn-N and Mn-Mn bond lengths in the bulk chain are 1.98 and 3.10 Å, which are significantly larger than the corresponding values on the surface. Thus, the change in magnetic coupling when going from surface to bulk is associated with the change in bond length. We also performed calculations for a finite chain consisting of 3 Mn atoms along [0001] direction on the surface by using a large $\text{Ga}_{50}\text{Mn}_6\text{N}_{56}$ supercell and 4x4x2 k-point mesh. The separation between the finite chain and its image in [0001] direction is 5.2 Å. Again AF state is found to be more stable than the FM state with the energy difference of 0.06eV/Mn atom. The Mn-N bond length on the surface layer is 1.82 Å, and the Mn-Mn distance is 2.91 Å. Thus it is clear that the AF coupling in the thin film is due to bond contraction.

From the standpoint of technological applications, doping of Mn beyond 1% is relatively easy only in the case of ‘‘soft’’ semiconductors like GaAs, InAs, or CdTe. This is not the case with ‘‘hard’’ semiconductors like GaN, which needs relatively high growth temperatures to obtain good crystalline quality. In order to obtain a high concentration of Mn, a highly nonequilibrium growth process is necessary. However, under those conditions Mn atoms in GaN will migrate to the surface layers upon annealing [33]. The bond length contraction in the surface layers would result in antiferromagnetic coupling. Thus to maintain ferromagnetic coupling between Mn atoms on the surface layer, their separation distance has to be increased by other means such as choosing appropriate substrate for film growth or surface coating.

In summary, we have shown that in (Ga,Mn)N system Mn-Mn separation distance plays a critical role in their magnetic coupling: The antiferromagnetic coupling on or near the surface layers is driven by Mn-Mn bond length contraction. Thus if the sample growth conditions are such that Mn atoms are buried in the bulk, the coupling is FM. However, if Mn atoms migrate to the surface, the coupling is AF. Our results provide an understanding of the seemingly different experimental results.

Table 1 Relative Energies $E(\text{FM})$ and $E(\text{AF})$ of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ (11 $\bar{2}$ 0) thin film. ΔE is the energy difference between anti-ferromagnetic (AF) and ferromagnetic (FM) states. In the configuration column, the positions of Mn ions are specified, as shown in figure 1.

Table 2 Changes in magnetic state and bond length ($\bar{?}$) when going from the surface to the inside of bulk.

layer	Coupling	R_{Mn-N}	R_{Mn-Mn}
1st	AF	1.822	2.978
2nd	AF	1.920	3.093
3rd	FM	1.951	3.111
Bulk	FM	1.990 2.01±0.03 (exp)*	3.233

*from Ref. [32]

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Configuration	E(FM)	E(AF)	?E
I {1-3, 33-35}	+0.403	0.0	-0.403
II {2-3,33-36}	+1.722	+1.694	-0.028
III {1-2, 35-36}	+1.773	+1.708	-0.065
IV {3-6, 29-33}	+2.550	+2.465	-0.085
V {5-6, 29-30}	+3.438	+3.226	-0.212

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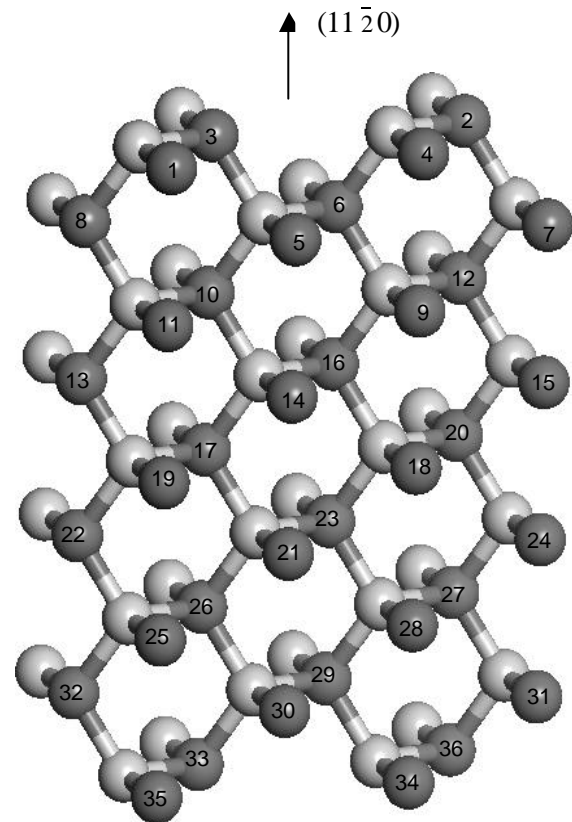


Fig.1. The super cell of $Ga_{1-x}Mn_xN$ ($11\bar{2}0$) slab consisting of 36 Ga and 36 N atoms. The numbered atoms are Ga.

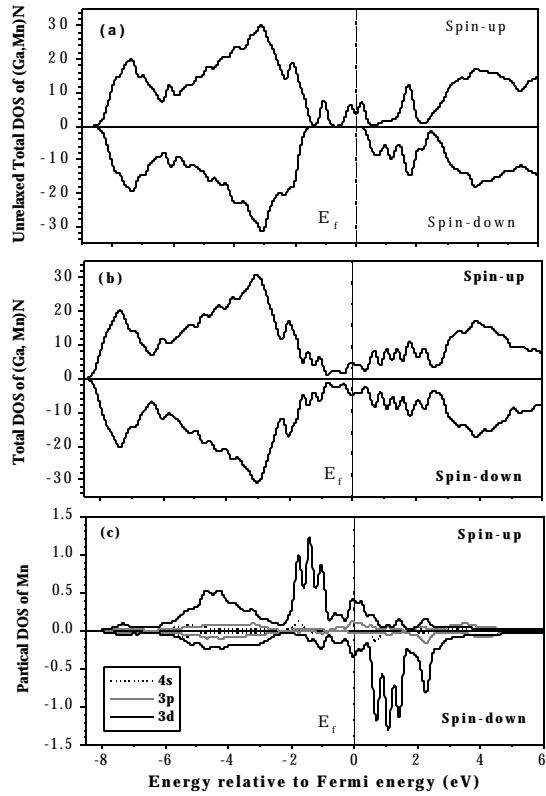


Fig. 2 Total DOS for (a) unrelaxed (FM) and (b) relaxed Ga_{1-x}Mn_xN thin film in the anti-ferromagnetic state. The corresponding partial DOS of Mn atom are shown in (c).