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Ferromagnetic GaN–Cr Nanowires

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ABSTRACT

Using first-principles theory, we predict ferromagnetism in Cr-doped GaN nanowires irrespective of the sites that the Cr atoms occupy. This is in contrast to Mn-doped GaN nanowires in which the magnetic coupling between the Mn atoms is sensitive to the Mn–Mn and Mn–N distances, although the ground state of Mn-doped GaN nanowires is ferromagnetic. Each Cr atom carries a magnetic moment of about 2.5 μ_B. The magnetic moment at the N site, however, is small and is aligned antiferromagnetically to the moments at the Cr atom. The magnetization axis is perpendicular to the axis of the wire, but the anisotropy energy is rather small. The easy solubility of Cr in GaN and the lack of sensitivity of ferromagnetic coupling to Cr distribution suggest that Cr-doped GaN nanowires may be a more suitable system for applications in spintronics than Mn-doped GaN nanowires.

Dilute magnetic semiconductor (DMS) materials have become a topic of great current interest because both the charge, arising out of the s and p electrons of the semiconductor, and spin, arising out of the magnetic impurity, can be used in novel spintronics devices. Much of the recent work, therefore, has focused on finding materials that are not only ferromagnetic (FM) at room temperature but also those in which the doping of transition metals is easy. The material that has attracted the most attention is Mn-doped GaN because it was predicted to be FM at room temperature.[1,2] However, the initial promise of this material has not been realized because the magnetic properties of Mn-doped GaN are found to depend strongly on the sample preparation conditions. Various experimental groups have reported rather conflicting results ranging from FM[3−11] to antiferromagnetic (AFM) and spin glass behavior[12−16] of the material. In addition, the reported Curie temperature of materials varies over a wide range (10−945 K).[3−11] These results are believed to be due to structural defects such as clustering that may exist in thin film materials.[12,17,18]

Recently, focus has shifted to low dimensional nanostructures such as single-crystalline nanowires of Mn-doped GaN. Several groups[19−22] have succeeded in synthesizing Mn-doped GaN nanowires having diameters of 10−100 nm and lengths up to tens of microns by using the reaction of Ga_2O vapor with NH_3 in the presence of multiwalled carbon nanotubes. These materials are free of defects, perfectly single crystalline, and have a homogeneous distribution of Mn. More importantly, the Mn-doped GaN nanowires are FM with a Curie temperature of up to 300 K.[19−22] The DMS nanowires are expected to have interesting magnetoelectronic properties because of the confinement of carriers in the radial direction and large magnetic anisotropy energy. Using first-principles theory, we have shown recently that Mn-doped GaN nanowires with diameters of 0.45 and 1 nm are FM. However, this FM coupling between the Mn spins, driven by a double exchange mechanism, is sensitive to the Mn−Mn and Mn−N distances. For some distributions of Mn atoms, the materials can be AFM, although they are higher energy states.

In this Letter we report a theoretical study of the magnetic properties of Cr-doped GaN nanowires. In contrast to the Mn-doped GaN nanowires, the GaN/Cr nanowire is found to be FM irrespective of the distribution of the Cr atoms. In addition, the binding energy of Cr to the GaN wire is larger than that of Mn, suggesting that it may be possible to dope the GaN nanowire with Cr more easily than with Mn. Thus, the GaN/Cr nanowire could prove to be a robust system for applications. In the following, we describe our theoretical procedure and results.

The GaN nanowire has been created from a ($7 \times 7 \times 2$) supercell of GaN having the wurtzite structure (see Figure 1a). We have removed the atoms outside the circled area in Figure 1a and replaced them with a vacuum space of about 12 Å along the $[10\bar{1}0]$ and $[01\bar{1}0]$ directions. The supercell consists of 96 atoms ($Ga_{48}N_{48}$). The wire extends to infinity along the [0001] direction through the periodic repetition of the supercell (as shown in Figure 1b). The 12-Å vacuum space ensures that the wires in neighboring supercells do not interact with each other. The diameter of the wire in

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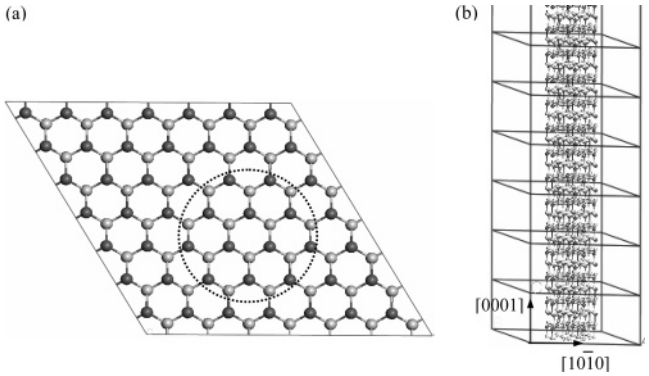

Figure 1. (a) Top view of a 7 × 7 × 2 GaN supercell having wurtzite structure. (b) $Ga_{48}N_{48}$ supercell that has infinite length along the [0001] direction.

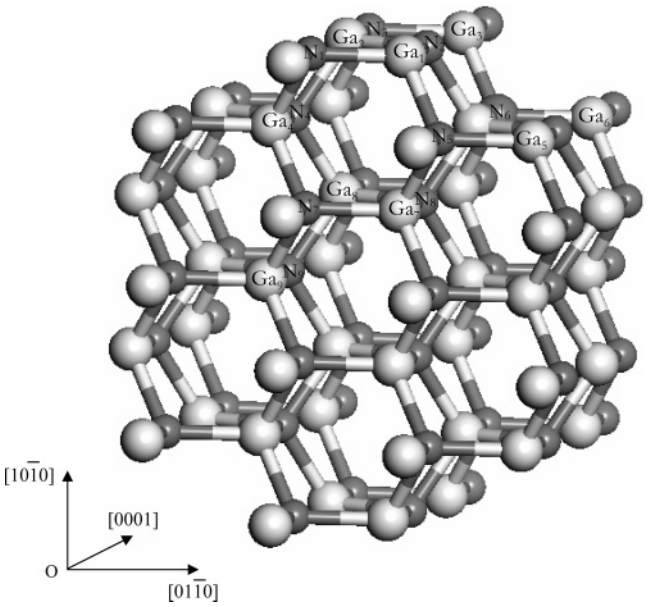

Figure 2. Schematic representation of the GaN nanowire supercell ($Ga_{48}N_{48}$). The lighter spheres are Ga, and the darker spheres are N.

Figure 1b is 1 nm. Two of the Ga atoms in the supercell were selectively replaced by Cr to study their magnetic coupling. This corresponds to a Cr concentration of 4.2%. In Figure 2 we present the $Ga_{48}N_{48}$ supercell. Some of the Ga and N atoms are numbered to facilitate our discussion as we replace various Ga sites by Cr.

The equilibrium structure of the supercell with and without Cr substitution, the total energies, the electronic structure, and the magnetic properties of the GaN/Cr nanowire were calculated using spin polarized density functional theory and generalized gradient approximation for exchange and correlation.[23] The calculations were carried out using the Vienna ab initio simulation package (VASP) and plane wave basis sets.[24] The projector augmented wave (PAW) potentials[25] were used for Ga, N, and Cr. These potentials are known to be more accurate than conventional or ultrasoft pseudopotentials in treating magnetic systems. The energy cutoff was set at 300 eV and the convergence in energy and force was set at 10^{-4} eV and 10^{-3} eV/Å, respectively. The geometries of the supercells with and without Cr doping were fully optimized without using any symmetry constraint. Because it is a priori not clear which Ga sites the Cr atoms would replace, we have studied eight different configurations by selectively replacing two Ga atoms by Cr. These are identified in Table 1. For example, configuration I corresponds to substituting two Ga atoms at sites marked Ga_7 and Ga_9 in Figure 2 with Cr. For each configuration, we also calculated the total energies of the FM and AFM states with and without full geometry optimization.

Table 1. The Energy Difference ΔE_0 (ΔE) between AFM and FM States ($\Delta E = E_{AFM} - E_{FM}$, in eV), the Relative Energy $\Delta\epsilon_0$ ($\Delta\epsilon$) (in eV) Calculated with Respect to the Ground State Configuration VI without (with) Geometry Optimization, and the Optimized the Cr−N and Cr−Cr Distances (in Å)

configurations	ΔE_0	$\Delta\epsilon_0$	ΔE	$\Delta\epsilon$	coupling	d_{Cr-N}	d_{Cr-Cr}
I (Ga_7,Ga_9)	0.155	1.679	0.274	1.539	FM	1.896	3.103
II (Ga_7,Ga_8)	0.097	1.883	0.193	1.786	FM	1.889	3.096
III (Ga_7,Ga_1)	0.109	0.929	0.079	0.978	FM	1.827	3.114
IV (Ga_1,Ga_4)	0.106	0.349	0.095	0.591	FM	1.827	3.113
V (Ga_1,Ga_5)	0.088	0.103	0.064	0.152	FM	1.821	3.272
VI (Ga_1,Ga_2)	0.132	0.000	0.130	0.000	FM	1.819	3.030
VII (Ga_1,Ga_3)	0.020	0.162	0.010	0.262	FM	1.829	5.190
VIII (Ga_1,Ga_6)	0.006	0.168	0.007	0.247	FM	1.821	5.517

We begin the discussion of our results by first concentrating on the atomic relaxation of the pure GaN nanowire. The total energy of the relaxed cell was found to be 10.628 eV lower than the unrelaxed one, corresponding to an energy gain of 0.221 eV/Ga−N dimer. The relaxed Ga−N bond length on the outermost surface layer along the [0001] direction (i.e., Ga_1-N_2 in Figure 2) is 1.869 Å, which corresponds to a contraction of −5.89% from the bulk value. The Ga−N bond lengths in the inner two layers (i.e., Ga_4-N_4, Ga_7-N_8), however, are 1.974 Å and 1.984 Å, which correspond to a contraction of only −0.6 and −0.05%, respectively. The distance between Ga and N atoms that form a zigzag chain approximately along the [01$\bar{1}$0] direction on the outermost surface (i.e., Ga_1-N_1 or Ga_2-N_2) changes from 1.930 to 1.891 Å, amounting to a contraction of −2.02%. The corresponding angles $\angle N_1-Ga_1-N_2 = \angle Ga_1-N_2-Ga_2$ change from 108.40° to $\angle N_1-Ga_1-N_2 = 118.34°$ and $\angle Ga_1-N_2-Ga_2 = 105.93°$. It is obvious that the relaxation of the atoms in the inner sites is negligible as compared to that in the outermost surface layer. The total electronic density of states (DOS) for spin-up and spin-down electrons corresponding to the pure GaN nanowire supercell is plotted in Figure 3a. It shows that the Fermi level is located in the gap region and the DOS curves for spin-up and spin-down are identical. Thus the GaN nanowire is a nonmagnetic semiconductor.

In Table 1 we present the main results of our paper. In column I we indicate the Ga atoms that were substituted by Cr. In columns II and IV we list the energy difference, ΔE, between the FM and AFM states for all these configurations without and with full geometry optimization, respectively. Configuration VI, in which the two Cr atoms form nearest neighbors on the outer surface layer of the GaN nanowire, is found to be the lowest energy configuration in which the Cr atoms are coupled ferromagnetically. The AFM config-

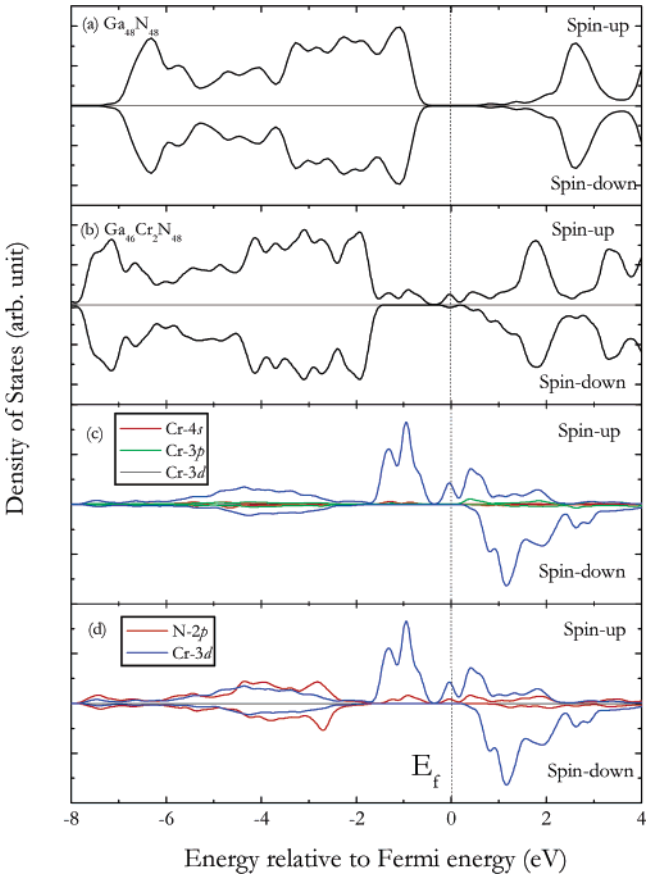

Figure 3. (a) Total DOS corresponding to the pure $Ga_{48}N_{48}$ nanowire surpercell, (b) total DOS of the Cr-doped GaN nanowire, (c) partial spin DOS of Cr in $Ga_{46}Cr_2N_{48}$, (d) orbital resolved spin DOS of Cr 3d and N 2p in $Ga_{46}Cr_2N_{48}$.

uration lies 0.132 eV higher in energy. Using this ground-state energy as the reference, we have tabulated the relative energies, $\Delta\epsilon$, of all of the other configurations in columns III and V without and with geometry optimization. Thus, comparison of the results in columns II and III with those in columns IV and V indicate the effect of relaxation. We note that the relaxation does not affect the magnetic properties qualitatively. The preferred magnetic coupling and the distance between Cr and N and that between Cr and Cr are given in the last three columns of Table 1. It is important to realize that irrespective of the sites that the Cr atoms occupy in the supercell in Figure 2 the FM state is lower in energy than the AFM state. The energy difference diminishes as the Cr−Cr distance increases and nearly vanishes when the Cr atoms are more than 5 Å apart. At this distance, the magnetic coupling is small because this is mediated mainly by the N atom that connects the two Cr atoms.

In Table 2 we list the magnetic moments at each Cr and its nearest-neighbor N and Ga atoms for all eight configurations. In the brackets, the moment located on 3d orbitals of Cr atoms are given. The magnetic moments at the two Cr sites are slightly different because these atoms are not equivalent and have different Cr−N distances. In the ground state, that is, the FM state of configuration VI, the Cr atom replacing the Ga_1 site carries a moment of 2.571 μ_B, which arises mainly from the Cr 3d orbitals (2.50 μ_B). The neighboring N atom (N_2 in Figure 2) is polarized antiferromagnetically with a magnetic moment of −0.168 μ_B. The Cr atom replacing the Ga_2 site carries a moment of 2.588 μ_B, which comes mainly from the Cr 3d orbital (2.512 μ_B). The overall magnetic moment at the Cr site, therefore, is about 2.5 μ_B and these are antiferromagnetically coupled to a small moment at the N site. Similar results were also found in Cr_2N cluster in which the two Cr atoms couple ferromagnetically to each other but antiferromagnetically to the N atom.[26,27]

To gain an understanding of the electronic structure of the GaN/Cr nanowire and the origin of the FM coupling between Cr atoms, we plot the total DOS of the $Ga_{46}Cr_2N_{48}$ supercell in Figure 3b. The orbital resolved partial DOS at the Cr and N sites are plotted in Figure 3c and d, respectively. We note from Figure 3b that the Fermi energy passes through the gap in the spin down DOS and the system is half-metallic and FM. As stated before, much of the magnetic moment resides at the Cr site and originates from the Cr 3d states (see Figure 3c). The FM coupling between the Cr atoms is mediated by the N atom as can be seen from the overlap in the DOS between the N 2p and Cr 3d states especially occurring in the majority orbitals, as shown in Figure 3d. It is well known that a Cr atom has five unpaired electrons that align to give spin $S = {}^5/_2$ in the 3d level. Similarly, N forms $S = {}^3/_2$ states in the 2p orbitals according to Hund's rule. In the ground state of the Cr-doped GaN nanowire, the two Cr atoms are too far apart (3.030 Å) to allow significant direct overlap of the unpaired electron wave functions, thus ruling out the possibility of a substantial direct exchange mechanism. Hence, one can suggest a Cr−Cr indirect exchange interaction via the N atom. The coupling involves the N 2p orbitals polarized antiferromagnetically with respect

Table 2. Magnetic Moments (in μ_B) at Each Cr and Its nearest Neighbor N and Ga Sites for Each Configuration before (μ_0) and after (μ) Geometry Optimizations[a]

configurations	μ_{0Cr1} (μ_0^d)	μ_{0Cr2} (μ_0^d)	μ_{Cr1} (μ^d)	μ_{Cr2} (μ^d)	μ_N	μ_{Ga}
I	2.341 (2.299)	2.329 (2.288)	2.491 (2.438)	2.490 (2.437)	−0.030	0.026
II	2.350 (2.307)	2.266 (2.220)	2.513 (2.455)	2.516 (2.468)	−0.0121	0.025
III	2.658 (2.599)	2.250 (2.215)	2.513 (2.448)	2.374 (2.334)	−0.050	0.057
IV	2.745 (2.686)	2.089 (2.065)	2.647 (2.576)	2.075 (2.047)	−0.025	0.024
V	2.678 (2.608)	2.680 (2.610)	2.570 (2.498)	2.570 (2.422)	−0.090	0.033
VI	2.725 (2.662)	2.686 (2.622)	2.571 (2.500)	2.588 (2.512)	−0.168	0.026
VII	2.652 (2.589)	2.652 (2.601)	2.560 (2.487)	2.560 (2.416)	−0.020	0.026
VIII	2.631 (2.572)	2.633 (2.573)	2.542 (2.474)	2.531 (2.463)	−0.020	0.042

[a] The moments arising out of 3d orbitals are shown in parentheses.

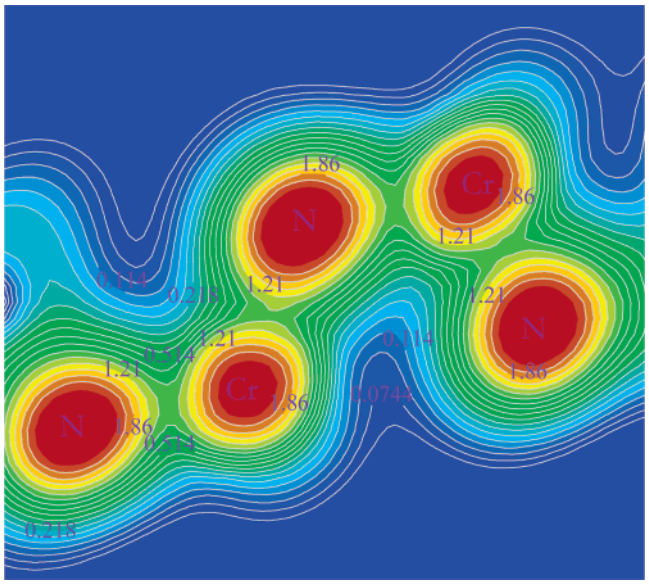

Figure 4. Charge density distribution of $Ga_{46}Cr_2N_{48}$ in the plane containing two Cr atoms and neighboring N atoms forming the zigzag chain. The charge densities in $Å^{-3}$ are listed on a few of the contours.

to the two Cr 3d orbitals. This causes a lowering of energy and makes the two Cr atoms couple ferromagnetically to each other. Therefore, the mechanism responsible for the FM coupling can be classified as the double exchange mechanism.[28,29] In Figure 4 we plot the charge density distribution of the $Ga_{46}Cr_2N_{48}$ supercell in a plane containing the two Cr atoms and neighboring N atoms forming a zigzag chain. Note that there is a considerable charge overlap between the Cr and N atoms unlike that between Ga and N atoms. This picture supports our earlier finding in Figure 3d in which the N 2p and Cr 3d orbitals overlap. It is very encouraging to note the recent experimental findings of room-temperature FM in Cr-doped GaN thin films.[30,31]

We have also calculated the anisotropic energies by orienting the magnetization axis along the $[10\bar{1}0]$, $[01\bar{1}0]$, and [0001] directions. We find the preferred direction of magnetization to be along the $[10\bar{1}0]$ direction, which is perpendicular to the axis of the wire. The energies corresponding to the magnetization along the [0001] and $[01\bar{1}0]$ directions are, respectively, 0.3 and 0.5 meV higher than that along the $[10\bar{1}0]$ direction.

In conclusion, we have shown that the GaN/Cr nanowire is FM. The magnetic moments at the Cr atoms are about 2.5 μ_B and these are coupled antiferromagnetically to a small moment at the N site. The FM coupling results from a charge overlap between the N 2p and Cr 3d states and the coupling is driven by a double exchange mechanism. In contrast to the GaN/Mn nanowires, we find that the Cr atoms are coupled ferromagnetically irrespective of the sites that Cr atoms occupy. The energy gain in replacing two Ga sites by Cr is 2.53 eV, which is substantially larger than replacing two Ga sites by Mn, namely, 0.54 eV. Thus, GaN/Cr nanowires may be a more robust system for applications in spintronics compared to GaN/Mn nanowires because it is not only easy to dope Cr into GaN but the FM coupling may also be less sensitive to sample conditions. Experimental verification of our prediction is eagerly awaited.

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