Ferromagnetic GaN–Cr Nanowires

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Received June 15, 2005; Revised Manuscript Received June 24, 2005

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 μB. 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 FM3–11 to antiferromagnetic (AFM) and spin glass behavior12–16 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 groups19–22 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 Ga2O vapor with NH3 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 × 7 × 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 [1010] and [0110] directions. The supercell consists of 96 atoms (Ga48N48). 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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The calculations were carried out using the Vienna generalized gradient approximation for exchange and correlation. The magnetic properties of the GaN/Cr nanowire were studied by replacing various Ga sites by Cr. Ga and N atoms are numbered to facilitate our discussion as we replace various Ga sites by Cr.

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 Ga₄₈N₄₈ supercell that has infinite length along the [0001] direction.

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. The calculations were carried out using the Vienna ab initio simulation package (VASP) and plane wave basis sets. The projector augmented wave (PAW) potentials 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 Ga₇ and Ga₉ 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 $\Delta E_0$ ($\Delta E$) between AFM and FM States ($\Delta E = E_{AFM} - E_{FM}$, in eV), the Relative Energy $\Delta E_0$ ($\Delta e$) (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).

<table>
<thead>
<tr>
<th>configurations</th>
<th>$\Delta E_0$</th>
<th>$\Delta e$</th>
<th>$\Delta E$</th>
<th>$\Delta e$ coupling</th>
<th>$d_{Cr-N}$</th>
<th>$d_{Cr-Cr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (Ga₇,Ga₉)</td>
<td>0.155</td>
<td>0.274</td>
<td>1.539</td>
<td>FM</td>
<td>1.896</td>
<td>3.103</td>
</tr>
<tr>
<td>II (Ga₇,Ga₈)</td>
<td>0.097</td>
<td>0.193</td>
<td>1.768</td>
<td>FM</td>
<td>1.889</td>
<td>3.096</td>
</tr>
<tr>
<td>III (Ga₇,Ga₁)</td>
<td>0.109</td>
<td>0.079</td>
<td>0.978</td>
<td>FM</td>
<td>1.827</td>
<td>3.114</td>
</tr>
<tr>
<td>IV (Ga₇,Ga₈)</td>
<td>0.106</td>
<td>0.095</td>
<td>0.591</td>
<td>FM</td>
<td>1.827</td>
<td>3.113</td>
</tr>
<tr>
<td>V (Ga₇,Ga₉)</td>
<td>0.088</td>
<td>0.064</td>
<td>0.152</td>
<td>FM</td>
<td>1.821</td>
<td>3.272</td>
</tr>
<tr>
<td>VI (Ga₁,Ga₂)</td>
<td>0.132</td>
<td>0.130</td>
<td>0.000</td>
<td>FM</td>
<td>1.819</td>
<td>3.030</td>
</tr>
<tr>
<td>VII (Ga₁,Ga₃)</td>
<td>0.020</td>
<td>0.010</td>
<td>0.262</td>
<td>FM</td>
<td>1.829</td>
<td>5.190</td>
</tr>
<tr>
<td>VIII (Ga₁,Ga₆)</td>
<td>0.006</td>
<td>0.007</td>
<td>0.247</td>
<td>FM</td>
<td>1.821</td>
<td>5.517</td>
</tr>
</tbody>
</table>

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, $\Delta E$, 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 FM config-
The magnetic moment 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 Ga1 site carries a moment of 2.571 \( \mu_B \), which arises mainly from the Cr 3d orbitals (2.50 \( \mu_B \)). The neighboring N atom (N2 in Figure 2) is polarized antiferromagnetically with a magnetic moment of −0.168 \( \mu_B \). The Cr atom replacing the Ga3 site carries a moment of 2.588 \( \mu_B \), which comes mainly from the Cr 3d orbital (2.512 \( \mu_B \)). The overall magnetic moment at the Cr site, therefore, is about 2.5 \( \mu_B \) and these are antiferromagnetically coupled to a small moment at the N site. Similar results were also found in Cr2N 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\(_2\)N\(_{48}\) 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 \( S = \frac{5}{2} \) in the 3d level. Similarly, N forms \( S = \frac{3}{2} \) 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 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 Ga1 site carries a moment of 2.571 \( \mu_B \), which arises mainly from the Cr 3d orbitals (2.50 \( \mu_B \)). The neighboring N atom (N2 in Figure 2) is polarized antiferromagnetically with a magnetic moment of −0.168 \( \mu_B \). The Cr atom replacing the Ga3 site carries a moment of 2.588 \( \mu_B \), which comes mainly from the Cr 3d orbital (2.512 \( \mu_B \)). The overall magnetic moment at the Cr site, therefore, is about 2.5 \( \mu_B \) and these are antiferromagnetically coupled to a small moment at the N site. Similar results were also found in Cr2N cluster in which the two Cr atoms couple ferromagnetically to each other but antiferromagnetically to the N atom.26,27

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![Figure 3.](image-url)
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. In Figure 4 we plot the charge density distribution of the Ga56Cr2N48 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.

We have also calculated the anisotropic energies by orienting the magnetization axis along the [1010], [0110], and [0001] directions. We find the preferred direction of magnetization to be along the [1010] direction, which is perpendicular to the axis of the wire. The energies corresponding to the magnetization along the [0001] and [0110] directions are, respectively, 0.3 and 0.5 meV higher than that along the [1010] direction.

In conclusion, we have shown that the GaN/Cr nanowire is FM. The magnetic moments at the Cr atoms are about 2.5 \( \mu_B \) 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.

Acknowledgment. The work was supported in part by a grant from the Office of Naval Research. We thank the staff of the Center for Computational Materials Science, the Institute for Materials Research, Tohoku University (Japan), for their continuous support of the HITACH SR8000 supercomputing facility.

References


Figure 4. Charge density distribution of Ga56Cr2N48 in the plane containing two Cr atoms and neighboring N atoms forming the zigzag chain. The charge densities in Å2 are listed on a few of the contours.