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## Mg-doped GaN nanostructures: Energetics, magnetism, and H<sub>2</sub> adsorption

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Using density functional theory and generalized gradient approximation for exchange and correlation potential we show that Mg-doped GaN nanocages and nanotubes can be magnetic with Mg-contributed spins distributed over the neighboring N sites. Mg atoms show no tendency for clustering due to the positive charge residing on them; they can trap hydrogen in molecular form via the charge polarization mechanism. The binding energies of hydrogen lie in the range of 0.1–0.2 eV/H<sub>2</sub>, which are ideal for storage applications under ambient thermodynamic conditions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3067836]

Magnesium (Mg), the seventh most abundant element on earth, has many attractive properties. It is nontoxic, is cheaper than many other metals, can be recycled, and its metallurgy is easy. Consequently, Mg-based materials have received considerable attention. Among them, Mg-doped *p*-type GaN is particularly interesting as it has potential applications in nanoscale electronics, optoelectronics, and biochemical sensing. GaN, a wide band gap (3.4 eV) semiconductor, also has applications in light-emitting diodes, ultraviolet or blue lasers, full color displays, etc.<sup>1</sup> It has been shown<sup>2</sup> that *p*-type GaN can greatly improve the performance of GaN-based devices. Mg is a suitable dopant for *p*-type GaN. Since the ionic radius of Mg is comparable with that of Ga, Mg doping can be expected to eliminate self-compensation effects. Thus, synthesis of Mg-doped *p*-type GaN for fabrication of optoelectronic devices has been hotly pursued.<sup>3–7</sup> For example, Li *et al.*<sup>4</sup> prepared Mg-doped GaN powders using direct nitridation of Ga<sub>2</sub>O<sub>3</sub> under a flowing NH<sub>3</sub> gas. They found that the powders exhibit bright blue-violet emission at around 3.05 eV. Garcia *et al.*<sup>5</sup> developed a new and inexpensive method for growing highly luminescent Mg-doped GaN thin films. Lam *et al.*<sup>6</sup> synthesized a Mg-doped GaN cap layer for photodetectors. Dussaigne *et al.*<sup>7</sup> established a method for doping high levels of Mg in GaN layers grown at low temperature.

It has recently been shown that a Mg<sup>2+</sup> ion can bind a large amount of hydrogen in molecular form.<sup>8</sup> The mechanism responsible for this binding is due to charge polarization discussed by Rao and Jena more than a decade ago.<sup>9</sup> Although MgH<sub>2</sub> hydride contains high wt % of hydrogen (7.6%), the strong bonding between Mg and H atoms results in poor kinetics. Thus, methods for embedding Mg atoms in substrates/matrices to make them ionlike for adsorption of hydrogen molecules have become a new subject in materials design.

In this study, we have explored the effect of Mg doping on the magnetism and hydrogen adsorption in GaN nanocages and nanotubes. Our main objectives are to study the energetics of Mg doping, namely, is it exothermic or endothermic? When Mg is substitutionally doped in GaN, holes and spins from the unpaired electrons are concurrently introduced since Mg has one valence electron less than Ga. How are these Mg dopants and the introduced spins distributed in the system? Do Mg atoms prefer to cluster? Furthermore, due to the charge transfer, Mg atoms would behave like ions when doped in GaN at Ga sites. Do these Mg ions adsorb H<sub>2</sub> molecules as has been found for free Mg<sup>2+</sup> ions? In this letter we provide a systematic theoretical study of the energetics, magnetism, and H<sub>2</sub> adsorption of Mg-doped GaN nanocages and nanotubes.

Our study is based on first-principles calculations using density functional theory and generalized gradient approximation for exchange and correlation. We used the supercell approach where the clusters were surrounded by 15 Å of vacuum space along the *x*, *y*, and *z* directions. The  $\Gamma$  point was used to represent the Brillouin zone because of the large supercell. The total energies and forces and geometry optimizations were carried out using a plane-wave basis set with the projector augmented plane-wave method<sup>10</sup> as implemented in the Vienna *ab initio* simulation package (VASP).<sup>11</sup> The PW91 form<sup>12</sup> was used for the exchange and correlation potential. The geometries of the nanostructures were optimized without symmetry constraint using the conjugate-gradient algorithm. The energy cutoff and convergence in energy and force were set to 400 eV, 10<sup>-4</sup> eV, and 1 × 10<sup>-3</sup> eV/Å, respectively. The accuracy of our numerical procedure for GaN and hydrogen-related systems has been demonstrated in our previous work.<sup>13–16</sup> For Mg atom, we obtained the ionization potential of 7.892 eV, in good agreement with the experimental value of 7.646 eV.<sup>17</sup>

We begin our discussion with the Ga<sub>12</sub>N<sub>12</sub> nanocage, which was found to be composed of six four-membered rings having *T<sub>h</sub>* symmetry,<sup>18</sup> as shown in Fig. 1(a). There are two

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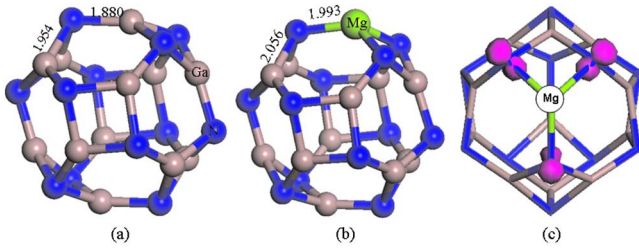


FIG. 1. (Color online) (a) Geometry of  $\text{Ga}_{12}\text{N}_{12}$ . (b) Geometry and (c) spin density of  $\text{MgGa}_{11}\text{N}_{12}$ . The lighter (brown) spheres are Ga and the darker (blue) spheres are N.

unequivalent Ga–N bonds: the Ga–N bond inside the four-membered ring has a length of 1.954 Å, while that between the four-membered rings has a length of 1.880 Å. When one Ga atom is replaced by Mg, the energy cost is found to be 1.818 eV, and the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is reduced from 1.532 to 0.103 eV in the pure  $\text{Ga}_{12}\text{N}_{12}$  cage, indicating that Mg doping greatly changes the electronic structure of GaN. This is in agreement with experimental findings that Mg doping can improve the conducting behavior of GaN.<sup>2</sup> Mg doping also results in some changes in bond length [see Fig. 1(b)] due to the small difference between the atomic size of Ga and Mg. The unpaired electron in  $\text{Mg–Ga}_{11}\text{N}_{12}$  introduces a spin moment of  $1.0\mu_B$ , which is distributed among the three N sites adjacent to the Mg site, as shown in Fig. 1(c).

Next we studied the distribution of Mg atoms and the effect of Mg concentration on the introduced magnetic moment in the Mg-doped GaN case. To this end, we first considered two different configurations [see Figs. 2(a) and 2(b)] where two Ga atoms are replaced by Mg at different sites. In the first configuration, the Mg–Mg distance is the shortest (2.915 Å), while in the second it is the longest (6.393 Å). We find that the second configuration is 0.130 eV lower in energy than the first one, and both of them carry a magnetic moment of  $2\mu_B$ . So it is clear that there is no tendency for Mg atoms to form clusters in the nanocage and the two spins introduced by Mg are ferromagnetically coupled. Based on this finding, we then doped three Mg atoms separately in the cage [Fig. 2(c)] and calculated the magnetic coupling between the three introduced spins. In the  $\text{Mg}_3\text{Ga}_9\text{N}_{12}$  cage, the induced moment is found to be  $3.0\mu_B$ , confirming that the coupling remains ferromagnetic. The magnetic moments are again distributed over the neighboring N sites.

To further study the effect of geometry and dimensionality on magnetism in Mg-doped GaN, we performed calculations on nanotubes. We chose the (5, 5) configuration of GaN tubes with hydrogen termination at both ends of the tube. This leads to a  $\text{Ga}_{45}\text{N}_{45}\text{H}_{20}$  supercell. We first replaced

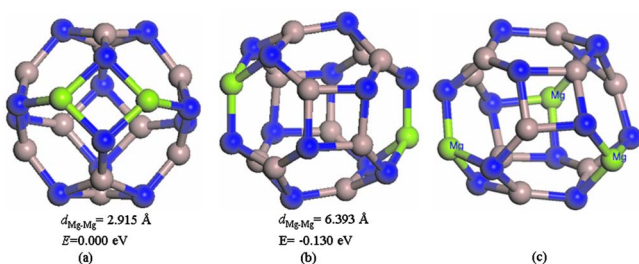


FIG. 2. (Color online) [(a) and (b)] Two configurations for  $\text{Mg}_2\text{Ga}_{10}\text{N}_{12}$ . (c) Configuration for  $\text{Mg}_3\text{Ga}_9\text{N}_{12}$ .

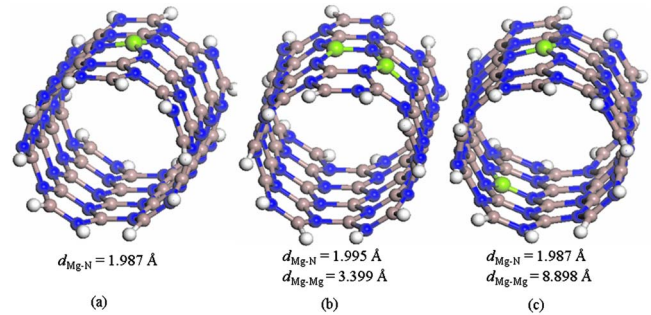


FIG. 3. (Color online) Geometries of one and two Mg atom doped GaN nanotube.

one Ga atom with Mg in the tube [Fig. 3(a)]. It was found that the energy cost for this replacement is 2.342 eV, which is 0.506 eV more than that in the  $\text{MgGa}_{11}\text{N}_{12}$  cage. We then replaced two Ga atoms with Mg at different sites, generating two configurations with Mg–Mg distances of 3.399 and 8.898 Å, respectively [Figs. 3(b) and 3(c)]. We found that the energy difference between these two configurations is only 0.02 eV, namely, the two configurations are energetically degenerate. This indicates that Mg can be homogeneously doped in GaN nanotubes. The induced spin moment for the  $\text{Mg}_2\text{Ga}_{43}\text{N}_{45}\text{H}_{20}$  nanotube was found to be  $2\mu_B$ , indicating that the spins couple ferromagnetically, as in the Mg-doped GaN nanocage. We note that the HOMO-LUMO gap changes dramatically when the Ga atom is replaced with Mg in the tube.  $\text{Ga}_{44}\text{N}_{45}\text{H}_{20}$  has a gap of 2.248 eV, indicating the semiconducting properties and the electronic stability of the nanotube. However, the HOMO-LUMO gap is reduced to 0.05 eV, exhibiting metallic properties when one Mg atom is introduced into the supercell ( $\text{MgGa}_{44}\text{N}_{45}\text{H}_{20}$ ). Of further note, the Mg doping makes the neighboring N atoms more reactive, as the frontier orbitals of the HOMO and LUMO are found to be predominantly contributed from the N sites.

Next we studied the adsorption of  $\text{H}_2$  molecules. We first determined if the GaN nanocage can adsorb hydrogen since it has been demonstrated<sup>9</sup> that a charged metal atom can bind a large amount of hydrogen in nearly molecular form due to the charge polarization mechanism. For example, a  $\text{Li}^+$  ion can adsorb<sup>9</sup> six  $\text{H}_2$  molecules with a binding energy of around 0.2–0.3 eV/ $\text{H}_2$ . Although the binding in GaN nanocages is primarily covalent, we first performed calculations to determine if a pure  $\text{Ga}_{12}\text{N}_{12}$  nanocage can adsorb hydrogen. We found that when the first  $\text{H}_2$  is directly introduced at the Ga site, the hydrogen molecule moves away from the Ga site to a distance of 2.530 Å after geometry optimization, and the binding energy is only 0.026 eV/ $\text{H}_2$ . This is a characteristic of physisorption. However, the situation changes when a Mg atom replaces a Ga site. As mentioned before, the Mg atoms, when doped at the Ga site in GaN, carry a positive charge and hence may bind hydrogen in molecular form. We found that when one  $\text{H}_2$  is introduced at the Mg site, hydrogen is indeed bound in molecular form with an adsorption energy of 0.209 eV [see Fig. 4(a)]. The  $\text{H}_2$  molecule is 2.261 Å away from the Mg site. The adsorption makes the  $\text{H}_2$  bond length elongate from 0.740 to 0.760 Å in its free state. When one more  $\text{H}_2$  is added, the adsorption energy decreases to 0.170 eV/ $\text{H}_2$ , resulting in a longer Mg–H distance (2.421 Å) and a shorter H–H bond length (0.757 Å) [see Fig. 4(b)]. When the number of  $\text{H}_2$  is further increased to 3 [Fig. 4(c)], the absorption energy becomes 0.149 eV/ $\text{H}_2$ , and the –H

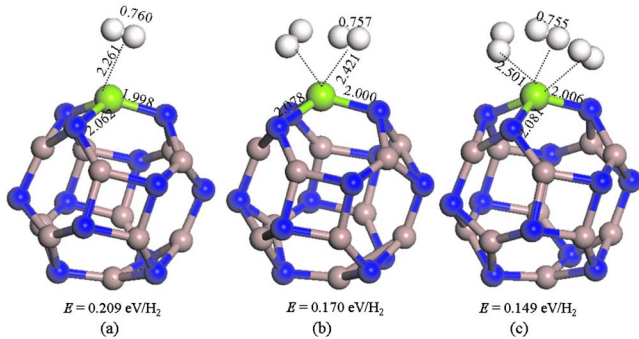


FIG. 4. (Color online) Bond length and absorption energy  $E$  of H<sub>2</sub> on the MgGa<sub>11</sub>N<sub>12</sub> cage.

bond length is found to be 0.755 Å. We note that as the number of H<sub>2</sub> increases, the polarizing interaction of the Mg ion with the hydrogen molecules decreases gradually. However, the adsorption energy still remains large enough so that the materials can be suitable for applications under ambient thermodynamic conditions.

We have also studied the hydrogen adsorption on Mg-doped GaN nanotubes. The results are given in Fig. 5. Note that hydrogen is again bound in molecular form independent of how many hydrogen molecules are attached. We are able to attach up to three H<sub>2</sub> to the Mg atom. The hydrogen adsorption energies are found to be 0.145, 0.114, and 0.101 eV/H<sub>2</sub>, respectively, when one, two, and three hydrogen molecules are introduced to the Mg site in the MgGa<sub>44</sub>N<sub>45</sub>H<sub>20</sub> nanotube. Although the magnitudes of these adsorption energies are smaller than each of the corresponding values in the MgGa<sub>11</sub>N<sub>12</sub> nanocage, they are still in the favorable energy window for ambient hydrogen storage.

From nanocage to nanotube, the effect of geometry and dimensionality on the properties of Mg-doped GaN system is clear. Unlike the fullerene cage, the Ga<sub>12</sub>N<sub>12</sub> cage has four-membered rings and the stress is larger than that for the GaN nanotube which has similar morphology to the (5, 5) carbon nanotube. The larger hydrogen adsorption energy and smaller Mg doping energy in GaN cage can be attributed to the highly stressed structure of the nanocage. Based on this finding, one can expect that reducing the radius of Mg-doped GaN nanotube can improve its performance for storing hydrogen. This is because when the radius of nanotubes gets smaller, the curvature will become larger, and hence the bond stress will increase. On the other hand, in GaN surfaces or thin films, the curvature is 0. Therefore, the doping energy should be larger and the hydrogen adsorption energy should be smaller. Thus our results suggest that the energetics of Mg doping and the ability of hydrogen adsorption in GaN nanostructures can be controlled by tuning the size and dimensionality of GaN nanostructures.

In conclusion, we have investigated the effects of geometry and dimensionality on the energetics, induced spin moment, and hydrogen adsorption in Mg-doped nanocages and nanotubes using first-principles calculations. We have shown that Mg doping not only introduces carriers and induces magnetism in GaN nanostructures but also changes its chemical reactivity. Geometry and dimensionality can be

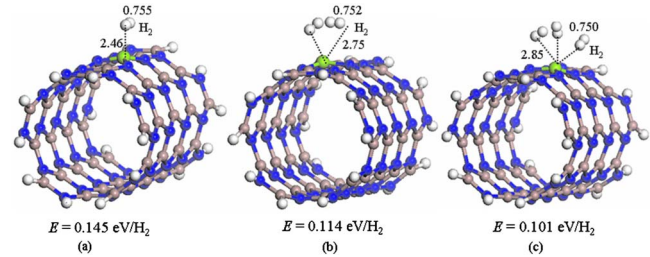


FIG. 5. (Color online) Hydrogen absorption on the Mg-doped GaN nanotube.

used as additional variables to modify the properties of the system. The present study sheds light on the physics of Mg-doped GaN nanostructures, providing new insights on this promising material for nanoscale optoelectronic devices as well as for the potential applications in H<sub>2</sub> storage. Furthermore, because of the biocompatibilities of Mg and GaN, the metallic and magnetic properties of Mg-doped GaN nanostructures might have potential biomedical applications as carriers for drug delivery or as sensors as the movement and properties of the nanostructures can be easily controlled and detected using an external electric field or magnetic field. We also find that hydrogen does not affect the properties of Mg-doped GaN since the hydrogen remains in nearly molecular form and hence does not take part in chemical interaction.

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