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Influence of Mn-doping on the chemical shielding tensors of ^{71}Ga and ^{15}N in the armchair GaN nanotubes: A DFT study

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ABSTRACT

The chemical shielding (CS) tensors of Gallium-71 and nitrogen-15 are computed for the first time in order to investigate the influence of Mn-doping on the electronic properties of the (5, 5) Gallium nitride nanotube (GaNNT). A GaNNT consisting of 40 Ga and 40 N atoms and having a 1.2 nm length was considered. One portal of the nanotube was capped by ten hydrogen atoms and other-end was kept open. Additionally, two other forms of this model of Mn-doped GaNNT were considered where a Mn-atom was substituted for a Ga atom either in the first or in the second layer. The calculations reveal that in both models of Mn-doped GaNNTs, the N atoms that are directly connected to the Mn atom have the smallest isotropic chemical shielding among other N atoms. These calculations were performed at the level of the density functional theory (DFT) using GAUSSIAN 03 package. The basis sets for Ga and N atoms were chosen to be 6-31G (d) and those for Mn atom were chosen to be LanL2DZ.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], electronic and mechanical properties of carbon and non-carbon nanotubes have been investigated by various groups. Different types of semiconducting nanotubes and nanowires such as SiGe nanotubes [2], BN nanotubes [3], and GaN nanorods [4] have been fabricated. GaN nanotubes were also synthesized by an "epitaxial casting" approach by Yang and co-workers recently, who used ZnO nanowires as templates [5]. However, the single-wall GaNNTs have not yet been synthesized. GaN plays an important role in modern material science. Due to its large direct band gap, GaN-based high-efficiency blue and green light-emitting diodes were fabricated successfully by Nakamura et al. [6] in 1994.

Density functional theory was used to predict stability, electronic structures of GaN nanotubes [7], and excitonic states [8]. Recently, Mn-doped GaN, as a dilute magnetic semiconductor material, has attracted considerable attention for its promising applications in a new class of spintronic devices with novel functionality [9,10]. Hao et al. showed that in the GaN nanotube and its Mn-doped form, the interaction between dangling bonds of Ga (or Mn) and N atoms at the open-end promotes the self-closing of the tube mouth and formation of a more stable semi-cone top with an open other-end. They also suggested that armchair open GaN nanotube arrays doped with a finite number of magnetic atoms may find application as electron source for spintronic devices in the future [11].

Nuclear magnetic resonance (NMR) is among the most versatile spectroscopic techniques to study the physical properties of matters in the solid phase [12–15]. Nuclei with nuclear spin angular momentum greater than zero (magnetic nuclei) e.g. Ga-71 and N-15, are detected by NMR. The chemical shielding (CS) tensors arise at the electronic sites of magnetic nuclei and protect the nuclei from feeling the full strength of the employed external field, which is experimentally measured as chemical shift by NMR. Both experimental and theoretical NMR studies carried out on CNTs, successfully reveal that NMR parameters are powerful tools to determine and characterize structures of nanotubes. In recent years, AlNNTs [16] and BNNTs have been theoretically and experimentally studied using NMR spectroscopy [17–22].

We report on our study of the three GaN model systems: a 'pure' or isolated GaN with one semi-cone end, a first-layer Mn-doped tube, and a second-layer Mn-doped tube. These systems were considered by Hao et al. [11] and we have adopted their GaNNT structures [11]. In particular, the influence of Mn-dopant on the chemical shift tensors at the sites of Ga-71 and N-15 has been computed for the above model systems using density functional theory (DFT).

2. Models and computational methods

We considered three models of (5, 5) armchair single-wall GaNNTs having a length of 1.2 nm. Model No. 1 (isolated) is a

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one-end-open armchair (5, 5) GaN nanotube consisting of eight-layer atoms stacked along the tube axis, including 40 Ga and 40 N atoms (Fig. 1). One end of this model is capped by 10 H atoms. Model No. 2 has a Mn-atom replacing a Ga atom at the first layer (Fig. 2a). Model No. 3 is a Mn substituted GaN model, where a Mn atom has replaced a Ga atom on the second layer (Fig. 2b). Our calculations for finite length, isolated, and Mn-doped GaN nanotubes were performed in the framework of density functional theory (DFT) by GAUSSIAN 03 package [23]. NMR values calculated with density functional theory are only somewhat sensitive to the basis set [24], and for Ga and N atoms 6-31G (d) [25] and for Mn atoms LanL2DZ [26] basis set have been recommended. Firstly, the considered models were allowed to fully relax during the geometrical optimization by the B3LYP exchange-functional method [27]. The basis sets were chosen to be 6-31G (d) for Ga and N atoms, and LanL2DZ for Mn atom. Secondly, the natural population analysis (NPA) and the quantum chemical calculations were performed on the three geometrically optimized models by B3LYP method and the above-mentioned standard basis sets were used to evaluate natural charges and the N-15 and Ga-71 NMR parameters.

The quantum chemical calculations yield the chemical shift (CS) tensors in the principal axes system (PAS) ($\sigma_{11} < \sigma_{22} < \sigma_{33}$); therefore, Eqs. (1) and (2) are used to evaluate the isotropic chemical shielding (ICS) and anisotropic chemical shielding (ACS) parameters [28].

$$\text{ICS (ppm)} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \tag{1}$$

$$\text{ACS (ppm)} = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \tag{2}$$

3. Results and discussion

3.1. Geometries

The optimized morphology of the isolated GaN nanotube is shown in Fig. 1b. It is shown that the Ga–N pairs at the open-end spontaneously interact with their nearest-neighbors, so that the

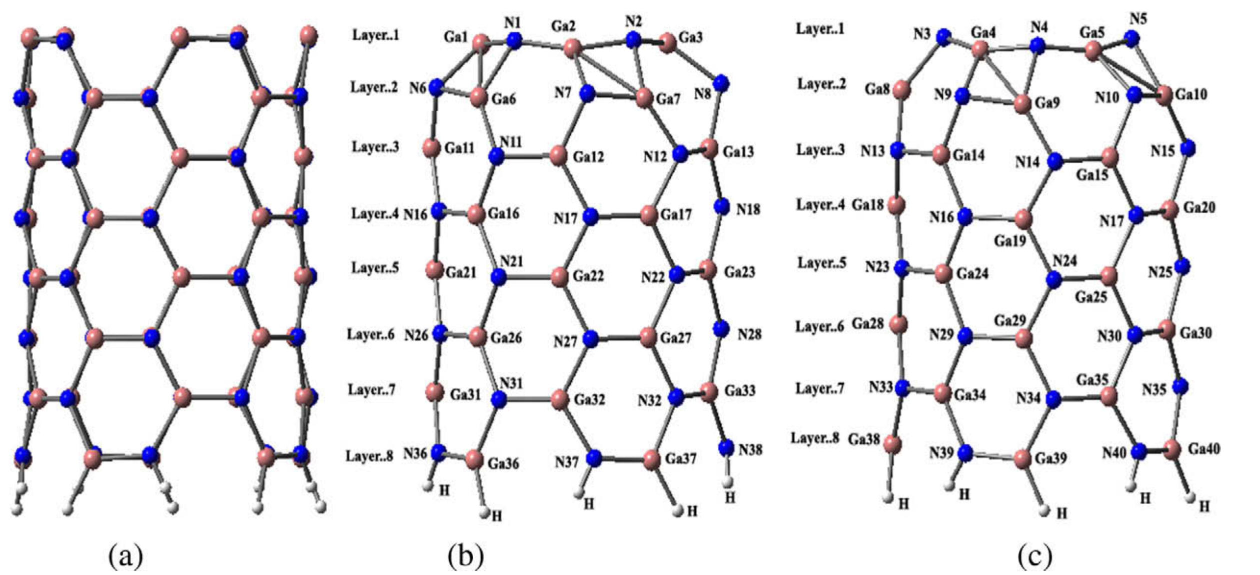

Fig. 1. Geometerical structure of (a) open-ended armchair (5, 5) GaN nanotube before optimization, (b) after optimization (front side) and (c) back side.

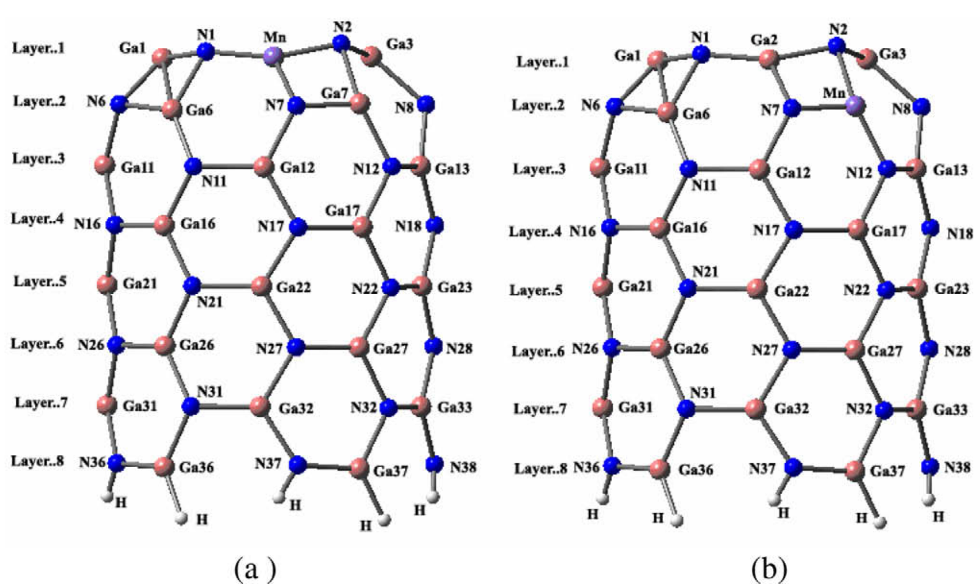

Fig. 2. (a) 2D views of first-layer Mn-doped GaNNT after optimization, front side. (b) Second-layer Mn-doped tube after optimization, front side. The labels for back side are the same labels of isolated model.