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Chemical shielding properties for BN, BP, AlN, and AlP nanocones: DFT studies

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ABSTRACT

The properties of boron nitride (BN), boron phosphide (BP), aluminum nitride (AlN), and aluminum phosphide (AlP) nanocones were investigated by density functional theory (DFT) calculations. The investigated structures were optimized and chemical shielding (CS) properties including isotropic and anisotropic CS parameters were calculated for the atoms of the optimized structures. The magnitudes of CS parameters were observed to be mainly dependent on the bond lengths of considered atoms. The results indicated that the atoms could be divided into atomic layers due to the similarities of their CS properties for the atoms of each layer. The trend means that the atoms of each layer detect almost similar electronic environments. Moreover, the atoms at the apex and mouth of nanocones exhibit different properties with respect to the other atomic layers.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is among the most important techniques to investigate the properties of matters in solid state [1,2]. However, due to the complexity of the electronic environment of the nanostructures, performing experimental NMR measurements is almost a formidable task for these materials [3]. Quantum chemical calculations could play dominant roles in reproducing reliable NMR parameters for the nanostructures prior to the experiments [3–6]. In present work, the properties of the III–V families of nanocones with 240° disclination angle including boron nitride (BN), boron phosphide (BP), aluminum nitride (AlN), and aluminum phosphide (AlP) are

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investigated (Fig. 1). To achieve the purpose, we have performed density functional theory (DFT) calculations to optimize the geometrical structures and subsequently, we have calculated the NMR parameters for the optimized structures. It is important to note that the nanocones have been observed as caps of the ends of nanotubes and also as free standing nanostructures through either computations or experiments [7–9].

In addition to the carbon nanotubes and nanocones, which are almost the pioneering nanostructures, the tubular and conical structures of combinations of the elements of groups III and V are also considered as important categories of nanostructures due to their expected always semiconducting behaviors [10,11]. In contrast with the tubular carbon structures, which show metallic or semiconducting behaviors, those of III–V counterparts are expected to be always semiconductors [10,11]. Previous investigations indicated that the nanocones, with topological defects such as pentagonal rings at the apexes, are built from planar hexagonal sheets [12]. In the case of our investigated III–V nanocones, this kind of defect yields homonuclear bonds such as B–B, Al–Al, N–N, and P–P bonds which are in contrast with the initial heteronuclear nature of the III–V compounds. However, in previous DFT investigations, to avoid the defective pentagonal rings and homonuclear bonds, we have shown that the hexagonal rings could also be existed at the apex of the stabilized BN nanocones [13,14]. Other investigations have also been performed to indicate the types of defects at the apexes through computations [15,16]. The models of our investigated III–V nanocones in present study only consist of hexagonal rings without defects and all the structures are composed of the heteronuclear III–V bonds (Fig. 1).

2. Computational details

In this research, the conical structures with the stoichiometries of $III_{33}V_{33}H_{14}$ (Fig. 1), in which III represents for B or Al atoms and V represents for N or P atoms, are considered as the representative models of BN, BP, AlN, and AlP nanocones with 240° disclination angles. The models only consist of hexagonal rings to avoid the defects and the homonuclear bonds, which are resulted by the pentagonal rings. The role of hydrogen atoms is to saturate the apex and the tips of nanocones to avoid the dangling effects [3]. To ease, the hydrogen atoms are not shown in Fig. 1. The geometries of the structures have been optimized based on the earlier examined level of computations employing the B3LYP exchange–correlation functional and the 6-31G* standard basis set [17]. Subsequently, the NMR parameters have been calculated at the same level of computations based on the gauge-included atomic orbital (GIAO) approach [18]. It is noted that, in order to reproduce the NMR parameters, chemical shielding (CS) tensors (σ_{ii}) are calculated in the principal axes system ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) for the ^{11}B, ^{27}Al, ^{15}N, and ^{31}P atoms and they are converted to isotropic (CS^I) and anisotropic (CS^A) CS parameters employing Eqs. (1) and (2) to directly relate with the experiments [1]. The CS parameters are

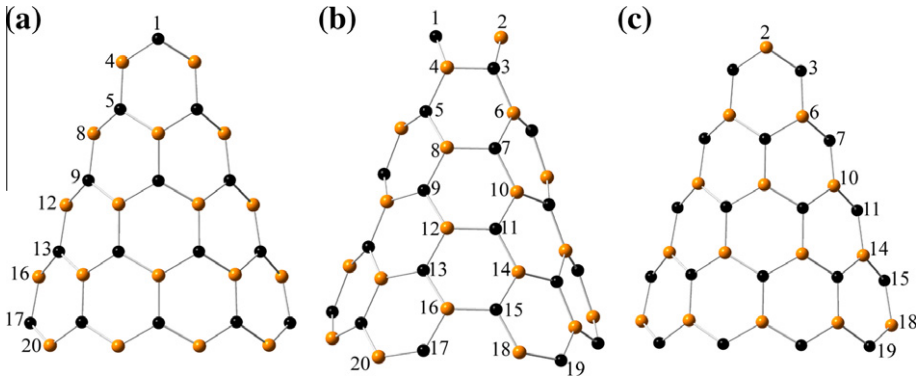

Fig. 1. The 2D views of different sides (by a 90° rotation) of III–V nanocones. To ease, the hydrogen atoms are not shown. The odd numbers are the elements of group III (B or Al) and the even numbers are the elements of group V (N or P).