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ORIGINAL PAPER

DFT calculations of NMR properties for GaP nanotubes

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Abstract Density functional theory calculations were performed to investigate representative models of (6,0) *zigzag* and (4,4) *armchair* gallium phosphide nanotubes (GaPNTs). Nuclear magnetic resonance properties including isotropic and anisotropic chemical shielding parameters (CS^I and CS^A) were calculated for ^{69}Ga and ^{31}P atoms of the optimized structures. The calculated CS parameters indicated that the P atoms detect slight changes of electronic environment in the GaPNT structures, but the changes for the Ga atoms are more significant. Moreover, *armchair* GaPNTs could be considered a more reactive material than the *zigzag* model for interactions with other atoms or molecules.

Keywords Density functional theory · Gallium phosphide · Nanotube · Chemical shielding

Introduction

Nuclear magnetic resonance (NMR) properties including isotropic and anisotropic chemical shielding parameters (CS^I and CS^A), which are among the most important elements to study the properties of matter, could be well reproduced by quantum calculations [1, 2]. Earlier studies indicated the usefulness of calculations of CS parameters for the investigation of properties of nanotubes [3, 4]. Indeed, due to the electronic complexity of nanotubes, performing experimental NMR measurements on these materials is a formidable task; therefore, calculations of these parameters are advantageous [4]. Studies on various types of carbon nanotubes (CNTs) have revealed that these materials are metals or semiconductors depending on the tube diameter and chirality, which makes their synthesis for specific applications difficult [5]. On the other hand, such tubular structures consisting of counterpart atoms of the third and fifth groups of elements are always viewed as semiconductors, independent of any restricting factors [6]. Among the new family of nanotubes, the structures of nitride compounds of atoms of the third group of elements, e.g., boron nitride (BN), have been investigated more often than phosphide compounds, e.g., boron phosphide (BP) [7–15].

Wu et al. [14] reported successful synthesis and the optical properties of gallium phosphide nanotubes (GaPNTs), which are suggested for future applications in optoelectronics due to their novel semiconducting behaviors. Other nanostructures of GaP counterparts, e.g., nanowires and nanocrystals, have also been investigated [16, 17]; however, to date, no more attention has been paid to characterization of the properties of GaPNTs. In this work, we investigated representative structures of (6,0) *zigzag* and (4,4) *armchair* GaPNTs (Fig. 1) by performing density functional theory (DFT) calculations of NMR properties of the optimized structures. In two recent contributions, we have shown that the properties of boron phosphide nanotubes (BPNTs) and aluminum phosphide nanotubes (AlPNTs), which belong to the category of phosphide compounds of atoms of the third group, could be well investigated by using calculated CS parameters [12, 13]. In this work, we employ these useful parameters to study the properties of GaPNTs.

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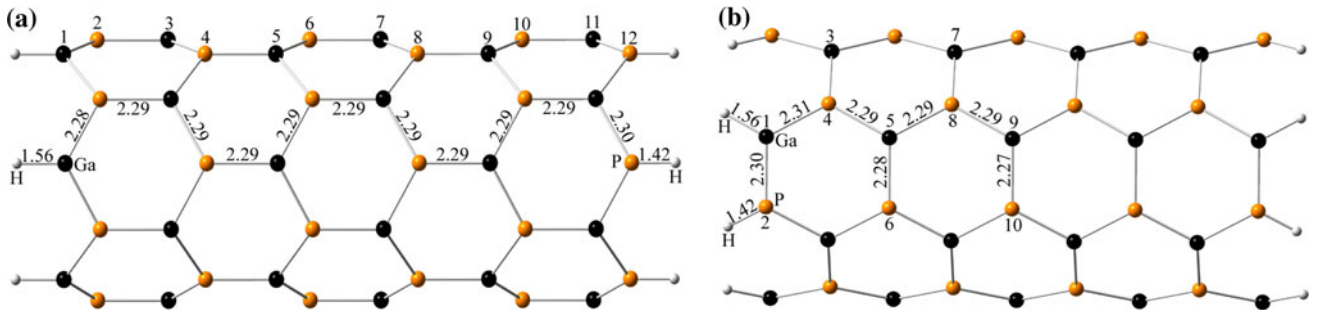

Fig. 1 Two-dimensional (2D) views of **a** the (6,0) *zigzag* model and **b** the (4,4) *armchair* model of the investigated GaPNTs. The Ga atoms are denoted by *odd numbers* and the P atoms are denoted by *even numbers*. Average bond length values (Å) are shown

Results and discussion

Figure 1a, b shows the (6,0) *zigzag* and (4,4) *armchair* structures of the investigated GaPNTs, where the optimized bond lengths are shown for selected, representative bonds. Comparing the Ga–P bond lengths with those of the Al–P and B–P bonds from earlier studies indicates that the average Ga–P bond length value (∼2.29 Å) is close to that for Al–P bonds (∼2.31 Å) [13] but notably longer than that for B–P bonds (∼1.89 Å) [12]. Previous studies have proposed that longer bond lengths of nanotubes could yield better surfaces for interactions with other atoms or molecules [18], so the longer bond lengths of GaP and AlP nanotubes make them better than BP nanotubes as components of interacting systems.

Calculated NMR properties, consisting of CS^I and CS^A parameters for ^{69}Ga and ^{31}P atoms of the optimized (6,0) GaPNTs, are presented in Table 1. In agreement with earlier studies [12, 13], the calculated CS parameters for atoms of the *zigzag* GaPNT could be divided into layers based on similarities of their values for the atoms of each layer. Since the CS parameters originate from the electronic sites of the atoms, they could be related to the electronic environments that each atom detects in the nanotube structure. Based on this trend, different electronic environments are observed for the ^{69}Ga and ^{31}P atoms of the *zigzag* GaPNT. The layers of ^{69}Ga atoms, with the exceptions of the Ga^3 and Ga^{11} layers, have similar values of the CS^I parameter, which means that the average electronic densities at the sites of these atoms are similar. However, different values of the CS^A parameter indicate that the orientations of the CS tensors are not similar for the Ga atoms of the mentioned layers. Among the layers of Ga atoms, the properties of atoms of the Ga^7 and Ga^9 layers are similar, whereas those of other layers are different. The values of the CS^A parameter for atoms of the Ga^1 layer, which makes the Ga tip, and the Ga^{11} layer, which is close to the P tip of *zigzag* nanotubes, are the largest among the Ga atom layers. This trend may show that atoms of the Ga^1 and Ga^{11} layers are more appropriate for interactions with other atoms or molecules. Among the layers of ^{31}P atoms, the atoms of the P^{12} layer, which makes the P tip of *zigzag* nanotubes, have the largest value of the CS^I parameter and the smallest value of the CS^A parameter. These results indicate no similarities for the layers of P atoms in the *zigzag* GaPNT, for which different values of the CS parameters are observed for different layers of P atoms. However, it is noted that the magnitude of the changes of the CS parameters is smaller for the P layers than for the Ga layers. The values of the CS^A parameter indicate that atoms of the P^2 and P^{10} layers could be considered as the best P atoms for interactions with other atoms or molecules among the available layers of P atoms of the *zigzag* GaPNTs. Comparing the results of the *zigzag* models of GaPNT and BPNT indicates that the CS parameters for P atoms are similar; however, significant differences are observed for the CS parameters for P atoms of the *zigzag* models of GaPNT and AlPNT [12, 13]. Larger values of the CS parameters for P atoms of *zigzag* AlPNTs than for P atoms of *zigzag* GaPNTs are observed.

Table 2 shows the calculated NMR properties (CS^I and CS^A parameters) for the optimized structure of the (4,4) *armchair* GaPNT (Fig. 1b). As for the *zigzag* model, the results indicate that the CS parameters of the *armchair* model also could be divided into layers due to similarities of their values for atoms of each layer. The values of the CS^I parameter indicate that Ga atoms of the Ga^1 and Ga^3

Table 1 NMR properties for the (6,0) *zigzag* GaPNT

^{69}Ga atoms	CS^I (ppm)	CS^A (ppm)	^{31}P atoms	CS^I (ppm)	CS^A (ppm)
Ga^1	1,531	294	P^2	404	300
Ga^3	1,484	64	P^4	397	245
Ga^5	1,532	146	P^6	390	264
Ga^7	1,532	125	P^8	384	259
Ga^9	1,533	124	P^{10}	416	313
Ga^{11}	1,422	357	P^{12}	420	158

See Fig. 1a

Table 2 NMR properties for the (4,4) *armchair* GaPNT

^{69}Ga atoms	CS^I (ppm)	CS^A (ppm)	^{31}P atoms	CS^I (ppm)	CS^A (ppm)
Ga^1	1,472	389	P^2	435	226
Ga^3	1,471	155	P^4	412	298
Ga^5	1,594	135	P^6	448	262
Ga^7	1,559	132	P^8	421	255
Ga^9	1,585	144	P^{10}	419	252

See Fig. 1b

layers have similar electronic densities, but different densities are observed for Ga atoms of other layers. Interestingly, similar values of the CS^A parameter are observed for atoms of the Ga_5 and Ga_7 layers, indicating that the orientations of the CS tensors at the sites of these atoms are similar. The observed largest values of the CS^A parameter for atoms of the Ga^1 layer, which makes the tip of the *armchair* nanotube, indicate it as the best layer for interactions with other atoms or molecules among the Ga atoms. Slight changes of the CS parameters are observed for the P atoms of different layers in the structure of *armchair* GaPNT. This trend means that the P atoms of *armchair* GaPNT detect slightly different environments in which the atoms of the P^4 layer could be considered as the best layer of P atoms for interactions with other atoms or molecules. In comparison with *zigzag* GaPNTs, the values of the CS parameters for Ga and P atoms of the *armchair* model are larger, which means that the *armchair* model could be more reactive than the *zigzag* model of GaPNT. Moreover, comparing the results of CS parameters for P atoms of *armchair* GaPNT, AlPNT, and BPNT indicates that the P atoms detect significantly different electronic environments in the three types of III-P nanotubes, with the value of the CS parameters differing between the mentioned structures [12, 13].

Conclusions

DFT-calculated CS parameters for (6,0) and (4,4) models of GaPNT indicate that the structure of nanotubes could be divided into layers based on similarities of the CS parameter values for atoms of each layer. The CS parameters for the layers of P atoms exhibit only slight changes, but notable changes are observed for the layers of Ga atoms. Moreover, comparison of the results for the *zigzag* and *armchair* models indicates that the *armchair* model could be considered as a more reactive material for interactions with other atoms and molecules due to the larger values of the CS parameters than for *zigzag* GaPNT.

Computational details

The representative structures of the (4,4) *armchair* and the (6,0) *zigzag* single-walled GaPNTs (Fig. 1) were investigated by DFT calculations employing the B3LYP exchange functional and the 6-31G* standard basis set. The formula for both nanotubes is $Ga_{36}P_{36}$, in which the tips are saturated by hydrogen atoms to avoid dangling effects [4, 19]. All geometrical coordinates were allowed to relax during the optimization process, and the CS parameters were subsequently calculated for the optimized structures. To calculate the CS parameters for the ^{69}Ga and ^{31}P atoms, the gauge-included atomic orbital (GIAO) approach was employed [20]. The calculated CS tensors in the principal axes system (PAS) were converted to the isotropic CS (CS^I) and anisotropic CS (CS^A) parameters using Eqs. 1 and 2 [1]. It is important to note that the CS parameters could be experimentally measured by NMR spectroscopy; however, the complexity of the electronic environment of nanotubes makes NMR experiments on these materials almost impossible [4]. Tables 1 and 2 show the evaluated NMR properties, consisting of the absolute values of the CS^I and CS^A parameters for ^{69}Ga and ^{31}P atoms of (6,0) *zigzag* and the (4,4) *armchair* models of GaPNT (Fig. 1). The Gaussian 98 package [21] was used to perform the DFT calculations of this study.

$$CS^I(\text{ppm}) = \frac{1}{3}(\sigma_{33} + \sigma_{22} + \sigma_{11}), \quad (1)$$

$$CS^A(\text{ppm}) = \sigma_{33} - \frac{1}{2}(\sigma_{22} + \sigma_{11}); (\sigma_{33} > \sigma_{22} > \sigma_{11}). \quad (2)$$

References

1. Bovey FA (1988) Nuclear magnetic resonance spectroscopy. Academic, San Diego
2. Mirzaei M, Mirzaei M (2010) J Mol Struct (Theochem) 953:134
3. Mirzaei M, Mirzaei M (2010) Monatsh Chem 141:491
4. Zurek E (2004) Autschbach J 126:13079
5. Harris PJF (1999) Carbon nanotubes and related structures. Cambridge University Press, Cambridge
6. Loiseau A, Willaime F, Demoncy N, Schramcheko N, Hug G, Colliex C, Pascard H (1998) Carbon 36:743
7. Li XM, Tian WQ, Huang XR, Sun CC, Jiang L (2009) J Mol Struct (Theochem) 901:103
8. Nirmala V, Kolandaivel P (2007) J Mol Struct (Theochem) 817:137
9. Mirzaei M, Seif A, Hadipour NL (2008) Chem Phys Lett 461:246
10. Chen GX, Zhang JM, Wang DD, Xu KW (2010) J Mol Struct (Theochem) 956:77
11. Qian Z, Hou S, Zhang J, Li R, Shen Z, Zhao X, Xue Z (2005) Physica E 30:81
12. Mirzaei M (2010) Z Naturforsch A 65:844
13. Mirzaei M, Mirzaei M (2010) J Mol Struct (Theochem) 951:69
14. Wu Q, Hu Z, Liu C, Wang X, Chen Y (2005) J Phys Chem B 109:197

15. Tang C, Bando Y, Liu Z, Golberg D (2003) Chem Phys Lett 376:676
16. Seo HW, Bae SY, Park J, Kang M, Kim S (2003) Chem Phys Lett 378:420
17. Cui DL, Pan JQ, Zhang ZC, Huang BB, Qin XY, Jiang MH, Gao SM (2000) Prog Cryst Grow Charact Mater 40:145
18. Bodaghi A, Mirzaei M, Seif A, Giahi M (2008) Physica E 41:209
19. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251
20. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98. Gaussian Inc., Pittsburgh
21. Mpourmpakis G, Froudakis GE, Lithoxoos GP, Samios J (2006) Nano Lett 6:1581