

# Quantum Chemical Treatment of Large Nanotubes via Use of Line Group Symmetry: Structural Preferences of Magnesium Dichloride Nanotubes

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Nanotubes with diameters in the magnitude of 10 nm can be treated by quantum chemical methods, made possible by utilization of line group symmetries. The methodology presented here is applied for magnesium dichloride nanotubes. The structural preferences of  $\text{MgCl}_2$  nanotubes are strongly dependent on the tube diameter. The rolled layer of a crystalline sheet becomes favorable above a diameter of 3.4 nm, below which alternative stable coordination modes dominate. Application of the methodology for other nanotubular compounds, including multiwalled nanotubes, is expected to be straightforward.

## Introduction

Nanotubes of several inorganic compounds, both layered and nonlayered, have been synthesized recently.<sup>1</sup> In theoretical investigations, the molecular structures of nanotubes generated from layered compounds are generally interpreted as a cylindrical form of the corresponding sheet,<sup>2</sup> in analogy with rolling of a graphene sheet into carbon nanotubes.<sup>3</sup> The structural characteristics of nonlayered nanotubes are less straightforward to understand. Attempts have been made for the cases of single-walled oxides of aluminum<sup>4</sup> and silicon.<sup>5</sup>

Limitation of inorganic nanotubes to cylindrical form of the respective layered compounds should not be a necessity; in the case of AlN nanotubes, there is both experimental<sup>6</sup> and theoretical evidence<sup>7</sup> that nonlayered faceted structures are actually favored over cylindrical ones. It is apparent that the thickness of the tube plays a significant role in determination of the preferred coordination mode. Theoretical predictions of Seifert et al. suggest that cylindrical single-walled metal chalcogenide nanotubes should be larger than approximately 6 nm in thickness to be stable.<sup>8</sup> Numerous tubular noncylindrical isomers can be devised, some of which may possess significant stability compared to cylindrical ones, particularly in the region below 6 nm in diameter. From the computational point of view, identification of the preferred coordination mode for inorganic nanotubes is a challenge, requiring systematic investigations of very large systems. Quantum chemical studies of inorganic nanotubes have been so far focused to diameters of about 1–2 nm.<sup>2</sup> An order of magnitude increase would be desirable, particularly if multiwalled nanotubes are considered.

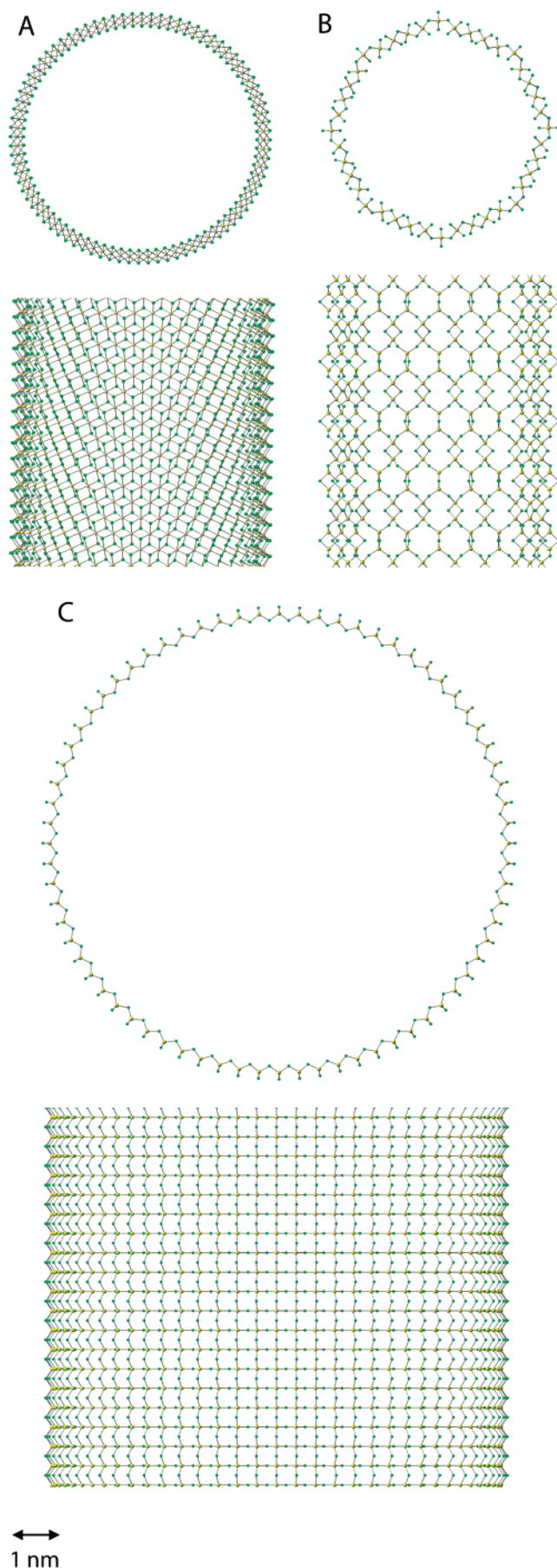
This paper introduces a methodology for the theoretical treatment of nanotubes of a magnitude of 10 nm thickness. The approach is applied for the determination of preferred coordination modes of single-walled magnesium dichloride nanotubes. While several metal halide nanoparticles are experimentally known,<sup>9</sup>  $\text{MgCl}_2$  nanotubes are still waiting for their discovery. We had three motives for the selection of magnesium dichloride as the prototype system: (a) The plausibility of an alternative coordination mode was recently demonstrated for single-walled

nanospheres of  $\text{MgCl}_2$ .<sup>10</sup> (b) Quantum chemical treatment of transition metal compounds is often cumbersome, mainly due to near-degeneracy correlation<sup>11</sup> and relativistic effects.<sup>12</sup> This is usually not the case for lighter elements; the Hartree–Fock method has been performed with a significant accuracy for clusters of magnesium dichloride.<sup>13</sup> (c) Magnesium dichloride is a common catalyst carrier in the Ziegler–Natta olefin polymerization process.<sup>14</sup> The paper aims at encouraging experimentalists toward synthesis of magnesium dichloride nanotubes, as such tubes could make excellent catalyst carriers due to their ultimate surface area.

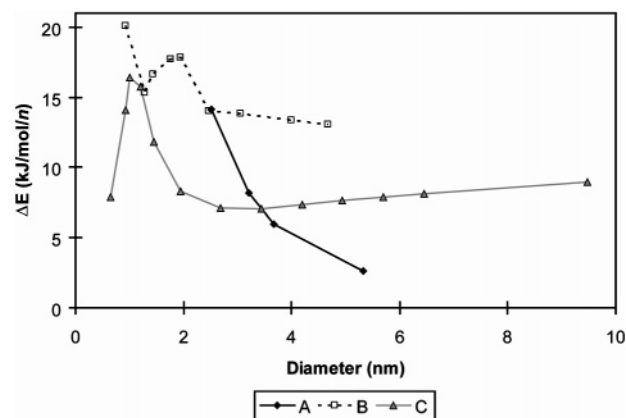
## Results and Discussion

Open-ended tubular structures can be treated as rolled infinite layers of the material. Both layers and tubes are periodic in two dimensions: layers are along two axes,<sup>15</sup> whereas tubes are only periodic along one axis but possess an  $n$ th order rotational axis. The symmetries of nanotubes can hence be described with line groups.<sup>16</sup> By taking advantage of the line group symmetries, greatly reducing computational requirements, we performed full geometry optimizations for open-ended magnesium dichloride nanotubes of infinite length. Three coordination modes were considered for the tubes. Cylindrical form (A), where coordination numbers of Mg and Cl are 6 and 3, respectively, was obtained by rolling a sheet of  $\text{MgCl}_2$  crystal lattice. Coordination mode B, in which Mg atoms are connected via alternating single and double chlorine bridges, is adopted from previous work on  $\text{MgCl}_2$  nanospheres.<sup>10</sup> Here, the respective coordination numbers of Mg and Cl are 4 and 2. Coordination mode C is identical to the preferred structures of single-walled  $\text{SiO}_2$  nanotubes.<sup>5</sup> C consists of singly bridging chlorines and has coordination numbers of 4 and 2 for Mg and Cl, respectively. Structures and relative stabilities of the isomeric tubules were investigated as a function of tube diameter up to sizes necessary for drawing conclusions of structural preferences. While not necessary for determination of the preferred structural mode, the scalability of the approach for systems with diameters of about 10 nm was demonstrated for the case of isomeric form C. The largest of the studied structures of each family are illustrated in Figure 1. Adopting the naming convention of carbon nanotubes,<sup>17</sup> the zigzag tubes are A (42,0), B (20,0), and C (72,0).

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**Figure 1.** Tube end and side view for largest optimized nanotubes of each structural family: A (42,0), B (20,0), and C (72,0).



**Figure 2.** Stabilities of selected magnesium dichloride nanotubes relative to an infinite (001) monolayer sheet of  $\beta$ -MgCl<sub>2</sub>.

All calculations were performed by the CRYSTAL03<sup>18</sup> program, which allows utilization of line group symmetries for systems with 1-fold to 6-fold rotational axes, excluding systems with a 5-fold axis. The Hartree–Fock method was applied in combination with basis set 3 from the work of Barrera et al.<sup>19</sup> The basis sets are specifically optimized for the case of magnesium dichloride and are extensions for 8-5-11G\* (Mg) and 8-6-311G\* (Cl) developed by Harrison and Saunders.<sup>20</sup> Basis set 3 of Barrera et al. has further optimized 3sp, 4sp, and 3d functions for Mg and 4sp, 5sp, and 3d functions for Cl, together with added 4d functions for Cl. Convergence criteria of  $10^{-8}$  hartree was used for both eigenvalues and total energies.

Since the tubes considered here are single-walled, it is of interest to compare their energies with that of an infinite (001) monolayer sheet of  $\beta$ -MgCl<sub>2</sub>, rolling of which generates the cylindrical (A) form of the nanotubes. The comparison is presented in Figure 2 and is summarized in Table 1. In the case of cylindrical tubes, the increase in stability as a function of tube diameter is nearly hyperbolic, approaching an energy of 0.06 kJ/(mol MgCl<sub>2</sub> unit) above that of the corresponding monolayer sheet.<sup>21</sup> The A (18,0) tube, with a diameter of 2.51 nm, lies 14.2 kJ/(mol  $n$ ) above the energy of an infinite sheet. The Mg–Cl bond lengths of A (18,0) range from 2.50 Å in the inner circle to 2.68 Å in the outer circle. For a point of comparison, the Mg–Cl bond length in the optimized monolayer sheet is 2.55 Å and it is 2.51 Å in the experimental crystal lattice.<sup>22</sup> As the size of the tube increases, the bond lengths approach those of an infinitely thick tube, i.e. the sheet. Nanotube A (42,0), which lies only 2.6 kJ/(mol  $n$ ) above the infinite sheet and has a diameter of 5.3 Å, has Mg–Cl bond lengths of 2.53 Å and 2.59 Å in inner and outer circles, respectively.

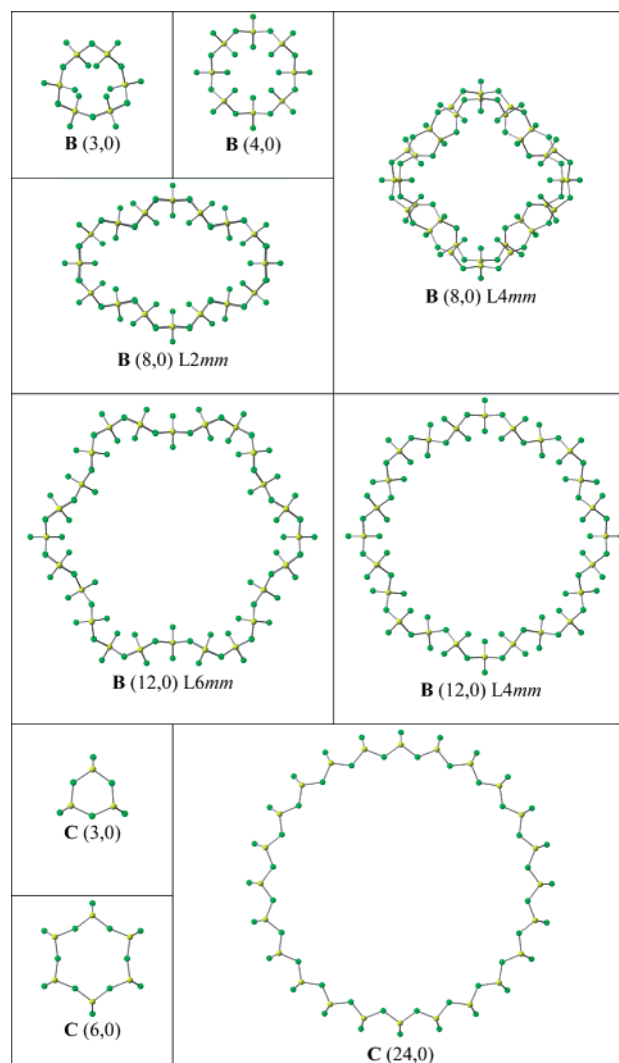
The relevance of alternative coordination modes (B and C) for magnesium dichloride nanotubes becomes apparent from Figure 2. Structures of type B are favored over the cylindrical ones (A) at diameters shorter than 2.5 nm. This is understandable, as rolling of the monolayer sheet of MgCl<sub>2</sub>, with three layers of atoms, into a small cylinder induces strain particularly at the inner circle. It is notable, however, that type B tubes possess significant stability, being within 20 kJ/(mol  $n$ ) from the (001) monolayer sheet of  $\beta$ -MgCl<sub>2</sub>. If one compares the result to carbon nanotubes, for which the strain energy due to rolling of a sheet of graphene into a (5,5) carbon nanotube is more than 20 kJ/(mol  $n$ ) at the same level of theory,<sup>5c</sup> the stability is striking. Tube end views of selected tubules discussed here are shown in Figure 3. Of the B-type structures below a diameter of 2.5 nm, B (4,0) is favored in energy. The smaller B (3,0) tube is destabilized due to repulsion between chlorines

**TABLE 1: Line Groups, Diameters, and Stabilities Relative to an Infinite (001) Monolayer Sheet of  $\beta\text{-MgCl}_2$  for Magnesium Dichloride Nanotubes**

nanotube	line group	diameter (nm)	$\Delta E/n$ (kJ/mol)
A (18,0)	L18mm	2.51	14.2
A (24,0)	L24mm	3.21	8.1
A (28,0)	L28mm	3.67	6.0
A (42,0)	L42mm	5.32	2.6
B (3,0)	L3	0.92	20.1
B (4,0)	L4mm	1.28	15.3
B (5,0)	L5mm	1.43	16.6
B (6,0)	L6mm	1.76	17.7
B (7,0)	L7mm	1.94	17.9
B (8,0)	L4mm	2.26	16.6
B (8,0)	L2mm	2.47	14.0
B (12,0)	L6mm	3.17	16.5
B (12,0)	L4mm	3.05	13.9
B (12,0)	L3mm	2.90	14.4
B (12,0)	L2mm	3.05	13.9
B (18,0)	L6mm	3.89	15.4
B (18,0)	L3mm	4.00	13.4
B (20,0)	L4mm	4.67	13.1
C (3,0)	L3mm	0.65	7.9
C (4,0)	L4mm	0.92	14.1
C (5,0)	L5mm	1.01	16.4
C (6,0)	L6mm	1.20	15.7
C (8,0)	L8mm	1.45	11.8
C (12,0)	L12mm	1.94	8.3
C (18,0)	L18mm	2.69	7.1
C (24,0)	L24mm	3.44	7.1
C (30,0)	L30mm	4.19	7.3
C (36,0)	L36mm	4.94	7.7
C (42,0)	L42mm	5.70	7.9
C (48,0)	L48mm	6.45	8.1
C (72,0)	L72mm	9.48	9.0

pointing inward in the thin tube. The repulsions is so strong that it requires B (3,0) to distort from L3mm to L3 symmetry. A shift from B (4,0) up to B (7,0) results in slightly decreased stabilities due to an increase in structural strain. Here, an increase in ring size forces the angle between Mg atoms and singly bridging chlorines to straighten, which is unfavorable for Cl with its lone pairs. The Cl–Mg–Cl angles remain constant, around  $110^\circ$  (excluding  $\text{Mg}_2\text{Cl}_2$  squares), typical for tetrahedral orientation. Straightening of the Mg–Cl–Mg bonds eventually leads to puckering of the smooth structures from B (8,0) on and lowering of the symmetry, in the same fashion as boron nanotubes recently studied by Kunstmann and Quandt.<sup>23</sup> Puckering, which enables preferred Mg–Cl–Mg bond angles of  $120\text{--}130^\circ$ , clearly improves the stabilities of the tubes. In the case of B (8,0), an isomer having only a 2-fold rotational axis is preferred, whereas B (12,0) favors L4mm symmetry. On the basis of this observation, the largest of the studied B-type nanotubes, B (20,0), was constrained to L4mm symmetry. At tube diameters beyond 2.5 nm, the stabilities remain practically unchanged.

While the preference of B-type magnesium dichloride nanotubes over the cylindrical ones (A) is apparent at diameters below 2.5 nm, it turns out that structural mode C is actually the more relevant alternative. Tube C (3,0) with a small diameter of 0.65 nm, lies only 7.9 kJ/(mol  $n$ ) in energy above the (001) monolayer sheet of  $\beta\text{-MgCl}_2$ . Structural strain determines the relative stabilities here, as well. A shift from C (3,0) up to C (5,0) forces the Mg–Cl–Mg angles to straighten, leading to increase in energy. From C (6,0) on, this structural strain is relieved by the chlorines turning inward, the ring center thus being capable of adopting Mg–Cl–Mg angles closer to the optimal value of around  $120\text{--}130^\circ$ . The minimum energy, 7.1 kJ/(mol  $n$ ) above the (001) monolayer sheet of  $\beta\text{-MgCl}_2$ , is reached at C (24,0). Interestingly, type C nanotubes are favored

**Figure 3.** Tube end view for selected magnesium dichloride nanotubes.

over the cylindrical ones (A) up to a diameter of 3.4 nm, which is the diameter of the preferred C-type tube, C (24,0). Type A structures are ultimately preferred at larger diameters, where the structural strain due to rolling of the planar sheet becomes less significant than the benefit of maximization of coordination numbers.

The methodology of utilizing line groups symmetries in theoretical treatment of open-ended nanotubes, introduced here and applied for the case of magnesium dichloride, should be straightforwardly extendable to other compounds, as well. One could expect the approach to turn out particularly useful in the studies of nanotubes of nonlayered compounds such as alumina and silica, which so far, being multiwalled and relatively thick, have been far beyond the reach of accurate quantum chemical methods. In addition to the structure determination of synthesized nanotubes, the methodology basically provides means to scan through the periodic table to search and predict the possible existence and properties of yet unknown nanostructured materials.

## Conclusions

By taking advantage of line group symmetries, nanotubes with diameters in the magnitude of 10 nm can be treated with pure quantum chemical methods using CRYSTAL03 software. Currently, the approach is limited to a 6th order rotational axis. Implementation of higher order rotational axes into the software



would remove the size limits in cylindrical systems altogether. The methodology was applied for the case of single-walled magnesium dichloride nanotubes, which was selected as a prototype system. The relative stabilities of three coordination modes of  $\text{MgCl}_2$  nanotubes were investigated as a function of tube diameter. The preference of a cylindrical form of a sheet from the crystal lattice cannot be taken for granted, the diameter of the tube having a significant influence on structural preferences. In the case of  $\text{MgCl}_2$  nanotubes, the rolled sheet of crystal lattice, with the respective coordination numbers for Mg and Cl of 6 and 3, becomes the favored coordination mode at diameters above 3.4 nm. Below that, another cylindrical form, but with coordination numbers of 4 and 2 for Mg and Cl, respectively, is preferred in energy. The  $\text{MgCl}_2$  nanotubes, once synthesized, are expected to contribute to the future applications of nanotechnology. Owing to the ultimate surface area, they may turn out as useful catalyst carriers in olefin polymerization catalysis. The introduced methodology is not limited to the nanotubes of magnesium dichloride, enabling ab initio level structure determination of various nanotubular compounds, including multiwalled ones.

## References and Notes

- (1) (a) Tenne, R. *Chem.—Eur. J.* **2002**, *8*, 5296–5304. (b) Tenne, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 5124–5132. (c) Rao, C. N. R.; Nath, M. *Dalton Trans.* **2003**, 1–24. (d) Remskar, M. *Adv. Mater.* **2004**, *16*, 1497–1504.
- (2) (a) Rubio, A.; Corkill, J. L.; Cohen, M. L. *Phys. Rev. B* **1994**, *49*, 5081–5084. (b) Côté, M.; Cohen, M. L.; Chadi, D. J. *Phys. Rev. B* **1998**, *58*, 4277–4280. (c) Lee, S. M.; Lee, Y. H.; Hwang, Y. G.; Elsner, J.; Porezag, D.; Frauenheim, T. *Phys. Rev. B* **1999**, *60*, 7788–7791. (d) Boustani, I.; Quandt, A.; Hernández, E.; Rubio, A. *J. Chem. Phys.* **1999**, *110*, 3176–3185. (e) Fagan, S. B.; Baierle, R. J.; Mota, R.; da Silva, A. J. R.; Fazzio, A. *Phys. Rev. B* **2000**, *61*, 9994–9996. (f) Seifert, G.; Terrones, H.; Jungnickel, G.; Frauenheim, T. *Phys. Rev. Lett.* **2000**, *85*, 146–149. (g) Seifert, G.; Terrones, H.; Terrones, M.; Jungnickel, G.; Frauenheim, T. *Solid State Commun.* **2000**, *114*, 245–248. (h) Seifert, G.; Terrones, H.; Terrones, M.; Frauenheim, T. *Solid State Commun.* **2000**, *115*, 635–638. (i) Seifert, G.; Hernández, E. *Chem. Phys. Lett.* **2000**, *318*, 355–360. (j) Zhang, P.; Crespi, V. H. *Phys. Rev. Lett.* **2002**, *89*, 056403–1–4. (k) Barnard, A. S.; Russo, S. P. *J. Phys. Chem. B* **2003**, *107*, 7577–7581. (l) Guerini, S.; Piquini, P. *Microelectr. J.* **2003**, *34*, 495–497. (m) Cabria, I.; Mintmire, J. W. *Europhys. Lett.* **2004**, *65*, 82–88. (n) Ponomarenko, O.; Radny, M. W.; Smith, P. V. *Surf. Sci.* **2004**, *562*, 257–268. (o) Chang, H.; In, E.; Kong, K.; Lee, J.-O.; Choi, Y.; Ryu, B.-H. *J. Phys. Chem. B* **2005**, *109*, 30–32. (p) Jhi, S.-H.; Roundy, D. J.; Louie, S. G.; Cohen, M. L. *Solid State Commun.* **2005**, *134*, 397–402.
- (3) Iijima, S. *Nature* **1991**, *354*, 56–58.
- (4) (a) Linnolahti, M.; Pakkanen, T. A. *Inorg. Chem.* **2004**, *43*, 4482–4486. (b) Linnolahti, M.; Luhtanen, T. N. P.; Pakkanen, T. A. *Chem.—Eur. J.* **2004**, *10*, 5977–5987.
- (5) (a) de Leeuw, N. H.; Du, Z.; Li, J.; Yip, S.; Zhu, T. *Nano Lett.* **2003**, *3*, 1347–1352. (b) Bromley, S. T. *Nano Lett.* **2004**, *4*, 1427–1432. (c) Linnolahti, M.; Kinnunen, N. M.; Pakkanen, T. A. *Chem.—Eur. J.* **2006**, *12*, 218–224.
- (6) Wu, Q.; Hu, Z.; Wang, X.; Lu, Y.; Chen, X.; Xu, H.; Chen, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10176–10177.
- (7) (a) Zhao, M.; Xia, Y.; Tan, Z.; Liu, X.; Li, F.; Huang, B.; Ji, Y.; Mei, L. *Chem. Phys. Lett.* **2004**, *389*, 160–164. (b) Chen, X.; Ma, J.; Hu, Z.; Wu, Q.; Chen, Y. *J. Am. Chem. Soc.* **2005**, *127*, 7982–7983. (c) Zhang, M.; Su, Z.-M.; Yan, L.-K.; Qiu, Y.-Q.; Chen, G.-H.; Wang, R.-S. *Chem. Phys. Lett.* **2005**, *408*, 145–149.
- (8) Seifert, G.; Köhler, T.; Tenne, R. *J. Phys. Chem. B* **2002**, *106*, 2497–2501.
- (9) (a) Rosenfeld Hachon, Y.; Grunbaum, E.; Tenne, R.; Sloan, J.; Hutchison, J. L. *Science* **1998**, *395*, 336–337. (b) Popovitz-Biro, R.; Twersky, A.; Rosenfeld Hachon, Y.; Tenne, R. *Isr. J. Chem.* **2001**, *14*, 7–14. (c) Rosenfeld Hachon, Y.; Popovitz-Biro, R.; Grunbaum, E.; Prior, Y.; Tenne, R. *Adv. Mater.* **2002**, *14*, 1075–1078. (d) Sallacan, N.; Popovitz-Biro, R.; Tenne, R. *Solid State Sci.* **2003**, *5*, 905–908. (e) Popovitz-Biro, R.; Sallacan, N.; Tenne, R. *J. Mater. Chem.* **2003**, *13*, 1631–1634. (f) Rosenfeld Hachon, Y.; Popovitz-Biro, R.; Prior, Y.; Gemming, S.; Seifert, G.; Tenne, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1644–1651. (g) Armstrong, A. R.; Canales, J.; Bruce, P. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4899–4902.
- (10) Luhtanen, T. N. P.; Linnolahti, M.; Pakkanen, T. A. *Inorg. Chem.* **2004**, *43*, 4482–4486.
- (11) Siegbahn, P. E. M. *Adv. Chem. Phys.* **1996**, *93*, 333–387.
- (12) Pykkö, P. *Chem. Rev.* **1988**, *88*, 563–594.
- (13) Luhtanen, T. N. P.; Linnolahti, M.; Laine, A.; Pakkanen, T. A. *J. Phys. Chem. B* **2004**, *108*, 3989–3995.
- (14) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503–1546.
- (15) Ceulemans, A.; Chibotaru, L. F.; Fowler, P. W.; Szopa, M. *J. Chem. Phys.* **1999**, *110*, 6916–6926.
- (16) Damnjanović, M.; Vuković, T.; Milošević, I.; Nikolić, B. *Acta Crystallogr.* **2001**, *A57*, 304–310.
- (17) (a) Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579–1581. (b) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2204–2206.
- (18) Saunders, V. R.; Dovesi, R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Harrison, N. M.; Doll, K.; Civalieri, B.; Bush, I. J.; D'Arco, Ph.; Llunell, M. *CRYSTAL2003 User's Manual*; University of Torino: Torino, Italy, 2003.
- (19) Barrera, G. D.; Allan, N. L.; Soriano, M. R. *Chem. Phys. Lett.* **1997**, *278*, 267–271.
- (20) Harrison, N. M.; Saunders, V. R. *J. Phys.: Condens. Matter* **1992**, *4*, 3873–3882.
- (21) Modified hyperbolic fit  $y = a + b/x^c$  was applied in the extrapolation of cylindrical tubes to an infinite diameter, i.e., to the corresponding sheet.
- (22) Bassi, I. W.; Polato, F.; Calcaterra, M.; Bart, J. C. Z. *Kristallogr.* **1982**, *159*, 297–302.
- (23) Kunstmann, J.; Quandt, A. *Chem. Phys. Lett.* **2005**, *402*, 21–26.