Symmetry Properties of Single-Walled BC$_2$N Nanotubes

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Abstract The symmetry properties of the single-walled BC$_2$N nanotubes were investigated. All the BC$_2$N nanotubes possess nonsymmorphic line groups. In contrast with the carbon and boron nitride nanotubes, armchair and zigzag BC$_2$N nanotubes belong to different line groups, depending on the index $n$ (even or odd) and the vector chosen. The number of Raman-active phonon modes is almost twice that of the infrared-active phonon modes for all kinds of BC$_2$N nanotubes.

Keywords BC$_2$N nanotubes · Symmetry · Group theory

Introduction

Carbon nanotubes have been extensively studied because of their interesting physical properties and potential applications. Motivated by this success, scientists have been exploring nanotubes and nanostructures made of different materials. In particular, boron carbon nitride (B$_x$C$_y$N$_z$) nanotubes have been synthesized [1, 2]. Theoretical studies have also been carried out to investigate the electronic, optical and elastic properties of BC$_2$N nanotubes using the first-principles and tight-binding methods, respectively [3–6]. Besides the elastic and electronic properties, theoretical and experimental research on phonon properties of BC$_2$N nanotubes is also useful in understanding the properties of the nanotubes. For example, the electron–phonon interaction is expected to play crucial roles in normal and superconducting transition. Furthermore, symmetry properties of nanotubes have profound implications on their physical properties, such as photogalvanic effects in boron nitride nanotubes [7]. Studies on the symmetry properties of carbon nanotubes predicted the Raman- and infrared-active vibrations in the single-walled carbon nanotubes [8], which are consistent with the experimental data [9] and theoretical calculations [10]. A similar work was carried out by Alon on boron nitride nanotubes [11], and the results were later confirmed by first-principles calculations [12]. And the symmetry of BC$_2$N nanotube was reported [13]. The purpose of this study is to extend the symmetry analysis to BC$_2$N nanotubes and to determine their line groups. The vibrational spectra of BC$_2$N nanotubes are predicted based on the symmetry. The number of Raman- and infrared (IR)-active vibrations of the BC$_2$N nanotubes is determined accordingly.

Structures of BC$_2$N Nanotubes

Similar to carbon or boron nitride nanotubes [14, 15], a single-walled BC$_2$N nanotube can be completely specified by the chiral vector which is given in terms of a pair of integers ($n$, $m$) [3]. However, compared to a carbon and boron nitride nanotubes, different BC$_2$N nanotubes can be obtained by rolling up a BC$_2$N sheet along different directions, as shown in Fig. 1a, because of the anisotropic...
geometry of the BC$_2$N sheet. If we follow the notations for carbon nanotubes [14], at least two types of zigzag BC$_2$N nanotubes and two types of armchair nanotubes can be obtained [6]. For convenience, we refer the two zigzag nanotubes obtained by rolling up the BC$_2$N sheet along the $a_1$ and the $a_2$ directions as ZZ$_{-1}$ and ZZ$_{-2}$, respectively, and two armchair nanotubes obtained by rolling up the BC$_2$N sheet along the $R_1$ and $R_2$ directions as AC$_{-1}$ and AC$_{-2}$, respectively. The corresponding translational lattice vectors along the tube axes are $T_{a1}$, $T_{a2}$, $T_{R1}$, and $T_{R2}$, respectively, as shown in Fig. 1a. It is noted that $T_{a2}$ is parallel to $R_2$, $T_{R1}$ to $b_1$, and $T_{R2}$ to $a_2$. An example of each type of BC$_2$N nanotubes is given in Fig. 1b–f.

**Symmetry of BC$_2$N Nanotubes**

We first consider the achiral carbon nanotubes with the rotation axis of order $n$, i.e., zigzag ($n$, 0) or armchair ($n$, $n$). The nonsymmorphic line-group [16] describing such achiral carbon nanotubes can be decomposed in the following way [17]:

$$G_n = \frac{C_{138}}{C_1} = \frac{LT_z}{C_2} \frac{D_{nh}}{C_2} \frac{E}{C_8} \frac{S_{2n}}{C_1}$$

where $LT_z$ is the 1D translation group with the primitive translation $T_z = |T_z|$, and $E$ is the identity operation. The screw axis $S_{2n} = z \rightarrow z + T_z/2, \varphi \rightarrow \varphi + \pi/n$ involves the smallest nonprimitive translation and rotation [11].

The corresponding BC$_2$N sheet of the zigzag ($n$, 0) BC$_2$N nanotubes (ZZ$_{-1}$) (Fig. 1b) is shown in Fig. 2. They have vertical symmetry planes as indicated by $g$. In this case, the $D_{nh}$ and $D_{nd}$ point groups reduce to $C_n$, due to the lack of horizontal symmetry axis/plane, and $S_{2n}$ vanishes for the lack of the screw axis. Thus,

$$G_{zz}^{-1}[n] = L_{T_z} \times C_{nv} \times E$$

The point group of the line group is readily obtained from Eq. 2,

$$C_{0}^{zz^{-1}}[n] = C_{nv}. \quad (3)$$

To determine the symmetries at the $\Gamma$ point of the 12 N ($N$ is the number of unit cells in the tube and $N = n$ for ZZ-1 BC$_2$N nanotubes) of phonons in ZZ-1 BC$_2$N nanotubes and the number of Raman- or IR-active modes, we have to associate them with the irreducible representations (irrep’s) of $C_{nv}$. Here, two cases need to be considered.

**Case 1**

$n$ is odd (or $n = 2m + 1$, $m$ is an integer)

The character table of $C_{2(m+1)v}$ possesses $m + 2$ irrep’s [18], i.e.,

$$\Gamma_{C_{2(m+1)\nu}} = A_1 \oplus A_2 \oplus \sum_{j=1}^{m} E_j \quad (4)$$

The 12 N phonon modes transform according to the following irrep’s:
\[ \Gamma_{12N}^{\text{ZZ}} = \Gamma_{o}^{\text{ZZ}} \otimes \Gamma_{v} = 8A_{1} \oplus 4A_{2} \oplus \sum_{j=1}^{m} 12E_{j} \]  

(5)

where

\[ \Gamma_{o}^{\text{ZZ}} = 4A_{1} \oplus \sum_{j=1}^{m} 4E_{j}(N = n) \]  

(6)

stands for the reducible representation of the atom positions inside the unit cell. The prefactor of 4 in \( \Gamma_{o}^{\text{ZZ}} \) reflects the four equivalent and disjoint sublattices made by the four atoms in the ZZ-1 BC\(_{2}\)N nanotubes. \( \Gamma_{v} = A_{1} \oplus E_{1} \) is the vector representation. Of these modes, the ones that transform according to \( \Gamma_{v} = A_{1} \oplus E_{1} \oplus E_{2} \) (the tensor representation) or \( \Gamma_{v} \) are Raman- or IR-active, respectively. Out of the 12 N modes, four have vanishing frequencies \([19]\), which transform as

\[ \Gamma_{12}^{\text{ZZ}} \Rightarrow n_{\text{Raman}}^{\text{ZZ}} = 30 \]  

(7)

\[ \Gamma_{12}^{\text{IR}} \Rightarrow n_{\text{IR}}^{\text{ZZ}} = 18 \]  

(8)

\textbf{Case 2}

\( n \) is even (or \( n = 2m, m \) is an integer)

The character table of \( C_{2m} \) possesses \( m + 3 \) irrep’s \([18]\), i.e.,

\[ \Gamma_{(n+1)\nu}^{C_{2m}} = A_{1} \oplus A_{2} \oplus B_{1} \oplus B_{2} \oplus \sum_{j=1}^{m-1} E_{j} \]  

(9)

The 12 N phonon modes transform according to the following irrep’s:

\[ \Gamma_{12N}^{\text{ZZ}} = \Gamma_{v}^{\text{ZZ}} \otimes \Gamma_{v} = 8A_{1} \oplus 4A_{2} \oplus 8B_{1} \oplus 4B_{2} \oplus \sum_{j=1}^{m-1} 12E_{j} \]  

(10)

where

\[ \Gamma_{v}^{\text{ZZ}} = 4A_{1} \oplus 4B_{1} \oplus \sum_{j=1}^{m-1} 4E_{j}(N = n) \]  

(11)

\( \Gamma_{v} = A_{1} \oplus E_{1} \) is the vector representation. Of these modes, the ones that transform according to \( \Gamma_{v} = A_{1} \oplus E_{1} \oplus E_{2} \) (the tensor representation) or \( \Gamma_{v} \) are Raman- or IR-active, respectively. Out of the 12 N modes, four (which transform as \( \Gamma_{v} \) and \( \Gamma_{R} = A_{2} \)) have vanishing frequencies \([16]\).

\[ \Gamma_{12N}^{\text{ZZ}} \Rightarrow n_{\text{Raman}}^{\text{ZZ}} = 30 \]  

(12)

\[ \Gamma_{12N}^{\text{IR}} \Rightarrow n_{\text{IR}}^{\text{ZZ}} = 18 \]  

(13)

\textbf{Case 1}

\( n \) is odd (\( n = 2m + 1 \))

The character table of \( C_{2m+1} \) possesses \( 4m + 2 \) irrep’s \([18]\), i.e.,

\[ \Gamma_{(n+1)\nu}^{C_{2m+1}} = \hat{A} \oplus \hat{A}^{\prime} \oplus \sum_{j=1}^{m} \left\{ E_{j}^{k} \oplus E_{j}^{s} \right\} \]  

(16)

The 12 N phonon modes transform according to the following irrep’s:

\[ \Gamma_{12N}^{\text{AC}} = \Gamma_{o}^{\text{AC}} \otimes \Gamma_{v} = 8\hat{A} \oplus 4\hat{A}^{\prime} \oplus \sum_{j=1}^{m} \left\{ 4E_{j}^{k} \oplus 8E_{j}^{s} \right\} \]  

(17)

where

\[ \Gamma_{o}^{\text{AC}} = 4\hat{A} \oplus \sum_{j=1,3,5,...}^{m} 4E_{j}^{k} \oplus \sum_{j=2,4,6,...}^{m} 4E_{j}^{s}(N = n) \]  

(18)
and \( \Gamma_v = A^v \oplus E_1^{\pm} \) is the vector representation. Of these modes, the ones that transform according to \( \Gamma_v = A^v \oplus E_2^{\pm} \oplus E_3^{\pm} \) (the tensor representation) or \( \Gamma_v \) are Raman- or IR-active, respectively. Out of the 12 N modes, four (which transform as \( \Gamma_v \) and \( \Gamma_{IR} = A^v \)) have vanishing frequencies [19].

\[
\Gamma_{AC-2}^{Raman} = 7A^v + 4E_2^{\pm} + 8E_4^{\pm} \Rightarrow n_{Raman}^{AC-2} = 19
\]

\[
\Gamma_{IR}^{AC-2} = 7A^v + 3E_1^{\pm} \Rightarrow n_{IR}^{ZZ-1} = 10
\]

Case 2

\( n \) is even \( (n = 2m) \)

The character table of \( C_{2mh} \) possesses 4m irrep’s [18], i.e.,

\[
\Gamma_{C_{2mh}} = A_g \oplus B_g \oplus A_u \oplus B_u \oplus \sum_{j=1}^{m-1} \left \{ E_{1g}^{\pm} \oplus E_{2g}^{\pm} \right \}
\]

The 12 N phonon modes transform according to the following irrep’s:

\[
\Gamma_{AC-2}^{12N} = \Gamma_{AC-2} \otimes \Gamma_v
\]

\[
= 8A_g \oplus 4B_g \oplus 4A_u \oplus 8B_u \oplus 4E_{1g}^{\pm} \oplus 8E_{2g}^{\pm} \oplus 4E_{3g}^{\pm}
\]

\[
\oplus \cdots \oplus \left \{ 6 + 2(-1)^{m-1}E_{(m-1)g}^{\pm} \right \} \oplus 8E_{1u}^{\pm} \oplus 4E_{2u}^{\pm}
\]

\[
\oplus 8E_{3u}^{\pm} \oplus \cdots \oplus [6 + 2(-1)^{m}]E_{(m-1)u}^{\pm}
\]

where

\[
\Gamma_{AC-2} = 4A_g \oplus 4B_g \oplus \sum_{j=2,4,6,\ldots}^{m-1} 4E_{1g}^{\pm} \oplus \sum_{j=1,3,5,\ldots}^{m-1} 4E_{2g}^{\pm} (N = n)
\]

The numbers of Raman- and IR-active modes are 19 and 10, respectively, for AC-1 BC2N nanotubes in irrespective of n. The numbers of Raman- and IR-active phonon modes for ZZ-1 BC2N nanotubes are Raman- and/or IR-active, respectively. Out of the 24 N modes, four (which transform as \( \Gamma_v \) and \( \Gamma_{IR} = A^v \)) have vanishing frequencies [19].

\[
\Gamma_{AC-2}^{Raman} = 7A_g \oplus 4E_{1g}^{\pm} \oplus 8E_{2g}^{\pm} \Rightarrow n_{Raman}^{AC-2} = 19
\]

\[
\Gamma_{IR}^{AC-2} = 3A_u \oplus 7E_{1u}^{\pm} \Rightarrow n_{IR}^{ZZ-1} = 10
\]

The nonsymmorphic line group describing the \( (n, m) \)-chiral carbon nanotubes can be decomposed as follows:

\[
G[N] = L_\tau \times D_d \times \left \{ \sum_{j=0}^{N/d-1} S_{N/d}^j \right \} = L_\tau \times D_1 \times \left \{ \sum_{j=0}^{N-1} S_N^j \right \}
\]

where \( N = 2(n^2 + m^2 + n'm')/d_R \); where \( d_R \) is the greatest common divisor of \( 2n + m' \) and \( 2m + n' \); \( d \) is the greatest common divisor of \( n' \) and \( m' \); \( S_{N/d} \) and \( S_N \) are the screw-axis operations with the orders of \( N/d \) and \( N \), respectively. The point group of the line group is obtained from Eq. 26,

\[
G_0[N] = \sum_{j=0}^{N/d-1} C_j^{N/d} \times D_d = \sum_{j=0}^{N-1} C_j^N \times D_1 = D_N
\]

where \( C_{N/d} = (\phi \rightarrow \phi + 2d\pi/N) \) and \( C_N = (\phi \rightarrow \phi + 2\pi/N) \) are the rotations embedded in \( S_{N/d} \) and \( S_N \), respectively.

For chiral \( (n, m) \) BC2N nanotubes, the point group \( D_N \) reduces to \( C_N \) due to the lack of \( C_2 \) axes. Here, \( N = (n^2 + m^2 + n'm')/d_R \) \( (n' = 2n, m' = m) \), where \( d_R \) is the greatest common divisor of \( 2n + m' \) and \( 2m' + n' \); \( d \) is the greatest common divisor of \( n \) and \( m \). The BC2N sheets corresponding to ZZ-2 and AC-2 are shown in Fig. 4a and b, which are chiral in nature. The \( \sigma_c \) and \( \sigma_d \) vanish in Fig. 4a and b, respectively, for ZZ-2 and AC-2 BC2N nanotubes, \( N = 4n \). The point group corresponding to the two models is expressed as:

\[
G_0[N] = \sum_{j=0}^{N/d-1} C_j^{N/d} \times C_d = \sum_{j=0}^{N-1} C_j^N \times C_1 = C_N
\]

The character table of \( C_N \) has \( N \) irrep’s, i.e.,

\[
\Gamma_{C_N}^N = A \oplus B \oplus \sum_{j=1}^{N/2-1} E_j^{\pm}
\]

The 12 N phonon modes transform according to the following irrep’s:

\[
\Gamma_{ch}^{12N} = \Gamma_{ch}^A \otimes \Gamma_v = 12A \oplus 12B \oplus \sum_{j=1}^{N/2-1} 12E_j^{\pm}
\]

where \( \Gamma_{ch}^A = 4 \left ( A \oplus B \oplus \sum_{j=1}^{N/2-1} E_j^{\pm} \right ) \) and \( \Gamma_v = A \oplus E_1^{\pm} \). Of these modes, the ones that transform according to \( \Gamma_v = A \oplus E_1^{\pm} \oplus E_2^{\pm} \) and/or \( \Gamma_v \) are Raman- and/or IR-active, respectively. Out of the 24 N modes, four (which transform as \( \Gamma_v \) and \( \Gamma_{IR} = A^v \)) have vanishing frequencies [19].

\[
\Gamma_{Raman}^{ch} = 10A \oplus 11E_1^{\pm} \oplus 12E_2^{\pm} \Rightarrow n_{Raman}^{ch} = 33
\]

\[
\Gamma_{IR}^{ch} = 10A \oplus 11E_1^{\pm} \Rightarrow n_{IR}^{ch} = 21
\]

Experimentally, only several Raman/IR-active modes can be observed. The observable Raman-active modes are with the range of \( 0-2000 \) cm\(^{-1}\). The \( E_{2g} \) mode around 1580 cm\(^{-1}\) is related to the stretching mode of C–C bond. The \( E_{2g} \) mode around 1370 cm\(^{-1}\) is attributed to B–N vibrational mode [20, 21]. The experimental Raman
spectra between 100 and 300 cm\(^{-1}\) should be attributed to \(E_{1g}\) and \(A_{1g}\) modes [22].

**Conclusions**

In summary, the symmetry properties of BC\(_2\)N nanotubes were discussed based on line group. All BC\(_2\)N nanotubes possess nonsymmorphic line groups, just like carbon nanotubes [8] and boron nitride nanotubes [11]. Contrary to carbon and boron nitride nanotubes, armchair and zigzag BC\(_2\)N nanotubes belong to different line groups, depending on the index \(n\) (even or odd) and the vector chosen. By utilizing the symmetries of the factor groups of the line groups, it was found that all ZZ\(_{-1}\) BC\(_2\)N nanotubes have 30 Raman- and 18 IR- active phonon modes; all AC\(_{-1}\) BC\(_2\)N nanotubes have 19 Raman- and 10 IR-active phonon modes; all ZZ\(_{-2}\), AC\(_{-2}\), and other chiral BC\(_2\)N nanotubes have 33 Raman- and 21 IR-active phonon modes. It is noticed that the numbers of Raman- and IR-active phonon modes in ZZ\(_{-1}\) BC\(_2\)N nanotubes are almost twice as in AC\(_{-1}\) BC\(_2\)N nanotubes, but which is almost the same as those in chiral, ZZ\(_{-2}\), and AC\(_{-2}\) BC\(_2\)N nanotubes. The situation in BC\(_2\)N nanotubes is different from that in carbon or boron nitride nanotubes [8, 11].

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