First-principles study of the electronic structure of aluminate nanotubes

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Abstract. We report the results of first-principles theoretical calculations for the electronic structure of aluminate nanotubes. A tubular structure in the form of AlO$_2$ is energetically stable and exhibits metallic conduction. Due to weak interactions between Li atoms and nanotubes, Li doping does not alter the stability of AlO$_2$ nanotubes and only increases the Fermi level. On the other hand, stable AlO nanotubes can be obtained by hole doping with Be and Mg impurities.

1. Introduction

Recently, one dimensional nanostructures have attracted considerable attention due to a wide variety of applications in nano-scale devices. Since the discovery of carbon fullerenes and later carbon nanotubes [1], various tubular forms derived from chemical compounds with a layer structure have been reported, such as BN [2,3], WS$_2$ [4,5], and MoS$_2$ [6,7]. Very recently, using the surfactant templating method without the addition of any organic solvant, lithium containing aluminate nanotube bundles have been successfully produced [8].

It is known that lithium aluminate, LiAlO$_2$, exists in five allotropic forms, monoclinic, rhombohedral $\alpha$, orthorhombic $\beta$, and tetragonal $\gamma$ and $\delta$ ones [9,10,11]. In the $\alpha$-phase, a layered AlO$_2$ has a metal layer sandwiched between two O layers. Aluminate nanotubes can be constructed by wrapping up a single AlO$_2$ sheet into a cylindrical tube, where each Al atom is bonded to six O atoms, with each three on the inner and outer shells. The rolling index can be defined, similar to carbon nanotubes, as shown in Fig. 1. Similarly, AlO nanotubes can be formed by a double layer of single Al and O layers. Transmission electron microscopy images and x-ray diffraction patterns showed that aluminate nanotubes have the characteristics of the $\alpha$-phase [8]. Experiments further suggested that a bundle of synthesized lithium containing nanotubes mainly consist of AlO nanotubes with central Li cores. However, our recent theoretical calculations showed that aluminate nanotubes are energetically stable in the form of AlO$_2$, while AlO nanotubes are generally disintegrated into clusters after full relaxations [12,13].

In this work we report the results of first-principles calculations for the electronic structure of aluminate nanotubes. All the AlO$_2$ nanotubes are metallic with pseudogaps right above the Fermi level. Due to weak interactions between the Li atoms and nanotubes, Li doping does not alter the stability of AlO$_2$ nanotubes and only increases the Fermi level. On the other hand, AlO nanotubes which can be stabilized by hole doping eventually turn into semiconducting nanotubes, similar to BN nanotubes.
Figure 1. Ball-and-stick models for (a) alpha-LiAlO$_2$, (b) single AlO$_2$ sheet, (c) armchair (4,4), and zigzag (7,0) AlO$_2$ nanotubes. In the AlO$_2$ sheet, the primitive lattice vectors are represented by $a$ and $b$, and O$_{in}$ and O$_{out}$ denote the inner and outer O atoms, respectively, which will be positioned in the tube.

2. Calculational method
To study the stability and electronic structure of aluminate nanotubes, we use a first-principles pseudopotential method within the density functional theory [14,15]. We use the generalized gradient approximation for the exchange-correlation potential [16]. We employ ultrasoft pseudopotentials to efficiently treat the localized nature of the O orbitals [17]. The wave functions are expanded in plane waves with the kinetic energy cutoff of 30 Ry. All the calculations are done for tetragonal supercells with the tube-tube distances of 15-22 Å. The Brillouin zone summation is performed by using a set of 3 k-points. We test 8 and 12 k-point sets and find that the total energies are accurate with the numerical accuracy of 1 meV per AlO$_2$ unit formula.

We examine various armchair ($n,n$) and zigzag ($n,0$) nanotubes with diameters ranging from 6.0–11.5 Å, which correspond to $n = 4$ and 7 for the armchair tubes and $n = 6$, 7, 9, and 11 for the zigzag tubes. For the (3,3) nanotube with a small diameter of 5.2 Å, a single tubular structure is unstable against disintegration. In zigzag tubes, the Al–O bond lengths in the inner O shell are generally smaller than those in the outer shell, while those for armchair nanotubes are similar. In the zigzag (5,0) tube with a small diameter, since the complex planar structure is not likely amenable to be rolled up into a tube, each of the outer O atoms is only bonded to one Al neighbor. Similarly, in the small diameter (4,4) tube, the Al–O network is more severely distorted, where each of the outer O atoms is closer to its right-hand Al neighbor and vice versa for the inner O atoms. In the sheet, each O atom is effectively bonded to three neighboring Al atoms, as shown in Fig. 1 (b), while two Al–O bond lengths are slightly larger than the other one due to the curvature effect in the zigzag tubes.

3. Results and discussion
The band structures of the AlO$_2$ nanotubes are generally similar to that for a single AlO$_2$ sheet, as shown in Fig. 2. Since the single AlO$_2$ sheet has a lack of one electron per unit formula to form completely ionic bonds, it shows the metallic band structure with a pseudogap of 6.7 eV just above the Fermi level. This pseudogap in fact corresponds to the energy gap of bulk LiAlO$_2$, which is the energy separation between the bonding and antibonding states of the Al–O bonds. In carbon nanotubes, their electronic structure is mainly determined by whether allowed wave vectors cross the Fermi point or not, i.e., the K point in the hexagonal Brillouin zone [18]. The single AlO$_2$ sheet has an indirect
pseudogap, with the conduction band edge located at the zone center point. Since allowed wave vectors always cross the $\Gamma$ point, the pseudogap intrinsically appears in the AlO$_2$ nanotubes. The size of pseudogaps is sensitive to variations in the Al–O and Al–Al bond distances. The pseudogap tends to decrease with increasing of the Al–O bond length. Due to the curvature effect, the Al–O bond lengths in the outer O shell are larger by about 0.10 – 0.38 Å than those for the single sheet, while the inner O shell has similar Al–O bond lengths. The Al–Al bond lengths also increase by 0.2 – 0.3 Å in

![Figure 2](image.png)

**Figure 2.** The band structures for the (a) single AlO$_2$ sheet, (b) zigzag (7,0), and (c) armchair (4,4) AlO$_2$ nanotubes, with the Fermi level set to zero.

![Figure 3](image.png)

**Figure 3.** The projected densities of states onto the Al and O atoms in the (a) zigzag (7,0) and (b) armchair (4,4) AlO$_2$ nanotubes, with the Fermi level set to zero.
the tubular form. The pseudogaps of the AlO₂ nanotubes considered here are smaller by about 2.8–3.3 eV than for the AlO₂ sheet, while it eventually reaches the value for the AlO₂ sheet as the diameter goes to infinite. For the zigzag tubes, the pseudogap increases from 3.7 to 3.9 eV when the tube index changes from \( n = 7 \) to 11, while it is 3.4 and 3.7 eV for the (4,4) and (7,7) tubes, respectively.

The projected densities of states (PDOSs) onto the Al and O atoms for the AlO₂ nanotubes are shown in Fig. 3. Similar to the AlO₂ sheet, the \( s^- \) and \( p^- \)-derived bands are well separated and the Fermi levels are located just below the O \( p^- \)-derived band edge. However, since the Al-O bond lengths on the outer O shell are larger than those on the inner shell, both the O \( s^- \) and \( p^- \)-derived bands split into two bands for the (7,0) nanotube. Due to shorter Al–O bond lengths, the O atoms on the inner O shell are more strongly bonded to the Al atoms, resulting in the lowering of the bonding states. Since the inner \( O p^- \) band is lowered, the Fermi level is located in the outer O \( p^- \) band. The plot of electron charge densities around the Fermi level shows that electron conduction is more contributed from the outer Al–O network. In the large diameter (11,0) nanotube, since the difference between the outer and inner Al-O bond lengths is much reduced, the electron conduction from the inner shell is enhanced. On the other hand, in the armchair tubes, the Al–O bond lengths are similar for both the O shells, thus, the whole tube wall contributes to electron conduction. As the tube diameter increases, the width of the O \( p^- \) band decreases for both the zigzag and armchair nanotubes. When Li atoms are encapsulated inside the tube cavity, electron charges are transferred from the dopant atoms to the nanotubes. In this case, the inner Al–O bond lengths slightly elongated, while the outer Al–O bond lengths decrease. Since interactions between the Li atoms and the nanotubes are weak, the band structure is little affected, only raising the Fermi level. With increasing the concentration of the Li dopants to one Li atom per Al atom, the metallic AlO₂ nanotubes eventually turn into semiconducting nanotubes.

The AlO nanotubes, which are formed by a double layer consisting of single Al and O sheets, are generally unstable in their neutral charge state. Since the ionic Al–O bonds have one extra electron per bond in the absence of one O shell, the Fermi level lies in the conduction band, resulting in metallic AlO nanotubes. However, these bonds are very weak, and the nanotubes easily disintegrate into cluster. If the Li impurities are doped, the AlO nanotubes maintain the metallic band structure, thus, it is still difficult to form the stable tubular structure. Our calculations rule out the possibility that a bundle of lithium aluminate nanotubes experimentally synthesized [8] consists of the AlO nanotubes. On the other hand, if the Be or Mg impurities substitute for the Al sites, the Fermi level decreases. When one hole per unit formula is doped, the tubular structure is found to be very stable, with circular cross sections for the (7,0) tube, while square cross sections appear for the (9,0) and (11,0) tubes with larger diameters, as shown in Fig. 4. The projected densities of states show that the Fermi level lies in the band gap. Thus, the AlO nanotubes doped with one hole per Al atom resemble the BN nanotubes [19]. The hole doping is also achievable with the F atoms as interstitial dopants. Since the F atom is more electronegative than the O atom, the electron charges will transfer from the AlO nanotubes into the F

**Figure 4.** Ball-and-stick models for the positively charged (a) (7,0), (b) (9,0), and (c) (11,0) AlO nanotubes, with one hole per unit formula.
atoms. In fact, the stable tubular structure is obtained when the F atoms are encapsulated in the tube cavity, although these atoms tend to directly bind with the Al atoms.

4. Summary
Based on the first-principles calculations, we suggest that a bundle of lithium aluminate nanotubes, which has been experimentally synthesized [8], consists of the AlO2 nanotubes. The AlO nanotubes containing lithium are extremely unstable, disintegrating into clusters, and these tubes can only be stabilized by hole doping. All the AlO2 nanotubes are metallic due to the lack of one electron per unit formula, with the Fermi level lying in the O p-derived band. As the doping level increases with the Li impurities, the Fermi level increases, and the AlO2 nanotubes eventually becomes semiconducting, with the pseudogap turned into the real gap. Since individual AlO2 nanotubes are chemically very active, these tubes will be strongly bound together when they are self-organized into bundles [20].

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