Structural and electronic properties of MgO nanotube clusters

G. Bilalbegović
Department of Physics, University of Rijeka, Omladinska 14, 51000 Rijeka, Croatia
(Received 25 January 2004; revised manuscript received 29 April 2004; published 12 July 2004)

Finite magnesium oxide nanotubes are investigated. Stacks of four parallel squares, hexagons, octagons, and decagons are constructed and studied by the pseudopotential density functional theory within the local-density approximation. Optimized structures are slightly distorted stacks of polygons. These clusters are insulators and the band gap of 8.5 eV is constant over an investigated range of the diameters of stacked polygonal rings. Using the Löwdin population analysis a charge transfer towards the oxygen atoms is estimated as 1.4, which indicates that the mixed ionic-covalent bonding exists in investigated MgO nanotubes.

DOI: 10.1103/PhysRevB.70.045407 PACS number(s): 61.46.+w, 73.22.--f, 36.40.Cg, 81.07.De

I. INTRODUCTION

Studies of nanotubes and nanowires are important for recent research in nanotechnology. Experimental and theoretical investigations of cylindrical nanostructures for many different organic and inorganic materials already exist. As new arrangements of atoms these structures are interesting for basic science. There is also a possibility to use cylindrical nanostructures as electrical and mechanical parts in nanodevices. Some technological applications of nanotubes and nanowires already exist, most notably for carbon nanotubes. Magnesium oxide is important in applications. It is known as an inert material with a high melting point, as a catalyst in important chemical reactions, and as a good substrate for many chemicals, for example metals, group III-V elements, and high-temperature superconductors. MgO is also used as an optical material and a component of composites. A bulk magnesium oxide crystallizes in the rocksalt structure. It is an insulating ionic simple oxide.

Properties of materials at a finite scale of lengths are often different in comparison to their bulk. For example, a pronounced covalent contribution to the ionic bonding exists in small MgO nanoparticles, whereas almost pure ionic bonds are typical for the bulk of this compound. Therefore, a crossover from a mixed covalent and ionic bonding to dominantly ionic one occurs in MgO nanostructures of an intermediate size. Small clusters of MgO have been investigated by several experimental and theoretical methods. A study of MgO clusters and their nucleation from the gas phase has been used to explore one possible process of a cosmic iron-magnesium-silicate dust formation in the last phase of life. Mass spectroscopy and collision-induced-magnesium-silicate dust formation in the last phase of life.
from the MgB$_2$ powders. Cubic MgO nanowires with diameters of about 100 nm and lengths of up to several micrometers have been synthesized by heating the Mg powder above its melting point in a flow of 20% O$_2$ and 80% Ar. Recently MgO nanotubes have been synthesized using a liquid metal assisted growth. They have been filled with gallium and this nanoscopic device is proposed as a thermometer with better properties than previously constructed one based on a carbon nanotube. The fabricated MgO nanotubes are cubic, several micrometers long, and exhibit both interior and exterior square cross sections. Their outer diameters are 30–100 nm, whereas interior ones are 20–60 nm. MgO nanorods have been used to produce columnar defects in high-temperature superconductors. Small MgO nanotubes studied in this work are also candidates for applications as components in the bulk, film, or wire composites of superconducting and other materials.

In this work MgO nanotubes having between 16 and 40 atoms, and made of stacks of four polygons are investigated. By stacking four polygons on top of each other and optimizing these structures, slightly distorted nanotubes of the length from 0.5782 to 0.5925 nm are formed. The structure, energetics, and electronic properties of these MgO nanotube clusters are studied using computational methods based on a pseudopotential density functional theory in the local-density approximation (LDA). The rest of the paper is organized as follows. Section II gives an outline of the method. In Sec. III the results and discussion are presented. Conclusions are summarized in Sec. IV.

II. COMPUTATIONAL METHOD

In this work ab initio density functional theory calculations are performed to study the structural and electronic properties of finite magnesium oxide nanotubes. The plane-wave pseudopotential method is applied. The density functional theory within the same plane-wave pseudopotential framework has already been used to calculate properties of the bulk MgO under high-temperature and high-pressure conditions which are important for geophysics and planetary physics. Recent density functional theory study of the high-pressure behavior of MgO at the generalized gradient approximation (GGA) level has shown an agreement with the LDA calculations of Refs. 25 and 26. Within the same plane-wave pseudopotential model as used in this work, it has been shown that the LDA approximation for the bulk of MgO and other alkaline-earth oxides yields good agreement with available structural and vibrational experimental data.

In this calculation LDA and parametrization of Perdew and Zunger for the exchange-correlation energy is applied. The pseudopotentials generated by the method of von Barth and Car for magnesium, and by one of Troullier and Martins for oxygen are used. The configurations 2$s^22p^6$ of O, and 3$s^2$ of Mg are taken as valence states. The calculations are performed with a kinetic-energy cutoff of 60 Ry. In the studies of MgO under geophysical conditions the cutoff of 90 Ry has been used, and this is important for a behavior of materials at high pressures. In the studies presented in this work (as well as in Ref. 28) it has been found that the results converge for the kinetic-energy cutoffs below 60 Ry. The cluster is positioned in the center of a large supercell of side 30 a.u. Such a choice ensures that the minimum distance between two clusters in the neighboring cells is in the worst case larger than 9.375 Å, which is found to be sufficient to prevent their interaction. The Brillouin zone is sampled using the Γ point.

Structural relaxation for MgO nanotube clusters is carried out by performing a series of self-consistent calculations and computing the forces on atoms. Rings and stable stacks of rings for MgO clusters have already been suggested by empirical and Hartree-Fock calculations. Therefore, here a cylindrical distribution of atoms in the form of stacks of polygons is assumed and interatomic distances are varied to find a minimum energy configuration. Starting nanotubes are constructed as strictly parallel stacks of regular polygons.
TABLE I. The geometry of optimized nanotubes, \( a \) is the length of the polygon side, \( l \) is the distance between opposite atoms on the top and bottom polygons. Indices \( o \) and \( i \), respectively, label outer (i.e., when at least one atom is in the top and bottom polygons) and interior bonds. Units are nm. The range of values is given if more than two values appear for a certain distance.

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>4 × 4</th>
<th>6 × 4</th>
<th>8 × 4</th>
<th>10 × 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_o )</td>
<td>0.1937</td>
<td>0.1895; 0.1900</td>
<td>0.1883; 0.1884</td>
<td>0.1874–0.1880</td>
</tr>
<tr>
<td>( a_i )</td>
<td>0.2101</td>
<td>0.2029</td>
<td>0.2007; 0.2009</td>
<td>0.1997–0.2004</td>
</tr>
<tr>
<td>( l_o )</td>
<td>0.1919; 0.1956</td>
<td>0.1950–0.2000</td>
<td>0.1961; 0.2017</td>
<td>0.1963–0.2019</td>
</tr>
<tr>
<td>( l_i )</td>
<td>0.1922</td>
<td>0.1954</td>
<td>0.1961</td>
<td>0.1969</td>
</tr>
<tr>
<td>( L )</td>
<td>0.5782</td>
<td>0.5883; 0.5886</td>
<td>0.5918</td>
<td>0.5925</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSION

Figure 1 presents the structures of MgO nanotubes which correspond to the minimum energy. This visualization is performed using the RASMOL package.\(^{24,35}\) The results show that stacked ring structures are stable during a pseudopotential density functional theory minimization. As presented in Fig. 1, the bonds and angles slightly change during the geometry optimization. The deviation from planarity of initial polygons is small. Similar, but slightly more distorted structures have been obtained by Wilson using an empirical compressible ion potential model.\(^{11}\)

It is found here that the square cross-section of the smallest 4 × 4 nanotube evolves to the rhombus. For the top and bottom rhombuses the O-Mg-O angle is 96.3°, whereas the Mg-O-Mg angle is 83.5°. The 6 × 4, 8 × 4, and 10 × 4 nanotubes after optimizations have a barrel shape as shown in Fig. 1. The optimized structural parameters are shown in Table I. The length of nanotubes increases with the number of atoms in the cluster. In optimized structures majority of the Mg-O distances decrease in comparison with initial ones of 0.2 nm. Total energies as a function of the initial diameter of MgO cylinders are shown in Table II.

The electronic density of states (DOS) for the 8 × 4 nanotube is shown in Fig. 2. The separation of bands is about 8.5 eV for all investigated nanotubes. When the diameter of a nanotube increases DOS does not change substantially, and the peaks only increase in their heights. A gap of 5.5 eV independent of the tube diameter and chirality has been found, for example, found for tubular boron nitride nanotubes.\(^{36}\) The band gap value of about 9 eV has been calculated for the 64 atoms cubelike MgO cluster using the density functional DMOl package.\(^{12}\) However, there the decrease of the band separation when the size of cubes increases has been reported. It has been calculated that for the (MgO)\(_4\) cubelike cluster the band separation is 12 eV. The increase of the number of atoms changes the number of neighbors for a cube cluster geometry where the coordination in larger clusters approaches the bulk value. Conversely, the coordination in the (MgO)\(_n\) nanotube clusters studied here does not approach the bulk value for large \( n \). A strong shape dependence of electronic properties in small MgO clusters has been found by Moukouri and Noguera using a tight binding calculation.\(^{3,5,6}\) It is known that both LDA and GGA exchange correlation functionals underestimate the electronic band gap. The band gap of 7.7 eV has been calculated in the GW approximation to the bulk electronic structure of MgO, in agreement with the experimental value of 7.8 eV.\(^{37}\) The LDA approximation used within various methods of electronic
structure calculations gives 4.19–6.6 eV for the bulk band gap of MgO.\textsuperscript{37} Therefore, the band gaps of 8.5 eV calculated in this work for MgO nanotubes within LDA, and 9 eV found in Ref. 12 for the cubelike (MgO)\textsubscript{12} cluster in the same approximation, are much larger than the values for the LDA bulk gap reported in the literature. An increase of the band gap in nanoparticles in comparison to the bulk also occurs for other materials. The origin of this phenomenon is a confinement in finite systems which increases the separation between energy levels. The value of the band gap of various MgO clusters has not been measured, and this subject certainly deserves an investigation.

The Löwdin population analysis has been carried out.\textsuperscript{38} The charges on the atoms and the average charge transfers are shown in Table III. The spilling parameter \( S \) measures the difference between the plane-wave eigenstates and their projection into the atomic basis, i.e., the amount of the total charge lost in the projecting process.\textsuperscript{39} Identical atoms with different coordination on the same nanotube sometimes have a different charge. The large charge transfer, but still less than 2, shows that the mixed ionic and covalent bonding exists in these nanotube clusters. As in Refs. 5–7, the term ionocovalent is used here to label the mixed ionic and covalent bonding. Although in a population analysis and other calculations involving the charge of ions the values depend upon the calculation model and method, a short discussion of several results follows. This point strengthens a connection between structural features of nanoparticles and the charges on the ions. The analysis of cubelike MgO clusters\textsuperscript{9} has shown that charges depend on the size of nanoparticles and on the coordination number of atoms. Moukouri and Noguera have found a large charge reduction as the coordination number decreases yielding to the charge in the MgO dimer of only half that of the bulk ions.\textsuperscript{5,6} In an early study based on the rigid ion approximation and two polarizable ion shell models, Ziemiann and Castleman have found that cubelike structures of (MgO)\textsubscript{n} correspond to the model with ion charges \( \pm 1 \).\textsuperscript{3} In their second model with ion charges \( \pm 2 \) spherical geometries composed of hexagons and squares have been optimized. Similar results have been obtained by a genetic algorithm method.\textsuperscript{8} Using an empirical potential with fluctuating charges Calvo has found that for cubelike (MgO)\textsubscript{n} clusters, when \( n \) changes from small values to the bulk regime, the charge transfer increases from 1 to 2.\textsuperscript{13} The crossover from ionocovalent to ionic bonds has been estimated to occur in these clusters at 300±100 MgO molecules. In the nanotube geometry studied here the coordination numbers are the same for all clusters and for larger clusters do not approach the bulk value. Therefore, the charge transfer of about 1.4, and the ionocovalent bonds are typical for these MgO nanotube clusters. The contour graphical representation of the charge density for the 6\times4 cluster is presented in Fig. 3. This visualization is performed using the XCRYSDEN package.\textsuperscript{40} Charges are mostly located on the oxygen atoms, but the covalent contribution to the ionic bonding exists.

### IV. CONCLUSIONS

MgO nanotubes consisting of four stacked planar \( n \)-polygonal rings (\( n=4,6,8,10 \)) are investigated by the first-principles density functional theory method in the pseudopotential approximation. These calculations show that MgO nanotube clusters are stable slightly distorted stacks of...
polycrystals. They have a large insulating band gap of 8.5 eV independently of their radius. The Löwdin population analysis indicates that the average charge transfer to oxygen atoms is 1.4. Therefore, the covalent contribution to the ionic bonding exists in these MgO nanotubes.

Experimental studies of various MgO clusters, for example, done by photoemission and electron microscopy techniques, are desirable. Recently an atomic resolution imaging of the Mg(001) surface has been reached using a dynamic scanning force microscopy. This experiment shows that similar imaging of MgO nanotubes is also feasible. It will be interesting to prepare, study, and use multilayered MgO nanowires similar to carbon and gold ones. MgO nanotubes are cylindrical structures with large interstitial regions of carbon nanotubes and these structures were imaged by electron microscopy. It is possible to prepare similar templates based on MgO nanotubes. Rectangular MgO nanorods have been recently used for the growth of embedded In nanowires. Such MgO composite nanostructures are promising candidates for antioxidation coating of metal nanowires, and as insulating layers in nanoelectronic devices. As for the BN nanotubes, a radius independent band gap calculated in this work offers a possibility to use grown samples of MgO nanotubes containing different sizes, but with similar electronic properties. Therefore, many possibilities for synthesis and experimental investigations, as well as for applications in various fields of nanotechnology exist. Some important applications of MgO cylindrical nanostructures have already been described.

ACKNOWLEDGMENTS

This work has been carried under the HR-MZT Project No. 0119255 “Dynamical Properties and Spectroscopy of Surfaces and Nanostructures.” The Pwscf package has been used. Part of the calculations has been done on the cluster of PC’s at the University Computing Center SRCE, Zagreb. I would like to thank Darko Babic for many advices and discussions about parallel computing. I am also grateful to Tone Kokalj for making available the Cygwin version of his Xcrysdex.