

Chapter 1

Introduction

Extensive experimental and theoretical investigations of nanostructures began in 1991 after the discovery of carbon nanotubes as tubular forms based on the graphite sheet (graphene) [1]. The results of carbon-based nanostructures studies (both experimental and theoretical ones) are summarized in several books [2–9]. The point defects influence on different properties of carbon nanotubes was studied in [10, 11]. In [11] the special attention was paid to the changes in the electronic properties of carbon nanotubes induced by the substitution of nitrogen, boron, or oxygen for C atoms.

However nanostructures are produced not only from carbon. In the last 20 years nanostructures of different inorganic compounds have been discovered and investigated. Researchers have synthesized not only inorganic nanotubes, but also inorganic nanoribbons, nanowires (nanorods) and nanowiskers [12, 13]. There have been reports on a variety of synthetic inorganic nanotubes [14], such as tungsten sulfide [15], silicon and boron nitrides [16, 17], vanadium, titanium and rare earth oxides [18–20]. Several reviews have appeared for the studies of inorganic nanotubes [21–27]. In [14] essential studies and topics are described concerning the synthesis, characterization and properties of individual nanotubular compounds or families.

Nanotubular materials are classified into three types [14]: single- and multi-walled rolled up nanotubes (that correspond to one or more sheets rolled into nanotube single or concentric cylindrical forms with no edge atoms) and a scrolled nanotube generated from a single straight sheet with both ends kept free.

Rolled up single- and multi-walled nanotubes are constructed from folded two-periodic (2D) layers, consisting of one or several sheets of atoms.

Multi-layered inorganic compounds (ZnO, for example) which have tubular forms are known, exhibit layers with the same hexagonal atom arrangement which have carbon nanotubes.

Examples of nonhexagonal layered structures, which may also form tubular structures are shown in Fig. 1.1 [25].

If the surface and interior of a finite-diameter 1D nanoobject is rigidly occupied by atoms, it is often called a nanowire or nanorod, and sometimes a “quantum” wire or “quantum” rod. The polyhedral nanotubes with a regular polyhedral shape are formed by nanowires with a hollow core.

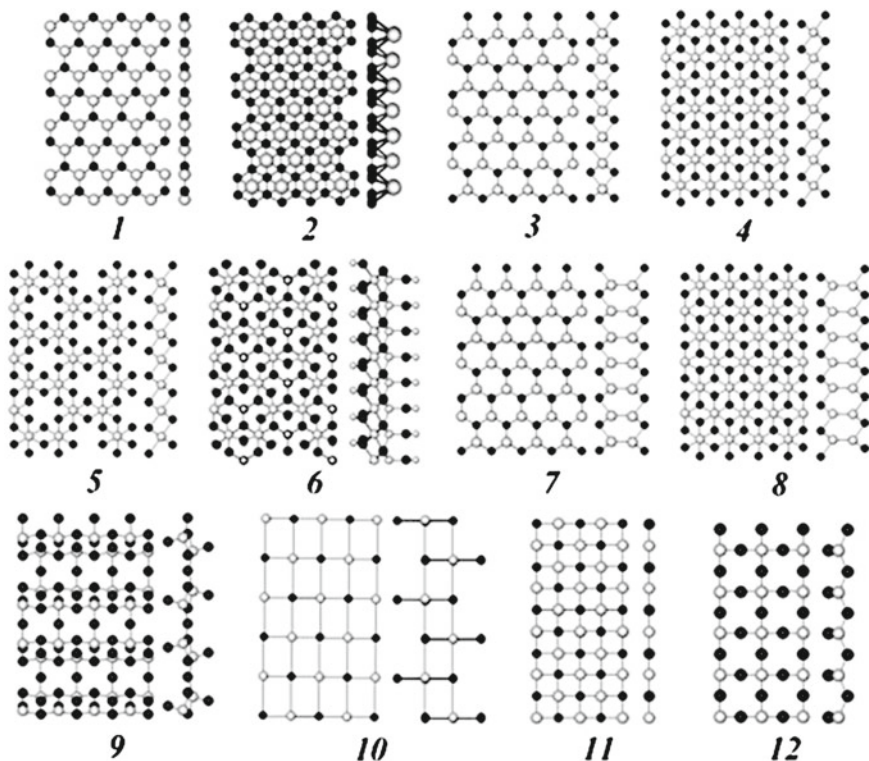


Fig. 1.1 Structures of the monolayers of some inorganic compounds: 1 BN, 2 AlB_2 , MgB_2 , 3 MoS_2 , WS_2 , NbSe_2 , 4 TiS_2 , ZrS_2 , anatase TiO_2 , NiCl_2 , 5 FeCl_3 , MoO_3 , 6 imogolite $\text{Al}_2\text{O}_3(\text{OH})_3\text{Si}(\text{OH})_4$, 7 GaS, GaSe, 8 metastable InS with a hexagonal lattice, 9 rectangular V_2O_5 , 10 centered rectangular lepidocrocite TiO_2 , 11 square MgO and 12 SiO_2 . The empty circles represent metal atoms, while full circles stand for nonmetal atoms, [25]

It has become common in the literature to use the designation “nanowire (nanorod)”. The implication is that nanowire is the preferred terminology, and nanorod means nothing essentially different [28].

The qualifier “quantum” applied to dots, wires (or rods), is ambiguous, for it does not indicate whether the system is a free standing fragment of a crystal, or a region embedded in a host crystal, as in gate-patterned regions of a two-dimensional layer in a 3D crystal. In the opinion of Philip B. Allen [28], it is better not to use “quantum” except for the latter case, or unless the ambiguity is intentional.

Ordered nanowires fall into several structural classes, [28]: (1) helical nanowires, (2) molecular nanowires, and (3) nanocrystalline nanowires (NCNW).

Helical nanowires are filled nanotubes. Potassium halide-filled BN nanotube is an example of a helical nanowire, [29]. Its fillings are usually single crystals with lengths up to several micrometers.

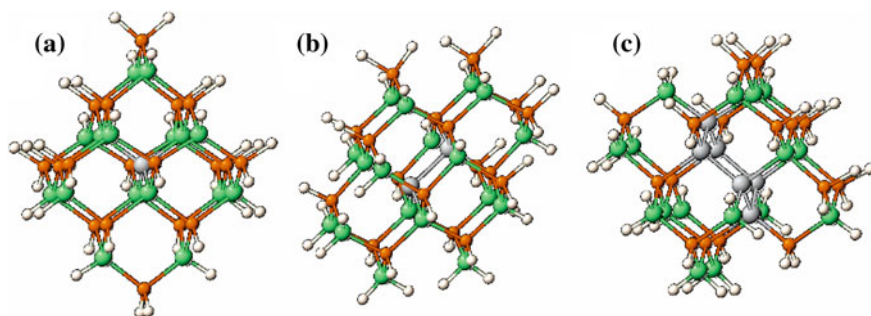


Fig. 1.2 Ball and stick model for the different nanocrystal symmetries. The atoms in *gray* represent the *center* of the nanocrystal. *Green* balls are for Se, *orange* for Cd, and *white* for pseudo-hydrogen atoms. **a–c** represent atom-centered (AC), bond-centered (BC), and hexagonal interstitia-centered (HC) nanocrystals, respectively (Reprinted figure with permission from Dalpian et al. [31], Copyright (2006) by the American Chemical Society)

Molecular nanowires can be fragments of quasi-1D crystals. For example, the non-helical inorganic polymer $(Mo_6S_6)_N$ (a fragment of the quasi-1D bulk crystal $M_2Mo_6X_6$, where M is an alkali and X = S, Se) is an example of a molecular nanowire, which has been studied experimentally and theoretically.

Finally, nanocrystalline nanowires (NCNW) are 1D fragments of bulk crystals where the bulk was a 3D (not a quasi-1D) material, [28]. The term “nanocrystal” is used for the fragments of bulk crystals that have only point group symmetry (0 D) typical of the molecules (the term “molecular cluster” is also used [30]). As an example, Fig. 1.2 shows nanocrystals constructed by cutting a spherical fragment of a CdSe bulk crystal with a zinc blende structure [31]. Point group symmetries are usually very important when one deals with molecules. Different symmetries usually lead to different properties in molecules, and this has been studied widely in the literature. Also it is very natural to expect symmetry to play an important role in the properties of nanocrystals [31].

Two parameters enter in the definition of a spherical nanocrystal: its radius and its center [31]. Nanocrystals with different centers and similar radii have different symmetries. For example, if a nanocrystal is centered in an atom (AC), as can be seen in Fig. 1.2a, it will have a T_d point group symmetry. The same will happen if the center is in a tetrahedral interstitial. These nanocrystals will be nonstoichiometric, that is, they will have a different number of cations and anions. Nanocrystals centered in a bond (BC) or in a hexagonal interstitial (HC), as can be seen in Figs. 1.2b, c, will be stoichiometric but will have lower symmetries (C_{3v}).

Simulations on monoperiodic nanostructures for different classes of inorganic substances are widely performed now, simultaneously with their synthesis and experimental study. A deep understanding of the composition and structure at the atomic level is key to understanding the relations between the unique properties of nanomaterials when compared with the bulk phase [32].

The theoretical difficulties one encounters in nanostructure study are as follows, [28]: (1) the precise atomic structure of inorganic nanomaterials is rarely known; (2) the computer techniques to exploit rotational as well as translational symmetry are not well developed.

Progress in nanoscience is becoming increasingly dependent on simulation and modeling, which is due to a combination of three factors [33]: the reduced size of nano-objects, the increasing power of computers and the development of new theoretical methods. The book by Delerue and Lannoo [33] is one of the first attempts to provide the theoretical background needed to simulate nanodevices, quantum dots and molecular devices.

The second edition of our previous book *Quantum Chemistry of Solids* [30] includes a chapter dealing with symmetry properties and the recent applications of the LCAO first-principles method to inorganic nanotubes, based on BN, TiO_2 and SrTiO_3 compounds. The chapter demonstrates the efficiency of first-principles calculations for predicting the structure and stability of single- and double-walled nanotubes.

In this book we discuss the symmetry and the results of the theoretical study of inorganic nanolayers, nanotubular materials and nanowires. Computational modeling is an essential part of this study so that our book effectively deals with **computational nanoscience**.

We present the basic results of the theoretical modeling of the structural and electronic properties of inorganic diperiodic (nanolayers) and monopерiodic (nanotubes and nanowires) nanostructures with different shapes and morphologies. Three models of monopерiodic nanostructures are considered: (i) nanocrystalline nanowires (obtained from 3D parent crystal structure sectioning it along the crystalline planes parallel to the chosen direction of the nanowire translation), (ii) rolled up nanotubes—single- and multi-walled (rolled from 2D nanolayers of parent crystal thin film) and (iii) polyhedral nanotubes. The symmetry of these models is described within the formalism of monopерiodic (line) symmetry groups for the conventional nanotubes. The nanowires and the polyhedral nanotube symmetry are described by 75 rod groups, forming a subset of an infinite number of line groups.

The three-dimensional triperiodic (3D) symmetry groups of the bulk crystals and the two-periodic (2D) layer symmetry groups of thin films are considered as the basis for the generation of monopерiodic (1D) symmetry groups of the nanostructures.

The formalism of the line symmetry groups is discussed and applied to the description of nanotubes and nanowires symmetry. The symmetry aspects of the nanotubes rolled up from the diperiodic layer are considered using the connection between the three dimensional diperiodic layer groups and monopерiodic line groups. The three-dimensional rod and layer subperiodic groups are considered in the context of three-dimensional space along with their concomitant relationships with the three-dimensional space groups. These relationships are the basis for the symbols and classification of the subperiodic groups, which are used in the symmetry description of nanowires and polyhedral nanotubes.

The first-principles methods applied to the LCAO and Plane Wave calculations of the electronic and vibrational properties of nanostructures are thoroughly described.

Understanding the theoretical aspects presented here provides greater scope for the synthesis of monoperiodic nanostructures with predictable morphology and a better interpretation of their properties.

Part II Applications gives numerous examples of the first-principles calculations of different inorganic nanostructures. We consider nanostructures based on: (1) α -Boron and metal diborides MeB_2 ($\text{Me} = \text{Al, Be, Mg, Ti}$); (2) tetravalent semiconductors—silicon, germanium, silicon carbide SiC , germanium silicide; (3) Boron and Group III metal nitrides; (4) binary oxides (ZnO , TiO_2 , ZrO_2); (5) ternary oxides $\text{Sr}(\text{Ba})\text{TiO}_3$, SrZrO_3 ; (6) disulfides MoS_2 , WS_2 , TiS_2 , ZrS_2 .

It is demonstrated that the properties of the inorganic nanostructures differ from those of the corresponding bulk crystal. This material helps the reader to understand potential of computer modelling for predicting the existence and describing the properties of inorganic nanostructures.

The majority of the first-principles 1D nanostructure DFT calculations were performed using Plane Waves (PW) basis requiring that periodic boundary conditions be used to model these nanostructures. Therefore an artificial vacuum space is inserted in the xy plane to separate adjacent nanowires, while the length of the 1D nanostructure is created by replication along the z-direction. In LCAO methods such an artificial periodicity is not necessary.

To determine the stability of nanoscale structures studied computationally, formation or binding energy was calculated. These energies are compared as a function of nanostructure dimension, usually diameter, as well as shape, and can give an indication of the relative stability of nanowires and nanotubes compared to the bulk or sheets. It is expected that when the dimensions of a material are reduced into the nano-region, unique and novel shapes and morphologies can form and, as a result, the bond distances and angles often differ from those in the bulk material [34]. It is therefore highly important to examine the structural changes of various nanostructures that affect their electronic and magnetic properties, including the density of states and band structure.

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