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Computational Studies of Electronic Properties of ZrS₂ Nanotubes[#]

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Abstract

Motivation. The discovery of carbon nanotubes (NT) with unique properties has stimulated the search for new quasi-one-dimensional (1D) nanoscale inorganic materials (NTs, nanowires etc.). Numerous *d*-metal dichalcogenide MX₂ (M = Mo, W; X = S, Se) nanotubes were prepared and investigated in the last decade. Quite recently (2002) the first ZrS₂ nanotubes were produced. As distinct from the group V and VI metal disulfide NTs, the electronic properties and chemical bonding of 1D nanomaterials based on group IV metal (Ti, Zr and Ta) disulfides have not been studied up till now. In the present paper, the electronic band structure and bond indices of ZrS₂ NTs were calculated for the first time and analysed in comparison with other MS₂ (M = Mo, W, Nb) nanotubes.

Method. The electronic band structure, densities of states, crystal orbital overlap populations and total band energies of ZrS₂ nanotubes and strips (E_{tot}) have been obtained using the tight-binding band structure method.

Results. The atomic models of *zigzag*- and *armchair*-like open-end ZrS₂ nanotubes have been constructed. The electronic structure and bond indices of ZrS₂ nanotubes have been calculated and analysed as a function of the tubes diameters (D) in the *armchair*- and *zigzag*-like forms. Our calculations for the *zigzag* (*n*,0)- and *armchair* (*n*,*n*)-like ZrS₂ nanotubes (*n* = 8 ÷ 29) showed that all NTs with D > 2 nm are uniformly semiconducting and their energy spectra are similar to the DOS of the bulk ZrS₂. The band gap tends to vanish as the tube diameters decrease. Zr–S covalent bonds were found to be the strongest interactions in ZrS₂ tubes, whereas Zr–Zr bonds prove to be much weaker, and the covalent S–S interactions are absent (COOPs < 0). According to our results, the *zigzag*-like configurations of the single-walled ZrS₂ NTs are more stable. Possible atomic structures of ZrS₂ nanotube caps and ZrS₂ fullerene-like molecules were also proposed and discussed.

Conclusions. Computer simulation of the band structure and bonding indices of non-chiral ZrS₂ nanotubes has been performed as the first step to understand the electronic properties of 1D nanomaterials of group IV *d*-metal disulfides which may be of interest, in particular, as hydrogen-storage materials and insertion materials of lithium batteries.

Keywords. ZrS₂ nanotubes; computer simulation; atomic structure models; electronic band structure; stability; intra-atomic chemical bonding.

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

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1 INTRODUCTION

The discovery of carbon nanotubes (NTs) with unique properties has simulated the synthesis of quasi-one-dimensional (1D) nanoscale materials (NTs, nanofibers, nanorods) from different inorganic compounds with a layered structure, see reviews [1–8]. Following the synthesis of WS₂ and MoS₂ NTs, numerous other *d*-metal dichalcogenide MX₂ (M = Mo, W, Ta; X = S, Se) nanotubes and nanofibers (and also fullerene-like molecules) have been reported [4–13]. Important progress was achieved in the last years in producing new NTs of InS [14], ZnS [15], Bi₂S₃ [16], ReS₂ [17], W_xMo_yC_zS₂ [18].

Quite recently (2002, [19]) the first ZrS₂ nanotubes have been prepared by thermal decomposition of the crystalline zirconium trisulfide ZrS₃ in a stream of H₂ and Ar at 900°C. TEM analysis showed that the reaction product contained ZrS₂ nanorods and onions in addition to capped nanotubes.

In the present paper, atomic simulation of the structure of non-chiral nanotubes constructed from ZrS₂ single molecular layer is performed. The electronic band structure and bond indices are calculated and analysed as a function of the tubes diameters (D) in *armchair*- and *zigzag*-like forms. The results are compared with earlier band structure calculations of related MoS₂, WS₂ and NbS₂ NTs [20–23]. Some atomic structures of ZrS₂ fullerene-like molecules and ZrS₂ nanotube caps were also proposed.

2 MODELS AND COMPUTATIONAL DETAILS

ZrS₂ crystallizes in the CdI₂ structural type (space group *P3m1*) with the lattice parameters $a = 0.3662$, $c = 0.5813$ nm and one formula unit per unit cell ($Z = 1$). The hexagonal ZrS₂ consists of triple (S–Zr–S) layers, where a Zr sheet is sandwiched between two sulfur sheets. The metal atoms are surrounded by six anions with approximately octahedral spheres. Each sulfur atom is coordinated to three zirconium atoms with a trigonal pyramidal geometry. The interatomic distances are Zr–S = 0.2568 and S–S = 0.3601 nm, see [24].

The atomic models of tubular ZrS₂ structures are constructed by mapping a triple (S–Zr–S) layer onto the surface of a tube. These “single-walled” tubes consist of three coaxial S–Zr–S cylinders, see Figure 1. The geometry of ZrS₂ NTs was described by the basis vectors (\mathbf{a}_1 and \mathbf{a}_2) of the Zr atom net introducing the so-called chiral vector $\mathbf{c}_h = n\mathbf{a}_1 + m\mathbf{a}_2$, whose modulus equals the perimeter of the Zr atom cylinder. As in single-walled carbon [1–8] or Mo,W,Nb disulfides NTs [20–23], three groups of ZrS₂ nanotubes can be obtained depending on the rolling direction \mathbf{c}_h : non-chiral *armchair* (n,n)-, *zigzag* ($n,0$)- and chiral (n,m)-like nanotubes. We have calculated the electronic structure of all ($n,0$) and (n,n) ZrS₂ NTs as a function of n in ranges from (8,0) to (29,0) and from (4,4) to (29,29), which correspond to the intervals of the inner sulfur cylinders diameters

(D^{in}) 0.554 – 3.074 and 0.376 – 5.562 nm, respectively, Table 1. We have performed the band calculations of planar strips of ZrS_2 monolayers having the cells of the same atomic dimensions as in the nanotubes. Such calculations permit evaluating the differences in the energy states of 1D planar and tubular forms due to the bending strain [23].

Table 1. The number of atoms in unit cells and diameters (D , nm) for some single-walled ZrS_2 nanotubes

NT	Cell size	$D^{\text{in}}(\text{S})^a$	$D^{\text{out}}(\text{S})$	$D(\text{Zr})$
(8,0)	48	0.554	1.176	0.936
(9,0)	54	0.680	1.298	1.054
(10,0)	60	0.806	1.420	1.170
(15,0)	90	1.414	2.020	1.754
(16,0)	96	1.534	2.140	1.872
(18,0)	108	1.772	2.376	2.106
(20,0)	120	2.010	2.614	2.340
(22,0)	132	2.246	2.850	2.574
(24,0)	144	2.484	3.086	2.808
(26,0)	156	2.720	3.322	3.044
(28,0)	168	2.956	3.438	3.278
(29,0)	174	3.074	3.676	3.394
(8,8)	48	1.260	1.874	1.622
(9,9)	54	1.470	2.208	1.824
(10,10)	60	1.678	2.288	2.028
(15,15)	90	2.710	3.314	3.040
(16,16)	96	2.914	3.518	3.244
(18,18)	108	3.322	3.926	3.648
(20,20)	120	3.730	4.334	4.054
(22,22)	132	4.138	4.740	4.460
(24,24)	144	4.546	5.148	4.866
(26,26)	156	4.952	5.554	5.270
(28,28)	168	5.360	5.962	5.676
(29,29)	174	5.562	6.164	5.876

^a D^{in} and D^{out} are diameters of the inner and outer cylinders made up of sulfur atoms, see Figure 1

To calculate ZrS_2 nanotubes and strips, the tight-binding band structure method within the extended Hückel theory (EHT) approximation [25] was employed. Besides the electronic band structure, this approach allowed us to investigate the chemical bonding based on the Mulliken analysis scheme. The densities of states (DOS), crystal orbital overlap populations (COOPs) and the total band energies of the nanotubes (E_{tot}) were obtained. For comparison with 1D nanostructures, the self-consistent band structure calculation of the crystalline ZrS_2 was performed using the full-potential LMTO method [26] with the local density approximation (LDA) for the exchange-correlation potential [27].

3 RESULTS AND DISCUSSION

Figure 2 shows the calculated values of E_{tot} (per ZrS_2 unit) versus the zirconium disulphide NT diameters. It is seen that according to our results the zigzag-like configurations of the ZrS_2 NTs are more stable. For these NTs (in the considered D interval), the E_{tot} dependence follows a $\sim 1/D^2$

behaviour indicative of a decrease in the tubes stability with decreasing D . An analogous dependence is typical of *armchair*-like NTs with $D < 4$ nm, which was also obtained in earlier calculations of MoS₂, WS₂ and NbS₂ NTs [20–23].

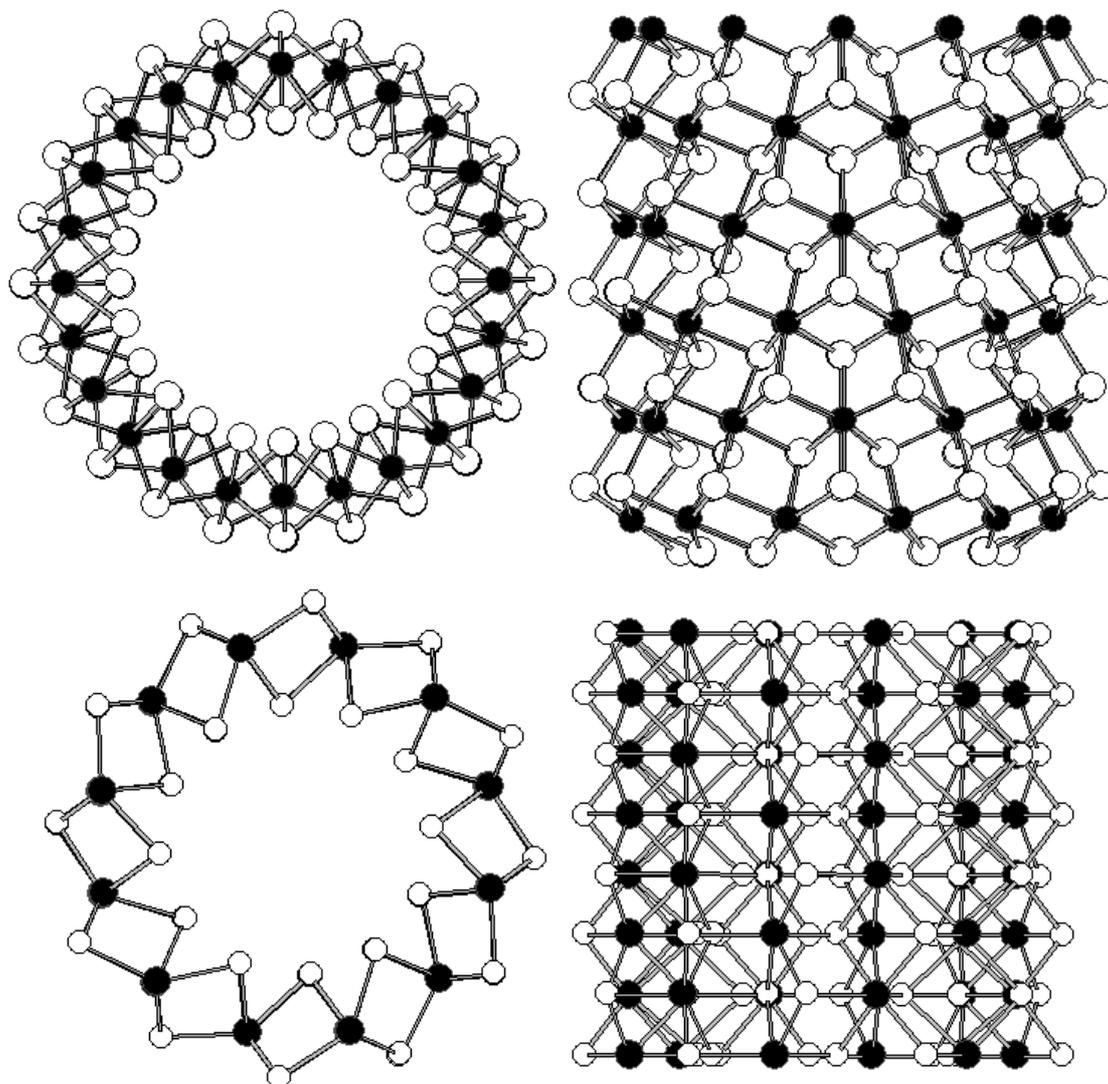


Figure 1. Atomic structures of the open-end (1) *zigzag*-like (12,0) and (2) *armchair*-like (6,6) ZrS₂ nanotubes. Side views and views along the tube axis are shown.

For $D < 4$ nm, the energy (per ZrS₂ unit) in the NTs is higher than in the corresponding infinite planar strips (with the same number of the atoms) due to the bending strain. However the tubular structures beginning with $D > 4$ nm may be energetically more favorable than strips: E_{tot} for these tubes becomes somewhat smaller. In comparison with the corresponding planar strips, the stabilization effect in such nanotubes can be explained by the absence of “dangling” bonds. Obviously, the additional contribution to the stabilization of the tubular structures is made by the Van der Waals interaction between the walls of adjoining coaxial (S–Zr–S) cylinders giving rise

predominately to multi-walled ZrS₂ NTs of rather large diameters.

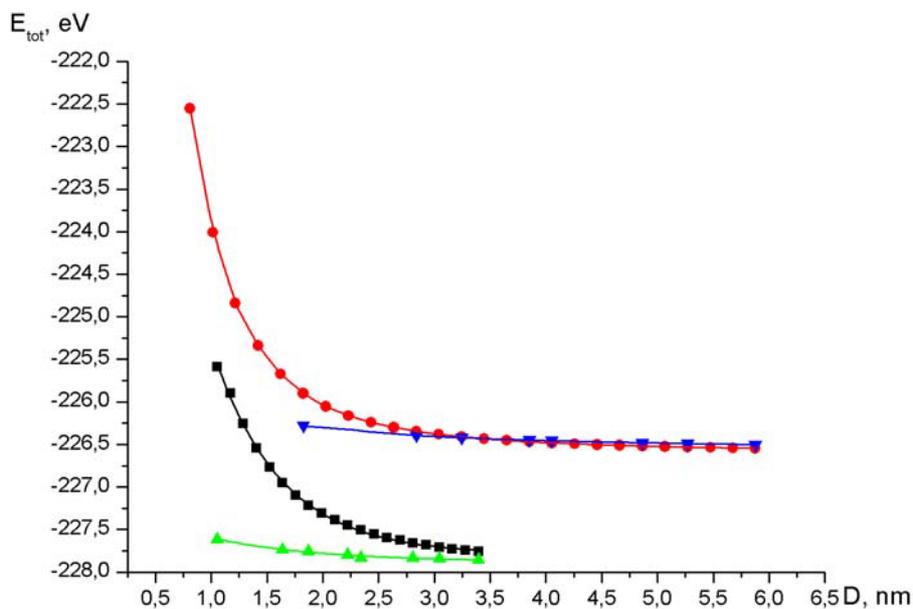


Figure 2. Total energies (per ZrS₂ unit) as a function of the diameter of Zr cylinders for ZrS₂ tubes of the *armchair*- (●) and *zigzag*-like (■) configurations. E_{tot} of some corresponding infinite planar strips (with the same number of the atoms) are also presented (Δ).

The synthesized ZrS₂ NTs are multi-walled, and their outer and inner diameters (D^{out} , D^{in}) are very large: ~ 125 and 60 nm respectively, which is likely to be due to specific experimental conditions [19]. For example, stable NTs of the isoelectronic and isostructural ZrS₂ analogue – TiS₂ produced recently [28] by low-temperature gas reaction $\text{TiCl}_4 + 2\text{H}_2\text{S} \rightarrow \text{TiS}_2 + 4\text{HCl}$ have much smaller diameters: $D^{\text{out}} \sim 20$ nm and $D^{\text{in}} \sim 10$ nm. D^{out} and D^{in} of multi-walled TiS₂ NTs prepared by chemical transport reaction [29] with the use of a mixture of titanium metal and sulfur powder (in the atomic ratio S/Ti = 2) are respectively ~ 30 and ~ 10 nm.

Let us consider the band structures of (n,n)- and ($n,0$)-like ZrS₅ NTs. As is known [24], the band structure of the semiconducting crystalline ZrS₂ consists of two valence-band groups: the lower quasi-core sulfur 3s bands (located at ~ 12 eV below the Fermi level and clearly separated from the other states of the valence band by a gap) and the fully occupied upper valence band composed mainly by the S3p states hybridized with the Zr4d states having an insignificant admixture of Zr5s,5p states.

These features are very well seen in Figure 3 displaying the total and partial DOSs of ZrS₂ as obtained in our FLMT0 calculation. The S3p-like DOS profile of the bulk ZrS₂ contains three basic DOS peaks (A–C) reflecting the anisotropic distribution of the S3p states: in the sulfur atoms net, inside molecular S–Zr–S layers, and between neighboring molecular layers. The indirect band gap (BG, Γ – L transition) between the valence and conduction bands is about 0.8 eV. The bottom of the conduction band (peaks D, E) consists chiefly of the Zr4d states.

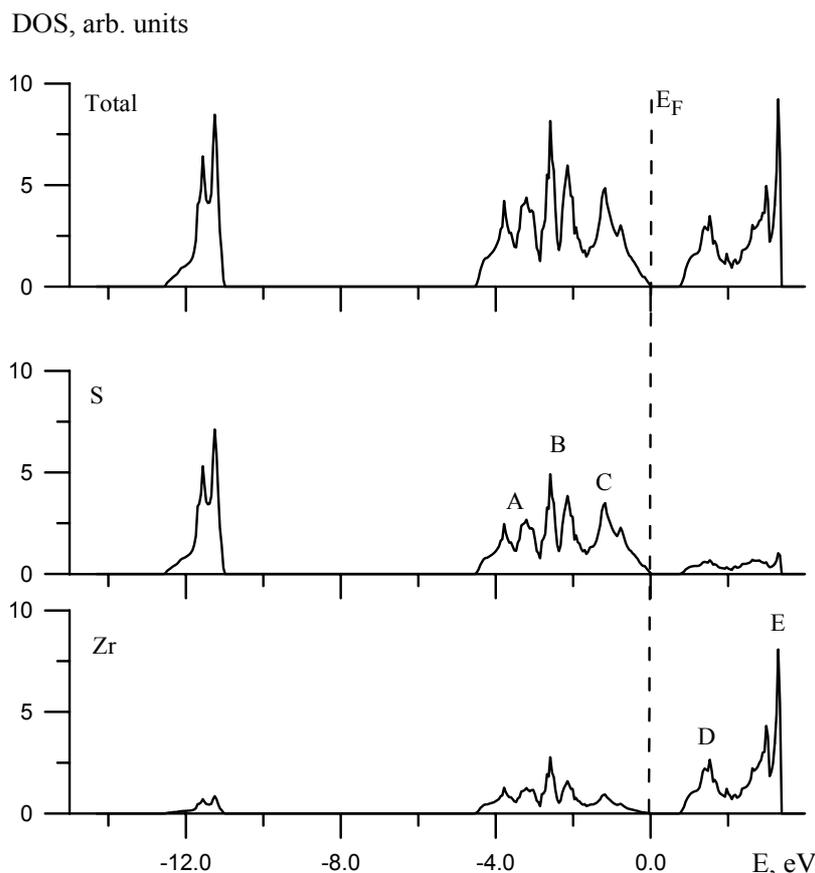


Figure 3. Total and partial DOSs of the bulk ZrS₂. FLMTO data.

As follows from our calculation, all ZrS₂ NTs with $D > 2$ nm are semiconducting and their energy spectra are similar on the whole to the DOS of the bulk ZrS₂, Figure 4. The main differences in the electronic states of the *armchair*- and *zigzag*-like NTs are connected with the DOS shape of the occupied Zr4*d*-S3*p* band and the lower-energy part of the conduction band. From Figure 4 it is seen that for the *armchair*-like NTs an appreciable energy separation of the electronic states of the Zr4*d*-S3*p* band into two groups takes place as a result of the sharp anisotropy of the Zr-S bonds, see below. This effect is much less pronounced for the *zigzag*-like NTs, whose DOS shape is more similar to that of the bulk ZrS₂. The above features depend on the tube geometry and diameter and determine the variation in the band gap width, Figure 5.

The BG decreases with diminishing NT diameters, for the NTs of different configurations and comparable D the BG values for the *armchair*-like NTs being still higher (by ~ 0.15 eV) than those for the *zigzag*-like NTs. A similar dependence between the BG and the tube diameter was reported recently for the semiconducting MoS₂ and WS₂ NTs [20,22]. For the considered NTs with the maximal diameter (minimal curvature), the BG values are ~ 0.55 eV (*armchair*-like (29,29)NT) and ~ 0.35 eV (*zigzag*-like (29,0)NT) as compared with the calculated value of ~ 0.8 eV for the bulk ZrS₂.

DOS, arb. units

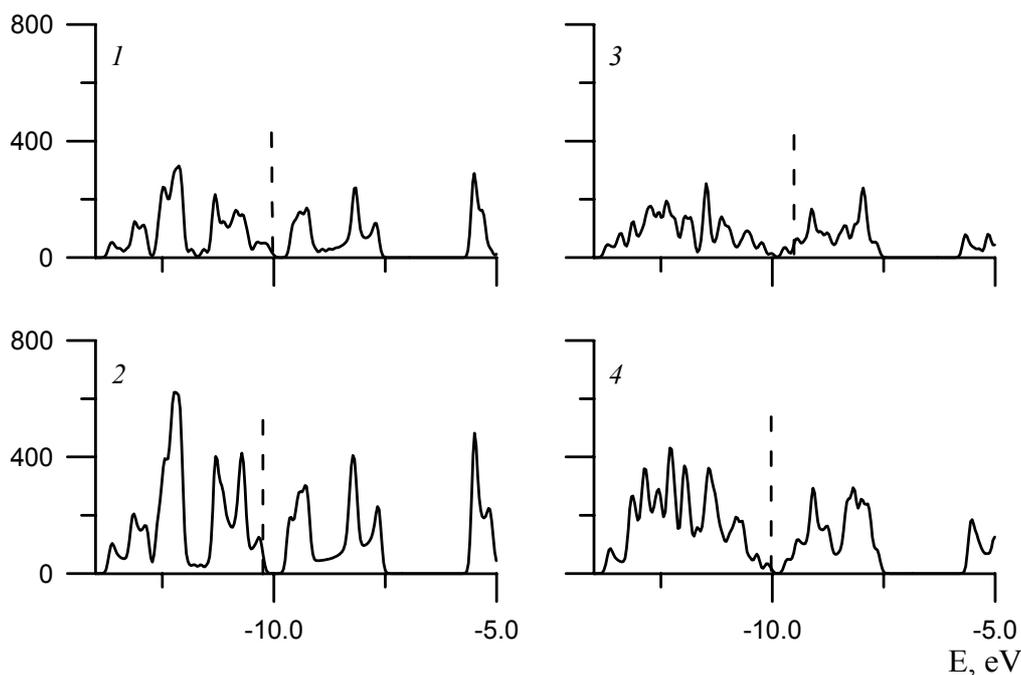


Figure 4. Total DOSs of 1–(15,15), 2–(28,28), 3–(15,0) and 4–(28,0) ZrS₂ nanotubes.

The strength of covalent bonds in the ZrS₂ tubes can be discussed using the COOP values, Table 2. For all the tubes, (a) the main bonds are Zr–S interactions (COOPs $\sim 0.40 - 0.60$ e); (b) the population of the Zr–Zr bonds is by an order of magnitude smaller ($\sim 0.01 - 0.03$ e); (c) the covalent S–S interactions are absent (COOPs < 0).

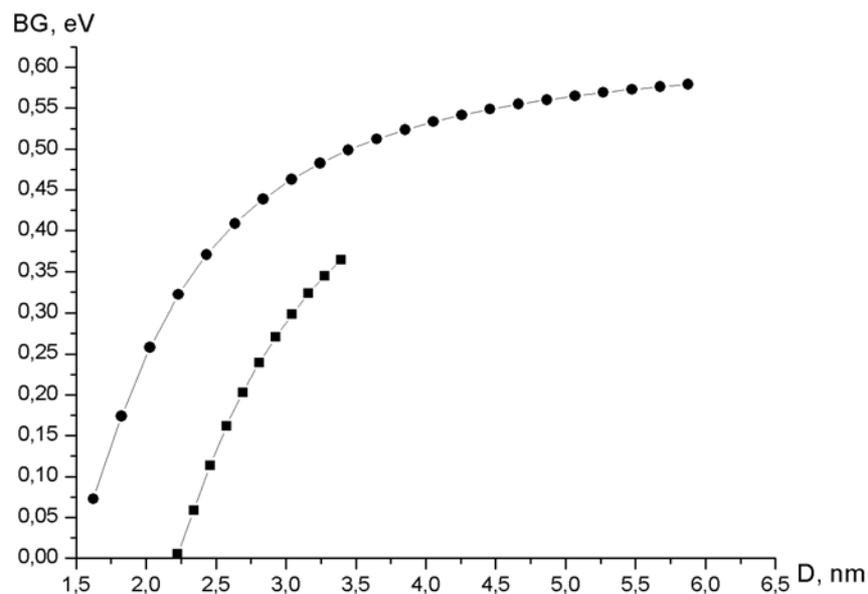


Figure 5. Band gaps of *armchair*- (●) and *zigzag*-like (■) ZrS₂ NTs as a function of the diameter of the “central” Zr cylinder.

There is anisotropy of the Zr–S bonds depending both on their orientation (across or along) relative to the NT axis and positions of S atoms belonging to inner or outer cylinders (Zr–Sⁱⁿ, Zr–S^{out} bonds, Table 2). For the *armchair*-like NTs, the COOPs values of Zr–Sⁱⁿ (along) are greater than those for Zr–S^{out}, whereas the COOPs values of Zr–S^{out} and Zr–Sⁱⁿ bonds (across) are comparable. As the NTs D increases, the COOPs values of Zr–Sⁱⁿ increase whereas those of Zr–S^{out} decrease. This suggests the higher reactivity of the outer sulfur atoms, in particular, as a possibility of their rearrangement (outer cylinder deformation) and also for the formation of various atomic defects. Such defects are more likely to form near the tube tips, which are considered [19] as active points of the tube growth. Note also that COOPs values of Zr–S^{out} bonds are much more considerable for the *zigzag*-like tubes, which are more stable than the *armchair*-like tubes judging by E_{tot} estimates, Table 2.

Table 2. Indices of intra-atomic bonds (COOPs, e) for some single-walled ZrS₂ nanotubes. COOPs of paired bonds of Zr–Zr and zirconium atoms with sulfur atoms forming outer (S^{out}) and inner (Sⁱⁿ) cylinders depending on their orientation relative to the NT axis (across or along) are presented.

NTs	Zr–Zr along	Zr–Zr across	Zr–S ⁱⁿ along	Zr–S ⁱⁿ across	Zr–S ^{out} along	Zr–S ^{out} across	NTs	Zr–S ^{out} along	Zr–S ^{out} across
(8,8)	0.022	0.024	0.379	0.509	0.317	0.551	(8,0)	0.703	0.520
(9,9)	0.025	0.018	0.391	0.526	0.315	0.543	(9,0)	0.697	0.521
(10,10)	0.026	0.016	0.403	0.534	0.312	0.543	(10,0)	0.699	0.522
(11,11)	0.026	0.015	0.413	0.539	0.309	0.544	(11,0)	0.694	0.525
(12,12)	0.026	0.014	0.422	0.543	0.306	0.545	(12,0)	0.685	0.528
(13,13)	0.026	0.013	0.429	0.545	0.303	0.546	(13,0)	0.675	0.533
(14,14)	0.026	0.013	0.435	0.547	0.300	0.547	(14,0)	0.666	0.536
(15,15)	0.026	0.012	0.441	0.549	0.298	0.548	(15,0)	0.657	0.538
(16,16)	0.026	0.012	0.446	0.550	0.296	0.549	(16,0)	0.650	0.541
(17,17)	0.026	0.012	0.450	0.551	0.294	0.549	(17,0)	0.644	0.542
(18,18)	0.026	0.011	0.454	0.552	0.293	0.550	(18,0)	0.638	0.543
(19,19)	0.026	0.011	0.457	0.552	0.291	0.550	(19,0)	0.634	0.544
(20,20)	0.026	0.011	0.461	0.553	0.290	0.551	(20,0)	0.624	0.549
(21,21)	0.026	0.011	0.463	0.553	0.288	0.551	(21,0)	0.621	0.549
(22,22)	0.026	0.011	0.466	0.554	0.287	0.552	(22,0)	0.618	0.550
(23,23)	0.026	0.011	0.468	0.554	0.286	0.552	(23,0)	0.615	0.550
(24,24)	0.026	0.011	0.471	0.554	0.285	0.552	(24,0)	0.612	0.550
(25,25)	0.026	0.010	0.473	0.555	0.284	0.553	(25,0)	0.610	0.551
(26,26)	0.026	0.010	0.474	0.555	0.283	0.553	(26,0)	0.607	0.551
(27,27)	0.026	0.010	0.476	0.555	0.283	0.553	(27,0)	0.605	0.551
(28,28)	0.026	0.010	0.478	0.555	0.282	0.553	(28,0)	0.603	0.551
(29,29)	0.026	0.010	0.479	0.555	0.281	0.553	(29,0)	0.601	0.552

Up to this point we have been discussing the models of infinitely long NTs only. The microscopic image [19] reveals the presence of closed ZrS₂ NTs with an unusual tip morphology in the form of rectangular caps. In order to explain possible ZrS₂ tube caps (and fullerene-like ZrS₂ hollow nanoparticles [19]), we have constructed the atomic models of some polyhedral structures preserving the stoichiometry of the system (S/Zr = 2).

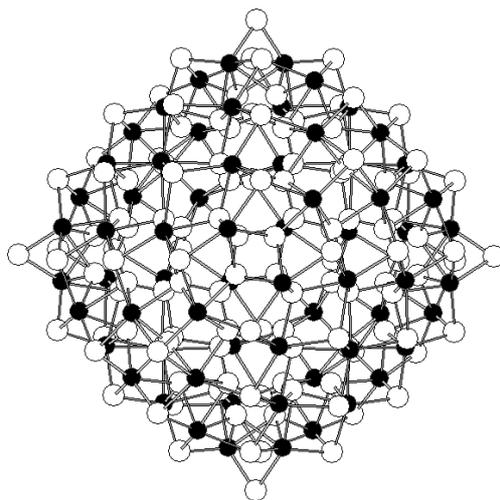


Figure 6. Atomic structure of the fullerene-like molecule $(\text{ZrS}_2)_{64}$.

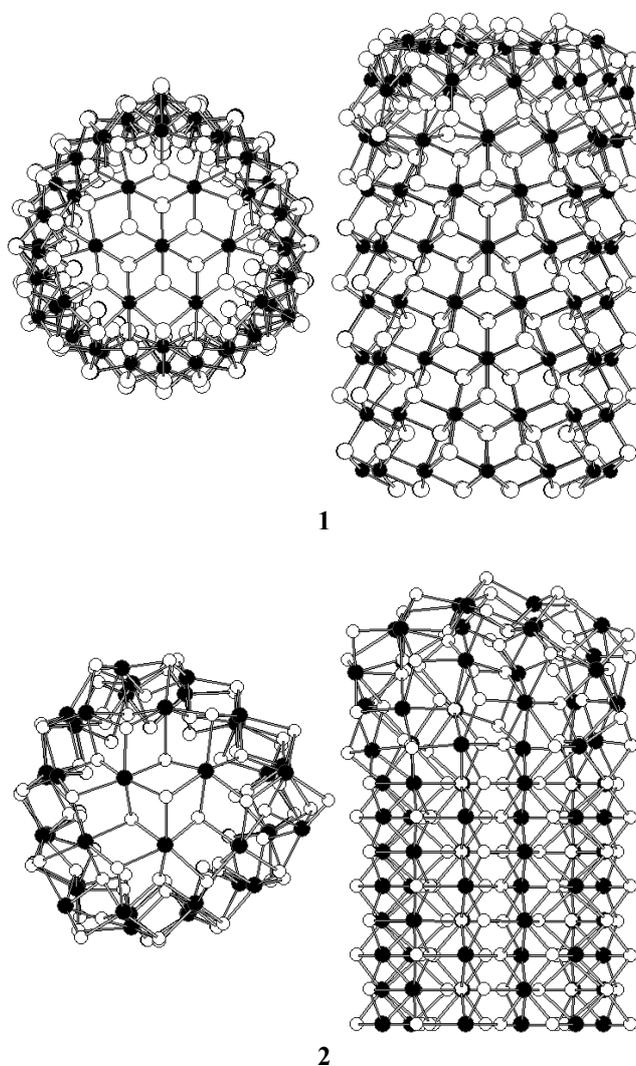


Figure 7. Atomic structures of the (1) *zigzag*-like (12,0) and (2) *armchair*-like (6,6) ZrS_2 nanotubes tips. Side views and views along the tube axis are shown.

For example, a series of fullerene-like molecules (FM, (ZrS₂)_n, where $n = 12, 16, 36, 48, 64$, etc.) can be created from triple layer (S–Zr–S) fragments. These structures can be described as triple-shell molecules consisting of concentric polyhedral shells, the outer and the inner shells being formed by S atoms, whereas the middle shell is formed by Zr atoms, Figure 6. The majority of Zr and S atoms in FM (both in the bulk and tubular forms of ZrS₂) preserve six- and three-fold coordination respectively. Each FM includes also a group of 4 Zr and S atoms with coordination numbers respectively 5 and 2. Similarly to C_n fullerenes, whose fragments are closed carbon NTs caps [30,31], these FM may be also viewed as possible caps models for ZrS₂ NTs of the corresponding diameters. Atomic models of the (1) *zigzag*-like (12,0) and (2) *armchair*-like (6,6) ZrS₂ nanotubes tips involving topological defects (TD) are shown, Figure 7. Similar square-like and octagonal-like TD were introduced to produce positive and negative Gaussian curvatures, respectively, of MoS₂, WS₂ NTs [20].

4 CONCLUSIONS

In summary, atomic models of single-walled ZrS₂ nanotubes have been constructed and their electronic properties and bond indices have been investigated using the tight-binding band method. We show that both *zigzag*- and *armchair*-like nanotubes are semiconducting, and the band gap trends to vanish for very small NT diameters. *Zigzag*-like nanotubes were found to be more stable for diameters comparable with those observed experimentally. It was established that Zr–S covalent bonds are the strongest interactions in zirconium disulfide NTs, whereas Zr–Zr bonds are much weaker.

However, there are numerous issues of interest for future studies. First of all, an important problem is the effect of “interlayer” interactions on the properties of multi-walled ZrS₂ tubes. Further explorations are needed to clarify the role of wall defects, in particular, inter- and intralayer stacking faults, and also the effects of non-stoichiometry ($S/Zr < 2$) in the region of the tube tips. This information should be the basis for constructing adequate theoretical models of the electronic structure, properties and growth mechanism of actually produced (Ti,Zr,Ta)S₂ nanotubes [8], which may be of interest, in particular, as hydrogen-storage materials [29] and insertion materials of lithium batteries.

Elaborating the theory of ZrS₂ and related metal disulfide nanotubes it may be interesting to construct atomic models and explore the electronic properties of hitherto unknown “composite” nanotubes composed by layers of various lamellar *d*-metal chalcogenides. Such tubes may be considered as hypothetical 1D allotropes of the well-known families of various misfit layer compounds, see [32,33]. We were the first to study the “superstoichiometric” Nb_{1+x}Se₂ NTs [34] as models of a 1D nanoform of the “autointercalated” layer 2H–NbSe₂ system (Nb_{1.27}Se₂ [35]).

New multi-walled metal disulfide nanotubes containing various intercalates (for instance organic or organometallic “guests” [36,37]) between the tube walls may also become a variation of those tubular composites. It is noteworthy that some similar composite 1D nanoscale materials are familiar: starting from V_2O_5 as a vanadium oxide precursor, different VO_x NTs have been fabricated [38–41], which are actually nanocomposites containing VO_x layers separated by organic templates (amine, diamine, etc.). For example, the average composition of the V_2O_5 -based NTs synthesized from the alkoxide precursor is $VO_{2.46\pm 0.06}(C_nH_{2n+4}N)_{0.27\pm 0.01}$ ($22 \geq n \geq 12$) [40].

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