Electronic properties of NiCl$_2$ tubular nanostructures

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Atomic models of zigzag ($n$, 0)- and armchair ($n$, $n$)-like NiCl$_2$ nanotubes ($n = 4$ - 29) formed by rolling (100) single layers of the bulk NiCl$_2$ which crystallizes in the CdCl$_2$-type structure, are constructed and their electronic properties and bond indices are investigated using the tight-binding band theory. The calculations performed show that all the considered nanotubes in non-magnetic state are uniformly metallic-like. The density of states at the Fermi level contains a considerable contribution from Ni$3d$ states, its value depends on the atomic configuration and diameter of the tubes. The Ni-Cl covalent bonds were found in NiCl$_2$ tubes, whereas Ni-Ni and Cl-Cl covalent interactions are almost absent. According our estimations, the zigzag ($n$, 0)-like NiCl$_2$ nanotubes are more energetically favorable.

Quasi-one-dimensional (1D) inorganic nanotubes (NTs) attract much interest due to wide prospects of technological application of materials produced on their basis. Besides carbon (see [1, 2, 3]), the first inorganic compounds, which were the basis for nanotube production, were layered hexagonal boron nitride [9, 10, 11] and metal-dichalcogenides MX$_2$ (M = Mo, W, Ta; X = S, Se) [6, 12, 13, 14, 15], having structures analogous to that of graphite. Recently, NTs of other sulfides were successfully synthesized: InS [16], ZnS [17], Bi$_2$S$_3$ [18], ReS$_2$ [19], W$_x$Mo$_y$C$_z$S$_2$ [20], ZrS$_2$, HfS$_2$ [21, 22].

Along with the above-mentioned NTs, a large number of other inorganic nanotubes have been produced or predicted. Among them there are new 1D tubular structures of metals (Na, Cu [23], Ni [24], Ag, Au [25, 26], Bi [27, 28]), boron [29], and silicon [30]. Some efforts are reported in synthesis and modeling of nanotubes based on inorganic compounds with planar or quasi-planar structures: BC$_3$, BC$_2$N, CN$_x$ (see reviews [6, 7, 8]), metal diborides MB$_2$ (M = Mg, Al, Sc, Ti, Zr) [31, 32, 33], ALB$_2$-like ternary silicides Sr(Ga$_x$Si$_{1-x}$)$_2$, Ca(Al$_x$Si$_{1-x}$)$_2$ [34] etc. A large number of 1D nanomaterials (nanowires, nanorods, nanotubes) based on metal oxides such as TiO$_2$ [35, 36, 37, 38, 39, 40], V$_2$O$_5$ [41, 42, 43, 44, 45, 46, 47], Co$_3$O$_4$ [48, 49], MnO$_2$, WO$_3$ [50], MoO$_3$, ReO$_2$ [51] and also on ZnO [52], SiO$_2$ [53, 54] etc. have been obtained. Important progress was achieved in producing nanotubes of semiconducting materials: SiGe, InAs/GaAs, InGaAs/GaAs, SiGe/Si InGeAs/GaAs [55, 56, 57].

Recently, the synthesis of closed-cage nanoclusters and nanotubes NiCl$_2$ which is the first representative of layered metal-halogen compounds, was reported [58, 59]. High-resolution transmission electron microscopy analysis (HRTEM) and electron diffraction measurements showed that NiCl$_2$ layers forming the walls of those multi-walled NTs were completely crystalline. Taking into account that bulk NiCl$_2$ is of ferro- and weak antiferromagnetic Ni-Ni coupling type in and across the layers, respectively, it is suggested [58] that unique magnetic properties may be expected for NiCl$_2$ NTs.

In this communication, the atomic simulation of the nanotubes constructed from NiCl$_2$ single layers is performed and their electronic band structure and bond indices are calculated and analyzed as a function of the tubes diameters (D) in armchair- and zigzag-like forms.

NiCl$_2$ crystallizes in the CdCl$_2$ structural type (space group $P3m$) with the lattice parameters $a = 0.3483$, $c = 1.7400$ nm. The bulk NiCl$_2$ consists of layers of a Ni sheet sandwiched between two chlorine sheets (Cl-Ni-Cl). Within the layers there exist ionic-covalent Ni-Cl bonds; the neighboring (Cl-Ni-Cl) layers interact with each other due to weak Van der Waals forces. The atomic models of tubular NiCl$_2$ structures were constructed analogously to the nanotubes of layered Mo, W, Nb dichalcogenides [60, 61, 62, 63, 64] by mapping a "triple" (Cl-Ni-Cl) layer onto the tube surface. Such "single-walled" tubes consist of three coaxial Cl-Ni-Cl cylinders built up of wrapped hexagonal Ni, Cl monoatomic sheets, Fig. 1. As for single-walled carbon NTs, see [1, 2, 3], three groups of NiCl$_2$ NTs can be classified as non-chiral (armchair ($n$, $n$)-, zigzag ($n$, 0)-like) and chiral ($m$, $n$)-like nanotubes. The majority of the synthesized [59] NiCl$_2$ NTs were non-chiral.

We calculated the electronic structure of non-chiral ($n$, 0) and ($n$, $n$) NiCl$_2$ 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 diameters of "outer" chlorine cylinders ($D_{out}$) 2.272 - 7.096 and 1.984 - 11.902 nm, respectively, Table 1.

The tight binding band structure method within the extended Hückel theory (EHT) approximation [65] was employed. Besides the electronic spectra, the densities of states (DOS), crystal orbital overlap populations (COOPs),

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and total band energies of the nanotubes \( E_{\text{tot}} \) were obtained.

Figure 2 shows the calculated values of \( E_{\text{tot}} \) (per NiCl\(_2\) unit) versus NT diameters. The \( E_{\text{tot}} \) dependence follows a \( 1/D^2 \) behavior indicative of a decrease in NTs stability with decreasing \( D \). Analogous dependences of strain energy (the difference between the energies of the plane atomic layer and the corresponding NT characterizes the chemical stability of tubular structures) are known for carbon and the majority of non-carbon NTs.

It is worth noting that according to our results for all the considered tubes, zigzag-like configurations of the NiCl\(_2\) nanotubes are more stable.

Within non-magnetic approach, all NTs are metallic-like. The electronic DOSs for the \((15, 15)\) and \((15, 0)\) NiCl\(_2\) nanotubes are showed in Fig. 3. The pronounced very sharp DOS peak near the Fermi level consists mainly of Ni3d states. Hence the magnetic instability can occur and it may be assumed that the near-Fermi Ni3d states will play a large role in the magnetic properties of NiCl\(_2\) NTs. However this aspect remains to be considered.

It is significant that the shape of the electronic spectrum is essentially modified by the tube geometry, see Fig. 3. For example, for armchair \((15, 15)\) NTs, the near-Fermi bands are separated from the filled valence bands by a forbidden gap, which is absent for zigzag \((15, 0)\) NTs.

To analyze the covalence of intra-atomic interactions, the COOPs of paired bonds were examined. It was established that Ni-Cl covalent interactions are the strongest bonds (Table 2), whereas Ni-Ni and Cl-Cl covalent-type interactions are absent (COOPs less 0). There is also sharp anisotropy of separate Ni-Cl bonds depending both on their orientation relative to the NT axis and the coordination of chlorine atoms belonging to "inner" or "outer" cylinders, as well as on the tube geometry. It is seen that the ratio of COOPs values for Ni-Cl\(_{\text{in}}\) and Ni-Cl\(_{\text{out}}\) bonds differs drastically for armchair \((n,n)\) - and zigzag \((n,0)\)-like tubes. In particular, for zigzag-like tubes the COOPs values of Ni-Cl\(_{\text{in}}\) are much greater than those for Ni-Cl\(_{\text{out}}\). This suggests higher reactivity of the "outer" chlorine atoms and a possibility of their rearrangement. The above features of interatomic bonds depending on the tube geometry may become an important factor in developing microscopic models of NiCl\(_2\) tubes growth both in zigzag- and armchair-like (and also chiral) forms.

In conclusion we have constructed atomic models of single-walled NiCl\(_2\) nanotubes in zigzag- and armchair-like forms and investigated their electronic properties and bond indices by the tight-binding band method. We show that both zigzag- and armchair-like nanotubes in non-magnetic state are metallic-like, with a very sharp DOS peak near the Fermi level predominantly of Ni3d character. This points to magnetic instability and a possibility of magnetic phenomena in NiCl\(_2\) NTs. Zigzag-like NiCl\(_2\) nanotubes were found to be more stable. It was established that Ni-Cl covalent bonds are the strongest interactions in nickel dichloride NTs.

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TABLE I: Radii (R, nm)* for NiCl$_2$ nanotubes.

| Nanotubes | R$^{in}$(Cl) | R$^{out}$(Cl) | R(Ni) |
|-----------|--------------|--------------|-------|
| (8,0)     | 0.535        | 1.136        | 0.904 |
| (9,0)     | 0.657        | 1.254        | 1.011 |
| (10,0)    | 0.778        | 1.371        | 1.126 |
| (11,0)    | 0.897        | 1.488        | 1.243 |
| (12,0)    | 1.015        | 1.604        | 1.356 |
| (13,0)    | 1.132        | 1.720        | 1.469 |
| (14,0)    | 1.249        | 1.836        | 1.582 |
| (15,0)    | 1.365        | 1.951        | 1.695 |
| (16,0)    | 1.481        | 2.066        | 1.808 |
| (17,0)    | 1.596        | 2.180        | 1.921 |
| (18,0)    | 1.711        | 2.295        | 2.034 |
| (19,0)    | 1.826        | 2.409        | 2.147 |
| (20,0)    | 1.940        | 2.524        | 2.260 |
| (21,0)    | 2.055        | 2.638        | 2.373 |
| (22,0)    | 2.169        | 2.752        | 2.486 |
| (23,0)    | 2.283        | 2.866        | 2.599 |
| (24,0)    | 2.397        | 2.980        | 2.712 |
| (25,0)    | 2.512        | 3.093        | 2.825 |
| (26,0)    | 2.625        | 3.207        | 2.938 |
| (27,0)    | 2.739        | 3.321        | 3.051 |
| (28,0)    | 2.853        | 3.435        | 3.164 |
| (29,0)    | 2.967        | 3.548        | 3.277 |
| (4,4)     | 0.364        | 0.992        | 0.783 |
| (5,5)     | 0.588        | 1.200        | 0.979 |

* R$^{in}$(Cl) and R$^{out}$(Cl) - radii of "inner" and "outer" chlorine cylinders.

TABLE II: Indices of intra-atomic bonds (COOPs, e) for some NiCl$_2$ nanotubes.

| Nanotubes | Ni-Cl$^{in}$ | Ni-Cl$^{out}$ | Ni-Cl$^{in}$ |
|-----------|--------------|--------------|--------------|
| (22,0)    | 0.281        | 0.242        | 0            |
| (23,0)    | 0.280        | 0.244        | 0            |
| (24,0)    | 0.287        | 0.244        | 0            |
| (25,0)    | 0.285        | 0.248        | 0            |
| (26,0)    | 0.288        | 0.248        | 0            |
| (27,0)    | 0.293        | 0.247        | 0            |
| (28,0)    | 0.291        | 0.250        | 0            |
| (29,0)    | 0.290        | 0.253        | 0            |
| (22,22)   | 0.104        | 0            | 0.241        |
| (23,23)   | 0.105        | 0            | 0.243        |
| (24,24)   | 0.105        | 0            | 0.243        |
| (25,25)   | 0.105        | 0            | 0.241        |
| (26,26)   | 0.105        | 0            | 0.241        |
| (27,27)   | 0.106        | 0            | 0.242        |
| (28,28)   | 0.106        | 0            | 0.240        |
| (29,29)   | 0.107        | 0            | 0.239        |

*Ni-Cl$^{in}$ and Ni-Cl$^{out}$ - couplings of Ni with atoms of "inner" and "outer" chlorine cylinders. For Ni-Cl$^{in}$ bonds, COOPs values for non-equivalent bonds "along" and "across" the tube axis are given.
FIG. 1: Atomic structures of: 1 - armchair (15,15)- and 2 - zigzag (15,0)-like NiCl$_2$ NTs. Side views and views along the tube axis are shown.
FIG. 2: Total energies (per NiCl$_2$ unit) as a function of the diameter of Ni cylinders for NiCl$_2$ tubes of armchair ($n,n$) (rings) and zigzag ($n,0$) (squares) forms.
FIG. 3: Total (solid line) and Ni3d-like DOS (dotted line) of: 1 - armchair (15,15)- and 2 - zigzag (15,0)-like NiCl$_2$ nanotubes.