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Electromechanical Properties of Small Transition-Metal Dichalcogenide Nanotubes

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Abstract: Transition-metal dichalcogenide nanotubes (TMC-NTs) are investigated for their electromechanical properties under applied tensile strain using density functional-based methods. For small elongations, linear strain-stress relations according to Hooke's law have been obtained, while for larger strains, plastic behavior is observed. Similar to their 2D counterparts, TMC-NTs show nearly a linear change of band gaps with applied strain. This change is, however, nearly diameter-independent in case of armchair forms. The semiconductor-metal transition occurs for much larger deformations compared to the layered tube equivalents. This transition is faster for heavier chalcogen elements, due to their smaller intrinsic band gaps. Unlike in the 2D forms, the top of valence and the bottom of conduction bands stay unchanged with strain, and the zigzag NTs are direct band gap materials until the semiconductor-metal transition. Meanwhile, the applied strain causes modification in band curvature, affecting the effective masses of electrons and holes. The quantum conductance of TMC-NTs starts to occur close to the Fermi level when tensile strain is applied.

Keywords: transition-metal dichalcogenide nanotubes; electromechanical properties; quantum conductance; density functional-based methods

1. Introduction

In the past few years, transition-metal dichalcogenides (TMCs) have become a class of materials most widely investigated in the fields of physics, materials science or nanotechnology. Especially, two-dimensional (2D) layered forms of TMCs are of great interest, as they can be easily manufactured to monolayers using chemical or mechanical exfoliation and chemical deposition techniques [1–3]. They possess desirable intrinsic band gaps ranging from about 1.0 to 2.0 eV, and they were utilized in nanoelectronic applications to produce field-effect transistors, logical circuits, amplifiers and photodetectors [4–7]. The electronic properties of 2D TMCs can be tuned by various means, including quantum confinement [8–11], mechanical deformations [12–14], electric fields [15,16] or local defects [17–19].

Similar to carbon, tubular and fullerene-like nanostructures can be formed from other inorganic materials, including sulfo-carbides [20], boron-carbon-nitrides [21] or TMCs [22,23]. Though less than their carbon counterparts, in particular MoS₂ and WS₂ nano-onions and nanotubes have been investigated both theoretically and experimentally [24–30]. TMC nanotubes (TMCs-NTs) behave as exceptional lubricants [31,32], and it has been shown that when the MoS₂ NTs or nano-onions are added to base grease, the friction coefficient remains low, even at very high loads [33]. The mechanical properties of TMC-NTs have been investigated experimentally, where tubes were subject to tensile strain using atomic force microscopy [34–37]. Elastic deformations were predicted from linear strain-stress relation up to the fracture point (at 13 GPa and 12% strain for WS₂ TMC-NTs), and fracture was directly related to the formation of local defects [35]. The mechanical properties of WS₂ NTs under axial tension and compression [36] shows that they are ultra-strong and elastic, which distinguishes them from other known materials. Quantum-mechanical simulations showed that under squeezing, MoS₂ NTs start to form platelets, partially attached to the grips, which provide good lubrication at the position of closest contact. This is interpreted as ‘nano-coating’.

Single-walled TMC-NTs have interesting electronic properties that depend on their diameter and chirality. Zigzag (n,0) NTs are direct band gap semiconductors, resembling 1H TMC forms, while armchair (n,n) NTs are indirect band gap materials, similar to the 2H TMC structures [24,29]. Zigzag tubes are, therefore, suggested for luminescent devices, an application that would not be possible for carbon NTs. With increasing tube diameter, the band gaps increase and eventually approach the single-layer limit.

Doping inorganic semiconducting NTs may lead to new optoelectronic nanomaterials. Ivanovskaya *et al.* [38] have investigated the effect of Mo to Nb doping on the electronic structure of MoS₂ NTs using the density functional based tight-binding (DFTB) method. It has been found that composite Mo_{1-x}Nb_xS₂ NTs are more stable than the corresponding mixture of pure tubes. This effect was even stronger for larger tube diameters. The authors reported that all doped NTs were metallic, independent of their chirality, diameters or the substitutional patterns. The density of states close to the Fermi level of Nb-substituted MoS₂ NTs can be tuned in a wide range by the degree of doping.

Electromechanical properties have been widely investigated theoretically for TMC monolayers [14,39,40], but they remain to be explored for the associated tubular structures. Because of their excellent lubricating properties, the application of tensile stress on 2D TMC systems is rather difficult

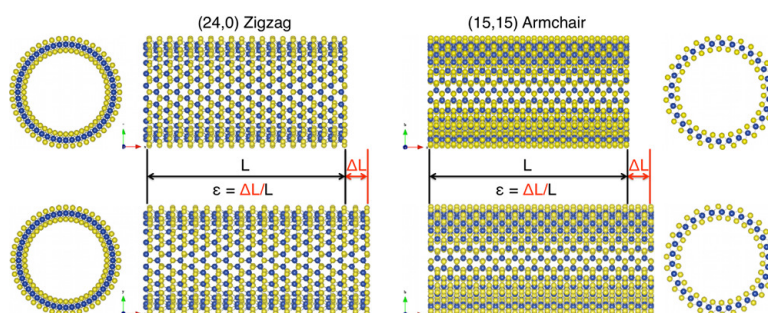
in experiments. The experimental setup for direct tensile tests of TMC-NTs is, however, state-of-the-art [35,37]. We have recently shown that the electronic properties of large-diameter TMC-NTs can be tuned by an external tensile strain for nanoelectromechanical applications [41] and that Raman spectroscopy is an ideal tool to monitor the strain of the individual tubes due to a linear correlation between the Raman shift and the strain. These results hold, however, for large diameter nanotubes. For small diameter tubes, finite size effects are expected.

In this work, we have investigated the electromechanical properties of small diameter TMC nanotubes by applying axial tensile strain. Stress-strain relations, the electronic structure and quantum conductance response to the mechanical deformations were compared between Mo- and W-based NTs with different chalcogen atoms. The results were compared to the available experimental and theoretical works. Our calculations show that up to 2%–5% elongations, the stress-strain relations scale linearly, and we obtained Young's moduli of about 200 GPa for armchair and zigzag tubes, with the notable exception of much softer WTe_2 . The shape of the band structures is strongly affected, the conduction bands have a loose dispersion for zigzag tubes, while the dispersion deepens for armchair materials. We find nearly a linear decrease in the band gap for all types of nanotubes, and eventually, the semiconductor-metal transition occurs. This is, however, observed at larger elongations than for the corresponding layered forms. Tensile strain enhances conductance closer to the Fermi level.

2. Computational Details

We have investigated the (n, n) armchair and the $(n, 0)$ zigzag TX_2 nanotubes ($T = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}, \text{Te}$) with $n = 21$ and 24 (see Figure 1). All structures were fully optimized (atomic positions and lattice constants) employing helical boundary conditions as implemented in the Crystal09 software package [42].

Figure 1. Front and sided views of zigzag and armchair TX_2 NT structures at equilibrium and under tensile strain (ε).



For the strained structures, only the atomic coordinates have been re-optimized, while the unit cell parameter along the tube axis was kept fixed, as reported in our previous works [14,41]. The tensile strain is defined as $\varepsilon = (L - L_0)/L_0$, where L_0 and L are equilibrium and strained lattice values, respectively (cf. Figure 1). The elastic properties of the tubes under tensile stress were calculated as force, F , acting on the area, A . The area can be calculated as follows:

$$A = 2\pi R_0 \delta \quad (1)$$

where R_0 is the tube radius, defined as the distance between the center of the tube and the metal atom, and δ is the thickness of tube wall, taken as the interlayer distance of the bulk material. The Young's modulus, Y , is obtained from the second derivative of the total energy with respect to the applied strain at the equilibrium volume, V_0 :

$$Y = \frac{1}{V_0} \frac{\partial^2 E}{\partial \varepsilon^2} \quad (2)$$

where $V_0 = AL_0$.

Structural and electromechanical properties have been calculated using density functional theory (DFT) in the representation by Perdew, Burke and Ernzerhof (PBE) [43], a method that was validated for the TMC systems earlier [11,29,41]. The all-electron 86-311G* basis was chosen for sulfur atoms, while for the heavier elements, the effective core potential (ECP) approach with large cores was employed, accounting for scalar relativistic effects [44,45]. The shrinking factor was set to eight, resulting in 5 k points in the irreducible Brillouin zone according to the Monkhorst–Pack sampling [46]. Band structures were calculated along the high symmetry points using the $\Gamma - X$ path.

The coherent electronic transport calculations were carried out using the density functional based tight-binding (DFTB) [47–49] method in conjunction with the non-equilibrium Green's function technique [50,51] and the Landauer–Büttiker approach. The present approach was already validated and described in detail in our previous works on various TMC materials [14,41,52].

3. Results and Discussion

We have calculated the electromechanical properties of TX_2 nanotubes by applying tensile strain (ε) to the tubes along their axis. Tensile strain causes changes in the geometry and results in the elongation of the T–X bonds (see Figure 2). These bond lengths increase nearly linearly with ε and are more severe for zigzag NTs. This trend is similar to the corresponding mechanical deformations in the 2D TMC structures [14,41]. In nanotubes, one needs to distinguish between T–X bond lengths in the outer and inner walls, the latter being slightly shorter. While for armchair NTs, outer and inner bonds change in the same way, this is not the case for zigzag NTs. At larger ε , the inner bonds undergo stronger elongations, eventually approaching the same values as for the outer bonds. We obtain elongation of 0.8–1.0 pm and 0.5–0.6 pm per 1% of strain for the zigzag and armchair NTs, respectively. Stronger elongations of bonds in the zigzag NTs can be understood, such that along the tube, where the tensile strain is applied, there are many bonds oriented exactly parallel to the axis, while this is not the case in armchair tubes. These bonds can be easily stretched, resulting also in a reduction of the X–T–X angles.

Once the tubes are subject to ε , also the tube diameters change, namely they have to shrink to compensate for the elongations along the tube axis. On average, the tube diameters shrink by 0.6 Å and 0.2 Å per 1% of strain for zigzag and armchair NTs, respectively.

The stress-strain relations for all the studied tubes are shown in Figure 3. If the curves are fitted to the harmonic approximation for small deformations according to Hooke's law, the stress-strain plots are linear, and the plastic deformations for larger strain values could not be observed. From this fitting, however, we have obtained the Young's moduli for all the tubes (see Table 1). Our results are in agreement with the available experimental and theoretical values. For example, the

experimental Young's modulus of multi-wall WS₂ NTs is found to be 152 GPa [36], 171 GPa [34] and 223 GPa [37]. For single-wall MoS₂ NT ropes, the lowest measured Young's modulus was 120 GPa [26], whereas theoretical values estimated from DFTB calculations for MoS₂ NTs are 200 GPa [53] and 230 GPa [30,54]. Moreover, Li *et al.* [55] have reported 150 and 127 GPa for (6, 6) and (10, 0) MoS₂ NTs, respectively.

Figure 2. The metal-chalcogen bond length (T-X) change with the applied tensile strain of exemplary MoS₂ and WSe₂ NTs. Similar linear changes are obtained for other transition-metal dichalcogenide-NTs.

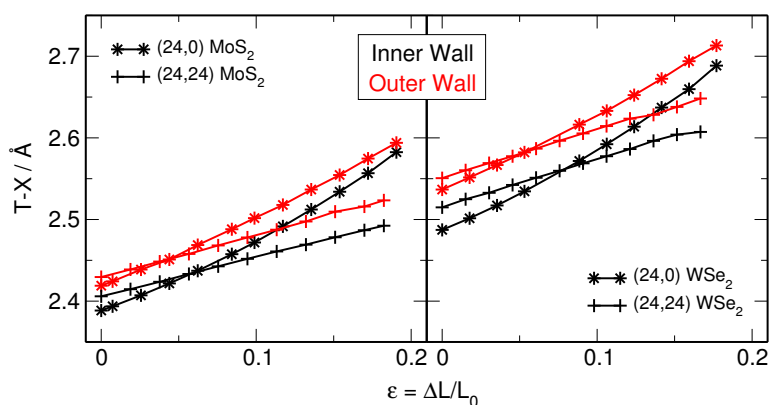


Figure 3. The calculated strain-stress relation of TX₂ NTs under applied tensile strain along the tube axis. Note the different scale on *x*- and *y*-axes of TTe₂ NTs.

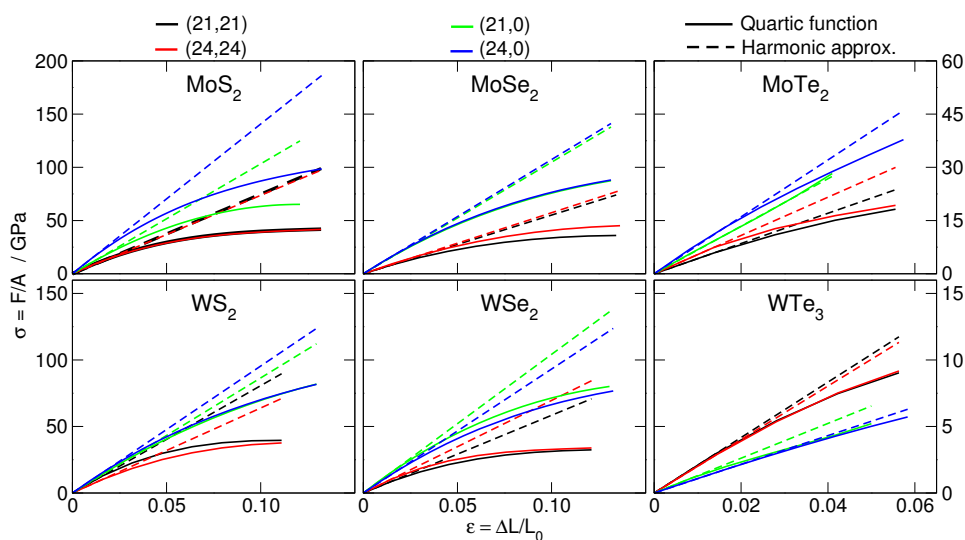


Table 1. The calculated Young’s moduli of all the studied NTs. The numbers are obtained from the harmonic approximation following Hooke’s law for small values of tensile strain.

System	Chirality			
	(21,0)	(24,0)	(21,21)	(24,24)
MoS ₂	191	259	235	232
MoSe ₂	184	188	165	174
MoTe ₂	110	132	119	150
WS ₂	160	177	256	203
WSe ₂	184	165	177	211
WTe ₂	44	36	59	57

If the curves are fitted to a higher order polynomial (here, the fourth order polynomial was chosen), we observe that already, for the ε of 3%–5% (for sulfides and selenides) or 2%–3% (for tellurides), the curves deviate from linearity.

Changes in the geometry of TMC NTs under mechanical deformations also affect the electronic structure of these materials. The band structure responses to the tensile strain are shown in Figures 4 and 5 for zigzag and armchair NTs, respectively. In the equilibrium, zigzag NTs are direct band gap semiconductors at Γ , while armchair NTs are indirect band gap materials with the valence band maximum (VBM) at Γ and the conduction band minimum (CBM) at $2/3$ between Γ and X . This is in close agreement with the DFTB calculations of Seifert *et al.* [24]. These features are unaffected by ε ; however, the CBM of armchair tubes shifts slightly towards the X point.

Figure 4. The calculated band structure response to the applied tensile strain of zigzag TX₂ NTs. (a) MoX₂ and (b) WX₂.

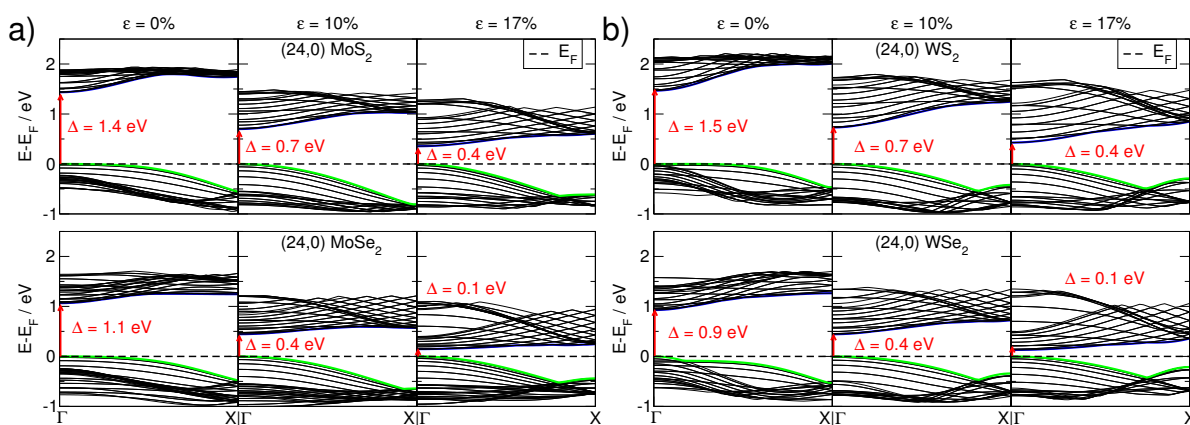
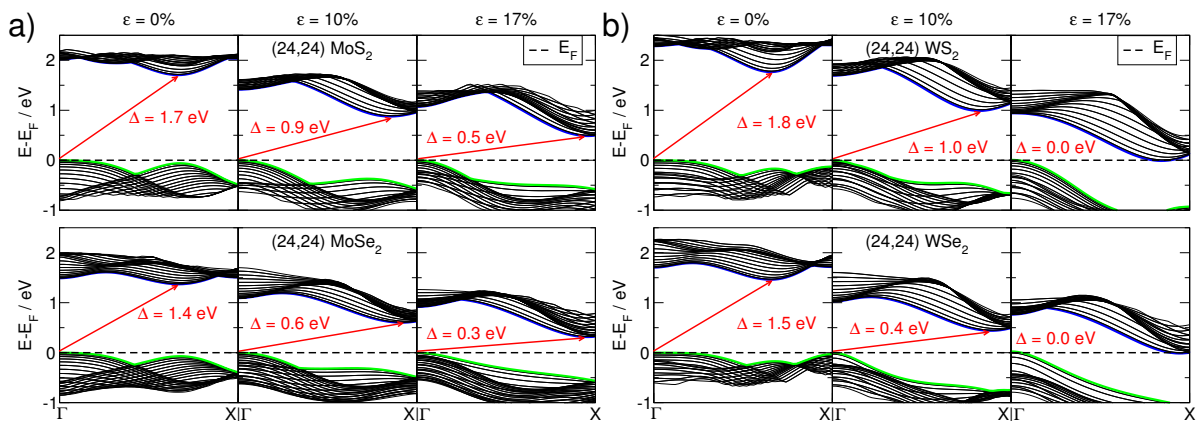


Figure 5. The calculated band structure response to the applied tensile strain of armchair TX_2 NTs. (a) MoX_2 and (b) WX_2 .



Both the valence and the conduction bands are affected by the mechanical deformations. While in the zigzag NTs, the CBM loses its dispersion with the applied strain, it is opposite in the case of armchair tubes. In the latter, the dispersion deepens, and the CBM position shifts towards the X point. The valence bands get more dispersed along the $\Gamma - X$ paths for larger deformations, and this is chirality-independent.

The band gap evolution with the tensile strain is shown in Figure 6. Nearly linear scaling is found for ε of 10%–12%. The semiconductor-metal transition occurs for elongations much larger than in the case of layered 2D forms [14,41], but it is faster for the NTs with heavier chalcogen atoms, as they have a smaller intrinsic band gap. We have noticed that for armchair NTs, there is almost no band gap dependency on the tube diameter for the whole range of ε , as it is in the zigzag forms.

Figure 6. The calculated band gap evolution with the applied tensile strain of zigzag and armchair TX_2 NTs.

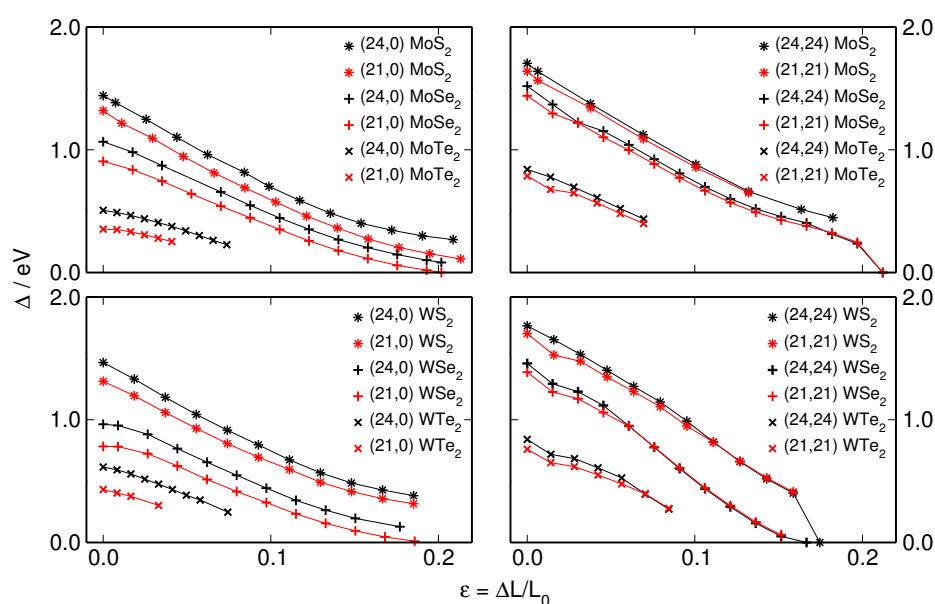


Figure 7 shows the intrinsic quantum conductance ($\mathcal{G}$) calculated along the TX_2 NTs with respect to the applied tensile strain. As the materials are stretched along the tube axis, $\mathcal{G}$ starts to appear closer to the

Fermi level, and eventually, the transport channel opens. For all NTs, the conductance below the Fermi level reduces with strain; however, above the E_F , it stays unchanged (it increases) for zigzag (armchair) NTs. Our quantum transport calculations aim to describe the intrinsic conductance of the entire tubes along their principal symmetry axis. Note that the quantum transport calculations are carried out using the DFTB method, which tends to overestimate the electronic band gap.

We have calculated the effective masses of electrons and holes at the CBM and VBM, respectively (see Table 2). The effective masses of holes are reduced with the tensile strain, which is consistent with stronger dispersion in the VBM. The masses of electrons at the equilibriums are similar for zigzag and armchair NTs of the same type. These numbers are larger for heavier chalcogen atoms, similar to the electron effective masses. We expect the effective masses of electrons to increase (decrease) for zigzag (armchair) NTs with ε as the dispersion of bands decreases (increases). The effective masses are calculated from the harmonic approximation and fitting to the energy point close to the VBM and CBM. This, therefore, strongly depends on the number of k -points along the path in the Brillouin zone. We have chosen very fine k -point sampling of 150 points between Γ and X . Thus, we do not observe as clear trends as expected in the effective masses of electrons. For the (6,6) and (10,0) MoS₂ NTs, Li *et al.* [55] have obtained effective masses of electrons and holes of 0.53, 0.51, 0.83 and 1.55, for armchair and zigzag forms, respectively.

Figure 7. The electron quantum conductance of TX₂ NTs under applied tensile strain along the tube axis.

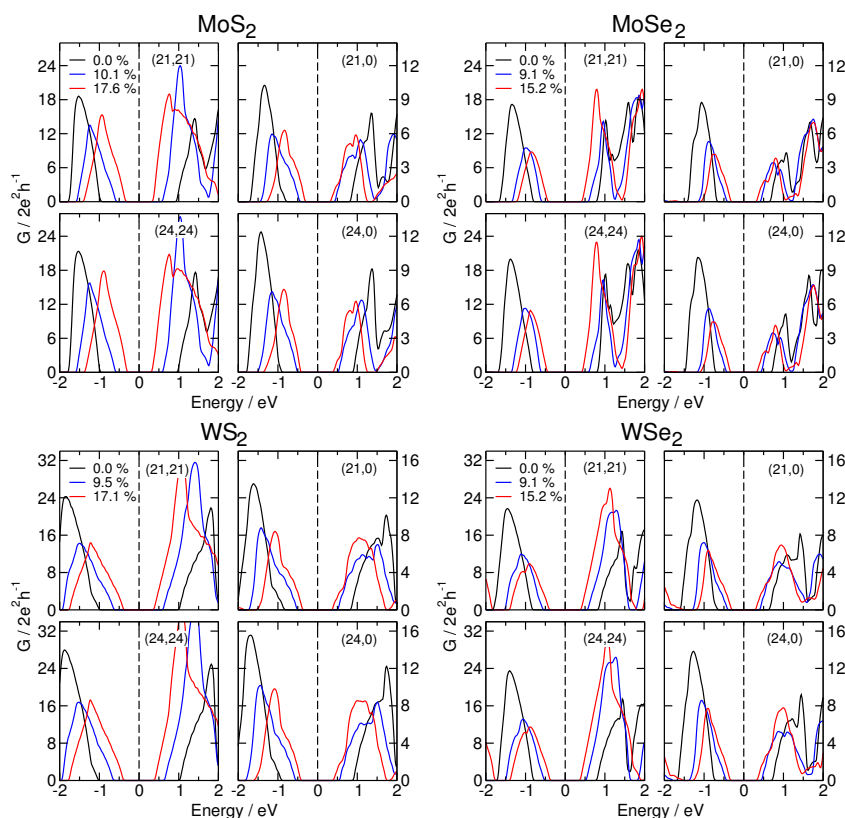


Table 2. The calculated effective electron and hole masses (in m_0 units) of TX_2 NTs with respect to the applied tensile strain (ε). For zigzag NTs, both effective masses are calculated at the Γ point; for armchair NTs, effective masses of holes are calculated at Γ and of electrons between Γ and X . Note, for the latter, we do not specify the exact k -point as the conduction band minimum (CBM) shifts with ε . The negative values of hole effective masses come from the band curvature at the valence band maximum (VBM).

System	Chirality	Electron masses			Hole masses		
		0%	5%	10%	0%	5%	10%
MoS ₂	(24,24)	0.621	0.631	0.707	−6.209	−1.684	−0.974
	(24,0)	0.655	0.621	0.660	−10.03	−1.990	−1.033
MoSe ₂	(24,24)	0.868	0.938	0.884	−15.366	−2.233	−1.140
	(24,0)	1.092	0.998	0.739	−0.485	−3.079	−3.461
WS ₂	(24,24)	0.434	0.457	0.524	−11.498	−1.934	−0.498
	(24,0)	0.475	0.434	0.467	−12.348	−3.171	−1.270
WSe ₂	(24,24)	0.621	0.715	0.659	−15.147	−2.285	−7.922
	(24,0)	0.585	0.714	0.916	−1.362	−2.846	−1.396

4. Conclusions

We have investigated the electromechanical properties of inorganic nanotubes of the TX_2 -type under applied tensile strain. The tubes undergo changes in geometry, namely the T–X bond lengths are elongated. More pronounced changes are obtained for the zigzag NTs, in which some of the bonds are oriented parallel to the tube axis, which means along the acting deformation force. The stress-strain relation fitted to the harmonic approximation for small deformations gives Young's moduli of about 200 GPa, with the exception of WTe₂, which produces notably smaller values around 50 GPa.

The electronic properties and the quantum transport are particularly affected by mechanical deformations. Nearly a linear change in the band gap is observed for elongations up to 12%. The semiconductor-metal transition is eventually obtained for all type of tubes; however, it is much faster for heavier chalcogen atoms. Nanotubes require larger tensile strain to become metallic than the corresponding 2D materials.

The dispersion of the valence and conduction bands changes strongly with the applied strain. Notably, the VBM deepens the dispersion, which results in the lowering of the hole effective masses. The CBM is chirality dependent, and the dispersion is lost (enhanced) for zigzag (armchair) NTs. The transport channels start to open closer to the Fermi level for larger ε .

The electronic properties and the possibility to tune by tensile strain suggest that inorganic NTs, such as TMC materials, could be considered in nanoelectronic applications, for example as switching materials.

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Author Contributions

N. Zibouche, M. Ghorbani-Asl, A. Kuc and T. Heine generated, analyzed and discussed the results. T. Heine conceived of this project. All authors contributed in writing this paper.

Conflicts of Interest

The authors declare no conflict of interest.

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