Strain engineering of the electronic and thermoelectric properties of titanium trisulphide monolayers

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Keywords: 2D materials, thermoelectrics, strain, DFT, seebeck coefficient

Abstract
The goal of this work is to evaluate the effect of mechanical strain on a number of electronic and thermoelectric properties of TiS₃ monolayers. We have used density-functional theory (DFT) calculations at the hybrid HSE06 level to evaluate the response of the electronic band gap and mobilities, as well as the thermopower, the electrical conductivity, the electronic contribution to the thermal conductivity and the power factor. Our calculations indicate that the band gaps can be increased by 44.25%, reaching a value of 1.55 eV from that of the undeformed case of 1.07 eV. The behaviour of HSE06 band gaps agrees well with that calculated at the G0W0 level of theory. We evaluate the variation of electron mobilities with strain and discuss the possible causes of the existent disagreement between experiments and simulations. In addition, our calculations predict small changes in the Seebeck coefficient, whose $S_y$ component can be enhanced by up to 11% with a compression of 5% along the $y$-axis. On the other hand, the electrical conductivity experiences higher variations, nearly doubling its value from the undeformed case under the semiconductor regime of doping and mechanical deformation. Finally, our predicted power factors can be enhanced by nearly twice under the same conditions by which the electrical conductivity is also improved, indicating that the latter drives the optimisation of the former.

1. Introduction

Thermoelectric materials have attracted much attention because they produce electricity without moving parts [1], which makes them ideal to engineer reliable devices that require minimal maintenance for long periods for applications such as harvesting human body heat [2], solar generators [3], waste recovery energy in power plants and combustion engines [4, 5]. This electricity production is caused by the Seebeck effect by which an applied temperature difference $\Delta T$ throughout the material induces a voltage difference $\Delta V$. The Seebeck coefficient $S$ (also referred to as thermopower) is defined as $S = \Delta V / \Delta T$. In turn, this parameter and the electrical $\sigma$ and thermal $\kappa$ conductivities define the figure of merit $zT = S^2\sigma T / \kappa$ that dictates the efficiency of a thermoelectric material: the higher the value of $zT$, the higher the efficiency of the thermoelectric device [6]:

$$\eta = \eta_C \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + 1}$$  \hspace{1cm} (1)

where $\eta_C$ is the Carnot efficiency. For example, equation (1) states that a thermoelectric material with a rather high $zT$ value of 1.4 has an efficiency of 10.34% working with a $\Delta T$ of 300 K. Given these low values, new strategies are necessary to enhance the figure of merit and hence the efficiency. This parameter indicates that attempts to achieve this purpose must focus on increasing the Seebeck coefficient and electrical conductivity and decreasing the thermal conductivity. However, conflicts exist between these strategies. For metals and highly-doped semiconductors, the Seebeck coefficient can be expressed as
\[
S = -\frac{\pi^2 k_B T}{3e} \frac{\partial \ln(\sigma(E))}{\partial E} \bigg|_{E=E_F},
\]

where \(E_F\) is the Fermi level, \(k_B\) is the Boltzmann constant, and \(e\) the elemental charge. Using \(\sigma(E) = e^2 (g(E) \tau v_0)_{E = E_F}\) with \(v_0\) being the electron’s drift velocity and \(\tau\) its relaxation time, the Seebeck coefficient can be rewritten as

\[
S = -\frac{\pi^2 k_B^2 T}{3e} \left( \frac{g(E)}{n} + \frac{\partial \mu}{\mu \partial E} \right) \bigg|_{E=E_F},
\]

where \(\mu\) and \(n\) are the carriers’ mobility and concentration and \(g(E)\) is the density of states [7]. The Seebeck coefficient is then improved by reducing the concentration and mobility of charge carriers. However, if the concentration and the mobility diminish, so does the electrical conductivity. In addition, the thermal conductivity is the sum of the electronic \(\kappa_e\) and phononic \(\kappa_{ph}\) contributions. Therefore, decreasing the electrical conductivity implies shrinking the electronic part as the latter is proportional to the former as dictated by the Wiedemann–Franz law \(\kappa_{el} = L\sigma T\), where \(L\) is the Lorentz number.

Most of current work made to maximise the figure of merit is based on creating nanostructures that take advantage of quantum confinement [8, 9]. The most popular example is the seminal work by Hicks and Dresselhaus [10], who predicted increases of the figure of merit in multilayers of Bi$_2$Te$_3$ by factors of up to 13, due to highly anisotropic effective-mass tensor. In this context, a common strategy is to manufacture two-dimensional flakes from exfoliating materials stacked with van der Waals forces. Upon this exfoliation, the flake’s electronic structure is in general different from the bulk’s near the valence and conduction band edges, as the chemical bonding between the outmost atomic layers adjusts as their constituent particles are now in contact with the vacuum or air. For instance, the band gap in MoS$_2$ shifts from being indirect in bulk to direct in a single layer [11]. Another effect is that surface states might emerge in the forbidden band gap [12], with the potential of filling the values of \(g(E)\) near \(E_F\), that in turn might increase the Seebeck coefficient as predicted by equation (3), while the other thermoelectric parameters remain practically unchanged. Hence, a large number of new two-dimensional materials have been created in recent years [13].

Among all these layered materials, here we are interested in the family of trichalcogenides MX$_3$, where M is the transition metal Ti, Zr, or Hf and X can be S, Se, or Te [14, 15], and in particular on titanium trisulphide (TiS$_3$). TiS$_3$ is an n-type [16, 17] semiconductor formed by abundant and non-toxic elements that is attractive for thermoelectric applications because of its large Seebeck coefficient of \(-650 \mu V K^{-1}\) at 300 K, a low thermal conductivity of 3.7 W/(m \cdot K) at 325 K with a carrier concentration of \(1.24 \times 10^{16} \text{ cm}^{-3}\) [18]. Previous works reported similar measurements with a thermopower of around \(-700 \mu V K^{-1}\) at 300 K [19] with an electrical conductivity at around 200 K between 0.5 and 5.0 (\(\Omega \cdot \text{cm}\))$^{-1}$ [20]. The electronic properties of TiS$_3$ has been also reported with a direct band gap of 1.0 ± 0.1 eV for thin films with a thickness of around 300 nm [21]. Although the behaviour of the thermopower of bulk TiX$_3$ under hydrostatic pressures of up to 9 GPa was studied by Hsieh et al [18] little is known on the effects of exerting uniaxial and biaxial strains on the thermoelectric properties on their monolayers.

The goal of this study is thus to evaluate the electronic and thermoelectric properties of titanium trisulphide monolayers as a function of the uniaxial and biaxial strains with first-principles calculations. We employ these calculations because they have been shown to be a valuable tool to study strain effects on other nanostructures such as \(\gamma\)-graphyne nanotubes [22]. In particular, we use density-functional theory (DFT) calculations that employ plane waves and the generalised gradient approximation (GGA) to relax the geometry of unit cells.

We then recalculate the electronic structure using two approaches: (i) the hybrid exchange–correlation functional HSE06 [22] and (ii) the G$_0$W$_0$ approach [23, 24], which open the underestimated electronic band gap of the GGA calculation and allow recovering a good agreement with the experimental values. Our intention is to make sure that little disagreement exists between the band gaps predicted with HSE06 and G$_0$W$_0$ under extreme mechanical conditions, as it has been reported that the thermoelectric properties of a semiconductor depend on finding a precise difference between the valence band maximum and the conduction band minimum. For instance, it was theoretically proven that the optimum band gap \(E_{gap}\) must be larger than 6\(\hbar\gamma T\) (i.e. 0.16 eV at 300 K) to maximise the figure of merit in direct-gap semiconductors [25]. In that study, it was also proposed that the band gap varies the effective mass under the approximation \(m^* = 3h^2 E_{gap}/4P^2\), where \(P\) is the Kane matrix element [26]. This approximation implies that \(\sigma\) and in turn \(\kappa_{el}\) also depend on the electronic band gap, which is subject to analysis later in this manuscript. Another theoretical study showed that the Seebeck coefficient maximises near one-half the energy gap divided by \(eT\) [27], evidencing the importance of correctly positioning the Fermi level by setting first an accurately energy gap. In addition, in the present work we discuss the large discrepancy existing between the electron mobilities predicted with DFT and those reported from experiments, with a disagreement reaching up to three orders of magnitude [28–30].
The manuscript is organised as follows. In section 2, we briefly describe the technical aspects of the DFT calculations and the methodology to calculate the charge mobilities, the Seebeck coefficient and other relevant thermoelectric magnitudes. In section 3, we present the band gaps of TiS$_3$ monolayers as a function of uniaxial and biaxial strains. We next show the behaviour of the electron mobilities as a function of these strains, as well as those of the thermoelectric properties (Seebeck coefficient, electrical conductivity, and electronic contribution to the thermal conductivity) and evaluate the resulting power factor. We compare to a certain extent the values we obtain for these properties with those reported in the literature from experimental measurements. Finally, section 4 concludes our main findings and implications for future work.

2. Theoretical methods

We use the Vienna *Ab initio* Package (VASP) [31–33] to relax the positions and cell parameters of TiS$_3$ monolayers. These monolayers are initially represented as a unit cell belonging to the P2$_1$/m space group as shown in figure 1. Reciprocal space integrations are made using a mesh of $10 \times 14 \times 1$ k-points centred at $\Gamma$ in the Brillouin zone. The geometry relaxation is carried out setting thresholds of 0.1 eV nm$^{-1}$ for the forces and $1 \times 10^{-6}$ eV for the self-consistency solution of the wavefunction. We use GGA for the exchange-correlation potential in the Perdew–Burke–Ernzerhof (PBE) [34] parameterization and the projector augmented wave method (PAW) [35]. We expand the valence orbitals with a plane wave basis with an energy cutoff of 350 eV. Long-range van der Waals forces are included using the Zero damping Grimme’s DFT-D3 scheme [36]. We choose this scheme because for TiS$_3$ it gives a better agreement with bulk lattice parameters with respect to other descriptions of the van der Waals forces available in VASP.

Once the geometry of the TiS$_3$ monolayer is relaxed, we obtain the following parameters: $a = 0.496$ nm, $b = 0.339$ nm, with an angle between them $\gamma = 90.0^\circ$; as a reference, bulk values obtained by Furuseth et al [14] are $a = 0.458$ nm, $b = 0.340$ nm, and $c = 0.878$ nm with angles $\alpha = 90.0^\circ$, $\beta = 97.320^\circ$, and $\gamma = 90.0^\circ$. A vacuum buffer of nearly 2 nm is used to separate the monolayer from its periodic images. After the structures are relaxed, we apply uniaxial strains and biaxial strains up to 7% along the x and y directions in increments of 1%. For uniaxial strains in the x (or y) directions, the lattice vector in this direction is kept fixed in order to reproduce the target strain, while the cell is free to relax along the y (or x) axis. After each relaxation is completed, we then used the optimised geometry and the HSE06 functional to obtain a more precise representation of the electronic structure from which we can obtain reliable thermoelectric transport properties with the BoltzTraP code [37, 38]. This code uses semiclassical Boltzmann theory under the constant relaxation time approximation. However, BoltzTraP expresses the electrical conductivity and the electronic contribution to the thermal conductivity as a function of the carrier’s relaxation time, which is defined as [39]

$$\tau_i = \frac{\mu_i m_i^*}{e},$$

where $m_i^*$ is the effective mass and $\mu_i$ is the carrier’s mobility along the $i$th direction, which can be calculated using Bardeen and Shockley’s deformation potential theory [40].

Figure 1. Representation of the TiS$_3$ unit cell (a) with atoms of sulphur painted in blue and titanium in grey and monolayer of $4 \times 4$ unit cells along the x and y directions (b).
3. Results and discussion

3.1. Electron mobilities

Table 1. Uniaxial values of the elastic modulus $C$, the deformation potential constant $E_0$, effective mass $m^*$ (in units of the relaxed electron’s mass $m_0$), mobility $\mu$ and relaxation time $\tau$ of holes and electrons in the x and y directions calculated using HSE06 calculations for an undeformed monolayer.

| Direction | Carrier | $C$ (eV Å$^{-2}$) | $E_0$ (V) | $m^*$ (m$_0$) | $\mu$ (x 10$^3$ cm$^2$/V·s) | $\tau$ (x 10$^{-13}$ s) |
|-----------|--------|-----------------|----------|--------------|------------------------|-------------------|
| X         | Hole   | 5.97            | 4.43     | $-0.45$      | 0.35                   | 0.88              |
| Y         | Hole   | 8.50            | $-5.14$  | $-3.81$      | 0.01                   | 0.11              |
| X         | Electron | 5.97          | 0.67     | 1.92         | 0.82                   | 8.98              |
| Y         | Electron | 8.50          | 1.38     | 0.32         | 9.69                   | 17.86             |

$$\mu_i = \frac{2}{3} \frac{e^3 C_i}{k_b T (m^* i)^2 E_{0,i}}$$

for uniaxial strains $\varepsilon$, where $E_{0,i}$ is the constant that couples a dilation $\Delta$ produced by applying a strain $\varepsilon$ with the energies $E(\varepsilon) = E_{0,i} + E_{1,i}\Delta$ of the electronic band $i$ with $E_{0,i}$ being a fitting parameter, and $C_i$ is the elastic modulus in the x and y directions for uniaxial deformations or both for biaxial cases. The deformation constant is calculated as the variation of the valence band maximum for holes and conduction band minimum for electrons with respect to the vacuum level versus the strain. These elastic moduli are calculated using

$$C_i = \frac{\partial^2 E_{tot}}{\partial \varepsilon_i^2} \bigg|_{A_0}$$

where $E_{tot}$ is the total energy and $A_0$ is area of the unstrained monolayer. The elastic moduli and deformation constants are determined from a number of simulations VASP/PBE where the monolayer is subject to strains between $-2.0$ and $2.0\%$ in increases of $0.5\%$ in the two in-plane directions. The effective mass is obtained using the dispersion relation

$$E_i(k_i) = E_{0,i}(k_i) + \frac{\hbar^2}{2m^*_i}(k_i - k_{0,i})^2$$

where $E_{0,i}(k_i)$ is the energy band maximum/minimum at a given position $k_i$ in the Brillouin zone along the $i$th direction, $m^*_i$ is the $i$th component of the effective mass tensor for holes if we fit around the valence band maximum and electrons near the conduction band minimum, and $k_{0,i}$ is the wave vector at the position where these two edges are found. We have carefully ensured that the band gap is direct for all strains between $-7\%$ and $7\%$; thus, the fitting is made around the $\Gamma$ point along the directions connecting the points in the Brillouin zone $\Gamma = [0.0, 0.0, 0.0]$ to $Z = [0.5, 0.0, 0.0]$ and $\Gamma = [0.0, 0.0, 0.0]$ to $Y = [0.0, 0.5, 0.0]$.

The deviation between theoretical and experimental values can in principle be attributed to three factors: first, the TiS$_3$ materials in experiment are multilayers rather than a monolayer modelled in DFT studies; second, the effects of the substrate employed to encapsulate the TiS$_3$ sample in the laboratory; and third the presence of crystallographic defects or surface impurities in experimental samples [42]. The first factor can be discarded as the DFT electron mobilities for a bilayer only decrease moderately with respect to the monolayer’s as listed in table 2. Therefore, we argue that the disagreement between experiments and theory can be partially reduced by evaluating the substrate’s effect on the electronic transport in TiS$_3$. Our argument is based on the data given by Lipatov et al [43] who reported mobilities of nanowhiskers between 18 and 24 cm$^2$/V·s on Si/SiO$_2$ at room temperature, which increase up to 43 cm$^2$/V·s on Al$_2$O$_3$. Recent data by Papadopoulos et al contain measurements of around 250 cm$^2$/V·s encapsulated in hexagonal boron nitride (hBN) at 90 K [44]. Deposited samples of graphene [45] and MoS$_2$ [46] on this material showed comparable mobilities as those of...
3.2. Band gaps

Figures 3(a) and (b) show the variation of the electronic band gaps determined with GGA-PBE, HSE06, and G0W0 levels of theory as a function of uniaxial strains. When no strains are present, the TiS3 monolayers have direct band gaps located at the Γ point of 0.24 eV for PBE and 1.07 eV for HSE06 and G0W0. When strains are applied, we see that the relative variation of PBE gaps show the highest increase because of its much lower unstrained value and goes up to 0.61 eV with a 7% stretching in the y-axis. This increase for PBE has been also previously reported [47], which supports the methodology employed in this study. However, since this GGA functional severely underestimates the experimental value with no deformation, we focus hereinafter on those predicted by HSE06 and G0W0. The band gaps computed with these two levels of theory show similar variations with strain, with a maximum value of 1.55 eV with a stretching of 7% along the axis. Nonetheless, we find that the HSE06 values behave more smoothly with increasing strain, which suggests that G0W0’s electronic structure is more sensitive to the mechanical deformation. In addition, we find that HSE06 yields direct band gaps for all strains applied with the exception of the 7% biaxial compression where it is indirect though quite near the Γ point at \( \varepsilon_y < -0.02 \).

For all three levels of theory, the different response shown in figures 3(a) and (b) of the band gap with the applied strains in x and y directions evidences the central role played by the anisotropy of the TiS3 monolayer. As a result of this anisotropy, we infer that the strain exerted along the y-direction drives the band gap variations when applying biaxial deformations illustrated in figure 3(c). For these biaxial deformations, the band gaps reach value of 1.31 eV for HSE06 and G0W0. On the one hand, the band gaps are severely reduced under compressions between 4 and 7% with values as low as 0.11 eV for HSE06 and 0.16 eV for G0W0. The reduction of the band gap under tension from along the x-direction is caused by the increase with valence band maximum with strains \( \varepsilon_x \leq -1\% \). In contrast, the valence band maximum increases monotonically with strains \( \varepsilon_y \) from −7% to 7%.
The different behavior of the band gap both directions adds another anisotropic feature of the electronic structure of the TiS₃ single layer. The reduction of the band gap under compression might induce a metallic behavior in the monolayers and are object of special study when evaluating the electrical conductivity in section 3.4. In addition, our simulations reveal that, for compressive strains larger than 2% (i.e. \( \varepsilon_y < -2\% \)), these deformations are plastic as the induced stretching in the x-direction is no longer linear as shown by figure 4(b). In contrast, figure 4(a) shows that a more moderate deviation from this linearity when strains are applied in the x-direction. Overall, we determine the Poisson’s ratios of \( \nu_{xy} = 0.13 \) and \( \nu_{yx} = 0.19 \).

3.3. Seebeck coefficient

We now analyse the strain effects on the thermoelectric properties, with an emphasis on the data obtained around 1.24 × 10¹⁸ electron · cm⁻³, which is taken as a reference since measurements for bulk crystalline TiS₃ are available at this concentration [17]. Figure 5 illustrates the variation of the in-plane Seebeck components \( S_x \) and \( S_y \) in the range of electron concentrations between 5 × 10¹⁵ and 5 × 10¹⁸ cm⁻³ for a number of uniaxial and biaxial strains. For uniaxial deformations induced in the x-direction, the component \( S_x \) remains practically constant, whereas the component \( S_y \) slightly decreases by 1.85% at 1.24 × 10¹⁸ cm⁻³ from −500.92 μV K⁻¹ to −491.62 μV K⁻¹ and by 2.14% −376.19 μV K⁻¹ to −368.14 μV K⁻¹ at 5.0 × 10¹⁸ cm⁻³ (the maximum electron concentration shown in our figure 5) with a stretching of 7%, which coincides with the band gap decreasing to only 0.95 eV. In contrast, when the structure is compressed by 7%, both thermopower components slightly decrease as the band gap slightly reduces to 0.88 eV. On the other hand, stronger changes occur when deforming
the structure along the $y$-axis, in particular with compressions of 7%, where the band gap is reduced to 0.11 eV, inducing a metallic behaviour in the electronic transport of the monolayer. As a result, both Seebeck components significantly worsen throughout the entire carrier concentration range, reaching values of approximately $-200 \mu V K^{-1}$. In contrast, a compression of 5% is able to enhance the $S_y$ component (i.e. increase its absolute value) by roughly 11% between $5.0 \times 10^{15}$ and $5.0 \times 10^{18} \text{ cm}^{-3}$, coinciding with a moderate drop of the band gap to 0.52 eV. In addition, we realise that this response with deformations along the $y$-axis drives the thermopower’s behaviour for a 5% biaxial compression. Overall, we observe that the in-plane Seebeck coefficients for the undeformed monolayer are $S_x = -442.96 \mu V K^{-1}$ and $S_y = -500.85 \mu V K^{-1}$, which are in the range those found experimentally with a value of $-650 \mu V K^{-1}$ for $1.24 \times 10^{18} \text{ cm}^{-3}$ for bulk crystal TiS$_3$.

### 3.4. Electrical conductivity

We next examine the changes of the electrical conductivity with strain. Since BoltzTraP yields electrical conductivities as a function of the charge’s relaxation times, the absolute values of the former are subject to that choice. In this work, we collect electron relaxation times $\tau_{x,DFT} = 897.76 \text{ fs}$ and $\tau_{y,DFT} = 1786.35 \text{ fs}$ by employing our predicted mobilities. In contrast, if we take the experimental mobilities reported in Ref[38],

![Figure 3. Variation of the electronic band gap versus the uniaxial strains using the PBE and HSE06 functionals, and G$_0$W$_0$ method along the x (a) and y (b) directions and biaxial strains (c).](image-url)
\( \mu_{x,\text{exp}} = 10.87 \text{ cm}^2/\text{(V \cdot s)} \) and \( \mu_{y,\text{exp}} = 25.00 \text{ cm}^2/\text{(V \cdot s)} \), and plug them into equation (4), we obtain the corresponding relaxation times \( \tau_{x,\text{DFT-exp}} = 11.87 \text{ fs} \) and \( \tau_{y,\text{DFT-exp}} = 4.61 \text{ fs} \), which in turn yield electrical conductivities at \( 1.24 \times 10^{18} \text{ cm}^{-2} \) of \( \sigma_{x,\text{DFT-exp}} = 2.60 \text{ (}\Omega \cdot \text{cm})^{-1} \) and \( \sigma_{y,\text{DFT-exp}} = 3.77 \text{ (}\Omega \cdot \text{cm})^{-1} \), which, as
expected, have a much better agreement with the experimental measurements than if we use our values that are two orders of magnitude higher.

With these two semi-empirical values we now analyse in figure 6 how the in-plane electrical conductivities vary as a function of the uniaxial and biaxial strains. For uniaxial strains exerted in the x-axis, figure 6(a) shows the component $\sigma_x$ significantly enhances with compressions, with its maximum values increased by nearly 1.5 times with 5% and doubled with 7% with respect to that of the undeformed case, coinciding moderate reductions of the band gap of 3.13% and 11.26%, respectively. In contrast, the component $\sigma_y$ is almost halved with a stretching $\varepsilon_y = 7\%$ even though the band gap at these conditions is 0.11 eV. For uniaxial strains applied along the y-axis, figure 6(c) illustrates how the component $\sigma_y$ behaves in the same manner with deformations made along the x-axis, but exhibiting a large increase with a 7% shrinking due to the emergence of the metallic behaviour in the monolayer. A similar picture is seen $\sigma_y$ with respect to $\varepsilon_y$ in figure 6(d) but with smaller variations for the highest electron concentrations. Thus, the uniaxial response of both in-plane components explains the similar picture observed with biaxial strains as displayed in figures 6(e) and 6(f). In all these figures we find that once the monolayer is loaded with a sufficiently high content of charge carriers of $10^{17} \text{ e}^{-} \text{cm}^{-3}$ or more, the electrical conductivity increases with increasing strain, a trend that is consistent with the electron mobility also enhancing with this deformation as predicted by Drude model’s definition of the electrical conductivity $\sigma = ne\mu$.

### 3.5. Electronic contribution to the thermal conductivity

We next analyse the variations on the electronic contribution to the thermal conductivity. Figure 7 shows the that the variations experienced by the component $\kappa_{el,x}$ and $\kappa_{el,y}$ described a similar behaviour as those exhibited by the electrical conductivity’s. This similarity can be explained in terms of the Wiedemann–Franz law

$$\kappa_{el} = L\sigma T,$$

where $L$ is the Lorentz number equal to $L = \pi^2 k_B^2/3e^2 = 2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$ [48], even though in principle is valid for metals. However, this law can also be applied for semiconductors, as long as the Lorentz number is modified accordingly [49], and therefore it guides us to find the conditions at which the electronic contribution to the thermal transport can be reduced to maximise the figure of merit and hence to increase the monolayer’s thermoelectric efficiency. However, a compromise exists as reducing this electronic contribution means a decline of the electrical conductivity, lowering in turn the monolayer’s power generation.

By using the semi-empirical relaxation times of $\tau_{x,\text{DFT-exp}} = 11.87 \text{ fs}$ and $\tau_{y,\text{DFT-exp}} = 4.61 \text{ fs}$, we find that the in-plane contributions are $\kappa_{el,x} = 1.64 \times 10^{-2} \text{ W/(m} \cdot \text{K)}$ and $\kappa_{el,y} = 2.29 \times 10^{-2} \text{ W/(m} \cdot \text{K)}$ at $1.24 \times 10^{18} \text{ e}^{-} \text{cm}^{-3}$. These values show that these contributions can be assumed to be negligible to the thermal transport since the thermal conductivity at 325 K was measured at 3.7 W/(m · K) for bulk crystalline TiS$_3$ in Ref [17]. As a result, we deduce that phonons are entirely responsible for the thermal transport in TiS$_3$ monolayers, as the maximum electronic contribution is barely 0.1 W/(m · K) in the concentration range of electrons considered in this work [30].
Finally, we analyse the trends of the in-plane power factors \( (S^2 \sigma) \). The power factor is very useful in thermoelectricity as it lumps the contributions of the thermopower and electrical conductivity to the electronic transport per unit temperature. Taking our previous semi-empirical values for the electrical conductivity, we obtain absolute power factors for the undeformed monolayer of \((S^2 \sigma)_x = 5.11 \times 10^{-5} \text{W/(m} \cdot \text{K}^2)\) and \((S^2 \sigma)_y = 9.46 \times 10^{-5} \text{W/(m} \cdot \text{K}^2)\) at 1.24 \( \times 10^{18} \text{e}^{-} \text{cm}^{-3}\). Figure 8 illustrates the response of the two in-plane components of the power factor to strain, from which it can be deduced that only \((S^2 \sigma)_x\) is significantly improved by shrinking the monolayer in the \(x\)-axis, as this component is nearly up to 1.5 and 2.0 times larger with 5% and 7% deformations. Moreover, as we compare it with the response exhibited by the thermopower and the electrical conductivity, we realise that the variation of the power factor is mainly driven by the latter. For uniaxial strains applied along the \(y\)-axis, we see that the metallic behaviour induced by a heavy compression of 7% has a minor effect on \((S^2 \sigma)_x\) and \((S^2 \sigma)_y\) despite the large increase of its electrical conductivity. In contrast, these two power factors experience higher variations under bidirectional strains: a larger increase upon compression and decrease with stretching of nearly 50% in each case.

**Figure 7.** Effect of the electron concentration on the directional components of the electronic contribution to the thermal conductivity \(\kappa_{el,x}\) (a) and (b) when a number of strains are applied in the \(x\) direction and \(\kappa_{el,y}\) (c) and (d) in the \(y\) direction and in both axes (e) and (f) of TiS₃ monolayers.

**Figure 8.** Effect of the electron concentration on the directional components of the power factor \((S^2 \sigma)_x\) (a) and (b) when strain is applied in the \(x\) direction and \(S^2 \sigma)_y\) (c) and (d) in the \(y\) direction and in both axes (e) and (f) of TiS₃ monolayers.

### 3.6. Power factor

Finally, we analyse the trends of the in-plane power factors \((S^2 \sigma)_x\) and \((S^2 \sigma)_y\). The power factor is very useful in thermoelectricity as it lumps the contributions of the thermopower and electrical conductivity to the electronic transport per unit temperature. Taking our previous semi-empirical values for the electrical conductivity, we obtain absolute power factors for the undeformed monolayer of \((S^2 \sigma)_x = 5.11 \times 10^{-5} \text{W/(m} \cdot \text{K}^2)\) and \((S^2 \sigma)_y = 9.46 \times 10^{-5} \text{W/(m} \cdot \text{K}^2)\) at 1.24 \( \times 10^{18} \text{e}^{-} \text{cm}^{-3}\). Figure 8 illustrates the response of the two in-plane components of the power factor to strain, from which it can be deduced that only \((S^2 \sigma)_x\) is significantly improved by shrinking the monolayer in the \(x\)-axis, as this component is nearly up to 1.5 and 2.0 times larger with 5% and 7% deformations. Moreover, as we compare it with the response exhibited by the thermopower and the electrical conductivity, we realise that the variation of the power factor is mainly driven by the latter. For uniaxial strains applied along the \(y\)-axis, we see that the metallic behaviour induced by a heavy compression of 7% has a minor effect on \((S^2 \sigma)_x\) and \((S^2 \sigma)_y\) despite the large increase of its electrical conductivity. In contrast, these two power factors experience higher variations under bidirectional strains: a larger increase upon compression and decrease with stretching of nearly 50% in each case.
4. Conclusion

In summary, in this study we have investigated the variation of electronic and thermoelectric properties of TiS₃ monolayers with uniaxial and biaxial in-plane strains between −7% and 7% using first-principles calculations based on density functional theory. Our calculations with the hybrid functional HSE06 indicate that the electronic band gap decreases with increasing compressing strains in both directions, reaching a point at which it vanishes with compression of 7% along the y-axis. In contrast, in this direction the gap can be increased from 1.07 eV to 1.55 eV with tensions of 7%. Overall, our calculations suggest that the band gap under biaxial stress behaves as that by the strain imposed along the y-axis. Our DFT band gaps are in good agreement with those also calculated with the G_{0}W_{0} level of theory, as long as one refers to the values obtained with HSE06. In addition, we have evaluated the influence of the mechanical strain on the electron mobilities and the possible causes between the existent disagreement between experiments [19, 38] and simulations [27−29] for this electronic property. We then employ deformation potential theory to calculate the electron relaxation times that are then evaluated as a function of uniaxial and biaxial strains. Furthermore, our calculations predict small changes in the Seebeck coefficient, which can be enhanced by 11% with a compression of 5% along the y-axis. If this compression is stronger, the thermopower exhibits a metallic behaviour. On the other hand, the electrical conductivity experiences higher variations, nearly doubling its x-component from the undeformed case under the semiconductor regime of doping and mechanical deformation in the same direction. Furthermore, we have evaluated the electronic contribution to the thermal conductivity, but we have determined that even though it can be tuned with strain and doping, its values are negligible and we and therefore assume that thermal transport in TiS₃ monolayers is mainly driven by phonons. Finally, our predicted power factors can be enhanced by nearly two times in the x-axis under the same conditions by which the electrical conductivity is also improved, indicating that the latter drives the optimisation of the former.

Overall, our calculations suggest that engineering of the band gap and thermoelectric behaviour is dependent on the direction along which monolayer deformation is applied. In addition, we want to mention that our DFT results are indicative for high shrinkages as we will need to confirm that experimentally these monolayers do not buckle. Note that buckling will induce further shear strains in these layers, which are out of the scope of this study. As a future work, we plan to extend this study by evaluating the effect of mechanical strain and electron doping on the thermal conductivity.

Acknowledgments

We acknowledge the financial received from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 793726 (TELIOTES - Thermal and electronic transport in inorganic-organic thermoelectric superlattices) and the support of The Supercomputing Center of Galicia (CESGA) where the calculations have been made. We are also grateful for the financial support received from the Ministerio de Economía, Industria y Competitividad (MINECO) under grant FEDER-MAT2017-90024-P and the Severo Ochoa Centres of Excellence Program under Grant SEV-2015-0496 and by the Generalitat de Catalunya under grant no. 2017 SGR 1506. The authors also thank with Dr Andrés Castellanos-Gomez and Dr Jesús Carrete for their helpful comments. The authors declare no conflict of interest.

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