Enhanced piezoelectricity and modified dielectric screening of 2-D group-IV monochalcogenides

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We use first principles calculations to investigate the lattice properties of group-IV monochalcogenides. These include static dielectric permittivity, elastic and piezoelectric tensors. For the monolayer, it is found that the static permittivity, besides acquiring a dependence on the interlayer distance, is comparatively higher than in the 3D system. In contrast, it is found that elastic properties are little changed by the lower dimensionality. Poisson ratio relating in-plane deformations are close to zero, and the existence of a negative Poisson ratio is also predicted for the GeS compound. Finally, the monolayers shows piezoelectricity, with piezoelectric constants higher than that recently predicted to occur in other 2D-systems, as hexagonal BN and transition metal dichalcogenide monolayers.

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I. INTRODUCTION

Piezoelectric materials are used in very diverse fields of application as sensors, actuators, electric field generators, and in general in any other applications requiring a conversion between electrical and mechanical energy. Recently, the availability of piezoelectric nanowires and nanobelts inspired the design of a class of ‘nanopiezotronic’ devices which make use of both their piezoelectric and semiconducting properties. These include, for example, nano-generators, field-effect transistors, and piezoelectric diodes. Lead-free biocompatible piezoelectric materials are also sought for, as components for biomedical devices.

Piezoelectric crystals can also be found amongst 2D materials. Some of these, like BN and 2H-stacked transition metal dichalcogenides, are centrosymmetric in bulk form, but loose the inversion symmetry if the number of layers is odd. Exfoliation of W and Mo dichalcogenide monolayers thus produces 2D piezoelectric crystals with strain-induced polarisation change in plane. This has been confirmed experimentally for MoS$_2$ by direct piezoresponse measurements and electrical characterisation of MoS$_2$ devices under strain$^2$. For a few transition metal dichalcogenides, the in-plane $d_{11}$ components of the piezoelectric tensor have been predicted to be superior to quartz$^2$. Here, we concentrate on yet another family of layered materials that are piezoelectric in the monolayer form. These are the group-IV monochalcogenides SnS, GeS, SnSe and GeSe. Due to the hinge-like structure similar to that of black phosphorus (Fig. 1), group-IV monochalcogenides are very ductile along the direction perpendicular to the zigzags, stretching in that direction when out-of-plane strain is applied. Since the direction perpendicular to the zigzags is also the main polar direction, this results in a very large piezoelectric coefficient, exceeding by at least one order of magnitude that of other known 2D piezoelectrics.

In addition, group-IV monochalcogenides present nearly vanishing or negative Poisson ratio. This is also a consequence of their anisotropic structure, as was recently reported$^2$ that a monolayer of black phosphorus (phosphorene) also possesses a negative Poisson ratio.

In this article, we use first principles calculations to predict the lattice response properties of this family of materials, comprising static dielectric constant, and elastic and piezoelectric constants.

A. Computational details

We use first-principles calculations to obtain structural properties of monochalcogenides. We employ a first-principles approach based on Kohn-Sham density functional theory (KS-DFT), as implemented in the Vienna ab initio simulation package (VASP)$^{1,2}$, which was used for calculation of elastic, piezoelectric and static dielectric tensors. The core and valence electrons are treated by the projector-augmented wave (PAW) method$^{10}$. The exchange correlation energy was described by the generalized gradient approximation (GGA) using the PBE$^{11}$ functional. For all materials, van der Waals interactions are taken into account by the method proposed by Tkatchenko and Scheffler$^{12}$ (TS), which presents a charge-density dependence of the dispersion coefficients and damping function. The Kohn-Sham orbitals were expanded in a plane-wave basis with a cutoff energy of 550 eV. The Brillouin-zone (BZ) was sampled using a $\Gamma$-centered $1\times20\times20$ grid for the monolayers, following the scheme proposed by Monkhorst-Pack$^{13}$. The results for bulk were obtained with a $6\times16\times16$ grid. Structural optimization has been performed with a very stringent tolerance of 0.001 eV/Å.

For comparison, we also performed calculations with the QUANTUM ESPRESSO code$^{14}$ in that case using Troullier-Martins pseudopotentials$^{15}$. There was good agreement between the two codes whenever direct com-
comparison could be established. All results shown were obtained with VASP, with exception of the Poisson ratio calculations, which were performed with QUANTUM ESPRESSO to take advantage of the implementation of geometry optimization constraints.

The supercells are periodic in the monolayer plane and large vacuum regions (> 17 Å) are included to impose periodic boundary conditions in the perpendicular direction. Convergence tests with greater vacuum thickness were performed, and the values used are enough to avoid spurious interaction between neighboring images.

II. RESULTS

A. Structure

Bulk group-IV monochalcogenides SnS, SnSe, GeS and GeSe have an orthorhombic structure with eight atoms per unit cell, four of each species. They belong to the space group Pnma. This structure is also known as the α phase of SnS, a naturally occurring mineral\(^{16}\). The waved structure adopted by these materials is similar to that of black phosphorus, with which these compounds are isoelectronic. All atoms are three-fold coordinated and tetrahedral coordination results from the repulsion of the lone pairs. In the monolayer, the translational symmetry along the x direction is lost, and with it the inversion symmetry, and the resulting structure belongs to the Pmn2\(_1\) space group. In this work, the axes system is chosen as the layers sit on the y-z plane, with the y axis parallel to the puckering direction, as shown in Fig. 1. The layers are stacked together along the x axis to form the bulk.

The calculated lattice parameters of these materials, for both bulk and monolayer, have been discussed in previous theoretical studies\(^{17−19}\), including our previous work at the GGA level\(^4\). Aware of the importance of van der Waals (vdW) interactions in layered materials, in this work we include these effects in order to obtain even more accurate structural properties of these materials. Table I presents the optimized lattice parameters for pure GGA and including vdW by Tkatchenko-Scheffler (TS) method. Available experimental data for bulk SnS\(^20,21\) and SnSe\(^22\) are also presented.

B. Static Dielectric Tensor

The static dielectric tensor \(\epsilon\) is calculated from the force constant (\(K\)) and Born dynamical effective charges (BEC) (\(Z\)) tensors\(^{23}\)

\[
\epsilon_{ij} = \epsilon_{ij}^{\infty} + V_{0}^{-1} Z_{mi}(K^{-1})_{mn}Z_{nj}.
\]

The tensors \(K\) and \(Z\) are second derivative response functions and are calculated using density functional perturbation theory.

The electronic contribution \(\epsilon_{ij}^{\infty}\), or ion-clamped static dielectric tensor, has been given in Ref.\(^4\). Here, we will concentrate on the lattice contribution, which for static electric fields, exceeds the electronic contribution.

For orthorhombic materials, the dielectric permittivity tensor has the form

\[
\epsilon_{ij} = \begin{bmatrix}
\epsilon_1 & 0 & 0 \\
0 & \epsilon_2 & 0 \\
0 & 0 & \epsilon_3
\end{bmatrix},
\]

TABLE I. Optimized lattice parameters (in Å) for α phase of SnS, SnSe, GeS, GeSe. We present results for PBE-GGA and including vdW by Tkatchenko-Scheffler (TS) method. Experimental data for bulk SnS\(^20,21\) and SnSe\(^22\) are also presented.

| Material | Monolayer | Bulk |
|----------|------------|------|
|          | b c        | a b c|
| SnS      | PBE        | 4.07 4.24 | 11.37 4.02 4.35 |
|          | vdW-TS     | 4.08 4.25 | 11.12 4.00 4.27 |
|          | Expt.      | - -       | 11.20 3.98 4.33 |
| SnSe     | PBE        | 4.30 4.36 | 11.81 4.22 4.47 |
|          | vdW-TS     | 4.27 4.37 | 11.58 4.20 4.47 |
|          | Expt.      | - -       | 11.50 4.15 4.44 |
| GeS      | PBE        | 3.68 4.40 | 10.81 3.68 4.40 |
|          | vdW-TS     | 3.73 4.30 | 10.41 3.67 4.34 |
| GeSe     | PBE        | 3.99 4.26 | 11.31 3.91 4.45 |
|          | vdW-TS     | 4.00 4.22 | 10.93 3.90 4.39 |
where we have contracted a two-index into a one-index notation. The values calculated for bulk are given in Tab. III. While for the tin chalcogenides the calculated values are in excellent agreement with estimates obtained from comparing the LO-TO splitting of the vibrational bands with the dielectric constants obtained from reflectivity data, for the germanium chalcogenides there is some discrepancy. This can be due to many factors, including crystal quality. In particular, the dielectric response along the $x$ axis is difficult to measure, explaining the range of variation of the measured values.

For two-dimensional materials, the dielectric constant is not well defined, depending on the interlayer distance $L$ as \[\epsilon_i = \delta_i + \frac{4\pi \chi^{2D}}{L}, \] where the 2D polarizability $\chi^{2D}$ (which includes both ionic and electronic contributions) is a constant and $\alpha, \beta = 2, 3$, in accordance with our convention of the layers in the $y - z$ plane. The $1/L$ dependence on the interlayer spacing of the electronic contribution to the susceptibility in the 2D systems has been verified in previous works. In this work, we verified that the same behaviour applies to the ionic contribution. In practice, this can be calculated using the same method as bulk (Eq. I) but replacing the volume by the area. The ionic contribution to $\chi^{2D}$ for the monolayers is given in Tab. III.

For comparison, if the interlayer distance $L$ in the monolayer is taken to be the same as in bulk, the vdW-TS calculations for SnS results in static ionic contributions to the permittivity with values 61 and 23, respectively, along the $y$ direction, and 39 and 14, respectively, along the $z$ direction, showing an increase of $\sim 2.5$ times when comparing the 2D and 3D systems. For SnSe and GeSe the ionic contribution to $\epsilon$ in monolayer reaches values three to four times higher than in their respective bulk forms. In the other hand, GeS presents just slightly higher values for $\epsilon$ from bulk to monolayer. The increase in the screening for SnS, SnSe and GeSe can be explained by two factors: (i) increase in Born effective charges (BEC) and (ii) softening of polar modes due to the absence of interlayer binding. The increase in the BEC can be as high as 28% for SnS, SnSe and GeSe, while for GeS $Z$ differs by less than 3%. To have a better understanding of the contribution of lattice vibrational mode softening to the increase of the static dielectric constant, we consider the contribution of different modes to the components of the static dielectric tensor, by writing $\epsilon_{ij}$ as in Ref. 31 and 32:

\[\epsilon_{ij} = \epsilon_{ij}^{\infty} + \frac{4\pi}{V_0} \sum_m \frac{S_{m,ij}}{\omega_m^i}.\]

where $V_0$ is the volume of the cell. $S_{m,ij}$ is called the mode-oscillator strength of the $\omega_m$ mode along the $i, j (= x, y, z)$ directions of the material and it is related to the eigendisplacements $U_m(\kappa i)$ and Born effective charge tensors $Z^*_m, ij$ by:

\[S_{m,ij} = \left( \sum_{\kappa i} Z^*_m, ij U^*_{m q=0}(\kappa i) \right) \left( \sum_{\kappa' j} Z^*_m, j \epsilon_{\kappa' j} U_{mq=0}(\kappa' j) \right). \tag{5}\]

$k$ is the index for the ions in the primitive cell. The ionic contribution to $\epsilon$ is then given by the second term in the right side of Eq. I. The expression for $S_{m,\alpha\beta}$ shows that and increase in the BEC increases the contribution of the ionic part of $\epsilon$. However, the dominant contribution comes from the $\omega_m$ modes. In Tab. III we present the frequency of the modes with major contribution to the static dielectric constant for monolayer and bulk monochalco- genides, along the in-plane directions. For all materials, just one mode contributes significantly to the $yy$ component of $\epsilon$, while there are two modes which contributes almost equally to the $zz$ components in bulk SnS and monolayer and bulk SnSe and GeSe. A significant softening of the contributing modes occurs when going from 3D to 2D forms, probably due to the lack of interaction with upper and bottom layers, observed in bulk. SnSe presents the largest softening in the contributing modes, with $\omega_m^{3D}/\omega_m^{2D} = 1.9$ along the $y$ direction up to $\omega_m^{3D}/\omega_m^{2D} = 2.5$ along $z$. GeS, however, presents the smallest softening of the modes, where we have $\omega_m^{3D}/\omega_m^{2D} = 1.1$ and 1.5 for the contribution to the $yy$ and $zz$ components of $\epsilon$.

C. Elastic Constants and Poisson ratio

a. Elastic constants: The elastic constant (stiffness) tensor is defined in the linear regime by Hooke’s law:

\[\sigma_{ij} = C_{ij} \epsilon_j, \tag{6}\]

where $\sigma$ and $\epsilon$ are the stress and strain tensors, respectively, $C_{ij}$ are the elastic constants. In this equation, and the following, there is an implicit sum over repeated indexes. Numerically, the elastic constants are easily determined using the equation of state. The change in the total energy $E(V_0)$ of a system due to an external strain ($\epsilon$) is given by

\[E(V_0, \epsilon) = E(V_0) + \frac{V_0}{2} C_{ij} \epsilon_i \epsilon_j, \tag{7}\]

where $V_0$ is the volume of the unstrained material. Here, the electric field term vanishes because of the periodic boundary conditions ($d\tilde{E} = 0$). For the monolayer system, the area ($A_0$) should figure instead. However, to facilitate the comparison with 3D systems and previous calculations, we use an effective thickness $d_0$. The most obvious choice is to take $d_0$ to be the distance between the layers in bulk, as is common practice in graphene.
shows the total energy versus strain along presented in this table are obtained considering vdW interactions and do not take into account LO-TO splitting effects. The values from Eq. \( C \) torque the \( \sigma \)alent to \( \text{static dielectric tensor as defined in Eq. 4.} \) The values are nine independent nonvanishing elements \( C_{ij} \), \( C \) are observed when compared to the PBE-GGA results. The stress components \( \sigma_{21} \) and \( \sigma_{31} \) are calculated using the effective thickness \( d_0 \) to define the lateral area of the layers. We have calculated \( C_{ij} \) both in clamped-ion and relaxed-ion conditions, by fixing the atomic coordinates or allowing them to relax, respectively, for each distortion of the lattice vectors. The results for bulk and monolayer group-IV monochalcogenides are presented in Table IV for calculations with and without vdW effects. Using the definition of \( d_0 \), the elastic constants are of the same order of magnitude for monolayer and bulk. In most cases though, they are slightly higher for the bulk for both relaxed and clamped-ion coefficients, indicating that the monolayers are less stiff for in-plane deformations. The main effects of vdW interactions in bulk are observed in the elastic constant components related to the \( x \) direction of the materials (those with index 1, \( j=1,2,3 \) as well as 55 and 66). The \( C_{11} \) constants are the most affected by the vdW forces, as expected, and differences up to 50\% are observed when compared to the PBE-GGA results.

Figure 2 shows the total energy versus strain along the \( y \) and \( z \) directions for a SnSe monolayer. The quadratic dependence of energy to the applied strain and the anisotropy between the perpendicular in-plane directions of the layer is given by

\[
\Delta E(V, \varepsilon) = \frac{V_0}{2} ( C_{22} \varepsilon_2^2 + C_{33} \varepsilon_3^2 ) + V_0 C_{23} \varepsilon_2 \varepsilon_3
\]

\[ (9) \]

where \( \Delta E(V, \varepsilon) = E(V, \varepsilon) - E(V_0, \varepsilon = 0) \) and \( C_{32} = C_{23} \). The results for SnS, GeS and GeSe are very similar, differing only in the ratio between elastic constants. It is also noteworthy that \( C_{22} \) (the elastic constant for the zig-zag direction) is much lower for group-IV monochalcogenides than for black-phosphorus \( (18.6 \times 10^{10} \text{ N/m}^2) \), in contrast with other elastic constant elements which are little changed\[22\].

|       | Monolayer | Bulk  | Expt.  |
|-------|-----------|-------|--------|
|       | \( \chi_{2D}^2 \) | \( \chi_{3D}^3 \) | \( \varepsilon_2 \) | \( \varepsilon_3 \) | \( \varepsilon_2 \) | \( \varepsilon_3 \) |        |
| SnS   | PBE       | 35.8  | 21.5  | 78.0  | 50.1  | 14.9  | 31.7  | 18.3  | 16±6 | 32±7 | 18±6 | Ref. (a) |
|       | vdW-TS    | 27.3  | 17.2  | 61.7  | 39.0  | 27.5  | 22.6  | 13.8  | 18.4 | 34.5 | 20.7 | Ref. (d) |
| SnSe  | PBE       | 73.6  | 26.4  | 156.5 | 56.0  | 21.3  | 39.1  | 12.1  | 26±7 | 45±8 | 32±7 | Ref. (a) |
|       | vdW-TS    | 76.4  | 37.7  | 165.7 | 82.0  | 25.7  | 32.0  | 15.9  | 17.5 | 32.5 | 18.5 | Ref. (d) |
| GeS   | PBE       | 5.3   | 3.1   | 12.4  | 7.4   | 6.8   | 11.8  | 7.6   | 20.0 | 17.5 | 10.3 | Ref. (b) |
|       | vdW-TS    | 7.1   | 3.6   | 16.1  | 8.6   | 16.7  | 12.9  | 8.5   | 10.6 | 14.0 | 10.6 | Ref. (d) |
| GeSe  | PBE       | 24.0  | 7.7   | 53.3  | 17.1  | 6.9   | 12.3  | 5.7   | 11.3 | 8.5  | 3.2  | Ref. (c) |
|       | vdW-TS    | 28.6  | 10.1  | 65.7  | 24.3  | 14.3  | 15.7  | 7.7   | 9.7  | 12.5 | 9.6  | Ref. (d) |

TABLE II. Ionic contributions to the 2D polarizability \( \chi_{2D}^2 \) and \( \chi_{3D}^3 \), macroscopic static dielectric tensor components \( \varepsilon_2 \) and \( \varepsilon_3 \) for \( y \) and \( z \) directions of the monolayers, and \( \varepsilon_1 \), \( \varepsilon_2 \) and \( \varepsilon_3 \) for \( x \), \( y \) and \( z \) directions of bulk. Results for PBE-GGA and taking into account van der Walls interactions are included. Our calculations for the bulk can be compared to experimental values from the previous works: (a) Ref. [27], (b) Ref. [28], (c) Ref. [24], (d) Ref. [30].

|       | \( \chi_{2D}^2 \) | \( \chi_{3D}^3 \) | \( \varepsilon_2 \) | \( \varepsilon_3 \) |
|-------|-----------------|-----------------|-----------------|-----------------|
| SnS   | 104             | 158             | 62              | 102             |
|       | 56              | 78              | 132             | 86              |
| GeS   | 180             | 207             | 77              | 116             |
| GeSe  | 94              | 145             | 137             | 76              |

TABLE III. Modes (cm\(^{-1}\)) at \( q=0 \) with largest contribution to the static dielectric tensor as defined in Eq. \( C \). The values presented in this table are obtained considering vdW interactions and do not take into account LO-TO splitting effects.
|          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|          |          |          |          |          |          |          |          |          |
| SnS      | PBE      | C-i      | 9.59     | 8.81     | -        | -        | 5.68     | 5.50     | -        |
|          |          | R-i      | 7.59     | 3.67     | -        | -        | 3.19     | 3.44     | -        |
| vdW-TS   | C-i      | 9.65     | 9.29     | -        | -        | 5.70     | 5.25     | -        |          |
|          | R-i      | 7.72     | 3.85     | -        | -        | 2.68     | 2.81     | -        |          |
| SnSe     | PBE      | C-i      | 7.90     | 7.26     | -        | -        | 4.54     | 4.81     | -        |
|          |          | R-i      | 6.92     | 3.32     | -        | -        | 2.77     | 2.32     | -        |
| vdW-TS   | C-i      | 5.68     | 5.34     | -        | -        | 2.96     | 3.28     | -        |          |
|          | R-i      | 5.04     | 2.89     | -        | -        | 1.83     | 1.80     | -        |          |
| GeS      | PBE      | C-i      | 9.51     | 8.92     | -        | -        | 6.08     | 5.41     | -        |
|          |          | R-i      | 8.48     | 2.82     | -        | -        | 4.00     | 3.44     | -        |
| vdW-TS   | C-i      | 9.41     | 9.25     | -        | -        | 6.17     | 5.52     | -        |          |
|          | R-i      | 8.26     | 3.02     | -        | -        | 3.93     | 3.49     | -        |          |
| GeSe     | PBE      | C-i      | 9.78     | 8.46     | -        | -        | 5.34     | 6.00     | -        |
|          |          | R-i      | 8.87     | 3.59     | -        | -        | 3.44     | 4.10     | -        |
| vdW-TS   | C-i      | 10.19    | 9.37     | -        | -        | 5.42     | 6.04     | -        |          |
|          | R-i      | 9.19     | 4.41     | -        | -        | 3.40     | 3.81     | -        |          |
|          |          |          |          |          |          |          |          |          |          |
| SnS      | PBE      | C-i      | 12.12    | 9.53     | 8.31     | 2.45     | 2.56     | 5.51     | 5.29     | 2.56     | 2.43     |
|          |          | R-i      | 4.85     | 7.99     | 3.42     | 1.31     | 1.80     | 3.16     | 3.47     | 1.95     | 2.00     |
| vdW-TS   | C-i      | 12.15    | 9.68     | 8.79     | 2.64     | 3.07     | 5.59     | 5.37     | 3.15     | 2.74     |
|          | R-i      | 6.59     | 7.70     | 3.84     | 1.86     | 2.66     | 2.80     | 3.24     | 2.87     | 2.50     |
| SnSe     | PBE      | C-i      | 10.99    | 8.39     | 7.61     | 1.76     | 2.03     | 5.09     | 5.20     | 1.93     | 1.77     |
|          |          | R-i      | 4.35     | 6.93     | 3.48     | 0.74     | 1.23     | 2.99     | 3.32     | 1.37     | 1.07     |
| vdW-TS   | C-i      | 11.72    | 9.30     | 8.29     | 1.87     | 2.44     | 5.23     | 5.40     | 2.44     | 1.97     |
|          | R-i      | 6.09     | 7.49     | 4.27     | 0.99     | 2.12     | 2.86     | 3.29     | 2.09     | 1.24     |
| GeS      | PBE      | C-i      | 12.40    | 10.47    | 8.83     | 2.79     | 2.67     | 6.00     | 5.75     | 3.18     | 2.93     |
|          |          | R-i      | 3.78-96  | 3.02     | 0.97     | 0.72     | 3.31     | 3.65     | 1.69     | 1.73     |
| vdW-TS   | C-i      | 12.84    | 10.93    | 9.48     | 2.72     | 2.91     | 5.94     | 6.13     | 3.61     | 3.35     |
|          | R-i      | 5.31     | 8.94     | 3.41     | 1.11     | 1.44     | 2.81     | 3.76     | 2.90     | 2.51     |
| GeSe     | PBE      | C-i      | 12.14    | 10.47    | 8.59     | 1.98     | 2.05     | 6.45     | 6.52     | 2.43     | 2.42     |
|          |          | R-i      | 3.20     | 8.72     | 3.75     | 0.29     | 0.82     | 3.91     | 3.93     | 1.15     | 0.96     |
| vdW-TS   | C-i      | 12.53    | 10.02    | 8.63     | 1.73     | 2.22     | 5.64     | 5.67     | 2.92     | 2.44     |
|          | R-i      | 4.16     | 8.06     | 3.85     | 0.26     | 1.38     | 3.05     | 3.50     | 2.08     | 0.88     |

**TABLE IV.** Calculated clamped-ion (C-i) and relaxed-ion (R-i) components of the elastic tensor $C_{ij}$ for bulk and monolayer. The elastic constants for the monolayer assume an effective layer thickness $d_0 = a/2$ to allow direct comparison with bulk. All values are given in $10^{10}$ N/m$^2$.

**b. Young modulus and Poisson ratio** The Young modulus and Poisson ratio are derived mechanical properties that can give direct information on how a system
FIG. 2. (Color online) The three-dimensional surface plot of total energy (in eV) versus uniaxial strain along \(y\) and \(z\) directions of a SnSe monolayer. Projections on the \(\varepsilon_2 = 0\), \(\varepsilon_3 = 0\) and \(\varepsilon_2 = \varepsilon_3\) planes show the quadratic dependence of the energy of the system to the applied strain, from where the elastic constants can also be calculated.

behaves under uniaxial stress i.e. when \(\sigma_i \neq 0\) and \(\sigma_j = 0\) for all \(j \neq i\). Here, we calculate these moduli to highlight the role of anisotropy on the mechanical response of group-IV monochalcogenides.

We define the Young modulus as

\[
Y_i = \frac{\partial \sigma_i}{\partial \varepsilon_i}. \tag{10}
\]

Since the materials in consideration here are orthorhombic, and the choice of principal direction is arbitrary, \(i\) can be any of the principal directions of the crystal. Similarly, we define multiple Poisson ratios \(\nu_{ij}\), corresponding to the negative ratio of the strain response at a \(i\) direction to the strain applied along a transversal \(j\) direction:

\[
\nu_{ij} = -\frac{\partial \varepsilon_i}{\partial \varepsilon_j}. \tag{11}
\]

for \(i \neq j\).

In order to calculate Poisson ratio and Young modulus of monolayer monochalcogenides, according to Eq. 10 and 11 strains from -6% to 6% were applied in the in-plane and out-of-plane directions of the layers. As the elastic constants of single-layers are not considerable modified by introduction of vdW effects (Tab. IV), we include only the results for calculations performed with the PBE-GGA functional.

Most of the materials have a positive Poisson ratio, which means that when a compressive strain is applied along one direction, the others expand. Conversely, if the material is stretched along one direction, it will compress along the perpendicular directions. This due to the materials’ tendency to conserve their volume. However, since group-IV monochalcogenides are very anisotropic, the values for the Poisson ratio vary greatly for different combination of directions \(i, j\).

FIG. 3. (Color online) Response of monolayer monochalcogenides under uniaxial stress along (a) \(\hat{x}\), (b) \(\hat{y}\) and (c) \(\hat{z}\) directions of the layers. Strain components for the directions perpendicular to the external force are plotted as a function of the strain component along the direction of the external force.

This is apparent in Figure 3 which illustrates the response of the monolayers under uniaxial stress. Firstly, it is clear that the linear region where the Young modulus
and Poisson ratio given by Eqs. 10 and 11 are constant is quite narrow, in some cases less than 2% strain.

In particular, if $i = 1$ or $j = 1$, the Poisson ratio is very close to zero, indicating that distortion along the in-plane directions and the direction perpendicular to the plane are practically decoupled. A very interesting exception is found in GeS: this is the only material in group-IV monochalcogenides that shows a negative linear Poisson ratio in the out of plane $x$ direction. The calculated value of $\nu_{12} = -0.137$ for GeS is about five times larger than the value calculated for phosphorene in Ref. 33, which report $\nu_{12} = -0.027$ for this material.

In contrast, the ratios $\nu_{23}$ and $\nu_{32}$ for in-plane uniaxial stress are in the ranges 0.3-0.5 and 0.7-1.6. The Poisson ratio is intrinsically linked with the anisotropy. Plotting the Poisson ratio against the anisotropy of the monolayer crystals ($b/c$), it becomes evident why GeS departs from the other materials (Fig. 4). Amongst all four materials, GeS has the smallest $b/c$ ratio, and is located far away from GeSe, SnS and SnSe. This behavior is more evident in the plot of $\nu_{21}$ and $\nu_{31}$ (left panel in Fig. 4), obtained by applying uniaxial strain in the out-of plane $x$ direction.

![FIG. 4.](Color online) Poisson ratio versus the degree of anisotropy, given by the ratio between in-plane lattice constants $b$ and $c$, for monolayer crystals. The values for phosphorene (P) taken from Ref. 33 are also included.

### D. Piezoelectric tensor

Non-centrosymmetric crystals display a change of polarisation $P_i$ under mechanical stress,

$$ P_i = d_{ij} \sigma_j. \tag{12} $$

Equation 12 shows that application of a stress $\sigma_j$ along the $j$-direction of a piezoelectric material induces a change of polarisation of magnitude $P_i$ in its $i$-direction. $P_i$ is related to $\sigma_j$ by a piezoelectric tensor with components $d_{ij}$. This is known as the direct piezoelectric effect. In the same way, the converse piezoelectric effect occurs when a strain $\epsilon$ is induced in a material under an external electric field. The converse effect can be written:

$$ \epsilon_j = d_{ij} E_i, \tag{13} $$

where $E_i$ is the component of the applied electric field in the $i$ direction. The piezoelectric coefficients $d_{ij}$ in Eqs. 12 and 13 are the same, and the proof of such equality is based on thermodynamical arguments. In addition, other piezoelectric coefficients can be defined, for example $\epsilon_{ij}$, that directly relates $E$ and $\sigma$ by:

$$ \epsilon_{ij} = -\frac{\partial \sigma_j}{\partial E_i} = \frac{\partial P_i}{\partial \sigma_j}. \tag{14} $$

For a constant electric field, the piezoelectric tensors $d_{ij}$ and $\epsilon_{ij}$ are related via the elastic tensor $C_{ij}$ as:

$$ \epsilon_{ij} = \sum_{k=1}^{6} d_{ik} C_{kj}. \tag{15} $$

However, in the case of a 2D system it is more meaningful to define a 2D polarisation per unit area, $P_{i}^{2D}$. Thus, we redefine $\epsilon_{ij}^{2D}$

$$ \epsilon_{ij}^{2D} = \frac{\partial P_i^{2D}}{\partial \sigma_j}. \tag{16} $$

The number of non-zero coefficients $\epsilon_{ij}^{2D}$ are completely defined by the symmetry of the system. The layered group-IV monochalcogenides are centrosymmetric in bulk (and even-numbered layers) and therefore are not piezoelectric. However, single layers belong to the polar space group $Pmn2_1$. In this space group, there are five non-zero piezoelectric constants: $\epsilon_{15}^{2D}$, $\epsilon_{24}^{2D}$, $\epsilon_{31}^{2D}$, $\epsilon_{32}^{2D}$, and $\epsilon_{33}^{2D}$, where we use the Voigt’s notation with 1, 2 and 3 corresponding to $x$, $y$ and $z$ directions, respectively. As for the calculation of the elastic constants, we consider only in-plane strain components for computation of the $\epsilon_{ij}^{2D}$ constants, which limit our discussion to $\epsilon_{32}^{2D}$, $\epsilon_{33}^{2D}$ and $\epsilon_{33}^{2D}$. The calculated values are presented in Table VII.

$$ \epsilon_{ij}^{2D} = \begin{bmatrix} 0 & 0 & 0 & 0 & \epsilon_{15}^{2D} & 0 \\ 0 & 0 & 0 & \epsilon_{24}^{2D} & 0 & 0 \\ \epsilon_{31}^{2D} & \epsilon_{32}^{2D} & \epsilon_{33}^{2D} & 0 & 0 & 0 \end{bmatrix} \tag{17} $$

For the best of our knowledge, there is still no experimental data on the piezoelectric properties of odd-number layers group-IV monochalcogenides. However, we take for comparison single layer TMDCs and h-BN, of which piezoelectric coefficients have been theoretically calculated, and object of recent experimental measurements.

Similar to h-BN and TMDC, the piezoelectric elements $\epsilon_{32}$, $\epsilon_{33}$ and $\epsilon_{24}$ of group IV monochalcogenides are enhanced as we move downward in the periodic table. The value of $\epsilon_{33}$ (for both relaxed and clamped-ion case) seems also to be directly related to the degree of anisotropy of the materials as given by the ratio between in-plane lattice parameters $b/c$.

For SnS and SnSe, $\epsilon_{33}$ is one order of magnitude higher than for other known 2D piezoelectric materials. This
### TABLE V. Poisson ratio and Young modulus (in GPa) for the mono layers monochalcogenides. The data for monolayer phosphorene from Refs. 36 and 37 are included for comparison. \( b/c \) is the ratio between in-plane lattice parameters.

|        | \( \varepsilon_1 \) | \( \varepsilon_2 \) | \( \varepsilon_3 \) | \( \nu_{12} \) | \( \nu_{21} \) | \( \nu_{13} \) | \( \nu_{23} \) | \( \nu_{32} \) | \( \nu_{31} \) | \( b/c \) | \( Y_1 \) | \( Y_2 \) | \( Y_3 \) |
|--------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------|-----------|-----------|
| SnS    | 0.097 | 0.277 | 0.025 | 0.861 | 0.067 | 0.419 | 0.97 | 32.4 | 15.1 | 8.7 |            |           |           |           |
| SnSe   | 0.120 | 0.153 | 0.046 | 0.733 | 0.065 | 0.474 | 0.99 | 30.4 | 16.2 | 11.3 |            |           |           |           |
| GeS    | -0.214 | 0.940 | -0.137 | 1.512 | 0.126 | 0.451 | 0.84 | 26.8 | 7.8 | 2.2 |            |           |           |           |
| GeSe   | 0.128 | 0.181 | 0.051 | 0.919 | 0.068 | 0.389 | 0.94 | 30.2 | 15.9 | 7.9 |            |           |           |           |
| P      | - | - | -0.027 | 0.930 | 0.046 | 0.400 | 0.88 | 44.0 | 166.0 | - |            |           |           |           |

### TABLE VI. Nonzero ion-clamped and relaxed-ion piezoelectric coefficients \( (10^{-10} \text{ C/m}) \). The tensor components are calculated according to \( e_{ij} = -\frac{\partial \sigma_i}{\partial E_j} \), where the values for the other 2D materials h-BN, MoS\(_2\) and MoTe\(_2\) are taken from Ref. 2 and included for comparison.

|        | \( e_{2D}^{\text{clamped-ion}} \) | \( e_{2D}^{\text{relaxed-ion}} \) |
|--------|----------------|----------------|
| SnS    | -4.73 | -4.39 |
| PBE    | 0.29 | 15.70 |
| vdW-TS | 2.27 | 15.54 |
| SnSe   | -4.89 | -4.67 |
| PBE    | 0.53 | 28.17 |
| vdW-TS | 4.42 | 15.82 |
| GeS    | -6.69 | -7.11 |
| PBE    | -1.25 | 7.28 |
| vdW-TS | -4.97 | 0.37 |
| GeSe   | -7.16 | -7.37 |
| PBE    | -0.26 | 13.26 |
| vdW-TS | -3.00 | 8.25 |
| h-BN   | -3.71 | -3.13 |
| MoS\(_2\) | -3.64 | -3.64 |
| MoTe\(_2\) | -5.43 | -5.43 |

### III. CONCLUSIONS

The group-VI monochalcogenides SnS, SnSe, GeS and GeSe have an orthorhombic structure similar to phosphorene. This structure results in in-plane anisotropy of the static permittivity, elastic constants and piezoelectric coefficients. In this study, we investigated those properties both for monolayer and bulk systems by including van der Waals effects, highlighting the differences resulting from the lower dimensionality. The electric susceptibility in the 2D systems is known to have an \( 1/L \) dependence on the interlayer spacing\(^{24} \). This has been verified for electronic contribution to the low-frequency susceptibility\(^{25} \). In this work, we verified numerically that the same applies to the ionic contribution. However, if we extrapolate the ionic contribution to the 2D permittivity to \( L = a/2 \), where \( a/2 \) is the inter-layer spacing in bulk, we notice a great enhancement for SnS, SnSe and GeSe. This is mainly due to the larger softening of the modes in the 2D systems, but also partially accounted for the effective Born charges in the 2D material.

In contrast, elastic constants remain nearly unchanged in monolayer, compared to bulk, if an equivalent volume of material is considered. The most remarkable amongst the elastic properties of group-VI monochalcogenides is the Poisson ratio. The Poisson ratio \( \nu_{12} \) and \( \nu_{21} \), relating strain and uniaxial strain for the direction perpendicular...
lar to the plane and the armchair in-plane direction are very small or even negative for GeS, the most anisotropic amongst the four materials.

Finally, while in bulk the presence of inversion symmetry forbids piezoelectricity, in monolayer there is one polar direction coinciding with the $C_2$ axis ($z$). Piezoelectric constants are higher than that recently predicted to occur in other 2D-systems, as hexagonal BN and transition metal dichalcogenide crystals.