Phosphorene analogues: isoelectronic two-dimensional group-IV monochalcogenides with orthorhombic structure

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The group-IV monochalcogenides SnS, GeS, SnSe and GeSe form a family within the wider group of semiconductor ‘phosphorene analogues’. Here, we used first principles calculations to investigate systematically their structural, electronic and optical properties, analysing the changes associated with the reduction of dimensionality, from bulk to monolayer or bilayer form. We show that all those binary phosphorene analogues are semiconducting, with bandgap energies covering part of the infra-red and visible range, and in most cases higher than phosphorene. Further, they usually have multiple valleys in the valence and conduction band, with spin-orbit splitting of the order of 19-86 meV.

I. INTRODUCTION

Two-dimensional (2D) materials have been extensively studied ever since a monolayer graphene was isolated by mechanical exfoliation.1 Thereafter, the interest was promptly extended to other 2D materials, such as hexagonal boron nitride (h-BN), layered metal dichalcogenides (LMDCs) and phosphorene, to name a few.2–4 In special, phosphorene, a monolayer of black phosphorus, adopts an orthorhombic structure different from graphene and transition metal dichalcogenides.5,6 This anisotropic structure is in the origin of some of phosphorene’s interesting properties, such as superior flexibility under tensile strain,7 and giant thermoelectric coefficient.8

However, the waved structure of phosphorene is shared by yet another class of 2D materials that has so far eluded attention. In the bulk form, group-IV monochalcogenides GeS, GeSe, SnS and SnSe all assume structures that can be considered derivatives of the orthorhombic black phosphorus, belonging to the space group Pnma-D16h (lower than black phosphorus, which has only one element and therefore belongs to Bmab-D18h). This is the α-phase of SnS, also known as Herzenbergite, a naturally occurring but rare mineral.9

Currently the most important prospective application of α-SnS is as absorber material for film photovoltaic (PV) cells. Although other chalcogenide materials as CdTe and CuInGaSe2 also show high PV efficiencies11–13, many factors make their usage difficult such as the high cost and toxicity of Cd13,14. In contrast, SnS is made of abundant and nontoxic elements, and its optical band gap of ~1.3 eV13,16 is right in the range of the optimal values for solar cells (1.1 to 1.5 eV). Moreover, according to a recent study, solar conversion efficiencies achieved so far for SnS can be well beyond the potential limit for the material due to the poor choice of band alignment in the devices.17 In addition, group-IV monochalcogenides may show to be superior to other 2D semiconductors in properties where anisotropy plays an important role, as patent in the record thermoelectric coefficient recently reported for SnSe (ZT=2.6 at 923 K).18

Besides, these binary ‘phosphorene analogues’ are expected to reveal distinct intrinsic properties in monolayer form, as some of the lattice symmetry operations, including inversion, are only present in bulk and in even-numbered layer systems. In this sense they are different from phosphorene,19 where inversion symmetry prevents spin-orbit splitting. In contrast, as shown in the present article, group-IV monochalcogenide monolayers show a large intrinsic spin-orbit splitting at valence and conduction band valleys. However, even though a few theoretical and experimental works have reported on the electronic and optical properties of monolayer or few layer SnS,13,20 monolayer properties remain poorly explored.

In this work, we use first-principles calculations to investigate electronic, structural and optical properties of the four aforementioned group-IV monochalcogenides MX, with M=(Sn, Ge) and X=(S, Se), in the phosphorene-like α-phase. We compare the properties of monolayer and bilayer with those of bulk for each of these materials, highlighting the differences in the electronic and optical properties.

II. METHODS

We use first-principles calculations based on density-functional theory to obtain the electronic, structural and optical properties of monochalcogenides. We employ a first-principles approach based on Kohn-Sham density functional theory (KS-DFT)21, as implemented in the QUANTUM ESPRESSO code.22. The exchange correlation energy was described by the generalized gradient approximation (GGA) using the PBE23 functional. In-
interactions between valence electrons and ionic cores are described by Troullier-Martins pseudopotentials [24]. The Kohn-Sham orbitals were expanded in a plane-wave basis with a cutoff energy of 70 Ry, and for the charge density, a cutoff of 280 Ry was used. The Brillouin-zone (BZ) was sampled using a Γ-centered 1×10×10 grid following the scheme proposed by Monkhorst-Pack [25]. For the optical properties (dielectric constant and conductivity), a finer 1×40×40 grid is employed. The calculation of the spin-orbit splitting was performed using noncollinear calculations with fully relativistic pseudopotentials.

In addition, a hybrid functional approximation for the exchange-correlation term (HSE06) [29] is employed in order to give reliable results for the gap energies, which are well known to be underestimated when employing semilocal GGA approximations. For the hybrid functional bandstructure calculations, we used the Vienna ab initio simulation package (VASP) [26, 27] with the projector-augmented wave potentials [28]. An energy cutoff of 40 Ry was used for the plane-wave basis set and integrations over BZ were performed using samples of 1×8×8 k-points for monolayers and bilayers and 4×8×8 k-points for bulk structures.

For monolayer and bilayer models, we used periodic boundary conditions along the three dimensions, with vacuum regions of 8 and 9 Å, respectively, between adjacent images in direction perpendicular to the layers. Convergence tests with greater vacuum thickness, and the values used are enough to avoid spurious interaction between neighboring images.

The optical conductivity was calculated directly from the joint density of states i.e. taking into account only direct excitations. The real part of the dielectric function is then calculated using the Kramers-Kronig relationship.

III. RESULTS

A. Crystal Structure

The bulk α phase has an orthorhombic structure with eight atoms per primitive unit cell, four of each species. The primitive unit cell contains two puckered layers, stacked as shown in Fig. 1b. The bi-layer is obtained just by increasing the lattice supercell vector perpendicular to the plane of the layers. The monolayer has four atoms per unit cell, as in Fig. 1a. Each atomic species is covalently bonded to three neighbors of the other atomic species (Fig. 1), forming zig-zag rows of alternating elements. Thus, there is in each atom a lone pair pushing its three bonds towards a tetrahedral coordination, just like in black phosphorus, resulting in its characteristic waved structure.

We adopted the axes system used by previous works [11, 12, 30], where layers are chosen to sit on the y-z plane i.e. perpendicular to the x-direction. Note that this is different from the axes system conventionally used for black phosphorus, which take c to be perpendicular to the layers. The atomic positions, in units of the unit cell vectors a, b and c, are ±(x, 1/2, z; 1/2 + x, 1/2, z). For SnS, for example, our calculated fractional atomic coordinates are x(Sn)=z(Sn)=0.12, x(S)=0.85 and z(S)=0.48. The lattice parameters and fractional atomic positions do not deviate much from those in the parent black phosphorus structure. As can be seen in Fig. 1 the most noticeable difference is that the height of the atoms (along a) is no longer constant, rather cation and anion have different heights alternating along z. The lattice is also more compact along z, but less compact along the y direction, to decrease the repulsion between the atoms of the same type aligned up along the ripples (Table I). Full details of the structure of the other compounds, including the calculated x(M,X) and z(M,X), can be found in the Supplemental Material (SM).

The calculated lattice parameters are in good agreement with experimental data for bulk SnS [31] (a=11.20 Å, b=3.98 Å and c=4.33 Å) and bulk SnSe (a=11.50 Å, b=4.15 Å, and c=4.44 Å). Our results are also in agreement with previous theoretical studies of SnS [13, 14, 30]. It is interesting to note that the lattice parameters show little variation amongst the four compounds, differing less than 7%. This is due to the similar electronegativity of Se and S, and of Ge and Sn, and consequently to the similar bond strengths. Thus, the lattice parameter trend is mostly dominated by the ionic radius of the constituents, the most compact structure being that of GeS. The lattice parameters of the sulphides remain nearly unchanged for different number of layers, while those of the selenides show variations of ~ ± 2%.

![FIG. 1. (Color online) Structure of group-IV monochalcogenides with phosphorene-like structure. We show the unit-cells for (a) monolayer and (b) bilayer, which are repeated along the \( \hat{x} \) direction. The respective BZ is shown in (c).](image-url)
FIG. 2. (Color online) Projection of the structure in the $\hat{y}$-$\hat{z}$ plane. The lattice vectors $\mathbf{b}$ and $\mathbf{c}$ are also shown.

Table I. Optimized lattice vectors (Å) for $\alpha$ phase of SnS, SnSe, GeS, GeSe along with those of phosphorene (P).

|       | Monolayer | Bilayer | Bulk  |
|-------|-----------|---------|-------|
|       | $\mathbf{b}$ | $\mathbf{c}$ | $\mathbf{a}$ | $\mathbf{b}$ | $\mathbf{c}$ | $\mathbf{a}$ | $\mathbf{b}$ | $\mathbf{c}$ |
| SnS   | 4.07      | 4.24    | 4.05  | 4.28  | 11.37 | 4.02  | 4.35  |
| SnSe  | 4.30      | 4.36    | 4.25  | 4.42  | 11.81 | 4.22  | 4.47  |
| GeS   | 3.68      | 4.40    | 3.67  | 4.42  | 10.81 | 3.68  | 4.40  |
| GeSe  | 3.99      | 4.26    | 3.97  | 4.31  | 11.31 | 3.91  | 4.45  |
| P     | 3.30      | 4.60    | 3.31  | 4.57  | 11.69 | 3.51  | 4.57  |

TABLE II. (Color online) ($\Delta k_y$; $\Delta k_z$): Positions of the VBM and CBM along the $\Gamma$-$Y$ and $\Gamma$-$Z$ lines in the BZ. The values are given in units of $2\pi/|\mathbf{b}|$ and $2\pi/|\mathbf{c}|$ for $\hat{k}_y$ and $\hat{k}_z$ directions, respectively.

|       | Monolayer | Bilayer | Bulk  |
|-------|-----------|---------|-------|
|       | CBM       | VBM     |       |
| SnS   | (0.74; 0.00) | (0.70; 0.00) |       |
| SnSe  | (0.20; 0.00) | (0.00; 0.30) |       |
| GeS   | (0.76; 0.00) | (0.00; 0.00) |       |
| GeSe  | (0.00; 0.20) | (0.00; 0.80) |       |

Most of the group-IV monochalcogenide phosphorene analogues have indirect gap, except for monolayer SnSe, bulk GeS and monolayer and bilayer GeSe, as shown by our calculated bandstructures in Fig. 3. This is different from black phosphorus and phosphorene, which has a well defined direct or nearly-direct gap.

In the following we examine in detail the bandstructure of each one of the compounds. The energy gaps given were obtained with the HSE functional, unless otherwise stated, and without considering spin-orbit coupling. Last, we will consider the spin-orbit splitting.

a. SnS has indirect gap independently of the number of layers. The indirect bandgaps calculated with HSE are $E_g = 1.96, 1.60$ and $1.24$ eV for monolayer, bilayer and bulk SnS, respectively. The results for bulk agree very well with the experimental measured gap energies compiled in Ref. [15], which presents bandgap energies extrapolated to zero temperature around 1.2-1.3 eV, agreeing very well with our calculated values. However, previous theoretical studies using the GW method [33, 34], obtained $E_g = 2.57, 1.57$ and 1.07-1.26 eV for monolayer, bilayer and bulk SnS, respectively [13, 15]. Another previous study [35] found a bandgap of 1.11 eV for bulk using HSE06, but different from our study used the experimental lattice parameters as input. The agreement is very good except for monolayer, and this difference may be due to several factors. One of them is the presence of shallow core $d$ bands in SnS, as discussed in Ref. [17].

We now turn to the details of the bandstructure. In all cases (monolayer, bilayer and bulk), VBM and CBM are located along the Z-$\Gamma$ and $\Gamma$-$Y$ lines. In the monolayer, there are other competing local CBM and VBM,
FIG. 3. (Color online) Electronic band structures for monolayer, bilayer and bulk calculated using the HSE hybrid functional. The VBM and CBM are highlighted by green and red full circles, respectively. Dashed black arrows indicate possible direct transitions ($T_1$ and $T_2$) to points very close in energy to the CBM and VBM.

very close in energy to the band edges. By considering this, in addition to the indirect band gap observed for the monolayer, two direct gaps higher in energy by 75 meV (represented by transition 1, $T_1$, in Fig. 3) and 0.22 eV ($T_2$) are also identified along Z-Γ and Γ-Y lines, respectively. For the bulk, we also observe a competing point along the Γ-Y line, defining a direct gap of 1.40 eV. The situation is similar for the other compounds studied.

b. SnSe For monolayer SnSe, the direct gap of 1.44 eV is calculated along the Z-Γ line. A second maxima at 0.16 eV above VBM is obtained in the Γ-Y direction, defining an additional direct transition at 1.60 eV ($T_1$). The bilayer bandstructure shows some differences. The CBM is now in the Γ-Y direction, and the material
### TABLE III. (Color online) Gap energies ($E_g$) for monolayer, bilayer and bulk monochalcogenides and phosphorene from GGA and hybrid functional calculations. The star (*) indicates direct band gaps. All values are given in eV.

|        | Monolayer | Bilayer | Bulk |
|--------|-----------|---------|------|
|        | GGA-QE    | HSE     | GGA-QE | HSE | GGA-QE | HSE |
| SnS    | 1.40      | 1.96    | 1.14  | 1.60 | 0.83   | 0.82 |
| SnSe   | 1.01*     | 0.96*   | 1.44* | 0.79 | 0.76   | 0.55 |
| GeS    | 1.69      | 2.32    | 1.55  | 1.55 | 2.02   | 2.04 |
| GeSe   | 1.14*     | 1.54*   | 1.02* | 0.98*| 1.45*  | 0.59 |
| P      | 0.90      | -       | -     | -   | 1.30   | 0.07 |

FIG. 4. (Color online) Energy gap as a function of the lattice parameters $b$ and $c$ for monolayer chalcogenides.

is characterized by an indirect gap of 1.20 eV, with the VBM still located in the Z-$\Gamma$ direction.

For the bulk model, the CBM is also observed in the $\Gamma$-$\Psi$ direction, and an indirect gap of 1.00 eV is defined with the VBM in the Z-$\Gamma$ direction. In this case, the second point nearest in energy to the VBM, lower in energy by 0.17 eV, is located along the $\Gamma$-$\Psi$ direction, and defines a direct gap of 1.17 eV ($T_1$ in Fig. 3).

c. GeS Monolayer GeS has an indirect band gap of 2.32 eV. This is defined by the CMB and VBM along the $\Gamma$-$\Psi$ and the Z-$\Gamma$ lines. The lowest energy direct transition is at the $\Gamma$ point (represented by $T_1$ in Fig. 3).

TABLE IV. Smallest direct gaps obtained from the HSE calculations. The respective transitions are indicated by black arrows in Fig. 4.

|        | Monolayer | Bulk |
|--------|-----------|------|
|        | $T_1$ | $T_2$ | $T_1$ | $T_2$ |
| SnS    | 2.03   | 1.40 | -   | - |
| SnSe   | 1.60   | 1.17 | -   | - |
| GeS    | 2.62   | 1.83 | -   | - |
| GeSe   | -      | -   | -   | - |

This direct gap is only 0.3 eV higher in energy than the indirect gap. In bilayer GeS, the gap is also indirect and 0.12 eV lower in energy than that of monolayer. The CBM in this case is still along $\Gamma$-$\Psi$, but the VBM is at the $\Gamma$ point. A second VB maximum at the Z point is almost degenerate in energy with the VBM at $\Gamma$.

Bulk has an indirect gap of 1.81 eV. The direct gap at the $\Gamma$ point is only 20 meV higher in energy than the indirect one. Our results are in excellent agreement with the bulk GeS gap energies extrapolated to zero temperature given in Ref. [15], which range from 1.74 to 1.96 eV for different experiments.

d. GeSe For GeSe monolayer, our calculations produce a direct gap $E_g=1.54$ eV along the $Z$-$\Gamma$ line. For the bilayer structure, a direct gap of 1.45 eV is calculated in the $Z$-$\Gamma$ direction, near the $Z$ point.

Similar to mono- and bilayer GeSe, the electronic structure for the bulk also shows the VBM and CBM in the $Z$-$\Gamma$ direction. However, the calculated gap of 1.07 eV is indirect in this case, as the CMB is located closer to the $\Gamma$ point. Also in this case our calculated results are in very good agreement with experimental results, where optical measurements have indicated bulk GeSe as an indirect band gap semiconductor with $E_g=1.14$ eV [36].

1. Spin-orbit splitting

The spin-orbit coupling gives rise, in the case of monolayer, to a splitting of the bands. This is different from monolayer phosphorene, where the inversion symmetry, together with time reversal symmetry, requires that the bands for the two spins are degenerate. No spin-orbit splitting is expected in bulk and even-numbered layer group-IV monochalcogenides for the same reason.

In order to quantify the effect of spin-orbit (SO) coupling, a fully relativistic calculation based on GGA was performed for the monolayer of all compounds. Figure 6 shows the calculated electronic bands for monolayer SnSe with and without spin-orbit coupling. The results for the other materials, given in SM, are very similar. So, for sake of simplicity, we discuss only the SnSe case. The SO-coupling changes little the shape of the bands, except
the thickness is reduced to a few layers, due to the presence of band nesting [38].

The complex dielectric function $\varepsilon(\omega)$ and optical conductivity $\sigma(\omega)$ of a material are related by:

$$\varepsilon(\omega) = 1 + \frac{i}{\omega \varepsilon_0} \sigma(\omega), \quad \sigma(\omega) = -i \omega \varepsilon_0 [\varepsilon(\omega) - 1]. \quad (1)$$

where $\omega$ is the frequency of the incoming electromagnetic wave and $\varepsilon_0$ the vacuum permittivity. The above functions are completely equivalent. By comparing their real and imaginary parts, we can see that the real part of the conductivity is directly related to the imaginary part of the dielectric constant by:

$$\sigma_r(\omega) = \omega \varepsilon_0 \varepsilon_i(\omega). \quad (2)$$

These quantities give us information about the conduction in the material. In the same way, $\sigma_\alpha(\omega)$ and $\varepsilon_\alpha(\omega)$ are also equivalent, and describe polarization.

The imaginary part of the dielectric tensor $\varepsilon_{\alpha \beta}(\omega)$ can be obtained from the first-principles bandstructure using

$$\varepsilon_i(\omega)_{\alpha \beta} = \frac{4\pi^2 \varepsilon^2}{m^2 \omega^2} \sum_{i,f} \left[ \mathbf{M}_{\alpha \beta} f_i(E_{kn}) (1 - f_f(E_{kn})) \right] \times \delta(E_{f - E_i} - \hbar\omega) d^3k \quad (3)$$

with $\mathbf{M}_{\alpha \beta} = \langle f|p_\alpha|i\rangle\langle f|p_\beta|i\rangle$ representing the squared matrix elements for the $\alpha$ and $\beta$ directions of the crystal, $f(E_{kn})$ is the Fermi distribution, and subscripts $i$ and $f$ correspond to initial and final states respectively. Note that this includes only direct transitions. Since the integral over the Brillouin Zone needs a very large number of points to converge, we use the GGA functional for the calculation, but applying a rigid shift to correct the bandgap.

For two-dimensional materials, the integral in Eq. 3 is over $d^2k$. Thus, in order to compare the results for 2D and 3D systems, we used an effective layer thickness taken to be $a/2$.

From [38], the real part of $\varepsilon(\omega)$ can be obtained via the Kramers-Kronig relations:

$$\varepsilon_r(\omega)_{\alpha \beta} = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_i(\omega')_{\alpha \beta}}{\omega'^2 + \omega^2} d\omega' \quad (4)$$

1. Conductivity $\sigma(\omega)$

The optical conductivity, $\sigma_r(\omega)$ shows a general similar behavior for all materials. The main difference is the optical threshold energy, which in our calculation is given by the direct gap. The highest peak, corresponding to a band nesting region, is slightly above the absorption edge. Then $\sigma_r(\omega)$ decays, while still showing some peaks.
with approximately half intensity compared to the maximum. After this, conductivity smoothly decreases until it reaches zero. The increase of conductivity due to band nesting in two dimensions is clear when comparing monolayer to bulk for all materials $\sigma_r(\omega)$ assumes values $\sim 2$ times larger for monolayer. The calculated $\sigma_r(\omega)$ for all compounds, monolayer and bulk, are shown in Fig. 7.

a. SnS. For SnS monolayer, the $yy$ and $zz$ components of the real part of the optical conductivity are very similar. The optical conductivity edge is at $\sim 2.0$ eV (corresponding to the direct transition $T_1$), where we observe a sharp increase that reaches a maximum at 3 eV. Three more pronounced peaks are observed at 3.8 eV, 7.3 eV and 8.8 eV, which are seen to decrease as we increase the energy. At 19 eV, $\sigma_r$ drops to zero. For bulk model, an anisotropic behavior is observed for the three directions. The maximum of $\sigma_r$ for $\hat{x}$ direction occurs at 4 eV, and at 2.6 eV and 3.6 eV for $\hat{y}$ and $\hat{z}$ directions. A fast increase is observed from $\sim 1.4$ eV, the direct energy gap $T_2$. For all directions we observe a “shoulder” from $\sim 7$ eV, where the conductivity shows small variations, except for $\hat{z}$ direction, where a small peak is observed around $\omega = 8.4$ eV. After these intervals, a fast decrease is observed, and $\sigma_r$ drops to 0 at $\sim 19$ eV.

![FIG. 7. (Color online) Real part of the optical conductivity $\sigma_r(\omega)$ for monolayer (black lines) and bulk (green dashed lines) monochalcogenides. A remarkable increase of conductivity is observed for the lower dimensional systems.](image)

b. SnSe. For SnSe, the optical conductivity $yy$ and $zz$ are very similar. The monolayer shows a fast increase for small energies, reaching a peak at 2.4 eV, before dropping quickly. At 6 eV, the intensity starts to increase again, and two smaller peaks of almost the same intensity are observed at 7 eV and 8 eV. A smooth decrease takes place until the optical conductivity drops to zero, at $\sim 20$ eV. The general trend of $\sigma_r$ for bulk is similar to the monolayer: after the onset at the direct gap energy $\sim 1.17$ eV, a sharp increase takes place, and the maximum is reached at 4.0 eV, 2.6 eV and 3.7 eV, for $\hat{x}$, $\hat{y}$ and $\hat{z}$ directions, respectively. After these peaks, the conductivity has a decaying tail with minor shoulders, and is practically vanished at $\sim 19$ eV. The most remarkable difference between monolayer and bulk is the intensity, which is greater in monolayer by a factor of $\sim 2$.

c. GeS. For monolayer GeS, a different scenario is observed if compared to the other materials considered here. The real part of conductivity $\sigma_r(\omega)$, shows slight different appearance for $\hat{y}$ and $\hat{z}$ directions, reflecting the anisotropy of the bandstructure. For both directions, we observe a fast increase of $\sigma_r$ from $\sim 2.6$ eV, the direct gap energy at the $\Gamma$ point, after which a region of many peaks very close in energy (separated by $\sim 0.5$ eV) can be identified. The maxima are observed at $\sim 5$ eV for $\hat{y}$ and $\hat{z}$ directions, followed by one more peak of slight lower intensity localized at $\sim 1$ eV above in energy. After a fast decrease, a second region with peaks of high intensity of the maximum values are also observed before which a smooth decrease takes place until $\sim 24$ eV, when conductivity goes to zero.

For bulk, the optical conductivity is also anisotropic, showing some contrast between the in plane ($\hat{y}$ and $\hat{z}$) and out of plane ($\hat{x}$) directions. For the $\hat{x}$ direction, a faster increase is observed from $\sim 2$ eV to $\sim 3$ eV, when a region of $\sim 1$ eV with approximately constant intensity is observed. This is followed by a second region where the optical conductivity increases again, reaching the maximum value at 4.7 eV. For $\hat{y}$ and $\hat{z}$ directions, this intermediary region of constant intensity is not observed, and well defined peaks are localized at 5 eV for $\hat{y}$ and $\hat{z}$ directions. For all directions, a fast decrease occurs until $\sim 8.5$ eV, before a second region of peaks of high intensity, compared to the maximum values. After that, a smooth decrease is observed until $\sim 22$ eV, when $\sigma_r$ drops to zero.

d. GeSe. For GeSe, $\sigma_r$ at $\hat{y}$ and $\hat{z}$ directions also show high isotropy. The highest peak is observed at 2.60 eV, followed by a fast decrease until $\sim 8$ eV, followed by a smaller peak at 8.5 eV. After this, $\sigma_r$ has a decreasing tail until about 22 eV. Bulk also presents a fast increase of the conductivity with maxima at 4.4 eV, 3.6 eV and 3.9 eV for $\hat{x}$, $\hat{y}$ and $\hat{z}$ directions, respectively. This is followed by a region where $\sigma_r$ is approximately constant, after which a smooth decrease occurs until about $\sim 20$ eV.

A characteristic common to all compounds is the sharpest and more intense optical conductivity for monolayer, compared to bulk. This is due to band-nesting in two-dimensions. Another is the in-plane isotropy of the optical conductivity of group-IV monochalcogenides.
despite the great anisotropy of the material. A likely explanation for this is the more ionic character of the bonding, as compared to phosphorene. As the electrons are more tightly bound, the bandstructure and optical characteristics are dictated mostly by the local atomic environment and therefore are similar for both in-plane directions.

2. Dielectric function $\epsilon(\omega)$

We now consider the real part of the clamped ion dielectric function. As the imaginary part, it has a similar qualitative behaviour for all the four compounds. The main difference is the value of $\epsilon$ in the low frequency regime ($\epsilon_0$), below or near the absorption edge, which is typically smaller than for bulk. In the high frequency regime, $\epsilon(\omega)$ follows the trend defined by the free electron gas approximation

$$
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2},
$$

where $\omega_p = \sqrt{\frac{4\pi ne^2}{m}}$ is the plasma frequency of the material. The plasma frequency of the monolayer is smaller than for bulk (where it is typically $\sim 15 - 20$ eV), and $\epsilon$ is close to zero over most of the high frequency regime, approaching values below 1 in the high frequency limit.

In the following, we consider in more detail the frequency dependence of $\epsilon$ for each material.

a. SnS For SnS monolayer, the electronic part of the dielectric function assumes a value of 3.8 for both $\hat{y}$ and $\hat{z}$ directions, while for bulk it is slightly anisotropic, assuming the values 9.7, 10.8 and 10.1 for $\hat{x}$, $\hat{y}$ and $\hat{z}$ directions respectively. For monolayer, $\epsilon$ is nearly zero from about 5 eV onwards. For bulk, however, the calculated plasma frequency is around 16 eV. For very high frequencies, the limiting values $\epsilon_\infty$ are 0.91 and 0.76 for monolayer and bulk, respectively.

b. SnSe For monolayer SnSe, $\epsilon_0$ is $\sim$4.8. The calculated $\omega_p$ is 5 eV, and for very high frequencies, $\epsilon(\omega)$ approaches the $\sim$ constant value of 0.93. For bulk, we have $\epsilon_0 = 9.9$, 11.5 and 10.9 for $\hat{x}$, $\hat{y}$ and $\hat{z}$ directions. The plasma frequency is $\omega_p = 14.5$ eV, and for higher frequencies, the dielectric function approaches 0.8.

c. GeS For monolayer GeS, the static dielectric function is 3.3. The plasma frequency $\omega_p \sim 8$ eV defines the high frequency limit where $\epsilon$ approaches 0.90. For bulk, $\epsilon_0$ is $\sim$ 9 for all directions. The calculated $\omega_p$ is 20 eV.

d. GeSe For monolayer GeSe, we have $\epsilon_0 = 5$. The plasma frequency is around 7 eV, and in the limit of high $\omega$ we found $\epsilon_\infty \rightarrow 0.9$. For bulk, the static value of $\epsilon$ is 9.7 in $\hat{x}$ direction and 11 for $\hat{y}$ and $\hat{z}$ directions. The plasma frequency is $\omega_p = \sim$17 eV for all directions, and $\epsilon_\infty = 0.74$.

**IV. CONCLUSIONS**

We have performed a systematic study of the electronic and optical properties of the family of phosphorene analogues SnS, SnSe, GeS and GeSe, and explored the consequences of lower dimensionality and symmetry breaking.

One of the most interesting facets of these materials is that, from bulk down to monolayer, they cover a wide range of bandgap energies, from $\sim 1.0$ to 2.3 eV according to hybrid functional calculations. The bandgap increases as the number of layers is reduced, thus making it possible to extend the absorption edge up to the green region of the spectrum. Further, the optical conductivity per layer thickness increases in monolayers, acquiring sharp peaks due to band nesting.

In parallel, this family of materials has the advantage of showing little variation in lattice parameters. This makes alloying a very promising direction for tuning the optical and electronic character of the materials. This is illustrated in Fig. 4 which maps calculated band gaps for the monolayer models as a function of the lattice parameters $b$ and $c$.

Further, the smallest lattice mismatch between SnS and GeSe compounds, for both lattice parameters (Fig. 4), can be an indication of these materials as good candidates for formation of hybrid structures.

Phosphorene itself has a small lattice mismatch to some of these materials, with which it can be combined.
Additionally, the inversion symmetry breaking in monolayer allows for spin-orbit splitting of the conduction and valence band valleys. This effect is absent in bulk group-IV monochalcogenides and in phosphorene. The spin-orbit splitting can be as large as 86 meV in SnS. The large spin-orbit splitting is likely due to the character of the VBM and CBM.

The properties described here open the possibility of using group-IV monochalcogenides for optoelectronics and spintronics. Despite, to our knowledge, there being still no experimental reports of isolation of monolayers of the monochalcogenides considered here, few-layers of these materials are already on the focus of recent experimental works [17, 20], and it is just a matter of time until exfoliation and transfer methods are applied to these materials.

Finally, this illustrates that phosphorene is the parent structure of a whole class of orthorhombic 2D materials, whose potential is to be revealed once they are isolated in monolayer or few-layer form.

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