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First-principle study on the electronic, optical and transport properties of monolayer α and β-GeSe

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The extraordinary properties and the novel applications of black phosphorene induce the research interest on the monolayer group-IV monochalcogenides. Here using the first-principles calculations, we systematically investigate the electronic, transport and optical properties of monolayer α- and β-GeSe, revealing a direct of 1.61 eV of monolayer α-GeSe and an indirect band gap of 2.47 eV of monolayer β-GeSe. For monolayer β-GeSe, the electronic/hole transport is anisotropic with an extremely high electron mobility of $2.93 \times 10^3 \text{cm}^2/\text{V} \cdot \text{s}$ along the armchair direction, and comparable to that of black phosphorene. Furthermore, for β-GeSe, robust band gaps nearly disregarding the applied tensile strain along the armchair direction is observed. Both monolayer α- and β-GeSe exhibit anisotropic optical absorption in the visible spectrum.

I. INTRODUCTION

The atomic-monolayer materials, also called as two-dimensional (2D) materials, have received tremendous attentions since the experimental realization of graphene[1-3]. Nowadays, 2D materials have formed a large material family, involving various kinds of layered crystal structures and chemical elements, e.g. graphene[4-6], transition metal dichalcogenides (TMDs)[7-10], stanene[11, 12], penta-graphene[13, 14], and etc.

Recently, black phosphorene, a monolayer material composed of phosphorus atoms with puckered structure, attracts much attention for its extraordinary properties. Black phosphorene is a semiconductor with a direct band gap of 1.5 eV [15, 16], and it has strongly anisotropic transport property with a high hole mobility comparable to graphene [16-19], which make it a promising candidate for future electronic and optoelectronic applications. Many efforts have been devoted on the discovery of new 2D materials with “phosphorene analogues” puckered structure[20], since the successful prediction of black phosphorene. Followed by the prediction approach proposed as the “atomic transmutation” method[21], that one type of elements is changed (transmutationed) into its neighboring elements in the periodic table but the total number of valence electrons is kept unchanged, the monolayer of group-IV monochalcogenides MX (M=Ge, Sn; X=S, Se) with similar puckered structures is believed to possess similar properties with black phosphorene, and can be regarded as a family of “phosphorene analogues”[20, 22-24].

The properties of the material family MX in the bulk form have been intensely investigated and revealed to be excellent thermoelectric materials with high figure of merit[25], especially for the crystal SnSe with an extraordinarily high thermoelectric ZT value of $2.6 \pm 0.3$ at 923K[26]. Much attention has been devoted on studying electronic and optical properties[20, 22, piezoelectricity[23, 24], thermoelectric and phonon transport[25] properties of monolayer MX. Recently Rohr et al. predicted a new member of MX family, i.e. β-GeSe, which is a polymorph of GeSe[27] with a boat conformation for its Ge-Se six-membered ring. Experimental measurement and theoretical calculations reveal that monolayer β-GeSe, similar to another polymorph of GeSe, i.e. α-GeSe[28], is a semiconductor with a moderate band gap as well, which make it promising for future electronic and optoelectronic applications. Further investigations on monolayer β-GeSe and some related monolayer MX crystals are thus necessary to gain insights on this new kind of 2D materials.

In this work, we systematically investigate the electronic, transport and optical properties of monolayer α- and β-GeSe by using first-principles calculations. We demonstrate that the direct band gap of monolayer α-GeSe is smaller than the indirect band gap of β-GeSe. Both monolayers of α- and β-GeSe have exceptionally high electron mobility, which are predicted to be $4.71 \times 10^3 \text{cm}^2/\text{V} \cdot \text{s}$ and $2.93 \times 10^3 \text{cm}^2/\text{V} \cdot \text{s}$ respectively with strong anisotropy. Furthermore, we also investigate the strain-engineering and optical properties of these two ma-
II. METHOD AND COMPUTATIONAL DETAILS

The calculations are performed using the Vienna ab-initio simulation package (VASP) based on density functional theory[29]. The exchange-correlation energy is described by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. The calculation is carried out by using the projector-augmented-wave (PAW) pseudopotential method with a plane wave basis set with a kinetic energy cutoff of 600 eV. Furthermore, for Ge and Se atoms, we considered d and p semicore states respectively as valence states by choosing Ge$^d$ and Se pseudopotentials. When optimizing atomic positions, the energy convergence value between two consecutive steps is chosen as $10^{-5}$ eV and the maximum Hellmann-Feynman force acting on each atom is $10^{-3}$ eV Å$^{-1}$. For $\alpha$–GeSe monolayer, the Monkhorst-Pack scheme is used for the Brillouin zone integration with k-point meshes of $17\times15\times1$ and $25\times21\times1$ for geometry optimization and self-consistent electronic structure calculations, respectively. And for $\beta$ phase, we use $17\times11\times1$ and $25\times15\times1$ Monkhorst-Pack k meshes for the structure relaxation and electronic structure calculations, respectively. To verify the results of the PBE calculations, the electronic structures of $\alpha$– and $\beta$–GeSe are calculated using the much more computationally expensive hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional[30, 31]. Generally, HSE06 improves the precision of band gap by reducing the localization and delocalization errors of PBE and HF functionals. Hereby, the screening parameter $u$ is set to 0.2 Å$^{-1}$. The complex dielectric functions $\epsilon(\omega)$ of monolayer $\alpha$– and $\beta$–GeSe are calculated by using HSE06 hybrid functional on a grid of $11\times11\times1$. The tetrahedron method with Bloch corrections are used as the smearing scheme. The effect of the van der Waals (vdW) interactions between adjacent layers was considered by using the empirical correction scheme of the Grimme’s DFT-D2 (PBE-D2) method[32, 33].

The properties of monolayer $\alpha$– and $\beta$–GeSe are obtained based on the results of complex dielectric function, i.e., $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part of dielectric tensor $\epsilon_2(\omega)$ is determined by a summation over empty band states as follows [34],

$$\epsilon_2(\omega) = \frac{2\pi e^2}{\Omega \epsilon_0} \sum_{k,v,c} \frac{\left| \langle \Psi_k^c | u \cdot r | \Psi_k^v \rangle \right|^2}{\epsilon_k^c - \epsilon_k^v - \hbar \omega}, \tag{1}$$

where $\epsilon_0$ is the vacuum dielectric constant, $\Omega$ is the crystal volume, $v$ and $c$ represent the valence and conduction bands respectively, $\hbar \omega$ is the energy of the incident photon, $u \cdot r$ is the vector defining the polarization of the incident electric field, $u \cdot r$ is the momentum operator, $\Psi_k^c$ and $\Psi_k^v$ are the wave functions of the conduction and valence band at the $k$ point, respectively. The real part of dielectric tensor $\epsilon_1(\omega)$ is obtained by the well-known Kramers-Kronig relation[35],

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\epsilon_2(\omega')\omega'}{\omega^2 - \omega'^2 + i\eta} d\omega', \tag{2}$$

where $P$ denotes the principle value. The absorption coefficient $\alpha(\omega)$ and reflectivity $R(\omega)$ can be subsequently given by [36–38]

$$\alpha(\omega) = \frac{2\omega}{c} \left\{ \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} \right\}^{1/2} - \epsilon_1(\omega) \right\}^{1/2}, \tag{3}$$

$$R(\omega) = \frac{|\epsilon_1(\omega) + i\epsilon_2(\omega) - 1|}{|\epsilon_1(\omega) + i\epsilon_2(\omega) + 1|^2}. \tag{4}$$

By using the deformation potential theory for semiconductors, which was proposed by Bardeen and Shockley[39], the intrinsic carrier mobility $\mu$ of monolayer group-IV monochalcogenides: $\alpha$–GeS, $\alpha$–GeSe, $\alpha$–SnS, $\alpha$–SnSe, and $\beta$–GeSe is calculated and investigated in details herein. In the long-wavelength limit, when only considering the interaction between electron and longitudinal acoustic phonon[39, 40], the carrier mobility of 2D semiconductors is given by [41–44],

$$\mu = \frac{e\hbar^2 C^{2D}}{k_B T m^*_e m_d E_I^2}, \tag{5}$$

where $e$ is the electron charge, $\hbar$ is the reduced Planck’s constant, $T$ is the temperature equal to 300 K throughout the paper. $C^{2D}$ is the elastic modulus of a uniformly deformed crystal by strains and derived from $C^{2D} = \partial^2 E / \partial^2 (\Delta l/l_0)$, in which $E$ is the total energy, $\Delta l$ is the change of lattice constant $l_0$ along the transport direction, and $S_0$ represents the lattice volume at equilibrium for a 2D system, $m^*_e$ is the effective mass along the transport direction given by $m^*_e = \hbar^2 (\partial^2 E(k)/\partial k^2)^{-1}$ (k is wave-vector, and $E(k)$ denotes the energy) ( either $m^*_e$ or $m^*_d$ along the a or b direction, respectively), $m_d$ is the average effective mass defined by $m_d = \sqrt{m^*_e m^*_d}$. $E_I$ is the deformation potential (DP) constant defined by $E_I^{(k)} = \Delta E_{CBM(VBM)} / (\Delta l/l_0)$, where $\Delta E_{CBM(VBM)}$ is the energy shift of the band edge with respect to the vacuum level under a small dilation $\Delta l$ of the lattice constant $l_0$.

III. RESULTS AND DISCUSSION

A. Geometric structure of monolayer $\alpha$– and $\beta$–GeSe

The top and side view of the fully optimized structure of monolayer $\alpha$– and $\beta$–GeSe both with space group of
TABLE I. Structural informations, cohesive energies ($E_c$), SOC strength ($E^{SOC}$) and band gaps of monolayer $\alpha$- and $\beta$-GeSe. The bond angles of $\theta$ and bond lengths of $d$ are indicated in Fig. 1.

<table>
<thead>
<tr>
<th>phase</th>
<th>$a$</th>
<th>$b$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$E_c$ [eV/atom]</th>
<th>$E^{SOC}$ [eV]</th>
<th>$E_{\text{a}}$ [PBE(SOC)/HSE06(SOC)] [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>3.97(3.83[27])</td>
<td>4.29(4.39[27])</td>
<td>2.54</td>
<td>2.66</td>
<td>96.59</td>
<td>97.41</td>
<td>-1.20</td>
<td>-0.016</td>
<td>-0.040</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.67(3.83[27])</td>
<td>5.91(5.81[27])</td>
<td>2.55</td>
<td>2.72</td>
<td>96.65</td>
<td>93.91</td>
<td>-1.17</td>
<td>-0.016</td>
<td>-0.041</td>
</tr>
</tbody>
</table>

For monolayer $\alpha$-GeSe shown in Fig. 2 (a), both the conduction band minimum (CBM) and the valence band maximum (VBM) are located along the $\Gamma$ − $Y$ direction denoted by $C_y$ and $V_y$ respectively. The formation of the band gap of $\alpha$-GeSe shows that it is a semiconductor with a direct band gap of 1.16 eV, which is well consistent with the reported results (1.16 eV in Ref. [25] and Ref. [47], 1.22 eV in Ref. [49]). However, it is worthy to mention that the energy difference (0.014 eV) between the local CBMs ($C_X$ and $C_Y$ in Fig. 2 (a)) and the CBM at $k_{\text{CBM}}$ is very small, and such nearly degenerate CBMs suggest that it is feasible to apply some kinds of external controls (e.g. strain), to tune monolayer $\alpha$-GeSe direct to indirect semiconductors, or vice versa. Since Ge and Se are relatively heavy elements, the SOC effect may influence the band structures obviously, which is confirmed by the calculated band structures with SOC involved, as shown in Fig. 2 (a) (the red dashed line). The corresponding HSE06 calculation without SOC (with SOC) in Fig. 2 (b) (Fig. 2 (c)) gives a larger band gap of 1.61 eV (1.67 eV) compared to the PBE result of 1.16 eV, since PBE calculations always underestimate the value of band gaps of semiconductors.

As mentioned above, the $\alpha$-structure of group-IV monochalcogenides MX can be regarded as the results of material design by “atomic transmutation” from monolayer black phosphorene, in which the P atom is changed by group-IV atom (Ge/Sn) and group-VI atom (S/Se) and the total number of valence electrons is kept unchanged. Therefore the similarity of electronic band
FIG. 2. (a) and (d) are PBE calculations with and without SOC of electronic band structure and PBE calculated density of states (DOS) of monolayer α−GeSe and β−GeSe along high-symmetry directions respectively. (b) and (e) are the electronic band structures under HSE06 hybrid functional of monolayer α−GeSe and β−GeSe respectively, and (c) and (f) are the HSE06 band calculations with SOC.

structures between monolayer black phosphorene and α−MX is expected (results shown in the Supplemental Material[47]), resulting from the structural similarity and the similar p-orbital electrons contributions. By comparison with the band gaps of black phosphorene and other monolayer α−MX under investigations here (Supplemental Material[47]) it is found that only black phosphorene and α−GeSe possess direct band gaps, while the other “phosphorene analogues” including β−GeSe possess indirect band gaps, which means that only monolayer black phosphorene and α−GeSe possess good ability to absorb photons, while the photon-absorption abilities of β−GeSe and other α−MX are relatively poor since photons are necessarily involved.

The PBE calculations with and without SOC for the electronic band structure and DOS of monolayer β−GeSe are presented in Fig. 2 (d), which shows that, monolayer β−GeSe is a semiconductor with an indirect band gap with $E_g = 1.76$ eV. The CBM locates at the midpoint along Γ − Y direction and the VBM locates near the Γ point along the Γ − X direction. The obtained band gap decreases to 0.80 eV when the SOC is involved. The HSE06 calculations with and without SOC effects for β−GeSe give the band gap of 2.53 eV and 2.47 eV, respectively, which are larger than that of α−GeSe.

As for the SOC effects, since the calculated SOC strength is negative as shown in Table. I, the calculated band gaps for both α− and β−GeSe decrease when SOC is involved.

In order to clarify the contributions from different orbitals to the band structures around the Fermi level of α− and β−GeSe, we calculate the total and partial density of states (DOS) as shown in the right part of Fig. 2 (a) and (e). Analysis on the PDOS (Ge-4s, 4p and Se-4s, 4p orbitals) of α−GeSe reveals that Ge-4p and Se-4p orbitals dominate the electronic states near the Fermi level. The contributions from the Ge-4p to the total DOS of the conduction bands is larger than that from Se-4p, while in the valence band, the Se-4p orbitals have more contributions than those from Ge-4p. Analysis on the PDOS of monolayer β−GeSe reveals the dominant contributions from Ge-4p and Se-4p orbitals to the total DOS near the Fermi level, and the respective contribution from the Ge-4p and Se-4p orbitals is similar to the case of α−GeSe. Similar analysis of PDOS on other α−MX also leads to the result that the p orbital of group-IV (group-VI) atoms dominates the conduction (valence) bands. It is worthy to note that, to correct the underestimation of the bandgap of standard DFT calculations, the DFT+U approach can be used by setting the on-site Coulomb parameter $U$ and $J$ to Ge atoms.
The calculated electronic band structures performed by both PBE (with and without spin-orbital-coupling, SOC) and HSE06-hybrid functional method for monolayer $\alpha$− and $\beta$−GeSe along high-symmetry directions of Brillouin zone (BZ) are shown in Fig. 2. The above-mentioned PDOS analysis on the orbitals contributions to the formation of CBM and VBM is validated by the partial charge densities associated with the CBM and VBM is validated by the formation of CBM and VBM. When compressive strains are applied along $a$ direction, the values of $V_X$ and $C_Y$ increase, while the value of $C_X$ decreases, leading to a transition from direct to indirect semiconductor of monolayer $\alpha$−GeSe even at a small compression with $\varepsilon_x=-1\%$. When a compressive strain of $\varepsilon_x=-8\%$ is applied, a semiconductor-to-metal transition takes place as shown in Fig. 4 (d).

However, when applying a tensile strain along $a$ direction, the changes of the local VBM and CBM are different. When the tensile strain increases, the value of local $V_Y$ decreases, and the values of $C_X$ and $V_X$ increase, while the value of $C_Y$ keeps nearly unchanged, subsequently leading to a transition from direct to indirect semiconductors at $\varepsilon_x=9\%$. So, the direct band gap characteristic of monolayer $\alpha$−GeSe keeps unchanged for small compression and moderate stretching along $a$ direction (from $\varepsilon_x=-1\%$ to $\varepsilon_x=9\%$).

The change of the band structures of monolayer $\alpha$−GeSe when applying an external strain along $b$ direction ($\varepsilon_y$) is much smaller than that for strains along $a$ direction, similar analysis on the evolution of band structures for compressive and tensile strains, as shown in Figs. 4 (b) and (d), show that, for applied strains from -10% to 10%, a transition from direct to indirect semiconductor happens, while the transition from semiconductor to metal does not takes place in the strain region.

When applying strains along the $bi$ direction from -10% to 10%, the changes of the band structures are more similar to those for strains along the $a$ direction, and the transitions for both direct-to-indirect semiconductor and semiconductor-to-metal happen, as shown in Figs. 4 (c) and (d), except that the latter transition occurs at a compressive strain of $\varepsilon_{xy}=-6\%$.

In addition, the evolution of band gaps in $\alpha$−GeSe under various strains are shown in Fig. 4 (d), indicating that the values of the calculated band gaps increase with the increase of tensile strains in the region from -10% to 10%, disregarding the directions along which the the strains were applied.

Fig. 5 shows the evolutions of band structures and values of band gap of monolayer $\beta$−GeSe as a function of compressive and tensile strains with the strength from -10% to 10%. The behavior of $\beta$−GeSe under strains is quite different compared to that of $\alpha$−GeSe. Monolayer $\beta$−GeSe without strain is an indirect semiconductor described by VBM of $V_X$ and CBM of $C_Y$. When compressive strains are applied along $a$ direction, the values of $V_X$, $C_X$ and $C_Y$ decrease, while $V_S$ increase, leading to another type of indirect semiconductor. When applying a tensile strain along $a$ direction, the change of these VBM and CBMs are on the contrary tendencies compared to that of compressive strain. We compared the evolutions of band structures under strain along $b$ and $bi$ directions as shown in Fig. 5 (b) and (c), and came to the conclusion that the tendency of $V_X$, $C_X$ and $C_Y$ are simi-
FIG. 4. Electronic band structures of monolayer $\alpha$−GeSe under applied strains along (a) $a$ direction, (b) $b$ direction and (c) $b$1 direction. (d) shows the evolution of band gaps for $\alpha$−GeSe as a function of the applied strain.

lar with that of along $a$ direction, but with large changes of $V_S$ in the strain range from -10% to 10%. Furthermore, there is no transition from semiconductor to metal in this strain region.

It should be noted here that, although the band gap of monolayer $\beta$−GeSe decreases when the applied compressive strains increase, which is similar to the case of $\alpha$−GeSe, however, the decreasing tendency of band gap when increasing tensile strains is opposite to that of $\alpha$−GeSe. More interestingly, as shown in Fig. 5 (b,d), for applied tensile strains along $b$ direction from 0% to 10%, both VBM ($V_x$) and CBM ($C_x$) locate along $\Gamma$−$X$ direction and the values of VBM and CBM keep nearly unchanged, which means that the calculated band gaps subsequently keep nearly unchanged, around 1.73 eV. Such robust band gap nearly disregarding the tensile strains also leads to the nearly overlap of bandgap curves for the two respective cases by applying tensile strains along $a$ and $b$1 directions, as shown in Fig. 5(d).

As we know that band gap is related to the bonding-antibonding splitting, which is determined quantitively by the overlap integral $V$ of atomic orbitals. The overlap integral $V$ decreases with increasing the interatomic distance, following the $d^{-2}$ principle ($d$ is the bond length) in covalent solids[53], i.e. $V \propto d^{-2}$. Thus, the energy width of each band increases when compressive strains are applied, since the corresponding value of $V$ increases due to a smaller of $d$, as shown in Fig. 4 (a,b) and Fig. 5 (a,b). Similarly, when the tensile strains are applied, the band structure for covalent solids tends to be flat gradually, due to the smaller value of $V$ caused by a larger $d$. As shown in Table. 1 and Fig. 1 (d), monolayer $\beta$−GeSe has a relatively large bond length ($d_2$) along $b$ direction. It means that the overlap integral along $b$ direction is smaller than that along $a$ direction, indicating that the change of band gap when applying tensile strains along $b$ direction will be much weaker.

To further understand the bond characteristics and then the mechanism of the robust band gap for monolayer $\beta$−GeSe, we have calculated the electronic localization function (ELF)[54–57] as shown in Fig. 6. ELF is a position dependent function with values that range from 0 to 1. ELF = 1 corresponds to perfect localization and ELF = 0.5 corresponds to the electron-gas like pair probability. 3D plot of the ELF in Fig. 6 (a) shows that the covalent bond strength along $b$ direction is trivial compared with that along $a$ direction, which is reflected as well by the charge densities distribution for VBM and
FIG. 5. Electronic band structures of monolayer $\beta$–GeSe under applied strains along (a) $a$ direction, (b) $b$ direction and (c) $bi$ direction. (d) shows the evolution of band gaps for $\beta$–GeSe as a function of the applied strain.

FIG. 6. (a) Top view of 3D ELF and 2D ELF profiles of monolayer $\beta$–GeSe along the (b) $a$ and (c) $b$ direction, respectively.

CBM shown in Fig. 3. 2D plots of ELF profiles in Fig. 6 (b) and (c) show that, electrons are localized on Se-atom sites, and the Ge-Se bond strength along $b$ direction is weaker than that along $a$ direction. Therefore, when applying tensile strains along $b$ direction, the overlap integral will not fluctuate greatly due to the weak covalent bonds along $b$ direction, which may subsequently lead to the robust band gap insensitive to the tensile strains along $b$ direction as shown in Fig. 5(d).

D. Transport properties of black phosphorene, monolayer $\alpha$–MX and $\beta$–GeSe

To investigate the transport properties of $\alpha$– and $\beta$–GeSe, we systematically calculate carrier mobilities of black phosphorene, monolayer $\alpha$–MX ($\alpha$–GeS, $\alpha$–GeSe, $\alpha$–SnS and $\alpha$–SnSe) and $\beta$–GeSe. According to the deformation theory, i.e. Eq. (5), three parameters, namely carrier effective mass $m^*$, the deformation potential $E_l$ and the elastic modulus $C^{2D}$ in the propagation direction determine the behaviors of carrier mobility of semiconductors[43, 58]. Although the PBE calculations always underestimate the band gap, the curvatures of valence and conduction bands calculated by PBE method are generally correct enough and the calculated carrier mobilities are subsequently in good agreement with experiments for numerous 2D materials[41–43, 58, 59]. We calculate the effective masses of holes ($m^*_h$) and electrons ($m^*_e$) along $a$ and $b$ directions by fitting parabolic func-
tions to the band curve close to the VBM and CBM, respectively, as shown in Table II.

For black phosphorene, it is remarkable that along the $a$ direction (band structure along $\Gamma$-X direction in Supplemental Material[47]), the valence of band is nearly flat close to the $\Gamma$ point (VBM), with the effective hole mass of 11.16 $m_0$, 9 times larger than the effective electron mass (1.24 $m_0$). And along $b$ direction (Y-$\Gamma$ in band structure), the effective carrier masses are 0.14 $m_0$ (hole) and 0.15 $m_0$ (electron) respectively, mainly due to the more dispersive $s$ and $p$ characters of VBM and CBM as shown in the band structure along the $\Gamma$-Y direction (see Supplemental Material[47]).

As mentioned above, monolayer $\alpha$-MX can be regarded as the “phosphorene analogues” produced by the so-called “atomic transmutation” method, the band structures of the four monolayer $\alpha$-$\text{MX}$s, i.e. $\alpha$-GeS, $\alpha$-GeSe, $\alpha$-SnS and $\alpha$-SnSe, indeed show similar patterns, which are shown in Fig. 2(a) and Supplemental Material[47]. All the four monolayer $\alpha$-$\text{MX}$s possess CBM along the $\Gamma$-X and VBM along the $\Gamma$-Y directions. According to the $d^{-2}$ principle[53], the orbital overlapping integral $V$ also determines the bandwidth of a specific band, and generally a band with a larger bandwidth has a larger band curvature at the CBM/VBM points, which thus leads to a smaller effective electron/hole masses for covalent solids. As shown in the Table, $\text{S1}$, the bond lengths $d_{1/2}$ for all the monolayer $\alpha$-$\text{MX}$s have the tendency of $d_{\text{GeS}} < d_{\text{GeSe}} < d_{\text{SnS}} < d_{\text{SnSe}}$, therefore, the orbital overlapping $V$ should be $V_{\text{GeS}} > V_{\text{GeSe}} > V_{\text{SnS}} > V_{\text{SnSe}}$, since the conduction and valence bands of all the monolayer $\alpha$-$\text{MX}$s are formed by $M-p$ and $X-p$ orbitals respectively. Subsequently, the effective masses for all the monolayer $\alpha$-$\text{MX}$s can be ordered by $m^*_{\text{GeS}} > m^*_{\text{GeSe}} > m^*_{\text{SnS}} > m^*_{\text{SnSe}}$, due to the opposite tendency of the bandwidths for these four monolayer $\alpha$-$\text{MX}$s. The relation of the effective masses for all the monolayer $\alpha$-$\text{MX}$s is shown and confirmed in Table II. as well.

By linearly fitting the band energy (CBM and VBM positions) shift with respect to the vacuum level under strain $\varepsilon (\Delta l/l_0)$ along $a$ and $b$ directions, the DP constant $E_l$ for both electrons and holes can be calculated. As shown in Fig. 7 (a) and (b), the responses of CBM and VBM for $\alpha/\beta$-GeSe to the applied strain appear to be anisotropic as well. The response for black phosphorene, $\alpha$-GeS, $\alpha$-SnS and $\alpha$-SnSe are shown in Supplemental Material[47]. The obtained DP constants $E_l$ are listed in Table II.

The elastic constant $C^{2D}$ can be calculated from the relation between the total energy and lattice dilations. Such relations for all the 2D materials under investigation here are shown in Fig. 7 (c-d) and Supplemental Material[47]. The calculated elastic constants are listed in Table II.

Based on the obtained $m^*_e$, $E_l$ and $C^{2D}$, the carrier mobilities of black phosphorene, monolayer $\alpha$-MX ($\alpha$-GeS, $\alpha$-GeSe, $\alpha$-SnS and $\alpha$-SnSe) and $\beta$-GeSe at room temperature ($T=300$ K) are calculated and listed in Table II. For black phosphorene, it has a large hole carrier mobility of $1.13 \times 10^4 \text{cm}^2/\text{V} \cdot \text{s}$ along the $a$ direction, even with large hole effective mass of 11.16 $m_0$, but with large elastic modulus of 102.59 N/m which is expected from the hybridized covalent $sp^3$ bonds and extremely small band edge deformation potential constant of 0.12 eV, which can be understood by considering the band edge wave function that the distribution of electron state can have a significant impact on the lattice deformation[21]. Table II also shows the transport properties of monolayer $\alpha$-MX, which show strongly anisotropic transport properties and high carrier mobilities along $a$ or $b$ directions.

The predicted carrier mobilities for both $\alpha$- and $\beta$-GeSe are anisotropic along the $a$ and $b$ directions. Both $\alpha$- and $\beta$-GeSe show high electron mobilities along the $b$ direction ($\mu_b$), i.e. $4.71 \times 10^4 \text{cm}^2/\text{V} \cdot \text{s}$ for monolayer $\alpha$-GeSe and $2.93 \times 10^4 \text{cm}^2/\text{V} \cdot \text{s}$ for monolayer $\beta$-GeSe, respectively. The calculated value of $\mu_b$ for $\beta$-GeSe is comparable to that of black phosphorene ($1.13 \times 10^4 \text{cm}^2/\text{V} \cdot \text{s}$), which suggests that monolayer $\beta$-GeSe is also a promising candidate material for future electronic and optoelectronic applications, considering the high electron mobilities and stability in ordinary environment[27].

E. Optical properties of monolayer $\alpha$- and $\beta$-GeSe

Fig. 8 presents the in-plane optical absorption spectra $\alpha(\omega)$ and reflectivity $R(\omega)$ of monolayer $\alpha$- and $\beta$-GeSe for the incident light with the polarization of the electric field $E$ along the $a$ ($E//a$) and $b$ ($E//b$) directions respectively. In 2D materials, compared to the band gap calculated by quasi-particle GW method which considers the excitonic effects, the optical band gap obtained by HSE06 is usually close to the real optical band gap due to the underestimation of band gap by neglecting excitonic effects[21]. Thus, we only perform HSE06 cal-
TABLE II. Calculated band gap $E_g$, effective mass $m^*$ (with $m_0^*$ being the static electron mass), deformation potential constant $E_i$, 2D elastic modulus $C$ and carrier mobility $\mu$ along the $\Gamma - X$ and $\Gamma - Y$ directions respectively. The electron and hole carrier mobilities $\mu$ are calculated by using Eq. (5) at $T=300$ K.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_g$ (HSE06)</th>
<th>carrier type</th>
<th>$m_a$ [$m_0$]</th>
<th>$m_b$ [$m_0$]</th>
<th>$E_{l-a}$ [eV]</th>
<th>$E_{l-b}$ [eV]</th>
<th>$C_a$ [N/m]</th>
<th>$C_b$ [N/m]</th>
<th>$\mu_a$ [cm$^2$/V·s]</th>
<th>$\mu_b$ [cm$^2$/V·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>black phosphorene</td>
<td>1.49</td>
<td>hole</td>
<td>0.11.16</td>
<td>0.14</td>
<td>0.12</td>
<td>2.79</td>
<td>102.59</td>
<td>23.60</td>
<td>1.13×10$^4$</td>
<td>3.66×10$^7$</td>
</tr>
<tr>
<td>α−GeS</td>
<td>2.75</td>
<td>hole</td>
<td>0.87</td>
<td>0.25</td>
<td>4.57</td>
<td>6.45</td>
<td>42.36</td>
<td>12.89</td>
<td>1.06×10$^2$</td>
<td>5.70×10$^1$</td>
</tr>
<tr>
<td>α−GeSe</td>
<td>1.61</td>
<td>hole</td>
<td>0.30</td>
<td>0.22</td>
<td>5.91</td>
<td>4.03</td>
<td>38.43</td>
<td>17.08</td>
<td>3.07×10$^2$</td>
<td>4.71×10$^3$</td>
</tr>
<tr>
<td>α−SnS</td>
<td>1.50</td>
<td>hole</td>
<td>0.16</td>
<td>0.14</td>
<td>8.40</td>
<td>4.74</td>
<td>41.65</td>
<td>21.32</td>
<td>5.40×10$^2$</td>
<td>9.42×10$^2$</td>
</tr>
<tr>
<td>α−SnSe</td>
<td>0.98</td>
<td>hole</td>
<td>0.16</td>
<td>0.14</td>
<td>4.74</td>
<td>8.40</td>
<td>41.65</td>
<td>21.32</td>
<td>5.40×10$^2$</td>
<td>9.42×10$^2$</td>
</tr>
<tr>
<td>β−GeSe</td>
<td>2.47</td>
<td>hole</td>
<td>0.10</td>
<td>0.84</td>
<td>2.68</td>
<td>1.99</td>
<td>42.00</td>
<td>41.00</td>
<td>1.19×10$^2$</td>
<td>2.71×10$^2$</td>
</tr>
</tbody>
</table>

![Absorption](image1)

![Reflectivity](image2)

**Fig. 8.** HSE06 calculations of (a) optical absorption spectra and (b) reflectivity of monolayer α− and β−GeSe for incident light with the polarization along the $a$ and $b$ directions.

Calculations of optical properties here. And it deserves further investigations on excitonic effects on electronic and optical properties of monolayer α− and β−GeSe. The corresponding imaginary part of the dielectric function are shown in Supplemental Material[47].

The absorption coefficient is defined as the decay of light intensity spreading in a unit length, i.e. Eq. (3). For monolayer α− and β−GeSe, the absorption coefficient shows an obvious anisotropy along different directions, and both materials exhibit obvious optical absorption with the frequency covering some part of the visible spectrum. The frequency region for high absorption along the $b$ direction of β−GeSe is larger than that along the $a$ direction shown in Fig. 8 (a), and is even larger than those of α−GeSe irrespective of polarization directions. Such a significant anisotropic optical property can be used to identify the monolayer β−GeSe in experiments.

**IV. CONCLUSION**

In summary, we have performed first-principles calculations on the structure, electronic, transport and optical properties of monolayer α− and β−GeSe. α−GeSe is a puckered structure similar to that of black phosphorene with Ge and Se atoms substituted for P atoms alternately, while β−GeSe consists of six-rings with the vertices arranged in an uncommon boat conformation. They all have strongly anisotropic properties. For monolayer α−GeSe, the direct-semiconducting characteristic is robust for small compression and moderate stretching along $b$ direction (from $\varepsilon_x=-1\%$ to $\varepsilon_x=9\%$), and an extremely high electron mobility of 2.93×10$^4$cm$^2$/V·s for β−GeSe is observed along the armchair direction. Furthermore, the band gaps of monolayer β−GeSe keep nearly unchanged under tensile strain from 0% to 10%. The calculated optical properties of monolayer α− and β−GeSe shows anisotropic behaviors and large absorption in some part of visible spectrum. Due to the ultrahigh electron mobilities and the abnormal behavior of robust band gap disregarding the applied tensile strains, monolayer β−GeSe is promising in the future electronic and optoelectronic applications.
ACKNOWLEDGEMENT

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[47] See supplemental material at [url will be inserted by publisher] for details of data analysis.


