Efficient strain-induced light emission in lonsdaleite germanium

Jens René Suckert, Claudia Rödl, Jürgen Furthmüller, Friedhelm Bechstedt, and Silvana Botti

Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany and European Theoretical Spectroscopy Facility

(Dated: September 15, 2020)

Lonsdaleite germanium has a direct band gap, but it is not an efficient light emitter due to the vanishing oscillator strength of electronic transitions at the fundamental gap. Transitions involving the second lowest conduction band are instead at least three orders of magnitude stronger. The inversion of the two lowest conduction bands would therefore make hexagonal germanium ideal for optoelectronic applications. In this work, we investigate the possibility to achieve this band inversion by applying strain. To this end we perform \textit{ab initio} calculations of the electronic band structure and optical properties of strained hexagonal germanium, using density functional theory with the modified Becke-Johnson exchange-correlation functional and including spin-orbit interaction. We consider hydrostatic pressure, uniaxial strain along the hexagonal \( c \) axis, as well as biaxial strain in planes perpendicular to and containing the hexagonal \( c \) axis to simulate the effect of a substrate. We find that the conduction-band inversion, and therefore the transition from a pseudo-direct to a direct band gap, is attainable for moderate tensile uniaxial strain parallel to the lonsdaleite \( c \) axis.

I. INTRODUCTION

Integration of silicon-based active optical devices into the common metal-oxide semiconductor (CMOS) technology is hampered by the indirect band gap of the diamond-structure phase of silicon (Si), germanium (Ge), and SiGe alloys [1, 2]. In fact, none of these semiconductors can emit light efficiently, and therefore they are not suitable for applications that require optoelectronic functionalities. Using heterogeneous integration, III–V semiconductors can be implemented as active light sources onto chips [1]. However, it would be desirable to have light sources available that are chemically compatible with Si, tolerated by the CMOS technology, and capable of emitting light efficiently. It is therefore an important technological challenge to achieve low-threshold lasing in group IV semiconductors.

Strain and alloying are the most investigated strategies to tailor absorption and emission properties of Si and Ge [3, 4]. Another explored way is to search for non-diamond-structure polymorphs with a modified band structure. The hexagonal lonsdaleite phase of Si (hex-Si) with space group \( P6_3/mmc \) can be stabilized under ambient conditions using different growth techniques [5–7]. Even if the size of the direct gap at \( \Gamma \) is reduced to 1.6 eV by band folding [8], the fundamental gap remains indirect with the conduction-band minimum (CBM) at the \( M \) point of the hexagonal Brillouin zone (BZ). Biaxial tensile strain larger than 4\% has been predicted to transform hex-Si into a direct semiconductor [8].

Ge also has an excellent CMOS compatibility [1]. The band structure of Ge in the cubic diamond structure features an indirect band gap with the CBM at the \( L \) point and a direct gap at \( \Gamma \) that is only about 0.1 eV larger [9, 10]. Ge in the hexagonal lonsdaleite crystal structure (hex-Ge) has been predicted to have a direct gap of about 0.3 eV at the \( \Gamma \) point [10–14]. Experimentally, hex-Ge has been obtained by low-pressure ultraviolet laser ablation [15, 16]. Alternatively, high-quality crystals of hex-Ge or hex-SiGe alloys can be grown on templates of wurtzite (\( wz \)) GaP or GaAs nanowires [17, 18]. Recently, direct-band-gap emission has been demonstrated for Ge-rich hex-SiGe alloys, with emission wavelength tunable by controlling the alloy composition [18].

The energy levels of hex-Ge at the \( \Gamma \) point are shown in Fig. 1. The CBM possesses \( \Gamma_{7v} \) symmetry. In agreement with group theory [19], optical dipole transitions from the three highest valence bands with symmetries \( \Gamma_{9v}^+, \Gamma_{7v}^+, \) and \( \Gamma_{7v}^- \) to the lowest conduction band are dipole forbidden except for the transition \( \Gamma_{9v}^+ \rightarrow \Gamma_{7v}^- \) that is dipole allowed for light polarization perpendicular to the hexagonal \( c \) axis [10]. However, its oscillator strength is three orders of magnitude smaller than the oscillator strength of typical dipole-active transitions in semiconductors [10]. Thus, hex-Ge can be called a pseudo-direct semiconductor that, despite having a direct band gap, is not optically active at the band-gap energy. However, there is a second conduction band with \( \Gamma_{7c} \) symmetry about 0.3 eV above the \( \Gamma_{8c} \) CBM. Except for the \( \Gamma_{8v}^+ \rightarrow \Gamma_{7c}^- \) transition for...
light polarization parallel to the $c$ axis, all transitions from the three highest valence bands to $\Gamma_{7c}$ are (strongly) dipole active [10, 19].

In this work, we use accurate $ab$ initio calculations to investigate if the ordering of the two lowest conduction bands can be inverted by applying moderate lattice strain to obtain a CBM with $\Gamma_{7c}$ character and make hex-Ge an efficient light emitter. We also explore the possibility to tune the wavelength of light emission by strain [20]. A brief review of the used methods is given in Sec. II. The influence of strain on the atomic structure is studied in Sec. III. Section IV is dedicated to the analysis of strain effects on the electronic band structure. In Sec. V, we focus on the optical properties of strained hex-Ge. Finally, in Sec. VI, we present a summary and draw conclusions.

II. COMPUTATIONAL DETAILS

All calculations were performed in the framework of density-functional theory (DFT) as implemented in the Vienna $ab$-initio Simulation Package (Vasp) [21, 22]. The wave functions are described using the projector-augmented wave (PAW) method [23] with a plane-wave cutoff of 500 eV. The Ge 3d electrons are treated as valence electrons and spin-orbit coupling (SOC) is included in all calculations. Unless otherwise noted, a $12 \times 12 \times 6 \Gamma$-centered $k$-point mesh is used for the BZ integration.

For the calculation of structural and elastic properties under strain, exchange and correlation are described in the generalized gradient approximation (GGA) using the PBEsol [24] functional. It has been previously shown that the PBEsol functional provides excellent lattice parameters for hexagonal Ge [10, 18]. The strained structures were optimized under constraint until the Hellmann-Feynman forces for all free atomic coordinates were below 1 meV/Å. Symmetry-reducing strain on hexagonal nanowire facets is simulated in an orthorhombic supercell of the primitive hexagonal cell using a $12 \times 6 \times 6$ $k$-point mesh.

Electronic band structures were obtained with the meta-GGA functional MBJLDA, i.e., the modified Becke-Johnson exchange potential [25–27] together with the local-density approximation (LDA) for correlation. This meta-GGA functional yields excellent band gaps at low computational cost [9, 10, 14, 28], even though deviations from experiment or more sophisticated approaches (e.g., hybrid functionals or many-body perturbation theory) occur for electronic states further away from the band gap. Since we are mainly interested in the near-gap electronic structure here, this does not pose a problem for the present study. We carefully validated the choice of this functional for electronic-structure calculations of hex-Ge in Ref. [10].

Optical spectra and radiative lifetimes were calculated in the independent-particle approximation starting from the meta-GGA electronic band structure using a denser BZ sampling with $60 \times 30 \times 30 \Gamma$-centered $k$ points.

III. STRUCTURAL AND ELASTIC PROPERTIES

A. Equilibrium structure

The equilibrium geometry was obtained by constant-volume relaxation and a subsequent fit of the resulting energy-over-volume curve to the Birch-Murnaghan equation of state (EOS) [29]. For the lattice parameters of unstrained he-Ge, we found $a_0 = 3.996\,\text{Å}$, $c_0 = 6.592\,\text{Å}$, and the internal cell parameter $u = 0.3743$. Both $u$ and the ratio of $c_0/a_0 = 1.6496$ are close to the values $(c/a)_{\text{id}} = \sqrt{8/3}$ and $u_{\text{id}} = 3/8$ of the ideal lonsdaleite structure. The lattice parameters are in very good agreement with available experimental data [18]. The EOS fit yields $B_0 = 67.6$ GPa for the isostructural bulk modulus and $B_0' = 4.69$ for its pressure derivative.

B. Symmetry-conserving strain

For sufficiently small strains, the relation between the stress tensor $\sigma$ and the strain tensor $\epsilon$ is linear, i.e., Hooke’s law

$$\sigma_{ij} = \sum_{j=1}^{3} C_{ij} \epsilon_{j} \quad (1)$$

holds, with the tensor of elastic constants $C_{ij}$ in Voigt notation [30] (1, ..., 6 = $xx$, $yy$, $zz$, $yz$, $zx$, $xy$). For hexagonal crystals, the symmetric elastic tensor has only five independent non-vanishing components [31–33]: $C_{11} = C_{22}$, $C_{33}$, $C_{12}$, $C_{13} = C_{23}$, $C_{44} = C_{55}$, and $C_{66} = \frac{1}{2}(C_{11} - C_{12})$.

First, we consider only normal stresses that leave the spacegroup symmetry unchanged. In this case, Hooke’s law reduces to

$$\sigma_{xx} = \sigma_{yy} = (C_{11} + C_{12}) \epsilon_{xx} + C_{13} \epsilon_{zz} \quad (2a)$$

$$\sigma_{zz} = 2C_{13} \epsilon_{xx} + C_{33} \epsilon_{zz} \quad (2b)$$

in hexagonal crystals, with the normal strains

$$\epsilon_{xx} = \epsilon_{yy} = (a - a_0)/a_0 \quad (3a)$$

$$\epsilon_{zz} = (c - c_0)/c_0 \quad (3b)$$

that are given by the deviations of the strained lattice constants $a$ and $c$ from their equilibrium values $a_0$ and $c_0$.

1. Hydrostatic pressure

When a hydrostatic pressure $P$ is exerted on the system, the stress tensor reduces to $\sigma_{ij} = -P \delta_{ij}$. Inserting this constraint into Eq. (2) yields the relation $\epsilon_{zz} = R_h \epsilon_{xx}$ between out-of-plane and in-plane strain, where $R_h$ is the hydrostatic ratio

$$R_h = \frac{(C_{11} + C_{12}) - 2C_{13}}{C_{33} - C_{13}}. \quad (4)$$
Table I. Lattice parameters \( a_0 \) (in Å), \( c_0 \) (in Å), and \( u_0 \), elastic constants \( C_{ij} \) (in GPa), Young modulus \( E \), biaxial modulus \( Y \), isothermal bulk modulus \( B_0 \) (in GPa) and its pressure derivative \( B'_0 \) as well as hydrostatic ratio \( R_h \), biaxial ratio \( R_b \), and Poisson ratio \( \nu \) of hex-Ge. As explained in the text, the elastic properties have been obtained in two ways: directly calculated from the strained system and using ELASTIC.

| Strain (PBEsol) | \( a_0 \) | \( c_0 \) | \( u_0 \) | \( C_{11}+C_{12} \) | \( C_{11} \) | \( C_{12} \) | \( C_{13} \) | \( C_{33} \) | \( C_{44} \) | \( C_{66} \) | \( E \) | \( Y \) | \( B_0 \) | \( B'_0 \) | \( R_b \) | \( R_h \) | \( \nu \) |
|----------------|--------|--------|--------|----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| ELASTIC (PBEsol) | 3.996 | 6.592 | 0.3743 | 177.8 | 23.4 | 159.5 | 153.3 | 170.9 | 67.6 | 4.69 | 1.023 | 0.294 | 0.132 |
| Ref. [34] (LDA) | 4.030 | 6.649 | 156 | 106 | 50 | 19 | 150 | 35 | 28 | 90 | 60 | 0.250 |
| Ref. [35] (exp.) | 193.1 | 155.6 | 37.5 | 27.7 | 169.3 | 41.1 | 59.1 | 74.0 |
| Ref. [18] (exp.) | 3.9855 | 6.5772 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

The isothermal bulk modulus \( B_0 = -V_0 \frac{\partial p}{\partial V} \bigg|_{p=0} \) relates hydrostatic pressure to infinitesimal volume changes. For sufficiently small volume changes and pressures,

\[
p = -B_0 \frac{\Delta V}{V_0} = -B_0 \left( 2\epsilon_{xx} + \epsilon_{zz} \right)
\]

holds. Combining Eqs. (2), (4), and (5), the bulk modulus is given by

\[
B_0 = \frac{(C_{11} + C_{12})C_{33} - 2(C_{13})^2}{(C_{11} + C_{12}) + 2(C_{33} - 2C_{13})}.
\]

We simulate hex-Ge under hydrostatic pressure by a constrained relaxation of the atomic coordinates at a given fixed cell volume.

2. Biaxial strain

Biaxial strain perpendicular to the hexagonal c axis is characterized by \( \sigma_{xx} = \sigma_{yy} \) and \( \sigma_{zz} = 0 \), i.e. the forces along the c axis vanish. Using Eq. (2), the out-of-plane strain can be linked to the in-plane strain by \( \epsilon_{zz} = -R_b \epsilon_{xx} \), where the biaxial ratio \( R_b \) is given by

\[
R_b = \frac{2C_{13}}{C_{33}}.
\]

The in-plane stress is related to the in-plane strain as \( \sigma_{xx} = Y \epsilon_{xx} \), with the biaxial modulus \( Y \) that reads

\[
Y = C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}}.
\]

To model biaxial strain perpendicular to the c axis in hex-Ge, the lattice constant \( a \) is fixed and all other degrees of freedom of the atomic geometry are determined by total-energy minimization.

3. Uniaxial strain

For uniaxial strain along the c axis, the in-plane normal stresses \( \sigma_{xx} = \sigma_{yy} = 0 \) vanish and only \( \sigma_{zz} \) is nonzero. Inserting this condition into Eq. (2) yields the relation \( \epsilon_{xx} = -\nu \epsilon_{zz} \) between the in-plane and out-of-plane strains with the Poisson ratio

\[
\nu = \frac{C_{13}}{C_{11} + C_{12}}.
\]

The uniaxial stress \( \sigma_{zz} = E \epsilon_{z} \) is related to the strain in this direction through the Young modulus \( E \)

\[
E = C_{33} - \frac{2C_{13}^2}{C_{33}}\]

which follows immediately from Eq. (2).

Uniaxial strain can be modeled by fixing the c lattice constant and relaxing all other atomic coordinates.

4. Elastic constants

For the situations of hydrostatic pressure, biaxial strain, and uniaxial strain, we determined the ratios between out-of-plane and in-plane strains for the smallest strains we investigated (about 1%) and found \( R_b = 1.023 \), \( R_h = 0.294 \), and \( \nu = 0.132 \), respectively. Taking as additional input the bulk modulus \( B_0 = 67.6 \) GPa from the EOS fit, the three elastic constants \( C_{11} + C_{12} = 177.8 \) GPa, \( C_{13} = 23.4 \) GPa, and \( C_{33} = 159.5 \) GPa, the biaxial modulus \( Y = 170.9 \) GPa, and the Young modulus \( E = 153.3 \) GPa can be computed.

C. Symmetry-reducing strain

All elastic constants \( C_{ij} \) can be obtained by calculating normal and tangential stresses for specific deformations of the crystal lattice and solving Hooke’s law, as implemented in the code ELASTIC [36, 37]. The elastic constants obtained with ELASTIC confirm the values calculated for hex-Ge under hydrostatic pressure, biaxial strain, and uniaxial strain. A summary of structural parameters and elastic constants, including a comparison with results in literature, can be found in Table I.
Figure 2. Band structure of hex-Ge for the unstrained equilibrium geometry (a), a volume change of $\Delta V/V_0 = +5\%$ (b), a biaxial strain of $\varepsilon_{xx} = \varepsilon_{yy} = -4\%$ (c), and a uniaxial strain of $\varepsilon_{zz} = +3\%$ (d). The VBM is used as energy zero. The gap region is shaded.

IV. ELECTRONIC PROPERTIES

A. Symmetry-conserving strain

The band structure of unstrained hex-Ge is displayed in Fig. 2(a) along with the labels of relevant high-symmetry states [10]. Besides the energy levels at the $\Gamma$ point, the $U_{5c}$ CBM is of particular interest, as it is close in energy to the CBMs at $\Gamma$. Under some strains, the $U_{5c}$ state on the $L-M$ line becomes the lowest conduction level and turns hex-Ge into an indirect semiconductor which is, of course, not desirable for high light-emission efficiency, as this CBM would act as a carrier trap. The strain dependence of the band-edge energies is plotted in Fig. 3 for hydrostatic pressure, biaxial strain, and uniaxial strain. Here, the $\Gamma_{9v}$ state, that is the VBM for the unstrained structure, serves as reference level for all strain-induced energy shifts.

1. Hydrostatic pressure

In general, we observe an increased splitting of all states at the $\Gamma$ point when hydrostatic pressure is exerted. Figure 3(a) shows that the VBMs at $\Gamma$ and the $U_{5c}$ CBM shift only marginally in the investigated range of volume changes. However, the energy of the two CBMs at $\Gamma$ increases strongly with rising pressure. The effect is particularly pronounced for
the $\Gamma_{7c}$ state, as it forms an $sp$ gap with the $\Gamma_{9v}^-$ VBM [11].

Negative hydrostatic pressure corresponding to a volume increase of about 5% would lead to the desired conduction-band inversion of the $\Gamma_{8c}^-$ and $\Gamma_{7c}^-$ states with a pseudodirect-to-direct-gap transition at a gap of 0.17 eV. In Fig. 2(b), the band structure of hex-Ge for a volume dilatation of 5% is shown, illustrating how the two CBMs approach. At even larger negative pressure, for 7.6% volume increase, a semiconductor-to-metal phase transition occurs. Experimentally, negative hydrostatic pressures are hard, if not impossible, to realize, which is why this does not represent a promising route to engineer the electronic structure of hex-Ge. More sophisticated strains have to be explored.

2. **Biaxial strain**

Figure 3(b) shows that the band ordering in hex-Ge is more sensitive to biaxial strain perpendicular to the hexagonal $c$ axis than to hydrostatic pressure. The $\Gamma_{7c}$ state exhibits a highly nonlinear behavior leading to a conduction-band inversion for compressive biaxial strains larger than 2.2%. Unfortunately, a direct-to-indirect-semiconductor transition with a $\Gamma_{8c}^- \rightarrow U_{8c}$ fundamental gap occurs already at smaller compressive strains. The resulting band structure is illustrated in Fig. 2(c) for 4% of tensile biaxial strain.

For tensile biaxial strain, the system becomes metallic at a strain of about 2%. The band ordering resembles that of zincblende HgTe or $a$-Sn [38] as a negative gap appears. Above 3% of tensile strain, the band ordering changes to $\Gamma_{7v}^+ > \Gamma_{9v}^- > \Gamma_{8c}^-$ and a small gap opens at $\Gamma$ between the empty $\Gamma_{7v}^+$ and the filled $\Gamma_{9v}^-$ state.

3. **Uniaxial strain**

Uniaxial strain along the hexagonal $c$ axis offers great potential to engineer the electronic states, as the two CBMs $\Gamma_{8c}^-$ and $\Gamma_{7c}^-$ shift in opposite directions [see Fig. 3(c)]. Already for a small tensile uniaxial strain of about 1.5%, a pseudodirect-to-direct gap transition occurs: hex-Ge becomes a direct-gap semiconductor with a gap of 0.4 eV and strong dipole transitions at the gap energy. The gap stays direct, but shrinks for larger strains until a semiconductor-to-metal transition occurs at about 4% tensile strain. Similar behavior has been observed experimentally for wz-GaAs [20] and wz-GaP [39] under uniaxial strain. The strain range between 1.5 and 4% is likely to be experimentally accessible and further offers the possibility to tune the band gap between 0 and 0.4 eV. Figure 2(d) shows the band structure of hex-Ge for 3% of tensile uniaxial strain illustrating the direct band gap and the band inversion at $\Gamma$.

For tensile uniaxial strains above 4% or compressive uniaxial strains above 3%, we predict a band inversion of conduction and valence bands.

| State   | $E_0$ (eV) | $\Xi_h$ (eV) | $\Xi_b$ (eV) | $\Xi_0$ (eV) |
|---------|------------|--------------|--------------|-------------|
| $\Gamma^+_{7v}$ | $-0.433$ | $0.51$ | $8.93$ | $-6.51$ |
| $\Gamma^+_{7v}$ | $-0.120$ | $0.15$ | $2.73$ | $-1.91$ |
| $\Gamma^+_{9v}$ | $0.000$ | $0.00$ | $0.00$ | $0.00$ |
| $\Gamma^-_{8c}$ | $0.298$ | $-1.95$ | $-15.76$ | $8.79$ |
| $\Gamma^-_{7c}$ | $0.633$ | $-8.75$ | $-6.83$ | $-13.62$ |
| $U_{5c}$ | $0.620$ | $-0.35$ | $6.98$ | $-6.93$ |

4. **Deformation potentials**

In Table II, the deformation potentials of the most important energy levels are compiled for the three considered symmetry-conserving strains. The deformation potentials $\Xi_j$ are defined as the linear expansion coefficients of the energy levels as a function of strain,

$$E(\epsilon_j) \approx E_0 + \Xi_j \epsilon_j,$$

with $j = h$ for hydrostatic pressure ($\epsilon_h = \Delta V/V_0$), $j = b$ for biaxial strain ($\epsilon_b = \epsilon_{xx} = \epsilon_{yy}$), and $j = u$ for uniaxial strain ($\epsilon_u = \epsilon_{zz}$). Note in particular that for biaxial and uniaxial strain, the strain dependence of the energy levels quickly becomes nonlinear. In these cases, the explicitly calculated values for the larger strains can be taken from Fig. 3.

The volume deformation potentials are very small for the states $U_{5c}$, $\Gamma^+_{7v}$, and $\Gamma^-_{7v}$. The potential $\Xi_h = -8.7$ eV of the $sp$ gap $\Gamma_{9v}^- \rightarrow \Gamma_{7c}^-$ is in excellent agreement with the value of $-8.8$ eV for cubic Ge [40]. It is also close to the value of $-8.25$ eV computed for wz-GaAs [41]. The volume deformation potential $\Xi_b = -1.9$ eV for the $\Gamma_{9v}^- \rightarrow \Gamma_{8c}^-$ gap is significantly smaller. Also in this respect, hex-Ge behaves very similarly to wz-GaAs [41].

On average, the absolute values of the biaxial and uniaxial deformation potentials are larger than the volume deformation potentials, even when taking the relation $\Delta V/V_0 \approx 2 \epsilon_{xx} + \epsilon_{zz}$ for the strain amplitudes into account. For all studied states except $\Gamma_{7c}$, the biaxial and uniaxial deformation potentials have opposite sign. However, their absolute values differ, as tensile (compressive) biaxial strain and compressive (tensile) uniaxial strain do not represent the same physical situation.

B. **Symmetry-reducing strain**

Pseudomorphic growth of hex-Ge on top of, e.g., wz-GaAs or wz-GaP substrates along the hexagonal $c$ axis does not permit to reach the preferential situation of tensile uniaxial strain. Growing instead on wz-GaAs or wz-GaP nanowire facets [17] represents a viable alternative to strain Ge along its hexagonal axis. However, the lattice mismatch between Ge and the nanowire substrate leads to a biaxial strain along the
bands, $\Gamma'_{8c}$ and $\Gamma'_{7c}$, as well as the size of the band gap at the $\Gamma$ point for symmetry-reducing biaxial strain are shown in Fig. 5.

In view of laser applications, only strain configurations with a direct band gap are relevant, therefore only those will be discussed here.

The conduction-band ordering for biaxial strain along the $\{1100\}$ facet is largely dominated by the strain component $\epsilon_{zz}$. The strain along the $\{1120\}$ direction has almost no impact. Consequently, the general picture is very similar to uniaxial strain. A tensile strain of $1\%$ -- $2\%$ yields the desired conduction-band inversion. Further increasing the strain reduces the value of the band gap until the material becomes metallic.

For biaxial strain in the $\{1120\}$ plane, the conduction-band ordering is also dominated by the strain in $c$ direction. The conduction-band inversion occurs for $\epsilon_{zz} > 1\%$ -- $2\%$. Also here, the band gap decreases with increasing strain. Only for compressive strains $\epsilon_{zz} > 2\%$ in the plane perpendicular to the $c$ axis, the $\epsilon_{zz}$ component has an equally strong influence and the conduction-band inversion occurs for lower $\epsilon_{zz}$. However, in this region, the gap is already very small. Therefore, we can conclude that the desired band ordering, which can be obtained for uniaxial strain, is stable with regard to small additional strains perpendicular to the $c$ axis.

We also checked whether a particular substrate can lead to lattice strain in the interesting regime. Some wurtzite substrates and their lattice mismatch relative to hex-Ge are listed in Table III, and the resulting strain of the most interesting substrates is indicated in Fig. 5. None of the considered substrates could induce the desired results, but one could use either wz-GaAs or wz-AlAs as a substrate to grow almost strain-free hex-Ge. Wz-InP (wz-GaP, hex-Si) can serve as substrate for tensile (compressive) strain in hex-Ge overlayers.

### V. OPTICAL PROPERTIES

Always in view of optoelectronic applications, we analyze how the pseudodirect-to-direct band-gap transition induced by tensile uniaxial strain affects the optical properties near the fundamental band edge.

We calculate the dielectric tensor components $\delta_{ij}(\omega)$ in the independent-particle approximation using the optical matrix elements $\langle \epsilon|\mathbf{p}|\mathbf{v}\rangle$ of the momentum operator $\mathbf{p}$ between conduction band $c$ and valence band $v$ at a given $k$-point applying the longitudinal gauge [43]. The diagonal elements of the imaginary part of the dielectric tensor are given by

$$
\text{Im} \delta_{ii}(\omega) = \frac{1}{\Omega} \sum_{\mathbf{k},\mathbf{v}} w_k \left| \langle \epsilon \mathbf{k} | \mathbf{p} | \mathbf{v} \rangle \right|^2 \times \\
\delta(\omega_{c\mathbf{k}} - \omega_{v\mathbf{k}} - \omega), \tag{12}
$$

where the valence and conduction band energies are denoted by $\hbar \omega_{c\mathbf{k}}$ and $\hbar \omega_{v\mathbf{k}}$, respectively. The crystal volume is denoted by $\Omega$ and $w_k$ is the $k$-point weight.

The global effect of tensile uniaxial strain on optical properties is illustrated in Fig. 6, where we show the imaginary part of the frequency-dependent dielectric tensor components $\delta_{ij}(\omega)$.
(a) biaxial strain along the [11\(\overline{2}\)0] and [0001] directions

(b) biaxial strain along the [\(\overline{1}100\)] and [0001] directions

Figure 5. Conduction-band ordering at \(\Gamma\) and size of fundamental band gap for biaxial strain in the \{\(\overline{1}100\}\} plane along the [11\(\overline{2}\)0] and [0001] directions (a) and in the [1\(\overline{1}00\)] plane along the [1\(\overline{1}00\)] and [0001] directions (b). In the white areas, the system is either metallic or the fundamental gap is indirect. The relative lattice mismatch of hex-Ge assuming pseudomorphic growth on wz-GaAs, wz-AlAs, and wz-InP substrates is indicated (see Table III).

\((j = \perp, ||)\) and the temperature-dependent radiative lifetimes \(\tau\) which are calculated as detailed in Ref. [10].

Unstrained hex-Ge does not exhibit an absorption peak at the fundamental band gap of 0.3 eV. The first peak rather occurs at 0.6 eV, the energy of the strong dipole transition between the highest valence band and the \(\Gamma_{7c}\) state. For increasing tensile uniaxial strain, this absorption peak shifts to lower energies, until it coincides with the band-gap energy for tensile uniaxial strains above 1.5% as a consequence of the conduction-band inversion. For strains beyond the band-inversion point, the slope of the absorption edge is much steeper which is typical for a direct semiconductor with dipole-allowed transitions at the absorption edge. The analysis of the optical transition matrix elements at \(\Gamma\) as a function of uniaxial strain along the \(c\)-axis reveals an overall rather weak effect on the optical matrix elements. The smaller band gap for increasing strain induces an increased value of the dielectric function component at the absorption edge, that is not compensated by the concomitant slight decrease of the optical matrix element of the \(\Gamma_{9v}^+ \rightarrow \Gamma_{7c}^-\) transition.

The occurrence of band inversion for moderate uniaxial strain along the \(c\)-axis is also obvious from the behaviour of the radiative lifetime. Tensile uniaxial strain above 1.5% gives rise to drastic changes of the radiative lifetime. Below 1.5% of strain, the lifetime curve shows the typical behavior of a system with two decay channels: a low-energy transition with small matrix element and a high-energy transition with large matrix elements [10]. Upon increasing temperature, the impact of the high-energy transition becomes stronger and the lifetime drops by several orders of magnitude. The large low-temperature lifetime of \(\sim 10^{-4}\) s is typical for a non-emitting system, the high-temperature value of \(\sim 10^{-7}\) s rather corresponds to a direct semiconductor. For uniaxial strains above the pseudodirect-to-direct gap transition, the lifetime is of the order of \(\sim 10^{-3} - 10^{-7}\) s and largely constant over the entire temperature range. This behaviour is characteristic for a
system with one dominating decay channel as the band-edge transition in direct semiconductors [10] and shows that the strong dipole transition at the band gap outweighs all the rest. The optical properties of uniaxially strained hex-Ge show that the material is an efficient light absorber with a dipole active direct-gap transition and low radiative lifetimes. Therefore, it is an interesting candidate material for silicon-technology based active optical devices which can compete with the light-emission efficiency of present-day III-V semiconductor devices.

VI. SUMMARY AND CONCLUSIONS

In summary, we have explored various possibilities to turn hexagonal Ge in the lonsdaleite phase with its pseudodirect band gap into a direct semiconductor with light-emission efficiencies suitable for technological applications. To this end, we investigated the impact of hydrostatic pressure, biaxial strain, and uniaxial strain on the electronic structure and the optical properties of hex-Ge. Hydrostatic pressure turns out unsuitable to obtain the desired modification of the conduction-band ordering and the concomitant pseudodirect-to-direct gap transition, as it occurs only for technically not accessible negative pressures. For biaxial strain within the hexagonal plane, either an insulator-to-metal transition occurs or the material becomes indirect before the conduction-band ordering changes.

For moderate tensile uniaxial strains between 1.5 % and 4 %, the desirable band inversion between the \( \Gamma_{8c} \) and \( \Gamma_{7c} \) conduction states is predicted by our calculations. The resulting gaps vary between 0.4 and 0 eV. Such strains are within reach of experimental realization. We could also show that small additional strain within the hexagonal plane, as they may occur in practical technological growth processes, have only little impact on the electronic structure. Uniaxially strained hex-Ge could, for instance, be pseudomorphically grown on the facets of III-V wurtzite-semiconductor nanowires.

The inversion of the two lowest conduction minima at \( \Gamma \) makes hexagonal germanium an excellent absorber or emitter, with a radiative lifetime smaller by three order of magnitudes than the one of the unstrained material. Provided that a suitable growth method can be found, hex-Ge can be used as a direct light emitter compatible with CMOS technology. Another unexplored route that deserves future attention is the combination of strain with alloying of Ge and Si to control the size of the band gap and the conduction-band ordering at \( \Gamma \) at the same time.

ACKNOWLEDGMENTS

This work is supported by the European Commission in the framework of the H2020 FET Open project SiLAS (GA No. 735008). C. R. acknowledges financial support from the Marie Sklodowska-Curie Actions (GA No. 751823). Computing time was granted by the Leibniz Supercomputing Centre on SuperMUC (project No. pr62ja).

1. D. A. B. Miller, Proc. IEEE 97, 1166 (2009).
2. S. Srinivasan, A. Arrighi, M. J. R. Heck, J. Hutchinson, E. Norberg, G. Fish, and J. E. Bowers, IEEE J. Sel. Top. Quantum Electron. 20, 8 (2014).
