

Ab initio study of elastic, vibrational, and thermal properties of lonsdaleite $\text{Si}_x\text{Ge}_{1-x}$ alloysPedro Borlido,^{1,2,3} Friedhelm Bechstedt,^{1,2} Claudia Rödl,^{1,2} and Silvana Botti^{4,1,2,*}¹*Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany*²*European Theoretical Spectroscopy Facility (ETSF)*³*CFisUC, Department of Physics, University of Coimbra, Rua Larga, 3004-516 Coimbra, Portugal*⁴*Research Center Future Energy Materials and Systems of the University Alliance Ruhr and Interdisciplinary Centre for Advanced Materials Simulation, Faculty of Physics and Astronomy, Ruhr University Bochum, Universitätsstraße 150, D-44801 Bochum, Germany*

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We investigate elastic, vibrational, and thermal properties of hexagonal (lonsdaleite) $\text{Si}_x\text{Ge}_{1-x}$ alloys in the framework of density functional theory. We calculate elastic stiffness constants and phonon frequencies across the full composition range and analyze their dependence on chemical composition and atomic arrangement. While the elastic moduli show an almost linear composition dependence, phonon energies and dispersion are significantly affected by the specific arrangement of Si and Ge atoms on the hexagonal lattice sites. From the elastic properties, we determine the propagation of sound waves and the critical layer thickness for epitaxial growth. We further analyze global thermal quantities including heat capacities and thermal expansion coefficients as functions of composition and temperature, revealing negative thermal expansion at low temperatures. All calculated properties are compared with theoretical and experimental results for cubic $\text{Si}_x\text{Ge}_{1-x}$ alloys, revealing remarkable quantitative similarities, attributed to the identical tetrahedral coordination of both structures.

DOI: [10.1103/h7wy-1srx](https://doi.org/10.1103/h7wy-1srx)**I. INTRODUCTION**

Since the invention of the transistor, modern technology has been closely linked to the development of semiconductor materials. Among these, silicon (Si), which crystallizes in the cubic diamond structure, stands out as the most pivotal. This semiconductor possesses remarkable properties, including abundance on Earth, high purity, strong covalent bonding, low thermal expansion, presence in different crystal structures, and an indirect energy gap. The stability of its oxide SiO_2 , which acts as an excellent insulator and passivation layer, is vital for the creation of high-quality electronic components and renders Si a preeminent choice for the microelectronics industry [1]. Furthermore, by incorporating germanium (Ge) into Si to form $\text{Si}_x\text{Ge}_{1-x}$ alloys, it becomes possible to finely tune the material's electronic characteristics, achieving reduced energy gaps with smaller energy separation between direct and indirect band transitions, and enhancing transport properties by modulating the effective carrier masses [2].

However, the inherent indirect band gap of cubic $\text{Si}_x\text{Ge}_{1-x}$ alloys presents a significant hurdle for their application in active optoelectronic devices and inter-chip communication [3]. Fortunately, both theoretical and experimental advancements

have demonstrated that this limitation can be surmounted by adopting hexagonal $\text{Si}_x\text{Ge}_{1-x}$ alloys, known for their direct semiconductor properties and, in particular, a strong light emission when the Ge content is above $\sim 65\%$ [4,5].

These alloys are based on metastable Ge and Si allotropes with the lonsdaleite (2H) crystal structure (space group $P6_3/mmc$, D_{6h}^4 , see Fig. 1) [4,6]. Lonsdaleite-structure Si is the most extensively studied Si polytype following cubic diamond-structure (3C) Si, and it has been successfully synthesized through a range of methods, as documented in various studies [7–13]. Notably, lonsdaleite Si has been found in core-shell nanowires [11,14,15]. The recent discovery of 4H-Si nanoplatelets further expands the range of applications by other polytypes [16]. The transformation of cubic Si into hexagonal polytypes has been observed in various scenarios, including high-temperature indentation [17], plastic deformation [18], ion implantation [19], low-pressure chemical vapor deposition [20], pulsed laser-beam annealing [21], and nanoribbon growth [22]. Production of lonsdaleite Ge ribbons within a diamond-structure Ge matrix dates back three decades, as evidenced by earlier studies [23–25]. More recently, researchers have harnessed innovative techniques, such as room-temperature nano-indentation [26] and low-pressure ultraviolet laser ablation [27,28], to induce the formation of hexagonal phases of Ge. Much like for their Si counterparts, various pathways to achieve hexagonal Ge nanowires have been explored [5,15,29–31]. Notably, in addition to the 2H polytype, other hexagonal forms of Ge, such as 4H-Ge, have also been documented in previous studies [32–35].

Despite the successful growth of $\text{Si}_x\text{Ge}_{1-x}$ alloys on various substrates [5] and the initial experimental characterization

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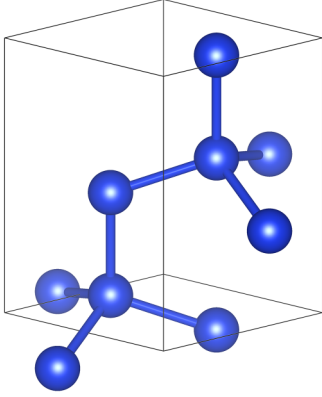


FIG. 1. Lonsdaleite (2H) unit cell prototype. The different four-atom alloys used in this work, derived from this structure, are presented in Fig. S1 in the Supplemental Material (SM) [36], along with symmetry information.

of lattice dynamics [37], complemented by theoretical explorations from first principles [38–40], crucial structural properties of these hexagonal materials remain less studied when compared to their cubic counterparts. Among the enigmatic aspects are the composition dependence of their elastic properties and lattice vibrations, as well as the composition effects on epitaxy and temperature-dependent behavior.

The primary objective of this study, therefore, is to conduct an exhaustive investigation of elastic, vibrational, and thermal properties of 2H-Si_xGe_{1-x} alloys using the framework of density functional theory (DFT). This research encompasses an in-depth exploration of phonon-dispersion relations, elastic coefficients and their implications for potential pseudomorphic growth, as well as the effects of lattice vibrations on temperature-dependent lattice expansion, energetics, and caloric properties. A deep understanding of these aspects is, in fact, essential in shaping the future of research into epitaxial structures for the practical utilization of this emerging material.

II. METHODS

All DFT calculations were conducted with the VIENNA AB-INITIO SOFTWARE PACKAGE (VASP, version 5.4.4) [41,42]. A kinetic-energy cutoff of 500 eV was consistently applied in all calculations. Γ -centered $\mathbf{k}$ -point grids with a density of 5000 $\mathbf{k}$ points per reciprocal atom were used throughout the calculations, which corresponds to a Γ -centered $12 \times 12 \times 6$ grid for the primitive Ge lonsdaleite cell. Geometry optimizations were performed until all forces on atoms were less than 10^{-3} eV/Å. Except for phonon calculations, we used the Perdew-Burke-Ernzerhof revised for solids (PBEsol) [43] approximation to the exchange-correlation functional.

Bulk moduli were calculated by fitting the Vinet equation of state [44] to the energy-versus-volume curve of structures optimized at fixed volume, over a range of approximately $\pm 5\%$ of the lattice vectors (equivalent to about $\pm 15\%$ of the optimized volume).

The ordered alloys under study in Fig. S1 in the Supplemental Material (SM) [36] belong to either the $6/mmm$, $\bar{6}m2$, or $3m/\bar{3}m$ point groups. For these point groups, the stiffness

tensor (using Voigt's notation [45]) has the general form [46],

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{pmatrix}, \quad (1)$$

where $C_{66} = (C_{11} - C_{12})/2$ (and $C_{14} = 0$ for $6/mmm$ and $\bar{6}m2$ structures). The physical significance of this relationship stems from the symmetry constraints of the hexagonal crystal system. We strained the cells according to the deformation potentials and strain tensors indicated in Table S3 in the SM [36], in steps of 1% within $\pm 5\%$. From the fit to the resulting data, a set of linear equations for the nonzero C_{ij} was obtained and solved. We note that this is a simpler approach than the one used in high-throughput studies [47] and that it is in our case manageable thanks to the simple form of the stiffness tensor for the small cells in question.

Under the reasonable assumption of an isotropic polycrystalline material, we can use the Hill average [48] of the bulk and shear moduli (B_H and G_H , respectively) to calculate the speed of sound [49]. The Hill average represents the arithmetic mean of the Voigt (upper) and Reuss (lower) bounds and provides a reliable estimate of the effective elastic properties of polycrystalline materials. For longitudinal waves, the speed of sound is given by

$$v_l = \sqrt{\frac{B_H + \frac{4}{3}G_H}{\rho}} \quad (2)$$

and for transversal waves by

$$v_t = \sqrt{\frac{G_H}{\rho}}, \quad (3)$$

where ρ is the mass density of the alloy. These equations describe the propagation speed of pressure waves (longitudinal) and shear waves (transversal) through the material. We also define their average,

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3}, \quad (4)$$

which is needed for the calculation of the Debye temperature.

From the latter quantity, we can obtain an estimate of the Debye temperature as [49]

$$T_D = \frac{h}{k_B} \left[\frac{3}{4\pi} \frac{N_A n \rho}{M} \right]^{1/3} v_m, \quad (5)$$

where h and k_B are Planck's and Boltzmann's constants, N_A is the Avogadro number, M is the molecular weight of the solid, and n is the number of atoms in the unit cell. We can simplify the expression using the definition of the volume per atom in the unit cell, denoted as $V_a = M/(N_A \rho n)$. The Debye temperature provides a characteristic temperature scale for the vibrational properties of the material and is related to the maximum phonon frequency in the material.

For phonon calculations, we applied the local-density approximation (LDA), relying on the Perdew-Zunger

parametrization for the correlation energy of the homogeneous electron gas (PZ91) [50]. The dynamic matrices were calculated using the finite-differences method, as implemented in the PHONOPY package [51,52]. To this end, supercells of dimensions $4 \times 4 \times 2$ were chosen to ensure convergence of the phonon frequencies (see Fig. S5 in the (SM) [36] for a detailed convergence analysis).

For the substrate compatibility analysis, we used the Materials Project database [53] to identify potential substrates for epitaxial growth. We calculated the lattice mismatch f between the SiGe alloys and potential substrates using the formula $f = (a_{\text{sub}} - a_{\text{SiGe}})/a_{\text{sub}}$, where a_{SiGe} is the in-plane lattice parameter of the alloy and a_{sub} is the corresponding substrate parameter.

The critical thickness for epitaxial growth was estimated using Fischer's model [54], which balances the forces on dislocation lines. This model provides the critical thickness as a function of the Burgers vector, the geometric arrangement of dislocations, and the strain due to lattice mismatch.

Thermal properties (thermal expansion coefficient, lattice heat capacity, etc.) at constant pressure were obtained using the quasi-harmonic approximation, which accounts for the volume dependence of phonon frequencies. This approach involves fitting phonon calculations performed on the optimized structure at different volumes, as implemented in the PHONOPY package [51,52]. The thermal expansion coefficient was calculated from the temperature dependence of the equilibrium volume, while heat capacities were obtained by taking appropriate derivatives of the Helmholtz free energy.

Directionally averaged Raman spectra were computed within the nonresonant approximation using the `vasp_raman` tool [55]. We used the phonon frequencies and amplitudes obtained with LDA. To address the inadequate description of the electronic structure of Ge-rich compounds by standard LDA/GGA functionals, we computed the dielectric tensor from the $\omega \rightarrow 0$ limit of the frequency-dependent dielectric function calculated with the modified Becke-Johnson potential [56]. We neglect ionic contributions, expected to be small given the covalent nature of the material. We validated this approach by comparing our results with other methods, as presented in the SM [36].

III. RESULTS

A. Elastic properties

We begin our investigation by examining the bulk modulus B , defined as

$$B = -V \frac{\partial p}{\partial V}, \quad (6)$$

where p is the hydrostatic pressure. For 2H-Si_xGe_{1-x} alloys, we analyze how this fundamental elastic parameter varies with composition. These calculations were performed for all unique eight-atom cells of ordered SiGe alloys (see Ref. [57] for the construction of the cells), and the resulting data points are presented in Fig. 2.

For pure hexagonal Ge and Si, we obtain bulk moduli of 68 GPa and 94 GPa, respectively, which align closely with previous findings [4,6,58,59]. Notably, these values are remarkably similar to those reported for cubic polymorphs,

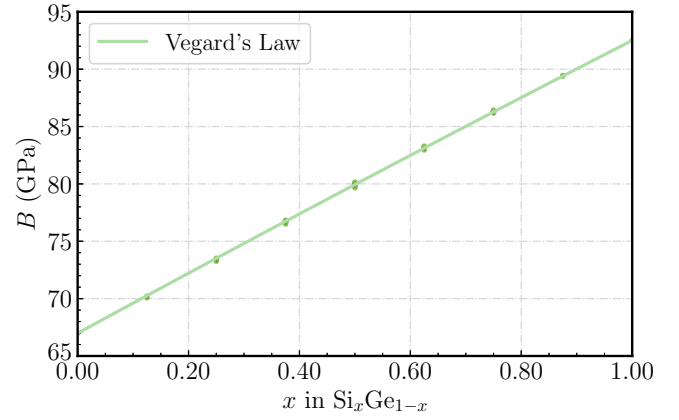


FIG. 2. Evolution of the bulk modulus as a function of Si content for hexagonal Si_xGe_{1-x} alloys. The continuous line represents the linear fit to Eq. (7).

reflecting the comparable tetrahedral coordination in both structures.

For the alloy compositions, we observe an almost linear variation of the bulk modulus B with Si content. At $x = 0.5$ (the composition with the most significant dispersion), the maximum difference between different atomic arrangements is only 0.5 GPa, representing less than 1% of the average bulk modulus at that composition. Fitting the data to a quadratic equation with a bowing parameter [60,61],

$$B(x) = B_{\text{Si}}x + (1-x)B_{\text{Ge}} + bx(1-x), \quad (7)$$

yields a bowing parameter b of 0.93 GPa. This value corresponds to only 1.1–1.5% of the bulk modulus across the observed compositional range, confirming the near-linear relationship between composition and bulk modulus. Although we cannot directly extrapolate this linear behavior to all other mechanical and dynamical properties of Si_xGe_{1-x} alloys, it serves as an important indicator of the compositional dependence of elastic properties.

A more comprehensive understanding of the mechanical behavior of these ordered alloys requires calculation of the complete stiffness tensor. Here, we focus on the four-atom unit cells described earlier. Table I presents the calculated elastic constants C_{ij} for these ordered alloys, along with the bulk moduli obtained from the Vinet equation of state. Due to the high symmetry of these materials, the bulk modulus can be expressed directly in terms of the elastic constants as

$$B = \frac{(C_{11} + C_{12})C_{13} - 2C_{13}^2}{C_{11} + C_{12} + 2(C_{33} - C_{13})}. \quad (8)$$

The values obtained through this relationship agree well with those derived from equation-of-state fitting.

As expected, we observe a systematic increase in elastic constants from 2H-Ge to 2H-Si, corresponding to the observed increase in stiffness with increasing Si content. We note that, as discussed in the Methods section, some of the C_{14} constants should be 0 from symmetry arguments, but are actually extremely small (albeit finite). This result is likely due to numerical inaccuracies and provides an estimate of our computational precision on the constants. The results for the

TABLE I. Elastic constants C_{ij} (in GPa) of the ordered hexagonal $\text{Si}_x\text{Ge}_{1-x}$ compounds with four atoms in the unit cell. The bulk moduli B (in GPa) obtained from the Vinet equation of state are also listed. For comparison, values for the cubic (3C) polymorphs are given in the Cartesian system where the z axis is aligned with the [111] crystallographic direction (calculated using values from Ref. [62]), see also Table S1 in the SM [36].

ID	x	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	C_{66}	B
Ge	0.00	138	41	25	0	161	38	49	68
SiGe_3	0.25	153	44	27	0	175	42	54	74
$\text{Si}_2\text{Ge}_2\text{-I}$	0.50	167	45	29	1	191	45	61	81
$\text{Si}_2\text{Ge}_2\text{-II}$	0.50	166	46	29	-1	189	44	60	81
$\text{Si}_2\text{Ge}_2\text{-III}$	0.50	162	49	30	-1	188	43	57	81
Si_3Ge	0.75	176	51	33	-1	201	46	63	87
Si	1.00	185	54	38	0	211	47	65	94
3C-Ge	0.00	138	39	27		149	44	50	
3C-Si	1.00	180	56	44		192	56	62	

three different atomic arrangements at $x = 0.5$ show relatively small dispersion, further confirming that composition has a more significant impact than the specific atomic configuration in this hexagonal group-IV system.

To facilitate direct comparison with cubic polymorphs, we calculated the elastic constants of 3C-Si and 3C-Ge in a reference frame where the z axis aligns with the [111] crystallographic direction [63,64] (see the (SM) for details [36]). The resulting values, computed from the PBEsol elastic constants reported in Ref. [62], are presented in the bottom rows of Table I.

These results reveal that not only are the bulk moduli of 2H and 3C polymorphs nearly identical for both Si and Ge, but the individual elastic constants also exhibit remarkable similarity. This correspondence stems from the tetrahedral coordination that is common to both crystal structures, which dominates the elastic response despite the different crystal symmetries.

Using the stiffness tensor, we can characterize the directional elastic response of the material through three fundamental parameters: Young's modulus E , the shear modulus G , and the Poisson ratio ν . Young's modulus is the most straightforward of these quantities, measuring the stress-to-strain ratio along a single specified direction. In contrast, both Poisson ratio and shear modulus depend on two directions—one for the applied strain and another perpendicular direction for measuring the response—making their full characterization more complex. To address this complexity, we analyze the maximum and minimum values of ν and G by systematically varying the orientation of the second direction, following the methodology described in Ref. [65]. Detailed directional plots of these elastic parameters are provided in Figs. S2–S4 in the SM [36].

Our analysis reveals macroscopic isotropy in the xy plane, consistent with the hexagonal symmetry of the crystal structure. In contrast, the elastic response in the xz and yz planes exhibits a pronounced lobular structure, reflecting the anisotropy between in-plane and out-of-plane properties. As expected, both the maximum and minimum values of Young's modulus ($E_{\max}$ and $E_{\min}$) increase systematically with Si concentration, reflecting the stronger covalent bonding in Si

compared to Ge. Interestingly, the anisotropy ratio $E_{\max}/E_{\min}$ remains nearly constant across the composition range, indicating that the directional character of the elastic response is preserved regardless of composition. Similar behavior is observed for the shear modulus, suggesting that the underlying bond directionality determines the elastic anisotropy pattern.

Beyond single-crystal properties, we also examine the average elastic response of untextured polycrystalline materials. This polycrystalline analysis serves two important purposes. First, it provides predictions relevant to experimental characterization, as many measurements are performed on polycrystalline samples due to the challenges in growing high-quality single crystals. Second, it enables meaningful comparisons between materials of different crystallographic symmetries by evaluating their orientation-averaged properties.

For polycrystalline materials, the elastic moduli (Young's modulus E , shear modulus G , bulk modulus B , and Poisson ratio ν) are bounded by the Voigt and Reuss averaging schemes [45,66], which provide theoretical upper and lower limits, respectively. The Voigt average assumes uniform strain throughout the polycrystal, while the Reuss average assumes uniform stress. The Hill average [48], which is the arithmetic mean of these two bounds, typically provides a reliable estimate of the effective elastic properties. Throughout this work, we denote these different averaging schemes using the subscripts V, R, and H, respectively.

From the average moduli, we calculate the universal anisotropy index [67]

$$A_U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6. \quad (9)$$

This dimensionless parameter provides a unified measure of elastic anisotropy that is valid for all crystal systems [68]. Values of $A_U = 0$ indicate perfect isotropy, while positive values quantify the degree of anisotropy. We also calculate the sound velocities and Debye temperature using Eqs. (2) through (5). Table II summarizes these polycrystalline averaged properties.

Since the differences between Voigt and Reuss averages are small for these systems, Table II presents only the Hill averages (the complete set of Voigt, Reuss, and Hill averages is provided in Table S4 in the SM [36]). The ratios $B_V/B_R \approx 1$ and $G_V/G_R \approx 1$ across the entire composition range, which is characteristic for hexagonal crystals with moderate anisotropy [47,67]. Notably, the polycrystalline elastic properties of cubic Si and Ge closely match those of their hexagonal counterparts, with cubic Ge showing slightly smaller values and cubic Si exhibiting slightly larger values than their respective hexagonal polymorphs.

All elastic moduli (B_H , E_H , and G_H) show a systematic increase with Si concentration, reflecting the stronger interatomic bonding in Si. This compositional stiffening directly influences the sound propagation, with the average sound velocity increasing from 3.3 km s^{-1} for 2H-Ge to 5.6 km s^{-1} for 2H-Si. The Poisson ratio, however, remains nearly constant at approximately 0.22–0.23 across the composition range. The universal anisotropy index A_U shows only a modest increase from 0.21 for 2H-Ge to 0.25 for 2H-Si, indicating that

TABLE II. Hill averages of the bulk modulus B_H , Young's modulus E_H , shear modulus G_H , and Poisson ratio ν_H , along with the universal anisotropy index A_U , the transverse, longitudinal, and mean sound velocities (v_t , v_l , and v_m , respectively) and Debye temperature T_D for the hexagonal $\text{Si}_x\text{Ge}_{1-x}$ ordered alloys. Sound velocities and Debye temperatures were calculated using Eqs. (2) through (5). For comparison, corresponding values for cubic Si and Ge are included. Values for the cubic polymorphs were computed using the elastic constants from Ref. [62].

ID	x	B_H (GPa)	E_H (GPa)	G_H (GPa)	ν_H	A_U	v_t (ms ⁻¹)	v_l (ms ⁻¹)	v_m (ms ⁻¹)	T_D (K)
Ge	0.00	69	115	47	0.22	0.21	2981	4987	3299	347
SiGe ₃	0.25	75	127	52	0.22	0.22	3340	5570	3695	393
SiGe-I	0.50	81	139	57	0.22	0.24	3803	6315	4205	452
SiGe-II	0.50	81	137	56	0.22	0.25	3769	6291	4170	448
SiGe-III	0.50	81	133	54	0.23	0.24	3719	6253	4118	442
Si ₃ Ge	0.75	87	144	59	0.23	0.25	4305	7236	4766	518
Si	1.00	93	149	60	0.23	0.25	5097	8646	5648	619
3C-Ge	0.00	68	119	49	0.21	0.34	3055	5029	3375	354
3C-Si	1.00	93	152	62	0.23	0.25	5153	8694	5707	625

the degree of elastic anisotropy is largely preserved across the composition range.

The Debye temperature follows the same compositional trend observed in cubic $\text{Si}_x\text{Ge}_{1-x}$ alloys [69]. The higher value for Si (619 K) compared to Ge (347 K) stems from Si's lower atomic volume, lower density, and higher elastic moduli. These calculated values for the hexagonal polymorphs closely match those of their cubic counterparts (354 K for cubic Ge and 625 K for cubic Si) and agree well with experimental measurements of 360–374 K and 625–645 K, respectively [70,71].

B. Epitaxial growth considerations

Currently, hexagonal $\text{Si}_x\text{Ge}_{1-x}$ alloys have been produced only in nanowire configurations [5], limiting their applicability. Achieving desirable opto-electronic integration remains an open challenge. From a theoretical perspective, we can explore two critical aspects of epitaxial growth: identifying suitable substrates with minimal lattice mismatch and determining the critical thickness for pseudomorphic growth before defect formation.

For pseudomorphic growth, the material and substrate must have similar in-plane lattice parameters. When this condition is not met, the lattice mismatch generates internal strains or stresses, leading to the growth of islands in the Volmer-Weber or Stranski-Krastanov modes, rather than the desirable two-dimensional Frank-Van der Merwe growth [72]. A fundamental consequence of lattice mismatch is the accumulation of interfacial stress at the heterointerface. The epitaxial film can accommodate this stress only up to a certain thickness—the critical thickness—beyond which the formation of defects or dislocation lines becomes energetically favorable, disrupting pseudomorphic growth. To determine this critical thickness, we employ the theoretical model developed by Fischer *et al.* [54], which is based on the force balance of dislocation lines. This model provides the critical thickness h_c for a heterostructure as the solution to the implicit equation

$$h_c = \frac{b \cos \lambda}{2f} \left[1 + \frac{1 - \nu \cos^2 \alpha}{4\pi(1 + \nu) \cos^2 \lambda} \ln \left(\frac{h_c}{b} \right) \right], \quad (10)$$

where b represents the magnitude of the Burgers vector, α is the angle between the Burgers vector and the misfit dislocation direction, and λ is the angle between the Burgers vector and the direction in the interface normal to the dislocation line [54,73]. The parameter f denotes the strain with respect to the substrate, while ν represents the Poisson ratio, which for growth along [0001] with equibiaxial strain equals $\nu = 2C_{13}/C_{33}$.

Although 2H- $\text{Si}_x\text{Ge}_{1-x}$ has thus far been synthesized only in nanowire configurations, we can gain valuable insights by examining similar wurtzite and wurtzitelike materials (e.g., InGaN [74] or AlGaN [75]). For wurtzite systems grown along the [0001] direction, the most energetically favorable slip systems are $1/3\langle 11\bar{2}3 \rangle\{11\bar{2}2\}$ and $1/3\langle 11\bar{2}3 \rangle\{1\bar{1}01\}$ [74,76]. We adopt these as reasonable approximations for our hexagonal $\text{Si}_x\text{Ge}_{1-x}$ system.

Figure 3 presents the calculated critical thickness for 2H- $\text{Si}_x\text{Ge}_{1-x}$ films deposited on 2H-Ge (0001), obtained using Eq. (10). These values were determined by linearly interpolating the relevant parameters between the pure end compounds.

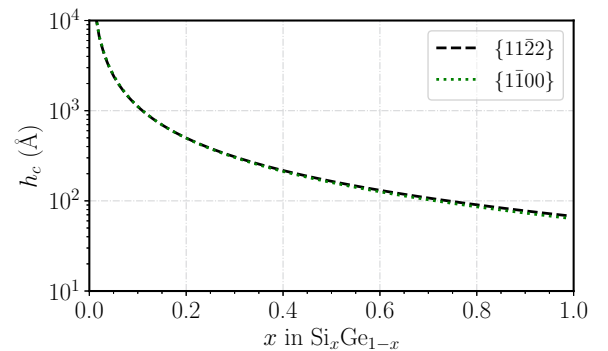


FIG. 3. Estimated critical thickness for the $1/3\langle 11\bar{2}3 \rangle\{11\bar{2}2\}$ and $1/3\langle 11\bar{2}3 \rangle\{1\bar{1}01\}$ slip systems of 2H- $\text{Si}_x\text{Ge}_{1-x}$ alloys deposited on [0001] 2H-Ge, as a function of Si concentration. For the application of Fischer's formula, we considered $b = \sqrt{a^2 + c^2}$, $\alpha = \pi/2$, and $\lambda = \arccos(a/\sqrt{a^2 + c^2})$ for the $1/3\langle 11\bar{2}3 \rangle\{11\bar{2}2\}$ system; for the $1/3\langle 11\bar{2}3 \rangle\{1\bar{1}01\}$ system, we used $b = \sqrt{a^2 + c^2}$, $\alpha = \arccos(1/2 \cdot a/\sqrt{a^2 + c^2})$, and $\lambda = \arccos(\sqrt{3}/2 \cdot a/\sqrt{a^2 + c^2})$.

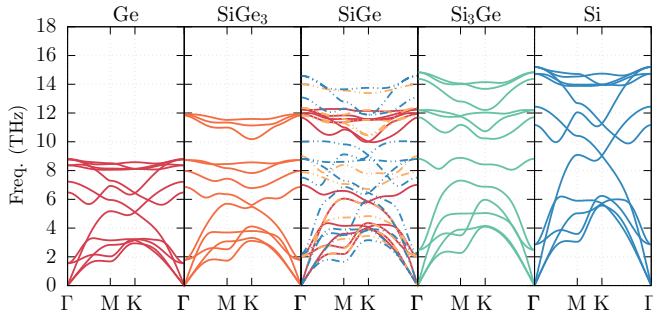


FIG. 4. Phonon band structures of the four-atom unit cells. Composition is indicated above the respective plot. For Si_2Ge_2 , the only case where there are multiple cells, the red, orange, and blue dashed curves correspond to the Si_2Ge_2 -I, Si_2Ge_2 -II, and Si_2Ge_2 -III arrangements, respectively.

The compositional dependence closely resembles the one observed in cubic Si/Ge heteroepitaxial systems, which can be expected given the mechanical similarities between the different polymorphs.

It is *a priori* possible to identify materials which in theory provide a decent substrate for growth, using for example the algorithm of Zurr and McGill [77] alongside available crystal structure databases. This will in fact provide several options within the necessary lattice mismatch range (see the SM [36]). However, it is important to note that this analysis does not account for growth temperature effects, kinetic limitations, or initial dislocation densities—factors that would require more sophisticated modeling beyond the scope of this study.

C. Phonons and thermodynamics

In Fig. 4, we present the phonon band structures for the ordered $2\text{H-Si}_x\text{Ge}_{1-x}$ structures with four atoms in the unit cell. The convergence of phonon branches and related thermal properties is demonstrated in Fig. S5 in the SM [36]. Our calculations show good agreement with previous theoretical investigations [38]. The evolution of the phonon density of states with composition is shown in Fig. S6 in the SM [36].

Qualitatively, the phonon band structures of 2H-Ge and 2H-Si exhibit similar features despite their different frequency ranges. The most significant differences can be attributed to the mass difference between the constituent atoms. Given that $M_{\text{Ge}}/M_{\text{Si}} \approx 2.6$, simple harmonic oscillator physics suggests that $\omega_{\text{Si}}/\omega_{\text{Ge}} \approx 1.6$, which is consistent with our calculated frequency ratios. For the intermediate compositions, several distinct features emerge as a consequence of the varying arrangements of Ge-Ge, Si-Si, and Ge-Si bonds. Notably, we observe phononic band gaps of varying magnitudes across the ordered alloy structures. However, it is important to recognize that these gaps are characteristic of the perfectly ordered configurations and would likely be diminished in real random alloys, where a broader distribution of local atomic environments exists. The dispersion of the three lowest acoustic phonon branches remains real for all structures, confirming the dynamic stability of all atomic arrangements.

Since we have access to the phonon frequencies, we can also examine the Raman spectra of the ordered alloys. The

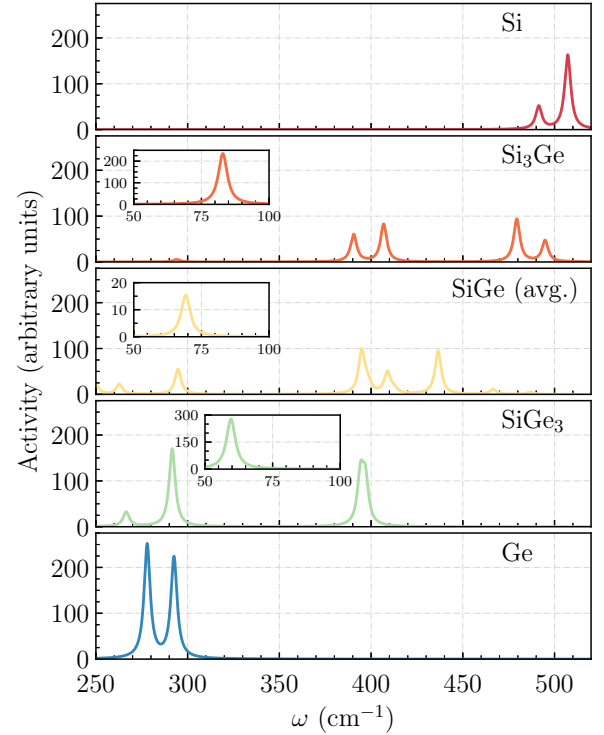


FIG. 5. Comparison of Raman spectra for the different compositions. For the case of SiGe, the average of the three nonequivalent cells is presented.

results, presented in Fig. 5, are in general agreement with previous calculations [40] and experimental measurements [37] and showcase the expected behavior for alloying. Unlike carbon lonsdaleite where the A_{1g} and E_{1g} modes are well separated [78], in hex-Si and hex-Ge the frequencies associated with these modes are separated by less than 1 cm^{-1} , making it difficult to resolve these Raman-active peaks. For intermediate compositions, the spectra become more complex due to additional features associated with different Si-Ge bonding configurations. However, these features should be interpreted carefully given that we are not considering effects of disorder. For example, prominent Raman-active peaks that appear for Si_3Ge , SiGe_3 , and one of the SiGe cells (associated with E, E, and E" modes, respectively) will likely become less intense and broader in a real alloy [79].

To further understand the vibrational properties under different conditions, we also investigated the effects of external stress and strain. As an illustrative example, we examined the influence of hydrostatic pressure by performing calculations on cells optimized at the same fixed volume steps used for determining the bulk modulus.

The most striking observation under pressure is the development of a pronounced soft mode at the M point of the Brillouin zone in lonsdaleite structures, as illustrated in Fig. 6. As pressure increases, this mode softens progressively until it becomes imaginary, signaling a dynamical instability at higher pressures (lower volumes). For clarity, we focus primarily on 2H-Si, although similar behavior was observed across all compositions, with the precise pressure threshold varying with the alloy composition. Figure 6 illustrates the

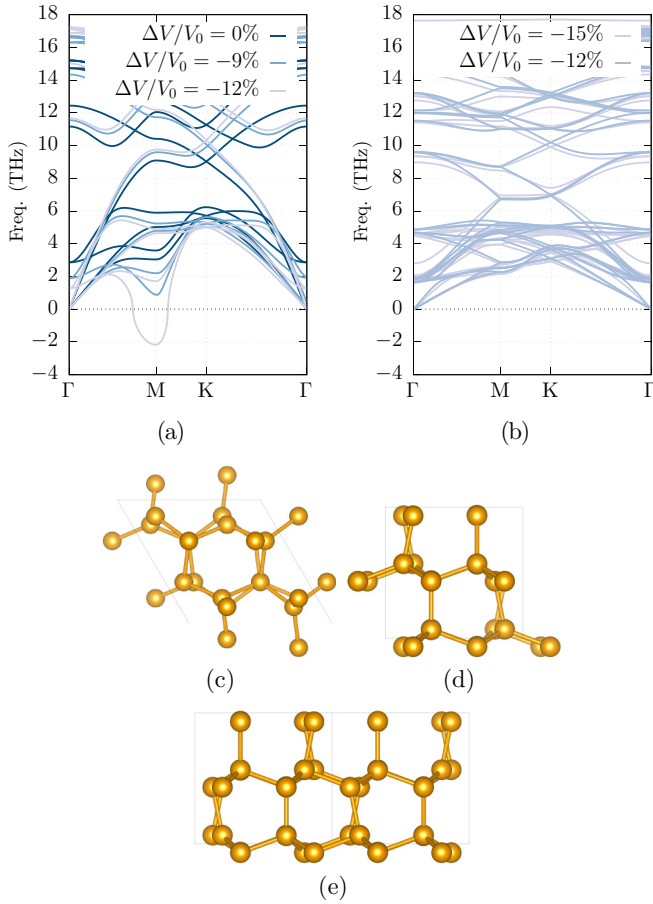


FIG. 6. Phonon band structure of 2H-Si under pressure. Panel (a) shows the four-atom unit cell results, while panel (b) presents the band structure of a $2 \times 2 \times 1$ supercell with 16 atoms, relaxed under pressure. The crystal structure of the supercell at $\Delta V/V_0 = -15\%$ is visualized from three crystallographic directions: (c) [0001], (d) $[1\bar{1}00]$, and (e) $[1\bar{1}20]$.

evolution of the phonon band structure for 2H-Si under increasing pressure. The transition to instability occurs between volume compressions of $\Delta V/V_0 = -9\%$ and -12% (corresponding to pressures of approximately 11 GPa and 15 GPa, respectively), where the optical phonon mode along the M direction in the Brillouin zone becomes imaginary. To explore the structural transformation associated with this instability, we constructed a $2 \times 2 \times 1$ supercell (containing 16 atoms) and performed fixed-volume optimizations on compressed structures, introducing small atomic displacements to break the initial symmetry. As evident in Fig. 6, the optimized atomic positions in the supercell at $\Delta V/V_0 = -12\%$ and -15% deviate significantly from their original high-symmetry positions. The resulting lower-symmetry structure belongs to the trigonal crystal system (space group 163), contrasting with the original lonsdaleite structure (space group 194). Importantly, this distorted structure exhibits lower energy than the undistorted configuration, with energy differences of 0.9 meV/atom and 8 meV/atom at volume compressions of $\Delta V/V_0 = -12\%$ and -15% , respectively. This phase transition matches the general behavior of silicon compounds under stress, which has been studied in the literature [80].

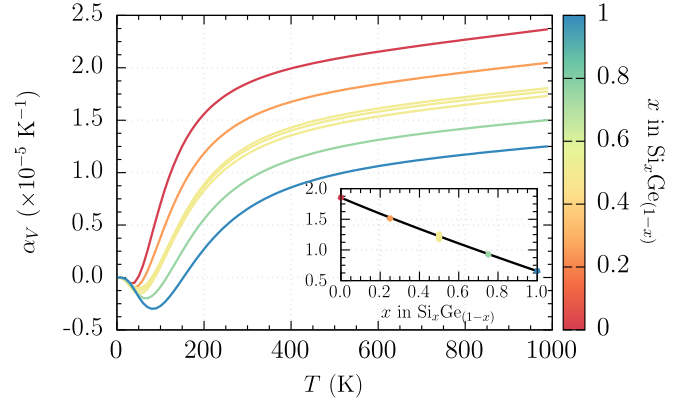


FIG. 7. Volume thermal expansion coefficient α_V as a function of temperature for the four-atom ordered alloys. The inset shows the variation of α_V with Si concentration x at $T = 300$ K.

Using our phonon calculations within the quasiharmonic approximation [81], we can determine various thermal properties of these materials, including thermal expansion coefficients and heat capacities. We first examine the volume thermal expansion coefficient, defined as $\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T}$. Figure 7 presents α_V as a function of temperature for the ordered alloys under investigation. All compositions show a rapid increase in α_V at low temperatures, reaching a linearlike regime above 200–300 K (depending on composition). The magnitude of α_V at $T = 300$ K decreases systematically with increasing Si content, ranging from $1.9 \times 10^{-5} \text{ K}^{-1}$ for 2H-Ge to $0.7 \times 10^{-5} \text{ K}^{-1}$ for 2H-Si. A particularly interesting feature is the presence of negative thermal expansion at low temperatures—a counterintuitive phenomenon where the material contracts upon heating. For 2H-Si, this negative expansion regime extends up to 150–160 K, while for 2H-Ge, it is confined to a narrower temperature range of 40–50 K. These thermal expansion characteristics closely parallel those of cubic counterparts: experimental values for cubic Si and Ge are approximately $0.8 \times 10^{-5} \text{ K}^{-1}$ and $2 \times 10^{-5} \text{ K}^{-1}$, respectively [82–85]. Negative thermal expansion regions have also been experimentally confirmed in these cubic materials [86]. The physical origin of negative thermal expansion at low temperatures can be attributed to the selective population of phonon modes with specific Grüneisen parameters. At very low temperatures, only acoustic phonons with low energies are thermally populated, particularly those near high-symmetry points at the Brillouin-zone boundary that exhibit negative Grüneisen parameters [87]. As temperature increases, longitudinal acoustic and optical phonons with positive Grüneisen parameters become increasingly populated, eventually dominating the thermal response and leading to the normal positive thermal expansion observed at higher temperatures.

The heat capacities at constant pressure C_p at $p = 0$ and constant volume C_V for these alloys are presented in Fig. 8. At high temperatures, all compositions approach the classical Dulong-Petit limit [70,71] of approximately $3R$ per mole of atoms, where R is the gas constant. In the low-temperature regime, the heat capacity follows the expected power-law behavior:

$$C_V \propto \left(\frac{T}{T_D} \right)^3,$$

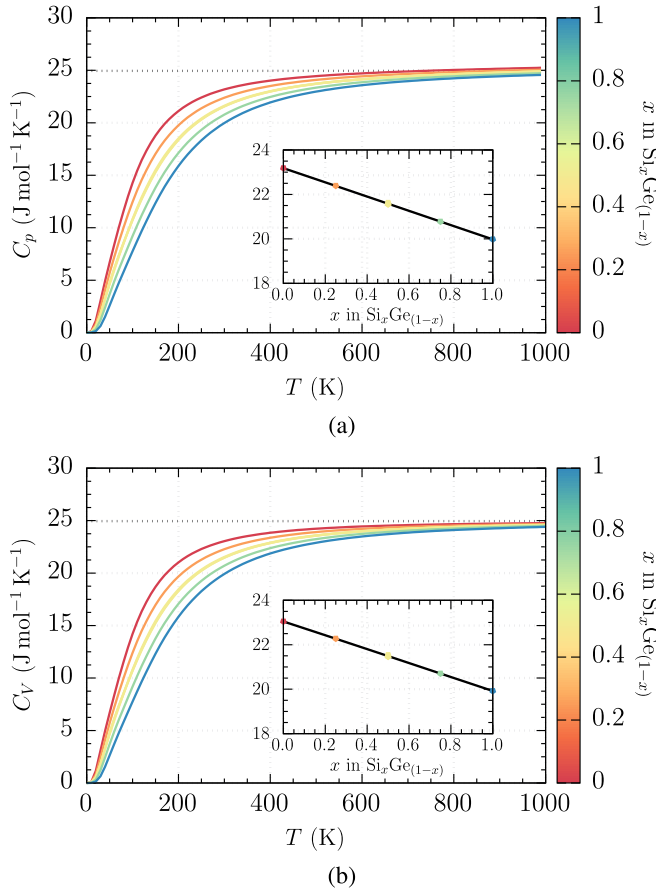


FIG. 8. Temperature dependence of (a) constant-pressure lattice heat capacity at $p = 0$ and (b) constant-volume lattice heat capacity for the four-atom ordered alloys. The insets show the composition dependence at room temperature.

where T_D is the Debye temperature. The values presented in Table II corroborate this scaling relationship and explain the compositional variation in the low-temperature heat capacity curves. At any fixed temperature, we find that the heat capacity varies nearly linearly with composition. For instance, at $T = 300$ K, the constant-volume heat capacity can be approximated as $C_V = ax + b$, where $a = -3$ and $b = 23 \text{ J mol}^{-1} \text{ K}^{-1}$, with x representing the Si fraction.

IV. CONCLUSIONS

In this study, we have conducted a comprehensive first-principles investigation of hexagonal (lonsdaleite) silicon-germanium ($2\text{H-Si}_x\text{Ge}_{1-x}$) alloys and uncovered key relationships between alloy composition and physical properties. Our findings reveal that an increase in Si concentration systematically enhances the bulk modulus and elastic constants, directly reflecting the strengthening of the covalent bonding network within the alloy structure.

The elastic properties of $2\text{H-Si}_x\text{Ge}_{1-x}$ alloys follow an almost linear dependence on composition, which suggests that predictable mechanical behavior can be achieved through precise compositional control. This predictability is crucial for engineering applications that require specific mechanical performance. Furthermore, our analysis of critical thickness

for epitaxial growth provides essential guidelines for experimental synthesis and identifies several promising substrate candidates for future growth attempts of $2\text{H-Si}_x\text{Ge}_{1-x}$ with direct-band-gap characteristics.

Our investigation of phonon band structures reveals that, while elastic properties show linear composition dependence, the lattice dynamics exhibit more complex behavior influenced by the specific arrangement of Si and Ge atoms. This finding is particularly relevant for understanding thermal transport and stability in these materials. Under hydrostatic pressure, we identified a structural phase transition, which demonstrates the sensitivity of these metastable alloys to external stimuli.

The calculated thermal properties—including thermal expansion coefficients and heat capacities—show systematic trends with composition, with the notable feature of negative thermal expansion at low temperatures. These characteristics are essential for predicting the behavior of $2\text{H-Si}_x\text{Ge}_{1-x}$ alloys in device applications across various operating conditions.

Perhaps most remarkably, the behavior of $2\text{H-Si}_x\text{Ge}_{1-x}$ alloys closely mirrors that of their cubic counterparts across multiple properties, which can be attributed to the identical tetrahedral coordination of atoms in both structures. This similarity suggests that the extensive knowledge base for cubic $\text{Si}_x\text{Ge}_{1-x}$ can serve as a valuable reference point for understanding and predicting many properties of the hexagonal variants.

This work establishes a foundation for future investigations into hexagonal $\text{Si}_x\text{Ge}_{1-x}$ alloys, but several important challenges remain. The effects of disorder on alloy properties require detailed exploration, as real materials contain other polytypes with mixed hexagonality. The influence of extended defects—including dislocations, grain boundaries, and stacking faults—on both structural and electronic properties needs to be quantified. Additionally, the growth kinetics and thermodynamic stability of these metastable structures under various synthesis conditions deserve further investigation.

The path toward practical optoelectronic applications of $2\text{H-Si}_x\text{Ge}_{1-x}$ alloys necessitates bridging the gap between theoretical understanding and experimental realization. Our findings provide critical insights for this journey, offering guidance on composition selection, substrate choice, and processing parameters that could enable the development of group-IV-based direct-gap semiconductors for integrated photonics and optoelectronic applications. In particular, the present work focused on pristine configurations of the alloys, but in real samples, point defects and grain boundaries will have measurable and important effects on the material electronic structure, growth kinetics, and thermodynamics [88–91]. We plan to address these aspects in future work.

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10.54499/UIDP/04564/2020, respectively) and Contract No. 2020.04225.CEECIND, as well as LCA - Laboratory for Advanced Computing at University of Coimbra for computer resources through Project No. 2023.11003.CPCA.

DATA AVAILABILITY

The data that support the findings of this article are openly available [103].

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