

First-Principles Investigation of the Structural and Electronic Properties of Tetra-Germanene

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1. Introduction

- The discovery of graphene has driven intensive research on two-dimensional (2D) group IV materials, especially germanene, a Ge-based analogue with mixed sp^2/sp^3 hybridization.
- Unlike planar graphene, germanene adopts a buckled honeycomb structure with longer Ge–Ge bonds and larger lattice constants, giving it greater flexibility and surface reactivity.
- The structural diversity of Ge allotropes has led to the discovery of square-like phases such as tetragonal and tetra-germanene, suggesting rich possibilities for tunable 2D materials [1].
- Limited prior studies on tetra-germanene motivate this work to evaluate its structure, stability, and electronic behavior, determining whether it is a viable and tunable 2D material for future applications

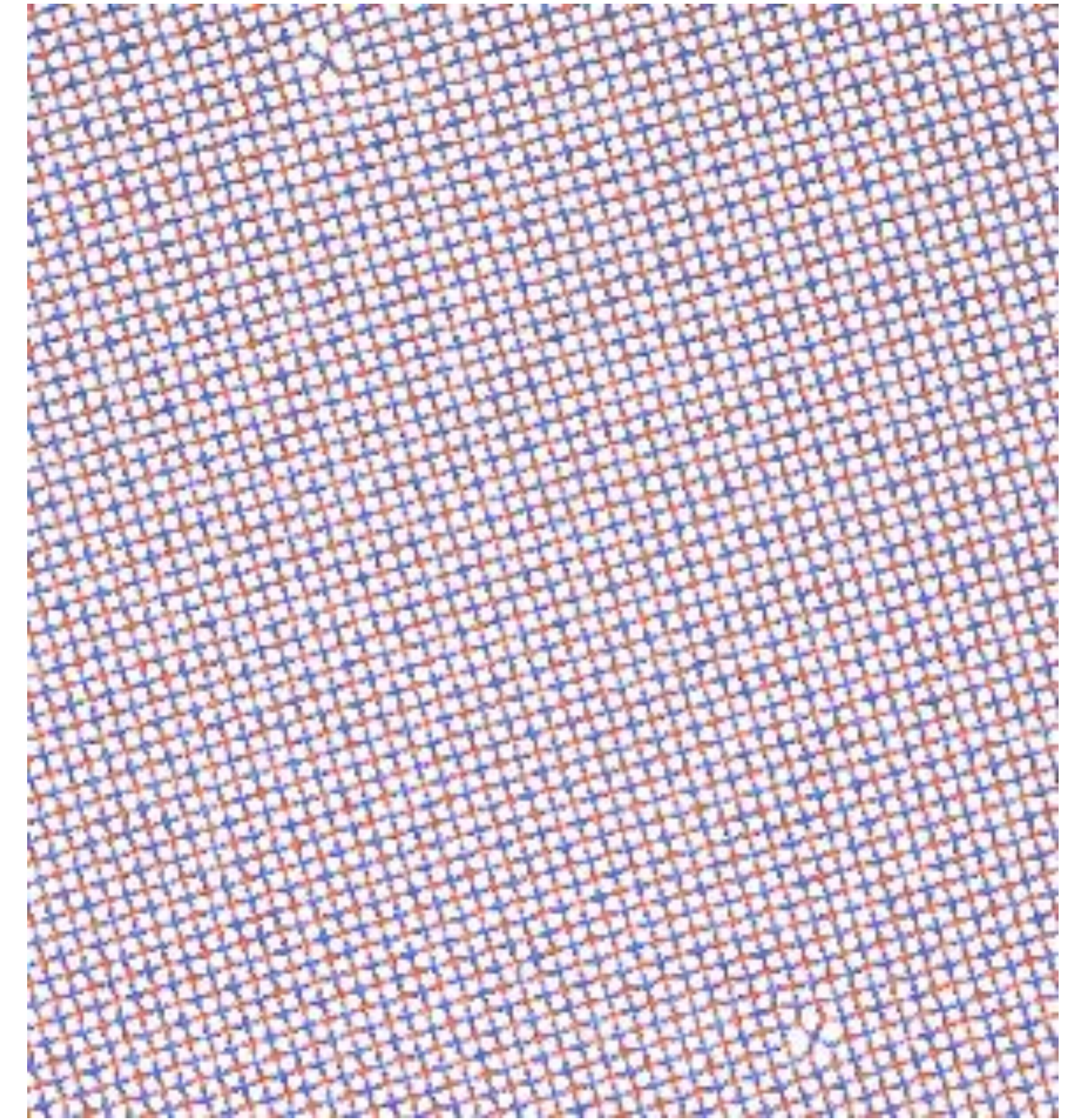


Fig. 1 MD snapshot of the 6000-atom germanene system after compression and relaxation at 300 K.

2. Computational Method

- Initial structure:
 - Extracted from previous molecular dynamics simulations of a 6000-atom germanene system (Fig. 1) [2].
 - A 64-atom tetra-germanene segment was selected from a symmetric, defect-free region as the DFT starting model.
- DFT setup (SIESTA) [3]:
 - Exchange–correlation: GGA-PBE functional with norm-conserving pseudopotentials.
 - Basis set: Double- ζ + polarization; vacuum gap: 40 Å along z.
 - k-point convergence test: adopted $5 \times 5 \times 1$ for the 64-atom cell.
 - Convergence criteria: 1×10^{-4} eV Å⁻¹; mesh cutoff: 500 Ry.
- Final Model:
 - Simplified 64-atom cell \rightarrow 4-atom unit cell, maintaining tetra-germanene symmetry (Fig. 2).
 - Hexagonal germanene optimized under identical parameters for comparison.

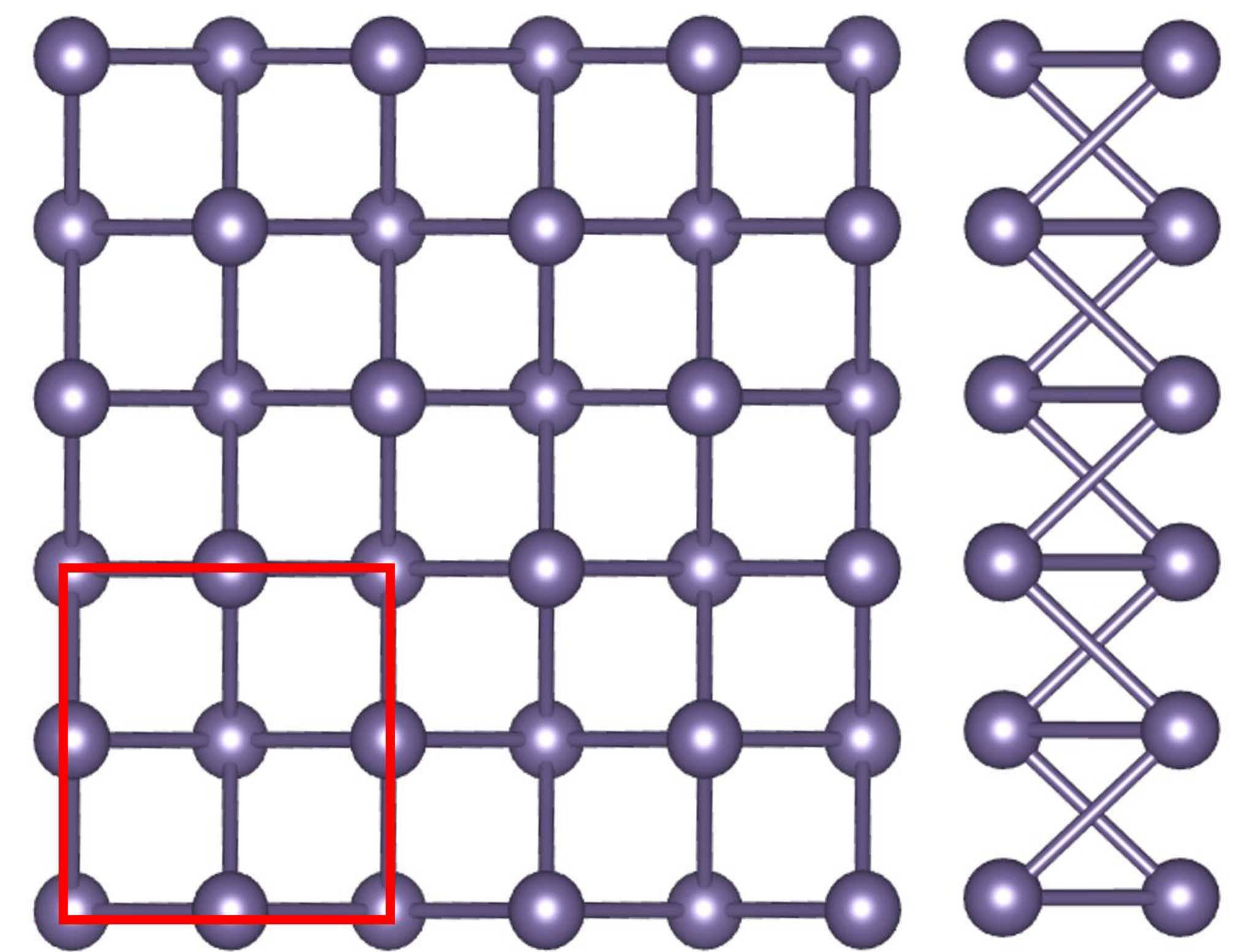


Fig. 2 Relaxed 64-atom tetra-germanene model and reduced 4-atom DFT unit cell.

3. Result and Discussion

A- Lattice Structural

- Relaxed tetra-germanene formed a near-square lattice with parameters $a = 4.012$ Å, $b = 4.171$ Å, $c = 40$ Å, and angles $\alpha = 89.977^\circ$, $\beta = 90.013^\circ$, $\gamma = 90^\circ$, confirming an square in-plane geometry.
- First-neighbor Ge–Ge bond increased from 2.48 Å (MD) to 2.91 Å (DFT) (Fig.3); out-of-plane distortion rose from 0.737 Å to 2.18 Å;
- Cohesive energy 5.135 eV/atom for tetra-germanene vs. 4.763 eV/atom for hexagonal germanene \rightarrow indicates greater energetic favorability.

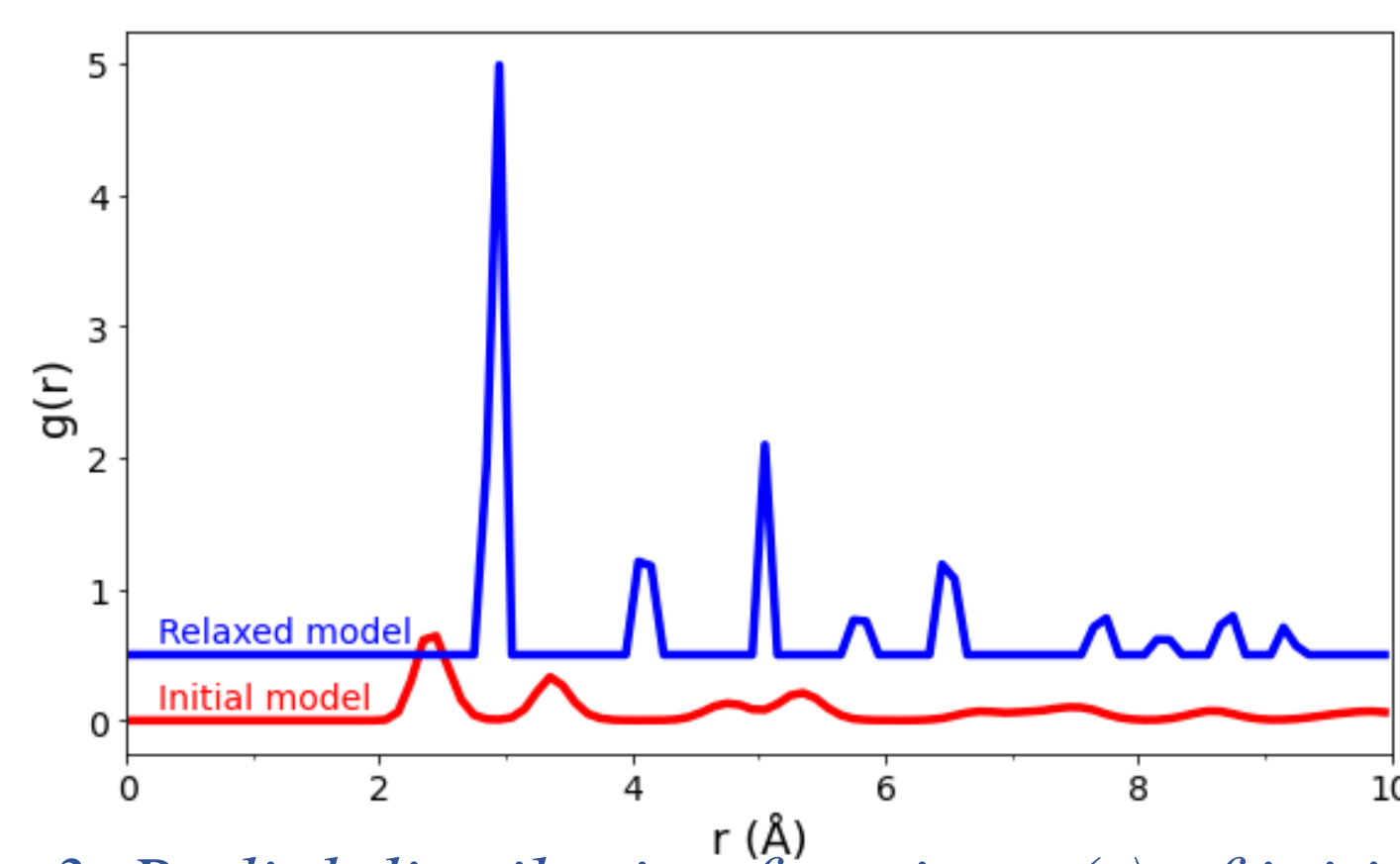


Fig. 3. Radial distribution function $g(r)$ of initial (red) and optimized (blue) tetra-germanene models

B – Electronic Properties

- Square-planar Ge–Ge bonding suggests dsp^3 hybridization and higher atomic coordination.
- Strong Ge 4d contributions below the Fermi level confirm mixed dsp^3 hybridization.
- Band structure shows no band gap or Dirac crossings, confirming metallic behavior distinct from hexagonal germanene.

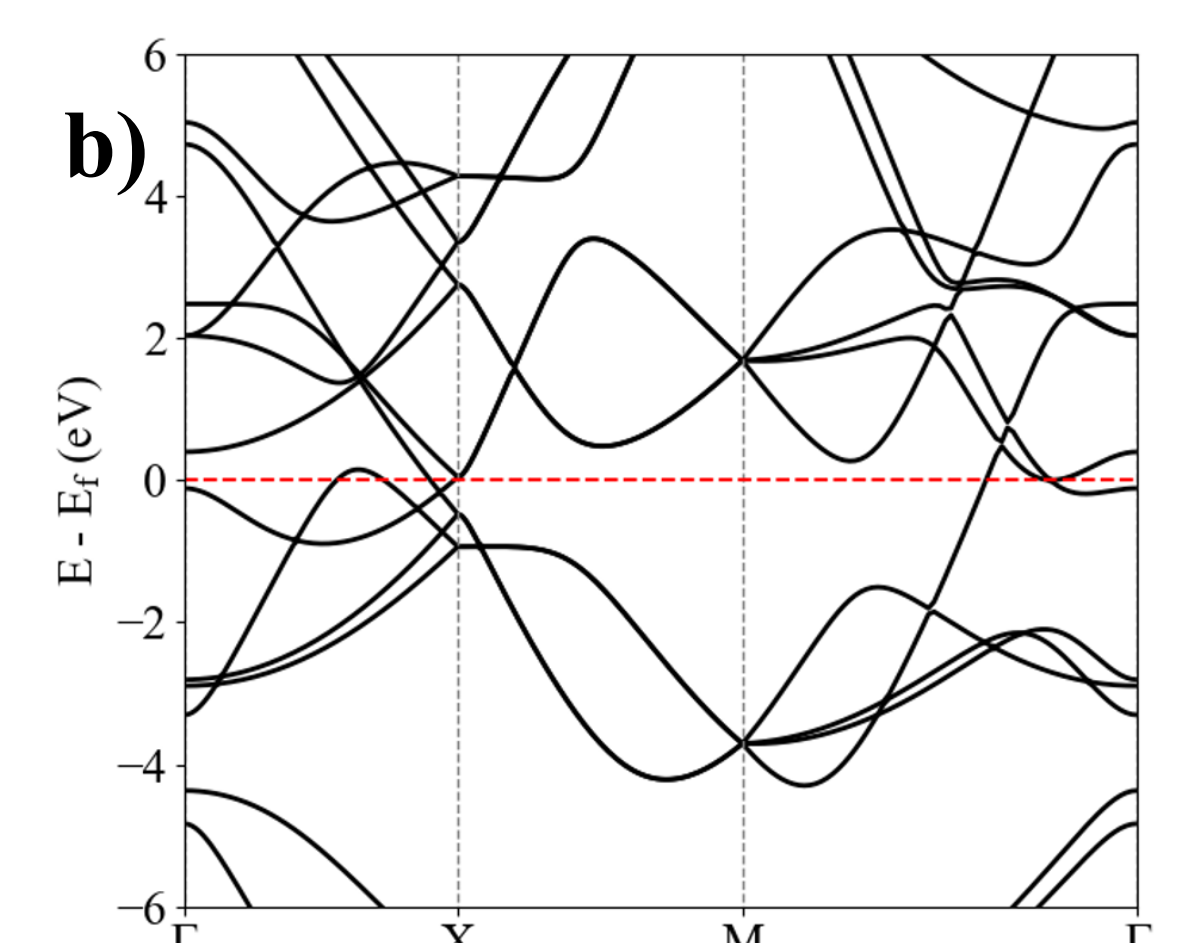
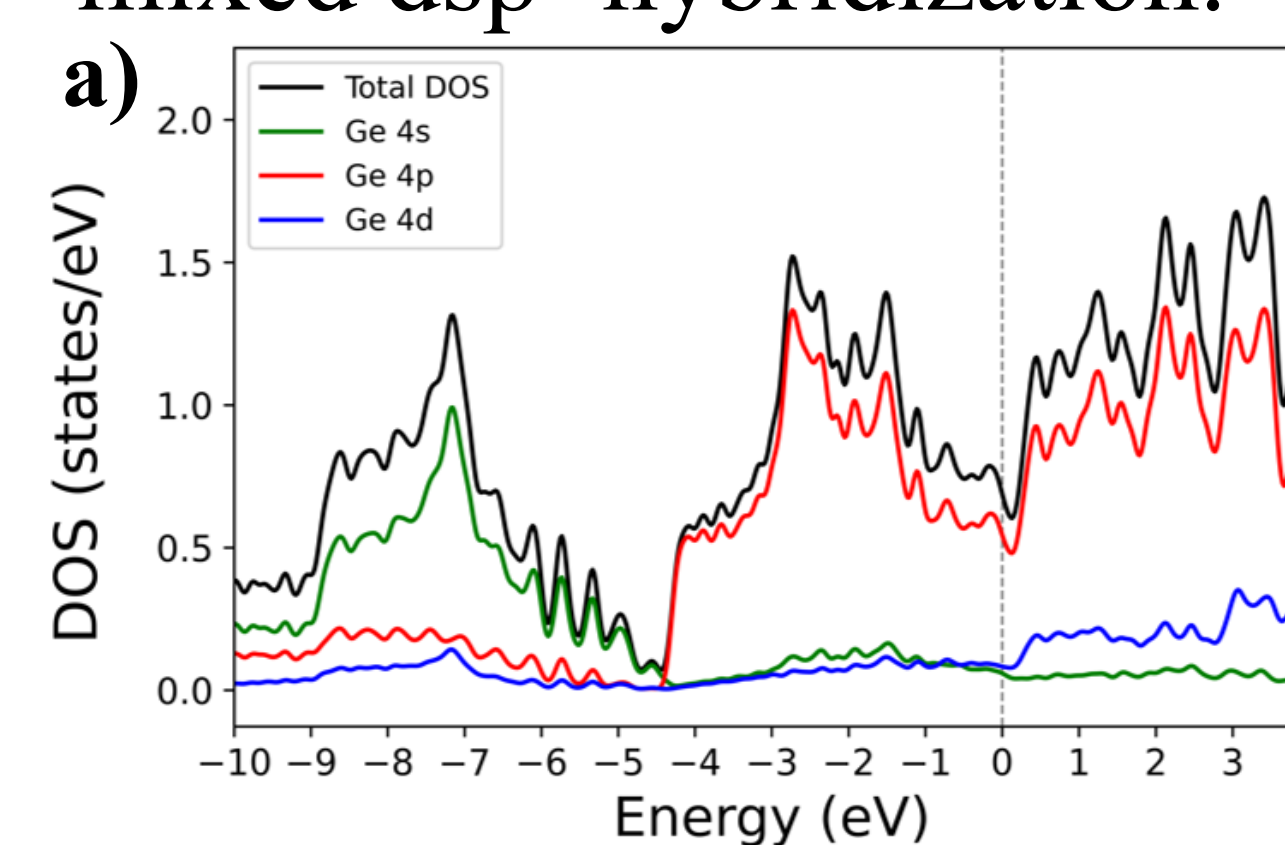


Fig. 4 (a) Partial density of states and (b) band structure of tetra-germanene.

4. Summary

- Tetra-germanene, a square-like 2D allotrope, was studied using DFT based on MD-derived structures.
- It relaxed into a near-square lattice ($a = 4.01$ Å, $b = 4.17$ Å) with 2.18 Å buckling and 5.14 eV/atom cohesive energy, showing higher stability than hexagonal germanene.
- Square-planar Ge–Ge bonds indicate dsp^3 hybridization with strong 4d orbital involvement.
- Metallic band structure with no band gap or Dirac crossings confirms a distinct, tunable electronic character for advanced 2D applications.

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[1] Chegel, R. Tunable band gap and enhanced thermoelectric performance of tetragonal Germanene under bias voltage and chemical doping. *Sci. Rep.* 2023, 13, 12023.

[2] Ngoc, et. al. Compression-induced hexa-to-tetra phase transition of confined germanene. *J. Mol. Graph. Model.* 2023, 124, 108553.

[3] Soler, J. et. al. The SIESTA method for *ab initio* order- N materials simulation. *J. Phys.: Condens. Matter* 2002, 14, 2745–2779.