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Ge(110) c(8×10) reconstructions stabilized by vibrations

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ABSTRACT

Determining the atomic structure of a surface is essential for reliable simulations and in-depth exploration of chemical and atomic-scale physical processes. Using Ge(110) $c(8 \times 10)$ as a case study, this work employs Density Functional Theory (DFT) calculations to examine the role of vibrational entropy in surface reconstruction stability. The Ge(110) $c(8 \times 10)$ unit cell consists of interstitial-based pentamers (Universal Building Block model, UBB) interspersed with regions appearing in STM images as unreconstructed. DFT calculations predict that adding more pentamers *lowers* the surface energy, contradicting experimental findings. This discrepancy is resolved when vibrational entropy is accounted for and *surface divacancies* are introduced in addition to the UBB pentamers. These divacancies are similar to those proposed earlier in the Tetramer-Heptagonal and Tetragonal Ring (THTR) reconstruction model. The nearest neighbors of the vacancy sites are rebonded as on monatomic step edges. The differences in the vibrational entropy contributed by pentamers, divacancies, and unreconstructed surface stabilize Ge(110) $c(8 \times 10)$ reconstructions with the pentamer density observed experimentally. The presence of divacancies is conceptually consistent with the presence of monatomic steps in Ge(110) " 16×2 ", the most stable reconstruction of this surface.

1. Introduction

Germanium has recently been used as a substrate for direct, metalfree synthesis of graphene [1-3]. Its surfaces reconstruct into structures similar to those of their silicon counterparts. Ge or Si bulk truncated by a {110} plane has high energy because it consist of $< 1\overline{10} >$ zigzags of threefold-coordinated atoms, and this geometry does not allow for the recombination of broken bonds. Some of these broken bonds can be saturated by adatoms, but this requires mass transport over large distances. Certain adatom clusters significantly reduce the (110) surface energy, but the associated reconstructions are among the most complex on Ge and Si. These reconstructions of (110) surfaces were studied by electron diffraction [4-8], photoemission [9] and by scanning tunneling microscopy (STM) [7,8,10-15]. Depending on the sample-tip bias, the most prominent structural component of this surface orientation appears in STM images as a pentagonal spot, a pentamer, or a tetramer of spots. Several models have been proposed for its structure and examined using ab inito DFT calculations [7,10-12,17-30]. The most recent model [19,20], the Universal Building Block (UBB), is compatible with both stable and transient reconstructions, including ubiquitous $\{17\ 15\ 1\}$ facets. It consists of three $[1\overline{1}0]$ zigzag atoms and two adatoms. These adatoms are supported by an interstitial atom [10], similarly to the stabilization of pentamer-like clusters on Si(113) [16],

and are further stabilized by subsurface rearrangement [19].

While the present DFT study confirms the stability of UBB, it also finds that UBBs are "too stable" – so stable that their predicted areal density in Ge(110) c(8 × 10) is nearly twice as high as what is seen by STM. Resolving this contradiction was the primary motivation of this project. The results demonstrate that thermodynamic stability of the observed phase is imposed by vibrational degrees of freedom. Vibrations affect the surface structure of metals [31] and oxides [32] and have recently been shown to be important also on a silicon surface, stabilizing its famous (111) 7×7 reconstruction [33]. Vibrational entropy favors these structural transitions, which rise the density of vibrational modes with low vibrational frequencies [34].

Ge(110) c(8 × 10) is a metastable but persistent structure. STM and LEED studies have shown that Ge(110) evolves from disordered to ordered pentamers (identified as UBBs), with UBB rows separated by monatomic steps [6,14]. These steps may form staircases (up-up-up) or alternate their vertical direction (up-down-up). The first case corresponds to {17 15 1} facets and is less stable, while the second corresponds to the "16×2" structure, the most stable one (see Ref. 6 for details). Each terrace between the steps contains one UBB row. Ge(110) "16×2" forms during annealing between 430 °C and 380 °C. Ge(110) c(8 × 10) is an intermediate, metastable structure, which appears when the sample is rapidly cooled through the 430 °C-380 °C

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range and annealed below 380 °C. It resembles " 16×2 ", but differs in that (1) the direction of UBB rows is slightly altered, (2) there are no steps in the unit cell, and (3) each second UBB row is missing, reducing the UBB density to approximately half. The c(8 × 10) unit cell contains four UBBs. The original UBB model [19], dubbed here 4UBB, assumes that the region between the UBB rows consists of [110] zigzags that lack of adatoms or vacancies. Each c(8 × 10) cell contains five such zigzags. Similar to relaxed but unreconstructed, bulk-terminated (110) surfaces, these zigzags tend to buckle, with alternating atoms moving upward and downward. The buckling phase may vary along and across zigzags, so that phase boundaries may occur, resulting in numerous low-energy metastable excited states in the regions between UBB rows.

This paper is organized as follows. First, it is shown that the DFT surface energy of Ge(110) c(8 \times 10) can be reduced either by adding more UBBs between the UBB rows or by introducing divacancies (pairs of atoms missing from a zigzag) resembling the divacancies proposed in the Tetramer Heptagonal- and Tetragonal Ring (THTR) model [28]. The nearest neighbors of these vacancies are back-bonded in a manner similar to edge atoms in " $16 \times 2^{"}$ steps. However, the energy gain from divacancies is smaller than that from additional UBBs. These conclusions are verified using various PBE [35] pseudopotentials, with and without dispersive forces, approximated using the RVV10 functional [36]). Second, it is demonstrated that vibrational entropy has a substantial influence on the thermodynamics of Ge(110) defects, raising the Helmholtz free energy F = U - TS of surfaces covered with only UBBs or only with divacancies and lowering H of surfaces containing both defects. This stabilizes the UBB density observed on Ge(110) $c(8 \times 10)$, but stabilization of vacancy-free 4UBB occurs only provided that UBB-divacancy vibrational interaction is neglected. Third, STM images simulated with and without vacancies are compared to experimental data.

2. Approach

Plane-wave ab initio calculations were performed with the pw.x tool of Quantum Espresso [37–39]. Most calculations employed the RVV10 exchange-correlation (xc) functional [36], which accounts for van der Waals dispersive forces, along with ultrasoft pseudopotentials (ps = Ge_04_PBEUS_r [43], see Table 1). The energy cutoff was set to $E_{cut} = 15$ Ry, with Brillouin zone sampling at Γ . The simulation slabs consisted of six Ge layers, with one side saturated by H atoms. Slabs were periodically repeated in all three dimensions. Periodicity along the surface-normal direction was a computational construct imposed by the plane wave basis set, leading to electrostatic coupling. This long-range coupling was eliminated using the standard dipole correction. The vacuum layer was 11.5 Å in the basic setup. Of the six Ge layers, five were fully relaxed, while the bottom Ge layer was fixed at bulk positions. The saturating H atoms were relaxed once, with all six Ge layers

Table 1

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constrained to bulk positions. Although these conditions do not guarantee fully converged results, they provide an efficient and reliable scan of structures, with the energy sequence remaining unaffected. Full convergence was achieved using a slab separation of 20 Å, eight Ge layers, and Brillouin zone sampling with a c(16×20) surface k-point set with offset, (2 2 1 1 1 0) in Quantum Espresso notation. For ps = Ge_04_PBEUS_r, the energy cutoff needed for full convergence was $E_{cut} = 20$ Ry.

Convergence of total energy calculations was verified in terms of key aspects: energy cutoff, Brillouin zone sampling, vacuum thickness, number of Ge layers, pseudopotentials (Table 1), and exchange and correlation functional (RVV10 [36], PBE [35], and PBEsol [42]). Table 1 compares the converged bulk lattice constants and bulk moduli for the pseudopotential and exchange-correlation functionals used in this work. Convergence tests for surface structures and surface energy differences are described in Section 3.1.

Total energy differences ΔE_{AB} between structures (surface phases) A and B with different number of Ge atoms NA and NB were calculated assuming equilibrium with Ge bulk:

$$\Delta E_{\rm AB} = E_{\rm A} - E_{\rm B} + \mu (N_{\rm B} - N_{\rm A}), \tag{1}$$

where μ is the chemical potential of bulk Ge, computed with the numerical conditions as in Table 1. Vibrations were accounted for by estimating the contributions to internal thermal energy E_{vib}

$$E_{\rm vib} = \frac{1}{2} \sum_{i} h \nu_i + \sum_{i} \frac{h \nu_i}{e^{\gamma_i} - 1} = E_{\rm ZPE} + E_{\rm therm}$$
 (2)

(E_{ZPE} is the zero-point energy and E_{therm} is the vibrational thermal energy) and to vibrational entropy S_{vib}

$$S_{\text{vib}} = k_{\text{B}} \sum_{i} \left(\frac{\gamma_{i} e^{-\gamma_{i}}}{1 - e^{-\gamma_{i}}} - \ln(1 - e^{-\gamma_{i}}) \right), \tag{3}$$

where *h* and k_B are the Planck and Boltzmann constants, $\gamma_i = h\nu_i/k_BT$, and ν_i is the frequency of the *i*-th vibrational mode. For computational efficiency, vibrations obtained in smaller cells were used to estimate E_{vib} and S_{vib} in a model outlined further on in this Section and described in detail in Section 3.2. Configurational entropy S_{conf} was included only to provide a rough estimate of surface coverages θ_m by each c(8 × 10) phase *m*, whereby the entropy of mixing (accounting for contributions arising from the variety of relative positions of more than two components) and phase boundary energies were ignored:

$$S_{\text{conf}}(\theta_m) = -k_{\text{B}} \sum_m \left(\ln \theta_m + \left(\theta_m^{-1} - 1 \right) \ln(1 - \theta_m) \right). \tag{4}$$

First, occupation x_m was obtained separately for each state m assuming equilibrium with the ground-state m = g in a two-state system: $\Delta(E_{\text{tot}} + E_{\text{vib}} - TS_{\text{vib}}) = T(S_{\text{conf}}(\theta = 1 - x_m) - S_{\text{conf}}(\theta = x_m)).$

Converged lattice constants a_0 and bulk moduli B_{mod} of Ge, as obtained with various pseudopotentials with exchange-correlation XC, energy cutoff E_{cut} and with a $16 \times 16 \times 16$ equidistant k-point mesh with offset (16 16 1 1 1 in Quantum Espresso notation) in the first Brillouin zone of the bulk primitive unit cell. ^aLattice constant from [40]. ^bBulk modulus from [41]. [†]Pseudopotentials included for comparison and not used in surface calculations. [‡]PBEsol is PBE optimized for bulk calculations [42]. [Ar] is a shortcut for the electronic configuration of argon. [*] indicates pseudopotentials created for this work with ld1.x tool of Quantum Espresso, see Supporting Material for technical details and Ref. 43 for UPF files.

Pseudopotential	source	frozen	valence	XC	$E_{\rm cut}$ Ry	a_0 Å	$B_{\rm mod}$ GPa
(experiment)	[40,41]	-	-	-	-	5.658 ^a	$70-78^{\mathrm{b}}$
Ge_04_PBEUS_r	[*,43]	[Ar]3s ¹⁰	$4s^24p^2$	RVV10	20	5.658	65
Ge_04_PBEUS_loc1	[*,43]	[Ar]3s ¹⁰	4s ² 4p ²	PBE	20	5.659	66
Ge.pbe-kjpaw	[44]	[Ar]3s ¹⁰	4s ² 4p ²	PBE	40	5.776	60
Ge.pbe-kjpaw	[44]	[Ar]3s ¹⁰	$4s^24p^2$	RVV10	40	5.828	57
Ge.rel-pbe-dn-kjpaw [†]	[45]	[Ar]	3s ¹⁰ 4s ² 4p ²	PBE	60	5.758	59
Ge.pbe-dn-kjpaw_psl.0.2.2	[46]	[Ar]	3s ¹⁰ 4s ² 4p ²	PBE	60	5.763	59
$Ge_ONCV_PBE-1.2^{\dagger}$	[47]	[Ar]	$3s^{10}4s^24p^2$	PBE	40	5.770	60
Ge_dojo_stringent [†]	[48]	[Ar]	$3s^{10}4s^24p^2$	PBE	120	5.763	59
Ge.pbesol-dn-kjpaw_psl.1.0.0 †‡	[49]	[Ar]	$3s^{10}4s^24p^2$	PBEsol [‡]	80	5.676	67

Subsequently, the values of θ in a multi-state ensemble were estimated from the x_m set by renormalization, assuming $\theta_m/\theta_g \approx x_m/(1-x_m)$ for $m \neq g$ and imposing $\sum_{m\neq g} \theta_m + \theta_g = 1$ (Eq. (4) was not applied self-consistently thereafter):

$$\theta_m \approx \frac{x_m}{(1-x_m)\sum_{k=1}^{k}}.$$
(5)

While these coverages are approximate and should be taken with care also because only the structures with local c(8 × 10) periodicity were considered and because only the most favorable configuration in each structure class was accounted for and the entropies due to the possibility of rearrangement of elements within each unit cell were neglected, they help to assess if there is a clearly dominating structure, by translating free energy differences $\Delta(E_{tot} + E_{vib} - TS_{vib})$ into equilibrium abundances θ of these structures.

Vibrational frequencies were obtained only for ps = Ge 04 PBEUS r. Due to computational constrains, a full $c(8 \times 10)$ treatment was not feasible; instead, vibrational frequencies were calculated for 3×3 surface cells, each containing a single object of interest (e.g., UBB, divacancy, or adatom). The slabs consisted of six Ge layers separated by 20 Å of vacuum and were decoupled by truncating the Coulomb interaction [50]. Frequencies were computed using ph.x, based on the linear response theory within a 2D framework. Vibrations were allowed in the topmost four, five, or six Ge layers, while the fixed and displaced parts of the dynamic matrix were separated by setting interaction elements to zero. Vibrational terms were extrapolated to infinitely thick slabs by assuming an inverse proportionality to the number of vibrating layers. A similar procedure was applied to bulk vibrations, where S_{vib} , E_{ZPE} , and E_{therm} were computed for bulk for phonons at the Γ point for 6, 12, 24, and 48 layers and then extrapolated to infinite thickness. See Section 3.2 for details on how c(8 \times 10) $E_{\rm vib}$ and $S_{\rm vib}$ were estimated from these 3 \times 3 data.

Constant-current STM images were simulated within the Tersoff approach [51] from electron densities computed with pp.x using ps = Ge_04_PBEUS_r, $E_{cut} = 15$ Ry, Brillouin zone sampling corresponding to the L point of the rectangular 16×20 surface (Quantum Espresso 2 2 1 1 1 0), six Ge layers, and 50 Å vacuum. These conditions guarantee that the images are converged and that they can be simulated also for large average sample-tip separations representative of small sample-tip

currents. The images were generated by an R-language [52] script and processed (Gaussian-broadened) by Gwyddion software [53].

For experimental STM images, Ge(110) surfaces were cleaned in UHV (base pressure below 10^{-10} mbar, background pressure 10^{-2} mbar) by 200 eV Ar ions in repeated sputter – anneal cycles. The images were captured in situ at room temperature using a SPECS Aarhus 150 microscope and processed (leveled and calibrated) using Gwyddion. For more scans (including 0.5 μ m \times 0.5 μ m), see Supporting Material.

3. Results and discussion

Fig. 1a) provides a snapshot from an early stage of surface evolution. The surface is predominantly covered by a dense UBB lattice gas with weak short-range order, as in region A. Region B shows the emergence of embryonic $c(8 \times 10)$ order, with the $c(8 \times 10)$ unit cell indicated by a vellow rhombus. This region is magnified in Fig. 1b The UBB density remains high along domain boundaries (C). At the edge of the ordered strip additional UBB pairs (D) are visible - each located between two UBB rows, where one row is regular and the other contains a displaced or missing UBB. Defects also occur in the form of smaller single spots (E) or pairs of such spots (F), in many cases located between closely spaced UBBs (see Supporting Material for a high-resolution scan). At a high negative bias of -2.0 V, UBBs appear as large, single, pentagonal, and bright spots (Fig. 1b-c). At lower biases, they resolve into pentamers consisting of five separate bright spots (Fig. 1d). The row pattern is complex; it remains regular in the regions between perfectly ordered rows (Fig.1c), but in areas where rows contain order defects, it depends on the local UBB registry (Fig. 1d).

3.1. Stability of 4UBB versus structures with other number of Ge surface atoms

Prolonged low-temperature annealing is known to convert Ge(110) surfaces from a state similar to that in Fig. 1a) into $c(8 \times 10)$ domains large enough to be detected by LEED [6]. UBBs are repelled from sites between their rows; in particular, additional UBBs (D in Fig. 1a) are less stable than perfect rows. This observation appears to conflict with the ab initio surface energy ordering (Fig. 2a-b, fully converged data).

Indeed, the structure with the lowest formation energy per unit cell is



Fig. 1. (a) STM image of occupied states at -2.0 V. (b) Enlarged fragment with the primitive $c(8 \times 10)$ unit cell (yellow rhombus) and with atoms of 4UBB model in Wigner-Seitz unit cell. [110] zigzags are green, the pentamer is red, the interstitial in its center is violet, the atoms strongly displaced by UBB are purple. (c) -2.0 V with better resolution. (d) At lower biases (here, -1.1 V) UBBs resolve into pentamers of spots. (For color version of this figure, the reader is referred to the web version of this article.).



Fig. 2. (a) Energy difference between 4UBB and most favorable structures with dGe atoms added from bulk.¹ (b) Coverage with these structures at 400 °C. (c-j) Selected reconstructions. UBB pentamers are red, other UBB atoms are violet, zigzags are green, single adatoms are blue, and divacancies are orange. (For color version of this figure, the reader is referred to the web version of this article.).

The overall energy gain relative to UBB is only about 0.2 eV per added UBB (three added Ge atoms) and does not exceed 0.1 eV per divacancy (two removed Ge atoms). It was therefore verified whether the UBB stability loss could result from insufficient accuracy. Eliminating residual electrostatic coupling between layers had no significant impact on energy differences. Similarly, increasing the number of Ge layers one by one to ten, as well as improving the energy cutoff and Brillouin zone sampling, produced no substantial effect. The most influential is the chemical potential (μ) of Ge, since formation energy is proportional to μdN , where dN is the number of atoms exchanged with the bulk (Eq. (1)) – a quantity that can vary by twenty or more. When μ becomes less negative (i.e., when the bulk phase becomes less favorable), atom transfer from the bulk to the surface is enhanced, increasing the stability of structures with more Ge adatoms than in 4UBB. Conversely, when μ becomes more negative, structures with more Ge vacancies become increasingly stable. Since the structures more stable than 4UBB include both Ge-rich (adatom-based) and Ge-deficient

¹ CIF files can be downloaded from Ref. [43], converged structures set.

not 4UBB (Fig. 2e), but 7UBB, which contains three additional pentamers between the UBB rows (Fig. 2c). Insertion of a pentamer pair between the rows also lowers the energy (Fig. 2d; see also object D in Fig. 1a). Similarly, creating divacancies between UBB rows (Fig. 2f-j) reduces the energy, though to a lesser extent. As a result, structures with additional pentamers are predicted to dominate at 400 °C and lower temperatures (Fig. 2b).

(vacancy-based) reconstructions (Fig. 2a), an adjusted μ can either stabilize or further destabilize vacancy-related structures with respect to adatom-related ones – but it cannot stabilize 4UBB. Moreover, although vacancy stabilization could explain the observed repulsion of additional pentamers, a converged correction to μ still retains 7UBB as the most stable configuration.

Another potential source of inaccuracy could be the reduced transferability of the Ge 04 PBEUS r pseudopotential [43], which was aggressively optimized for a low energy cutoff (Table 1). To assess this, test calculations were performed using established pseudopotentials (Table 1), with both PBE and RVV10 exchange-correlation (xc) functionals. Two types of tests were conducted. In the first set, approximately 40 reconstruction variants were selected, with dGe=0 (4UBB) and dGe = -4 (two divacancies) with the lowest energies in each category. The impact of pseudopotentials and xc functionals on energy differences (ΔE) relative to the most favorable case obtained with Ge 04 PBEUS r [43] (alias csr) was examined. The test included csr, Ge 04 PBEUS loc1 [43] (csp), and Ge.pbe-kjpaw [44] (kjpaw), using the following combinations: csr + RVV10, csp + PBE, kjpaw + PBE, and kjpaw + RVV10. While the ordering of a few metastable surface states was affected, the most favorable structures remained unchanged (see Supporting Material, Section 2). Figure 3 illustrates the difference between kipaw and csr. The influence of RVV10 was similar in the csp + PBE / csr + RVV10and kjpaw + PBE / kjpaw + RVV10 pairs, but in the former, the effect was less pronounced. The ΔE differences between csr + RVV10 and kjpaw + RVV10 remained within ± 0.1 eV (Fig. 3a), potentially due to transferability loss and/or due to the Ge bulk lattice constant being 3 % too large for kipaw + RVV10 (Table 1). This was less prominent than ΔE differences between kjpaw + PBE and kjpaw + RVV10 (Fig. 3b).

The second test set contained reconstructions with a single lowenergy structure from each class (Fig. 4). It was conducted using csr + RVV10, kjpaw + PBE and 14kjpaw + PBE, where 14kjpaw refers to Ge. pbe-dn-kjpaw_psl.0.2.2 [46] (Table 1). In 14kjpaw, Ge 3d¹⁰ electrons were included as valence electrons, meaning that 14 electrons per Ge atom are treated self-consistently in the total energy calculations. In contrast, csr, csp, and kjpaw include only four valence electrons $(4s^24p^2)$. The test was performed on structures identified in the intermediate stage of the project as the most favorable in each dGe class. Since this test was computationally intensive, it was not repeated in the final stage, meaning that the tested structures are similar but not identical to those shown in Fig. 2. However, the observed trends (Fig. 4a) are unequivocal and support the premise that 4UBB is not the most stable reconstruction. Although compared to kipaw + PBE and 14kipaw + PBE, csr + RVV10 slightly increases the predicted equilibrium abundance of structures with four UBBs (i.e., of 4UBB + divacancies), this effect is weak and nearly vanishes once the structure optimizations converge (Fig. 1a-b). Thus, the issue must be addressed in another way.

However, it should be stressed that while the older, intuitive pentamer model [24] remains in use [30,3], the present study confirms the recent conclusion [19] that the UBB cluster has a significantly lower energy.

In summary, ab initio calculations of surface energy differences for $Ge(110) c(8 \times 10)$ models suggest a ground state radically different from that observed experimentally by STM. The key discrepancy lies in the areal density of the characteristic pentamer-shaped spots, identified as UBBs. This conclusion remains unaffected by the choice of the pseudopotential or the use of PBE instead of RVV10 exchange-correlation.

3.2. Influence of vibrational energy and vibrational entropy

Vibrational modes can affect the stability and abundance of atomic structures in two ways. First, quantum mechanics imposes a minimal level of vibrations, meaning that the lowest realizable energy of an atomic ensemble does not correspond to the static total energy minimum, but rather to this minimum plus the Zero Point Energy (ZPE) – the sum of the energy of these unavoidable vibrations (E_{ZPE} in Eq. 2). This

correction is temperature-independent and is primarily determined by differences in the hardest vibrational modes (i.e., those with the highest frequencies, in other words – the highest vibrational energies). Second, soft modes in the energy range of k_BT can be thermally populated, contributing to the entropy (S_{vib}) and to the internal energy (E_{vib}) of the system. This temperature-dependent correction (Eq. (3) and E_{vib} in Eq. 2) is dominated by low-energy vibrations.

Ge(110) reconstructions are complex – a six-layer model of the c(8 × 10) unit cell contains more than 500 atoms. Due to this complexity, rather than simulating the entire vibrational spectrum of each structure, characteristic vibrational entropy and energy were assigned to each structural component *m* of interest (e.g., a pentamer, an adatom, or a divacancy; Fig. 5a-F). These parameters were obtained from calculations on a 3 × 3 cell with approximately 130 atoms. The contribution $\Delta_m^{3\times3}$ of component *m* to $S_{\text{vib},m}^{3\times3}$ was defined as the difference from a perfect surface with buckled zigzags (Fig. 5 g) and was extrapolated to infinitely thick slab by including vibrations from *L* = 4, 6, and 5 layers, assuming inverse proportionality to *L* (Fig. 5h):

$$\Delta_m^{3\times3} S_{\text{vib}} = S_{\text{vib},m}^{3\times3} - S_{\text{vib},\text{perfect}}^{3\times3} + s_{\text{vib},\text{bulk}}^{\infty} \left(N_{\text{perfect}} - N_{\text{m}} \right) \underset{n \to \infty}{\to} \Delta_m^{3\times3} S_{\text{vib},m}^{\infty} \quad (6)$$

The term $s_{\text{vib,bulk}}^{\infty}(N_{\text{perfect}} - N_{\text{m}})$ accounts for the conservation of the number of atoms, analogous to $\mu(N_{\text{B}} - N_{\text{A}})$ in the expression for the total energy difference between structures with N_A and N_B atoms (Eq. 1). Here, $s_{\text{vib,bulk}}^{\infty}$ represents the vibrational entropy per atom in bulk Ge, computed using Γ phonons of $3 \times 3 \times L$ bulk, where *L* is the number of (110) layers, set to 6, 12, 24, and 48. This was then extrapolated to an infinite number of layers, assuming inverse proportionality to *L* (Fig. 5i). Since the regions between the UBB rows of 4UBB (Fig. 2a) resemble the perfect surface (Fig. 5 g), the vibrational entropy $S_{\text{vib,c}}$ of any c(8 × 10) structure *c* built as 4UBB with additional components from Fig. 5a-F) can be defined relative to $S_{\text{vib,4UBB}}$ using Eq. (6), as a sum of the contributions from these components. Contributions to internal vibrational energy were estimated in the same way and account for roughly 10 % of $F_{\text{vib,c}}$ at T = 400 °C.

The left-hand side of Fig. 5h) shows that the bulk term favors vacancies, as expected, since it accounts for the entropy of atoms transferred to the bulk. But differences between surface structures reduce its effect.

Fig. 6 presents three extreme scenarios for how vibration influence c (8 × 10) reconstruction. They differ in mapping the 3 × 3 components to those in c(8 × 10) structures. The first scenario (Fig. 6a) assumes that vacancies from the pentamer-divacancy pair (PDV-P in Fig. 5a,d, $\Delta F_{vib,v} = -0.16 \text{ eV}$, v = A,B,C) are representative of all divacancies in Fig. 6d within the strip between pentamers. This assumption favors 4UBB + 5DV (Fig. 2j). The second scenario (Fig. 6b) averages the contributions from PDV-P and DV for vacancies A ($\Delta F_{vib,A} = 0.02 \text{ eV}$), as the divacancy from PDV is near two pentamers (Fig. 5d). The remaining vacancies are treated as DV (Fig. 5f, $\Delta F_{vib,B} = \Delta F_{vib,C} = 0.20 \text{ eV}$). This results in fewer vacancies, favoring configurations as 4UBB + 2DV (Fig. 2g) and 4UBB + 4DV (Fig. 2i). The third scenario (Fig. 6c) classifies all vacancies as DV. This destabilizes pentamers and vacancies, ultimately favoring plain 4UBB (Fig. 2e, dGe=0).

Although the vibrational entropies and energies were estimated from simplified structures and detailed stability predictions vary depending on the assumptions used, the trends clearly indicate that vibrations significantly hinder the accumulation of additional UBBs. It follows that incorporating vibrational entropy helps recover the experimentally observed UBB density. However, this may come at the costs of abandoning the assumption of the $1\overline{10}$ zigzags in Ge(110) c(8 × 10) remaining intact, as presumed in the original 4UBB model [19]. Indeed, only the scenario that neglect interactions between vacancies and UBBs (Fig. 6c) predicts the stabilization of c(8 × 10) unit cells that are free from divacancies and additional pentamers.



Fig. 3. Pseudopotential tests, set 1. (a) kjpaw vs. csr, both with RVV10. (b) kjpaw + RVV10 vs. csr + PBE. See Section 3.3 for the discussion of structural corrections to the original Zhachuk 4UBB reconstruction.



Fig. 4. Pseudopotential tests, set 2. (a) Formation energies with respect to 4UBB (b) Estimated surface coverages at 400 °C. The tested structures are similar but not identical to those shown in Fig. 2.

3.3. Measured and simulated Scanning Tunneling Microscopy images

These conclusions were further verified by comparing experimental STM images to those simulated for 4UBB with and without vacancies. As an experimental reference, high-resolution images of well-developed Ge (110) $c(8 \times 10)$ reported by Ichikawa [11] were used. To reduce noise in the experimental data, multiple instances of the $c(8 \times 10)$ unit cell and its surrounding region were averaged by superimposing them as separate semi-transparent layers in GIMP [54]. The computed STM images were broadened using a 4-pixel Gaussian filter in Gwyddion [53].

The $1\overline{10}$ zigzags in the perfect surface strips between UBB rows are buckled, meaning that every second atom shifts upward, while the others shift downward. This allows for the formation of intrinsic phase boundary defects in zigzags, where two neighboring atoms shift in same direction (Fig. 7a). Among these, the "both neighbors down" is more stable than "both neighbors up".

Additionally, the buckling phase can differ between neighboring zigzags, leading to extrinsic phase boundaries that run parallel to the zigzags (Fig. 7b). In STM images, an extrinsic phase boundary appears as either a black row (B1) or a bright row (B2). An intrinsic phase boundary appears as a dark saddle within the zigzag, accompanied by a black spot

and a bright spot on either side (C in Fig. 7b). The buckling phase is pinned by atoms P, which are strongly displaced downward by UBBs (Fig. 7b).

The calculations indicate that the ground state of 4UBB is free of intrinsic phase boundary defect, but it contains two extrinsic phase boundaries as in Fig. 7b). In contrast, the original structure predicted by Zhachuk [19], using different physical approximations (LDA exchange-correlation and a localized basis set), contains in addition five intrinsic phase boundaries and an inverted buckling defect between two UBBs, labelled V in Fig. 8a. When computed with RVV10, the energy of this structure is about 0.7 eV above the ground state, with V contributing 0.07 eV (compare the blue and the red point in Fig. 3a) and each intrinsic phase boundary contributing an average of 0.12 eV. Experimental images confirm that the defect V is absent (Fig. 8a). However, neither of these two structures reproduces the experimental pattern observed between UBB rows. The 4UBB ground state with no intrinsic phase boundaries fails completely (Fig. 7b). The Zhachuk structure, which includes intrinsic phase boundaries, produces better STM images, but it still deviates from experiment. Besides the defect V, where the contrast in the bottom-left half is reversed relative to experimental data, it also predicts spurious bright spots in other regions (A, B, and C in



Fig. 5. Vibrational contributions to free energy differences at 400 °C, with respect to 4UBB. (a-f) Structural components and their contributions $\Delta_m^{3\times3} E_{\text{vib},m}^{\infty} - T\Delta_m^{3\times3} S_{\text{vib},m}^{\infty}$; pendiv is pentamer-divacancy pair. (g) The perfect surface. (h) Extrapolation to infinitely thick slab. The bulk term is shown separately on the left. (i) Extrapolated bulk TS_{vib} ; for comparison with literature, see Ref [55] and Supporting Material.

Fig. 8a).

Compared to Zhachuk 4UBB, the STM image simulated for the most abundant structure predicted by scenario 1 (4UBB + 5DV, see Fig. 2j) more closely matches the experimental data - the discrepancies labelled V, B and C disappear (Fig. 8b). However, at least one issue remains unsolved and scenario 2 (Fig. 6b) does not provide further improvement. Although due to a nearby vacancy, artifact A changes in appearance (the number of spots is reduced) and the result is nearly acceptable, a closer inspection reveals inconsistencies in the contrast distribution in the bottom-right surrounding of A (Fig. 8c). Fig. 8d highlights this issue by comparing profiles extracted along the yellow lines in Fig. 8c. The discrepancy occurs between 0 and 1.2 nm. Moreover, while the buckling pattern of the original Zhachuk 4UBB model reasonably describes the 0 to 0.6 nm region, the 4UBB + 5DV model fails in this range. This failure may be due to limited transferability of the extremely soft Ge_04_PBEUS_r pseudopotential (Table 1). The associated inaccuracy (Fig. 3a) may be sufficient to overlook the formation of an intrinsic phase boundary at this specific location.

Because divacancies and phase boundaries are difficult to distinguish solely from their appearance in STM images, and since the contributions of defects (divacancies and additional pentamers) to free energy was only estimated, it is possible that plain 4UBB remains stable if pentamer-divacancy vibrational coupling is weak (Scenario 3, Fig. 6c). One could therefore hypothesize that perfect Ge(110) c(8 \times 10) consists only of 4UBB rows, without additional pentamers or divacancies. This would however imply that at 400 °C, several buckling phase boundaries remain frozen between the UBB rows. Given that at absolute zero, each boundary costs about 0.1 eV, formation of these boundaries must be

accompanied by a vibrational entropy increase comparable to the values estimated per surface defect atom (about ± 0.1 eV, Fig. 5a-F). This contribution was not explicitly obtained in the current work, as is even more challenging to decouple from other contributions than it is for divacancies. Addressing this issue would likely require direct calculations of vibrations in c(8 \times 10) cells, which is beyond the scope of this project.

4. Divacancies and the phase transition to Ge(110) " $16 \times 2''$

The abovementioned results indicate that the same local rebonding that occurs at Ge(110) " $16 \times 2^{"}$ step edges may be already present on Ge (110) c(8 \times 10), in the form of rebonding between surface and subsurface atoms on both edges of surface divacancies (Fig. 9). This provides insight into the mechanism of phase transitions on Ge(110). In this picture, serves c(8 \times 10) as an intermediate state, from where approximately half of the pentamers of the initial disordered surface are repelled, while the remaining ones condense into UBB rows. This rearrangement becomes thermodynamically favorable due to the formation of divacancies between these rows (Fig. 9a). As evolution continues, more vacancies form and condense into low terraces, separated from the UBB rows by monatomic steps (Fig. 9b). Simultaneously, residual atoms from the strips between the rows reorganize into UBB pentamers, reducing the surface energy of intermediate structures with steps. Combined with an adjustment of the UBB row direction to better accommodate the strain field caused by rebonding at the step edges, this ultimately leads to the " 16×2 " reconstruction.



Fig. 6. Influence of vibrations on stability of Ge(110) reconstructions. The structures are the same as in Fig. 2. Background histograms show approximate coverages at 400 °C. (a) Vacancies A, B and C (see panel d) contribute as PDV-P (Fig. 5a,d). (b) Vacancies A contribute as a mean of PDV-P and DV, vacancies B and C as DV (Fig. 5f). (c) All vacancies contribute as DV. (d) The most stable energetically is vacancy A (close to a strongly displaced, purple zigzag atom of UBB), vacancy B is close to the other side of UBB and less stable energetically, vacancy C is equidistant to two UBB and has the highest formation energy.

5. Summary and conclusions

This study shows that ab initio total energy calculations, combined with a simple ab-initio based model for vibrational contribution to Helmholtz free energy balance, offer a potential solution to a significant inconsistency between the evolution of Ge(110) reconstructions as observed in STM measurements, and the energy sequence of these reconstructions obtained from ab initio calculations. This inconsistency arises because, on the one hand, the measurements show that a surface annealed below 380 °C evolves from dense coverage with randomly distributed pentamers to a mixture of small c(8 \times 10) domains with approximately half the initial pentamer density (four pentamers per unit cell). On the other hand, the calculations predict that the c(8 \times 10) surface energy decreases when two or three more pentamers are added.

First, this ab initio energy ordering was confirmed to be independent of the approximations used, including slab thickness, vacuum layer thickness, Brillouin zone sampling, energy cutoff, pseudopotential choice, number of frozen core electrons, and inclusion of van der Waals dispersive forces. Second, while including the vibrational internal energy term ($E_{\rm vib} = E_{\rm ZPE} + E_{\rm therm}$) did not alter this result, incorporating vibrational entropy contributions ($-TS_{\rm vib}$)shifted the thermodynamic equilibrium toward c (8 \times 10) structures, in which surface divacancies form in place of additional pentamers, thereby recovering the experimentally observed pentamer density.

Third, although STM images do not easily distinguish between surface divacancies and phase boundaries arising from buckling of $[1\overline{1}0]$ zigzags, the simulated STM patterns and profiles for the vacancycontaining structures predicted in this work agree much better the experimental observation than those simulated for the original c(8 × 10) model, which contained four UBBs and no vacancies [19,20]. The remaining difference between simulated and measured UBB images may be attributed to local variations in buckling phase, associated with energy changes below the calculation accuracy estimated for this study.

Finally, while it cannot be entirely ruled out that vibrations stabilize pure 4UBB structures (without divacancies or additional UBBs), such stabilization would require that the vibrational contribution from divacancies is comparable to that estimated assuming negligible



Fig. 7. STM images (occupied states) of phase boundaries between buckling domains of $1\overline{10}$ zigzags in Ge(110) c(8 \times 10), simulated for the 4UBB reconstruction class (dGe=0). Side views are cross-sections along the red lines. (a) Intrinsic phase boundary A; compare the areas surrounded by the yellow dashed line in both panels. (b) Extrinsic phase boundaries B1 (black row) and B2 (bright row). The part between zigzags in phase is marked C. The atom P is strongly displaced downwards by UBB and pins the buckling phase. (For color version of this figure, the reader is referred to the web version of this article.).



Fig. 8. (a-b) Simulated STM images (occupied states at -1.0 V: colored images and small grayscale insets on the left) compared to experiment (large grayscale rectangles, data from Ref. [11]). The solid rhombus is the c(8 × 10) unit cell. Regions A, B, C, and V highlight differences to measurements. In the simulated images they are rendered in greyscale with contrast matched to that in the experimental image. (a) 4UBB with the buckling pattern predicted by Zhachuk [19]. (b) 4UBB+5DV (Fig. 2j), coverage 67 % according to scenario 1 (Fig. 6a). (c) Enlarged surroundings of A and B. (d) Height profiles along the yellow lines in panel c.

vibrational coupling between divacancies and UBB pentamers, and that intrinsic buckling phase boundaries increase vibrational entropies by about 0.1 eV per boundary. Verifying this would require direct computation of vibrational entropies for $c(8 \times 10)$ structures, which is beyond the scope of the current study.

The results presented here illustrate the importance of surface vibrations for the thermodynamic stability of complex surface structures. In general, this stability affects surface properties such as adsorption energies, energy barriers, and the diffusivity of the adsorbed species, ultimately influencing chemical reactivity and catalytic activity (for example, during decomposition of precursors in chemical vapor deposition of films). Vibrational entropy has recently been shown to invert the reconstruction stability order on another semiconductor surface, Si (111), stabilizing the 7 \times 7 reconstruction in place of the 5 \times 5 reconstruction, which is the surface energy ground state at absolute zero [33].



Fig. 9. Comparison between rebonding in divacancies and on the step edge. Step edge atoms from the surface layer are marked S. $[1\overline{10}]$ zigzag atoms are green, UBB pentamer atoms are red, the UBB interstitial is violet, strongly displaced UBB atoms are purple, subsurface atoms are sepia. (a) Rebonding of divacancy nearest neighbors; dGe=-2. The removed atoms are indicated by empty circles with crosses, the divacancy surface neighbors are marked D, its subsurface neighbors are marked B. (b) Rebonding of atoms of a monatomic step edge in an illustrative arrangement with multiple vacancies condensed into a lower terrace with a UBB pentamer (P2 with interstitial i2); dGe=-15. Since the strip separating two UBB rows of the upper terraces is narrower in $c(8 \times 10)$ cells than in " $16 \times 2^{"}$ cells, the step edge is here closer to the pentamers than it is in the stable " $16 \times 2^{"}$ reconstruction [20], rising the energy of the $c(8 \times 10)$ structure.

atomistic mechanism of phase transitions on Ge(110) by highlighting structural similarities between monatomic step edges in the most stable " 6×2 " reconstruction and the elements stabilizing the transient c(8 × 10) reconstruction (divacancies).

On the technical side, this work introduces a numerically efficient Ge pseudopotential Ge_04_PBEUS_r (four valence electrons, energy cutoff 15 Ry to 20 Ry), optimized for use with RVV10. This pseudopotential [43], whose generation data is provided in the Supporting Material, accurately reproduces the experimental lattice constant and bulk modulus of Ge, and provides standard bulk entropy with PBEsol accuracy.

Finally, it is noted that accounting for van der Waals interactions may also be necessary to accurately reproduce subtle surface energy differences between certain reconstructions of clean surfaces of covalently bonded crystals, particularly when considering adatom-related structures.

CRediT authorship contribution statement

Jarek Dąbrowski: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2025.122761.

Data availability

https://doi.org/10.24435/materialscloud:eq-s8 (CIF and UPF files are available in Materials Cloud Archive,)

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