

## Do We Know the True Structure of $\text{Ge}(111)c(2 \times 8)$ ?

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We present the first *ab initio* determination of the surface structure and electronic properties of  $\text{Ge}(111)c(2 \times 8)$ . New features emerge, in addition to the basic adatom–rest-atom architecture. In agreement with LEED, which shows weak but nonvanishing quarter-order reflections, we find that an asymmetry is present in the surface unit cell, related to a small buckling between the two rest atoms, as well as to in-plane asymmetries of the rest atoms, adatoms, and first bilayer atoms. This inequivalence also produces a splitting of both the rest-atom and the adatom dangling-bond states, which explains the difference in their apparent heights as seen recently with scanning tunneling microscopy.

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The low-temperature stable surface of  $\text{Si}(111)$  has a  $(7 \times 7)$  structure, while that of  $\text{Ge}(111)$  is  $c(2 \times 8)$ . In both reconstructions a crucial role is played by the adatom–rest-atom mechanism [1–11]: About  $\frac{3}{4}$  of the ideal surface dangling bonds are saturated by “adatoms,” where extra electrons are mainly captured away by the remaining  $\frac{1}{4}$  of surface atoms (“rest atoms”). In the simplest adatom–rest-atom structure [with either a  $(2 \times 2)$  or a  $c(2 \times 4)$  unit cell] this charge transfer leads to filled and empty surface-state bands, mostly localized on the rest atoms and the adatoms, respectively; all partly filled dangling-bond states are then eliminated, and the surface is stable [1]. Experience with the  $(7 \times 7)$  structure of Si, however, has shown that many subtler but important effects accompany this main phenomenon [2]. Similar effects should also be present in the  $\text{Ge}(111)c(2 \times 8)$  surface [3,4]. Particularly, scanning-tunneling-microscopy (STM) studies find differences in the charge distributions of the two adatoms and the two rest atoms within the  $c(2 \times 8)$  unit cell [4]. These differences—reminiscent of those between the faulted and unfaulted halves of the unit cell of  $\text{Si}(111)(7 \times 7)$  [2,5]—suggest the occurrence of structural asymmetries in the  $c(2 \times 8)$  cell, also qualitatively indicated by low-energy electron diffraction (LEED) [6]. The nature of these secondary distortions and asymmetries has not been described so far. Also not understood is the microscopic reason why the surface is in reality  $c(2 \times 8)$  and not  $(2 \times 2)$  or  $c(2 \times 4)$  [12]. As indicated by recent calculations for  $\text{Si}(111)$  [13], these difficult problems are now within the reach of modern *ab initio* methods [14].

In this Letter we present first-principles calculations of the structural and electronic properties of  $\text{Ge}(111)c(2 \times 8)$ , where the full periodicity of this surface is treated correctly for the first time. Previous theoretical studies have been simplified to an adatom structure with  $(2 \times 2)$  periodicity [1,7].

We find significant differences in the structures of the  $(2 \times 2)$  and  $c(2 \times 4)$  subunits of the  $c(2 \times 8)$  unit cell, and show that these are consistent with the LEED results in

Ref. [6]. The rest atoms have a relative buckling of the order of  $0.03 \text{ \AA}$ , and in-plane asymmetries of the order of  $0.1 \text{ \AA}$ , while differences are smaller for the adatoms. The  $(2 \times 2)$  subunit rest atom, which is raised more, acquires slightly more electron charge than the other. In addition, there is a splitting of the occupied (empty) rest-atom (adatom) dangling-bond states, so that there are states mostly localized either in one or in the other of the rest atoms (the effect is smaller for the adatoms), in agreement with STM results [4]. We also find a small contribution of the adatoms to filled states, thus indicating that the adatom  $\rightarrow$  rest-atom charge transfer is not complete.

Our calculations were performed by the *ab initio* molecular-dynamics (MD) scheme [14], well tested in a previous study of the  $(111)(2 \times 1)$  surface of Ge [15]. We adopt a repeated slab geometry, each slab consisting of six layers of sixteen Ge atoms each, corresponding to two primitive  $c(2 \times 8)$  cells. The four adatoms are added to the top surface; the other surface is saturated by sixteen hydrogen atoms. The five topmost layers of Ge and the adatoms are allowed to move; the sixth layer and the H atoms are frozen. Consecutive slabs are separated by an empty space  $7.6 \text{ \AA}$  wide. Only electronic states at  $\mathbf{k}=0$  have been included, which is reasonable in view of the large size of our unit cell. The wave functions have been expanded in plane waves with kinetic energy cutoff  $E_{\text{cut}}=8 \text{ Ry}$ . Convergence was checked by separate calculations using different supercells and/or  $E_{\text{cut}}=10 \text{ Ry}$ . Computational details will be given elsewhere [16].

To determine the optimal  $c(2 \times 8)$  structure, we have used a combined electronic and ionic steepest-descent relaxation starting from an ideal  $\text{Ge}(111)(1 \times 1)$  surface covered by adatoms located at  $T_4$  sites [17]. To check that the resulting structure was the true minimum, a few somewhat different starting configurations were also tried. The same result was achieved in all cases, indicating the absence of energy barriers between initial and final geometries. Moreover, the stability of the final structure was further checked by a long microcanonical thermal MD run ( $\sim 0.45 \text{ ps}$ ) at  $T \sim 300 \text{ K}$ . The full re-

laxed surface structure was first of all found to retain exact  $c(2 \times 8)$  symmetry, in spite of the larger  $c(4 \times 8)$  simulation cell. Its total energy was found to be lower than that of the ideal  $(1 \times 1)$  surface (calculated using the same surface supercell) by  $\sim 0.33$  eV/[ $(1 \times 1)$  cell], and lower than that of Ge(111) $(2 \times 1)$  by  $\sim 0.05$  eV/[ $(1 \times 1)$  cell] [18].

The optimal  $T=0$  structure of Ge(111) $c(2 \times 8)$  is shown in Fig. 1. The agreement between our atomic coordinates (to be presented in detail elsewhere [16]) and x-ray experiments [8] is excellent [19]: van Silfhout has shown that the structure factor intensity along the  $(10)$  rod calculated using our atomic positions [averaged to yield a  $(2 \times 2)$  cell] fits the x-ray results as well as his best-fit coordinates [9]. Since we do not impose a  $(2 \times 2)$  unit cell, our surface structure does not have threefold symmetry. For the first-layer atoms F1, F2, and F3 (F4, F5, and F6) that are bonded to adatom A1 (A2), only a reflection plane between atoms F1 and F3 (F4 and F6) survives. This appears to be a true effect in the real  $c(2 \times 8)$  surface [10]. In addition, we find a remarkable inequivalence of the two rest atoms (their relative buckling is  $\sim 0.03$  Å, and in-plane asymmetries are of the order of 0.1 Å), whereas the inequivalence is quite small for the adatoms. With respect to their ideal positions, the adatoms are lowered by  $\sim 0.41$  Å; the two rest atoms R1 and R2 are raised by 0.55 and 0.52 Å, respectively; atoms

F1, F2, F3 (F4, F5, F6) move laterally toward the adatom A1 (A2): F1 and F3 (F4 and F6) by 0.14 (0.08) Å, and F2 (F5) by 0.11 (0.2) Å. Rest atom R1 (R2) has bond angles of  $96.8^\circ$ ,  $96.1^\circ$ , and  $96.2^\circ$  ( $101.6^\circ$ ,  $95.0^\circ$ , and  $95.0^\circ$ ) with its neighbors. This compares well with an average value of  $98.5^\circ$  extracted in Ref. [8]. Second-layer atoms S1, S5 (below the adatoms) are strongly displaced downwards by 0.55 Å. Other second-layer atoms move upwards by 0.07–0.12 Å. These changes in turn produce some displacements of atoms in the second bilayer. The adatom–rest-atom structure corresponding to A1–R1, i.e., to the  $(2 \times 2)$  subunit of the  $c(2 \times 8)$  cell, is clearly more symmetric with respect to  $120^\circ$  rotations than that corresponding to A2–R2 in the  $c(2 \times 4)$  subunit.

LEED results [6] show that fourth-order spots, although very weak, are not missing, contrary to expectations for a perfectly symmetric  $c(2 \times 8)$  cell. LEED intensities of the integer-, half-, eighth-, and quarter-order beams are in the ratios of 1000:100:10:1 (Fig. 2). For a rough comparison we estimate the kinematic Bragg intensity in the simple form  $I(\mathbf{G}) = |\sum_i \exp(i\mathbf{G} \cdot \mathbf{r}_i) \exp(-z_i/\lambda)|^2$ , where  $\sum_i \exp(i\mathbf{G} \cdot \mathbf{r}_i)$  is the structure factor of the atoms at positions  $\mathbf{r}_i = (x_i, y_i, z_i)$ , and  $\exp(-z_i/\lambda)$  accounts for the penetration depth  $\lambda$  of the electrons. In Fig. 2 we plot this intensity along the  $[1\bar{1}0]$  direction (where integer-, half-, and quarter-order reflections lie) using  $\lambda = 8$  Å as a value rather typical for LEED electrons. It can be seen that all the spots are present, and the order of magnitude of the intensity ratios is consistent with experiment.

The structural asymmetries which we have just described must be accompanied by an energy gain, as well as by corresponding asymmetric features in the electronic properties of the Ge(111) $c(2 \times 8)$  surface. We find a small excess electron charge near the outermost rest atom R1 relative to R2. No quantitatively similar effect is seen for the adatoms. Hence the  $(2 \times 2)$  subunit is slightly

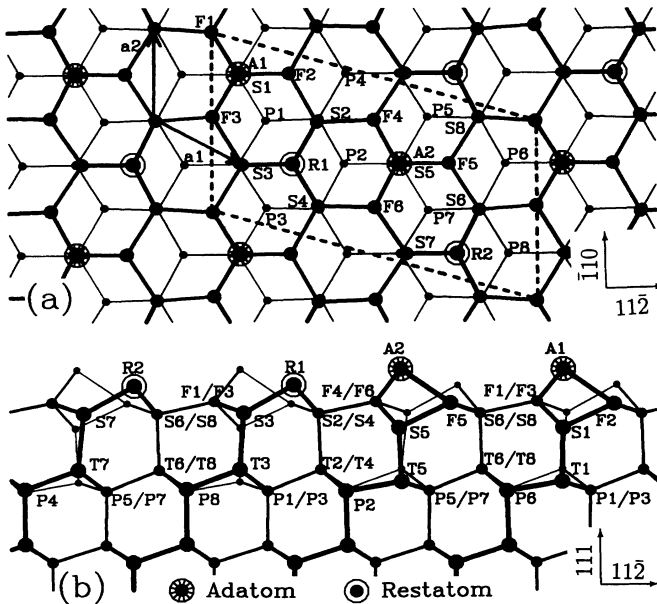


FIG. 1. Atomic structure of the reconstructed Ge(111)  $\times c(2 \times 8)$  surface. (a) Top view of the surface showing the adatoms and the first three layers of atoms.  $a_1$  and  $a_2$  are the lattice vectors of the unreconstructed surface and have a length  $a = a_0/\sqrt{2}$  ( $a_0$  is the bulk lattice constant). (b) Side view of the surface in the  $(1\bar{1}0)$  plane passing through A2 in (a). Bigger dots and thicker lines represent atoms and bonds closer to the viewer.

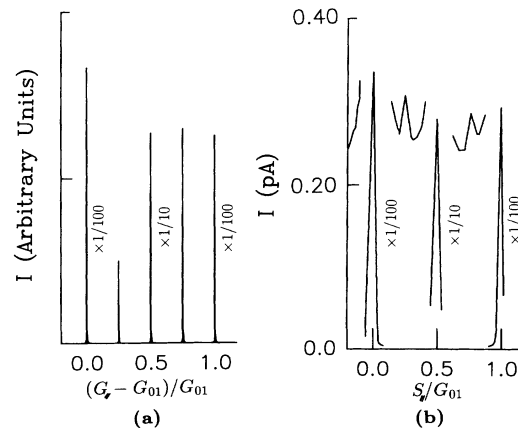


FIG. 2. LEED intensity, plotted along the  $[1\bar{1}0]$  direction, showing integer-, half-, and quarter-order spots. (a) Theory (this work); (b) LEED data of Ref. [6].

more electron rich than the  $c(2\times 4)$ . Electrostatic (Madelung) energies associated with this structural and charge modulation asymmetry have the right sign for stabilizing  $c(2\times 8)$  relative to either  $(2\times 2)$  or  $c(2\times 4)$ . For a quantitative evaluation of this stabilization energy, we have performed a separate calculation of the  $c(2\times 4)$  structure (no asymmetry) also in a 16-atom cell, and obtained an energy  $\sim 0.06$  eV/(1 $\times$ 1) higher than our  $c(2\times 8)$  results. The extra stability of asymmetric  $c(2\times 8)$  probably can be seen as a form of wall-wall attraction, similar to that proposed between steps [20].

Analysis of the surface states at the two  $\mathbf{k}$  points which fold into the  $\Gamma$  point of our  $c(4\times 8)$  cell also reveals asymmetric features [Fig. 3(a)]. We find two occupied rest-atom dangling-bond bands, s4 and s5, with s4 (s5) localized mostly on R1 (R2). Similarly, the empty ada-

tomlike band is split in two, s8 and s9, but the charge density of both states is evenly distributed on A1 and A2. s1 and s2 are first-layer dangling-bond states coupled to  $p_x, p_y$  adatom orbitals [21]. s3 is also a backbond state similar to s1 and s2, but with some charge density on R2. s6 and s7 are backbond states mostly localized in the first bilayer, with some weight in the second.

In Fig. 3(c) we show the surface density of states (SDOS) and compare it with angle-resolved photoemission (ARPES) [3] and inverse photoemission (IPE) [22] [Fig. 3(b)]. In Fig. 3(d) results of scanning tunneling microscopy (STS) [5,11] are also displayed. There is general agreement in the number and position of the filled-state peaks between our results and the different experiments. Features corresponding to adatom and rest-atom dangling bonds and to backbond states are easily identified. The predicted splitting between, e.g., s4 and s5 appears to be too small for detection within the resolution of the data. A peak (corresponding to the states s6 and s7) is found very close to the Fermi level at the  $\Gamma$  point, in agreement with ARPES. These states are not dangling-bond-like and are very delocalized both in plane and vertically, reaching down to the second bilayer. This is consistent with the large dispersion seen in ARPES. The agreement is poorer for empty states (a shift of  $\sim 0.7$  eV is needed), possibly reflecting a standard difficulty of local density calculations.

In Fig. 4 (left) we show a grey-scale image of the local density of states  $\rho(\mathbf{r}, E)$  in a plane at  $z \sim 1$  Å above the adatoms, and at  $E = -0.5$  eV measured from the Fermi energy  $E_F$  [23]. In the simplest approximation this plot corresponds to the STM images of our structure, taken at voltage  $V = E$ . The right-hand panel shows actual STM

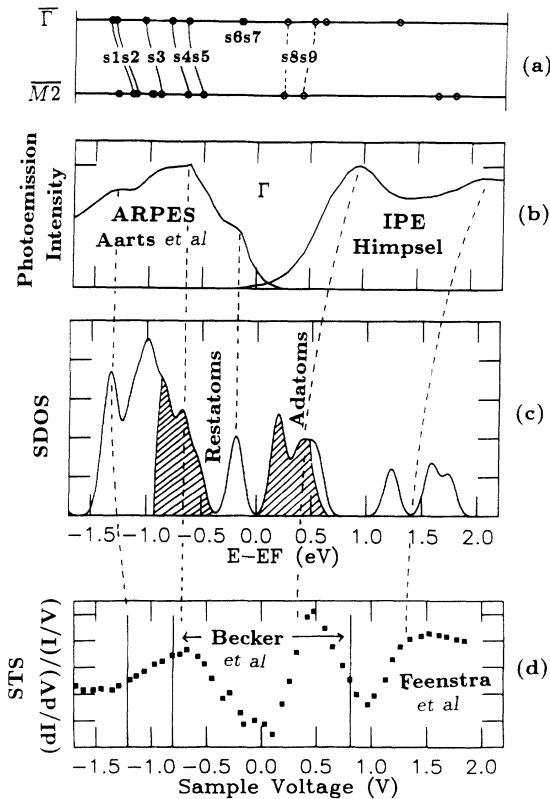


FIG. 3. (a) Surface states at the two  $\mathbf{k}$  points,  $\bar{\Gamma}(0,0)$  and  $\bar{M}_2(\pi/2a, \pi/4a\sqrt{3})$ , sampled in this calculation. Solid (open) circles denote occupied (empty) states. Lines connecting states of similar origin at  $\Gamma$  and  $\bar{M}_2$  represent the expected surface bands. (b) ARPES [3] and IPE [22] results at  $\Gamma$ . (c) Calculated SDOS (this includes all states whose weight in a region including the first two layers and the adatoms is greater than 0.5). The discrete levels have been broadened with Gaussians of width 0.1 eV. Shaded areas indicate rest-atom and adatom states. (d)  $(dI/dV)/(I/V)$  from STS [11]. Vertical lines give the position of the peaks in Ref. [5]. Dashed lines connecting corresponding features in panels (b)–(d) are meant as a guide to the eye.

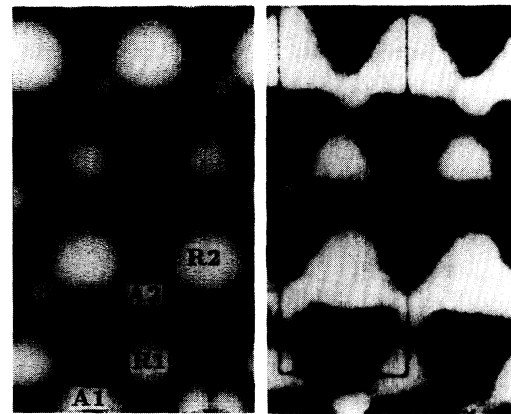


FIG. 4. Theoretical (left) STM images of  $\text{Ge}(111)c(2\times 8)$  at  $E \sim -0.5$  eV compared with experimental results of Ref. [4] at  $V \sim -0.7$  eV (right) (the slight energy shift is required by residual inaccuracies in band energy location). White denotes more current; black, less current. Note the large asymmetry of the rest atoms R1 and R2, and also current from the adatoms, indicating partial charge transfer.

data [4]. The rest atoms R2 are the brightest features, both in calculations and experiments. As in experiment, we also have weaker features originating from the adatoms A1 and A2, thus indicating that the charge transfer from the adatoms to the rest atoms is in reality incomplete. At a lower voltage of  $-0.9$  eV (not shown), the situation is changed, and now the two different rest atoms are about equally bright. Conversely at energies above  $E_F$  our images are entirely dominated by the adatoms, which appear rather symmetric again in agreement with the STM results.

In conclusion, we have presented a new *ab initio* study of Ge(111) $c(2\times 8)$  where the full periodicity is respected, and all related asymmetries and distortions are permitted. Differences in structure and electronic charge distribution between the rest atoms belonging to the  $(2\times 2)$  and  $c(4\times 2)$  subunits of the  $c(2\times 8)$  cell are found, which explain recent LEED and STM data. These differences suggest an analogy with the known asymmetries in the unit cell of Si(111) $7\times 7$  [2]. Their role in stabilizing the  $c(2\times 8)$  over the  $(2\times 2)$  and  $c(2\times 4)$  structures has been addressed microscopically.

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- [18] For this comparison, a new calculation for Ge(111) $2\times 1$  was made using a  $(2\sqrt{3}\times 4)$  supercell with 16 atoms/layer. The  $(2\times 1)$  structure was found to be lower than the ideal (calculated with the same cell) by  $\sim 0.28$  eV/[ $(1\times 1)$ ]. This value is slightly different from that reported in Ref. [15], where a smaller cell was used.
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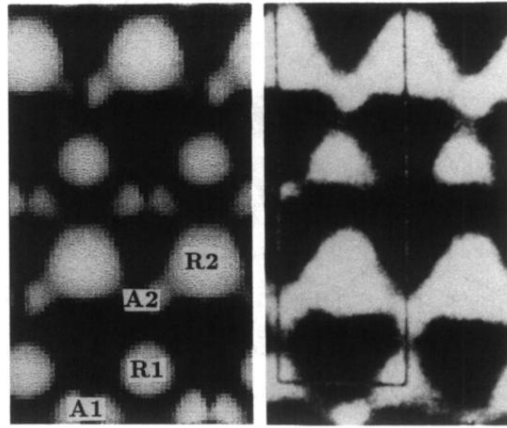


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