PHYSICAL REVIEW B VOLUME 44, NUMBER 24 15 DECEMBER 1991-II

Structural and electronic properties of the (111)2 × 1 surface of Ge from first-principles calculations

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(Received 25 July 1991)

We present results of a first-principles determination of the surface structure and electronic properties of Ge(111)2 × 1. We have found that the most stable state of this surface has a π-bonded chainlike structure. This structure has two different isomers with the tilt angle of the uppermost chains in opposite directions, and energetically very close to each other. The isomers exhibit a similar buckling of the surface chains, much larger than that of Si(111)2 × 1. They also show a very similar surface-state dispersion, which agrees well with the angle-resolved photoemission data of Nicholls *et al.*

I. INTRODUCTION

The (111) surface of germanium shows a (2 × 1) reconstruction following cleavage at room temperature. Although no direct experimental structural determination of Ge(111)2 × 1 is available so far, this surface is believed to have a π-bonded chain geometry[1] similar to that of Si(111)2 × 1. This idea is supported not only by the chemical similarity between Si and Ge, but also by the fact that surface-state dispersions calculated on the basis of the π-bonded chain geometry agree reasonably well with a large variety of spectroscopic data.[2]

However, there are also a number of experimental results suggesting that the cleavage surface of Si and Ge might have somewhat different characteristics. While the cleaved surface of Si always shows a 2 × 1 low-energy electron diffraction (LEED) pattern, independent of the cleavage temperature T_{cl}, there seems to be evidence that the Ge(111) surface structure depends on T_{cl}.[3] In particular, while at $T_{\mathrm{cl}} \geq 60$ K Ge(111) shows a well-defined 2 × 1 reconstruction, at $T_{\mathrm{cl}} < 40$ K LEED pictures where the extra spots of the 2 × 1 structure are anisotropically broadened, or altogether missing are found.[3]

The electronic structure of the (111)2 × 1 surface of Ge is not completely clear either. Nicholls *et al.* (NHUF),[4,5] using angle-resolved photoemission (ARUPS), have found a band dispersion for the dangling-bond surface state that agrees well with LDA (Ref. 6) and quasiparticle calculations[7] based on the π-bonded chain model. However a different photoemission experiment by Solal *et al.*[8] (SJBSPP) found a band with a very small dispersion which is inconsistent with the π-bonded chain model.

The surface optical absorption data of Chiarotti *et al.*[9] indicates a surface interband, or excitonic transition peaked around 0.5 eV, very close to that of Si(111)2 × 1, 0.45 eV. This is also somewhat surprising, since the bulk gap of Ge is only half that of Si. If a π-bonded chain model is the explanation, it must still differ somehow from that of Si(111)2 × 1.

Prompted by these conflicting or at any rate unexplained results, we have performed a detailed first-principles study of the structural and electronic properties of Ge(111)2 × 1 which, unlike previous *ab initio* calculations, is not biased by a given (e.g., π-bonded chain) model of the surface structure. In our calculations the optimum surface structure is directly searched using the Car-Parrinello molecular-dynamics approach[10] which has already been tested successfully in the study of silicon surfaces.[11,12] Our results show that the most stable state of the (111)2 × 1 Ge surface is indeed a π-bonded chain structure. However, two chainlike structures with different tilt angles of the topmost chains are found. These two structures have, within the precision of our calculations, the same energy. Remarkably, they both exhibit a huge buckling of the surface chains, 0.8–0.9 Å in comparison with 0.3–0.4 Å (Ref. 13) for the Si(111)2 × 1 surface. The existence of these two degenerate structures implies the possibility of different domains under different cleavage conditions, which may be at the origin of the cleavage-temperature-dependent effects.[3] The surface-state dispersions of both structures are in good agreement with photoemission data by NHUF,[4] and can also explain very well the optical peak position.[9]

This paper is organized as follows. In Sec. II we describe our computational method and some technical details. Our results for the structural and electronic properties are presented in Secs. III and IV, respectively. A discussion and the conclusions are given in Sec. V.

II. COMPUTATIONAL METHOD

Our calculations are performed within the *ab initio* molecular-dynamics scheme, using a repeated slab geometry. Each slab consists of six (111) layers of Ge atoms. It has one free surface while the other surface is saturated by hydrogen atoms. Neighboring slabs are separated by an empty space 7.6 Å wide. Two different surface supercells have been used: one with eight atoms/layer and ($\sqrt{3} \times 4$) in-plane periodicity (hereafter referred to as cell A), and the other with 12 atoms/layer with a ($2\sqrt{3} \times 3$) periodicity (cell B). In both cases, only the Γ point of the surface supercell Brillouin zone was sampled. The **k** points of the conventional surface Brillouin zone (SBZ) which fold into this point are (in units of $\pi\sqrt{2}/a_0$, a_0 being the bulk lattice constant) $\bar{\Gamma} \equiv (0,0), \bar{J} \equiv (1,0)$, and $(\frac{1}{2},0)$ in the case of cell A; $\bar{\Gamma} \equiv (0,0), \bar{J}' \equiv (0,1/\sqrt{3}),(\frac{2}{3},0)$, and $(\frac{2}{3},1/\sqrt{3})$ in the case of cell B (see Fig. 1). The wave functions are expanded in plane waves with a kinetic energy cutoff E_{cut}=8 Ry, which gives well-converged bulk energies.[14] The norm-conserving pseudopotential is taken from Ref. 15, and includes both s and p nonlocal terms, which are treated within the Kleinman-Bylander scheme.[16] Details about this are to be discussed elsewhere.[14] A steepest-descent (SD) algorithm (see, e.g., Ref. 17) is used for electronic energy minimizations at fixed ionic positions. This is combined with a similar steepest-descent dynamics of the ions to determine the optimum surface structure. Although a global surface structure optimization via simulated annealing was not carried out, we have checked the local stability of several structures by performing short microcanonical MD runs at finite temperatures. In all these calculations only the five topmost layers of Ge are allowed to move, while the sixth layer of Ge and the H atoms are fixed at the ideal positions.[18]

III. SURFACE STRUCTURE

To determine the optimal surface structure (compatible with our choice of the surface supercell), we have first performed various steepest-descent relaxations starting from different initial ionic configurations and using the two different surface supercells described above. In the following we shall first describe the results obtained with cell A.

When starting from the clean unreconstructed (111) surface [Fig. 2(a)], we found that the system evolves to the structure shown in Fig. 2(c). This is a (2×1) chainlike structure where the tilt angle of the uppermost chains is reversed with respect to the standard Pandey-like geometry.[1,13] The path of the transformation can be described as follows. One of the topmost atoms in the (2×1) unit cell [atom 1 in Fig. 2(a)] starts going down in the $[\bar{1}\bar{1}\bar{1}]$ direction until its vertical position is almost at the same height of the second layer of atoms. Meanwhile, atom 3 moves in the $[\bar{1}\bar{1}2]$ planar direction. In this initial stage of the transformation the movement of atom 1 and the gain in potential energy are very fast, so that the total gain in energy with respect to the ideal surface reaches values of the order of 0.3 eV per (1×1) surface cell. Once the Ge atoms reach the configuration shown in Fig. 2(b) (after ~ 2000 SD steps), the changes in atomic positions and the energy gain per step become very slow. However the atoms in the first and second

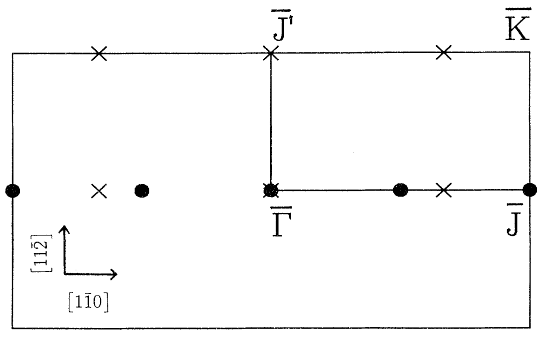
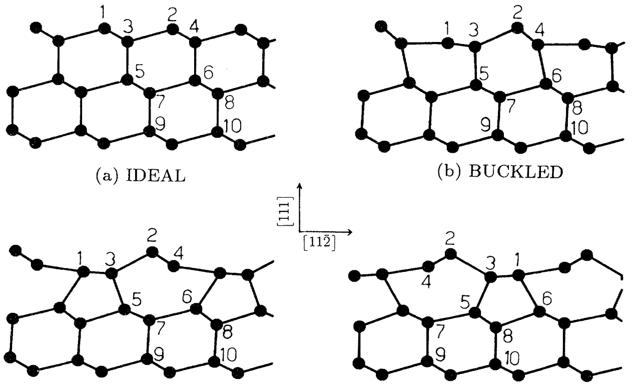


FIG. 1. Surface Brillouin zone of the Ge(111)2×1 surface. Solid dots (crosses) denote the **k** points which fold into the Γ point of supercell A (B).



(a) IDEAL

(b) BUCKLED

(c) CHAIN LEFT

(d) CHAIN RIGHT

FIG. 2. Schematic side view of selected atomic structures characterizing the relaxation starting from the ideal (1×1) surface: (a) initial (ideal unreconstructed); (b) intermediate (buckled); (c) final ("chain left"). In (d) we show the final ("chain right") structure obtained by relaxation of the standard Pandey chain model (see text).

layers keep moving slowly in the $[\bar{1}\bar{1}2]$ direction and the bonds between atoms 4 and 6 in Fig. 2(b) start to break. Finally the bonds between atoms 1 and 6 are formed and the fivefold and sevenfold rings typical of the π-bonded structure are completed [Fig. 2(c)]. This took altogether ~ 7000 SD steps. The final direction of the tilt angle of the π-bonded chain is reversed relative to the standard π-bonded structure of Si(111) 2 × 1 (Refs. 1 and 13) (we call this the "chain left" structure). In order to check the stability of this chain left structure, we performed a long thermal Car-Parinello MD run (0.55 ps, corresponding to 2300 time steps) where the temperature was gradually raised (by rescaling the ionic velocities) from 100 to 200 K. The structure was found to be stable in this temperature range.

Instead, when we started our steepest-descent minimization from a standard Pandey-like structure (with the tilt angle of the topmost chains in the other direction) the "chain right" structure of Fig. 2(d) was obtained. Within the accuracy of our calculations, the two chain structures are found to have essentially the same energy: 0.419 and 0.417 eV/(1 × 1) cell lower than the ideal surface for the chain right and left, respectively. The fact that both structures appear locally stable indicates the existence of an energetic barrier between them, which prevents spontaneous transformation of one into the other. These two structures also have other features in common. The bonds along the topmost chains are slightly contracted with respect to the ideal bulk length of 2.43 Å (Ref. 19) (2.42 Å for both the chain right and chain left). The bonds between atoms 3 and 5 in Figs. 2(c) and 2(d) are strong (2.42 and 2.40 Å for the chain right and left, respectively), while the bonds between atoms 1 and 6 are very weak (2.50 and 2.59 Å). There is a larger buckling in the case of the chain left structure (0.88 against 0.78 Å for the chain right). However, in both cases the chain buckling is much larger than in previous theoretical calculations.[6,7] It is also much larger than for Si(111)2×1, where the experimental value is ~0.38 Å,[13] and the value obtained by *ab initio* MD is ~0.49 Å.[11]

We have checked the influence of the slab size, and the thickness of the vacuum, by increasing the number of Ge layers from six to eight (the first six layers of Ge were allowed to relax), and the width of the vacuum region from 7.6 to 10.8 Å. Our results for the energy gain relative to the ideal surface and the buckling of the chain right structure are shown in Table I. It is apparent that our results do not depend significantly on the thickness of the slab and of the vacuum.

We have also checked how our results are affected by the choice of the surface supercell (i.e., of the **k**-point sampling), by repeating our calculations with the surface supercell *B*. When starting with the ideal Ge(111) surface, and applying steepest descent, we found that the initial stages of the relaxation were the same as for cell *A*. However, for cell *B* the relaxation terminated at an intermediate (2 × 1) buckled structure similar to that shown in Fig. 2(b), having a substantially higher energy than the (2 × 1) π-bonded chain (see Table II). Only subsequently, by performing a thermal MD run, we found that at a temperature T ~200 K this buckled (2 × 1) structure transformed into the lower energy π-bonded chain left geometry. In Table II we show the energy gain with respect to the ideal unreconstructed surface of the buckled, the chain left, and the chain right structures, obtained with the supercell *B*. For the π-bonded chain structures, the magnitude of the buckling is also given. If we compare these results with the ones in Table I, we see some differences. These differences, as well as the fact that with cell *B* the buckled structure is a local (shallow) minimum, can probably be understood as an effect of the different sampling of the **k** points in the (2 × 1) SBZ. It is interesting to note that for Si(111) no extra local minimum such as the buckled (2 × 1) structure occurs when using a surface supercell either of type *A* or *B*. The final T=0 coordinates obtained with eight atoms/cell and 12 atoms/cell are given in Tables III and IV.

TABLE II. Energy gain with respect to the ideal unreconstructed surface [in eV/(1 × 1) surface cell], and buckling of the π-bonded chain, using a 12 Ge atoms/layer supercell (supercell *B*).

Structure	ΔE [eV/(1 × 1) cell]	Buckling (Å)
chain right	0.334	0.69
chain left	0.340	0.77
buckled	0.209	

TABLE I. Energy gain with respect to the ideal unreconstructed surface [in eV/(1 × 1) surface cell], and buckling of the π-bonded chain for different sizes and separations of the slab. These results have been obtained using the surface supercell with eight atoms/layer (supercell *A*) and refer to the chain right structure.

Slab	ΔE [eV/(1 × 1) cell]	Buckling (Å)
six layers of Ge + one layer of H + 7.6 Å of vacuum	0.419	0.78
six layers of Ge + one layer of H + 10.8 Å of vacuum	0.423	0.73
eight layers of Ge + one layer of H + 10.8 Å of vacuum	0.399	0.76

TABLE III. Atomic positions of the Ge(111)2 × 1 surface. Atoms are numbered as in Fig. 2. Positions are given by $\mathbf{r} = c_1\mathbf{a}_1 + c_2\mathbf{a}_2 + c_3\mathbf{a}_3$, with $\mathbf{a}_i$ defined in the conventional cubic coordinate system as $\mathbf{a}_1 = (a_0/2)(-1,0,1)$, $\mathbf{a}_2 = (a_0/2)(1,-2,1)$, $\mathbf{a}_3 = a_0(1,1,1)$. The coordinates are taken from our calculations with cell A and averaged over the different 2 × 1 unit cells. There is a small breakdown in the $(1\bar{1}0)$ mirror plane symmetry.

Atom	Ideal			Chain left			Chain right		
no.	c_1	c_2	c_3	c_1	c_2	c_3	c_1	c_2	c_3
1	0.500	0.500	1.000	0.500	0.361	0.905	0.001	0.507	0.909
2	0.000	0.000	1.000	0.001	0.836	1.039	0.501	−0.010	1.052
3	0.000	0.667	0.917	0.000	0.564	0.896	0.502	0.300	0.898
4	0.500	0.167	0.917	0.501	0.021	0.949	0.000	0.844	0.973
5	0.000	0.667	0.667	0.000	0.661	0.659	0.499	0.183	0.662
6	0.500	0.167	0.667	0.500	0.190	0.667	0.000	0.655	0.670
7	0.500	0.833	0.583	0.500	0.845	0.591	0.500	0.839	0.595
8	0.000	0.333	0.583	0.000	0.341	0.565	−0.001	0.337	0.564
9	0.500	0.833	0.333	0.500	0.832	0.336	0.500	0.830	0.339
10	0.000	0.333	0.333	0.000	0.327	0.322	0.000	0.328	0.322

IV. SURFACE ELECTRONIC STATES

Using the geometry of the chain structures obtained with the Car-Parrinello method, we performed standard first-principles self-consistent pseudopotential calculations to investigate the electronic structure of the (111)2 × 1 surface of Ge. In these calculations we use the same plane-wave kinetic-energy cutoff of 8 Ry employed for the structural determinations. An evenly spaced sampling grid of eight **k** points in the surface Brillouin zone of the (2 × 1) reconstructed surface is used for the calculation of the electronic charge density during the iteration to self-consistency. On changing from three **k** points to eight **k** points the energy changes by less than 0.03 eV/surface atom. After self-consistency is reached, the electronic band structure of the system was calculated along the symmetry directions $\bar{\Gamma}\bar{J}\bar{K}$. Contour plots of the occupied and empty surface states at $\bar{J}$ for the chain left and chain right structures are shown in Figs. 3 and 4. For both structures the occupied surface state is completely localized on the top atom of the π-bonded chain [Figs. 3(a) and 4(a)], while the empty surface state is completely localized on the down atom of the chain [Figs. 3(b) and 4(b)]. A similar feature has been observed in the case of Si(111)2 × 1 by scanning tunneling spectroscopy.[20]

Comparison between our calculated surface-state dispersions and experiments is shown in Fig. 5 (the band dispersion of SJBSPP is shown in Fig. 6). In Fig. 5 the theoretical and experimental curves have been rigidly shifted so that at $\bar{J}$ they all coincide with the value of

TABLE IV. Atomic positions of the Ge(111)2 × 1 surface (using cell B). Coordinates and same comment as in Table III.

Atom	Buckled			Chain left			Chain right		
no.	c_1	c_2	c_3	c_1	c_2	c_3	c_1	c_2	c_3
1	0.511	0.487	0.942	0.503	0.329	0.897	0.000	0.515	0.906
2	0.004	−0.005	1.041	0.004	0.833	1.038	0.500	0.016	1.047
3	0.013	0.685	0.912	0.003	0.536	0.896	0.500	0.308	0.897
4	0.509	0.142	0.917	0.504	−0.010	0.958	0.000	0.852	0.976
5	−0.008	0.668	0.659	0.001	0.649	0.660	0.500	0.183	0.660
6	0.497	0.170	0.666	0.501	0.181	0.659	0.000	0.654	0.668
7	0.495	0.838	0.577	0.501	0.830	0.592	0.500	0.834	0.595
8	−0.001	0.335	0.579	0.000	0.328	0.561	0.000	0.332	0.565
9	0.499	0.833	0.329	0.500	0.834	0.337	0.500	0.834	0.338
10	0.000	0.333	0.330	0.000	0.331	0.320	0.000	0.333	0.322

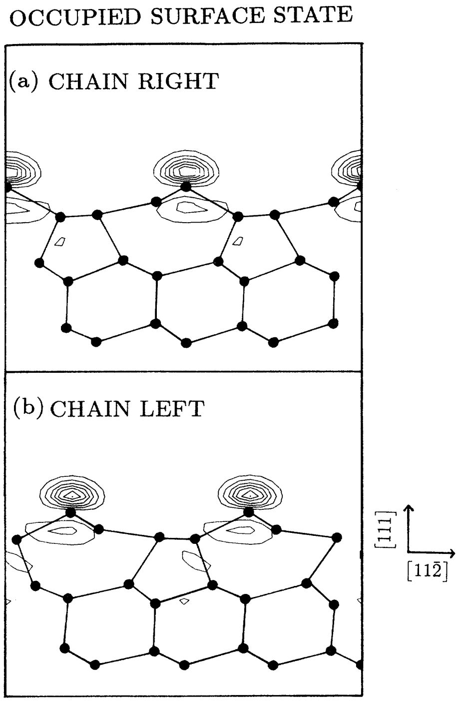


FIG. 3. Contour plot of the occupied surface state at $\bar{J}$, in the (110) plane passing through the up atom: (a) chain right structure, (b) chain left structure. Note the "mirror" similarity of the two.

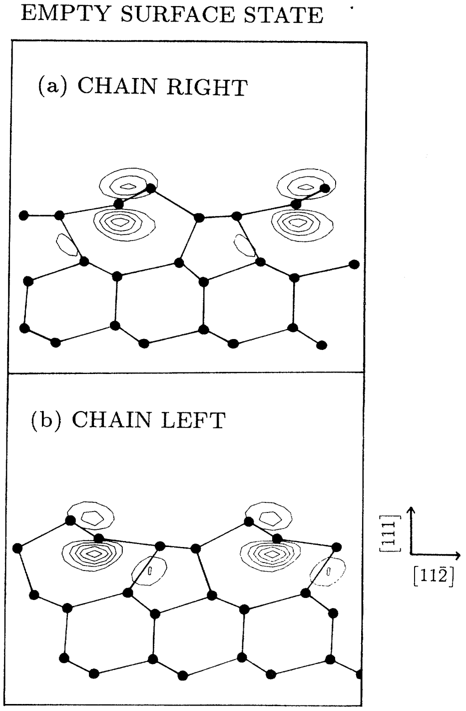


FIG. 4. Contour plot of the empty surface state at $\bar{J}$, in the (110) plane passing through the down atom: (a) chain right structure, (b) chain left structure. Same comment as in Fig. 3.

the NHUF experiment with photon energy 10.2 eV (other curves from the same experiment are left in the original position). The Fermi level is taken to be at 0.1 eV above the valence-band maximum according to experiments.[8,5]

In Table V we compare the gap between the occupied and empty surface states, and the corresponding bandwidth with experimental results and with other theoretical calculations. We found a gap of 0.54 and 0.56 eV for the chain left and chain right structures respectively.[19] These values are larger than that found

TABLE V. Gap between the occupied and empty surface states at $\bar{J}$ [$E_{\text{gap}}(\bar{J})$], and surface-state bandwidths (W^{occ}, W^{emp}), as calculated in this work together with previous theoretical and experimental results.

	Previous theory		Present work		
	LDA	QP	Chain left	Chain right	Experiment
$E_{\text{gap}}(\bar{J})$	0.24	0.67	0.54	0.56	0.50[a,b] 0.52[c] 0.57[d] 0.65[e]
W^{occ}	0.83	0.82	0.65	0.56	0.75[f] 0.25[g]
W^{emp}	1.19	1.25	1.11	1.11	

[a] Reference 24.
[b] Reference 21.
[c] Reference 22.
[d] Reference 25.
[e] Reference 26.
[f] Reference 4.
[g] Reference 8.

in previous LDA calculations by Northrup and Cohen,[6] but smaller than the recent calculation of Zhu and Louie using the quasiparticle self-energy approach.[7] The value of our gap is surprisingly close to the values from optical measurements,[2,21–23] direct photoemission from a heavily n-type doped Ge sample,[24] and EELS,[25] while combined inverse photoemission (IPE) and photoemission (PE) results give a larger gap of about 0.65 eV.[26] The difference between optical experiments and combined PE-IPE is believed to be due to excitonic effects present in the optical processes.[27,28]

From Table V it appears that the angle-resolved photoemission measurements of NHUF and SJBSPP yield very different bandwidths for the occupied surface states. The one by NHUF shows a big energy dispersion between the $\bar{\Gamma}$ and the $\bar{J}$ point, with a bandwidth of 0.75 eV, while the experiment by SJBSPP give a very flat band with only 0.25 eV dispersion. The NHUF dispersion for the occupied band is slightly higher than the bandwidth of the occupied states in our calculations. However, from Fig. 5 it appears that our theoretical occupied bands (especially those for the chain left structure) match closely the experimental band from PE and PE of a heavily doped surface. Based on these surface band structures we believe that the two π-bonded chain structures of our calculations represent the 2×1 surface of the experiment of NHUF, and not that of SJBSPP.

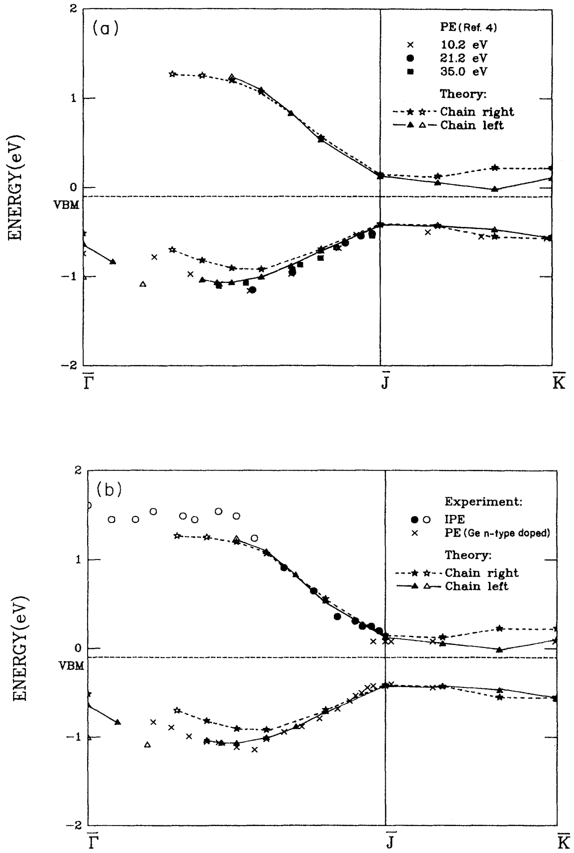


FIG. 5. Dispersion of theoretical surface-state energies compared with different experimental techniques: (a) direct PE, with various photon energies; (b) direct PE of a heavily doped surface and inverse PE. Solid points indicate strong features, open points denote weak features. The agreement with the chain left structure (solid lines) is slightly better.

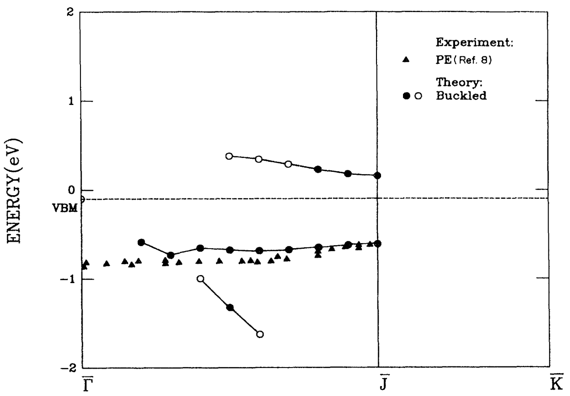


FIG. 6. Comparison of the surface band structure of the buckled structure with the PE experiments by Solal *et al.*

Out of curiosity, we calculated the surface band structure of the metastable buckled structure [Fig. 2(b)] found in our Car-Parrinello calculation using cell B. Interestingly, we found a flat occupied band, with only 0.13 eV of energy dispersion that agrees very well with the SJBSPP photoemission experiments (see Fig. 6). However, our buckled structure is not stable at and above 200 K, while that of SJBSPP was obtained by cleaving at room temperature. If this buckled structure is indeed the one observed by SJBSPP, it must have been stabilized in some way, possibly by defects or by impurities, as proposed by NHUF.[5] A buckled structure stabilized by surface defects was indeed found in our earlier studies of Si(111).[12]

V. DISCUSSION AND CONCLUSIONS

In a scanning-tunnel-microscope study of the Si(111)2×1 surface,[29] pictures of the surface with some asymmetries along the $[2\bar{1}\bar{1}]$ were observed. These asymmetries were explained as due to a tilt or translation of the chains in response to strain arisen from nearby structural defects. Having found two degenerate chain structures for Ge(111)2×1, "domains" related to a change of the tilt angle of the chains are likely to occur also for this surface. These domains are separated by boundaries which represent the defects in this case.

In order to estimate approximately the energy of such boundary defects, we created a structure where adjacent chains had different tilt angle directions (this calculation was performed using the surface cell B). After relaxation, we found that this configuration is only 0.008 eV/surface atom higher in energy than the Pandey structure. We have considered also the situation where the tilt angle changes along a given chain. Using the A surface cell (which has eight atoms along the [110] direction), we introduced a change of the tilt angle along the chain. After relaxation, we found that this structure is 0.084 eV/surface atom higher than the chain right. This energy cost, however, would probably decrease with longer supercells allowing a more efficient relaxation around the defect.

Domains of these two different ground-state structures, may explain, following the original proposal by Grazhulis, the lack of 2 × 1 long-range order in his low-temperature cleavage experiments. The "defect" calculations reported above supports this idea, suggesting that the boundary energy involved in creating these different domains is not very high. However, it is at present still quantitatively unclear why cleave above 60 K would allow defects to disappear.

In summary, the present first-principles study shows that the most stable state of the (111)2 × 1 Ge surface is a π-bonded chainlike structure. In particular, two stable isomers with different directions of the tilt angle of the topmost chains and almost identical energy are found. Both isomers show a big buckling ($\sim$0.8 Å) of the surface chains and have a surface-state dispersion which agrees well with the experimental data of NHUF. The existence of two different structures with the same energy allows disordered domains, which may explain the absence of the 2 × 1 ordering under some cleavage conditions.

Note added in proof. We tested the influence of $E_{\rm cut}$ in the buckling of the π-bonded chains, increasing $E_{\rm cut}$ to 10 Ry without finding any significant difference.

ACKNOWLEDGMENTS

We would like to thank Dr. F. Ancilotto for providing us with some of the computer codes used in this work. This work was supported by INFM, and also in part by the European Research Office of the U.S. Army.

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