LETTER TO THE EDITOR

A theoretical case study: the Sn/Ge(111)–(3 × 3) surface

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Abstract. We present a theoretical analysis of the Sn/Ge(111)–(3 × 3) surface. The (3 × 3) atomic structure is searched using a combination of local-orbital and plane-wave density functional methods. We find a ground state geometry that presents two different types of Sn adatoms whose vertical positions differ by ∼ 0.3 Å. The electronic structure of the surface is analysed including electron correlation effects. The comparison with recent experimental studies, both on the atomic and electronic structure of this surface, gives a strong support to the structural model presented in this work.

(Some figures in this article appear in colour in the electronic version; see www.iop.org)

The α phase induced by the adsorption of 1/3 of a monolayer of Pb or Sn atoms on the Ge(111) surface displays a puzzling transition [1, 2]. Low energy electron diffraction (LEED) experiments show a gradual and reversible change from the $(\sqrt{3} \times \sqrt{3})$ pattern to a (3×3) periodicity as the temperature is lowered. In the scanning tunneling microscopy (STM) images, all the adatoms appear equivalent at room temperature (RT), forming a two-dimensional $(\sqrt{3} \times \sqrt{3})R30°$ lattice, in agreement with the accepted T_4 adatom model (see below) for these surfaces. At low temperatures (LT), however, the adatoms do not appear equivalent in the STM images, showing the new (3×3) symmetry: one out of three Sn (Pb) atoms appears brighter in the filled state images and darker in the empty state images; the contrary is true for the other two Sn (Pb) adatoms (i.e. they appear darker in the filled state images and brighter in the empty state images).

The $(\sqrt{3} \times \sqrt{3})$ structure for Pb/Ge(111) or Sn/Ge(111) is widely believed to consist of a layer of equivalent Sn (Pb) adatoms on T_4 sites over a Ge(111) surface [1–3]. In this geometry, the T_4 adatoms sit on top of second layer Ge atoms and are bonded to three Ge atoms of the first Ge-layer. A key element for understanding the $(3 \times 3) \leftrightarrow (\sqrt{3} \times \sqrt{3})$ transition in these systems is the determination of the ground state (3×3) atomic geometry. This also presents a theoretical challenge because in previous density functional theory (DFT) calculations for the Pb/Ge(111) system [1], a (3×3) structure was found which is lower in energy than the $(\sqrt{3} \times \sqrt{3})$ by ∼ 0.02 eV per adatom; in this structure, two inequivalent Pb atoms are found in the unit cell whose vertical positions differ only by $\Delta z = 0.05$ Å. Similar calculations for the Sn/Ge(111) system [2], however, did not find any stable (3×3)-distortion, i.e. no (3×3) structure was found to be lower in energy than the $(\sqrt{3} \times \sqrt{3})$. This theoretical information, together with the experimental information discussed above, suggested that the (3×3) phase is a two-dimensional charge density wave (CDW) [1], and that the transition to the CDW state is driven mainly by electron correlation effects [2, 4].

In this paper we argue that for analysing new geometries, like the Sn/Ge(111)–(3 × 3) surface, one should try to find a balance between the use of very accurate numerical methods

and less accurate but more efficient calculations. This is related to the need of exploring a large configurational phase-space in order to get the appropriate structure of the system. In this line, we have found a new (3×3) ground state geometry using a combination of local-orbital (LO) and plane-wave (PW) DFT methods. This new structural model presents two different types of Sn adatoms, both on T_4 sites but whose vertical positions differ by ~ 0.3 Å. As it will be shown below, this ground state geometry provides a good explanation of the different experimental observations.

The first step of our theoretical analysis consists in an exploration of the ground state atomic geometry of the Sn/Ge(111)–(3×3) system by means of an efficient molecular dynamics technique (the Fireball96 code) [5]. The advantage of using a suitable LO method (like the Fireball96 code) resides in the fact that it requires much less computational resources (both CPU time and memory) than a PW method to perform the same calculation. This allows a more complete exploration of the configurational phase-space where the absolute energy minimum of the surface might be found [6]. Therefore, we have run Fireball96 simulations for which the atoms are initially placed in a (3×3) unit cell made up of three equivalent $(\sqrt{3} \times \sqrt{3})$ unit cells. Then, the atoms are given random initial velocities (according to a Maxwell–Boltzmann distribution for a given temperature), and move following free dynamics for ~ 100 time steps, Δt ($\Delta t = 2.0\,fs$). In these calculations the Sn/Ge(111)–(3×3) surface is represented by a slab with 4 layers of Ge and a layer of H atoms saturating the bonds of the deeper Ge layer. Both the H layer and the last (fourth) Ge layer are kept fixed during the relaxation to mimic the bulk termination. The geometry of minimum energy is then searched by removing kinetic energy at certain time steps, following a dynamical quenching procedure. The main feature of the (3×3) atomic geometry of minimum energy obtained in this way is a vertical distortion of the Sn-layer in which one Sn atom (A_0, see figure 1) is displaced upwards and the other two Sn
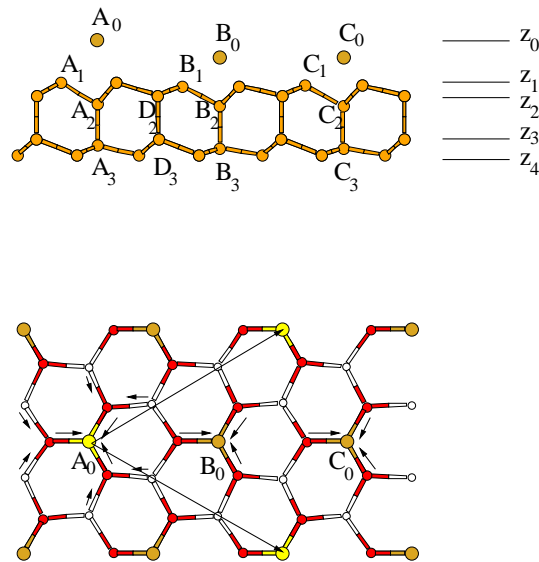

Figure 1. Atomic geometry of the Sn/Ge(111)–(3×3) surface. (Top) Side view: subscript '0' refers to Sn atoms while subscripts 1–4 indicate Ge atoms of the first four Ge-layers. (Bottom) Top view, showing the Sn atoms (large dots) and the Ge atoms of the first (small dark dots) and second (white dots) layers; the long arrows show the unit cell vectors and the short arrows indicate the direction of the in-plane displacements $\Delta \perp_i$. See table 1.

Table 1. Structural parameters (in Å) for the Sn/Ge(111)–(3 × 3) reconstruction. Δz_i is the vertical displacement of the different atoms in each layer with respect to the average layer vertical position, z_i. $\Delta \perp_i$ corresponds to the in-plane displacements. See figure 1 for details. The atomic geometry obtained in this work is compared with two experimental data sets, LEED/SXRD [10] and SXRD [11].

		This work	LEED/SXRD	SXRD
$z_0 - z_1$		1.75	1.86	1.85
$z_1 - z_2$		0.84	0.86	0.87
$z_2 - z_3$		2.43	2.48	2.49
$z_3 - z_4$		0.75	0.79	0.80
	A_0	+0.18	+0.25	+0.17
Δz_0	B_0	−0.08	−0.12	−0.07
	C_0	−0.08	−0.12	−0.10
	A_1	+0.10	+0.11	+0.07
Δz_1	B_1	−0.05	−0.06	−0.04
	C_1	−0.06	−0.06	−0.04
	A_2	−0.36	−0.37	−0.42
Δz_2	B_2	−0.39	−0.37	−0.35
	C_2	−0.39	−0.37	−0.43
	D_2	+0.18	+0.19	+0.20
	A_3	−0.24	−0.28	−0.29
Δz_3	B_3	−0.32	−0.28	−0.24
	C_3	−0.32	−0.28	−0.33
	D_3	+0.15	+0.14	+0.15
	A_1	0.20	0.17	0.19
$\Delta \perp_1$	B_1	0.12	0.05	0.17
	C_1	0.12	0.05	0.18
$\Delta \perp_2$		0.05	0.15[a]	0.04

[a] This displacement is in a different direction (see [10]).

atoms (B_0 and C_0) are displaced downwards, with $z(A_0) - z(B_0, C_0) \sim 0.3$ Å (a preliminary report of this (3 × 3) atomic structure has been presented in [7]). This distortion in the Sn-layer is accompanied by a related distortion in the first 4 Ge-layers (see tables 1 and 2). The energy difference between this reconstruction and the minimum energy ($\sqrt{3} \times \sqrt{3}$) structure is less than 10 meV per Sn atom [8].

The Sn/Ge(111)–3 × 3 atomic structure was subsequently studied with a PW–DFT method (CETEP [9]), both in the LDA and GGA approximations. These calculations require an intense use of computational resources and, therefore, have to be run on a parallel computer. We have used 16 special k–points in the Brillouin zone and a PW cutoff of 12 Ry (increasing the cutoff to 15 Ry changes the energy differences in less than 1 meV). In this case, the (3 × 3) atomic structure obtained with Fireball96 was used as the starting atomic geometry, and then was fully relaxed. The resulting atomic structure obtained with the GGA approximation (LDA calculations yield very similar results for the structure and energy differences) shows the same trends obtained with the LO method, with quantitative differences less than 0.04 Å in all the structural parameters (see table 2), except for the average vertical distance of the Sn layer to the first Ge layer where the difference is 0.08 Å. This structure is lower in energy than the ($\sqrt{3} \times \sqrt{3}$) surface (which is a local minimum), although only by ~ 5 meV per Sn atom. Another local minimum, with a total energy difference less than 1 meV/Sn atom with respect to the ($\sqrt{3} \times \sqrt{3}$) structure, was also found. In this structure the vertical distortion between

Table 2. Main changes in the structural parameters (in Å) for the Sn/Ge(111)–(3 × 3) surface when increasing the number of Ge-layers in the calculations.

| | | PW | Fireball96 | | |
		4 Ge-layers (PW)	4 Ge-layers	6 Ge-layers	10 Ge-layers
	A_0	+0.22	+0.26	+0.25	+0.22
Δz_0	B_0	−0.11	−0.13	−0.11	−0.10
	C_0	−0.11	−0.14	−0.13	−0.11
	A_2	−0.29	−0.26	−0.32	−0.33
Δz_2	B_2	−0.32	−0.33	−0.41	−0.40
	C_2	−0.32	−0.34	−0.42	−0.41
	D_2	+0.15	+0.16	+0.19	+0.19
	A_3	−0.16	−0.17	−0.24	−0.25
Δz_3	B_3	−0.22	−0.25	−0.36	−0.35
	C_3	−0.22	−0.25	−0.37	−0.36
	D_3	+0.10	+0.11	+0.16	+0.16
	A_4			0.04	0.04
$\Delta \perp_4$	B_4			0.08	0.07
	C_4			0.08	0.07

the two different types of Sn atoms is 0.1 Å. The PW calculation confirms the prediction of the Fireball96 method that a 3 × 3 reconstruction with a large vertical distortion among the Sn atoms is the global energy minimum.

The reduced number of Ge layers included in these calculations can affect the displacements of the second and third Ge layers, since fourth-layer Ge atoms are kept fixed at bulk positions and are not allowed to relax. We have analysed the effect of increasing the number of Ge layers in the structural parameters performing Fireball96 calculations with 6 and 10 Ge layers. Table 2 shows that while the top-most layers are only slightly affected, the relaxation of the fourth Ge layer, although small, allows the Ge atoms which are directly below the Sn atoms in second and third Ge layers to further move towards the bulk. This extra relaxation is significant and therefore has to be taken into account when comparing with the experimental results.

The structural parameters for the Sn/Ge(111)–(3×3) surface deduced from our calculations are shown in table 1. These structural parameters are obtained by adding to the PW results discussed above a correction to take into account the relaxation of the deeper Ge-layers. This correction is obtained from the Fireball96 calculations as the difference between the results for 10 and 4 Ge-layers (see table 2). The atomic geometry obtained in this way is compared in table 1 with the results of two recent experimental structural studies (LEED/SXRD [10] and SXRD [11] columns). The first point to note is that the difference between the vertical displacements of Sn atoms is 0.26 Å in our work, a value that is obtained when the corrections due to increasing the number of Ge-layers in the calculations are included. This is smaller than 0.33–0.40 Å, as obtained using only 4 Ge-layers [7]. That vertical displacement is in good agreement with recent data of Bunk *et al*. On the other hand, the overall agreement between our different displacements and the experimental data of Zhang *et al* and Bunk *et al* is remarkable; this agreement between experiment and theory strongly supports the proposal that the Sn/Ge(111)–(3 × 3) surface presents a reconstruction with two different Sn atoms with a significant vertical distortion [7].

We now proceed to discuss the electronic structure of this surface reconstruction. Figure 2 shows the Sn/Ge(111)–(3 × 3) LDA surface bands appearing close to E_F, as calculated with
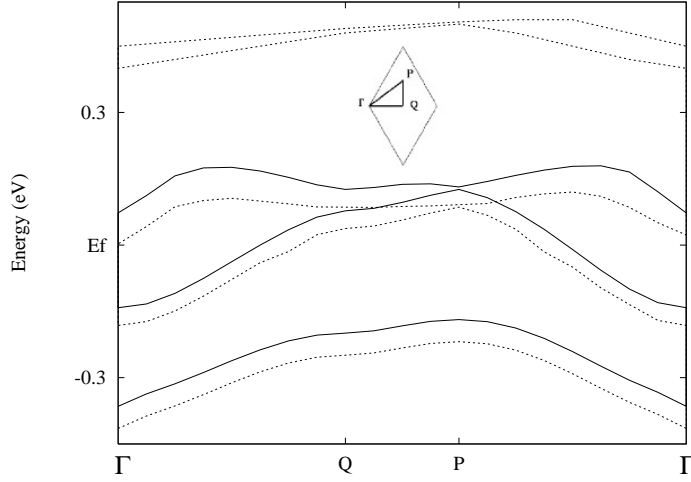
Figure 2. Electronic structure of the Sn/Ge(111)–(3 × 3) surface. LDA (solid lines) and correlated (dashed lines) surface bands along the Γ–Q, Q–P and P–Γ directions (see inset).

Fireball96. These three bands are associated with the three Sn dangling-bonds [12]. For the Sn atom displaced upwards, rehybridization makes its dangling bond to have a more *s*-like character and a corresponding lower energy. The lower surface band in figure 2 is associated with that atom and it is doubly occupied. On the other hand, the other two surface bands, located around E_F, are associated with the two dangling bonds of the Sn atoms displaced downwards.

Correlation effects on these bands can be important: the width of the surface bands, ~ 0.2 eV, is small compared with the effective intrasite Coulomb interaction, U^{eff}, that has been calculated to be ~ 0.55 eV [13]. We have analysed the electron correlation effects on these surface bands by using a generalized Hubbard Hamiltonian. The different electron–electron interaction parameters appearing in this Hamiltonian are determined from a set of LDA calculations for the full surface; then, the correlated surface bands are obtained by solving the generalized Hubbard Hamiltonian using a local self-energy. A detailed explanation of this procedure to study many-body effects in two-dimensional systems can be found in [13]. The correlated surface bands are also shown in figure 2, for the sake of completeness. The main effect of electron correlations is the new density of states (DOS) that appears ~ 0.5 eV above E_F, which presents a total weight of one electron. The occupied DOS is only slightly modified by electron correlations.

The occupied DOS close to E_F has been measured using valence band photoemission spectroscopy (PES) [7, 14]. These experiments show that the Sn/Ge(111)–(3 × 3) surface presents two dispersive surface states below E_F, one of them crossing E_F. The width of these two states is ~ 0.2–0.3 eV, both reaching their minimum value at the Γ point of the (3 × 3) Brillouin zone. The lower band is ~ 0.2–0.3 eV below the upper one. All these features are in good agreement with the theoretical result (see figure 2), therefore further supporting the structural model for this surface described in tables 1 and 2.

As mentioned above, this surface changes from the LT (3 × 3) structure to a ($\sqrt{3} \times \sqrt{3}$) periodicity at RT. High-resolution PES experiments [7, 14] show that the electronic structure of the Sn/Ge(111)–($\sqrt{3} \times \sqrt{3}$) surface is very similar to the electronic structure of the LT phase, Sn/Ge(111)–(3 × 3): in valence-band PES two dispersive surface bands are also observed

close to E_F, one of them crossing E_F and the other band located ~ 0.2–0.3 eV below; in core-level PES two (or three [15]) different Sn–$4d$ components are found. The fact that PES experiments yield a similar electronic structure for the LT (3×3) and the RT $(\sqrt{3} \times \sqrt{3})$ Sn/Ge(111) surfaces indicates that a simple T_4 adatom model, in which all the Sn atoms are equivalent, is inadequate to describe the α-$(\sqrt{3} \times \sqrt{3})$ Sn/Ge(111) surface. Therefore, what is the nature of the RT α–Sn/Ge(111) phase? This question has been investigated by means of first-principles molecular dynamics simulations [7]. These computer simulations show how the (3×3) ground state structure gives rise to the observation of a $(\sqrt{3} \times \sqrt{3})$ symmetry at RT.

 (i) At $T \sim 125$ K the Sn atoms have large vertical displacements (0.2–0.3 Å) while keeping the (3×3) periodicity (one of the three Sn atoms oscillates in a higher position than the other two).
(ii) At higher temperatures the oscillations become larger and an interesting process takes place: at certain moments two Sn atoms interchange vertical positions (while staying at the same T_4 site), the upper Sn atom becoming one of the two lower Sn atoms, and one of the lower Sn atoms becoming the upper Sn atom.

These dynamical fluctuations explain the different experimental observations for the $(\sqrt{3} \times \sqrt{3})$ surface. For example, STM measures the average position of the Sn atoms and, therefore, at RT all the Sn atoms appear at the same height with a $(\sqrt{3} \times \sqrt{3})$ symmetry. On the other hand, in PES experiments an 'instantaneous' picture of the system is obtained, revealing the similarity of the $(\sqrt{3} \times \sqrt{3})$ and (3×3) electronic structures.

In summary, we have explored the Sn/Ge(111)–(3×3) atomic structure using a combination of LO and PW DFT methods. The use of a suitable LO method allows a fast and, therefore, more detailed exploration of the configurational phase-space; the PW method is used to confirm and refine the LO results. We find a surface reconstruction in which one Sn atom (per unit cell) is displaced upwards and the other two Sn atoms are displaced downwards, with a total vertical distortion of ~ 0.3 Å. This atomic model for the Sn/Ge(111)–(3×3) surface and the corresponding electronic structure have been contrasted with the experimental evidence, yielding a strong support to the theoretical finding.

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