Surface Soft Phonon and the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ Phase Transition in Sn/Ge(111) and Sn/Si(111)

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Density functional theory calculations show that the reversible Sn/Ge(111) $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition can be described in terms of a surface soft phonon. The isovalent Sn/Si(111) case does not display this transition since the $\sqrt{3} \times \sqrt{3}$ phase is the stable structure at low temperature, although it presents a partial softening of the 3×3 surface phonon. The rather flat energy surfaces for the atomic motion associated with this phonon mode in both cases explain the experimental similarities found at room temperature between these systems. The driving force underlying the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition is shown to be associated with the electronic energy gain due to the Sn dangling bond rehybridization.

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A soft phonon is a vibrational mode of a crystalline material whose frequency decreases as T falls, eventually reaching zero. At this point the crystal is unstable in relation to the corresponding atomic displacements and undergoes a transition to a lower symmetry phase. Typical examples are the high-low transition in quartz, the ferroelectric transition in $BaTiO_3$, and the ferroelastic transition in $SrTiO_3$ [1]. On semiconductor surfaces, different mechanisms, such as Peierls transitions or charge density waves, have been proposed as the origin of two dimensional phase transitions. However, no soft phonon transition has been unambiguously identified in these systems so far.

In this Letter we consider the Sn/Ge(111) $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition, which is a prototypical example of a T-induced reversible change of symmetry at a semiconductor surface. The driving force underlying this phase transition has been under intense debate since its discovery on the Pb/Ge(111) system [2]. Different physical mechanisms have been proposed to play an important role in this transition: surface Fermi wave vector nesting or electron correlations, leading to the formation of a charge density wave [2,3] at low T; dynamical fluctuations of an underlying 3×3 structure, giving rise to the observation, on average, of a $\sqrt{3} \times \sqrt{3}$ symmetry at room temperature [4]; and the interaction between the 3×3 periodicity and Ge-substitutional defects that act as nucleation centers [5]. Recently, several groups [6–9] have also considered the isovalent Sn/Si(111) system and have found strong similarities and some striking differences with the Ge case. The electronic structure is very similar in both cases, with two major components in the Sn $4d$ core level spectra and two surface bands close to the Fermi level [6], associated with two different Sn dangling bonds. At variance with the Sn/Ge(111), where a transition to a 3×3 pattern is clearly observed at low T, the Sn/Si(111) surface shows a $\sqrt{3} \times \sqrt{3}$ pattern both in LEED and scanning tunneling microscopy, for temperatures as low as 70 K [6], even in the presence of a significant density of Si-substitutional defects [7]. Moreover, the two surface bands mentioned above are not as clearly resolved at low T as they are in the Sn/Ge(111) case [6]. By analyzing theoretically the Sn/Ge and Sn/Si systems, we conclude that the $\sqrt{3} \times \sqrt{3} \rightarrow 3 \times 3$ transition is due to a surface soft phonon. The frequency of this mode in Sn/Ge(111) goes to zero for a $\bar{k}$ vector corresponding to a reciprocal lattice vector of the 3×3 periodicity. For Sn/Si(111) we find that the $\sqrt{3} \times \sqrt{3}$ is the stable structure at low T, and therefore this system should not display the $\sqrt{3} \times \sqrt{3} \rightarrow 3 \times 3$ transition. The comparison of the Sn/Ge and Sn/Si systems with their corresponding H-covered cases shows that the driving force for this transition is the electronic energy gain associated with the surface band splitting induced by the 3×3 distortion.

The atomic displacements associated with the $\sqrt{3} \times \sqrt{3} \rightarrow 3 \times 3$ transition in Sn/Ge(111) provide the clue for the soft mode responsible for this transition. The signature of the 3×3 structure is the upward displacement of one of the three Sn adatoms, and the corresponding downward movement of the other two [10]. Figure 1 and Table I show how these upward and downward movements are interconnected: as one of the Sn atoms (Sn_1) moves upwards, the three Ge nearest neighbors (A_1) follow this motion by moving towards it (with both upward and in-plane displacements). These Ge displacements force corresponding in-plane movements of the Ge (labeled D_2) towards the position of Sn_1. Since the Ge-D_2 atoms are also bonded to first-layer Ge atoms (B_1, C_1) linked with the two other Sn atoms (Sn_2 and Sn_3), these are forced to move downwards.

Does the Sn/Si(111) surface present a similar 3×3 structure at low T? We have studied this possibility by means of density functional theory (DFT) calculations [11]. In this analysis, we start from a $\sqrt{3} \times \sqrt{3}$ structure (in a 3×3 unit cell), where the three Sn atoms are equivalent; we select one of them (Sn_1) and force it to move in the direction perpendicular to the surface. For each of these displacements, the other Sn atoms (Sn_2 and Sn_3) and all the semiconductor atoms are allowed to relax (up to the fifth layer) to their zero force positions under the constraint of

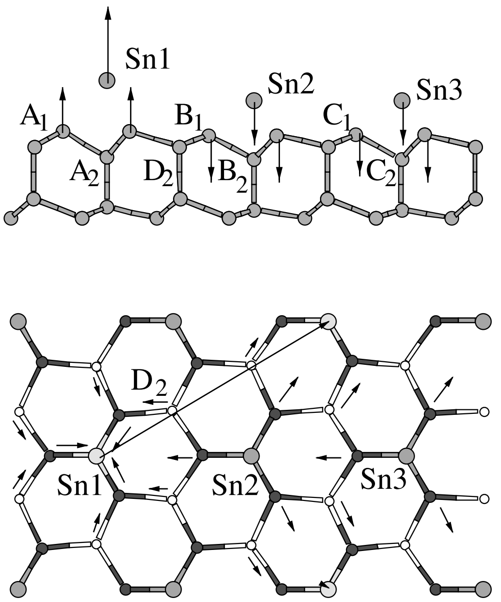

FIG. 1. Ball-and-stick model of the Sn/Ge(111)-(3 × 3) reconstruction. The arrows show the direction of the atomic displacements (up/downwards on top, in-plane on bottom figure) with respect to the $\sqrt{3} \times \sqrt{3}$ geometry. Notice that the Ge atoms move in-plane towards the position of the upper (Sn_1) and away from the two other Sn atoms. The atoms D_2 connect the Ge atoms which are nearest neighbors of the different Sn atoms.

the Sn_1 displacement. These calculations were performed for both the Sn/Si and Sn/Ge systems (see Fig. 2). The energy vs Sn_1 displacement is very flat for Sn/Ge(111); the ground state corresponds to a 3 × 3 geometry with a Sn_1 displacement of ~0.18 Å, as found in previous calculations [10,12] and in agreement with the experimental evidence [13,14]. The Sn/Si(111) surface, however, does not present any stable 3 × 3 distortion; i.e., the $\sqrt{3} \times \sqrt{3}$ is the stable structure at low T.

The inset in Fig. 2 shows another interesting finding: Sn_2 and Sn_3 move together in the opposite direction to the constrained motion of the Sn_1 atom, *for both the Sn/Ge(111) and Sn/Si(111) surfaces.* These results suggest a correlated up/down motion of the Sn atoms [4] that, at a sufficiently low temperature, is frozen into the 3 × 3 structure in the case of Ge (but not in the case of Si). As reflected in Table I, the displacements associated with this motion are essentially localized in the tetrahedra formed by a Sn atom and the three Ge of the first layer bonded to it. In order to analyze the corresponding normal modes associated with the up/down motion of the tetrahedra, we have considered a force constant model which includes effective interactions between first nearest neighbor tetrahedra:

TABLE I. Atomic displacements (in Å) associated with the Sn/Ge(111)-(3 × 3) surface measured with respect to the $\sqrt{3} \times \sqrt{3}$ geometry.

	Sn_1	Sn_2	Sn_3	A_1	B_1	C_1
Δz	0.18	−0.08	−0.08	0.08	−0.04	−0.03
$\Delta\perp$	0.00	0.00	0.00	−0.04	0.02	0.02

	A_2	B_2	C_2	D_2
Δz	0.02	0.00	0.00	0.00
$\Delta\perp$	0.00	0.00	0.00	0.04

$$F_i = -\alpha z_i + \beta \sum_{j,nn} (z_j - z_i), \tag{1}$$

where F_i, the force acting on each tetrahedron, is proportional to its center-of-mass displacement (with respect to the $\sqrt{3} \times \sqrt{3}$ structure), z_i, and the differences in displacement between nearest neighbors, $z_j - z_i$.

The force constants α and β can be determined from the calculations presented above. These calculations provide the accurate information required for this purpose, since they are focused precisely on the deformations we are analyzing here. Imposing that F_2 and F_3 are zero in the above equations yields a relation between the force constants and the displacements z_1 and $z_2(= z_3)$: $3\beta/\alpha = -z_2/(z_2 - z_1)$. For small displacements, $(-z_2)$ is around $0.5z_1$ for Ge, while it is only $0.35z_1$ in Si. Therefore, we obtain $3\beta/\alpha = -1/3$ for Ge and $3\beta/\alpha = -0.23$ for Si.

The phonon dispersion relation of this mode is easily found, using Eq. (1), to be

$$M\omega^2 = (\alpha + 6\beta) - \beta \sum_j \cos(\bar{k} \cdot \bar{R}_j), \tag{2}$$

where $\bar{k}$ is the momentum parallel to the surface, $\bar{R}_j$ is the coordinates of the six first nearest neighbors, and M is the tetrahedron mass. In this approach, the atoms outside the tetrahedra are treated *adiabatically;* i.e., we neglect their mass and assume that they follow "instantaneously" the displacement imposed by the motion of the tetrahedra. This means that the forces between, say, the Ge-D_2 atoms

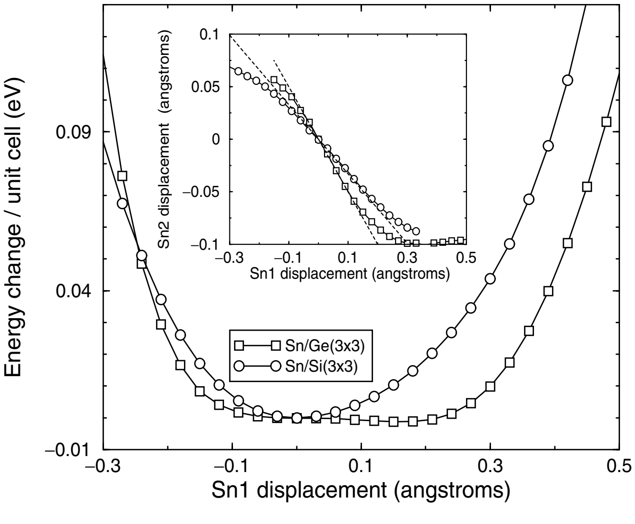

FIG. 2. Total energy as a function of the Sn_1 for the Sn/Ge(111) and Sn/Si(111) surfaces. The energy of the $\sqrt{3} \times \sqrt{3}$ structure is taken as the reference. Inset: displacements (in Å) of the Sn_2, Sn_3 atoms as a function of the Sn_1 displacement. All the displacements are referred to the $\sqrt{3} \times \sqrt{3}$ structure.

(see Fig. 1) and the atoms in the tetrahedra are automatically included in the force constants of Eq. (1) and in the phonon dispersion relation of Eq. (2). We have estimated the error introduced by this adiabatic approximation in the phonon frequencies by comparing the kinetic energies of the atoms whose inertia is neglected in our approach with that of the atoms in the tetrahedra. This yields errors of 7% and 16% for the Si and Ge cases, respectively. These values set the order of magnitude of the accuracy that our model presents for the phonon frequencies.

Figure 3 shows the phonon dispersion curves for Ge and Si, compared with the projected phonon bulk band structure. Notice that we find a zero-frequency mode at the $\bar{K}'$ point for Ge. The corresponding $\bar{k}$ vector defines the new 3×3 periodicity associated with this soft mode. For Si, the phonon dispersion relation shows only a minimum at the $\bar{K}'$ point, with a phonon energy of 5.5 meV. These results are in agreement with our previous comments on the stability of the Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) structure, as shown in Fig. 2.

The phonon branches shown in Fig. 3 provide an explanation for the main similarities and differences between the Si and Ge cases. At low T, while for Ge we can expect a phase transition to the 3×3 structure, there is no stable 3×3 phase for Si. On the other hand, at high T (say, for $k_B T \gg 6$ meV, room temperature is a high T limit) we can expect Ge and Si to be alike. This can be understood by considering the energy curves in Fig. 2: at room T the Sn atoms vibrate with a large amplitude in both surfaces (with displacements between -0.2 and 0.3 Å for Ge and -0.2 and 0.2 Å for Si). In this vibration, Sn atoms are correlated with their Sn nearest neighbors. This is true even in the Si case, because although the 3×3 structure is not a stable minimum, due to the fact that the vibration associated with the 3×3 structure is a minimum of the phonon dispersion, the atomic motion can be expected to be dominated by this mode. For the Sn/Ge(111)-($\sqrt{3} \times \sqrt{3}$) phase, anharmonic effects renormalize the frequency of the soft phonon mode to a nonzero value [15], as shown schematically in Fig. 3.

The atoms involved in this vibration spend most of the time around the turning points of their classical trajectories, where the atom velocity goes to zero. At these turning points, the electron occupation of the Sn dangling bonds is different: atoms in "up" positions have a fully occupied dangling bond, while those at "down" positions present only a partial occupation of their dangling bonds [10]. This explains the double peak observed in the x-ray photoemission spectroscopy Sn 4d core level spectra of both systems, as originally proposed in the dynamical fluctuations model [4] to explain the Sn/Ge(111) $3 \times 3 \rightarrow \sqrt{3} \times \sqrt{3}$ transition. In this model, Sn atoms display correlated up/down vibrations which present, at room temperature, large amplitudes, but keep memory of the underlying 3×3 phase. The soft phonon shown in Fig. 3 is responsible for this atomic motion and provides the physical mechanism for the dynamical fluctuation model.

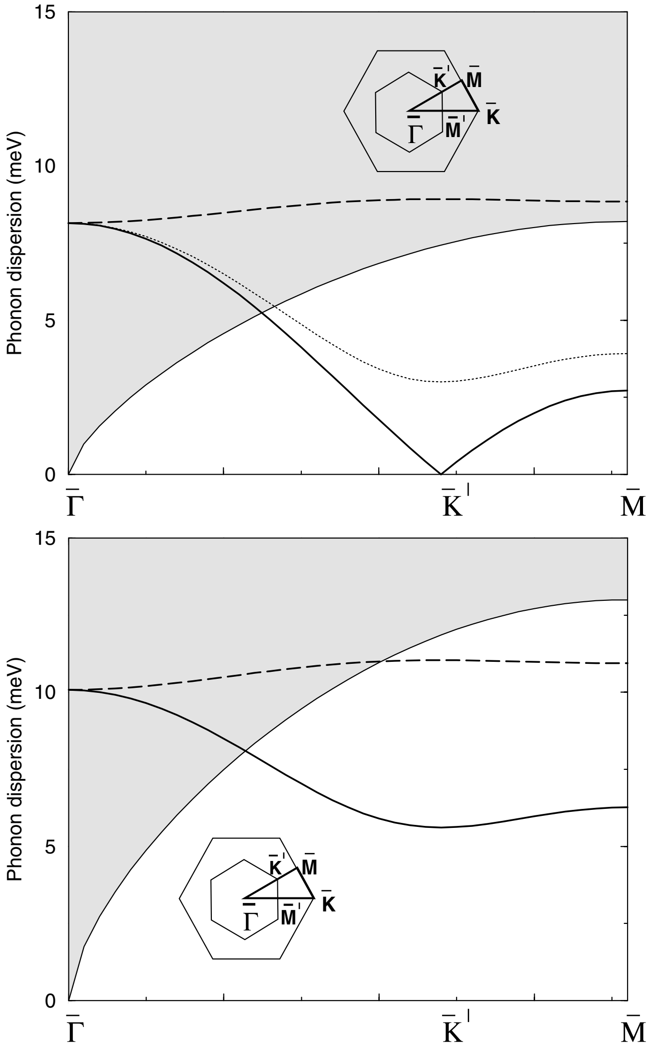

FIG. 3. Phonon dispersion curves for the Sn/Ge(111) (full line, top) and Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) (full line, bottom) surfaces. Dashed lines correspond to the H-saturated Sn/Ge(Si)(111)-($\sqrt{3} \times \sqrt{3}$) surfaces. Shaded areas represent the projection of the corresponding phonon bulk band structure. The phonon branches are plotted along the $\bar{\Gamma}\bar{M}$ direction in the first Brillouin zone (BZ) of the ideal (111) surface (see inset). The inner hexagon corresponds to the BZ of the $\sqrt{3} \times \sqrt{3}$ surface. $\bar{K}'$ defines the new 3×3 periodicity associated with the soft phonon in Ge. At room temperature, the frequency of the soft mode should be renormalized to a nonzero value, as shown schematically by the dotted line.

We have also addressed the problem of which driving force is softening the surface mode associated with the 3×3 structure. As Si and Ge are isovalent atoms and the electronic structure of both interfaces is very similar, one might expect the difference in the relative stability of the two structures to be related to the different elastic properties of the two materials. In order to single out the elastic contribution from the one associated with the Sn-dangling-bond rehybridization [16] and corresponding surface-band splitting [10], we have studied the surface phonons of these surfaces with hydrogen atoms saturating the Sn dangling bonds. As shown in Figs. 3a and 3b, the dispersion curves for the H-saturated surfaces are rather different from the Sn surfaces; in particular they display no "softening" of the mode at $\bar{K}'$. This different behavior is related to the Sn-dangling-bonds rehybridization.

In order to quantify these effects, we have considered the relaxed Sn surfaces discussed above (see Fig. 2) for two different Sn_1 displacements, namely, 0.0 Å (the $\sqrt{3} \times \sqrt{3}$ geometry) and 0.18 Å (the "3×3" geometry). The elastic contribution is calculated, in each case, as the difference in energy between the two geometries *with H atoms saturating the Sn dangling bonds*. Subtracting this elastic contribution from the total energy difference for the Sn surfaces, the energy contribution due to the Sn-dangling-bonds rehybridization is obtained. These calculations provide the following results: $E_{\mathrm{elastic}}(\mathrm{Ge}) = 156$ meV and $E_{\mathrm{electronic}}(\mathrm{Ge}) = -158$ meV; $E_{\mathrm{elastic}}(\mathrm{Si}) = 131$ meV and $E_{\mathrm{electronic}}(\mathrm{Si}) = -112$ meV [17]. Therefore, the main difference between the Sn/Ge and Sn/Si cases is the different hybridization between Sn and the surface atoms. A comparison of the surface bands for both cases confirms this result: the Ge case presents in the 3×3 geometry a larger band splitting, 152 meV as compared with 93 meV for Si. This effect can be related to the different sizes of Si and Ge [16]. When Sn is closer in size to the semiconductor atom the surface rehybridization is stronger and the surface gains more energy by means of the surface band splitting caused by the 3×3 distortion.

In conclusion, we have shown via state-of-the-art DFT calculations that the reversible $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition in Sn/Ge(111) is associated with a surface soft mode. The 3×3 structure is not stable in the Sn/Si(111) case, although it is a minimum in the phonon dispersion, and consequently this surface should not display the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ transition. Comparing the Sn/Ge and Sn/Si cases, and considering the corresponding H-covered surfaces, we have found that the driving force underlying the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition lies in the electronic energy gain due to the Sn-dangling-bond rehybridization.

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