Dynamical Fluctuations as the Origin of a Surface Phase Transition in Sn/Ge(111)

J. Avila,[1] A. Mascaraque,[2] E. G. Michel,[2] M. C. Asensio,[1] G. LeLay,[3] J. Ortega,[4] R. Pérez,[4] and F. Flores[4]

[1]*Instituto de Ciencia de Materiales, CSIC, 28049 Madrid, Spain*
and LURE, Université Paris-Sud, F-91898 Orsay, France
[2]*Departamento de Física de la Materia Condensada and Instituto Nicolás Cabrera, Universidad Autónoma, 28049 Madrid, Spain*
[3]*CRMC2-CNRS and UFR-SM, Université de Provence, 3 Place Victor Hugo, 13003 Marseille, France*
[4]*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma, 28049 Madrid, Spain*

The Sn/Ge(111) interface has been investigated across the $3 \times 3 \rightarrow \sqrt{3} \times \sqrt{3} R 30°$ phase transition using core level and valence band photoemission spectroscopies. We find, both above and below the transition, two different components in the Sn $4d$ core level and a band splitting in the surface state crossing the Fermi energy. Theoretical calculations show that these two effects are due to the existence of two structurally different kinds of Sn atoms that fluctuate at room temperature between two positions and are stabilized in a 3×3 structure at low temperature.   [S0031-9007(98)08264-7]

The investigation of phase transitions in low-dimensional surface systems provides insight in several fundamental fields of condensed matter physics [1], due to the variety of different mechanisms which may act as the driving force behind the phase transition. Carpinelli *et al.* [2] have recently reported a surface phase transition from the room temperature (300 K, RT) $\alpha\sqrt{3} \times \sqrt{3} R 30°$-Pb/Ge(111) phase [3,4] (in the following $\alpha\sqrt{3}$) to a 3×3 structure at low temperature (100 K, LT). They proposed that the structural phase transition is due to the stabilization of a surface charge density wave [5,6] due to Fermi surface nesting. They stressed the critical role that electron correlation effects could play in the stabilization of the LT phase, which was found to be semiconducting, in contradiction with the metallic character predicted from a simple electron counting. An investigation on the closely related Sn/Ge(111) system [7] revealed that, although the same phase transition was observed, the Fermi surface nesting did not play a role in the phase transition. Thus, it was suggested that many body effects were of importance in the ground state of this system [7,8]. These experiments showed, however, that the surface remains metallic across the phase transition.

In this work we present a combined experimental and theoretical study of the origin of the phase transition in Sn/Ge(111). State-of-the-art angle-resolved ultraviolet photoemission has been used to investigate in detail the electronic structure of the valence band and the core levels of Sn/Ge(111). We find, both at LT and RT, two different surface states close to the Fermi energy (E_F) and two different components in the Sn $4d$ core level line shape, associated with the adatom Sn layer. We have analyzed theoretically this behavior by means of detailed density-functional theory (DFT) calculations. From these studies we conclude, at variance with previous results [7,9], that the LT 3×3 phase presents two structurally different Sn atoms, with a vertical distortion of ~0.35 Å. The $3 \times 3 \rightarrow \alpha\sqrt{3}$ transition is explained as a dynamical effect

in which inequivalent Sn atoms interchange their vertical positions, without having to resort to many body effects.

The experiments were performed in an ultrahigh vacuum chamber equipped with an angle-resolving hemispherical analyzer receiving synchrotron light from the SU6 beam line of the Super-Aco storage ring in Orsay at the Spanish-French station. For more details on the sample preparation and the characteristics of our apparatus we refer the reader to Ref. [10].

The stabilization of a 3×3 reconstruction from the RT $\alpha\sqrt{3}$ unit cell means that inequivalent Sn atoms must appear at LT. One suitable tool to analyze this expected asymmetry is core level photoemission spectroscopy. In this technique, the line shape of inner core levels is obtained. The existence of components with different binding energies is related to a different chemical environment (initial state effect). Different screening properties may also affect the binding energy (final state effects) [11]. The $4d$ core levels of Sn were monitored along the adsorption process on Ge(111) (see Fig. 1). For a coverage of 0.25 monolayers (ML), Sn atoms form a well ordered structure with a 2×2 symmetry in the low-energy electron diffraction (LEED) pattern. Following standard procedures [12,13], the core level was fitted using a single component with an intrinsic Lorentzian width of 220 meV (Gaussian broadening 320 meV). For a coverage of 1/3 ML, LEED shows an $\alpha\sqrt{3}$ reconstruction at RT and a 3×3 pattern at LT. The Sn $4d$ line shape for the $\alpha\sqrt{3}$ reconstruction is much broader [12,14] and can only be reproduced using two components (Fig. 1). The intensity ratio between the two components is close to 1:2 for 1/3 ML coverage, and is not sensitive to the polar emission angle, indicating that both come from the adatom top layer. We can also discard the fact that they are due to any kind of defects, since the line shape was the same for many different preparations [12]. At the LT 3×3 phase, both components are preserved (see Fig. 1), and there is only a small change of their relative intensities. The existence
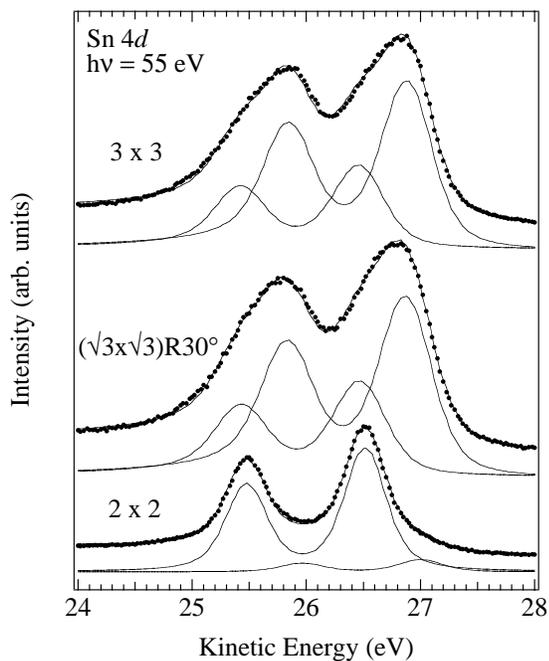
FIG. 1. Sn $4d$ core level for different surface reconstructions. From bottom to top, the core levels found for the 2×2, $\alpha\sqrt{3}$, and 3×3 reconstructions.

of two distinct components in the core level at LT means that two inequivalent kinds of atoms exist at the surface in the 3×3 reconstruction, as expected, but surprisingly the two kinds of atoms subsist at RT.

A similar behavior is observed in the valence band. The experimental valence band data for LT are presented in the lower panel of Fig. 2 (right). A scheme of the reciprocal space direction probed is shown in the top panel of Fig. 2. We concentrate here on the data obtained for the surface band in the vicinity of E_F and for the third Brillouin zone. Each Sn atom contributes with four electrons to the valence band and bonds to three Ge atoms with one unpaired electron each. One would expect from electron counting arguments the existence of a half-filled surface band. The broad peak detected in the vicinity of the Fermi level is due to this dispersing surface band. However, the asymmetric line shape found reveals the existence of two close surface bands at LT. The surface peak has been deconvoluted in two components in Fig. 2. We used a Voigt line shape for the peaks, convoluted with a Fermi function, and a χ^2 fitting procedure to reproduce the line shape of the peak area. The fitting parameters of the two peaks were obtained from the spectrum at a 29° emission angle, where the two components are best distinguished, and they were maintained in all the series. The intrinsic widths found ($\sim$300 meV) are 3 times larger than our experimental resolution, indicating that they constitute an intrinsic property of the electronic states. The existence of a split surface band is not predicted in previous DFT calculations [7]. The left panel of Fig. 2 shows a comparison with equivalent RT spectra. Rather

broad peaks were observed at RT, suggesting that the splitting is preserved, but it is hardly resolved. This is clear from the spectrum taken at $\sim\overline{K}_2$ (27° off). The corresponding binding energy (BE) vs parallel momentum plots are shown in the middle panels of Fig. 2. Note the parabolic dispersions both at RT and LT.

In order to understand the splitting of the valence band and the existence of two components in the Sn $4d$ core level, we have analyzed theoretically this interface by means of a combination of local-orbital and plane-wave (PW) DFT methods. First, we have explored the geometry of the 3×3 surface using an efficient molecular-dynamics (MD) technique based on a local-orbital self-consistent DFT approach (the FIREBALL96 code) [15]. The ground state 3×3 geometry found with this method presents a unit cell with one Sn atom displaced upwards and the other two Sn atoms displaced downwards, with a total
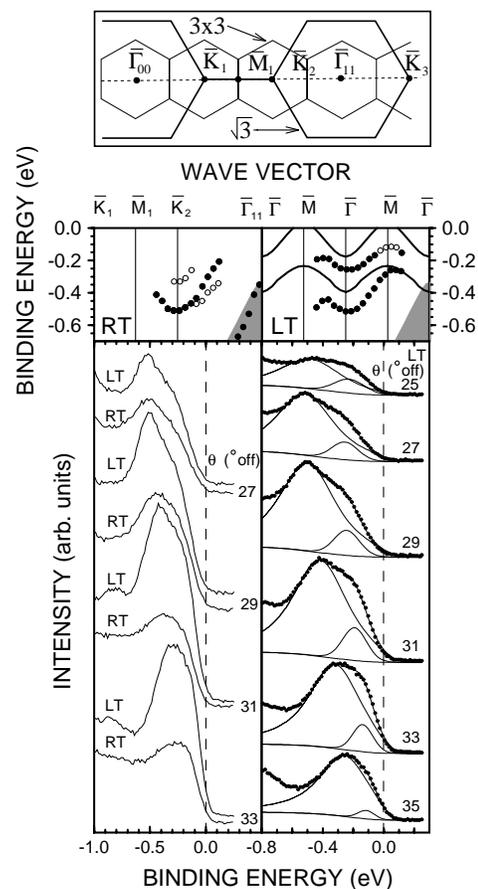

FIG. 2. Bottom panel (right): Valence band spectra (filled circles) of 3×3-Sn/Ge(111) as a function of emission angle ($h\nu = 32$ eV). The lines represent the two components observed and their sum. Bottom panel (left): A comparison of selected spectra at RT and LT vs emission angle ($h\nu = 32$ eV). Middle panels: Binding energy vs parallel momentum for the experimental bands (filled circles, empty circles are less-intense peaks) at RT and LT and the theoretical LDA calculation (lines). Top panel: Reciprocal space area probed. Symmetry points belong to the $\alpha\sqrt{3}$ unit cell.

vertical distortion of ~0.35 Å. The corresponding vertical distortion of the Ge last layer atoms is ~0.20 Å, the Sn-Ge distance being quite similar (2.68–2.74 Å) for both types of Sn atoms. In these calculations the 3×3 reconstruction is lower in energy than the $\alpha\sqrt{3}$ by 40 meV per Sn atom. The accuracy of these results has been checked using the more rigorous PW DFT method [16]. This method is very demanding in computational resources and, therefore, has been used here only to test and refine the FIREBALL96 results. Both the local density approximation (LDA) and the generalized gradient approximation have been used, and they provide very similar results for the geometries and for the total energy differences between the $\alpha\sqrt{3}$ and 3×3 reconstructions. The PW calculations confirm the local-orbital results. Both structures are local minima of the total energy and their geometries, in particular, the vertical distortion of the Sn atoms, are very similar to the ones found by the local-orbital method. The 3×3 structure is the most stable one, although the absolute energy minimum for it is found only 5 meV per Sn atom below the energy minimum of the $\alpha\sqrt{3}$ reconstruction [17].

In Fig. 2 we compare the occupied LDA-surface bands (obtained with FIREBALL96) with the experimental bands at LT. Another empty band, not shown in the figure, appears 0.15 eV above E_F. The experimental band topology is well reproduced by the theory, although a shift of 0.2 eV is found between both cases. In particular, the experimental splitting is reproduced, and we find for the 3×3 reconstruction a surface band crossing E_F along the $\overline{\Gamma M}$ line. The atomic origin of the surface bands can be traced back to the corresponding Sn dangling bonds. The band with higher BE, filled by two electrons, is mainly weighted on the Sn atom displaced upwards, while the two surface bands with lower BE, occupied only by one electron, are associated with the other two Sn atoms displaced downwards. This charge transfer between surface bands explains the energy gain between the 3×3 and the $\alpha\sqrt{3}$ structures, although we have to emphasize that the *total* charges in the different Sn atoms for the 3×3 structure are very similar. The reason for this is that the valence charge, localized below the valence-band maximum, tends to screen that charge difference associated with the Sn dangling bonds.

Correlation effects on the surface bands for the 3×3 reconstruction can be important [7,8]. In fact, the width of the surface bands, ~0.2 eV, is small compared with the effective intrasite Coulomb interaction, U, that we have calculated to be 0.55 eV for the Sn dangling bonds. This is obtained using a restricted LDA calculation [18], by changing the filling factors of the surface bands and calculating its effect on the surface band levels. Then, correlation effects can be calculated using a local self-energy [19]. This analysis shows, however, that correlation effects tend to modify substantially only the empty surface band given by the LDA calculation, leaving

practically unmodified the two bands shown in Fig. 2. Therefore, correlation effects do not modify the metallic character of the 3×3 structure.

In the next step, we have studied the effect of temperature and the $3 \times 3 \rightarrow \alpha\sqrt{3}$ transition, by means of first-principles MD simulations. First, we have calculated the critical temperature (T_c) of the phase transition by using a simple Ising model with a triangular lattice and by fitting the nearest-neighbor interaction in the model to the energy difference between the two structures, ΔE. This model yields $T_c = 240$ K (30 K) for $\Delta E = 40$ meV (5 meV), depending on the values of the two calculations discussed above; the experimental T_c is ~210 K. This result suggests that, although the intrinsic precision of the LDA approach is probably not enough to calculate ΔE with the high accuracy needed, the MD simulations commented on below (for which $\Delta E = 40$ meV) provide a qualitative description of the dynamics of this system.

In the different MD simulations, we start with the atoms in the same 3×3 ground state positions, but with random velocities chosen, in each case, from a different Maxwell-Boltzmann distribution. Then, we follow the time evolution of the system using LDA forces in a typical MD simulation [15]. Figure 3 shows the time evolution of the z coordinate (perpendicular to the surface) of the three Sn atoms in the 3×3 unit cell for the temperatures
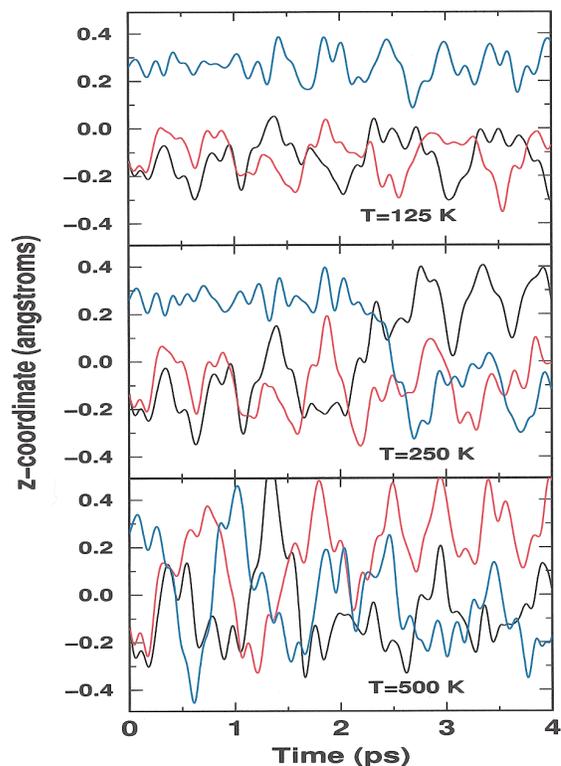

FIG. 3(color). Time evolution of the z coordinate (perpendicular to the surface) of the three Sn atoms (blue, red, and black lines) in the 3×3 unit cell for the temperatures $T \sim 125$, 250, and 500 K in the MD simulations.

$T \sim 125$, 250, and 500 K. For $T \sim 125$ K, the Sn atoms fluctuate around their equilibrium positions, one at higher z (blue) and two at lower z (red and black). For $T \sim 250$ K an upper Sn atom and one of the two lower Sn atoms exchange heights. For $T \sim 500$ K the system fluctuates very quickly, with the Sn atoms exchanging between the upper and lower heights.

These results show that the Sn layer at RT or above keeps memory of its LT ground state, and that the phase transition can be described as the dynamical evolution of a floating Sn layer with the atoms located instantaneously, at high temperature, in one of the two predominant positions, defined by the LT phase. This scenario is able to explain the experimental data available: (i) First, in scanning tunneling microscopy (STM), individual Sn atoms are seen at RT, on the average, at the same height, the surface presenting an $\alpha\sqrt{3}$ reconstruction [7]. (ii) In photoemission experiments, the spectra appear at RT as an average of the different geometries that are dominated by the local 3×3 environment that we have found at LT. This suggests that the surface bands should appear at RT as in the LT case, as shown in Fig. 2, with a striking similarity between both cases. (iii) Finally, core level BE shifts at high temperature should also show the two-level peaks associated with the two Sn sites observed at LT, as seen in Fig. 1. Since the photoemission process takes place in a subfemtosecond time scale, the two extreme positions of the fluctuating Sn layer are still detected at RT. This behavior is similar to the one found for the analogous case of Si(100) along the $c(4 \times 2) \rightarrow 2 \times 1$ phase transition [20,21]. The relative intensities of the two core level components are in agreement with this model. The core level component shifted to lower BE (higher kinetic energy in Fig. 1) has twice the weight of the other one. This is consistent with our interpretation of the $\alpha\sqrt{3}$ reconstruction, if we realize that these core level shifts are dominated by a final-state relaxation effect [22]. This is due to the metallic character of the surface bands associated with the two Sn atoms displaced downwards.

Concerning other experimental data, our results agree with the complementarity of the STM images observed with positive and negative sample biases at LT [7]. STM images depend both on the local density of states and the tip-atom distance. Although the downward Sn atoms are located 0.35 Å below the upward Sn atom, the relation between the hole density of states associated with the two sites (which is mainly localized in the downward atoms) more than compensates for the difference in height, producing a corrugation complementary of the one imaged with the negative bias.

In a recent structural investigation, Baddorf et al. [9] have found that the Sn/Ge interface contains two kinds of Sn atoms at LT. They conclude that a large root mean square vibrational displacement is expected for both structures, in agreement with the model proposed here, although they found a negligible vertical distortion at LT. This conclusion was mainly based on the analysis of a limited reciprocal space portion for 3×3 rods. A structural study on Pb/Ge(111) and Sn/Ge(111) [23], where a much larger reciprocal space range was analyzed, reveals, however, an excellent agreement with the model proposed here for Sn/Ge(111).

We conclude that the 3×3 phase is due to a reordering within the Sn/Ge layer giving rise to two inequivalent Sn atoms. This structure explains the existence of two components in the Sn $4d$ core level and in the surface state band crossing E_F. The dynamical fluctuations of this overlayer at RT give rise to the observation of an $\alpha\sqrt{3}$ structure.

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