Nature of the Low-Temperature 3 × 3 Surface Phase of Pb/Ge(111)

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The structure of the low-temperature 3 × 3 surface phase of Pb/Ge(111) has been determined by surface x-ray diffraction experiments. Analysis of the data reveals that the Pb layer exhibits a vertical corrugation of ~0.4 Å, affecting also the two top Ge layers. Significant distortions are found down to the third Ge layer. This structural model supports that the 3 × 3 ground state can be best described as a cooperative distortion stabilized by a gain in electronic energy. [S0031-9007(99)08749-9]

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Critical phenomena are a fascinating area of current research in solid state physics. The complex phenomenology of phase transitions can be analyzed in the more simple playground of low-dimensional systems [1]. Carpinelli *et al.* [2] have reported a temperature-driven phase transition for a Pb layer deposited on Ge(111). At room temperature (300 K), 1/3 of the monolayer of Pb atoms occupy T_4 sites of the Ge(111) surface, giving rise to a $\sqrt{3} \times \sqrt{3} R30°$ surface periodicity [3] (in the following $\sqrt{3}$). As temperature decreases below ~250 K, a 3 × 3 surface phase appears. The 3 × 3 ground state was described as the stabilization of a charge density wave in the Pb layer [2], driven by electron-phonon coupling in the two-dimensional Fermi surface [2]. The 3 × 3 surface periodicity was observed with scanning tunneling microscopy (STM), and it was attributed to valence charge redistribution in the Pb layer and not to a rippled topography [2]. First-principles density-functional theory (DFT) calculations showed that the ground state for Pb/Ge(111) was a 3 × 3 phase with a slight rippling in the Pb layer (~0.05 Å) [2], but it was proposed that electron correlation played a crucial role in the stabilization of the 3 × 3 phase. A similar phenomenology has been observed for Sn/Ge(111) [4,5]. A structural study for this interface [6] found no significant rippling in the Sn layer and attributed the 3 × 3 phase to lateral atomic displacements in the first Ge layer.

This scenario has been recently questioned in several aspects. First, the experimental Fermi surface for Pb/Ge(111) exhibits no significant nesting [7], a crucial point in the theoretical model proposed in Ref. [2]. Second, valence-band photoemission results [7–9] do not support the fact that electron correlation plays a major role in 3 × 3 phases. The surface valence bands at low temperature (LT) are split [7], in disagreement with theoretical calculations [2]. Core-level photoemission for Sn/Ge(111) indicates the existence of two kinds of Sn atoms in the 3 × 3 phase [8,9]. All these experiments could be interpreted assuming a corrugated Sn or Pb layer, but this idea disagrees with the structural model found by Baddorf *et al.* [6] for Sn/Ge(111).

In this Letter we present a structural investigation on (3 × 3)-Pb/Ge(111). This information is crucial to determine the correctness of the different mechanisms put forward to explain the phase transition, and it is also required to clarify the apparent contradictions found between theory [2,9] and different experimental results [2,4–9]. State-of-the-art surface x-ray diffraction (SXRD) experiments were used to obtain the atomic positions of the 3 × 3 phase. We propose a new model for this phase consistent with other experimental [7–9] and theoretical results [9]. In the T_4 adsorption site, each Pb atom is bonded to three Ge atoms (see Fig. 1). This four-atom cluster is repeated three times in the 3 × 3 unit cell. We find that the reconstruction is due to a vertical displacement of the three clusters, two inwards and one outwards, keeping approximately equal bond lengths and bond angles in all three. The distortion affects strongly other Ge atoms in the first and second bilayers. Thus, the reconstruction can be described as an overall rippling of the Ge crystal which gives rise to a vertical distortion of the Pb layer of ~0.4 Å. This result supports the fact that the 3 × 3 phase is stabilized by the electronic energy gained after a strong structural distortion. The reconstruction can be described as a quasi-two-dimensional cooperative Jahn-Teller process that involves not only the Pb layer but also the top three bilayers of the Ge crystal.

The crucial point to determine the nature of 3 × 3 phases is to find out reliably both the in-plane and the out-of-plane distortions. To this end, we performed SXRD in-plane and out-of-plane measurements, probing extensive portions of the reciprocal space. In this way, SXRD becomes sensitive to the structure of both the top and deeper layers. The data analysis is simplified with respect to other surface sensitive techniques, since only kinematical scattering theory is needed [10]. The experiments were performed on the surface diffraction beam line at ESRF. For details on the experimental

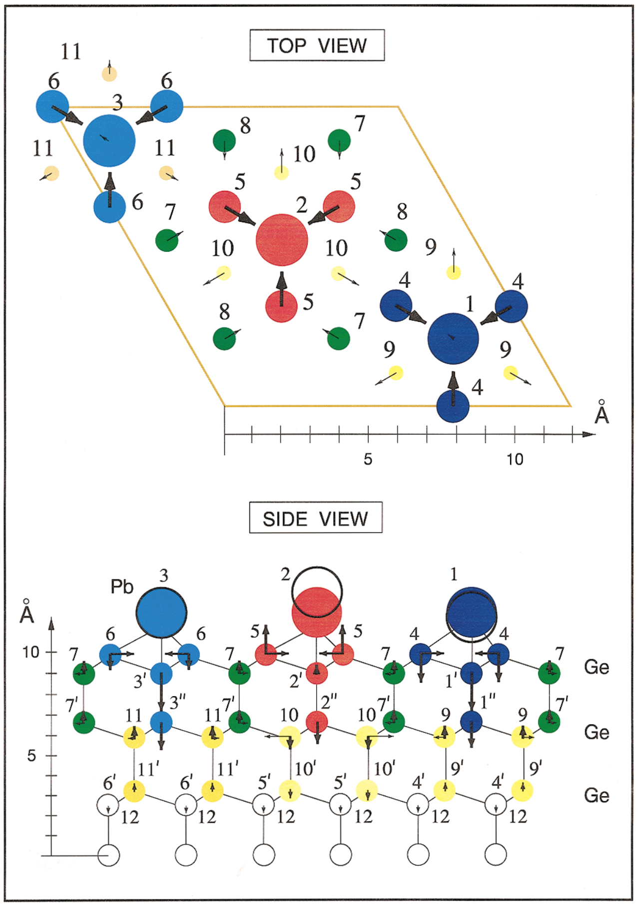

FIG. 1(color). Structural model found for the 3 × 3 phase. Ge atoms are located at ideal bulklike positions. Pb atoms (colored) occupy ideal T_4 sites (bond length: 2.94 Å), while circles represent the final position found. Arrows indicate the direction of atomic displacements and are proportional to them, but the scale of lateral movements has been exaggerated. Thin arrow lengths are multiplied by a factor of 10.

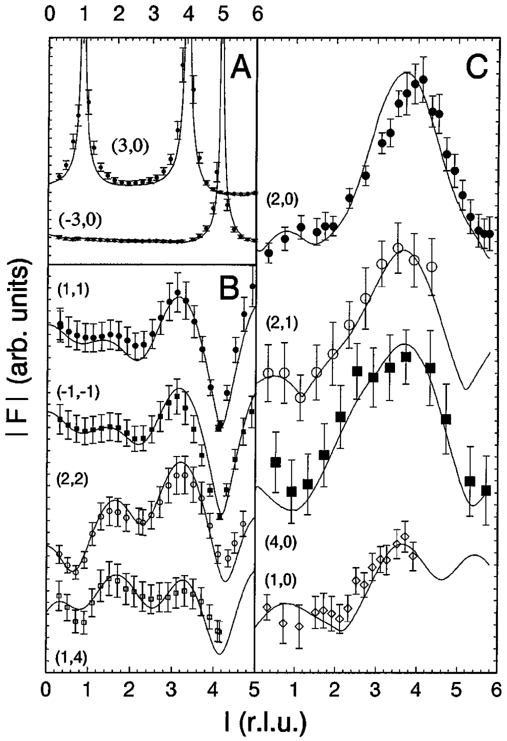

FIG. 2. Integrated intensities of experimental rods (points) and best fit to the data (lines) for the crystal truncation rods [panel (A)] and fractional order rods [panels (B) and (C)]. Rods in panel (C) are specific of the 3 × 3 reconstruction. The vertical scale of panel (C) [(A)] is multiplied by a factor of 6.6 [0.4] with respect to panel (B). Curves are uniformly shifted in the vertical direction in each panel.

setup we refer the reader to Ref. [11]. The quality of the Ge(111) surface was judged by measuring the 1/8 x-ray reflections coming from the $c(2 \times 8)$ reconstruction, characteristic of the clean surface. Pb was deposited from a carefully calibrated Knudsen cell, following the preparation method described in Ref. [7]. The surface was cooled down to 50 K during the measurements. The 3 × 3 superstructure peaks appeared gradually upon cooling with a signal-to-background ratio approximately 10 times smaller than comparable $\sqrt{3}$ peaks (see Fig. 2). All reflections are indexed with respect to a 3 × 3 unit cell given by $\mathbf{a}_1 = \frac{3}{2}[10\bar{1}]_{\text{cubic}}$, $\mathbf{a}_2 = \frac{3}{2}[\bar{1}10]_{\text{cubic}}$ in the surface plane, and $\mathbf{a}_3 = [111]_{\text{cubic}}$ normal to the surface. The data set was averaged over symmetry related reflections of the $p3$ plane group, leading to 55 in-plane irreducible structure factor intensities (25 of them from 3 × 3 specific reflections) and 165 out-of-plane irreducible structure factor intensities reaching $l \simeq 6$ reciprocal lattice units (71 of them from 3 × 3 specific reflections). In addition to this, 60 irreducible structure factors were measured for crystal truncation rods. The total number of structure factors determined was 280. The model developed below used a total of 30 independent parameters, including the possible domains of the reconstruction. This gives a rate of ~9 experimental points per parameter. The angle of incidence was 0.225°, close to the experimental critical angle. This enhanced the surface sensitivity for 3 × 3 fractional rods.

An inspection of the in-plane data set (see Fig. 3) and of the fractional order rods (see Fig. 2) reveals that the structure factor of 3 × 3 specific reflections is small in the vicinity of $l = 0$. Since the atomic number of Pb is 2.5 times larger than that of Ge, its contribution to the diffracted intensity is about 6 times more important. This suggests that the 3 × 3 reconstruction does not contain a significant in-plane distortion at the topmost surface layer (Pb atoms). In fact, STM pictures do not reflect large lateral displacements in the Pb layer [2]. On the other hand, all 3 × 3 fractional rods have a significant intensity around $l = 4$ (see Fig. 2). This fact, and the strong modulation of all fractional rods (see Fig. 2), requires a 3 × 3 distortion with large out-of-plane

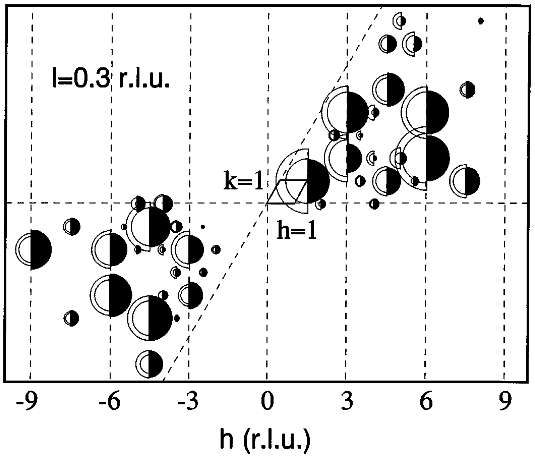

FIG. 3. Irreducible in-plane structure factors. Radii of empty semicircles are proportional to measured structure factors and reflect their uncertainties. Filled semicircles correspond to calculated structure factors. The relative intensity of 3 × 3 specific reflections is multiplied by a factor of 2.

relaxations that extend over several atomic layers. A side view of the model used to fit the data is represented in Fig. 1. Within the 3 × 3 unit cell, three Pb atoms and three full Ge bilayers were distorted in the fitting process.

As a starting point, we used the in-plane data set to determine the atomic lateral displacements. The most important lateral displacement needed to fit the in-plane data set comes from the three Ge groups 4, 5, and 6 (see Fig. 1) that were laterally relaxed independently. In a first approximation, all groups 4, 5, and 6 are displaced ~0.15 Å towards Pb atoms (1, 2, and 3) [12]. The next step was to obtain the displacements in the vertical direction. In view of STM information [2], we allowed Pb atoms to relax in the vertical direction independently. Ge groups 4, 5, and 6, bonded to each of them, also had to be relaxed vertically and followed the movement of Pb atoms. Thus, we consider a cluster of five atoms, one Pb and four Ge, including the three Ge atoms directly bonded to Pb and the one underneath. The 3 × 3 unit cell contains three of these clusters, highlighted in colors blue, red, and cyan in Fig. 1. By allowing an independent vertical relaxation of these three clusters, the model reproduced already most of the features observed in both the in-plane and the out-of-plane data. A χ^2 of 5.3 was reached after finishing this process. Two of the clusters had to be relaxed inwards (blue and cyan) in approximately the same amount, while the third (red) was displaced outwards. Obviously, these kinds of relaxations also affect all other Ge atoms in the two top bilayers. Their positions will be described next, but the basic 3 × 3 distortion was clarified after this first fit: it consists of a rippling of both Ge and Pb atoms, affecting strongly the top Ge bilayer.

The refinement of this model was achieved by including horizontal and vertical displacements down to the third bilayer of the substrate (see Fig. 1). In-plane and out-of-plane Debye-Waller factors were introduced in the fit, but they did not bring a significant improvement for the LT data set shown in this Letter, probably due to the low temperature reached during the measurements (~50 K). They are relevant for data taken at higher temperatures [13]. The refinement included the in-plane data set, the fractional rods, and the crystal truncation rods. We note that the atomic movements found (see Table I for details) reflect the elastic response of the Ge crystal to the basic distortion described before [14]. For instance, green Ge atoms in the top bilayer (see Fig. 1, groups 7 and 8) are also displaced upwards, as are the Ge atoms directly underneath, and exhibit a small lateral relaxation [15]. Thus, the downward displacement of two Pb-Ge clusters (blue and cyan in Fig. 1) is accompanied by an upward displacement of the central Pb-Ge cluster (red in Fig. 1) that is followed by the intermediate Ge atoms $1'$, $2'$, and $3'$ [16]. The final χ^2 of the refined model was 1.6.

Several characteristics make the 3 × 3 reconstruction unique. First, it involves the displacement of three atomic clusters. The Pb-Ge bond lengths (2.93 ± 0.02 Å and 2.95 ± 0.02 Å) and bond angles (49° ± 1° and 47° ± 1° off vertical) are equal within experimental accuracy for the three clusters. The 6% stretching of the Pb-Ge bond length with respect to the sum of covalent radii allows a smaller bending of the Ge dangling bond. The vertical displacement of each cluster induces an overall distortion of the crystal. The tendency observed is to keep Ge-Ge bond lengths as close to the bulk value as possible. All Ge-Ge bonds are equal to the bulk value of 2.44 Å within 2.5%, excluding the bond between atoms $2'$ and $2''$, that is stretched to 2.63 Å ([17]; see also below). The rippling found in the top Pb layer (atoms 2-1: 0.42 ± 0.01 Å; atoms 2-3: 0.382 ± 0.003 Å), is reduced to a ~60% for Ge atoms in the second bilayer, and it is less than 10% in the third Ge bilayer. Thus, the 3 × 3 distortion is shared between the top bilayers, a process that reduces the strain. On the other hand, lateral displacements in the second bilayer are significant (~0.1 Å) for atoms 10. This group is laterally displaced by the upward movement of atoms 7 and 8 and provokes a downward displacement of atom $2''$. This favors the stretching of the weakened $2'$-$2''$ bond [17]. In-plane displacements are critical to obtain the final fit and, in particular, to reproduce the shape of fractional order rods at low l, but they are much smaller than comparable vertical displacements. The reconstruction should be described as a periodic vertical rippling rather than a lateral displacement [6] without significant vertical distortion [2,6].

The structure described in this Letter for (3 × 3)-Pb/Ge(111) agrees well with the ground state found using DFT in the local density approximation for Sn/Ge(111) [9]. In this calculation, the Sn layer reached a vertical distortion of 0.35 Å. The phase transition was attributed to the stabilization at LT of vertical fluctuations

TABLE I. Atomic displacements (in Å) found for (3×3)-Pb/Ge(111). Numbers and direction of displacements are shown in Fig. 1. Ge displacements are referred to ideal bulk positions and Pb displacements to the T_4 site described in Fig. 1. Numbers in parentheses are error bars calculated as in Ref. [10].

Atom	Δ (lateral)	Δ (vertical)	Atom	Δ (lateral)	Δ (vertical)	Atom	Δ (lateral)	Δ (vertical)
1	0.013(2)	0.076(9)	2	0.000(1)	0.384(2)	3	0.025(5)	0.002(1)
4	0.114(6)	0.20(4)	5	0.148(5)	0.21(2)	6	0.114(6)	0.10(1)
$1'$	0.001(1)	0.4(1)	$2'$	0.001(1)	0.022(1)	$3'$	0.000(1)	0.4(1)
$1''$	0.001(1)	0.37(7)	$2''$	0.001(1)	0.156(6)	$3''$	0.000(1)	0.33(8)
7	0.03(1)	0.090(3)	8	0.02(1)	0.085(3)	$7'$	0.03(1)	0.024(1)
$8'$	0.02(1)	0.046(1)	9	0.04(1)	0.01(1)	10	0.08(2)	0.04(2)
11	0.008(2)	0.02(1)	$9'$	0.000(1)	0.03(2)	$10'$	0.000(1)	0.01(1)
$11'$	0.000(1)	0.07(5)	12	0.000(1)	0.011(4)			

in the Sn layer, in agreement with the two extreme positions found in this work for (3×3)-Pb/Ge(111). We conclude now that the LT distortion affects several Ge layers, in a process driven by a gain in electronic energy. A strong surface distortion can lift the degeneracy of $\sqrt{3}$ bands, so that 3×3 bands are split [7]. The new electronic band structure reflects a bond reordering. This process provides an energetic gain large enough to prevail over the elastic energy needed to create the distortion. Rippled reconstructions of this kind were proposed some time ago as metastable states for a Si(111) surface [19], stabilized by the presence of vacancies. The structure of the 3×3 phase found here reflects a similar elastic response, but it has a much more complex unit cell. It can be best described as a cooperative Jahn-Teller distortion of the top layers of a Pb-covered Ge crystal. It has been proposed that electron correlation effects are crucial in the stabilization of the 3×3 phase [2,4,5]. Electron correlation could certainly affect the band structure, but the atomic displacements found in the 3×3 phase are too large to be driven only by electron correlation, in agreement with other findings [8,9].

Baddorf *et al.* have performed a SXRD study on the related system Sn/Ge(111) [6]. The model proposed is different from the one found here. Their periodic lattice distortion involves a negligible vertical ripple of the Sn layer (less than 0.05 Å) and a large (0.22 Å) lateral displacement of Ge atoms 4, 5, and 6. The maximum l reached for the only 3×3 fractional rod measured was $l = 1.8$, a value too low to show the intensity increase detected around $l = 4$. This modulation cannot be reproduced without significant vertical distortion and also appears in the case of Sn/Ge(111) [20].

We conclude that the origin of the 3×3 phase is a strong rippling (~0.4 Å) of the Pb layer that affects the three top Ge bilayers. The stable LT phase can be described as a result of a cooperative Jahn-Teller distortion, by which a significant gain in electronic energy allows large atomic displacements. Our results do not support the theory that electron correlation effects are relevant for the stabilization of the 3×3 phase.

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