# Direct Observation of a $(3 \times 3)$ Phase in $\alpha$-Pb/Ge(111) at 10 K

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We have investigated the recently reported structural phase transition at low temperature (LT) for $\alpha$-Pb/Ge(111) [from a $(3 \times 3)$ symmetry to a disordered phase] using scanning tunneling microscopy (STM). By tracking exactly the same surface regions with atomic resolution while varying the sample temperature from 40 to 140 K, we have observed that substitutional point defects are not mobile, in clear contrast to previous assumptions. Moreover, STM data measured at the lowest temperatures ever reported for this system (10 K) show that while filled-state images display the apparent signature of a glassy phase with no long-range order, in empty-state images honeycomb patterns with $(3 \times 3)$ periodicity, and not distinguishable from data measured at much higher temperatures, are clearly resolved. These new observations cast serious doubts on the nature and/or on the existence of a disordered phase at LT.

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Low-dimensional systems are an ideal playground for the analysis of critical phenomena. In particular, structural phase transitions occurring at surfaces have been the subject of intense experimental and theoretical research for the last few decades. The development of new experimental techniques such as scanning tunneling microscopy (STM) at cryogenic temperatures has widened, much more recently, our view of the microscopic aspects of some of such transitions. A prototypical example has been the case of the Si(001) surface, where a wealth of new phases has been detected by low temperature (LT) STM. Some of these observations, however, are not exempt of an intense debate as the STM in itself can have some influence on the phase transitions, especially when very low differences in energy separate some of these phases [1–9]. Another important example of new discoveries in this field stimulated by STM observations are the LT phase transitions occurring in the 1/3 monolayer (ML) $\alpha$ phases of Pb/Ge(111) and Sn/Ge(111) and the $\beta$ phase of Pb/Si(111). For all of these systems, reversible phase transitions from a $(\sqrt{3} \times \sqrt{3})R30°$ reconstruction ($\sqrt{3}$ in the following) at room temperature (RT) to a $(3 \times 3)$ periodicity at LT do exist [10–13]. Very recently, Guo *et al.* [14] have reported a new phase transition on $\alpha$-Pb/Ge(111) at lower temperatures ($T_c \sim 76$ K) from the $(3 \times 3)$ symmetry to a disordered "glassy"-like phase. This phase transition, discovered and experimentally characterized only by filled-state STM imaging, had previously been predicted by some of the same authors [15] as a result of the delicate balance between two driving forces: the long-range electron-mediated interaction and the elastic stress imposed to the substrate.

In the present work, we have performed a thorough study of this new phase transition by STM at LT. Some puzzling observations are revealed by this investigation. First, we have observed that point defects are not mobile, in clear contrast to previous assumptions. Second, STM data measured at 10 K show that while filled-state images display the apparent signature of a glassy phase with no long-range order (LRO), in empty-state images honeycomb patterns with $(3 \times 3)$ periodicity are clearly resolved. Third, at 40 K large regions presenting $(3 \times 3)$ periodicity at both bias polarities can coexist with regions displaying a disordered nature only in filled-state images. And fourth, reversible switching between the $(3 \times 3)$ and the disordered phase can be induced just by increasing the tunneling current when filled-state imaging is used. The nature and/or the existence of a disordered phase at LT is seriously questioned by all these new findings.

The experiments were carried out in two independent ultrahigh vacuum (UHV) systems. All the data at temperatures between RT and 40 K were measured in a UHV system equipped with a home-made ultrastable variable temperature (VT)-STM [13,16]. Data at 10 K were acquired with a home-made UHV LT combined dynamic atomic force microscope/STM operated in the STM mode [17]. Sample preparation consisted in depositing $\sim$0.5 ML Pb on clean reconstructed Ge(111)-$c(2 \times 8)$ surfaces ($n$-type, RT resistivity $\leq 0.4$ Ohm $\cdot$ cm) followed by annealing. This procedure leads a sharp $\sqrt{3}$ LEED pattern at RT and large terraces presenting the $\sqrt{3}$ reconstruction with lower densities of defects (mainly substitutional Ge adatoms) than those reported in previous STM images in the literature [10,14]. All data were acquired and processed with the WSXM program [18].

Figures 1(a)–1(c) show filled-state STM images summarizing observations on the 1/3 ML Pb/Ge(111) surface at temperatures between RT and 40 K. When lowering the temperature from RT to 95 K, a phase transition from the $\sqrt{3}$ phase [Fig. 1(a)] to the $(3\times3)$ phase [Fig. 1(b)] can be observed in good accord with previous STM results [10]. LT filled-state images [Fig. 1(b)] are characterized by a hexagonal array of bright protrusions with $(3\times3)$ periodicity, corresponding to a corrugated surface where one Pb atom out of three in the unit cell is slightly higher ($\approx$0.4 Å) [19]. Upon further cooling down, filled-state STM images on areas free of defects reveal the disappear-

 

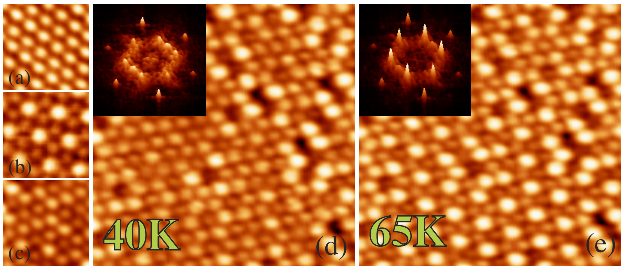


FIG. 1 (color online). (a), (b), (c) $3.7 \times 3.7\ \mathrm{nm}^2$ filled-state STM images on $\alpha$-Pb/Ge(111) measured at RT (a), 95 K (b) and 40 K (c). The sample bias is $-1.5$ V. The tunneling currents are: (a) 1 nA, (b) 0.1 nA, and (c) 0.2 nA. (d) and (e) two $10 \times 10\ \mathrm{nm}^2$ frames extracted from a STM movie [20] measured while varying the sample temperature from 40 K to 65 K. Sample bias and tunneling current are $-1.5$ V and 0.2 nA. The insets in (d) and (e) show FTs of the corresponding STM images.

ance of the $(3 \times 3)$ periodicity. Some atoms appear brighter than others [Fig. 1(c)], but no LRO can be observed. The disappearance of LRO in filled-state images has been interpreted by Guo *et al.* [14] as the reversible transition from the $(3 \times 3)$ to a new disordered glassy-like phase at the lowest temperatures. As with our VT-STM it is possible to image exactly the same surface regions with atomic resolution while varying the sample temperature [13], the evolution from disordered to $(3 \times 3)$-ordered images can be tracked by recording STM movies. An example of such exceptional kind of movies [20] is shown in Figs. 1(d) and 1(e) where the same surface spot was tracked from 40 to 65 K. The disappearance of the $(3 \times 3)$ LRO at the lowest temperatures can be observed both in real space images and in their Fourier transforms (FT). All these observations are in general good accord with previous filled-state STM imaging at LT by Guo *et al.* [14].

An important issue, although subject to certain controversy, in the $\sqrt{3}$ to $(3 \times 3)$ phase transitions for Sn/Ge(111), Pb/Si(111), and Pb/Ge(111) is the role of point defects (substitutional Ge or Si atoms). For Sn/Ge(111) it was reported that a large interaction between defects with a $(3 \times 3)$ periodicity does exist that forces them to move from the random distribution they present at RT to the alignment onto one honeycomb sublattice found at LT [21–23]. Surprisingly, Pb/Si(111) does not exhibit such mobile point defects as the phase transition takes place [13]. For Pb/Ge(111) it is unknown whether such an alignment accompanies the $\sqrt{3}$ to $(3 \times 3)$ phase transition, though it has been assumed that it should exist as in the Sn/Ge(111) case [14]. For the newly reported transition to the disordered phase it has been suggested that a second disordering of the defects should accompany the phase transition for temperatures lower than $T_c \sim 76$ K [14]. This suggestion was based on filled-state STM images on different defective regions measured above and below $T_c$. Thus, in order to clarify this relevant issue to the new phase transition (i.e., the possibility of point defect mobility at temperatures close to $T_c$), defective regions have been imaged continuously from 40 to 140 K. Figure 2 summarizes a typical example of such measurements: three selected frames (filled-state images) are displayed as well as an empty-state image (measured simultaneously with the corresponding filled-state image) that serves as a reference to outline the defects' location at the lowest temperature. Although filled-state images reveal an evolution from a disordered surface to the $(3 \times 3)$ periodicity as in Fig. 1, none of the defects in this region has changed its location while varying the temperature in such large range. In fact, we have never detected any motion of substitutional defects in any of our temperature-dependent movies. Point defects mobility was considered to be closely related to the newly reported phase transition [14], thus the absence of such mobility cast a first doubt on the nature of this phase transition.

Further and stronger evidence against a simple situation in this apparent phase transition can be extracted from inspection of empty-state STM images at the lowest temperatures ever used for the Pb/Ge(111) system. Figure 3 shows simultaneously measured filled and empty-state STM images of this surface at 10 K. The filled-state image displays the same disordered appearance as that already observed at 40 K. Amazingly, the simultaneous empty-state image shows a clear LRO corresponding to a honeycomb pattern with $(3 \times 3)$ periodicity (one dark and two bright protrusions per unit cell). Its FT displays sharp maxima with this $(3 \times 3)$ periodicity. As a matter of fact, empty-state images of this surface at 10 K cannot be distinguished from those measured at much higher temperatures, i.e., above $T_c$ for the glassy phase transition. As an example, simultaneous filled and empty-state images measured at 95 K are shown in Figs. 3(d) and 3(e). According to all these observations, it could be stated that, while a loss of LRO can be observed in filled-state

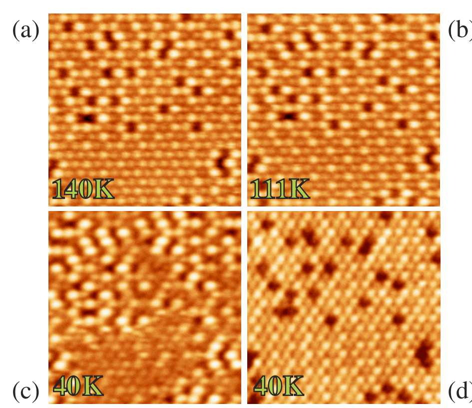


FIG. 2 (color online). STM images measured exactly on the same $12 \times 12\ \mathrm{nm}^2$ region at different sample temperatures. (a), (b), and (c) correspond to filled states (sample voltage: $-1.5$ V), while (d) corresponds to empty states (sample voltage: $+1.5$ V). The time lapse between (a) and (c) is 27 600 s. The tunneling current is 0.1 nA for all images.

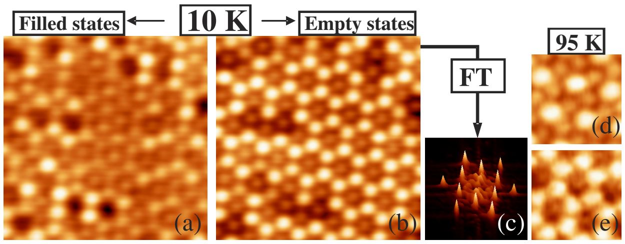


FIG. 3 (color online). (a) and (b) Filled and empty-state STM images simultaneously measured at 10 K. (c) FT of (b) displaying sharp peaks corresponding to the $(3 \times 3)$ periodicity. Typical filled (d) and empty-state (e) STM images of the $(3 \times 3)$ phase measured at 95 K are shown. The size of the images is $7.5 \times 7.5\ \mathrm{nm}^2$ for (a) and (b) and $3.1 \times 3.1\ \mathrm{nm}^2$ for (d) and (e). The tunneling parameters are: $-1.0$ V, 1.0 nA (a); $+1.0$ V, 1.0 nA (b); $-1.5$ V, 0.2 nA (d); and $+0.75$ V, 0.2 nA (e).

STM images, from the point of view of empty-state images, there is not a second phase transition even at the lowest temperatures in the Pb/Ge(111) system.

At 10 K, most of the surface presents this dual appearance depending on the bias polarity in a wide range of tunneling conditions: bias ranging from $\pm 0.15$ to $\pm 1.5$ V; set point tunneling current from 50 pA to 3 nA. This is not, however, the situation at higher (but well below $T_c$) temperatures. At 40 K, surface regions presenting this dual appearance can coexist with very wide areas displaying the $(3 \times 3)$ periodicity at both bias polarities. This is illustrated in Figs. 4(a) and 4(b) where the largest $(3 \times 3)$ region ever reported for Pb/Ge(111) (see Refs. [10,14]) is shown at a temperature well below 76 K. This region coexists with other patches presenting a disordered (ordered) appearance for filled (empty)-state images [Figs. 4(c) and 4(d)]. In order to understand this puzzling behavior, the tunneling conditions were varied. Figures 5(a)–5(c) display three filled-state images measured on the same location at 40 K with different set point currents. The data reveal that while for high set point currents most of the surface presents a disordered appearance, when decreasing the current, well-developed $(3 \times 3)$ regions start to appear. This can be quantified by measuring the ratio of the amplitude of the $(3 \times 3)$ peaks to that of the $\sqrt{3}$ ones in the FT of the STM images as a function of the set point current [Figs. 5(d) and 5(e)]. These plots show a continuous decrease of this ratio (considered by Guo *et al.* [14] the order parameter of the phase transition) as the tunnel current is increased. These induced transformations between disordered-ordered appearance are reversible.

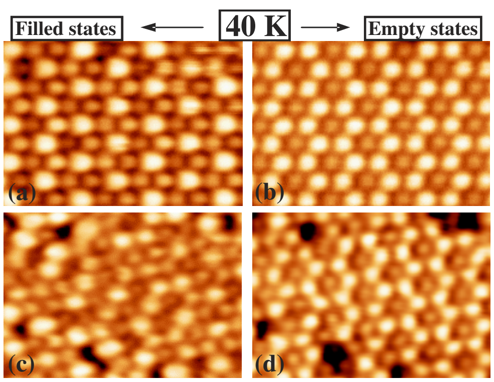


FIG. 4 (color online). STM images measured at 40 K on a region displaying $(3 \times 3)$ order at both polarities (a) and (b) and on a region displaying $(3 \times 3)$ order only in empty states (c) and (d). Empty and filled-state images were measured simultaneously. The size of the images are: $7.0 \times 5.0\ \mathrm{nm}^2$ [(a) and (b)] and $8.0 \times 5.6\ \mathrm{nm}^2$ [(c) and (d)]. The sample voltages and tunneling currents are: $-1.0$ V, 0.2 nA (a); $+1.0$ V, 0.2 nA (b); $-1.5$ V, 0.1 nA (c); and $+1.5$ V; 0.1 nA (d).

All the facts here presented tend towards a scenario where the nature and/or existence of a glassy phase at LT is seriously questioned. Similar problems have already been encountered in Si(001) at LT. For instance, the origin of the surprising STM observation of $(2 \times 1)$ symmetric dimers below 65 K [3–5] as well as the fluctuation between two different phases, $p(2 \times 2)$ and $c(2 \times 4)$, depending on the tunneling parameters have been the subject of an intense debate. Different explanations involving an STM influence have been envisaged: direct tip-surface interactions [4,6], STM field-induced effects [24], and local surface charging [4,8,24], among others. Moreover, the defect

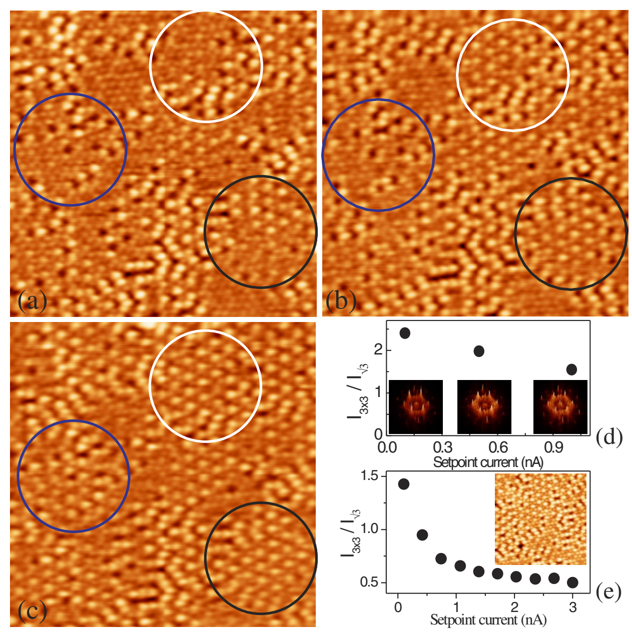


FIG. 5 (color online). (a)–(c) Filled-state ($-1.5$ V) STM images measured on the same $24 \times 24\ \mathrm{nm}^2$ area at 40 K and at different set point currents: 1.0 nA (a), 0.5 nA (b), and 0.1 nA (c). The circles denote regions where changes between $(3 \times 3)$ and disorder are observed. Notice that the images were acquired in the following time sequence: (c) then (a) then (b). (d) Intensity ratio ($I_{3\times 3}/I_{\sqrt{3}}$) obtained from the FT of (a) to (c) (shown in the inset) vs set point current. (e) Intensity ratio vs set point current obtained from another data set on the $16 \times 16\ \mathrm{nm}^2$ region shown in the inset (bias: $-1.5$ V) [20].

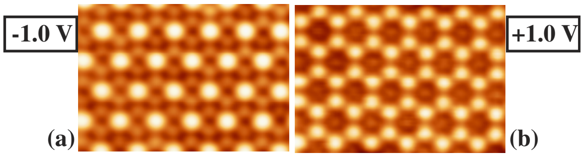


FIG. 6 (color online). $7.0 \times 5.0\ \mathrm{nm}^2$ STM images measured at 10 K on Pb/Si(111) displaying the $(3 \times 3)$ phase at both polarities. The tunneling current is 3 nA for (a) and (b).

concentration seems to also play an important role [9]. In our present case, all the data suggest that the disappearance of the LRO of the $(3 \times 3)$ reconstruction only in filled-state images at temperatures below $\sim$76 K could be an STM artifact. Indeed, surface electronic transport limitations in STM experiments have already been detected in Ge(111)-$c(2 \times 8)$ surfaces at LT ($\sim$60 K and below) [25,26]. We suggest that in $\alpha$-Pb/Ge(111) a hindered surface conductivity related to the immobile defects could produce some local charging at the lowest temperatures. This charging would start to manifest itself at intermediate temperatures (between 76 K and 40 K) for typical STM tunneling currents (50 pA to 3 nA). Upon further cooling down to 10 K, even the smaller currents (50 pA) could induce local charging preventing the observation of LRO for filled-state images. According to this scenario, it is quite possible that such STM-induced effects would influence the delicate balance between electronic and elastic energies responsible for the stabilization of the $(3 \times 3)$ reconstruction [15,27,28].

As a further experimental confirmation of this scenario, we have also measured the closely related system Pb/Si(111) at 10 K. Very large $(3 \times 3)$ regions with a very low density of defects can be prepared in Pb/Si(111) [13]. It should be expected, then, that such samples should display larger surface conductivity and hence lower charging artifacts for STM. As it is shown in Fig. 6, this is in fact the case: STM images measured at 10 K and high tunneling current on Pb/Si(111) present clear $(3 \times 3)$ patterns for both bias voltages. In contrast to the Pb/Ge(111) system, no traces of an apparent glassy phase have been found in Pb/Si(111) at such LT even when varying the tunneling parameters in the same large range as for Pb/Ge(111). This fact strongly supports that the $(3 \times 3)$ phase is the ground state for both systems.

In summary, by analyzing the $\alpha$-Pb/Ge(111) phase with STM at the lowest temperatures ever reported for this system, we have shown that serious doubts can be cast on the nature and/or on the existence of a recently reported phase transition from the well-known $(3 \times 3)$ to a disordered glassy-like phase. Our puzzling new findings can be rationalized as the result of a strong STM influence on the measurements. A tentative explanation is proposed based on a hindered surface conductivity, where the immobile substitutional defects could play some role, which can alter the delicate balance between electronic and elastic energies at the lowest temperatures. We expect that these results would stimulate further experimental and theoretical work on this subject.

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[1] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).
[2] H. Shigekawa *et al.*, Jpn. J. Appl. Phys. **35**, L1081 (1996).
[3] T. Yokoyama and K. Takayanagi, Phys. Rev. B **61**, R5078 (2000).
[4] T. Mitsui and K. Takayanagi, Phys. Rev. B **62**, R16251 (2000).
[5] Y. Kondo *et al.*, Surf. Sci. **453**, L318 (2000).
[6] K. Hata, S. Yoshida, and H. Shigekawa, Phys. Rev. Lett. **89**, 286104 (2002).
[7] K. Sagisaka, D. Fujita, and G. Kido, Phys. Rev. Lett. **91**, 146103 (2003).
[8] M. Ono *et al.*, Phys. Rev. B **67**, 201306(R) (2003).
[9] D. Riedel *et al.*, Phys. Rev. B **69**, 121301(R) (2004).
[10] J. M. Carpinelli *et al.*, Nature (London) **381**, 398 (1996).
[11] J. M. Carpinelli *et al.*, Phys. Rev. Lett. **79**, 2859 (1997).
[12] J. Ortega, R. Pérez, and F. Flores, J. Phys. Condens. Matter **14**, 5979 (2002); L. Petersen, Ismail, and E. W. Plummer, Prog. Surf. Sci. **71**, 1 (2002), and References therein.
[13] I. Brihuega *et al.*, Phys. Rev. Lett. **94**, 046101 (2005).
[14] J. Guo, J. Shi, and E. W. Plummer, Phys. Rev. Lett. **94**, 036105 (2005).
[15] J. Shi *et al.*, Phys. Rev. Lett. **91**, 076103 (2003).
[16] O. Custance *et al.*, Phys. Rev. B **67**, 235410 (2003).
[17] N. Suehira *et al.*, Rev. Sci. Instrum. **72**, 2971 (2001).
[18] WSXM, free software from http://www.nanotec.es.
[19] A. Mascaraque *et al.*, Phys. Rev. Lett. **82**, 2524 (1999).
[20] See EPAPS Document No. E-PRLTAO-95-014547 for STM movies. This document may be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
[21] A. V. Melechko *et al.*, Phys. Rev. Lett. **83**, 999 (1999).
[22] H. H. Weitering *et al.*, Science **285**, 2107 (1999).
[23] A. V. Melechko *et al.*, Phys. Rev. B **61**, 2235 (2000).
[24] K. Seino, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **93**, 036101 (2004).
[25] G. Dujardin, A. J. Mayne, and F. Rose, Phys. Rev. Lett. **89**, 036802 (2002).
[26] R. M. Feenstra, G. Meyer, and K. H. Rieder, Phys. Rev. B **69**, 081309(R) (2004).
[27] R. Pérez, J. Ortega, and F. Flores, Phys. Rev. Lett. **86**, 4891 (2001).
[28] G. Ballabio *et al.*, Phys. Rev. Lett. **89**, 126803 (2002).