New $(\sqrt{3} \times \sqrt{3})R30^\circ$ Phase of Pb on Ge(111) and Its Consequence for the Melting Transition

M. F. Reedijk,[1] J. Arsic,[1] D. Kaminski,[1] P. Poodt,[1] J.W. M van Kessel,[1] W. J. Szweryn,[1] H. Knops,[2] and E. Vlieg[1]
[1]*NSRIM Department of Solid State Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*
[2]*Institute of Theoretical Physics, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

(Received 17 July 2002; published 6 February 2003)

Depending on the preparation method, we find two different structures of the Pb/Ge(111) system at a nominal coverage of $\frac{4}{3}$ monolayer that exhibit different melting points. One is the well studied β phase that melts at 270 °C, but the other is a new and metastable phase that melts at 330 °C. Using surface x-ray diffraction the atomic structure of both phases is found to be surprisingly similar. The difference in melting points can be explained by the distribution of the excess Pb present on the surface, which has a direct effect on the vacancy density. We propose a modified phase diagram, in which the melting temperature of the β phase depends strongly on coverage.

DOI: 10.1103/PhysRevLett.90.056104 PACS numbers: 68.35.Rh, 68.08.De, 68.35.Ct

Phase transitions on surfaces have proven to be an area where interesting phenomena take place. Owing to the low dimensionality, the local structure, defects, and thermal fluctuations are more important than in bulk material [1,2]. One type of system that has been found to be particularly rich is the metal-semiconductor interface, of which a lot is known thanks to their importance in electronics [3,4]. Prime examples are Pb and Sn monolayers on Si(111) and Ge(111). Despite (or because of) many studies, various phases and phase transitions on these systems have remained controversial, e.g., the low-temperature and low-density phase transition from a $(\sqrt{3} \times \sqrt{3})R30^\circ$ to a 3×3 reconstruction [5] that is possibly driven by a charge-density wave, and the high-temperature "melting" of the high-density $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase to a 1×1 phase [1,6]. In the latter case the different observations can be reconciled by assuming that the "molten" surface layer has both liquid and solid properties [7,8]. This high-temperature phase can additionally be considered a model system for a solid-liquid interface in which the ordering in the liquid and the effect of coverage and mismatch are more easily studied than in thicker solid-liquid interfaces that are relevant for, e.g., crystal growth and lubrication [9].

In this Letter we focus on the Pb/Ge(111) system that we find to be more subtle in its behavior than previously thought. The phase diagram of this system as derived by Ichikawa [10] and Grey *et al.* [6,11] shows two $(\sqrt{3} \times \sqrt{3})R30^\circ$ ($\sqrt{3}$ in short) phases, a low-coverage phase at $\frac{1}{3}$ monolayer (ML) known as the α phase and a dense β phase at $\frac{4}{3}$ ML. de Vries *et al.* [7] confirmed that the saturation coverage of the β phase is $\frac{4}{3}$ ML, with one Pb atom located at an H_3 site and the other three located on off-center bridge positions between the T_1 and T_4 sites ("OCT_1"), see Fig. 1.

In the course of investigating the phase transition at a coverage of $\frac{4}{3}$ ML [12], we found a difference between the as-deposited structure and the annealed structure. If at least $\frac{4}{3}$ ML of Pb is deposited, a $\sqrt{3}$ phase forms (that we will call the β' phase) that exhibits a phase transition to a 1×1 phase at ~330 °C. This is an irreversible transition, and after cooling down the well-known β phase emerges with a lower transition temperature of ~270 °C. The latter transition is reversible; thus the β phase is stable. In this Letter we present the structural differences between the two phases and show that the vacancy density plays a dominant role in the melting mechanism.

Surface x-ray diffraction was used to determine the atomic structure of the two $\sqrt{3}$ phases. The truncation of a crystal at the surface gives rise to tails of diffuse scattering connecting the bulk Bragg peaks in the direction perpendicular to the surface that are called crystal truncation rods. The exact shape of the rods is determined by the atomic structure of the surface [13]. The experiment was performed at the DUBBLE beamline at the ESRF in Grenoble [14]. The Ge(111) samples were cleaned by repeated cycles of sputtering and annealing. All data were measured at a wavelength of 1.13 Å, with a constant incoming angle of 1° and varying exit angles.

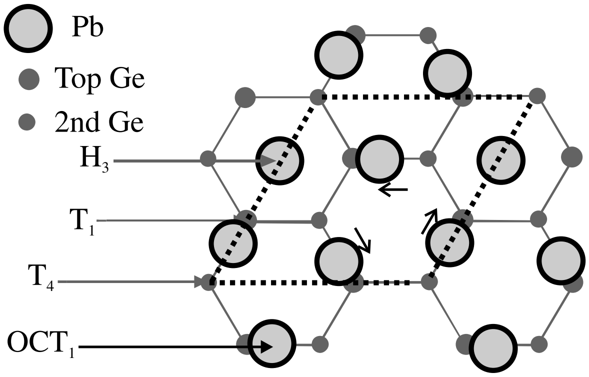

FIG. 1. Schematic top view of the structural model for the β phase. The $\sqrt{3}$ unit cell is indicated by the dotted lines. One Pb atom is positioned at the H_3 site, and three Pb atoms are placed on bridged positions between the T_1 and T_4 sites. The displacement direction of the bridged atoms is shown with an arrow.

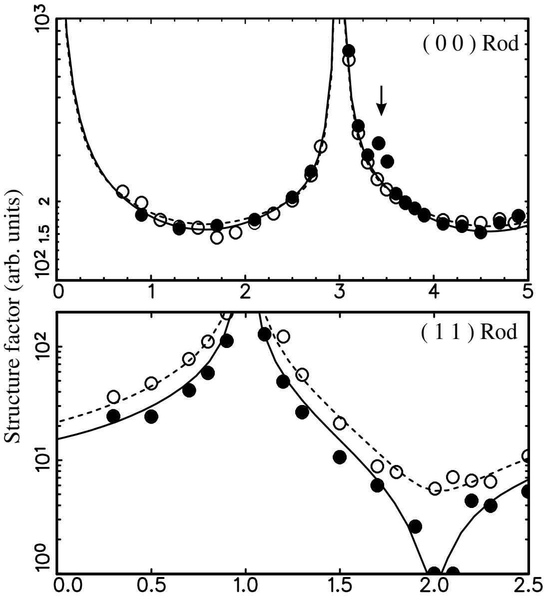

FIG. 2. Structure factor amplitudes along the (0 0) and (1 0) crystal truncation rods for the annealed (open circles) and as-deposited (filled circles) structures. The lines are the best fit calculations. The peak near $l = 3.4$ in the as-deposited specular rod arises from bulk Pb.

To denote the surface structure, we use a 1 × 1 surface unit cell for Ge(111) whose lattice vectors are expressed in terms of the conventional cubic lattice by $\mathbf{a}_1 = \frac{1}{2}[10\bar{1}]$, $\mathbf{a}_2 = \frac{1}{2}[\bar{1}10]$, and $\mathbf{a}_3 = [111]$. The cubic coordinates are in units of the germanium lattice constant (5.66 Å at 300 K). The corresponding reciprocal lattice vectors $\mathbf{b}_i$ are defined by $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. The momentum transfer $\mathbf{Q}$ is denoted by the diffraction indices hkl in reciprocal space: $\mathbf{Q} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$. The indices (hk) refer to the in-plane component of the momentum transfer and (l) to the perpendicular component.

After cleaning, Pb was deposited using a Knudsen effusion cell while monitoring a $\sqrt{3}$ reflection in order to control the total amount of deposited lead [7]. We used low deposition rates in the range from 0.02–0.04 ML/ min. During deposition the sample temperature was 230 °C. To prepare the "as-deposited" β' structure, somewhat more than $\frac{4}{3}$ ML of Pb is deposited. After slowly cooling the surface to room temperature a full data set is measured. To prepare the β phase the temperature is raised above the (irreversible) transition temperature of 330 °C. Subsequently, the surface is cooled to room temperature, where a second data set is measured. A data set consists of a specular rod, crystal truncation rods and an extensive in-plane data set. All measured intensities were converted into structure factors by applying a standard procedure [15]. Model calculations and fitting were done using the ROD program [16].

Despite the large difference in transition temperatures for the two structures, the measured data show a large resemblance. Figure 2 shows the measured data for the (0 0) and (1 1) rods. The main difference can be found in the (0 0) rod near $l = 3.4$, where the β' structure shows a fairly sharp peak. The position of this peak corresponds to the (111) Pb Bragg peak at this wavelength. This indicates the excess Pb to be ordered in (111)-oriented islands. From the width of the peak the thickness of the islands is determined to be 20 ML. The β phase does not show this peak, showing that the excess Pb is reorganized upon the anneal.

The β' phase shows an irreversible phase transition at a high temperature. Preparations with different initial Pb coverages and different heating rates reproducibly yielded a phase transition temperature of ~330 °C. The melting behavior of the transition was monitored by measuring the $(\frac{2}{3}, \frac{2}{3}, 0.3)$ reflection. No large changes in structure factor were observed until the transition temperature, at which the reflection completely disappeared. Also the width of the peak, a measure of the domain size, remained small. It is important to note that the β' phase is stable for at least several hours when heated to temperatures close to its own transition point, i.e., well above the transition temperature of the β phase. In contrast, the β phase shows a lower transition temperature, with a different melting behavior. Above the melting point, the $(\frac{2}{3}, \frac{2}{3}, 0.3)$ reflection significantly broadens, showing critical scattering, while the intensity gradually drops [12].

To determine the structural difference between the two structures, both data sets are fitted starting from the $\sqrt{3}$ structure as determined by de Vries *et al.* [7] (Fig. 1). The parameters used for fitting are the surface fraction, height of the H_3 atom, height and in-plane displacement of the OCT_1 atoms, and anisotropic Debye-Waller parameters of the Pb atoms. With this model both structures could be fitted very well; see Fig. 2. Table I shows the best-fit parameters. The difference in the (1 1) rod near $l = 2$ turns out to be mainly due to the difference in vacancy density.

The β structure is equivalent to the structure at 1.25 ML measured by de Vries *et al.*, and the atomic positions of the Pb atoms are in excellent agreement (Table I). The main difference is the coverage (1.28 vs 1.19 ML). The difference in Debye-Waller parameters is caused by the difference in experimental temperatures. The structural similarity is expected, because in both cases the reconstruction was formed by cooling down the disordered 1 × 1 phase.

The β' structure is slightly, but significantly, different from the β structure in both the coverage and the height of the Pb atoms. The Pb atom at the H_3 position is 0.2 Å lower than the bridge atoms in the β' phase, compared to 0.08 Å higher in the β phase. Earlier discrepancies in the literature for the height determination [4,7,17] may

TABLE I. Best fit parameters.

Parameter	β' phase	β phase	1.25 ML [7]
Surface fraction	1.00(1)	0.96(1)	0.89
Height H_3 (Å)	2.63(9)	2.83(5)	2.88
Height OCT_1 (Å)	2.83(6)	2.75(2)	2.76
OCT_1 (Å)	0.36(1)	0.36(1)	0.39
$DW_{\parallel}$ (OCT_1)	3.4(5)	3.6(3)	6.3
$DW_{\parallel}$ (H_3)	5.2(8)	3.6(3)	6.3
Coverage	1.33(2)	1.28(1)	1.19
χ^2	2.22	1.74	

therefore be partly explained by the different preparation methods.

The structural differences between the two phases are small, and the most convincing argument that we have two different structures is the large and reproducible difference in the transition temperature and behavior. An important question is now what causes this large difference in transition temperature and melting behavior?

It seems unlikely that this difference is caused by the small height differences between the two structures, knowing that a Debye-Waller parameter of 3.4 corresponds to a mean-square displacement of 0.04 Å^2. A more important factor may be the lower coverage of the β phase that can provide an explanation within the concept of vacancy-induced melting [18]. For example, the melting temperature of N_2 adlayers on graphite is reduced for coverages below the saturation coverage because the presence of vacancies facilitates melting [19].

The same mechanism might explain the different melting temperatures for the two $\sqrt{3}$ structures. However, the analogy between the Pb/Ge system and the N_2-graphite system is not perfect. The total amount of Pb available is $> \frac{4}{3}$ ML, and the melting transition of the β' phase is irreversible. Another point that needs an explanation is the high energy barrier between the two structures, i.e., the high-temperature necessary for the transition between the two structures.

In order to arrive at a consistent picture that combines all our observations, we need to include the distribution of the excess Pb on the surface. In the β' phase, we found from the specular rod that the surface is covered by Pb islands with a thickness of approximately 20 ML. Since there is an excess Pb of about 0.3 ML, approximately 1.5% of the surface is covered by these islands. While we have no direct observation, by considering similar systems [20] we may assume that the Pb will form many small islands, which will preferably be located at the step edges. Each terrace is thus in contact with at least one of these Pb islands. This situation is sketched in Fig. 3. In order for the β' phase to melt, vacancies need to be generated. The Pb islands, however, act as a source of Pb atoms, and none of the $\sqrt{3}$ domains can create the vacancies that are necessary for melting. When the bulk melting point of Pb is reached, the small islands melt and merge into a much smaller number of large islands; see Fig. 3 (bottom). Most terraces are no longer in contact with bulk Pb, and they will melt [21]. Our absolute temperature calibration is not very precise, but the melting point of the β' phase is fully consistent with the bulk melting point of Pb of 327.5 °C. The fact that the fractional-order reflections show no broadening during the melting of the β' phase is added proof for this model. The rearrangement of the Pb is irreversible, which explains the irreversible transition of the β' phase. The apparent high energy barrier between the β and β' phase is, in fact, the difference between the melting temperature of the β phase and the bulk melting point of Pb.

After the excess Pb is rearranged and the sample is cooled down, the β phase is formed which has a normal and reversible melting behavior in which the $\sqrt{3}$ peaks continuously broaden when approaching the phase transition. We find that the β phase has a coverage that is slightly less than $\frac{4}{3}$ ML and thus that it contains already vacancies (or antiphase domain walls) at room temperature.

The observation of peak broadening at a coverage of 1.28 ML is in contradiction with the phase diagram as proposed by Grey *et al.* In this regime, the β phase was assumed to be in equilibrium with a (1×1) phase for temperatures above 180 °C. When the temperature is increased, part of the surface covered by the β phase transforms to the (1×1) phase according to the lever rule, until eventually the whole surface is covered with the (1×1) phase. Thus, no peak broadening of the fractional-order reflections should occur, but only an intensity drop. The experimental peak broadening we find was also observed earlier by de Vries *et al.* [7] at 1.25 ML. In addition, Grey [11] observed critical scattering above the melting point of the β phase at 1 ML and 180 °C. In order to explain the broadening, we propose a modification of the phase diagram of the Pb/Ge(111) system in which the β phase is stable between 1.25 and $\frac{4}{3}$ ML (Fig. 4). Thus, the β phase can exist over a wider coverage range, similar to the α phase around $\frac{1}{3}$ ML. The sharp increase in the melting transition from 1.25 to $\frac{4}{3}$ ML is

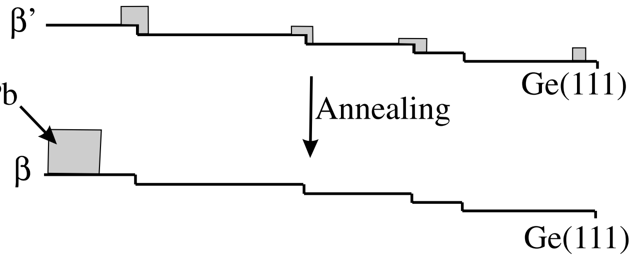

FIG. 3. The excess lead is equally distributed on the surface in small islands for the β' phase. After annealing, the Pb is redistributed in larger islands and most terraces have no access to bulk Pb.

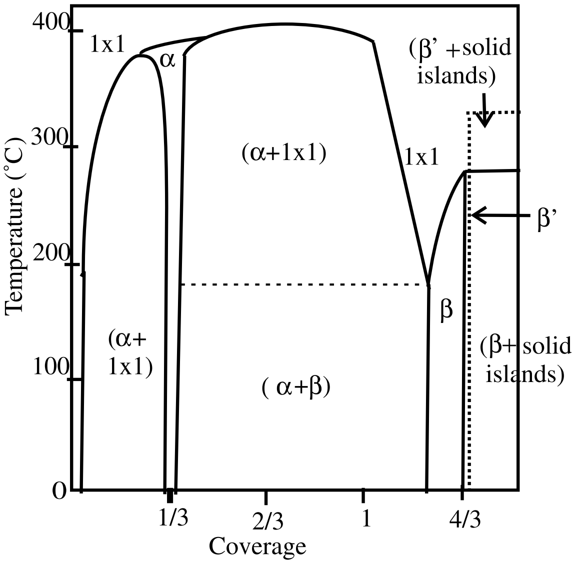

FIG. 4. The modified phase diagram of Pb/Ge(111) in which the β phase exits over a coverage range from 1.25 to 1.33 ML. This area was previously assigned to exist of a β phase mixed with an α phase (below 180 °C) or a 1×1 phase (above 180 °C). The β' phase is shown as a dotted line in the phase diagram.

now explained by the vacancy-induced melting mechanism as described earlier for the N_2/graphite system. The main reason to propose a (1×1) β-phase coexistence region near $\frac{4}{3}$ ML in the original phase diagram was the observation of both $\sqrt{3}$ reflections and liquid rings [11]. However, near the phase transition the Pb monolayer will have both liquid and solid properties [7,8], and thus these earlier observations are compatible with our new phase diagram.

The metastable β' phase forms a line in the phase diagram at a coverage of $\frac{4}{3}$ ML that ends at the melting point of lead. The phase diagram predicts that a molten β phase can be converted back into a β' phase by adding Pb, and this is indeed what we observed. At a sample temperature of 230 °C we found that after adding ~0.06 ML (very close to the difference in coverage listed in Table I) the β' phase is formed again. With continued deposition the signal from thin 3D islands reappears.

In conclusion, we have shown that at a nominal coverage of $\frac{4}{3}$ ML two different $\sqrt{3}$ structures exist which combine small structural differences with a large difference in transition temperature and melting behavior. This can be explained by the distribution of the excess Pb atoms on the surface that inhibits the β' structure from melting until the bulk melting point is reached. A microscopic technique (e.g., STM or low energy electron microscopy) is necessary to confirm our hypothesis for the behavior of the excess Pb. Our results are a clear example of how defects (vacancies in this case) can modify a phase transition. The results also show that the density at a solid-liquid interface is a crucial parameter in the behavior of the liquid.

We thank the staff of the DUBBLE beamline at the European Synchrotron Radiation Facility for their assistance during the measurements. This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), and was made possible by financial support from the Netherlands Organization for Scientific Research (NWO).

---

[1] I. Hwang and J. Golovchenko, Phys. Rev. Lett. **71**, 255 (1993).
[2] F. Ancilotto, A. Selloni, and R. Car, Phys. Rev. Lett. **71**, 3685 (1993); A.V. Melechko, J. Braun, H. H. Weitering, and E.W. Plummer, Phys. Rev. Lett. **83**, 999 (1999).
[3] D. R. Heslinga, H. H. Weitering, D. P. Vanderwerf, T. M. Klapwijk, and T. Hibma, Phys. Rev. Lett. **64**, 1589 (1990).
[4] H. Huang, C. M. Wei, B. P. Tonner, and S. Y. Tong, Phys. Rev. Lett. **62**, 559 (1989).
[5] J. M. Carpinelli *et al.*, Phys. Rev. Lett. **79**, 2859 (1997); J. Avila *et al.*, Phys. Rev. Lett. **82**, 442 (1999).
[6] F. Grey, R. Feidenhans'l, J. S. Pedersen, and M. Nielsen, Phys. Rev. B **41**, 9519 (1990).
[7] S. A. de Vries, P. Goedtkindt, P. Steadman, and E. Vlieg, Phys. Rev. B **59**, 13 301 (1999).
[8] M. F. Reedijk, F. K. de Theije, M. T. McBride, K. F. Peters, and E. Vlieg, Phys. Rev. B **64**, 033403 (2001).
[9] E. Johnson, Science **296**, 477 (2002); E. Vlieg, Surf. Sci. **500**, 458 (2002).
[10] T. Ichikawa, Surf. Sci. **140**, 37 (1984).
[11] F. Grey, Ph.D. thesis, Copenhagen University, Copenhagen, 1988.
[12] M. F. Reedijk *et al.* (to be published).
[13] I. Robinson and D. Tweet, in *Handbook on Synchrotron Radiation*, edited by G. Brown and D. Moncton (Elsevier Science Publishers BV, New York, 1991), Vol. 3, p. 221.
[14] M. Borsboom *et al.*, J. Synchrotron Radiat. **5**, 518 (1998).
[15] E. Vlieg, J. Appl. Crystallogr. **30**, 532 (1997).
[16] E. Vlieg, J. Appl. Crystallogr. **33**, 401 (2000).
[17] B. N. Dev, Phys. Rev. Lett. **64**, 1182 (1990); L. Seehofer, G. Falkenberg, and R. L. Johnson, Surf. Sci. **290**, 15 (1993); F. Ancilotto, A. Selloni, and R. Car, Phys. Rev. B **50**, 15 158 (1994).
[18] Note that for both phases the total amount of Pb deposited is larger than $\frac{4}{3}$ ML; the coverages mentioned here are those of the $\sqrt{3}$ phases.
[19] R. D. Etters, B. Kuchta, and J. Belak, Phys. Rev. Lett. **70**, 826 (1993).
[20] G. Meyer, M. Michailov, and M. Henzler, Surf. Sci. **202**, 125 (1988); N. Boutaoui, H. Roux, and M. Tholomier, Surf. Sci. **239**, 213 (1990); A. D. van der Gon, R. M. Tromp, and M. C. Reuter, Thin Solid Films **236**, 140 (1993).
[21] The higher chemical potential of the smaller islands is an additional argument why the small islands have a larger effect.