Ge(001)-(\(\frac{2}{5}\))\(^{-\frac{1}{3}}\))-Pb ↔ (\(\frac{2}{5}\))\(^{-\frac{1}{6}}\))-Pb: Low-temperature two-dimensional phase transition

O Bunk†‡§, M M Nielsen‡, J H Zeysing†, G Falkenberg†, F Berg-Rasmussen‡, M Nielsen‡, C Kumpf‡∥, Y Su†, R Feidenhans’l‡ and R L Johnson†
† II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany
‡ Condensed Matter Physics and Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark
∥ present address: Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Abstract. The Ge(001)-(\(\frac{2}{5}\))\(^{-\frac{1}{3}}\))-Pb surface reconstruction with a lead coverage of 5/3 monolayer is on the borderline between the low-coverage covalently-bonded and high-coverage metallic lead overlayers. This gives rise to an unusual low-temperature phase transition with concomitant changes in the bonding configuration. Both the room-temperature and low-temperature phases of this system were investigated by surface x-ray diffraction using synchrotron radiation. The room-temperature Ge(001)-(\(\frac{2}{5}\))\(^{-\frac{1}{3}}\)) phase is best described by a model with dynamically flipping germanium dimers underneath a distorted Pb(111) overlayer with predominantly metallic properties. In the low-temperature Ge(001)-(\(\frac{2}{5}\))\(^{-\frac{1}{6}}\)) phase the dimers are static and the interaction between adsorbate and substrate and within the adsorbate is stronger than at room temperature. These results suggest that the phase transition is of order-disorder type.

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§ To whom correspondence should be addressed: Oliver.Bunk@desy.de
1. Introduction

Surfaces and interfaces determine many chemical and physical properties of materials and play a key role in nanoscale electronic devices. A well-known example of the influence of an interface on electronic properties is the Schottky barrier at metal-semiconductor interfaces. In principle, the height of the barrier is determined by the difference between the work function of the metal and the electron affinity of the semiconductor, but experimental investigations showed that the atomic structure directly at the interface may influence the barrier height considerably [1]. Model systems chosen to study this phenomenon were, e.g., lead adsorbed on different silicon and germanium surfaces, since for these systems abrupt interfaces with planar layers free of alloying were expected. Extensive scanning tunneling microscopy (STM) investigations of the different phases of lead on Ge(001) surfaces for different lead coverages and preparation temperatures partially confirmed and partially disproved this simple idea [2, 3]. For lead coverages above \( \sim 1.5 \) monolayer (ML) quite flat and uniform lead overlayers forming a commensurate \( (\frac{1}{3} \times \frac{2}{3}) \) and at higher coverage an incommensurate \( c(8 \times 4)i \) reconstruction are observed. That the latter overlayer exhibits metallic properties is evident from the low STM tip bias of 20 mV used to image this surface [3]. Below 1.5 ML lead coverage and at preparation temperatures below 300°C commensurate reconstructions with \( (2 \times 2) \) and \( c(8 \times 4) \) unit-cells are formed. Both reconstructions are described by lead dimers covalently bonded to the germanium substrate. For the Ge(001)-\((2 \times 2)\)-Pb reconstruction with a nominal lead coverage of 0.5 ML the germanium substrate is still dimerized whereas in the \( c(8 \times 4)i \) phase with a nominal lead coverage of 0.75 ML half the dimer bonds are broken [3] – as confirmed recently by first-principle total energy calculations [4, 5]. The lead dimers in these two reconstructions are tilted to avoid the energetically unfavourable configuration of two approximately sp\(^3\) hybridized lead atoms each with a half-filled “dangling bond”. This buckling is static as opposed to the clean Si(001)- and Ge(001)-(2\( \times 2 \)) surfaces where the dimers flip dynamically at room temperature [6]. The lead-induced reconstructions of the Ge(001) surface described so far more or less exhibit the expected flat overlayer necessary for an ideal Schottky barrier model system – although only the phases with a sufficiently high lead coverage fulfill the condition of being metallic. At low lead coverages below 1 ML and preparation temperatures above \( \sim 300°C \) the surface exhibits a completely different morphology. This phase is not well ordered and has been described as the “rough phase” [3] with height differences of more than five atomic layers. The formation of this phase with an unusually high roughness for lead overlayers may be explained by the significant stress induced by the incorporation of lead atoms with a covalent radius of 1.47 Å on germanium lattice sites (covalent radius 1.22 Å), i.e., an unexpected alloying may occur at low lead coverages and high preparation temperatures.

The lead-induced surface reconstructions of the Ge(001) surface described so far possess a wide diversity of properties. But the Ge(001)-\((\frac{2}{3} \times \frac{1}{3})\)-Pb reconstruction, formed at an intermediate lead coverage of around 5/3 ML seems to be even more interesting.
From the point of view of coverage it resides between the low-coverage covalently-bonded and the high-coverage metallic phases and may share properties common to both.

Based on thorough STM investigations and some diffraction results a structural model was proposed for the Ge(001)-(\(\frac{2}{3}\)\(\sqrt{3}\))-Pb reconstruction with 5/3 ML lead in a distorted Pb(111) layer on top of a completely dimerized Ge(001) substrate [3, 7]. The complete dimerization of the germanium substrate is surprising since at lower lead coverage in the Ge(001)-c(8\(\times\)4)-Pb reconstruction the dimerization of the (even lower coverage) Ge(001)-(2\(\times\)2)-Pb surface and the clean Ge(001)-(2\(\times\)1) is already partially removed. To verify the proposed structural model for the room-temperature phase and to elucidate the properties of the novel Ge(001)-(\(\frac{2}{3}\)\(\sqrt{3}\))-Pb low-temperature phase [8] we investigated both systems in a surface x-ray diffraction (SXRD) experiment using synchrotron radiation.

2. Experimental

2.1. Preparation and measurements

The sample was prepared in an ultra-high vacuum (UHV) system equipped with reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) facilities. A clean (2\(\times\)1) reconstructed Ge(001) sample was prepared by the standard procedure of cycles of sputtering at 350-450°C for 30-60 min using 500 eV Ar\(^{+}\) ions and annealing at 600-650°C for 15 min. Lead was deposited while observing the RHEED-patterns: Starting from the (2\(\times\)1) reconstruction of the clean surface first the c(8\(\times\)4)-Pb and finally the Ge(001)-(\(\frac{2}{3}\)\(\sqrt{3}\))-Pb phase was observed. The change from c(8\(\times\)4) to (\(\frac{2}{3}\)\(\sqrt{3}\)) periodicity is accompanied by the disappearance of the characteristic c(8\(\times\)4)-streaks and the emergence of half-order reflections in the (1\(\overline{1}\)) azimuth. The long-range order of the surface reconstruction was improved by annealing the sample at 150°C.

The sample was then transferred to a portable UHV chamber equipped with a helium closed-cycle two-stage sample cooling system and brought to the BW2 wiggler beamline at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) for the x-ray diffraction measurements. The x-ray photon energy was set to 10 keV (\(\lambda = 1.24 \text{ Å}\)) and the glancing angle of incidence to 0.65° (i.e. above the critical angle to reduce the uncertainties in the measured intensities arising from mechanical displacements). A data-set consisting of 182 in-plane reflections, 236 reflections along nine fractional-order rods and 81 reflections along three integer-order rods (so-called crystal truncation rods, CTRs) was recorded for the Ge(001)-(\(\frac{2}{3}\)\(\sqrt{3}\))-Pb structure determination. After completing the room-temperature measurements the sample was cooled until the temperature of the sample holder reached 20 K. For the low-temperature (\(\frac{2}{3}\)\(\sqrt{3}\))-phase 313 in-plane reflections, 371 reflections along 18 fractional-order rods and 106 reflections along four CTRs were recorded.
2.2. Data-analysis

The integrated intensities were corrected for the Lorentz factor, polarization factor, active sample area and the rod interception appropriate for the z-axis geometry [9]. The in-plane data were averaged assuming that all four domains which are possible within the p2-symmetry are equally populated. In this way the room-temperature in-plane data set was reduced to 96 and the low-temperature in-plane data set to 223 symmetry-inequivalent reflections. The recording of extensive data sets with 413 symmetry-inequivalent data points for the room-temperature and 700 data points for the low-temperature phase was necessary to determine all the relevant parameters in these complex reconstructions with large unit cells.

The conventional surface coordinate system with \( a = \frac{1}{2}[110]_{\text{cubic}} \), \( b = \frac{1}{2}[\bar{1}10]_{\text{cubic}} \), and \( c = [001]_{\text{cubic}} \) is used. The cubic coordinates are in units of the germanium lattice parameter of 5.66 Å at 300 K and therefore \(|a| = |b| = 4.00\) Å and \(|c| = 5.66\) Å.

Only seven layers were included in the data-analysis to describe the substrate relaxations, i.e., less than the ten layers used for the analysis of the clean surface [10] to keep the number of free parameters reasonably low. In addition the elastic energy calculated using the Keating algorithm [11,12] was used as a constraint on the substrate parameters in the data analysis. The Keating term restricts the substrate parameters if the optimization runs into a shallow \( \chi^2 \) minimum. Nevertheless the data analysis was only possible using a computer program with the ability to handle efficiently the 152 parameters necessary to describe the atomic positions in the low-temperature phase together with further parameters describing thermal motion and disorder and the Keating constraints for 105 of the parameters.

The overall good agreement between the result of the structural refinement and the measured data is apparent from figure 1 for the room-temperature results and figure 2 for the low-temperature data. Using in total 82 parameters a reduced \( \chi^2(|F|) \) value of 2.2 was obtained for the room-temperature phase. For the low-temperature phase in total 155 parameters were determined and the reduced \( \chi^2(|F|) \) was 3.3. From a technical point of view the number of parameters is exceptionally large for a surface structure determination.

3. Results and discussion

In the following two subsections we focus on the most important results and suggest a possible interpretation.

3.1. Room-temperature phase

The analysis of the room-temperature data basically confirmed the structural model with a distorted Pb(111) layer on top of the dimerized germanium substrate proposed previously by Falkenberg et al [3] (see figure 3 and table 1). We could confirm that the
germanium dimers of the clean surface broken when forming the Ge(001)-c(8×4)-Pb reconstruction are reestablished at a higher lead coverage of 5/3 ML. In addition to this remarkable result some interesting details are revealed.

The atomic displacement parameter (ADP) used in the analysis of diffraction data describes both thermal motion and static disorder [13]. The ADP listed in table 1 for the lead atoms 1-9 (see figure 3) is anisotropic – larger in the surface plane than perpendicular to it. This suggests the picture of a metallic overlayer with static disorder and a significant mobility of the individual atoms around their equilibrium position. An extra ADP was necessary to describe the behavior of lead atom 10. This atom is on a high-symmetry site and has a larger distance to the germanium substrate than the other lead atoms. It is therefore more weakly bonded. This is reflected in its higher ADP.

There is a striking anisotropy in the ADP of the first layer germanium atoms. The amplitude of 0.4 ± 0.1 Å in the z-direction (perpendicular to the surface plane) matches well to the values of 0.50 Å [10] and 0.42 Å [14] for the clean surface. This may indicate that, similar to the clean surface, the germanium dimers are dynamically flipping beneath the lead overlayer. This analogy to the clean surface seems to be obvious, although static disorder and dynamic movement cannot be distinguished by SXRD. The bond length of 2.45 ± 0.08 Å for two germanium dimers (12-13 and 14-15) is in excellent agreement with the value of 2.44 ± 0.01 Å for the clean Ge(001)-(2×1) reconstruction [10]. The simple picture of an unperturbed germanium surface layer is supported by this fact. However, a bond length of 2.68 ± 0.07 Å was determined for the germanium dimer 11-16. This is an increase of 9 % compared to the substrate bond length of 2.45 Å. Since the germanium atoms 11 and 16 have the smallest observed Ge-Pb distance of 2.71 ± 0.06 Å to their next neighbor atoms 7 and 8 (drawn dark grey in figure 3) a stronger, partially covalent Pb-Ge interaction weakening the Ge-Ge dimer bonds may cause the observed increase in the dimer bond length.

To summarize the results for the Ge(001)-(3 3 1/3)-Pb room-temperature phase, the following model is consistent with the observed structural parameters: A distorted, metallic Pb(111) overlayer is only weakly bonded within the layer and to the substrate and has an increased in-plane motion or disorder compared to the out-of-plane direction. A partially covalent interaction between one germanium dimer and the two next neighbor lead atoms per unit-cell stabilizes the overlayer. This interaction tends to make the overlayer commensurate with the substrate and to weaken the corresponding dimer bond under the lead layer. The remaining two substrate dimers per unit-cell continue the dynamic flipping movement characteristic of the clean surface. The delicate balance between covalent and metallic behavior of the surface atoms indicates that this system is likely to respond to small changes of the total energy, e.g., by simply changing the temperature. The structural parameters derived from the SXRD measurements suggest that this system is predisposed to structural changes as a function of the temperature.
3.2. Low-temperature phase

Apart from the additional reflections characteristic of the \((\frac{3}{2}\,l)\)-periodicity the in-plane data measured at room and at low temperature look quite similar (see figure 1(a) and figure 2(a)) – mainly due to the characteristic ring pattern formed by the strongest reflections. This indicates that the fundamental framework of the reconstruction remains intact upon cooling. But despite the similarities there are definite differences as can be seen by the comparison of the fractional-order rod scans shown in figure 5. The differences are not artifacts caused by choosing incorrect scaling factors since they are not uniform along all rods and they are not just caused by changes in thermal motion since they occur in some cases only in a certain range of \(l\)-values (see, e.g., the \((2,3/2,l)\)-rod for \(l > 2\)) and in other cases along the whole rod (see, e.g., the \((8/3, 5/3, l)\)-rod).

The parameters determined in the detailed data analysis are listed in table 2 and table 3 and the model is shown in figure 4. The weakly bonded lead atom (number 10 in figure 3) remains in a high-symmetry site upon cooling (numbers 10 and 20 in figure 4). The differences to a similar structural model for the low-temperature \((\frac{3}{2}\,l)\)-reconstruction with lead atom 2 on a high-symmetry trench site amounts only up to 0.09 Å for most atoms. But the height (i.e. \(z\)-position) difference of 1.48 Å for the high-symmetry site atoms 10 and 20 is necessary to describe the data adequately and therefore the chosen symmetry is unambiguously the one occurring in the low-temperature phase.

For the lead layer the lowering of the \(z\)-position of atom 20, causing the described height difference, and the outward displacement of the next neighbor lead atoms 16 and 19 by 0.77 Å are the most pronounced changes in comparison to the room-temperature structure. All lead atoms are adequately described by one in-plane and one out-of-plane ADP. The ADP amplitudes of 0.21 ± 0.03 Å in the surface plane are smaller than the 0.26 ± 0.04 Å and 0.34 ± 0.10 Å at room temperature, but not as low as one would expect solely from a thermal effect. Static disorder would explain the larger in-plane ADP-amplitudes. The counterpart of the “floating” lead overlayer at room temperature, which is only weakly pinned to its commensurate position, is probably a network made up of a variety of very similar low-temperature structures, which forms due to a broad minimum of the total energy as a function of the in-plane position.

The germanium atoms in the low-temperature phase are well described by an isotropic ADP with a value close to zero. This is clear evidence of a well-ordered substrate structure at low temperatures. The precise value of this ADP does not strongly influence the reduced \(\chi^2\) and therefore it was fixed at a constant small value.

The germanium dimers close to the lead atoms 10 and 20 are statically tilted in alternate directions and probably the dynamical motion is frozen out at low temperatures. The germanium dimer atoms next to lead atom 10 have a \(z\)-position difference of 0.29 ± 0.06 Å. The germanium dimer atoms next to lead atom 20, which has a significantly lower \(z\)-position than at room temperature, have a larger \(z\)-position difference of 0.54 ± 0.05 Å. Both values are smaller than the corresponding values for the clean surface: 0.74 ± 0.15 Å [10] and 0.69 ± 0.04 Å [14] for the room-temperature
phase and $0.84 \pm 0.02 \text{ Å}$ [15] for the low-temperature phase. This indicates a stronger interaction of the adsorbate with the substrate at low temperature than at room temperature. In addition the dimers 21-27 and 30-32, which probably have a partially covalent interaction with the lead layer at room temperature are (within the uncertainty of the measurements) symmetric at low-temperature. A symmetrical configuration would be energetically unfavourable without germanium-lead interactions arising from the adsorbate layer. It is interesting that not only the distance from these germanium atoms in a symmetric configuration to their next neighbor lead atoms is close to the covalent bond distance, but also the approximately sp$^3$ hybridized germanium atoms 26 and 31 of the statically tilted dimers have a distance similar to the covalent bond length to the lead atoms 1 and 3. Therefore, we conclude that the lead layer in the low-temperature phase is more firmly bonded to the substrate with a more covalent character than it is the case at room temperature.

The covalent bond length for lead is $2.94 \text{ Å}$. The lead atom pairs (1,6), (3,9), (11,16) and (13,19) have a distance of $3.0 \pm 0.05 \text{ Å}$ between the atoms of each pair. This may indicate the presence of partially covalent bonds even within the overlayer. This assumption is supported by figure 6. In this figure the number of lead atoms with next neighbor distances (within the lead layer) below a certain threshold value versus the threshold value distance is shown. The only significant difference between the curves for the room and low-temperature phase (dashed and solid line respectively) is a plateau from $\sim 3.0 \text{ Å}$ to $\sim 3.2 \text{ Å}$ for the low-temperature phase curve. That means the small distances within the lead layer are a significant feature of the low-temperature phase. It is interesting to note that the lead atom pairs with small interatomic distances surround the lead atoms 10 and 20, which exhibit a pronounced height difference compared to their position at room temperature.

Assuming that there are partially covalent Ge-Pb and Pb-Pb bonds immediately raises the question of the hybridization of the lead atoms and the electron density distribution within the lead layer. As a first approximation one may assume that one germanium atom of each buckled dimer has approximately two electrons for a Pb-Ge bond and that the electron density within the lead layer is not strongly influenced by these bonds. Each germanium atom of the symmetric dimers has approximately one electron and the lead overlayer has to donate one electron for each covalent Pb-Ge bond. A completely covalent Pb-Pb bond would localize two electrons. Therefore, covalent bonds from symmetric germanium dimers to lead atoms and within the lead layer will lower the electron density in other parts of the overlayer which means that the number of partially covalent bonds in the energetically most favorable configuration is limited. The formation of stronger covalent bonds is inherently inhibited by the basic atomic structure of the system; the pathway for lowering the total energy of the system by the formation of covalent bonds is inherently frustrated. The only way out of this frustration would be the formation of a completely new structure with a lower total energy. However no such structure with a lead coverage of 1.5 ML has been observed and it is unlikely that the activation energy for this phase transition involving considerable
mass transport would be available at low temperatures.

Considering the classification of the phase transition the results of the structure determination presented here suggest that it is of order-disorder type. The low-temperature phase with static germanium dimers and stronger bonding is the ordered form of the room-temperature phase with dynamically flipping dimers and a “floating” lead overlayer. We propose that within the Pb/Ge(001) system there is a delicate balance of different pathways for lowering the total energy of the system and that the true nature of the system is probably more complex than our simplistic bonding arguments would suggest.

It is instructive to compare the phase transition described here with the transition from the hexagonal incommensurate phase of lead on Si(111) to the Si(111)-([3\times\overline{1}])-Pb low-temperature structure [16]. In both systems the adsorbate forms a Pb(111) overlayer. The overlayer is incommensurate (Pb/Si(111)) or weakly pinned to a commensurate position (Pb/Ge(001)). In both low-temperature phases interatomic distances indicate the presence of Pb-substrate bonds with predominantly covalent character. The major differences arise from the substrate; in the case of Si(111) the lowest energy structure, the (7\times7) reconstruction, is removed by lead deposition and annealing – the silicon substrate of the hexagonal incommensurate phase has essentially the undisturbed bulk-truncated structure which is not stable without the lead overlayer. In the case of Ge(001) the dimers in the (2\times1)-reconstruction of the clean surface are partially removed by lead deposition and reestablished themselves at larger lead coverages. Therefore, the lead overlayer of the Ge(001)-([\overline{2}\times\overline{1}])-Pb reconstruction stabilizes the reconstructed substrate and the lead overlayer of the hexagonal incommensurate phase on Si(111) stabilizes the bulk-truncated structure of the substrate. Both systems lower their total energy upon cooling by the formation of bonds with covalent character and the capability of forming such bonds plays a key role in determining the substrate structure.

4. Summary

At room temperature the topmost germanium layer of the Ge(001)-([\overline{2}\times\overline{1}])-Pb reconstruction is similar to the clean (2\times1) reconstructed surface which is described by dynamically flipping germanium dimers. The mainly metallic lead overlayer is probably pinned to a commensurate registry with the substrate by weak covalent interactions to one germanium dimer per unit-cell.

Upon cooling, the dimers with a weak covalent bond to the adsorbate at room temperature remain in a symmetrical position. The remaining dimers are statically tilted in alternate directions as in the Ge(001)-(2\times1) surface reconstruction at low-temperatures. Within the lead overlayer the main difference to the positions at room temperature is a height difference of the two lead atoms that are weakly bonded on high-symmetry sites at room temperature. Additional partially covalent interactions between the substrate and adsorbate and within the adsorbate layer stabilize the system.

The structural changes are consistent with the occurrence of an order-disorder phase
transition in this system. The phase transition is partially frustrated by the mutual exclusiveness of different pathways for lowering the total energy.

Total energy calculations for this complex system with such a large unit-cell are definitely a challenge but, with regard to the interesting properties and the expected insight in the delicate energy balance, probably worth the effort. We hope that the determination of the detailed atomic structure reported here will pave the way for theoretical investigations of the Ge(001)-(2\textsuperscript{1}1\textsuperscript{1}0)-Pb reconstruction at $T = 0$ K and at elevated temperatures.

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Table 1. Atomic positions in the Ge(001)-(\(\frac{1}{2}\frac{1}{2}\))--Pb room-temperature phase. The atomic positions determined in the SXRD data analysis are given in surface coordinates. The deviation from a bulk-like position and the atomic displacement parameter amplitudes are given in Å. The uncertainty is estimated to be ±0.04 Å (±0.02 Å in \(x, y\) and \(z\)) for the Pb atom positions and ±0.09 Å (±0.05 Å in \(x, y\) and \(z\)) for the Ge atom positions. Due to the high ADP in the z-direction the uncertainty for the \(z\)-position of the Pb atom number 10 is around ±0.5 Å.


Table 2. Atomic positions in the Ge(001)-(2\frac{1}{2} \times 1\frac{1}{2})-Pb low-temperature phase (lead atoms and substrate layers 1-3). The atomic positions determined in the SXRD data analysis are given in surface coordinates. The deviation from a bulk-like position and the atomic displacement parameter amplitudes are given in Å. The uncertainty is estimated to be ±0.06 Å (±0.03 Å in x, y and z) for the Pb atom positions and ±0.1 Å (up to ±0.06 Å in x, y and z) for the Ge atom positions.
Table 3. Atomic positions in the Ge(001)-(2\(1\)

| no. | type | pos. [surf. coord.] | dev. [Å] | ADP xy/z [Å] |
|-----|------|---------------------|----------|---------------|
| 57  | Ge   | (1.997,1.005,-1.001) | (0.02,-0.01,0.13) | 0.14 0.04 |
| 58  | Ge   | (2.005,1.005,-1.000) | (0.00,-0.04,0.11) | 0.12 0.04 |
| 59  | Ge   | (1.994,5.986,-1.004) | (-0.01,-0.02,0.11) | 0.12 0.04 |
| 60  | Ge   | (1.944,5.998,-0.741) | (-0.08,0.02,0.19) | 0.21 0.04 |
| 61  | Ge   | (1.999,6.017,-1.001) | (-0.03,0.07,0.18) | 0.19 0.04 |
| 62  | Ge   | (0.497,5.000,-0.778) | (-0.02,0.01,0.10) | 0.10 0.04 |
| 63  | Ge   | (1.021,5.002,-1.001) | (0.01,0.02,0.21) | 0.12 0.04 |
| 64  | Ge   | (1.500,5.000,-0.726) | (0.00,0.00,0.25) | 0.25 0.04 |
| 65  | Ge   | (1.979,4.998,-0.999) | (-0.01,-0.02,0.21) | 0.21 0.04 |
| 66  | Ge   | (0.503,4.000,-0.778) | (-0.02,-0.04,0.11) | 0.10 0.04 |
| 67  | Ge   | (1.987,2.008,-1.005) | (0.02,0.02,0.18) | 0.19 0.04 |
| 68  | Ge   | (0.944,1.002,-1.001) | (0.02,0.02,0.18) | 0.19 0.04 |
| 69  | Ge   | (1.008,0.985,-1.006) | (0.02,-0.06,0.15) | 0.16 0.04 |
| 70  | Ge   | (2.008,0.974,-1.006) | (0.02,0.06,0.15) | 0.16 0.04 |
| 71  | Ge   | (1.992,3.015,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |
| 72  | Ge   | (0.961,3.015,-1.006) | (0.02,0.00,0.13) | 0.14 0.04 |
| 73  | Ge   | (0.501,3.010,-0.778) | (0.00,0.04,0.11) | 0.12 0.04 |
| 74  | Ge   | (1.973,0.985,-1.006) | (-0.02,0.01,0.13) | 0.14 0.04 |
| 75  | Ge   | (1.982,0.974,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |
| 76  | Ge   | (1.973,0.974,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |
| 77  | Ge   | (0.501,0.974,-1.006) | (0.02,0.00,0.13) | 0.14 0.04 |
| 78  | Ge   | (1.982,0.974,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |
| 79  | Ge   | (1.982,0.974,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |
| 80  | Ge   | (1.982,0.974,-1.006) | (-0.02,0.06,0.15) | 0.16 0.04 |

Table 3. Atomic positions in the Ge(001)-(2\(1\)

- Pb low-temperature phase (substrate layers 4-7). See table 2 for further explanations.
Figure captions

![Graph showing SXRD data for the Ge(001)-(210)-Pb room-temperature phase.](image)

**Figure 1.** SXRD data for the Ge(001)-(210)-Pb room-temperature phase. (a) In-plane data measured at a small $l$-value of 0.13. Unaveraged data are shown to display the characteristic pattern of twelve reflections with high intensity which originates from the lead overlayer with (approximately) sixfold symmetry on the germanium substrate with twofold symmetry. The areas of the filled (empty) semi-circles are proportional to the measured (calculated) intensities. (b) Fractional-order and (c) integer-order rod scans. The solid line is calculated using the model shown in figure 3 with the parameters given in table 1.
Figure 2. SXRD data for the Ge(001)-\((\frac{3}{2}, 0)\)-Pb low-temperature phase. (a) In-plane data measured at a small \(l\)-value of 0.13. The areas of the filled (empty) semi-circles are proportional to the measured (calculated) intensities. (b) Integer-order and (c) fractional-order rod scans. The solid line is calculated using the model shown in figure 4 with the parameters given in table 2 and table 3.
Figure 3. Atomic structure of the Ge(001)-(2\frac{1}{2} 1\frac{1}{2})-Pb room-temperature phase. The (2\frac{1}{2} 1\frac{1}{2}) unit-cell is indicated by a dashed line. Lead atoms are drawn black or dark grey. The dark grey lead atoms are 2.7 Å above the substrate. Germanium atoms are the small circles. The numbers shown correspond to table 1. Lead atoms 2 and 10 are on high-symmetry sites. For simplicity all atoms have separate labels irrespective of the p2-symmetry restrictions.
Figure 4. Atomic structure of the Ge(001)-\(\begin{pmatrix} 2 \\ 1 \\ 0 \\ 6 \end{pmatrix}\)-Pb low-temperature phase. (a) Top-view. The \(\begin{pmatrix} 2 \\ 1 \\ 0 \\ 6 \end{pmatrix}\) unit-cell is indicated by a dashed line. Lead atoms are drawn black or dark grey. For the dark grey lead atoms the distance to the substrate is in the range from 2.6 Å to 2.8 Å and indicates a partially covalent bond. Pb-Pb distances of 3.0 Å are indicated by a dotted line. Germanium atoms are drawn as small circles. The dark grey germanium atoms have a lower z-position indicating sp\(^2\)-like hybridization. The numbers shown correspond to table 2 and table 3. Lead atoms 10 and 20 are on high-symmetry sites. (b) Side-view to show the height difference of the lead atoms 10 and 20 and the germanium dimer buckling.
Figure 5. Comparison of some fractional-order rod scans for the Ge(001)-(\(\frac{2}{3}, \frac{1}{3}\))-Pb room-temperature phase (data points: asterisks, calculated intensity: solid line) and the Ge(001)-(\(\frac{2}{3}, \frac{1}{3}\))-Pb low-temperature phase (data points: squares, calculated intensity: dashed line). Despite the overall similarities there are some significant differences, e.g., for high \(l\)-values along the (2,3/2,\(l\))-rod and for all measured \(l\)-values along the (8/3,5/3,\(l\))-rod.
Figure 6. Number of lead atoms with a next neighbor distance within the lead layer below a certain threshold value versus the threshold value distance for the Ge(001)-(210)-Pb room-temperature (dashed line) and the Ge(001)-(216)-Pb low-temperature phase (solid line). There is a pronounced difference in the region from 3.0 Å to 3.2 Å indicating stronger interaction between the lead atoms in the low-temperature phase than in the room-temperature phase. The interaction may have partially covalent character.