

Low- and high-temperature phases of a Pb monolayer on Ge(111) from *ab initio* molecular dynamics

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We present an *ab initio* molecular dynamics study of the structure and dynamics of a close-packed monolayer of Pb on the Ge(111) surface, with coverage $\Theta = 4/3$, at different temperatures. The room-temperature ($\sqrt{3} \times \sqrt{3}$) structure is characterized by large in-plane fluctuations of the Pb adatoms, and agrees well with recent x-ray standing wave data. At $T \sim 800$ K we observe a (1×1) disordered structure showing in-plane diffusion of the Pb atoms. Disorder is confined to the plane of the overlayer. A strong correlation with the solid Ge substrate is present, leading to preferential residence sites and diffusion paths of the Pb atoms on the surface. The calculated local density of states for the high temperature phase is found to agree with recent scanning tunnel microscope observations, which show a simply Pb-terminated (1×1) surface with an apparent coverage $\Theta = 1$.

I. INTRODUCTION

The study of structures and phase transitions of thin adlayers weakly interacting with the substrate (physisorption regime) has been the subject of extensive experimental and theoretical research for many years. More recently increasing attention has instead focused on the properties of overlayers with stronger interactions with the substrate (chemisorption regime). The systems formed by ultrathin Pb overlayers on the Ge(111) surface can be considered as prototype examples for this study. Since Pb atoms at low coverages neither desorb nor diffuse into the substrate over a wide range of temperatures, Pb/Ge(111) is a model of a nearly two-dimensional (2D) system. In addition, like most semiconductor surfaces and interfaces, the Pb/Ge(111) system is also expected to show an interesting interplay of atomic and electronic structures. For these reasons it has been recently the subject of numerous experimental investigations. However, despite considerable effort, several aspects of the Pb/Ge(111) phase diagram at monolayer and submonolayer Pb coverages (Θ) are still rather unclear.

One question which has been debated for many years concerns the coverage and structure of the low-temperature, dense ($\sqrt{3} \times \sqrt{3}$)R30 phase known as the β phase. On the basis of reflection high-energy electron-diffraction (RHEED), X-ray, and low-energy electron-diffraction (LEED) measurements¹⁻⁴ a model [hereafter referred to as the x-ray electron-diffraction (XED) model] has been proposed, which consists essentially of a (111) fcc overlayer of Pb, rotated by 30° with respect to the

Ge lattice, and with some distortions to accommodate the misfit with the substrate. The Pb coverage for such a structure is $\Theta = 4/3$ (we define $\Theta = 1$ as corresponding to one Pb atom per one surface Ge atom). Real-space scanning tunneling microscopy (STM) images⁵ have been found to be consistent with a $\Theta = 4/3$ model having one Pb atom (per unit cell) on the hollow (H_3) site and three Pb atoms at off-centered (OC) T_4 sites. This model is similar to the XED model, except that in the latter the three Pb atoms occupy OC T_1 sites (i.e., directly above surface Ge atoms). By contrast, a completely different structural model has been proposed by Hwang and Golovchenko,⁶ again based on STM images. The saturation coverage of this model (hereafter referred to as the trimer model) is $\Theta = 1$. It consists of three Pb atoms (per unit surface cell) slightly displaced from the T_1 sites to form trimers which are centered at the H_3 sites of the Ge substrate. However, new x-ray standing wave (XSW) measurements⁷ are again consistent with a $\Theta = 4/3$ structure, ruling out the trimer as well as other $\Theta = 1$ models of the β phase. This conclusion agrees with the results of a recent first principles molecular dynamics study,⁸ where a "chain" model of the β phase, with $\Theta = 4/3$, has been proposed. This model is characterized by the presence, at $T = 0$, of (weakly) covalently bonded Pb chains running along a $[1\bar{1}0]$ direction of the substrate, which however are disrupted, at room temperature, by large in-plane fluctuations of the Pb atoms. The properties of this structure are found to agree well with several experimental results, largely reconciling the conflicting interpretations which had been proposed for

the different data.

As the temperature is raised, an apparently continuous, reversible structural transition from the $(\sqrt{3} \times \sqrt{3})$ β phase to a (1×1) phase is observed to take place. The transition temperature T_c is found to depend strongly on coverage. Just below monolayer completion T_c remains close to $\sim 170^\circ\text{C}$, whereas very close to monolayer coverage there is a sharp increase in the transition temperature to $\sim 300^\circ\text{C}$.^{1,6} The transition point falls down to 190°C as the monolayer becomes defective.^{1,9} The character of this transition as well as the properties of the high- T (HT) (1×1) phase are also controversial. Ichikawa,¹ based on RHEED data, attributed the (1×1) phase to a 2D isotropic liquid, essentially unperturbed by the underlying Ge substrate. An x-ray diffraction study by Grey *et al.*¹⁰ showed a ring of diffuse scattering in the (1×1) phase at $q \sim 2.05 \text{ \AA}^{-1}$, as expected for a 2D liquid scattering. However, the ring was found to be azimuthally anisotropic, which was attributed to interaction of the Pb layer with the Ge substrate. Instead, from the fact that the LEED pattern remained sharp above the transition temperature, Metois and Le Lay⁹ argued that the HT phase is actually an ordered Pb layer with coverage $\Theta = 1$. XSW measurements³ above T_c found a nonzero value of the amplitude of the (220) Bragg reflection of the adsorbate, suggesting the existence of local order. This was attributed to the presence, above T_c , of small domains of the low- T β phase. The $(\sqrt{3} \times \sqrt{3}) \rightarrow (1 \times 1)$ transition was thus interpreted as an order-disorder transition. An interpretation in terms of an order-disorder transition has been recently proposed also by Franklin *et al.*⁷ on the basis of XSW measurements. Surprisingly, these results seem to indicate that at higher temperatures there is a higher degree of correlation with the Ge substrate than at room temperature, i.e., as T increases the Pb-Pb correlations decrease, so that the Ge substrate potential plays a more important role in determining the structure of the HT β phase. The results of Ref. 7 also suggest that no structural change occurs normal to the surface, i.e., the phase transition is truly two dimensional. Finally, the high-temperature STM images of Ref. 6 seem to indicate that the HT (1×1) phase is basically a simple Pb-terminated Ge(111)- (1×1) surface. The $(\sqrt{3} \times \sqrt{3}) \rightarrow (1 \times 1)$ transition is interpreted as an order-order phase transition, where thermal fluctuations of the Pb atoms disrupt the trimers observed in the low-temperature β phase, while the Pb-Ge bonding remains basically the same as in the low- T β phase.

In this paper we present a study of the low- ($T < T_c$) and high- ($T > T_c$) temperature properties of a Pb monolayer on Ge(111) based on first principles molecular dynamics¹¹ (MD) calculations. Starting from the $T = 0$ "chain" structure with coverage $\Theta = 4/3$, we have studied its temperature behavior via MD simulations at two different average temperatures, $T \sim 550 \text{ K}$ and $T \sim 800 \text{ K}$. These are here representative of $T < T_c$ and $T > T_c$, as the properties of our system at these two temperatures are found to correspond to those of the room-temperature $(\sqrt{3} \times \sqrt{3})\beta$ and HT (1×1) phases, respectively. Since this study amounts already to a quite heavy computational effort, a more detailed investigation

as a function of T and/or Θ has not been pursued. At $T \sim 550 \text{ K}$ the dynamics of the Pb overlayer is that of a thermally disordered solid phase, whose structure agrees well with the XSW results of Ref. 7. At higher T in-plane diffusive motion of the Pb atoms is observed. The role of the solid Ge substrate results in imposing preferential residence sites and diffusion paths on the mobile Pb atoms. The structural and dynamical properties both below and above T_c are studied and compared with experiments. Calculated STM images of the HT phase show a remarkable resemblance with the real-space STM images of Ref. 6, where a simply Pb-terminated Ge(111) surface appears, with an apparent coverage $\Theta = 1$.

II. COMPUTATIONAL DETAILS

Our calculations have been performed using the *ab initio* MD approach,¹¹ which allows one to take fully into account the role of electronic states in the atomic dynamics. Details of the method and a number of applications have been reviewed recently.¹² The Ge(111) surface is modeled as a periodically repeated slab consisting of six layers of 12 Ge atoms each, corresponding to four $(\sqrt{3} \times \sqrt{3})R30$ cells. $N = 16$ Pb adatoms are present on the top surface, while the other surface is saturated by 12 hydrogen atoms. The four topmost layers of Ge plus the Pb overlayer were allowed to move and/or relax, while all other layers were kept fixed. Consecutive slabs are separated by an empty space 10 \AA wide. Norm-conserving pseudopotentials with s and p nonlocality in a separable form are used. The wave functions are expanded in plane waves with kinetic energy up to 8 Ry. Only the Γ point of our supercell was used, corresponding to four points in the Brillouin zone (BZ) of the primitive $\sqrt{3}$ cell. For a few selected atomic geometries, total energies have been checked with calculations including 13 k points in the BZ. In MD simulations, the temperature was controlled by means of a Nosé-Hoover ionic thermostat.¹³ Another Nosé-Hoover thermostat was used to control the classical kinetic energy of the electronic degrees of freedom, following the prescription of Ref. 14.

III. THE ROOM-TEMPERATURE STRUCTURE

We have discussed the low-temperature properties of the β phase previously.⁸ The results presented in that work provide evidence that the coverage of this phase is $\Theta = 4/3$. The $T = 0$ structure was determined via a simulated annealing procedure, where the XED model proposed on the basis of LEED and x-ray measurements⁴ was first fully relaxed, then heated and equilibrated¹⁵ at $\sim 500 \text{ K}$, and finally quenched again to zero temperature. A very long minimization procedure was required for the determination of the registry of the overlayer with respect to the Ge substrate, as this was found to correspond to a very flat region of the potential energy surface. The minimization was stopped when residual forces were less than $\sim 0.02 \text{ eV/\AA}$. The resulting structure has three Pb

atoms per $\sqrt{3}$ cell in OC T_1 sites whereas the fourth Pb atom is in an OC T_4 position. All the Pb atoms are approximately at the same height, $z \sim 2.7$ Å, above the Ge surface. Weak covalent Pb-Pb bonds give rise to “chains” along a $[1\bar{1}0]$ direction of the substrate (see the total valence charge density in Fig. 1), breaking the threefold symmetry of the ideal Ge(111) surface (only a mirror plane symmetry remains).

To study the structural modifications and the dynamics of the Pb/Ge(111) system at finite temperature, we started from the chain structure and performed a long ($\sim 73\,000$ time steps corresponding to ~ 23 ps) MD run where the temperature of the Pb/Ge system was varied between ~ 500 and ~ 800 K. We will use in the following “low T ” and “high T ” to distinguish between two different portions of the MD run. The low-temperature part, consisting of ~ 8.8 ps, was performed at temperature $T_L = 550 \pm 50$ K, while for the high-temperature part (~ 14.2 ps) a temperature $T_H = 800 \pm 100$ K was used.¹⁶ These two temperatures will be for us representative of $T < T_c$, in particular, room temperature (RT), and $T > T_c$, respectively. We used these temperatures, which are higher than the corresponding experimental temperatures, in order to have faster atomic motions during the limited time of our simulations. This can be *a posteriori* justified by the fact that the properties of our system at $T_L \sim 550$ K and $T_H \sim 800$ K turn out to agree well with the experimental RT and HT properties of the β phase.

In the “low- T ” run, the Pb atoms fluctuate around an average ($\sqrt{3} \times \sqrt{3}$) structure which is almost coincident with that resulting from the average of the three $T = 0$ equivalent chain structures with different $[1\bar{1}0]$ orientations. These are in turn obtained by rotating the Pb atoms at the OC T_4 sites by $\pm 120^\circ$ around their closest T_4 site (see Fig. 1). However, thermal fluctuations disrupt long-range Pb chains, thus restoring the threefold symmetry of Ge(111).¹⁷ In the low- T run we find very large in-plane rms displacements of the Pb atoms

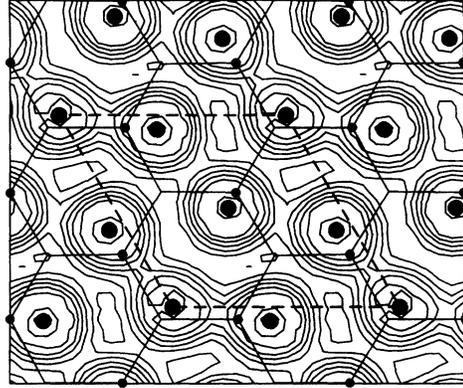


FIG. 1. Contour plots of the total valence charge density for the chain structure, in a plane ~ 1.3 Å above the Pb overlayer. The underlying Ge lattice is outlined: dots represent surface Ge atoms. Bigger dots indicate Pb atoms. The $\sqrt{3}$ unit cell is also shown with dashed lines.

($\langle u_{\text{par}}^2 \rangle^{1/2} = 0.54$ Å), the displacements being particularly large for the Pb adatoms at the OC T_4 sites, which have a weaker bond with the substrate (for these $\langle u_{\text{par}}^2 \rangle^{1/2}$ is 0.63 Å, whereas for the Pb atoms close to T_1 sites it is 0.51 Å). The motion of the OC T_4 adatoms can be approximately described as a rotation around the corresponding T_4 site. It is precisely this motion that restores in the average low- T structure the C_{3v} symmetry of the Ge substrate. By contrast, the calculated rms displacement perpendicular to the surface is rather small, $\langle u_{\text{perp}}^2 \rangle^{1/2} = 0.18$ Å. For comparison, a value $\langle u_{\text{perp}}^2 \rangle^{1/2} = 0.24$ Å has been inferred from a fit of the experimental XSW data at RT.⁷ From the total amplitude $\langle u^2 \rangle = \langle u_{\text{par}}^2 \rangle + \langle u_{\text{perp}}^2 \rangle$ and using the 3D relation between the mean-square displacement and temperature $\langle u^2 \rangle \sim 3T/Mk_B T_D^2$, we obtain a Debye temperature of the Pb monolayer $T_D \sim 34$ K ($T_D \sim 36$ K using

TABLE I. Coherent fraction (F) and coherent position (P) for the chain structure (both at $T = 0$ and RT), and along the “low-” and “high-” T MD runs (see text), compared with experimental XSW data of Franklin *et al.* (Ref. 7). Results for the chain structure at RT are obtained by including a Debye-Waller factor (the same for all Pb atoms), with atomic mean-square displacements derived from the “low- T ” MD simulations and rescaled to RT. Calculated $F_{1\bar{1}\bar{1}}$ and $P_{1\bar{1}\bar{1}}$ for the chain model, MD “low” and MD “high” are obtained by averaging over $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, and $(\bar{1}\bar{1}1)$. Error bars are the corresponding rms deviations.

| Source | $F_{1\bar{1}\bar{1}}$ | $P_{1\bar{1}\bar{1}}$ | $F_{1\bar{1}\bar{1}}$ | $P_{1\bar{1}\bar{1}}$ |
|-----------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Chain, $T = 0$ | 0.99 | 0.96 | 0.30 ± 0.12 | 1.22 ± 0.02 |
| Chain, RT | 0.96 | 0.96 | 0.25 ± 0.10 | 1.22 ± 0.02 |
| MD, “low” | 0.93 | 0.98 | 0.24 ± 0.06 | 1.02 ± 0.01 |
| MD, “high” | 0.86 | 1.00 | 0.26 ± 0.06 | 0.93 ± 0.02 |
| Expt., RT | 0.90 ± 0.03 | 0.91 ± 0.01 | 0.24 ± 0.04 | 1.01 ± 0.09 |
| Expt., $T \sim 200^\circ\text{C}$ | 0.88 ± 0.02 | 0.92 ± 0.01 | 0.33 ± 0.04 | 1.06 ± 0.09 |

the in-plane displacement $\langle u_{\text{par}}^2 \rangle$). Tonner *et al.*¹⁸ found $T_D \sim 41$ K, while the x-ray results of Ref. 7 give $T_D \sim 32$ K. Note that the bulk-Pb Debye temperature is $T_D = 81$ K.

In Table I we present the structure factors $S(\mathbf{G}) \equiv F_{\mathbf{G}} e^{-2\pi i P_{\mathbf{G}}}$, with $\mathbf{G} \equiv (1, 1, 1)$ and $(1, 1, \bar{1})$, for the chain structure (both at $T=0$ and RT, simulated through the introduction of a common Debye-Waller factor for all the Pb atoms¹⁹) and along the low- T MD run. For comparison, the XSW results of Ref. 7 are also given. The agreement of the MD data with experiment is very good, especially for the $(11\bar{1})$ factors, which probe the in-plane structure of the overlayer.²⁰ The proper inclusion of thermal fluctuations appears to be very important in the comparison between theory and experiment.

IV. THE HIGH TEMPERATURE PHASE

As the temperature of our MD run is raised to ~ 800 K, the motion of the Pb overlayer becomes diffusive, while the Ge atoms remain close to their low-temperature equilibrium sites, the simulation temperature being always much lower than the Ge melting temperature. This behavior is shown Fig. 2, where the mean-square displacements $\langle |r(t) - r_0|^2 \rangle$ of Pb and Ge atoms are plotted as a function of the simulation time. By contrast, the Pb rms displacement perpendicular to the surface remains small, $\langle u_{\text{perp}}^2 \rangle^{1/2} = 0.30$ Å, showing that the disordering effects are essentially confined to the plane of the overlayer, i.e., the disordering transition is truly 2D. From $\langle |r(t) - r_0|^2 \rangle$ we estimate a 2D Pb surface diffusion co-

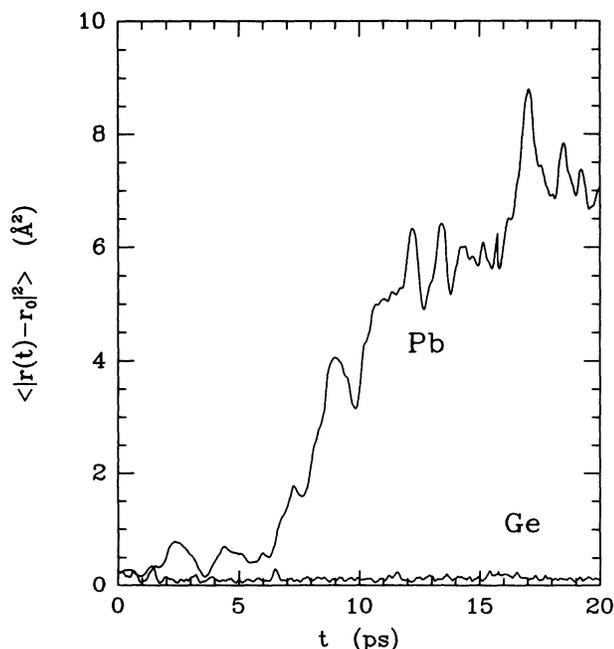


FIG. 2. Mean-square displacement as a function of time along our MD simulation for the Pb atoms in the overlayer and the Ge substrate. The first ~ 6 ps correspond to our low- T run (see text).

efficient $D = (1.2 \pm 0.3) \times 10^{-5}$ cm²/s, which is about half the value of the bulk diffusion coefficient of liquid Pb at the melting temperature ($T_M \sim 600$ K). Analysis of the singly resolved Pb displacements $|r_i(t) - r_i^0|$ indicates the occurrence of correlated motions where several Pb atoms displace almost simultaneously to neighboring sites. This correlation is most likely an effect of the high atomic density in the overlayer. For a pair of Pb atoms the motion is so highly correlated as to suggest the formation of a dimer. This dimer remains surprisingly stable as it moves over the surface, the average distance of the two Pb atoms involved being 3.20 ± 0.25 Å at $T = 800$ K (the calculated $T = 0$ bond length of an isolated Pb dimer is 2.86 Å). In our run we have also observed the formation of a vacancy in the Pb overlayer, with the concomitant appearance of an adatom just above the defective monolayer. Events of this kind are frequently observed in MD simulations of metal surfaces near the bulk melting temperature,²¹ where they are identified as the main mechanism of surface disordering. Here the creation of the adatom-vacancy pair does not appear to play a crucial role, as this event takes place when the disordering of the overlayer is already well established.

In Fig. 3 we show the in-plane atomic trajectories of the Pb atoms at four instants of our run. The symbols indicate the three symmetry sites (T_1 , T_4 , and H_3) of the ideal Ge surface. It appears that the in-plane diffusion of the Pb takes place preferentially along $[11\bar{2}]$ directions, i.e., perpendicularly to the $T = 0$ Pb chains, and that, while diffusing, the Pb atoms still spend an important fraction of time close to symmetry sites. The overall qualitative character of the diffusion, however, is neither clearly jumplike, as in the presence of significant activation barriers, nor continuous, as expected for a 2D liquid (where barriers should be of the order of kT). In the following we shall often use the word “jump” to describe the motion of the Pb atoms, even in cases where this may not be perfectly appropriate. By defining conventional occupations of T_1 , T_4 , and H_3 ,²² in our high- T MD run we find that, out of the 16 Pb atoms in our supercell, on the average 9.3 occupy T_1 sites, 2.2 occupy T_4 sites, and 4.5 occupy H_3 sites. The average time spent close to a T_1 site is 58%, close to a T_4 site is 14%, and close to a H_3 site is 28%. Thus T_1 is by far the preferred residence site also at high T , while the high occupation of H_3 can be in part understood by taking into account the low energetic cost of registry shifts of the overlayer. From the analysis of the Pb trajectories when diffusion starts, it appears that (i) atoms initially in OC T_4 sites tend to jump to (or close to) T_1 sites, either directly or passing through an H_3 hollow site; and (ii) atoms initially in OC T_1 sites either jump to a nearest T_1 site (possibly passing through H_3) or spend some time in H_3 or (but less frequently) in T_4 sites.²³ From Fig. 3, it also appears that a few Pb atoms never jump away from their initial equilibrium sites, but always fluctuate (even if with large rms displacements) around these. This indicates that the relaxation times in the system are very long and the time duration of our simulation is not enough to allow for a complete equilibration (see also Ref. 17). On the other hand, we also observe that some Pb atoms are able to make a few jumps

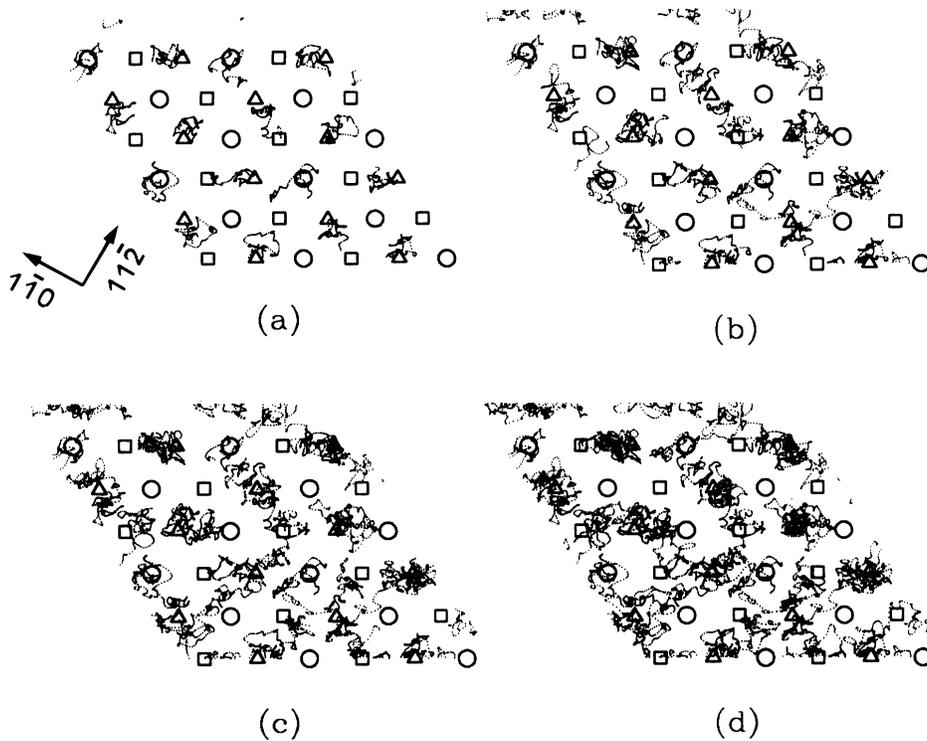


FIG. 3. Trajectory plots showing motions of Pb adatoms projected in the (x, y) plane, superposed with ideal sublattice sites. Triangles, circles, and squares indicate the T_1 , T_4 , and H_3 sites of the Ge surface, respectively.

during the length of our run, e.g. after a first jump they spend some time (a few to several picoseconds) near a symmetry site, and then move to another site. These observations suggest that the picture offered by Fig. 3, where both diffusing and nondiffusing Pb adatoms are present, should represent a typical configuration of the system, confirming that diffusion in the overlayer is not a purely 2D liquidlike diffusion but has important lattice-gas-like (i.e., jumplike) features. We expect that nonliquidlike features should be comparatively more important at the typical experimental temperatures, $\sim 200^\circ\text{C}$, i.e., 300°C lower than in our simulation. As a rough estimate, residence times at $T \sim 200^\circ\text{C}$ should be enhanced with respect to those observed in our run by a factor ranging from ~ 10 , for diffusion barriers $E_b \sim 0.2$ eV, to ~ 100 , for $E_b \sim 0.5$ eV (this holds if the diffusion mechanisms do not change with temperature, as it seems reasonable to assume). The former value of E_b represents a typical value for the diffusion barriers in our system, that we infer from the residence times in our simulation,²⁶ while $E_b \sim 0.5$ eV should be an upper bound.²³ These estimates indicate that residence times at $T \sim 200^\circ\text{C}$ should be of the order of nanoseconds, so that these motions are much too fast to be resolved by STM.

The disordering of the Pb overlayer is reflected in the change with temperature of the structure factors. Since the small size of our surface supercell allows us to sample only a rather coarse mesh of wave vectors \mathbf{G} in reciprocal space, we are not able to make a detailed comparison with the structure factor obtained in the x-ray diffraction experiment of Ref. 10. We can instead make contact with the XSW data of Franklin *et al.*,⁷ as shown in Table I, where the coherent fraction F_G (modulus)

and position P_G (phase) of the experimental XSW structure factors for $\mathbf{G} \equiv (1, 1, 1)$ and $(1, 1, \bar{1})$ are compared with our calculated values. We remark that the experimental data show little variation from below to above the $(\sqrt{3} \times \sqrt{3}) \rightarrow (1 \times 1)$ transition. This has been interpreted as an indication that the transition is of the order-disorder type. Moreover, the slight increase of $F_{11\bar{1}}$ with temperature has led to the suggestion that at higher temperature there is a higher degree of correlation with the Ge substrate than at room temperature. The overall behavior of the experimental data is well reproduced by our results. This indicates that the small variation of the XSW factors from below to above T_c does not exclude the presence of diffusive motion in the HT (1×1) phase. In particular, we find a good agreement with the experiment for the temperature dependence and the absolute values of F_{111} , P_{111} , and $F_{11\bar{1}}$. For $P_{11\bar{1}}$ we find a slight decrease with increasing T , in contrast with the experiment, where a slight increase is observed (note, however, that this increase is smaller than the error bars in the experimental $P_{11\bar{1}}$ value). There are a few possibilities which may account for this difference, most noticeably the difference in temperature between our run and the experiment, and/or the fact that, as mentioned previously, our system may not be sufficiently equilibrated.

To make contact with RHEED (Ref. 1) and LEED (Ref. 9) data, in Fig. 4 we show the low- and high- T peak intensities $I(\mathbf{q})$, where \mathbf{q} is the surface wave vector along the (11) reciprocal space direction. As a simple approximation, we use for $I(\mathbf{q})$ the expression $I(\mathbf{q}) = |\sum_i f_i(\mathbf{q}) \exp(i\mathbf{q} \cdot \vec{R}_i) e^{-\lambda(z-z_i)}|^2$, where f_i are the atomic form factors of individual (Pb and Ge) atoms, and \vec{R}_i are the positions of the atoms inside the unit

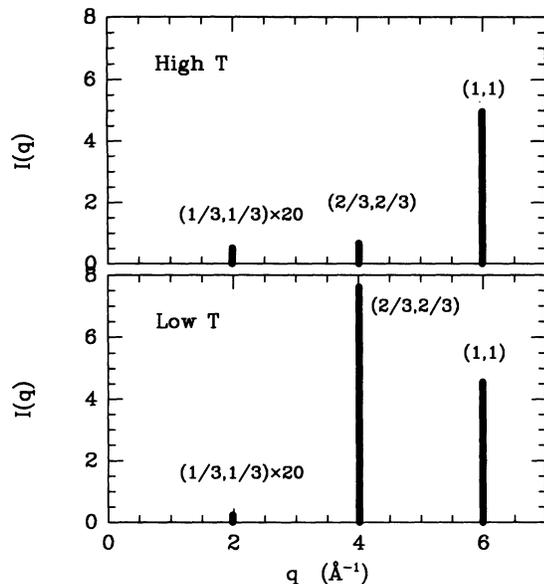


FIG. 4. Calculated LEED structure factors. For clarity, the intensity of the $(1/3, 1/3)$ diffraction peak has been multiplied by 20.

cell. The exponential weight simulates the probing depth of the scattering electrons, where $\lambda = 4.5 \text{ \AA}$ is typical for low-energy electron penetration. At low- T we find a strong $(2/3, 2/3)$ peak (which is one of the most characteristic features of the β phase), a weaker $(1, 1)$ peak (originating from the substrate), plus an extremely weak $(1/3, 1/3)$ peak, consistent with experiments where it appears to be two orders of magnitude smaller in intensity than the $(2/3, 2/3)$ peak. At high temperature, the $(1, 1)$ peak dominates the structure factor, in qualitative agreement with experiments. The $(2/3, 2/3)$ peak, although strongly reduced in intensity, is still visible, suggesting some persistence of 2D ordering in the Pb overlayer.

To obtain some insight into the character of this ordering, in Fig. 5 we show the Pb-Pb radial distribution func-

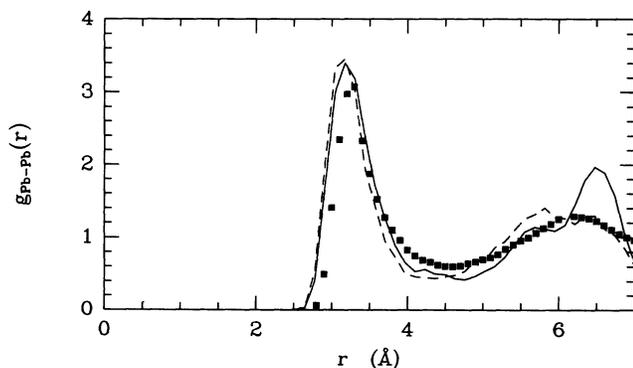


FIG. 5. Pair correlation function $g_{\text{Pb-Pb}}(r)$, for the Pb atoms in the overlayer at low (full line) and high (dashed line) temperature. For $r > 6 \text{ \AA}$, $g_{\text{Pb-Pb}}(r)$ is extrapolated from our data following the procedure in Ref. 28. Filled squares show the experimental pair correlation function for liquid Pb at $T = 340 \text{ }^\circ\text{C}$, taken from Ref. 27.

tions $g_{\text{Pb-Pb}}(r)$ at low (solid line) and high (dashed line) temperatures, together with the experimental pair correlation function for bulk liquid Pb (l -Pb) at $T = 340 \text{ }^\circ\text{C}$.²⁷ The calculated HT correlation function has features intermediate between the lower- T and the l -Pb results. The two calculated curves are quite similar up to $\sim 6 \text{ \AA}$, which include the first two neighbor shells, but show significant differences at larger distances. The agreement between our high- T $g_{\text{Pb-Pb}}(r)$ and the experiment for l -Pb is rather good in the whole range considered, but in our result the peaks are somewhat sharper, indicating a higher degree of ordering.

The similarity between the low- and high- T local structure is confirmed by the behavior of the Pb vibrational spectral density (Fig. 6), that we obtain from the temporal Fourier transform of the time-averaged velocity-velocity correlation function.²⁹ At both low and high T the spectrum is dominated by a sharp peak at $\sim 5 \text{ meV}$, arising from z -polarized Pb-Ge stretching modes. On the low- and high-frequency sides of this peak there are x, y -polarized in-plane modes. At low T , the low-frequency shoulder of the 5 meV peak can be associated with the motions which disrupt the $T = 0$ Pb chains. This feature is strongly suppressed at high T , but at the same time the spectrum acquires a finite zero-frequency value related to the Pb in-plane diffusion. The features associated with the high-frequency x, y modes become broader but do not show any substantial change at high T . Overall, the HT spectrum is quite different from that of a typical liquid, suggesting instead a resemblance (except for the finite zero-frequency value) to the vibrational density of states of a hot solid.

Turning finally to the electronic properties, we recall⁸ that, while the $T = 0$ chain structure is found to exhibit a small ($\sim 0.1 \text{ eV}$) gap, no gap is present at RT, where the system is metallic. Such metallic character is main-

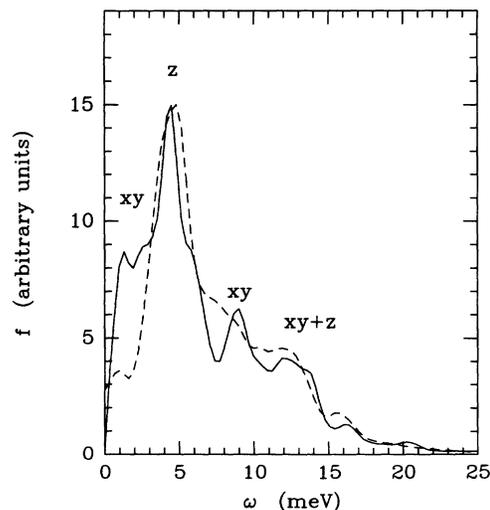
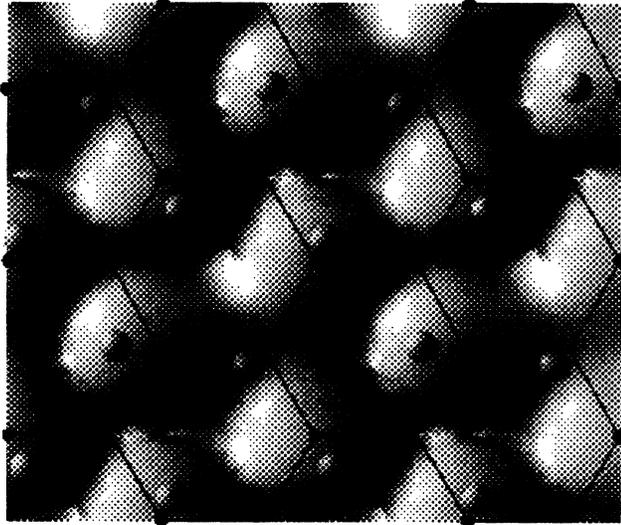
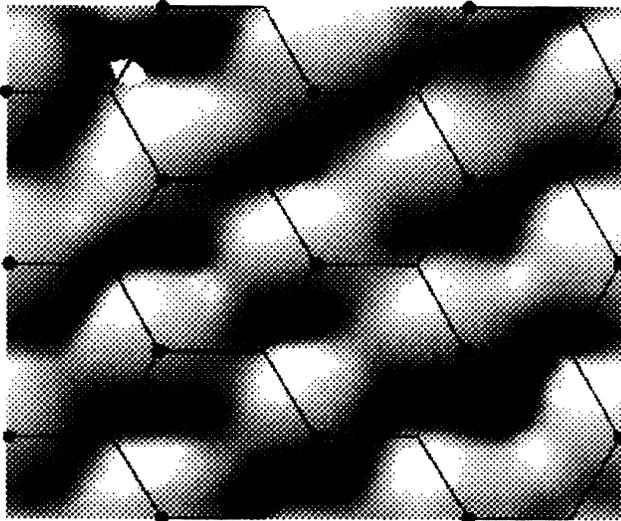


FIG. 6. Vibrational density of states for the Pb overlayer obtained from the Fourier transform of the velocity-velocity correlation function. The full and dashed curves refer to low and high T , respectively. Labels indicate the main polarization character of the modes contributing to the spectrum.

tained at HT. The peak of Pb-induced states at $\sim 0.7 - 1$ eV below E_F , which is also discussed in Ref. 8, although broader, is well defined also at high temperature. Using the simplest approximation, we obtain “theoretical” STM images from the local density of states³⁰ (LDOS) $\rho(\vec{r}, E_F - eV) \equiv \sum_i |\Psi_i(\vec{r})|^2 \delta(E - (E_F - eV))$, where the $\Psi_i(\vec{r})$ are the single-electron Kohn-Sham orbitals. The calculated low-temperature STM image resulting from filled states at ~ 0.7 eV below the top of the valence band is shown in Fig. 7(a). An array of trimerlike pro-



(a)



(b)

FIG. 7. Theoretical STM images of the high-coverage phase of Pb/Ge(111) from topographic maps of constant local density of states (see text). The images are taken at ~ 2.5 Å above the Pb layer. The underlying Ge lattice is always shown, while for better clarity Pb atoms (indicated by the big dots) are shown only in the upper panels.

trusions is present, in agreement with the results of Refs. 6, 31, and 32. As discussed in Ref. 8, the reason why only three out of four Pb atoms per $\sqrt{3}$ cell show up in the charge density map is that these states have $p_{x,y}$ character, and thus a node at the OC T_4 Pb adatom site. At high T , we have calculated the STM images by averaging over the LDOS’s of 10 independent configurations generated during the MD run and using again states at about 0.7 eV below the top of the valence band. Our results [Fig. 7(b)] suggest a rather ordered, Pb-terminated (1×1) surface structure in qualitative agreement with the STM images of Ref. 6 several degrees above the transition temperature. In spite of the diffusive behavior of the Pb overlayer, STM images show an apparent $\Theta = 1$ structure, quite similar to a thermally disordered (1×1) Ge surface. Evidently, only the orbitals with p_z (or $s + p_z$) character, that describe the bonding (or antibonding) states between the Pb adatoms and the Ge surface, are able to show up in these images, the contribution of other orbitals either being insignificant or being anyway averaged out during the thermal motion of the Pb atoms.

V. CONCLUSIONS

In this paper we have presented first principles MD simulations of the room- and high-temperature phases of a Pb monolayer on the Ge(111) surface. This approach allows us to take fully into account the connection between electronic structure and atomic dynamics, but restricts us in a number of ways. The main limitations of our calculations are the small size of the system, the short duration of our runs, and finally the fact that only two temperatures could be studied. In spite of this, the agreement of our results with the available experimental information is remarkable.

One of the main characteristics of the calculated RT ($\sqrt{3} \times \sqrt{3}$) phase is the occurrence of very large in-plane fluctuations of the Pb atoms around their equilibrium sites. Taking properly into account these fluctuations turns out to be very important for a comparison with experimental data, as shown by the results in Table I.

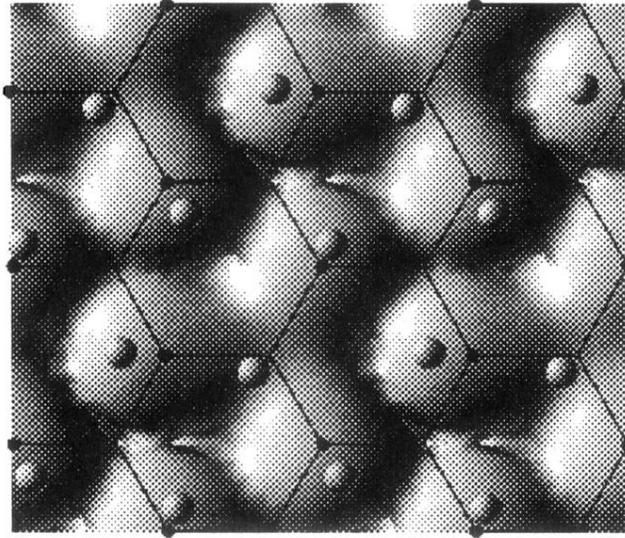
The picture of the high-temperature (1×1) phase which emerges from our calculations is characterized by two main features. On the one hand, the Pb monolayer shows a diffusive in-plane motion with a diffusion coefficient of the order of that of l -Pb, which is suggestive of a 2D liquidlike layer, similar to the model proposed by Grey *et al.*¹⁰ On the other hand, a strong correlation with the Ge solid substrate is maintained, resulting in preferential residence sites for the Pb atoms and the persistence of local order in the overlayer up to medium-range distances. This is consistent with the models^{3,6,7} for which correlations with the substrate play a dominant role in determining the structure of the HT phase of Pb/Ge(111). The character of the diffusion process that we can infer from the analysis of the atomic trajectories is intermediate between a jumplike mechanism characteristic of a lattice-gas model and a continuous diffusion typical of a 2D liquid. Considering that the temperature

used in our simulation is rather elevated in comparison to experiment, we expect that at the usual experimental temperatures lattice-gas features should be more pronounced. However, since typical diffusion barriers in this system are rather small, we believe that diffusion is an important characteristic of the (1×1) phase observed experimentally, as well as an essential mechanism of the $(\sqrt{3} \times \sqrt{3}) \rightarrow (1 \times 1)$ disordering transition.

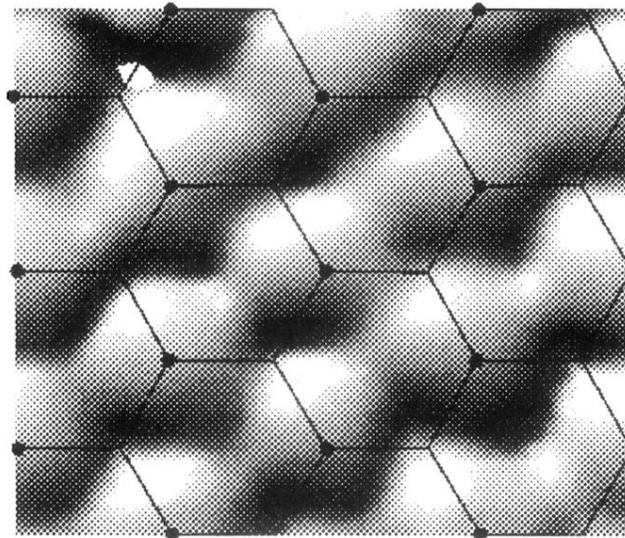
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- ¹⁵ This equilibration corresponds to the initial part of the "low- T " run described below.
- ¹⁶ In the low- T part of the run, the first ~ 2.5 ps are considered as "equilibration" (Ref. 15), and are thus not included in the computation of "low- T " statistical averages. For the "high- T " part of the run, we verified that the pair correlation function calculated along different sections of the run did not change appreciably.
- ¹⁷ Due to the limited duration of our run, the symmetry recovery is actually not perfect. Thus, for instance, differences in the structure factors $S(\mathbf{G})$ for $(11\bar{1})$, $(\bar{1}\bar{1}1)$, and $(\bar{1}11)$ are still present also in the low- (and even in the high-) T runs, although much smaller than at $T = 0$ (see Table I).
- ¹⁸ B.P. Tonner, H. Li, M.J. Robrecht, M. Onellion, and J.L. Erskine, *Phys. Rev. B* **36**, 989 (1987).
- ¹⁹ Using different Debye-Waller factors for the atoms at OC T_1 and OC T_4 , the agreement of $P_{11\bar{1}}$ with experiments is somewhat improved (we find $P_{11\bar{1}} = 1.12 \pm 0.01$), while the other factors are substantially unchanged.
- ²⁰ See, e.g., E. Vlieg, E. Fontes, and J.R. Patel, *Phys. Rev. B* **43**, 7185 (1991).
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- ²² To define these occupations, we calculate at each instant of the MD run to which type of site (T_1 , H_3 , or T_4) each Pb atom is closest. In this way Pb atoms are always assigned to a site, even when they are actually "flying" between sites.
- ²³ In a different context, thermally activated, single hops between T_4 and H_3 sites with activation energy $E_b \sim 0.5$ eV have been observed for isolated Pb adatoms on Ge(111) (Refs. 24 and 25).
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- ²⁶ This is done using for the residence time τ a simple Arrhenius expression $\tau = \nu^{-1} \exp(E_b/kT)$, where ν is an effective attempt frequency. Taking $\nu \sim 10^{12} \text{ s}^{-1}$, which approximately corresponds to the value of the Pb-Ge bond stretching frequency in Fig. 6, we find that a value $E_b \sim 0.2$ eV leads to $\tau \sim 15$ ps at $T = 800$ K. This is somewhat larger than, but of the order of, the residence times we observe in our simulation.
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- ³² Note, however, that, experimentally, trimers appear to be centered at H_3 sites (Ref. 6), whereas in our calculated images [including Fig. 7(a)] trimers are usually centered at T_4 sites, except at large distance from the surface where they may appear centered at H_3 , as discussed in Ref. 8.



(a)



(b)

FIG. 7. Theoretical STM images of the high-coverage phase of Pb/Ge(111) from topographic maps of constant local density of states (see text). The images are taken at ~ 2.5 Å above the Pb layer. The underlying Ge lattice is always shown, while for better clarity Pb atoms (indicated by the big dots) are shown only in the upper panels.