Surface relaxations in quantum-confined Pb

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The relationship between electronic and atomic structure of quantum confined objects is a key issue in nanoscience. We performed low-energy electron diffraction to determine the surface relaxations of ultrathin Pb films on Si(111)7×7 with thicknesses ranging from four to nine atomic layers. The results indicate a contraction of the first interlayer spacing d_{12} for all films. The d_{12} contraction exhibits a small bilayer modulation as a function of thickness, indicative of a quantum size effect. The oscillatory relaxations furthermore suggest an interesting correlation with the work function oscillations predicted from density functional theory [Wei and Chou, Phys. Rev. B **66**, 233408 (2002)] and can be understood qualitatively on the basis of the jellium model.

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I. INTRODUCTION

The ongoing miniaturization of solid state electronic devices toward the nanoscale regime underscores the need for understanding quantum size effects (QSEs) in small metallic objects. Experimental studies of quantum size phenomena in thin metal films date back to the 1970's when Jaklevic and Lambe first observed the QSE by means of tunneling experiments in metal-oxide-metal junctions.¹ Subsequent studies, most of these performed on Pb, have highlighted the importance of the QSE for the electronic properties and growth mode of the film.^{2–5} In particular, the interplay between the QSE and morphological evolution of the films received considerable attention following the discovery of a “magic thickness” and preferred island heights in ultrathin metal films grown at moderately low temperature.^{6–10} The influence of the quantum size effect on lattice relaxations, however, has hardly been investigated. This is surprising, considering the fact that the interplay between quantum confinement and atomic arrangement is one of the most fundamental questions in nanoscience.

The literature does not present a very coherent picture regarding the magnitude of lattice relaxations induced by the QSE. For instance, a recent low-energy electron microscopy study¹¹ of Ag on W(110) showed an increased layer spacing at the film-substrate interface, but no significant changes in the layer-to-layer relaxations were reported. Most efforts have focused on ultrathin Pb films, however. Scanning tunneling microscopy¹² (STM) and helium atom scattering (HAS) for Pb on Si(111),⁴ Pb on Cu(111),¹³ and Pb on Ge(100) (see Refs. 14 and 15) all indicated large oscillatory surface relaxations as a function of thickness, though neither technique probes the actual core positions. Instead, STM and HAS are very sensitive to the electron density above the surface. X-ray diffraction and low-energy electron diffraction (LEED) are expected to produce more reliable relaxations. An x-ray diffraction study by Floreano *et al.*¹⁵ indicated that the first interlayer spacing (near the solid-vacuum interface) oscillates around the bulk equilibrium layer spacing with an amplitude of about 5% (i.e., surface layers are either expanded or contracted, depending on the film thickness). The reliability of these results requires further scrutiny, however,

because of the large number of fitting parameters and relatively small data set. Another x-ray study of Pb on Si(111)¹⁶ indicated quasibilayer oscillations [i.e., bilayer oscillations that are modulated by a 9 monolayer (ML) superperiod] in the internal structure of the films. Interestingly, the first interlayer spacing was contracted for all layer thicknesses. Density functional theory (DFT) slab calculations on free-standing Pb films^{17,18} have predicted thickness-dependent relaxations in thin films, but it remains difficult to include the incommensurate substrate in these calculations.

In this paper, we present a dynamical LEED structure determination study of Pb films on Si(111)7×7 as a function of thickness in the quantum size regime. Dynamical LEED [or LEED- $I(V)$] has proven to be a reliable technique to determine the atomic arrangement of surfaces.^{19–22} It is found that the surface relaxations are correlated with the QSE. All films (4–9 ML) show a contraction of the first interlayer spacing d_{12} . The magnitude of the contraction (Δd_{12}) oscillates with a bilayer periodicity although the amplitude of this QSE oscillation is quite small. The bilayer oscillation can be linked to the calculated work function of the films and appears to be consistent with the Finnis-Heine model for surface relaxations.²³ The results will furthermore be compared to STM data, He scattering experiments, and DFT predictions.

II. EXPERIMENTAL PROCEDURE

The experiments were performed in an UHV chamber located at Delft University of Technology. The system was equipped with Auger electron spectroscopy (AES), LEED with automated data acquisition, ion gun, and liquid nitrogen sample cooling capability. The base pressure was 4×10^{-11} mbar. To obtain a clean 7×7 reconstructed Si(111) surface the sample was flashed by e-beam heating to 1100 °C. After this flash, no traces of contaminants were found by AES, while LEED showed a very sharp and low background 7×7 pattern.

High purity Pb (5N) was evaporated from a Knudsen cell at a temperature of 595 °C. The angle of incidence was 40° from the surface normal to allow for real-time monitoring of

FIG. 1. Intensity of the combined Pb/Si NOO/LVV Auger spectra as a function of Pb coverage used for calibration of the Pb coverage. The intensity saturates at 0.65 ML Pb. (One monolayer is defined as a close-packed Pb(111) layer; see text).

the Auger electron spectrum in order to calibrate the deposition rate. The sample was kept at room temperature during the calibration run. The peak-to-peak intensity of the combined Pb(NOO, 96 eV-Si(LVV, 92 eV) Auger line decreases sharply during Pb deposition until the coverage saturates at 0.65 ML Pb (Fig. 1). The absolute coverage at the break point was determined by *ex situ* Rutherford backscattering spectrometry (RBS). The Pb coverage is expressed in terms of a close-packed Pb(111) monolayer ($1 \text{ ML} = 9.43 \times 10^{14} \text{ atoms/cm}^2$). Following this calibration procedure, the sample was flashed again and subsequently cooled to 110 K. Pb was then deposited using the same growth rate as above; the growth rate in all experiments was of the order of 0.15 ML/min. At 110 K, the films show quasi-layer-by-layer growth,^{10,16,28,29} i.e., layer $N+1$ starts to grow before layer N is completed.

The experimental $I(V)$ curves were obtained from the LEED images using home-built software. The program places a circle around a spot in the diffraction pattern and adds the intensity of all pixels within the circle. The background intensity is corrected for by subtracting the intensity of a nearby circle, not placed on a spot, that is located at a similar distance from the center of the pattern. The resulting $I(V)$ curves are checked to be independent of the size of the circle used, and are normalized to the incident electron beam current.

III. EXPERIMENTAL RESULTS

A. Morphology of the films

The growth of Pb on Si(111) 7×7 has been investigated intensively during the last decades.^{24–26} Therefore, the initial stages of growth are well known and have been observed many times by different groups and with different experimental methods.

At room temperature, in the initial stages of Pb growth (up to 0.15 ML) Pb atoms occupy six distinct sites in the 7×7 unit cell, while maintaining the 7×7 symmetry.²⁵ At

FIG. 2. LEED patterns of characteristic Pb formations on Si(111) 7×7 grown at 110 K. (a) The Pb wetting layer with 7×7 symmetry. (b) Pb(111) crystals on top of the wetting layer, at a total coverage of 2.5 ML. (c) Closed Pb(111) film.

higher coverages Pb atoms cover more of the Si substrate, until a full wetting layer has developed, still having the 7×7 symmetry. During the growth of this wetting layer, the fractional order spots in the sharp Si(111) 7×7 LEED pattern gradually disappear. The only fractional order spots that remain visible are the ones neighboring the integer order spots ($\frac{1}{7}$, $\frac{6}{7}$, and $\frac{8}{7}$ spots) and the ones located along the main crystallographic directions [Fig. 2(a)]. Combined LEED, STM, and RBS studies^{24,25} identify this phase as having a Pb coverage of 0.66 ML. From the STM results, the authors proposed a model with 8 Pb atoms along the Si(111) 7×7 unit cell axes, while the remaining Pb atoms are distributed over sites above the top layer of Si atoms. The kink in the combined Pb-Si Auger line at 0.65 ML (Fig. 1) is likely to be caused by the stacking of Pb atoms on Pb atoms and was taken as our reference point for the calibration of the absolute coverage.

For the purpose of LEED- $I(V)$, Pb films were grown at 110 K. Beyond 1 ML coverage, the LEED background initially increases, until Pb crystallites start to grow, with Pb(111) facets parallel to the Si(111) surface. The Pb islands

are mainly oriented along the substrate axes, i.e., $[110]\text{Pb}||[110]\text{Si}$, but exhibit a 6° mosaic spread [Fig. 2(b)]. The LEED pattern shows six-fold symmetry, in contrast to the three-fold symmetry of the Si(111) substrate. This shows that ABC and ACB stacked domains are present in (nearly) equal amounts. These domains are rotated 60° with respect to each other, thus averaging the (10) and (01) diffracted intensities. This leads to equal intensity in the six (10) beams, the six (11) beams and the six (20) beams from the Pb layer.

The LEED intensity from the Pb islands shows some overlap with the fractional order spots of the wetting layer. The reason for this is the 10% smaller (in-plane) lattice parameter of Pb compared to Si(111). Consequently, the $\frac{8}{7}$ wetting layer spots coincide with the Pb(111) (10) spots. Within the 12° angular spread, the LEED intensity is equally distributed. There is no indication of a preferred coordination within this interval, in contrast with a previous LEED study²⁶ where a preference was observed for the 6° rotated island.

Upon further deposition at 110 K, the Pb film closes (at ~ 3 ML). The fractional order spots of the wetting layer disappear first. The Si integer order spots disappear next and finally only banana shaped spots of the Pb crystallites remain visible in LEED. As the film is closed the mosaic spread narrows significantly [Fig. 2(c)]. The spots remain banana shaped, but the angular spread is reduced. Figure 2(c) is representative of the LEED patterns from which the $I(V)$ curves are obtained for the structure determination of the Pb films on Si(111) 7×7 .

For the purpose of structure determination, Pb films of 4, 5, 7, 8, and 9 ML nominal Pb coverage were grown at 110 K on Si(111) 7×7 .²⁷ At this temperature, the films grow quasi-layer-by-layer.^{10,16,28,29} LEED intensity spectra [$I(V)$ curves] of the (10), (11), (20), and (21) beams were measured for each thickness, except for the 9 ML film, of which only the (10) and (20) have been measured. The six symmetry-equivalent beams from the various films always showed mutual R -factors smaller than 0.10, which is indicative of a good quality data set. Symmetry-equivalent beams were averaged before data analysis. The incident electron energy ranges from 50 to 250 eV with 1 eV increments, which is sufficient for sampling the peaks present in the intensity spectra. The large energy range also indicates good film quality. For comparison, in the Pb(111) bulk crystal LEED study of Ref. 30 spots were no longer visible above 200 eV beam energy.

TABLE I. Mutual Pendry R -factors of (10) beams in experimental data sets. The energy of the $I(V)$ curves ranges from 50 to 220 eV.

(10) beams	4 ML	5 ML	7 ML	8 ML	9 ML
4 ML		0.137	0.085	0.105	0.175
5 ML	0.137		0.076	0.132	0.062
7 ML	0.085	0.076		0.094	0.095
8 ML	0.105	0.132	0.094		0.139
9 ML	0.175	0.062	0.095	0.139	

TABLE II. Mutual Pendry R -factors of (11) beams in experimental data sets. The energy of the $I(V)$ curves ranges from 117 to 181 eV.

(11) beams	4 ML	5 ML	7 ML	8 ML	9 ML
4 ML		0.276	0.090	0.073	0.149
5 ML	0.276		0.170	0.199	0.174
7 ML	0.090	0.170		0.040	0.091
8 ML	0.073	0.199	0.040		0.091
9 ML	0.149	0.174	0.091	0.091	

B. R -factor analysis

The quantized energy levels in the film determine the stability, and are likely to influence the multilayer relaxation at the surface of the films. Strictly speaking, the electronic structure and stability of the Pb films exhibit *quasi*-bilayer oscillations, i.e., bilayer oscillations are interrupted by even-odd crossovers that are separated by 9 ML.^{31,32} Here we focus on films between 4 and 9 ML thick. In this range, even thicknesses are energetically stable while odd thicknesses are unstable. Hence, the periodicity of these oscillations is exactly 2 ML.

Since the total charge density shows a 2 ML periodicity, one might also expect bilayer oscillations in the structural parameters of the film, as the lattice relaxations should be proportional to the derivative of the charge density variations (linear response regime¹⁶). The magnitude of this effect may be small, however, as we will learn from the following discussion.

A first check for a possible bilayer periodicity in the structure of the films is to calculate the mutual (Pendry) R -factors³³ of the experimental $I(V)$ curves. If the structural parameters would indeed exhibit bilayer periodicity, then the mutual R -factors from the N and $(N\pm \text{even})$ monolayer films should be systematically smaller for identical (h,k) diffracted beams. Alternatively, the mutual R -factors of N and $(N\pm \text{odd})$ monolayer films should be higher.

This analysis has been performed on the (10), (11), and (20) beams of Pb films grown at 110 K in the quasi-layer-by-layer mode. The results are shown in Tables I–III for the (10), (11), and (20) beams, respectively. The tables are symmetrical around the diagonal axis. Figure 3 shows the experimental beams used in this analysis. The energy range of the (21) beam was too limited to calculate a reliable R -factor and

TABLE III. Mutual Pendry R -factors of (20) beams in experimental data sets. The energy of the $I(V)$ curves ranges from 125 to 196 eV.

(20) beams	4 ML	5 ML	7 ML	8 ML	9 ML
4 ML		0.106	0.115	0.067	0.188
5 ML	0.106		0.038	0.023	0.096
7 ML	0.115	0.038		0.032	0.075
8 ML	0.067	0.023	0.032		0.099
9 ML	0.188	0.096	0.075	0.099

FIG. 3. Experimental $I(V)$ curves of the 4, 5, 7, 8, and 9 ML Pb films on Si(111) 7×7 used in the R -factor analysis. (a) (10) beams, (b) (11) beams, (c) (20) beams, and (d) (21) beams.

TABLE IV. Average Pendry R -factors of beams from thicknesses differing even and odd number of layers.

Beam	(10)	(11)	(20)
Average R (N vs $N \pm \text{even}$)	0.090	0.127	0.072
Average R (N vs $N \pm \text{odd}$)	0.127	0.141	0.094

was not included in this analysis. A low R -factor of two $I(V)$ curves means that the $I(V)$ curves are similar, while a high R -factor means lesser similarity between the two curves. Bilayer periodicity in the R -factors implies a bilayer periodicity of the surface structure.

Inspection of the tables shows that the expected bilayer periodicity in the R -factors is present for some beams, but is less pronounced in others. For example, the (10) beam from the 5 ML film shows low R -factors when compared with identical beams from the 7 and 9 ML films (0.072 and 0.062, respectively). Comparison with the 4 and 8 ML films yields significantly higher R -factors (0.137 and 0.132, respectively). Some other beams do not show this behavior. Clearly, not all beams show a systematic bilayer trend, which is possibly due to scatter in the data as well as possible variations in the film quality, such as surface roughness.

To check for an overall trend, R -factors from all [N versus $N \pm \text{even}$] and from all [N versus $N \pm \text{odd}$] numbered layers have been averaged. Table IV shows the results for the (10), (11), and (20) beams. The average R -factor from the [N versus $N \pm \text{even}$] numbered layers shows a significantly lower value than the [N versus $N \pm \text{odd}$] numbered layers. Thus, even in the absence of a full-blown LEED- $I(V)$ analysis, inspection of the raw $I(V)$ data strongly suggests a bilayer periodicity in the structural parameters of the films.

C. Structure determination results

To obtain quantitative information about the atomic structure and relaxations of the individual films, the $I(V)$ spectra were analyzed with the Van Hove SATLEED software package.³⁴ The structural parameters to be optimized were the real and imaginary part of the inner potential V_{0r} and V_{0i} , the Debye temperature Θ_D and the first and second interlayer spacings d_{12} and d_{23} . No more than two interlayer spacings were included in the fit, since Pb is a strong scatterer and the spectra therefore do not obtain much information about the deeper layers. The third and higher interlayer spacings were kept fixed at their bulk values. The values of V_{0r} , d_{12} , and d_{23} were optimized by the fitting routines of the SATLEED program, while V_{0i} and Θ_D had to be fitted manually.

In the dynamical treatment of the scattered intensities, a set of 13 relativistic phase shifts was used ranging from 50 to 350 eV, calculated by the Barbieri/Van Hove phase shift package.³⁴ The 14th and higher phase shifts gave very small numbers and were not included in the calculations. Since the SATLEED program only allows for the use of a single trial structure, the treatment of the domains present in the films needs attention. The 60° rotated domains average the observed LEED intensities of the (10) and (01) beams,

FIG. 4. Pendry R -factor as a function of imaginary part of the inner potential V_{0i} (a) and Debye temperature Θ_D (b) for the 7, 8, and 9 ML data sets. The optimum values are -8 eV and 125 K, respectively.

for example, making it impossible to distinguish them. Therefore, in the SATLEED code the $I(V)$ curves of the (10) and (01) beams are both calculated and subsequently averaged. The routine that optimizes the atomic structure and R -factors now compares the averaged $I(V)$ curve with the measured one. Or, in general, the program must average those $I(V)$ curves that are also averaged in the experiment due to, e.g., domains.

The first step in the search for the optimized structures was the determination of the values for V_{0i} and Θ_D . All of the five experimental data sets gave values for V_{0i} between -7 and -9 eV. The relaxations and R -factors only showed very small changes when varying V_{0i} between -7 and -9 eV, and a value of -8 eV for V_{0i} was taken for all thicknesses during the remainder of the optimization procedure. The same holds for Θ_D and a final value of 125 K was chosen, which is slightly larger than the literature value of 105 K.³⁵ Figure 4 shows the total Pendry R -factor of three different data sets as a function of V_{0i} (a) and Θ_D (b). The overall similarity of the data sets with respect to these two parameters is represented by the coincidence of the minima. The vibrational amplitude of the topmost Pb layer is enhanced in the search by a factor of $\sqrt{2}$, to take the reduced coordination of the surface atoms into account.

The five structures were optimized with a constant in-plane lattice parameter of 3.489 Å. The (11) beams were not

TABLE V. Structure determination results for several Pb coverages on Si(111) 7×7 . The in-plane lattice parameter is fixed at 3.489 Å. Deviations from the bulk interlayer spacings are given as percentages.

Thickness (ML)	4	5	7	8	9
$\Delta(d_{12})$ (%)	-2.9	-3.3	-2.8	-2.3	-2.8
$\Delta(d_{23})$ (%)	+1.6	+0.5	+0.5	+1.1	+0.6
V_{0R} (eV)	4.9	4.8	5.1	5.5	4.1
$R_{P,tot}$	0.142	0.257	0.166	0.193	0.225
R_{10}	0.09	0.19	0.13	0.15	0.16
R_{20}	0.26	0.35	0.25	0.30	0.34
R_{21}	0.23	0.12	0.09	0.15	—

included in the fit, because that produced high R -factors (>0.4 in all data sets). The influence of the (11) beam on the structure determination results will be discussed in Sec. III D, where it will also be shown that the omission of the (11) beam does not significantly affect the fitted layer relaxations. The total Pendry R -factor $R_{P,tot}$ is a geometric average of the individual R -factors, and their weights were taken proportional to the energy range of the individual beams.²¹ The results of the layer relaxations are given in Table V. The search for the global R -factor minimum for each film thickness started from a variety of trial structures, including the large relaxations observed in STM and HAS. All calculations converged toward the same global R -factor minimum. The experimental and calculated $I(V)$ curves of the 7 ML data set are shown in Fig. 5, and are representative of all data sets.

To check for systematic errors introduced by a possible roughness of the growth front, the following procedure has been implemented: we generated various geometrical averages of the calculated $I(V)$ curves of the optimized structures in Table V, to be used as “experimental” input for a new structure determination. The resulting fits to the generated data produced within 0.1% the geometrical average of the original layer relaxations, though the R -factors increased slightly. Evidently, coexisting layer thicknesses would produce LEED- $I(V)$ spectra that can be optimally fitted to an average layer relaxation. The slight increase of the overall R -factor can be attributed primarily to the (11) beam, indicating that the (11) beam is the beam most sensitive to surface roughness. We will discuss the significance of this geometrical averaging in Sec. IV when we compare the layer relaxations from LEED- $I(V)$ to those from other experimental studies.

Figure 6 shows a contour plot of the total Pendry R -factor around the global minimum of the 7 ML film at $R_P=0.166$ as a function of $\Delta(d_{12})$ and $\Delta(d_{23})$. The minimum is indicated by the black square at the center. This R -factor landscape is typical for all five data sets. The SATLEED program does not allow for keeping the real part of the inner potential constant in the fit; it is always optimized. Therefore, R -factors outside the minimum tend to be underestimated, because V_{0R} is always optimized at each location in the R -factor landscape of Fig. 6. The figure shows that the R -factor depends much more strongly on $\Delta(d_{12})$ than on $\Delta(d_{23})$; i.e., the curvature of

FIG. 5. Experimental (solid line) and calculated (dotted line) LEED- $I(V)$ curves from a 7 ML Pb film on Si(111)7 $\times$ 7.

the landscape is stronger in the horizontal than in the vertical direction. Clearly, the parameter d_{12} is the dominant contributor to the R -factor.

The uncertainties in the values of $\Delta(d_{12})$ and $\Delta(d_{23})$ can be obtained³³ from the variance σ of the total Pendry R -factor:

$$\sigma = R_{P,min} \sqrt{\frac{8|V_{0i}|}{\Delta E}}, \quad (1)$$

with $R_{P,min}$ the Pendry R -factor at the global minimum and ΔE the total energy range of the experimental data set. The uncertainty in $\Delta(d_{12})$ is given as $\Delta(d_{12})(R_{P,min} + \sigma) - \Delta(d_{12})(R_{P,min})$. All five data sets show similar curvature of

FIG. 6. Contour plot of the total Pendry R -factor $R_{P,tot}$ as a function of $\Delta(d_{12})$ and $\Delta(d_{23})$ in Å for the 7 ML optimized structure. The minimum ($R_{P,tot}=0.166$) is indicated by the black square in the center.

the R -factor landscape as a function of d_{12} and d_{23} . Taking into account the systematic underestimation of R_P in the R -factor landscape, this leads to uncertainties in $\Delta(d_{12})$ and $\Delta(d_{23})$ of 0.6% and 0.8% of the bulk interlayer spacing, respectively. The meaning of these numbers will be addressed in Sec. IV.

D. Stacking faults and the (11) beam

The fact that the structure determination in the previous sections is performed without the (11) beam raises the question what influence this beam has on the results. We already alluded to the possibility that surface roughness affects the (11) beam. However, since the (11) beam is also the beam most sensitive to stacking faults on fcc(111) and hcp(0001) surfaces,³⁶ it has to be investigated whether the high R -factor of this beam can be related to deviations from the Pb fcc stacking sequence. Therefore, the 8 ML data set has been investigated for the existence of stacking faults.

Assuming that the top layer Pb atoms are located in the “A position” of a closepacked stacking arrangement, we can place the second layer atoms in either the B or C positions. We already know that both possibilities occur with equal probability since the LEED pattern has the sixfold symmetry (Sec. III A). This twinning (i.e., the coexistence of $ABCABC\dots$ and $ACBACB\dots$ stacked domains) was already taken into account in the $I(V)$ analysis (see Sec. III C). Therefore, in order to explore whether the high R -factor of the (11) beam is related to stacking faults, we must consider deviations from the above fcc stacking sequence. As we move into the crystal, we only need to consider the following faulty stacking sequences: $ABABCABC\dots$ and $ABACABCABC\dots$ (For the unavoidable symmetry reasons mentioned above, these are averaged with $ACACBACB\dots$ and $ACABACBACB\dots$, respectively). Both cases amount to a stacking fault between the second and the third layers. Stacking faults in deeper layers are not included because of the very low sensitivity of the LEED experiment to the atomic positions in deeper layers.²⁰

TABLE VI. Pendry R -factors of the 8 ML data set for twinned fcc stacking and for two different stacking-fault sequences.

Structure	R	fcc	ABAB...	ABAC...
Without (11) beam	$R_{P,tot}$	0.19	0.20	—
With (11) beam	$R_{P,tot}$	0.28	0.33	0.32
With (11) beam	$R_{P,11}$	0.43	0.62	0.59

The 8 ML data set has been tested for the two detectable stacking faults with and without inclusion of the (11) beam. The results are displayed in Table VI. If we exclude the (11) beam from the analysis, the R -factor shows a slight increase for the ABABCABC... stacking sequence, while for the other stacking fault sequence, no R -factor minimum was found. However, if all four beams are included in the analysis, the total Pendry R -factor increases significantly upon the introduction of the stacking fault. This increase can be attributed *exclusively* to the increase of R_{11} from 0.4 to 0.6; the R -factors of the other beams did not change. This analysis proves that the (11) beam is indeed the most sensitive to stacking faults. The only other plausible imperfection leading to a large R -factor for the (11) beam would be surface roughness, as indicated in the previous section. We therefore conjecture that the poor fit of the (11) beam must be attributed to the presence of minority stacking fault domains and/or roughness at the growth front. We finally note that the relaxations in the optimized structure including all four beams differ only marginally from the three-beam fit in Table V; $\Delta(d_{12})(4 \text{ beams}) = -2.1\%$ and $\Delta(d_{23})(4 \text{ beams}) = 1.0\%$. In summary, the (11) beam is very sensitive to structural imperfections; the omission of the (11) beam from the $I(V)$ data analysis only marginally affects the fitted layer relaxations.

IV. DISCUSSION AND CONCLUSIONS

Because similar multilayer relaxations lead to similar spectra, diffraction theory would predict low mutual R -factors for layers having similar relaxations. The results of Tables I–IV show that the Pendry R -factors for the (N versus $N \pm \text{even}$) numbered layers are significantly smaller than for the (N versus $N \pm \text{odd}$) numbered layers. The R -factor analysis of the experimental spectra thus provides direct evidence for a bilayer periodicity in the multilayer relaxations of the films, without the need for a dynamical analysis of the intensities. The quantitative LEED analysis confirms the existence of bilayer oscillations in the surface relaxation, although the variations are quite small (Table V). Notice that *the first interlayer spacing d_{12} is always contracted, regardless of the film thickness.*

The literature is quite confusing with regard to the magnitude of the multilayer relaxations in quantum confined films. The helium atom scattering^{13–15} and scanning tunneling microscopy¹² data have shown extremely large relaxations up to -30% for $\Delta(d_{12})$ and $+15\%$ for $\Delta(d_{23})$ around the bulk equilibrium spacing.¹⁴ These very large relaxations must be attributed to electronic effects such as charge spilling from the quantum well into the vacuum, not to the relax-

ations of the atomic core positions. Similar arguments can be given for the giant oscillatory behavior of the step heights observed in STM.¹² Clearly, reliable structure parameters can only be obtained via x-ray diffraction or LEED- $I(V)$ analysis.

There have been few attempts recently to measure the multilayer relaxations in quantum confined Pb films with x-ray diffraction and x-ray reflectivity. Floreano *et al.*¹⁵ concluded that the outer layer spacing (d_{12}) oscillates around the bulk equilibrium value with an amplitude of 5%. They noted that these oscillations are much smaller than those in their HAS experiments. The fitting of their rod scans required many parameters and hence, it is not easy to assess the reliability of the fit. Czoschke *et al.*¹⁶ on the other hand used a simple theoretical model to reduce the number of fitting parameters. They fitted the x-ray reflectivity data from a 10 ML Pb film on Si(111)($\sqrt{3} \times \sqrt{3}$)–Pb by modeling the film as a one-dimensional quantum well system with hard wall potential barriers. (These films were grown under conditions similar to ours; i.e., layer-by-layer.) The total charge density $\rho(z)$ in the film was calculated by summing over all occupied, free-electron subbands. To include the effects of charge spilling, the width of the well was adjusted on both sides, which introduces the “charge spilling parameter.” The displacement of the atomic planes from their bulk positions was then taken proportional to the derivative $\partial\rho/\partial z$ of the theoretical charge density at the bulk location of the atomic planes. The resulting displacement pattern was then fitted to the experimental reflectivity data which produced a d_{12} contraction of 9% for 10 ML of Pb. (A 5% contraction was found for a 9 ML film.³⁷) This model also produced very large relaxations, although not as large as the HAS and STM results would suggest.

The model, though very transparent and elegant, remains rather crude. The charge distribution used for the fitting of the data is model dependent and may not be accurate, especially in the surface region, while the validity of the linear response approximation is questionable for relaxations as large as 9%. Attempts to fit our LEED- $I(V)$ data to relaxations of that magnitude were unsuccessful. The fits always converged to d_{12} contractions of order 2–3% (Table V) while the reported 9% relaxation¹⁶ is clearly far outside our experimental margin of error [0.6%; see Eq. (1)]. If the small relaxations from LEED- $I(V)$ were the result of geometrical averaging over a rough growth front, producing a *systematic* error in LEED- $I(V)$, then the minus 9% d_{12} relaxation of the 10 ML film^{16,37} would have to be balanced by a small outward expansion for the neighboring thicknesses (see discussion on geometrical averaging in Sec. III C). This would not only be at odds with the x-ray reflectivity study of Czoschke and coworkers^{16,28} but also with the results from DFT. DFT calculations of Pb(111) slabs^{17,18} show that d_{12} is always contracted, regardless of the film thickness. The calculations also produce layer relaxations much smaller than the above HAS, STM, and x-ray reflectivity experiments would suggest.

Our LEED- $I(V)$ results are qualitatively consistent with DFT but indicate slightly smaller variations: -2.5 to -3% for $\Delta(d_{12})$ and $+1\%$ for $\Delta(d_{23})$, with a superimposed bilayer oscillation in $\Delta(d_{12})$ of $\approx 5\%$ (0.01 to 0.02 Å). The even layers

FIG. 7. First interlayer relaxation from LEED- $I(V)$ (black squares) and calculated work function data from C. M. Wei and M. Y. Chou (see Ref. 32) (open circles).

show a smaller d_{12} contraction than the odd layers, also consistent with DFT. In contrast to the STM and HAS results, both LEED and DFT indicate a contraction of the first interlayer spacing for all thicknesses. Our LEED- $I(V)$ results are consistent quantitatively with a dynamical LEED- $I(V)$ study³⁰ of bulk Pb(111), which reported $\Delta(d_{12}) = -3.5 \pm 10\%$ and $\Delta(d_{23}) = +0.5 \pm 1.4\%$. The discrepancy between the absolute magnitude of the relaxations in LEED and DFT can be attributed in part to thermal expansion of the lattice in the LEED experiment because the DFT result only applies to $T = 0$ K. Furthermore, it should be noticed that the layer relaxations were only calculated for freestanding slabs.

One could argue that the observed amplitude of the bilayer oscillation in the relaxation lies within the error bars of the method. We have two reasons to believe that our observations are significant. First, the R -factor analysis of the bare spectra (Sec. III B) shows clearly that the even and odd layers have different structures; i.e., the bilayer oscillation is directly observable in experiment (without data fitting). Secondly, the relaxation of the second interlayer spacing $\Delta(d_{23})$ also shows a bilayer oscillation. It is hardly conceivable that the $I(V)$ data consistently fit to a bilayer oscillation pattern for *both* $\Delta(d_{12})$ and $\Delta(d_{23})$, if the effect were statistically insignificant. The amplitude of the superimposed quasibilayer oscillation in $\Delta(d_{12})$ of about 0.5% originates from the thickness-dependent modulation of the valence charge density. For comparison, this relaxation amplitude is similar to the structure modulations in weakly coupled incommensurate charge density wave systems.^{38,39} Although our data are qualitatively consistent with the DFT calculations, this does not automatically offer insight into the fundamental aspects that drive the layer relaxations. In the following, we will attempt to correlate quantum electronic structure with surface relaxations.

A parameter that is very sensitive to the surface charge density is the work function. The work function of freestanding Pb films was calculated by Wei and Chou (open circles in Fig. 7).³² The calculated work function also reveals quasibilayer oscillations. Comparison of Table V with the calculated work function (both shown in Fig. 7) shows that the even-numbered layers with smaller contraction have the largest

work function, while the odd-numbered layers with increased contraction have the lowest work function. Preliminary DFT calculations of the surface relaxation indeed indicated a correlation between work function and surface relaxation.^{17,40} This oscillating work function must be related to the oscillations in the Fermi energy and/or oscillations in the charge spilling from the quantum well (“surface dipole”).⁴¹ It is not clear how QSE oscillations in the Fermi energy would affect the surface relaxations. On the other hand, the correlation between the surface dipole and relaxations is straightforward, at least within a jellium description, and we therefore base our arguments on the jellium model. The tails of the wave function extending into the vacuum constitute a surface dipole layer and therefore contribute to the work function. The more charge spilling, the larger the dipole, the larger the work function. This suggests that charge spilling is largest for the even films, which also turn out to be the most stable ones.³¹

At first sight, this observation seems counterintuitive, since the quantum well states of the even films are supposed to be deeper in energy than those of odd films^{31,32} and should therefore spill less charge into the vacuum. However, in order to calculate the total surface charge density, one has to consider the full two-dimensional subband dispersion, not just the states near Γ . Detailed jellium calculations show that the total charge spilling is smallest when the bottom of subband is located right at the Fermi level, and largest when the Fermi level is located exactly in between the highest occupied and the lowest unoccupied level at the Γ point.⁴²

It now appears that the relaxation data and the theoretical work function results (both shown in Fig. 7) can all be understood on the basis of this simple charge spilling concept. The theoretical maxima in the work function coincide with the smallest contraction of the first interlayer spacing. According to the Finnis-Heine model,²³ close-packed (111) surfaces usually show minimal relaxations, as opposed to open surfaces that are usually contracted [e.g., cubic (100) surfaces]. On close-packed surfaces, there is not much “room” for Smoluchowski charge smoothing and, consequently, much of the charge density remains located above the surface. In fact, many (111) surfaces show small expansions as the ion cores move away from the crystal to compensate the excess charge density above the surface (Smoluchowski smoothing would lead to a contraction). Although there are many exceptions to this simple electrostatic argument [see, e.g., Feibelman,⁴³ in fact, the 3.5% contraction of the (111) surface of bulk Pb (Ref. 30) is also an anomaly], this jellium argumentation appears to work quite well to explain the layer-by-layer variations of the d_{12} contraction. The larger work functions of the even layers correspond to more charge spilling and hence the outer layer expands relative to its bulk equilibrium value, meaning less contraction. This is consistent with the smaller contractions of the even layers in Table V. Figure 8 illustrates the increased charge spilling and work function in the even (and stable) layers with respect to the odd (and unstable) layers.

This line of argument should of course be checked against the STM and HAS results which are also very sensitive to surface charge density. STM results of Pb on Si(111) 7×7 indicate that the step height between a 7 and 8 ML terrace is

FIG. 8. Schematic drawing of the increased charge spilling (and work function) in the even layers with respect to the odd layers. In the even layers the first layer atoms are pulled outwards, reducing the contraction.

reduced while the step height between a 6 and 7 ML terrace is expanded (Su *et al.*,¹² this counting scheme includes the wetting layer). This suggests that the charge spilling from the $N=7$ terrace is large while the charge spilling from the $N=8$ terrace would be small, opposite to the scenario outlined above (Fig. 8). However, STM experiments are most sensitive to states near the Γ point,⁴⁴ while the step height is strongly dependent on bias voltage. Apparent step heights calculated with DFT for Pb(111) slabs¹⁸ are in antiphase with He scattering data¹³ for Pb on Cu(111). To circumvent this discrepancy, the authors artificially strained the slabs to mimic the presence of a mismatched substrate, which produced reasonable agreement between theory and experiment. This “trick” cannot be applied in the Pb on Si(111) case, because the Pb films appear to be fully relaxed. Helium scattering data are also very confusing. For instance, the results presented by Crottini *et al.*¹⁴ suggest an expansion of step height between 7 and 8 ML, whereas the data presented Floreano *et al.*¹⁵ indicate the opposite. The issue of apparent step heights in He scattering and STM clearly warrants further experimental and theoretical investigation.

V. SUMMARY

The surface relaxation of quantum confined Pb films has been determined with LEED- $I(V)$. The interlayer relaxations

$\Delta(d_{12})$ and $\Delta(d_{23})$ have small values that are quite typical for close-packed fcc surfaces, showing a few percent contraction for the first interlayer spacing and a somewhat smaller expansion for the second layer spacing. The relaxations oscillate as a function of layer thickness although the amplitude of the oscillations is very small and comparable to the margin of error. The (11) beams consistently produce poor data fits, indicating the presence of stacking fault domains and/or residual roughness at the growth front. Roughness would lead to an underestimation of the oscillatory relaxations. The oscillatory pattern of the layer relaxations can be associated with the bilayer oscillations in the electronic structure (i.e., the QSE). The observed decreased contraction in d_{12} for the even films can be explained within the jellium model by the expected increase of charge spilling from the quantum well. In this way, a relationship between the relaxation and work function is suggested: even (odd) films show an increased (decreased) charge spilling and work function. The extremely large relaxations observed in He scattering and STM must be attributed to charge spilling effects, as these measurements probe the tails of the electronic charge distribution above the surface, not the atom core positions.

We finally remark that much effort has been devoted toward understanding surface relaxations on simple metal crystals. The usual approach is to compare the surface relaxations of different elements and different crystal orientations. These comparative studies have had mixed success.^{43,45,46} Quantum confined Pb films, on the other hand, prove to be unique model system to test the simple electrostatic Finnis-Heine model of surface relaxations because the surface charge density of Pb(111) can be tuned by tuning the layer thickness. The layer-to-layer variations of the surface relaxation appear to be in line with the Finnis-Heine argument, although fully relaxed DFT calculations are clearly needed to further corroborate this simple picture. Such calculations would have to include the substrate as the substrate is known to affect the location of the even-odd crossovers in the quantum electronic properties.

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