# Structure and melting of lead overlayers on Cu(100) studied with thermal-energy atom scattering

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The highest-coverage ordered overlayer of Pb on Cu(100) is the  $c(5\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure. It has been investigated by measuring the intensities of specularly scattered He atoms upon varying the incidence angles. From a simple kinematical analysis, a new model for this structure is proposed. It is similar to the previously reported by Höesler and Moritz [Surf. Sci. 117, 196 (1982)] except that two atoms per unit cell are sitting on threefold sites at 1.8 Å above the Pb overlayer. Upon melting of the overlayer, these two atoms appear to become embedded in the underlaying Pb layer since the molten layer is atomically flat. The thermal behavior of the lowest-coverage ordered Pb structure,  $c(4 \times 4)$ , was investigated by measuring the intensities of several diffracted beams. The structure disorders at 545 K, exhibiting a rather complex phenomenology, since the critical exponent  $\beta$  is found to be zero (indicative of a first-order transition), but at the same time the transition displays some characteristic features of second-order transitions.

### I. INTRODUCTION

Lead overlayers on single-crystal substrates have received considerable interest in the last few years as model cases for studying two-dimensional (2D) phase transitions such as melting or disordering. In addition, several ordered overlayer structures have been investigated in detail due to its intrinsic value for understanding the atomic structure of epitaxial films exhibiting large misfits in lattice parameters with the substrate. The early papers by Rhead *et al.*<sup>1-3</sup> showed that Pb grows in a Stranski-Krastanov form on the low-index faces of Cu. Before completion of the first monolayer, several ordered overlayer structures are formed such as  $c(4 \times 4)$ ,  $c(2 \times 2)$ , and  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  on Cu(100),  $c(2\times2)$  and  $p(5\times1)$  on the (110) face, and  $p(4 \times 4)$  on the (111) face. The highcoverage structures of  $c(5\sqrt{2}\times\sqrt{2})R45^{\circ}$  and  $p(4\times4)$ were interpreted by those authors in terms of dense pseudohexagonal-close-packed layers. Few years later a quantitative low-energy electron diffraction (LEED) analysis by Moritz et al. using dynamical theory revealed that the  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  was not pseudohexagonal but instead that the Pb atoms basically occupy the hollow sites of the Cu(100) substrate and arrange in narrow domains of a strained  $c(2 \times 2)$  structure.<sup>4-6</sup> This structural model was based on a previously published paper by Bibérian et al.<sup>7</sup> which proposed that ordered  $c(2 \times 2)$  structures on (100) fcc substrates could evolve to  $c(n\sqrt{2}\times\sqrt{2})R45^{\circ}$  (*n* integers) structures by increasing coverage. The latter structures consisted of  $c(2 \times 2)$ domains where the adatoms sit in hollow sites bounded by rows of pairs of atoms in analogy with the lines separating antiphase domains of  $c(2 \times 2)$  overlayers. These rows are similar to the domain walls characteristic of incommensurate structures.<sup>8</sup> For Pb on Cu(100), Moritz et al. proposed<sup>6</sup> a unit cell for the  $c(5\sqrt{2}\times\sqrt{2})R45^{\circ}$ structure that was atomically very flat with a corrugation below 0.05 Å. To achieve such a flat structure, containing the above-mentioned row of pairs of atoms, a compression of the Pb lattice parameters of almost 10% was required. The authors rationalized this large compression by comparing it with the atomic radii of Pb in several alloys.

In the present paper we have further investigated this overlayer structure by utilizing thermal-energy atom scattering (TEAS).<sup>9</sup> To do that, the specularly scattered intensity was measured as a function of the incidence angle (rocking curves). This procedure results in direct information on the atomic corrugations at the surface. The rocking curves were analyzed with an extremely simple kinematical approach that allowed to deduce the main features of the surface structure. It is concluded that our data are inconsistent with the previously proposed structural model since the Pb unit cell is found to possess a large atomic corrugation (1.8 Å). A model to account for this result is given.

As a second topic in this paper, the results of an investigation of the melting of the different Pb structures are presented. A great deal of interest has been devoted the last few years to 2D phase transitions. In particular the melting of Pb overlayers has been found to exhibit a rich phenomenology. In the early paper of Rhead et al.<sup>1</sup> it was found that the melting temperatures of the overlayers on several Cu substrates were well below the melting temperature of Pb. Later studies<sup>10</sup> demonstrated that on Cu(110) substrates Pb exhibits commensurateincommensurate and an incommensurate-melting transitions. Very recently it has been found<sup>11</sup> that the so-called  $p(4 \times 4)$  structure of Pb on Cu(111) is in reality incommensurate. The same authors found that for coverages of Pb close to completion of the monolayer, the overlayer structure is laterally compressed in 3.2%; this compressed layer melts at a temperature well above the melting point of Pb, and after melting the lateral compression is removed.

We have also investigated the melting of the three different ordered structures of Pb on Cu(100). An interesting result is that the large atomic corrugation of the  $c(5\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure becomes zero above the melting temperature (490 K). The rocking curve above the melting temperature is practically identical to the corresponding one of the  $c(2\times 2)$  structure.

The  $c(4\times4)$  structure exhibited measurable intensities of several diffracted beams in addition to the (00) one. By measuring the intensity and angular width of the  $(\frac{1}{2}0)$ and  $(0\frac{1}{2})$  reflections we found that a phase transition at  $T_c = 545$  K occurs consistent with a critical exponent  $\beta=0$  (i.e., first-order-like). Angular peak width was not constant upon crossing the temperature transition and the peak shape becomes Lorentzian type as in a secondorder phase transition.<sup>12,13</sup>

## **II. EXPERIMENT**

The experiments were performed in a UHV system described elsewhere.<sup>14</sup> The incident He beam was generated from a nozzle source at room temperature. Its kinetic energy was 63 meV  $(k = 11 \text{ Å}^{-1})$  with a full width at half maximum (FWHM) of 0.35°. Coherent length at  $\theta_i = 75^\circ$ was estimated to be 350 Å. Detection of the scattered beam was accomplished with a movable quadrupole mass spectrometer. Due to its mechanism setup for movement, the available incidence angle  $\theta_i$ , measured from the surface normal was restricted to an interval ranging from 45 to 90°. Scattered beams having an intensity larger than  $10^{-3}$  times that of the direct beam were measurable. Peak profiles were measured at intervals of 0.04° with an average time of 5 min in each position to improve statistics. The system had also LEED and Auger-electronspectroscopy (AES) facilities.

The crystal was of (100) orientation as determined by the Laue technique and mechanically polished before insertion into the vacuum chamber. It was cleaned by successive ion bombardment cycles and annealing at 1100 K. After this treatment it displayed a sharp LEED pattern. The temperature was monitored by a chromel-alumel thermocouple clipped to one side of the sample. Temperature stabilization within 4 K was achieved. Lead was deposited in situ from a resistively heated furnace. Deposition was always performed while having the Cu surface around 400 K. Before performing measurements, annealing up to 550 K was done to improve surface ordering. Intensity measurements were taken allowing the system to get stabilized by waiting 10 min after each variation of temperature. The Pb coverage was determined with AES and TEAS.15

### III. RESULTS AND DISCUSSION A. The clean Cu(100) surface

After several cycles of  $Ar^+$  etching and annealing to 1100 K the Cu(100) surface exhibited a sharp  $(1 \times 1)$ LEED pattern and no traces of contamination as viewed by AES. He scattering resulted in a single scattered beam along the specular direction as expected from a close-packed metallic surface where the surface corruga-



FIG. 1. Curve (a), specular intensity in logarithmic scale of the He beam vs incidence angle (rocking curve) of the clean Cu(100) at T = 500 K. Dots, experiment values; solid curve, eye guide. Lateral intensity falls are apparatus effects. Curve (b), logarithmical representation of  $[1 + \cos(\Delta k_{\perp} h)]$  with h = 1.80Å. Only peak positions have to be compared. Dashed lines correspond to maxima positions in curve (a).

tion is too small to give nonzero diffracted beams. At room temperature and 75° of incidence angle the surface reflectivity i.e., the ratio of the specular intensity to the intensity of the incident beam was around 30%. To further characterize the Cu surface, the intensity of the specular beam was monitored as a function of the incidence angle as shown in Fig. 1. The rocking curve exhibits maxima and minima indicating that the surface is not flat within the coherent zone of the beam.<sup>16</sup> A crystal surface with an imperfect cutting or polishing is expected to consist of flat terraces bounded by steps. If h denotes the step height at the surface, then from the Bragg law,  $2hk \cos\theta_i = \pi n$  (*n*, integer), one has constructive (*n*, even) or destructive (n, odd) interference of specular beams scattered from adjacent terraces. Due to that, the specular intensity displays maxima and minima for in-phase and out-of-phase scattering conditions, respectively. In Fig. 2, the dependence of  $\cos \theta_i$  versus *n* is displayed. It exhibits a linear relationship as expected from the Bragg law; the slope determines the h value, obtaining  $h = 1.80 \pm 0.04$  Å in excellent agreement with the bulk value of 1.804 Å given by the x-ray diffraction for the (100) interlayer spacing of copper. This result illustrates that the surface steps are monoatomic in height. The surface was further characterized by measuring the rela-



FIG. 2. Cosine of incidence angles satisfying Bragg law for destructive (circles) and constructive (dots) interference. These angles correspond to the maxima and minima shown in Fig. 1, curve (a).

tive number of atoms in steps or what is equivalent the average size of the surface terraces. This was done by utilizing a titration technique consisting in decorating the surface steps with foreign atoms deposited from the vapor phase. It has been described in detail in a previous paper<sup>17</sup> and will not be discussed here. The result was 425-450 Å for the mean terrace size a value which is comparable in magnitude to the length of the coherence zone of the beam (around 350 Å, see Sec. II).

### B. The ordered lead overlayers

Starting with the clean and ordered Cu(100) substrate, Pb deposition at room temperature causes three different ordered structures depending on coverage. These are a  $c(4\times4)$ , a  $c(2\times2)$ , and a  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  that have been previously reported.<sup>1</sup> Relative to the intensity of the specularly reflected He beam before Pb deposition, the specular intensities, at the completion of these ordered structures were measured to be 0.08, 0.32, and 0.39, respectively.

The  $c(4\times4)$  structure becomes fully developed at a lead coverage of  $\frac{3}{8}$  of a monolayer<sup>15</sup> [a monolayer is defined from the atomic density of the Cu(100) substrate; thus a Pb coverage of 0.6 monolayers represents an ideally Pb adlayer that completely covers the substrate]. In addition to the specular beam, the  $(\frac{1}{2}0)$  and  $(0\frac{1}{2})$ diffracted beams were measurable. Their intensity relative to the direct beam was 0.01 at 445 K and  $\theta_i = 75^\circ$ . Due to the low intensity of the specular beam of the  $c(4\times4)$  structure, we were not able to measure rocking curves with enough quality to be properly analyzed.

The  $c(2\times 2)$  and  $c(5\sqrt{2}\times \sqrt{2})R45^\circ$  structures become fully developed at 0.5 and 0.6 deposited monolayers respectively. In both cases the scattered intensity was concentrated along the specular direction and no diffracted beams [other than the (00)] could be measured with our apparatus.

### C. The $c(2 \times 2)$ structure: Analysis of the rocking curve

Figure 3, curve (c) shows the rocking curve corresponding to the  $c(2\times2)$  structure (coverage 0.5) grown at 440 K. The data points in the figure were taken while having the surface at 467 K temperature. As in Cu(100) (Sec. III A) maxima and minima are visible. The maxima occur at incidence angles of 81.5°, 73.6°, and near 63°. The minima at 78.3° and ~68.4°. Figure 4 shows a plot of  $\cos\theta_i$  versus *n* in the same way as was done for clean Cu in Sec. III A. The resulting slope determined from the Bragg law as  $n/2k \cos\theta_i$  is  $1.97\pm0.05$  Å which is significantly different from the value of  $1.80\pm0.04$  Å obtained from the clean substrate.

The obtained value of 1.97 Å deserves some analysis in order to be rationalized. For the experiment in Fig. 3 curve (c), as the coherence length of the incoming beam is similar to the mean Cu(100) terrace dimensions, the probability of having at least one step within the coherence zone should be high. For simplicity let us assume that a coherent zone contains one step that separates an upper and a lower terrace. One may view the scattered intensity measured in Fig. 3 curve (c) as being due to



FIG. 3. Specular intensity vs incidence angle depicted in logarithmic scale for (a) the Pb monolayer  $c(5\sqrt{2}\times\sqrt{2})R45^{\circ}$  at T=504 K (disordered phase), (b) the  $c(2\times2)$  at T=553 K (disordered phase), (c) the  $c(2\times2)$  at T=467 K (ordered phase). Dots, experimental values; solid curve, eye guide. (d) Logarithmic representation of Eq. (2) with h=1.80 Å,  $E_1=0.50$  Å, and  $E_2=0.27$  Å. Dashed lines correspond to maxima positions in curves (a), (b), and (c).

(apart from some instrumental effects that do not need to be considered here) the sum over the area illuminated by the incoming beam of the coherently scattered intensities that result from the kinematical interference conditions on the scattered amplitudes in the coherence zones. Within a coherence zone, if an ordered overlayer of Pb sitting on the Cu substrate exists, then if the structure of the adlayer is identical at the upper and lower terraces one should always obtain from the rocking curve the value 1.80 Å corresponding to the Cu step height *provided* the simple Bragg law  $2hk \cos\theta_i = \pi n$  be valid. For this reason, the obtained value of 1.97 Å cannot be explained with this model and the unit-cell corrugation should be taken into account.

For a kinematical scattering approach, the specularly scattered amplitude from a coherence zone is

$$A(\Delta K, \Delta k_{\perp}) \propto \sum_{j} e^{i \Delta k_{\perp} z_{j}} e^{\Delta K(x_{j} + y_{j})}$$

where the sum extends to the coherence zone and  $z_i$ 



FIG. 4. Cosine of incidence angles vs intereference order n for the maxima (dots) and minima (circles) corresponding to curves (a), (b), and (c) of Fig. 3.

denotes coordinates along the surface normal.  $\Delta K$  is the parallel component of the scattering vector **k** with respect to the surface plane, and  $\Delta k_{\perp} = 2k \cos \theta_i$  is the perpendicular component. For the specular beam  $\Delta K = 0$ , then

$$A(0,\Delta k_{\perp}) = A \propto \sum_{j} e^{i\Delta k_{\perp} z_{j}}$$

In the mean coherence zone at the surface and within the simple above mentioned assumption, one would have for the clean Cu(100) substrate before deposition that the last expression reduces to

$$A \propto 1 + e^{i \Delta k_{\perp} h}$$

since half of the coherence zone belongs to the lower terrace (z=0) and the other half to the upper one (z=h). The last expression leads to

$$I \propto 1 + \cos(\Delta k_{\perp} h)$$

for the scattered intensity in the specular direction. Figure 1, curve (b) shows a logarithmic plot of this intensity for h = 1.80 Å. As it is visible the calculated intensity displays maxima that coincide with the experimental ones [curve (a)] within  $\pm 0.50^{\circ}$  which is the accuracy of the experimental values.

In order to extract some information on the structure of the  $c(2\times 2)$  Pb overlayer, a similar analysis has been performed but allowing additional surface levels within the coherence zone. The  $c(2\times 2)$  structure has been previously studied by LEED intensity analysis<sup>4,5</sup> and it has been found to consist of Pb atoms sitting on the hollow sites of the (100) substrate mesh. As the atomic diameter of Pb is 10% smaller than the distance between two nearest-neighbor hollow sites, the Pb atoms may sit in these sites without any lateral compression.

As it is well known<sup>18</sup> in the He scattering experiments, the He atoms "see" surface corrugations determined by constant electronic density contours of a charge density of the order of  $10^{-4}$  electrons per cubic Bohr radius. These electronic densities occur typically at distances of 3 Å beyond the plane of surface atoms.

For a  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$  unit cell, one expects to have three kinds of heights that should be relevant for the electronic corrugation of the surface: one top site height, located on top of the Pb atoms, two bridge site heights between two adjacent Pb atoms, and a hollow site height with fourfold coordination in the middle of the cell. Let us assign z = 0,  $z = E_1$ , and  $z = E_2$  to the hollow, top, and bridge sites, respectively. This is equivalent to locate the origin of the z coordinate at a distance from the surface plane of atoms on the constant contour surface above a hollow site. To obtain a rough description of the structure we are going to assume that z = 0;  $E_1$  and  $E_2$  can be considered as the most relevant variables in determining the corrugation of the unit cell. In this case the scattering amplitude from a coherence zone could be written as

$$A \propto \sum_{\substack{j \\ \text{coherence} \\ \text{cone}}} e^{i \Delta k_{\perp} z_{j}} = (1 + e^{i \Delta k_{\perp} z_{j}}) \left( \sum_{\substack{j \\ \text{terrace}}} e^{i \Delta k_{\perp} z_{j}} \right)$$
(1)

and

$$\sum_{\substack{j \ \text{terrace}}} e^{i \,\Delta k_{\perp} \, z_{j}} \propto \sum_{\substack{j \ \text{unit cell}}} e^{i \,\Delta k_{\perp} \, z_{j}}$$

$$\propto 1 + e^{i \,\Delta k_{\perp} \, E_{1}} + 2e^{i \,\Delta k_{\perp} \, E_{2}}.$$

This leads to a specular intensity given by

$$I \propto \{3 + 2\cos[\Delta k_{\perp}(E_{1} - E_{2})] + \cos(\Delta k_{\perp}E_{1}) + 2\cos(\Delta k_{\perp}E_{2})\}[1 + \cos(\Delta k_{\perp}h)].$$
(2)

By taking h = 1.80 Å as determined in Sec. III A and  $\Delta k_{\perp}$  as given by the incidence angle and the wave vector of the incoming beam, we varied  $E_1$  and  $E_2$  in order to fit the angles at which the measured maxima of Fig. 3, curve (c) occur. The result is shown in curve (d) of Fig. 3 that corresponds to  $E_1 = 0.50$  Å and  $E_2 = 0.27$  Å. As it can be observed from the figure, the measured maxima in curve (c) occur at 81.5°, 73.6°, and 64.1° and in curve (d)at 81.3°, 72.3°, and 62.7°. The fit is more sensitive to  $E_1$ than to  $E_2$  because a 15% decrease in  $E_1$  produces the extinction of the 62.7° maximum while varying  $E_2$  in the same percentage produces peak shifts of around 1°. Within variations of  $\pm 5\%$  in  $E_1$  and  $\pm 10\%$  in  $E_2$  the maxima positions are well reproduced. Taking into account the simplicity of the above analysis, the agreement can be considered as satisfactory.

In order to know if the adjusted parameters  $E_1$  and  $E_2$ are physically reasonable, a calculation of the electronic charge distribution has been performed by simulating the external p orbital of the Pb atoms by the Slater wave function

$$\Psi(r) = Nr^{n-1}e^{-\alpha r}Y_{lm}(\theta, \Psi)$$

where r,  $\theta$ , and  $\Psi$  are polar coordinates, N the normalizing factor and in our case n = 4.2 and  $\alpha = (Z - s)/n$  being Z = 82 and  $s = 3 \times 0.35 + 18 \times 0.85 + 60$ .<sup>19</sup> The results of the calculation are depicted in Fig. 5. Figure 5(a) shows several constant density contours obtained by adding charge densities from the Slater wave functions for two Pb atoms separated at 3.62 Å (the lattice parameter of the  $(\sqrt{2} \times \sqrt{2})R45^\circ$  unit cell) along the direction defined by two consecutive Pb atoms. The contour corresponding to an electronic density of  $10^{-4}$  a.u. (electrons per cubic Bohr radius) is indicated in the figure. Between two consecutive contours there is a factor-of-5 change in electronic density. As previously mentioned, thermalenergy He atoms (kinetic energy 63 meV in our case) are reflected at charge densities around  $10^{-4}$  a.u. From the contour of the figure, an electronic corrugation of 0.29 Å is obtained as it is illustrated.

Figure 5(b) shows constant electronic density contours for two Pb atoms separated at 5.12 Å (i.e.,  $3.62 \times \sqrt{2}$ ) along the diagonal of the  $(\sqrt{2} \times \sqrt{2})R45^\circ$  unit cell. The midpoint in the abscissa axis corresponds to the hollow site. From the contour at  $10^{-4}$  a.u. one obtains a corrugation of 0.50 Å from the top site to the hollow site positions. Referring to the parameters of the fitting of the rocking curve mentioned above, z = 0 would correspond to point P in Fig. 5(b) which is the deepest site in the Pb



FIG. 5. Charge-density contours for two Pb atoms along the side of the  $c(2\times 2)$  unit cell (a) and along its diagonal (b). Consecutive curves have charge-density values differenced by a factor of 5.

unit cell. Then for Fig. 5 one would obtain  $E_1 = 0.50$  Å and  $E_2 = 0.50 - 0.29 = 0.21$  Å in very good agreement with the previously obtained values. This agreement may be considered as an indication of the suitability of the analysis of the rocking curve that we performed.

In summary this section shows that from a simple analysis of the rocking curve of the  $c(2\times 2)$  Pb structure on Cu(100) at room temperature, one may obtain information on the main characteristics of the corrugations of the Pb unit cell.

As it will be described in detail in Sec. III F, the  $c(2\times 2)$  solid overlayer suffers a phase transition at T = 498-K. Curve (b) in Fig. 3 is a rocking curve recorded 55 K above the phase transition. It is virtually identical to curve (c) indicating that no important change in the surface corrugation occurs upon melting the  $c(2\times 2)$  structure.

### **D.** The $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ structure: Analysis of the rocking curve

In this section, a completely similar analysis to the one discussed in Sec. III C is presented for the highest coverage Pb structure. The  $c(5\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure was obtained by depositing 0.6 monolayers of Pb on the Cu(100) substrate at 440 K. Figure 6, curve (a) shows the data points of the rocking curves recorded while having the surface at T = 475 K. As it is visible, five maxima are resolved at 82°, 77.8°, 74.8°, 69.9°, and 63.9° and a shoulder is scarcely visible around 59.4°. Figure 7 shows the  $\cos\theta_i$  versus n plot from its slope and the Bragg law one obtains  $\pi n/2k\cos\theta_i = 4.02\pm 0.04$  Å. Again, as in Sec. III C this value cannot be rationalized in a straightforward way. Its magnitude suggests that large corrugations exists on the surface. From LEED analysis data<sup>6</sup> and from the arguments in Ref. 7, we assumed that the



FIG. 6. Curve (a) specular intensity, in logarithmic scale, vs incidence angle for the  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  at T = 475 K (ordered phase). Dots, experimental values; solid line, eye guide. Curve (b), Eq. (4) in logarithmic scale with h = 1.80 Å,  $E_1 = 2.30$  Å, and  $E_2 = 0.27$  Å.

 $c(5\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure was based in a unit mesh with some additional complications due to the matching of antiphase  $c(2\times 2)$  cells. Within the assumptions on the coherently scattered amplitude done in Sec. III C one may utilize Eq. (1) to intend extracting some information on the corrugations of the highest-coverage structure. For the scattering from a terrace, we take

$$\sum_{\substack{j \ \text{terrace}}} e^{i \,\Delta k_{\perp} \, z_{j}} \propto \sum_{\substack{j \ \text{unit cell}}} e^{i \,\Delta k_{\perp} \, z_{j}} \propto 1 + e^{i \,\Delta k_{\perp} \, E_{1}} + e^{i \,\Delta k_{\perp} \, E_{2}} ,$$
(3)

where again the first term (z=0) would correspond to the deepest surface levels (the hollow sites),  $E_1$  to the top sites, and  $E_2$  to the bridge sites. Naturally, these assignations to the E's somewhat arbitrary since the unit mesh is expected to be noticeably more complicated than the  $c(2\times 2)$  one. For reasons that will become clear below, we weighted all sites equivalent. From the above amplitude and by assuming as above that the coherence zone contains, on the average, two terraces separated by a monoatomic step, one gets for the intensity



FIG. 7. Cosine of incidence angles vs interference order for the interference maxima (dots) and minima (circles) in Fig. 6, curve (a).

$$I \propto \{3 + 2\cos[\Delta k_{\perp}(E_1 - E_2)] + 2\cos(\Delta k_{\perp} E_1) + 2\cos(\Delta k_{\perp} E_2)\}[1 + \cos(\Delta k_{\perp} h)].$$
(4)

 $E_1$  and  $E_2$  were varied to fit the angular positions where the maxima in curve (a) of Fig. 6 occur. The result of the fitting was  $E_1 = 2.3$  Å and  $E_2 = 0.27$  Å. The corresponding calculated intensity is displayed in Fig. 6, curve (b) that exhibits maxima at the values: 81.8°, 77.6°, 73.3°, 68.9°, 64.4°, and 60.4° in good agreement with the experimental values. The existence and position of the calculated maxima are very sensitive to the values of  $E_1$  and  $E_2$ . For example, an increase of 10% in  $E_1$  produces peaks shifts of 1° and the maximum at 64.4° disappears. By decreasing  $E_1$  in the same amount, the peak at 77.6° becomes neglectful. Variations in  $E_2$  presented similar characteristics. In summary, an interval of approximately  $\pm 5\%$  around  $E_1$  and  $E_2$  can be defined where the maxima positions of the experimental rocking curve are well reproduced.

Notice that the value of  $E_2$  obtained from the fit is identical to the one for the  $c(2\times 2)$  structure. However  $E_1$ , i.e., the top-hollow corrugation distance in the  $c(2\times 2)$  structure was 0.5 Å whereas for the  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  is 2.3 Å. This value is easily rationalized with a hard-sphere model for the surface structure.

Figure 8 shows a top view and side view of the unit mesh. It is basically identical to the one proposed by Moritz *et al.*<sup>6</sup> except for the positions of the two shaded atoms in the figure. In their model, those atoms were located at less than 0.05 Å from the atomic plane of the underlying Pb atoms. By locating the shaded atoms on the threefold sites without any compression (i.e., by maintaining the atomic radius equal to the bulk value of metallic Pb), the center of these atoms lies at 1.8 Å from the atomic planes of the underlaying Pb atoms as indicated in the figure. With this arrangement, the value for  $E_1$  that one obtains is 1.8+0.5=2.3 Å where the second term arises from the top-hollow corrugation. This value coincides exactly with the previous one obtained from the fit. Therefore we propose a modification of the structural



FIG. 8. Curve (a) schematic top view of the model proposed for the  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  unit cell. Dashed circles are Pb atoms "resting" on 1, 2, 3, and on 4, 5, 6 Pb atoms, 1.80 Å above their planes. The directions shown correspond to the Cu substrate. Curve (b) side view along [011] direction.

model by Moritz *et al.* consisting in "raising" the shaded atoms just for keeping their underformed atomic radii. Now it becomes clear why  $E_1$  and  $E_2$  were weighted identically in Eq. (3): in the unit cell proposed exists the same number of top sites and bridge sites.

As it will be described in detail in Sec. III G, the  $c(5\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure exhibits a phase transition at T = 490 K that has been named as melting in the literature.<sup>1</sup> An important observation is that above melting there is an noticeable change in the structure of the adlayer as deduced from the analysis of the rocking curve.

Curve (a) of Fig. 3 is the rocking curve measured 14 K above the transition temperature. As it can be seen from the figure it is practically identical with those of the  $c(2 \times 2)$  structure solid [curve (c)] and melted  $c(2 \times 2)$ [curve (b)] where only three maxima appear instead of the five maxima characteristic of the solid phase. The analysis of curve (a) leads therefore to the corrugation characteristic of the  $c(2 \times 2)$  which is an atomically flat structure. Thus this means the shaded atoms in the unit cell of Fig. 8 that are the responsible for the high corrugation of the solid phase, are not there above the melting transition. It looks as if those atoms became embedded in the atomic plane of the underlying Pb atoms. In this case, in order to accomodate those atoms without any lateral compression, the melted adlayer should exhibit a pseudohexagonal array as previously suggested by Rhead et al. in Ref. 1.

# E. Phase transition of the $c(4 \times 4)$ structure

As was shown in a previous work,<sup>15</sup> by monitoring the specular intensity of the He beam versus Pb coverage, i.e., evaporating time, allowed us to detect when an ordered structure was well developed. In the case of the  $c(4\times4)$  a more reliable method was used by choosing the  $(\frac{1}{2}0)$  or  $(0\frac{1}{2})$  diffracted peaks instead of the specular peak.

The lowest-coverage ordered structure  $c(4 \times 4)$  was complete at  $\theta = \frac{3}{8}$  within experimental error. Thermal behavior of this structure has been studied by recording specular intensity and diffracted intensities versus surface temperature. All of them had the same characteristic features, namely, an initial Debey-Waller type variation in intensity followed by an abrupt decrease in a shorttemperature range. Within experimental uncertainty, this process was reversible. On the other hand, the He specular intensity from the clean Cu surface decreased monotonously with temperature indicating that no phase change of the substrate occurred over the considered temperature range. Also, it was checked by AES and TEAS that neither Pb dissolution into the bulk nor Pb desorption took place at T < 730 K. All these facts indicate that in this range of temperature and coverage the Pb overlayer is a 2D "closed system" and the abrupt decrease in intensity of the diffracted and specular beams has to be ascribed to a phase transition within the overlayer.12

A detailed analysis required subtraction of the Debey-Waller effect and temperature-dependent background correction.<sup>13</sup> In Fig. 9, the normalized intensity resulting



FIG. 9. Normalized peak intensity and FWHM vs temperature for the  $(\frac{1}{2}0)$  beam at  $\theta = \frac{3}{8}$  ML. Circles, measured peak intensity corrected by a Debye-Waller factor; solid line, fit with Eq. (6).  $\beta = 0.003$  and  $T_c = 545$  K. Dots, measured FWHM.

for the  $(\frac{1}{2}0)$  beam is shown. The same figure presents also the measured temperature-dependent FWHM of the angular intensity distribution of the diffracted peak. The broadening of the FWHM and the inexistence of hysteresis is an indication of a continuous phase transition.<sup>12,20</sup> The theory of critical phenomena predicts that in the vicinity of the transition temperature  $T_c$ , the normalized intensity varies according to a power law,<sup>21</sup>

$$I_N(T) \propto (T - T_c)^{2\beta} , \qquad (5)$$

where  $\beta$  is the critical exponent associated with long-range order.

The real 2D system is expected to contain domains of finite size. This is due to the existence of imperfection of the substrate and possible "frozen-in" antiphase boundaries.<sup>20</sup> In addition, we introduce a finite-width Gaussian distribution of critical temperatures and fit the measured  $I_N(T)$  with the formula

$$I_{N}(T) = \frac{I_{0}}{\sqrt{2}\pi\Delta t} \times \int_{T-T_{c}}^{\infty} \left[\frac{T_{c}-T+t}{T_{c}+t}\right]^{2\beta} \exp\left[-\frac{1}{2}\frac{t}{(\Delta t)^{2}}\right] dt ,$$
(6)

 $\Delta t$  being the Gaussian distribution width and  $I_0$  a normalization constant.

For the  $(\frac{1}{2}0)$  diffracted beam of the  $c(4\times 4)$  structure, the best intensity fit, shown in Fig. 9, is obtained with the values of Table I. The values of  $\Delta t$  and  $I_0$  are reason-



FIG. 10. Peak profiles of the  $(\frac{1}{2}0)$  beam above  $T_c$ . Solid curves, parametrized Lorentzian fits; dots, measured values.

able<sup>20</sup> and  $\beta$  is practically indistinguishable from zero. The abruptness of the intensity fall already suggested a very low value for  $\beta$ . This corresponds to a logarithmical variation of the order parameter with temperature near the critical point.

In Fig. 9, the FWHM evolution of the  $(\frac{1}{2}0)$  beam with surface temperature is depicted. Below  $T_c$ , peak profiles are well described with a Gaussian curve of 0.36° FWHM. This value is attributed to the instrument response function at these diffraction conditions. Above  $T_c$ , the beam widths increase monotonously and the peak profiles fit Lorentzian curves. To evaluate the critical exponent v for  $T > T_c$ , the measured angular profiles of the  $(\frac{1}{2}0)$  beam, after subtraction of the diffuse background were compared with a parametrized Lorentzian function convoluted with an instrument response function<sup>13</sup> which was taken from the angular profile of the beam at low temperature ( $\sim 300$  K). Figure 10 represents two peak profiles above transition temperature with their respective fits. The temperature dependence of the FWHM of the adjusted Lorentzian is shown in Fig. 11. These data are then fitted for  $T > T_c$  by a power law similar to Eq.

TABLE I. Phase transition temperature  $T_c$  and critical exponent  $\beta$  for three different ordered structures of Pb/Cu(100)

Structure	Spot	$T_c$ (K)	β	$\Delta t$ (K)	I <sub>0</sub>
$c(4 \times 4)$	$(\frac{1}{2}0)$	545±5	$0.003 {\pm} 0.003$	7±2	$1.01 {\pm} 0.02$
$c(4 \times 4)$	(ÕO)	545±5	$0.003 {\pm} 0.003$	10±2	$1.01 {\pm} 0.02$
$c(2 \times 2)$	(00)	498±5	$0.003 \pm 0.003$	10±3	$1.01 {\pm} 0.02$
$\frac{c(5\sqrt{2}\times\sqrt{2})R45^{\circ}}{2}$	(00)	490±5	$0.003 {\pm} 0.003$	7±2	$1.01 {\pm} 0.02$



FIG. 11. FWHM of the  $(\frac{1}{2}0)$  short-range component vs temperature. Solid curve, power-law fit.

(5) changing the critical exponent to  $\nu$ . The obtained value is  $\nu = 1.5 \pm 0.2$ . Due to the small temperature range available, no great number of data were taken and consequently the value of  $\nu$  remains somewhat imprecise. Finally, it was also found that the position in reciprocal space of the  $(\frac{1}{2}0)$  and the  $(0\frac{1}{2})$  beams did not vary upon crossing  $T_c$ .

The specularly scattered intensity from the  $c(4\times4)$ overlayer diminished upon increasing the surface temperature and exhibited a sharp drop at  $T_c = 545$  K. Above this temperature its value was not zero and decreased continuously by increasing T. This nonzero value was due to a nonzero vanishing surface reflectivity for the He atoms indicative of surface flatness. The peak profile was Gaussian and its angular width (0.35° FWHM) remained unchanged upon crossing  $T_c$ . After Debye-Waller and reflectivity corrections, the normalized intensity was fitted as in the previous case. The fitting parameters are shown in Table I. The results are in agreement with the previous ones obtained from the diffracted beam and they confirm the value of  $\beta$ .

As a summary, the observed main characteristic features of the disordering at 545 K of the Pb overlayer are (i)  $\beta = 0$ , (ii) no hysteresis, (iii) the line shapes of the diffracted beams are Lorentzian above  $T_c$ , and (iv)  $v \approx 1.5$ . Point (i) is more characteristic of first-order transitions while (ii), (iii), and (iv) are fingerprints of second-order transitions.<sup>22</sup>

The Landau-Lifshitz symmetry rules for classifying critical phenomena would predict in this case a first-order transition due to the square symmetry of the array of substrate sites.<sup>23,24</sup>

This situation could be originated by finite-size effects that induce characteristics of continuous transitions in first-order transitions.<sup>25</sup>

### F. Phase transition of the $c(2 \times 2)$ structure

With our apparatus diffracted beams were not detected due to the lower corrugation of this structure. The study of its thermal stability was restricted to the analysis of the specular beam. It was also checked that the Pb overlayer in this coverage range constitutes a 2D closed system for T < 680 K and no hysteresis effects were noticed. The values of the best-fit parameters of the normalized intensity are shown in Table I. No broadening peaks



FIG. 12. Normalized peak intensity vs temperature for the (00) beam corresponding to a Pb monolayer. Circles, measured peak intensity corrected by a Debye-Waller factor; solid curve, Eq. (6) fit with  $\beta = 0.003$  and  $T_c = 490$  K. Dots, measured FWHM.

were detected. Landau-Lifshitz theory predicts a possible second-order phase transition to the disordered phase with a critical behavior belonging to the Ising universality class.<sup>23</sup> The Ising model predicts a  $\beta$  critical exponent of  $\frac{1}{8}$ .<sup>24</sup> Disagreement with our experimental value is obvious, what is an indication of not being a second-order transition. It appears to be first order on the basis of the experimentally available determined  $\beta=0$  value.

### G. Phase transition of the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ structure

In spite of being a highly corrugated structure no diffracted beams were found. No desorption of Pb atoms was found to occur below 580 K. A phase transition showing no hysteresis was observed at  $T_c = 490$  K. It was analyzed as in the precedent cases and the normalized intensity depicted in Fig. 12 was obtained. The solid line that fits the data points corresponds to Eq. (6) using the fit parameters of the Table I. Peak width remains constant upon crossing the temperature transition. Landau criterion is not applied to this case because no equivalent adsorption sites exist. Then,  $\beta$  exponent cannot theoretically be checked and its small value suggests a first-order transition.

#### **IV. SUMMARY AND CONCLUSIONS**

This paper demonstrates that with a very-simple analysis of the rocking curves of the different Pb structures on Cu(100), one may obtain the main characteristics of their surface corrugation.

For the  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  structure at low temperatures, it has been found that in order to fit the angles where the maxima of the rocking curve occur, a new structural model for the unit cell needs to be introduced. It is basically identical to the one proposed previously by Höesler and Moritz in Ref. 6 except that two atoms per cell are located in threefold sites at 1.8 Å above the underlying plane of the Pb atoms (see Fig. 8). Upon melting the rocking curve is practically identical to the one obtained for the  $c(2\times 2)$  structure (which is atomically flat), indicating that those atoms have become embedded in the underlying atomic plane of Pb. This is compatible with a flat and compact fluid where all the Pb atoms "touch" the Cu substrate.

On the other hand, all possible order-disorder transitions have been studied by recording the temperature evolution of the scattered intensity. The lowest-coverage structure  $c(4\times4)$ , disorders at 545 K, the critical exponent  $\beta$  is zero (indicative of a first-order transition) but it displays also some features that are characteristics of second-order transitions. The  $c(2\times2)$  and  $c(5\sqrt{2}\times\sqrt{2})R45^\circ$  structures suffer phase transitions at 498 and 490 K, respectively, both with  $\beta=0$ .

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