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Three-dimensional structure of the ordered phases of Hg on Cu(001)

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The structures of ordered phases following adsorption of mercury on Cu(001) have been identified using helium-beam scattering and low-energy electron diffraction. We found that three of the four observed ordered submonolayer phases are high-order commensurate phases. The three-dimensional structure of these phases brought about by a periodic variation of the height of the Hg atoms above the Cu(001) plane has been measured. Furthermore, from a combined analysis of helium-beam scattering and angle-resolved photoemission data for a low-density Hg ordered overlayer, we deduce and quantify the departure from the atomic electron distribution of Hg due to adsorption. A model to analyze diffraction data from all these phases is also presented. We show that second-layer structural and electronic properties are influenced by those of the first layer. Adsorption at the lowest substrate temperature obtainable proceeds in a layer-by-layer mode up to three layers.

I. INTRODUCTION

The study of lattice-mismatched materials often reveals a subtle interplay of forces.¹ Qualitatively different behaviors or effects are expected for systems in which weakly attractive forces are present (physisorption) as compared with systems in which strong, localized adsorption occurs (chemisorption). In the former regime, as exemplified by the case of adsorption of rare gases on graphite² or (111) metal surfaces,³ commensurate or triangular incommensurate structures are most often observed; in other cases, such as Ar on MgO(001),⁴ partial or high-order commensuration occurs in which only a fraction of the atoms of the ordered overlayer in the most energetically favored sites of the substrate, the other atoms lying in other non-high-symmetry sites. In the latter regime, represented, for example, by the ordered phases of oxygen on tungsten,⁵ strong, localized, fully commensurate adsorption usually occurs,⁶ though there exist a large number of exceptions.⁷

The ordered submonolayer phases of mercury on Cu(001) seem to represent an intermediate case. While adsorption is stronger⁸ than in the typical physisorption case, mercury overlayers do not exhibit large electronic rearrangements, as evidenced by angle-resolved photoemission results.^{9,10} Qualitatively similar results have also been obtained for Hg adsorption on other metals.¹¹⁻¹³

More recently, we have used atom beam scattering and angle-resolved photoemission to study the metal-nonmetal transition in monolayer and bilayer mercury on the (001) surface of copper.¹⁰ It was found that the two submonolayer mercury phases show a nonmetallic behavior in which the mercury atom hardly hybridizes with other adatoms, while the bilayer is metallic.¹⁰

Miedema and Dorleijn¹⁴ speculated that unsupported Hg monolayers should be bound chiefly by van der Waals interactions because of the large promotion energy from occupied *s*- to empty *p*-electron levels. Jansen *et al.*¹⁵ showed that an unsupported Hg monolayer should undergo an insulator-metal transition as the lattice parameter of the triangular lattice decreases below a critical value. Singh and Jones¹⁶ measured the electronic and structural properties of mercury overlayers on several transition metals and, in the case of Hg on Ni(111), confirmed the main results of the calculation of Jansen *et al.*

Here we report a complete analysis of the ordered structures of Hg on Cu(001) in the submonolayer regime. We will see that standard empirical models based on He-surface interaction potentials deduced from gas-phase data cannot reproduce the observed structures. Instead a model which uses both structural and electronic data as input will be presented and shown to be in agreement with the experimental data. An analysis will be given to quantify the departure of the Hg structures from an ideal two-dimensional (2D) overlayer. Correlations between energetics of adsorption (as deduced from atom beam scattering and temperature programmed desorption data), atomic structures, and electronic properties will be given. We will also comment on the mechanism of growth and on the influence of first-layer adsorption on structural and electronic properties of the second layer.

II. EXPERIMENT

Our apparatus consists of three main parts.¹⁷ The first is the beam formation stage, composed of three differentially pumped chambers. We use a supersonic helium beam which is obtained through the expansion of

a research grade helium gas at up to 1100 psi through a 5- μm nozzle. For these experiments the beam source has been cooled to 85 K, yielding a beam energy of 18.3 meV and a velocity distribution with full width at half maximum (FWHM) of below 1.2% at the highest pressure.¹⁸ Thus the high forward intensity and very narrow velocity distribution of these beams are well suited for studying the structure and dynamics of surfaces.

The UHV chamber is divided in two parts. At the top there is a sample preparation chamber with an argon-ion gun and a 400 l/s turbomolecular pump. On top of this chamber a long-ravel manipulator is mounted. The sample preparation chamber is separated by an 8-in. gate valve from the scattering chamber below. This chamber is pumped by a CTI 10-in. cryopump and contains the detector housing and a four-grid low-energy electron diffraction (LEED) and Auger system. The detector is a quadrupole mass spectrometer placed in a housing with a $\frac{1}{32}$ -in. collimator and differentially pumped by a turbomolecular pump. The detector and pump are placed on a 13.25-in. doubly differentially pumped platform which can be rotated by 190° around the sample. The sample can be rotated around the manipulator axis (polar angle) or its normal (azimuthal angle) and can be cooled to 120 K and heated by electron bombardment to 1200°C.

In the Hg experiments, triple-distilled Hg is introduced in the preparation chamber through an UHV leak valve. Typically, a pressure of 1×10^{-8} Torr (value uncorrected for gauge sensitivity) is maintained for the desired amount of time. Coverages are deduced with the aid of LEED and atom beam scattering (ABS) features as discussed in Refs. 8 and 13. Coverage determinations up to the first layer are more accurate than the ones for subsequent layers since the former were obtained by an analysis of LEED structures, intensity of the Hg (78 eV) Auger signal, and atom beam scattering. Thermal programmed desorption data, discussed below, show an almost constant sticking coefficient for Hg on Cu(001) up to the completion of the first layer. For adsorption at the lowest temperatures, the sticking coefficient is nearly constant up to the completion of the third layer. Otherwise, coverages quoted for phases on the second layer are deduced from the structural models proposed.

The Cu(001) sample is cleaned prior to each run by Ar-ion bombardment, first with the surface at room temperature and then at 350°C. Then the sample is annealed at 580°C and slowly cooled. The best test of the condition of the surface is the quality of the helium scattered signal. The best prepared Cu surfaces yield more than 50% of the incident beam in the specular reflection and the FWHM of the specular peak approaches the detector angular resolution, presently at 0.7°. No oscillations in polar scans (specular intensity versus incident angle) have been detected, thus indicating a rather step-free surface. The best gauge of surface cleanliness turns out to be Hg adsorption. If the surface is even only slightly contaminated and/or disordered, Hg hardly adsorbs. The reproducibility of adsorption curves, in which the specular signal is monitored as a function of time, and therefore coverage (see Fig. 8 in the next section), is used to judge the

quality of the layers formed. Once the layer is formed, little contamination occurs. The layer is removed by ramping the sample temperature to 300°C. No trace of Hg is then left on the surface as monitored by Auger electron spectroscopy.

A four-grid LEED system is used to check, when necessary, the symmetry of ordered phases and to position the sample azimuth for He-beam diffraction measurements. No effects on the deposited layers due to the electron beam have been observed.

III. RESULTS

A. High-temperature phases

In Fig. 1(a) we show the phase diagram for up to the completion of the first layer of Hg on Cu(001). Shown

FIG. 1. (a) Phase diagram for Hg adsorbed on Cu(001) at surface temperature $T > 200$ K. Empty symbols show beginning of an ordered phase; filled symbols are maxima in ABS or LEED diffraction spots. Only a few representative points are shown. The line at $T = 200$ K is the coexistence of two energetically different Hg phases from TPD data. (b) Same as in (a) but for $T < 200$ K. Crossed region: various phases coexist; cross-hatched region: disordered phase. The bottom part of the figure shows a (0, -1) He diffraction peak intensity for the (3 $\times$ 3) phase vs Hg coverage.

FIG. 2. He diffraction peaks for the $c(2 \times 2)$ phase. $\theta_i = 60^\circ$, $E_i = 18.3$ meV. In the inset: a schematic drawing of the $c(2 \times 2)$.

are a few representative points of maximum intensity of LEED or ABS diffraction spots. For temperatures greater than about 300 K a net desorption of mercury occurs under UHV conditions. The proposed structures, following an analysis of LEED and ABS data, are given in Figs. 2 and 3. Diffraction peaks are labeled according to the reciprocal lattice vectors of the overlayer. Preliminary reports on the $c(2 \times 2)$ [coverage of 0.5 of Cu(001)] and the $c(4 \times 4)$ (coverage of 0.62) have been published

FIG. 3. Same conditions as in Fig. 2; but for the $c(4 \times 4)$ phase. In the inset, Hg atoms in high-symmetry sites are shaded; the other Hg atoms are in black. The $(0, -2)$ peak belongs to both the $c(2 \times 2)$ and $c(4 \times 4)$ phases.

recently,^{8,10,19-21} therefore, here we will mainly discuss in detail the results of our analysis using a method described in the next section.

We point out that the $c(4 \times 4)$ is actually a high-order commensurate structure consisting of a mercury square net (lattice parameter $a = 3.22$ Å) rotated by 18.4° with respect to the $\langle 110 \rangle$ direction of Cu; the supercell contains five atoms, of which four are not in high-symmetry sites of the substrate. In the range of coverage and temperature studied, the $c(4 \times 4)$ phase coexists with the $c(2 \times 2)$. Since at a given energy the LEED spots of the $c(2 \times 2)$ constitute a subset of the $c(4 \times 4)$, we cannot use LEED data to check whether the two phases coexist or not. On the other hand, ABS diffraction patterns for the $c(2 \times 2)$ and $c(4 \times 4)$ are different. Specifically, it is shown in Fig. 4 that a $c(4 \times 4)$ diffraction peak emerges while the $c(2 \times 2)$ one does not disappear. It is hard to quantify the amount of each phase present, since it happens that the $(0, -2)$ peak of the $c(4 \times 4)$ is coincident with the $(0, -1)$ peak of $c(2 \times 2)$. On the other hand, we think, based on an analysis of all the $c(4 \times 4)$ peaks, that the $(0, -2)$ peak (which is a third-order peak) should be much smaller than the $(0, -1)$ peak of the $c(2 \times 2)$ (which is a first-order peak). Further evidence is provided by thermal programmed desorption (TPD) data.²² The horizontal line at about 200 K [Fig. 1(a)] shows the coexistence region between two energetically different arrangements of atoms as determined by analysis of TPD data.²² If tentatively we identify these two phases observed in TPD with the two actual structures, i.e., $c(4 \times 4)$ and $c(2 \times 2)$, then the coexistence region is wider than the one obtained from LEED and ABS measurements. At present, it is unclear whether this discrepancy is due to the higher sensitivity of TPD to low-coverage energetically different phases or other factors, such as stabilization of different types of ordered structures by different density and/or types of defects of the two samples.

FIG. 4. Diffraction peaks of the $c(2 \times 2)$ and $c(4 \times 4)$ phases are plotted as a function of Hg exposure. Surface temperature is 225 K, $\theta_i = 60^\circ$.

B. Low-temperature phases

In Fig. 1(b) we show the phases obtained upon Hg adsorption on Cu(001) held below 200 K. These are labeled (3×3) and $c(2 \times 6)$ (ideal coverage of 0.66 and 0.83, respectively), where this notation indicates the symmetry of the superstructure cell. The (3×3) is a metastable phase in the sense that upon warming it converts into $c(4 \times 4)$, but cannot be obtained by cooling from the high-temperature phases. This happens for the $c(2 \times 6)$ as well and is confirmed by TPD results.²² Otherwise, these phases appeared to be stable during our experiments and reproducible under various adsorption conditions. A narrow, disordered phase separates the (3×3) from the $c(2 \times 6)$; the loss of the (3×3) order is very abrupt, as measured by the disappearance of the ABS diffraction peaks of the (3×3) phase [Fig. 1(b)]. Furthermore, the bottom panel of Fig. 1(b) shows that Hg atoms form (3×3) islands readily, since diffraction peaks are observed at very small coverages.

The structures deduced from LEED and ABS data are shown in Figs. 5 and 6. In all these phases but the $c(2 \times 2)$, ABS diffraction peaks are chiefly due to the modulation in the z direction of (i.e., perpendicularly to) the Hg layer because of the occupation of nonequivalent sites. An analysis of these diffraction patterns yielding the amount of “buckling” or “rumpling” of the overlayer in the z direction is given in the next section. Notice that this information is not easily extracted from LEED data,

FIG. 5. Same conditions as in Fig. 2, but for the (3×3) . In the inset, shading of Hg atoms indicates different heights of Hg atoms vs the Cu(001) plane. The supercell is also indicated. $|a_1| = 3.6 \text{ \AA}$, $|a_2| = 5.7 \text{ \AA}$, $\alpha = 71.6^\circ$.

FIG. 6. (a) Same conditions as in Fig. 2, but for the $c(2 \times 6)$. A schematic LEED pattern is shown in (b). In the drawing of the real space structure, shaded atoms are Hg atoms in high-symmetry sites. The lines indicate the supercell, $|a_1| = 5.1 \text{ \AA}$, $|a_2| = 8.1 \text{ \AA}$, $\alpha = 71.6^\circ$.

since a calculation fitting the spot intensities is prohibitively lengthy for such complicated structures and acceptable convergence of theory with experiment doubtful.

C. Second-layer structures and multilayer adsorption

Figure 7(a) shows the structure of the second layer when it is formed on top of the $c(4 \times 4)$ structures. Atoms in the second layer form, at low coverage, a “true” low-coverage $c(4 \times 4)$.²¹ In our model, atoms go in the depressions of the first-layer supercell due to first-layer buckling. The bilayer has been shown to be metallic.¹⁰ When the second layer is formed on top of the $c(2 \times 6)$ (which occurs for adsorption on a low-temperature substrate), a different LEED pattern is obtained [Fig. 7(b)]; Fig. 7(c) shows ABS diffraction peaks from this low-temperature adsorbed second layer. From an analysis of both LEED and ABS data, we propose the structure shown in Fig. 7(b).

Figure 8 shows an ABS adsorption curve. Here the specular intensity of the helium beam is monitored as a

function of exposure to Hg and, therefore, coverage [the initial sticking coefficient is constant and near unity as measured by TPD (Ref. 22)] and is indicative of a mobile precursor stable to adsorption. The very sharp drop of the He reflected signal occurring at the beginning of the deposition is due to the larger cross section Σ for He scattering from an isolated Hg atom.²³ An analysis of this type of data was presented elsewhere¹⁹ and gave $\Sigma = 50 \text{ \AA}^2$. The reflected signal is observed to peak at the completion of ordered structures as indicated in the figure. The fact that the He specular signal does not re-

FIG. 7. (a) He diffraction and proposed structure for a second Hg layer adsorbed on top of the $c(4 \times 4)$. (b) Observed LEED pattern and proposed real space structures are also shown for second layer on top of $c(2 \times 6)$. $\alpha = \tan^{-1}(\frac{1}{2})$, shaded atoms are first-layer atoms [see Fig. 6(b)], dark atoms are second-layer atoms. (c) shows the He diffraction pattern from the second layer on top of the $c(2 \times 6)$.

FIG. 8. Hg adsorption monitored by He specular reflectivity vs exposure. In the inset, signatures of completion of three layers are seen. Main panel: He specular peak for in-phase ($\theta_i = 50^\circ$) and out-of-phase ($\theta_i = 57^\circ$) conditions. Surface temperature is 150 K.

cover to the value obtained for the clean copper surface is due to the smaller Debye temperature of the overlayer [measured to be about 134 K for the $c(2 \times 2)$ and likely lower for the second layers] and due to defects in the layer (the curve in the figure was obtained in real time with no annealing). In the inset, the ABS adsorption curve shows the layer-by-layer growth up to three layers. This has been confirmed by analyses of the Auger Hg (78 eV) peak versus exposure¹⁸ and angle-resolved photoemission data.⁹ Very similar results (layer-by-layer growth) have also been observed for Hg on Ag(100).¹³ Although we cannot exclude it, we think that little or no growth in the next layer occurs before the current layer is completed. In fact, peak shape analysis, TPD, and Debye-Waller data are consistent with a layer-by-layer growth up to the third layer.

We took adsorption curves for different angles of incidence (θ_i) of the beam; two adsorption curves are shown for in- and out-of-phase conditions. In the first curve, the incident angle is chosen so as to have constructive interference in the reflection of He from Hg islands and the Cu plane; in the second, destructive interference is observed. The condition for maximum constructive interference is given by $2hk \cos \theta_i = 2n\pi$ (n , integer),²⁴ h denotes step height, k is the He-beam wave vector. From the difference in angles and knowing the incident wave vector ($5.93 \pm 0.08 \text{ \AA}^{-1}$), we obtain that the Hg layer is, on average, about $2.4 \pm 0.1 \text{ \AA}$ above the Cu plane, where the error comes from a conservative estimate of where the maxima and minima of intensity occur in an intensity versus incidence angle plot.

IV. ANALYSIS OF THE ABS DIFFRACTION DATA

In order to interpret the ABS data, an interaction potential for the He-Hg overlayer-Cu substrate system has to be developed. Furthermore, to understand the ener-

getics of Hg adsorption, a Hg-Cu(001) interaction potential has to be built as well. Most of the discussion is devoted to the analysis of the $c(2 \times 2)$ phase, where no buckling takes place and firm conclusions from analyses of photoemission data¹² can be used.

A. Construction of the Hg-Cu(001) potential

We used standard combination rules to determine the parameters of the Hg-Cu potential from the Lennard-Jones 6-12 potentials of Hg-Hg and Cu-Cu. For the Hg-Hg potential parameters we took the spectroscopic determination of the Hg-Hg well depth and position of the energy minimum of van Zee, Blankespoon, and Zwier.²⁵ For Cu-Cu we used a Lennard-Jones 6-12 potential fitted to embedded atom method functions given in Ref. 26. We obtained the following parameters for a Lennard-Jones Hg-Cu pair potential: $\sigma = 2.69$ Å, and $\epsilon = 99.6$ meV. The laterally averaged Hg-Cu(001) potential has a ground-state energy of 543 meV in good agreement with isosteric heat data at low coverage, 500 ± 50 meV,⁸ which was obtained by measuring the adsorption isobars from room temperature upwards; on the other hand, TPD (Ref. 22) gives a much larger value of 0.74 eV but includes activation barriers to desorption. The z position of the potential minimum, $z_{\min} = 2.65$ Å, is comparable with the result obtained above from ABS interference measurements.

B. Construction of the He-Hg $c(2 \times 2)$ -Cu(001) potential

To obtain the He-Hg overlayer plus Cu(001) potential we need to sum the He-Hg pair potential over all Hg atoms and then sum the He-Cu(001) interaction. We took the spectroscopic data of Duval, Jouvet, and Soep²⁷ for the ground state of the He-Hg dimer: $E_0 = 0.99$ meV and $R_{\min} = 4.6$ Å and used it to produce a Lennard-Jones 6-12 potential. For the He-Cu(001) potential we considered the attractive term of the He-Cu(001) interaction [$\sim -c_3/(z - z_0)^3$, see Ref. 28 for details] since the repulsive part has no contribution at these distances. By summing the He-Hg layer contribution to this term we obtain a complete He-Hg plated-Cu(001) potential.

First, we present a qualitative analysis of the $c(2 \times 2)$ structure. The He-Hg $c(2 \times 2)$ -Cu(001) potential gives a well depth, 5.5 meV, typically encountered in the interaction of He with metal surfaces.²⁸ If we evaluate this potential at the classical turning points of a He atom of kinetic energy of 19 meV, we obtain a corrugation, or modulation, of the repulsive part across the unit cell as a function of the perpendicular coordinate z , of 0.9 Å from top to fourfold hollow site (in a quantitative comparison, one should calculate all the diffraction intensities—this will be done below). Even if we take into account that the functional form of the Lennard-Jones potential usually exaggerates the corrugation, we find that this value of 0.9 Å is rather large for a metal surface. If we calculate the corrugation using experimental data and the eikonal scattering theory (see below for details), we get a value of 0.13 Å. Evidently this large difference, 0.9 versus 0.13 Å, cannot be ascribed alone to the use of the eikonal approximation in calculating the scattering intensities (on the

contrary, the eikonal approximation is believed to give reliable results²⁹ in this regime of weak diffraction).

C. The effective-medium-theory model

Since this empirical method did not work, we decided to use the so-called effective medium theory (EMT), in which the interaction potential near the classical turning point of an approaching He atom is directly proportional to the charge density of the overlayer at that point.^{30–32} In its simple form EMT gives for the repulsive part of the interaction

$$V(x, y, z) = \alpha \rho(x, y, z) \quad (1)$$

where ρ is the electron charge density of the solid, and α is a constant which depends on the incoming atom, for He being 53 eV Å³. It has been shown^{33,34} that Eq. (1) can be derived using different and independent methods. Although the usefulness of applying this method to interpret atom beam scattering data has been questioned,³² it gives reasonable results if the charge density is known accurately.^{35,36} For example, we were successful in fitting our experimental ABS data for an ordered lead layer on Cu(001) using the superposition of charge densities of lead atoms.³⁷ However, one should keep in mind that, when discrepancies arise with experimental data, other factors might influence the final results.^{38,39}

A good approximation to the actual surface charge density seen by the He atom can be obtained by summing the individual atomiclike contributions of the top-layer atoms (if no charge transfer is involved between adsorbate atoms or between an adsorbed atom and an atom of the substrate).³² We used the Herman-Skillman values⁴⁰ to obtain the tail of the charge distribution of a Hg atom. Again, we obtain a very large value of the corrugation, 0.4 Å from top to fourfold adsorption site. The discrepancy between this value and the experimentally determined one (0.13 Å) is too large to be ascribed just to the typical encountered discrepancies between experimental values and EMT results.³⁸ The conclusion we draw from our analysis is that even in the simple case of the $c(2 \times 2)$ structure, where the almost closed-shell Hg atoms are far apart from one another—3.6 Å as compared to a nearest-neighbor distance of 3.0 Å in solid mercury—one cannot assume that Hg will maintain an atomiclike electronic structure. Similarly, it has been shown, in the case of the (001) surface of MgO,³⁶ that intercrystal charge densities have to be used, rather than the atomiclike ones.

The clue on how to improve upon our interaction potential comes from the observation that photoemission data indicate a screening of the Hg 5d orbitals larger than the atomic case. A model interpreting photoemission data is given in detail elsewhere.⁴¹ Here we will summarize its salient features.

The photoemission screening length (to which all electrons contribute but which is dominated by 6s and 6p electrons) is proportional to the density n_s of conduction electrons (6s and p electrons) as

$$l_s = \frac{2\pi e^2 n_s}{\kappa E_d} \quad (2)$$

where κ is the dielectric constant of the film and E_d is the diffusion energy.⁴¹ For a photoemission (excitonlike) core-hole pair, a trial wave function (for the 2D film) of the type

$$\phi(r) = N \exp(-\beta r) \quad (3)$$

can be used to describe the extent of the core-hole photoelectron pair. Screening will affect the overlap of the Coulomb potential between the hole and the excited electron, resulting in a change of the partial cross section. The photon energy of the delayed maximum in the partial cross section $E = E_{\max} - E_{\text{onset}}$ is roughly proportional to l_s , which allows us to obtain β^2 since $\beta^2 \propto 1/l_s$ when orbital hybridization changes are neglected (i.e., for a nonmetalliclike layer). We can therefore estimate the change in β from the cross-section maximum shift of a shallow core-level partial cross section. For the mercury 5d levels $E_{\text{onset}} \simeq 15$ eV, while $E_{\max}$ is 37 eV for atomic Hg and 55 eV for the $c(2 \times 2)$. This implies a change of β of 0.74. In the z direction, no changes need to be invoked. This analysis suggests that the charge density of each Hg atom probed by the He atom, consisting essentially of electrons from s and p levels, is an ellipsoid.

Our conclusion is that the shape of the individual Hg atoms adsorbed on Cu(001), as determined by a constant-electron-density contour, is not spherical as it would be for isolated Hg atoms. The following analysis takes into account this asymmetry. From Ref. 42, we write

$$\begin{aligned} V(x, y, z) &= \alpha \rho(x, y, z) + V_a(x, y, z) \\ &= \alpha \sum_i \rho_i(x, y, z) + V_a(x, y, z) \end{aligned} \quad (4)$$

and

$$\rho_i(x, y, z) = \rho_0 \exp[-(\lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2)^{1/2}], \quad (5)$$

where ρ_i is the charge density of a Hg atom, and λ_x , λ_y , and λ_z are coefficients for the decay of the atomic charge density. V_a is the attractive part of the potential which can be written as

$$V_a(x, y, z) = - \sum_j \frac{C_6}{r_j^6} f_6(r_j) - \frac{C_3}{z^3} f_3(z), \quad (6)$$

where $f_{6,3}$ are damping functions which have been calculated elsewhere.⁴³ We are interested in evaluating the charge density profile across the unit cell for a value of the charge density given by^{31,36}

$$\rho = \frac{E_{\text{inc}}}{\alpha} \simeq \frac{18.3 \text{ meV}}{53 \text{ eV } \text{\AA}^3} \simeq 3.5 \times 10^{-4} \text{ \AA}^{-3}. \quad (7)$$

For each x, y point in the unit cell we solve for z , obtaining the profile shown in Fig. 9(a). We then use the profile determined above as a "corrugation function" for a scattering calculation. This profile essentially represents the locus of points where the He atom is repelled back in the gas phase. A close-coupling calculation is then performed to obtain the probability of diffraction of a helium atom in the various elastic channels. In the calculation we keep $\lambda_z = 2.62 \text{ \AA}^{-1}$ as given by the Herman-Skillman

tables and we let $\lambda_x = \lambda_y$ be a free parameter. A fit to experimental ABS data (corrected for the Debye-Waller effect) (Ref. 19) gives $\lambda_x = 2.2 \text{ \AA}^{-1}$, see Table I. Data and calculations are shown for $\theta_i = 60^\circ$ and $E_i = 18.3 \text{ meV}$. Little variation in the overall diffraction pattern is observed for $50^\circ < \theta_i < 70^\circ$. The preexponential factor is adjusted to give a well depth of 5.5 meV, as obtained from the summation of Lennard-Jones potentials described above. Therefore the ratio λ_x / λ_z gives a measure of the ellipticity of the Hg electron charge density probed by the He atom. This value, 0.84, should be compared with the value of 0.74 obtained from an analysis of resonant photoemission features, as discussed above. Exact agreement would be surprising since photoemission is a final-state spectroscopy, while ABS probes a surface potential close to the photoemission initial state.

We should remark that this simple model, although it gives the main features of the corrugation, yields too small a value for the $(-1, -1)$ peak, see Table I. No

FIG. 9. (a) Hg $c(2 \times 2)$ layer profile obtained from superposition of Hg charge densities, Eq. (5). (b) Best-fit corrugation function [Eq. (8)] profile.

change in λ_x (or even λ_z or the preexponential factor) could fit all the peaks, although a simple corrugation function such as

$$\xi(x,y) = \xi_{0,1} \left[\cos \left[\frac{2\pi}{a} x \right] + \cos \left[\frac{2\pi}{a} y \right] \right] + \xi_{1,1} \cos \left[\frac{2\pi}{a} x \right] \cos \left[\frac{2\pi}{a} y \right] \quad (8)$$

with $a = 3.6 \text{ \AA}$ and $\xi_{0,1} = 0.032 \text{ \AA}$, $\xi_{1,1} = 0.015 \text{ \AA}$ could. This function yields a profile very similar to the one from charge density summation, especially in terms of peak-to-valley corrugations, see Fig. 9(b). This is indicative that, in order to obtain the experimental value for $(-1, -1)$, we need to make changes in the shape of the charge density profile. These changes are quite subtle, since the charge density method and Eq. (8) give very similar peak-to-valley corrugation. Nonetheless, these changes cannot be obtained using the model summarized in Eq. (4). We turn to photoemission data to obtain clues as the possible nature of these subtle changes in the ABS diffraction pattern.

In angle-resolved photoemission, a Δ_1 [$a C_{4v}$ point-group representation of states of symmetry (s, p_z, d_{z^2})] character density of states is observed near E_F and below E_F for Hg on Cu(001) (Ref. 10) for the $c(2 \times 2)$, $c(4 \times 4)$, and (3×3) structures; these features are highly localized states and are believed¹⁶ to be a result of the multiconfigurational ground state of Hg.⁴⁴ Such localized states would certainly affect ABS since the principal contributions to these states are $6s$ and $6p$ wave functions.⁴⁰ Since this trend is observed also for the other

structures, see below, one might conclude that the smoothness of the charge density functional form chosen cannot give higher Fourier components large enough to reproduce the experimental data. While for the other phases we must wait for a better determination of the He-Hg potential, we show below that a semiquantitative analysis of departure of these phases from ideal two dimensionality can be carried out with a little computational effort.

The analyses of the other structures are intrinsically more complicated because some of the Hg atoms are out of registry with respect to Cu(001). Our method is similar to the one described above except $V_a = 0$ (Ref. 45) and we use the eikonal approximation. Hg atoms are placed on the Cu(001) lattice according to the calculated Hg-Cu(001) potential. Because not all Hg atoms reside in the fourfold hollow sites, the actual charge density profile "seen" by a He atom is due to both the "shape" of the Hg atoms [as for the $c(2 \times 2)$ phase discussed above] and the shift in the z direction of the whole Hg atom due to the corrugation of the Cu surface. These structures are significantly more compact than the others; in fact, one, the $c(2 \times 6)$, is metallic.⁴⁶ For these structures the photoemission analysis presented above is no longer valid as the above theory is (for photoemission) based on a simple spherical screening approximation to an oversimplified potential for the photohole. Consequently, we have no choice but to take $\lambda_x = \lambda_y = \lambda_z$. Mercury atom positions are relaxed in the z direction to obtain the best fit. These z values are higher for some phases, such as the (3×3) , than for the ones calculated using the Hg-Cu pair (Lennard-Jones) potential. This is expected both because the values from the potential should be considered as in-

TABLE I. Experimental and calculated diffraction probabilities as percentage of specular peak. Experimental diffraction peaks have been extrapolated to 0 K using the Debye-Waller formula given in Ref. 19. The ξ and ΔZ 's units are $\text{\AA}$ and λ 's units are $\text{\AA}^{-1}$. Most of the data presented are for $\theta_i = 60^\circ$ and $E_i \approx 18.3 \text{ meV}$.

$c(2 \times 2)$				(3×3)			
Calculated I_G/I_0				Calculated I_G/I_0			
(m,n)	Experiment I_G/I_0	Charge density $\lambda_x = 2.21$ $\lambda_z = 2.622$	Corrugation function $\xi_{01} = 0.032$ $\xi_{11} = 0.015$	(m,n)	Experiment I_G/I_0	Charge density $\lambda = 2.622$ $\Delta Z = 0.23$	Corrugation function $\xi_{01} = 0.08$ $\xi_{11} = 0.025$ $\xi_{12} = 0.024$
$(0, -1)$	4.2	4.2	4.2	$(0, -1)$	24.4	24.1	24.2
$(-1, -1)$	1.1	0.38	1.2	$(-1, -1)$	2.6	6.0	2.83
				$(-1, -2)$	3.2	0.6	3.02
$c(4 \times 4)$				$c(2 \times 6)$			
(m,n)	Experiment I_G/I_0	$\lambda = 2.622$ $\Delta Z = 0.1$	$\xi_{01} = 0.02$ $\xi_{02} = 0.037$ $\xi_{03} = 0.015$ $\xi_{11} = 0.022$ $\xi_{21} = 0.02$	(m,n)	Experiment I_G/I_0	$\lambda = 2.622$ $\Delta Z = 0.04$	$\xi_{01} = 0.009$ $\xi_{10} = 0.015$ $\xi_{02} = 0.017$ $\xi_{03} = 0.011$ $\xi_{12} = 0.013$
$(0, -1)$	1.4	1.5	1.39	$(0, -1)$	0.2	0.28	0.25
$(0, -2)$	4.8	0.15	4.76	$(-1, 0)$	0.7	0.087	0.83
$(0, -3)$	0.7	0.07	0.71	$(0, -2)$	1.1	0.021	1.17
$(-1, -1)$	1.1	0.6	1.09	$(0, -3)$	0.6	0.002	0.58
$(-2, -2)$	1.1	0.05	1.15	$(-1, -2)$	0.7	0.013	0.8

dicative rather than a firm prediction, and, perhaps more importantly in this case, because of the presence of the other Hg atoms. In fact, the metallic $c(2 \times 6)$ phase shows a considerably lesser buckling than the (3×3) , consistent with the itinerant band structure and close packing of Hg.

The effect of rumpling is typically the dominant effect as far as the He diffraction pattern is concerned. To check this quantitatively, we calculated the diffraction pattern from the (3×3) with a Δz relaxation of only 0.05 Å and obtained a much lower diffraction intensity pattern, for example, the $I(0, -1)/I(0, 0)$ is now 1%. By using different parameters and fitting functions we checked that the *first-order diffraction peak is indeed the one which dominates the overall corrugation profile*; the other peaks have an influence mostly on the details of the shape.

Experimental and calculated diffraction probabilities for the $c(4 \times 4)$, (3×3) , and $c(2 \times 6)$ phases are reported in Table I, together with the amount of relaxation obtained from the charge density model. We also reported the results of fitting the diffraction peaks with a more flexible function which is usually employed in this type of analysis:

$$\xi(x, y) = \sum_{\mathbf{G} (\neq 0)} \xi_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{R}}. \quad (9)$$

This function fits the peaks very well on account of the fact that more fitting parameters are used and subtle change in shapes are accommodated. We find that the fitting of the smaller peaks is largely independent of fitting of the first-order peaks, in agreement with our conclusions above. The overall corrugation for each structure is very similar to the results of the charge density model, see Table I.

V. DISCUSSION

He diffraction from a Hg overlayer gives some unexpected results. First, it is well known that He diffraction from compact, unreconstructed surfaces of fcc metals is negligible [including Cu(001)].²⁹ In our case, we observe that diffraction features are dominated by the relaxation of Hg atoms with respect to an ideally flat, on an atomic scale, Cu(001) surface. Second, while Hg can be considered to be an almost closed-shell atom with a weak interaction with the substrate, the diffraction patterns clearly show that the overlayer *cannot* be described in terms of a collection of unperturbed Hg atoms. Independent analysis of ABS and photoemission data shows that there is an enhanced spreading of Hg charge density on the Cu(100) plane rather than perpendicular to it. Third, the charge density method (using the superposition of atomiclike charge densities), while giving the overall corrugation, does not seem to be able to give the subtle changes of the shape of the electron density profile which are responsible for the smaller diffraction peaks.

The rumpling of the Hg first layer has an effect on the

structure of the second layer. For example, when Hg is adsorbed at $T > 200$ K, the second-layer atoms form a (low-coverage) $c(4 \times 4)$ with Hg atoms likely positioned in the depressions caused by the registered atoms of the first layer, see Fig. 7(a). This bilayer has a two-dimensional band structure and photoemission final-state screening characteristic of a very itinerant band structure (i.e., metallic).

Similarly, when Hg is adsorbed on top of the $c(2 \times 6)$ nearly hexagonal-close-packed structure, a quasihexagonal overlayer is formed, a different structure than for the second layer obtained at high temperature. Because of the large effect of the Debye-Waller factor for this loosely bound second layer, the ABS diffraction intensities were too low to be used in a detailed structural analysis. Based on the LEED pattern and the measured ABS peaks, we propose the structure shown in Fig. 7(b). Contrary to what has been observed for the adsorption of Hg on the Ni(001) surface, but similar to Hg on Ag(001),¹³ both the first- and second-layer structures are not simply related to planes of orthorhombic bulk solid mercury.

VI. SUMMARY

Here are the main conclusions of our study: (1) four ordered phases are observed up to one layer coverage of Hg on Cu(001); Hg adsorbs rather weakly (0.5 eV) with attractive Hg-Hg interaction; (2) the large lattice mismatch causes Hg to form mostly high-order commensurate phases; the amount of buckling of these phases has been measured; (3) the first-layer structure influences the growth of the second layer; (4) even in the low-coverage phase, the outermost Hg electron shell is distorted from the gas-phase case; calculations fitting ABS data and, independently, photoemission data point to an elliptical spreading of the Hg charge parallel to the surface with an aspect ratio of 1.2 to 1.3.

We also showed that, at least for this type of system, a more sophisticated calculation of the surface charge density is needed. It is possible that in these insulating phases [all except the $c(2 \times 6)$], charge localization produces extra features which cannot be obtained by a naive summation of unperturbed atomiclike charges. In fact, periodic charge localization for the $c(2 \times 2)$, $c(4 \times 4)$, and (3×3) phases would explain the anomalous ABS results, as well as provide a basis for the presence of the observed *localized* density of states near E_F in photoemission.¹⁰

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FIG. 3. Same conditions as in Fig. 2; but for the $c(4 \times 4)$ phase. In the inset, Hg atoms in high-symmetry sites are shaded; the other Hg atoms are in black. The $(0, -2)$ peak belongs to both the $c(2 \times 2)$ and $c(4 \times 4)$ phases.

FIG. 5. Same conditions as in Fig. 2, but for the (3×3) . In the inset, shading of Hg atoms indicates different heights of Hg atoms vs the Cu(001) plane. The supercell is also indicated. $|a_1| = 3.6 \text{ \AA}$, $|a_2| = 5.7 \text{ \AA}$, $\alpha = 71.6^\circ$.

FIG. 6. (a) Same conditions as in Fig. 2, but for the $c(2 \times 6)$. A schematic LEED pattern is shown in (b). In the drawing of the real space structure, shaded atoms are Hg atoms in high-symmetry sites. The lines indicate the supercell, $|a_1| = 5.1 \text{ \AA}$, $|a_2| = 8.1 \text{ \AA}$, $\alpha = 71.6^\circ$.

FIG. 7. (a) He diffraction and proposed structure for a second Hg layer adsorbed on top of the $c(4 \times 4)$. (b) Observed LEED pattern and proposed real space structures are also shown for second layer on top of $c(2 \times 6)$. $\alpha = \tan^{-1}(\frac{1}{2})$, shaded atoms are first-layer atoms [see Fig. 6(b)], dark atoms are second-layer atoms. (c) shows the He diffraction pattern from the second layer on top of the $c(2 \times 6)$.