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Order-disorder transition of the $c(2\times2)$ phase in the Pb/Cu(110) system: Significance of surface defects

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The tight-binding method has been combined with Monte Carlo simulations to study the structure and order-disorder transition of a Pb half-monolayer on a Cu(110) surface. Using coverage dependent lateral interactions a low-temperature $c(2\times2)$ structure and its transition to a disordered state was obtained. The general behavior of the two-dimensional (2D) order-disorder transition was found to be in very close agreement with experimental findings. Equilibrium surface Pb-Cu alloying was also observed during the disordering transition. The critical behavior of the system is shown to depend crucially on the initial order in the 2D overlayer: a continuous Ising type with initially perfect $c(2\times2)$ ordering, and first-order when in the initial configuration of the adlayer, has ''frozen-in'' distortions. [S0163-1829(98)03740-0]

I. INTRODUCTION

The growth of Pb and its overlayer structure on a Cu (110) surface has been the subject of many experimental and theoretical studies.[1–11] This two-dimensional system exhibits a large variety of structural phase transitions in the submonolayer range of coverage θ. Below $\theta<0.35$ Pb adatoms partly substitute the Cu atoms of the outermost layer and form a lattice gas.[7] Close to one monolayer, but in a quite narrow range, $0.75<\theta<0.80$, the system forms a series of $p(n\times1)$ superstructures ($n=4,5,9,13,17$) that have been observed recently by thermal energy atom scattering measurements.[3,4] Scanning tunneling microscopy thermal energy atom scattering (TEAS) studies[9,10] revealed that the above superstructures are formed by regular sequences of rows of Pb atoms that entirely substitute $\langle 100\rangle$ rows of Cu atoms. In the middle coverage range $\theta\approx0.5$ the appearance of $c(2\times2)$ diffraction patterns have been observed, indicating island growth of this phase at coverages $\theta>0.37$ with Pb emerging from the surface Cu lattice.[7,8] At its saturation coverage $\theta_{sat}=0.5$ the Pb $c(2\times2)$ structure undergoes with temperature an order-disorder transition. From symmetry arguments applied to the lattice model the phase transition ''$c(2\times2)$–disorder state'' is expected to belong to the Ising universality class.[12] With increasing temperature a surface alloying of Pb $c(2\times2)$ with Cu could take place even at θ_{sat}. This may influence its disordering phase transition behavior. Recent TEAS measurement[5,6,8] indicated an order-disorder transition at $T=437$ K. The determined critical exponents γ and ν associated with short-range correlation show a good coincidence with the theoretical prediction of the Ising universality class, while a strong deviation of the critical exponent β that describes the decay of the long-range order is observed. In the present paper, it is demonstrated that Monte Carlo (MC) simulations using energies computed via a tight-binding model reveal a Pb $c(2\times2)$ structure at saturation coverage $\theta_{sat}=0.5$ on the Cu(110) substrate. Also found is an occurrence of order-disorder phase transition. The corresponding critical temperature is calculated and the nature of the ordering is discussed.

II. MODEL

The tight-binding model (TBM) has been shown to be an appropriate way to account for the bulk interactions in the case of transition metals.[13,14] It has also been used to investigate properties of transition-metal surfaces[15,16] and microclusters.[17,18] Applying TBM some very good results have also been obtained for s,p metals such as Al and Pb.[14,19] In TBM the atom-atom interactions are described as a combination of a short-range repulsive pair potential plus an effective band term. In this approach the total cohesive energy is written for an atom i:

$$E_i=E_i^r+E_i^b, \tag{1}$$

with E_i^r being the repulsive energy given by

$$E_i^r=\sum_{j,\mathbf{r}_{\alpha\beta}<\mathbf{r}_c} A_{\alpha\beta}\exp\left[-p_{\alpha\beta}\left(\frac{\mathbf{r}_{ij}}{\mathbf{r}^0_{\alpha\beta}}-1\right)\right], \tag{2}$$

where α,β denote the chemical nature of atoms, $r_{\alpha\alpha}$ is the first-neighbor distance of the pure metal, and $\mathbf{r}^0_{\alpha\beta}=(\mathbf{r}_{\alpha\alpha}+\mathbf{r}_{\beta\beta})/2$ if $\alpha\neq\beta$, $\mathbf{r}_{ij}$ is the distance between atoms i and j, and $\mathbf{r}_c$ is the cutoff distance for the interaction. E_i^b is the band energy obtained in the from of the second moment of the electron density of states, which is expressed by

$$E_i^b=-\sqrt{\sum_{j,\mathbf{r}_{ij}<\mathbf{r}_c}\xi^2_{\alpha\beta}\left[-2q_{\alpha\beta}\left(\frac{\mathbf{r}_{ij}}{\mathbf{r}^0_{\alpha\beta}}-1\right)\right]}, \tag{3}$$

where ξ is an effective hopping integral and q describes its dependence on the relative interatomic distance.

In the present paper the equilibrium properties of a three-dimensional (3D) continuum space model of Pb on the Cu(110) substrate were studied using canonical MC sampling[20] along with Verlet tables[21] of the neighbors of each particle that were updated after every 10 MC steps. The summation in Eqs. (2) and (3) is performed over all atoms within a sphere of radius 3 times the Cu nearest-neighbor (NN) distance. The contribution to the internal energy of adsorbate atoms placed at longer distances was found to be less than 5% and was not accounted for. The parameters A, p, q and ξ of the interaction potentials for Pb and Cu are given in Ref. 19. In the absence of experimental data,

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the parameters of the Pb-Cu interaction are estimated by taking the average of the constants of pure metal interactions.

We have simulated Pb/Cu(110) system using two different models of substrate atom behavior: (i) model I, the atoms of the uppermost substrate layers are allowed to move; (ii) model II, the substrate atoms are fixed to their ideal sites in the fcc (110) lattice.

Allowing the substrate Cu atoms to move in the same manner as Pb atoms we could investigate their relaxation due to presence of adsorbate atoms as well as possible exchange events of atoms between different layers. This process of surface alloying has been recently experimentally observed not only for Pb/Cu(110) (Ref. 7) but also for Pb/Cu(100) (Ref. 23) and even in the case of the most closely packed Pb/Cu(111) (Ref. 24) system.

The fcc (110) lattice planes form rectangular lattices with lattice constants 1 and $\sqrt{2}$ where we choose an unit system in which the lattice constant $b/\sqrt{2}$ of the substrate is unity. The linear dimension L_x and L_y are multiples of 1 and $\sqrt{2}$, respectively, so that the influence of box size on the adsorbate's structure is kept minimal. The Z axis is perpendicular to the planes, pointing from the surface [$Z=0$ corresponds to the centers of the top layer substrate atoms fixed to their ideal sites in fcc (110) lattice] into the adsorbate space. In our simulation, lattice size $M=L_x \times L_y$, where $M=14 \times 10$, 20×14, and 28×20, has been used with periodic boundary conditions. For each simulation, 10^5 MC moves were attempted per atom. A single MC displacement consists of a sequential selecting a new atom position R_i in the simulation box, and calculating the energy change in energy for the proposed move. MC events related to atom moves with an energy change of less than or equal to zero were automatically accepted. Displacements that cost energy difference dE were accepted with probability $\exp(-dE/kT)$, (k Boltzman constant; T, temperature), by comparison with a random number. The maximal single displacement was considered temperature and species dependent, so that an acceptance rate of 50% of trial states for each species was maintained during the run. After the equilibration of 2×10^5 moves per atom, the structure factor was calculated from a surface configuration generated every 10^3 MC steps and the results averaged. The equilibrium state is established after the total system energy reaches its minima and fluctuates around its constant value at a given temperature. The θ_{sat} is defined as the half from the number of substrate atoms at the Cu(110) surface that corresponds to the atom density of a perfect $c(2\times 2)$ phase.

III. RESULTS AND DISCUSSION

First we analyze the structure of the adsorbate layer at θ_{sat} and low temperatures T. According to experimental observations the Pb atoms alloy in the outermost substrate Cu(110) layer at low coverages.[7,10] Increasing the coverage the alloyed Pb atoms emerge from their substituted positions with Cu atoms in the topmost substrate layer and arrange in a $c(2\times 2)$ structure. It should be pointed out that no indication of a $p(2\times 1)$ Pb/Cu(110) structure is experimentally observed, although the Pb-atomic densities of both $c(2\times 2)$- and $p(2\times 1)$-Pb structures on Cu(110) at θ_{sat} are the same. On the other hand, the relations of effective Pb-atomic areas in Pb-bulk crystal layers (111), (100), and (110) to a $c(2\times 2)$-Pb layer on Cu(110) are 1.73, 1.5, and 1.06, respectively. Although a strong misfit of the lattice constants of the adsorbate and surface Pb:Cu 1.36:1 is present, the Cu surface potential relief clearly opposes the formation of densely packed islands with a Pb-Pb lattice spacing. However, we failed to obtain a $c(2\times 2)$ structure of Pb on Cu(110) in the experimentally determined temperature range employing the parameters of Eqs. (2) and (3), which give a good agreement with the experimental bulk cohesive energy and bulk modulus. The calculated substrate potential relief shows that while an adatom has experienced a rather high potential barrier along the $\langle 001\rangle$ direction, it is almost free to move along the $\langle 1\bar{1}0\rangle$ direction. Obviously, the substrate corrugation is not strong enough to attach the adatoms to a specific lattice position along $\langle 1\bar{1}0\rangle$ channels. Thus, the $c(2\times 2)$ structure is determined by the delicate interrelation of the elasticity of the adsorbate layer and the surface potential relief.

The structural rearrangement with increasing coverage of Pb on the Cu(110) surface suggests a coverage dependent character of the Pb-Pb interactions.[22] A similar behavior of the lateral adsorbate interactions is proposed for the Pb adsorption onto other low-index Cu(111) (Refs. 24,25) and Cu(100) (Ref. 23) faces too. Let us recall that in the TBM the repulsive interaction part is included in order to ensure bulk crystal stability and is expected to be important in compressed rather than more loosely packed Pb-layer configurations.[26] First-neighbor distance in $c(2\times 2)$ structure exceeds nearly 1.3 times the NN Pb-bulk distance. On the other hand, the hopping integral ξ in a band energy term (3), describes overlapping of tight-binding wave functions of neighbor atoms and, hence, is strongly influenced by atomic environment changes.[14,27] Indeed, accounting for the adsorbate atomic relaxation effects near impurities, vacancies and surfaces, there is charge-density redistribution modifying the potential and, thus the tight-binding parameters.

In order to obtain an experimentally observed $c(2\times 2)$ structure at θ_{sat} and low T we modify the value of $\xi_{\alpha\alpha}(\alpha=\mathrm{Pb})$ appropriate for the bulk Pb crystal. The change of this parameter not only leads to the appearance of a Pb $c(2\times 2)$ structure but also controls its order-disorder transition temperature. In the case of initially perfectly ordered Pb atoms on exact $c(2\times 2)$ sublattice positions, the system demonstrates the following behavior after reaching an equilibrium state. (i) The $c(2\times 2)$ phase is stable below 120 K but disappears above this T when bulk values of the interaction potential in Eq. (1) are used. (ii) The temperature range for a $c(2\times 2)$ structure appearing becomes wider when the bulk value of a hopping integral ξ decreases. Pb atoms are distributed around fourfold symmetry sites, Fig. 1(a). (iii) We do not observe any indication of a $p(2\times 1)$ structure (that could also be formed for purely geometrical reasons) which is in agreement with experimental observations. (iv) No substitution of Pb atoms with the Cu atoms in a topmost surface layer at low temperatures is detected.

Applying a random initial configuration of adsorbed Pb atoms on the substrate we also obtain a $c(2\times 2)$ structure. However, in this case some local distortions due to higher (lower) Pb concentrations with respect to the ideal $c(2\times 2)$ order are present. In the regions with lower adatom concen-

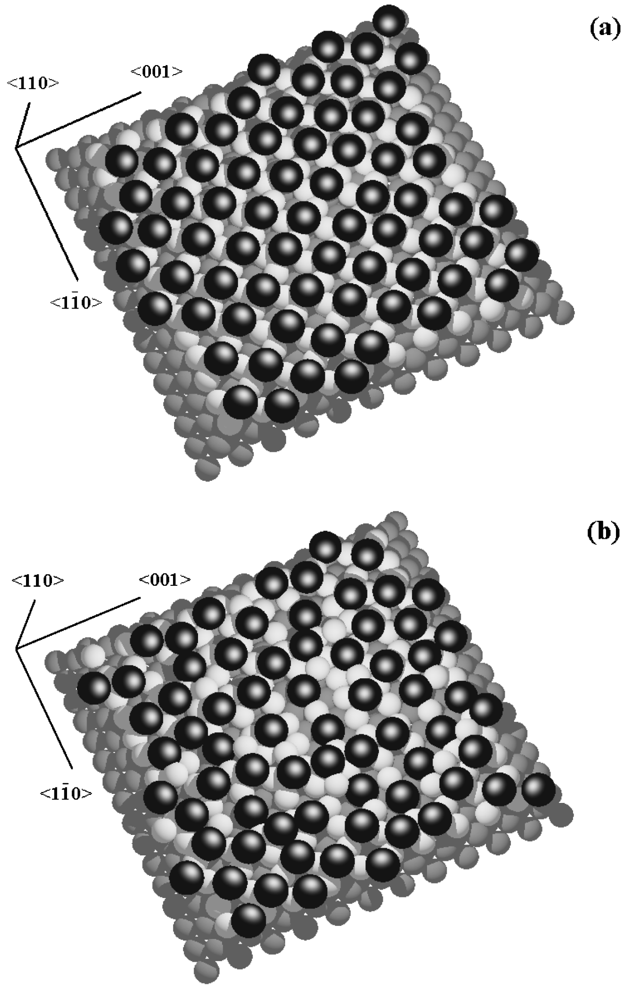

FIG. 1. Snapshot of a randomly chosen configuration from the MC simulation of the 0.5 ML Pb (dark balls) on (110) Cu surface (light gray balls, first Cu layer including lattice dynamics; gray circles, second and third layer with fixed atoms in exact positions). (a) $T=300$ K, a perfect $c(2\times2)$ structure; (b) $T=500$ K, the disordered Pb layer is seen as well as Pb-Cu interface mixing. Pb atoms embedded in the first substrate layer exactly replace Cu atoms.

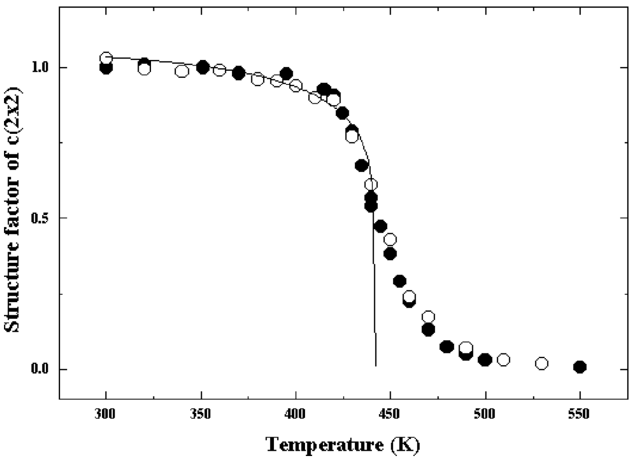

FIG. 2. Temperature dependence of the structure factor for the $c(2\times2)$-Pb structure on Cu(110) surface with fixed atoms (open circles) and with atoms allowed to move (dark circles). Solid curve is fit ($\beta=0.124$, $T_c=443$ K) with the exact equation of the Ising model (Ref. 41).

tration some Pb atoms are embedded in the lattice of the topmost Cu layer. The removal of these local distortions in the adsorbate lattice proceeds extremely slowly and increases the necessary statistical efforts. A strong anisotropy of the surface Cu(110) potential relief could be the reason for the observed slowing down of the equilibration procedure. A rather strong potential barrier for surface diffusion substantially restricts jumps of adatoms along the $\langle 001\rangle$ direction. The incorporation of one atom in the chain of adatoms along the $\langle 1\overline{1}0\rangle$ channels present in the case of ideal $c(2\times2)$ lattice can be easily accommodated with the interaction potentials used in this study. The influence of these ''frozen-in'' distortions on the temperature stability of the $c(2\times2)$ structure is discussed later.

We have done simulations with fixed Cu atom positions of the surface layer. The low-temperature structure undergoes order-disorder phase transition at $T_c\approx180$ K. Decreasing the bulk value of the parameter ξ by 25% increases the temperature range for appearance of a $c(2\times2)$ structure. It also leads to its disordering transition in an experimentally determined temperature range. Thus, the model system I (first layer substrate atoms allowed to move) substantially change the balance of the adsorbate-adsorbate to the adsorbate-substrate interactions in comparison to the model II (fixed Cu atom positions). The higher correction involved to ensure the appearance of a Pb $c(2\times2)$ structure in a model I suggests that relaxation of a surface Cu layer exerts a more rigorous influence on the Pb-Pb interactions. This may be understood as an increased charge transfer between the Pb atom and the Cu atoms in their neighborhoods due to the simultaneous relaxation of the adsorbate and substrate lattices. This assumption is in agreement with recent numerical simulations[15,28] and experimental studies.[29–31] It is shown that a strong relaxation of the outermost substrate layers beneath the adsorbate layer occurs in order to reduce the bond length between adsorbate and next-nearest neighbor substrate atoms. Consequently, repulsive NN interaction between adatoms may appear and stabilize the $c(2\times2)$ structure. As argued above we incorporate presumed changes in the electronic state of an adatom in the parameter ξ, characterizing band overlapping with its nearest Pb neighbors.

In order to investigate the order of the adsorbate layer during the disordering process, we have calculated the two-dimensional structure factor,

$$S(\mathbf{k})=\frac{1}{N}\left\langle\left|\sum_j \exp(i\mathbf{k}\mathbf{r}_j)\right|^2\right\rangle. \tag{4}$$

The summation is over adatoms, $\mathbf{k}$ is the wave vector in reciprocal space, $\mathbf{r}_j$ is the position of atom j, N is the number of adatoms, and the angular brackets denote an average over configurations.

Figure 2 shows the structure factor evaluated for Pb atoms at (1/2,1/2) diffraction condition as a function of temperature. The transition temperature (defined as the inflection point in the curve) is found at around 440 K. This result is in an excellent agreement with the experimental value of 437 K (Refs. 5,6,8) and is obtained after decreasing 4.5 times the bulk Pb value of the parameter ξ in Eq. (3). The structure

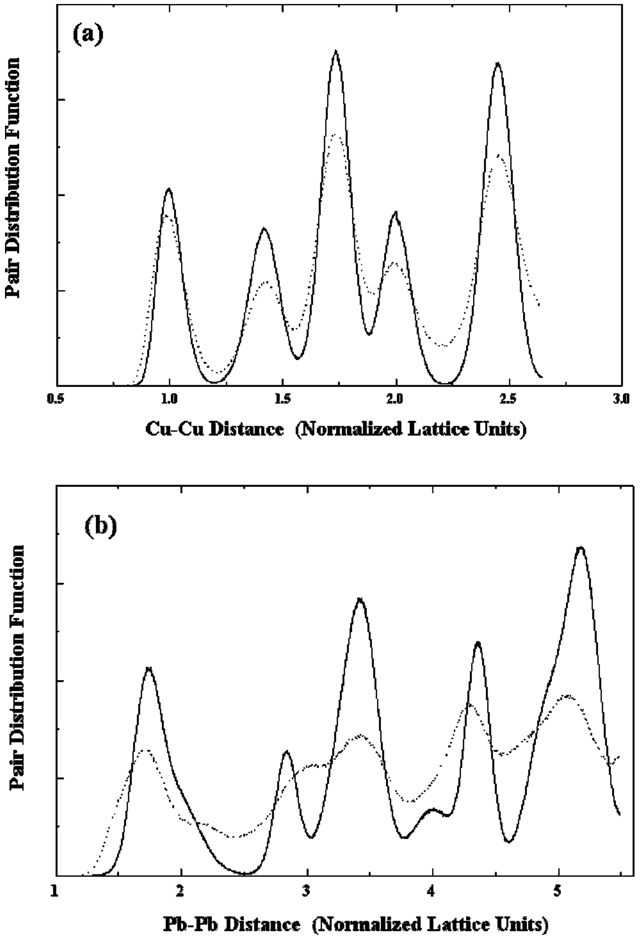

FIG. 3. Pair distribution function: (a) Cu(110) surface layer covered with 0.5 ML Pb, 300 K (solid line), and 500 K (dotted line). At low T no surface alloying is observed, while at 500 K an equilibrium concentration of Pb atoms embedded in the Cu overlayer is found. (b) The Pb layer on Cu(110) at 300 K (solid line) reflects $c(2\times2)$ ordering and 500 K (dotted line) the disordered state.

factor for the Pb layer on a surface with Cu atoms fixed at ideal (110) sites has a similar temperature dependence except that the bulk Pb value of ξ is decreased only 1.4 times.

There is another important difference in the Pb layer behavior in different treatments of the Cu(110) surface atoms. Approaching the temperatures where the steep decrease of the structure factor begins, a small fraction (1%) of Pb atoms in the adlayer substitute the Cu atoms from the surface layer in a model system I. An increase of temperature is accompanied not only by a decrease of the order in the adsorbate but also by an increase of the fraction of Pb atoms alloyed in a substrate layer. We obtain that already at 500 K where the structure factor almost disappears, a saturation concentration of 15% of Pb atoms substitute Cu atoms from the upper (110) layer of the substrate, Fig. 1(b).

The exchange of the larger Pb atoms with the Cu atoms leads to a compression in the outermost Cu layer that is manifested by the pair distribution function (PDF) [Fig. 3(a)]. The positions of the first maximum corresponding to the first-neighbor distance in a Cu(110) layer is steadily shifted to shorter distances. The observed slight shift (2%) of the positions of the first maximum of the PDF suggests that the substrate layer maintains its initial (110) structure. Nevertheless, the variation of the slope of the structure factor of the integral order spots is experimentally observed.[5,6,8] It is assumed that the observed intensity decrease results from the surface corrugation change during the Pb $c(2\times2)$ disorder phase transition.[32] Our calculations clearly show that disordering transition is accompanied by surface alloying. That certainly may modify the surface phonon modes and, thus the behavior of the integral order beam intensities. On the contrary, increasing the temperature the dramatic change of the order in the Pb layer is clearly manifested in the PDF [Fig. 3(b)]. The close values of adatom positions and their oscillations make barely distinguishable the first and second NN distances along the $\langle 1\overline{1}0\rangle$ and the $\langle 110\rangle$ directions, respectively, even at low T. The following peaks correspond to the third- and fourth-. . . neighbor distances. As temperature increases the PDF continuously looses its low T features that signify disordering of the $c(2\times2)$ structure.

The site exchange of part of Pb and Cu atoms and rearrangements of the Cu layer involved during disordering transition of the adsorbate imply unusual critical behavior and ordering phenomena. The predictions of the critical properties of this complicated phase transition is not obvious from simple symmetry considerations. Indeed, the experimentally determined value of the critical exponent β of the order parameter decay is nearly two times smaller with respect to theoretically estimated values. However, the temperature behavior of the normalized structure factor of a $c(2\times2)$ Pb layer in our simulations on both surface models is identical, Fig. 2. In order to extract additional information on the transition the temperature dependence of the structure factor was fitted with the power-low form $S(T)\approx|t|^{2\beta}$, where $t=1-T/T_c$ is the reduced temperature and β- the critical exponent depicting order parameter decay. Following the procedure described in (Ref. 33) we found $\beta=0.121\pm0.014$ and $T_c=444\pm3$ K.

It is important to note that the phase transition behavior of both studied model systems is identical and in good agreement with the expected Ising model, although in a model I the decay of the adsorbate order is accompanied with alloying with the uppermost substrate layer. We point out here that in some other 2D systems observed order-disorder phase transition of the adlayer is proposed to involve structural rearrangements of the substrate layer. It has been shown that the continuous phase transition of a $p(2\times1)$-O onto W(001) induces a deconstruction transition of the substrate.[34] This system is predicted to belong to the XY model with cubic anisotropy with nonuniversal critical exponents. Recently it was shown that the three-state Potts model behavior of Au $(\sqrt{3}\times\sqrt{3}R30°)$ on Si(111) has not been influenced by the expected model of the mechanism of disordering, involving local surface distortions, nor by the presence of three-dimensional Au islands during the transition.[35] Let us note that the Ising model prediction follows from the existence of two $c(2\times2)$ sublattices on the fcc (110) substrate. The appearance of local defects: impurities, vacancies, local distortions, etc., during the phase transition does not directly affect its nature if they do not lead to the systematical preference of one or the other sublattices. Our results indicate that the occurrence of surface alloying in the studied Pb/Cu system during the order-disorder transition do not influence its critical behavior. On the other hand, experimentally detected changes in the intensity behavior of the integral order spots coincide with the disordering transition of the adsorbate. This may be attributed to the local structural distortion in the uppermost substrate layer due to Pb-Cu alloying.

The structure and phase transition observed here are in fairly good agreement with the experimental evidence. A strong discrepancy, however, exists between the determined values of the critical parameter β in our simulations and TEAS measurements that gave a nearly two times smaller value. It is evident that finite-size effects, e.g., mean terrace width, antiphase boundaries, point defects, etc., influence the behavior of the real system in the critical region. That is the case when the correlation length is comparable to the system's size.[36,37] Apparently, the quality of a crystal used in the experimental study with a mean terrace width of 100 Å may substantially influence the behavior of the critical exponent at $T \leqslant T_c$. On the other hand, in the region $T > T_c$, i.e., in the disordered phase of the adsorbate, the correlation length is the distance over which an ordered region extends since the range it measures refers to fluctuations about configurations with no long-range order. Hence, when the correlation length becomes smaller than system size the short-range order fluctuations will not be affected by boundary effects. Accordingly, experiments gave for the critical exponents that describe the fluctuation of the short-range order γ and the decay of the correlation length ν values close to those appropriate for the Ising universality model.

Our results show a negligible shift of -0.25% for $T_c(L)$ obtained in simulations compared to the larger system size $T_c(L_y=20)$. This strongly suggests that the observed different decay of the long-range order cannot be explained only by finite-size effects imposed by the relatively small mean terrace width in the experimental system. Nagl *et al.*[31] have shown with scanning tunneling microscopy measurements that Pb atoms predominately decorate the step edges and easily incorporate (alloy) through these edges in the Cu matrix of the upper terraces. This process can influence the decay of long-range order in two ways. First, it may lead to effective smearing out the effect of steps and to disrupt the critical fluctuation across them. This can lower the symmetry than the flat surface, thus, crucially violating the theoretical expectations based on the symmetry considerations. Second, preserving part of Pb atoms on the terraces in substituted position with Cu atoms (frozen-in defects) even after high-temperature annealing. That may change the energetics in the adsorbate layer and in that way influence the nature of long-range order decay.[38] Our simulations show that the frozen-in distortions that could not be removed during the runs with initially random distributed Pb atoms on the substrate, drastically influence the order of the 2D adsorbed layer. The $c(2\times2)$ order-disorder phase transition occurs at lower T and with abrupt first-order-like behavior. Similar deviation from the expected Ising model behavior due to the influence of surface defects is found in the Pb/Cu(100).[39] Gomez and Dieb[19] obtained defects and domains in their MC simulations of a Pb $c(5\sqrt{2}\times5\sqrt{2})R45°$ onto Cu(100) after random initial configurations of adatoms. However, no information is reported on the influence of these defects of the temperature Pb layer structure stability.

IV. SUMMARY

In the present study we have revealed some important features of the 2D order-disorder phase transition behavior of $c(2\times2)$ Pb/Cu(110) system using a ''realistic'' many-body potential. Assuming coverage-dependent Pb-Pb interactions our MC simulation results are in excellent agreement with the recent experimental observations. In the framework of the model described above we obtained (i) formation of $c(2\times2)$ structure at temperature $T<400$ K, (ii) order-disorder transition in experimentally determined critical region at $T=443\mp3$ K, (iii) surface alloying in the system depending on the temperature.

Considering statements (ii) and (iii) we are able to provide a simple explanation of experimentally detected change in the slope of the integral order peak intensities. This explanation is based on the surface alloying process, taking place during the phase transition in the 2D adlayer. The intermixing is observed even at low T and it is much more pronounced in the disordered state, where 15% of Pb atoms replace Cu atoms in the first substrate layer at $T=500$ K. We found a rather subtle dependence of the order-disorder transition behavior on the kinds of defects and distortions in a Pb layer. The adlayer with frozen-in distortions undergoes a first-order-like phase transition. On the contrary, initially perfectly ordered $c(2\times2)$-Pb layer shows continuous order-disorder transition, although it is accompanied by Pb-Cu surface alloying. In that case the system exhibits Ising universality model behavior. Considering the experimental findings on Pb/Cu system, it should be pointed out that any thermal treatment (usually applied to reach equilibrium state) may change irreversibly the ''perfection'' of both the substrate and 2D layer and thus crucially influence the critical behavior of the system.

Finally, applying the same lateral and normal interactions in the system, as in Eq. (1), in the range of coverages $0<\theta<0.5$ our results show the lattice gas adsorbate ordering in agreement with those experimentally observed.[1,7] Depending on both coverage and temperature we found an equilibrium surface alloying and dealloying process in the system.[40]

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