SOS model of overlayer induced faceting

Czesław Oleś

Institute of Theoretical Physics, University of Wrocław,
Plac Maksy Borna 9, 50-204 Wrocław, Poland
(Dated: March 4, 2003)

A solid-on-solid model is proposed to describe faceting of bcc(111) metal surface induced by a metal overlayer. It is shown that the first order phase transition occurs between faceted (211) or (110) and disordered phases. The ordered phases consist of large 3-sided pyramids with (211) facets or (110) facets. It is shown that the high-temperature disordered phase has not planar bcc(111) structure but faceted disordered structure. Hysteresis effects were observed when the system was warmed above the transition temperature and then cooled down. Temperature dependence of LEED patterns for faceted and disordered phase are calculated in kinematic approximation.

PACS numbers: 68.35.Rh, 68.43.De, 64.60.Cn

I. INTRODUCTION

Recent experiments have demonstrated that surfaces such as W(111) and Mo(111) covered by a single physical monolayer of certain metal, e.g., Pd, Pt, undergo massive reconstruction from planar morphology to microscopic faceted surface after annealing to $T > 700 K$. The reconstructed surface consists of 3-sided pyramids with mainly (211) facets, and pyramid dimensions range from \( \sim 1 \) to 100 nm. It has been shown that facets are composed of substrate atoms, and the monolayer of adsorbate remains on the outermost surface layer during the faceting transformation. Another type of massive reconstruction has been very recently found in STM and LEED experiment for Pd on Ta(111) system\(^7\). The reconstructed surface consists of (011) facets, which form large triangular pyramids. The third type of reconstructed structure, coexistence of small (011) facets with large (211) facets, has been observed in Pd on W(111) for prolonged annealing time (for short annealing time only (211) pyramids occurred). An important step in understanding the thermal stability of reconstructed surfaces was LEED experiment performed in high temperatures for Pd on Mo(111) by Song et al.\(^8\). They demonstrated existence of reversible phase transition between faceted (211) and planar phases and they found that this transition has a large hysteresis, i.e., the transition temperature in cooling cycle \( T \approx 830 \) is lower than that in the heating cycle \( T \approx 870 \).

In theoretical studies of overlayer-induced faceting\(^9,10\) the first principle method have been used to calculate the surface formation energy of fcc metals (Pd, Pt, Au, Ag, Cu) adsorbed on Mo and W. Results of these calculations performed for pseudomorphic adsorbate overlayer on (111), (211), and (011) flat surfaces show that (111) surface becomes unstable at the coverage of one physical monolayer, where the energy of (211) orientation has the lowest value. However, such energy calculation (at $T=0$) are not sufficient to explain why some of these metals do not induce faceting, e.g., Ag/Mo(111). On the other hand, the first principle calculation confirmed that critical coverage to induce faceting is approximately equal to one physical monolayer (PML) and that the growth mode is Stransky-Krastanov as the surface energy increases at coverage higher than 1 PML.

Theoretical studies of surface reconstruction and surface phase transitions in bimetallic system are complicated problems mainly due to occurrence of long range many-body interactions. One of approaches to such problems is application of simple solid-on-solid models\(^11,12,13,14\), in which the crystal is represented by two-dimensional array of columns. They were employed to study roughening transition\(^11,12\), missing-row reconstruction\(^12\), growth of the surfaces\(^12\), surface diffusion\(^12,16\), adsorption\(^14\), phase transitions in two component crystals\(^13\), etc.

In this paper we introduce a simple SOS model for bcc(111) surface covered by one physical monolayer of adsorbed atoms to describe surface reconstruction and phase transitions. Using Monte Carlo simulation we study change of the surface structure during the heating and cooling processes, phase transitions to a faceted phases, phase diagram, LEED patterns and temperature dependence of diffracted intensity calculated in kinematic approximation.

II. THE SOS MODEL

To study faceting in bimetallic system one needs to know interaction potentials. There are many-body potential for Mo-Mo and W-W interactions derived by Finnis and Sinclair\(^17\) but to our knowledge there is only Ni-Mo many-body potential\(^18\) for interaction between (Mo, W) and fcc metals. However in Ni/Mo(111) system the faceting does not occur\(^18\). Therefore we are going to study overlayer induced faceting using a simple solid-on-solid (SOS) model which describe a surface formation energy in agreement with result of the first principle calculation.

In order to construct a model of overlayer-induced faceting on bcc(111) surface (BCCSOS) we are taking into account some experimental evidences. There is a critical coverage, approximately equal to 1PML, to induce faceting on W(111) and Mo(111)\(^4\). When the cover-
age exceeds 1PML, extra adsorbate atoms form 3D clusters on the top of faceted surfaces. Hence to simplify
problem it will be assumed that coverage is constant and
equal to 1PML. Such coverage is equivalent to 3, 2, and
1 geometric monolayers of adsorbate on bcc (111), (211),
and (011) surfaces, respectively. A second assumption is
that substrate atoms (B) can take position in discrete bcc
lattice. It has been shown3, in the case of Pd/W(111),
that both {011} facets and {112} facets of W are cov-
ered by pseudomorphic monolayer of Pd. Therefore we
assume that adsorbate atoms (A) are also located in
positions of the bcc structure. There are three types
of interaction energies in this SOS model: adsorbate-
adsorbate interaction $\epsilon_{AA}$, adsorbate-substrate interac-
tion $\epsilon_{AB}$, and substrate-substrate interaction $\epsilon_{BB}$, with
the range of interaction up to forth neighbors ($i = 1, 2, 3,
4$).

It is convenient to choose the coordinate system with the
Z axis parallel to [111] direction and X, Y axes along
[101], [121] directions in the (111) plane. Atoms along
the closed packed direction (parallel to the z axis) form
columns which positions in the (x, y) plane are described
by three triangular sublattices $l = 0, 1, 2$ shown in Fig. 1
Column height $z_i$ at site $i$ in the $l$th sublattice is defined
as $z_i = h_i a \sqrt{3}/6$ where $a$ is bcc lattice constant, $h_i =
3n_i + l$ and $n_i$ is the number of atoms in $l$th column. The
assumption on constant coverage equal to 1PML means
that there is exactly one A atom in each column placed
on its top. As we are going to study reconstruction only,
not desorption or crystal melting, the typical restriction
of SOS models on columns heights will be assumed. The
$h_i$ difference between nearest neighbor sites are forced to
be $\pm 1, \pm 2$.

Let us define the Hamiltonian as surface formation en-
ergy of A material on B (111) surface

$$H = E_{A/B}(N_A, N_B) - E_{A}^{bulk}(N_A) - E_{B}^{bulk}(N_B),$$

where $E_{A/B}(N_A, N_B)$ denotes energy of $N_A$ atoms A on
bcc(111) surface consisting of $N_B$ atoms B, $E_{A}^{bulk}(N_A)$,
$E_{B}^{bulk}(N_B)$ are energies of A, B atoms in their bulk
environments. Now taking into account above assumptions
we can express Hamiltonian Eq. (1) in terms of column
heights $h_i$ in the following form

$$H = \frac{1}{2}\sum_j \left\{ \sum_{i,j} J_{ij} \delta (|h_i - h_j| - 1) + K_{ij} \delta (|h_i - h_j| - 2) \right\}
+ \sum_{j,j} 2J_{jj} \delta (|h_i - h_j|) + (2J_2 + K_2) \delta (|h_i - h_j| - 3)
+ J_2 \delta (|h_i - h_j| - 2) + \delta (|h_i - h_j| - 4) \right\} + N J_0,$$

where

$$J_0 = \frac{1}{2} \epsilon_1^B + \epsilon_1^A,$$

$$J_1 = \frac{1}{2} (\epsilon_2^B + \epsilon_3^B + 2\epsilon_4^B) + \epsilon_2 + \epsilon_3 + \epsilon_4,$$

$$K_1 = \frac{1}{2} (\epsilon_1^B + 2\epsilon_3^B + \epsilon_4^B) + \epsilon_1 + \epsilon_3 + \epsilon_4,$$

$$J_2 = \frac{1}{2} \epsilon_4^B + \epsilon_4,$$

$$K_2 = \frac{1}{2} \epsilon_3^B + \epsilon_3 - \epsilon_4,$$

$$\epsilon_i = \epsilon_i^{AB} - \epsilon_i^{AA},$$

and sums over $j_1$, $j_2$, and $j_3$ denotes summing over first,
second, and third neighbors of a column at site $i$. In
what follows, we will treat $J_1$, $J_2$, $K_1$, and $K_2$ as model
parameters. It is worth noting that this BCCSOS Hamil-
tonian of overlayer-induced faceting at constant coverage
can also be used to study a clean bcc(111) surface by
setting $\epsilon_i^{AB} = \epsilon_i^{AA} = \epsilon_i^B$.

A. Energies of (111), (211), and (110) faces at $T=0$

First, we will check the stability of ideal surfaces (111),
(211), and (110) covered with 3, 2, 1 geometric monolay-
ers of A, similarly as it was performed in first principles
calculations. This allows us to estimate values of model
parameters for reconstruction, from (111) surface to
{112} or to {011} faceted surface, under assumption
that edge energies are neglected.

Using the Hamiltonian Eq. (2) we get the following
expressions for surface energy per site for ideal face of
orientation $(hkl)$

$$E_{111} = E_r + 7J_2,$$

$$E_{210} = E_{111} + 2J_0 + 2K_2,$$

$$E_{211} = E_{111} + K_2,$$

where

$$E_r = J_0 + K_1 + 2J_1.$$
Thus, the stability conditions are:

\[ K_2 \geq 0, \quad J_2 + K_2 \geq 0 \quad \text{for (111) surface}, \]
\[ J_2 + K_2 \leq 0, \quad 2J_2 + K_2 \leq 0 \quad \text{for (110) surface}, \]
\[ K_2 \leq 0, \quad 2J_2 + K_2 \geq 0 \quad \text{for (211) surface}. \]

It easy to see that transformation from (111) surface to \{211\} facets will be possible for negative values of \( K_2\) and appropriate positive \( J_2\). To satisfy these conditions, the range of interactions \( \epsilon^3_{ij}\) should be not smaller than \( r_4 = a\sqrt{11}/2\). On the other hand, it is easy to ensure stability of bcc(111) surface at zero coverage (\( \epsilon_i = 0\)) by choosing \( \epsilon^3_{12} < 0 \) and \( \epsilon^4_{ij} < 0\). Thus, there is general possibility to chose a set of interactions \{\( \epsilon^3_{12}, \epsilon^4_{ij}, \epsilon_3, \epsilon_4\}\} in such a way that at zero coverage the bcc(111) surface is stable whereas for coverage equal to one physical monolayer the bcc(211) surface become stable.

It is worth noting that surface energies per site \( E_{hkl}\) are related to surface energies per surface atom \( \sigma_{hkl}\) (used in first principles calculations\(^2,9\)) in the following way \( \sigma_{111} = 3E_{111}, \sigma_{211} = 2E_{211}, \sigma_{110} = E_{110}\), as the number of surface atoms is \( N/3, N/2, \) and \( N\), respectively. Moreover, above stability conditions correspond to faceting conditions\(^2,9\) expressed in terms of scaled \( \sigma_{hkl}\), e.g., the conditions \( E_{211} \leq E_{111}, E_{211} \leq E_{110}\) are equivalent to \( 3\sigma_{211}/2 \leq \sigma_{111}, 3\sigma_{211}/2 \leq 3\sigma_{110}\) for transformation (111) \( \rightarrow \) \{112\}.

Independence of stability condition on parameters \( J_0, J_1, K_1\) comes from assumptions on constant number of adsorbate atoms A and the restriction on column heights. Therefore we neglect these parameters in further analysis what corresponds to shifting of the surface energy by \( -E_r\). Moreover, by choosing \( J_2\) as the unit of energy we will work with dimensionless quantities: energy \( \tilde{H} = H/J_2\), temperature \( \tilde{T} = k_B T/J_2\), and parameter \( \tilde{K} = K_2/J_2\) (in what follows, the tilde will be omitted).

### III. SIMULATION OF FACETING

We will discuss here results of the annealing process investigated by Monte Carlo (MC) simulation in canonical ensemble. Let us start with some details concerning the simulation method. Configurations of BCCSOS model are generated via the classic Metropolis algorithm. A new configuration in Markov chain is generated from the previous configuration by moving one B atom from a site \( i \) to a site \( j \), what is equivalent to the following change of heights: \( (h_i, h_j) \rightarrow (h_i - 3, h_j + 3)\). It is important to note that such change of heights is possible only if \( h_i\) is the local maximum (with respect to the nearest neighbors) and \( h_j\) is the local minimum because of the restriction on column heights. Let us remember one of the model assumption that adsorbates always stay on the column tops as we study reconstruction of B surface covered by the physical monolayer of A material.

MC simulation were carried out on rectangular lattice of linear size \( L_x, L_y\) along x, y direction, respectively with periodic boundary conditions (PBC). To check the role of PBC additional simulations were performed with boundary atoms fixed at positions of the flat bcc(111) surface. The results are consistent with those obtained for calculation with PBC.

First, we investigate properties of the system with coupling constant \( K = -1.25\) during warming up process. At each temperature \( T_i = T_{i-1} + \Delta T\) system spends the same annealing time \( \tau\) measured in Monte Carlo steps per site. The ideal bcc(111) surface is used as a starting configuration at \( T_0\). We also investigate properties of the system during cooling down the sample. Results of simulations for the following parameters: \( L_x = 192, L_y = 336, \Delta T = 0.03\) and \( \tau = 3 \times 10^5\) are presented in Fig. 2-Fig. 5. Let us notice that these sizes of the lattice correspond to the area of 426Å × 431Å on the bcc(111) surface with the lattice constant \( a = 3.14\)Å.

The surface formation energy decreases as temperature is elevated (see Fig. 2) what indicates reconstruction of the surface. At \( T \approx 0.4\) very small 3-sided \{211\} pyramids are formed on the surface and further warming up causes growth of pyramids sizes (see Fig. 4). By the \{211\} pyramid we mean the pyramid built of (211), (121), and (112) facets. A big jump of the surface energy is observed at \( T = 1.26\) where the phase transition to disordered phase occurs. On the other hand, discontinuous change of the surface energy is observed at \( T = 1.20\) when the system is cooling down. The hysteresis loop seen in Fig. 2 indicates that the phase transition is of first order.

The surface is undercooled or overheated because system rest in metastable state separated from the stable state by the free energy barrier. The hysteresis effects, dependence of temperature of the phase transition on cooling and warming, has been observed in LEED experiment for Pd/Mo(111). When system is cooling down we observe formation of large pyramids with defected faces and edges just below the temperature of the phase transition (see Fig. 3). Facets of similar shapes and sizes were ob-
served at this temperature on warming. During further cooling defects disappear and pyramids take nearly ideal shapes at \( T \approx 1 \). Therefore the dependence of surface energy on cooling is very week in the ordered faceted phase.

It is very interesting that in the disordered phase the surface is not planar as suggested in experimental work\(^6\). The structure of disordered phase contains randomly distributed small facets mainly of \{112\} orientations what is shown in Fig. 5 where the cross section of the disordered phase is compared to cross sections of faceted \{211\} and ideal bcc(111) surfaces. Moreover, we calculated the average number of atoms on a facet of orientation \{211\} which in the disordered phase is nearly 10. So we will call this phase as disordered faceted phase (DFP). In very narrow temperature range, we observed a coexistence of both faceted and DFP, e.g., in simulation at \( T = 1 \) denoted by the triangle in Fig. 2. A surface structure in this case looks like surface of ordered phase where large pyramids are removed and on their place DFP is present. On the other hand, there are 3-sided pyramidal holes built of large facets of \{112\} orientation. Sometimes, DFP is located also at the bottom of these holes. It is worth noting that coexistence of both faceted and disordered phases has been observed\(^7\) in LEED experiment in Pd/Mo(111) system. However, it was suggested that coexistence is due to the inhomogeneity of the surface.

One of quantities measured in MC simulation is the square mean width of the surface,

\[
\delta h^2 = \left\langle \frac{1}{N} \sum_j (h_j - \langle h \rangle)^2 \right\rangle. \quad (3)
\]

Behaviour of the \( \delta h^2 \) during warming up and cooling down processes allows us to study dependence of mean vertical sizes of pyramids on temperature. In Fig. 6 we present results of simulation for 3 different annealing times \( \tau = 2 \times 10^3, 2 \times 10^4, 3 \times 10^5 \). In all cases the hysteresis loop is present near the phase transition and for shorter time a larger hysteresis is observed. It is easy to explain because it is more probable to overcome the free energy barrier in longer time. In the warming up process the size of pyramids does not depends on the annealing time \( \tau \) up to \( T \approx 1 \). When temperature approaches \( T \approx 1 \) then a rapid growth is observed and for longer annealing time \( \tau \) greater pyramids are formed on the surface. Pyramids reach maximal sizes just below the temperature of the phase transition where dependence of sizes on annealing time is the strongest. It worth noting that dependence of facets size on temperature qualitatively agrees with the experimental results\(^4\). The value of \( \delta h^2 \) rapidly decreases above the phase transition where very weak dependence on temperature is observed. In the cooling down process large pyramids are formed just below the phase transition temperature, and further de-
increasing of temperature practically does not change the size of pyramids.

We check dependence of surface growth on the initial temperature $T_0$ and we find that the behaviour of $\delta h^2$ near the transition point is very similar to that in Fig. 6 for process which starts at $T_0 = 0.3$ or $T_0 = 1.0$. Finally we analyze the influence of the temperature increment, $\Delta T$, on the surface energy and the $\delta h^2$ near the phase transition for $\tau = 3 \times 10^5$. We found that for $\Delta T = 0.01$ the hysteresis loop slightly increases, there are more points where the faceted and disordered phases coexist but it seems that sizes of pyramids do not depend on the temperature increment.

We observe that the growth of the facets on warming base on formation of a larger pyramid from several smaller pyramids. Probability of such rebuilding of the surface is very small at low temperature. This is reflected in the acceptance ratio $f$, a fraction of accepted configurations in the Markov chain, which is very low at low temperatures, $f \approx 0.002$ below $T = 0.3$ and $f = 0.01$ at $T = 0.7$. On the other hand, the acceptance ratio is of the same order for $T = 1.0$, $f = 0.1$, and close to the phase transition, $f = 0.2$, but we observe difference in facets sizes at these temperatures. Looking at snapshots of the surface after annealing at temperature up to $T \approx 1.1$ on warming, we found that pyramids have nearly ideal shapes (see for example Fig. 8). We think that all above observation can be explained in the following way. The system is passing through metastable states - local minima of the free energy - as temperature is increased. There are barriers between local minima hence the growth of facets depends on the annealing time.

The stability analysis of flat (111), (211), and (110) surfaces in Sec. IIA shows that at $T = 0$ the (211) surface is stable for $-2 \leq K < 0$ whereas for $K < -2$ the (110) surface is stable. Whether these findings are generally correct we can check constructing phase diagram in the (T, K) plane by using MC simulations. Most of simulations were performed at constant K varying temperature. To check the results some simulations were performed at constant temperature. To identify different phases we calculated masses of clusters of different facet orientations (111), {110}, and {112}. A cluster of orientation (hkl) is defined in similar way as percolation cluster on the (hkl) plane. We also recorded equilibrium configurations at each investigated point of the (T, K) plane. We found that for $K < 0$ the phase diagram (see Fig. 7 contains three phases

1. Faceted $\{112\}$ phase consisting of 3-sided $\{112\}$ pyramids.
2. Faceted $\{110\}$ phase consisting of 3-sided $\{110\}$ pyramids.
3. Disordered faceted phase.

The surface of the faceted $\{110\}$ phase is built of (110), (101), and (011) facets which form 3-sided pyramids on the bcc(111) surface. Such surface has been observed experimentally in Pd on Ta(111) system[7]. The phase transition between the disordered phase and one of ordered is of first order as surface energy, the square mean width of the surface $\delta h^2$, and the structure factor (see Sec. IV) change discontinuously at the transition point. The transition temperature between $F\{211\}$ and disordered phase is bounded from above by maximum $T_c = 1.20$ at $K = -1.50$. If we chose this point to estimate model parameters for Pd/Mo(111) with $T_c = 850$ K we get

IV. PHASE DIAGRAM

![FIG. 6: Temperature dependence of the $\delta h^2$ during the heating and the cooling cycles for 3 different annealing times. Each label contains symbols for heating, cooling and the number of MC steps](image1)

![FIG. 7: Phase diagram: T versus K.](image2)
\[ J_2 = 0.06 \text{ eV}, \text{ and } K_2 = -0.09 \text{ eV}. \] On the other hand the transition temperature from F\{110\} to the disordered phases is increasing function of \(|K|\) and it might reach large value. The present model does not include the desorption, thus we can expect that transition temperature might be above the desorption temperature in some systems especially where the faceted F\{110\} phase occurs. In such cases the phase transition to the disordered faceted phase could not be observed but rather deconstruction induced by desorption would be expected.

There is difficult to study phase transition between ordered phases using MC simulation because for \(K \approx -2\) we observed coexistence of two types of facets \{011\} and \{112\}. The mixed phase does not contain separated pyramids of two types but mixture of facets, e.g., on the (211) facet a smaller (011) facet can occur.

V. SIMULATION OF LEED PATTERNS

Low energy electron diffraction (LEED) experiments play an important role in investigation of structures and phase transitions of faceted surfaces. Very recently, Song et al.\(^7\) where able to study LEED patterns of Pd/Mo(111) system in high temperatures up to 1200K. They demonstrated the existence of reversible planar/faceted phase transition with transition temperature different for heating cycles (\(T \approx 870\text{K}\)) and for cooling cycles (\(T \approx 830\text{K}\)).

In this section we employee the BCCSOS model to analyze the temperature dependence of LEED patterns. The diffracted intensity is proportional, in the kinematic approximation, to the structure factor

\[
S(k) = \left| \sum_j \exp(ik\mathbf{R}_j) \right|^2,
\]

where summing is over surface atoms, \(k = k_f - k_i\), and \(k_i, k_f\) is the wave vector of incident electron, scattered electron, respectively. Position of surface atoms \(\mathbf{R}_j\) is expressed by column height \(h_{r_j}\) in site \(r_j = (x_j, y_j)\) in the following way \(\mathbf{R}_j = a(3\sqrt{2}x_j, \sqrt{6}y_j, \sqrt{3}h_{r_j})/6\). In a SOS model not all atoms from column tops are surface atoms. Therefore in calculation of diffracted intensity sometimes the shadowing factor is used. In this paper we consider the contribution to \(S\) only from surface atoms. As a surface atom in any configuration we choose the atom from the top of column which has at least four lower nearest neighbors. In the case when number of higher columns is equal to 3 then atom is regarded as surface atom if is not surrounded by the higher neighbors. Such case occurs for atoms on \{110\} facets. We will calculate structure factor only for a set of \(k_f\), chosen in such a way to describe diffraction on faces \{111\} and \{211\}. For each of these faces we construct a pair of inverse lattice vectors \(g_1, g_2\) parallel to the face, e.g., for (121) \(g_1 = 2\pi/a(\sqrt{2}/2, 0, 0)\) and \(g_2 = 2\pi/a(0, 4\sqrt{6}/9, 2\sqrt{3}/9)\). Then, the wave vectors of scattered electrons, \(k_f\), for given face are chosen to satisfy condition of constructive interference \((k_f - k_i)\parallel = l\mathbf{g}_1 + m\mathbf{g}_2\), where \(l, m = 0, \pm 1, \ldots\) and the symbol \(\parallel\) denotes vector component parallel to the face.

We calculated structure factors for the wave vector of the incident electron, \(k_i = 2\pi/a(0, 0, 1.43)\), normal to the bcc(111) surface. Thus energy of incident electrons is equal to 31 eV for \(a = 3.14\text{Å}\), similarly as in LEED experiment for Pd/Mo(111) surface. Figure 8 shows LEED patterns obtained in computer simulation for the model parameter \(K = -1.25\). In the ordered phase \{211\} we see besides 3 clovers (groups of 3 spots) observed experimentally, the forth clover in the center of the image, and six single spots more distant from the center. The pattern of disordered phase consists of three spots which positions correspond to the centers of external clovers in the diffracted pattern of the faceted phase. Apparent lack of spots from bcc(111) surface confirms that disordered phase has not the planar structure.

Temperature dependence of the structure factors were calculated using MC simulation and changing temperature in the way described in Sec. Most of simulations were performed on the lattice with \(L_x = 90, L_y = 132\). The spots of disordered phase have the same diffracted intensities. Their temperature dependence (see Fig. on
TEMPERATURE DEPENDENCE OF THE STRUCTURE FACTOR

The temperature dependence of the structure factor for the wave vector corresponding to a spot of the disordered phase on warming (triangles) and on cooling (squares). The hysteresis loop for large lattice $L_x = 192, L_y = 336$, is shown in the inset. The warming and on cooling shows the presence of hysteresis loop in behaviour of $S(T)$ close to the phase transition what is in agreement with experimental results. The hysteresis loop calculated for large lattice with $L_x = 192, L_y = 336$ is shown in the inset in Fig. 9. There are several points where the structure factor takes intermediate values because at these temperatures coexistence of faceted and disordered phases has been observed. More coexistence points where found on warming than on cooling. We observe also discontinuity of the structure factor at the transition temperature. Thus hysteresis and discontinuity of the structure factors are another argument for the first-order phase transition between faceted and disordered phases. During the process of warming up the system the $S$ decreases with temperature and becomes very small when on the surface large enough $\{211\}$ facets are formed.

The diffracted intensities of a spot in the ordered phase was calculated for $k_f$ fulfilling the condition of constructive interference and also for vectors from a very small surroundings of $k_f$. Then maximal value of $S$ were chosen to represent the intensity of spot at this $k_f$. We use such procedure because the surface does not consist of ideal flat $\{211\}$ facets during warming up and cooling processes, therefore spots can change shapes, intensities, and positions. The diffracted intensities of spots of faceted phase are different because areas of facets of different orientation are not equal. Moreover, their dependence on temperature during warming the system shows irregular behaviour (see Fig. 10) because of facets grow i.e., from several small facets a bigger one arises. We observe rapid growth of $S$ at temperature $T \approx 0.9$ when large pyramids are formed on the surface. During the cooling cycles, the $S$ reaches nearly maximal value just below transition temperature what confirms formation of large $\{211\}$ facets. The maximal values of $S$ in the faceted phase are nearly ten times smaller than in the disordered phase because in former case only $\sim 1/3$ surface atoms contribute to $S$, i.e., surface atoms placed on facets of the same orientation.

VI. DISCUSSION

We have presented here the BCCSOS model to study overlayer induced faceting. Although it might seem that model is very simple it gives many results in agreement with experiments. It has been shown that bcc(111) surface covered by a physical monolayer undergoes reconstruction upon annealing. We obtained two types of reconstructed surfaces: faceted $\{211\}$ covered by 3-sided pyramids as observed in Pd/Mo(111) and faceted $\{011\}$ surface found in Pd/Ta(111). The sizes of facets depend on annealing temperature and annealing time. At high temperature the phase transition to disordered phase occurs. We have shown that LEED diffraction patterns can be calculated, in kinematic approximation, in warming up and cooling down processes for different electron energies. In dependence of diffracted intensities on temperatures the hysteresis effect was observed close to temperature of the phase transition.

On the other hand, we can investigate some properties not reported in experimental papers. First of all the phase transition can be studied in details using this model. It is shown that the phase transition is of first order because quantities such as surface energy, the structure factor change discontinuously as temperature reaches the transition point. Moreover the hysteresis effects are observed when system is warming up and then cooling down. We can analyze the structure of the surface...
in disordered phase as well as in the coexistence of the faceted and disorder phase close to the transition temperature. We found that the disordered phase consists of many small \{211\} facets randomly distributed. Hence it is not planar bcc(111) surface. It would be interesting to check experimentally this prediction. It was suggested that coexistence of faceted and disordered phases is due to the inhomogeneity of the adsorbate coverage but we have demonstrated that the coexistence could also exist for homogeneous coverage.

It seems that this model can be applied to study reconstruction of curved bcc surfaces where reconstructed surface has different structure than faceted bcc(111) surface. In case of Pd deposited on a needle-shaped tungsten, step like \{211\} microfacets has been observed. Using the present model we have not obtained the faceted phase with large \{211\} pyramids and small \{011\} pyramids as observed in Pd/W(111) for prolonged annealing time. This might be due to lack of density fluctuation. So we are going to extend the model including dependence on coverage. The most general extension should base on replacing of the interactions $\epsilon_{ij}^{\alpha\beta}$ by many-body potentials. To construct such potentials, e.g., for Mo-Pd, W-Pd systems, the results of the first-principle calculations could be used.

**Acknowledgements**

I would like to thank prof. Jan Kołaczkiewicz and dr Andrzej Szczepkowicz for discussions. This work was supported by the Polish State Committee of Scientific Research (KBN) Grant No 2 P0 3B 107 19.

---

* Electronic address: oleksy@ift.uni.wroc.pl

1. T. E. Madey, C.-H. Nien, K. Pelhos, J. J. Kolodziej, I. M. Abdelrehim, and H.-S. Tao, Surf. Sci. 438, 191 (1999).
2. C.-H. Nien, T. E. Madey, Y. W. Tai, T. C. Leung, J. G. Che, and C. T. Chan, Phys. Rev. B 59, 10335 (1999).
3. T. E. Madey, J. Guan, C.-H. Nien, C.-Z. Dong, H.-S. Tao, and R. A. Campbell, Surf. Rev. Lett. 3, 1315 (1996).
4. C.-Z. Dong, J. Guan, R. A. Campbell, and T. E. Madey, in *The Structure of Surface IV*, edited by X. Xie, S. Y. Tong, and M. A. van Hove (World Scientific, Singapore, 1994) p. 328.
5. C.-H. Nien and T. E. Madey, Surf. Sci. 380, L527 (1997).
6. C.-Z. Dong, L. Zhang, U. Diebold, and T. E. Madey, Surf. Sci. 322, 221 (1995).
7. Ker-Jar Song, J. C. Lin, M. Y. Lai, and Y. L. Wang Surf. Sci. 327, 17 (1995).
8. R. Szukiewicz and J. Kolaczkiewicz, *Thermal stability of the Ta (111) surface covered with Pd* (unpublished, submitted to Surface Science).
9. J. G. Che, C. T. Chan, C. H. Kuo, and T. C. Leung, Phys. Rev. Lett. 79, 4230 (1997).
10. C. T. Chan, J. G. Che, and T. C. Leung, Progress in Surface Science 59, 1 (1998).
11. H. van Beijeren, Phys. Rev. Lett. 38, 993 (1977).
12. S. Prestipino, G. Santoro, and E. Tosatti, Phys. Rev. Lett. 75, 4468 (1995).
13. G. Mazzeo, E. Carlon, and H. van Beijeren, Phys. Rev. Lett. 74, 1391 (1995).
14. V. P. Zhdanov and B. Kaseno, Phys. Rev. B 56, R10067 (1997).
15. G. Santoro, M. Vendruscolo, S. Prestipino, and E. Tosatti, Phys. Rev. B 53, 13169 (1996).
16. P. C. Searson, R. Li, and K. Sieradzki, Phys. Rev. Lett. 74, 1395 (1995).
17. M. W. Finnis and J. E. Sinclair, Philos. Mag. A 50, 45 (1984).
18. Q. Zhang, W. S. Lai, and B. X. Liu, Phys. Rev. B 58, 14020 (1998).
19. A. Szczepkowicz and A. Ciszewski, Surf. Sci. 515, 441 (2002).