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Formation of stripe structure without longer range interactions

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We propose the model with two interaction constants (nearest-neighbor pair repulsion v_1 and trio in a line attraction v_t) which demonstrates stripe domains formation on hexagonal lattice in absence of longer range interactions usually required for stripes formation. Stripe domains of the simplest stripe structure, (2×1), are obtained at low concentration of particles and $|v_t|/v_1=1.0-1.3$. Phase diagrams of this model are obtained by Monte Carlo simulation and mixed (2×1)+gas phase stability is analyzed. It is demonstrated that the (2×1)+gas phase can be the ground-state structure at very low concentrations of particles, as well as the metastable structure characterized by large and very stable domains.

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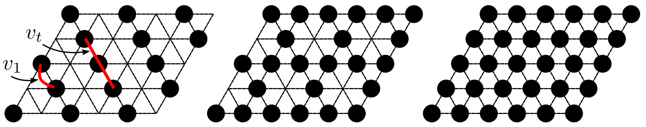
I. INTRODUCTION

Self-organized stripe structures are observed in two-dimensional (2D) systems with competing short- and long-range interactions of electrostatic, magnetic, or elastic origin. Stripes were experimentally found in very different (some of them, nanoscale) materials: binary liquids,[1] surface-adsorbate systems,[2–5] ferroelectrics,[6] ferromagnetic,[7] and Langmuir films.[8] Stripes and liquid crystalline electron states are also found[9] in two-dimensional electron systems with competing short- and long-range interactions.

Stripe structures in ultrathin magnetic layers [e.g., Fe/Cu(001) (Ref. 7)] are caused by competition of short-range ferromagnetic exchange and long-range antiferromagnetic dipole interactions. The phase-transition model describing the physics of this competition was introduced by MacIsaac *et al.*[10] and is called dipolar Ising model. The thermodynamics of this model is very well studied both for square (see, e.g., Refs. 10 and 11 and references therein) and hexagonal[12,13] lattices. Stripe phases characterized by periodic stripe domains of one magnetization direction alternating with stripe domains of opposite direction are found in the phase diagram of this model. The width of stripe domains depends on a ratio of short- and long-range interactions. When dipole interactions are dominating the stripes are thin. Wide stripes are observed when exchange interactions are larger than the dipole ones.

Historically, the simplest stripe structure with stripe domain width equal to one lattice constant was obtained in 1960s-70s in a model with the nearest-neighbor (NN) interaction v_1 and next-nearest-neighbor (NNN) interaction v_2 (Refs. 14 and 15) on a square lattice. This structure, called superantiferromagnetic phase, is characterized by periodic alternation of one chain of "up" spins with one chain of "down" spins. In surface-science (lattice-gas) notations it is called (2×1) and has the stoichiometry at concentration $c=0.5$. Two other phases obtained using this model on a square lattice are the ferromagnetic (1×1) phase $(c=1)$ and the "checkerboard" antiferromagnetic (2×2) phase $(c=0.5)$. It is seen from the ground-state phase diagram[14] that (2×1) phase occurs when $2v_2<-|v_1|$, and v_2 has to be repulsive, but v_1 can be both attractive and repulsive. For example, in Refs. 15 and 16 the formation of the (2×1) phase was demonstrated for repulsive v_1 and v_2. Comparing this model with the mentioned dipole Ising model one can notice that v_2 is playing the role of longer range repulsion which allows for two chains of spins of the same magnetization direction to form not closer than at $2a$ distance apart, and thus leading to formation of the (2×1) phase at low temperature.

Here we present the model in which the (2×1) phase forms on a 2D hexagonal lattice with adsorption on the fcc sites only as a very stable structure without inclusion of longer range forces (NNN and further interactions). The main motivation for this study were the reports of stripe phases formation at very low concentrations of particles in systems, where more compact structures are believed to be energetically favorable. In particular, we were stimulated by recent analysis of the vibrational spectra[3,4] which revealed that Si-O-Si-O stripe structures are formed during room-temperature decomposition of silane (SiH_4) on oxidized Pd and Pt(111) surfaces. These findings were supported later by density-functional theory (DFT) calculations.[5] According to the DFT results, at low silicon coverage SiO complexes start to connect into stripes with O shifted into a "bridge" position between two Si atoms. Analyzing the DFT results[5] we managed to extract the main interactions responsible for the chain-structure formation in SiO/Pd(111) system. This is possible if to compare the formation energies of various low-energy structures obtained from DFT calculations to the energies of these structures given by lattice-gas expansion of the energy. The calculation of interaction constants by comparison of the energies was previously performed, e.g., for O/Rb(0001),[17] Ag/Pt(111),[18] and O/Pt(111).[19] Performing such a comparison to different SiO structures on Pd(111), we found that, in order to obtain the chain structures, the NN pair interaction of two SiO "particles" has to be repulsive. We also found that the isotropic interaction of three SiO particles in a line (v_t) has to be attractive and of the same order of magnitude as v_1. Therefore our idea was that the mechanism of stripe formation in SiO/Pd(111) system might be governed simply by competition of these two main interactions. Such a model neglects the interactions longer than the NN (v_t attraction is responsible only for intrachain formation). The model is also quite unusual for stripe forma-



(a) $c = 0.5$ (2×1) (b) $c = 0.75$ (2×2)–3 (c) $c = 1$ (1×1)

FIG. 1. (Color online) (a) (2×1), (b) $(2\times2)-3$, and (c) (2×1) phases of adsorbed particles (solid circles) on a triangular lattice. The sites of this lattice correspond to the fcc sites of a hexagonal lattice. The interactions v_1 and v_t shown in (a) correspond to pair and trio in a line interactions between adsorbed atoms, respectively.

tion, since there is no interaction which would maintain the (2×1) phase domain, i.e., hold the chains with unidirectional spins at *exactly* $\sqrt{3}a$ distance.

Considering the literature on statistical models in which NN pair interactions are supplemented by the three-body interactions, the references might be roughly divided into those published in pre-DFT and past-DFT era. The ground-state analysis of different Ising-type models (see Refs. 20 and 21 and references therein) and use of certain trio interactions to obtain better agreement of statistical models with the experimental data (see, e.g., Refs. 16 and 22) are the typical examples of the pre-DFT papers. Calculations,[17–19,23,24] combining *ab initio* schemes with lattice-gas expansion of the energy up to the trio interactions and Monte Carlo calculations, characterize past-DFT approach. Some specific cases are more widely reviewed in Ref. 25. The works of Ehrlich *et al.*,[26] in which pair and trio interactions are derived from measurements of the probability of existence of atom pairs and trios, might be attributed to the third group of papers. Most of the mentioned models are characterized by attractive (ferromagnetic) NN pair interaction and smaller contribution of next-NN and trio interactions, the latter coming mostly from the triangle three-body forces. Here we propose the model with competing repulsive (antiferromagnetic) NN pair and attractive trio in a line interactions.

II. MODEL

In lattice-gas description the Hamiltonian of our model is

$$\mathcal{H} = \sum_{\text{NN}} v_1 n_i n_j + \sum_{\text{trio in a line}} v_t n_i n_j n_k, \tag{1}$$

where n_α $(\alpha = i,j,k)$ is equal to 1 if the site is occupied by a particle, and zero—otherwise. Since the formation of stripes was observed on Pt and Pd(111) lattices, the calculation was carried out on a 2D hexagonal lattice of fcc sites only which is equivalent to a simple triangular lattice with interaction constants v_1 and v_t, Fig. 1. The concentration of particles is $c = \langle n_i \rangle$. We performed the calculation of thermodynamics of this model for different concentrations and values of the ratio v_t/v_1. For our Monte Carlo calculations we employed Metropolis algorithm and Kawasaki dynamics with fixed number of particles. The particle participating in a diffusion process was chosen randomly, and the diffusion of the particle to the NN site was performed with the probability $\exp[-(E'-E)/k_BT]$, where E' and E are the system energies after and before the step, respectively. The optimal lattice size was 96×96 sites. The chosen time of calculation was 10^6 Monte Carlo steps per site. Our aim was to find the limits of the (2×1) phase, i.e., to calculate the phase diagrams of the model in k_BT/v_1 vs v_t/v_1 coordinates for different concentrations of particles and, finally, to obtain the k_BT/v_1 vs c diagrams for fixed v_t/v_1 values. The phase diagrams were obtained in two sets of calculations: one, when each run at new temperature value starts from random configuration of particles and another—when it starts from configuration obtained at previous temperature. This distinction demonstrates rather different results and is aimed to separate between stable and metastable states.

Depending on k_BT/v_1 and v_t/v_1 values, the model Eq. (1) allows the formation of domains of one of three phases shown in Fig. 1: (2×1) (stoichiometric at $c=0.5$), $(2\times2)-3$ $(c=0.75)$ and "ferromagnetic" (1×1) phase $(c=1)$. The $(2\times2)-3$ structure might be obtained from the simple $p(2\times2)$ structure with $c=0.25$ $[(2\times2)-1]$ by inversion of empty and occupied sites. Note that we studied this model at concentrations which were much lower than stoichiometric concentrations of these phases. Then, at finite temperature and close to the "particle-gas" phase, a considerable part of particles is still "free" and not connected into the dense domain of evolving structure. Thus, actually we studied the formation of two-phase structures when one phase was either (2×1), $(2\times2)-3$, or (1×1) phase and the other phase was the particle gas. If all three ordered structures were pure phases, their ground-state energies per one particle at each corresponding stoichiometry would be equal to: $E_{(2\times1)} = v_1 - |v_t| = -\epsilon$, $E_{(2\times2)-3} = 2(v_1 - |v_t|) = -2\epsilon$, and $E_{(1\times1)} = 3(v_1 - |v_t|) = -3\epsilon$. A simple estimation of the energy of a mixed phase at chosen concentration and temperature $T=0$ yields: $E_{\text{x+gas}}(c) = E_{\text{x}} c / c_{\text{x}}$, where E_{x} and c_{x} correspond to pure phase energy and stoichiometry, respectively, and x denotes one of the phases: (2×1), $(2\times2)-3$, or (1×1). Thus, at $v_1 < |v_t|$ the highest energy at any concentration should have mixed (2×1)+gas phase $[E_{(2\times1)+\text{gas}}(c) = -2\epsilon c]$ and the lowest energy—mixed (1×1)+gas phase, $E_{(1\times1)+\text{gas}}(c) = -3\epsilon c$ [inset to Fig. 2(a)].

Seemingly, in the phase diagram of the model Eq. (1) the mixed (2×1)+gas phase [as well as $(2\times2)-3$+gas phase] can occur only at higher temperatures due to higher entropy of (2×1) or $(2\times2)-3$ phase domain to compare with that of the (1×1) phase. This viewpoint, correct at high concentration of particles $(c>0.4)$, is, however, not completely correct for lower concentrations.

III. RESULTS AND DISCUSSION

The $(k_BT/v_1, c)$ phase diagram obtained by Monte Carlo simulation starting from random configuration is presented in Fig. 2. Our simulation shows that the domains of the (2×1) stripe structure occur at $|v_t|/v_1 \gtrsim 1$, immediately after the chains start to be formed. Thus, the (2×1)+gas phase occupies a certain region of the phase diagram only at very low concentrations. Further increase in $|v_t|/v_1$ and concentration gradually promotes the occurrence of denser structures, $(2\times2)-3$+gas and (1×1)+gas phases. The (2×1)

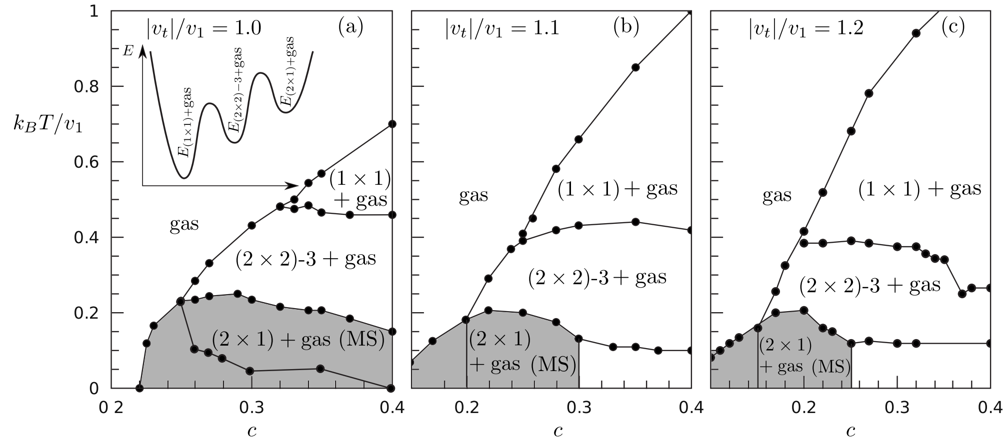


FIG. 2. Phase $(k_BT/v_1, c)$ diagrams of the model for (a) $|v_t|/v_1=1.0$, (b) 1.1, and (c) 1.2 obtained when simulation at each temperature starts from random configuration. The (2×1)+gas phase regions are colored gray. (2×1)+gas (MS) depicts metastable (2×1)+gas region to separate it from the "ground-state" region (see the text). Inset in (a): energies of all three mixed phases at zero temperature and arbitrary concentration $c<0.5$. The barriers between the phases are emphasized schematically.

+gas phase is not found at the phase diagram at $c>0.4$ and, in general, it is well defined only up to the "step" in the (2×1)+gas-to-$(2\times2)-3$+gas phase-transition curve: nice domains of this phase are still found up to $c=0.4$, 0.3, and 0.25 for $|v_t|/v_1=1.0$, 1.1, and 1.2, respectively. As an illustration the snapshots of (2×1) and $(2\times2)-3$ phase domains just below and above the phase-transition point are presented in Fig. 3. Particle diffusion in the region immediately adjacent to the (2×1)+gas phase region at low temperature is much slower due to low temperature, higher concentration and, in particular, due to higher values of $|v_t|/v_1$. As temporal metastable structures we obtain there "frozen" fragments of (2×1) and $(2\times2)-3$ phase domains.

Simple ground-state analysis yields impossibility of (2×1)+gas formation at low temperatures while Monte Carlo results demonstrate that this phase is very stable at low concentrations and $1\lesssim|v_t|/v_1\lesssim1.3$. Thus, the important question arises—if the (2×1)+gas phase can be the ground state of the model Eq. (1), i.e., at which values of the model parameters it is a stable structure and at which—metastable and favored only due to high barriers between potential minima of existing phases. To answer this question we performed the simulations with decreasing temperature when the run at each temperature value starts from configuration obtained at previous temperature.

These results are shown in Fig. 4. The (2×1)+gas phase is the ground-state structure at those values of concentration and $|v_t|/v_1$, where it exists below the transition line to the gas phase in the phase diagram of Fig. 2. When the (2×1)+gas phase is found below the $(2\times2)-3$ phase in the phase diagram, the answer depends on $|v_t|/v_1$ value. At $|v_t|/v_1=1$ the (2×1)+gas phase is still the most probable ground-state structure up to $c=0.4$. This is demonstrated in Fig. 5(a), where we present the calculation of order parameters (OPs) of the (2×1) and $(2\times2)-3$ [or (1×1)] phase domains, when the calculation at each new temperature value starts from the previous configuration. With decreasing temperature $(2\times2)-3$ phase domain (for $c<0.32$) or (1×1) phase domain (for $c>0.32$) grows up to some value of temperature, but later starts to decrease. In contrast, the domain of the (2×1) phase starts to increase at this point and finally at low temperature, $\mathrm{OP}_{(2\times1)}>\mathrm{OP}_{(2\times2)-3/(1\times1)}$. Thus, the $(2\times2)-3$ or (1×1) domain stretches out creating the 2×1 phase domain as shown in snapshots of Figs. 5(b) and 5(c), where $\mathrm{OP}_{(2\times1)}\approx\mathrm{OP}_{(2\times2)-3/(1\times1)}$.

Further increase in $|v_t|/v_1$ drastically reduces the possibility of the (2×1)+gas structure to be the ground state when this structure in the phase diagram exists below the $(2\times2)-3$+gas and (1×1)+gas phases. The general rule, which follows from comparison of (b) and (c) parts in Figs. 2 and 4, says that if several phases exist in the phase diagram (at any temperature), the phase with the densest domain is the ground-state structure for given concentration at $|v_t|/v_1\geq1.1$. At $|v_t|/v_1=1.1$ the (2×1)+gas, $(2\times2)-3$+gas, and (1×1)+gas phases are the ground-state structures at $0.15<c<0.2$, $0.2<c<0.25$, and $c>0.25$, respectively. At $|v_t|/v_1=1.2$ these intervals shrink for (2×1)+gas and $(2\times2)-3$+gas phases (to 0.10–0.15 and 0.15–0.18, respectively), but the ground-state interval of the (1×1)+gas phase widely increases.

It is seen comparing Figs. 2 and 4 that (2×1)+gas structure occurs at very low concentration of particles ("ground-state" region) and also occupies a region at a bit higher con-

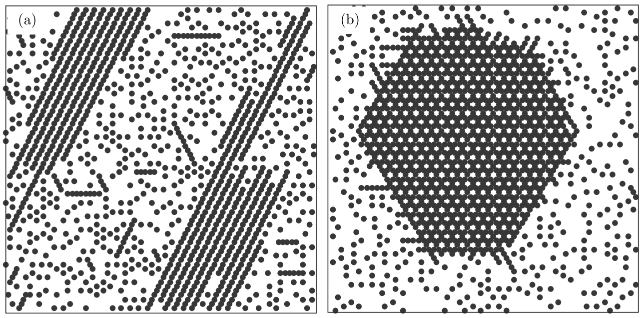


FIG. 3. Snapshots of phase domains just below and above the phase-transition point (a) (2×1) at $k_BT/v_1=0.195$ and (b) $(2\times2)-3$ at $k_BT/v_1=0.205$. Other parameters: $c=0.25$, $|v_t|/v_1=1.1$.

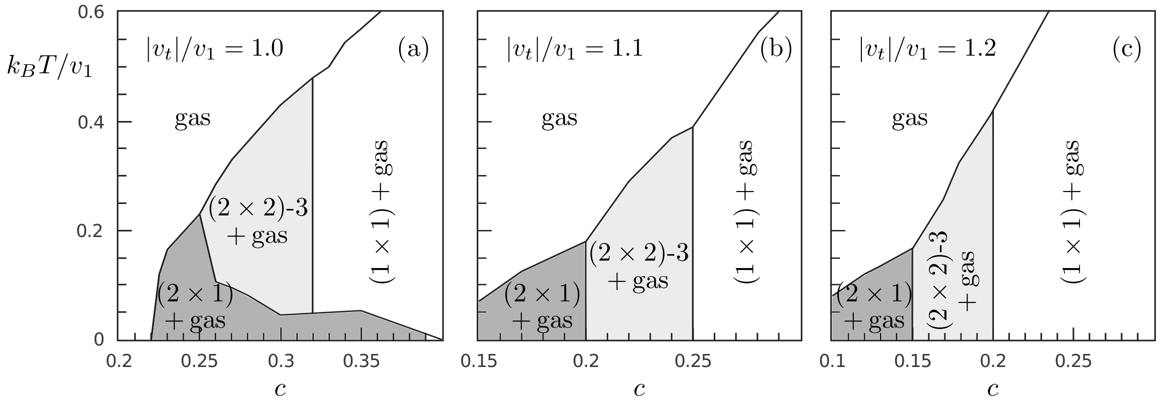


FIG. 4. Phase diagrams obtained with decreasing temperature when calculation at each new temperature value starts from the configuration obtained at previous temperature.

centration, where this phase is metastable. In spite of metastability, the phase in this region is characterized by large and stable domains of the (2×1) stripe structure, like the one shown in Fig. 3(a). These domains form very easily in calculations starting from random configuration and they are so stable that increase in simulation time by two orders of magnitude does not destroy them. This metastable (2×1) + gas state region is the largest at $|v_t|/v_1=1$ and extends up to $|v_t|/v_1=1.3$, where it is still found at $0.2<c<0.25$.

It is easy also to understand, why the (2×1)+gas structure is so stable in the "metastability region" shown in Fig. 2, even though its energy is higher than those of (1×1)+gas and $(2\times2)-3$+gas phases. Two particles in the NN sites increase the energy of the system ($+v_1$) but such states inevitably occur even at low concentration of particles. When the third particle comes in a line, system's energy decreases by ($+v_1-|v_t|$). This reasoning is valid also for fourth, fifth, etc., particle which are going to extend the chain. But if to a pair of particles in the NN sites the new particle (or few particles) is added forming the triangle (or square, etc.) rather than chain, the energy would increase, at least in the beginning. For example, it is needed first to form the hexagon domain of seven particles with the (1×1) structure, that the addition of the eighth particle would result in decrease in such system's energy. When the concentration is small probability of such a conglomerate is negligible. Therefore the chain or stripe structure formally having higher energy can exist in practice for a very long time. This is the most likely reason why it was observed in SiO/Pd(111) system at low concentrations of reacting silane.[3–5] Due to surface strains or defects such metastable structure might be even more stable.

The most interesting question is how the compact (2×1)+gas phase, but not some other structure characterized by set of stripes, occurs in our model. As we have demonstrated, some regions on the phase diagram at $1.0<|v_t|/v_1<1.3$ is characterized by easily nucleating and disintegrating short chains. Frequent encounter of nonparallel chains at repulsive v_1 leads to their easy dissociation and gradual forma-

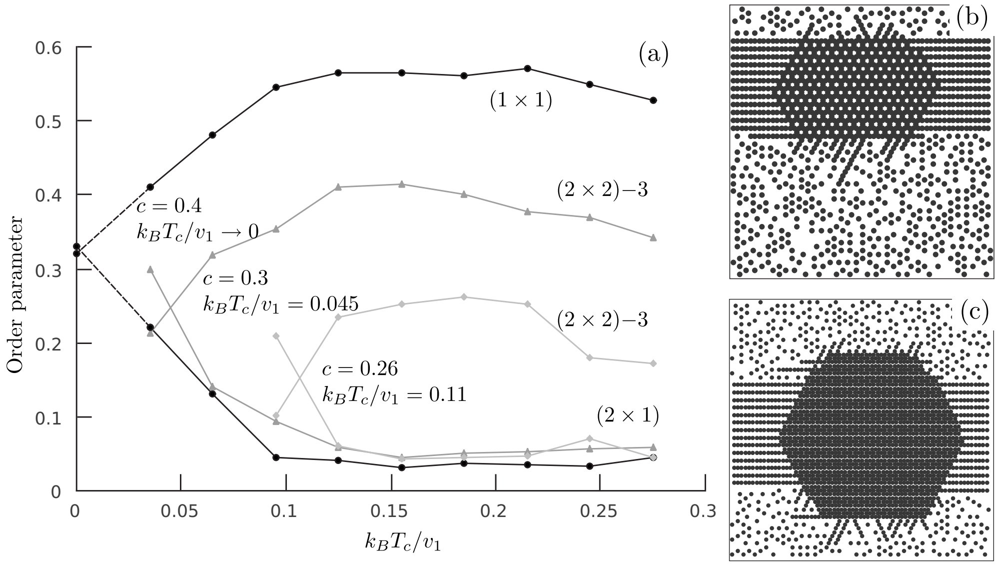


FIG. 5. (a) Temperature dependences of order parameters of (2×1) and $(2\times2)-3$ (c=0.26 and 0.3) and (1×1) (c=0.4) phases, obtained with decreasing temperature when calculation at each new temperature value starts from the configuration obtained at previous temperature. [(b) and (c)] Snapshots of domain fragments at low temperature and $|v_t|/v_1$=1.0 when order parameters of both phases are of similar magnitude. Concentration (b) c=0.3 and (c) c=0.4.

tion of parallel chains structure. Thus, the system eventually is favoring the parallel orientation of chains. It is more difficult to understand why the domain maintains the compact (2×1) form with not larger than exactly $\sqrt{3}a$ distance in between the parallel chains. We think that in such a way the system tries to avoid for the single particle to get in between the chains: the energy would increase, if the inclusion is at the NN distance from the chain. If the chains are further apart, the inclusions can start to create a new chain. Thus, when the number of free particles exceeds the number of particles in chains, the (2×1) structure is formed due to an "internal pressure" created by diffusion of free particles.

IV. CONCLUSIONS

In conclusion, we have shown that the simplest stripe structure in a form of the (2×1) phase domain can be obtained in a model with two interaction constants on triangular lattice: pair repulsion v_1 and three-body attraction in a line v_t, i.e., without inclusion of the next-nearest-neighbor and longer range forces. Our results support the idea that Si-O-Si stripe structures obtained during room-temperature decomposition of silane (SiH_4) on oxidized Pd and Pt(111) surfaces at very low concentrations of silicon (0.1–.2) (Refs. 3–5) are formed mainly due to competition of these two interaction potentials. Analyzing the results of the model we determined the stability regions of the (2×1)+gas phase. We found that this phase can be the ground-state structure of the model and also can exist as a "very stable" metastable phase at low values of concentration and $|v_t|/v_1=1.0-1.3$. The existence of stripe structure in the phase diagram, which was obtained when calculation at each new temperature value starts from the configuration obtained at previous temperature (Fig. 4) is possible in a rather small "window" of temperature and interaction parameters, the result which would hardly satisfy the experiment. However, we also found that for calculations starting from random configuration the (2×1) stripe domain persistently occurs and exists in wide regions of the phase diagram (Fig. 2). Extension of equilibration time by 2–3 orders of magnitude keeps this stripe domain stable, the fact which suggests very high barriers between competing phases. At the same time, the range of temperature and interaction parameters, where this phase exists as a metastable phase (Fig. 2), is much larger than that in the diagram of Fig. 4.

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