

## Low-Temperature Ultrafast Mobility in Systems with Long-Range Repulsive Interactions: Pb/Si(111)

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A realization of the numerous phases predicted in systems with long-range repulsive interactions was recently found in Pb/Si(111). Surprisingly, these numerous phases can be grown at low temperatures  $\sim 40$  K over macroscopic distances. This unusual observation can be explained from theoretical calculations of the collective diffusion coefficient  $D_c$  in systems with long-range repulsive interactions. Instead of a gradual dependence of  $D_c$  on coverage, it was found that  $D_c$  has sharp maxima at low temperatures for every stable phase (i.e., for every rational value of the coverage  $\theta = p/q$ ) in agreement with the experiment.

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Recent experiments on the Pb/Si(111) to study the phase transitions close to coverage  $4/3$  ML have revealed that numerous phases form and that this is one of the best realizations of an outstanding prediction in theoretical physics, i.e., the “devil’s staircase” (DS) [1]. As predicted 25 years ago in systems with long-range (LR) repulsive interactions, in principle, an infinite number of ordered phases can form at low temperatures, even with minute changes in coverage, because it is always possible to rearrange the atoms into new 1D patterns and lower the energy of the system [2–4]. This realization is important, both for fundamental science (because it shows how a complex theoretical prediction is observable) but more importantly because the numerous 1D phases provide templates of variable periodicity to study 1D physics. This discovery, however, has only addressed the issue of energetic stability of these phases but not the kinetics of their formation. Even if it is shown that for a given minute coverage change from  $\theta$  to  $\theta + \Delta\theta$  there exists a drastically novel atom arrangement with lower energy, it is still not clear what is the kinetic pathway (i.e., the optimal temperature, time, etc.) for the system to find this new arrangement and how fast it is reached. This implies that it is necessary to understand how the collective diffusion coefficient  $D_c$  (which is the appropriate parameter accounting for the relaxation of small concentration fluctuations) behaves in systems with LR interactions.

It was already shown some years ago that in other interactive overlayers with simpler short-range interactions,  $D_c$  is a sensitive parameter of phase transitions: upon crossing the phase boundary  $D_c$  can go through extrema which depend on which parameter is varied—coverage or temperature. It is in fact possible to map out phase boundaries and thermodynamic singularities from  $D_c(T, \theta)$  [5,6]. This is easily seen from the factorization of  $D_c$  into

$$D_c = D_J(\partial(\mu/k_B T)/\partial \log \theta), \quad (1)$$

the product of  $D_J$ , the jump rate diffusion coefficient (or kinetic factor), times the coverage derivative of the chemical potential, the thermodynamic factor. Close to a second order phase transition critical fluctuations are so large  $[(\partial\mu/\partial\theta)^{-1} \rightarrow \infty]$  that no diffusion currents can eliminate them, which implies  $D_c \rightarrow 0$ . In addition to the temperature dependence of  $D_c$  close to a phase transition, the coverage dependence of  $D_c$  (for fixed temperature  $T < T_c$ ) can show maxima (or minima) as the ideal coverage of the ordered phase  $\theta \rightarrow \theta_c$  is approached, since at  $\theta_c$  the perfect defect-free phase is least compressible. Such studies were performed for models with short-range (SR) interactions [7] but not for systems with LR interactions.

The evidence supporting the DS in Pb/Si(111) (and therefore the presence of LR repulsive interactions) was based on showing the existence of two generating phases ( $\sqrt{7} \times \sqrt{3}$  with  $\theta = 6/5$  ML and  $\sqrt{3} \times \sqrt{3}$  with  $\theta = 4/3$  ML) [1]. When  $n\sqrt{7} \times \sqrt{3}$  and  $m\sqrt{3} \times \sqrt{3}$  unit cells are combined they form the phase denoted by  $(n, m)$  with  $n, m$  any integers. These phases were imaged both in real and reciprocal space with complementary techniques: with atomic resolution using STM and with high resolution electron diffraction (SPA-LEED) to show that these phases cover macroscopic distances ( $\sim 0.2$  mm). Because of the bilayer structure of the Si(111) as shown in [1] the interactions between the Pb atoms can be anisotropic and the DS 1D model is a very good fit to the system as seen from the  $\mu$  vs  $\theta$  isotherm predicted by the 1D model [1]. The  $T$ - $\theta$  phase diagram was also measured and the transition from the 1D DS phases to phases of different symmetry (hexagonal HIC and striped SIC phases) was mapped out in detail [8].

In this Letter we report that different DS phases are realized at very low temperature,  $\sim 40$  K after very small deposition  $\Delta\theta \sim 0.006$  ML of Pb on top of an initial DS phase of coverage  $6/5$  ML  $< \theta < 4/3$  ML. Since the coverage modulation  $\Delta\theta/\theta \ll 1$  corresponds to a small fluctuation

tuation from equilibrium and since, as shown in Ref. [8], identical equilibrium phases form either by deposition or thermal annealing, the experiment is sensitive to equilibrium long wavelength relaxation in the system.

Motivated by these unexpected and intriguing observations we have performed calculations of the parameter which is sensitive to the equilibrium relaxation, i.e., the collective diffusion coefficient  $D_c$ , in model systems with LR interactions having chemical potential  $\mu$  vs coverage  $\theta$  isotherms analogous to the DS isotherms: plateaus of width  $\Delta\mu$  in  $\theta$  vs  $\mu$ , corresponding to the ordered phases and with phases of higher stability having larger  $\Delta\mu$ . It is found that in these models the  $D_c$  vs  $\theta$  plot shows sharp maxima corresponding to all ordered phases and that higher maxima of  $D_c$  correspond to more stable phases.

A value of  $D_c$  can be estimated from the measurements using  $D_c = L^2/4\tau$  where  $L = 200$  nm is the coherence length of the diffractometer and  $\tau$  is less than 3 sec (the time for the  $\Delta\theta$  fluctuation to relax at 40 K). This gives  $D_c > 10^{-14}$  cm<sup>2</sup>/sec since the ordering length scale can be larger than  $L$  and 3 sec is the fastest we can observe the decay of the fluctuation. This is an unusually high value of  $D_c$  for any metal system at 40 K.

These results, different when compared to the  $D_c$  vs  $\theta$  dependence found in models with SR interactions [5,6], map the fractal nature of the DS  $\mu$  vs  $\theta$  isotherms into a kinetic quantity  $D_c$ . In addition, they can explain why the transition between different DS phases is so rapid at low temperatures:  $D_c$  is high despite the low temperatures.

The conclusions are also relevant to other systems where LR repulsive interactions are present: Pb/Cu(111) [9], and Te/W(211) and Te/Mo(110) [10,11] for which, however, the fast kinetics was observed above room temperature. Theoretical predictions for the Ba-induced Si(111)3 × 2

reconstruction suggest that this can also be a DS realization [12]. Large numbers of phases of different symmetry were also predicted for the incommensurate-commensurate (I-C) transition [13,14] and the fast kinetics presented in the current work should be relevant in these systems too.

These transformations into phases of minute coverage differences but different symmetry are illustrated more clearly when the transition from the linear DS to HIC phases is presented as seen in Fig. 1. The temperature used (202 K) is above the U-shaped curve separating linear DS from HIC phases. Other transformations from linear to linear DS phases have been observed at as low as  $T = 40$  K, the lowest temperature that can be reached in the STM chamber. This result is unique to the system with LR repulsive interactions and, as theoretical modeling shows, results in maxima of  $D_c$  at low temperatures, as long as the coverage is within the regime in which the DS phases form.

Figure 1 shows ten patterns observed with increasing coverage starting at the bottom left with the  $\sqrt{7} \times \sqrt{3}$  phase ( $\theta = 6/5$  ML). High resolution 1D scans along  $[\bar{1}\bar{1}2]$  and centered at  $(\bar{1}/3\bar{1}/3)$  are used to determine spot position with an accuracy better than 0.1% of the Brillouin zone. Each successive scan was obtained after a deposition of an additional  $\Delta\theta \sim 0.01$  ML. It is clear that after every deposition there is a change into a new pattern which is as sharp as the one before, indicating a global phase change over the whole surface. The predominant phases determined by the distance in reciprocal space between the two primary spots are marked above each scan. The first three scans correspond to linear DS phases of decreasing periodicity. The second panel has a main periodicity of  $19a_0$  and changes to a pattern with main periodicity  $9a_0$  [with  $a_0 = 3.84$  Å the lattice constant of Si(111)]. With continuing deposition an even more dra-

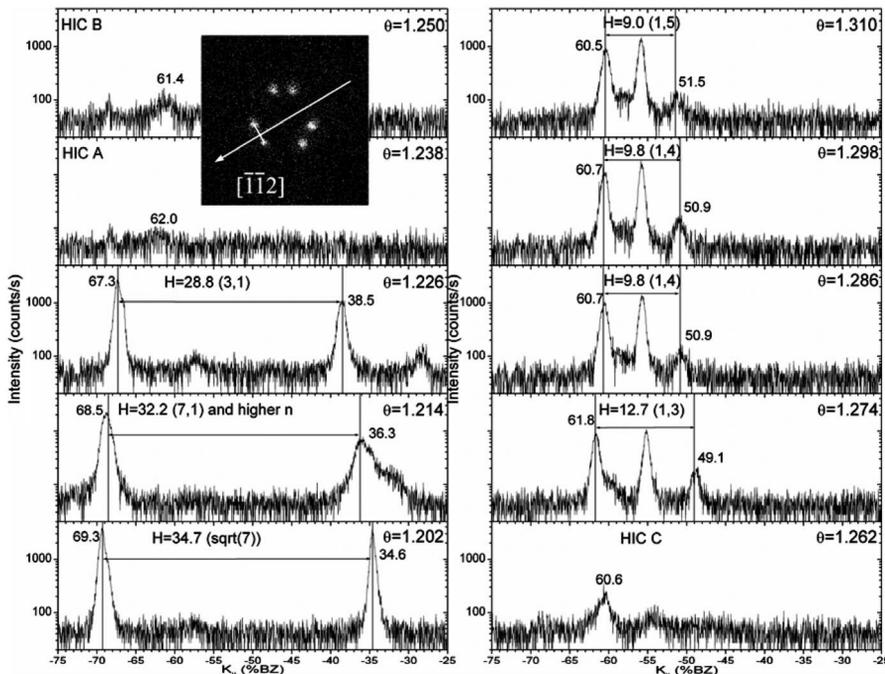


FIG. 1. SPA-LEED 1D scans along  $[\bar{1}\bar{1}2]$  and close to the  $(\bar{1}/3\bar{1}/3)$  spot showing the transformation of phases differing in coverage by less than  $\sim 0.01$  ML. The phases are marked at the top of each panel. The inset shows that for the HIC phases only the projection onto the  $[\bar{1}\bar{1}2]$  direction is seen in the 1D scans.

matic rearrangement occurs as seen for  $\theta = 1.238$  ML with the formation of the HICA phase, which was identified both with the projection of the slightly off-axis spots onto the  $[\bar{1}\bar{1}2]$  direction (see inset of Fig. 1) as well as from 2D scans. This involves more extensive rearrangement of the linear DS phases since the HIC phases have a threefold symmetry with their triangular unit cells consisting of  $\sqrt{3} \times \sqrt{3}$  cells which are separated by domain walls of the “almost”  $\sqrt{7} \times \sqrt{3}$  phase [15]. The rearrangement is also seen in Fig. 2 with STM, where an initial  $25 \times 25$  nm<sup>2</sup> area with the  $\sqrt{7} \times \sqrt{3}$  phase transforms into the (2,1) phase after Pb deposition of  $\Delta\theta \sim 0.035$  ML, followed by the (3,1) phase after an additional  $\Delta\theta \sim 0.04$  ML at 135 K.

These intriguing results raise the question what is the  $D_c$ : can it be so high for all the numerous ordered phases and at such low temperatures? To answer these questions we calculated  $D_c$  in models with LR repulsive interactions relevant to Pb/Si(111) as suggested by the statics [1].

As seen from Eq. (1) the calculation requires both the thermodynamic factor (obtained from the  $\mu$  vs  $\theta$  isotherm) and the kinetic factor which is determined by how the hopping barrier is modified by the LR interactions. Traditionally, the calculation of these quantities was carried out either within the quasichemical approximation (and its close variations) or with Monte Carlo simulations [7]. Recently, an analytic method was proposed for lattice gas models with arbitrary interactions between the atoms. The method is described in [16,17], with [17] dealing specifically with its application to systems with LR interactions in 1D.

Different models with DS realization have been proposed both in 1D [2–4] and 2D [18]. The 1D model with LR elastic interactions of the form  $J/r^s$  with  $s = 2$  (the results depend very weakly on  $s$ ) and  $r$  the separation between any two Pb atoms was shown to be applicable to Pb/Si(111) [1]. In addition, if only the high symmetry Pb atoms are assumed to be involved in the interaction (which effectively amounts to a renormalization of the interaction constant  $J$ ) then the coverage in the real system is mapped into  $1/5$  ML  $< \theta < 1/3$  ML [1]. One other difference is that in the real system the two generating phases  $\sqrt{7} \times \sqrt{3}$

and  $\sqrt{3} \times \sqrt{3}$  differ by two lattice constants [1]—this does not affect the hierarchical structure of the DS phases.

So far, the theoretical analysis in the DS 1D model has been carried out to calculate the  $\theta$  vs  $\mu$  isotherm at  $T = 0$ , but no work has been performed to calculate kinetic parameters like  $D_c$ . Despite, however, the impossibility of performing exact calculations in the DS model the main conclusions about  $D_c$  can be deduced by comparing the results for  $D_c(\theta)$  in two other solvable models from which an extrapolation to the DS case is unequivocal.

The isotherms for the DS model are calculated in Ref. [1] for the interaction energy  $J/r^2$  from the stability  $\Delta\mu$  of a phase with coverage  $\theta = p/q$

$$\Delta\mu(p/q) = \sum_{l=1}^{l=\infty} lq\{J(lq+1) + J(lq-1) - 2J(lq)\}, \quad (2)$$

which results in the characteristic DS fractal structure of the isotherm. The stability of the phase (i.e., the value  $\Delta\mu$ ) depends only on the period of the phase  $q$ .

Two other models were studied at finite  $T$ . A model labeled SR with nearest neighbor repulsive interaction has a  $(2 \times 1)$  ordered phase at  $T = 0$  and  $\theta = 1/2$ . At other coverages there is coexistence between the vacant state ( $\theta = 0$ ) and  $(2 \times 1)$  for  $\theta < 1/2$  ML or the full state ( $\theta = 1$ ) and  $(2 \times 1)$  for  $\theta > 1/2$  ML. The other model, introduced in [19], has “screened” LR repulsive interactions only between neighboring atoms. Stable phases are possible only for coverages with  $\theta = 1/q$  ( $q = 1, 2, 3, \dots$ ). For other coverages there is coexistence between the adjacent phases, i.e., the phase with  $\theta = 1/q$  coexists with the next phase  $\theta = 1/(q-1)$ . This model is labeled a staircase (S) interaction model. The width of the plateaus monotonically increases as one approaches  $\theta = 1$ .

$D_c$  was calculated according to Eq. (1). The thermodynamic factor can be expressed as the inverse of the mean square number fluctuation  $\langle N \rangle^2 / (\langle N^2 \rangle - \langle N \rangle^2)$ . At coverages at which there is a plateau in  $\mu$  and at  $T = 0$  this quantity diverges because the system is “locked” into the same coverage over a finite interval of  $\mu$ . In fact, at finite temperature the isothermal compressibility can be approximated at  $\theta = p/q$  for the DS model by

$$\frac{\partial(\mu/k_B T)}{\partial\theta} = \frac{1}{2} \left(\frac{p}{q}\right)^2 \exp\left(\frac{1}{2} \frac{\Delta\mu}{k_B T}\right). \quad (3)$$

The dramatic increase of the thermodynamic factor still depends monotonically on phase stability  $\Delta\mu$ .

For the full determination of the behavior of  $D_c$  one needs to determine also the kinetic factor  $D_j$  in Eq. (1). It accounts for the local barrier an atom needs to overcome from its initial to its final position. The hopping algorithms depend on the change of the energy at the initial  $\delta E_i$  and final site  $\delta E_f$  due to interactions [7], but it can also depend on the energy change due to interactions at the saddle point of the activated state, as shown in [5]. This change was necessary to explain a moderate dependence of  $D_c$  on  $\theta$  in CO/Ru(111).

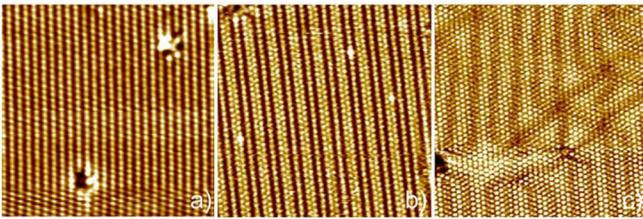


FIG. 2 (color online).  $25 \times 25$  nm<sup>2</sup> area showing initially the  $\sqrt{7} \times \sqrt{3}$  phase with  $\theta = 1.2$  ML (left) transforming into the (2,1) phase with  $\theta = 1.235$  ML (middle) followed by the (3,1) phase with  $\theta = 1.28$  ML after deposition of  $\Delta\theta \sim 0.04$  ML at 135 K.

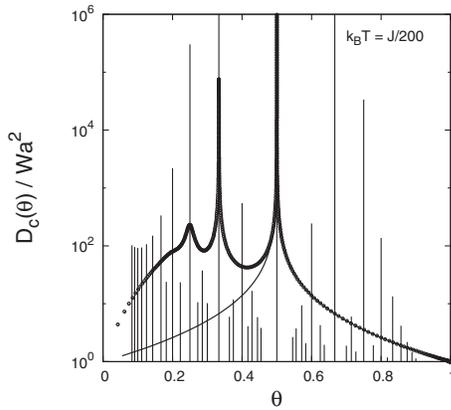


FIG. 3.  $D_c$  vs  $\theta$  dependence for the SR model (symmetric solid line around  $\theta = 1/2$  ML), for the S model (circles), and the thermodynamic factor for the DS model (vertical lines). For weakly coverage dependent kinetic factor,  $D_c$  follows the maxima of the thermodynamic factor in good agreement with the experiment.

The choice of the barrier change for the activated state should be guided by the experimental system. For Pb/Si(111) the fast rearrangement of the system to new DS phases for all coverages at low temperature can be reproduced with the choice of the saddle point barrier energy change being  $\delta E_s = \min(\delta E_i, \delta E_f)$ . With this choice, the kinetic factor was calculated using analytical results for the SR and S models. The results for  $D_c(\theta)$  and  $J/k_B T = 200$  are shown in Fig. 3.  $D_c$  is scaled to the single particle diffusion coefficient  $Wa^2$  (itself depending on  $T$ ). The choice of the barrier height modification model  $\delta E_s = \min(\delta E_i, \delta E_f)$  is the most relevant for Pb/Si(111): it can account for the observed intriguing result, i.e., fast low-temperature preparation of the DS phases in Pb/Si(111) independently of the initial phase of the system. The resulting weakly coverage-dependent kinetic factor leads to  $D_c$  which follows the maxima of the thermodynamic factor in good agreement with the experiment.

This statistical mechanics analysis is phenomenological and describes correlations between the diffusing adatoms, but the choice of the parameters relevant to Pb/Si(111) would ideally require first principles calculations. Unfortunately, no such calculations are available in the literature and are beyond the scope of this Letter. However, the unusual structure of the dense maxima in  $D_c$  vs  $\theta$  persists even for  $J/k_B T$  as low as  $J/k_B T = 25$ ; although the values of the maxima are reduced. Density-functional theory (DFT) calculations in the literature on other metal systems have shown the presence of LR interactions in Ag/Ag(111) which can account for the anomalously low terrace diffusion prefactors [20]. The importance of LR interactions in metal/semiconductor systems was confirmed in Ba/Si(111) [12]. DFT energies of this system were mapped to 1D antiferromagnetic Ising model showing that the LR interactions are of electronic

origin. LR interactions are present in Pb/Cu(111), and result in unusually self-organized patterns [21]. The reason for the higher diffusion activation energy in Pb/Cu(111) was that mass transport is through vacancy diffusion.

In summary we have described low-temperature experiments on Pb/Si(111)- $\alpha\sqrt{3} \times \sqrt{3}$  showing extensive overlayer rearrangement over macroscopic distances from phases of different symmetry and periodicity, induced by minute changes in coverage  $\Delta\theta$ . These extensive rearrangements indicate a very high diffusion coefficient  $D_c$  in the system. By calculating  $D_c$  in model systems with LR repulsive interactions, we show that the  $D_c$  vs  $\theta$  dependence consists of sharp maxima at all coverages corresponding to the stable phases at low temperatures in good agreement with the experiment.

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