Surface Diffusion of Pt on Pt(110): Arrhenius Behavior of Long Jumps

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The one-dimensional diffusion of Pt adatoms in the missing row troughs of the (1×2) reconstructed Pt(110) surface is monitored directly from atomically resolved time-lapsed scanning tunneling microscopy images. For this self-diffusion system, it is surprisingly found that not only jumps between nearest neighbor sites but also *long jumps*, i.e., jumps between next nearest neighbor sites, participate. The hopping rate for these long jumps is found to follow an Arrhenius dependence with an activation barrier for diffusion ($E_{d2} = 0.89$ eV) slightly larger than that for single jumps ($E_{d1} = 0.81$ eV). [S0031-9007(97)03476-5]

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The diffusion of adatoms on metal surfaces is one of the most fundamental processes in surface science and is of crucial importance in such diverse areas as crystal and thin film growth, heterogeneous catalysis and oxidation. This has spurred a tremendous interest in understanding the nature of surface diffusion on the atomic scale. In the conventional picture of surface diffusion, the adatom migration occurs through a series of uncorrelated displacements over the minimum energy barrier between nearest neighbor binding sites on a static substrate. The time honored technique for direct observation of surface diffusion processes is field-ion microscopy (FIM), where the migration of adatoms is followed on small terraces at the apex of very sharp FIM tips [1,2]. This technique has over the years led to the discovery of many novel atomic scale diffusion mechanisms [1–3]. More recently also scanning tunneling microscopy (STM) has given valuable information about surface diffusion although in most cases in an indirect manner from nucleation and growth experiments [4–8]. In a few cases it has also been possible by means of STM to follow the diffusion processes directly at the atomic level [9–11], but so far attempts at studying metal on metal diffusion by tracking the individual atoms have not been successful [8].

In spite of the increased knowledge of diffusion processes, a number of fundamental questions still remain unsolved. In particular, it has been speculated that *long jumps* may occasionally occur where a diffusing adatom, once promoted to a transition state, spans several lattice spacings before retrapping rather than migrates in the ordinary fashion between nearest neighbor lattice sites. The presence of long jumps may, for instance, affect the activation barrier determined from measurements of the mean-square displacement of diffusing adatoms since a long jump would contribute strongly to this quantity [12–14]. Long jumps are believed to be common at high temperatures where $k_B T$ is comparable to the activation barrier for diffusion. At lower temperatures, long jumps are thought to occur if the energy dissipation to the substrate lattice is weak [15], and from molecular dynamics (MD) simulations they have been found to play a significant role in the diffusion of adsorbed gases on metal surfaces [14,16]. However, for metal on metal diffusion the coupling to the lattice is much stronger. This is especially true for self-diffusion where the equal masses of adsorbate and substrate atoms cause the energy transfer in collisions to be at a maximum [17]. Thus for self-diffusion long jumps are expected to be less likely. Experimental observations of long jumps are still very scarce. In an FIM study by Senft and Ehrlich [13], a significant contribution from long jumps was revealed for the diffusion of Pd on W(211), whereas for self-diffusion of W on W(211) no long jumps were found to occur.

Several questions arise in this connection. Do these long jumps exist for other systems than Pd on W(211), and is it generally so that they do not exist for metal self-diffusion? Does the rate for long jumps follow a simple Arrhenius dependence with temperature? If so what is the activation barrier for long jumps, and does it differ from the activation barrier for single jumps?

In this Letter we will address these fundamental questions by presenting results on the surprising finding that a significant proportion of long jumps participate in the *self*-diffusion of Pt on the Pt(110)-(1×2) surface. The Pt adatoms are confined to the troughs of the (1×2) missing row reconstruction, where their one-dimensional (1D) migration has been monitored directly from time-lapse STM movies.

The experiments are performed in a UHV chamber equipped with a variable temperature STM as well as standard facilities for sample preparation and characterization. The Pt(110) crystal was sputter cleaned with 1.5 kV Ne ion bombardment followed by annealing to 980 K. This treatment left the surface in its clean (1×2) reconstructed state. The Pt adatoms are deposited on the surface by resistive heating of a thoroughly outgassed 0.4 mm diameter 99.995% pure Pt wire. After deposition, the sample is transferred to the STM for imaging at temperatures ranging from 280 to 380 K. The image acquisition time is varied according to the atomic mobilities, values ranging from 2

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to 20 sec per image (256 × 256 pixels). All STM movies are obtained in the constant current mode with $I = 1$ nA and $V = 100$ mV.

Figure 1 shows an STM image of the Pt(110)-(1 × 2) missing row reconstructed surface after Pt has been deposited. The deposited Pt atoms are found in the 1D troughs of this (1 × 2) missing row surface, and the close-packed Pt rows separating these troughs are imaged with atomic resolution. The image is acquired after the sample has been held at the deposition temperature of 313 K for more than 4 hours. Obviously there must be some thermal mobility at this temperature since otherwise the adatoms would not have been able to meet, nucleate, and form the one-dimensional islands. On the other hand, since single adatoms are still left on the surface, the mobility is sufficiently low for the nucleation and growth process not to cease even after several hours.

To gain detailed insight into the adatom migration, we have acquired many consecutive STM images. When played back as a STM movie, these images impart a vivid impression of the diffusion process; examples can be found at our World Wide Web (WWW) site [18]. The migration of the adatoms in the troughs becomes immediately clear by inspecting these movies. We never observe events where an adatom traverses from one missing row to another, and the diffusion is thus truly 1D at temperatures up to at least 380 K. To reduce adatom-adatom interactions as much as possible, all movies are acquired at very low coverages where only 5–20 adatoms are within the field of view of 160 × 160 Å^2 at a time. Since the movies usually consist of 300–500 images, the number of observations, that is, the number of times an atom is observed in two consecutive images, displaced or not, amounts to several thousand. To quantify the information on surface diffusion contained in the movies, the adatom positions are tracked as a function of time, using a semiautomatic pattern-recognition routine.

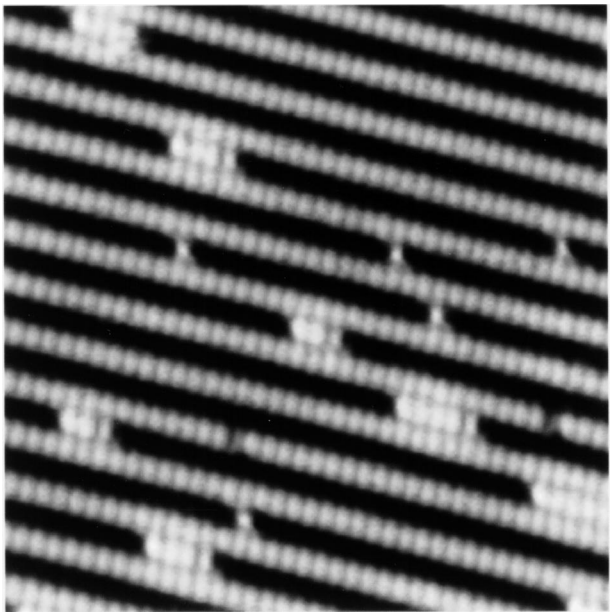

FIG. 1. STM image showing the Pt(110)-(1 × 2) surface after a submonolayer amount of Pt has been deposited at 313 K. The presence of single adatoms as well as nucleated islands in the troughs of the missing row reconstruction are evidence for a low thermal mobility (97 × 102 Å^2).

When determining the adatom hopping rate from the found positions, one has to be aware that the observed displacements of adatoms between consecutive images cannot simply be equated with the actual adatom jumps. An adatom might perform several jumps between consecutive images, which would be observed as either a displacement over several lattice spacings or, if the atom jumped back and forth, no displacement at all. The appropriate analysis of a 1D random walk in continuous time, including the possibility that an adatom can make long jumps has been carried out in detail by Ehrlich and co-workers [12]. They find that the probability $P_x(t)$ of an atom, initially at position $x = 0$ at time $t = 0$, to be at lattice site x at some later time t is given by

$$P_x(t) = \exp[-(h_1 + h_2)t] \sum_{j=-\infty}^{\infty} I_j(h_2 t) I_{x-2j}(h_1 t), \quad (1)$$

where I_n are the modified Bessel functions of the first kind of order n, and h_1 and h_2 are the rates for single and double jumps, respectively. The expression is easily extended to include rates for longer jumps. In the present context, t is the time interval between consecutive images [19]. The adatom hopping rates, h_1 and h_2, are determined by fitting the expression for $P_x(t)$ to the probabilities obtained from the measured distributions of adatom displacements.

In Fig. 2 we show an example of an experimentally determined displacement distribution together with the best fits of the expression for $P_x(t)$ when we allow for (i) only single jumps ($h_2 = 0$) and (ii) both single and double jumps. The fitted distributions are normalized to the same number of observations as the measured one, and we have imposed the usual [12] constraint that the fitted distribution should have the same mean-square displacement, $\langle \Delta x^2 \rangle$, as the measured one. The fit allowing for both single and double jumps is clearly seen to be superior, and thus we conclude that it is imperative to include double jumps to account for the observed displacement distribution. We will return to the question of the statistical significance of the data below.

The determined hopping rates for single and double jumps are plotted in Fig. 3 versus $1/T$. The ratio between double and single jumps, that is, h_2/h_1, increases slightly with temperature, but lies in the (5–10)% range. The hopping rate for the single jumps is seen to exhibit an Arrhenius dependence on temperature. More importantly, however, such an Arrhenius dependence is for the first time seen to hold also for the double jump rate. By fitting

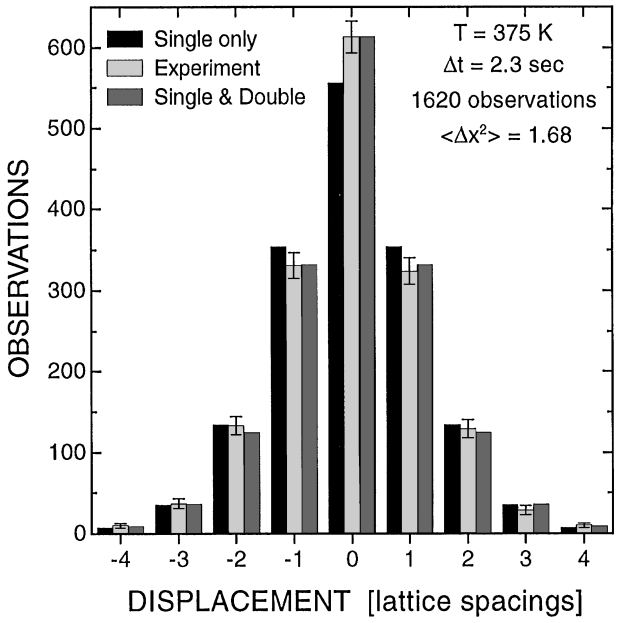

FIG. 2. Distribution of displacements for the self-diffusion of Pt on Pt(110)-(1 × 2) at 375 K. The best fit (dark gray) is obtained with a double to single jump ratio $h_2/h_1 = 9.5\%$. The distribution corresponding to diffusion by single jumps only is shown in black.

to the Arrhenius form, $h = \nu \exp(-E_d/k_B T)$, where ν is the prefactor, k_B is Boltzmann's constant, T is the temperature, and E_d is the activation barrier for diffusion, we obtain for the single jumps $E_{d1} = 0.81 \pm 0.01$ eV, $\nu_1 = 10^{10.7\pm0.2}$ sec^{-1}, and for the double jumps $E_{d2} = 0.89 \pm 0.06$ eV, $\nu_2 = 10^{10.9\pm0.8}$ sec^{-1} [20].

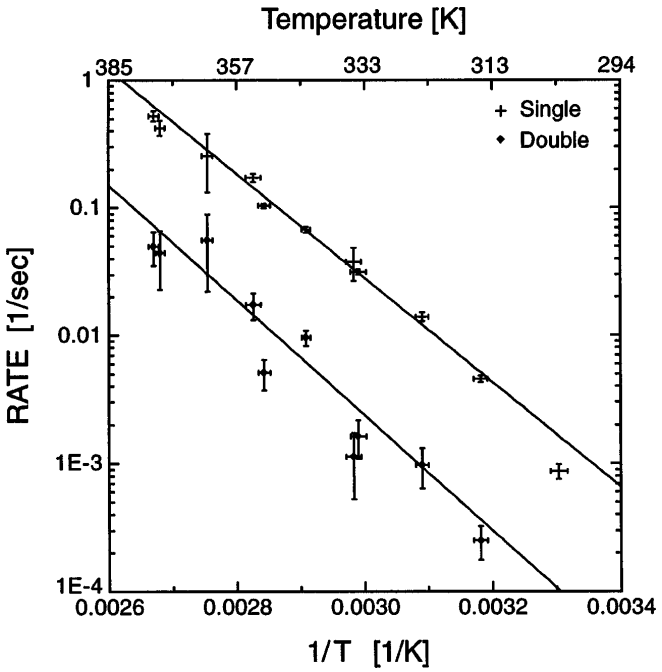

FIG. 3. Arrhenius plot of the determined rates for single and double jumps, h_1 and h_2.

Before we further discuss the implications of the above findings, we will briefly address the issue of the statistical significance of the data. When the relative rate for double jumps, h_2/h_1, becomes low, the question arises whether the changes to the displacement distributions brought about by the double jumps are sufficiently large that the double jump rate, h_2, can be reliably determined. To address this issue, a kinetic Monte Carlo (KMC) routine is used to simulate 1D random walks for different h_2/h_1 ratios. The resulting displacement distributions are subsequently fitted with the expression for $P_x(t)$ [12]. We have verified that it is indeed possible, for the number of observations and mean-square displacements experimentally encountered, to regain the input value for h_2 precisely down to a range of $h_2/h_1 \approx (1-2)\%$ if averaging is done over a large number of runs. It is similarly verified that if *no* double jumps are allowed in the simulations, the double jump rates resulting from the fitting are, indeed, negligible. Thus, the only problem in determining double to single jump ratios, at the level of (5–10)% encountered experimentally, stems from the statistical scatter in the measurements. This quantity is assessed by performing sets of KMC simulations for each movie, where the input parameters are those relevant for the particular conditions. The confidence intervals (in either direction) shown on Fig. 3 correspond to one standard deviation evaluated from such simulations. From Fig. 3 we therefore conclude that the existence of long jumps is indeed statistically significant.

In the analysis presented above, it is implicitly assumed that the adatom migration is a random walk between equivalent sites with jump rates independent of time. If strong correlations exist between adatoms or if the diffusivity is influenced by the presence of the STM tip, systematic errors could occur. As already mentioned, all data are acquired in a regime of very low coverage. If, in spite of this, an adatom comes within a few lattice spacings of another adatom in the same row, its displacements are excluded from the analysis. In general, adatoms that pass each other in adjacent rows are included in the analysis. However, in a test case it was verified that if the relatively small number of such events were also excluded, no significant change in the determined jump rates resulted.

The question of a possible tip influence has been thoroughly investigated, and details will be reported elsewhere. In brief we find two different regimes for the dependence of the hopping rate on the tunnel junction resistance, R. For values of $R \geq 50$ MΩ the adatom hopping rate is found to be independent of R, whereas for lower values of R there is a considerable increase in the hopping rate. Since the present results are all acquired at $R = 100$ MΩ tip influence is negligible.

We now return to a discussion of the determined activation barriers for single and double jumps. The data presented here constitute the first experimental demonstration that the rate for double jumps follow an Arrhenius dependence on temperature. Even though this result might

have been expected from general considerations of activated processes, it has to our knowledge never been shown in any of the previous theoretical papers on this subject. However, in very recent MD simulations such a behavior has indeed been verified [21].

If we in the expression for the double jump rate, $h_2 = \nu_2 \exp(-E_{d2}/k_B T)$ assume that $E_{d2} = E_{d1} + \Delta E$, we find from Fig. 3 that $\Delta E = 0.08 \pm 0.06$ eV. This ΔE may be interpreted as an additional energy required for a long jump to occur. The dissipation of energy when an adatom diffuses over the surface has been modeled as a friction term in a generalized Langevin equation by Ferrando *et al.* [15]. They find a characteristic energy associated with the work performed by the frictional force as the atom moves over one lattice spacing. Although it is unclear whether this energy can be directly associated with the additional energy ΔE mentioned above, the fact that ΔE for Pt on Pt(110) is found to be small seems to indicate that the energy dissipation to the substrate is low in this system. This is surprising since a strong coupling is generally expected for a self-diffusion system where adatoms and substrate atoms have equal masses. The present findings seem to differ from the FIM studies of Pd and W on W(211) [13]. In this case no long jumps were found for W on W(211), whereas for Pd the long jumps disappeared by a lowering of the temperature from 133 to 122 K. This led the authors to suggest that the barrier for a double jump in this latter system was roughly twice as big as that for a single jump.

In conclusion, we have found that a significant amount of long jumps occur for self-diffusion of Pt on the Pt(110)-(1×2) missing row reconstructed surface. The hopping rate for the long jumps is found to follow an Arrhenius dependence on termperature, and the activation barriers for single and double jumps are determined to be $E_{d1} = 0.81$ eV and $E_{d2} = 0.89$ eV, respectively. This energy difference may be interpreted as a measure of the energy dissipation of the Pt adatoms on the Pt(110)-(1×2) surface. Hopefully the present experimental findings will stimulate new theoretical studies.

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[18] http://www.dfi.aau.dk/condensm/surface/stmlab/ptmovies/ptmovies.htm
[19] More precisely, t is the time that elapses between the moments when the tip is at the same position in consecutive images. Because of the gradual scanning of the image, atoms that have moved will be imaged with time intervals slightly different from t. This effect proves insignificant in the present case. Conceptually, however, the effect constitutes a fundamental difference between STM and FIM diffusion measurements. Further discussion will be published elsewhere.
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