VOLUME 92, NUMBER 16 PHYSICAL REVIEW LETTERS week ending 23 APRIL 2004

Long Jump Rates in Surface Diffusion: W on W(110)

Grazyna Antczak[1,2] and Gert Ehrlich[1]
[1]Materials Research Laboratory and Department of Materials Science and Engineering,
University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, USA
[2]Institute of Experimental Physics, University of Wroclaw, Wroclaw, Poland

(Received 9 September 2003; published 23 April 2004)

We have reexamined the diffusion of W adatoms on W(110) using the field ion microscope. The diffusivity is in good agreement with previous results and reveals no unusual features, but from observations of the distribution of displacements, corrected for diffusion during temperature transients, we have for the first time been able to measure the temperature dependence of rates for nearest-neighbor and double jumps, as well as for vertical and horizontal transitions. Activation energies and frequency factors for all the long jumps are significantly larger than for single jumps, and a simple model is proposed to account for our observations.

DOI: 10.1103/PhysRevLett.92.166105 PACS numbers: 68.35.Fx, 68.35.Ja, 81.10.Aj, 81.15.Kk

During the last decade, long jumps, that is jumps between other than nearest-neighbor sites in diffusion, have been identified on a number of different surfaces in studies which have determined the ratio for long-jump rates compared to that for single jumps [1–7]. What has so far not been possible to do is to establish the actual rate law governing long jumps. How does this rate law compare with that of the usual single jumps between nearest-neighbor sites, and how do such jumps come about? No information at all is available about these matters, even though they are important for diffusion as well as for chemical reactions. It is our objective here to probe these two questions. In this effort we concentrate on examining the behavior of tungsten atoms on the W(110) plane, for which much is already known [7–9].

We first examine the diffusivity, which describes the overall rate of mass transfer in surface diffusion. This is easy to establish using techniques such as field ion microscopy or scanning tunneling microscopy that reveal the location of individual adsorbed atoms on a surface. A measurement of the mean-square displacements on an infinite surface yields the diffusivity D through the relations

$$\langle \Delta x^2 \rangle = 2D_x t, \tag{1}$$

$$\langle \Delta y^2 \rangle = 2D_y t, \tag{2}$$

where t is the diffusion time interval. For tungsten atoms diffusing on W(110), we have made measurements in a field ion microscope [10] of the mean-square displacements at temperatures ranging from 301 to 364 K. At each temperature, a minimum of 1200 observations was taken. To derive the diffusivity D, however, still requires corrections. In our studies, atom motion is observed on planes with a diameter in the neighborhood of ~25 lattice spacings, not on an infinite surface. Displacements that occur within ~2 distances of the lattice edges are rejected, in order to avoid edge effects. Furthermore, to correct for diffusion occurring on a finite surface, Monte Carlo simulations are made of the mean-square displacement during a time interval t on a surface of the same dimensions as in the actual experiments, until a jump rate is found in the simulations which agrees with the experimental value of $\langle \Delta x^2 \rangle$. Especially at elevated temperatures, however, some atom movement occurs both while the surface is being heated to the set temperature and after heating is stopped. The mean-square displacement during this transient period is measured in separate experiments in which the heating current is cut off once the temperature reaches the set value [11]. This zero-time value of the mean-square displacement, also based on a minimum of 1200 observations, is then subtracted from the value in the original experiments to derive $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ in Eqs. (1) and (2). The diffusivities for W atoms on W(110), given by the Arrhenius relation $D = D_0 \exp(-E_D/kT)$, are plotted in Fig. 1 as a function of $1/T$. What is important here is that this plot is quite linear over a temperature range of more than 60 K. For D_x it yields an activation energy $E_D = 0.92 \pm 0.02$ eV and a prefactor $D_0 = 1.61(\times 1.6^{\pm 1}) \times 10^{-3}$ cm^2 s^{-1}; for D_y, $E_D = 0.93 \pm 0.01$ eV and $D_0 = 5.21(\times 1.4^{\pm 1}) \times 10^{-3}$ cm^2 s^{-1}. The prefactors have the magnitude standard in surface diffusion; also, both results are in good agreement with more limited earlier experiments [9] and reveal *no* unusual effects.

The all important question now concerns the nature of the jumps made by an atom in diffusing at different temperatures and their rates. Possible jump processes have been previously explored [7] and are sketched in Fig. 1. In addition to nearest-neighbor jumps α there is the possibility of double jumps β spanning two nearest-neighbor distances along the close packed $\langle 111 \rangle$; we also have to consider the possibility of horizontal δ_x transitions and vertical δ_y jumps. Long jumps are expected to raise the diffusivity above its usual value, but this is not a reliable guide to the presence of such transitions, and there is no indication of any such effect in our results. Information about jump processes important in

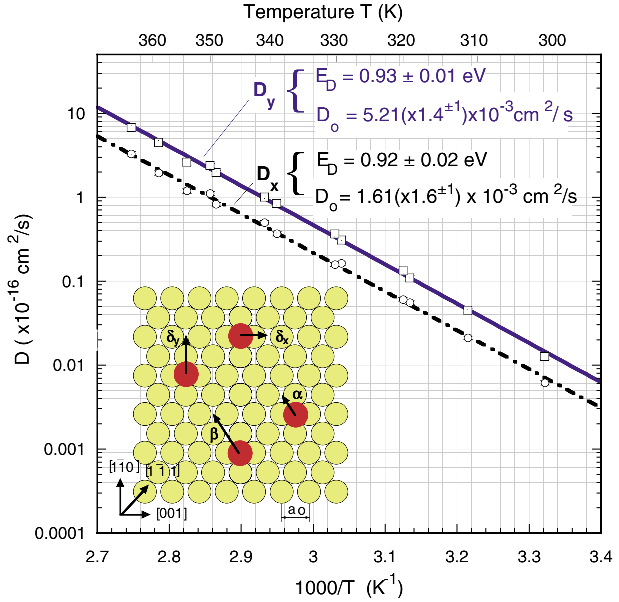

FIG. 1 (color online). Temperature dependence of diffusivities for W atoms on W(110) derived from mean-square displacements; these were obtained from a minimum of 1200 observations at each temperature. Diagram at bottom left illustrates possible jump processes on W(110).

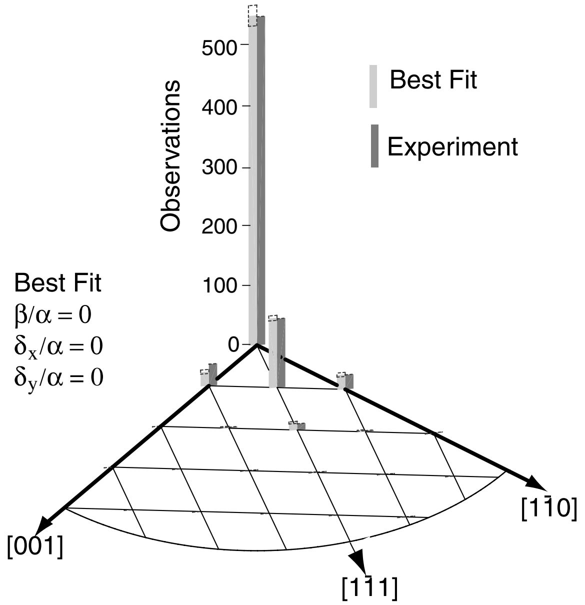

FIG. 2. Distribution of W atom displacements at 319 K on W(110) derived from 1200 observations. Best fit obtained with only single α jumps in diffusion.

diffusion requires additional measurements of the frequency with which different displacements occur [12]. Once this distribution is known, corrections have to be made for the finite plane size. Monte Carlo simulations are carried out, again on a plane of the same dimensions as in the experiments, for different values of the possible jump rates; this simulation is continued until the distribution of displacements achieved in the simulations is in good agreement with that from the actual observations [2]. From this rate we can then evaluate the mean-square displacements on an infinite plane [13]. At elevated temperatures, this distribution again has to be corrected for atom motion during temperature transients, but in a more elaborate way [11,14]. A rate R is deduced from the distance distribution for experiments extending over a total time interval t; the rate r_0 during the transient interval of length t_0 also has to be determined separately. The actual rate r at the set temperature during a corrected time period t_c is obtained by taking the total number of jumps, Rt, subtracting the number found in zero-time experiments, $r_0 t_0$, and then dividing by the time t_c at the set temperature; the rate r is thus found as $r = (Rt - r_0 t_0)/t_c$ [15].

The distribution of displacements derived in this way from observations at 319 K, a low temperature for the diffusion of tungsten atoms on W(110), is shown in Fig. 2. The best fit to the experiments is obtained with just single α jumps between nearest-neighbor sites [16]; other processes make negligible contributions. Much the same is true at other low temperatures below 342 K. At higher temperatures [17], longer jumps are known to participate [7]. The distribution of displacements at 364 K, for example, is shown in Fig. 3. To achieve a fit requires a ratio of double to single jumps $\beta/\alpha = 0.17$ and also horizontal as well as vertical jumps at $\delta_x/\alpha = 0.23$ and $\delta_y/\alpha = 0.26$.

These results do not yet give us the actual jump rates at the set temperature, $T = 364$ K. The displacement distribution during transients at the set temperature of 364 K is shown in Fig. 4, and with this information we can finally arrive at the rate ratios. We note here that at really elevated temperatures the zero-time corrections are quite significant, as considerable atom motion occurs before and after the set temperature is achieved. Measurements have been made on a total of 13 temperatures, and the results for

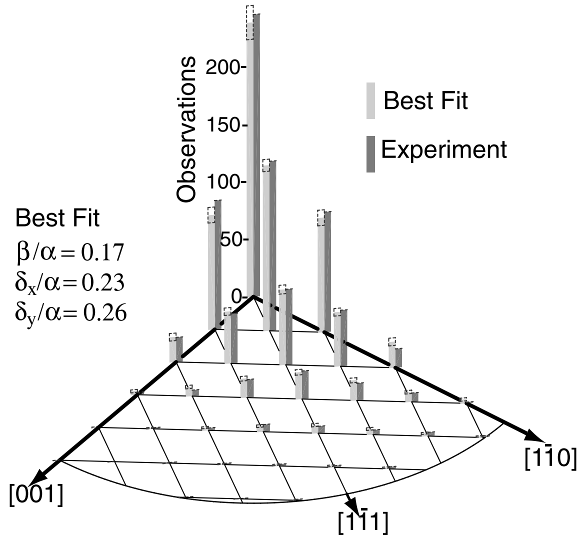

FIG. 3. Distribution of displacements for W atoms on W(110) at 364 K, based on 2400 observations.

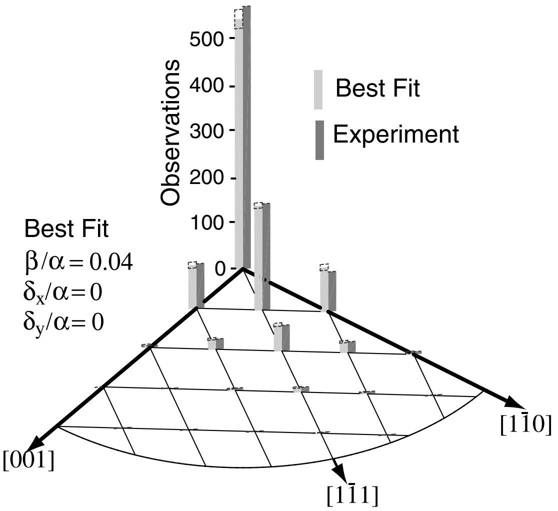

FIG. 4. Distribution of W atom displacements during temperature transients in diffusion experiments at 364 K obtained from 2400 observations.

significant rate ratios and for the fraction of long jumps are collected in Table I. It is clear again that as the temperature is raised the role of long jumps becomes much more important in the diffusion process.

How do we understand these results? As shown in Fig. 5, at high temperatures the rate α diminishes significantly below the values extrapolated from low temperatures. With the single jump rate α now known, we can arrive at the rates for the other jumps β, δ_x, and δ_y, which are shown in Figs. 5 and 6. For the first time we have information about the actual rate law governing long jumps, not just about rate ratios; the prefactors and activation energies for the rates are given in Table II. Because of the uncertainties in the rate ratios, there is considerable scatter in these rates, especially in δ_x, and δ_y [18]. For all the long jumps, however, both the prefactor and the activation energies are significantly higher than for single jumps, the latter by roughly 30% or more.

The questions that now remain are how to account for the strange behavior of the nearest-neighbor single jump rate α, the value of which actually diminishes at higher temperature, and how to understand the linear behavior of $\ln(D_x)$ with $1/T$, where long jumps do not increase the overall rate at high temperatures. We make the following proposal. The basic jump process for tungsten atoms on W(110) takes place along the close-packed direction $\langle 111 \rangle$ as indicated in the inset of Fig. 7. This rate R_l is given by the expression for the low temperature rate of α jumps. At low temperatures, jumping atoms condense at nearest-neighbor sites to make an α transition. At elevated temperatures, however, a jumping atom can deviate from this path in various ways, as given by a conversion probability p_i [19]. The atom can continue along the $\langle 111 \rangle$

TABLE I. Rate ratios for W on W(110).

T (K)	β/α	δ_x/α	δ_y/α	Fraction long jumps
320	0.0490	0.0357	0.0357	0.107
329	0.0221	0.0244	0.0244	0.0662
330	0.0300	0.0389	0.107	0.149
339	0.00	0.0528	0.0792	0.117
341	0.0227	0.0227	0.0227	0.0639
349	0.0318	0.0388	0.133	0.169
350	0.166	0.198	0.295	0.397
354	0.122	0.0663	0.178	0.268
359	0.214	0.206	0.335	0.430
364	0.755	1.257	1.417	0.774

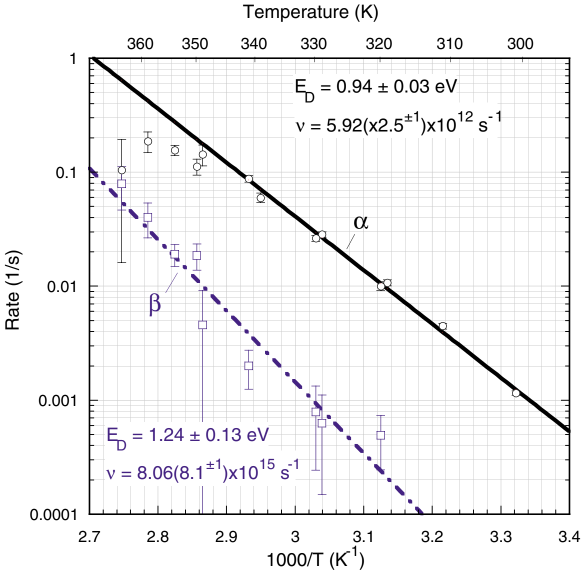

FIG. 5 (color online). Arrhenius plot for nearest-neighbor jump rate α and for the double jump rate β. Linear plot for α shows the fit for low temperatures.

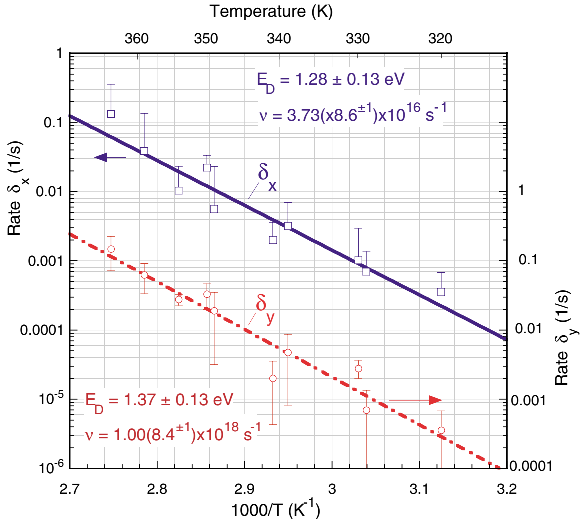

FIG. 6 (color online). Temperature dependence for jump rates δ_x and δ_y of W atoms on W(110). For the sake of clarity, only the upper error bar is plotted for the jump rate δ_x.

TABLE II. Rate parameters on W(110).

Rate	Activation energy E_D (eV)	Frequency factor ν (s^{-1})
α (low temp)	0.94 ± 0.03	$5.92(\times 2.5^{\pm 1}) \times 10^{12}$
β	1.24 ± 0.13	$8.06(\times 8.1^{\pm 1}) \times 10^{15}$
δ_x	1.28 ± 0.13	$3.78(\times 8.6^{\pm 1}) \times 10^{16}$
δ_y	1.37 ± 0.13	$1.00(\times 4.4^{\pm 1}) \times 10^{19}$

direction to make a double jump β. Also possible are deviations to the right or left, to give a δ_x or a δ_y jump. These long transitions of course diminish the rate of jumps α to nearest-neighbor sites, and this reduces the effect of long jumps on the diffusivity at higher temperatures. However, a plot of the logarithm of the sum of all the jump rates against $1/T$ should give a single straight line [20], as the number of jumps is set by the basic jump process; as seen in Fig. 7, that is in fact the case.

The rate of a long jump is given by the product $R_l p_i$. Since the conversion probability p_i can be written as $\nu_i \exp(-E_i/kT)$, we can also rationalize the high values found for both the long-jump prefactors and activation energies: the former are given by the product of the frequency factor for the basic jump and for the probability of a deviation, which may itself be sizable; the latter is always the sum of two activation energies. It still remains to ascertain the effects bringing about the deviations in the direction of the jumping atom as well as the energetics of these events, which at present are not really understood, but the overall picture accounts for our findings. It will now be interesting to establish the extent to which this view describes diffusion in other systems.

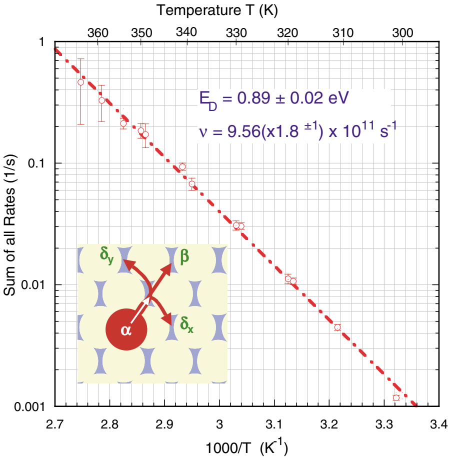

FIG. 7 (color online). Inset: Schematic of jump rates on W(110). Basic process is jump along ⟨111⟩, which at higher temperatures can deviate from nearest-neighbor endpoint. Main graph: Sum of all the jump rates shown as an Arrhenius plot of the log against $1/T$. One straight line fits all the data.

This work was carried out with support from the Department of Energy under Grant No. DEFG02-96ER45439 to the F. Seitz Materials Research Laboratory. We also acknowledge the donors of the Petroleum Research Fund, administered by the ACS, for partial support under Grant ACS PRF No. 36919-AC5. We are much indebted to Dr. S.-M. Oh, for his help in starting this project, and to Dr. M. Lovisa, for his early work with this system.

[1] D. C. Senft and G. Ehrlich, Phys. Rev. Lett. **74**, 294 (1995).

[2] D. C. Senft, Appl. Surf. Sci. **94/95**, 231 (1996).

[3] T. R. Linderoth, S. Horch, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **78**, 4978 (1997).

[4] F. Montalenti and R. Ferrando, Phys. Rev. B **58**, 3617 (1998).

[5] H. T. Lorenson, J. K. Norskov, and K. W. Jacobsen, Phys. Rev. B **60**, R5149 (1999).

[6] S.-M. Oh, S. J. Koh, K. Kyuno, and G. Ehrlich, Phys. Rev. Lett. **88**, 236102 (2002).

[7] S.-M. Oh, K. Kyuno, S. J. Koh, and G. Ehrlich, Phys. Rev. B **66**, 233406 (2002).

[8] T. Ala-Nissila, R. Ferrando, and S. C. Ying, Adv. Phys. **51**, 949 (2002).

[9] G. L. Kellogg, Surf. Sci. Rep. **21**, 1 (1994).

[10] Instrumentation is described by D. A. Reed and G. Ehrlich, Surf. Sci. **151**, 143 (1985).

[11] M. F. Lovisa and G. Ehrlich, Surf. Sci. **246**, 43 (1991).

[12] J. D. Wrigley, M. E. Twigg, and G. Ehrlich, J. Chem. Phys. **93**, 2885 (1990).

[13] The mean-square displacements are related to the rate ratios just found through [12] $\langle \Delta x^2 \rangle = 4\alpha t[1 + 2\delta_x/\alpha + 4\beta/\alpha](a/2)^2$, $\langle \Delta y^2 \rangle = 4\alpha t[1 + 2\delta_y/\alpha + 4\beta/\alpha](\sqrt{2}a/2)^2$, where a is the lattice constant, so that all rate ratios and α can be obtained from these two equations.

[14] In Ref. [7], no corrections were attempted for motion during transients, allowing only semiquantitative conclusions.

[15] S. J. Koh, Ph.D. thesis, University of Illinois at Urbana–Champaign, 1998, Sec. III.B3.

[16] Minimization is carried out as described by S. Dedoussis, M. Chardalas, and S. Charalambous, Comput. Phys. Commun. **31**, 29 (1984).

[17] Some of our high temperature results were obtained by carrying out an additional 1200 experiments and then combining these with data in Ref. [7]. All the results were then analyzed keeping the difference between $\langle \Delta y^2 \rangle$ and $\langle \Delta x^2 \rangle$ fixed at the experimental value and varying α, β/α, and δ_y/α.

[18] Errors in the rates have been roughly estimated by doing Monte Carlo simulations of the displacement distribution at each temperature and then analyzing the distributions.

[19] A similar idea has been proposed in diffusion on channeled surfaces by F. Montalenti, Ph.D. thesis, University of Genova, 1999, Sec. 2.44.

[20] Note that this is *not* implicit in the linear dependence of $\ln(D)$ on $1/\mathrm{T}$.