

Atomic jumps in surface self-diffusion: W on W(110)

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(Received 18 June 2002; published 18 December 2002)

Although surface diffusion has been studied on the atomic level for decades, little is known about jump processes in self-diffusion. The diffusion of W atoms on the densely packed W(110) plane has therefore been examined, using the field ion microscope to probe contributions of jumps other than between nearest-neighbor sites. Measurements of the mean-square displacements of atoms along the x and y axes ($\langle 001 \rangle$ and $\langle 110 \rangle$, respectively) and of the detailed spatial distribution of atomic displacements serve to define the nature of the jumps important in diffusion. It is shown that, in addition to nearest-neighbor and second-nearest-neighbor transitions along the close-packed $\langle 111 \rangle$, atoms also carry out jumps along $\langle 001 \rangle$ and $\langle 110 \rangle$, and that the contribution from these processes increases rapidly with temperature.

DOI: 10.1103/PhysRevB.66.233406

PACS number(s): 68.35.Fx, 68.35.Ja, 81.10.Aj, 81.15.Kk

In recent years it has become clear that atomic diffusion on surfaces is not a simple event.¹ In some instances, diffusion occurs by an exchange process, in which the adatom replaces an atom in the underlying lattice.² Even when atoms migrate by jumping over the surface, these are not always transitions between adjacent sites: more complicated jumps have been identified in diffusion both on channeled, essentially one-dimensional surfaces such as W(211)^{3,4} and Pt(110)-(1 \times 2),⁵ as well as on the two-dimensional W(110) plane.⁶ Little has so far been done to characterize self-diffusion on a two-dimensional (2D) surface, however. Here we therefore report an exploratory study of how individual W adatoms diffuse over the most densely packed plane of tungsten, the (110) plane, a schematic of which is shown in Fig. 1. The obvious view of diffusion on this surface is that it takes place by single jumps between nearest-neighbor positions, that is, between adjacent sites along the close-packed $\langle 111 \rangle$ directions, in what we designate as α transitions. However, other transitions may perhaps also be possible. Among these are β double jumps, covering two nearest-neighbor distances along $\langle 111 \rangle$, δ_y jumps in the $\langle 110 \rangle$ directions, or possibly δ_x jumps along $\langle 001 \rangle$. Our purpose here is to explore if other than nearest-neighbor transitions play a significant role in self-diffusion on W(110), and what these might be.

To this end, we have used the field ion microscope⁷ to measure the displacements of a single tungsten atom on the W(110) plane at ten temperatures ranging from 310 to 375 K. At least 200 observations were accumulated at each temperature, but at four temperatures in the range 350 to 365 K the number measured was increased by a factor of ~ 6 . From the mean-square displacement $\langle \Delta x^2 \rangle$ along the x axis (that is along $\langle 001 \rangle$) during a time interval t , we derive the diffusivity D_x using the Einstein relation

$$\langle \Delta x^2 \rangle = 2D_x t. \quad (1)$$

All measurements have been carried out on a surface with a radius of ~ 14 lattice spacings a . To avoid the altered environment at the edges of the (110) plane, observations within a distance of $4a$ from the plane boundaries are rejected. Nevertheless, diffusion occurs on a plane of finite size, not on the

infinite surface envisioned in the Einstein relation. Corrections for this finite size effect^{4,8} are made by Monte Carlo simulation of diffusion on a bcc (110) plane of the same dimensions as in the experiments; the diffusion parameters in the simulations are adjusted until good agreement is achieved between the mean-square displacement in the simulations and in the experiments.⁹ The diffusivity D_x derived in this way (in length units of $a/2$) is shown as a function of the temperature in Fig. 2. Nothing appears unusual in this Arrhenius plot, and the activation energy ΔE_D as well as the diffusivity prefactor D_0 are in reasonable agreement with previous results reported for this system.¹¹

From the same set of displacement measurements, the mean-square displacement $\langle \Delta y^2 \rangle$ along $\langle 110 \rangle$ was also derived, and yields the diffusivity D_y along the y axis (in length units of $\sqrt{2}a/2$). If diffusion occurs entirely by jumps along $\langle 111 \rangle$, the close-packed direction, then the diffusivity D_y should be the same as D_x . However, as is evident from Fig. 2, where the difference between the diffusivities along the y

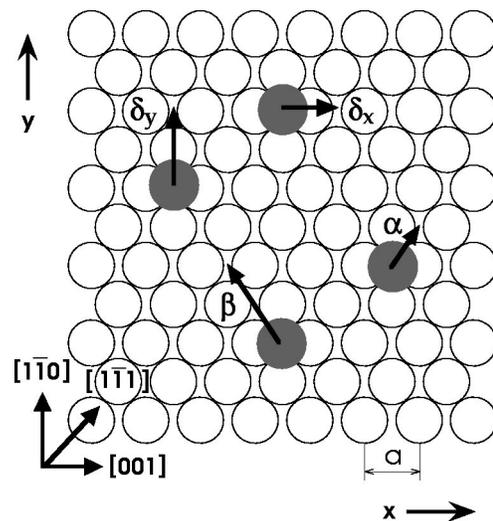


FIG. 1. Schematic of bcc (110) plane, showing possible jump processes in surface diffusion of self-adsorbed atoms.

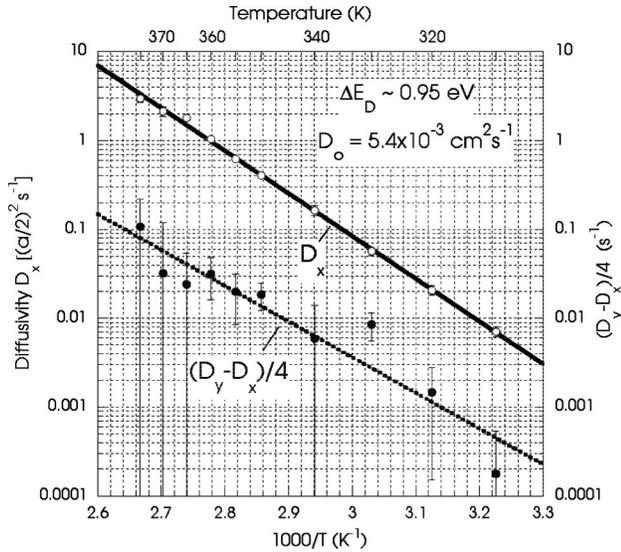


FIG. 2. Temperature dependence of the diffusivity in self-diffusion of W atoms on the W(110) plane. D_y and D_x , the diffusivities along $\langle 110 \rangle$ and $\langle 001 \rangle$ in length units of $\sqrt{2}a/2$ and $a/2$, respectively, are not equal to each other as they would be for jumps along $\langle 111 \rangle$; dotted line indicates trends only.

and x axes is plotted as $(D_y - D_x)/4$, the two are *not* the same: even though the scatter in the difference is large, D_y consistently exceeds D_x .

If all the transitions depicted in Fig. 1 contribute to self-diffusion, the mean-square displacements can be written as^{12,13}

$$\langle \Delta x^2 \rangle = 4t[\alpha + 2\delta_x + 4\beta], \quad (2)$$

$$\langle \Delta y^2 \rangle = 4t[\alpha + 2\delta_y + 4\beta], \quad (3)$$

and the difference between the diffusivities becomes

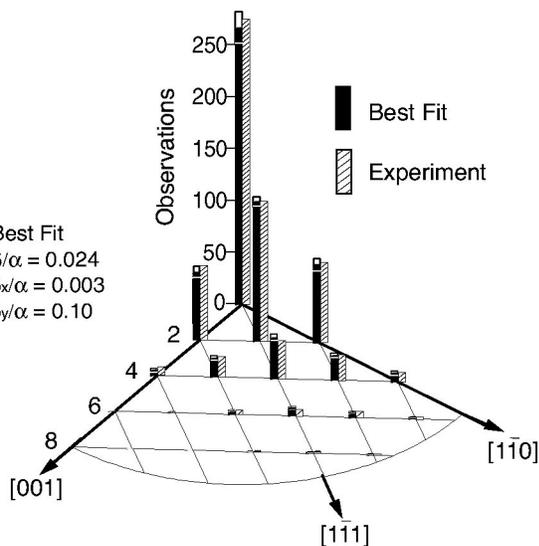


FIG. 3. Measured distribution of displacements, as well as best fit from simulations, mapped into first quarter, for W atom diffusing over W(110) for 3 s at 350 K. Displacements along x axis in units of $a/2$, along the y axis in units of $\sqrt{2}a/2$.

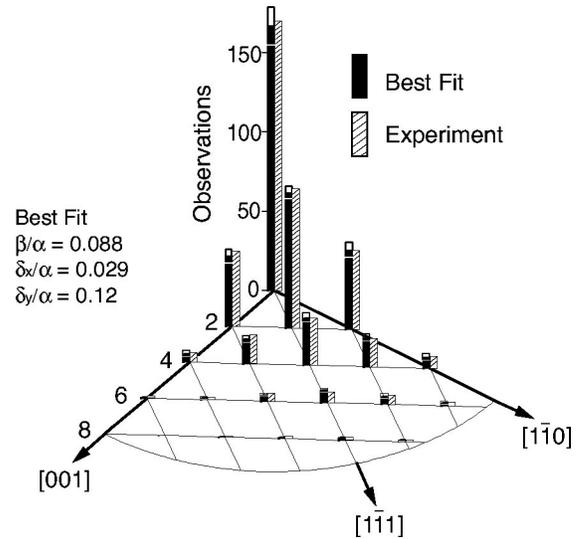


FIG. 4. Distribution of displacements for W atom diffusing over W(110) for 2.5 s at a set temperature $T = 355$ K. Non-nearest-neighbor jumps have become more important.

$$D_y - D_x = 4(\delta_y - \delta_x). \quad (4)$$

From the difference in diffusivities found in Fig. 2 it is evident that jumps between other than nearest-neighbor sites contribute in a significant fashion in the self-diffusion of W atoms on W(110): at the very least, vertical jumps δ_y are important.

More detailed information about the transitions that actually participate in the diffusion of self-adsorbed W atoms can be derived from an analysis of how the atomic displacements are distributed over the (110) plane.¹² In Fig. 3 are plotted the number of displacements to different locations, mapped into the first quadrant, observed after a diffusion interval of 3 s at a set temperature of 350 K. To interpret this distribution,^{4,8} we simulate diffusion on a (110) plane of the same size and shape as in the experiments, assuming values for the mean-square displacements along x and y , as well as

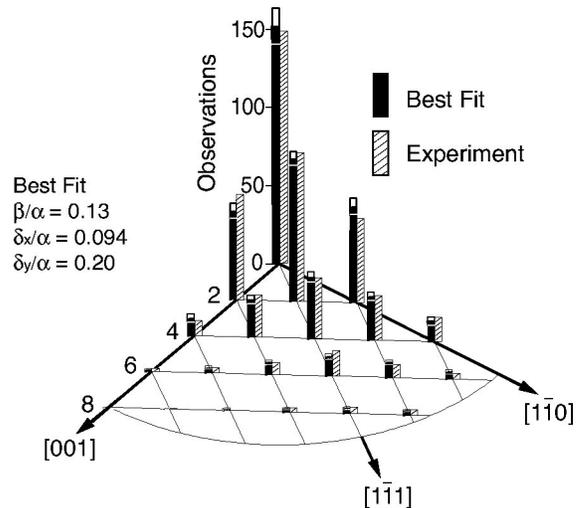


FIG. 5. W atom displacements on W(110) during 2-s interval at 360 K. Vertical δ_y transitions are double the value at 350 K.

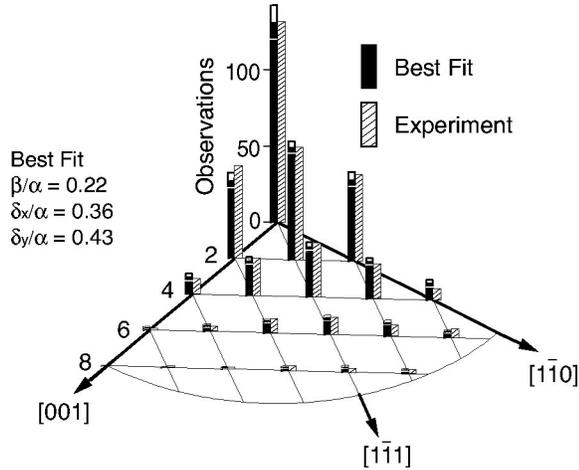


FIG. 6. Displacement distribution of W atoms diffusing on W(110) for 1.3 s at 365 K. Non-nearest-neighbor jumps now roughly comparable in number to nearest-neighbor transitions.

for the ratios of double to single jumps β/α and for horizontal to single jumps δ_x/α . The four parameters are then varied until agreement is obtained between the observed distribution and that in the simulations. At 350 K the best fit is found if the ratio of double to single jumps, β/α , as well as the ratio of horizontal to single jumps, δ_x/α , is negligibly small. However, the ratio of vertical to single jumps, δ_y/α , is significant at ~ 0.1 . Even at this relatively low temperature, it appears that diffusion involves jumps to other than nearest-neighbor sites.

As the diffusion temperature is raised, this trend continues. Displacements have also been measured at 355 K, and the distribution shown in Fig. 4 reveals a significant increase in the contribution of β double jumps. At 360 K, however, the rise in non-nearest-neighbor transitions is especially noticeable. To approximate the distribution measured at this temperature, in Fig. 5, we have to invoke a significantly larger contribution of vertical jumps, with $\delta_y/\alpha = 0.20$; horizontal transitions now give the ratio $\delta_x/\alpha = 0.094$. A 10 K rise in the temperature has increased the participation of non-nearest-neighbor jumps from 12 to 30%. A further increase in the temperature by 5 K, to 365 K, dramatically lowers the importance of single jumps to nearest-neighbor sites. The distribution of displacements at this temperature, in Fig. 6, is best represented by much larger contributions from non-nearest-neighbor jumps: $\beta/\alpha = 0.22$, $\delta_x/\alpha = 0.36$, and $\delta_y/\alpha = 0.43$. These transitions now make up $\sim 50\%$ of the total.

In the self-diffusion of W atoms on W(110), summarized in Table I, we see behavior in some ways similar to what has previously been documented in diffusion of Pd atoms, both on W(211),^{3,4} a channeled plane, and on W(110).⁶ The contributions of other than nearest-neighbor transitions in all these systems increase rapidly with temperature, in the present case to almost 50% over a span of 15 K; these non-nearest-neighbor jumps appear to be of considerably higher

TABLE I. Rate parameters for self-diffusion of W atoms on W(110).

T (K)	t (s)	Observations	$\langle \Delta x^2 \rangle$ $(a/2)^2$	β/α	δ_x/α	δ_y/α
350	3.0	1545	2.42	0.024	0.003	0.10
355	2.5	1170	3.10	0.088	0.029	0.12
360	2.0	1403	4.16	0.13	0.094	0.20
365	1.3	1200	4.67	0.22	0.36	0.43

energy than transitions to nearest-neighbor sites. Self-diffusion of W atoms does, however, differ in some important aspects from the previously studied movement of Pd on the same surface. For the latter, it was possible to define a reduced characteristic temperature $T_c = kT/E_D = 0.036$ for the onset of non-nearest-neighbor jumps.^{3,6} Straightforward extrapolation from this value to the self-diffusion of tungsten suggests we should expect longer jumps at temperatures $T \geq 400$ K. Because of the better mass match for W compared to Pd atoms on W(110), energy transfer, and therefore also the characteristic temperature T_c for W atoms should be higher still. In our experiments, however, we already find such transitions at a much lower temperature, at $T = 350$ K. It appears that this characteristic temperature has only limited utility.

The diffusion of W atoms on W(110) is similar to that of Pd adatoms⁶ in that at relatively low temperatures, vertical transitions to sites along $\langle 110 \rangle$ already contribute. However, for W atoms, horizontal transitions, to sites along $\langle 110 \rangle$, are increasingly important as the temperature is raised, whereas for Pd atoms, no such transitions were isolated in the temperature range explored. One possibility is that atoms making horizontal as well as vertical transitions start out as jumps along the close-packed $\langle 111 \rangle$, but subsequently change their direction in interactions with the substrate. The deviation from the original jump direction is larger for horizontal than for vertical transitions. For tungsten atoms, which are 73% heavier than Pd, energy transfer is easier to accomplish, and this may favor horizontal transitions.

Much remains to be done still, most notably to establish the temperature dependence of non-nearest-neighbor jumps quantitatively. However, one thing is already clear from the present measurements: surface self-diffusion of atoms on W(110) is a complicated process, involving many different types of jumps between other than nearest-neighbor sites, which rapidly become important at higher temperatures.

This study was done with support from the Department of Energy under Grant No. DEFG02-96ER45439 to the F. Seitz Materials Research Laboratory. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research under Grant ACS PRF No. 36919-AC5. We are indebted to Dr. G. Antczak for help in the final stages of this work.

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