Long jumps in one-dimensional surface self-diffusion: Rebound transitions

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The diffusivity as well as the distribution of displacements of tungsten atoms have been examined on the W(211) plane. An Arrhenius plot of the diffusivity does not indicate long jumps, but the distributions of displacements at $T \geqslant 300$ K show both double transitions between sites two spacings apart, as well as single jumps; double jumps have a high activation energy, $E_\beta = 1.44 \pm 0.13$ eV. At temperatures $T > 320$ K, atom motion over the surface is entirely by longer transitions. Most interesting is the fact that the sum of all measured jump rates does not agree with expectations, indicating for the first time that rebound transitions, in which jumping atoms immediately return to the origin, are significant.

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Self-diffusion of tungsten atoms on W(211) has been examined in the past, but only jumps between nearest-neighbor sites were found even at the highest temperature studied.[1] A variety of long transitions was, however, established in self-diffusion on a two-dimensional surface, on W(110).[2,3] Is it a characteristic of self-diffusion in channels that only nearest-neighbor jumps are important? That is the question we address here, but in closely examining the diffusion of tungsten atoms on the (211) plane of tungsten, we have also found quite unexpected results.

In our work, the displacements of tungsten adatoms deposited on the surface were observed in an ultrahigh-vacuum field ion microscope. The tip was prepared from (211) oriented single crystal wire, 0.007 in. in diameter, by electrochemical etching in 2*N* NaOH. Images were obtained in helium gas at a pressure of $\sim 10^{-4}$ Torr; other details of the technique have been described previously.[4] From 1200 observations at each temperature above 295 K, the mean-square displacement $\langle \Delta x^2 \rangle$ was evaluated, giving the diffusivity D through

$$\langle \Delta x^2 \rangle = 2Dt. \tag{1}$$

For a multijump process, the mean-square displacement can also be written as

$$\langle \Delta x^2 \rangle = 2l^2(\alpha + 4\beta + 9\gamma)t, \tag{2}$$

where α is the rate of jumps between nearest-neighbor sites, β the rate of double jumps between sites two spacings apart, and γ the rate of jumps covering three spacings; l is the nearest-neighbor distance, and t is the time interval for diffusion. These relations are valid for infinite surfaces, but since measurements were done on planes ~ 17 spacings long, Monte Carlo simulations on a plane of exactly the same size and structure as in the experiments were used to determine the diffusivity. Diffusion during temperature transients before and after the set temperature is reached, that is zero-time measurements,[5] were also done, and the main results were corrected for this effect.

We expect longer jumps to manifest themselves in the diffusivity at higher temperatures. However, from an Arrhenius plot of the diffusivity over 60 K, shown in Fig. 1, we obtain an activation energy $E_D = 0.81 \pm 0.02$ eV and a diffusivity prefactor $D_o = 3.41(\times 2.40^{\pm 1}) \times 10^{-3}$ cm^2/s. These values are in good agreement with the work of Senft,[1] and with earlier studies,[6,7] and give no clear indication of any unusual jump processes. If jumps of different length occur independently, then from Eq. (2), we expect for the diffusivity a deviation from a linear Arrhenius plot; that is *not* seen, however.

The nature of the jumps contributing to diffusion can be ascertained directly by measuring the distribution of dis-

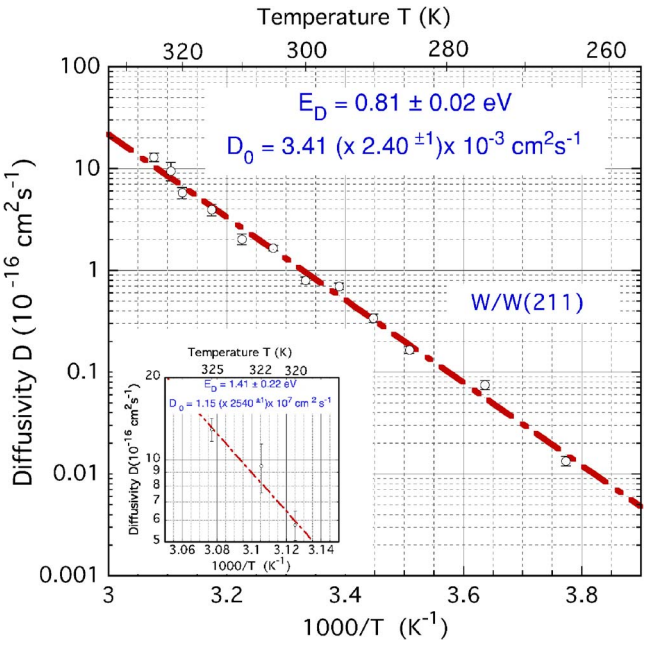

FIG. 1. (Color online) Arrhenius plot for the diffusivity of tungsten atoms on W(211) surface in the temperature range $T = 260-325$ K. Inset: Possible Arrhenius plot for the three highest temperatures. Characteristic values derived from this plot are comparable to those for double transitions.

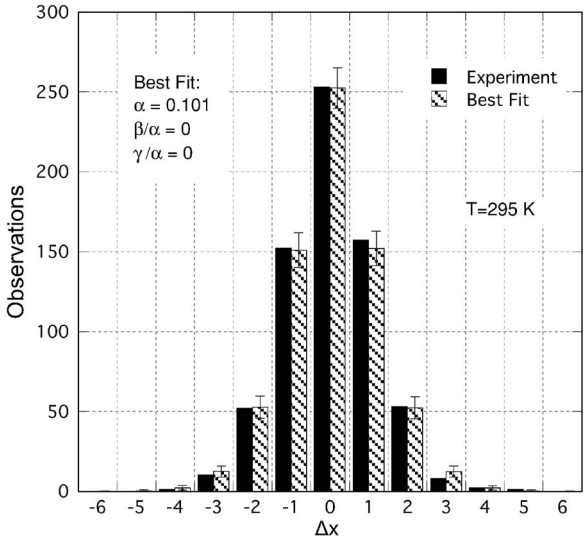

FIG. 2. Distribution of displacements of a tungsten atom in a W(211) channel ~17 atomic spaces long at a temperature $T=295$ K. Distribution determined in experiment is shown in black, the Monte Carlo best fit appears striped. Only single transitions can be identified.

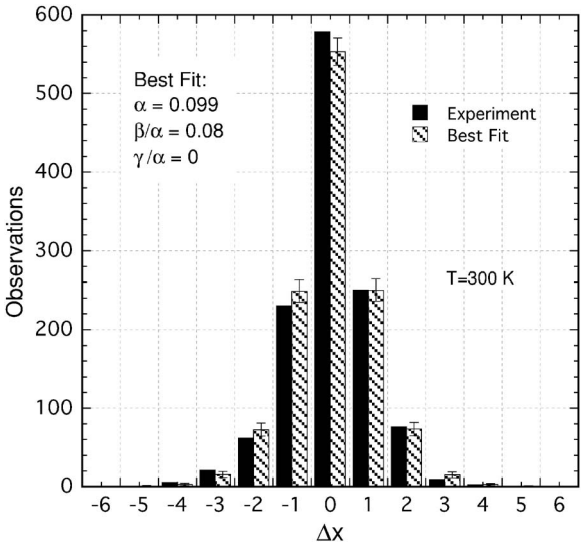

FIG. 3. Distribution of displacements for W atom on W(211) plane at a temperature $T=300$ K. A small number of double transitions is detected for the first time.

placements $p_x(t)$ for jumps occurring on the (211) plane. On an infinite surface, this distribution is given by[8]

$$p_x(t) = \exp[-2(\alpha+\beta+\gamma)t] \sum_{k=-\infty}^{\infty} I_k(2\gamma t) \sum_{j=-\infty}^{\infty} I_j(2\beta t) \times I_{x-2j-3k}(2\alpha t) \quad (3)$$

and should reveal the presence of jumps at rates β and γ to other than nearest-neighbor sites; $I_x(y)$ is the modified Bessel function of order x. Since our observations were made on small planes with reflection at the ends, we have again resorted to Monte Carlo simulations with different rates for the single, double, and triple jumps to fit the experimentally measured values of $p_x(t)$.

The distribution of 750 displacements measured at a temperature of 295 K is shown in Fig. 2. The best fit to the data gives no indication of jumps other than between nearest neighbors. Distributions of displacements have also been determined at a series of higher temperatures. In the distribution at $T=300$ K in Fig. 3, based on 1200 observations, the best fit is obtained with a ratio of double to single jumps, β/α, equal to 0.08, the first indication of transitions longer than between nearest neighbors. The influence of long jumps increases with increasing temperature; at $T=310$ K the ratio of double to single jumps is $\beta/\alpha=0.1$, at 320 K, β/α is even bigger, amounting to 0.12, and at the highest temperature tested, at $T=325$ K, the ratio of double to single jumps achieves a huge value of 0.66, as shown in Fig. 4. No triple jumps were found in the range of temperatures investigated. However, from these observations, it is clear for the first time that long jumps do occur in one-dimensional self-diffusion; it is just a matter of exploring more elevated temperatures.

Here we note that these distributions do not give us the jump rate at a constant temperature, as some diffusion may occur during temperature transients while heating and cooling the specimen. To correct for such effects, we have also measured the distributions in zero-time experiments,[5] in which the heating to the sample is cut off as soon as the set temperature is reached. If the jump rate in the normal experiment is given by R, and during the zero-time measurements by r_o, then a rate r corrected for temperature transients is obtained from

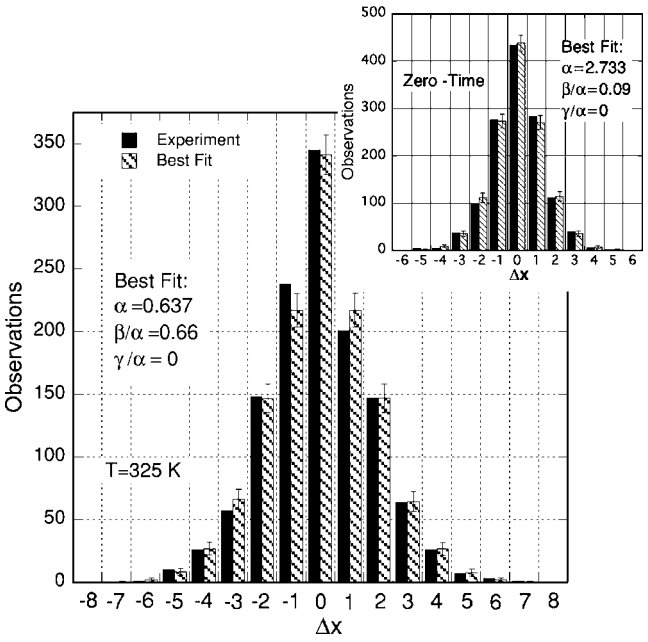

FIG. 4. Distribution of displacements for W on W(211) at $T=325$ K. Double transitions have increased significance, but there are no triple jumps. Inset shows the distribution of displacements for transitions occurring during warming and cooling sample to $T=325$ K.

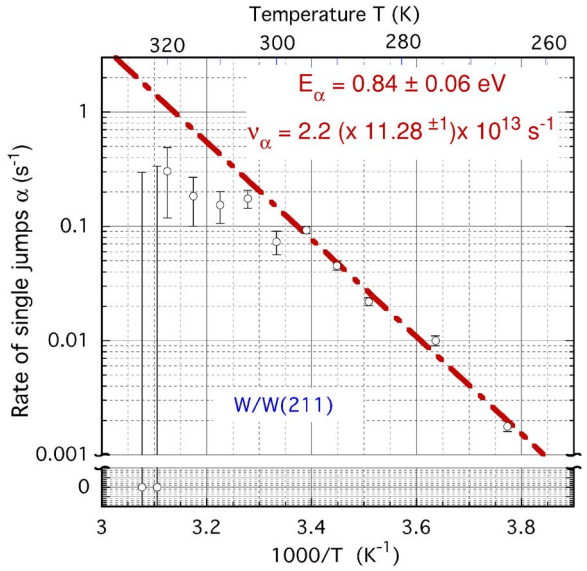

FIG. 5. (Color online) Temperature dependence of single jumps α. A diminution of single jump rate due to increase in number of double transitions is observed. Arrhenius line and diffusion characteristics are based on low temperature rates only.

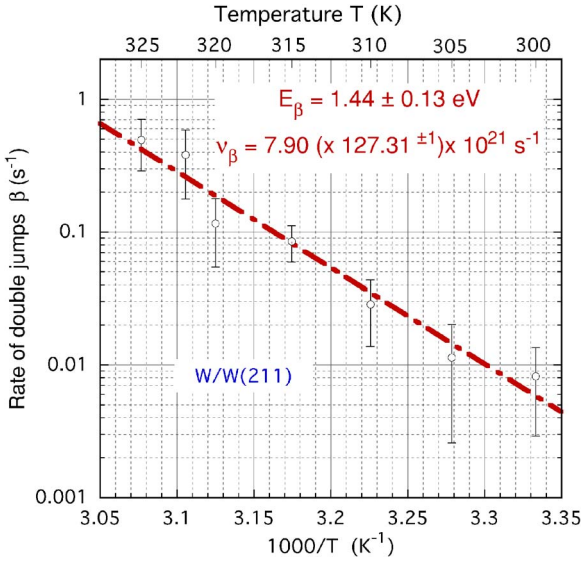

FIG. 6. (Color online) Semilogarithmic plot for the temperature dependence of double jump rate β. A much higher activation energy and frequency prefactor is found for double jumps than for single transitions.

$$r = (Rt - r_o t_o)/t_c, \tag{4}$$

where t is the time interval for normal experiments, t_o for zero-time observations, and t_c the time at the temperature set for diffusion. Zero-time distributions for the higher temperatures were measured and an example is given as an inset of Fig. 4, together with the normal measurements. It should be noted that zero-time experiments in the temperature range we investigated have mostly contributions from single jumps; only at the highest temperature do some double transitions start appearing during temperature transients.

Jump rates corrected for zero-time effects at various temperatures are shown graphically in Figs. 5 and 6. At 325 K, for example, these corrections have eliminated all single α jumps. The question now arises about how good the distance distributions are. This we have estimated roughly by doing Monte Carlo simulations of ten distributions at each temperature, all with input values and number of observations the same as in the experiments, but different in the random number used to start the simulation. Each simulated distribution is analyzed in the same way as the experiment, to get a rough idea of the standard deviation.

From the results plotted in Fig. 5, it is clear the rate α of single jumps begins to deviate from a linear relation of the logarithm with $1/T$ once the temperature increases beyond ~300 K. At lower temperatures, we find an activation energy $E_\alpha = 0.84 \pm 0.06$ eV and a frequency prefactor $\nu_\alpha = 2.2(\times 11.3^{\pm 1}) \times 10^{13}$ s^{-1}, agreeable with values from measurements of the diffusivity. At higher temperatures, however, the rate begins to deviate from a linear Arrhenius plot, achieves a maximum at ~315 K, and then diminishes rapidly to reach zero at ~322 K. At the same time, however, the plot of the rate of double jumps β in Fig. 6 follows a linear curve over the entire investigated temperature range, and yields a much higher activation energy, $E_\beta = 1.44 \pm 0.13$ eV and a much higher prefactor $\nu_\beta = 7.9(\times 127^{\pm 1}) \times 10^{21}$ s^{-1}. The energy for double jumps is close to double the activation energy for single jumps, which explains the steep transition from single and to double jumps. This transition proceeds without the presence of longer jumps; this does not appear to be a general feature, however, since in diffusion of palladium on W(211), double and triple jumps were observed together.[1,9]

The behavior of the jump rates suggests they are not independent; instead, double jumps seem to arise from nearest-neighbor transitions when at higher temperatures, the diffusing atom does not come to rest at the first site encountered and continues on. The greater the number of double jumps found, the smaller should be the number of single transitions. This also accounts for the unusual characteristics of the long jumps. We can write the rate of double jumps R_β as

$$R_\beta = R_1 p. \tag{5}$$

Here, R_1 is the basic rate extrapolated from the rate of single jumps at low temperatures at which they are the only transitions, and p is the probability of converting a single jump to a double transition. The single jump rate is given by

$$R_1 = \upsilon_o \exp(-E_1/kT), \tag{6}$$

and the probability of conversion by

$$p = \upsilon_{op} \exp(-E_p/kT). \tag{7}$$

Here, E_p and υ_{op} are characteristic of the conversion. The activation energy for double jumps is therefore the sum of the individual activation energies, which according to our results are roughly comparable. The prefactor is the product of the contributions from the two processes, and will, therefore, also be high.

Judging from Eq. (2) for the mean-square displacement, the diffusivity should be affected by the onset of longer

jumps and should reflect a higher diffusion barrier as single jumps, between nearest neighbors disappear. Our diffusivities do not clearly show such a trend, but that may be because a large fraction of the measurements were taken at lower temperatures, where double jumps are not yet significant in number. If, however, we do something unusual, and examine only the three determinations at the highest temperatures, from 320 K to 325 K, as is done in the inset to Fig. 1, then the activation energy for these three points amounts to 1.41 ± 0.22 eV and with a prefactor of $1.15(\times 2540^{\pm 1}) \times 10^7$ cm^2/s. These values are quite close to the characteristics of β double jumps, as in this temperature range contributions from single jumps are unimportant. Although this analysis is only suggestive, it does indicate that further studies, to demonstrate that the diffusivity at higher temperatures may directly reveal contributions of long transitions, are desirable.

For the mechanism we propose, that single transitions are converted to double jumps, we expect the sum of all the jump rates should be given by the rate law for single jumps (at low temperatures) and should be represented by a linear Arrhenius plot. A plot of the sum of all the jump rates measured is given in Fig. 7, and it is clear that this expectation is *not* met; at the higher temperatures, the sum falls significantly below the value extrapolated linearly from lower temperatures. Evidently, double jumps do not entirely replace the single jumps. Our measurements are not accounting for all the jumps occurring at higher temperatures.

We propose that at higher temperatures, $T \geqslant 310$ K, an adatom that has just made a jump and lands at a nearest-neighbor site can do two things. With a probability p, it can continue to a site two spacings from the start; however, as an alternative, the atom can bounce back to the starting position at the rate β_R shown in the inset to Fig. 7. At higher temperatures, rebounds become more frequent, increasing the deviation from the line linearly extrapolated from low temperatures. Rebounding has previously been seen in molecular dynamics simulations,[10] but here, for the first time, is found in an experiment and clearly plays an important role.

Our work has shown that at temperatures only $\sim 1/10$ of the melting point, self-diffusion over the (211) plane of tungsten occurs primarily by double jumps spanning two spacings along ⟨111⟩. At even more elevated temperatures than those explored here, we expect longer transitions, such as triple jumps, to manifest themselves. Only at low temperatures, at $T \leqslant 295$ K, is atom diffusion carried by single jumps between nearest neighbors, the traditional picture of surface diffusion. In addition, we have demonstrated the unexpected presence of rebound transitions, in which atoms making a jump return to their start rather than continuing further on. These transitions become more frequent at higher temperatures. In any event, for both one-dimensional and two-dimensional diffusion, on the (211) and (110) planes of tungsten, long jumps are important. What has to be checked now is if these effects are general, and not limited to tungsten.

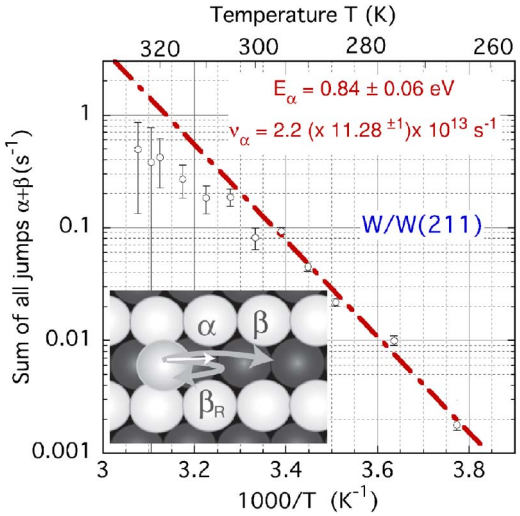

FIG. 7. (Color online) Arrhenius plot for the sum of single plus double transition rates vs reciprocal temperature. The line and characteristic values are for low temperature single jump rates. A deviation at higher temperatures is clear. Inset: schematic of jumps predicted on W(211) in investigated temperature range.

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