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Kinetics of atom rebounding in surface self-diffusion

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Self-diffusion of tungsten atoms as well as the distribution of displacements has in the past been examined on the channeled W(211) plane. In addition to simple nearest-neighbor jumps and double transitions, rebound jumps, in which an atom jumps but returns immediately to its starting position, have been identified. The kinetics of rebounds have now been determined. Rebounds occur on W(211) at temperatures as low as 300 K, with an activation energy of 1.03 eV and a frequency prefactor of 1.40×10^{16} s^{-1}; they have not been found in diffusion on W(110).

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For decades surface diffusion was understood as a random walk of atoms making jumps between nearest-neighbor sites. However, around 1980 molecular dynamics simulations[1,2] showed that at elevated temperatures such a simple picture can be misleading; the simulations predicted long transitions on the surface. Experimental proof of such transitions had to wait until 1995, when Senft[3,4] found that in diffusion of palladium on W(211), not only double but also triple jumps occurred at a low temperature of 133 K. Surface diffusion is clearly not as simple as was previously thought. In this Brief Report we present another transition, rebound jumps, and their kinetics.

Recently, atom self-diffusion on the (211) plane of tungsten has been examined in detail,[5] and single as well as double jumps, between sites two spacings apart, have been identified in the distribution of displacements consisting of 1200 observations per temperature measured on planes with 17 adsorption sites along a channel. Zero time corrections were also performed to account for transitions occurring while the sample was heating and cooling, and atoms close to the edges were withdrawn from the experimental data. The rate laws governing these two processes have been established using kinetic Monte Carlo simulations on a plane with the same structure and geometry as in the experiments, and it has been demonstrated that single and double transitions are correlated; double jumps start out as single transitions, in which the adatom does not come to rest at an adjacent site, but instead continues on to a neighboring position. At higher temperatures the rate of such double jumps becomes more important, and single jumps eventually diminish in number and then disappear. For such related processes, the *sum* of the individual rates should plot as a simple Arrhenius graph with the same activation energy and prefactor as for single jumps at low temperatures. This behavior has been previously demonstrated for the diffusion of tungsten and iridium adatoms on W(110).[6,7]

In the previous paper[5] the jump rates were measured in self-diffusion on W(211), and from Fig. 7 there it is clear that the sum of the single plus double jump rates does *not* coincide with the line extrapolated from self-diffusion at low temperatures. As the temperature rises above 300 K, the sum of the rates falls more and more below the linear plot. Evidently this sum does *not* account for all the jump processes important in the diffusion. What has been neglected is the rate of atoms starting on a single transition, but then immediately rebounding to the origin. Such rebounding was predicted from molecular dynamics simulations of self-diffusion on bcc(211) surfaces,[8] and was subsequently also found in simulations for diffusion on fcc(111) planes.[9,10]

What is usually measured in diffusion studies is the mean-square displacement $\langle \Delta x^2 \rangle$, and this does not detect rebounds, as their displacement is zero. They lower the overall diffusivity since rebounds originate in single jumps, but then return to the origin, decreasing the detectable displacement of the atom. However, what was not derived previously was the kinetics of rebound jumps.

Recently it became clear that the rate of rebound transitions is easy to determine provided all other jump rates are known. It is just given by the difference between the sum of single plus double transitions on the one hand, and the line for the total number of jumps, which is the extrapolation of the low-temperature jump rate, on the other. All these quantities are known, and for the first time the rate of rebounds has been determined. It is plotted in Fig. 1 as a function of

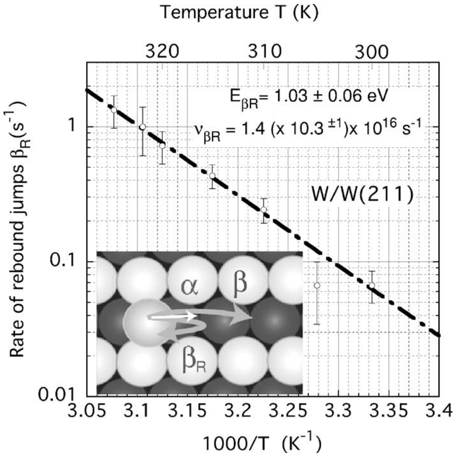

FIG. 1. Rate of rebound jumps β_R obtained as the difference between the sum of single plus double jumps and the total rate extrapolated from low temperatures. The inset shows a schematic of atomic jumps on the W(211) plane.

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TABLE I. Jump rates for W on W(211). (Data on single and double jumps from Ref. 5).

	Activation energy E (eV)	Frequency prefactor ν (s^{-1})
Single jumps α	0.84 ± 0.06	$2.2(\times 11.3^{\pm 1}) \times 10^{13}$
Double jumps β	1.44 ± 0.13	$7.9(\times 127.3^{\pm 1}) \times 10^{21}$
Rebound jumps β_R	1.03 ± 0.06	$1.4(\times 10.3^{\pm 1}) \times 10^{16}$

$1/T$ and is represented by a straight line with an activation energy $E_{\beta R} = 1.03 \pm 0.06$ eV, and a prefactor of $V_{\beta R} = 1.40$ $(\times 10.3^{\pm 1}) \times 10^{16}$ s^{-1}.

A comparison of the different jump rates measured on W(211) is given in Table I, and it is clear that the characteristics of the rebound process lie between those of single and double jumps; rebound transitions will occur at lower temperatures than do double jumps. At a first look, atom behavior on W(211) seems to differ from what has been found in molecular dynamics simulation on a Cu(111) surface;[10] there, the number of rebounds diminishes with temperature as the longer transitions increase. However, in my experiment a more limited range of temperatures is explored, in which only singles and doubles plus rebounds are active. At more elevated temperatures, longer jumps will take place and this should lower the number of rebounds as well. The present work is an experiment to measure the rate of rebounding, and to discover if rebounding already occurs at low temperatures.

It is interesting to compare these studies on W(211) with previous work on W(110). There diffusion has been extensively studied; Fig. 15 in Ref. 7 shows plots of the sum of the measured jump rates. For both tungsten and iridium adatoms, the sum of the individual rates overlaps with the plot of the single jump rate extrapolated from low temperatures. The activation energy and frequency prefactor for single jumps $(\mathrm{W/W(110)}: E_\alpha = 0.94\ \mathrm{eV},\ \nu_\alpha = 5.45 \times 10^{12}\ \mathrm{s}^{-1};\ \mathrm{Ir/W(110)}: E_\alpha = 0.94\ \mathrm{eV},\ \nu_\alpha = 5.92 \times 10^{12}\ \mathrm{s}^{-1})$ agree within experimental error with values obtained from the sum.[6,7] This means that on the W(110) plane, if there is rebounding, its importance is negligible in the range of temperatures I explored. The difference between the two types of planes may lie in their structure. The (110) plane is densely packed and adatoms carry out two-dimensional diffusion, whereas on the (211) atoms move in channels that confine the movement of the adatom on the surface and seem to further rebound after an initial jump. It is important, however, to point to the differences in diffusion on W(110) and what has been found in simulations on fcc(111) planes.[10] On these planes, rebounds are found at low temperature [200 K for Cu(111)]. The difference emphasizes once again the contrasting structure and diffusion behavior on close-packed fcc(111) and bcc(110) surfaces.[11] In any event on the (211) plane of tungsten, atom rebounds make a significant contribution to the atomic processes in diffusion and cannot be neglected.

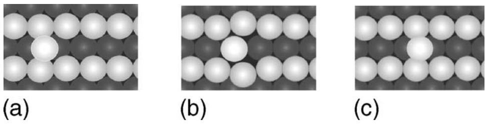

FIG. 2. Schematic of an atom jump along the ⟨111⟩ channel on W(211). (a) Adatom at the equilibrium point before jump. (b) Channel walls have bulged out, allowing adatom to move. (c) Adatom in nearest-neighbor site after jump.

That rebounding occurs more frequently than double jumps, as shown in Table I, is surprising, since one might expect that continuing in the direction of the original jump should be easier than a reversal of the direction of the atom. However, rebounds as well as double jumps originate in nearest-neighbor transitions and for the temperatures of these measurements their rates can be described by the equation

$$R_{\beta R} = R_1 \times p_{\beta R}, \tag{1}$$

where R_1 is the basic rate extrapolated from the rate of single jumps at low temperatures, and $p_{\beta R}$ is the probability of an atom turning back to its original position. This relation is valid as long as higher transitions are negligible in surface diffusion; it cannot be extrapolated to more elevated temperatures where processes occurring on the surface are not known. It does show that atom jumps over the surface are correlated with the dynamics of the lattice, and for long jumps as well as for rebounds this correlation is important. The probability of a continuing transition depends on a widening of the channel, shown in Fig. 2, being correlated with the position of the moving atom, and at this moment it is difficult to predict what is more probable: continuation or turning back. What is clear, however, is that we expect similar rebounds in diffusion on planes similarly structured, such as the fcc (110).

In summary, we have recognized and characterized three kinds of atomic processes in self-diffusion on W(211). At low temperatures the movement of atoms proceeds by single jumps between nearest-neighbor sites with an activation energy of 0.84 eV. At slightly elevated temperatures (around 300 K) the single jumps are replaced with double and rebound jumps with an activation energy of 1.44 and 1.03 eV, respectively. For W(211) the transition between these processes is very steep, much steeper than for W(110). One may wonder if such small changes in temperature can be responsible for so drastic a change in the mechanism of movement. The change in thermal energy between 300 and 320 K amounts to only ~0.0017 eV, but this small change increases the rate of rebound jumps by a factor of ~12. Of course other factors may be involved but the investigation was carried out only to 325 K, and further replacement of shorter jumps by longer transitions is possible at higher temperatures.

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[11] Fcc(111) and bcc(110) planes differ not just in packing density and geometry, but also in the energetics of diffusion compared to other planes. The self-diffusion energetics on copper are ~0.04 eV on Cu(111) (Ref. 12) and ~0.25 eV on Cu(110) (Ref. 13). On W(110) self-diffusion occurs with a barrier of 0.94 eV (Ref. 5), compared with 0.81 eV for W(211) (Ref. 6).

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