Correlated Jump-Exchange Processes in the Diffusion of Ag on Ag(110)

R. Ferrando

Dipartimento di Fisica dell'Università, Istituto Nazionale di Fisica della Materia and Centro di Fisica delle Superfici e delle Basse Temperature/CNR, Via Dodecaneso 33, 16146 Genova, Italy

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It is shown by molecular-dynamics simulations that correlated processes involving both jumps and exchanges become important in the diffusion of Ag/Ag(110) at temperatures around 600 K. Silver is modeled by many-body potentials derived in the framework of the tight-binding model. [S0031-9007(96)00322-5]

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The diffusion of adatoms on metal surfaces may occur by different mechanisms; not only uncorrelated jumps between nearest-neighbor sites are possible, but also exchanges and long jumps. In the exchange-mediated diffusion, the adatom enters the substrate and replaces one atom of the latter by pushing it above the surface; in the long-jump diffusion, the adatom starts from a given site, then it may make a flight and finally thermalize in a cell which is not a nearest neighbor of the cell of departure.

The occurrence of exchange-mediated diffusion has been shown in many different systems [1]. Interchannel diffusion on fcc (110) surfaces was discovered in Pt/Pt(110) and Ni/Ni(110) [2]; the exchange mechanism was then predicted by molecular-dynamics (MD) calculations [3] and experimentally discovered in W/Ir(110) [4]. The possibility of exchanges on the more compact (100) surfaces has been predicted by MD simulations [5] and discovered in different experiments [6]. Recently, MD simulations on the (100) faces of Cu [7] and other metals [8] have shown that complicated exchange mechanisms, involving the displacements of more than two atoms, occur at high temperatures.

The possibility of long jumps (often called correlated jumps) has been investigated both experimentally [9,10] and theoretically [11–13]; the experiments show that long jumps occur, for instance, in Ir/W(110), Na/Cu(001), and Pd/W(211).

In this Letter, we show by MD simulations that new mechanisms become important in the diffusion of Ag on Ag(110) as the temperature is raised to about 600 K: precisely, correlated jump-exchange, exchange-jump, and exchange-exchange processes (see Figs. 1–3). In that system, interchannel diffusion occurs by exchanges at any temperature; at high temperatures it happens that about 25% of the total interchannel-diffusion events is represented by correlated events of the above kinds. The Ag(110) surface presents close-packed rows and channels along the $[1\bar{1}0]$ direction (horizontal direction in the figures); the perpendicular direction is the [001]. Silver is modeled by many-body potentials of the kind developed by Rosato, Guillopé, and Legrand (RGL) [14,15] on the basis of the second-moment approximation to the tight-binding model [16]. Those potentials describe correctly relaxations and reconstructions of noble metals [15]; recently, they have been employed in the simulation of adatom and dimer diffusion on fcc transition metal surfaces [17,18]. In particular, it results that RGL potentials predict, in agreement with all known experimental results, whether exchange-mediated diffusion is a favorable process on different flat surfaces of the above metals [17]. The form and the parameters actually used in the present simulations are given in Ref. [19].

Our system consists of a (110) slab of the thickness of 12 layers; each layer contains 7×7 atoms; periodic boundary conditions are applied in the surface plane. On the topmost layer we put the diffusing adatom.

Before starting the high-temperature simulations, the static energy barriers for the elementary diffusion processes have been calculated by quenched molecular dynamics [20]. In particular, we computed the diffusion barrier for jumping along the channels $E_j^{\parallel}$, the one for jumping across the channels $E_j^{\perp}$ and the one for the simple exchange (which corresponds to processes e_1 and e_2 in Fig. 1) E_e. The results are reported in Table I, where

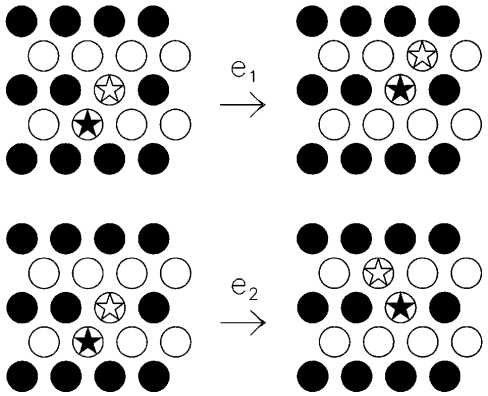

FIG. 1. Schematic representation of the simple exchanges e_1 and e_2. The black star represents the adatom initially in the channel; black circles correspond to the atoms of the surface rows; white circles correspond to those of the layer below. The row atom which participates in the exchange with the adatom is singled out as the white star.

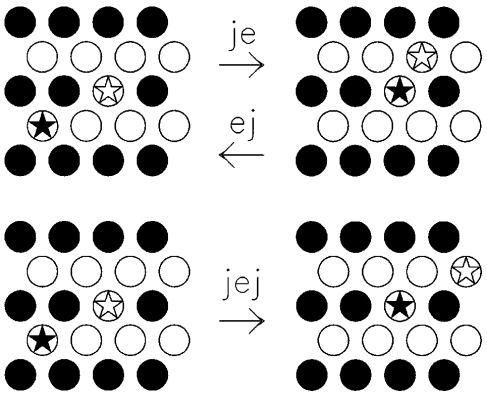

FIG. 2. Schematic representation of possible correlated jump-exchange (je), exchange-jump (ej), and jump-exchange-jump (jej) processes. Symbols as in Fig. 1

they are compared to those given by the corrected effective medium (CEM) theory obtained by Perkins and DePristo [21]; RGL and CEM results are in good agreement both for diffusion along the channels and for exchange. As one may expect, the easiest process is the diffusion along the channels; the interchannel mobility is possible only by exchanges, due to the very high value of $E_j^{\perp}$.

High-temperature diffusion is studied by running many independent microcanonical simulations at five different temperatures (450, 550, 600, 650, and 670 K). The solution of the equations of motions is achieved by the standard Verlet algorithm [22], with a time step of 7 fs. Some simulations were run with a time step of 3.5 fs as a check of the occurrence of the correlated events.

As we are interested in single-atom diffusion on the otherwise perfect surface, data are taken when only one adatom is present on the surface; if an atom of the topmost layer leaves the row by itself, without being pushed by

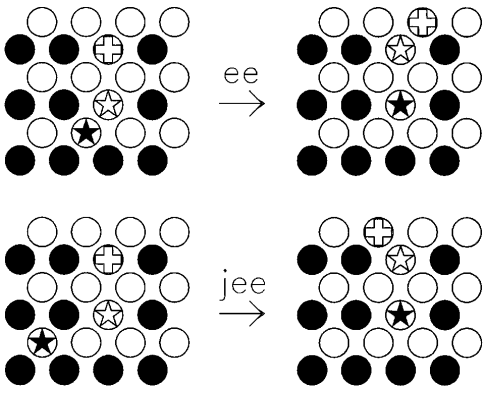

FIG. 3. Schematic representation of possible correlated exchange-exchange (ee) and jump-exchange-exchange (jee) processes. The black star represents the adatom initially in the channel; black circles correspond to the atoms of the surface rows; white circles correspond to those of the layer below. The row atoms which participate to the double exchange are singled out as the white star and the white cross.

TABLE I. Energy barriers. All data are in eV. $E_j^{\parallel}$ is the energy barrier for jumping along the channels, $E_j^{\perp}$ for jumping across the channel, E_e is the barrier for exchange. The CEM results are taken from Ref. [21].

	$E_j^{\parallel}$	$E_j^{\perp}$	E_e
RGL	0.28	0.83	0.38
CEM	0.26	···	0.34

the adatom, the simulation is stopped. Having stopped the simulations each time there is a spontaneous breaking of a row, the exchange events reported in Table II refer only to concerted exchanges [23], and not to events in which, at first, an isolated vacancy is created in a row and later the vacancy is filled by an incoming adatom. The spontaneous breaking of rows becomes rather frequent at the highest temperature. At the temperatures considered in the following, thermal dilation is not negligible. It has been determined at each temperature looking for the value of the lattice spacing which gives zero crystal pressure [19].

The high-temperature simulations display a rather rich phenomenology, with a large number of simple and correlated events. Therefore, the mobility of Ag is large, corresponding to diffusion coefficients in the range of $10^{-6} - 10^{-5}$ cm^2 s^{-1} even in the cross-channel direction. In order to discriminate the correlated events, a criterion must be given; we follow the one described in Ref. [19], with a cutoff time of $\tau = 2$ ps. The latter is comparable to the time necessary to cross a lattice spacing at the average thermal velocity. A particle is considered as thermalized in a given cell if it spends a longer time there than τ. For instance, let us assume that the adatom starts a jump from the first cell and finally stops in the third cell. This process is counted as a double correlated jump if the adatom spends in the second cell a time shorter than

TABLE II. Results of the MD simulations of diffusion of Ag on Ag(110). Five temperatures have been considered. t_0 is the total simulation time at each temperature (in ps). At each temperature, the numbers of single, double, and triple jumps along the channels (j_1, j_2, and j_3, respectively) and of the other events discussed in the text (see Figs. 1–3) are reported.

	450 K	550 K	600 K	650 K	670 K
t_0	13000	5900	4400	3700	2800
j_1	98	135	142	153	130
j_2	5	4	13	10	5
j_3	0	1	0	1	0
e_1	5	13	18	21	30
e_2	11	15	17	27	19
je and ej	0	0	8	10	12
jej	0	0	0	1	3
ee	0	2	1	2	1
jee	0	0	0	1	0

τ, otherwise two single jumps are counted. The same criterion applies to all the correlated processes.

The different diffusion processes are represented in Figs. 1–3, apart from jumps along the channels (single, double, and triple jumps, indicated by j_1, j_2, and j_3 in Table II). The total results, given in Table II, can be summarized as follows.

Jumps along the channels.—This kind of event gives the most important contribution to the diffusion in the $[1\bar{1}0]$ direction. Single jumps represent more than 90% of the total number of jumps at any temperature; almost all long jumps are double. This percentage is in agreement with the results of MD simulations concerning diffusion along straight steps on the (111) face of Ag [19]. The fraction of long jumps is not strongly temperature dependent. There is some indication of a slight increase up to 600 K and then of a rather sudden decrease at the highest temperatures. A slow increase of the fraction of long jumps with temperature is consistent with the result of a one-dimensional Brownian model of diffusion with temperature-independent friction [13,19]. Interchannel jumps never happened in the simulations.

Simple exchanges.—They correspond to processes e_1 and e_2 in Fig. 1. Event e_1 contributes to diffusion in both directions, whereas e_2 contributes only to diffusion in the [001] direction. From the data in Table II, both e_1 and e_2 seem to have essentially the same probability. This means that the memory of the initial direction of the incoming atom is lost in the exchange process. An explanation of this result may be related to the fact that, during the exchange mechanism, the two atoms have to pass through a dumbbell-like configuration [24,25], which is symmetric on the surface plane. This result indicates that Ag/Ag(110) may behave in a different way from Pt/Ni(110) and Ir/Ir(110). In the latter systems, the experiments [26,27] showed that mechanism e_1 is preferred.

Correlated exchange-jump and jump-exchange processes.—These events are formed by jumps along the channels correlated with exchanges with the atoms of the $[1\bar{1}0]$ rows. Examples of possible ej (exchange-jump), je (jump-exchange), and jej (jump-exchange-jump) are depicted in Fig. 2. At 550 K and below none of those events is observed but already at 600 K we find 35 simple exchanges and 8 correlated events of the above kinds. At 650 and 670 K the fraction of correlated events is even larger. The sudden appearance of correlated events within a rather small increase of temperature may resemble the field-ion-microscopy results in Ref. [10] about the diffusion of Pd on W(211). Diffusion on that channeled surface is one dimensional; it has been found that a large fraction (about 25%) of long jumps along the channels appears as the temperature is raised by less than 10% from 122 to 133 K. In the present simulations, however, we find a dramatic change in the frequency of events in which the correlation is between jumps and exchanges, whereas the occurrence of correlated jumps in the $[1\bar{1}0]$ direction is not dramatically affected by the temperature.

Correlated exchange-exchange processes.—Also exchange-exchange (ee, see Fig. 3) or jump-exchange-exchange (jee) events are possible, but they are rare at any temperature. The statistics is very poor and it is not possible to draw any conclusion from the data.

A qualitative explanation for the occurrence of the correlated processes described above may be given in the following terms. Around 600 K, a strong anharmonicity in the surface phonons on Ag(110) appears. This has been demonstrated both by helium scattering experiments [28] and by embedded-atom simulations [29]. We too have computed the mean-square vibrational amplitude $\langle u^2 \rangle$ of the top-layer atoms (the row atoms depicted by black circles in the figures); the results for the vibration perpendicular to the channel (along the [001] direction) are shown in Fig. 4. The latter vibration is in fact strongly anharmonic; its average amplitude increases strongly at high temperatures. As the amplitude of this vibration increases, it may happen, for instance, that the adatom, instead of making a long straight jump along the channel, is pushed or pulled in the perpendicular direction by a row atom, thus making a correlated jump-exchange process. This is consistent also with the observation of a drop in the frequency of long in-channel jumps at the highest temperatures, as the strong perpendicular row-atom vibrations reduce the availability of long straight paths.

In conclusion, we have shown that the high-temperature diffusion of Ag on Ag(110) may proceed by many different elementary mechanisms. Single and long jumps along the $[1\bar{1}0]$ direction and simple exchanges are common at

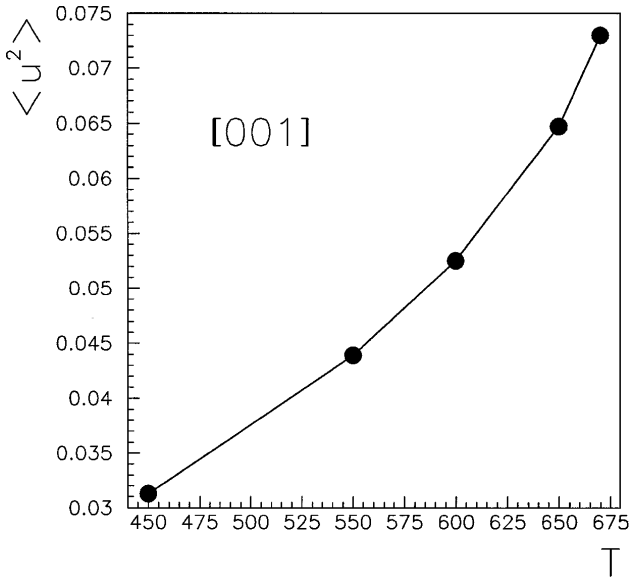

FIG. 4. Average square amplitude $\langle u^2 \rangle$ of the vibration of the top layer atoms (black circles in Figs. 1–3) in the [001] direction (perpendicular to the channels) at the temperatures of the simulations. $\langle u^2 \rangle$ is in Å^2 and T in K.

the lowest temperature considered here (450 K); simple exchanges are possible along the [001] direction (as in e_2) and in the diagonal direction (event e_1), essentially with the same probability. Correlated events involving exchanges become important as the temperature is raised to 600 K. These events can be of the jump-exchange, exchange-jump, exchange-exchange kinds, or even more complicated and, above 600 K, they amount to about one-quarter of the total exchanges.

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