PHYSICAL REVIEW B VOLUME 48, NUMBER 15 15 OCTOBER 1993-I

Diffusion of individual Pt atoms on single-crystal surfaces of rhodium

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(Received 22 March 1993)

The diffusion of individual Pt atoms on five low-index crystal planes of Rh has been investigated by field-ion microscopy. The activation energy of surface diffusion is found to depend strongly on the crystal plane and to increase in the order of $(111)<(311)<(110)<(331)<(100)$. It ranges from below 0.22 eV on Rh(111) to 0.92 eV on Rh(100). The diffusion mechanism on all surfaces is site-to-site hopping, with the exception of Rh(110), where convincing evidence for exchange displacements is obtained. The reflection barrier against migration off the plane edge also exhibits a strong structure sensitivity, from a large reflection on Rh(311) to essentially none on Rh(100) and Rh(331). The results are compared with previous field-ion-microscope studies of self-diffusion on Rh and Pt.

I. INTRODUCTION

A fundamental step in the growth of crystalline solids is the migration of individual atoms across atomically smooth terraces. Although it has been possible to study single-atom diffusion with the field-ion microscope for many years,[1-3] efforts to characterize atom motion on metal surfaces have recently been stimulated by (1) a practical interest in the fabrication of artificially structured materials involving metal-metal combinations, (2) the observation of unexpected diffusion modes for atoms on surfaces (e.g., migration by exchange displacements[4-16]), and (3) theoretical developments that permit realistic modeling of single-atom displacements.[17-20] Migration on the low-index surfaces of fcc metals has attracted much of the recent attention, as it is these surfaces that exhibit unexpected diffusion behavior and are amenable to theoretical study with a variety of semiempirical and first-principles approaches and also to experimental investigation with the field-ion microscope.

In this paper, I report the results of an experimental investigation to determine the diffusion behavior of Pt adatoms on five single-crystal surfaces of Rh. The aim is to add to the existing data base for metal diffusion on metal surfaces and to look for trends that may help elucidate the rules governing how atoms move on surfaces (e.g., by hopping or exchange displacements). Pt on Rh is of special interest in that it represents a combination of metals intermediate between Pt on Pt, a system for which exchange displacements are found to be energetically favorable on certain surfaces,[4,9] and Rh on Rh, a system which behaves normally (i.e., atoms migrate by ordinary hopping displacements on all surfaces examined[3]). In addition, the experimental results reported here are intended to provide quantitative measurements of surface diffusion barriers useful for the testing of theoretical approaches to the investigation of individual atoms on surfaces. The interaction of Pt adatoms with Rh surfaces is also of practical interest in that Pt, Rh, and their alloys are used to catalyze a variety of commercially important chemical reactions.

Schematic representations of the different planes examined are shown in Fig. 1. The drawings show a top view of each plane's atomic structure. The lightly shaded circles correspond to atoms in the topmost layer, and the darker shaded circle corresponds to the most likely adsorption site (i.e., the lattice-continuation site) for a deposited adatom. The mobility of Pt adatoms on each of the five surfaces was investigated, as was the possibility of exchange displacements taking place between the Pt adatom and Rh substrate atoms. Previous studies indicate that exchange displacements may occur for atoms on

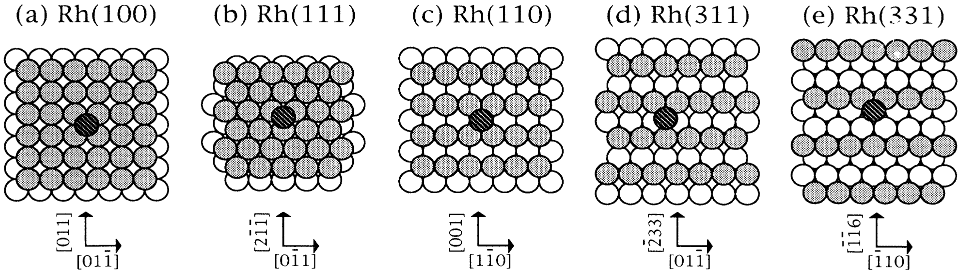

FIG. 1. Schematic representations of the five Rh surfaces examined in this investigation. Shown are top views of each plane's atomic structure. The lightly shaded circles correspond to atoms in the topmost layer, and the darker shaded circle corresponds to the most likely adsorption site (i.e., the lattice-continuation site) for the deposited Pt adatom.

both the (100) and (110) planes of fcc metals.[4–16]

Along with the quantitative studies of diffusion barriers for atoms on top of the crystal planes, qualitative observations of the interaction of the adatom with the step edge were made. Atom-step interactions obviously play a major role in the nucleation and growth process, and past studies indicate that, whereas the edges of some crystal planes act as a reflection boundary, others do not. In this work, the temperature at which adatom loss off the plane began to occur was noted and compared to the onset temperature for diffusion on top of the plane.

II. EXPERIMENTAL METHODS

The procedures used in field-ion-microscopic studies of single-atom surface diffusion are discussed in several review articles[21–24] and books[25,26] and will not be repeated here. In this section, I mention only a few experimental details relevant to the present investigation. The sample tips were prepared from 0.127-mm-diameter polycrystalline Rh wire etched in a 4:1 wt:wt ratio of molten $NaNO_3$ and NaCl. The tip surfaces were cleaned by thermal annealing, Ne-ion sputtering, and field evaporation. Pt adatoms were deposited on the Rh surface from thoroughly outgassed Pt-wire coils placed a few cm from the tip. The tip temperature was controlled and monitored using the standard four-probe resistance/resistivity technique commonly employed in field-ion-microscope surface diffusion studies.[3] Field-ion-microscope images of the Rh tip surface were obtained in 2×10^{-4}-Torr Ne at 77 K with an internal channel plate used for intensification. The images were recorded with a video camera/recorder system and were analyzed with an automated, computer-image-processing system.

III. EXPERIMENTAL RESULTS

A. Pt on Rh(100)

The main results relating to the diffusion of Pt adatoms on Rh(100) are reported in a separate article concerning the mobility and stability of Pt clusters on Rh(100).[16] A summary of the single-atom diffusion results is presented here for comparison to diffusion on the other surfaces. The atomic structure of the Rh(100) surface is shown in Fig. 1(a). The diffusion mechanism for Pt adatoms on Rh(100) is ordinary site-to-site hopping. This is deduced from the identification of the diffusing adatom as Pt, both before and after displacements have occurred. In exchange diffusion, an adatom pushes a substrate atom out of its lattice site and takes its place in the top layer of surface atoms. If the displacement process for Pt on Rh were exchange, the adatom under observation would change from Pt to Rh during the first displacement. However, Rh adatoms on the Rh(100) plane can be distinguished from Pt adatoms because the desorption field for Pt is significantly higher than that for Rh. By checking the desorption field of the adatom during a diffusion sequence, one finds that exchange displacements do not take place, i.e., the diffusion mechanism is ordinary hopping. Measurements of the mean-square displacement of the Pt adatom at four different temperatures between 314 and 346 K yield an activation energy of surface diffusion and diffusivity (Arrhenius prefactor) of 0.92 ± 0.13 eV and $2\times10^{-3\pm1.9}$ cm^2/s, respectively. Adatoms were lost off the edge of the plane at all temperatures investigated, i.e., there is no apparent "reflection" barrier at the edge of the Rh(100) plane.

B. Pt on Rh(111)

The atomic structure of the Rh(111) plane is shown in Fig. 1(b). The fcc(111) plane is the least corrugated of all the cubic surfaces. Quantitative measurements of the activation barrier for diffusion on Rh(111) were not possible in this investigation because Pt adatoms were found to be mobile on this surface even at the base temperature of 77 K. This result is consistent with previous results for self-diffusion on both Rh(111) (Ref. 3) and Pt(111).[4] If one makes the assumption that the generally accepted[27] Arrhenius prefactor of 1×10^{-3} cm^2/s is valid for this system, then the qualitative observation that Pt is mobile below 77 K places an upper limit of 0.22 eV on the activation energy for Pt diffusion on Rh (111). The appearance of stable Pt clusters after extensive deposition with the tip at 77 K indicates that adatom motion on this surface is due to conventional hopping, not exchange displacements. The inability to conduct the standard diffusion measurements precluded the possibility of estimating the reflection barrier for Pt adatoms on the Rh(111) plane.

C. Pt on Rh(110)

The fcc(110) plane is a corrugated surface consisting of close-packed rows of atoms along the $[1\bar{1}0]$ direction. The most likely adsorption site for a metal atom is in a quasifourfold hollow site within a surface channel, as indicated in Fig. 1(c). Adatom motion may occur from site to site within a given surface channel [e.g., self-diffusion on Rh (Ref. 3)] or cross channel by exchange displacements [e.g., self-diffusion on Pt,[4] Ni,[6] and Ir (Refs. 4 and 7)]. Field-ion micrographs illustrating typical results for Pt migration on Rh(110) are shown in Fig. 2. The photographs correspond to successive images with intermittent 30-s heating intervals at a temperature of 242 K. The short arrows in Figs. 2(a)–(c) show the position of a single Pt atom adsorbed in one of the surface channels. Accurate measurements of the adatom coordinates indicates that the adatom does not change its position from Figs. 2(a)–2(c). Figure 2(d) shows the same surface after one additional heating interval at 242 K. It is clear that the adatom is no longer on top of the (110) terrace. Analysis of Figs. 2(c) and 2(d) using a color superposition technique shows that during the one 30-s heating interval the adatom migrated off the plane to the step position indicated by the arrow in Fig. 2(d).

The diffusion sequence illustrated in Fig. 2 was reproducible over more than 20 experimental trials. At temperatures at or near 240 K, Pt adatoms were immobile for 1–25 diffusion cycles, and then in a single heating interval they would diffuse across the plane and off its edge. At lower temperatures the adatoms did not move at all

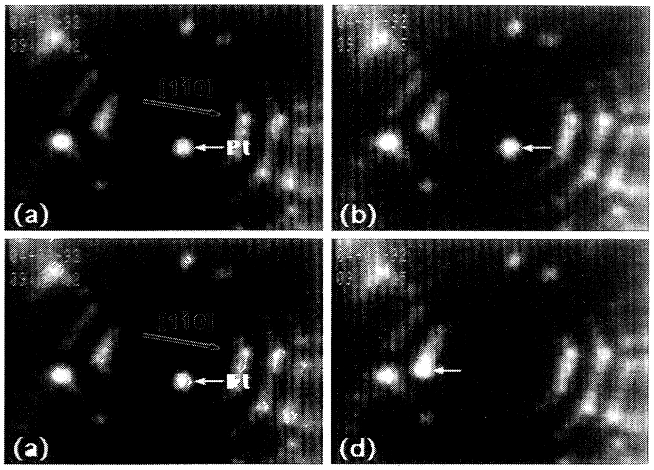

FIG. 2. Field-ion micrographs illustrating the diffusion behavior of Pt adatoms on the Rh(110) plane. The short arrows in (a)–(c) show the position of a single Pt atom adsorbed in one of the surface channels. Between each photograph the sample was warmed from its base value of 77 K to a temperature of 242 K for 30. No motion occurred in (a)–(c). The arrow in (d) indicates the position of an adatom in a step position. The sudden loss of the adatom off the plane indicates an exchange process as discussed in the text.

and at higher temperatures they disappeared more frequently. This behavior is quite different from that observed in typical single-atom diffusion experiments. Normally, at the onset temperature for adatom motion the individual displacements are small, with infrequent observations of jumps between neighboring binding sites. As the temperature is increased the displacements become monotonically larger, but diffusion off the plane is not observed until significantly higher temperatures (at least 30–50 K above the onset temperatures) are applied.

The sudden loss of Pt adatoms from the Rh(110) surface can be explained by the exchange process mentioned above. On fcc(110) surfaces, exchange displacements take place when the adatom pushes a substrate surface atom into a neighboring surface channel and takes its place in the channel wall.[4–8] The cross-channel exchange process is illustrated schematically in Fig. 3. In self-diffusion systems like Pt on Pt(110) and Ir on Ir(110), the chemical identity of the adatom before and after the displacement does not change, and the activation barriers for the first, second, and subsequent cross-channel displacements are the same. In the case of Pt on Rh, however, after the first exchange the adatom changes from Pt to Rh resulting in a different barrier for diffusion. From past studies of self-diffusion on Rh(110), it is known that Rh adatoms become mobile at 175 K and escape the edge of the plane at temperatures as low as 210 K.[3] Clearly, at 240 K, where Pt adatoms disappear from the Rh(110) surface, Rh adatom s are sufficiently mobile to move from anywhere on the plane to its edge and over. The behavior of Pt adatoms on Rh(110) is therefore the result of the activation barrier for exchange displacements being lower than that for hopping displacements. In this situation no motion occurs until an exchange displacement takes place at ~240 K. The exchange process generates a Rh adatom in a neighboring channel, which quickly diffuses off the plane. The Rh adatom is not seen on the plane because the probability of the diffusion interval ending just as the adatom is generated is very small. The location of the observed step-site atom in Fig. 2(d) is consistent with a cross-channel exchange followed by diffusion of a Rh adatom down the neighboring surface channel and off the plane.

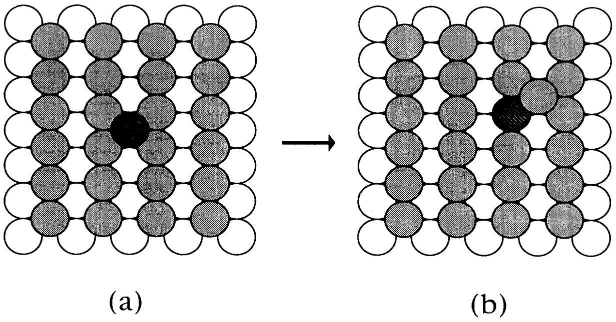

FIG. 3. A schematic representation of the cross-channel exchange process on fcc(110) surface.

It would be a simple matter to confirm the proposed mechanism if the atom located at the step site [e.g., Fig. 2(d)] could be identified as Rh, and a Pt atom could be detected within the top layer of Rh atoms. Exchange displacements involving Pt adatoms on the Ni(110) surface were confirmed in earlier studies in this way by identifying the adatoms based on differences in their desorption fields.[8] Although it is possible to distinguish Pt and Rh adatoms on top of the (110) plane from differences in their desorption fields, the desorption-field difference for atoms in step sites or within the Rh lattice is not large enough for this purpose. Since the field-ion microscope used in this study does not have an atom-probe capability, direct confirmation of the exchange process is not possible. However, even without this additional confirmation, the circumstantial evidence presented above (the sudden loss of the Pt adatoms) is sufficient to conclude that exchange displacements occur for Pt on the Rh(110) surface with a lower activation barrier than hopping displacements. From the onset temperature where movements are first observed, the activation barrier for the exchange process is estimated to be ~0.65 eV.

In a few experimental sequences (three out of 25), the diffusion behavior of Pt on Rh(110) was different from that described above. During 30-s heating periods at 242 K, the adatom was observed to make cross-channel and in-channel displacements to new locations on the surface without diffusing off the plane. This type of migration is illustrated by the field-ion micrographs shown in Fig. 4. The high-contrast spot in Fig. 4(a) corresponds to a Pt adatom on a Rh(110) plane. When this atom was initially deposited on the surface, it did not move for 20 diffusion cycles at 242 K, similar to that reported above. However, as seen in photographs in Figs. 4(b)–4(c), when motion did occur, the adatom remained on top of the plane (at least for a few diffusional intervals). From the direction of the surface channels indicated on the micro-

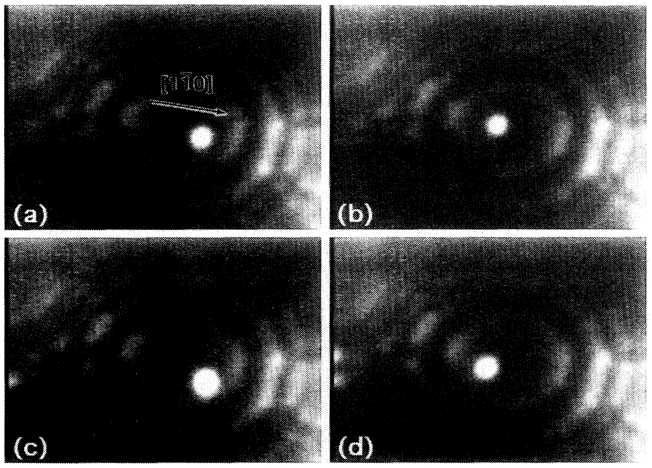

FIG. 4. Field-ion micrographs illustrating what appear to be cross-channel "hops" of a Pt adatom on a Rh(110) surface. Between each photograph the sample was warmed to 242 K for 30 s. These types of displacements were observed infrequently.

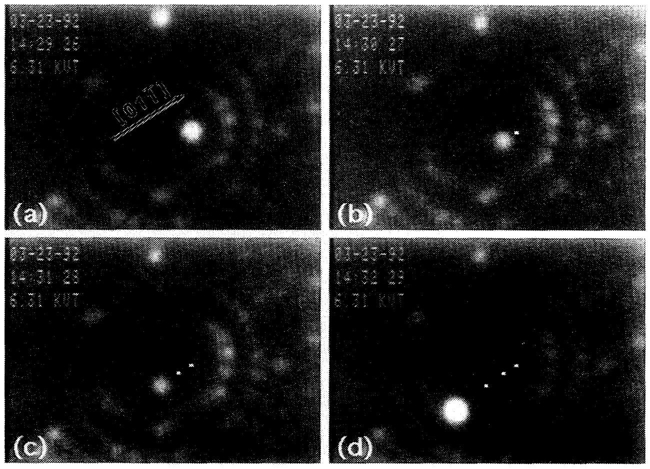

FIG. 5. Field-ion micrographs showing the diffusion of a Pt adatom on the Rh(311) plane at 191 K. The small white dots superimposed on the photographs show the positions of the adatom in the previous images. The motion of the adatom is confined to one dimension.

graph, it is clear that cross-channel displacements were involved in the migration. It could not be determined whether this cross-channel motion was due to Pt adatoms hopping over the channel walls or a Pt/Rh exchange followed by a Rh cross-channel exchange (the applied field was below the desorption field of either Pt or Rh). The intensity of the image spot did not change after the first cross-channel displacement, suggesting that exchange did not occur (i.e., Pt adatom hopping), but the notion of cross-channeling hopping at these temperatures is counterintuitive. Cross-channel exchange displacements for Rh and Rh(110) seem more likely, but these were not observed in earlier field-ion microscopy (FIM) studies of Rh self-diffusion.[3] Unfortunately, more detailed studies of this effect were impeded by the low probability of its observation. Theoretical investigations of the relative energy barriers for cross-channel exchange and hopping displacements would be very useful in explaining the observation.

D. Pt on Rh(311)

Like the fcc(110) surface discussed above, the fcc(311) surface is a channeled surface consisting of close-packed rows of atoms. However, the configuration of atoms around the surface sites on the (311) plane is different from those on the (110) plane [see Fig. 1(d)]. Specifically, there are no quasifourfold hollow sites similar to the presumed adatom binding sites on the (110) surface. It is not surprising, therefore, that the observed diffusion behavior of adatoms on the two surfaces is different. In general, the activation barrier for diffusion of like adatoms is found to be lower on (311) than on (110), and cross-channel (i.e., exchange) processes have not been observed on any fcc(311) surface investigated by field-ion microscopy.

The results for Pt on Rh(311) are consistent with these previous observations. Adatom motion is observed at significantly lower temperatures (onset $T \sim 165$ K) than on (110) and is found to be confined to within a given surface channel. Field-ion micrographs illustrating the diffusion of Pt on Rh(311) at 191 K are shown in Fig. 5. In just three diffusion intervals, the adatom moves from near one edge of the plane in Fig. 5(a) to the other in Fig. 5(d). The small white dots in Figs. 5(b)–5(d) show the positions of the adatom in the previous images. The one-dimensional nature of the adatom's motion is indicated by the linear arrangement of dots in Fig. 5 (along the $[01\bar{1}]$ direction) and is obvious from the site-visitation map shown in Fig. 6. This map is a plot of the adatom coordinates after each of 230 diffusion intervals at 191 K. The distortion of the site map (deviation from a true straight line) is due to the well-documented,[25,26] nonuniform magnification of the field-ion microscope. The

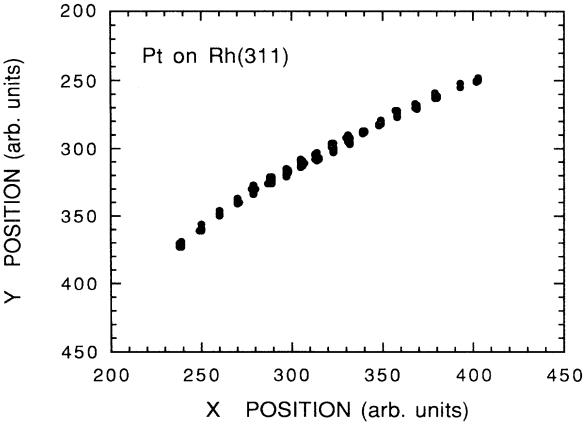

FIG. 6. A site-visitation map corresponding to 230 diffusion intervals for a Pt adatom migrating on the Rh(311) plane at 191 K. The linear arrangement of sites indicates that cross-channel displacements do not occur on this plane. The map is used to calibrate the distance scale.

configuration of sites over this large number of intervals indicates that cross-channel displacements do not occur for this system and, consequently, that the diffusion mechanism is ordinary hopping. The same type of site-visitation maps (i.e., one dimensional) are obtained for all diffusion temperatures investigated.

Besides demonstrating the absence of cross-channel displacements, site-visitation maps such as the one shown in Fig. 6 provide an accurate calibration of the displacement distances which are used to measure the adatom's mean-square displacement. The measured mean-square displacements as a function of temperature are then used to determine the diffusion parameters. An Arrhenius plot of the log of the mean-square displacement vs inverse temperature corresponding to diffusion at five temperatures in the range from 165–205 K is shown in Fig. 7. From the slope and intercept of this plot, the activation energy and diffusivity for Pt on Rh(311) are determined to be 0.44±0.02 eV and $1.6\times10^{-4\pm0.5}$ cm^2/s, respectively.

The edge of the Rh(311) plane is found to be an effective reflection barrier for Pt adatoms in the temperature range used to extract the diffusion parameters (165–205 K). In fact, adatom loss off the plane is not detected until the temperature is raised to well above 335 K. (Diffusion data for temperatures above 205 K were not used in the above analysis because the measured mean-square displacement was too large for the standard edge correction formula to be valid.) This "escape" temperature is slightly larger than that found for Pt on Rh(100), where adatom loss was noted at 325 K.

The large reflection barrier for Pt at the Rh(311) plane edge means that the adatom's location within the channel can be observed over many diffusion cycles. As shown in past studies of Re and W on W(211),[28] with sufficient observations it is possible to investigate preferences for particular binding sites across the surface by plotting the number of observations at a given site along the channel as a function of its location. For W on W(211) a strong preference for binding at the sites at the very ends of the channel was found.[28] In contrast, Re adatoms on W(211) were found to prefer the second position from the edge.[28] Figure 8 shows a frequency distribution plot for Pt on a Rh(311) surface channel consisting of 18 binding sites. Although the number of observations (230) is not sufficient to obtain quantitative differences in binding energies, it is clear that there are no strong preferences for binding at the edge or near-edge sites. It is therefore apparent that there is a strong chemical specificity in the site variation of adatom binding on different metal surfaces.

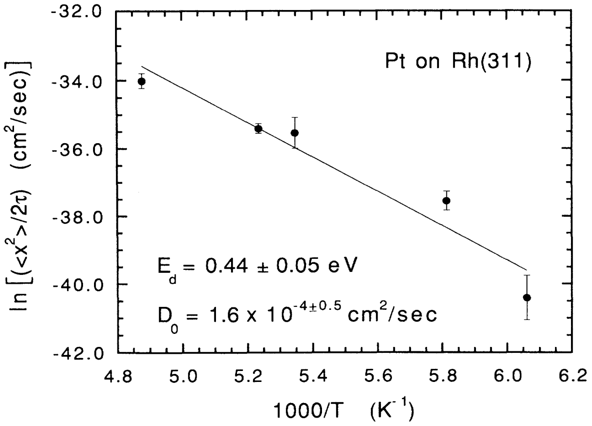

FIG. 7. The mean-square displacement of a Pt adatom on Rh(311) vs temperature plotted in Arrhenius form. The activation energy E_d and prefactor D_0, determined from a least-squares analysis, are stated on the figure.

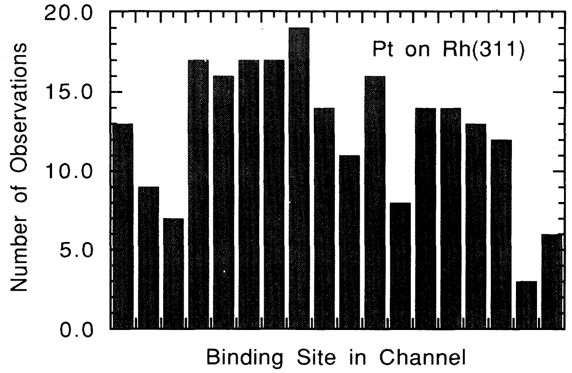

FIG. 8. A frequency distribution plot for a Pt adatom migrating within a Rh(311) surface channel consisting of 18 binding sites. The temperature was 191 K and the plot corresponds to 230 observations. No preference for the end sites is noted.

E. Pt on Rh(331)

The fcc(331) plane is a stepped surface made up of small (111)-like terraces and (110)-like steps [see Fig. 1(e)]. Symmetry suggests that adatoms on this surface would prefer to bind in the (110)-like grooves (the lattice-continuation site) with nearest neighbors in a configuration very similar to adatoms on the (110) plane. For those systems where hopping displacements are favored on both surfaces, one would expect diffusion on the (331) plane to be similar to that on the (110) plane because hopping displacements depend primarily on interactions of nearest-neighbor atoms. In agreement with this picture, the activation energies for self-diffusion on Rh(331) and Rh(110) have been found to be nearly equal. However, the activation barrier for exchange displacements, which involve the concerted motion of more than just the neighboring atoms, would be expected to be quite different for the (331) and (110) planes. Therefore, the occurrence of exchange displacements on the (110) surface does not imply that exchange displacements will be energetically favorable on the (331) surface.

The results for Pt on Rh(331) are consistent with these expectations. Whereas exchange displacements are preferred on for Pt on Rh(110), the diffusion of Pt on Rh(331) is found to occur by ordinary hopping. Analysis of Pt migration on Rh(331) at four temperatures in the range from 256 to 278 K yields an activation energy for surface diffusion of 0.72±0.02 eV. Because the temperature range over which reasonable statistics could be gathered was so small, this energy was not determined from the slope of an Arrhenius plot, but was calculated from the measured mean-square displacements directly with the assumption of the accepted[27] Arrhenius prefactor of 1×10^{-3} cm^2/s.

The loss of adatoms off the edge of the Rh(331) plane became quite noticeable at temperatures in excess of 300 K. This temperature is lower than that observed for diffusion off the (311) plane (~350 K) even though the barrier to diffusion on the (331) plane is considerably higher than on the (311) plane. Apparently, the additional barrier to diffusion off a given plane is not simply some fraction of the barrier to diffusion on the plane. This result is consistent with the qualitative observations reported for self-diffusion on Rh surfaces.[3]

IV. DISCUSSION

The activation energies for Pt diffusion on the different crystal planes of Rh measured (or estimated) in this study are given in Table I. For comparison, activation energies from previous investigations of self-diffusion on Rh (Ref. 3) and Pt (Refs. 4 and 11) are also listed. As indicated in the table, the general trend of increasing activation energy from (111) to (100) is very similar to the results for self-diffusion on Rh. The activation barriers tend to be slightly higher for Pt on Rh with the exception of the (311) plane, where the barrier for Pt on Rh is slightly lower. It has been noted previously[3] that the trend in activation energies $(111)<(311)<(110)<(331)<(100)$ is quite reasonable in view of the corrugation of the different surfaces. Diffusion is easiest on the close-packed (111) plane, more difficult on the channeled planes, and most difficult on the (100) where the corrugation in the direction of motion is the highest. Table I also indicates a similar trend for self-diffusion on Pt. However, there is a notable exception for diffusion on the (100) plane. The activation energy for self-diffusion on Pt(100) is about half that of the other two systems. This difference can be attributed to the difference in the diffusion mechanism, which is exchange for self-diffusion on Pt (Ref. 9) and hopping for Pt on Rh and presumably for Rh on Rh.[3]

Despite the development of a variety of theoretical approaches that can now treat the diffusion of individual metal atoms on metal surfaces, theoretical calculations of Pt/Rh diffusion barriers for comparison to experiment are scarce. First-principles and embedded-atom method (EAM) calculations of fcc/fcc diffusion barriers have been reported,[17–19] but these calculations have been confined to the case of self-diffusion. The only theoretically predicted diffusion barrier for Pt on Rh is that for displacements on the (100) plane, which was calculated using transition state theory (TST) and corrected effective-medium (CEM) potential-energy surfaces.[20] The value reported is 0.66 eV, considerably lower than the experimental result of 0.92 eV. The same theory does a much better job for self-diffusion on Rh (0.80 eV compared to the experimental value of 0.88 eV), indicating a possible problem with mixed metal systems. Hopefully, the experimental results reported here will help improve the theoretical modeling efforts, which, in turn, will provide further insight into the physics of the diffusion process.

TABLE I. Activation energies of surface diffusion for metal-metal combinations involving Pt and Rh.

Crystal Plane	Rh on Rh[a]	Pt on Pt[b]	Pt on Rh[c]
(111)	0.16 eV	<0.22 eV	<0.22 eV
(311)	0.54 eV	0.69 eV	0.44 eV
(110)	0.60 eV	0.81 eV*	~0.65 eV
(331)	0.64 eV	0.84 eV	0.72 eV
(100)	0.88 eV	0.47 eV	0.92 eV

[a] From Ref. 3.
[b] From Refs. 4 and 11.
[c] From this work.
*Average of in-channel and cross-channel barriers.

It was noted in Sec. I that one of the motivations for this work was to ascertain the diffusion mode (exchange vs hopping) on the various surfaces and identify possible trends or correlations with results obtained previously for other metal/metal combinations. The diffusion mode was found previously to be exchange for self-diffusion on the (100) and (110) planes of Pt and hopping for self-diffusion on the same planes of Rh. It was interesting to find that exchange displacements were favored for Pt on the Rh(110) surface, but that hopping displacements were preferred on the (100) surface. Typically, the diffusion mechanism for a given metal-metal combination has been found to be the same on the (100) and (110) planes (Pt on Ni is a possible exception[7]). The unusual behavior of Pt on Rh(110) reported above suggests that Pt on Rh represents a borderline system with only small differences in the exchange and hopping activation barriers. Further investigations employing an externally applied electric field to promote or inhibit exchange displacements[29] are planned to help determine the actual difference in the exchange and hopping activation energies.

Table II shows a compilation of the measured activation barriers and diffusion modes for diffusion on various fcc(100) surfaces including the present results for Pt on Rh. [It is generally assumed that the diffusion mode for self-diffusion on Ni(100) and Rh(100) is ordinary hopping, but so far this has not been confirmed by analysis of site-visitation maps.] It is interesting to note that before the present results for Pt on Rh(100), one could associate the preference for exchange displacements in heterogeneous systems with a thermodynamic driving force derived from heats of alloy formation.[16] Enthalpies of binary alloy formation based on the atomic model of Miedema[30] have been tabulated by de Boer *et al.*[31] From these tables, the calculated heats of formation for Pt/Ni compounds (both Pt in Ni and Ni in Pt) are found to range from −3 to −7 kJ/mol depending on the relative atomic concentrations. Similarly, the values for Re/Ir compounds range from −2 to −5 kJ/mol. In contrast, the values for Pt/Pd compounds range from +1 to +3 kJ/mol. Comparison of these values with the experimentally determined preference for exchange listed in Table II indicate that exchange displacements are correlated with a negative heat of alloy formation. However, the correlation does not hold for Pt on Rh(100). The calcu-

TABLE II. Activation energies of surface diffusion and diffusion modes for various fcc/fcc metal combinations.

	Ni(100)	Rh(100)	Ir(100)	Pt(100)
Ni	0.63 eV (Ref. 6) hop(?)			~0.45 eV (Ref. 12) exchange
Rh		0.88 eV (Ref. 3) hop(?)		
Re			0.95 eV (Ref. 14) exchange	
Pd				0.70 eV (Ref. 12) hop
Ir			0.93 eV (Ref. 10) exchange	
Pt	0.69 eV (Ref. 15) exchange	0.92 eV (Ref. 16) hop		0.47 eV (Ref. 9) exchange

lated enthalpies of formation for Pt/Rh compounds are found to range from −1 to −2 kJ/mol, suggesting that exchange should occur, but the present studies indicate that hopping displacements are preferred in this system.

Not only are the calculated heats of alloy formation inconsistent with the results for Pt on Rh(100), they provide no insight with respect to homogeneous systems where, as indicated in Table II, exchange displacements are energetically favorable on some fcc(100) planes and hopping displacements are favored on others. It is therefore not too surprising that the atomic interactions which determine whether exchange displacements are favored in a given system are more subtle than those inferred from macroscopic, thermodynamic properties. In past studies it has been shown that for Ni, Pd, and Pt adatoms on the Pt(100) surface, exchange displacements can be correlated with a larger adatom-induced lattice relaxation as determined from embedded-atom-method calculations.[12] It would be interesting to see if this correlation holds for the other systems mentioned above, but so far neither measurements nor calculations of the lattice relaxations in these systems are available. It is also evident that in order to establish any reasonable trends or correlations information on more metal/metal combinations will be required.

As mentioned in Sec. III the additional barrier to diffusion off the edge of the plane was found to be crystal-plane dependent. Because of the low migration temperature for Pt on the Rh(111) plane and the unusual diffusion behavior for Pt on the Rh(110) plane, the temperature at which adatom loss occurred could not be determined for these planes. However, it was possible to determine the "escape" temperature the other three surfaces. On (100) and (331), Pt adatoms frequently migrated off the plane during the heating cycles, but on (311) there was a large reflection barrier. Whereas motion on the (311) plane occurred at temperatures as low as 165 K, adatom loss off the plane did not occur until the temperature was raised to above 335 K. These results are in general agreement with those reported previously for self-diffusion on Rh.[3] It is interesting that the different behavior is not due so much to the difference in escape temperature as to the difference in diffusion temperature on the plane. In all cases adatom loss occurred at temperatures above 300 K, but on (100) and (331) these temperatures were required for diffusion on the plane as well. This suggests that one should not view the edge reflection barrier as an additional barrier given by some fraction of the diffusion barrier on the plane, but as a barrier whose height is relatively constant from one crystal plane to the next. For some systems it has already been shown that diffusion off the plane involves an exchange process and is nothing at all like the typical view of a marble rolling off a ledge.[32] It may be that the edge barrier is defined by how well the atomic configuration at the edge lends itself to these exchange processes. Given the importance of adatom-step interactions in crystal-growth processes, more systematic investigations of these escape barriers should provide a fruitful area for further investigation.

V. SUMMARY

Field-on-microscope investigations have shown that the activation energy of surface diffusion for Pt adatoms on Rh surfaces depends strongly on the crystal plane and increases in the order of (111)<(311) <(110)<(331) <(100). The activation energy ranges from below 0.22 eV on Rh(111) to 0.92 eV on Rh(100). The diffusion mechanism on all surfaces is site-to-site hopping, with the exception of Rh(110), where exchange displacements are inferred from the sudden loss of Pt adatoms. Qualitative observations of the temperature at which adatom loss off the edge of the plane becomes significant indicates a pronounced structure sensitivity in the reflection barrier, from a large reflection on Rh(311) to essentially no additional barrier on Rh(100) and Rh(331).

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under contract No. DE-AC04-76DP00789.

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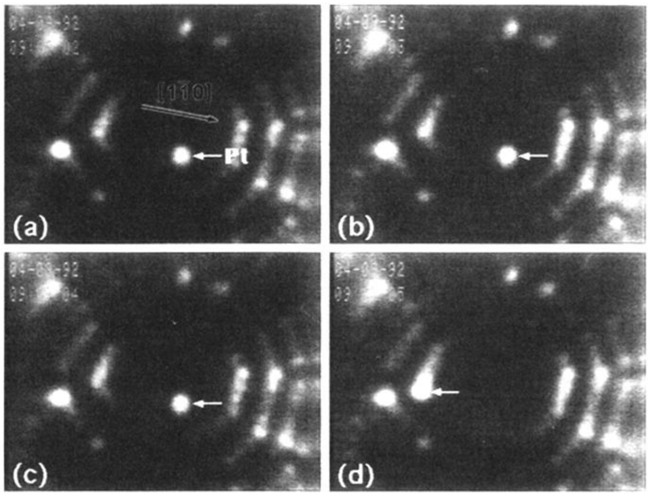

FIG. 2. Field-ion micrographs illustrating the diffusion behavior of Pt adatoms on the Rh(110) plane. The short arrows in (a)–(c) show the position of a single Pt atom adsorbed in one of the surface channels. Between each photograph the sample was warmed from its base value of 77 K to a temperature of 242 K for 30. No motion occurred in (a)–(c). The arrow in (d) indicates the position of an adatom in a step position. The sudden loss of the adatom off the plane indicates an exchange process as discussed in the text.

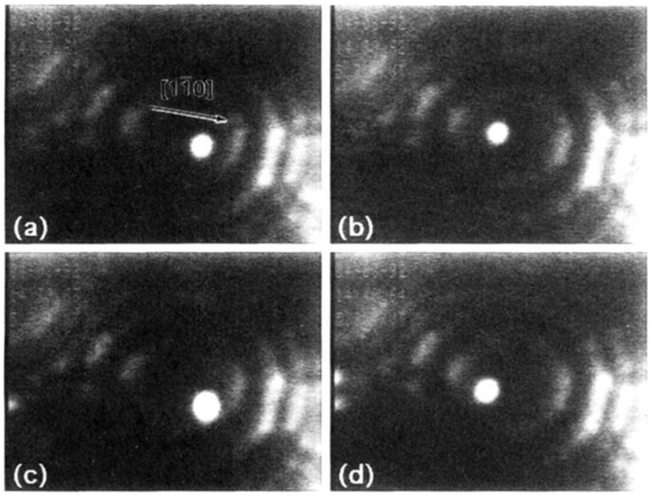

FIG. 4. Field-ion micrographs illustrating what appear to be cross-channel "hops" of a Pt adatom on a Rh(110) surface. Between each photograph the sample was warmed to 242 K for 30 s. These types of displacements were observed infrequently.

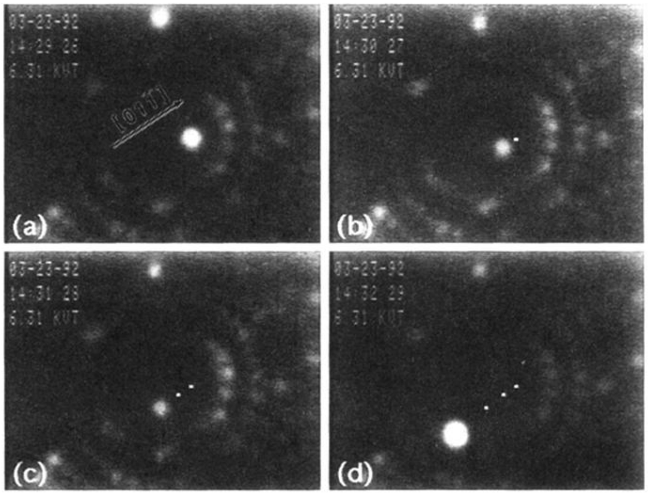

FIG. 5. Field-ion micrographs showing the diffusion of a Pt adatom on the Rh(311) plane at 191 K. The small white dots superimposed on the photographs show the positions of the adatom in the previous images. The motion of the adatom is confined to one dimension.