

Mechanisms of exchange diffusion on fcc(111) transition metal surfaces

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Exchange diffusion on unreconstructed fcc (111) transition metal surfaces has been studied through a combination of molecular dynamics with a friction force (quenched molecular dynamics) and the nudged elastic band method. Four homogeneous systems [Au/Au(111), Pt/Pt(111), Ni/Ni(111), and Cu/Cu(111)] provide evidence for the occurrence of exchange via the formation of a transient dimer (concerted exchange) when the following conditions are met. First, adatom and substrate are of the same nature, second, the exchange involves the original adatom and a surface atom in a nearest-neighbor position on the surface (short range exchange). Consideration of two heterogeneous systems, Co/Pt(111) and Co/Au(111), reveals that an alternative mechanism (two-steps exchange) may take place provided the tensile stress of the substrate is sufficiently high. This is the case in Co/Au(111) and in Co/Pt(111), when this latter is submitted to in-plane expansion. By focusing on mechanisms involving surface atoms next-nearest neighbors of the original adatom, we have highlighted two different kinds of medium range diffusion via exchanges. The first amounts to a concerted movement of the adatom and two surface atoms, one of them simply sliding on the surface in a position intermediate between the remaining two, moving upward and downward, respectively. The second occurs through a pair of two correlated short range exchanges. We found that exchange diffusion barriers are lowered by the medium range mechanism on Au(111) substrates. An atomic-scale rationale explaining this behavior is presented.

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I. INTRODUCTION

Exchange processes are peculiar diffusion modes on fcc(110) and (100) transition metal (TM) surfaces. This mechanism of migration is drastically different from conventional hopping between adjacent sites, since it consists of site replacements between an adatom and one (or several) surface atom. In the case of heterogeneous deposition, the occurrence of exchanges has implications for surface morphology and crystal growth. Exchanges promote the mobility on the surface provided energetics and kinetic effects favor this diffusion mode over hopping. Also, exchanges drive the incorporation of foreign atoms inside the substrate, leading to surface alloying. The mechanisms of exchange on fcc(110) and (100) TM surfaces have been elucidated via appropriate experimental probes and atomic-scale calculations.¹⁻⁶ Covalency effects and the role of tensile surface stress have proved crucial, by allowing to ascribe diffusion by site exchange to specific structural and bonding features.^{6,7} Less information is available for the case of fcc(111) TM substrates. Incorporation and exchanges have been observed in

conjunction with the reconstruction propensity of Pt(111) and Au(111).⁸⁻¹² In particular, on Au(111), preferential islands nucleation of Fe, Co, or Ni and burrowing of self-organized Co clusters have been tentatively rationalized by invoking mass transport through site exchanges.¹¹⁻¹⁴ These pieces of evidence motivate a thorough search of diffusion mechanism on relevant fcc(111) TM substrate. In addition, a preliminary study carried out on the reconstructed Au(111) substrate by classical molecular dynamics revealed that Co cluster formation and exchanges are intimately related.¹⁵ This calls for a precise understanding of the elementary steps underlying the replacement sequences on fcc(111) TM surfaces, with a special concern for adsorption on Pt(111) and Au(111).

In this paper we unravel the mechanism of exchange diffusion for the heteroatomic systems Co/Au(111) and Co/Pt(111) and we evaluate the corresponding diffusion barriers. To this end, we found it useful to consider also four cases of homoatomic exchange, namely, Au/Au(111), Pt/Pt(111), Ni/Ni(111), and Cu/Cu(111). Exchange diffusion paths are obtained by combining classical molecular

TABLE I. Parameters of the interatomic potentials. More details on the analytical expression and the fitting procedure can be found in Ref. 25.

System	A (eV)	p	ξ (eV)	q	r_0 (Å)	Reference
Au/Au(111)	0.210	10.35	1.818	4.178	2.880	This work
Cu/Cu(111)	0.080	11.17	1.260	2.441	2.556	This work
Ni/Ni(111)	0.035	18.01	1.323	1.685	2.531	This work
Pt/Pt(111)	0.242	11.14	2.506	3.680	2.770	Reference 25
Co/Pt(111)	0.245	9.97	2.385	3.320	2.635	Reference 25
Co/Au(111)	0.141	10.66	1.614	3.113	2.690	Reference 26

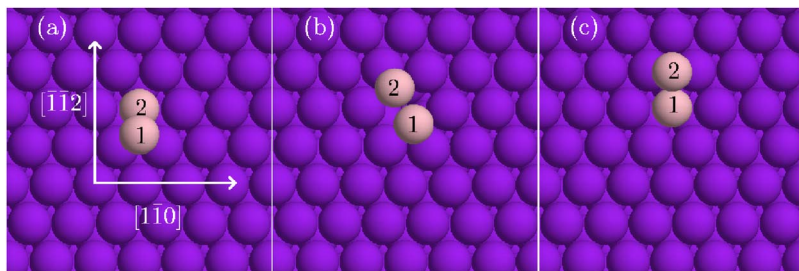


FIG. 1. (Color online) Concerted exchange mechanism. (a) Initial situation, (b) transient dimer at the saddle point, (c) final situation.

dynamics with a friction force (hereafter called quenched molecular dynamics), effective potentials and the nudged elastic band (NEB) method.^{16–18} Both short (nearest-neighbors) and medium range exchanges are considered for Co/Au(111), Co/Pt(111), Au/Au(111), and Pt/Pt(111). In addition, two further homogeneous systems [Ni/Ni(111) and Cu/Cu(111)] complete our study of the short range process. Focusing on this specific mechanism, we show that a sufficiently high tensile surface stress can drive the transition from a concerted motion with formation of a transient dimer to a two-step movement. This consists of insertion of the adsorbed atom followed by the ejection of the substrate atom. The concerted motion yields the most favorable energy path for homoatomic exchange. On the other hand, when a heteroatom is adsorbed, a two-step process can occur provided the insertion results in a release of the tensile stress. This mechanism is also observed when the tensile stress is sufficiently increased by an enlarged in-plane lattice constant.

Medium range exchanges are those involving the original adatom and at least one surface atom not nearest neighbor. In three cases [Pt/Pt(111), Au/Au(111), Co/Pt(111)], a concerted movement featuring the adatom and two surface atoms provides an alternative to the short range counterpart. A sequence made of two correlated short range processes is found for Co/Au(111). Medium range exchanges are more favorable on Au(111) substrates, as a result of a local rearrangement that optimizes tensile stress and equilibrium interatomic distances.

This paper is organized as follows. Our calculations are described in Sec. II. Section III is devoted to short range exchanges, while medium range exchanges are described in Sec. IV. Conclusive remarks are collected in Sec. V.

II. DETAILS OF CALCULATIONS

Exchange barriers and mechanisms are obtained via the nudged elastic band (NEB) method,^{16–19} that proved efficient to find the minimum energy path between given pairs of transition initial and final states.^{20,21} A set of 36 images has been taken with a spring interaction of $1 \text{ eV}/\text{\AA}^2$ between adjacent images. The optimization of the band, involving the minimization of the force acting on the images, is performed by means of a quench molecular dynamics procedure.²² The interatomic interactions are described in the framework of the second moment approximation of the tight binding theory. This framework has an extensive record of reliability for the modeling of TM surface properties, as detailed and

demonstrated in previous works.^{13,15,23,24} The parameters of the interatomic potential have been fitted to experimental data such as the cohesive energy, the elastic constants, and the bulk modulus (homoatomic interactions) and mixing energy (heteroatomic interactions). They are given in Table I. Our computational slabs are $12 \times 12 \times 12$ crystals cut perpendicular to the [111] direction with periodic bounding conditions along the $[\bar{1}10]$ and $[\bar{1}\bar{1}2]$ directions. For each combination of adatom and substrate, one adatom is placed onto the (111) surface. Throughout our calculations unreconstructed substrates only are considered. This choice does not imply any loss of generality due to predominance, in the reconstructed counterpart, of interatomic distances having values very close to the unreconstructed case.

III. SHORT RANGE MECHANISM OF EXCHANGE

Our four cases of homoatomic exchange have in common the formation of a transient dimer, found at the saddle point of the minimum energy path (see Fig. 1). This mechanism is analogous to the concerted motion observed on fcc(100) TM substrates, with the adatom and the surface atom entering and leaving the substrate, respectively, in a simultaneous move.^{3,4,6} The corresponding diffusion barriers are given in Table II, together with the value for hopping. We observe that the lower value for exchange found for Au(111) is associated with the substrate of highest tensile stress, due to the largest surface mismatch.²⁷ This finding is consistent with the rationale developed by Yu and Scheffler for fcc (100) TM surfaces and based on the crucial role of tensile surface stress for exchange diffusion.⁷ It is worthwhile to examine the variation of the site energy at the saddle point with respect to the initial configuration (adatom at the adsorption site). Values for the exchange barriers can be decomposed in three contributions. The largest one amounts to $\sim 60\%$ and can be ascribed to the lift of the surface atom, changing coordination from nine to three nearest neighbors. The second contri-

TABLE II. Hopping and exchange barriers for diffusion in the four cases of homogeneous systems considered in this work.

System	Hopping (eV)	Exchange (eV)
Au/Au(111)	0.112	0.878
Cu/Cu(111)	0.043	1.455
Ni/Ni(111)	0.049	2.050
Pt/Pt(111)	0.176	2.105

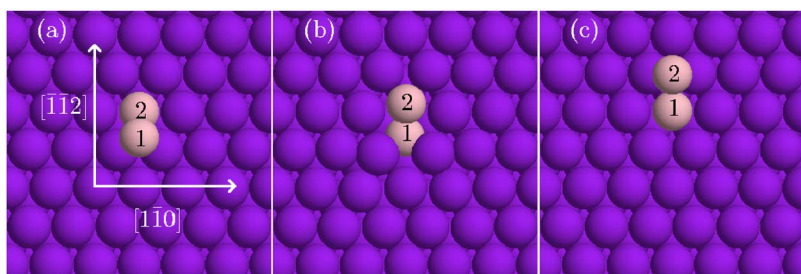


FIG. 2. (Color online) Two-step exchange mechanism. (a) Initial situation, (b) adatom insertion at the saddle point, (c) final situation.

bution (close to 40%) is due to the rearrangement of the surface atoms in the neighborhood of the transient dimer. The third and smallest is related to the adatom, weakly affected by the dimer formation since its coordination does not change significantly during the exchange. Lowest values for the ratios between the single contributions and the cohesive energies are again found for Au(111). This confirms the lowest energy cost for exchange on this substrate.

In view of these indications, the origin of heterogeneous exchange diffusion on fcc(111) TM substrates can be readily identified. For Co/Pt(111) we calculate an exchange barrier $E_{ex}^{Co/Pt(111)} = 2.065$ eV, very close to the value $E_{ex}^{Pt/Pt(111)} = 2.105$ eV. On the other hand, a reduction is found for Co/Au(111), $E_{ex}^{Co/Au(111)} = 0.536$ eV with respect to $E_{ex}^{Au/Au(111)} = 0.878$ eV. The underlying mechanisms are different for the two situations. In the case of Co/Pt(111) the exchange proceeds through the formation of a transient dimer, as for Pt/Pt(111). A two-step process characterizes the exchange for Co/Au(111). This consists of Co insertion followed by Au ejection (Fig. 2). We stress that ejection of Au takes place only after the completion of the Co insertion and not in concomitance with the movement of the latter. Such a difference is exemplified in Fig. 3, which shows the positions of the atoms involved in the exchange along the [111] direction. While Co and Pt move in a concerted fashion throughout the exchange [case of Co/Pt(111)], displacements are separated in time for Co and Au [case of

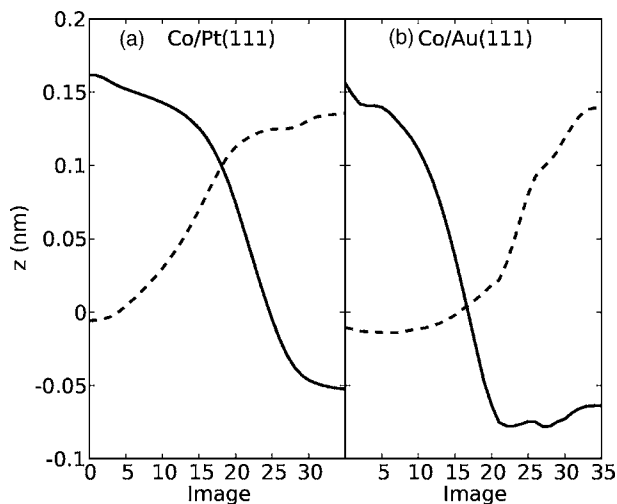


FIG. 3. Atomic position (along the [111] direction) of the atoms involved in the exchange mechanism in the case of Co/Au(111) and Co/Pt(111). Dashed line: substrate atom, full line: original adatom.

Co/Au(111)], with the Au atom beginning to move after complete insertion of Co. The reasons underlying the preference for a two-step process rest on the high tensile surface stress of Au(111) caused by a large surface mismatch. Unlike the insertion of an Au atom, insertion of the smaller Co atom does release this stress, due to local rearrangement caused by the shorter Co-Au distances. The question arises on whether this rationale has a general applicability to other adsorbate/substrate combinations. Our calculations on Co/Pt(111) with expanded Pt(111) substrates prove that this is indeed the case [Fig. 4(a)]. Within the range (0–0.25 %) of expansion, the exchange mechanism proceeds through the

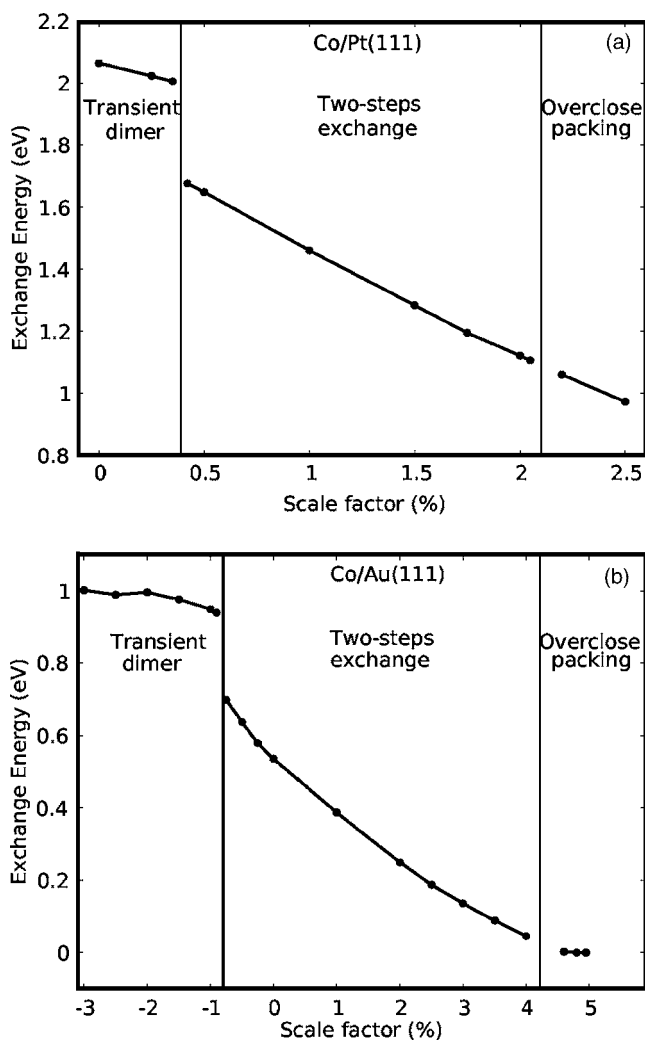


FIG. 4. Exchange barriers as a function of the in-plane expansion factor for the case of Co/Pt(111) (a) and Co/Au(111) (b).

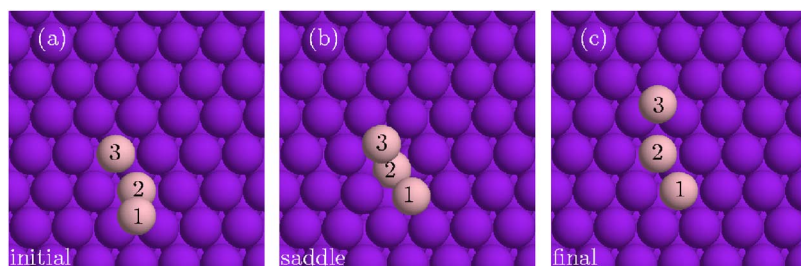


FIG. 5. (Color online) Medium range exchange mechanism. (a) initial situation, (b) saddle point configuration, (c) final situation.

formation of a transient dimer. For the interval (0.35–2.05 %), the two-step exchange mechanism is observed. When the expansion is larger than 2.2%, the relaxation of the final situation, namely, a Pt atom deposited on the Pt(111) surface with a Co atom inside, leads to the Pt adatom insertion into the surface without any Co or Pt ejection. This corresponds to an overclosed packing of the surface and to the disappearance of any saddle point in the profile of the energy barrier vs the reaction coordinate. Conversely, a compression of the Au(111) substrate drives the transition from the two-step exchange to the transient dimer formation [Fig. 4(b)]. The overclosed packing of the surface is observed for an expansion of between 4.0 and 4.4 %. The high energetic cost related to the lift of the surface atom is reflected by the sudden rise in the exchange energy values, up to 1 eV. It appears that removal of the tensile surface stress offsets the relaxation effects due to the Co atom, causing the recovery of concerted motion as for homoatomic exchange.

We attributed a finite exchange energy with the overclosed packing in Co/Pt(111) [Fig. 4(a)]. No energetic cost is associated with the analogous conditions in Co/Au(111) [Fig. 4(b)]. This choice is simply related to the disappearance of the saddle point between the initial and the final states E_i and E_f . For Co/Pt(111) E_f is found at higher energy and decreases with increasing expansion, while $E_f < E_i$ in Co/Au(111). We have expressed this difference in the energetics by taking $E_f - E_i$ and 0 as values for the exchange barrier in Co/Pt(111) and Co/Au(111), respectively.

IV. MEDIUM RANGE MECHANISM OF EXCHANGE

Molecular dynamics studies on the diffusion of Co adatoms and clusters on Au(111) suggest that site replacements involve Au atoms that are next-nearest neighbors of the Co adatom migrating into the substrate.^{13,15} This diffusion mechanism can be termed a “medium range” one. It implies a correlated set of displacements inducing a propagative movement in the uppermost surface layer. Such a process is in analogy with the high temperature behavior of Cu/Cu(100).^{28,29} We analyze the medium range exchange (MRE) diffusion mechanism for two cases of homogeneous diffusion [Pt/Pt(111), Au/Au(111)] and two cases of heterogeneous diffusion [Co/Pt(111), Co/Au(111)], closely related to current experimental interest.^{9,14} The Au atoms involved are next-nearest neighbors of the Co adatom. Figure 5 is representative of the MRE mechanism for Pt/Pt(111), Au/Au(111), and Co/Pt(111). Our calculations show a concerted process featuring, in a simultaneous fashion, the de-

scendent of the adatom [hereafter termed atom (1)] and the ejection of a surface atom [atom (3)]. The difference from the short range concerted exchange lies in the sliding of a second surface atom [atom (2)] located between atom (1) and atom (3) [see Fig. 6(a)]. This mechanism is very similar to the Knight mechanism observed in the case of (100) surfaces.³⁰ In Fig. 7, we compare the energetics of direct and medium-range exchanges along the reaction coordinate defined by the NEB procedure. For Pt/Pt(111), a vanishing difference is observed between short range ($E_{\text{Pt/Pt(111)}}^{\text{SR}} = 2.105$ eV) and medium range exchange ($E_{\text{Pt/Pt(111)}}^{\text{MR}} = 2.111$ eV). Medium range is more favorable than short range for Au/Au(111) ($E_{\text{Au/Au(111)}}^{\text{MR}} = 0.778$ eV, $E_{\text{Au/Au(111)}}^{\text{SR}} = 0.878$ eV). However, the opposite holds true for Co/Pt(111) ($E_{\text{Co/Pt(111)}}^{\text{MR}} = 2.248$ eV, $E_{\text{Co/Pt(111)}}^{\text{SR}} = 2.065$ eV).

To rationalize these findings, we describe the concerted exchange mechanism as the movement of a cluster [the trimer made of atoms (1), (2), and (3) as defined above] in the substrate environment. We decompose the exchange barrier E_{exch} in two contributions, the first due to the cluster E_{cl} and the second due to the substrate E_{sub} , this latter accounting for all remaining atoms. This decomposition highlights the

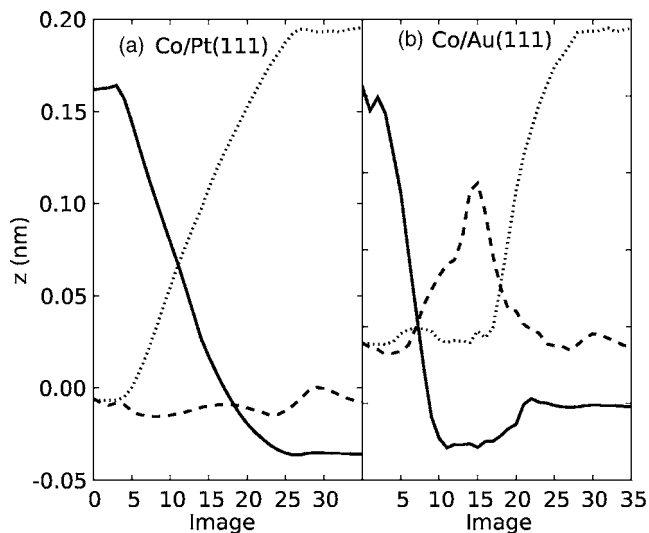


FIG. 6. Atomic position (along the [111] direction) of the atoms involved in the medium range exchange mechanism in the case of Co/Pt(111) and Co/Au(111). Case of Co/Pt(111), dotted line: substrate atom moving upward, dashed line: surface atom sliding in the surface plane, full line: original adatom. Case of Co/Au(111), full line: original adatom, dashed line: surface atom ejected during the first short range exchange process, dotted line: surface atom participating in a concerted exchange with the former surface atom.

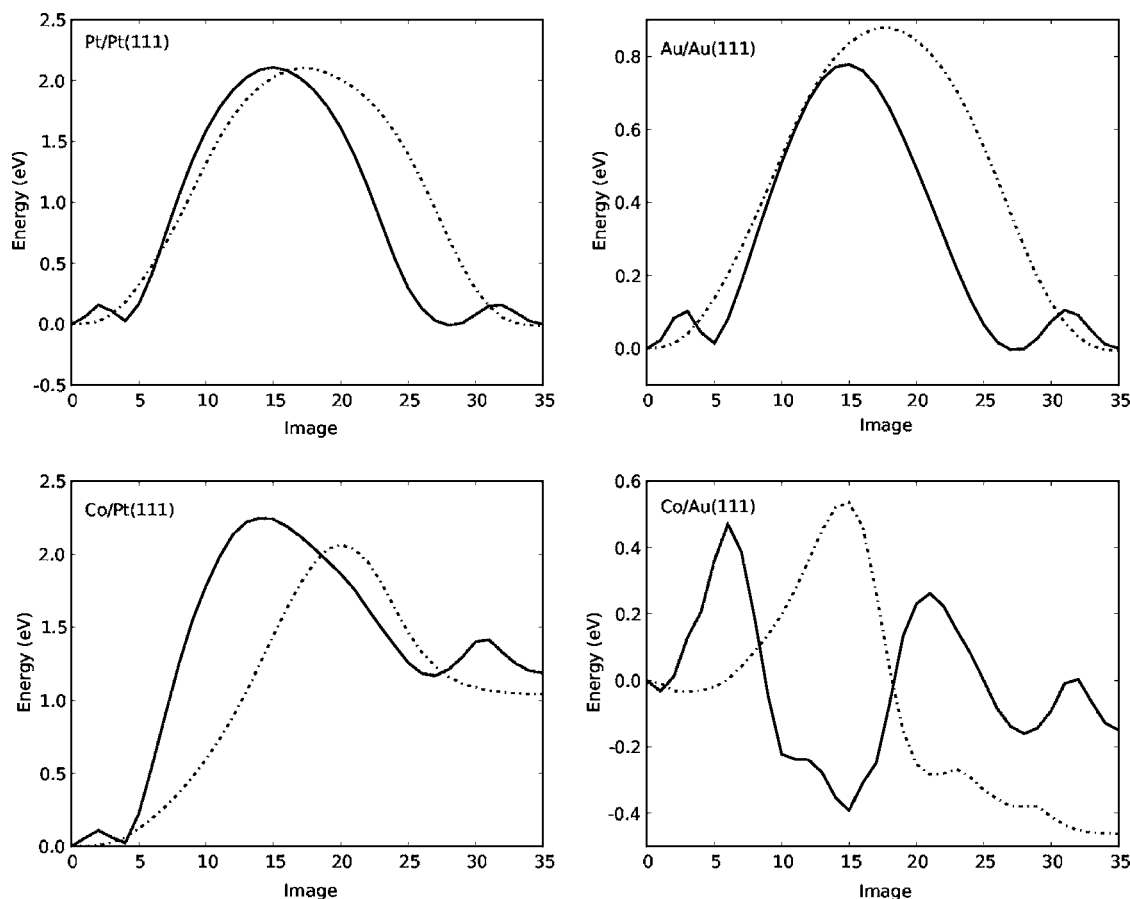


FIG. 7. Energy profiles along the reaction coordinate for the short range (dash-dotted line) and the medium range (full line) exchange mechanisms.

atomic-scale origins of exchange in terms of a partition between cluster and substrate effects. The variations in the barrier's values ΔE_{exch} from the short to the medium range exchange mechanism are given in Table III together with the different contributions ΔE_{cl} and ΔE_{sub} . The MRE mechanism lowers E_{cl} and increases E_{sub} in all cases with respect to the short range one. Concerning E_{sub} , a smaller increase is observed for Au/Au(111) than for Co/Pt(111) and Pt/Pt(111). Such a difference stems from the tensile stress inherent in the Au(111) substrate, more inclined to insertion and, as a consequence, less affected than the Pt(111) substrate by the compressive effect of adatom inclusion. As expected for systems sharing the same substrate, the values of ΔE_{sub} for Co/Pt(111) and Pt/Pt(111) are very close.

Also in Table III one notices that ΔE_{cl} is negative for the three cases, indicating a lowering of the cluster contribution

TABLE III. Variation ΔE_{exch} in the exchange barriers E_{exch} from the short range to the medium range mechanism. The different contributions due to the three atoms involved in the exchange (ΔE_{cl} , see text) and to the substrate atoms (ΔE_{sub}) are also given.

	Au/Au(111)	Pt/Pt(111)	Co/Pt(111)
ΔE_{exch} (eV)	-0.100	+0.005	+0.183
ΔE_{cl} (eV)	-0.221	-0.224	-0.021
ΔE_{sub} (eV)	+0.121	+0.229	+0.204

to the exchange barrier. The decrease of E_{cl} for the MRE mechanism has two main origins related to the role played by atom (2) and to coordination effects. The movement of atom (2) facilitates the insertion of atom (1) by increasing their interatomic distance. This allows us to minimize the loss of coordination of the ejected atom [atom (3)] by decreasing its interatomic distance with atom (2). The strength of this effect favors MRE over short range by -0.1 eV for Au/Au(111), ($\Delta E_{\text{cl}} = -0.221$ eV, $\Delta E_{\text{sub}} = 0.121$ eV). In Pt/Pt(111), substrate and cluster contributions are essentially equal in intensity but have opposite signs ($\Delta E_{\text{cl}} = -0.224$ eV, $\Delta E_{\text{sub}} = 0.229$ eV). For Co/Pt(111), we found that ΔE_{cl} is as small as -0.021 eV, favoring the short range exchange ($\Delta E_{\text{exch}} = 0.183$ eV). This inversion of tendency compared to the case of Pt/Pt(111) can be understood in terms of the shorter equilibrium Co-Pt distance. Such smaller value undermines the whole insertion-ejection sequence, by hampering not only the increase of the distance between atoms (1) and (2) but also the decrease of the distance between atoms (2) and (3).

We now turn to the details of the MRE mechanism for Co/Au(111). This consists of a sequence of two short range exchange processes [Fig. 6(b)]. First, we observe a two-step mechanism inducing the ejection of a Au surface atom and the incorporation of the Co adatom. Then, a concerted exchange takes place, involving the former Au surface atom, acting as an adatom, and a second Au atom. The barrier

(0.470 eV) to be overcome to complete the first step of the sequence is smaller than the one for a short range two-step mechanism (0.536 eV) (see Fig. 7). Indeed, although the two-step and the concerted exchange mechanisms occur in sequence, the latter begins before full completion of the former, causing an increase of the tensile stress and a reduction of the exchange barrier.

V. CONCLUSIONS

Exchange mechanisms on fcc (111) transition metal substrates have been found to play a crucial role in connection with preferential nucleation and surface reconstruction.^{8–14} In this paper we have resorted to atomic-scale simulation tools to highlight short range and medium range diffusion processes involving incorporation of adatoms and site exchange with surface atoms. In the case of exchange between the adatom and a nearest-neighbor surface atom (short range exchange), a concerted movement takes place in the homogeneous case, through the formation of a transient dimer. By analyzing in detail the case of two heterogeneous systems [Co/Pt(111) and Co/Au(111)], we have shown that a competition between the concerted motion and a two-step process (insertion well distinct in time from ejection) is driven by the surface tensile stress. Our results show that the larger the tensile stress, the higher is the tendency toward a two-

step process, more effective to release the stress by optimizing the surface configuration. In this respect, the Au(111) substrate, intrinsically characterized by a high tensile stress, provides a prototype example of a two-step short range exchange in the case of Co/Au(111). Medium range exchanges consist of the ejection of a surface atom in a location other than a nearest-neighbor position of the original adatom. This latter is incorporated in the substrate. The combined movement of the original adatoms and two surface atoms leads to a concerted motion for Pt/Pt(111), Co/Pt(111), and Au/Au(111). A sequence of two short range exchanges is found for Co/Au(111). Medium range exchanges lower the diffusion barriers on Au(111) substrates. In this context, it has to be recognized that the nudged elastic band method proved to be a powerful tool for the investigation of optimal exchange trajectories representative of low temperature behavior. Molecular dynamics calculations are in progress to complete our understanding of diffusion mechanism on TM fcc (111) surfaces via simulations at finite temperatures.

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