Physical origin of exchange diffusion on fcc(100) metal surfaces

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For the (100) surfaces of Pt and Ir, experiments revealed that self-diffusion proceeds by atomic exchange rather than hopping. Using density-functional theory we find that the physical origin of this phenomenon is different from that for Al, where it had been explained as being activated by the formation of directional bonds at the transition state. We predict that exchange diffusion should also occur on Au(100) and show that the tensile surface stress plays a crucial role for the exchange diffusion. This explains why the exchange process is favorable for the late 5d, but not for 3d and 4d fcc(100) metal surfaces.

Diffusion of adatoms on metal surfaces is of vital importance for many processes, such as, for example, adsorption, desorption, surface chemical reactions, and crystal growth. Surface diffusion may proceed by hopping of an adatom between minima of the potential energy surface, i.e., between stable or metastable adsorption sites. Or, alternatively, the adatom can replace a surface atom and the replaced atom then assumes an adsorption site. This is diffusion by atomic exchange and was first discussed by Bassett and Webber and Wrigley and Ehrlich for fcc (110) surfaces which consist of close-packed rows of atoms separated by surface channels. Even for the crystal bulk, namely Si, exchange diffusion has been discussed, actuated by the desire to keep the number of cut bonds low along the diffusion pathway.

On less corrugated fcc(100) surfaces diffusion by atomic exchange (see Fig. 1) was observed and analyzed only for Pt (Ref. 4) and Ir. An understanding of the underlying physical mechanism and why exchange diffusion occurs at Pt(100) and Ir(100) but apparently not at other fcc(100) transition-metal surfaces is still lacking.

For Al(100) Feibelman had performed a thorough theoretical analysis showing that also in this system self-diffusion proceeds by atomic exchange. The process is caused by the noticeable covalency of aluminum, which can form directional bonds (by sp hybridization) at certain atomic geometries. The transition state of exchange diffusion at Al(100) (see Fig. 1) may be described as a dimer, consisting of the adatom and the lift-up surface atom, located above a surface vacancy. Each atom of this dimer forms three chemical bonds, two with surface Al atoms and one with the other atom of the dimer. The covalent nature of Al thus lowers the energy of the geometry of Fig. 1(c). While this description is plausible for Al(100) it remains an open question why the 5d transition metals Pt and Ir behave similar to Al, but the other transition metals do not.

In this work we show and explain that the dependence of the energy barrier of surface diffusion on surface stress is qualitatively different for the hopping and exchange mechanisms: For the hopping diffusion the energy barrier increases with increasing tensile stress and for the exchange diffusion it decreases. Our results show that the formation of directional bonds does not play a role in the surface diffusion of Pt and Ir (100), but instead, the main origin of the exchange diffusion observed for these systems is the unusually high surface stress of the late 5d metals. These results can have interesting consequences for epitaxial growth of strained films: Strain affects the diffusion mechanism, and, e.g., for Ag(100), we predict that under tensile strain exchange diffusion will become relevant which will, for example, change the map of sites visited by a deposited adatom.

We performed density-functional theory (DFT) calculations for the self-diffusion on Au(100) and strained Ag(100). Norm-conserving, fully separable, scalar-relativistic pseudopotentials have been employed. Most calculations were done with the local-density approximation (LDA) of the exchange-correlation functional, but the main results were checked (and confirmed) using the generalized gradient approximation (GGA). The 5d states were treated as valence states, and the basis-set consists of plane waves up to a kinetic energy of 35 Ry (see also the discussion of Table I). For the gold crystal the calculated lattice constant is $a_0 = 4.07 \, \text{Å}$ and the bulk modulus is $B_0 = 1.90 \, \text{Mbar}$. These are the LDA results without taking zero-point vibrations into account. The corresponding GGA results are $a_0 = 4.19 \, \text{Å}$ and $B_0 = 1.32 \, \text{Mbar}$. The agreement with $T=0 \, \text{K}$ experimental data is good ($a_0^{\text{exp}} = 4.06 \, \text{Å}$, $B_0^{\text{exp}} = 1.72 \, \text{Mbar}$), as is that with other calculations.

To treat the adsorbate we use the supercell approach with a $(3 \times 3)$ surface unit cell, a four-atomic-layer-thick slab, and 8.6 Å of vacuum. The slab thickness is small but sufficient, because the adatom is adsorbed only on one side of the slab (see below). The k-space integration is replaced by a sum over a uniform mesh of 16 k points in the surface Brillouin zone.

FIG. 1. Top view of an adatom at (a) the fourfold hollow site, (b) the transition state for hopping diffusion (the twofold bridge site), and (c) the transition state for exchange diffusion. The gray scale of the atoms reflects their heights.
TABLE I. Convergence tests for the DFT-LDA diffusion barriers $E_d$ on the flat surfaces with respect to the cutoff energy $E_{\text{cut}}$, the number of atomic layers $N_l$, the number of relaxed layers $N_{r\text{relax}}$, and the number of $\mathbf{k}$ points in the SBZ $N_k$. A $(3 \times 3)$ surface unit cell is used.

<table>
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<tr>
<th>Calc. #</th>
<th>$E_{\text{cut}}$ (Ry)</th>
<th>$N_l$</th>
<th>$N_{r\text{relax}}$</th>
<th>$N_k$</th>
<th>$E_d$ (eV)</th>
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</thead>
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<td>2</td>
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</tr>
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<td>35</td>
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</table>

The result that self-diffusion on Au(100) proceeds by atomic exchange is in sharp contrast to the behavior of silver (100), which is isoelectronic and typically chemically rather similar to gold. For Ag(100) it is well established that surface diffusion at room temperature proceeds by hopping.\(^{18}\)
The above analysis of the exchange-diffusion transition state geometry emphasized the role of the tensile surface stress. We remind that the surface stress tensor is given by \( \sigma_{ij} = \gamma \delta_{ij} + \partial \gamma / \partial \epsilon_{ij} \) with \( \epsilon_{ij} \) the strain tensor and \( \gamma \) the surface energy. Indeed, the excess surface stress \( \tau = \partial \gamma / \partial \epsilon_{ij} \) of the late 5d metals is significantly higher than that at its 4d and 3d isoelectronic elements [e.g., \( \tau_{\text{Au(100)}} = 0.20 \text{ eV/Å}^2 \) compared to \( \gamma_{\text{Au(100)}} = 0.09 \text{ eV/Å}^2 \) and \( \tau_{\text{Ag(100)}} = 0.11 \text{ eV/Å}^2 \) compared to \( \gamma_{\text{Ag(100)}} = 0.07 \text{ eV/Å}^2 \) (Ref. 13)]. The difference has been traced back to relativistic effects, which play a noticeable role for the heavier 5d metals: The relativistic effects give rise to a contraction and energy lowering of s states, and as a consequence, the d band moves closer to a Fermi energy.\(^{13}\) This is also the reason why gold has a more reddish-yellow color than silver. Indeed, a relativistic treatment is most important in order to attain a good description of structural and elastic properties of 5d metals, while it is not important for the 4d metals. As a result of these relativistic effects, i.e., the increased bonding by d states, the tensile surface stress at 5d metals is considerably higher than that of the 4d metals. Thus, while the significant tensile surface stress of Au(100) pulls the dimer of the exchange transition state “into” the surface, lowers the energy of the transition state, and enables exchange diffusion, the surface stress at Ag(100) is too weak to have a significant effect.

The above analysis suggests an interesting prospect, which could be used to prove the above explanation. By heteroepitaxial growth it is possible to grow films with an enlarged lateral lattice constant. An enlarged lateral lattice constant implies an increase in the tensile surface stress. Thus, with respect to the stress, a strained silver film becomes more goldlike. We therefore analyzed the two diffusion mechanisms cross. This result strongly supports that the tensile surface stress plays the key role for the exchange diffusion on fcc(100) surfaces and predicts that for pseudomorphic Ag films (with increased parallel lattice constant) self-diffusion should get more and more influenced by the exchange mechanism.

Finally, we note also that for Al(100) the excess surface stress is high (\( \tau_{\text{Al(100)}} = 0.10 \text{ eV/Å}^2 \)) compared to \( \gamma_{\text{Al(100)}} = 0.07 \text{ eV/Å}^2 \), although the ratio \( \tau / \gamma \) is similar to that of Ag(100). Concerning the geometry of the exchange-diffusion transition state of Al/Al(100) we find that it is similar to that of Au/Au(100): The dimer is 0.90 Å above the surface.
surface layer, i.e., 55% closer to the center of the top layer than the interlayer distance in the bulk, which implies a closer packing and a local stress relief. We conclude also that for Al(100) the tensile surface stress plays an important role, but the covalent nature of Al (formation of sp hybrids at the transition state) is important as well and enables an even more efficient stress relief than that occurring at transition metal surfaces.

In summary, we presented density-functional theory calculations for atomic diffusion processes on Au(100), strained Ag(100), and Al(100). For Au(100) the surface diffusion is predicted to proceed by atomic exchange. In all these cases we find that the exchange diffusion is actuated by the high surface stress and its local relief at the transition state geometry noted in Fig. 1(c). This explains why Al(100) as well as the late 5d metals exhibit self-diffusion by atomic exchange, but the other fcc (100) surfaces, as these have much lower surfaces stresses, do not. We also note that the desire of local stress relief at highly stressed surfaces will also affect other surface properties, because locally stress will be modified by any surface perturbation, such as, for example, a step.

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14 The clean surface and the free atom are calculated with the same basis as the adsorbate system.
19 The Ag calculations are done with a (3 x 3) surface cell, a slab thickness of three layers (allowing the top layer and the adatom to relax), a basis set with E\textsubscript{cut} = 40 Ry, and nine k points in the SBZ.