RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 57, NUMBER 8 15 FEBRUARY 1998-II

First-principles diffusion-barrier calculation for atomic oxygen on Pt(111)

Alexander Bogicevic, Johan Strömquist, and Bengt I. Lundqvist
Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden

(Received 10 November 1997)

An inconsistency is pointed out in adsorption energy values for O diffusion on Pt(111) in three recent studies: (A) the scanning tunneling microscope (STM)-deduced value of 0.43 eV for the diffusion barrier [J. Wintterlin, R. Schuster, and G. Ertl, Phys. Rev. Lett. **77**, 123 (1996)]; (B) the calculated fcc-hcp adsorption-energy difference [P. J. Fiebelman, E. Stefanie, and M. Thomas, *ibid.* **77**, 2257 (1997)]; and (C) the STM-identified metastability of O in hcp sites [B. C. Stipe *et al.*, *ibid.* **78**, 4410 (1997)]. Using accurate first-principles density-functional methods we obtain full agreement with (B) and (C) and a diffusion barrier of 0.58 eV, consistent with a reinterpretation of the raw data in (A). We further report on oxygen-induced surface buckling. [S0163-1829(98)51908-X]

Oxygen adsorption on platinum surfaces is one of the central model systems of surface physics. Data of an impressive accuracy are accumulating, and a comprehensive and quantitative picture is developing. Here an inconsistency among some key data from three recent studies is pointed out, and first-principles electron-structure calculations are shown to be accurate enough to provide a resolution of it.

The O/Pt system plays a key role in numerous technologically important catalytic reactions, such as oxidation of CO and hydrocarbons in the catalytic treatment of automotive exhaust gases.[1–6] The mechanisms and detailed descriptions of these reactions have been shown to sometimes crucially depend on oxygen diffusion.[7] As an example, oxygen has been reported to be rate limiting in a later stage of H_2O formation from O and H via OH on Pt.[8] Furthermore, oxygen has been found to facilitate smooth layer-by-layer growth in Pt(111) homoepitaxy by acting as a surfactant floating on top of the growing Pt layers.[9] The diffusivity of oxygen is also important in discussions regarding the existence of ''hot'' atoms with transient mobility upon O_2 dissociation.[10–12]

One of the three studies (A) utilizes the scanning tunneling microscope (STM). Inspired by Harris and Kasemo,[11] Wintterlin and co-workers have confirmed previous claims of the existence of hot atoms in the course of O_2 dissociation on Pt(111).[10,12] They also have determined a value $E_d \simeq 0.43$ eV for the O/Pt(111) diffusion barrier that does not coincide with the one from earlier measurements by Lewis and Gomer.[13] In addition, they have deduced an anomalously low prefactor.[10]

The second study (B) is theoretical. Using a parallel linear combination of atomic orbitals implementation of the local-density approximation (LDA), Feibelman Stefanie, and Thomas[14] have calculated the oxygen binding energy difference between the hcp and fcc sites on the Pt(111) surface. They find it to be $\Delta E_{\mathrm{fcc/hcp}} \simeq 0.4$ eV (LDA). When diffusing on the Pt(111) surface, the oxygen atom must pass both hcp and fcc sites. This fact requires that E_d is larger than the difference in chemisorption energies of oxygen in the fcc and hcp sites (see Fig. 1).

The two observations might give the conclusion that the hcp site is extremely shallow with an activation barrier of only ~ 0.03 eV for the diffusion to an fcc site. Such a barrier would be of the order of the expected zero-point vibration energy (actually smaller than the calculated $\hbar\omega$, see below), rendering the hcp site totally unstable. However, this is very explicitly contradicted by the third study that we consider (C), involving recent STM measurements by Stipe and coworkers, primarily aimed at the possibility of STM-induced O_2 dissociation on Pt(111).[15] In this study oxygen atoms are identified in hcp sites as metastable at 50 K. Using simple transition-state theory, $\nu = \nu_0 e^{-E/k_B T}$, and estimating the ratio of STM scanning rate to attempt frequency to be 10^{-12}–10^{-13}, we deduce from this a lower bound for the hcp-fcc barrier of 0.12–0.13 eV. This strongly indicates that either the fcc-hcp diffusion-barrier value of paper A is too low or the calculated fcc-hcp energy-difference value of paper B is too large (see Fig. 1).

We have performed first-principles calculations based on density-functional theory to study the adsorption and diffusion of atomic oxygen on Pt(111). Thanks to recent progress in functionals, algorithms, and computers, this very useful tool[16–18] now makes it possible to calculate, e.g., six-dimensional potential-energy surfaces (PES) of such di-

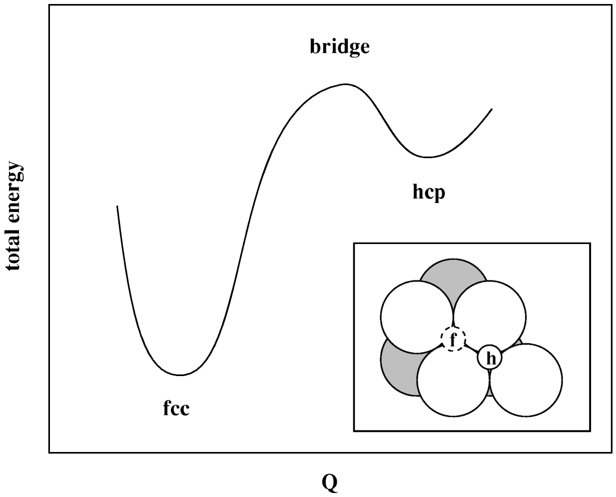

FIG. 1. Schematic illustration of the total energy for an oxygen atom diffusing on Pt(111). The *Q* coordinate indicates the diffusion path shown in the inset from the fcc site (f) to the hcp site (h).

TABLE I. Calculated adsorption energetics of atomic oxygen on Pt(111). The static diffusion barrier (bri*) is calculated when the surface is relaxed according to fcc adsorption but the oxygen atom is placed in the bridge site. The number of k-points is denoted n_{kp} and the number of Pt(111) layers n_l. The adsorption energies E_{LDA} and E_{GGA} are given in reference to fcc occupation (for chemisorption energies, see the main text). All values are stated in eV.

n_{kp}	n_l	site	E_{LDA}	E_{GGA}	Φ	$\Delta\Phi$
6	4	fcc	0.00	0.00	6.16	−0.03
	4	hcp	0.51	0.48	6.13	−0.09
	4	bri	0.68	0.59	6.16	−0.38
18	4	fcc	0.00	0.00	6.01	−0.12
	4	hcp	0.44	0.44	6.03	−0.08
	4	bri	0.70	0.60	6.03	−0.49
	4	bri*	0.80	0.69	6.04	−0.45
54	4	fcc	0.00	0.00	6.04	−0.11
	4	hcp	0.45	0.45	6.04	−0.09
	4	bri	0.68	0.58	6.05	−0.47
18	6	fcc	0.00	0.00	6.02	−0.12
	6	hcp	0.45	0.45	6.02	−0.08
	6	bri	0.66	0.56	6.03	−0.47

atomic molecules as CO or O_2 interacting with a transition metal surface.[19–21] Values for adsorption energies and diffusion barriers for this system are presented and compared to existing data. The ability of the calculations to reproduce the experimental parameters of surface buckling, as well as work functions, vibrational frequencies, and other quantities, constitutes a reference frame for the precision in the calculated results.

We use density-functional theory (DFT),[22,23] applying both the local-density (LDA),[24] and the generalized-gradient approximations (GGA),[25] for the exchange-correlation functional. The LDA calculations are performed self-consistently, whereas the semilocal exchange-correlation corrections of the GGA are calculated from LDA densities, so-called post-GGA. Extensive self-consistent calculations within the GGA have shown this to be an excellent approximation due to the variational property of the total energy functional.[25,26] The *ab initio* pseudopotential is generated within the LDA. As the adsorption properties of the surface are not expected to depend critically on the Pt core levels, which are the ones most affected by nonlocal exchange-correlation effects, we use this potential in the GGA study, as well. The use of LDA ionic coordinates in GGA calculations is also known to be a good approximation.[26] The Kohn-Sham equations are solved by alternating conjugate gradient minimizations and subspace rotations. We also use the density mix scheme of Kresse.[27] The occupation numbers are updated using a recently developed technique that is based on a minimization of the free energy functional.[28] To stabilize the k-point summation, the electronic temperature is set to 0.1 eV and the energy is extrapolated to zero temperature in a standard manner.[29]

TABLE II. Calculated binding parameters and surface relaxation for O on Pt(111). The parameter d_{01} is the distance between the oxygen atom and the center of mass (CM) of the topmost Pt(111) layer. Similarly, d_{12} is the distance between the CM of the first and second Pt layer, and so on. The four parameters b_1, b_2, c_1, and c_2 indicate the amount of surface buckling, while the six Δ and α values (α_{1b}, α_{2b} are always zero) denote the in-plane total lateral displacements and rotations of the radially expanding Pt atoms as seen from the oxygen atom (see Fig. 2). Since the relaxation parameters are very robust with respect to k-point sampling and system size, we choose to save some space by presenting them as averages (using the $n_l=4$, $n_{\mathrm{kp}}=18$, 54 and $n_l=6$, $n_{\mathrm{kp}}=18$ results). All distances are given in Å.

	fcc (calc.)	fcc (expt.[a])	hcp	bri
d_{01}	1.20	1.18±0.02	1.24	1.43
d_{12}	2.29	2.29±0.03	2.31	2.29
d_{23}	2.26	2.26±0.05	2.26	2.26
b_1	−0.13	−0.07±0.03	0.00	−0.14
c_1	0.00	0.00	−0.12	−0.09
b_2	0.11	0.09±0.10	0.00	0.09
c_2	0.00	0.00	−0.01	0.00
Δ_{1c}	0.06	0.07±0.1	0.00	0.09
Δ_{1a}	0.06	0.07±0.1	0.04	0.13
Δ_{1b}	0	0	0.04	0.10
Δ_{2c}	0.01	0.09±0.1	0.00	0.01
Δ_{2a}	0.01	0.09±0.1	0.01	0.02
Δ_{2b}	0	0	0.01	0.01
α_{1c}	0°	2.3±5°	0°	0°
α_{1a}	0°	2.3±5°	0.0°	4.9°
α_{2c}	0°	3.0±5°	0°	0°
α_{2a}	0°	3.0±5°	0.3°	0.3°

[a]Reference [30].

The supercell is made up of 4 Pt(111) layers and 4 layers of vacuum (>9 Å). The two topmost layers are fully relaxed using a damped molecular dynamics method, whereas the two bottom layers are kept fixed at fcc bulk positions. The oxygen atom is adsorbed so that the repeated cell forms the experimentally established[30] $p(2\times2)$ ordered overlayer on one side of the slab[31] (4 Pt atoms per layer). The oxygen atom and the Pt atoms are described by the soft pseudopotentials of Troullier and Martins.[32] The same pseudopotentials have previously been successfully used in determining the structure of κ-Al_2O_3.[33] The wave functions are expanded in plane waves with a kinetic energy cutoff of 650 eV, the high value required by oxygen.[33] The lattice constant for Pt is within LDA found to be 3.93 Å (650 eV cutoff), which is (unexpectedly according to traditional LDA wisdom) slightly larger than the measured value 3.91 Å. The surface Brillouin zone is sampled at 6/18/54 special k-points.[34] Calculations with two additional layers of Pt(111) (two layers kept fixed and four allowed to relax) induce a change of only about 10 meV to the diffusion barrier. The results are summarized in Tables I and II. The work function is denoted Φ, and the adsorbate-induced work function change $\Delta\Phi$.[31]

Results on the surface relaxation of Pt(111) when oxygen atoms are adsorbed in a (2×2) overlayer in fcc sites have been reported by Starke *et al.*.[30] The surface buckling and other relaxation effects are in detail reproduced by our calculations. We also find a similar buckling behavior for oxygen adsorbed in hcp and bridge sites. The results are illustrated in Fig. 2 and summarized in Table II. The height of the

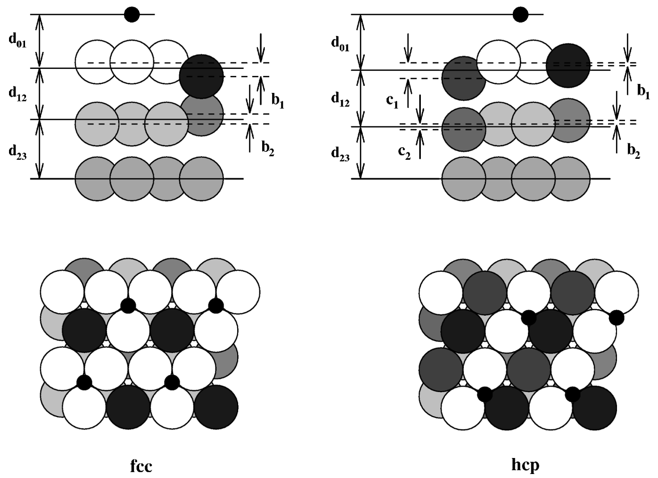

FIG. 2. Schematic display of the surface relaxation for the $p(2\times2)$-O/Pt(111) system with oxygen adsorbed in fcc and hcp sites. The buckling seen in the side views is somewhat exaggerated for illustration purposes. The distance between the oxygen atom and the first Pt layer (d_{01}) and the interlayer spacings (d_{12} and d_{23}) are measured between center-of-mass planes (solid lines). The buckling amplitudes are given by b_1, b_2, c_1, and c_2 (dashed lines). The top view illustrates the adsorption geometry. The three Pt atoms just underneath the oxygen atom expand radially outwards, with a tendency towards in-plane rotation in the hcp site. This effect is amplified when the oxygen is in the bridge site (not shown), and a relaxation intermediate between the ones seen for fcc and hcp adsorption is found. Table II summarizes the relaxation effects for all three cases. See also Fig. 2 in Ref. 30 for comparison.

oxygen atom above the surface has been measured experimentally, yielding values of 0.85±0.06 Å,[35] and 1.20 Å.[30] We get 1.20 Å, in agreement with the most recent measurement.

In order to get a reasonable value for the chemisorption energy, E_{chem}, it is necessary to perform a spin-polarized calculation of the oxygen atom alone in the same cell using 18 k-point sampling and a similar calculation of the clean Pt slab. The binding parameters of oxygen within the LDA and GGA approximations are presented in Table II. The calculated $E_{\mathrm{chem}}^{\mathrm{calc}}=5.18$ (LDA) and 4.13 eV (GGA) correlates well with the latest experimentally obtained values $E_{\mathrm{chem}}^{\mathrm{expt}}=4.8$ eV (low coverage), 4.5 eV for a coverage of 0.25 ML, which is the coverage of our calculations, and 3.8 eV (high coverage) by Parker, Bartram, and Koel.[36] Parker, Bartram, and Koel have also measured the work-function change $\Delta\Phi=0.2$ eV,[36] of the same magnitude as the calculated $\Delta\Phi=0.1$ eV. The work function for clean Pt(111) is calculated to be $\Phi=6.0$ eV, in good agreement with the experimental value of 5.8 eV.[37]

The barrier for oxygen diffusion on Pt(111) was first measured by Lewis and Gomer[13] some thirty years ago, using field emission microscopy, and reporting an activation energy of 1.2–1.5 eV. The Wintterlin, Schuster, and Ertl study of oxygen diffusion with STM was performed at a surface temperature of around 200 K. They have deduced an activation-barrier value of $E_d\simeq0.43\pm0.04$ eV, and a preexponential factor of $D_0\simeq10^{-6.3\pm1.0}$ cm^2/s.[10] The barrier difference between these two experiments is attributed to the incompatibility between random walk and macroscopic diffusion measurements.[10]

Our results for the diffusion-path energetics are plotted in Fig. 1. The calculations yield $\Delta E_{\mathrm{fcc/hcp}}=0.45$ eV within both LDA and GGA, in good agreement with the calculations by Feibelman, Stefanie, and Thomas.[14] The diffusion barrier from the fcc to hcp site is similarly $E_d=0.58$ (0.68) eV using GGA (LDA),[38] which is a reasonable value in perspective of the discussion above. The hcp site is less stable than the fcc site and presents an activation barrier of about 0.13 eV (0.21 eV within LDA) for diffusion to the fcc site. These results in several ways indicate that the diffusion barrier as measured by Wintterlin, Schuster, and Ertl is too low.

We notice that the difference of about 0.10 eV between LDA and GGA diffusion barriers stems from a lowering of E_{bri} by the same amount of energy within GGA (see Table I). This is understood by the fact that the mutual agreement between LDA and GGA is better in high density zones (fcc and hcp sites) than in regions of low electron density, such as the bridge site, where GGA is expected to do better. We refer to Ref. 26 for an illuminating discussion on this issue.

The calculations on surface relaxation show that as the oxygen atom moves from the lowest energy fcc site over the bridge and into the hcp site, the surface atoms reconstruct to lower the total energy. By placing the oxygen atom in the bridge site, yet maintaining the relaxed structure of oxygen in the fcc site, an estimate of the importance of surface relaxation for the diffusion barrier is obtained. The result is a 0.10 eV higher adsorption energy compared to when the Pt atoms are allowed to relax. By quickly moving to accommodate the diffusing oxygen atom, the Pt atoms thus lower the diffusion barrier by about 0.1 eV (Table I).

The perpendicular vibrational frequency of oxygen in the fcc site within the harmonic approximation is calculated to be $\hbar\omega_{\perp}=59$ meV, in agreement with measurements [59 meV,[39] 58 meV (Ref. 36)]. Similarly, the vibration frequency in the diffusion direction turns out to be $\hbar\omega_{\parallel}=60$ meV, implying a diffusion prefactor of $D_0\simeq10^{-3.0}$ cm^2/s, which falls into the expected range. For the bridge site, the perpendicular vibrational frequency is calculated to be $\hbar\omega_{\perp}=67$ meV, again within the harmonic approximation, and the in-plane vibrational frequency orthogonal to the diffusion direction (Fig. 1) $\hbar\omega^*=56$ meV. For temperatures below ~350 K, at which oxygen forms the well ordered $p(2\times2)$ overlayer and oxygen diffusion is relevant, these zero-point vibrations bring down the fcc-hcp diffusion barrier by about 30 meV.

The prefactor measured by Wintterlin, Schuster, and Ertl is thus three orders of magnitude lower than the calculated value $D_0=10^{-3.0}$ cm^2/s, which is a typical result for hopping diffusion. This fact, together with the indications of too low a barrier in this experiment, leads us to reexamine the data by Wintterlin, Schuster, and Ertl. We notice that the fit is based on data taken in a narrow temperature range of 191–205 K, and therefore (as noted by the authors) prone to large error bars; in fact, the reported value of E_d is not the main focus in paper A. Having calculated the diffusion prefactor, we use this value to perform a one-parameter fit to the raw diffusion data (paper A). This naturally results in a poorer fit, which however still falls within the error bars of all but two low-temperature points, and that yields $E_d=0.56$ eV. This value agrees much better with our calculations ($E_d = 0.55$ eV with zero-point vibrations taken into account), and resolves the adsorption discrepancy outlined above. We note, however, that the temperature regime is just too narrow and the data of insufficient accuracy to allow for more detailed comparisons.

In summary, we have presented density-functional calculations on the chemisorption and diffusion barrier of oxygen on Pt(111) that provide results accurate enough to resolve an important issue. The calculated energy barrier is somewhat higher than recently measured in an STM experiment. With other experiments and calculations supporting the present calculations, we reexamine the raw diffusion data and are able to reconcile all findings by lifting the diffusion prefactor to a more common level.

The authors acknowledge instructive discussions with Vladimir Zhdanov, Göran Wahnström, Mats Persson, and Bengt Kasemo, and motivating correspondence with Ove Hjortsberg. Financial support through the Materials Consortium no. 9, supported by the Swedish Board for Industrial and Technical Development (NUTEK) and the Swedish Foundation for Strategic Research (SFS), the Swedish Natural Science Research Council (NFR), and the Swedish Research Council for Engineering Sciences (TFR), together with allocation of computer time at the UNICC facilities at Chalmers University of Technology, are gratefully acknowledged.

---

[1] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley-Interscience, New York, 1994).

[2] T. Matsushima *et al.*, Surf. Sci. **127**, 403 (1983).

[3] M. Mieher and W. Ho, J. Chem. Phys. **91**, 2754 (1989).

[4] C. T. Rettner and J. Lee, J. Chem. Phys. **101**, 10 185 (1994).

[5] C. Åkerlund, I. Zoric, and B. Kasemo, J. Chem. Phys. **104**, 7359 (1996).

[6] A. C. Luntz, M. D. Williams, and D. S. Bethune, J. Chem. Phys. **89**, 4381 (1988).

[7] V. P. Zhdanov and B. Kasemo, J. Catal. **170**, 377 (1997).

[8] L. K. Verheij, M. Freitag, M. B. Hugenschmidt, I. Kempf, B. Poelsema, and G. Comsa, Surf. Sci. **272**, 276 (1992).

[9] S. Esch, M. Hohage, T. Michely, and G. Comsa, Phys. Rev. Lett. **72**, 518 (1994).

[10] J. Wintterlin, R. Schuster, and G. Ertl, Phys. Rev. Lett. **77**, 123 (1996).

[11] J. Harris and B. Kasemo, Surf. Sci. **105**, L281 (1981).

[12] H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, and R. J. Behm, J. Chem. Phys. **99**, 2128 (1993).

[13] R. Lewis and R. Gomer, Surf. Sci. **12**, 157 (1968).

[14] P. J. Feibelman, E. Stefanie, and M. Thomas, Phys. Rev. Lett. **77**, 2257 (1997).

[15] B. C. Stipe *et al.*, Phys. Rev. Lett. **78**, 4410 (1997).

[16] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[17] B. Hammer, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **70**, 3971 (1993).

[18] B. Hammer and J. K. Nørskov, Nature (London) **376**, 238 (1995).

[19] P. A. Gravil, D. M. Bird, and J. A. White, Phys. Rev. Lett. **77**, 3933 (1996).

[20] A. Eichler and J. Hafner, Phys. Rev. Lett. **79**, 4481 (1997).

[21] Y. Morikawa, J. J. Mortensen, B. Hammer, and J. K. Nørskov, Surf. Sci. **386**, 67 (1997).

[22] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[23] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1968).

[24] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[25] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

[26] B. Hammer, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **70**, 3971 (1993).

[27] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[28] L. Bengtsson (unpublished).

[29] M. Gillan, J. Phys.: Condens. Matter **1**, 689 (1989).

[30] U. Starke *et al.*, Surf. Sci. **287/288**, 432 (1993).

[31] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16 067 (1992).

[32] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[33] Y. Yourdshahyan, U. Engberg, L. Bengtsson, B. I. Lundqvist, and B. Hammer, Phys. Rev. B **55**, 8721 (1997).

[34] D. J. Chadi and M. Cohen, Phys. Rev. B **8**, 5747 (1973).

[35] K. Mortensen, C. Klink, F. Jensen, F. Besenbacher, and I. Stensgaard, Surf. Sci. Lett. **220**, L701 (1989).

[36] D. H. Parker, M. E. Bartram, and B. E. Koel, Surf. Sci. **217**, 489 (1989).

[37] B. E. Nieuwenhuys and W. M. Sachtler, Surf. Sci. **34**, 317 (1973).

[38] We emphasize that all GGA values are based on the structure, lattice constant, pseudopotentials, and electron density given by LDA.

[39] H. Steiniger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 1 (1982).