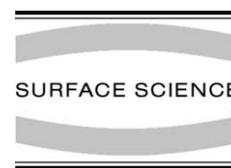




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Evidence for slow oxygen exchange between multiple adsorption sites at high oxygen coverages on Pt(1 1 1)

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Abstract

Thermal desorption (TPD) measurements using isotopically labeled oxygen were carried out on a Pt(1 1 1) surface for oxygen coverages θ_{O} between 0.25–0.7 monolayers (ML, 1 ML corresponds to $1.505 \times 10^{15} \text{ cm}^{-2}$). In these experiments, $^{18}\text{O}_2$ was used to produce $\theta_{\text{O}} = 0.25$ ML and then N^{16}O_2 was used to obtain larger values of θ_{O} at the surface. We observed differences in the peak shapes and temperatures maxima of the O_2 TPD peaks from the different combinations of labeled O_2 molecules ($^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$), and this provides direct evidence for multiple adsorption sites and slow oxygen exchange between these sites during dosing or heating in TPD. Also, we have reinvestigated the high resolution electron energy loss spectroscopy (HREELS) spectra of these surfaces. We find that there is only a 22 cm^{-1} shift of the loss peak due to Pt–O stretching vibrations for θ_{O} between 0.25–0.55 ML, consistent with similar Pt–O bond energies at the different sites occupied by oxygen adatoms at these coverages on the Pt(1 1 1) surface. © 2001 Published by Elsevier Science B.V.

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Oxygen adsorption at Pt surfaces is central to understanding the activity of Pt in many important catalytic reactions, e.g. gas-phase oxidation of NH_3 to NO_2 over Pt catalysts and liquid-phase oxidation of H_2 to H_2O over Pt electrodes in fuel cells. Thus, many studies have been devoted to measuring and simulating oxygen adsorption on single-crystal model surfaces, such as Pt(1 1 1) [1–11].

Dissociative adsorption of dioxygen (O_2) on Pt(1 1 1) surfaces under UHV conditions forms a p(2×2)-O structure with $\theta_{\text{O}} = 0.25$ ML [1]. This

structure can be obtained by either a saturation exposure of Pt(1 1 1) to O_2 at 300 K or heating a layer of molecularly chemisorbed O_2 , formed by exposing O_2 on Pt(1 1 1) at 100 K, to 300 K [2]. The oxygen adatoms occupy fcc threefold hollow sites and have a desorption energy E_{d}^0 of 55 kcal/mol in the low coverage limit. The O_2 desorption activation energy is strongly coverage dependent because of O–O repulsive interactions [3,4], and the oxygen desorption energy E_{d} can be described by a function $E_{\text{d}} = E_{\text{d}}^0 - B\theta_{\text{O}}$, where B is equal to 30 kcal/mol [5] in the region of $0 < \theta_{\text{O}} < 0.25$ ML. As a result, no adsorption on nearest-neighbor sites was detected with STM which found that the average O–O distance was greater than or equal to $2a$, where a is the Pt–Pt distance on Pt(1 1 1). The

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existence of small oxygen islands stable to 450–500 K [2] was explained by Zhdanov and Kasemo [5] to be result of high surface oxygen diffusion energy which freezes in this non-equilibrium distribution.

There have been several measurements and calculations of the O-atom diffusion energy on Pt(1 1 1) surfaces. These values vary from 27 kcal/mol as measured by field emission microscopy [6] to 13 kcal/mol as predicted by density-function (DFT) calculations [7] for $\theta_{\text{O}} = 0.25$ ML. Knowledge of an accurate value for the diffusion energy is important for understanding and explaining mechanisms of oxidation reactions on Pt(1 1 1), because O adatoms would be bound to the site where they were initially adsorbed for high values, while they would be fairly mobile for low values.

Oxygen coverages in excess of 0.25 ML could certainly be encountered in many applications, and these have been probed in a few studies on Pt(1 1 1) [8,9]. More recently, we showed that high oxygen coverages may be cleanly obtained in UHV by exposure of the Pt(1 1 1) surface to aggressive oxidants such as NO_2 [10] or O_3 [11]. TPD revealed that oxygen desorbs more readily from surfaces with $\theta_{\text{O}} > 0.25$ ML than at lower coverages [10], showing that such higher coverage oxygen adlayers are significantly destabilized, i.e. chemisorbed more weakly. E_{d} decreases from 40 kcal/mol at $\theta_{\text{O}} = 0.25$ ML to 28–30 kcal/mol for $0.25 < \theta_{\text{O}} < 0.75$ ML, and after accounting for the O_2 dissociation barrier, this leads to estimates of the Pt–O bond dissociation energy, $D(\text{Pt–O})$, equal to 80 kcal/mol at $\theta_{\text{O}} = 0.25$ ML and ≤ 71 kcal/mol for $0.25 < \theta_{\text{O}} < 0.42$ ML [10]. There are at least two reasons for such destabilization. First, repulsive oxygen–oxygen interactions become stronger as the average O–O distance decreases with increasing θ_{O} . Since possible O–O distances on the Pt(1 1 1) surface are not described by a continuous function but rather by a set of discrete values, the formation of a (2×1) -O overlayer may result in the appearance of a new TPD peak because of occupation of energetically different adsorption sites where the O–O distance is a instead of $2a$ as in the $p(2 \times 2)$ -O overlayer. Secondly, at $\theta_{\text{O}} > 0.25$ ML, oxygen may be forced to occupy sites that are less energetically favorable than fcc threefold hollow sites such as hcp threefold hollow sites (or less

likely, even twofold bridge or atop sites). While the importance of the first factor is expected because of the existence of the O–O repulsive interaction mentioned above, it is not clear whether the second factor plays any substantial role. Currently, there is no structural determination of O adatoms on Pt(1 1 1) occupying sites other than fcc threefold hollow sites.

Previous high resolution electron energy loss spectroscopy (HREELS) on Pt(1 1 1) with $0 < \theta_{\text{O}} < 0.25$ ML [8] and $\theta_{\text{O}} = 0.25$ and 0.75 ML [10] showed only one vibrational band near 470 cm^{-1} . This implies that all adsorbed oxygen atoms either occupy equivalent sites or that the Pt–O bond dissociation energy, $D(\text{Pt–O})$, is similar for all occupied sites. First-principles calculations by Feibelman [12] showed that the O–Pt bond length and O–Pt interaction within the top layer was little affected by the nature of the adsorption site, either fcc or hcp. These DFT calculations predict a decrease in oxygen adsorption energy of 0.47 eV for oxygen adsorbed at hcp sites compared to fcc sites, with Pt–O bond lengths of 2.13 and 2.09 Å, respectively [12]. The origin of the preferential adsorption at fcc sites is d -electron depletion that occurs between surface and subsurface Pt atoms that does not occur for adsorption at hcp sites, which causes less destabilization of surface and subsurface Pt bonding. This helps to explain the different desorption peaks in TPD and at the same time the presence of only one vibrational band in HREELS.

Our primary probe in these experiments for determining if two adsorption sites are populated at oxygen coverages larger than 0.25 ML was to use TPD and isotopically labeled oxygen, using different isotopes to populate sites characteristic of several distinct coverages. Occupation of non-equivalent sites and a slow oxygen exchange rate between those sites will cause difference in the TPD traces for different O_2 isotopic combinations. In addition, we were motivated to obtain new HREELS data by the lack of data specifically over the coverage range of 0.25–0.5 ML where we expect that a change of site could occur.

TPD and HREELS experiments were performed in two different UHV chambers. TPD was conducted in an UHV chamber equipped for

Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy ion scattering spectroscopy (LEISS), TPD, and low energy electron diffraction (LEED). The Pt(111) surface was cleaned by cycles of Ar⁺ ion bombardment and subsequent annealing to 1150 K. ¹⁸O₂ (99.1 at.%, BOC Limited) was dosed onto the Pt(111) surface via a glass microcapillary array doser. NO₂ (99.5 at.%, MG Industries) was dosed via a stainless steel tube doser. All exposures were carried out with the Pt(111) crystals at 330 K in order to avoid coadsorption of NO. Exposures given in this report have not been corrected for ionization gauge sensitivity nor doser-enhancement factor. TPD spectra were taken using a linear heating rate of 6 K s⁻¹. The ionizer region of the UTI quadrupole mass spectrometer (QMS) was covered with a stainless still shield to minimize background contributions to the signal.

HREELS experiments were performed in a three-level UHV chamber equipped with a cylindrical mirror analyzer for AES, UV-photoelectron spectroscopy (UPS), and XPS on the top level, LEED optics and a QMS for TPD and residual gas analysis in the middle level, and a LK2000 spectrometer for HREELS experiments in the bottom level. The sample cleaning and gas dosing procedures were the same as those described above. Both chambers had background pressure in the low 10⁻¹⁰-Torr range. The HREELS spectra were obtained using an incident beam energy of 4.5 eV.

Fig. 1 summarizes our TPD results using isotopically labeled oxygen. Except for the bottom trace, taken after a saturation ¹⁸O₂ exposure was used to create $\theta_{\text{O}} = 0.25$ ML, all of the O₂ TPD spectra in Fig. 1 were obtained after dosing NO₂ on a Pt(111) surface at 330 K that had been precovered with $\theta_{\text{O}} = 0.25$ ML by using ¹⁸O₂. O₂ TPD spectra were obtained from these surfaces monitoring the signals at 32, 34, and 36 amu to follow desorption of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂, respectively. Results are shown from three different experiments following exposure of 0.004, 0.012, and 0.06-L NO₂ to produce total oxygen coverages of $\theta_{\text{O}} = 0.31$, 0.53, and 0.66 ML, respectively, as determined from the integrated TPD areas. There are clear differences in the peak shapes and max-

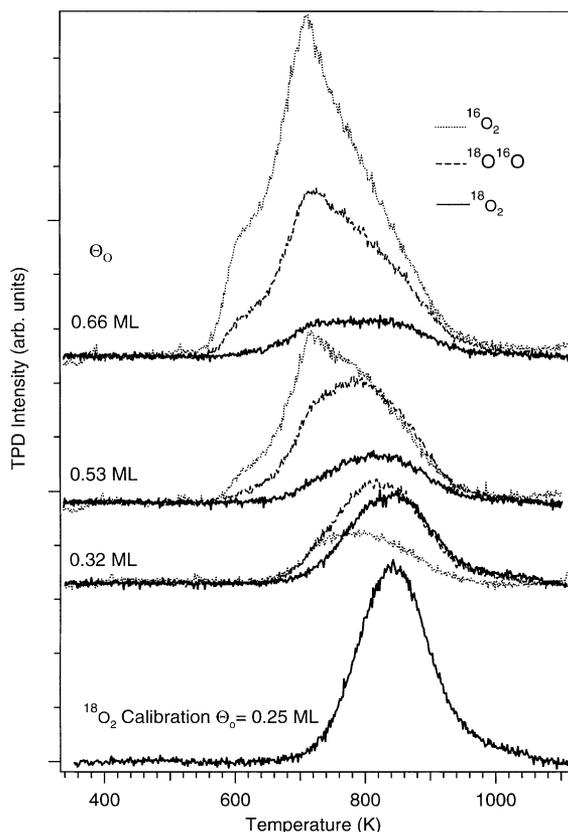


Fig. 1. O₂ TPD curves after N¹⁶O₂ was dosed onto a Pt(111) surface at 330 K which had been precovered with a saturation dose of ¹⁸O₂ to give $\theta_{\text{O}} = 0.25$ ML.

ima for the different, isotopically labeled O₂ molecules desorbed from these surfaces for all of the oxygen coverages examined. All three possible O₂ isotopes desorbed as separate peaks, with ¹⁶O₂ desorption occurring first, followed by ¹⁶O¹⁸O and ¹⁸O₂. There was a difference between the leading edges of the peaks of about 40 K for $\theta_{\text{O}} = 0.53$ ML. For the traces for $\theta_{\text{O}} = 0.53$ and 0.66 ML, there are also distinct shape differences between the desorbing O₂ isotopes. All of these differences are indications that ¹⁸O and ¹⁶O adatoms occupy different surface sites with different energies and there is only slow exchange between these different sites. Also, there is evidence for destabilization of the initially adsorbed ¹⁸O adatoms which is manifested in a lower temperature onset for desorption and an increased FWHM of the ¹⁸O₂ TPD peak

following adsorption of additional oxygen. The $^{18}\text{O}_2$ peak FWHM was 120 K for $\Theta_{\text{O}} = 0.25$ ML versus 240 K for $\Theta_{\text{O}} = 0.66$ ML. And, there is obviously a higher reactivity of the more weakly bound ^{16}O adatoms which show a propensity to recombine with other ^{16}O adatoms and also ^{18}O adatoms that exceeds that expected by statistics. This leads to non-statistical distribution of the isotopic products, e.g., $^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ yields of 5:4:2 rather than 1:2:1 at $\Theta_{\text{O}} = 0.5$ ML.

These observations allow us to estimate a lower bound on the activation energy for oxygen diffusion on the Pt(111) surface. Diffusion processes on metal surfaces can be described by an Arrhenius expression

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \quad (1)$$

where D is the diffusion constant, D_0 is an exponential prefactor, E_d is the diffusion activation energy, R is the gas constant, and T is the absolute temperature. The Einstein expression relates the value for the diffusion constant to the average displacement (r) and time of diffusion (t)

$$D = \frac{\langle r^2 \rangle}{2dt} \quad (2)$$

where d is the dimensionality of the diffusion space (two in this case). Eqs. (1) and (2) can be used to estimate the diffusion barrier that is necessary to prevent mixing of different oxygen isotopes during the timescale of the experiment. For different isotopes not to mix, the average displacement must be less than the distance between adjacent hcp and fcc hollow sites (1.6 Å) during the time of annealing (1 s) at temperature near beginning of the oxygen desorption (500 K). Using a typical value for the diffusion coefficient (D_0) on metallic surfaces of 10^{-4} cm²/s, we conclude that E_d must be larger than 28 kcal/mol. This estimate, which results from our measurements for $0.3 < \Theta_{\text{O}} < 0.75$ ML, is close to the value of 27 kcal/mol as measured by field emission microscopy [6], and excludes a value of 13 kcal/mol as predicted by density-function (DFT) calculations [7], for $\Theta_{\text{O}} = 0.25$ ML.

It is helpful to look at a structural model for oxygen adlayers as shown in Fig. 2 to interpret

these results. Fig. 2a shows the (2×2) oxygen adlayer on Pt(111) obtained by exposure of the Pt(111) surface to $^{18}\text{O}_2$. All oxygen atoms occupy fcc hollow sites to form a (2×2) structure with $\Theta_{\text{O}} = 0.25$ ML. There are two possibilities for placing additional O adatoms to obtain an oxygen coverage of 0.5 ML. The first is to continue filling fcc sites which could eventually form a (2×1) structure as shown in Fig. 2b. In this structure, all oxygen adatoms are energetically equivalent and thus there should be no differences in the shapes and onset temperatures for the O_2 TPD peaks from all three combinations of the two oxygen isotopes. We imagine that domain boundaries and defects affect all of the traces equally.

The second possibility is to start filling hcp sites as shown in Fig. 2c. This is a (2×2) structure, but non-primitive with two oxygen atoms per unit cell. Both structures are consistent with observations of a (2×2) LEED pattern at these oxygen coverages. In this case, however, O adatoms occupy energetically different sites with energies E_{fcc} and E_{hcp} . And so, TPD should reveal three separate curves because the two types of oxygen adsorption sites produce two terms plus a cross term with E_{fcc} and E_{hcp} in $E_d(\Theta)$ in the desorption rate expression for O_2 molecules formed from adatoms occupying different types of sites. Thus, we interpret our TPD results as indicating that oxygen occupies energetically distinguishable sites at $\Theta_{\text{O}} > 0.25$ ML and propose that these are hcp hollow sites based on theoretical predictions [13].

Rapid surface diffusion of oxygen adatoms would cause exchange between sites and a homogenous isotopic distribution over the different adsorption sites. This would result in identical TPD profiles for the different isotopically labeled O_2 molecules. Because such behavior is not displayed in Fig. 2, we conclude that oxygen diffusion and exchange on Pt(111) with $\Theta_{\text{O}} < 0.7$ ML is a relatively slow process under our conditions. Furthermore, to extend that the diffusion path from one fcc site to a neighboring fcc site proceeds through an intermediate hcp site, slow oxygen interchange between hcp and fcc sites also would imply slow diffusion between fcc sites.

HREELS spectra obtained at several oxygen coverages are shown in Fig. 3. The spectra ob-

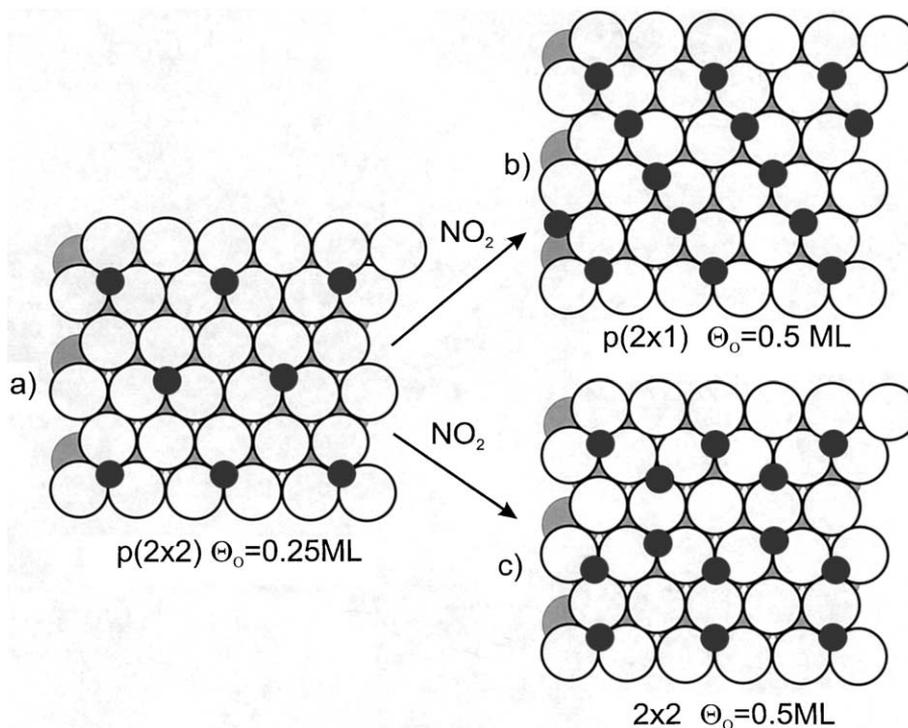


Fig. 2. Real-space models of oxygen adsorbed on a Pt(111) surface with exclusive occupation of threefold sites.

tained for $\Theta_0 < 0.25$ ML were taken on the Pt(111) surface exposed to $^{16}\text{O}_2$, while those for $\Theta_0 > 0.25$ ML were obtained after NO_2 exposure on a Pt(111) surface that had been precovered with $\Theta_0 = 0.25$ ML using $^{16}\text{O}_2$ in a manner identical to that described above except that here there were no differences in the oxygen isotopes used. At $\Theta_0 = 0.18$ ML, we observe only a single peak at 466 cm^{-1} with a width of 61 cm^{-1} (elastic peak FWHM = 53 cm^{-1}). This is consistent with a previous report [10] and the loss peak is assigned to the Pt–O stretching vibrational mode. With an increase of Θ_0 , there is a shift in this peak toward higher loss energy. At $\Theta_0 = 0.55$ ML, the peak was at 492 cm^{-1} with a width of 68 cm^{-1} . There is no evidence of a new loss peak at $\Theta_0 > 0.25$ ML in our spectra at this resolution, and in any event the shift of such a second peak would be less than 22 cm^{-1} .

This observation is an indication of similar Pt–O interactions at both hcp and fcc threefold hol-

low sites, as proposed by Feibelman [13]. The small shift of the Pt–O stretching band toward higher energies at higher coverages may be explained by dipole–dipole coupling that should be present based on a model for oxygen adsorption proposed by Zhdanov and Kasemo [5]. Oxygen–oxygen interactions at small O–O distances (high Θ_0) were considered to be dominated by dipole–dipole interactions. The energy of such interactions increases proportionally to $1/a^3$ (i.e., $\Theta_0^{1.5}$), where a is the O–O distance. Such interactions would result in stronger coupling of the Pt–O $^{\delta-}$ stretching modes at higher Θ_0 .

In summary, we have used $^{18}\text{O}_2$ and N^{16}O_2 to produce oxygen adatoms at distinct oxygen coverages and TPD from these surfaces to show strong evidence for energetically different adsorption sites for oxygen adatoms on Pt(111) at $\Theta_0 > 0.25$ ML. Based on previous theoretical calculations, we propose that oxygen adatoms adsorbed at $\Theta_0 > 0.25$ ML start to occupy hcp

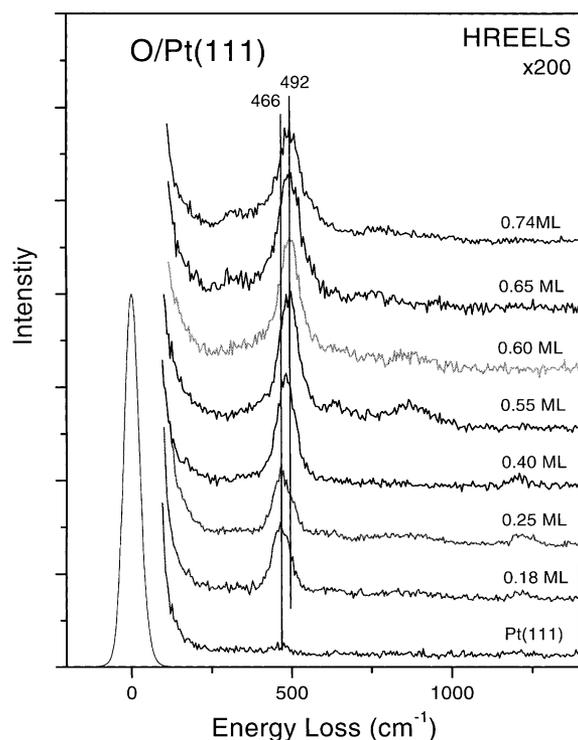


Fig. 3. HREELS spectra for oxygen-covered Pt(111) surfaces.

hollow sites on the Pt(111) surface. Furthermore, observations of separate isotopically labeled O_2 peaks in TPD experiments shows that diffusion of oxygen adatoms on the Pt(111) surface is a relatively slow process which does not result in extensive mixing of O adatoms occupying these different sites on the time scale of our experiment even at the elevated temperatures encountered during TPD. This implies that there is no oxygen

diffusion at room temperature. We observed only a small shift in the Pt–O stretching vibration in HREELS with increasing oxygen coverage, and this shift would be expected from dipole–dipole coupling. Thus, the Pt–O stretching modes at these two sites have the same energies (within 22 cm^{-1}) and similar Pt–O bonding interactions, which is consistent with theoretical predictions.

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References

- [1] N. Materer, U. Starke, A. Barbieri, R. Doll, K. Heinz, M.A. Van Hove, G.A. Somorjai, *Surf. Sci.* 325 (1995) 207.
- [2] J.L. Gland, E.B. Kollin, *J. Chem. Phys.* 78 (1983) 963.
- [3] B.C. Stipe, M.A. Rezaei, W. Ho, *J. Chem. Phys.* 107 (1997) 6443.
- [4] T. Zambelli, J.V. Barth, J. Wintterlin, G. Ertl, *Nature* 390 (1997) 495.
- [5] V.P. Zhdanov, B. Kasemo, *Surf. Sci.* 415 (1998) 403.
- [6] R. Gomer, *Rep. Progr. Phys.* 53 (1990) 917.
- [7] A. Bogicevic, J. Stormquist, B.I. Lindqvist, *Phys. Rev. B* 57 (1998) R4289.
- [8] J. Gland, B. Sexton, G. Fisher, *Surf. Sci.* 95 (1980) 587.
- [9] J.L. Gland, *Surf. Sci.* 93 (1980) 487.
- [10] D.H. Parker, M.E. Bartram, B.E. Koel, *Surf. Sci.* 217 (1989) 489.
- [11] N.A. Saliba, Y.L. Tsai, C. Panja, B.E. Koel, *Surf. Sci.* 419 (1999) 79.
- [12] M. Lynch, P. Hu, *Surf. Sci.* 458 (2000) 1.
- [13] P.J. Feibelman, *Phys. Rev. B* 56 (1997) 10532.