

## SURFACE PHONON DISPERSION OF CLEAN AND OXYGEN COVERED Pt(111)

Klaus KERN, Rudolf DAVID, Robert L. PALMER, George COMSA

*Institut für Grenzflächenforschung und Vakuumphysik der Kernforschungsanlage Jülich,  
P.O. Box 1913, D-5170 Jülich, Fed. Rep. of Germany*

and

Talat S. RAHMAN

*Cardwell Hall, Department of Physics, Kansas State University, Manhattan, KS 66506, USA*

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The dispersion of the vibrational modes of the Pt(111) surface in the absence of impurities as well as in the presence of oxygen has been measured by inelastic helium scattering along the  $\bar{\Gamma}\bar{M}$  azimuth. In the case of the ordered  $p(2 \times 2)O$  superstructure, the additional dispersion branch appearing as a result of the Brillouin zone folding was also measured. The experimental results show the first direct evidence for the appearance of a surface Rayleigh phonon gap at the new zone boundary. The gap was determined to be  $\sim 0.85$  meV at the  $\bar{M}_0$  point. Lattice-dynamical calculations show that this relatively large gap is due to bond stretching interactions between the adsorbate and substrate atoms. The dispersion curve in the presence of disordered oxygen, obtained by annealing (1200 K) the Pt surface in an oxygen atmosphere and assumed to be located subsurface on the basis of ion scattering data has been measured. The frequency of the Rayleigh phonon at the  $\bar{M}$  point is 12% below the clean surface value. This is at variance with the case of disordered oxygen on metal surfaces (O/Ni(100)) which has been shown to have a negligible influence on the Rayleigh dispersion curve. According to the lattice dynamical calculations this 12% frequency lowering corresponds to a reduction of the interlayer force constant  $k_{12}$  by about 30% and thus supports the subsurface location of the oxygen atoms.

### 1. Introduction

Much of the effort in surface physics is devoted to the question of the structure and local force field of clean and adsorbate covered surfaces. Surface phonon spectroscopy [1,2], which became feasible in the near past, has proved to be an excellent approach to understanding the dynamics of surfaces. In conjunction with advanced numerical methods for calculating surface vibrational phenomena, information on surface structure and the corresponding binding forces can now be extracted from the measured phonon dispersion

data. Despite the capability of high-energy resolution and extreme surface sensitivity inherent in inelastic He scattering, only few work has been done on adsorbate covered surfaces by this technique. In this paper we report on the results of the investigation of the inelastic scattering of thermal He atoms from the Pt(111) surface and the adsorbate induced changes in the surface phonon dispersion upon adsorption of ordered and disordered oxygen.

There is a large number of experimental data giving evidence for the existence of three states of oxygen on Pt(111). These phases are mainly determined by the surface temperature during oxygen adsorption. Below  $\sim 160$  K oxygen adsorbs in molecular form, above this temperature in two atomic phases. At temperatures below 800 K the "chemisorbed" phase, at temperatures above 800 K the so-called "oxide" phase is obtained. The latter one is attributed to a subsurface "oxide" [3] which is only obtained in the presence of impurities (for example Si) as contaminant [4,5], i.e. is a silicon oxide. While the nature of the "oxide" phase seems to be largely clarified, the location of the oxygen is not. Whereas ion scattering data [3] suggest the subsurface location, the Auger data [5] are compatible also with the formation of three-dimensional  $\text{SiO}_2$  clusters on top of the Pt(111) surface. The experimental results presented in section 4.3 support the subsurface location of the oxygen atoms.

## 2. Experimental

The details of the experimental apparatus have been described elsewhere [6,7]. Here only the features relevant to this experiment will be given. The total scattering angle is fixed, i.e.  $\vartheta_i + \vartheta_f = 90^\circ$ . Incident He beam energies in the range 10–35 meV are used; the velocity spread is  $\Delta v/v \approx 0.7\%$ . The overall energy resolution upon cross correlation analysis of the TOF distribution is 0.3–0.6 meV. The effective angular resolution of the apparatus is  $0.3^\circ$ . The Pt(111) crystal is mounted on a manipulator in a UHV chamber with a base pressure in the low  $10^{-11}$  Torr range. The Pt(111) single crystal is cleaned by repeated cycles of sputtering, oxygen and thermal cleaning until no traces of impurities can be detected by the CMA Auger spectrometer. The defect density of the clean crystal is less than  $10^{-3}$  [8]. The azimuthal alignment of the crystal is performed in situ by means of He diffraction [9].

The  $\text{p}(2 \times 2)$  oxygen overlayer ("chemisorbed" phase) is obtained by exposing the crystal to molecular oxygen with the crystal temperature at 300 K. The saturation coverage  $\theta_s \approx 0.25$  corresponds to an Auger peak ratio of  $\text{O}(510 \text{ eV})/\text{Pt}(237 \text{ eV}) \approx 0.4$  measured at 2 keV, 5  $\mu\text{A}$ , and 2 V peak-to-peak voltage ( $\theta = 1$  corresponds to  $1.5 \times 10^{15}$  atoms  $\text{cm}^{-2}$ ). Sharp  $\text{p}(2 \times 2)$  He-diffraction patterns with low diffuse background are observed. Indeed the He diffraction patterns show sharp half number extra spots; the analysis of the peak widths

allows an estimate of the domain size of  $\sim 400$  Å [10]. Under the given vacuum conditions, no contamination or depletion (by H or CO) of the oxygen overlayer could be observed after several hours.

The so-called "oxide" phase is produced by annealing the Pt crystal ( $T_s = 1200$  K) in an oxygen atmosphere of  $\sim 10^{-6}$  mbar. After 20 min exposure the same Auger ratio  $\text{O}(510 \text{ eV})/\text{Pt}(237 \text{ eV}) \approx 0.4$  is obtained. While the "chemisorbed" oxygen desorbs very rapidly after flashing the crystal to 600 K, the desorption rate in the "oxide" phase is negligible even at 1400 K.

## 3. Lattice dynamical model

The lattice dynamics of the platinum surface is treated in the harmonic approximation using pair potentials. The potential energy term in the model hamiltonian is based on nearest neighbour interactions and central forces. Equilibrium conditions then require that the first derivative of the pair potential vanishes, i.e. each atom has its equilibrium position at the minimum of the pair potential connecting the atom to its next neighbour. We have deliberately chosen a simple model so as to be free from too many unknown parameters and also to be able to obtain exact results using a quasi-analytic technique [11,12].

In the lattice dynamical calculations of the  $\text{p}(2 \times 2)\text{O-Pt}(111)$  system we have introduced in our calculations besides nearest neighbour central forces also an additional non-central force of the bond stretching type between adsorbate and the nearest neighbour substrate atoms. It was recently found that such non-central forces play an important role in the case of  $\text{p}(2 \times 2)$  structures [13]. The lattice-dynamical hamiltonian then has the following additional term:

$$V_{\beta S} = \frac{1}{2} k' \sum_{i \neq j} \Delta l_i \Delta l_j, \quad (1)$$

where

$$\Delta l_i = n_{b_i} [u(i) - u(0)], \quad (2)$$

with  $n_{b_i}$  being the unit vector from the adsorbate atom to the first layer substrate atom  $i$  and  $u(i)$  and  $u(0)$  are the displacements of the substrate and the adsorbate atom, respectively. This term correlates the stretching of the Pt–O bonds thereby introducing a three-body interaction between the adsorbate and substrate atoms. This affects not only the dispersion of the adsorbate modes but also that of the substrate phonons. A detailed analysis of this non-central force and the ensuing lattice dynamics analysis will be presented elsewhere [14].

## 4. Results and discussion

### 4.1. Pt(111)

The lattice dynamics of the clean Pt(111) surface has recently been investigated in detail experimentally [15–17] and theoretically [15]. A significant asymmetry of the surface phonon dispersion between the  $\bar{\Gamma}\text{M}$  and  $\bar{\Gamma}\text{K}$  azimuth is observed [15]. Most of the salient features of the measured dispersion curves can be reproduced in lattice dynamical calculations provided one assumes a substantial softening of the intralayer force constant  $k_{11}$  of the Pt atoms in the first layer [15]. The same behavior was recently inferred from the lattice dynamical calculations of Bortolani et al. [18] for the (111) surfaces of the noble metals (Cu, Ag, Au). Along the  $\bar{\Gamma}\text{K}$  azimuth a number of anomalous kinks in the Rayleigh mode have been noted [16,17]. It was suggested that these observed effects are due to a 2D surface Kohn anomaly [16].

In the following we want to address the question on the adsorbate-induced changes in the surface Rayleigh wave upon adsorption of ordered and disordered layers of oxygen. All measurements reported here are performed in

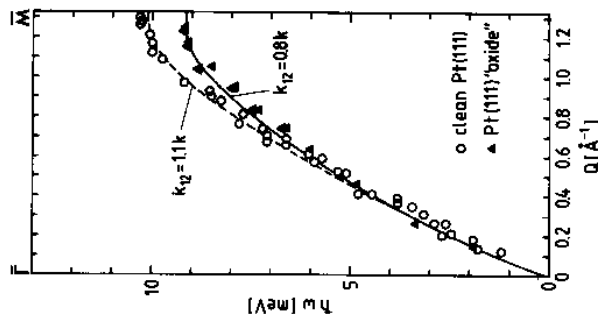


Fig. 1. Measured Rayleigh phonon dispersion curves of the "oxide" and of the clean surface in the  $\bar{\Gamma}\text{M}$  azimuth.

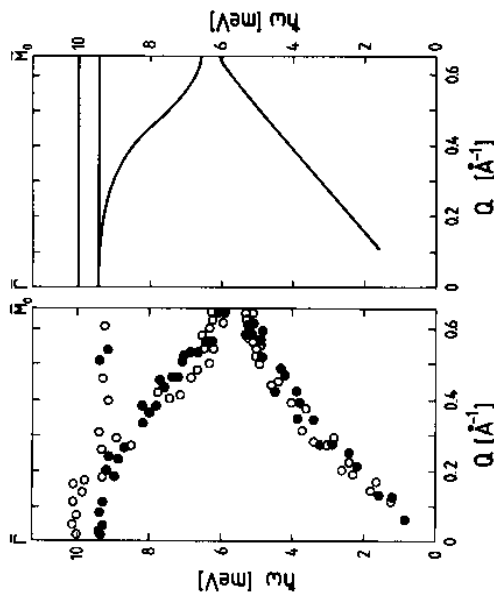


Fig. 2. Experimental (a) and theoretical (b) Rayleigh phonon dispersion curves of the  $p(2 \times 2)\text{-Pt}(111)$  surface, in the  $\bar{\Gamma}\text{M}_0$  direction, reduced to the first Brillouin zone. The phonon events belonging to the first Brillouin zone are denoted by open circles, those belonging to the second zone by filled circles.

the  $\langle 11\bar{2} \rangle$  crystal direction (sagittal and shear horizontal modes are decoupled in the  $\bar{\Gamma}\text{M}$  azimuth). The measured Rayleigh dispersion curve for the clean Pt(111) surface is shown in fig. 1. The force constants using in the best fit lattice dynamical calculation are  $k_{11} = 0.4k_{\text{bulk}}$ ,  $k_{12} = 1.1k_{\text{bulk}}$  where  $k_{\text{bulk}}$ , the bulk force constant, is  $4.83 \times 10^4$  dyn/cm.

### 4.2. $p(2 \times 2)\text{-O-Pt}(111)$

The presence of a superstructure on metal surfaces due to adsorption of ordered overlayers modifies the substrate Rayleigh phonon dispersion curve even in the absence of surface reconstruction. Experimental results reported so far show that, in spite of substantial quantitative changes, the shape of the Rayleigh curve remains qualitatively unchanged [19]. However, it has been predicted theoretically [20,21] that also qualitative changes, like the opening of phonon gaps at the new zone boundaries, might appear.

Fig. 2a shows the measured surface phonon dispersion of the  $p(2 \times 2)\text{-O-Pt}(111)$  system. Due to the periodicity imposed by the oxygen overlayer, the length of the reduced Brillouin zone of the  $p(2 \times 2)\text{-O}$  surface is half that of clean Pt(111) ( $\bar{\Gamma}\text{M}_0 = \frac{1}{2}\bar{\Gamma}\text{M}_{\text{Pt}}$ ). The data clearly demonstrate the existence of a phonon gap of  $0.85 \pm 0.2$  meV at the new zone boundary. It is for the first time that such a gap induced by an adsorbed layer in the Rayleigh curve is

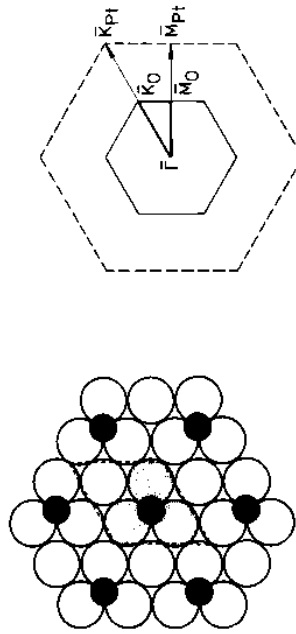


Fig. 3. Unit cell and 2D Brillouin zone of the  $p(2 \times 2)\text{O-Pt}(111)$  surface.

observed experimentally. Even an elementary argument makes the appearance of the phonon gap plausible. The elementary cell of the  $p(2 \times 2)\text{O-Pt}(111)$  surface (fig. 3) contains four Pt and one O atom. Assuming that the oxygen sits in the three-fold hollow site, three Pt atoms are loaded with an O atom, while the fourth Pt atom is not. This situation is very similar to the classical two mass chain in solid state text books and makes the appearance of the energy gap plausible.

In order to fit the size of the gap energy we have to introduce three-body forces as mentioned in section 3. A simple next neighbour central force model only leads to an energy gap of 0.06 meV [22]. In fig. 2b we plot the theoretical dispersion curve obtained with the refined model including three-body interactions. We assume that the adsorbate sits 1.38 Å above the Pt(111) surface and that the Pt-O force constant is  $1.85 \times 10^5$  dyn/cm in order to fit the oxygen-platinum stretch frequency of 59 meV [23]. For the inter- and intra-layer Pt-Pt force constant we choose the same values as for the clean surface. The bond stretching force constant  $k' = 2.31 \times 10^4$  dyn/cm gives the best fit. The comparison between theory and experiment in fig. 2 shows that by including three-body forces the gap energy is reasonably reproduced (0.5 to 0.85 meV). The theoretically predicted gap centre is about 0.5 meV higher than the experimental one. The calculations also predict two additional dispersion-less modes at  $\hbar\omega = 10.0$  and 9.5 meV, which are indeed observed in the experiment. The fact that the higher one is experimentally seen only in the first quarter of the first Brillouin zone is yet unclear.

#### 4.3. The "oxide" phase

In contrast to the diffraction results from the ordered  $p(2 \times 2)$  oxygen phase, the so-called "oxide" phase shows no extra spots in He-diffraction patterns. The diffraction pattern is nearly identical to that of the clean Pt(111) surface. The height of the specular peak (zeroth order) is slightly decreased by

about 15%, which in view of the sensitivity of He atom scattering is an indication for a very smooth surface. The same behaviour was also noted by Poelsema [24]. A very sensitive measure of the degree of disorder present on the surface (i.e. the flatness of the surface) is the diffuse elastic peak in TOF spectra, which is due to scattering at defects of the surface such as steps, kinks or randomly distributed adatoms. From the comparison with TOF spectra taken from surfaces with well known defect densities, a quantitative measure for the surface smoothness may be inferred. We have compared the diffuse elastic intensity from the "oxide" phase with the diffuse elastic intensity from a nearly perfect surface (clean Pt(111), less than 0.1% defects) and a slightly disordered surface (5% disordered oxygen on top of the Pt(111) surface\*). The measured ratio of the diffuse elastic intensities from: clean Pt, "oxide", and from slightly disordered surface is 1:2:6, respectively; this clearly demonstrates the smoothness of the "oxide" surface. Note that the oxygen coverage of the surface with "oxide" is about 25% (Auger peak ratio of O(510 eV)/Pt(237 eV)  $\approx 0.4$ ), that is five times larger than that of the much rougher disordered oxygen surface.

The smoothness of the outermost layer of the "oxide" surface is in principle consistent with the subsurface location of the oxygen as well as with the existence of 3D  $\text{SiO}_2$  clusters in form of very sharp  $\text{SiO}_2$  needles on top of the platinum surface. A distinction between these two possibilities is obtained on the basis of the measured surface phonon dispersion of the "oxide" phase.

Previous measurements [25] have shown that the presence of disordered oxygen on metal surfaces (O/Ni(100)) has a negligible influence on the Rayleigh dispersion curve. The very small frequency decrease is mainly due to the mass loading effect of the adatoms. An estimate of this mass loading effect of disordered adsorbates on the phonon frequency may be given following the work of Benedek and Nardelli [26]. If the adatom mass  $m_a$  is much smaller than the substrate atom mass  $m_s$  and the adatom does not effect the coupling between the substrate atoms, the phonon frequency is modified as a function of coverage  $\theta$ :

$$\omega^2 = \omega_0^2 [1 - (m_a/m_s)\theta], \quad (3)$$

where  $\omega_0$  is the frequency of the clean and  $\omega$  the frequency of the adsorbate covered surface. In the case of the "oxide" phase the total coverage of oxygen is almost 25% and we calculate a frequency decrease of about 1% at the  $\bar{M}$  point. Eq. (3) is strictly valid only when the phonon frequency is given by  $\omega = (\Phi''/m_s)^{1/2}$ , where  $\Phi''$  is the second derivative of the pair potential. This is surely not true for the Rayleigh wave at the  $\bar{M}$  point. Nevertheless this simple formula yields reasonable estimates of the mass loading effect [25].

\* This disordered phase is produced by adsorption at 100 K, where the oxygen is immobile.

In fig. 1 the measured dispersion curve for the "oxide" phase along the  $\bar{\Gamma}\bar{M}$  azimuth is compared with the dispersion curve of the clean platinum surface. The phonon frequency of the "oxide" phase is substantially decreased ( $\sim 12\%$ ) at the  $\bar{M}$  point. Thus, in order to fit the dispersion curve we have to introduce a softening of the interlayer force constant  $k_{12}$  between the first- and second-layer Pt atoms in our lattice dynamical calculations. The best fit is obtained by  $k_{12} = 0.8k_{\text{bulk}}$ . This softening of  $k_{12}$  by about 30% with respect to the clean platinum surface can only be understood assuming that the most of the oxygen is located between the first and second layer Pt atoms, i.e. the "oxide" phase is a subsurface oxide.

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