Electron-Energy-Loss Spectroscopy of Ordered Oxygen Overlayers on Ru(001)

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High-resolution electron-energy-loss measurements and relevant theoretical calcula-
tions for the vibrational structure of ordered oxygen overlayers on the Ru(001) surface
are presented. The vibrational spectrum of the $p(2 \times 2)$ overlayer shows a single dipolar-
active mode above the substrate phonon band. Because of a reduction in symmetry of the
threefold adsorption site, however, the vibrational spectrum of the $p(1 \times 2)$ overlayer is
fundamentally different, showing two dipolar-active modes above the substrate phonon
band.

Well before spectroscopic methods were de-
veloped for their observation, the existence of
vibrations localized at clean metal surfaces had
been predicted and described in lattice-dynami-
cal calculations.[1] Recently, significant improve-
ments in the resolution and spectral range of
electron-energy-loss (EEL) measurements has
rendered feasible the observation of *substrate*
vibrational modes in dipolar scattering from or-
dered adsorbate overlayers on single-crystal met-
al surfaces.[2] The adlayer provides a dipolar
coupling[3] of the incident electrons to the surface
resonance modes, and the activity (or absence)
of these modes in EEL spectra has been shown to
delimit the overlayer periodicity and adsorption
site. For example, detailed structural informa-
tion concerning the adsites of oxygen overlayers
on Ni(100)[4] and Ni(111)[5] surfaces has been ob-
tained via a comparison of calculated and experi-
mental EEL spectra.

Here we present the results of an experimental
and theoretical study of oxygen overlayers on the
Ru(001) surface. Oxygen forms two ordered over-
layers on Ru(001)—a $p(2 \times 2)$ structure at a frac-
tional surface coverage of $\theta = 0.25$ and three inde-
pendent domains of $p(1 \times 2)$ overlayers rotated
120° with respect to one another at $\theta = 0.50$,[6,7]
both of which give "(2×2)" LEED patterns and
similar calculated I-V beam profiles.[8] The EEL
spectra of these structures show dipolar loss fea-
tures at frequencies *below* the maximum sub-
strate phonon frequency similar to surface reso-
nance modes discussed previously,[2,4,5] and indica-
tive of the twofold periodicity of both overlayers.
Furthermore, we show for the first time that the
dipolar activity of modes *above* the maximum
bulk phonon frequency of the metal depends on

the symmetry of the *combined* overlayer plus sub-
strate structure and in this case serves to dis-
tinguish unambiguously the $p(2 \times 2)$ and $p(1 \times 2)$
overlayers in EELS measurements.

The $p(2 \times 2)$ overlayer and its two-dimensional
Brillouin zone are illustrated in Fig. 1(a). The
oxygen threefold absorption site,[5,8,9] including
all neighbors in the surface and adsorbate layers,
has three reflection planes perpendicular to the
surface and hence has a point group symmetry
that is C_{3v}. Because of the large difference in
mass of the adsorbate oxygen atoms and the sub-
strate Ru atoms, vibrational modes associated
with motion of the adsorbate atoms have their
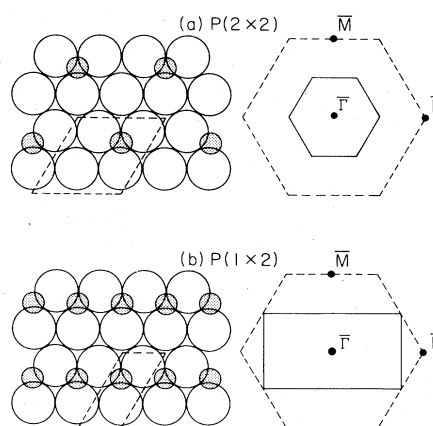displacements strongly localized in the adsorbate

FIG. 1. Overlayers and unit cells (left) and two-di-
mensional Brillouin zones (right) for (a) the $p(2 \times 2)$
structure and for (b) a single domain of the $p(1 \times 2)$
structure that oxygen forms on Ru(001). The dashed
lines represent the substrate Brillouin zone and the
solid lines represent the overlayer Brillouin zones.

layer at frequencies above the substrate phonon band. The substrate is therefore effectively "rigid" with respect to the adsorbate vibrations, and the three normal modes of the oxygen atom are the following: two degenerate modes of E symmetry, polarized strictly parallel to the surface plane and dipolar inactive[3]; and a single dipolar-active A_1 mode, henceforth referred to as $\nu_\perp$(Ru-O), polarized strictly perpendicular to the surface. Because of its twofold periodicity, the reciprocal-lattice vectors of the $p(2\times2)$ overlayer fold the $\bar{M}$ point of the substrate Brillouin zone into the $\bar{\Gamma}$ point. Thus, substrate modes at $\bar{M}$ should appear in the EEL spectrum if they couple to vertical motion of atoms in the threefold sites.[2,5]

In contrast, the threefold absorption site of the $p(1\times2)$ overlayer, a single domain of which is illustrated in Fig. 1(b), has only a single reflection plane perpendicular to the close-packed rows. Its symmetry is therefore lowered from C_{3v} to C_s, and the three normal modes of the oxygen atom are the following: a single, dipolar-inactive mode of A'' symmetry, polarized perpendicular to the reflection plane and parallel to the surface; and two dipolar-active modes of A' symmetry, polarized in the reflection plane. One of these, henceforth referred to as $\nu_\parallel$(Ru-O), involves motion of the oxygen atoms perpendicular to the close-packed rows and nearly (but not strictly) parallel to the surface, and the other is the perpendicular mode, $\nu_\perp$(Ru-O). The reciprocal-lattice vectors of the $p(1\times2)$ overlayer, shown in Fig. 1(b), fold the $\bar{M}$ point of the substrate Brillouin zone into the $\bar{\Gamma}$ point.[10]

To understand fully and interpret the data to be presented here, we have performed lattice-dynamical calculations to describe the vibrational structure of both the $p(2\times2)$ and the $p(1\times2)$ overlayers. In these calculations, the atoms interact only with their nearest neighbors through central forces. The details of the method used to calculate the inelastic scattering cross section for dipolar-enhanced modes have been presented previously,[5] and additional details specific to the $p(2\times2)$ and $p(1\times2)$ overlayers discussed here will be presented in a subsequent publication.[10]

We have calculated scattering amplitudes for the two overlayer structures with the oxygen atom at both threefold sites, i.e., the site over a second-layer Ru atom ("hcp" site) and the site over a second-layer vacancy ("fcc" site).[5] Oxygen-ruthenium bond lengths were estimated from a consideration of the covalent radii of O (0.73 Å)

and Ru (1.3 Å)[9] and adjusted, together with the Ru-O force constant, to give optimum agreement between theoretical and experimental results. The Ru-Ru force constant was obtained from a one-parameter fit to the maximum bulk phonon frequency of Ru, 310 cm^{-1}.[11]

It should be noted that the adsorption site (hcp versus fcc) only affects the calculated vibrational spectra below 310 cm^{-1}, where vertical motion of the oxygen adlayer couples differently to the various substrate modes for the two sites.[5,10] Calculated spectra for the two sites are nearly identical, differing significantly only in the relative intensities of modes below 310 cm^{-1}. Since these modes are near the limit of the experimental spectral range, no unambiguous conclusion concerning a preferred adsite for the oxygen can be drawn from the experimental data, and only the calculations for hcp sites are shown in the figures and discussed in the text.

The EEL spectrometer used for the measurements reported here and the vacuum system in which it is contained have been described previously.[12] The Ru(001) sample was prepared and cleaned by standard techniques.[6,7,13] EEL spectra were recorded in the specular direction ($\pm 1°$) with an incident beam energy of 4 eV, an elastically scattered count rate of 10^5 s^{-1}, and a resolution of 70 cm^{-1} full width at half maximum.

The experimental and calculated EEL spectra of the $p(2\times2)$ oxygen overlayer are shown in Figs. 2(a) and 2(b), respectively. For the calculation, the Ru-O bond length was chosen to be 2.05 Å giving a distance between the oxygen overlayer and the first substrate plane of $R_\perp = 1.3$ Å. Variation of $R_\perp$ between 1.2 and 1.6 Å did not affect the calculated spectrum significantly. The single feature above the substrate phonon band at 535 cm^{-1} in both spectra is the $\nu_\perp$(Ru-O) mode of oxygen in the threefold site.[13] The two narrow features in the calculated spectrum at 135 cm^{-1} and 260 cm^{-1} are surface resonance modes of the type discussed previously[4,5] and result, respectively, from the S_1 and S_2 surface phonons[14] at the $\bar{M}$ point of the surface Brillouin zone. The S_1 mode is indiscernible in the experimental spectrum, and S_2 appears as a shoulder near 250 cm^{-1}.

The experimental and calculated EEL spectrum of the $p(1\times2)$ overlayer are shown in Figs. 3(a) and 3(b), respectively. For the calculation, optimal agreement with the experimental data was obtained with a Ru-O bond length of 2.26 Å ($R_\perp = 1.6$ Å). Since measurements of the work-func-

FIG. 2. (a) Experimental and (b) theoretical EEL spectra for the $p(2 \times 2)$ oxygen overlayer.
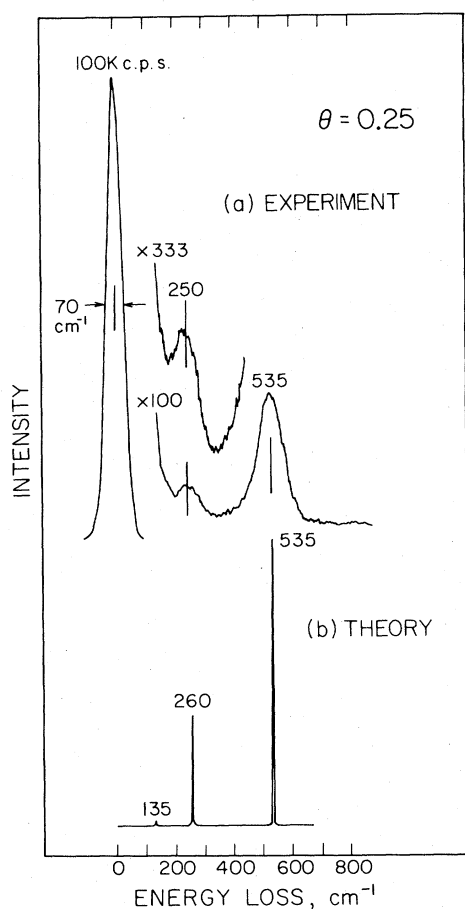
FIG. 3. (a) Experimental and (b) theoretical EEL spectra for the $p(1 \times 2)$ oxygen overlayer.

tion change upon adsorption indicate that the average static dipole moment per adsorbed atom is approximately 3 times as great for the $p(1 \times 2)$ as for the $p(2 \times 2)$ overlayer,[6] the use of different bond lengths in the calculations for the two overlayers is justifiable.

In addition to the $\nu_\perp$(Ru-O) mode at 585 cm^{-1}, the calculated spectrum shows a second feature above the substrate phonon band at 433 cm^{-1}. This is the $\nu_\parallel$(Ru-O) mode of A' symmetry in the $p(1 \times 2)$ overlayer, and results from motion of the oxygen atoms nearly parallel to the surface and perpendicular to the close-packed rows of the $p(1 \times 2)$ structure. A reduction of the adsorption-site symmetry from C_{3v} in the $p(2 \times 2)$ overlayer to C_s in the $p(1 \times 2)$ overlayer adds a new dipolar mode to the EEL spectrum. The vibrations of the oxygen atoms perpendicular and parallel to the surface are no longer decoupled, and the displacements of the substrate atoms no longer have triangular symmetry, but instead become vertical
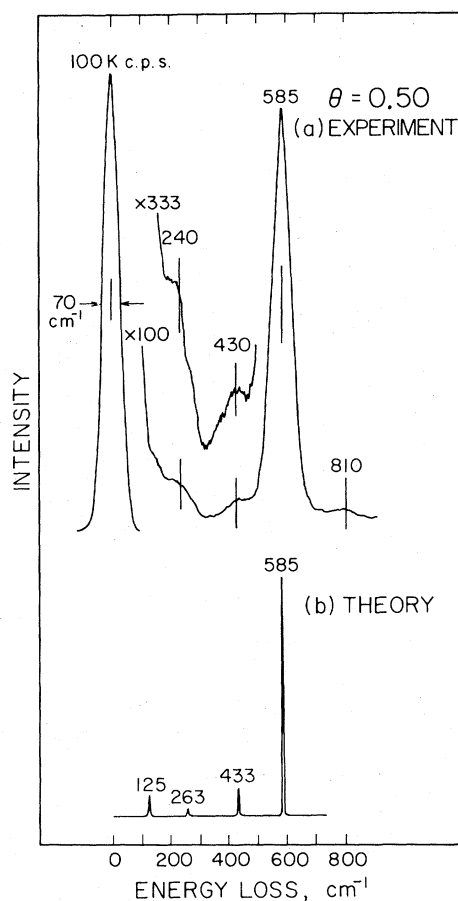
and horizontal "shear" motions. The corresponding dipolar-enhanced modes appear in the experimental spectrum at 585 and 430 cm^{-1}. The calculated spectrum also shows features at 125 and 263 cm^{-1}, again due to the surface phonons S_1 and S_2 at $\bar{M}$, respectively.[14] Although no feature near 125 cm^{-1} is discernible in the experimental spectrum, the S_2 mode appears near 240 cm^{-1}, and the weak feature at 810 cm^{-1} is due to the combination loss of S_2 and $\nu_\perp$(Ru-O).

Finally, it should be noted that the intensity of the 430 cm^{-1} mode depends more strongly on the *order* of the surface layer than on the coverage. In spectra recorded after annealing to 350 K to ensure surface order, the intensity of this mode increases with coverage from undetectable in the $p(2 \times 2)$, $\theta = 0.25$ spectrum, to the reproducible intensity shown in the $p(1 \times 2)$, $\theta = 0.50$ spectrum. In keeping with the symmetry arguments presented above, this increase in intensity occurs as oxygen adatoms fill the sites between those of the

$p(2\times2)$ overlayer. Addition of each adatom above $\theta = 0.25$ creates (on the average) two sites with broken symmetry and dipolar-active modes near 430 cm^{-1}.

In EEL spectra for *disordered* layers of oxygen adsorbed at 100 K, however, the 430 cm^{-1} mode appears for all coverages, but with intensity varying widely from spectrum to spectrum. Upon adsorption at 100 K, the oxygen adatoms are "frozen" into threefold sites at random, forming a disordered overlayer with some fraction occupying adjacent sites. In fact, the dipolar spectrum of *two atoms* on the surface, were it observable, would look very much like the $p(1\times2)$ spectrum if the two atoms happened to occupy adjacent sites, where interactions could lead to site-symmetry breaking. For coverages of disordered oxygen below $\theta = 0.25$, annealing to 350 K causes the mode at 430 cm^{-1} to vanish, as the overlayer orders into a configuration consistent with the $p(2\times2)$ structure.

To summarize, we have shown, via comparison of experimental to theoretical EEL spectra of $p(2\times2)$ and $p(1\times2)$ overlayers of oxygen on Ru(001), that the dipolar activity of the normal modes of a high-symmetry (threefold, C_{3v}) adsorption site can be modified by the presence of near neighbors in the adlayer which reduce the site symmetry (to C_s in this case).

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[1]See R. F. Wallis, Prog. Surf. Sci. 4, 233 (1973), and references therein.

[2]H. Ibach and D. Bruckmann, Phys. Rev. Lett. 44, 36 (1980); S. Andersson and M. Persson, Phys. Rev. B 24, 3659 (1981); S. Lehwald and H. Ibach, *Vibrations at Surfaces*, edited by R. Caudano, J. M. Gilles, and A. A. Lucas (Plenum, New York, 1982), p. 137.

[3]E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1972).

[4]T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. Lett. 46, 1469 (1981), and Phys. Rev. B 25, 883 (1981).

[5]T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. B 27, 4059 (1983).

[6]T. E. Madey, H. A. Engelhardt, and D. Menzel, Surf. Sci. 48, 304 (1975).

[7]S. L. Parrott, G. Praline, B. E. Koel, J. M. White, and T. N. Taylor, J. Chem. Phys. 71, 3352 (1979).

[8]C.-M. Chan and W. H. Weinberg, J. Chem. Phys. 71, 2788 (1979).

[9]M. Van Hove, in *The Nature of the Surface Chemical Bond*, edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979), Chap. 4.

[10]T. S. Rahman, to be published.

[11]R. R. Rao and J. V. S. S. N. Murthy, Z. Naturforsch. 34a, 724 (1979).

[12]G. E. Thomas and W. H. Weinberg, Rev. Sci. Instrum. 50, 497 (1979).

[13]G. E. Thomas and W. H. Weinberg, J. Chem. Phys. 69, 3611 (1978), and 70, 954 (1979).

[14]R. E. Allen, G. P. Allredge, and F. W. de Wette, Phys. Rev. B 6, 632 (1972).