

High resolution electron scattering from chemisorbed oxygen on the ruthenium (001) surface^{a)}

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Inelastic electron scattering spectroscopy has been used to measure energy-gain as well as energy-loss transitions of oxygen chemisorbed on the Ru(001) surface. The relative intensity of the energy-gain to the energy-loss transition was found to follow the expected Boltzmann distribution. The intensities of the inelastic peaks relative to the elastic peak were observed to increase with temperature. The temperature dependence and sources of experimental error are explained within the context of an approximate theory for the scattering of electrons from adsorbates on metal surfaces.

Electron energy loss spectroscopy is becoming increasingly popular as a probe of surface vibrations of adsorbed layers on metal surfaces. At temperatures for which $k_B T \gtrsim h\omega_0$, where ω_0 is the oscillator frequency, slow electrons also may be used to observe the emission of vibrational energy from adsorbed layers. Similar observations for surface phonons in *bulk* metal oxides were first made by Ibach¹ and recently by Dalmai-Imelik *et al.*²

In this work, we present measurements of emission in intensities from oxygen chemisorbed on the Ru(001) surface over a wide temperature range, and the first observations of energy-gain scattering from a chemisorbed layer. The intensity measurements are sensitive to the scattering angle and surface condition. To explain these effects and the observed temperature dependence, the results are interpreted in terms of a dipolar scattering theory.³⁻⁵

The electron energy distribution curves were obtained with a scattering system of the Kuyatt-Simpson type⁶ contained in a ultra-high vacuum system of which the base pressure is 4×10^{-11} torr. An electron beam with a kinetic energy of 4 eV was incident on the crystal at an angle of 62° with respect to the surface normal. The scattered beam was detected by a rotatable analyzer which was positioned approximately ($\pm 1^\circ$) in the direction of the specularly reflected beam, and which accepted electrons in a cone subtending a half-angle (θ_c) of 2.2° from that direction. The specularly reflected beam has a full angular width at half-maximum of approximately 2° , as measured by rotating the analyzer.

The Ru sample was cut and polished within 1° of the (001) plane using standard techniques.⁷ It was spot welded to Ta support wires and mounted on a Varian precision manipulator which had been modified to allow for resistive heating. The temperature of the crystal was monitored with a W-5% Re/W-26% Re thermocouple spot welded to its side. The crystal temperature was controlled using a programmable current source for resistive heating. A variable voltage reference was

compared to the thermocouple voltage to provide the temperature control.⁸ Since the current required to heat the crystal is on the order of 20 A, and a coaxial wiring arrangement is not practical, unacceptably high magnetic fields prohibit the simultaneous operation of the temperature controller and the electron spectrometer. Hence, the temperature controller was placed under the control of the computer (PDP 11/10) also used to control the spectrometer. The heater could be disabled momentarily under program control to permit operation of the energy analyzer and then re-enabled to allow the crystal temperature to recover. At the highest temperatures employed here (1000 K), it was necessary to heat 2 s for each second of data acquisition, and the sample cooled about 30 K during the 1 s of spectrometer operation. Better temperature control could be obtained at higher switching rates although this was not necessary in the results reported here.

Energy distribution curves have been obtained for saturation coverages of oxygen in the range 100 to 1000 K.⁹ In this work, the Ru surface was exposed to 10 L ($1 \text{ L} \equiv 10^{-6}$ torr s) of oxygen at 300 K and then heated to 1200 K. The resulting surface exhibited a single stretching frequency of 69 meV (range 67.5 to 70.5 meV), presumably due to a stretching mode of atomically bound oxygen. This variation in peak position is slightly more than usual experimental scatter (± 1 meV) and is due to the changing coverage of oxygen resulting from its diffusion into the bulk.¹⁰ The metal-oxygen stretching frequency varies from 64 meV at low coverage to 74 meV at saturation.⁹ The error in frequency is not significant to these results, and coverage effects are eliminated when the peak ratios are taken. The fact that only one stretching frequency was observed for oxygen on the Ru(001) surface (possibly due to the "dipole-normal selection rule")³ means that the atomic position of oxygen cannot be deduced from the energy-loss measurements in the specular direction. Since oxygen resides in threefold coordinated sites on the (111) surface of Ni,¹¹ this may also obtain on the Ru(001) surface. Dynamic low-energy electron diffraction calculations in our laboratory will decide this question unequivocally.

Representative spectra obtained at two temperatures are shown in Fig. 1. Between measurements at different temperatures, the oxygen-covered surface was heated to above 1000 K to remove all adsorbed gases

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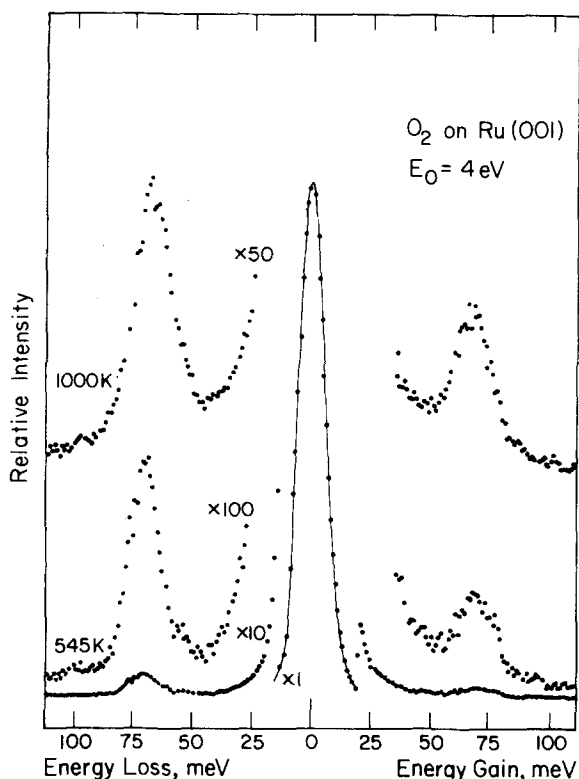


FIG. 1. Electron energy distribution curves obtained at 545 and 1000 K normalized to the elastic peak height.

except oxygen. The vibrational energy-gain peak was clearly observable at temperatures above 400 K. The areas of the inelastic peaks were obtained after subtracting the background intensity due to their proximity to the elastic peak. The intensity of the inelastic features relative to the intensity of the elastic peak is approximately 2% of that obtained on bulk metal oxides.^{1,2} This is expected due to the much larger relative inelastic cross section calculated for scattering from the surface phonon of an ionic material.^{1,3,5} The logarithm of the ratio of the inelastic intensities is plotted in Fig. 2 as a function of reciprocal temperature. The data are in good agreement with the theoretical line with a slope of 0.069 eV divided by the Boltzmann constant (k_B) and with an intercept of zero.

The cross section for inelastic electron scattering from surface vibrations in the forward direction has been calculated both semiclassically⁴ and quantum mechanically in the Born approximation.³ If temperature effects are considered, both calculations predict a cross section of the form

$$\frac{d\sigma}{d\Omega} = \frac{2C}{M\hbar\omega_0^2} (n+\gamma) \left(\frac{d\mu}{dz}\right)^2 \frac{(\theta \cos\alpha \cos\phi - \theta_0 \sin\alpha)^2 + \theta^2 \sin^2\phi}{(\theta^2 + \theta_0^2)^2 \cos\alpha} \quad (1)$$

in the approximation $\theta \ll 1$ and $\theta_0 \ll 1$. Here, θ and ϕ are polar and azimuthal angles, respectively, in a spherical coordinate system in which the specular direction lies along the z axis. M is the reduced mass of the oscillator, which together with its image has a dynamic dipole moment ($d\mu/dz$) perpendicular to the surface and a frequency ω . The electron is incident on the surface

at the angle α from the surface normal with velocity v . n is the occupation number at the temperature of interest, given by the Planck distribution $[\exp(\hbar\omega/k_B T) - 1]^{-1}$, and γ is one for energy loss and zero for energy gain. θ_0 is $\pm(\hbar\omega/mv^2)$, where m is the mass of the electron; θ_0 is positive for energy gain and negative for energy loss. The understood dependence on dipole density and surface reflectivity is included in the constant C , which is equal to $e^2 n_0 |R|^2$, where e is the electronic charge, n_0 is the surface unit cell density, and $|R|^2$ is the surface reflectivity. The simplifications leading to Eq. (1) do not allow for interadsorbate interactions,¹² or scattering of the electron from the short-range part of the molecular potential,¹³ but it is probably a reasonable form to use to examine the effects of temperature and angle on scattering near the specular direction.

The denominator of Eq. (1) is a strong function of θ , but it is independent of the sign of θ_0 and therefore has the same value for energy gain or energy loss. We see at once that the ratio of the energy gain intensity (I_{+1}) to the energy loss intensity (I_{-1}) is relatively insensitive to small errors in alignment. This is not true of the ratio of the inelastic to elastic peak intensities (I_{+1}/I_0). Since the inelastically scattered electrons are spread more in angle than the elastically scattered electrons, the ratio I_{+1}/I_0 will increase as the analyzer is moved out of the specular direction. If the acceptance cone of the electron energy analyzer is assumed to be centered on the specular direction, Eq. (1) can be compared directly with experiment by integrating over ϕ from 0 to 2π and over θ from 0 to the experimental cutoff angle θ_c (2.2° in this work).^{3,4} The result is

$$\sigma = \frac{\pi C (d\mu/dz)^2}{M\hbar\omega_0 v^2} \cos\alpha \left[\frac{(\tan^2\alpha - 2)\theta_c^2}{\theta_c^2 + \theta_0^2} + (\tan^2\alpha + 2) \ln\left(1 + \frac{\theta_c^2}{\theta_0^2}\right) \right] (n+\gamma) \quad (2)$$

This expression does not depend on the sign of θ_0 , so the ratio I_{+1}/I_{-1} is predicted to be

$$\frac{I_{+1}}{I_{-1}} = \frac{n}{n+1} = e^{-\hbar\omega/k_B T} \quad (3)$$

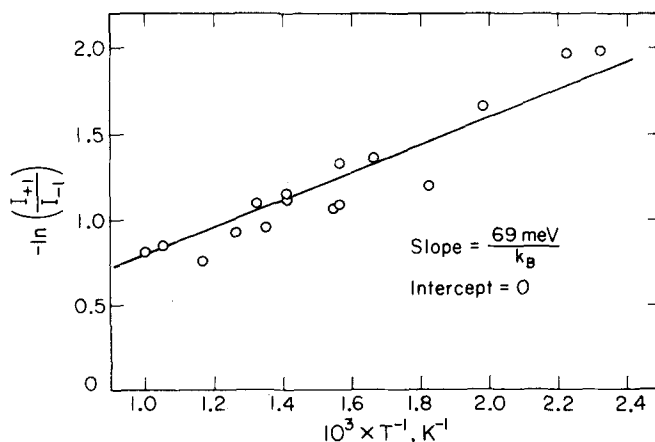


FIG. 2. The logarithm of the ratio of the energy-gain to energy-loss peak areas as a function of reciprocal temperature. The solid line is the theoretical dependence.

in agreement with the experimental results shown in Fig. 2. If the energy analyzer is not positioned exactly in the specular direction this ratio will, in addition, depend weakly on scattering angle. It would appear that movement of the Ru crystal on its support wires due to heating effects can explain the scatter in the data shown in Fig. 2.

Equation (1) also predicts that the ratios I_{+1}/I_0 and I_{-1}/I_0 will depend on temperature, and that they will be much more sensitive to alignment errors than the ratio I_{+1}/I_{-1} . Certainly, the data support qualitatively the conclusion that the inelastic intensity increases with temperature. However, the more severe alignment requirements for the accurate measurement of I_{+1}/I_0 prohibit a quantitative comparison. An additional, more fundamental, source of error in measuring the ratios, I_{+1}/I_0 at elevated temperatures is that the oxygen surface coverage may change. There is recent evidence that surface oxygen on Rh(111) and Ru(001) may diffuse into the bulk far below the desorption temperature.^{10,14}

In conclusion, vibrational scattering spectra have been measured for chemisorbed oxygen on Ru(001) over a wide range of surface temperature. The peak intensities are in agreement with the expected distribution functions.

The sources of error in these intensity measurements have been outlined in terms of the recent theories of electron scattering from vibrations in adsorbed layers.^{3,4}

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