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[12] Classical inertial waves can propagate at some angle with respect to the rotation axis, having a dispersion $\omega^2=(2\Omega\hat{m}\cdot\hat{z})^2$, where $\hat{m}$ is the wave-vector direction and $\hat{z}$ is the rotation axis. This dispersion does not have a minimum, however, the frequency going to zero as l increases at fixed k and $\hat{m}\cdot\hat{z}\rightarrow 0$.

[13] There is also an extremum of $\omega(l)$ at $l=0$. However, $|\partial^2\omega/\partial l^2|$ is relatively large there and, consistent with our observations, we do not expect an observable response peak at the corresponding frequency.

[14] In doing the lattice sums, following Ref. 6, we assumed a triangular array. Because, typically, l is a small fraction of a reciprocal-lattice vector, we do not believe that the results are sensitive to the particular lattice structure. The results depend weakly on the value of the core parameter a and we took it to be 2 Å.

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Observation of Surface Phonons on Ni(111) by Electron Energy-Loss Spectroscopy

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Surface phonons of metals at certain points of the two-dimensional Brillouin zone can be observed in electron energy-loss spectroscopy when suitable coupling is provided by commensurable adsorbate lattices.

Surface phonons on crystalline solids have been a matter of theoretical interest for quite some time.[1] Except for the acoustical surface modes and for the Fuchs-Kliewer surface modes[2] in ionic lattices, little experimental material is available on the subject because of the lack of appropriate spectroscopic tools. Recently we have shown[3] that surface vibrations along the step edges of the stepped platinum (111) surface can be excited by low-energy electrons via the dipole scattering mechanism.[4] The sufficiently high dynamic dipole moment was provided by the isolated position of the step atoms and their particular electronic properties. In this Letter we report on the observation of surface phonons of the flat Ni(111) surface. The appropriate dipole coupling with low-energy electrons specularly reflected from the surface is provided here by submonolayer amounts of oxygen, acetylene, and hydrogen.

The spectrometer was the same as described in previous papers.[5] Clean Ni(111) surfaces were prepared in ultrahigh vacuum by oxidation and reduction cycles and sputtering and annealing. The cleanness of the sample was controlled by Auger spectroscopy using a cylindrical mirror analyzer. A low-energy electron-diffraction (LEED) system to observe the surface structures was also available. In accordance with previous studies we found an ordered (2×2) adsorbate lattice with C_2H_2 (Ref. 6) and with H.[7] With oxygen we found two ordered adsorbate lattices,[8] $p(2\times2)$ and $(\sqrt{3}\times\sqrt{3})R30°$, corresponding to coverages of 0.25 and 0.33 monolayer, respectively. The vibrational spectrum for $p(2\times2)$ is shown in Fig. 1(a). The 580-cm^{-1} (72-meV) loss is the perpendicular vibration of oxygen located in a threefold site.[9]

A temperature of 275 K was chosen for record-

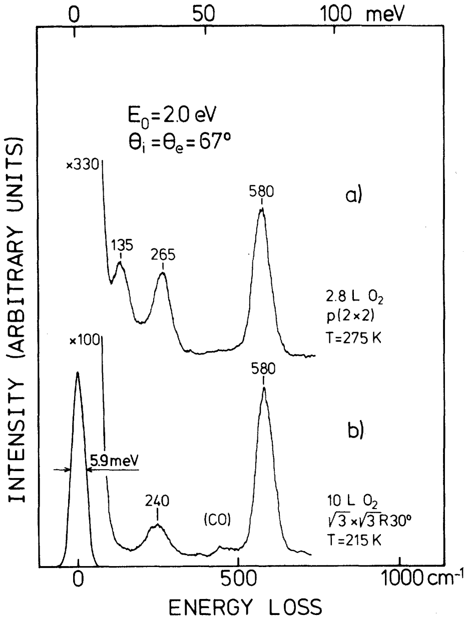

FIG. 1. Electron energy-loss spectra of Ni(111) with a $p(2\times2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ overlayer of oxygen, respectively.

ing this spectrum. The choice was made in order to have the temperature low enough to obtain a well-ordered $p(2\times 2)$ structure. We avoided lower temperatures since there a structural transition was noticed which involves the occupation of the other threefold site with the $p(2\times 2)$ structure retained.

In addition to the loss due to the oxygen vibration the spectrum Fig. (1a) shows losses at 135 cm^{-1} (16.7 meV) and 265 cm^{-1} (32.8 meV) which are in the range of the Ni phonon frequencies [$\omega_{\max} = 295$ cm^{-1} (36.6 meV)^{10}]. The loss at 135 cm^{-1} is directly connected to the $p(2\times 2)$ structure. This was established in two independent experiments: In the first experiment we dosed the sample with 2 L (where 1 L $= 10^{-6}$ Torr sec) of O_2. Cooling the sample from 450 K we observed the first diffuse half-order LEED spots at ~410 K which became sharp and intense below ~365 K. This order-disorder transition is reversible. Vibration spectra recorded with the same dosing and cooling program showed a diffuse background in the lower energy range which sharpened into the 135-cm^{-1} loss at ~365 K. In a second experiment we dosed the sample to higher coverages where the $p(2\times 2)$ pattern disorders and found that the 135-cm^{-1} loss disappeared.

The second loss behaves differently: It is observable also in the disordered state above 410 K (with $\omega = 245$ cm^{-1}). We also notice a frequency shift from 265 cm^{-1} down to 240 cm^{-1} when going from $p(2\times 2)$ to $(\sqrt{3}\times\sqrt{3})R30°$ (Fig. 1). In order to establish that the two losses at 135 and 265 cm^{-1} are due to substrate vibrations we performed further experiments with the (2×2) overlayers of acetylene and hydrogen at 150 K. The results in Fig. 2 show that the lower loss is observed at 140 cm^{-1} with both adsorbates; the higher one, however, is not excited with hydrogen, a point which will be rather significant in the interpretation below.

All losses occur in specular reflection only, which is characteristic of scattering by the perpendicular dipole moment associated with vibrations.^{4} Because of the scattering kinematics ($q_{\parallel} < 10^{-2}$ Å^{-1}) all losses correspond to the $\overline{\Gamma}$ point of the surface Brillouin zone. With ordered overlayers, however, one must distinguish between the surface Brillouin zone of the substrate surface and the surface Brillouin zone of the surface plus adsorbate. Since dipole coupling to the substrate is provided through the adsorbate lattice an excitation in the Γ point of the adsorbate atoms (in-phase motion of all adsorbate atoms) may well correspond to an excitation in other points than $\overline{\Gamma}$ of the substrate surface Brillouin zone. This is illustrated in Fig. 3(b) for the (2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ structures.

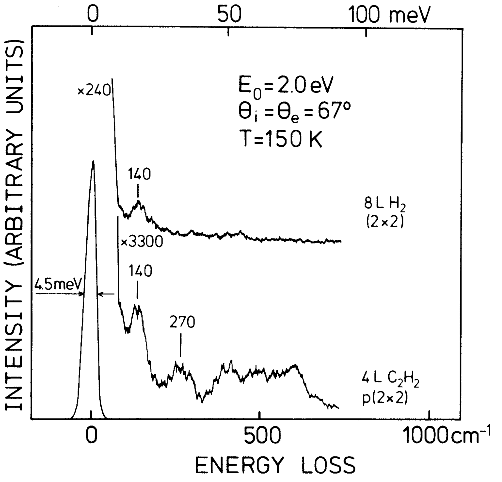

FIG. 2. Spectra of Ni(111) with other (2×2) overlayers. Upper curve, (2×2) overlayer of hydrogen. The ~270-cm^{-1} loss is not observed with H. Lower curve, $p(2\times 2)$ overlayer of C_2H_2. The higher losses are due to acetylene vibrations.

We have found the 135-cm^{-1} loss to be correlated to existence of the (2×2) structure. The loss is therefore a phonon excitation at $\overline{M}$ [Fig. 3(b)]. The losses at 265 and 240 cm^{-1} then correspond to $\overline{M}$ and $\overline{K}$, respectively. We believe that the phonons are not bulk phonons of the nickel lattice for the following reasons. (i) The different frequencies for the higher losses for the two ordered adsorbate lattices and disordered overlayers cannot be explained with bulk phonon excitation. (ii) There is no correlation between the observed loss energies and critical points of the bulk phonon spectrum.^{10} (iii) The excitation process is strictly localized to surface atoms; surface phonon excitation is therefore preferred. We therefore associate the observed losses with the surface phonons of the Ni(111) surface in $\overline{M}$ and $\overline{K}$, respectively.

This proposition is confirmed by comparing with rather extensive theoretical studies on the surface-phonon spectrum of a 21-layer slab by Allen, Alldredge, and de Wette^2 (AAdW). The potential used in this study was of the Lennard-Jones type. Although this is not a realistic potential for metals, qualitative conclusions should not be affected by the choice of the potential. For the (111) surface AAdW find five bands of surface

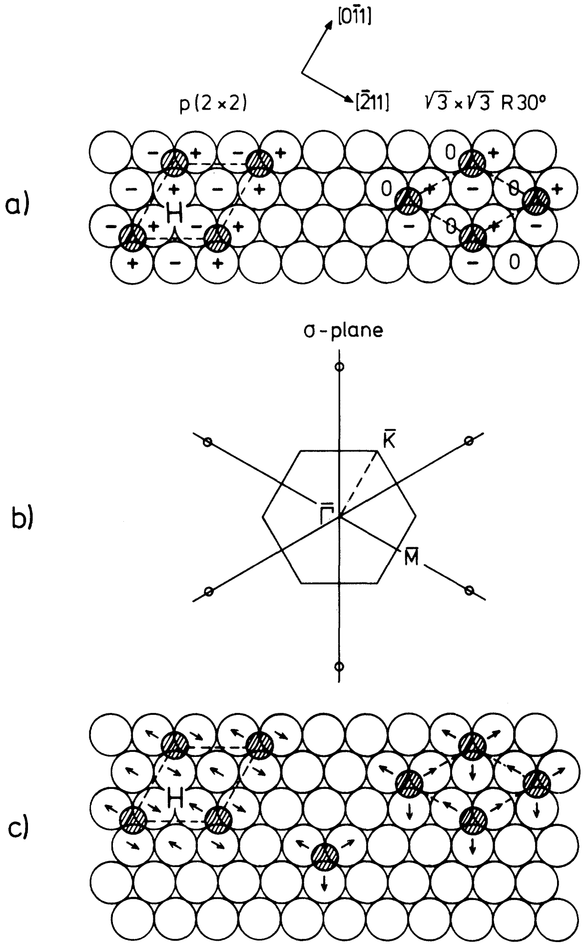

FIG. 3. (a) Structure of the $p(2\times 2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ oxygen overlayers. The plus, minus, and 0 signs depict the motion of the nickel atoms in a generalized Rayleigh wave S_1 in $\bar{M}$ and $\bar{K}$, respectively. Since the force field of the electron is perpendicular to the surface the Rayleigh wave can be excited in $\bar{M}$ with the $p(2\times 2)$ overlayer, but not, however, in $\bar{K}$ with the $(\sqrt{3}\times\sqrt{3})R30°$ structure. (b) Two-dimensional Brillouin zone of the (111) surface. Positions of substrate LEED reflexes are indicated by a 0. The LEED reflexes of the $p(2\times 2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ structures fall on $\bar{M}$ and $\bar{K}$. $\bar{\Gamma}$ points of the overlayers are therefore identical to $\bar{M}$ and $\bar{K}$ of the substrate for the two adsorbate layers, respecrively. (c) Motion of the nickel atoms in the surface phonon S_2 in $\bar{M}$ and $\bar{K}$, respectively. The polarization of S_2 is strictly longitudinal in $\bar{M}$. The motion in $\bar{K}$ is depicted to be consistent with the $(0\bar{1}1)$ symmetry plane and to point out the similarity to a localized vibration excited via adsorbate atoms [lower part of Fig. 3(c)]. The position of the extra hydrogen atom in the (2×2) cell is marked as H. With this hydrogen atom the excitation of S_2 in $\bar{M}$ is "symmetry forbidden" for a homogeneous perpendicular field, since the two hydrogen atoms move with a π phase shift.

modes (S_1–S_5). S_1 is a generalized Rayleigh wave which exists throughout the two-dimensional Brillouin zone. S_1 is primarily polarized perpendicular to the surface, and strictly so along $\bar{\Gamma}\bar{M}$. S_2 along $\bar{\Gamma}\bar{M}$ and $\bar{M}\bar{K}$ and S_4 along $\bar{\Gamma}\bar{K}$ are primarily longitudinal, S_3 is a shear-horizontal mode, and S_5 exists only in a narrow region around $\bar{K}$. In Fig. 3 we depict the motion of the nickel atoms in S_1 and S_2 in $\bar{M}$ and $\bar{\Gamma}$, respectively. As mentioned, the surface phonon S_1 is polarized perpendicular to the surface in $\bar{M}$ because of the $(0\bar{1}1)$ symmetry plane.[11] Scaling the frequencies of the crystal slab of AAdW to the maximum frequency of the LA bulk phonon would predict for S_1 a frequency of 110 cm^{-1} in $\bar{M}$, in reasonable agreement with the observed loss. In further calculations AAdW also show that an adsorbed layer of light atoms has only a small effect on the frequency of S_1. A closer inspection of Fig. 3 also explains why this mode can be excited with the (2×2) adsorbate lattice. S_1 at $\bar{M}$ corresponds to a vibration where alternate $[0\bar{1}1]$ rows of Ni atoms move with a π phase shift perpendicular to the surface. This mode can be excited via a perpendicular force field on a (2×2) lattice since the $(\bar{2}11)$ plane perpendicular to the surface along the adsorbate rows is not a symmetry plane. Vice versa the S_1 mode at $\bar{K}$ cannot be excited with the $(\sqrt{3}\times\sqrt{3})R30°$ lattice because $(0\bar{1}1)$ is a symmetry plane. Thus the force on the nickel atoms moving with alternate phases is equal. The excitation of S_1 at $\bar{K}$ is therefore "symmetry forbidden" insofar as electron spectroscopy selects the perpendicular excitation over the parallel, which it does by roughly a factor of 10^2–10^3.[12] Because of the reasonable agreement in frequency and the correct symmetry we identify the observed loss at 135–140 cm^{-1} with the excitation of the generalized Rayleigh wave S_1 in $\bar{M}$.

We now turn to the interpretation of the losses at 265 and 240 cm^{-1}, respectively. Similar losses have also been observed with a densely packed CO layer[13] and a $p(2\times 2)$ oxygen layer on Ni(100) (Ref. 14) and attributed to phonon losses; however, they were not studied in detail. We associate these losses with the excitation of S_2 at $\bar{M}$ and $\bar{K}$. As can be seen by inspection of Fig. 3(c) a perpendicular dipole moment for this mode is provided by the adsorbate atoms. The calculations of AAdW[11] predict frequencies of 265 and 240–245 cm^{-1} in $\bar{M}$ and $\bar{K}$, respectively, in very good agreement with the observed result.

As we have mentioned, the 245-cm^{-1} loss was also observed for disordered oxygen layers. It shifts to 265 cm^{-1} in ordering into the $p(2\times 2)$ lattice. For isolated adsorbate atoms only vibrations of A_1 symmetry of the C_{3v} point group [Fig. 3(c)] are excited. In the process of ordering into a $p(2\times 2)$ lattice the motion of the nickel atoms must change orientation to build up the strictly longitudinal surface phonon S_2 in $\bar{M}$. This could explain the observed frequency shift in ordering.

Finally, we comment on the observation that with hydrogen only the 140-cm^{-1} loss is observed. According to a very detailed experimental and theoretical LEED analysis of the system,[7] the (2×2) lattice of hydrogen corresponds to a coverage of 0.5 and is therefore not primitive. The suggested position for the extra hydrogen atoms is marked by an H in Figs. 3(a) and 3(c). We can easily see that this extra hydrogen atom makes the excitation of S_2 [Fig. 3(c)] (nearly) symmetry forbidden: Inspection of the motion pattern shows that the perpendicular components of the motion of the two hydrogen atoms forming the lattice base have a π phase shift relative to each other in in the case depicted in Fig. 3(c), while they are in phase in the S_1 mode shown in Fig. 3(a). (Here we have neglected the fact that the two hydrogen sites are not strictly equivalent.) The absence of the S_2 loss in the case of the (2×2) hydrogen lattice therefore is not only consistent with our interpretation of the observed losses as being surface phonon excitations, but also provides additional confirmation to the structural model proposed by Christmann *et al.*[7] Since alternative models discussed in this paper would not make the S_2 excitation "symmetry forbidden." In summary, we have shown that the excitation of surface phonons in certain points of the surface Brillouin zone is possible via electron energy-loss spectroscopy when ordered adsorbate structures provide the coupling. The new method should be particularly interesting for materials and surfaces where large commensurable adsorbate lattices with different lattice constants have been observed. It should be pointed out further that—via the dipole moment—the phonons should be observable also in far-infrared reflection spectroscopy.

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