

Dispersion of Adsorbate Vibrational Modes—the $c(2 \times 2)$ Oxygen Overlayer on Ni(100)J. M. Szeftel,^(a) S. Lehwald, and H. Ibach*Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich,
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The dispersion of surface vibrational modes associated with the $c(2 \times 2)$ adsorbate layer of oxygen on Ni(100) is measured throughout the two-dimensional Brillouin zone along the [110] direction. Two oxygen modes and two nickel surface phonons are observed. A lattice-dynamical analysis gives good agreement with the data when the oxygen atom sits at ~ 0.9 Å above the nickel surface at the fourfold hollow site.

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The understanding of the lattice dynamics of clean and adsorbate-covered surfaces requires the determination of the dispersion relations of surface modes in the two-dimensional Brillouin zone. Substantial progress has already been achieved with the measurement of the dispersion of acoustical surface modes using inelastic scattering of He atoms¹ and recently also low-energy electrons.² For physical reasons which lie in the nature of the scattering process it was not possible, however, to detect optical surface modes and modes within adsorbate layers on surfaces with the method of He scattering.³ In this Letter we show that electron scattering is not subject to the same constraints and we report the first measurement of the dispersion relation of adsorbate modes. We have chosen the $c(2 \times 2)$ oxygen layer on a Ni(100) surface to demonstrate the method since this is one of the most intensively investigated adsorption systems, and experimental procedures to prepare the ordered structure are well established. The experimental data are analyzed within the framework of a lattice-dynamical model. The analysis will allow us to make contact with the structural data for this surface system.

Our single-crystal nickel surfaces were prepared in the conventional way by use of cycles of heating and sputter cleaning in order to leach out

the sulfur and remove the carbon. Ordered overlayers of oxygen were produced by exposing the surface to oxygen at room temperature via a calibrated dosing system followed by annealing the surface to ~ 420 K for about 5 min. This procedure had to be performed with some care since underexposure leaves residues of the primitive (2×2) overlayer on the surface while overexposure leads to islands of oxide growth. Proper $c(2 \times 2)$ overlayers are characterized with electron energy-loss spectroscopy by the complete absence of an elastic diffracted beam at the \bar{X} point of the substrate Brillouin zone and also the absence of any vibrational loss at 545 cm^{-1} (in specular reflection) which would be indicative of the formation of nickel oxide.

Electron energy-loss spectra were obtained by use of a double-pass electron energy-loss spectrometer⁴ capable of employing a wide range of impact energies. This capability is important in order to optimize the inelastic signal from a certain phonon dispersion branch, and also to differentiate between surface phonons of different polarization, as we shall see. Earlier theoretical calculations of inelastic electron scattering for a different adsorbate system showed⁵ large variations in the cross sections as a function of energy and scattering angle. As no such calculations were at hand for Ni(100)- $c(2 \times 2)$ O, we had to ex-

plore a rather wide range of energies (4–200 eV) for each q_{\parallel} , for optimum intensities.

Dispersion relations are measured along the $\bar{\Gamma} \rightarrow \bar{X}$ ([110]) direction with the analyzer set to a fixed polar angle of 70° from the normal and the scattering plane aligned with the (110) plane of the sample. The polar angle of the incident beam was set to obtain the desired q_{\parallel} . Sample spectra for certain values of q_{\parallel} , taken at three different impact energies, are shown in Fig. 1. Peak positions of energy losses are displayed as data points in Fig. 2, along with a comparison with theory as discussed below. The upper two branches in Fig. 2 arise from vibrations associated with two degrees of freedom of the oxygen atoms. The lower two branches are nickel surface resonance modes of the type discussed earlier.⁶

By comparing the dispersion branches in Fig. 2 with the sample spectra in Fig. 1 we can see that depending on q_{\parallel} and E_0 , modes from a specific

branch appear predominantly in the spectrum. In Fig. 1(c), for example, the oxygen mode of the lower branch appears only as a slight shoulder on the loss caused by the mode of the upper branch. Vice versa only the mode of the lower oxygen branch appears in the spectrum in Fig. 1(d). The total set of data points in Fig. 2 was obtained by systematically exploiting the different cross sections of differently polarized modes for a large number of impact energies.

The results in Figs. 1 and 2 also show that only one mode is observed at $\bar{\Gamma}$ and only two out of three oxygen-associated dispersion branches along the $\bar{\Gamma}-\bar{X}$ direction. These two results are consistent with the generally accepted position of the oxygen atom in a fourfold hollow site: As the local symmetry is then C_{4v} , the oxygen modes at $\bar{\Gamma}$ are polarized strictly perpendicular (the A_1 mode) and parallel (the E mode) to the surface. The selection rules^{5,7} require that only the A_1

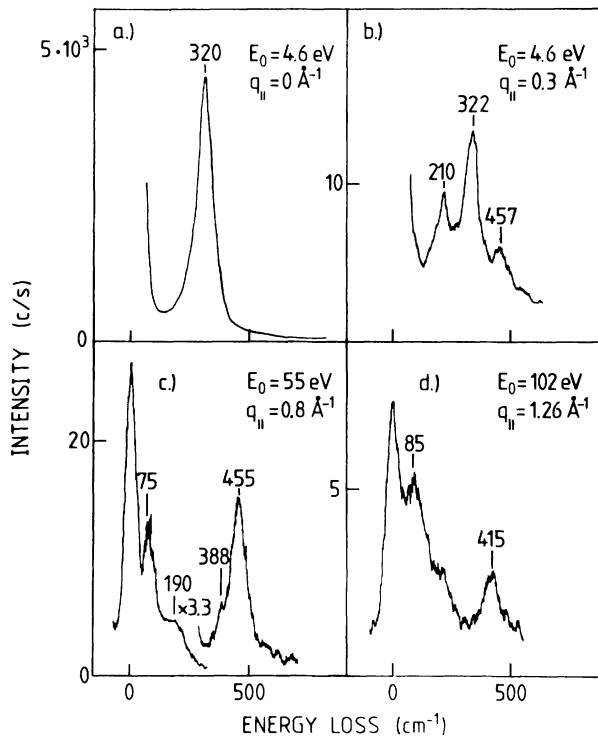


FIG. 1. Sample spectra for various q_{\parallel} and impact energies E_0 . Spectrum (a) shows the vertical motion of the oxygen atom at $\bar{\Gamma}$. Here the scattering mechanism is dipole scattering and the count rate is consequently large. The absence of a second feature in this spectrum is indicative of a high-symmetry site. Spectra (b)–(d) illustrate the varying sensitivity of modes of different polarization as a function of the scattering kinematics.

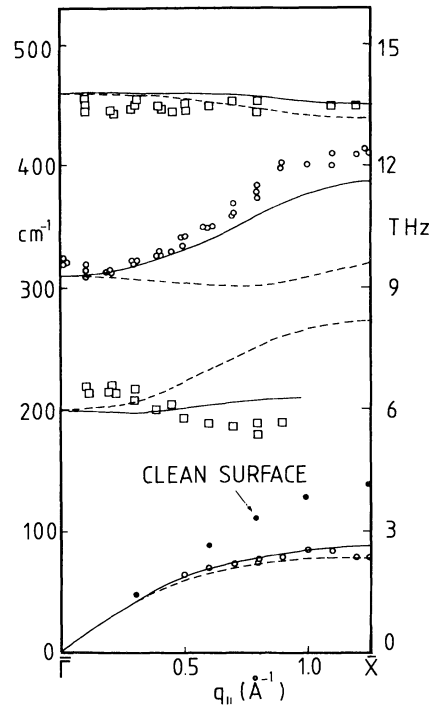


FIG. 2. Dispersion of adsorbate and substrate surface phonons for a Ni (100) surface with a $c(2 \times 2)$ oxygen overlayer. The solid-circle line is the S_4 -phonon dispersion for the clean surface (Ref. 2). Modes with predominantly perpendicular and predominantly parallel polarization are distinguished by use of circles and squares for the data points, respectively. The solid lines are theoretical calculations for oxygen 0.9 Å above the fourfold site, and the dashed lines the low-lying oxygen picture discussed in earlier papers (Refs. 6 and 9).

mode is observable at $\bar{\Gamma}$. Along the $\bar{\Gamma}$ - \bar{X} direction the symmetry reduces to C_s with the (110) plane being the plane of symmetry. Accordingly the E mode at $\bar{\Gamma}$ splits into two branches, one odd and one even with respect to the (110) plane. The branch which is A_1 at $\bar{\Gamma}$ also belongs to the even representation along the $\bar{\Gamma}$ - \bar{X} direction. The selection rules for impact scattering⁵ now require that the odd modes be forbidden when the scattering plane is aligned along the plane of symmetry. Consequently the branches in Fig. 2 must be even.

The reasoning also applies to the nickel surface resonance in Fig. 2. These resonances can exist despite being partly placed within the bulk continuum, because the bulk modes in the considered energy and momentum space belong to the odd representation so that the surface resonances cannot couple with the bulk modes. The surface resonance ceases to be a sharp feature in the spectra for $q_{\parallel} \geq 0.8 \text{ \AA}^{-1}$ since it dives into the bulk continuum⁸ of the same parity there. The acoustical surface branch is the equivalent of the S_4 mode of the clean surface,² although substantially reduced in frequency near \bar{X} . The reduction is distinct only for the $c(2 \times 2)$ oxygen overlayer whereas for a $p(2 \times 2)$ overlayer we find that the reduction is marginal.

We have carried out a theoretical analysis of large-angle electron scattering from the $c(2 \times 2)$ oxygen overlayer on Ni(100) by extending our earlier theory to large wave vectors.⁹ The model is supplemented by direct lateral interactions of central-force character between nearest-neighbor oxygen atoms. The results are summarized in Fig. 2. The solid curves are calculated with the oxygen placed 0.9 \AA above the surface in the fourfold hollow site, with the oxygen-Ni force constant adjusted to fit the 310-cm^{-1} feature at $\bar{\Gamma}$, and the dashed lines are predictions for the low-lying oxygen configuration discussed earlier.^{6,9} In the latter case, angle-bending interactions used previously⁹ were appended, to bring both high-frequency modes (parallel and perpendicular) into accord with the data at $\bar{\Gamma}$.

Consider first the two high-frequency surface phonons. With oxygen at 0.9 \AA , the choice of a single force constant fits both modes nicely at $\bar{\Gamma}$. This constant, while reduced substantially from that appropriate to the $p(2 \times 2)$ structure (almost a factor of 2 smaller), is not anomalously soft. We find that it lies between that appropriate to solid NiO and that of the diatomic molecule NiO. Lateral interactions affect the perpendicular sur-

face phonon branch modestly (not at all at either $\bar{\Gamma}$ or \bar{X}), and the simple model produces very large dispersion in this branch as observed. The dispersion in this branch thus arises almost entirely from indirect interactions between oxygen atoms, induced by motions of the substrate atoms. Lateral interactions leave the parallel branch unaffected at $\bar{\Gamma}$, but produce a 35-cm^{-1} upshift at \bar{X} , to give a nearly flat branch similar to the data. The low-lying oxygen model provides a qualitatively incorrect description of the lower branch, without further and likely substantial modification. This is strong evidence in favor of the 0.9-\AA position, in our view.

The feature just near 200 cm^{-1} is a resonance mode which appears in the data near $\bar{\Gamma}$; it appears in earlier calculations⁹ in the spectral density for parallel motions of the oxygen overlayer, and the present theoretical analysis (0.9-\AA position) shows its dispersion to be modest, and it progressively broadens and disappears as \bar{X} is approached, as observed. Once again, the low-lying oxygen model provides a poor account of this feature, with far too much dispersion and persistence of the feature all the way to \bar{X} .

As discussed earlier, the data show a dramatic softening of the S_4 mode at and near \bar{X} . It softens from 135 cm^{-1} on the clean surface (at \bar{X}) to 80 cm^{-1} . The mode frequency at \bar{X} is unaffected by changes in the intralayer couplings between Ni nearest neighbors in the outermost layer, but it is sensitive to interactions between Ni atoms in the first and the second layers. This force constant must be reduced to 30% of the bulk value to generate the theoretical curves, suggesting substantial outward relaxation of the outermost Ni layer.

Finally, in our calculations of the spectral density for perpendicular motion of the oxygen, we find a surface resonance mode at 166 cm^{-1} at \bar{X} , which is not present in the data. Since all of the signals reported here are weak, this feature may be absent in the data because the matrix element for coupling to it may be small. This point is under further study.

With this exception, the data are well accounted for by the nearest-neighbor central-force model with the oxygen at 0.9 \AA , supplemented by nearest-neighbor lateral interactions between adsorbates of central-force character. The data presented here also provide strong evidence for a marked outward relaxation of the outermost Ni layer; the frequency shift of the S_4 mode at and near \bar{X} is dramatic, with the consequence that

this conclusion is not model dependent. This and the substantial change in the O-Ni force constant suggest substantial changes in electronic structure as one moves from the $p(2 \times 2)$ with increasing coverage. The physics of this system remains intriguing.

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¹G. Brusdeylins, R. Bruce Doak, and J. P. Toennies, Phys. Rev. Lett. 46, 437 (1981).

²S. Lehwald, J. M. Szeftel, H. Ibach, T. S. Rahman, and D. L. Mills, Phys. Rev. Lett. 50, 518 (1983).

³J. P. Toennies, private communication.

⁴H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982), p. 16 ff.

⁵S. Y. Tong, C. H. Li, and D. L. Mills, Phys. Rev. B 24, 8906 (1981).

⁶T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. Lett. 46, 1469 (1981), and Phys. Rev. B 25, 883 (1982).

⁷Ibach and Mills, Ref. 4, p. 116 ff, and p. 171.

⁸R. J. Birgenau, J. Cordes, G. Dolling, and A. D. B. Wood, Phys. Rev. 136, A1359 (1964).

⁹T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. B 25, 883 (1982).

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