

Electron-Energy-Loss Spectroscopy and Oxygen Overlayers on the Ni(100) Surface

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We present an analysis of the electron-energy-loss spectra produced by dipole scattering from lattice vibrations of the $p(2 \times 2)$ and $c(2 \times 2)$ oxygen overlayer on the Ni(100) surface. We conclude that the distance between the oxygen layer and the Ni surface is very much smaller for the $c(2 \times 2)$ overlayer than for the $p(2 \times 2)$, in accord with a recent suggestion by Upton and Goddard.

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Quite recently, electron-energy-loss spectroscopy has been employed to study vibrations of ordered overlayers of oxygen on both the Ni(100) and the Ni(111) surfaces.¹ The experiments explore small angle scattering events, where electric dipole interactions provide coupling to the surface vibrations.² The data are intriguing, since the frequency regime below the maximum vibrational frequency of the substrate (295 cm^{-1} for Ni) has been explored, and well-defined structures are observed there. In this Letter, through use of a simple lattice-dynamical model which contains no adjustable parameters, we wish to show that these data have striking implications for the structure of the ordered overlayers of oxygen on the Ni(100) surface. The *ab initio* calculations of Upton and Goddard³ provide our basic input parameters, and our success in fitting the data shows their calculated potential-energy curves can be used to generate accurate force constants that may be incorporated into lattice-dynamical models.

This Letter describes a theoretical analysis of spectra taken from the $c(2 \times 2)$ and the $p(2 \times 2)$ oxygen overlayers on the Ni(100) surface. We obtain an excellent account of both spectra, but only if we let the $c(2 \times 2)$ layer be placed very much closer to the surface than the $p(2 \times 2)$ layer. Upton and Goddard,³ who have carried out *ab initio* calculations of the interaction energy between an oxygen atom and a finite cluster of Ni atoms arranged to mimic the semi-infinite Ni crystal with (100) surface, have conjectured that the $c(2 \times 2)$ layer is drawn in tightly against the Ni(100) surface.

The picture offered by the present analysis is very different from that deduced from low-energy electron-diffraction (LEED) data,⁴ which have been argued to imply that both the $p(2 \times 2)$ and the $c(2 \times 2)$ overlayers lie a distance of 0.9 \AA above the Ni surface. We note that recent x-ray photoemission spectroscopy studies of the $c(2 \times 2)$

layer of oxygen on Ni(100) also offer support for the picture proposed here,⁵ and of the conjecture by Upton and Goddard.

In our lattice dynamical model, all atoms are assumed to interact with only nearest neighbors through central-force interactions. This picture gives quite a good fit to the phonon spectrum of the bulk Ni crystal, and we determine the one parameter that enters the description of lattice dynamics in Ni by fitting the maximum phonon frequency of 295 cm^{-1} . The atoms in the oxygen overlayer are placed in the hollow site of fourfold symmetry, and each couples only to its four nearest-neighbor Ni atoms via central-force interactions. The work of Upton and Goddard³ provides a value for the distance R_{\perp} for the equilibrium position of the oxygen atom above the Ni(100) surface, along with the curvature of the potential-energy curve around the minimum, when the oxygen moves in the direction normal to the surface. The value of R_{\perp} allows one to compute $\sin \alpha$, where α is the angle between the normal to the surface, and a line directed to a nearest-neighbor Ni atom in the surface layer, assumed located at the site appropriate to a bulk Ni atom (see below). The potential energy for motion of the oxygen normal to the surface with Ni atoms fixed is then $\frac{1}{2} k u^2$, with u the displacement from equilibrium, $k = 4 \varphi'' \cos^2 \alpha$, and φ'' the derivative of the assumed two-body central-force potential between an oxygen and a nearest-neighbor Ni atom. Thus, the value of k provided by the *ab initio* calculations of Upton and Goddard³ combined with their R_{\perp} allows one to determine φ'' , and from this the dynamical matrix required for the lattice-dynamical analysis of the model. In all the spectra we calculate, once the value of φ'' is found, the substrate atoms participate fully in the motion.

Let $e_{\alpha}^{(s)}(\vec{Q}_{\parallel}, l_z)$ be the eigenvector of a normal mode of the structure with wave vector \vec{Q}_{\parallel} parallel to the surface. Here s is the remaining

quantum numbers required to designate the mode (surface phonon, bulk phonon), α is a Cartesian coordinate which specifies the direction of the displacement, and l_z the layer number with $l_z=1$ the adsorbate layer. Central to the analysis of the electron-energy-loss spectra are lattice-dynamical Green's functions of the form⁶

$$U_{\alpha\beta}(l_z, l_z'; \bar{Q}_{\parallel}, z) = \sum_s \frac{e_{\alpha}^{(s)}(\bar{Q}_{\parallel}, l_z) * e_{\beta}^{(s)}(\bar{Q}_{\parallel}, l_z')}{\omega_s^2(\bar{Q}_{\parallel}) - z^2}, \quad (1)$$

with $\omega_s(\bar{Q}_{\parallel})$ the frequency of the mode in question and z a complex frequency. We also require the spectral densities

$$\rho_{\alpha\beta}(l_z, l_z'; \bar{Q}_{\parallel}, \omega) = (\omega/\pi i) [U_{\alpha\beta}(l_z, l_z'; \bar{Q}_{\parallel}, \omega + i\epsilon) - U_{\alpha\beta}(l_z, l_z'; \bar{Q}_{\parallel}, \omega - i\epsilon)]. \quad (2)$$

For the model outlined above, we have obtained closed analytic forms for these Green's functions when $\bar{Q}_{\parallel} = 0$ for both the $c(2 \times 2)$ and the $p(2 \times 2)$ overlayer of oxygen on Ni(100). It is these spectral densities that are required to describe the small-angle scattering observed in the dipole regime and studied in the experiments described above. We may embellish the basic model by allowing for relaxation of the outermost atomic layer of Ni atoms; this is done by modifying the relevant force constants. For the case of the $p(2 \times 2)$ oxygen overlayer, we allow in addition for an outward static "breathing" distortion of the square of Ni atoms which lie just below each oxygen. For Ni, we believe the influence of such static relaxations on the energy-loss spectra are small, and can be ignored. Their influence is explored in a longer publication that will appear elsewhere.⁷

In Fig. 1(a), we reproduce the small-angle energy-loss spectrum measured for the $p(2 \times 2)$ structure. There are three loss peaks. The one at 430 cm^{-1} , well above the Ni phonon bands, is the "local mode" of the oxygen atoms, polarized normal to the surface; in the dipole dominated regime, a selection rule⁸ allows scattering only by dynamic dipole moments normal to the surface. In addition to the 430-cm^{-1} feature, two additional lines appear within the Ni phonon bands, one at 180 cm^{-1} and one at 230 cm^{-1} .

In Fig. 1(b), we show our calculated energy-loss spectrum. We have assumed, following Goddard *et al.*, that the $p(2 \times 2)$ layer lies 0.88 \AA above the surface. For this configuration, their *ab initio* calculations give 370 cm^{-1} for the combination $(k/M_0)^{1/2}$. This would be the frequency of the oxygen local mode, in the limit where the substrate mass is assumed infinite. The finite mass of the Ni atoms shifts this feature up to 445 cm^{-1} for the $p(2 \times 2)$ structure, a value very close to that obtained earlier⁹ for an isolated oxygen atom above the hollow site of fourfold symmetry. We

also find a doublet within the Ni phonon bands, with frequencies (180 cm^{-1} , 245 cm^{-1}) very close to those observed. These are not surface phonons, but resonance modes. One of these has its origin in a true surface phonon, twofold degenerate, on the *clean* Ni(100) surface. There is a surface mode within a gap in the bulk phonon spectrum at the point X of the two-dimensional Brillouin zone of the clean surface. This mode is the S_6 mode discussed first by Allen, Alldredge, and deWette.¹⁰ Its role in the energy-loss spectroscopy of the clean (100) surface and sensitivity to force-constant changes has also been discussed. [See Fig. (3) and Fig. 9(b) of Ref. 6]. With the $p(2 \times 2)$ overlayer present, the point X is folded back to the point Γ of the new Brillouin zone, and one of the two S_6 modes excites vertical motion in the oxygen adlayer, to become dipole active. The second S_6 mode fails to couple for sym-

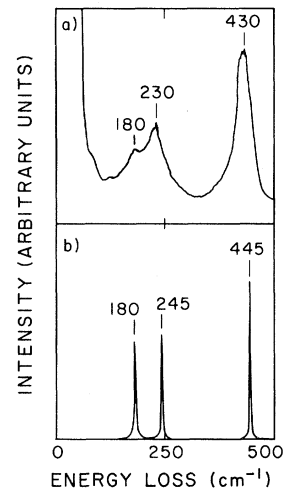


FIG. 1. (a) The data of Ibach and Bruchmann on the energy-loss spectrum of electrons scattered from the $p(2 \times 2)$ overlayer of oxygen on Ni(100). (b) The theoretical loss spectrum generated by the analysis described in the text. The oxygen is a distance $R_{\perp} = 0.88 \text{ \AA}$ above the surface.

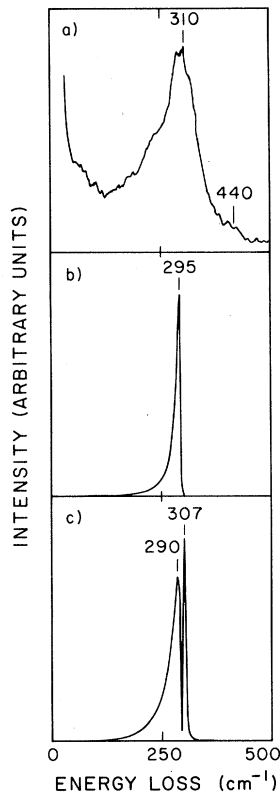


FIG. 2. (a) The data of Ibach and Bruchmann on the energy-loss spectrum of electrons scattered from the $c(2 \times 2)$ overlayer of oxygen on Ni(100). (b) The theoretical spectrum calculated as described in the text, for $R_{\perp} = 0.26 \text{ \AA}$. (c) The theoretical spectrum calculated as described in the text, for $R_{\perp} = 0.27 \text{ \AA}$.

metry reasons. With point X folded back to point Γ , the S_6 mode lies in the phonon continuum at Γ in the new zone, so it becomes a "leaky surface mode" or resonance mode, to use the terminology of bulk lattice dynamics. This is the origin of the 245-cm^{-1} line, and the 180-cm^{-1} feature is a second resonance mode of the surface structure.

In Fig. 1(b), and elsewhere in this paper, we assume the scattering is produced by motion of the surface layer of Ni atoms against the oxygen overlayer. If $u_0^{(\perp)}$ is the displacement of an oxygen atom normal to the surface in a mode with wave vector $\vec{Q}_{\parallel} = 0$, and $u_i^{(\perp)}$ ($i = 1, 2, \dots, 4$) that of the Ni atoms which lie just below the oxygen, the theoretical curves are the spectral density function of the correlation function $\langle X(t)X(0) \rangle$, where the coordinate $X(t) = u_0^{(\perp)}(t) - \frac{1}{4}[u_1^{(\perp)}(t) + \dots + u_4^{(\perp)}(t)]$. Of course, only the contribution from the modes with wave vector $\vec{Q}_{\parallel} = 0$ is retained. Such spectral density functions have been referred to by Allan and Lopez¹¹ as dipole-mo-

ment-density functions.

In Fig. 2(a), we show the experimental electron-energy-loss spectrum for dipole scattering from the $c(2 \times 2)$ structure. It differs qualitatively from that in Fig. 1(a). If, following the conclusions of the LEED analysis, we assume the oxygen still sits roughly 0.9 \AA above the surface, our calculated energy-loss spectra are in *qualitative* disagreement with the data. We find the oxygen local mode downshifted from 445 to 401 cm^{-1} , and virtually no scattering intensity within the Ni phonon bands, below 295 cm^{-1} . The data show no evidence of any features above $\approx 300 \text{ cm}^{-1}$ for the $c(2 \times 2)$ structure, and a strong asymmetric tail with a peak at $\approx 310 \text{ cm}^{-1}$, and which extends down into the Ni phonon bands.

Upton and Goddard argue that in the $c(2 \times 2)$ structure, there is substantial charge transfer between the Ni substrate and the oxygen overlayer, and this renders the high coverage structure qualitatively different from the low-density $p(2 \times 2)$. They mimic this with their cluster method and a single oxygen above to conclude that the equilibrium distance is $R_{\perp} \approx 0.26 \text{ \AA}$, a value very much smaller than the 0.88 \AA appropriate to the $p(2 \times 2)$ structure. For their proposed $c(2 \times 2)$ structure, they calculate $(k/M_o)^{1/2} = 265 \text{ cm}^{-1}$, a frequency which lies within the Ni phonon bands. Figure 2(b) shows our calculated energy-loss spectrum for this choice of parameters. We find no modes above the Ni phonon bands, and a large asymmetric tail that extends down into them, very much as in the data. We do a better job of mimicking the data if we make a rather small modification of their parameters. If we simply change R_{\perp} from 0.26 to 0.27 \AA , while the value of φ that enters the force constant k is left unchanged, we obtain the spectrum in Fig. 2(c). A local mode has split off from the phonon band, and the asymmetric tail is broadened. The experimental spectrum peaks at 310 cm^{-1} , distinctly above the maximum Ni phonon frequency of 295 cm^{-1} . We therefore believe there is a local mode just above the band, as in Fig. 2(c), but which is unresolved in the experiment, either because the resolution of the apparatus is not sufficient or very likely because the local mode is lifetime broadened, to merge with the phonon continuum. {We have set $z = \omega + i\epsilon$ in the Green's function [Eq. (1)] with ϵ small but finite, and so the δ function that describes the local mode contributions to the spectral density is slightly broadened.}

The present analysis suggests that the LEED

data on the $c(2 \times 2)$ oxygen layer on Ni(100) should be reexamined, to see if improved agreement between theory and experiment can be achieved by placing the oxygen layer quite close to the surface. It is our understanding that for the $p(2 \times 2)$, the fit between theory and experiment is excellent with the layer 0.9 Å above the surface, but the fit is less satisfactory for the higher-density $c(2 \times 2)$ structure.

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Level-Crossing Transition in the Cluster Compounds Nb_6I_{11} and HNb_6I_{11}

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The cluster compounds Nb_6I_{11} and HNb_6I_{11} exhibit a coupled structural and electronic phase transition. The structural deformation is accompanied by a *crossing* of electronic levels which leads to a reduction of the *spin* degeneracy. We expect such level-crossing transitions to occur in other compounds containing transition-metal clusters.

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There exists a large variety of ordered compounds where the building blocks are metal clusters rather than individual atoms.¹ With the exception of the so-called Chevrel phases, whose extraordinary superconducting properties have recently created wide interest,² such cluster compounds are usually considered too complicated for physical investigation. It is our belief that the physical properties of cluster compounds are highly varied, often interesting, and amenable to theoretical understanding. This we substantiate by considering the cluster compounds Nb_6I_{11} and HNb_6I_{11} which are built from the same cluster as the Chevrel phases but have cluster separations so large that the *d* electrons do not conduct but are localized onto the individual clusters. As a consequence each cluster may carry a magnetic

moment and we have found that Nb_6I_{11} and HNb_6I_{11} exhibit a coupled magnetic and structural phase transition which is not of the usual Jahn-Teller type.³ At the transition there is a reduction of *spin* degeneracy due to a *crossing* of electronic levels. In this Letter we present experimental and theoretical evidence for the existence of this crossing.

We first describe the structure of the two compounds.⁴⁻⁶ The unit, Nb_6I_8 , forms a distorted cube with I atoms at the corners and Nb atoms at the face centers. The Nb atoms thus form a distorted octahedron. There are six additional I atoms located approximately on the perpendiculars of the cube faces. Each of these additional I atoms are shared between two neighboring Nb_6I_8 clusters and hence provide the intercluster bond-