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Citation: *The Journal of Chemical Physics* **86**, 2986 (1987); doi: 10.1063/1.452052

View online: <http://dx.doi.org/10.1063/1.452052>

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Defects in C(2×2) oxygen overlayers on Ni(100): The effect on vibrational spectra

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(Received 17 September 1986; accepted 18 November 1986)

We have modeled vacancy defects in C(2×2) oxygen overlayers on Ni(100) to examine the effect which such vacancies have on the vibrational spectra as measured by inelastic scattering of low energy electrons (HREELS). Particular attention has been given to the change in frequency of the collective modes of the oxygen overlayer as a function of the wave vector of the mode. We find that this frequency dispersion is modified by the vacancies and that there are distinctive changes in the expected peak shapes as a function of the scattering geometry.

I. INTRODUCTION

Experimental studies of adsorbate vibrations have recently provided a significant amount of detailed information about the vibrations of simple ordered adsorbate systems on single crystal substrates. The periodicity of the ordered overlayers results in well-defined periodicity of the collective normal modes of vibration. Thus the relative amplitude of the motion of adsorbate atoms involved in a normal mode is described as a Bloch wave with a well-defined value of the momentum vector parallel to the surface (k_{\parallel}).¹ High resolution electron energy loss spectroscopy (HREELS) and high resolution inelastic helium atom scattering are now able to provide data on the dispersion (change in mode frequency with k_{\parallel}) of surface vibrations for ordered systems.^{2,3} Such data has led to the development of detailed models of the lattice dynamics of a few ordered atomic adsorbates.⁴ The lattice dynamical models which have been developed assume perfectly ordered overlayers and result in a force field for the system which is consistent with the available data. The purpose of the present study is to identify and provide estimates of the magnitude of the effects which defects would have on such measurements.

Defects in bulk solids and the resulting effects on vibrational properties have been the subject of an extensive literature. The reader is referred to one of the several reviews, and references therein, on this topic for background material.⁵ One of the simplest types of defects in an ordered adsorbate layer is a vacancy. Since vacancy defects disrupt the periodicity of the ordered overlayer, the normal modes of vibration are no longer associated with a single k_{\parallel} value. However, if the defect density is not too large only a few Bloch waves with distinct values of k_{\parallel} will contribute to each collective normal mode. As the result of the loss of perfect long range order one would expect to see changes in the dispersion of a vibrational mode.

Our approach is to use the well-studied C(2×2) oxygen overlayer on Ni(100) as a model system. A lattice dynamical model has been developed for this adsorbate system by

Rahman *et al.*⁶ which describes the measured dispersion curves for the two oxygen collective vibrations (perpendicular to the surface and parallel to the surface), as well as modes in the Ni phonon band which involve motion of the Ni surface layers as well as the oxygens. We have used an *FG* matrix method, in which the substrate is described by a cluster of atoms, to study the effect of vacancy defects in this system. We are using the previously described lattice dynamical model of Rahman *et al.* as the point of comparison for our calculations.

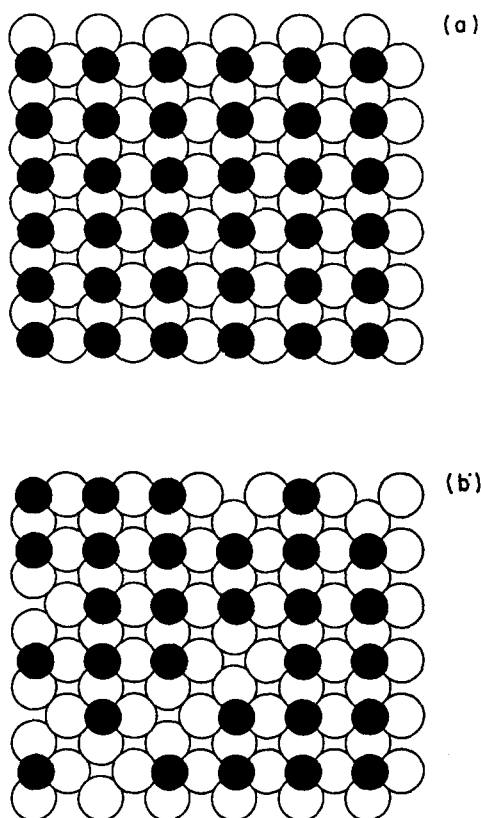


FIG. 1. Ball models of the clusters used in the defect overlayer calculations. The nickel substrate consists of 144 atoms in two layers. The filled circles indicate oxygen atoms. (a) The perfect C(2×2) overlayer with 36 oxygen atoms. (b) One of the defect structures with seven missing oxygen atoms.

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TABLE I. Parameters of the lattice dynamics model $C(2 \times 2)$ O/Ni(100).

$R_{\text{O-Ni plane}}$	$= 0.90 \text{ \AA}$
$f_{\text{Ni-O}}$	$= 0.950 \text{ mdyn/\AA}$
$f_{\text{O-O}}$	$= 0.095 \text{ mdyn/\AA}$
$f_{\text{Ni-Ni}}$	$= 0.379 \text{ mdyn/\AA}$

II. METHOD

In our calculations we utilize a finite cluster of metal atoms to describe the vibrational motions of the nickel substrate. Oxygen atoms are placed on the cluster in sites corresponding to the overlayer of interest. The computational method employed here is a modification of Wilson's *FG* matrix method, discussion of which can be found in standard texts on molecular vibrations.⁷ Once a cluster and oxygen overlayer is chosen, the vibrational problem is formulated in terms of internal (valence) coordinates such as bond stretches, angle bends, etc.⁸ All calculations are carried out within the harmonic approximation. We impose periodic boundary conditions on the calculations in the directions parallel to the surface of the cluster. The calculations result in normal mode vibrational frequencies and eigenvectors. In the case of a perfectly periodic overlayer the periodic boundary conditions allow us to assign values of k_{\parallel} to the eigenvectors (and thus eigenfrequencies). This allows us to construct

the dispersion curve for each mode. The number of k_{\parallel} values obtained from each calculation depends on the size and shape of the particular cluster chosen. The details of the method including the effects of cluster size and shape and the details of the periodic boundary conditions have been published previously.⁸

Figure 1(a) shows the cluster used in these calculations with a perfect $C(2 \times 2)$ oxygen overlayer. The cluster contains 144 Ni atoms in two layers and 36 oxygen atoms. We have shown previously that two-layer Ni clusters are sufficient to describe the vibrational modes which occur at frequencies above the maximum substrate phonon frequency.⁸ We generate a defective structure by leaving off a set of randomly chosen oxygen atoms. In all of the calculations described here we have used a 20% defect density (seven defects out of 36 total sites). Figure 1(b) shows one of the clusters used with 20% defects.

Since the clusters used in these calculations contain many atoms, simple ways of viewing the output of the calculation are useful. We typically display the output of the calculation as a spectral density function $\rho_{\alpha}(\omega, k_{\parallel})$ for the oxygen atoms. The general form for $\rho_{\alpha}(\omega, k_{\parallel})$ is given by

$$\rho_{\alpha}(\omega, k_{\parallel}) = \sum_s \sum_l [e_{\alpha}^s(l, k_{\parallel})]^2 \left[\frac{\gamma}{(\omega_s - \omega)^2 + \gamma^2} \right],$$

where l ranges over the oxygen atoms, s ranges over the eigenvalues, α labels a Cartesian coordinate, and $e_{\alpha}^s(l, k_{\parallel})$ is

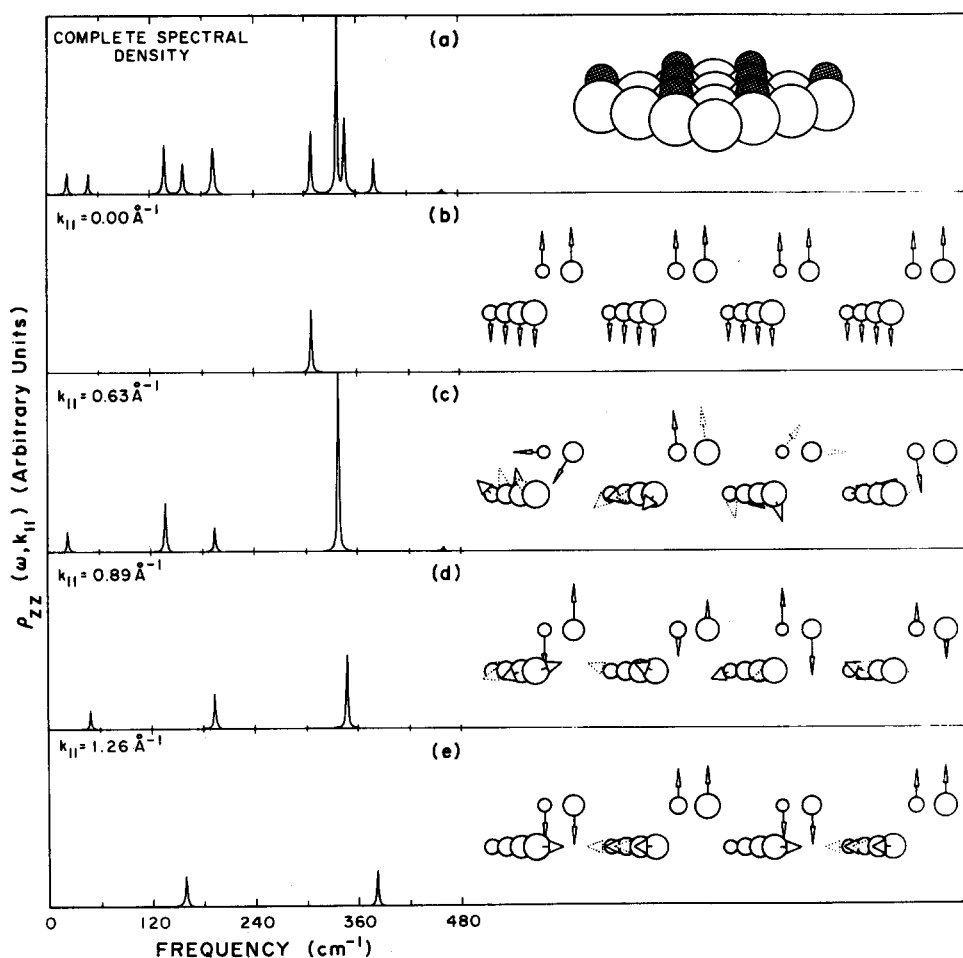


FIG. 2. An example of the direct result of a periodic cluster calculation and the subsequent decomposition into different k_{\parallel} components. The cluster shown is an 8-atom $C(2 \times 2)$ overlayer of oxygen on a 16-atom Ni(100) sheet. The complete perpendicular spectral density function for one of the oxygen atoms is shown in (a). The Fourier-transformed perpendicular spectral density functions corresponding to various k_{\parallel} values are shown in (b)–(e). The ball-and-arrow drawings illustrate the motions of atoms in the cluster for the oxygen-nickel perpendicular modes at frequencies between 308 ($k_{\parallel} = 0.00 \text{ \AA}^{-1}$) and 381 cm^{-1} ($k_{\parallel} = 1.26 \text{ \AA}^{-1}$).

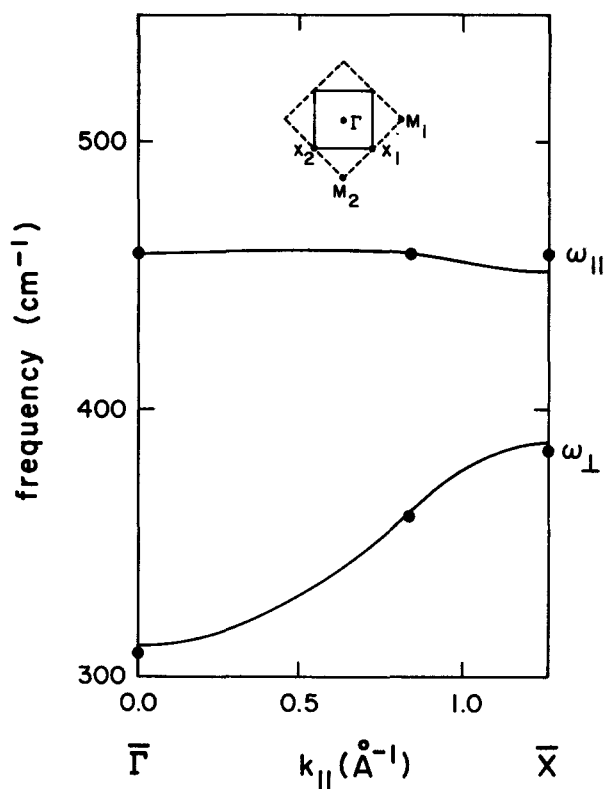


FIG. 3. Calculated dispersion curves for the perpendicular and parallel oxygen stretching modes for the $C(2 \times 2)$ oxygen overlayer on $Ni(100)$. The solid curves represent results from a Green's function lattice dynamics technique, while the circles mark points obtained via the cluster method employed here. $\bar{\Gamma}$ and \bar{X} are defined with respect to the substrate Brillouin zone (the dashed zone in the inset figure).

the appropriate displacement amplitude of the eigenvector. Separate spectral density functions are usually calculated for the motions of the oxygen atoms perpendicular to the substrate ($\alpha = z$) and parallel to the substrate ($\alpha = x, y$). In the case of the perfect overlayers, since all the oxygen atoms are equivalent, the summation over the oxygen atoms may be neglected. The Lorentzian frequency function is used for display purposes only, to broaden the delta functions which are the direct result of our calculations. In all the displays shown here a Lorentzian width of 2 cm^{-1} has been used. These spectral density functions provide a good description of the vibrational spectrum expected from a HREELS experiment.^{8,9}

The lattice dynamical model which we have used in these calculations as developed by Rahman *et al.*⁶ utilizes a single bond stretching force constant between Ni atoms, a Ni-O bond stretch with the oxygen in a fourfold hollow site, and a direct O-O interaction. The force constants and geometries used are listed in Table I. As we have mentioned previously this lattice dynamical model is consistent with the wide body of experimental evidence available for this system.

Figure 2 shows results for the perfect periodic overlayer. The results shown in Fig. 2 were generated for a cluster with a single Ni layer to make the eigenvector display less cluttered. As such, the modes below 200 cm^{-1} are not well described. However, the oxygen modes at frequencies well above the phonon band are well described. Figure 2(a)

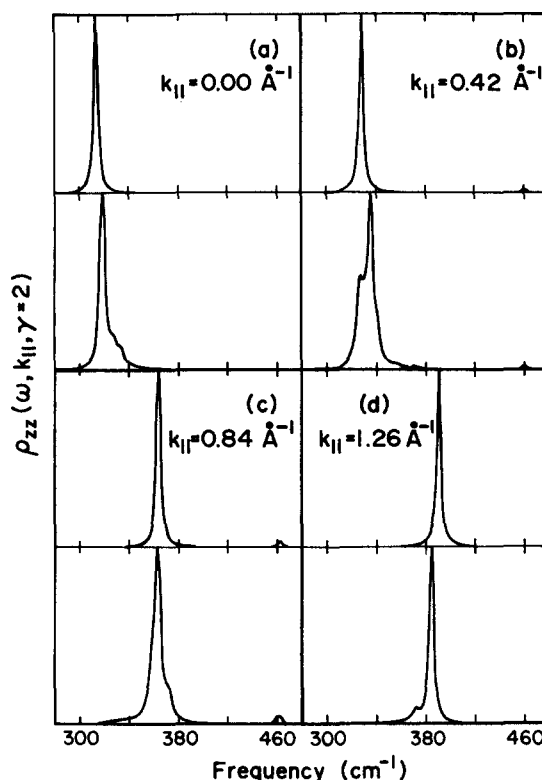


FIG. 4. Oxygen spectral density functions for motions perpendicular to the nickel surface. In each case the upper curve is for the perfect $C(2 \times 2)$ overlayer and the lower curve is the result of an average over five randomly chosen defect structures. (a)-(d) correspond to $k_{||}$ values of 0.00 \AA^{-1} ($\bar{\Gamma}$), 0.42 , 0.84 , and 1.26 \AA^{-1} (\bar{X}), respectively.

shows the spectral density function for oxygen motion perpendicular to the nickel surface. Figures 2(b), 2(c), 2(d), and 2(e) show the perpendicular spectral density function for specific values of $k_{||}$. Also shown are arrow diagrams illustrating the atomic motions corresponding to each oxygen collective normal mode in the $300\text{--}400 \text{ cm}^{-1}$ region. All of these modes are Ni-O stretching modes in the direction perpendicular to the surface. The dispersion in this motion from $k_{||} = 0$ (the $\bar{\Gamma}$ point, corresponding to all the oxygens moving in phase) to the maximum $k_{||}$ value of 1.26 \AA^{-1} (the \bar{X} point, corresponding to neighboring oxygens moving exactly out of phase) is 73 cm^{-1} . The complete dispersion curves for the oxygen mode perpendicular to the surface and the mode parallel to the surface are shown in Fig. 3. The results shown in Fig. 3 were calculated using a multilayer cluster with the force constants of Table I and correspond well to the experimentally measured dispersion curves.² The cluster used in these calculations contains 96 Ni atoms in four layers. The convergence of these calculations with cluster size has been described previously.⁸

The results of our calculations for defective overlayer structures are displayed as oxygen perpendicular spectral density functions in Fig. 4. Figures 4(a), 4(b), 4(c), and 4(d) each correspond to a different value of $k_{||}$. In each case, the upper spectrum corresponds to the result obtained for the perfect overlayer, while the lower spectrum was obtained by averaging the results from five different defective overlayers one of which is shown in Fig. 1(b). Each of the defec-

tive overlayers was obtained by randomly removing seven of the 36 oxygens. The first thing which should be noted from Fig. 4 is that the 20% vacancy density which we have used in these calculations does not completely remove the dispersion of the oxygen perpendicular motion. Three important results can be easily seen in Fig. 4. These are: (1) the total frequency dispersion from $\bar{\Gamma}$ to \bar{X} is decreased by about 10 cm^{-1} (12%) compared to the perfect overlayer case. (2) The frequency shift from the perfect overlayer to the defect structure is larger at $\bar{\Gamma}$ and \bar{X} (at the boundaries of the Brillouin zone) than in the middle of the zone ($k_{\parallel} = 0.42 \text{ \AA}^{-1}$ and $k_{\parallel} = 0.84 \text{ \AA}^{-1}$). Thus the shape of the dispersion curve is changed by the defects. In particular, the dispersion curve is flattened out near the zone boundaries. (3) The predicted shape of the modes changes in a characterizable way with k_{\parallel} for the defect structure. In particular, at the $\bar{\Gamma}$ point the observed mode should show a small shoulder to higher frequency while at \bar{X} the mode should show a small shoulder to lower frequency. In the center of the Brillouin zone the modes are essentially broadened in a symmetrical manner by the existence of the vacancy defects. We attribute the slight asymmetries shown in Figs. 4(b) and 4(c) to the fact that only five defect structures have been included in our averaged spectra.

The predicted k_{\parallel} dependence of the mode shape may be a useful experimental probe of the existence of defects. Such a change in shape with k_{\parallel} is a direct result of the positive dispersion of the mode from $\bar{\Gamma} \rightarrow \bar{X}$ coupled with the mixing of k_{\parallel} modes due to the lack of periodicity in the presence of defects.

The decrease in total dispersion and the flattening of the dispersion curve will be less useful in establishing the existence of defects since both of these properties of the dispersion are also quite sensitive to the details of the lattice dynamics model (the force constants and structural parameters).

In summary the HREELS vibrational spectra may be a sensitive measure of the existence of defects in an ordered overlayer. In particular the shapes of the vibrational modes as a function of k_{\parallel} should be particularly sensitive to defects which destroy the overlayer periodicity. This phenomena will only be easily observable for cases such as the C(2x2) O/Ni(100) system studied here which show sufficient dispersion for the perfect overlayer. It should also be noted that the details of the dispersion curves near the zone boundary may be slightly flattened due to defects. Thus care must be taken when such details of experimental dispersion curves are used to develop lattice dynamical models within the assumption of perfectly ordered overlayers.

ACKNOWLEDGMENTS

This work has been supported by the Office of Naval Research. One of us (K.G.L.) would like to acknowledge the support of a University of California Presidents Fellowship.

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