Adsorbate-Induced Soft-Phonon Reconstruction of the Ni(100) Surface

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A systematic study of the lattice dynamics of several (2×2) overlayers on Ni(100) leads to the conclusion that the reconstruction of the nickel surface with a carbon overlayer is of the soft-phonon type. The reconstruction is driven by the freezing of the S_1 nickel surface phonon.

The structure and dynamics of $c(2 \times 2)$ overlayers on Ni(100) surfaces have been studied extensively in recent years. Whereas $c(2 \times 2)$ overlayers of sulfur and oxygen leave the nickel surface unreconstructed[1] the overlayer produced with carbon gives rise to a reconstruction, so as to reduce the symmetry to a 2×2 unit mesh.[2] A particular feature of the structure is the existence of two perpendicular glide planes which cause systematic extinctions in the LEED pattern of the surface. The two structure models which are consistent with the observed extinction are shown in Figs. 1(a) and 1(b). A dynamical LEED analysis[2] favors the structure as displayed in Fig. 1(a) where the coordination of the carbon atom remains a fourfold hollow site, with the nickel atoms rotated clockwise and counterclockwise around the carbon atoms in alternate sequence. This structure is a rather interesting type of an adsorbate-induced reconstruction since the nearest-neighbor coordination of the carbon atoms and the size of the hollow site remain [Fig. 1(a)] as on the unreconstructed surface. Obviously, the driving force for the reconstruction is not the adsorbate-substrate interaction directly. Rather, the reconstruction seems to be driven by a modification of the coupling between the substrate atoms as induced by the adsorbate.

In this Letter we show that the reconstruction pattern shown in Fig. 1(a) arises from the softening of a particular surface phonon. The analysis to be presented here stems from a systematic study of commensurate superstructures of sulfur[3] and oxygen[4] on Ni(100). Contact between lattice-dynamical model calculations and surface phonon dispersion measurements have shown that for the $c(2 \times 2)$ overlayer of sulfur on Ni(100) the force constant between the first- and second-layer nickel atoms is unchanged from its value on the clean surface, while for the same overlayer of oxygen this force constant is reduced dramatically to 30% of its value for the coupling between the atoms in the bulk crystal. This result can be qualitatively understood in terms of the stronger oxygen-nickel bond which reduces the bonding of the nickel

surface atoms to their nearest neighbors in the layer below. The reduced nickel-nickel bonding is also evident from the relaxation of the interlayer spacing when oxygen is adsorbed.[5]

In the following we show that the particular reconstruction pattern in Fig. 1(a) may be understood as a natural consequence of a continuing trend of reduced nickel interlayer coupling, with stronger bonding to the adsorbate, so as to make an unreconstructed $c(2 \times 2)$ carbon-covered Ni(100) surface unstable. For this purpose let us, in a *Gedankenexperiment*, as-
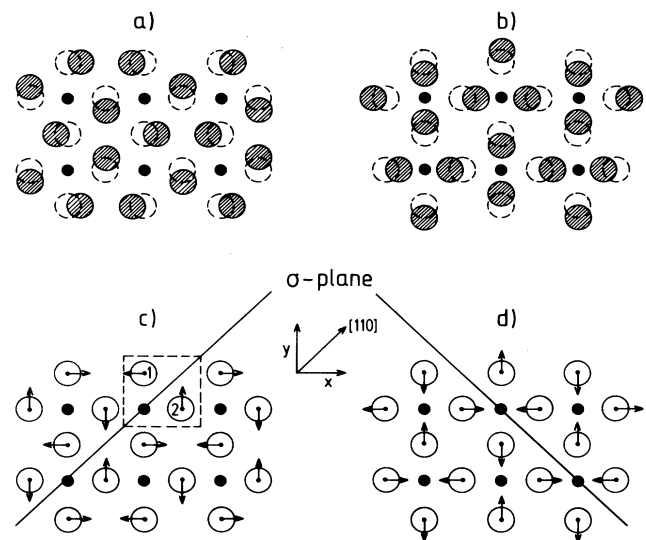

FIG. 1. (a),(b) The proposed models for the reconstruction of Ni(100) with a $c(2 \times 2)$ overlayer of carbon. The small dark circles are carbon atoms and the striped and the dashed circles are the first-layer nickel atoms in their displaced and undisplaced positions, respectively. In (a) the carbon atoms remain on a fourfold site on the reconstructed surface while in (b) they occupy the "twofold" bridge position. (c),(d) The two displacement patterns of the first-layer nickel atoms, with odd symmetry with respect to the σ plane. The pattern in (c) is also that of the linear combination of the S_1 nickel surface phonon for the two $\bar{X}$ points.

sume that the carbon atoms occupy the fourfold hollow site and that the Ni(100) surface is unreconstructed [Fig. 1(c)]. The displacement of the first-layer nickel atoms which would lead to the reconstructed phase (if the corresponding mode becomes soft) is of odd symmetry with respect to the symmetry plane as defined in Fig. 1(c). Obviously, the mode couples only to likewise odd modes in the carbon layer above and the nickel layers below. Thus the motion of the carbon atoms must be perpendicularly polarized to the σ plane.

This can be illustrated very easily by writing the equations for the atomic displacements. We do this with the aid of the Fourier-transformed Green's functions, which we construct from the atomic displacements, such that the function describing the propagation of a particular mode from an atom denoted by $l_z\kappa$, to another denoted by $l_z'\kappa'$, is

$$U_{\alpha\beta}(l_z\kappa, l_z'\kappa'; \mathbf{Q}_\|)$$
$$= \sum_s \frac{e_\alpha^{(s)}(\mathbf{Q}_\|; l_z\kappa)\, e_\beta^{(s)}(\mathbf{Q}_\|; l_z'\kappa')^*}{\omega^2 - \omega_s^2(\mathbf{Q}_\|)}, \qquad (1)$$

where $e_\alpha^{(s)}(\mathbf{Q}_\|; l_z\kappa)$ is the αth Cartesian component of the eigenvector for the displacement of the κth atom in the unit cell in layer l_z (in our notation $l_z = 0$ denotes the adsorbate layer, $l_z = 1$ the first substrate layer, and so on), $\omega_s(\mathbf{Q}_\|)$ is the frequency of the mode s with $\mathbf{Q}_\|$ the component of the wave vector parallel to the surface, and ω is a complex frequency. The parallel motion of carbon atoms which have odd symmetry with respect to the mirror plane in Fig. 1(c) is denoted by $U_\|^-(01; \mathbf{Q}_\|)$ such that

$$U_\|^-(01; \mathbf{Q}_\|)$$
$$= U_{xx}(01, 01; \mathbf{Q}_\|) - U_{yy}(01, 01; \mathbf{Q}_\|). \qquad (2)$$

The equation of motion for this Green's function and the subsequently emerging hierarchy of equations can be written by following the method developed in Ref. 4. Here we give only the equations for this particular displacement of the carbon atoms and those of the nickel atoms in the layer below to which it couples. To be more specific, we choose the wave vector $\mathbf{Q}_\|$ to lie along the $\bar{\Gamma}$-$\bar{X}$ direction, in the two-dimensional Brillouin zone. We then have

$$(\omega^2 - 2k_{00})U_\|^-(01; Q_\|) + 2k_{01}\cos(aQ_x)U_\|^b(1; Q_\|) - 2ik_{01}r_\perp \sin(aQ_x)U_\perp(1; Q_\|) = 1, \qquad (3)$$

and for the motion of the first-layer nickel atoms

$$[\omega^2 - 2k_{00}' - 2k_{11}\cos^2(aQ_x) - k_{12}]U_\|^b(1; Q_\|) + 2k_{01}\cos(aQ_x)U_\|^-(01; Q_\|)$$
$$+ 2k_{11}\cos^2(aQ_x)U_\|^q(1; Q_\|) + k_{12}\cos(aQ_x)U_\|(22; Q_\|) = 0, \qquad (4)$$

with

$$(\omega^2 - 2k_{00}'r_\perp^2 - 2k_{12})U_\perp(1; Q_\|) + 2ik_{01}r_\perp \sin(aQ_x)U_\|^-(01; Q_\|)$$
$$+ ik_{12}\sin(aQ_x)U_\|(21; Q_\|) - ik_{12}\sin(aQ_x)U_\|(22; Q_\|) = 0, \qquad (5)$$

and finally

$$[\omega^2 - 2k_{11}\cos^2(aQ_x) - k_{12}]U_\|^q(1; Q_\|) + 2k_{11}\cos^2(aQ_x)U_\|^b(1; Q_\|) + k_{12}\cos(aQ_x)U_\|(21; Q_\|) = 0. \qquad (6)$$

The Green's-function combinations appearing in the above equations are defined as

$$U_\|^b(1; \mathbf{Q}_\|) = U_{xx}(12; 01; \mathbf{Q}_\|) - U_{yy}(11; 01; \mathbf{Q}_\|),$$
$$U_\|^q(1; \mathbf{Q}_\|) = U_{xx}(11; 01; \mathbf{Q}_\|) - U_{yy}(12; 01; \mathbf{Q}_\|),$$
$$U_\perp(1; \mathbf{Q}_\|) = U_{zx}(12; 01; \mathbf{Q}_\|) - U_{zy}(11; 01; \mathbf{Q}_\|),$$
$$U_\|(2\kappa; \mathbf{Q}_\|) = U_{xx}(2\kappa; 01; \mathbf{Q}_\|) - U_{yy}(2\kappa; 01; \mathbf{Q}_\|),$$

$$(7)$$

while the force constants have the form

$$k_{00} = \frac{\Phi_{01}^\|}{M_a(1 + r_\perp^2)}, \qquad k_{01} = \frac{\Phi_{01}^\|}{(M_a M_s)^{1/2}(1 + r_\perp^2)}$$

and

$$k_{00}' = \frac{\Phi_{01}^\|}{M_s(1 + r_\perp^2)}, \qquad k_{11} = \frac{\Phi_{11}^\|}{M_s}, \qquad k_{12} = \frac{\Phi_{12}^\|}{M_s},$$

with $\Phi_{01}^\|$, $\Phi_{11}^\|$, and $\Phi_{12}^\|$ the second derivative of the pair potential between the carbon and the nickel atoms, the first-layer nickel atoms, and the nickel atoms in the first and second layers, respectively. Here $a = a_0/\sqrt{2}$ and $r_\perp = R_\perp/a$, with a_0 the nearest-neighbor distance and $R_\perp$ the vertical height at which the adsorbate sits over the fourfold hollow site.

At the $\bar{X}$ point of the two-dimensional Brillouin zone for the unreconstructed Ni(100) surface $aQ_x = \pi/2$, and it is easy to see from Eqs. (3)–(6) that the Green's function $U_\|^q(1; Q_\|)$ and $U_\|^b(1; Q_\|)$ decouple from the other terms. The frequency of the modes connected with these Green's functions are

$$\omega(U_\|^q) = (k_{12})^{1/2}, \qquad (8)$$
$$\omega(U_\|^b) = (2k_{00}' + k_{12})^{1/2}. \qquad (9)$$

As seen from the definition in Eq. (7) the motions described by $U_{\parallel}^{a}(1;Q_{\parallel})$ and $U_{\parallel}^{b}(1;Q_{\parallel})$, at the $\bar{X}$ point of the unreconstructed two-dimensional Brillouin zone, correspond to the displacement pattern depicted in Figs. 1(c) and 1(d), respectively. From Eqs. (8) and (9) we see that the $U_{\parallel}^{a}$ mode becomes soft as k_{12} approaches zero while the $U_{\parallel}^{b}$ mode maintains a finite frequency. It is thus clear that when k_{12} becomes vanishingly small or negative the surface reconstructs with the displacement pattern of the $U_{\parallel}^{a}$ mode [Fig. 1(c)] which is equivalent to the proposed reconstruction pattern. Hence our calculations provide a natural explanation as to why the reconstruction pattern in Fig. 1(a) is preferred over that in Fig. 1(b). Note that the displacement pattern in Fig. 1(c) is that of a linear combination of the S_1 modes at the two $\bar{X}$ points. We further note that the carbon-nickel bond angles are not changed to first order in the reconstruction pattern in Figs. 1(a) and 1(c). The $U_{\parallel}^{a}(1;Q_{\parallel})$ mode would therefore become soft even with finite angle-bending forces introduced in the equations. A lattice-dynamical analysis of other modes shows[6] that with nonvanishing angle-bending forces the above solution for the reconstruction pattern is unique.

In our calculations so far on the (2×2) overlayers on Ni(100),[4, 6] we have found the nearest-neighbor interaction to be sufficient for an adequate fit to the experimental dispersion curves. We have thus not attempted to extend the model to include next-nearest-neighbor interactions in any sophisticated manner. Preliminary results of total-energy calculations[7] suggest that, at least for the carbon atoms, second-nearest-neighbor coupling between the adatoms and the second-layer substrate atoms may not be negligible. Once second-neighbor interactions are introduced one also has to take into account that the first derivatives of the pair potential between the atoms need no longer be zero and that one might have internal stresses. It is straightforward to show, however, that even with this type of force field the $U_{\parallel}^{a}$ mode is the mode to become soft in a continuing trend in the force fields describing sulfur, oxygen, and carbon over-layers.[8]

A soft-phonon model for an adsorbate-induced surface reconstruction has been proposed previously by Fasolino, Santoro, and Tosatti[9] for H on W(100), where they have studied the effect of the force-constant changes on the frequency of various types of surface phonons. While it was shown by Fasolino, Santora, and Tosatti that with a particular choice of force constants the observed reconstruction pattern for H on W(100) could be reproduced, there is no independent evidence that the force constants actually assume their required values or that there is a trend towards such a softening, as in the case presented here. Furthermore, we have shown that the reconstruction induced by carbon on nickel (100) does not result from a direct adsorbate-substrate interaction. Although a comprehensive understanding of the mechanism for the force-constant changes will have to await a total-energy calculation, the study presented here may serve as a guideline for such calculations as to which interactions to focus on.

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