

Photoelectron-diffraction analysis of the structure of  $c(2 \times 2)\text{O}$  on Ni(001)

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Calculated energy-dependent photoelectron-diffraction (EDPD) curves for oxygen-nickel perpendicular spacings ( $d_{\perp}$ ) between 0.0 and 1.2 Å are presented and compared with experimental data for the  $c(2 \times 2)\text{O}$ -Ni(001) system. Using a normalized  $R$  factor, we found that the only acceptable agreement is for  $d_{\perp}$  spacings in the range 0.78–0.90 Å. The experimental observation that adsorbate-induced modulations remain strong over a wide energy range in EDPD curves, but not in low-energy electron-diffraction intensity curves, is explained.

## I. INTRODUCTION

Because of the site specificity of the photoelectron-diffraction (PD) process, angle-resolved photoelectron diffraction of core-level electrons has been used to determine the binding location of several adsorbate atoms and one molecule. The coherence length of the diffraction process is about equal to the mean free path of the final-state photoelectron (4–8 Å); therefore, the technique probes the local geometry surrounding the adsorbate site.

The  $c(2 \times 2)\text{O}$  on Ni(001) system is a very interesting case because studies using different techniques have produced two conflicting results:  $d_{\perp}$ , the spacing between the oxygen layer and the top-most nickel layer, has been found to be either 0.8–0.9 Å (Refs. 1–8) or  $\sim 0$  Å, i.e., the two layers are nearly coplanar (Refs. 9–13). Earlier, Rosenblatt *et al.*<sup>7</sup> used energy-dependent photoelectron diffraction (EDPD) to study this system. Searching over  $d_{\perp}$  spacings between 0.5 and 1.7 Å, they found good agreement at  $d_{\perp} = 0.90 \pm 0.04$  Å. Smaller  $d_{\perp}$  spacings were not tested due to difficulty in the computational method. Also, an  $R$ -factor analysis was not carried out for this system.

Because of reports of the near-coplanar adsorption site for O on Ni(001) we developed a method which allows calculation of emission and diffraction processes in layers having any  $d_{\perp}$  spacing, including

coplanar. We present here, for the first time, EDPD curves for  $c(2 \times 2)\text{O}$ -Ni(001) with  $d_{\perp}$  between 0.0 and 0.4 Å. The method is based on the combined-space formulation,<sup>14</sup> and its details are presented elsewhere.<sup>15</sup> EDPD curves at normal exit angle for  $d_{\perp}$  values from 0.0 to 0.4 Å were computed in steps of 0.05 Å, and from 0.5 to 1.2 Å in steps of 0.1 Å. Five phase shifts were used in the calculation. Other conditions and all dynamical inputs [e.g., phase shifts, inner potential (11.2 eV), inelastic damping, vibration amplitudes, etc.] are identical to those reported by Rosenblatt *et al.*<sup>7</sup> Finally, an  $R$ -factor analysis was carried out for the full range of  $d_{\perp}$  spacings.

## II. RESULTS AND DISCUSSION

The comparisons between calculated curves and measured data are shown in Figs. 1 and 2. Starting with the best agreement near 0.9 Å, the agreement worsens as  $d_{\perp}$  is decreased. At  $d_{\perp} = 0.5$  Å, all five experimental peaks (at 37, 66, 99, 155, and 193 eV) are in disagreement with theory. The worst agreement is in the range  $d_{\perp} = 0.2$ –0.6 Å. As  $d_{\perp}$  is further decreased, agreement improves somewhat in the low-energy range. However, even at  $d_{\perp} = 0.0$  Å, the agreement is poor above 80 eV. Thus according to our visual inspection, there is no acceptable agreement for  $d_{\perp}$  in the range 0.0–0.4 Å.

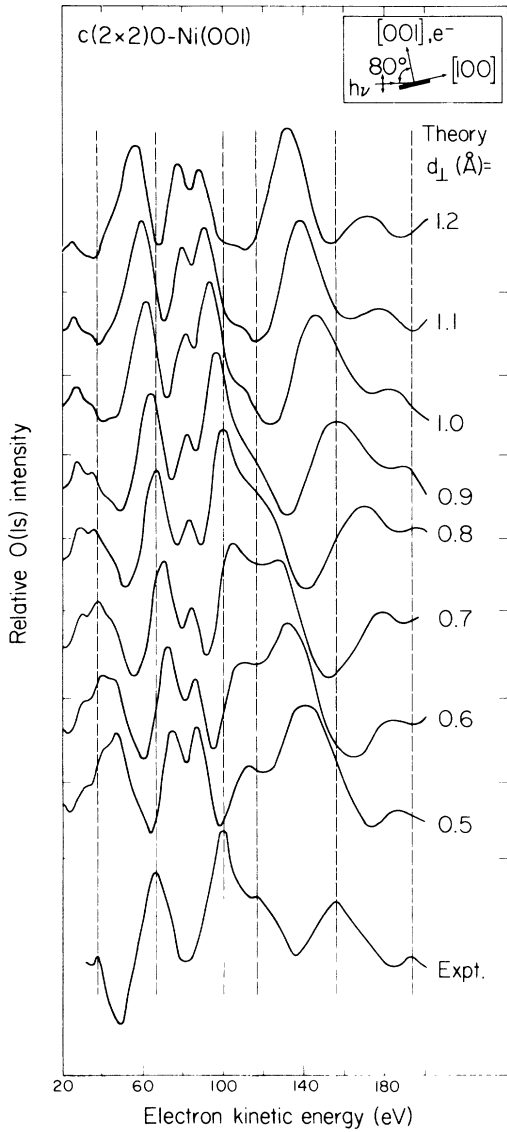


FIG. 1. Experimental normalized photoelectron-diffraction curve for  $c(2 \times 2)\text{O}(1s)\text{-Ni}(001)$ , compared with theoretical curves for  $d_{\perp} = 0.5\text{--}1.2$  Å (hollow site).

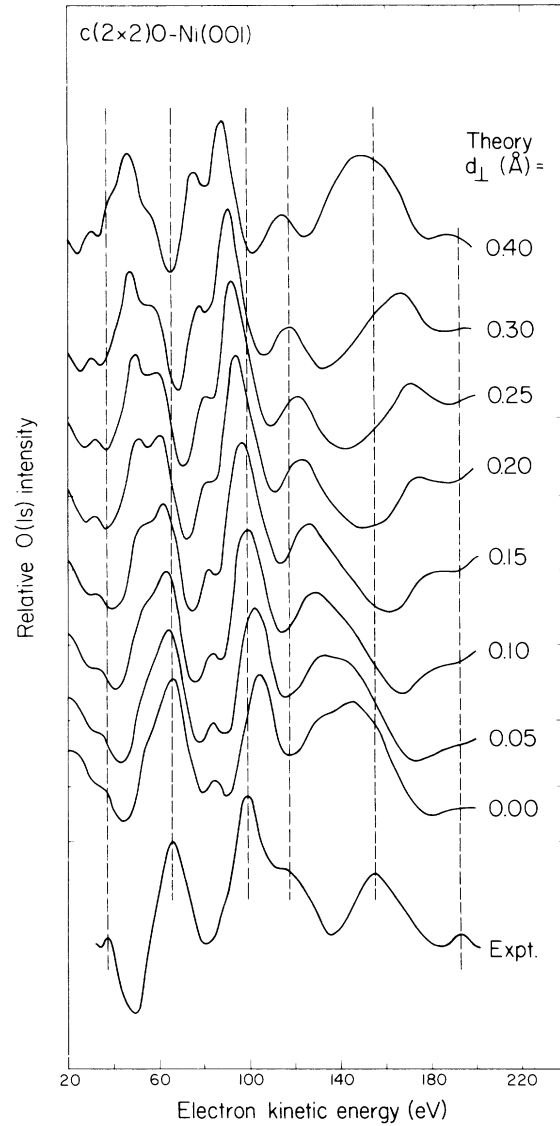


FIG. 2. Experimental normalized photoelectron-diffraction curve for  $c(2 \times 2)\text{O}(1s)\text{-Ni}(001)$ , compared with theoretical curves for  $d_{\perp} = 0.00\text{--}0.40$  Å (hollow site).

The  $R$ -factor analysis is shown in Fig. 3. We used a normalized  $R$  factor ( $R_N$ ) based on putting weights on six individual  $R$  factors which were discussed earlier.<sup>4,16</sup> The  $R$  factors  $R_1, \dots, R_6$  and  $R_N$  are defined as

$$R_1 = A_1 \Delta E_s / \Delta E_{\text{tot}} \quad (1)$$

$$R_2 = A_2 \int (I_e - cI_t)^2 dE \quad (2)$$

$$R_3 = A_3 \int (I'_e - cI'_t)^2 dE \quad (3)$$

$$R_4 = A_4 \int (I''_e - cI''_t)^2 dE \quad (4)$$

$$R_5 = A_5 \int \frac{|I'_e - cI'_t| |I''_e - cI''_t|}{|I'_e + \max |I'_t||} dE \quad (5)$$

$$R_6 = A_6 \int \frac{(Y_e - Y_t)^2 dE}{(Y_e^2 + Y_t^2) dE} \quad (6)$$

$$R_N = \frac{1}{6} (R_1 + R_2 + R_3 + R_4 + R_5 + R_6) \quad (7)$$

Here  $I_e$  are the experimental intensity data, and  $I'_e$  and  $I''_e$  refer to the first and second derivatives of  $I_e$  with respect to energy.  $I_t$ ,  $I'_t$ , and  $I''_t$  are the corresponding quantities for the calculated intensities.  $\Delta E_s$  is the energy range with slopes of opposite signs, and  $\Delta E_{\text{tot}}$  is the total energy range. Also,

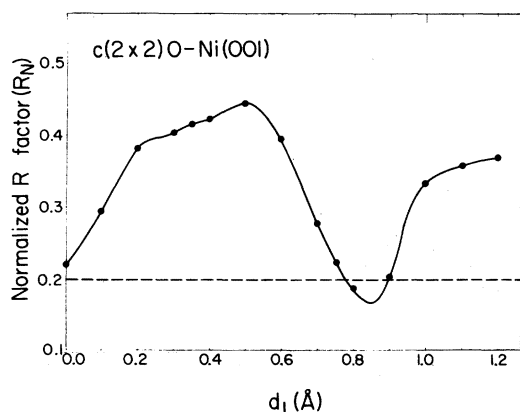


FIG. 3. Plot of normalized  $R$  factor ( $R_N$ ) vs  $d_1$  spacing.

$$c = \frac{\int I_e dE}{\int I_t dE}, \quad (8)$$

$$Y_{e,t} = \frac{I'_{e,t}/I'_{t}}{1 + V_I^2 (I'_{e,t}/I'_{t})^2} \quad (9)$$

$$V_I = 3.8 \left[ \frac{E + V_0}{90 + V_0} \right]^{1/3}, \quad (10)$$

where  $V_0$  is the inner potential and  $E$  is the electron energy, in electron volts, above the vacuum level. The weights are chosen such that the average value of each  $R$  factor over all geometries considered is the same. This ensures that the influence of each  $R$  factor is roughly the same, and in taking the overall average, no one  $R$  factor dominates the others. In earlier works<sup>4,16</sup> we have set the average of each  $R$  factor over all geometries considered to unity. In this work, in order to give  $R_N$  a quantitative meaning, we set each average equal to the average of the Zanazzi-Jona  $R$  factor<sup>17</sup> over all geometries tried ( $d_1 = 0.0$ – $1.2$  Å). Because the Zanazzi-Jona  $R$  factor is widely used, the  $R_N$  obtained here can be directly compared to the values of the Zanazzi-Jona  $R$  factor found in other works. The  $R_N$  has the additional features contained in  $R_1, \dots, R_6$ .

In the  $R$ -factor plot (Fig. 3), we note a deep minimum between 0.8 and 0.9 Å, in complete agreement with the previous discussion based on visual inspection. The minimum of the  $R$ -factor curve occurs at 0.85 Å. The value of  $R_N$  is a maximum at  $d_1 = 0.5$  Å. As  $d_1$  is further decreased, the value of  $R_N$  becomes smaller. However, at  $d_1 = 0.0$  Å, the value of  $R_N$  is still larger than 0.2, a value presently considered as the upper bound for a good fit between theory and experiment. In the full range of spacings,  $R_N \leq 0.2$  only in the region  $d_1 = 0.78$ – $0.90$  Å, again in agreement with our previous discussions

based on visual analysis. We also varied the inner potential in steps of 1 eV between 8.2 and 13.2 eV and found no improvement on the values of the  $R$  factor. We conclude from the  $R$ -factor analysis that  $d_1 = 0.85 \pm 0.04$  Å.

We now comment on the recent high-resolution electron-energy-loss spectroscopy (EELS) results. Data indicating a large downshift in the oxygen-nickel frequency from  $430 \text{ cm}^{-1}$  for  $p(2 \times 2)$  to  $310 \text{ cm}^{-1}$  for  $c(2 \times 2)$  were reported independently by Anderson<sup>9</sup> and by Lehwald and Ibach.<sup>10</sup> No such shift was observed between  $p(2 \times 2)$ S and  $c(2 \times 2)$ S on Ni(001).<sup>9</sup> If we accept the diffraction results using low-energy electron diffractions (LEED),<sup>1,4</sup> surface extended x-ray-absorption fine structure,<sup>5</sup> ion scattering spectroscopy,<sup>6</sup> and EDPD (this work and Ref. 7), then most of the  $c(2 \times 2)$  oxygen atoms are adsorbed at the 0.8–0.9-Å  $d_1$  spacing. To explain the large EELS frequency shift without a change in  $d_1$ , the force constant for O-Ni vibrations must decrease significantly from  $p(2 \times 2)$  to  $c(2 \times 2)$ . Whether such a large decrease is reasonable is unclear, because the surface chemical bond is very poorly understood. Surface-chemistry models published to date have not realistically accounted for the effects on bonding of  $c(2 \times 2)$  vs  $p(2 \times 2)$  coverage. These models rely on clusters of single oxygen atoms with many nickel atoms and do not take into account the effects of neighboring oxygen atoms in the  $c(2 \times 2)$  structure. Recent theoretical work by Bauschlicher *et al.*<sup>8</sup> has brought the prediction of a near-coplanar model for the  $c(2 \times 2)$ O system into question. It will be interesting to learn whether the EELS result is consistent with potential-energy curve calculations using larger slab geometries.

### III. COMPARISON BETWEEN EDPD AND LEED

The strength of our conclusions about  $d_1$  values as derived from EDPD results is based on the sensitivity of EDPD curves to  $d_1$  of the O-Ni separation explicitly. Because of the similarities between EDPD and LEED, it is useful to point out some important differences. In a LEED intensity-voltage ( $I$ - $V$ ) curve for an integral-order spot [e.g., the (00) beam], the diffraction interference between oxygen and nickel is obscured by intensity modulations from the nickel substrate. Assuming normal incidence, we can write the (00) beam intensity as

$$\begin{aligned} I_{00} &\sim |f_0 e^{i\phi_0} + e^{2ikx} R_s e^{i\psi_s} + \dots|^2 \\ &= R_s^2 + 2f_0 R_s \cos(2kx + \psi_s - \phi_0) \\ &\quad + f_0^2 + \dots, \end{aligned} \quad (11)$$

where  $f_0$  is the backscattering amplitude from the oxygen layer, and  $R_s$  is that from the nickel substrate slab. The quantities  $\phi_0$  and  $\psi_s$  are their respective phases,  $k$  is the electron wave vector, and  $x$  is the perpendicular distance between the O overlayer and the topmost Ni layer. We have taken only the incident beam and one reflected beam in Eq. (11). Inclusion of more beams will complicate matters but will not affect the following arguments. The first term  $R_s^2$  is the (00)-beam  $I$ - $V$  curve for clean nickel. We note that it *does not* contain the O-Ni spacing  $x$ . The second term contains  $x$  but is smaller by the ratio  $2f_0/R_s$ . Thus we have a cosine curve containing the unknown  $x$  superposed on  $I_{00}$  of clean Ni. At low energies, this produces shifts in peak positions and formation of split peaks and shoulders on  $I_{00}$  of clean nickel. At higher energies,  $f_0$  (backscattering from oxygen) decreases more rapidly than  $R_s$ , so we approach the clean nickel  $I$ - $V$  curve. It is also clear from Eq. (11) that the Fourier transformation of  $I_{00}$  does not readily give distances simply related to  $x$ .

In LEED, there is the option of studying an oxygen-induced spot [e.g., the  $(\frac{1}{2} \frac{1}{2})$  beam]. Again, taking only the incident beam and one scattered beam, we can write its leading terms as

$$I_{1/2,1/2} \sim 2R_s f_\theta^o f_{\pi-\theta}^o \cos(2kx + \psi_s + \psi_\theta - \psi_{\pi-\theta}) + R_s^2 f_\theta^{o^2} + \dots, \quad (12)$$

where  $\theta$  is the angle between the surface normal and the  $(\frac{1}{2} \frac{1}{2})$ -beam direction. We see from Eq. (12) the leading term of  $I_{1/2,1/2}$  does depend on  $x$ . However, its intensity is smaller as it contains two scatterings off the overlayer:  $f_\theta^o$  (backscattering) and  $f_{\pi-\theta}^o$  (large-angle forward scattering). The oxygen-induced spots are very sensitive to the unknown  $x$ , but these beams have strong intensities only at low energies. Good surface order and low-temperature measurements are essential for obtaining useful half-order LEED  $I$ - $V$  curves in a wide energy range.

In an EDPD curve, there are no integral- or half-order directions. Any exit-angle direction has a leading modulation term sensitive to  $x$ , the O-Ni spacing. For example, at emission normal to the surface, we can write<sup>18</sup>

$$I_{\theta=0} \simeq A_0^2 + 2A_0^2 R_s \cos(2kx + \psi_s + \phi^+ - \phi^-) = A_0^2 + 2A_0^2 \sum_{\alpha=1}^N R_\alpha \cos[2k(x + d_{1\alpha}) + \phi_\alpha + \phi^+ - \phi^-] + \phi^+ - \phi^-, \quad (13)$$

where  $A_0$  is the atomic emission amplitude,  $d_{1\alpha}$  the perpendicular distance from the first nickel layer to the  $\alpha$ th layer,  $R_\alpha$  the backscattering amplitude of the  $\alpha$ th nickel layer,  $\phi_\alpha$  is its phase, and  $\phi^+$  and  $\phi^-$  are the phases of emission in and out of the solid. Again, for simplicity, we have taken only the direct-emission and backscattered directions. The largest term in Eq. (13) is the first term, but this term is just the atomic emission cross section, which for states without a Cooper minimum, is a *smooth* function of energy. The second term in Eq. (14) contains the unknown  $x$  and is a cosine modulation. The normalized modulation term

$$\chi = \frac{I - I_0}{I_0} \sim 2 \sum_{\alpha=1}^N R_\alpha \cos[2k(x + d_{1\alpha}) + \phi_\alpha + \phi^+ - \phi^-], \quad (14)$$

where  $I_0 = A_0^2$ , is a sum of cosine functions whose Fourier transformation gives peaks related to distances  $(x + d_{1\alpha})$ . We note that either Eq. (13) or (14) is *independent* of the oxygen backscattering factor. Thus the modulations in EDPD curves depend mainly on the backscattering factors  $R_\alpha$  of nickel. Since  $R_\alpha$  is appreciable over a wide energy range, this allows measurements of EDPD curves of overlayer systems for a wide energy range at room temperature.

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