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X-ray photoelectron diffraction studies of surface structure: Use of high-angular resolution, R-factor analysis, and holography, with applications to carbon monoxide on Fe(001) and to oxygen and sulfur on the Ni(001) surface

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University of Hawaii, 1991
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OF SURFACE STRUCTURE: USE OF HIGH-ANGULAR RESOLUTION,
R-FACTOR ANALYSIS, AND HOLOGRAPHY, WITH APPLICATIONS TO
CARBON MONOXIDE ON Fe (001) AND TO OXYGEN AND SULFUR ON
THE Ni(001) SURFACE

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ABSTRACT

This dissertation discusses the use of x-ray photoelectron diffraction (XPD) for elucidating the surface structure of several different types of chemisorption systems.

The determination of the tilt angle and orientation of the \( \alpha_3 \)-state of CO on Fe(001) is a particularly interesting subject, since it could be a precursor state to atomic dissociation. A series of combined polar and azimuthal XPD scans was able to quickly determine that the CO molecule was indeed tilted by making use of the very strong intra-molecular electron forward scattering that permitted pinpointing the polar tilt angle and azimuthal orientation by simply sighting down the direction of the most intense photoelectron diffraction intensity.

The study of c(2×2)S on Ni(001) represents the first use of higher angular resolution (\( \leq \pm 1^\circ \)) XPD and R-factor comparisons of experiment to theory for a very well-defined adsorbate system. This overlayer consists of an atomic adsorbate that sits rather high above the surface plane at \( z = -1.3 \, \text{Å} \), and it is thus a challenging problem for forward-scattering-dominated XPD to resolve. Nevertheless, we show that high-angular resolution XPD is capable of not only answering the question of the \( z \)-distance, but also the even more difficult task of resolving the first-to-second Ni interplanar spacing problem. The additional diffraction fine structure that appears in both the experimental and theoretical data, along with an R-factor analysis, illustrate the usefulness of this new direction and its potential for applications to a wide variety of systems. We also consider the possibility of holographically analyzing such XPD data using Fourier transform methods. These results are found to be encouraging, even for the limited experimental data set available here; theoretical simulations also suggest interesting directions for future study.

Lastly, the determination of the various surface structures that appear on a clean Ni(001) surface upon its exposure to oxygen is investigated via a combined XPD/low energy electron diffraction (LEED) study. Although a much studied case, there is still some
controversy over the actual structure of both the c(2×2) O overlayer and the point at which oxide nucleation begins to occur. We conclude from our XPD data that oxide nucleation occurs quite early in the c(2×2)O chemisorption region and that this effect may have influenced prior studies of this structure. We have also discussed for the first time a NiO(001) superlattice that grows on the surface at saturation oxygen coverages; this is seen in our LEED results.
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<td>ARPEFS</td>
<td>Angle-resolved photoemission fine structure</td>
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<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
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<td>ESDIAD</td>
<td>Electron stimulated desorption ion angular distributions</td>
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<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>HP</td>
<td>Hewlett-Packard 5950A electron spectrometer used in this study</td>
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<td>SWIFT</td>
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<td>STM</td>
<td>Scanning tunneling microscopy</td>
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<td>TPD</td>
<td>Temperature programmed desorption</td>
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<td>UHV</td>
<td>Ultra high vacuum</td>
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<td>UPS</td>
<td>Ultra-violet photoemission spectroscopy</td>
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<td>VG</td>
<td>VG Scientific ESCALAB5 electron spectrometer used in this study</td>
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<td>XPD</td>
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CHAPTER 1

GENERAL INFORMATION

1.1. INTRODUCTION:

The study of the properties and structures of solid surfaces continues to yield fascinating new discoveries as recent technological improvements allow ever more powerful analytical tools to unlock the mysteries that lie in the near surface region of only a few atomic layers in thickness. The field of surface science remains one of continuing growth as our desire for ever greater technological advances demand a significantly more detailed chemical and physical understanding of the processes that occur at surfaces. This growth has been driven by the rapid advances in solid state electronics, as well as by the need to better understand such processes as catalysis, corrosion, lubrication, adhesion, and abrasion. Recent research has made it increasingly clear that the surface region of a solid can have markedly different properties from its bulk. The chemical composition at the surface, as well as both its atomic and electronic structure can differ radically from the corresponding bulk solid properties, and these differences can have an impact on the types of chemical and mechanical processes that occur on a surface. The "surface" of a solid can be defined to be the material that lies within the first few atomic layers--the region over which properties are found to differ significantly from bulk properties--and all of our discussion will be limited to this region. Since the foundation of any theoretical description of the chemical, mechanical, electrical and vibrational properties of a surface depends on detailed information
on the atomic arrangement or atomic geometry involved, surface structure determinations are a key starting point for understanding all of the interactions that occur.

This dissertation deals largely with the use of scanned angle x-ray photoelectron diffraction (XPD) for determining surface atomic geometries. In some cases, XPD has been used in conjunction with low energy electron diffraction (LEED) for observing the symmetry, periodicity, and quality of an overlayer. The XPD results are furthermore analyzed by using a reliability factor (R-factor) analysis to determine the fit to single scattering (SS) predictions of various proposed surface structures. An R-factor analysis is simply a mathematical means for quantifying the degree of agreement between two curves, data point by data point, using a function that measures the differences according to some algorithm.

There are currently a wide variety of experimental techniques that can be used to study surface structures. Some of the more common ones are low energy electron diffraction (LEED) [1], medium energy ion scattering (MEIS) [2], surface extended x-ray adsorption fine structure (SEXAFS) [3], and scanning tunneling microscopy (STM) [4]. All except STM require some kind of theoretical modeling in which the experimental features are compared to calculations for a given structure; in STM, by contrast, the atomic positions are in some cases sampled directly (more precisely, any structure in the surface density of states is sampled directly). LEED uses a monoenergetic beam of electrons that is scattered off a surface and the symmetry of the resulting diffraction pattern is observed. This information is sampled over a wide area of >100 Å in radius, and is most commonly used to monitor the quality of the prepared surface. A more sophisticated approach requires that the intensities of a number of these diffraction spots be measured as a function of the incident electron beam voltage, plotted versus beam voltage to yield a so-called I-V curve, and compared to very complex electron multiple scattering calculations using R-factors [5,
to derive the various structural parameters. MEIS on the other hand, typically uses monoenergetic He$^{+2}$ nuclei (or other suitable ions) in the range of 10,000-100,000 eV and monitors the energy distribution of these ions in various backscattering directions. This technique has been used to determine the elemental identity of buried species greater than 10 atomic layers deep, well beyond what can normally be detected by any of the other conventional surface techniques in use today. Through the further use of ion shadowing and blocking experiments, the position of adsorbates as well as surface reconstructions have been determined with an accuracy of $\pm 0.01$ Å. SEXAFS requires the use of a variable energy photon source which restricts its use to a synchrotron radiation facility; the x-ray absorption cross-section is measured as a function of photon energy at a point starting approximately 100-200 eV above some x-ray adsorption edge. Small oscillations of the adsorption cross-section are observed as the photon energy is swept to higher values up to $\sim 400-500$ eV above threshold. These oscillations are the result of photon-excited electrons scattering off of atoms adjacent to the emitting atom. Fourier transforms of SEXAFS data routinely report atomic spacings of very high accuracies ($\sim \pm 0.05$ Å) but often are restricted by the close proximity of other adsorption edges which limit the usefulness of the technique. On the other hand, STM is unique in that it is the only technique that has the ability in some cases to directly image the positions of single atoms on a surface. These images are the result of measuring the tunneling current between a specially prepared tip (most often of W) that is kept at a constant bias voltage while being mechanically scanned across the surface, all while hovering within a few angstroms of the surface plane. While the vertical resolution is quite impressive at $\sim 0.05$ Å, the lateral resolution is much poorer at $\sim 0.3$ Å, and positive identification of the types of atoms observed is impossible at present.

X-ray photoelectron diffraction has by now also established itself as a valuable tool for determining the atomic structures of surfaces and a number of review articles have been
published on this subject [7]. XPD is basically a refinement of the surface analytical technique known as x-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA). The XPS measurement is accomplished by irradiating a sample with monoenergetic soft x-rays (we have used both Al Kα and Mg Kα, at 1486.6 eV and 1253.6 eV, respectively) and observing the kinetic energy distribution of the emitted electrons (XPS), as well as their angular distributions (angle-resolved XPS or XPD). The basic energy conserving process was first described by Einstein in 1905 and termed the photoelectric effect [8]. Photons of sufficient energy that are incident on an atom residing in the near-surface region of a solid will eject an electron having a kinetic energy given by:

$$E_{\text{kin}} = h\nu - E_b - \phi_{\text{spect}}.$$  (1-1)

where $h\nu$ is the energy of the incident radiation, $E_b$ is the Fermi-referenced binding energy of the excited electron in the atom being irradiated (assuming that the electron is a core electron and thus atom-specific), and $\phi_{\text{spect}}$ is the work function of the spectrometer, which typically ranges between 4 and 5 eV depending on the interior material used. These photon-excited electrons are known as photoelectrons. The binding energy of a core electron may be simply regarded as the ionization energy of a particular atomic shell, perhaps with additional shifts or splittings due to chemical or magnetic effects. Measuring the energy distributions of the photoelectrons provides immediate chemical information on the various species present both on and in the surface region. A typical XPS overall energy distribution curve for clean Ni(001) using an Al Kα x-ray source is shown in Figure 1.1(b), where the Ni 2p1/2, Ni 2p3/2, Ni 3s and Ni 3p photoelectrons, as well as some Ni LMM Auger electron peaks at a kinetic energy range near 800 eV, are indicated. Exposing the cleaned surface to 1200 L of oxygen ($1 \text{ L} \equiv 1 \times 10^{-6} \text{ Torr-sec.}$) results in the formation of a thin
saturated oxide overlayer, shown here by the appearance of an O 1s photoelectron peak centered at $E_{\text{kin}} = 958$ eV in Figure 1.1(a). Quantitative analytical information can be obtained by integrating the intensity under the O 1s photoelectron peak (shown in the insert in Figure 1.1) after subtracting off the inelastically scattered background and comparing it to a similarly treated substrate emission peak, such as the Ni 2p$_{3/2}$. This process will be discussed in greater detail in Chapter 5.

Detailed structural information can be obtained if these adsorbates are deposited or grown on clean single-crystal substrates by observing the angular distributions of the photoelectron intensity. These angular distributions exhibit much structure due to the scattering interactions that these electrons undergo from neighboring atoms before escaping from the surface and being energy analyzed.

There are two main types of XPD as illustrated in Figure 1.2. In the scanned energy mode shown at right [also known as angle-resolved photoemission fine structure (ARPEFS)], the photon energy of the incident x-rays is allowed to vary while maintaining a fixed electron emission direction [9, 10]. Typically, the incident photon energy (as well as the kinetic energy of the emitted electrons) is swept upward over a range from about fifty to several hundred electron volts above the binding energy of the particular electron orbital, while at the same time the number of emitted photoelectrons is monitored. The tunable x-ray source required for this type of experiment is available only at a synchrotron radiation facility and will not be discussed further. The second type of XPD shown at left can be performed with a conventional fixed-energy x-ray tube as the excitation source and involves scanning emission angles so as to measure the angular distribution of a particular photoelectron intensity at fixed $h\nu$ (and thus fixed kinetic energy). Such an experiment requires an instrument capable of carrying out high-precision angle scans of two types in a general experimental geometry such as that shown in Figure 1.3. These are azimuthal angle
scans where both the polar angle ($\theta$) and photon energy remain fixed, and polar angle ($\theta$) scans where the azimuthal angle ($\phi$) and the photon energy are fixed. For simplicity, the $\phi$-angles will be referenced to some low index direction, while the $\theta$-angle will be measured with respect to the surface plane (i.e. $\theta = 90^\circ$ corresponds to emission along the surface normal $\hat{n}$). Throughout this dissertation, the surface normal is along the [001] direction and the $\phi$-angle is defined with respect to the [100] equivalent direction, as shown in Figure 1.3. Core-level electrons are generally used when measuring these angular distributions to avoid complex effects in the valence-level energy spectra due to multi-site chemical bonding, although a few scanned-angle valence-level studies have recently been done [11]. Another consideration is that valence levels tend to have much smaller cross-sections compared to fully occupied core levels, such that the latter result in significantly higher count rates and shorter data collection times, an important consideration when studying either unstable intermediate states or highly reactive surfaces.

The interpretation of XPD data so as to determine the details of the atomic positions in the surface region requires the comparison of the experimental diffraction data to theoretical simulations based on clusters having the proposed structures. The experimental data is based upon peaks representing elastic photoelectron scattering from the atoms adjacent to the emitting atom; these in fact are the features directly describable by Equation (1-1). (Only a couple of studies of the diffraction of inelastic peaks in XPS spectra have so far been done [12].) The elastic diffraction pattern is thus the result of a complex scattering interaction involving the direct, unscattered photoelectron wave interfering with the elastically scattered waves that have been produced by interaction with the atomic potentials of the neighboring atoms, as discussed more quantitatively in the next section.
1.2. THEORETICAL MODELING:

1.2.1. SINGLE-SCATTERING CLUSTER MODEL-

The theoretical model that has been found in the past to describe most of the features in XPD patterns quite well is the single scattering cluster (SSC) approach. Figures 1.3 and 1.4 illustrate the basic geometries that are used to describe the SSC model. Here, the angle $\alpha$ between the incident unpolarized x-ray beam and the observed direction or wave vector $\vec{k}$ of the exiting photoelectron is set to either 72° or 48° depending on the XPS spectrometer (HP or VG spectrometer, respectively, as described below).

As shown in Figure 1.4(a), the final-state wavefunction $\psi(\vec{r}, \vec{k})$ as measured along some electron emission direction $\vec{k}$, can be viewed as a superposition of a 'direct' or 'primary' wave $\phi_0(\vec{r}, \vec{k})$ with the summation of the individually scattered waves $\phi_j(\vec{r}, \vec{r}_j \rightarrow \vec{k})$ which result from the interaction of the direct wave and the $j$th scattering atom along the direction $\vec{r}_j$. This final wavefunction is thus simply:

$$\psi(\vec{r}, \vec{k}) = \phi_0(\vec{r}, \vec{k}) + \sum_j \phi_j(\vec{r}, \vec{r}_j \rightarrow \vec{k}) ,$$

and the observed photoelectron intensity is determined by simply squaring the amplitude of the final state wavefunction:

$$I(\vec{k}) \propto |\phi_0(\vec{r}, \vec{k}) + \sum_j \phi_j(\vec{r}, \vec{r}_j \rightarrow \vec{k})|^2 .$$

All of the structural parameters such as bond lengths, bond angles and interplanar separations are contained in the various diffraction peaks of the photoelectron intensity as a
function of $\vec{k}$. XPD is an atom-specific structural probe and, because of both the $1/e$ decay of the outgoing direct wave and the strong inelastic attenuation involved, it is also a probe of the short-range order surrounding the emitter. The local environment of each type of atom can be studied individually and will have a distinct diffraction pattern that is unique to the arrangement of the nearby atoms. The overall amplitudes of the diffraction effects are rather high, having anisotropy values in excess of $\frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}}} = 0.50$. The diffraction curves for azimuthal scans passing through different low-index directions are also quite distinct, as will be discussed in greater detail later.

To consider the SSC model in more detail, we can use Figure 1.4(a). Monochromatic x-ray radiation of polarization $\mathbf{E}$ is incident on the sample surface, and ejects a core-level photoelectron along some direction $\vec{k}$. The photoelectron intensity in this direction, will be given in the dipole approximation as:

$$I(\vec{k}) \propto \left| \langle \psi(\vec{r}, \vec{k}) | \mathbf{r} \cdot \mathbf{E} \psi_c(\vec{r}) \rangle \right|^2,$$

where $\psi_c(\vec{r})$ is the core orbital involved. With the detector placement along $\vec{k}$ taken to be essentially at infinity and further assuming that the photoelectron is the result of $s \rightarrow p$ emission, the final expression for the intensity in the simple plane-wave (PW) scattering SSC limit becomes:

$$I(\vec{k}) \propto |\mathbf{E} \cdot \vec{k} \exp(-L_0/2\Lambda_e) + \sum_j \frac{\mathbf{E} \cdot \hat{\mathbf{r}}_j}{r_j} | f_j(\theta_j) | W_j \exp(-L_j/2\Lambda_e) \exp\{-i[kr_j(1-\cos\theta_j) + \Psi_j(\theta_j)] \}|^2.$$
where \( \exp(-L_0/2A_e) \) and \( \exp(-L_j/2A_e) \) allow for inelastic attenuation of the primary and scattered waves respectively, with an inelastic mean free path of \( A_e \) and total path lengths for escape of \( L_0 \) and \( L_j \), respectively; \( r_j \) is the distance to scatterer \( j \); \( \theta_j \) is the associated scattering angle; \( |f_j(\theta_j)| \) is the magnitude of the PW scattering factor and \( \Psi_j(\theta_j) \) is its phase; and \( W_j \) is a Debye-Waller attenuation factor that takes into account reductions of the diffracted intensity due to thermal vibrations of the scatterers. \( W_j \) depends on the mean squared displacement \( \overline{U}_j^2 \) of each atom and it is given in the simplest approximation as:

\[
W_j = \exp[-2k^2(1-\cos \theta_j)\overline{U}_j^2(T)],
\]

(1.2)

where \( \overline{U}_j^2 \) is the one-dimensional, mean-squared displacement of the \( j^{th} \) atom with respect to the emitter. If the scattering angle of the \( j^{th} \) scatterer is \( \theta_j \), the quantity \( r_j(1-\cos \theta_j) \) represents the geometric pathlength difference between the direct wave and the scattered wave and it contains all of the geometric structural information about the cluster. [Note that the scattered wave also has a scattering phase shift \( \Psi_j(\theta_j) \), associated with it that is dependent on both the scattering angle \( \theta_j \) and the type of scattering atom, \( j \).] The complex PW scattering factor \( f_j(\theta_j) \) associated with the scattering interaction is calculated in a standard way from:

\[
f_j(\theta_j) = \left( \frac{1}{2ik} \right)^{\ell_{\text{max}}} \sum_{\ell=0}^{\ell_{\text{max}}} (2\ell+1) \exp(2i\delta_{\ell}) P_\ell(\cos \theta_j),
\]

for each type of atom present in the cluster, where \( \ell \) is the angular momentum of each partial wave, \( \ell_{\text{max}} \) is a cutoff on \( \ell \) that can be calculated from \( kR_{MT} \) (with \( R_{MT} \) equal to the
effective muffin-tin radius of the scattering potential), $\delta_{\ell}$ is the phase shift of the $\ell$th partial wave, and $P_{\ell}$ is the $\ell$th Legendre polynomial.

At the kinetic energies investigated in this work, significant electron scattering is observed only for small scattering angles, i.e. when $\theta_j$ is rather small ($\leq 20^\circ$–$30^\circ$); this results in the temperature-dependent Debye-Waller equation [see Equation (1-2)] approaching unity for all of the major scattering events, so that thermal effects are expected to be small. Some earlier SSC-PW calculations for Cu(001), found that the values of $U_j^2(T)$ could be varied by as much as a factor of four without noticeably altering the calculated diffraction patterns [13]. Thus, while the incorporation of vibrational effects into these SSC calculations is important for a complete picture of the scattering process, they do not significantly alter the peak positions of the principle forward scattering features unless a "wagging" surface molecule is involved [14]. In the past, these one-dimensional mean-squared displacements were given separate surface and bulk values (surface plane atoms are expected to display somewhat greater vibrational effects compared to bulk due to the extra degree of freedom there) and are available from sources such as LEED where the lower kinetic energies used make large-angle scattering more important and thus render this correction much more significant [1]. On the other hand, high-angular resolution XPD experimental data displays considerably more fine structure and it is important to incorporate thermal vibrations in a more correct manner. The SSC-PW calculations mentioned earlier used a rather simple uncorrelated model for vibration. However, the problem with this is that scatterers closer to the emitter vibrated with the same amplitude as for those further away. Since the atomic motions on real surfaces are correlated, the relative displacement of atoms closer to the emitter should be much reduced over an atom in the same atomic plane but further away from the emitting site. In other words, atoms that are adjacent to the emitting atom will tend to vibrate in unison with the emitter and thus show
lower relative displacements, but the relative displacements will get larger the further away one is from the central atom. At large distances, these displacements will approach the limiting value associated with the uncorrelated approach. Thus, in all of the SSC theory curves described here involving Ni as the substrate, the calculations utilized the correlated lattice vibrational model described in Sagurton et al. [15]. The relative mean squared displacement $\sigma^2_j(T)$ of each $j^{th}$ atom is given by:

$$
\sigma^2_j(T) = \frac{3\hbar^2}{2M_{Ni}k_B\theta_Dq_D^2} \left[ q_D^2 + \frac{4q_D^2}{\alpha^2} \left[ \frac{\pi^2}{6} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} + \frac{\alpha}{n} \right) e^{-n\alpha} \right] \right] - \frac{2}{|R_j - R_e|} (1 - \cos \beta_j)
$$

$$
+ \frac{4q_D}{|R_j - R_e|} \sum_{n=1}^{\infty} \frac{1}{n^2 + (\beta_j/\alpha)^2} \left( e^{-n\alpha}[\sin \beta_j + (\beta_j/\alpha)\cos \beta_j - \beta_j/\alpha] \right),
$$

(1-3)

where $\hbar$ is the reduced Planck's constant, $k_B$ is the Boltzman's constant, $T$ is the sample temperature, $M_{Ni}$ is the mass of a Ni atom, $\theta_D$ is the Debye temperature, $q_D$ is the Debye wave vector, $|R_j - R_e|$ is the distance separating the emitter from the $j^{th}$ scatterer, $\alpha = \theta_D T$, and $\beta_j = q_D |R_j - R_e|$.

The effect of electron refraction at the surface/vacuum interface is taken care of through the use of a substrate inner potential $V_0$. The effect of electron refraction could potentially result in a change of the electron trajectory outside the crystal by as much as a few degrees at grazing emission angles and is especially significant when higher angular resolution XPD is involved. The expression for the internal emission angle $\theta'$ inside the solid can be determined from:
\[ \theta' = \cos^{-1}\left[ \left( \frac{E_{\text{kin}}}{E_{\text{kin}} + V_0} \right)^{1/2} \cos \theta \right] \],

where \( E_{\text{kin}} \) is the kinetic energy of the electron outside the surface, \( V_0 \) is the substrate inner potential and \( \theta \) is the observed polar angle of electron emission outside the solid.

The most interesting feature of the electron-atom scattering factor discussed in Equation (1-2) is that it is dominated by a very pronounced peak in the forward scattering direction for energies above about 500 eV, as shown in Figure 1.5. Only at energies well below 500 eV does the backscattering direction become an important contributor to the overall picture. The ramifications of this effect are twofold. First, the electron kinetic energies looked at in our experimental data, fall very close to 1,000 eV, and thus the scattering is dominated by this "forward scattering" [7] or "forward focussing" [16] effect. A very direct measurement of the direction of the nearest neighboring atoms to a given emitter can be made by using these strong forward scattering peaks, as will be used in Chapter 2 to determine the tilt angle of the \( \alpha_3 \)-state of CO on Fe(001).

Not all of the diffraction features observed are directly due to forward scattering peaks, and significant modulations can come about from scattering through larger scattering angles (\( \theta_j \)) that may involve path length differences of 2, 3, or more times the electron De Broglie wavelength \( \lambda_e \).

The surface sensitivity of XPD is largely due to the strong interactions that photoelectrons have with the atoms of the solid. Depending on their kinetic energy (typically from 50-2,000 eV) and the type of substrate, electron inelastic attenuation lengths can range from about 5 to 30 Å [17]. In addition, by varying the polar electron emission angle, it is possible to further enhance this attenuation effect. At very low electron takeoff angles, it is possible to observe the "no-loss" photoelectron emission from as little as just the first 2-3 atomic layers, even though the incident photon radiation is able to penetrate
much deeper into the bulk. This makes XPD a very versatile probe of the short range order surrounding the emitter. In fact, previous studies have shown that the principle diffraction features are the result of scattering off of the first few (3-5) nearest neighbor atomic shells, although final convergence of all of the diffraction fine-structure may not occur until clusters of 20 to 25 Å in radius are used (see Figure 1.6), as well as discussed in further detail in Chapters 3, 4, and 5.

Finally, a great deal of effort has been expended to improve the theoretical modeling so as to go beyond the SSC-PW approach. Recent improvements include the incorporation of the correct spherical wave (SW) s→p final state by Sagurton et al. [15], and more recently a computationally simpler and far more general method for spherical-wave scattering described by Rehr and Albers [18]. Finally, a versatile cluster based, *multiple scattering* (MS) program by Kaduwela et al. [19] that incorporates the Rehr and Albers approximation and other refinements has recently been completed in our group; the results of this agrees quite well with those from other more time consuming or less accurate MS approaches to XPD by Tong et al. [16] and by Barton and Shirley [20].

In this thesis, all of the diffraction calculations are at least at the SSC-SW level discussed by Friedman and Fadley [21]; in a few cases, MS effects are also assessed using the program of Kaduwela et al. [19]. The principle MS effect of concern for the cases considered in this thesis is what has been termed "defocussing" in emission along dense linear chains of atoms at higher energies above about 500 eV [16(a)], as illustrated in Figure 1.4(b)-ii. In this effect, the intensities along such chain directions can be dramatically reduced relative to the predictions of SS theory if the emitter is at the bottom end of a chain of 3 or more atoms [16, 19]. We discuss this in Chapter 3 in connection with grazing emission from an adsorbate atom and scattering along rows of other adsorbate atoms in the same surface plane.
1.2.2. INPUTS TO THE ssc PROGRAMS-

Some of the values used in the calculation of the relative mean squared displacements $\sigma_j^2(T)$ from Equation (1-3) are: $T$ is the sample temperature in Kelvin = 295 K, $\theta_D$ is the Debye temperature for Ni (taken to be 375 K) [22], $q_D$ is the Debye wave vector for nickel (1.75580 Å$^{-1}$). A Ni inner potential of 11 eV was used for the c(2×2)O and c(2×2)S covered surface [23] while a somewhat larger value of 13.2 eV based on a band structure calculation by Mattheiss [24] was used for the saturated NiO. No inner potential was used in the analysis of the CO/Fe data due to the surface adsorption involved and the relatively large tilt angle associated with the intramolecular forward scattering. While it is possible to treat $V_0$ as an adjustable parameter, we have not done so in this thesis. The inelastic mean free path for Ni 2$p_{3/2}$ at 629 eV or $\Lambda_c^m(629 \text{ eV})$ was taken to be 10.0 Å for the clean metal [25] and assumed to scale as $E_{\text{kin}}^{0.52}$ in the oxide, leading to a value for the O 1$s$ peak at 954 eV of

$$\Lambda_c^{ox}(954 \text{ eV}) = (10 \text{ Å}) \left( \frac{954 \text{ eV}}{629 \text{ eV}} \right)^{0.52} = 12.3 \text{ Å}.$$  

Similarly, the mean free path for S 2$p$ emission from the S/Ni system at 1085 eV used was 13.3 Å. The mean free path for C 1$s$ (1206 eV) emission from CO/Fe(001) was arbitrarily set to 100 Å since the actual value used would not affect the outcome of the analysis due to large electron takeoff angle encountered and the small clusters used in the analysis. The surface cutoff of inelastic loss at the surface was arbitrarily set to occur at the Ni hard sphere distance of 1.24 Å above the centers of the topmost Ni plane. A similar treatment
was used in the CO/Fe analysis, although again, because of the large electron takeoff angle, it did not affect the SSC calculations.

1.3. EXPERIMENTAL PROCEDURES:

1.3.1. DESCRIPTION OF INSTRUMENTATION-

The experimental work presented in this thesis was done on two highly modified ultra-high-vacuum x-ray photoelectron spectrometer systems in our surface science laboratory. These machines are a Hewlett-Packard 5950A (= "HP") and a VG Scientific ESCALAB5 (= "VG") electron spectrometers and they have been modified to allow high-precision XPS data collection in both the polar- and azimuthal- directions under complete computer control, and faster data acquisition via very efficient Surface Science Laboratories resistive anode detectors [7(a), 26].

The HP 5950A spectrometer is equipped with a monochromatized Al Kα radiation source (1486.6 eV) in addition to a custom-built long-travel sample probe that permits the transfer of sample material from a separate preparation chamber to the main analysis chamber while under UHV conditions. The pressure in the main analysis chamber was typically maintained in the mid 10^{-11} Torr range, while the preparation chamber was able to maintain pressures in the mid 10^{-10} Torr range. The preparation chamber also included facilities for observing LEED patterns, in situ sample cleaning with an ion gun, and temperature monitoring with an infrared pyrometer. The purity of the admitted gases could also be checked with a mass spectrometer residual gas analyzer. Both chambers were fitted with separate ion and titanium sublimation pumps to maintain these UHV conditions. The solid angle to the electron analyzer has been determined from electron trajectory calculations.
to be a cone of $\sim3.5^\circ$ half angle, but with a value that is dependent on the kinetic energy of the incoming photoelectron [27].

The VG spectrometer features a very versatile twin x-ray anode that could provide both unmonochromatized Al and Mg K\text{$\alpha$} x-rays at an energy of 1486.6 and 1253.6 eV, respectively. A secondary monochromatic Al K\text{$\alpha$} x-ray source, although available, was not used in this study. The pressure in the analysis chamber was maintained at $5 \times 10^{-11}$ Torr using both oil-diffusion and titanium sublimation pumps. The higher angular resolution capability comes from the use of a set of fixed length-to-diameter tube arrays mounted on a rotatable plate and it allows several different angular acceptance cones to be brought into use [28]. Currently, two tube array assembles of $\pm1.5^\circ$ and $\pm3.0^\circ$ angular acceptance and a single open aperture of $\pm3.0^\circ$ are available, with the poorest resolution being a $\pm6.0^\circ$ aperture when the rotatable plate is moved completely out of the way. The higher angular resolution data comes at a very high cost, for $\pm1.5^\circ$ aperture there is a $56\times$ reduction in throughput intensity over the $\pm6.0^\circ$ aperture, with a corresponding increase in the data collecting time [28]. In situ sample cleaning via ion sputtering is available, along with temperature monitoring with an IR pyrometer and leak checking with a residual gas analyzer.

1.3.2. SAMPLE PREPARATION-

1.3.2.1. Fe(001)-

The sample described in Chapter 2 is a single crystal wafer of Fe(001) that was kindly donated to us by Dr. Stephen Cameron of Exxon Research and Engineering, and it
was used in the determination of the tilt angle of the $\alpha_3$-state of CO on Fe(001). This crystal was initially cut to the [001] face, polished and hydrogen furnace treated to reduce the bulk sulfur concentration. After arrival in Hawaii, this crystal surface was observed to have extensive rust formation, possibly from the humidity during storage by us, and it thus had to be repolished by Dr. Masamichi Yamada and Mr. Greg Herman. All repolishing was done with an oil-base diamond abrasive paste to reduce the amount of surface oxidation, using subsequently smaller grit sizes from 15 $\mu$m down to 0.25 $\mu$m. The misalignment from the [001] face after repolishing was less than ±0.5° as determined from back-reflection Laue measurements and the crystal was not subjected to the hydrogen furnace treatment. After mounting the sample in the sample preparation chamber using standard Mo sample clips, the sample wobble about the azimuthal axis was observed to be less than ±0.2° as determined from a laser alignment check.

The cleaning of Fe single crystals is complicated by the bcc $\rightarrow$ fcc phase transition at ~1190 K which prevents heating the sample above 1170 K, even though the melting point is much higher at ~1,770 K. This particular sample had an especially large amount of dissolved oxygen in the bulk, with lesser amounts of sulfur and carbon. No other contaminants were observed throughout the study. When annealing the Ar$^+$ sputtered crystal for a few minutes to 973 K or higher, the coverage of oxygen increased from about 0.20 ML to a saturation coverage of about 1.5 ML as determined from XPS intensity ratios. Continued heating at this temperature resulted in the replacement of the oxide layer with a sulfur layer. This sulfur layer (final coverage 1.0 ML) apparently replaces the oxide layer since no oxygen was detected by XPS at this stage. This sulfur overlayer was very stable and no change in the coverage was noted even on prolonged annealing.

The standard cleaning recipe in use at EXXON [29] at the time involved initial sputtering at 1073 K for a few hours to remove all traces of oxygen and sulfur from the
surface and near-surface region. Once cleaned, routine sputtering was done at 1073 K for 10 minutes (beam voltage not stated) then at 700 K for an additional 5 minutes before annealing at 700 K for another 5 minutes. Our experience is that sputtering at these elevated temperatures were counterproductive; while they do appear to bring the sulfur to the surface for removal by sputtering, we could not deplete the near-surface/bulk region quickly enough to notice a reduction in the surface impurity concentration after cleaning. Prolonged sputtering at elevated temperatures were also observed to result in the formation of very small pits in the surface requiring the crystal to be repolished. Since the high temperature anneals were not necessary to restore surface order after sputtering and since we were not interested in studies at elevated temperature, the high temperature sputtering cycle was eliminated in favor of a longer sputter at lower temperatures.

The recipe we settled on for routine cleaning was thus done at reduced temperatures. First annealing at 673 K for 1 hour to drive off the CO overlayer, then checking the XPS coverages. If the total contamination level was greater than 0.10 ML (about the cleanest that we could do), a one hour Ar⁺ sputter at 673 K and a beam voltage of 600 V was done. Without annealing after the sputtering, typical XPS coverages were as follows:

- 0.15–0.20 ML oxygen
- 0.10 ML carbon
- no evidence of sulfur

By annealing for several hours (usually overnight) at 673 K in the main chamber (<1.0 × 10⁻¹⁰ Torr during the anneal), typical coverages were found to be:

- 0.08—0.10 ML oxygen
- no evidence of carbon
- no evidence of sulfur
These results suggest that the freshly cleaned Fe(001) surface is extremely reactive and is quickly contaminated with CO present in the residual gas of the preparation chamber. A thorough check of the system with a residual gas analyzer (RGA) showed normal background levels of CO in the residual gas of a baked UHV system and no evidence for a leak of any kind.

By carefully controlling the annealing temperature after sputtering, it was possible to maintain the total O, C, and S contamination level to approximately 0.08 ML, with the principle contaminant being oxygen. In a subsequent study by Cameron et al. [30], this residual contamination of oxygen, if present as an overlayer on the surface, was found to simply block the adsorption of the CO molecule at those sites which they occupy and reduce the CO coverage accordingly.

The $\alpha_3$-state of CO was generated by introducing 15 L ($10^{-7}$ Torr $\times$ 150 sec) of CO to the sample at room temperature, with the following final XPS coverages being derived:

- 0.52 ML oxygen
- 0.33 ML carbon
- no evidence of sulfur

The oxygen coverage of 0.52 ML is thus consistent with the diffuse $c(2\times2)$ LEED pattern observed, with the ideal $c(2\times2)$ coverage being 0.50 ML. The lower carbon coverage of 0.33 ML is probably due to blocking of $\sim$ 0.17 ML of the $c(2\times2)$ sites by residual oxygen.

Longer exposures up to 100 L did not change the coverages of either carbon or oxygen, so this overlayer is effectively saturated. This CO overlayer was found to be relatively unstable and had to be renewed only after each combined C 1s/O 1s data run of approximately 20 hours duration.
1.3.2.2. \textit{Ni(001)}-

The \textit{Ni(001)} sample described in the remainder of this thesis was cut from a single crystal rod of this same material on a low speed diamond saw and oriented to within \( \pm 0.3^\circ \) of the [001] surface normal by back-reflection Laue. This sample was then mounted in a bakelite polishing ring with epoxy and allowed to setup overnight. The sample and ring were sanded with 600 grit silicon carbide paper, using water as a lubricant, on a mechanical polisher to get the sample face flush with the edge of the ring. The subsequent polishings were done using successively finer grades of diamond paste of 15 \( \mu \), 6 \( \mu \), 3 \( \mu \), and 1 \( \mu \), grit size before switching to the finest polishings of 0.30 \( \mu \), 0.1 \( \mu \) and finally 0.05 \( \mu \) alumina. The polishing ring was ultrasonically cleaned in methanol, while paying careful attention to prevent cross-contamination of the polishing abrasive. The epoxy was removed by soaking in methylene chloride, taking particular care to minimize any stress to the Ni sample from the expanding epoxy. The crystal alignment was again checked by Laue and found to have remained unchanged. The final dimensions of the sample were approximately 6 mm diameter by 2 mm thick.

Immediately prior to the installation of the Ni crystal into the sample preparation chamber, a final chemical etchant was used to remove any surface damage that could have come about by the mechanical polishing. The etchant used was a 10\% solution of 1:1 \textit{HNO}_3/\textit{H}_2\textit{SO}_4 and it was allowed to remain in contact with the sample for 10 minutes before rinsing with copious amounts of distilled water.

The initial cleaning of the \textit{Ni(001)} crystal in vacuum was done by cyclic \textit{Ar}^+ bombardment at a beam voltage of 600 volts for one hour at normal incidence. The argon pressure was maintained at \( 5.0 \times 10^{-5} \) Torr while heating the crystal to \( \sim 813 \) K throughout
the sputter. Immediately after sputtering, the sample temperature was raised to ~873 K for five minutes to anneal the surface damage and to degas the crystal bulk of argon. The contaminants in the highest concentration found on this crystal consisted of sulfur, carbon and oxygen that were noted in the full-range XPS survey scans. Their individual coverages were carefully monitored throughout the course of the experiments. Periodic survey scans did not reveal any other contaminants. The sulfur and oxygen were quickly removed by several repeated Ar\(^+\) bombardment and annealing cycles; however it was carbon at ~0.022 ML that resisted all early attempts at removal. Some success was achieved by exposing the sample to O\(_2\) before bombardment and after several attempts, the combined coverage of all three containments were kept below 0.02 ML throughout the course of the experiment.

Care must be exercised here because it is known [31] that oxygen will quickly diffuse into the bulk at temperatures above 500 K. Hence, heating the sample to high temperatures should not be attempted unless the the oxygen coverage is quite low (below 0.05 ML).

The c(2×2) sulfur overlayer was formed by exposing the cleaned Ni(001) surface to 30 L (10\(^{-7}\) Torr × 300 sec.) of H\(_2\)S at ambient temperature. The surface was then briefly annealed to 493 K for a few minutes. The c(2×2) sulfur LEED pattern was sharp and well-defined and remained so throughout the length of time required for data collection of approximately 20 hours in duration. There was no noticeable buildup of any O or C contamination at the end of this time period. Each azimuthal data set involved cleaning and redepositing of a new sulfur overlayer.

The O/Ni(001) experiments were performed in a manner similar to that which was done for S/Ni(001). The oxygen overlayer was made by carefully exposing the clean Ni surface to oxygen for various exposures that are described in Chapters 4 and 5. The uniformity of the chemisorbed oxygen and NiO overlayers were monitored by LEED both before and after an azimuthal or polar scan. A series of O 1s and Ni 2p\(_{3/2}\) core spectra
taken at various oxygen exposures are shown in Figures 1.7 and 1.8. In Figure 1.7, there appears to be a small 0.3 eV shift to higher kinetic energy in the O 1s position of the oxide peak as compared to the c(2x2) overlayer. This could be a chemical shift due to the formation of the oxide; however the effect is small and we did not investigate this further. The clean Ni 2p3/2 signal shown in Figure 1.8 shows the very characteristic 6 eV satellite that is due to a many electron transition and must be included in the integrated intensity measurements if accurate coverages are to be derived [25]. The Ni 2p3/2 peak for the saturated oxide at 1200 L is noticeably broadened, making the integrated intensity determination difficult if not impossible. This will be discussed in further detail in Chapter 5, when we carry out our estimations of the saturated oxide thickness.

The only contaminant noted for this series of experiments was the gradual appearance with time of a small shoulder in the O 1s XPS peak from the saturated oxide centered at approximately 1.3 eV lower kinetic energy, as shown in Figure 1.9, which compares the O 1s photoelectron peak taken at a polar angle of 46° and a similar peak taken at a polar angle of 11°. As this figure indicates that this contamination feature was only apparent at low θ angles, and only if the surface was not cleaned and redeposited for some time (~5 days). This minor surface contaminate is reported to be the result of H2O present in the residual gas that reacts with the NiO overlayer to form a hydroxide contaminant [31].

1.4. OUTLINE OF THESIS:

The specific cases studied in this thesis by XPD in combination with LEED represent several distinct and prototypical types of surface structure problems. In Chapter 2, we consider a diatomic adsorbate exhibiting a highly tilted geometry with respect to the surface [the α3 state of CO on Fe(001)], a case for which simple forward scattering peaks
are found to provide direct structural information on the nature of the tilt. In Chapter 3, we study a simple atomic adsorbate [sulfur on Ni(001)] in a well-ordered c(2×2) structure that has been used as a reference case to test new structural techniques, and we ask how much additional structural information can be derived with the use of high angular resolution experimental data and more quantitative R factor comparisons of experiment and SS theory. The potential influence of multiple scattering effects and the possibility of analyzing such data by holographic inversion methods are also considered here. In Chapters 4 and 5, we treat a more complex system representing the stages of oxidation of a metal [oxygen on Ni(001)], in which structures all the way from fractional-monolayer coverages of adsorbed O atoms to several monolayers of saturated oxide are analyzed.
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Figure 1.1. Overall x-ray photoelectron spectroscopy (XPS) energy distribution curves for Ni(001) taken with Al Kα radiation. (a) After a 1200 L exposure to oxygen that results in the formation of a thin oxide overlayer covering the Ni surface, and with an expansion of the O 1s spectrum shown as in the insert. (b) Clean Ni(001) with the positions of the Ni 2p1/2, Ni 2p3/2, Ni 3s, Ni 3p and Ni LMM Auger lines indicated.
Figure 1.2. The three basic types of photoelectron diffraction measurements are shown here. They include (1) an azimuthal (φ) scan at constant polar angle, (2) a polar (θ) scan at constant azimuthal angle, and (3) a variable-energy scan along some fixed emission direction. The scanned-energy mode (also called angle-resolved photoemission fine structure (ARPEFS) requires access to a synchrotron radiation facility.
Figure 1.3. Schematic diagram of the experimental geometry. The angle $\alpha$ is fixed at 48° and 72° for the VG and HP spectrometers respectively, and the radiation is unpolarized in both cases. Note that the θ-angle is measured with respect to the surface and φ is referenced against a low-index direction. In all cases discussed in this thesis, the low-index direction chosen is the [100] azimuth.
Figure 1.4. (a) Illustration of some of the assumptions used in the single-scattering cluster model (SSC), with the various quantities indicated. (b) Two types of multiple scattering effects that need to be considered. (i) At low energies << 500 eV, backscattering is important, but it can be ignored at the energies studied at in this thesis. (ii) Multiple forward scattering along rows of atoms reduces the observed intensity along the scattering direction and will be an important consideration above >500 eV.
Figure 1.5. Dependence of the magnitude of the plane-wave scattering factor $|f(\theta_{Ni})|$ for Ni as a function of scattering angle $\theta_{Ni}$ for various electron kinetic energies from 50 to 1320 eV. Note the increasing strength of the scattering factor in the forward direction as the electron kinetic energy increases and a reduction of strength in the backscattering direction.
Figure 1.6. (a) Some of the different-sized clusters used in a single-scattering analysis of c(2x2)O/Ni(001) to test for the convergence of the diffraction features. (b) Calculated curves for the various clusters at $\theta = 8^\circ$ and $z = 0.80$ Å. Note that a cluster of radius at least 20 Å is needed for optimal agreement.
Figure 1.7. O 1s spectra taken at various oxygen exposures from the clean metal to the saturated oxide at 1200 L. Note the small 0.3 eV shift to higher kinetic energy of the peak maxima in going from the c(2×2) overlayer to the saturated oxide.
Figure 1.8. Ni 2p3/2 spectra taken over the same oxygen exposure range as in Figure 1.7. Note that at 1200 L, the saturated oxide broadens the Ni peak and makes integrating the peak intensity more difficult.
Figure 1.9. O 1s spectra taken after an initial oxygen exposure of 1200 L and then exposure to the residual gas at $5.0 \times 10^{-11}$ Torr for 5 days. The shoulder that is very evident at the more surface sensitive angle of $\theta = 11^\circ$ is thought to be due to a surface contaminant brought about by the reaction of residual H$_2$O with the oxide surface, resulting in the formation of a hydroxide compound. Our surfaces were cleaned and redeposited after every 24-48 hours, and were not affected by this.
CHAPTER 2

STRUCTURE OF AN UNUSUAL TILTED STATE OF CO ON Fe(001) FROM X-RAY PHOTOELECTRON DIFFRACTION

2.1. ABSTRACT:

The highly tilted $\alpha_3$ state of CO on Fe(001) has been studied using combined polar and azimuthal x-ray photoelectron diffraction. A more accurate structural picture is derived, with the molecule being tilted at an angle of $55^\circ \pm 2^\circ$ with respect to the surface normal along <100> azimuths and probably occupying fourfold hollows. An estimate is also made of the vertical C distance above the Fe surface. The utility of combined $\theta/\phi$ x-ray photoelectron diffraction measurements for such unusual adsorbate structures is demonstrated.

2.2. DISCUSSION:

The existence of an "abnormal" or "unusual" type of surface bonding state of CO that involves a tilted or lying-down geometry and a considerably lowered CO stretch frequency has been discussed recently for several different transition-metal surfaces including Fe(001) [1-3], Cr(110) [4,5], and Mo(001) [6]. This state is of considerable interest because it may represent a precursor to dissociation with a weakened CO bond due to additional electronic interactions with the metal substrate [1]. However, little is known
about the exact geometric structure of the CO for any of these cases. For the case of α3 CO on Fe(001) that we will consider here, electron-energy-loss (EELS) measurements show a very low CO stretch frequency of 1210 cm\(^{-1}\) [1]. Near-edge x-ray-absorption fine-structure (NEXAFS) measurements on this state have been used to deduce an elongation of the CO bond by 0.07 ± 0.02 Å from a shift in the position of the σ resonance [3]. From the relative lack of a change in the absolute and relative intensities of the π and σ resonances with a change in radiation polarization, an estimated tilt angle with respect to normal of 45° ± 10° has been deduced [3]. However, the precision of this determination is not high, and it also was not possible in this study to specify whether there is any preferred azimuthal orientation of the tilt. Measurements of electron-stimulated-desorption ion angular distributions (ESDIAD) are consistent with such a high tilt in showing a very weak signal for O\(^+\), but no bond angle information could be derived, probably due to the strong image forces which deflect and attenuate the desorbing ions [2].

We have thus applied x-ray photoelectron diffraction (XPD) for the first time to this intriguing adsorption state in an attempt to better understand its structure, combining both polar and azimuthal scans of core-level intensity in a way that has not been attempted before for such adsorbate structure studies. This method makes use of the dominance of highly-peaked forward scattering in core-level emission at energies of greater than approximately 500 eV [7–10]. As these peaks have typical FWHM values of only about 20°, the precision of bond tilt determinations should be considerably higher than in measurements such as NEXAFS where the dependence on variable polarization goes as a more slowly varying \(\cos^2\) function [3, 8, 10]. Also, a simple single scattering cluster (SSC) model has been shown in prior studies to model very well this kind of intramolecular scattering [7–10], although useful structural conclusions can often be drawn directly from the position of the through-bond forward scattering without any comparison to theory [7–10]. For the case at
hand of a diatomic adsorbate, high kinetic energy, and high takeoff angles relative to the surface, multiple scattering effects should be completely negligible.

The instrumentation utilized is described in detail elsewhere [10] and consists of an x-ray photoemission spectroscopy (XPS) system equipped with a two-axis specimen manipulator capable of automated scanning of either the polar or azimuthal angles of electron emission with high precision (approximately ± 0.2°–0.3°). LEED characterization is also possible. The Fe(001) surface was cleaned and prepared using standard procedures [11, 12]. After cleaning, less than 0.1 ML of combined C and O impurity was present on the surface. CO was adsorbed on the clean surface at ambient temperature up to a total exposure of 15 Langmuirs (10⁻⁷ Torr × 150 sec). Prior work on this system using a combination of XPS, temperature-programmed desorption (TPD), and EELS [1, 11, 12] indicates that this should lead to a very high fraction of the CO being present in the desired α₃ state. From a comparison of our C 1s and O 1s core spectra with those published previously [11], we estimate this fraction to be greater than 80%. The C 1s and O 1s intensities yield coverages after adsorption of 0.33 ± 0.05 ML for C and 0.52 ± 0.05 ML for O; the latter number is in excellent agreement with recent work for the O coverage based upon XPS and TPD data [12] and the former suggests the presence of atomic oxygen from CO dissociation that blocks some CO adsorption sites and thus reduces the C coverage. Precise calibration of the polar (θ) and azimuthal (φ) scales was made by using strong, narrow XPD peaks in Fe 2p₃/₂ emission from the clean surface [10]; the accuracy of this calibration is ± 0.5°. Polar scans of both C 1s and O 1s intensities were carried out in two different azimuths above the (001) surface: [100] and [110]; the θ scale is measured with respect to the surface. Polar data will be reported as the normalized ratio I(C 1s)/I(O 1s) in order to approximately divide out the θ-dependent instrument response function [7, 10, 13]; in any case the I(O 1s) profile was smooth and structureless so that this division does not
affect any of our conclusions. Azimuthal C 1s scans were also carried out over a range of 200° for selected polar angles. All data shown represent sums of seven or more separate scans with cleaning and readsoption in-between. All features discussed here were reproducible in all of the individual scans.

In Figure 2.1(a), we show normalized polar scans of the C 1s intensity along the two types of azimuths studied. The difference between the two curves is striking: There is a clear peak in the curve for the [100] azimuth, centered at \( \theta = 35° \pm 2° \) and with a FWHM of 25°, whereas the curve for the [110] type azimuth is flat and featureless, with only one possible weak peak at \( \theta = 17° \). These same differences are seen in the raw data for the C 1s intensities before normalization; as noted above, the normalized O 1s curves for the two cases were smooth featureless curves with no indication of forward scattering peaks. These results alone thus immediately suggest that the CO is bound with the C atom down, that the peak at \( \theta = 35° \) is due to forward scattering from O, that the molecular tilt is approximately 55° with respect to the surface normal, and that the tilt is preferentially along <100> azimuths. The overall forward scattering effect for the [100] azimuth at 35° as judged by the quantity \( \frac{I(\text{maximum}) - \text{average of the minima at the edges of the peak}}{I(\text{maximum})} \) is 16% and thus is comparable to that observed for the case of c(2x2)CO/Ni(001), which exhibits bonding normal to the surface [7(a), 7(b)].

In order to further quantify these conclusions, we have also performed 200° azimuthal scans of the C 1s intensity at a polar angle of 35° chosen so that the emission directions will pass directly through the strong [100] peak in Figure 2.1(a). These results are shown in Figure 2.1(b). (Normalization with O 1s is not necessary in this case because \( \theta \) is constant.) This curve shows its strongest features at precisely those <100> azimuthal positions that are consistent with the peak in Figure 2.1(a). These azimuthal results thus lead to the overall conclusion that a high proportion of \( \alpha_3 \) CO is tilted in the <100>
azimuths, as shown schematically in Figure 2.1(c) for the most likely bonding position in a fourfold hollow site [1–3]. Note also the small, but reproducible, peak at $\phi = 45^\circ$ or along $<110>$ azimuths; this we will discuss further below.

A more quantitative analysis of these results can also be made by using the results of straightforward SSC calculations incorporating spherical-wave scattering [7, 10, 14]. Such calculations have been carried out for the C 1s intensities so as to model the normalized curve in Figure 2.1(a) and the absolute curve in Figure 2.1(b); the O 1s intensity is expected and found to have very little modulation due to the absence of any strong forward scatterers between it and the detector. The well-known dominance of forward scattering at the high energy of 1202 eV involved for C 1s also should lead to a very small effective cluster [7]: We have thus used only the tilted CO molecule plus five Fe atoms so as to include the four nearest neighbors and the next-nearest neighbor in an assumed fourfold hollow site, as shown in Figure 2.1(c). [The choice of the very open fourfold hollow site is based on its being the most likely site for a highly tilted molecular adsorption, as well as on prior experimental work based upon XPS, LEED, TPD, and ultraviolet photoemission spectroscopy [1, 3, 11, 12], and prior theoretical calculations for vertical-standing CO on Fe(001) [15].] Adding more Fe atoms to this cluster was indeed verified to produce very little change in any of the calculated curves. Reference calculations with no Fe atoms have also been carried out to determine precisely what the Fe near-neighbors contribute. For simplicity, the C atom is assumed to be centered in the fourfold hollow. The experimental data also suggest that we choose a tilt of $35^\circ$ with respect to the surface. In some calculations, the vertical position $z$ of the C with respect to the first Fe surface plane has been varied. Four equally probable $<100>$ directions of tilt have been assumed, with intensities from each of these site or domain types being added to yield the final polar or azimuthal curves. The presence of these four site types will reduce the peak-to-background
ratios in both polar and azimuthal scans due to the addition of relatively flat backgrounds of intensity from the nonforward scattering sites. Vibrational effects have been included via Debye-Waller factors only, although a more exact treatment including possible wagging or frustrated rotational motion would be expected to additionally broaden features and reduce experimental peak-to-background ratios [7(b)]. Shifting the tilt angle from 35° in the calculations was found to move the peak position in polar scans by exactly the amount of the angle shift; thus we can with certainty use 35° in the remainder of our calculations. Other theoretical results are summarized in Figures 2.2 and 2.3.

In Figure 2.2, our experimental azimuthal data is compared to calculated curves for an isolated CO molecule (for which z has no meaning) and for a cluster consisting of CO plus 5 Fe atoms [as shown in Figure 2.1(c)]. For the latter, z values of 0.0 (in-plane) to 1.0 Å that span the range of reasonable C-Fe distances in carbonyls [16] have been investigated, although only the curves for 0.3, 0.5 and 0.6 Å are shown. The simple forward scattering peaks along [100] and [010] are well predicted for all of the curves shown, and thus they do not provide any further information concerning vertical position. The weaker peak along [110] by contrast is found to oscillate with z, and its relative intensity I''/I is plotted as a function of z in the inset of the figure. The accuracy of our experimental I''/I values from these first results is only about ±0.2, although it could be improved by doing longer full 360° scans and fourfold averaging into one quadrant [10]. Comparing experiment and theory thus suggests the two z ranges of about 0.22 ± 0.10 Å and 0.63 ± 0.10 Å. An analysis of the diffraction calculations shows that the maxima of this weaker peak are the result of successive constructive interferences between a first-order scattering event (that is, with one wavelength difference between direct and scattered waves) from oxygen [7] and a second or third-order event (that is, with two or three wavelengths difference between direct and scattered waves) from the Fe atom in the [110] corner of the hollow. Such simply
interpretable features in XPD can thus be directly related to geometry, and this is the first time that they have been used for this. A more accurate analysis of such data should also include the effects of vibration [7], but these would be expected to more rapidly attenuate the higher order [110] peak due to the larger scattering angles involved [10]. Thus, our calculated $I'/I$ values should if anything be too low, perhaps favoring the higher values near $z = 0.2$ Å. The $z$ values between 0.2 and 0.6 Å that are suggested by this analysis are also found to yield C-Fe nearest neighbor distances of 1.64–2.04 Å that are very close to the distances found in CO-Fe complexes [16].

The experimental anisotropy $\Delta I/I_{\text{max}}$ is about 16%–18%, as indicated in Figure 2.2. The corresponding values for the theoretical curves of Figure 2.2 are about a factor of 2 larger. However, such discrepancies have been noted previously [7], and could be due to vibrational effects and/or C atoms present in other than the tilted $\alpha_3$ state.

In Figure 2.3, we compare experimental and theoretical curves for the polar variation of C 1s intensity, using for the solid curves a tilt angle of 35° and the two best-fit vertical heights of 0.3 and 0.6 Å. There is excellent agreement here as well, even as to the existence of the weaker feature due to first-order scattering from O that occurs rather near the normal at $\theta = 70^\circ$. Adding in the five Fe atoms for the two lower curves is found to change only the fine structure of the principal peak; vibrational effects would be expected to smear out these small changes and to cause all three solid curves to be in equal agreement with experiment [7(b)]. To illustrate the known sensitivity of the main peak to the tilt angle [7, 10], we also show curves for $\theta_{\text{tilt}} = 33^\circ$ (long-dashed curve) and $\theta_{\text{tilt}} = 37^\circ$ (short-dashed curve); it is clear that the peak position directly follows the tilt angle.

Thus, a fully self-consistent picture of the structure of this unusual bonding state of CO emerges from this study of the system by XPD: CO is tilted at $55^\circ \pm 2^\circ$ with respect to the normal with a preferred orientation in $<100>$ azimuths. This structure information
further supports the suggestion of a fourfold hollow bonding site [1, 3, 11, 12] and for this site, our data suggest that the C–Fe vertical distance is in one of the two ranges of $0.2 \pm 0.1$ and $0.6 \pm 0.1$ Å. This tilt angle is thus fully consistent with the less precise NEXAFS determination of $45^\circ \pm 10^\circ$ by Moon et al. [3], and, as they have conjectured from the insensitivity of the normalized $\pi$ resonance intensity to changes in polarization direction, it is also extremely close to the magic angle of $54.7^\circ$. Although we do not here determine the precise position of the C atom relative to the fourfold hollow including possible offsets from center, such a determination should be possible from similar analyses of additional polar and azimuthal scans of C 1s and O 1s [17], particularly if the azimuthal scans are made over a full $360^\circ$. Overall, the application of such combined polar- and azimuthal-XPD measurements to highly tilted bonding geometries such as CO on other transition metal surfaces [4–6] is highly promising.
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Figure 2.1. (a) Experimental polar scans of the C Is/O Is intensity ratio for the $\alpha_3$ state of CO on Fe(001). Curves are shown for two azimuths: [100] (solid curve) and [110] (dashed curve). (b) Experimental azimuthal scan of the C Is intensity for the $\alpha_3$ state of CO at a polar angle of 35° with respect to the surface. (c) The bonding geometry deduced from these data.
Figure 2.2. Comparison of the experimental C 1s azimuthal scan for the $\alpha_3$ state of CO with theoretical calculations assuming the molecule to be tilted at 35° with respect to the surface along <100> directions and to be in four equally populated site types or domains. In the top curve, no Fe scatterers are included. In the lower curves, five Fe scatterers are added, as shown in Figure 2.1(c). The C is taken to be centered in the fourfold hollow, and its vertical distance from the Fe surface plane has been varied from 0.0 to 1.0 Å. Inset: The relative intensity $I'/I$ of the weaker higher-order feature along <110> directions as a function of $z$. 
Figure 2.3. The experimental polar scan of the C 1s/O 1s ratio in a [110]-type azimuth is compared to theoretical calculations (solid curves) using the same assumptions as in Figure 2.2. Such curves (with $\theta_{\text{tilt}} = 35^\circ$) are shown for no Fe scatterers and for five Fe scatterers with vertical distances of 0.3 and 0.6 Å as indicated from a comparison of Figure 2.2 to experiment. Also shown are the predicted forward scattering peaks for tilt angles of 33° (long-dash curve) and 37° (short-dash curve).
3.1. ABSTRACT:

We have obtained azimuthal x-ray photoelectron diffraction (XPD) data with a high angular resolution of ±1.5° for S 2p emission from c(2×2)S on Ni(001). The relatively high position of the adsorbate with respect to the substrate makes this a stringent test case of the structural sensitivity of forward-scattering-dominated XPD. With this higher resolution, the data are nonetheless found to be sensitive to atomic structure, including in particular both the vertical height of S above Ni (z) and the first-to-second-layer Ni interplanar spacing (d_{12}). A single scattering cluster (SSC) theoretical analysis using R-factors to judge goodness of fit yields z = 1.39 ± 0.05 Å and d_{12} = 1.86 ± 0.05 Å, in excellent agreement with other recent experimental and theoretical studies. This analysis also indicates that clusters of up at least 25 Å in radius (200–250 atoms) are needed to accurately describe all of the diffraction fine structure observed; thus, although XPD is primarily a short-range-order probe, high resolution data provides sensitivity to order that may go out as far as 10–15 neighbor shells. For takeoff angles with respect to the surface of less than about 10°, multiple scattering effects appear to become more important, as verified by fully-converged multiple scattering cluster (MSC) calculations; however, for
takeoff angles larger than 10°, these effects fall away rapidly, making a single-scattering analysis of such data still a useful approach. Finally, we have analyzed our experimental data and SSC simulations of it using recently-suggested Fourier-transform holographic inversion methods. Although our data are too limited to permit fully accurate holographic imaging, features associated with the nearest-neighbor S atoms in the adsorbate overlayer are seen in both experimental and theoretical images. In addition, the theoretical calculations indicate that the atomic images can be improved if: the solid angle of the hologram is limited so as to exclude the strong forward scattering features at low takeoff angles; effects due to non-constant scattering factor amplitudes and phases are corrected out using the scattered-wave-included Fourier transform method of Saldin et al., and/or the hologram range is further limited so as to avoid the overlap of twin and real images. Several interesting directions for further study with such high-resolution data, SSC R-factor analyses, and holographic imaging are thus suggested.

3.2. INTRODUCTION:

Scanned-angle x-ray photoelectron diffraction (XPD) at energies of approximately 500 to 1,500 eV has by now been successfully applied to determining the structures of a number of chemisorption systems [1–6]. For simple molecular adsorbates such as CO/Ni(001) [1], CO/Ni(110) [2], and CO/Fe(001)[3], the strong intramolecular forward scattering effect for core-level emission at these energies can be used to great advantage in determining both the tilt angle and the preferred orientation of the chemisorbed molecule. In the case of atomically adsorbed species that lie rather near the first plane of substrate atoms, near forward scattering from substrate atoms also can produce strong diffraction effects for low takeoff angles with respect to the surface, with one example of this being
O/Cu(001) [4]. However, for atomic adsorbates that are bound fairly high above the substrate surface plane e.g. at a vertical distance \( z \geq 1.0 \) Å, such substrate forward scattering peaks are directed into the surface and thus are strongly suppressed except for very low electron takeoff angles. For such cases, the strongest diffraction peaks may in fact be the result of scattering along low-index rows of adsorbate atoms along the surface plane. Thus, for such high-\( z \) adsorbates, the adsorbate-substrate structural information in XPD must be due to larger scattering angles and is expected to be much weaker, as was shown in a prior study on the S/Ni system using lower angular resolution [5]. Figure 3.1(a) further illustrates this difficulty in XPD for the specific example of c(2×2)S on Ni(001), a case for which \( z \) is known to be \(~1.3 \) Å. It is clear that the scattering angle for Ni (\( \theta_{Ni} \)) is larger than that for sulfur (\( \theta_{S} \)), resulting in weaker modulations of the diffraction signal due to the substrate. To derive information concerning \( z \) and the even-more-difficult first-to-second layer substrate interplanar spacing (\( d_{12} \)) thus requires a greater sensitivity to the diffraction fine structure. Higher angular resolution azimuthal scans at low takeoff angles may provide this sensitivity.

In this paper, we report on the first study of such a high-\( z \) atomic adsorbate using high-angular resolution XPD. As a suitable test case for this kind of adsorbate, we use the well-defined c(2×2) sulfur structure on nickel (001). Azimuthal XPD data for S 2p emission were measured at a resolution of \( \pm 1.5^\circ \) and analyzed by comparing experiment to single scattering cluster calculations using R-factors so as to try to determine both \( z \) and \( d_{12} \). We also quantitatively consider the effects of multiple scattering on such data, as well as the possibility of analyzing it by holographic methods that have recently been suggested by Szöke [7] and Barton [8], and further refined by Saldin, Tonner, and co-workers [9].
3.3. EXPERIMENTAL:

The experimental system used for this study has been described in detail previously [6, 10] and consists of a Vacuum Generators ESCALAB 5 XPS spectrometer that has been modified for angle-resolved measurements by the installation of a high-accuracy two-axis specimen goniometer and a set of movable angle-defining stainless steel tube arrays mounted in front of the electron lens at the entry to the energy analyzer [10(a)]. The tube arrays allow angular resolutions of ±1.5° and ±3.0° to be selected. Prior studies have shown a dramatic increase in the amount of diffraction fine structure when the angular resolution is increased from the standard ~ ±6.0° to ±1.5° [6, 10(a)]. Unpolarized Mg Kα radiation (hv = 1253.6 eV) was used for excitation. The detector consisted of a single channeltron, although a multichannel detector has by now been installed in this system [10(b)]. Precision scanning of either the φ- or θ-electron emission angles [as defined in Figure 3.1(b)] was possible under direct computer control, with accuracies of ~ ±0.3° in selecting both angles.

The Ni(001) surface was cut and polished to within ±0.3° of the [001] direction and cleaned under UHV conditions by repeated Ar⁺ bombardment and annealing cycles using standard cleaning procedures for Ni [11]. Surface cleanliness and sulfur adsorbate coverage were monitored by XPS. After cleaning, less than a 0.02 ML total coverage of C, O, and S impurities was observed. The c(2×2) sulfur overlayer was formed by exposing the cleaned Ni surface to 30 L (10⁻⁷ Torr × 300 sec) of H₂S at ambient temperatures, followed by a five minute anneal to 493 K. Immediately after annealing, the overlayer showed a sharp c(2×2) low energy electron diffraction (LEED) pattern that persisted throughout a given angle scan. The surface was cleaned and the sulfur overlayer renewed after each data run of approximately 20 hours duration. All of the features in the S 2p diffraction data
discussed here have been reproduced in separate, individual scans with cleaning and readsorption of the surface overlayer between runs.

The precise calibration of the $\Theta$- and $\phi$-directions was done with high angular resolution using the strong and very narrow Ni 2p$_{3/2}$ XPD peaks from the clean surface that occur along the $\langle 110 \rangle$ directions [6]. This calibration had an accuracy of $\pm 0.2^\circ$. A series of S 2p azimuthal scans ($E_{\text{kin}} = 1085$ eV, electron wavelength = 0.37 Å) were taken over a $\phi$-range of 100° and at takeoff angles with respect to the surface of $\theta = 6^\circ$, 10°, 12°, and 16°. A schematic drawing of the experimental setup is shown in Figure 3.1(b); the angle $\alpha$ between x-ray incidence and electron exit is fixed for this spectrometer at 48°. Low takeoff angles were selected due to the strongly forward scattering nature of the high energy S 2p photoelectrons. As noted previously [cf., Figure 3.1(a)], strong diffraction effects are only expected to be observed within the narrow forward scattering cone of approximately 15°–20° with respect to the surface plane.

3.4. RESULTS AND DISCUSSION:

3.4.1. SINGLE SCATTERING ANALYSIS:

In Figure 3.2, we show as dashed curves the raw S 2p azimuthal data taken at polar angles with respect to the Ni surface of 6°, 10°, 12° and 16°. All of these curves represent sums from at least two separate adsorptions and intensity scans. This data has subsequently been mirror averaged across the [110] symmetry plane at $\phi = 45^\circ$ to improve the statistical reliability, as shown by the solid curves. Overall, there is excellent reproducibility of all features in comparing the raw data to its mirror-averaged counterpart. There is a high degree of diffraction fine structure present, especially at the lowest takeoff
angle of 6°. Some of the diffraction peaks have a FWHM of 3° or less and this is the first
time to our knowledge that such narrow features have been observed in adsorbate XPD
curves. The overall anisotropies of the data, defined as $\Delta l/l_{\text{max}} = (l_{\text{max}}/l_{\text{min}})$, are shown at
the right and they range from about 23% up to a very high 38%. The mirror averaging
process is found to decrease the anisotropy only slightly at a given $\theta$, by about 1–5%.

The single-scattering cluster (SSC) model used in most of our calculations has been
discussed in detail elsewhere [6, 12] and it incorporates both spherical-wave scattering and
the correct $p \rightarrow$ interfering $s + d$ final states involved in S 2p photoemission. The latter two
improvements make use of the Rehr-Albers separable Green's function approach [13]. The
clusters involved in the calculations contain approximately 47 adsorbate and 170 substrate
atoms or 217 total atoms that span the region up to 25 Å along the surface from the emitting
atom; this size was found necessary to insure full convergence of the XPD patterns. A
typical cluster is shown in Figure 3.3. The calculations were broadened in both the $\theta$ and $\phi$
directions to simulate an angular acceptance of ±1.5°. The R-factor program used in this
analysis was modeled after that proposed by Van Hove et al. for LEED [14] but we have
used a different normalization procedure that is found to yield more reliable results for XPD
data [11, 15]. Although only the results of the analysis based on "$R_1$" (the sum of the
absolute values of the differences between experiment and theory) are shown here, all five
R-factors ($R_1$, $R_2$, $R_3$, $R_4$, and $R_5$) discussed in this prior work [14] are found to give rise to
similar structural conclusions [15].

A global R-factor analysis that sums the results at all four polar angles is shown in
Figure 3.4(a) for clusters having various $z$ and $d_{12}$ values. The best overall fit is found at $z$
= 1.39 Å and $d_{12} = 1.86$ Å, with the latter corresponding to an approximately 5.7%
expansion of the first-to-second Ni interplanar spacing over the bulk value of 1.76 Å.
These results are in good agreement with recent determinations using angle-resolved
photoemission fine structure (ARPEFS) [16] ($z = 1.30 \, \text{Å}$, $d_{12} = 1.84 \, \text{Å}$), surface extended x-ray absorption fine structure (SEXAFS) [17] (1.37 Å, 1.86 Å), and LEED [18] (1.30 Å, 1.80 Å), as well as with total energy calculations [18] (1.36 Å, $d_{12}$ not determined).

A final comparison of the SSC calculations at the optimal geometry with the mirror-averaged experimental data is shown in Figure 3.4(b). There is generally excellent agreement between experiment and theory as to both the peak positions and their relative intensities, particularly for the takeoff angles of 10° and 12° where the anisotropies are largest. The agreement for $\theta = 16°$ is also very good. The only significant problem with the final fit is with the fine structure in the data taken at the lowest takeoff angle of 6°. About half of the fine structure has been reproduced in the single-scattering theoretical calculations as to both position and relative intensity. The principle discrepancies lie along the [100] and [110] directions corresponding to the most dense rows of S atoms along the surface (cf., Figure 3.3) and they therefore may be due to multiple-scattering effects that are known to be enhanced along such rows [6, 12(b), 12(c), 19]. These rows of S atoms that are in-plane to a S emitter will tend to display enhanced scattering over the deeper-lying Ni substrate atoms [cf., Figure 3.1(a)].

Several points concerning our single-scattering analysis up to this point should be noted:

(i) First, at low takeoff angles, the cluster size necessary can become an important indicator of the average domain size of the surface involved. At $\theta = 6°$ and 10°, tests on the convergence of SSC cluster calculations show that a minimum cluster size of at least 20 Å in radius is required to optimally describe the fine structure and that a larger cluster of 25 Å may in fact be necessary for final convergence. At larger emission angles for which forward scattering at larger distances from the emitter is
reduced, the effective lateral size of the cluster also is reduced, but nevertheless a
cluster size of 25 Å was used throughout our data analysis for self-consistency.

(ii) Another factor in the theoretical modeling which could have been significant was the
use of correct $p \rightarrow s + d$ final states. However, the simpler $s \rightarrow p$ final state
calculations used in many prior XPD analyses [6] are found to have diffraction
patterns that are nearly identical to the more exact method; there are only small
differences in the relative heights of some of the lesser features, with all major peak
positions and intensities remain unchanged. This result is consistent with a prior
analysis of these final-state effects in XPD at higher energies [12(a)].

(iii) Lastly, in R-factor plots such as Figure 4(a) but for the individual takeoff angles $\theta =
6^\circ$ and $10^\circ$, there is no real minimum in the $R_1$ values as $z$ is scanned for the optimal
d$_{12}$ spacing of 1.86 Å. That is, it is actually the data at $\theta = 12^\circ$ and $16^\circ$ that yield the
d$_{12}$ value from this SSC analysis. This may indicate that single scattering
calculations are not sufficiently accurate for fully describing the diffraction effects
observed at the lowest takeoff angles. As noted earlier, a full MS treatment may be
necessary for these angles, and we now examine this point further.

3.4.2. ASSESSMENT OF MULTIPLE SCATTERING EFFECTS-

In order to make a first estimate of the importance of multiple scattering at the
lowest emission angles, we have carried out such calculations using a newly-developed
general-purpose code due to Kaduwela et al. [12(b), 12(c)]. Current computer time
restrictions limit the number of scatterers to around 36 atoms. Thus, the 35 strongest
scatterers in addition to the emitter, as determined from a single-scattering analysis of this
problem, were used in the MS calculations. This 36-atom cluster is shown in Figure 3.3 as
the two types of shaded atoms; it includes virtually all of the sulfur atoms that lie within a 45° wedge and out to about 20 Å from the emitter and the 11 nearest Ni atoms that lie in the first layer only. No nickel atoms were included from the second or deeper layers, so there can clearly be no sensitivity to $d_{12}$ in a cluster that is this small.

Figure 3.5 compares all of our experimental data with SS calculations for both the fully converged 217-atom cluster and the 36-atom cluster, and with MS calculations for the 36-atom cluster. The R-factors shown give an indication of the goodness of fit of each theory curve to the experimental data. The SS calculations for this minimal 36-atom cluster at higher polar angles of 10°, 12° and 16° show little change when compared to those for the fully converged 217-atom cluster, as illustrated in Figures 3.5(b)-3.5(d). This supports our earlier conclusion that the effective lateral cluster size decreases as takeoff angle increases. However, Figure 3.5(a) shows a significant change in fine structure between the SS results for 217 atoms and 36 atoms, with the relative intensities of several peaks over $\phi = 30°-60°$ changing considerably, and the symmetry-equivalent regions from 0°-10° and 80°-90° showing even larger changes. Thus, as expected for very low takeoff angles, the 36-atom cluster is not converged in a single scattering limit, but it should nonetheless permit assessing qualitatively how important MS effects may be at this lowest angle.

Looking now at the SS and MS calculations for the 36-atom cluster at $\theta = 6°$ [Figure 3.5(a)], we see marked differences between the two curves, including a strong suppression in MS of the nearest-neighbor S forward scattering peak along $\phi = 0°$ and 90° that is probably due to defocusing [12, 19], and a much better prediction in MS of the doublet centered at $\phi = 45°$. It is also interesting that MS for 36 atoms predicts about an equal amount of fine structure to the SS calculation for 217 atoms. MS effects are thus expected to be important for this lowest takeoff angle. However, there is overall no better agreement between MS theory with a minimal cluster and experiment than there is between
SS theory with a fully-converged cluster and experiment. In fact, the R-factor for SS/217-atoms is slightly lower than that for MS/36-atoms (0.068 versus 0.076), with the best fit actually being SS/36-atoms (0.066). Thus, we can only conclude from this preliminary work that MS effects appear to be important in the analysis of XPD from adsorbates at very low takeoff angles, but that quantitatively using them to analyze data will require calculations on much larger clusters of ~100–200 atoms that are not yet possible to do.

Figures 3.5(b)–3.5(d) present the same sort of SS/MS comparisons for takeoff angles of $\theta = 10^\circ$, $12^\circ$, and $16^\circ$. There are certain important differences between these cases and $\theta = 6^\circ$. As noted before, the SS results for 217 atoms are, for all three higher takeoff angles, very similar to the SS results for 36-atoms. The MS results for 36 atoms are also much more similar to the SS results for 36 atoms for all three angles; i.e., MS effects are less important, probably due to the effectively smaller size of the cluster noted earlier and the resultant lack of long chains of atoms along the scattering pathways. Again for all three angles, MS is found to improve the agreement of certain features (although not all) in comparison with experiment, although the lowest R factors are still found in one or the other SS curve. At $\theta = 16^\circ$, MS does a better job in predicting the relative intensities and peak positions than either of the two SS curves; perhaps an even smaller SS cluster than the 36-atom used here would be adequate to describe this case. Overall, we thus conclude that a SS treatment with a smaller cluster should work reasonably well as $\theta$ is increased to above about $10^\circ$, with the likely reason being that all single scattering is then taking place outside of the strong forward scattering cone.

Finally, in Figure 3.6(a), we show the same three theoretical curves for a very high takeoff angle of $45^\circ$. The overall anisotropies are markedly reduced to only a few percent, as expected since the single scattering angles are all very large and thus well away from the dominant forward peak. There are some differences between SS and MS results for the 36-
atom cluster, but, in view of the small anisotropy, they would be very difficult, if not impossible, to detect experimentally. So these results for $\theta = 45^\circ$ further support the idea of effectively smaller clusters and a more nearly single scattering description as $\theta$ is increased. With reference to the latter point, we find that an R-factor calculated between the SS/36-atom and MS/36-atom results has a rather high value of 0.16 for $\theta = 6^\circ$, but monotonically falls to $\sim 0.002$ by $\theta = 45^\circ$, as shown in Figure 3.6(b).

3.4.3. HOLOGRAPHIC IMAGING FROM ADSORBATE XPD-

We now consider the potential utility of analyzing such azimuthal x-ray photoelectron diffraction data using the holographic imaging methods first suggested by Szöke [7] and Barton [8], and subsequently extended by Saldin, Tonner and co-workers [9], and by Tong et al. [20]. These procedures may in principle produce direct images of atomic positions in real space, although the few analyses of experimental data from multilayer crystals that are so far available indicate that the accuracy of such images may be only $\pm 0.5-1.0$ Å along the vertical and/or forward scattering directions. However, methods for improving this accuracy have been suggested by several authors [9, 20, 21], and it is certainly important to see how far one can go with holographic imaging. Even if such images were to only provide a good starting point for more refined searches using SS or MS calculations and R-factors, they could be very worthwhile.

The holographic method begins with a general expression for the intensity distribution above a surface expressed as a normalized $\chi(\mathbf{k})$ function [8, 22], where $\mathbf{k}$ is the electron wave vector. If the direct or unscattered component of an outgoing wave emanating from the origin is denoted by $\phi_0$ and the singly, and possibly also multiply, scattered component as it leaves for the detector from the $j$th scatterer at $\mathbf{r}_j$ is denoted by $\phi_j$, these
components can be written very generally as [8]: \( \psi_0(\mathbf{r}) = F_0(\mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{r}] \) and \( \psi_j(\mathbf{r}) = F_j(\mathbf{k}) \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)] \); here, \( F_0(\mathbf{k}) \) contains factors for the excitation matrix elements and inelastic attenuation, and \( F_j(\mathbf{k}) \) contains these factors as well, but also pathlength-dependent phase factors \( \exp[iK_L j] \), effective spherical-wave scattering factor(s) \( f_{j,\text{eff}}(k, \mathbf{r}_j) \), Debye-Waller-like factors \( \tilde{W}_j \) for vibrational attenuation, and a sum over the various single and multiple scattering pathways with different total lengths \( L_j \) that terminate in scatterer \( j \) just before going to the detector. Summing the direct wave and the scattered waves from all atoms \( j \) in a cluster, taking the square to get the intensity \( I(k) \), and then determining \( \chi(k) \) from \( [I(k) - I_0(k)]/I_0(k)^{1/2} \) (with \( I_0(k) \) being the intensity in the absence of any scatterers) then yields:

\[
\chi(k) \propto \sum_j \{ F_0^*(k) F_j(k) \exp[-ik \cdot r_j] + F_0(k) F_j^*(k) \exp[ik \cdot r_j] \} + \sum_j \sum_k \{ F_j^*(k) F_k(k) \exp[ik \cdot (r_j - \mathbf{r}_k)] + F_j(k) F_k^*(k) \exp[-ik \cdot (r_j - \mathbf{r}_k)] \} .
\]

As in prior work [8], the inversion proceeds by projecting \( \chi(k) \) onto the \( k_x, k_y \) surface plane and then doing a two-dimensional Fourier transform (FT) with \( z \) as a variable parameter to yield the image \( U \) in a given \( z \) plane as:

\[
U(x, y; z) \propto \iint \{ \chi(k) \exp[ik_z z] \exp[i(k_x x + k_y y)] \} dk_x dk_y .
\]

The first (single) sum in Equation (3-1) represents the usual hologram of optical holography and the second (double) sum the self-hologram [7, 8]. If the \( F_j \)'s did not depend on \( k \) (implying among other things an outgoing s-wave from the emitter and s-wave scattering), then the FT would be expected to yield peaks only at \( \pm r_j \) and at \( \pm (r_j - \mathbf{r}_k) \), that
is, at ± the atomic positions [the real and conjugate (or mirror) images, respectively] and at ± all of the differences of atomic positions (the image due to self-interference and its conjugate). In the further limit that \(|F_0| >> |F_j|\) for all \(j\), the double sum can be neglected and only the real image and its conjugate will be obtained; for the actual strengths of electron-atom scattering at \(-1,000\) eV, this neglect has been shown to be a useful, but borderline approximation [21]. In addition, some \(|F_j|\)'s are very large, and the dependence of the \(F_j\)'s on \(\vec{k}\) is very strong, including both the forward scattering dominance referred to above and possible multiple scattering pathways that introduce additional factors of \(\exp[i(k \mid \vec{r}_m - \vec{r}_n \mid)]\) for each step in a pathway. The anisotropy in \(|F_0|\) and \(|F_j|\), as well as the phase shifts introduced in each scattering event and possible multiple scattering character have been shown to introduce additional aberrations or artifacts in images [9, 20, 21].

As one method for correcting such images for both the anisotropic amplitude in \(|F_j|\) and the phase shift associated with each scattering event, Saldin et al. have proposed the scattered-wave-included Fourier transform (SWIFT) method [9]. In this procedure, Equation (3-2) is modified by dividing \(\chi(\vec{k})\) by some \(f_{j,\text{eff}}(\vec{k}, \vec{r})\), where this effective scattering factor may be calculated in either the plane-wave limit or in the more accurate spherical-wave picture that we have used here. The resulting corrected image \(U'\) is then calculated from:

\[
U'(x, y; z) \propto \int \int \left\{ \frac{\chi(\vec{k}) \exp(i k z)}{f_{j,\text{eff}}(\vec{k}, \vec{r})} \right\} \exp[i(k_x x + k_y y)] dk_x dk_y.
\]  

(3-3)

The coordinate \(\vec{r}\) in \(f_{j,\text{eff}}\) is here allowed to vary continuously over all space, even though the centers of the scatterers are found only at the positions \(\vec{r}_j\) that are to be determined. This is
possible to do in principle, because the modified integral in Equation (3-3) (it is no longer a simple two-dimensional Fourier transform) will be large only for regions near the atoms, and the divisions by \( f_{i,\text{eff}} \) in other regions should thus produce very little error in the corrected image function \( U'(x,y;z) \).

In applying this type of analysis to the case at hand, the first thing we have done is to compute the function \( \chi(k) \) over the full hemisphere above the \( c(2\times2)S\text{Ni}(001) \) surface, using the SSC spherical-wave method outlined above and the 217-atom cluster of Figure 3.3. This is shown in Figure 3.7(a), from which it is clear that the largest peaks in the interference pattern are for grazing emission; this is expected, since it is for these angles that scattering can take place within the strong forward scattering cone. As another indication of the dominance of the lower takeoff angles in producing diffraction features, we plot the calculated anisotropy \( \Delta I/I_{\text{max}} \) for each \( \theta \)-value as a function of \( \theta \) in Figure 3.7(b), together with the four experimental points for the data of Figure 3.2. It is clear from theory that the anisotropy drops off very rapidly as \( \theta \) is increased, probably falling to values too low to measure with present laboratory radiation sources by \( \theta = 30^\circ \). Thus, \( \theta \) values below 30\(^\circ\) would seem to be preferred for such measurements, although our past discussion suggests that, for \( \theta \) less than about 10\(^\circ\), multiple scattering effects might become more important, thereby complicating the holographic imaging process. The optimum hologram range is thus suggested to be \( \theta = 10^\circ-30^\circ \) for such an adsorbate system.

Our experimental data were not initially taken with the idea of holographic imaging in mind, and so consist of only four scans, with one being at an angle low enough that multiple scattering could play a role. In any event, we will Fourier transform this data set, as well as different regions of the full theoretical hologram in Figure 3.7(a), to see what sorts of images are produced.
In Figure 3.8, we show various Fourier transforms of the theoretical hologram according to Equation (3-2) that were done with \( z = 0.0 \text{ Å} \), that is, in the plane of the S atoms. The only variable changed is the opening angle of the hologram \( \alpha_o \), which is chosen to be 178° (only 2° from the maximum possible), 150°, and 120°. The two smaller opening angles of 150° and 120° should effectively cut out the forward scattering peaks in the hologram and, perhaps by eliminating this source of the non-ideal anisotropy in the scattering, thus improve the image quality, as suggested previously by Thevuthasan et al. [21]. Improvement is indeed seen for \( \alpha_o = 120° \) and 150°, for which the strong satellite peak that is significantly displaced from the true nearest-neighbor atomic position at 3.52 Å is much reduced, and a peak that is much closer to the true position is seen to become stronger. The optimal opening angle appears to be at about \( \alpha_o = 150° \), which excludes the first 15° of grazing emission, and we see a rapid buildup of satellite features clustering around the emitter by \( \alpha_o = 120° \).

Figure 3.9 shows the results of limiting the hologram range to what should be the experimentally optimal takeoff angles between 10° and 30°. Several kinds of images are shown here. In Figure 3.9(a), the full hologram has simply been Fourier transformed according to Equation (3-2), and the resulting image is almost as good as that in Figure 3.8(b) with a larger opening angle of 150°; there are strong satellite peaks associated with the nearest neighbors in both figures, but the peaks at lower \( |x| \) are closer to the actual distances in Figure 3.9(a). In Figure 3.9(b), the same 10°–30° data have been transformed using the SWIFT method of Equation (3-3). The double peak structure associated with the nearest neighbors moves inward, but now the minimum in it is located at the known atomic position. Thus, there has been no real improvement in our ability to locate these neighbors. The inherent reason why the SWIFT method will not work optimally for this case is that all twin images are expected to be broadened and shifted outward from the origin by the
scattering factor correction [9, 23]. Thus, since transforming the full hologram will for the c(2×2) overlayer in the z = 0 Å plane always result in a superposition of real and twin images at every atomic position, any improvement in the real image may be masked by a deterioration in the overlapping twin image.

One possible solution to the problem of overlapping real and twin images is shown in Figures 3.9(c) and 3.9(d). Here, we have taken advantage of the fact that the dominance of forward scattering effectively localizes the information on the position of a certain atom in a given region of the hologram, an effect that was first pointed out by Saldin et al. [9]. Thus, by analyzing only the right half of the hologram for the 10°–30° data, the nearest-neighbor atom at the far right in the image will be the only one found along the central y = 0 Å line, and its symmetric twin will appear in the left half, as shown in Figure 3.9(c). The satellite peaks seen before are now also gone. Now applying the SWIFT procedure to this half-hologram of data yields the asymmetric image in Figure 3.9(d) due to the inequivalent action of the correction on real and twin images. On the "real" right side of the image, the nearest-neighbor peak has indeed moved in to a position much closer to the actual distance, although it has broadened considerably. Even the next-nearest-neighbor ridges are now centered at the correct distances. The rightmost three features in Figure 3.9(d) would therefore permit estimating the positions of the nearest and next-nearest neighbors in this overlayer to within about 0.3 Å. Thus, the general procedure of using the SWIFT method on some fraction of the hologram that selects out certain atom(s) and eliminates twin/real overlap is very promising.

Finally, we turn in Figure 3.10 to the holographic analysis of our experimental data and analogous theoretical calculations. That is, we consider only the very limited data set of 360° azimuthal scans at polar angles of 6°, 10°, 12°, and 16°. In Figures 3.10(a) and 3.10(c), the simple Fourier transform of Equation (3-2) is applied to experiment and theory,
respectively. It is encouraging that both images are similar in showing broad peaks near the nearest-neighbor positions and ridges along the next-nearest-neighbor directions, although it would be difficult to say anything very quantitative about the structure from them. Figures 3.10(b) and 3.10(d) represent the same experiment/theory comparison after the SWIFT correction of the full 360° hologram. The two images are again similar, with the nearest-neighbor features moving toward the correct positions somewhat, and the next-nearest-neighbor ridges exhibiting more peaking near the correct positions. Thus, even for this small amount of data, some structural information appears to be derivable, and the agreement between experiment and single scattering theory suggests that this is not spurious. Carrying out the same kind of analysis for a larger data set (e.g., such as that represented in Figure 3.9) is certainly also a promising direction for future work.

3.5. CONCLUSIONS:

We have presented for the first time high-angular-resolution XPD azimuthal data from an atomic adsorbate and, in conjunction with large-cluster single-scattering cluster (SSC) calculations and R-factor analysis, have utilized the increased amount of fine structure to determine not only the vertical bonding distance of the adsorbate, but also to detect small changes in the interplanar spacing in the substrate. We find that the c(2×2)S structure on Ni(001) consists of S atoms in fourfold hollow sites at \( z = 1.39 \pm 0.05 \) Å and with \( d_{12} = 1.86 \pm 0.05 \) Å, in excellent agreement with other recent studies. A preliminary examination of the effects of multiple scattering on such analyses indicates that they may be significant at very low takeoff angles, but fall off rapidly in importance as the takeoff angle is increased to about 10° or higher. Nonetheless, we conclude that large-cluster SSC calculations can still be used to determine adsorbate surface structures, with improved
accuracy perhaps being achieved by avoiding the lowest takeoff angles lying more in the strong forward-scattering cones of the adsorbate overlayer. Moreover, such SS calculations with varying cluster sizes may be applicable to studying other more complicated adsorption systems that appear to have more than one domain type or size, or in which disorder may limit the domain size to \( \leq 25 \text{ Å} \) in radius. Finally, we have applied holographic imaging procedures to our experimental data and to SS theoretical simulations of it. Image quality is found to be improved by eliminating strong forward scattering peaks from the hologram before imaging, by applying the scattered-wave-included Fourier transform method, and by considering only some fraction of the hologram to eliminate the overlap of real and twin images. These results provide encouragement for future holographic imaging work on such adsorbates with larger data sets.
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Figure 3.1. (a) Schematic drawing of the $c(2\times2)$S structure on Ni(001). Adsorbate systems characterized by large $z$-distances have inherently weaker scattering effects from the substrate atoms. (b) General geometry of the x-ray photoelectron diffraction experiment. Specimen rotations are carried out on either the polar ($\theta$) or azimuthal ($\phi$) axes. The angle $\alpha$ separating the photon incidence and the electron emission directions is set at $48^\circ$. 
Figure 3.2. Experimental high angular resolution azimuthal scans of the S 2p intensity for low takeoff angles of $\theta = 6^\circ$, 10$^\circ$, 12$^\circ$ and 16$^\circ$. The raw data (dashed curves) are the result of summing two or more azimuthal scans taken over an azimuthal range of 100$^\circ$. The solid curves represent the same experimental data that have been mirror averaged across $\phi = 45^\circ$ (the [110] direction) to improve statistical reliability. Note the large amount of diffraction fine structure present at the lowest emission angle of $\theta = 6^\circ$. 
Figure 3.3. The cluster of about 25 Å radius and containing 217 atoms that was used in the single scattering cluster (SSC) analysis of our azimuthal data. Note that this cluster includes a second Ni layer. The shaded atoms are the 35 strongest scatterers plus the emitter, as determined from a single scattering analysis. This 36-atom cluster was used for a multiple scattering cluster (MSC) analysis of the data.
Figure 3.4. (a) R factors of the $R_1$ type summed over $\theta = 6^\circ$, $10^\circ$, $12^\circ$, and $16^\circ$ and plotted versus vertical height $z$ for various $d_{12}$-spacings from $d_{12} = 1.76$ Å (bulk value-no expansion) to $d_{12} = 1.96$ Å (+0.2 Å expansion). The optimum geometry is a fourfold hollow site at $z = 1.39$ Å and $d_{12} = 1.86$ Å. (b) Comparison of experiment and SS theory for the optimum geometry.
Figure 3.5. (a) Comparison of the experimental data at $\theta = 6^\circ$ with SSC theory using the fully converged 25 Å cluster as shown in the Figure 3.3, and with both the SSC and MSC results for a smaller 36-atom cluster as indicated by the darker shaded atoms in Figure 3.3. The individual $R_1$ values comparing experiment and theory are also indicated with each curve. (b) Same as in (a) but for $\theta = 10^\circ$. (c) Same as in (a) but for $\theta = 12^\circ$. (d) Same as in (a) but for $\theta = 16^\circ$. Note that, as $\theta$ increases, the difference between the SS/36-atom calculation and the MS/36-atom calculation steadily decreases.
Figure 3.6.  (a) As in Figure 3.5, but for theoretical calculations at the higher takeoff angle of $\theta = 45^\circ$ only.  (b) R-Factor ($R_1$) values comparing a SSC calculations for the 36-atom shaded cluster of Figure 3.3 with a corresponding MSC calculation for the same cluster are plotted versus takeoff angle $\theta$. 
Figure 3.7. (a) $\chi(\vec{k})$ taken from the results of SSC-SW calculations at 1085 eV over the full hemisphere ($\alpha_0 = 178^\circ$) above the c(2x2)S/Ni(001) surface. The fully converged 217-atom cluster of Figure 3.3 was used in the calculations. (b) Plot of the anisotropy $\Delta I / I_{max}$ at a given takeoff angle verses takeoff angle $\theta$. Both theoretical results based on the $\chi(\vec{k})$ data in (a) and the experimental XPD data are shown. The rapid dropoff in the theoretical anisotropy by $30^\circ$-$40^\circ$ suggests a practical limit on the experimental data range of $\theta \leq 30^\circ$. Avoiding multiple scattering effects also suggests $\theta \geq 10^\circ$. 
Figure 3.8. Fourier-transform holographic images of the $\chi(k)$ data in Figure 3.7(a) taken in the adsorbate S layer (here defined as $z = 0.0$ Å). (a) A contour stack plot of the Fourier transform obtained with the full opening angle of the hologram ($\alpha_o = 178^\circ$). (b) Same as in (a) except $\alpha_o = 150^\circ$. (c) Same as in (a) except $\alpha_o = 120^\circ$. 

Figure 3.8. Fourier-transform holographic images of the $\chi(k)$ data in Figure 3.7(a) taken in the adsorbate S layer (here defined as $z = 0.0$ Å). (a) A contour stack plot of the Fourier transform obtained with the full opening angle of the hologram ($\alpha_o = 178^\circ$). (b) Same as in (a) except $\alpha_o = 150^\circ$. (c) Same as in (a) except $\alpha_o = 120^\circ$. 
Figure 3.9. Fourier transform holographic images based upon only the $\chi(k)$ results of Figure 3.7(a) between $\theta = 10^\circ$ and $30^\circ$. Images are derived from: (a) the full $360^\circ$ hologram by simple Fourier transformation, (b) the full hologram with a scattered-wave included Fourier transform (SWIFT) correction, (c) as in (a) but for the right half of the hologram only, (d) as in (b), but for the right half of the hologram only.
Figure 3.10. Experimental and theoretical holographic images based only upon data at the takeoff angles of $\theta = 6^\circ$, $10^\circ$, $12^\circ$, and $16^\circ$. (a) Simple Fourier transform of the experimental data set. (b) Experimental data with the SWIFT correction. (c) As in (a), but for SSC theory over the same takeoff angles. (d) As in (b), but for SSC theory.
CHAPTER 4

OBSERVATION AND CHARACTERIZATION OF A STRAINED LATERAL SUPERLATTICE IN THE OXIDATION OF Ni(001)

4.1. ASTRRACT:

The saturated oxide formed on Ni(001) under UHV conditions has been studied by x-ray photoelectron diffraction (XPD) and low-energy electron diffraction. At ambient temperature and with a 1200 L exposure to oxygen, the saturation oxygen coverage is found to be 4.3 ± 0.4 monolayers (ML) as measured relative to the Ni(001) surface-atom density. [1 langmuir (L) = 10^{-6} Torr-Sec.] The oxide is furthermore found to grow primarily as NiO(001) in a highly strained superlattice for which the horizontal lattice constant is expanded by 1/6 compared to the underlying Ni(001). The XPD results are found to be very sensitive to the degree of short-range order in the oxide before and after light annealing, particularly when obtained with high-angular resolutions of approximately ±1.0°. Single-scattering calculations with spherical-wave scattering are found to give an excellent description of the XPD from the annealed and more-ordered overlayer. These results also suggest the general utility of high-resolution XPD for studying the degree of short-range positional order present in epitaxial overlayers.
4.2. INTRODUCTION:

We report here the first observation of a strained lateral superlattice in the ambient-temperature oxidation of Ni(001). This study makes use of both high-energy x-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) to determine the structural characteristics of the oxide overlayer formed. Although the reaction of Ni(001) with oxygen has been the object of numerous studies [1, 2], no such superlattice has been discussed previously. A somewhat similar superlattice has been proposed in an early stage of the high-temperature oxidation of Ni(111) by Christensen et al. [3], and we comment below on its relationship to the structure we observe. A prior XPD study by our group on O/Ni(001) has emphasized the structures formed at lower exposures [4]. We here will concentrate entirely on the saturated oxide of approximately 4 monolayers (ML) thickness which in this study was formed at ambient temperature with an oxygen exposure of 1200 langmuirs (L) [1]. (1 L = 10^-6 Torr sec.)

4.3. EXPERIMENTAL PROCEDURE AND SURFACE CHARACTERIZATION:

The modified Hewlett-Packard 5950A system on which this combined LEED-XPD study was performed is discussed in detail elsewhere [5]. In addition, several azimuthal XPD scans of O 1s intensity were carried out at a very high angular resolution of ±1.5° in a VG Scientific ESCALAB5 system equipped with angle-defining tube arrays [6]. Surface cleanliness and oxide coverage were monitored by x-ray photoelectron spectroscopy (XPS) using standard core-intensity relationships for different surface overlayer morphologies [5]. Al Kα radiation (1486.6 eV) was used for excitation in all spectra.
The saturated oxide thickness after 1200 L exposure at ambient temperature and a pressure of $1.0 \times 10^{-5}$ Torr was determined from the ratio of the O 1s intensity of the oxide to the Ni 2p$_{3/2}$ intensity from the clean Ni surface just before the exposure. Both intensities were measured at a point well away from any strong photoelectron diffraction features and chosen so as to represent averages over the XPD structure; doing such averaging has been shown to be crucial for deriving accurate overlayer coverages [7]. The intensity ratios so derived were found to be very reproducible, with values usually lying within ±5% of those used for deriving the coverages quoted here. The calculations incorporated full allowance for inelastic attenuation in the assumed uniform oxide overlayer, and also included the variation of analyzer solid angle with kinetic energy [7]. Theoretical relative differential photoelectric cross sections for O 1s and Ni 2p$_{3/2}$ were used [8]. The electron mean free path in the oxide at the O 1s kinetic energy (954 eV) was taken to be 12.3 Å [7]. This analysis yields an oxide thickness equivalent to $4.3 \pm 0.4$ ML of oxygen as measured with respect to the Ni(001) surface density of $1.61 \times 10^{15}$ atoms/cm$^2$. (Most of the uncertainty here stems from that in the mean free paths used.) Neglecting overlayer attenuation yields a value of 2.4 ML and demonstrates the considerable importance of this correction. Upon annealing briefly to approximately 523 K, the attenuation-corrected value drops to 2.0–3.0 ML, although this decrease was very sensitive to the time of annealing and not fully reproducible. Such a decrease could be due to oxygen diffusion into the bulk [1]. Also, a simple thickening of the oxide layer into islands leaving relatively low-exposure areas in between has been suggested previously [1, 9] and would yield the same effect on our attenuation-corrected numbers. This is because our analysis assumes a uniform overlayer, but in the case of thicker islands (yielding a patched overlayer), the oxygen at the bottom of each island would experience enhanced inelastic scattering. Thus, the total O 1s intensity
would be lowered for thicker patched islands, and our effective coverage based upon a uniform overlayer model would go down.

Our saturation coverages before annealing are thus significantly higher than the approximately 2-ML discussed in some prior studies in the literature [1, 9, 10]. In order to check our analysis procedure, we have used a well-defined point in the exposure-versus-coverage or kinetics curve that corresponds to the strongest region of the c(2×2)O LEED pattern. This point is defined as the minimum-slope exposure along a short c(2×2) plateau in the kinetics curve; it is found to occur at 30–40 L in our experiment. Assuming in this case that there is no attenuation in the partial monolayer formed and using all other inputs to the calculation as for the oxide overlayer, we get a result of $0.37 \pm 0.04$ ML that is in excellent agreement with most prior studies [1, 2, 9]. [It should be noted that higher coverages for saturation c(2×2)O can be achieved under different experimental conditions, such as exposing at 323–423 K above room temperature [11] and/or using annealing and re-exposing cycles]. Looking at our results in another way, the ratio of the O 1s intensity at saturation coverage to that at the c(2×2) reference point is found to be 6.63; this implies that the minimum coverage value at saturation (which would be calculated with neglect of overlayer attenuation) is $0.37 \times 6.6 = 2.4$ ML. Correcting this value for attenuation then yields the 4.3 ML that we finally derive. Previous XPS work on a different Ni(001) crystal and in a different laboratory [12] gave O 1s intensity ratios from saturation to c(2×2) that are fully compatible with the high coverage values we are suggesting. Both sets of XPS data show well-defined c(2×2) plateaus in their kinetics curves centered at rather high exposures of 30–40 L; this indicates a low defect density and rules out the possibility that the high saturation coverage is a result of poor surface quality. Thus, these combined XPS results provide a fully self-consistent picture and support a saturation coverage of about 4 ML at an exposure of 1200 L.
One possible source of the discrepancy between our results and others for saturation coverages is that several prior studies have found lower exposures in the 200 L range to yield saturation, whereas our crystal did not reach saturation until approximately 500-600 L. Another source is that prior electron spectroscopic studies may not have correctly allowed for the combined effects of both outgoing Auger-electron- or photoelectron-diffraction and overlayer attenuation. In support of this latter suggestion, we note that the x-ray fluorescence work of Mitchell et al. [10], in which attenuation corrections in x-ray emission from the overlayer should not be a problem, yield an O 1s ratio between saturation and c(2×2) coverage of approximately 10. Using an average value from the literature for the c(2×2) of 0.37 ML, which also agrees with our value, then yields a saturation coverage of $10 \times 0.37 = 3.7$ ML, a value not very far below our own of 4.3 ML. This fluorescence ratio cannot be consistent with a c(2×2) coverage of 0.4 ML and a saturation coverage of near 2 ML. We conclude, therefore, that the question of quantification of oxygen coverage at saturation conditions, generally accepted to be about 2 ML in the literature [1, 9, 10], needs reassessing. This problem will be dealt with in more detail in a later paper. For the present work, it is only necessary to establish that our saturated oxide layers are significantly thicker than 2 ML.

4.4. RESULTS AND DISCUSSION:

In Figure 4.1 we show LEED photographs and corresponding sketches of the spot patterns observed at an incident beam energy of 64 eV. In Figure 4.1(a), we show the pattern observed after the usual 1200 L exposure at ambient temperature (approximately 293 K). Here, one sees the square array characteristic of the underlying Ni(001) substrate, which is partly overlapping with a very diffuse square array of smaller dimension which is
thought to be due to NiO present in the (100) orientation [1, 9]. Also evident is the weaker 12-spot ring, which has been suggested to be caused by two domains of NiO in the (111) orientation that are rotated 30° apart [1, 9]. But beyond this we see a clear and fully reproducible splitting of the diffuse NiO(001) spots into a centered square, as shown schematically in the right panel. Direct measurements from these and similar photographs obtained in another experimental system [12] yields the following geometric relationships among the spots:

(i) The centered square has an outside dimension along each edge that is very close to $\frac{1}{\sqrt{7}} = 14.3\%$ of that of the primary square array for Ni(001). The actual values are 14.3–15.1% as measured from the photographs.

(ii) The first observation also implies that the primary square array for NiO(001) also has an outside dimension that is very close to $\frac{6}{\sqrt{7}} = 85.7\%$ of that of Ni(001), and this is found to be the case in direct measurement (84.9–85.7%).

(iii) Both the 12-spot ring and the centered squares of NiO(001) yield spots that are coincident in position with the primary square array of Ni(001).

Upon annealing this ambient-temperature oxide to about 523 K over a total of about 10 minutes, the spot patterns shown in Figure 4.1(b) are found. As noted previously for this system [1,9], the 12-spot ring disappears, the NiO(001) spots brighten, and there is also a very weak appearance of the same patterns seen with the c(2×2)O overlayer formed at much lower exposures. We also note that the centered-square splitting of the NiO(001) spots is removed by this annealing.

Our suggested explanation for the extra spot splitting observed with the ambient-temperature oxide is that a lateral superlattice is formed due to the growth of reasonably large domains of strained NiO(001) whose NaCl lattice constant is on average exactly $\frac{1}{6}$ larger than that of the underlying Ni(001). The two arrays of Ni atoms that would be thus
overlaid are shown in Figures 4.2(a) and 4.2(b), and it is clear from the overlay in Figure 4.2(c) that a new centered-square superlattice structure with dimensions that correspond to (6×6) NiO(001) unit cells on (7×7) Ni(001) unit cells is formed. Thus, since the electrons in LEED will tend to penetrate several layers and scatter both singly and multiply, the regular beating of these two commensurate lattices could give rise to the additional spot splitting seen. A direct simulation of this effect with reduced photographic negatives of Figures 4.2(a)–4.2(c) and a visible laser does indeed yield a spot splitting of the form and dimensions observed. The agreement between experiment and this optical simulation is furthermore best for an illuminated area of the negative of about (3×3) superlattice cells or about (18×18) NiO cells with overall dimensions of 74 Å × 74 Å. [that is, about the size of the arrays shown in Figure 4.2(c)], this provides a rough idea as to the possible domain sizes of the superlattices that may be involved.

Such a superlattice must be highly strained, however, since the positions of the Ni atoms in the NiO(001) structure can be totally in registry with those in the underlying Ni(001) only at the lighter centered-square positions that are obvious in Figure 4.2(c), but must pass through regions of very strong mismatch in between these points. Two unit cells of this proposed structure (assuming for the moment only 2 ML of oxide with 1/6 expansion) are shown in Figure 4.3(a) for the case of perfect registry in one corner, and even for this case, the edge atoms in the two cells begin to be significantly out of registry. The true structure would no doubt relax in various ways to accommodate the strain induced, with one reasonable consequence being a net bowing outward over regions of the strongest mismatch. Such an effect might, in fact, be observable in a scanning-tunneling-microscope (STM) study of this system, although none has as yet been performed.

Additional information on the properties of this ambient-temperature oxide can be obtained from azimuthal- and polar-angle XPD scans for the O/Ni(001) system, an
introduction to which appears elsewhere [4]. In Figures 4.4 and 4.5, we show two additional sets of O 1s azimuthal data obtained at a very high angular resolution of ±1.5°. These data were obtained as full 360° scans which exhibited to a high degree the full $C_{4v}$ point-group symmetry of the Ni(001) or NiO(001) surfaces and were then fourfold averaged into one quadrant. In Figure 4.4, the polar angle of emission has been chosen to be as close as possible to 35.3°, implying that strong forward-scattering events due to Ni atoms may occur along <111> directions for emission from O atoms lying in the second and subsequent layers of the NiO(001) (see arrows in Figure 4.3). Such strong diffraction peaks do indeed occur, as shown in the experimental curves for both the unannealed and annealed oxide at $\phi = 45°$ in Figure 4.4. The second case considered in Figure 4.5 is a polar angle of 45°, which should and does yield strong peaks for O emitters in second and subsequent layers due to forward scattering from O atoms lying along <110> directions at $\phi = 0°$ and 90° (see arrows in Figure 4.3); again these strong features are seen for both the unannealed and annealed oxide.

Annealing the oxide overlayer as described previously causes significant changes in the XPD patterns seen at both polar angles, as shown in the bottom solid curves in Figures 4.4 and 4.5. The dominant forward scattering peaks are present in both cases, but there are significant changes in the relative intensities and positions of the additional features in these curves. In general, there is considerably more fine structure after the anneal, particularly for $\theta = 45°$. This suggests that the oxide is more highly ordered, and perhaps thicker, after annealing. Thus, high-resolution XPD is shown to be sensitive to the subtle structural changes which have caused the LEED also to change between Figures 4.1(a) and 4.1(b).

To get a better idea of how such changes might be linked to a reduction of the degree of strain and positional disorder present in the ambient-temperature oxide, we have carried out single-scattering cluster (SSC) calculations with spherical-wave scattering [5] for
various possible oxide overlayer structures; these are shown as dashed curves in Figures 4.4 and 5. The calculations shown at the bottoms of Figures 4.4 and 4.5 are for ideal 2- and 3-ML overlayers of NiO(OO1) with long-range order, as well as for a sum of two domains of 2 ML of NiO(111) with long-range order that is consistent with the 12-spot ring seen before annealing. In both figures it is clear that the annealed oxide yields XPD curves that are in remarkably good agreement with those of the ideal 2 ML of NiO(OO1), with noticeably less agreement as to fine structure for an ideal 3 ML of NiO(OO1). Thus, we conclude that the annealed oxide exists as NiO(OO1) and that it has been well-ordered in the top 2 ML by the anneal. Some disordered oxide that is not as obvious in the XPD curves is probably still present below these top 2 ML, since our surface stoichiometry suggests that another 2–3 ML of oxygen may be present after the anneal, particularly if there is thickening and island formation. This more deeply buried and strained oxide may be responsible for the lower experimental anisotropy (37%) compared to theory (63%). A prior XPD analysis of the vertical separation of the oxide layers for the annealed oxide based upon the positions of forward scattering peaks in polar scans [4] also suggests that it is very close to the one-half of \( \frac{7}{6} \) of the Ni lattice constant (\( a_{Ni} \)) which is expected if the oxide has the same \( \frac{1}{6} \)-expanded lattice constant in all three dimensions. This assumption has thus been used in all of the calculations reported here.

Turning now to the ambient-temperature oxide that exhibits the superlattice structure, we have carried out several calculations to simulate some of the effects of strain and the loss of long-range order, considering the first 2–3 ML of oxide that would be most important in producing the photoelectron diffraction pattern. In the upper portions of Figures 4.4 and 4.5, we show theoretical calculations for three different clusters whose makeup is illustrated in Figure 4.3(b):

(i) A 35-atom cluster of 2 ML of NiO(OO1) spanning only about two unit cells.
(ii) The same 35-atom cluster with the surface-layer O atoms moved upward by only 0.21 Å (a displacement suggested by measurements of the precise θ positions of the forward scattering peaks in Figures 4.4 and 4.5 from separate polar scans).

(iii) And finally a five-atom cluster that includes only the emitter in the second layer plus the four atoms nearest to the emitter along the scan directions in the second layer [as indicated more darkly in Figure 4.3(b)].

In all of these calculations, we have assumed that both the vertical and lateral lattice constants of the oxide are expanded by 1/6 relative to the underlying \( a_{\text{Ni}} \) to give \( a_{\text{NiO}} = 4.11 \) Å.

In both Figures 4.4 and 4.5, the 35-atom curve of the undistorted cluster looks rather like that of ideal 2 ML NiO(001), a result which is consistent with the known short-range sensitivity of XPD [5]. (Recall that all calculations have been made for a 1/6 dilated oxide lattice.) However, there is considerable sensitivity of these curves to either a slight upward displacement of the O atoms in the 35-atom cluster or a much reduced cluster size, as shown in the second two theoretical curves in each figure. It is interesting here that either of these two cluster changes yields curves that agree better with the unannealed experimental results. Thus, although we cannot choose between these two possible structures in what may be a very strained system with a continuum of structural variations from point to point, it seems clear that our XPD results for the ambient-temperature oxide are fully consistent with the proposed strained superlattice.

We now consider the bottom theoretical curves in both Figures 4.4 and 4.5 for two symmetry-related domains of 2 ML of NiO(111) with long-range order, a case which might be expected to simulate whatever NiO(111) is present in domains of sufficient size and order to yield the relatively sharp (but weak) 12-spot ring in Figure 4.1(a). These NiO(111) curves do not yield any major features that are in agreement with those seen in the
unannealed oxide curves, and it is clear that the dominant species present is NiO(001). However, closer inspection does reveal that certain weaker features in the experimental data for the unannealed oxide may be at least partially caused by XPD from the minority NiO(111) present. For example, in Figure 4.4, the experimental data for the unannealed oxide exhibit a filling in of the valleys in the NiO(001) theoretical curves at $\phi = 12^\circ$ and $78^\circ$ that may be linked to the peaks at similar positions for NiO(111). In Figure 4.5, the shoulders at $\phi = 15^\circ$ and $75^\circ$ and the strong peak at $\phi = 45^\circ$ in the data for unannealed oxide all could contain contributions from the regular peaks for NiO(111) at the same positions. However, taking linear superpositions of the theoretical curves for unannealed NiO(001) and NiO(111) with various mixing coefficients $\chi$ and $(1-\chi)$ respectively indicates that the overall best fits to the unannealed data represent only about 5% NiO(111). The maximum amount possible is only 10%. We thus conclude that, even though some of the surface must exist in the (111) structure with sufficiently large domains to yield the relatively sharp 12-spot ring seen in Figure 4.1(a), the dominant species of oxide on Ni(001) is NiO(001).

Lastly, we comment briefly on the relative lattice constants exhibited by NiO in its growth on Ni(001). The lattice constant of bulk NiO in the NaCl structure is 1.184 times that of Ni. For the superlattice, we have proposed an average value of $7/6 = 1.167$ times, or a 1.7% contraction relative to bulk NiO. Thus, NiO(001) grows on Ni(001) with very nearly its normal lattice constant. For the two-domain NiO(111) structure thought to cause the 12-spot ring [9], the perfect matching of <110> row spacings of Ni(001) with those of the most closely spaced rows in (111) planes of NiO requires an NaCl lattice constant of 1.154 times Ni, or a 2.5% contraction relative to the bulk oxide. The amount of contraction required and thus the net energy change involved is very close for the two cases, and it is thus perhaps not surprising that they can coexist on the surface. However, the fact that the growth of NiO(001) requires less contraction may explain its statistical dominance. In comparative
data for another Ni surface, Christensen et al. [3] find evidence for a similar sort of superlattice in LEED measurements in an early stage of high-temperature oxidation of Ni(111). Here, a NiO(001) structure beats against the underlying Ni(111) surface; however, their simulations of the LEED pattern require a 7% expansion of the NiO lattice relative to its bulk value that is much larger than and in the opposite direction to ours.

4.5. CONCLUSIONS:

The oxidation of Ni(001) is dominated by the formation of NiO(001), which, at ambient temperature, grows in a strained lateral superlattice. This superlattice oxide is expanded in lattice constant by $1/6$ relative to Ni(001), as seen via extra spot splittings in LEED that have not been discussed previously. Azimuthal XPD data at high angular resolution further indicate that this oxide is highly strained, but that the first two layers can be very well ordered by a brief low-temperature anneal to approximately 523 K. Comparisons to calculated single-scattering diffraction curves are found to yield excellent agreement for the annealed oxide. Using such theoretical curves, the amount of NiO(111) present in the unannealed oxide is estimated to be 5%, and cannot be more than 10%, even though it is thought to be responsible for the presence of a 12-spot ring pattern in LEED. Both NiO(001) and NiO(111) are contracted by very nearly the same amount in lattice constant relative to bulk NiO, but NiO(001) is less so. Our total coverages of saturated oxide at 1200 L exposure are $4.3 \pm 0.4$ ML before annealing and 2.0–3.0 ML after annealing. The importance of both fully reaching saturation and allowing adequately for inelastic attenuation in the oxide overlayer have also been demonstrated.

Beyond these specific structural conclusions concerning the oxidation of Ni(001), we also note that this study has demonstrated for the first time a high sensitivity of XPD
with resolutions of approximately ±1° to relatively subtle changes in the degree of short-range order around a given type of emitter. Thus, such measurements should be very useful in studies of the growth of various types of strained epitaxial overlayers, islands, or clusters on single-crystal substrates. Prior work on epitaxial systems using either Auger-electron diffraction or XPD (References 13 and 14) has largely made use of lower-resolution data in which the principal diagnostic features are the strong forward-scattering peaks along near-neighbor directions. But the results presented here indicate that considerably more detailed structural information can be extracted from higher-resolution data which more clearly exhibit features due to higher-order interference phenomena. As one example of this kind of study, the growth of metastable crystal structures such as epitaxial fcc Fe on Cu(001) (Reference 15) must be associated with strain and misfit dislocations, particularly for thicker layers which often tend to revert to the normal crystal structure. High resolution XPD should be capable of studying the degree of disorder present near the surface as a function of thickness. Similarly, XPD from islands or clusters should be sensitive to both the size of the agglomeration and the degree of order within it [16].
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Figure 4.1. (a) LEED spot pattern observed for ambient-temperature saturated oxide on Ni(001) at an incident energy of 64 eV. (The specimen holder obscures some spots from left to right across the image.) At right the positions and suggested origins of the several structures are indicated. (b) Same as (a), but after a light anneal to approx. 523 K over about 10 minutes.
Figure 4.2. (a) The array of Ni atoms on the surface of Ni(001), with various directions noted. (b) The Ni atoms in our proposed superlattice of NiO(001) with a $1/6 = 16.7\%$ lattice constant expansion with respect to the Ni. (c) An overlay of the two structures in (a) and (b) indicating the nature of the commensurate superlattice formed, as well as regions of both good registry (lighter color) and high mismatch and/or strain (darker color).
Figure 4.3. (a) Two overlying unit cells from the superlattice in Figure 4.2(c), with an assumed 2-ML thickness of NiO(001) and perfect registry at one corner. Also indicated are the two types of directions along which strong forward scattering effects from near neighbor atoms is expected, one for $\theta = 35.3^\circ$ ($<111>$ directions) and one for $\theta = 45^\circ$ ($<110>$ directions). (b) Two types of clusters used to simulate the reduction of long-range order in the strained superlattice: a 35-atom cluster over about two unit cells, and a minimal five-atom cluster (atoms shown in heavier outline).
Figure 4.4. Experimental azimuthal scans of O1s intensity obtained with a high angular resolution of ±1.5° at θ = 35.3° before and after a light anneal of the oxide are compared to the results of theoretical diffraction calculations for several clusters. The NiO(001) clusters without long-range order are indicated in Figure 4.3(b) and described in the text.
Figure 4.5. As Figure 4.4, but for $\theta = 45^\circ$. 
CHAPTER 5

X-RAY PHOTOELECTRON DIFFRACTION AND LOW ENERGY ELECTRON DIFFRACTION STUDY OF THE INTERACTION OF OXYGEN WITH THE Ni(001) SURFACE:
c(2×2) TO THE SATURATED OXIDE

5.1. ABSTRACT:

We have carried out a combined x-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) study of the interaction of oxygen with Ni(001) at ambient temperature from the c(2×2) structure up to the saturated oxide. Several new conclusions are possible based on an R-factor comparison of an extensive series of azimuthal- and polar- O 1s XPD data to theoretical simulations based on a single-scattering cluster (SSC) model with spherical wave scattering. A new method for normalizing experimental and theoretical intensities for XPD R-factor analyses is also used. For the c(2×2) structure, we find that the oxygen sits in the fourfold hollow site, at a vertical distance \( z \) of approximately 0.75 Å above the first Ni plane, in excellent agreement with several prior studies. There is also strong evidence from the XPD results that oxide nucleation occurs very early in the chemisorption region and this effect could explain the proposals for in-plane bonding or pseudobridge bonding previously reported in the literature. The saturated oxide that forms at ambient temperatures is found from LEED and XPD to form a highly strained superlattice that is expanded by \( \frac{1}{6} \) with respect to the underlying Ni(001). We also find that the saturation oxide coverage is much larger than
that previously reported in the literature of 2–3 monolayers (ML), and that it is in fact 4–5 ML. Other qualitative conclusions concerning the nature of the strain in the oxide are also possible.

5.2. INTRODUCTION:

Despite being the object of intensive investigation by a variety of surface-structure techniques over the past 20 years, there is still much to be learned about the exact nature of the various structures that arise on the Ni(001) surface when it is exposed to oxygen [1–18]. In order to better understand this system, we have obtained an extensive set of both polar- and azimuthal-x-ray photoelectron diffraction (XPD) data, as well as low energy electron diffraction (LEED) observations, at a number of different oxygen coverages. Of particular interest was determining the geometric structures of both the c(2×2) structure and of the saturated oxide overlayer that grow at ambient temperature (~300 K) on this surface, and in assessing the degree of coexistence of these two structures. XPD has been shown to be very useful in deducing structural information from ordered adsorbate atoms lying in or near the surface plane or from thin epitaxial films on a substrate, especially at kinetic energies in the range of 500–1500 eV [19, 20]. XPD is also in comparison to LEED more of a short-range order probe (~25–50 Å range compared to ~100–200 Å for the latter). Photoelectron diffraction data at such high energies have furthermore been successfully analyzed using simple single scattering cluster (SSC) calculations to differentiate between the various proposed surface structures thought to be be present [19, 20]. In order to better quantify the degree of agreement between experiment and theory, we have also used an R-factor analysis.
We begin by introducing the main features of the O/Ni(001) system as known previously. It has been well established that the adsorption of oxygen on Ni(001) occurs in four major steps at ambient temperature [1], with a schematic of some of the structures involved being shown in Figure 5.1:

(i) Rapid submonolayer adsorption with no disruption of the crystal lattice in the surface region, first leading to an ordered p(2×2) and then a c(2×2) overlayer geometry that would have ideal coverages of Θ = 0.25 and 0.50 monolayers (ML), respectively. We will here restrict our consideration to the c(2×2) structure, whose completion is schematically indicated in Figure 5.1(a).

(ii) Initiation of a c(2×2) plateau, the width of which is highly dependent on the quality of the Ni(001) surface and on the substrate temperature. This plateau is thought to be due to the complete filling in of all remaining available sites for dissociation of the impinging oxygen molecules and subsequent chemisorption. The best c(2×2) overlayer has been observed experimentally at coverages in the range of 0.30–0.40 ML, or somewhat below the ideal coverage.

(iii) Penetration of oxygen into the Ni lattice resulting in the development of isolated NiO nuclei or islands, accompanied by a rapid upswing in the oxygen sticking coefficient at coverages greater than ~0.50 ML. With increasing oxygen exposures, these NiO islands grow predominantly, but not necessarily exclusively, in the (001) orientation. Here, oxide clearly coexists with the c(2×2) structure.

(iv) Saturation occurs when these islands coalesce at a coverage that has been estimated previously to be in the range of 2–4 ML of NiO [Figure 5.1(d)]. The characteristics of the saturated layer are dependent on the actual mixture of two distinct oxide epitaxial orientations thought to be present, specifically in the [001] and [111]
orientation, and this mixture is in turn dependent on the substrate temperature during exposure [14].

There also exists a very slow, diffusion-limited, vertical oxide growth on significantly higher oxygen exposures that is known as the "tarnishing" region.

At low oxygen coverages (Θ < 0.5 ML), there has been considerable controversy over the actual geometric positions of the oxygen atoms in the c(2×2) overlayer. Part of this problem can be traced back to a misunderstanding of the effect annealing has on the surface structure. Crystal annealing was carried out in some older studies primarily to sharpen and intensify the LEED spots associated with the overlayer. However, at temperatures as low as 450–600 K, annealing can cause atomic oxygen initially chemisorbed onto the surface to diffuse into the crystal bulk and possibly also to form oxide nuclei, thus interfering with the ensuing structural determination [1]. Simple inward diffusion should not be confused with oxide nucleation however. In the early 1980's, an XPD study by our group [5] suggested that the oxygen overlayer resided in the same plane as the topmost Ni layer for an oxygen coverage approaching 0.5 ML, the theoretical limit for an ideal c(2×2)O structure; in this work however, it was pointed out that the XPD patterns would be very sensitive to the presence of small oxide nuclei, an effect which could have biased the results towards an in-plane geometry [5]. The in-plane geometry was in conflict with an earlier LEED analysis by Demuth et al. [2] who originally proposed that the p(2×2) and c(2×2) overlayer structures had the same z-distance of 0.8 Å. A subsequent theoretical study by Upton and Goddard [7], however, supported the short Ni–O bond distance and initiated the "oxide state" controversy for the c(2×2) overlayer. In a subsequent LEED study by Tong et al. [8], the possibility that the oxygen overlayer resided in the same plane as the topmost Ni layer could not be differentiated from a situation where the oxygen atoms sat well above the surface at a distance of 0.8 Å. Stöhr et al. [9] used surface extended x-ray adsorption fine
structure (SEXAFS) to rule out the in-plane bonding site and found that both the p(2×2) and c(2×2) structures occupied the fourfold hollow sites and had identical z-distances of 0.86 Å. In a followup LEED study, Demuth et al. [10] however, suggested that the c(2×2) structure had a z-distance of 0.80 Å, but more importantly, that the oxygen atoms were displaced 0.3 Å from the fourfold hollow site along the <110>-directions. This was described as being the pseudobridge bonding site. Such an unusual displacement was claimed to be entirely consistent with an observed broadening of several of the peaks associated with scattering off of nearest neighboring Ni atoms in the χ-curves of the SEXAFS analysis. However in the most recent LEED analysis of this system [15], a multilayer, tensor approach has shown that the preferred structure has the oxygen atoms residing once again in the fourfold hollow sites, although at a somewhat shorter z-distance of 0.75 Å. We will present a new and more detailed XPD analysis of the c(2×2) structure in this paper.

Although, the interaction of oxygen with the Ni(001) surface at higher coverages (> 0.5 ML), is known to result in the onset of oxide nucleation and growth, it has also been concluded that the onset of oxide nucleation occurs well before the cessation of c(2×2) formation [1], although there is very little prior quantitative information concerning the relative amounts of oxygen in the c(2×2) and oxide structures. The actual oxidation of the Ni(001) surface is a remarkably complex interaction that is highly dependent on the temperature of the substrate during the oxygen exposure. In an earlier XPD/LEED paper on this system [13], Saiki et al. reported LEED observations of a (6×6) NiO(001) centered-square superlattice formation which grows on a (7×7) Ni(001) mesh, and that this coexists with two orientations of a minority NiO(111) species rotated 30° apart from each other and manifesting themselves as a 12-spot ring when viewed by LEED. (Various LEED photographs relevant to this discussion have previously been published in Reference 13).
These two co-existent oxide phases were first discussed by Holloway and Hudson [3] and first hypothesized to be NiO(001) and NiO(111) by Mitchell et al. [4]. Subsequent work by Wang et al. [14] has shown that room temperature is actually a crossover point for the formation of the (111) versus (100) orientations of NiO. At lower temperatures, NiO(111) is the majority species while the more stable (100) orientation is observed at room temperature and above. Although the (111) structure is clearly seen in our ambient temperature LEED pattern, it yields no observable peaks in the XPD curves, and has thus been estimated to comprise about 5% and no more than 10% of the total saturated oxide [13].

Annealing the saturated oxide for a few minutes to as little as 523 K results in the removal of both the NiO(111) 12-spot ring and the centered-square spot splitting of the superlattice, and also leads to the reappearance of a similar c(2×2) structure that is observed at lower oxygen coverages [13, 14]. This is postulated to be due to the formation of oxygen-rich and oxygen-depleted regions, as illustrated in Figure 5.1(e). The oxygen-rich regions appear to have greater order in the vertical direction that could be the result of the creation of a significantly thicker oxide layer. The LEED spots of NiO(001) after annealing are more intense, but remain centered very near their previous position and are rather diffuse, which suggests that the annealed oxide is still under considerable strain and/or exists in rather small domains. The oxygen-poor regions are thought to be covered by a c(2×2) oxygen overlayer that leads to the recovery of a c(2×2) structure in LEED after annealing.

The formation of two or more monolayers of ordered NiO(001) should result in significant modulations of the O 1s x-ray photoelectron spectroscopy (XPS) signal, similar to that expected from a single-crystal of NiO. In the prior XPD analysis of the annealed oxide layer [13], it was determined that the best fit of theoretical calculations to high-angular
resolution O 1s azimuthal XPD data at takeoff angles $\theta$ of 35.3° and 45.0° with respect to the surface occurred for a large NiO(001) cluster 2-ML thick that covered an area of approximately 20 Å in radius from the emitting oxygen atom. This cluster had a lattice constant expanded by $1/6$ over bulk Ni, that is $a_{\text{NiO}} = 7/6(3.52 \text{ Å}) = 4.11 \text{ Å}$, a value determined from measurements of the position of the oxide diffraction spots in LEED. Annealing does not fully relieve the expansion in the horizontal directions but retains the slight 1.4% compression below the bulk oxide lattice constant of 4.17 Å. However, the annealed oxide had an XPD pattern that was markedly different from the unannealed data, indicating that some type of irreversible structural changes were occurring in the process. These effects also are explored in greater detail in this paper.

In the following sections, we present a more detailed set of XPD results, and these are found to lead to several new conclusions concerning the structures of oxygen on Ni(001).

5.3. EXPERIMENTAL CONSIDERATIONS:

The two experimental systems used for this study have been described in detail previously [19(a), 21] and consist of Hewlett-Packard (HP) 5950A and VG Scientific ESCALAB5 x-ray photoelectron spectrometers that have been modified for angle-resolved measurements with the installation of high-accuracy two-axis specimen goniometers. The VG system also has a series of angle-defining stainless steel tube arrays mounted in front of the entry lens to the energy analyzer [21]. These tube arrays allow different angular resolutions of ±1.5°, ±3.0°, and ±6.0° (full open) to be selected. Prior studies have shown an increase in the amount of diffraction fine structure when the angular resolution is increased from the standard ±3.5° to ±6.0° to the current minimum ±1.5° [21], and that
such additional fine structure may be useful in deriving additional details of overlayer structures [19(c), 22]. An unpolarized Al Kα radiation source (hv = 1486.6 eV) was used for the primary excitation in either case. The experimental configuration is shown in Figure 5.2; the angle α between radiation incidence and electron exit was 72° in the HP system and 48° in the VG system. The detector consisted of a Surface Science Laboratories multichannel system on the HP and a single channeltron on the VG spectrometer, although the latter has subsequently been upgraded to include a similar multichannel detector [23]. Precision scanning of either the φ- or θ-electron emission directions was possible under direct computer control. Base pressures were maintained at better than 5 × 10⁻¹¹ Torr in the main analysis chamber. A LEED unit was available on the HP system to observe the surface symmetry of the various overlayer surface structures that were obtained.

The Ni(001) sample was cut from a single-crystal rod with a low-speed diamond saw and oriented to within ±0.3° of the (001) surface as determined by Laue back-scattering measurements. The surface was then mechanically polished with successively finer grades of diamond paste before final chemical etching in a 10% solution of 1:1 nitric/sulfuric acid to remove as much of the surface disorder from mechanical polishing as possible before mounting in the spectrometer. Surface cleanliness and oxygen coverage were monitored by XPS, as described in detail in the next section. The initial and subsequential cleanings were done by successive in situ Ar⁺ bombardments at 600 volts, followed immediately by annealing to approximately 873 K until the combined coverage of C, O, and S impurities totaled less than 0.02 ML and the LEED pattern showed a sharp p(1×1) pattern of the (001) surface with high contrast.

The oxygen exposures were performed at room temperature, with the oxygen pressure being monitored by a standard Bayard-Alpert ion gauge. The best compromise between the sharpest c(2×2) pattern and the most intense fractional-order spots was
observed at an exposure of 30 L (10^{-7} \text{Torr} \times 300 \text{sec.}); this also is found to be the location of the minimum slope in the uptake curve, as shown in Figure 5.3 and discussed in more detail below. The XPS-based coverages at this exposure were found to be 0.38 ± 0.04 ML, in excellent agreement with prior studies [1]; the determination of these coverages also is discussed below. The saturated-oxide exposure was somewhat arbitrarily set at 1200 L (10^{-5} \text{Torr} \times 120 \text{sec.}), since by this point the oxygen coverage (approximately 2.4 ML as measured with respect to Ni(001) and without correcting for attenuation by the oxide overlayer, so as to represent a minimum value) did not increase appreciably with significantly larger oxygen exposures [cf., Figure 5.3(a)]. In either c(2\times2)O or the saturated oxide, the O 1s/ Ni 2p_{3/2} intensity ratios used for quantitative analysis were taken along directions well away from any strong photoelectron diffraction forward scattering features and also chosen so as to represent an average intensity from the surface at a given \theta. The individual intensity measurements were found to be very reproducible, with values ranging within ±5% of the values reported in this paper. The importance of such care in these measurements will be explained later.

The precise calibration of the \theta– and \phi–angles with respect to the crystal axes (cf., Figure 5.2) was done with high angular resolution and using the strong and very narrow Ni 2p_{3/2} XPD peaks from the clean surface that occur along the <110> directions. This calibration had an accuracy of ±0.2°. A series of O 1s azimuthal scans (E_{\text{kin}} = 954 \text{ eV}, electron wavelength = 0.40 Å) were taken for both the c(2\times2) and saturated oxide structures over a \phi-range of 380° at grazing takeoff angles with respect to the surface of \theta = 8°, 11°, 14°, and 17° to yield enhanced surface sensitivity and at much larger angles near \theta = 35° and 45° to probe deeper lying structures. Polar scans were also measured in high-symmetry azimuths. All of this data will be discussed below.
5.4. THEORETICAL MODELING AND DATA ANALYSIS:

5.4.1. QUANTITATIVE ANALYSIS OF SURFACE COVERAGES-

The theoretical model used to describe the relationship between the integrated XPS peak intensities and different surface coverages in this study has been described in great detail elsewhere [19]. Basically, it assumes a uniform overlayer that is atomically flat, that the incident x-rays have penetration depths that far exceed the elastic escape depths of the photoelectrons, that any enhancements of the photocurrent due to diffraction effects from the uniform overlayer/substrate are either negligible or have somehow been averaged over, and that inelastic scattering can be adequately described by a simple exponential in the attenuation length or mean free path ($\Lambda_e$). Electron refraction due to the inner potential ($V_0$) can often be neglected due to the large takeoff angles and/or the high kinetic energies of the photoelectrons being utilized, but we have included it in our calculations for completeness.

For a bulk solid having little or no local order to produce diffraction, the relationship between the integrated intensity of a core level photoemission peak is given by [19(a)]:

$$I_k = I_0 \Omega_0(E_{\text{kin}}) A_0(E_{\text{kin}}) D_0(E_{\text{kin}}) \rho_k \frac{d\sigma_k}{d\Omega} \Lambda_e(E_{\text{kin}}),$$

where $I_0$ is the intensity of the incident monochromatic x-ray flux, $\Omega_0(E_{\text{kin}})$ is the effective solid angle of the detector, $A_0(E_{\text{kin}})$ is effective source area of the sample seen by the analyzer, $D_0(E_{\text{kin}})$ is the detector efficiency, $\rho_k$ is the density of the $k^{\text{th}}$ species under study, $\frac{d\sigma_k}{d\Omega}$ is the differential cross-section of the peak $k$ under study, and $\Lambda_e(E_{\text{kin}})$ is the inelastic attenuation length of the photoelectron in the solid.
XPS peak intensity ratios have been shown to be useful in determining the fractional monolayer coverages of adsorbates and the stochiometric ratios of the various elements present in the near surface region. The purely instrumental parameters $I_0$, $\Omega_0$, $A_0$, and $D_0$ will cancel out when intensity ratios of the various chemical species are examined, provided that the kinetic energies are reasonably close. If photoemission peaks with more widely differing energies are studied [as is the case for the O 1s (954 eV) and Ni 2p3/2-metal (629 eV) considered here], the change in the detector solid angle $\Omega_0(E_{\text{kin}})$ with energy can become significant, and suitable values for the particular spectrometers we have used have been tabulated and published [23, 24]. Similarly, the differential cross-sections have also been calculated and tabulated for many cases [25]; the same is true for the electron attenuation lengths of various solids [26]. The overall accuracy of such measurements are in the range of ±20% at the submonolayer concentration levels and the majority of the error is in the determination of $A_e(E_{\text{kin}})$, which is expected to vary roughly as the square root of the kinetic energy in a given material for the energies of interest here [26].

For the ideal case of a uniformly distributed adsorbate present at submonolayer quantities [the situation for c(2×2)O/Ni(O01)], the oxygen coverage can best be determined by assuming that the overlayer is completely non-attenuating [19(a)]. Comparisons of the Ni 2p3/2 intensities both before and after oxygen exposure to form c(2×2) showed essentially no change in absolute value and this supports our use of the completely non-attenuating overlayer model. The O 1s/Ni 2p3/2 (metal) intensity ratio for this dilute overlayer then becomes:

$$\frac{I_{O1s}(954 \text{ eV})}{I_{Ni2p(m)(629 \text{ eV})}} = \frac{\Omega_0(954 \text{ eV})}{\Omega_0(629 \text{ eV})} \cdot \frac{\frac{d\sigma_{O1s}}{d\Omega}}{\rho_{Ni(m)} \cdot A_e^{m}(629 \text{ eV}) \cdot \sin\theta} \cdot \frac{\frac{d\sigma_{Ni2p}}{d\Omega}}{S'}$$
where \( m \) = metal peak, \( S' \) = number of oxygen atoms per cm\(^2\), \( \rho_{Ni(m)} \) = atomic density in Ni metal = 9.14 \( \times \) 10\(^{22}\) atoms/cm\(^3\), and \( \Lambda_m^{629}\) (629 eV) = the mean free path in the metal at 629 eV. This can be rearranged to yield the c(2\times2) coverage as:

\[
S'[c(2\times2)] = \left[ \frac{I_{O1s}}{I_{Ni2p(m)}} \right] \cdot \frac{\Omega_o(629 \text{ eV})}{\Omega_o(954 \text{ eV})} \cdot \frac{\frac{d\sigma_{Ni2p}}{d\Omega}}{\frac{d\sigma_{O1s}}{d\Omega}} \cdot \rho_{Ni(m)} \cdot \Lambda_m^{629} \text{ eV} \cdot \sin \theta .
\]

Substituting in the relevant values,

\[
\frac{\Omega_o(629 \text{ eV})}{\Omega_o(954 \text{ eV})} = 1.44 \text{ (as derived previously for the HP spectrometer [24])},
\]

\[
\frac{d\sigma_{Ni2p}}{d\Omega} = 4.674 \text{ (calculated from data in Reference 25)},
\]

\[
\frac{d\sigma_{O1s}}{d\Omega} = 10.0 \times 10^{-8} \text{ cm \ [from Reference 26(c)]},
\]

and \( \theta = 45^\circ \), yields the number of monolayers of oxygen present with respect to the Ni(001) surface as:

\[
\# \text{ ML of } O = S'[c(2\times2)O] \cdot \frac{S[Ni(001)]}{S[Ni(O01)]} = 27.01 \cdot \left[ \frac{I_{O1s}}{I_{Ni2p(m)}} \right] ,
\]

(5-1)

where \( S[Ni(001)] \) = the surface density of Ni(001) = \( \frac{2 \text{ atoms}}{a_0(Ni)^2} = 1.61 \times 10^{15} \text{ atoms/cm}^2 \).

In determining coverages for the saturated oxide, we have measured the Ni 2p\(_{3/2}\) signal from the clean Ni surface and the O 1s signal from the reacted surface just after
exposure; this avoids the considerable difficulties in trying to distinguish the Ni 2p3/2(metal) and Ni 2p3/2(oxide) features in nickel spectra for the oxidized case. The overlayer of thickness \( t_{ox} \) is now assumed to be isotropically attenuating. The intensity ratio here becomes [19(a)]:

\[
\frac{I_{O1s}}{I_{Ni2p(m)}} = \frac{\Omega_o(954 \text{ eV})}{\Omega_o(629 \text{ eV})} \cdot \frac{\rho_{O(\text{ox})}}{\rho_{Ni(m)}} \cdot \frac{d\sigma_{\text{O1s}}}{d\Omega} \cdot \frac{\Lambda_e^o(954 \text{ eV})}{\Lambda_e^o(629 \text{ eV})} \cdot \left[ 1 - \exp \left( \frac{-t_{ox}}{\Lambda_e^o(954 \text{ eV}) \cdot \sin \theta} \right) \right],
\]

which on rearrangement and substitution of the various values, is then:

\[
t_{ox} = -\ln \left[ 1 - \left( C \cdot \frac{I_{O1s}}{I_{Ni2p(m)}} \right) \right] \cdot \Lambda_e^o(954 \text{ eV}) \cdot \sin \theta ,
\]

where:

\[
C = \frac{\Omega_o(629 \text{ eV})}{\Omega_o(954 \text{ eV})} \cdot \frac{\rho_{Ni(m)}}{\rho_{O(\text{ox})}} \cdot \frac{d\sigma_{\text{Ni2p}}}{d\Omega} \cdot \frac{\Lambda_e^o(629 \text{ eV})}{\Lambda_e^o(954 \text{ eV})} = 8.641 ,
\]

\( \Lambda_e^o(954 \text{ eV}) \) = electron mean free pathlength in the oxide layer, taken in our calculations to be 12.3 Å [26], and

\[
\rho_{O(\text{ox})} = \frac{1}{(1/6)^3} \cdot \rho_{Ni(m)} = 5.76 \times 10^{22} \text{ atoms/cm}^3 ,
\]
as calculated with allowance for the $7/6$ expansion relative to the Ni lattice observed in LEED. Thus we have finally,

$$t_{ox} (\text{Å}) = -8.72 \cdot \ln \left[ 1 - 8.641 \left( \frac{I_{O1s}}{I_{Ni2p(m)}} \right) \right]. \quad (5-2)$$

From the $7/6$ expansion relative to the underlying Ni(001), the oxide surface density becomes,

$$S'[\text{NiO(001)}] = \frac{2 \text{ atoms}}{[\text{a}_0(\text{Ni})]_2^2} = 1.185 \times 10^{15} \text{ atoms/cm}^2$$

and the "unrelaxed" vertical distance between planes is given by:

$$d_{100(ox)} = \left( \frac{1}{2} \right) (7/6)(a_0(\text{Ni})) = 2.054 \text{ Å}.$$

From Equation (5-2), the number of monolayers of oxide with respect to the oxide surface density is then given by:

$$\frac{t_{ox}(\text{Å})}{d_{100(ox)}} = -4.25 \cdot \ln \left[ 1 - 8.641 \left( \frac{I_{O1s}}{I_{Ni2p(m)}} \right) \right],$$

and the # ML's of oxide with respect to the Ni(001) surface density by:

$$\frac{t_{ox}(\text{Å})}{d_{100(ox)} \cdot (7/6)^2} = -3.12 \cdot \ln \left[ 1 - 8.641 \left( \frac{I_{O1s}}{I_{Ni2p(m)}} \right) \right]. \quad (5-3)$$
The inelastic attenuation lengths are an important ingredient in any such XPS surface analysis, and we have here used two different approaches to assess the difference they make. In the first approach already indicated above, an experimental value of $\Lambda^m_\epsilon(629\text{ eV}) = 10.0\text{ Å}$ for propagation in Ni metal was used as a starting point; this has been found to give excellent results for the XPS analysis of the well-defined c(2\times2)S overlayer by Connelly et al. [26(c)]. We will also see below that it gives a c(2\times2)O coverage of 0.38 ML that is in excellent agreement with those from several other methods [1, 18]. As no accurate experimental $\Lambda_\epsilon$ data are available for NiO, the 10.0 Å value for the metal was then scaled simply as $(E_{\text{kin}})^{0.52}$ to yield values for the oxide of $\Lambda^{\text{ox}}_\epsilon(629\text{ eV}) = 10.0\text{ Å}$ and $\Lambda^{\text{ox}}_\epsilon(954\text{ eV}) = 12.3\text{ Å}$. These latter values do not however, take into account the composition and density changes from metal to oxide. As another approach, we have used the equations and tabulations of Penn [27] to determine these values. These do not have a direct experimental calibration, but do take into account of the atomic makeup of each material. They yield $\Lambda^m_\epsilon(629\text{ eV}) = 8.2\text{ Å}$, $\Lambda^{\text{ox}}_\epsilon(629\text{ eV}) = 8.6\text{ Å}$, and $\Lambda^{\text{ox}}_\epsilon(954\text{ eV}) = 11.6\text{ Å}$, values which, with the exception of the first for Ni metal, are extremely close to those which we have used. Since our 10.0 Å value for $\Lambda^m_\epsilon(629\text{ eV})$ has experimental support from prior XPS studies of both c(2\times2)S and c(2\times2)O, we believe that this is in any case the most reliable value to use. The other two oxide values of 12.3 Å and 11.6 Å that are of relevance here in determining the saturated oxide thickness are very close in the two approaches. If anything, using the slightly lower 11.6 Å value would yield a somewhat thicker saturated oxide layer thickness. Thus, based upon the present state of our knowledge of the attenuation lengths in the oxide, we have used a highly reliable set of values.

Turning now to the actual values derived in this study, we note that the coverage of the c(2\times2)O structure at 30 L was determined from the ratio of the O 1s and Ni 2p3/2 peak areas immediately after O$_2$ exposure. Converting the intensity ratio to monolayers of
oxygen using Equation (5-1) gave a value of $0.38 \pm 0.04$ ML, in excellent agreement with currently accepted values [1, 18]. It is also significant here that a value of $0.35 \pm 0.04$ ML in complete agreement with ours was derived for this value in an independent XPS study by Brundle and Hopster [28] using an empirical O 1s intensity calibration via a saturated monolayer of CO on Ni(001) at liquid nitrogen temperature.

As noted above, the saturated oxide thickness after a 1200 L exposure at ambient temperature was determined from the ratio of the O 1s peak area of the oxide and the Ni 2p$_{3/2}$ peak area of the clean surface immediately before oxygen exposure. This procedure was used to avoid the complications of having to allow for the intensity of the chemically-shifted Ni 2p$_{3/2}$(oxide) peak [1, 29], as well as the attenuation of the Ni 2p$_{3/2}$(metal) peak in passing through an oxide layer of unknown thickness. Using this approach, only the attenuation due to the O 1s signal passing through the oxide layer needs to be considered. In order to illustrate the importance of electron attenuation, if we assume that the oxide overlayer is completely non-attenuating, we get from Equation (5-1) an oxygen coverage of 2.4 ML with respect to the Ni(001) surface density. This is an absolute minimum according to our XPS analysis, as it neglects overlayer attenuation. On the other hand, if the oxide overlayer attenuates the XPS signal, the more correct Equation (5-3) gives an oxygen coverage of $4.7 \pm 0.5$ ML, an increase of nearly a factor of two, thus underscoring the importance of attenuation corrections in coverage measurements. As stated in our earlier paper [13], this saturated oxide thickness is larger than the 2–3 ML that has previously been reported from some studies in the literature [1]. The absolute minimum of 2.4 ML that we find is furthermore inconsistent with the saturation coverage of 2.45 ML found recently by Pope et al. using nuclear reaction analysis [18], since the presence of any reasonable attenuation in the oxide overlayer in XPS would yield a higher value than 2.45. Our value of 4.7 ML with overlayer attenuation is however, consistent with, although somewhat higher
than, a very recent XPS study of O/Ni(001) by Hall et al. [30], who find a 4-ML thickness for the NiO(001) orientation that we find to be dominant at saturation.

5.4.2. PHOTOELECTRON DIFFRACTION CALCULATIONS-

The single scattering cluster (SSC) model used for the photoelectron diffraction calculations in this study has been discussed in detail elsewhere [19] and we have used it in a form that contains both spherical-wave scattering and the correct $s \rightarrow p$ final state in O 1s photoemission. The latter two improvements make use of the Rehr-Albers separable Green's function approach [31(a)] which simplifies the calculation of the effective scattering factors. In the case of O 1s emission from a multilayer system such as NiO(001) or NiO(111), where it is possible to have more than one type of emitter in each layer, it is important to correctly weigh the intensities of each emitting atom in the final intensity sum. The weight used is the number of each type of emitter per unit area in that layer divided by the total number of emitting atoms per unit area present in the layer. Attenuation of the photocurrent from each oxide layer is then provided by an exponential factor of the form $\exp\left(-\frac{z}{2\Lambda_c \sin \theta}\right)$, where $z$ is the depth below the surface. Such weighting considerations are also important in the estimation of the percentage of NiO (one O atom per Ni atom multiplied by the number of monolayers of NiO(001)) mixed in with c(2×2)O ($\frac{1}{2}$ O atom per Ni atom), a point that will be discussed in greater detail later.

A more sophisticated program that takes into account photoelectron multiple scattering (MS) events is also available to us, although computer-time constraints limit the size of the clusters that can be used at present to about 30–40 atoms [32, 33]. In general, MS effects in XPD are not significant unless there are long rows of atoms present in the cluster which lie within about 10$^\circ$ of the photoemission direction [32, 33]. MS also may
produce some effects for the thicker annealed oxide, where it would be expected to yield a reduction of the intensity of the forward scattered peaks predicted by SSC theory, but it is not expected to significantly influence the conclusions of this analysis.

The input parameters for the SSC program include the following for O 1s emission:

For the c(2×2) analysis, clusters of various sizes were investigated and it was found that a cluster having a minimum radius of 20 Å from the emitter is necessary to insure full convergence of all the diffraction features at the lowest takeoff angle of θ = 8° [see, for instance, Figure 16 in Reference 19(c)] and this was used throughout the analysis for consistency. An inner potential of 11.0 eV was used for the c(2×2) overlayer, along with an inelastic attenuation length in the overlayer of 12.3 Å, although small changes of ±20% in either value did not significantly change the outcome of the calculated diffraction curves.

For the oxide, a number of different clusters having two or more layers of NiO, as well as having different radii from a minimal five-atom cluster up to a fully converged cluster of 20 Å in radius, were used to investigate the effect that annealing has on the vertical and horizontal order of the oxide layer. For the oxide, the inelastic attenuation length remained unchanged at 12.3 Å, but the inner potential was increased to 13.2 eV, a number obtained from a band structure calculation by Mattheiss [34].

5.4.3. R-FACTORS FOR COMPARING EXPERIMENT AND THEORY-

The five R-factors (R₁–R₅) used in this study to judge the goodness of fit between experimental azimuthal data and theory are based essentially on the ideas of Van Hove, Tong, and Elconin [35]. However, a significant improvement we have incorporated is in the manner of normalizing the experimental data with the theory. This normalization is motivated by the observation that the theoretical anisotropies as judged by $(r_{\text{max}} - r_{\text{min}})/r_{\text{max}}$
typically exceed those of the experimental results by a factor of between two and three. Such a discrepancy can be attributed to MS effects, surface roughness, finite domain sizes, and other non-ideal surface effects. Our basic strategy is to force the normalized theory curve to have an anisotropy as close as possible to that of experiment before direct comparison. The normalization routine is as follows: The experimental diffraction curve is forced to have an amplitude between zero and one,

\[ I_{\text{exp}}^*(n) = \frac{I_{\text{exp}}(n) - I_{\text{exp}}^{\text{min}}}{I_{\text{exp}}^{\text{max}} - I_{\text{exp}}^{\text{min}}} \]

where \( I_{\text{exp}}^*(n) \) is the rescaled experimental intensity for the \( n^{\text{th}} \) channel in the azimuthal scan, \( I_{\text{exp}}(n) \) is the raw experimental data for the \( n^{\text{th}} \) channel, and \( I_{\text{exp}}^{\text{max}} \) (\( I_{\text{exp}}^{\text{min}} \)) are the maximum (minimum) values of \( I_{\text{exp}}(n) \) in the azimuthal scan. Next, the average value of both the rescaled experimental and original theoretical curves is set to zero by subtracting out the average value of the rescaled experimental and the raw theoretical curves:

\[ I_{\text{exp}}^{**}(n) = I_{\text{exp}}^*(n) - \frac{1}{n} \left[ \sum_n I_{\text{exp}}^*(n) \right] \]

and

\[ I_{\text{th}}^*(n) = I_{\text{th}}(n) - \frac{1}{n} \left[ \sum_n I_{\text{th}}(n) \right] . \]

The average value of both the rescaled experiment and theory is given by,
The rescaled theory, \( I_{th}(n) \), then is forced to have the same ±area relative to the average zero as the rescaled experimental data, \( I_{exp}^{**}(n) \). The final scaled theory curve is then \( I_{th}^{**}(n) \), as given by:

\[
I_{th}^{**}(n) = I_{th}^{*}(n) \left[ \frac{A_{exp}}{A_{th}} \right],
\]

where the ± areas, \( A_{exp} \) and \( A_{th} \), are given by:

\[
A_{exp} = \sum_{n} I_{exp}^{**}(n) \quad A_{th} = \sum_{n} I_{th}^{*}(n).
\]

In the final step in the normalization, a vertical offset is added to give the normalized theory curve approximately the same maximum value as the original experimental curve. This vertical offset is defined as:

\[
\text{offset} = I_{exp}^{*} + \frac{I_{min}^{exp}}{I_{max}^{exp} - I_{min}^{exp}}.
\]

so that,
Because these final normalized intensities are still absolute, with no background subtracted from them, they yield the very desirable property for XPD analyses that two curves with a lower percent effect (or lower overall anisotropy $= (I_{\text{max}} - I_{\text{min}})/I_{\text{max}}$) contribute less to four of the five R-factors defined below. Thus, the contributions of azimuthal scans with different anisotropies to $R$ are automatically weighted correctly in the summed $R$'s to be discussed below.

These normalized intensities are finally substituted into the five R-factors $R_N (N = 1, 2, 3, 4, 5)$ as defined by Van Hove et al. [35] to yield:

$$R_1 = \frac{\sum_n |I_{\text{exp}}(n) - I_{\text{th}}^+(n)|}{\sum_n |I_{\text{exp}}(n)|},$$

$$R_2 = \frac{\sum_n [I_{\text{exp}}(n) - I_{\text{th}}^+(n)]^2}{\sum_n (I_{\text{exp}}(n))^2},$$

$$R_3 = \text{percentage of angle range over which } I_{\text{exp}}(n) \text{ and } I_{\text{th}}^+(n) \text{ have slopes of different sign (+/-)}. $$
\[ R_4 = \frac{\sum_n |I'_\text{exp}(n) - I'_\text{th}(n)|}{\sum_n |I'_\text{exp}(n)|}, \]

where \( I'_\text{exp}(n) \) and \( I'_\text{th}(n) \) are the first derivatives of the experiment and normalized theory respectively, and lastly,

\[ R_5 = \frac{\sum_n \left[ I'_\text{exp}(n) - I'_\text{th}(n) \right]^2}{\sum_n (I'_\text{exp}(n))^2}. \]

Finally, for a set of azimuthal diffraction data from a given surface structure, we can calculate "global" or "summed" R-factors for any one of the five choices as:

\[ R_N(\text{total}, z) = \frac{1}{m} \sum_m R_N(m, z), \quad (5-5) \]

where \( N \) is the \( N^{th} \) R-factor, \( z \) is some structural parameter(s) that is being varied, and \( m \) is the number of azimuthal scans at different polar angles taken for that surface structure. In a large number of tests, we find that all five R-factors give very similar results (as will be illustrated below for one example) and that they are also consistent with straightforward visual evaluations of fit. These R-factors are also found to be superior for XPD to others that we have tested such as those of Zanazzi and Jona [36]. We have further found that the first R-factor (\( R_1 \)) provides an excellent description of the fit between curves by itself and it is this value that is reported in most cases throughout this paper.

\[ \]
5.5. RESULTS AND DISCUSSION:

5.5.1. SOME STRUCTURAL CONSIDERATIONS-

Figure 5.4 is a schematic drawing of the two primary structures that we will be concerned with on the Ni(001) surface. By varying the takeoff angle of the O 1s azimuthal scans, it is possible to tune the analysis from sampling preferentially near-surface features at low θ values to probing more bulk-like structural information at high θ values. From Figure 5.4(a) for c(2×2)O, we see that, in order to obtain structural information on the oxygen-to-nickel interplanar separation or z-distance, rather large scattering angles (θ_Ni) are involved, but these can be minimized by using grazing emission directions, thus increasing the scattering that comes from the underlying Ni atoms. The scattering angles for other O atoms (θ_O) are by contrast constant at θ_O = θ = takeoff angle. From Figure 5.4(b) for the oxide, we can also use grazing emission directions to derive structural information more sensitive to the surface plane, or larger polar angles to probe the structure of the oxide buried further beneath the surface. Due to the epitaxial nature of the NiO(001) oxide that forms on Ni(001), information on both the distance separating the first and second NiO planes (a_{12}) and that separating the second and third planes (a_{23}) is relevant.

5.5.2. KINETICS OF THE OXYGEN UPTAKE ON Ni(001) AND THE ONSET OF NiO FORMATION-

In order to systematically monitor the dependence of the oxygen coverage on exposure, the O 1s and Ni 2p_{3/2}(metal) XPS intensities were measured at various sequential
oxygen exposures up to 1300 L for a substrate temperature of ~300 K. These intensities were observed along $\theta = 45^\circ$ and $\phi = 13^\circ$, a direction chosen such that it represented an average over the Ni 2p$_{3/2}$ diffraction structure in order to minimize the influence of diffraction effects on the final oxygen coverages. The importance of this kind of correction has been discussed for c(2×2)S on Ni(001) by Connelly et al. [26(c)]. The intensity ratios were in this figure converted to monolayers coverage using the more approximate Equation (5-1), which assumes that the oxide layer is completely non-attenuating, and thus leads to too-low oxide coverages that are simply proportional to the O 1s/Ni 2p$_{3/2}$ intensity ratios. The results of these measurements and the concomitant LEED patterns are illustrated in Figure 5.3(a), with a blowup of the critical 10 L–120 L region also presented in Figure 5.3(b). Also included in the figures are the recent temperature-dependent O/Ni Auger ratio measurements for this system by Wang et al. [14] at 300 K (shown as the short dashed curve), 350 K (dashed curve), and 400 K (long dashed curve), all of which have been normalized to have the same magnitude as the XPS curve at an exposure of 30 L which corresponds to the minimum-slope reference point in our c(2×2) "plateau". All four curves display the characteristic two-step uptake curve that is in excellent agreement with the pioneering Auger results of Holloway and Hudson [3].

The length and relative flatness of our coverage curve near 30 L is in best agreement with the Auger results at 350–400 K, and suggest that, during XPS analysis, our specimen may have been heated somewhat above ambient temperature. However, the fact that our curve seems to reach saturation considerably more slowly than the other three also suggests that our surface could have had less surface defects and thus inherently lower reactivity. The dashed Auger ratio curve for 350 K further shows a final saturated oxide value that agrees very well with the results of our kinetics curve, indicating a degree of self-consistency between the XPS and Auger data.
The results of our LEED observations have been described in earlier figures in Reference 13. A very faint c(2×2) pattern was observed at a coverage of 10 L. This replaced a weak p(2×2) pattern that was present at 1 L. This c(2×2) pattern slowly increased in intensity and displayed its strongest and sharpest diffraction spots over the relatively flat c(2×2) plateau region from 30 L to 70 L, after which it slowly turned into rather large and hazy spots before disappearing altogether after a total exposure of 300 L. It is important to note that the final disappearance of the c(2×2) structure occurred well after the first appearance of the NiO LEED patterns at 150 L. The oxygen coverage showed a very rapid increase in the region of 100–300 L that is due to the rapid growth around existing oxide nuclei. At approximately 150 L or 0.85 ML coverage, the individual domains of NiO become sufficiently large to be observable with LEED. Two types of LEED patterns associated with this oxide are seen, a stronger p(1×1) of NiO(001) and a weaker 12-spot ring; the latter is thought to be characteristic of two orientations of NiO(111) rotated 30° apart. At our ambient-temperature exposure conditions, these two LEED patterns slowly increased in intensity with increasing oxygen exposure all the way up to saturation. As mentioned earlier, the last traces of all c(2×2) structure were finally removed at 300 L, but it was not until 800–1200 L that the oxygen uptake nearly ceased, indicating that the oxide had finally saturated the surface.

A careful inspection of the LEED pattern at 1200 L revealed the previously discussed splitting of the large and rather hazy NiO(001) spots into a centered square arrangement [13]. From the position of the NiO(001) spots and their rather diffuse nature, it was suggested by Saiki et al. that this is the result of the NiO(001) overlayer having a lattice constant parallel to the surface that is expanded by 1/6 relative to the underlying Ni(001) substrate. This oxide would thus be under considerable strain due to largely incommensurate growth on the underlying Ni(001) mesh. The superposition of (6×6)
NiO(001) unit cells on (7×7) Ni(001) unit cells creates a single NiO(001)/Ni(001) superlattice unit cell, which is believed to be the origin of the centered spot splitting that was reported earlier. Wang et al. [14] have also subsequently studied the LEED spot profiles and integrated intensities for this system as a function of temperature.

As noted earlier, the presence of small islands of NiO that apparently coexist with the majority c(2×2) species is thought to be the reason that a very early XPD study by our group reported that the oxygen position in the c(2×2) structure is a fourfold hollow site and very close to the in-plane position [1, 5]. (In fact, the exposure used to study c(2×2) in this prior work was 100 L, and the associated oxygen coverage was ~1.0 ML. In the present study, we have both used what appears to be a higher quality and less reactive surface, and chosen significantly lower exposures to minimize such oxide effects.) For such a structure, the diffraction data would be strongly affected by the forward-scattering effects from even a small amount of oxide present in the near-surface region, especially if the data were taken at grazing emission directions, as illustrated in Figure 5.4(b). Azimuthal data taken at sufficiently large takeoff angles should, at least in principle, be able to detect the presence of buried oxide islands provided that these islands are at least 2-ML thick and that they display some kind of epitaxial-like growth. Two such emission directions are shown by the arrows in Figure 5.5(a) for 2-ML of NiO(OOl) grown on the Ni(OOl) surface, and they correspond to oxygen forward scattering, which is expected along the [101] emission direction at $\theta = 45^\circ$ and $\phi = 0^\circ$, and also to nickel forward scattering along the [111] direction at $\theta = 35^\circ$ and $\phi = 45^\circ$.

In order to search for oxide nuclei effects, a series of O 1s azimuthal scans was taken at various oxygen exposures from 30 L up to the saturated oxide at 1200 L. The curves shown in Figure 5.6 were taken at $\theta = 36^\circ$, which is very close to passing through the $<1\overline{1}1>$ directions, while those in Figure 5.7 were taken at $\theta = 46^\circ$, close to the $<101>$
directions. Here, the experimental data are shown as the solid curves and they were compared with the results of different SSC calculations, which appear as dashed curves. The experimental data at 30 L represents the diffraction pattern for the best c(2×2) overlayer (Θ = 0.4 ML), 70 L should include some oxide nucleation (Θ = 0.5 ML), 150 L is the point where LEED first detects the presence of NiO (Θ = 0.8 ML), and of course, 1200 L represents the saturated oxide. Theoretical calculations were done for a c(2×2) overlayer with the oxygen sitting in the fourfold hollow sites at the generally agreed upon height of ℓ = 0.75 Å and for a saturated oxide made up of 2-ML of NiO(001), but with various cluster sizes to mimic the effect of small domains and/or strain. These oxide clusters include a minimal five-atom cluster having only short range order [dark-circled atoms in Figure 5.5(b)], an intermediate-sized 35-atom cluster covering about two unit cells [Figure 5.5(b)] whose a12-spacing has been expanded by 0.2 Å in an attempt to approximate the expected effect of relaxation in the vertical direction in response to the ~1.4% compression in both lateral directions, and by a much larger, fully converged cluster of ~20 Å in radius, containing approximately 200 atoms. Also shown is the calculated result for a fully converged 2-ML thick NiO(111) cluster, including a summation over two equally populated domains rotated by 30° with respect to one another. The theoretical curves make it clear that XPD is primarily sensitive to short range order, as calculations for both the minimal five-atom cluster and the intermediate 35-atom cluster contain all of the major diffraction features present in the much larger and fully converged 20 Å cluster.

The experimental diffraction pattern of the saturated oxide in Figure 5.6 clearly shows the effect of strong O-to-Ni forward scattering at φ = 45°, and the shape of the curve remains essentially unchanged until ~70 L where approximately 0.5 ML of oxygen is present. The experimental anisotropy has dropped from a high of 28%, down to only approximately 7% over this exposure range, and there is a corresponding increase in the
statistical uncertainty due to a reduction in the O 1s integrated intensity as the exposure is reduced. A similar effect is observed for the primary diffraction features in Figure 5.7 at $\theta = 46^\circ$. The primary peaks are centered at $\phi = 0^\circ$ and $90^\circ$ and are due to the slightly less intense O-to-O forward scattering. Qualitatively, the observed oxide diffraction patterns are not at all consistent with those expected from NiO in the (111)-orientation; by contrast, they are in rather close agreement with the predicted patterns for NiO in the (001)-orientation, especially for the minimal five-atom cluster and for the intermediate 35-atom cluster with the 0.2 Å vertical expansion.

Turning now to the c(2×2) overlayer at 30 L, we see that a comparison of the experimental data at 30 L with fourfold c(2×2) theory at $z = 0.75$ Å agrees reasonably well with the positions of some of the major diffraction peaks, even though such features are very weak, with experimental anisotropies in the 5–9% range and theoretical anisotropies of 20–4%, respectively. However, certain features in the experimentally-derived curves at 30 L appear to represent forward scattering effects due to a small amount of oxide or buried oxygen in the subsurface region. This conclusion is based on a filling-in of the central valley with a weak peak at $\phi = 45^\circ$ in Figure 5.6, and the much clearer oxide-like forward scattering peaks at $\phi = 0^\circ, 90^\circ$ seen in Figure 5.7. These forward scattering peaks in Figure 5.7 are quite intense and they persist down to 30 L, with a significant anisotropy of 8.6%, where they greatly exceed the anisotropy predicted for the c(2×2)O structure. These peaks thus clearly indicate the presence of buried oxygen emitters, probably in the form of small nuclei of NiO(001) mixed in with the c(2×2) overlayer. An R-factor analysis of the experimental data at 30 L and $\theta = 46^\circ$ (Figure 5.7) with theoretical curves generated by a simple mixing of the c(2×2) structure with various percentages of 2-ML of NiO(001) resulted in the conclusion that about 10–15% of the oxygen atoms are present in such buried sites. These results are consistent with a recent STM study of this system by
Wilhelm et al., who see evidence for oxide island formation at as low as 10 L O$_2$ exposure [16].

Such high-takeoff-angle XPD data is thus seen to be extremely sensitive to minority species that are somehow in subsurface sites, a generally useful characteristic for future studies of oxidation and epitaxy.

5.5.3. STRUCTURE OF NiO(001) ON Ni(001)-

In discussing our data for the saturated oxide, we will first consider O 1s polar scans, and then O 1s azimuthal scans. Figures 5.8(a) and 5.8(b) present O 1s polar scans for both the unannealed and annealed oxide at 1200 L exposure (solid curves), as taken along the <101>- and <111>- azimuths respectively. The accuracy of the shapes and positions of these curves was confirmed by comparing scans obtained along the four symmetry-equivalent azimuths 90° apart. These experimental data are also compared in these figures to several SS calculations (dashed curves) derived from a variety of clusters. The primary diffraction feature observed along the <101> azimuth for the unannealed surface is a strong peak centered at $\theta = 47.8^\circ$ which shifts to a lower angle of $\theta = 46.6^\circ$ on annealing. There are two other minor features, a weak peak at $\theta = 39^\circ$ for the unannealed case which appears as a shoulder in the annealed curve, and a weak shoulder at $\theta = 54^\circ$ that is more evident in the unannealed case. Along the <111> azimuth, the unannealed curve shows a single broad peak centered near $\theta = 37^\circ$–38°, which on annealing sharpens slightly to form the primary peak centered near $\theta = 39^\circ$; in addition, the annealed data shows weak additional features at $\theta = 28^\circ$ and $\theta = 49^\circ$.

While simple forward scattering arguments can be used to determine the approximate positions of all of the major diffraction features, the actual peak positions are
pushed upward by several degrees from the ideal <101>- and <1\bar{1}1>-emission directions at \( \theta = 45^\circ \) and \( \theta = 35.3^\circ \) respectively. These shifts are furthermore opposite in direction from those expected due to electron refraction by the substrate inner potential (\( V_0 \)). In this study, a value of 13.2 eV was used as the inner potential for the oxide surface in the SSC calculations [34], and this results in a downward shift of the external electron trajectories by about 0.5° at the polar angles examined. Thus, the observed upward shifts appear to be due to real structural effects.

Assuming for the moment that the oxide overlayer contains at least 2-ML of NiO(001) (we will later with our azimuthal data confirm that NiO(111) is a minority species under our conditions of exposure), the forward scattering peak along the <101>-direction would correspond to O-Ni scattering while the peak in the <1\bar{1}1>-direction would be due to O-O scattering, as indicated in Figure 5.5. It should then in principle be possible to determine whether there is any relative vertical relaxation of the O and Ni surface atoms within the surface plane from the corresponding shifts in the position of the forward scattering peak from the ideal polar angles of 45.0° and 35.3°. As described in a prior XPD/LEED paper on this system by Saiki et al. [13], the two-dimensional lattice constant in the surface plane was deduced from LEED measurements and it was concluded that the oxide was expanded by \( \frac{1}{6} \) or 16.7% over \( a_{Ni} = 3.52 \text{ Å} \), and that this expansion to \( a_{NiO} = 4.11 \text{ Å} \) remained essentially unchanged on annealing the oxidized surface. Since the lattice constant of bulk NiO is 1.184 times that of Ni, or 4.17 Å, there is a residual lateral compression of 1.4% in this model. The 1.2° shift of the primary diffraction peak along the <101>-direction to higher polar angle between the unannealed and annealed data thus could be due to a simple expansion of the unannealed oxide lattice in the vertical direction so as to reduce the strain imposed by being compressed laterally by the underlying Ni(001) mesh. Such a shift in the \( \theta \)-angle of 1° to 3° corresponds to a vertical expansion of between 0.1 Å
to 0.3 Å, a reasonable amount if the NiO(001) unit cell is actually trying to conserve its volume when compared to bulk NiO. In fact, in conserving volume relative to bulk NiO, the required expansion leads to a vertical unit cell height of 4.30 Å = a_{12} + a_{23}, or a 0.2 Å overall vertical expansion relative to the lateral a_{NiO}. In the unannealed data, a similar shift along the <1\bar{1}1>-direction was not so clearly observed; however, the rather broad peak featured in this data could easily hide such a shift. The annealed data for <1\bar{1}1> shows as much as a 4° shift. These results could imply that only the oxygen in the surface plane of the unannealed oxide has been displaced upward by ~0.2 Å, as suggested previously [13], but in the present analysis, we have expanded our search to include various increases in the a_{12} spacing (thus moving both O and Ni atoms upward equally), as discussed further below. Taking the <10\bar{1}> or <1\bar{1}1> data together, Figure 5.8 shows that the best fit for the polar unannealed data is finally found for an intermediate-sized 35-atom cluster where just the oxygen atoms are moved upward by 0.2 Å.

An attempt to model the annealed oxide was done using much larger and fully converged clusters of 20 Å in radius and with 2-, 3-, and 4-ML thicknesses. While the a_{1//} spacing was fixed at the value of a_{NiO} = 4.11 Å derived from our LEED results, the a_{12}-spacings in the perpendicular direction were allowed to vary. Two interesting observations were made. First, for those clusters having no vertical expansions and designated as being "cubic", the centers of the diffraction peaks along the <10\bar{1}>-direction were shifted downward by 0.5° to θ = 44.5°, as expected from simple electron refraction due to the surface inner potential. In order to explain the significant observed shift in the opposite direction, something more is clearly needed. As shown in Figure 5.8(a) for the 2-ML, 20 Å cluster that had a_{12} increased by 0.2 Å, this expansion is sufficient to shift the emission direction to the higher polar angles required. The second observation is that, along the
<111>-direction, the most intense diffraction feature in both experiment and theory occurs at $\theta = 39°-40°$ and is thus not simply relatable to the O-Ni forward scattering direction at $\theta = 35.3°$. Probably this peak has contributions from higher order interferences whose position is sensitive to both the expansion in the vertical direction and to the thickness of the oxide film. The best fit for the annealed data in this azimuth is found to be for a 2- or 3-ML cluster having either little or no expansion of the vertical interplanar spacing, but the evidently more complex nature of the interference effects involved with this direction make this conclusion less reliable.

A rigorous analysis of the polar data using R-factors was not possible due to the presence of a non-linear background that is caused by a difficult-to-measure instrumental response function for a multilayer thin film [19, 24]. This response function is expected to behave roughly as $\sin \theta$. Data obtained by fixing the polar angle and scanning over azimuthal angles do not exhibit such response function effects, and we consider these now.

Low angular resolution O 1s azimuthal data were taken for the unannealed oxide over the range of $\theta = 43°$ to $47°$ in 1° steps, although only the results at $\theta = 43°$, 45°, and 47° are shown in Figure 5.9. The experimental data (shown as the solid curves) were taken over the full 360° azimuthal range and fourfold averaged to improve the statistical reliability before being plotted over one quadrant from $\phi = 0°$ to $90°$. The primary diffraction features are the peaks centered at $\phi = 0°$ and $90°$; these correspond to the strong forward scattering that is expected along <101> emission directions (see, for example, Figure 5.5). These strong diffraction peaks also exhibit shoulders located approximately 14° to either side of their centers; these shoulders gradually decreases in significance as the polar angle is increased from $\theta = 43°$ to $\theta = 47°$. There is also a very strong diffraction feature centered at $\phi = 45°$ and it too, decreases in relative intensity as the polar angle is increased. As discussed in the prior XPD analysis of this system [13], this peak appears as a doublet in
the annealed oxide data (as will be discussed further below), but appears as a singlet in the unannealed data, providing a clear indication of the structural differences between the unannealed and annealed forms of the oxide. One contribution to the peak at $\phi = 45^\circ$ is first-order interference [19] associated with forward scattering along $<101>$ directions, although other forward scattering processes along higher-order directions also may contribute, as first pointed out for XPD from epitaxial Cu(001) films by Bullock and Fadley [37]. The anisotropy varies between 20–22% over the entire unannealed data set from $\theta = 43^\circ$ to $47^\circ$; this is quite low when compared to the annealed data to be discussed later, which yield 35–53%. These anisotropy results suggest less long-range order and/or smaller domain sizes of the individual NiO islands in the unannealed case.

These observations prompted our use of smaller clusters to simulate the loss of long-range order for the unannealed data. In Figure 5.9, we compare experiment to calculation for several different clusters: a 35-atom cluster such as that shown in Figure 5.5(b) in which $a_L$ and $a_H$ are equal ("no expansion" or "cubic"), the same cluster with the top-layer O atoms moved up by 0.2 Å, and the same cluster with $a_{12}$ increased by 0.2 Å (so that both O and Ni atoms are moved up). Also shown are theory curves for the minimal five-atom cluster in Figure 5.5(b). A visual comparison of experiment and theory readily indicates that the larger cluster with oxygen, and perhaps also nickel, displaced upward by ~0.2 Å best describes the data, although the agreement is not as good for $\theta = 47^\circ$ as for the two lower angles.

Continuing with the analysis of the unannealed data, we note that the intermediate-size 35-atom cluster covers an area of approximately 5 Å in radius or approximately two unit cells of NiO and yields results that are very similar in appearance to those of much larger 20 Å clusters that were used in a prior analysis of annealed XPD azimuthal data [13]. In order to better quantitate our analysis of this data, we have carried out an R-factor
analysis as summed over all of the azimuthal data using Equations (5-4) and (5-5), and these results for various $a_{12}$-expansions are summarized in Figure 5.10. The filled circles and solid curve represent 2-ML thick, 35-atom clusters whose $a_{12}$-distance has been expanded in 0.1 Å steps from the reference value of the $a_{||}$-spacing that is fixed at 4.11 Å. The best fit is found for an expansion of $a_{12}$ between 0.1 Å and 0.2 Å, and it is better than what is obtained by simply moving the oxygen atoms in the surface plane upward by 0.2 Å (upward pointing triangle), or by going to the minimum five-atom cluster (downward pointing triangle), with the latter two structures displaying about equally good fits. This expanded structure is consistent with the results of the earlier polar analysis that suggested a small expansion of the $a_{12}$-spacing is needed to match the tilt to higher polar angles of the principle forward scattering features.

Comparing experiment with theory at the optimal $a_{12}$-expansion of 0.2 Å in Figure 5.9, shows excellent agreement at the lower end of the $\theta$-range. At $\theta = 43^\circ$, the positions of all of the features are well very reproduced, with the only minor discrepancy being the relative peak height of the forward scattered peak at $\phi = 0^\circ$ and 90°. At $\theta = 45^\circ$, the primary discrepancy is that theory predicts too broad a feature at $\phi = 45^\circ$, a problem which becomes worse on going up to $\theta = 47^\circ$. The forward scattering peaks and their shoulders are a little too well-resolved compared to the experiment and this may indicate that a smaller cluster (i.e., less long-range order) would be useful and/or that a greater amount of surface disorder and strain may be present than is possible to take into account in the calculations.

To conclude this discussion of the unannealed oxide data, we find evidence in both polar and azimuthal data for vertical displacements in the top layer by approximately 0.2 Å, although the closeness of the R-factors for the several structures explored does not permit ruling out some mixture of structures with O, as well as Ni, shifted upward, and with less long-range order than our 35-atom cluster possesses. In fact, the (6×6) NiO/(7×7) Ni
superlattice that has been proposed previously [13] would be expected to lead to regions of more order/less strain and less order/higher strain over the superlattice unit cell. Thus, the XPD measurements will certainly be averaging over a number of local environments, and the best we can hope to do from this kind of analysis is to estimate the average or most typical type of structure.

We now consider analogous azimuthal data for the annealed oxide over the $\theta = 43^\circ$-$47^\circ$ range, but with the important difference that the angular resolution is now significantly better at $\pm 1.5^\circ$. These experimental data also were taken in $\theta$ steps of $1^\circ$, with the entire set being shown in Figure 5.11. The anisotropies of the experimental curves vary from a low of 36% up to a very high value of 53%, and there is much more fine structure than in the unannealed data of Figure 5.9. These curves posses a remarkable sensitivity to small changes in $\theta$ that has also been seen in the high-resolution work by Osterwalder et al. [38] on Ni 2p$_{3/2}$ substrate emission from clean Ni(001).

Figure 5.11 shows that the primary diffraction features common to this set of curves are the strong forward scattering peaks that appear along the $\langle 101 \rangle$-equivalent directions at $\phi = 0^\circ$ and $90^\circ$ (as seen also in Figure 5.9). The central region at $\phi = 45^\circ$ exhibits a wide, mesa-like peak at $\theta = 43^\circ$. This peak splits into a doublet as the emission angle is raised above $\theta = 44^\circ$, and this doublet is best resolved at $\theta = 45^\circ$. Other experimental diffraction features include a somewhat weaker peak that is strongest for $\theta = 43^\circ$ and centered at $\phi = 10^\circ$-$22^\circ$; this peak continuously decreases in height as the polar angle is increased, essentially disappearing at $\theta = 47^\circ$. Finally, a small shoulder is observed at $\theta = 43^\circ$ and $\phi = 23^\circ$, and this gradually increases in size until it is a well-defined although rather weak peak at $\theta = 47^\circ$. It is thus clear from Figure 5.11 that the richness of the diffraction fine structure can be used to clearly differentiate curves separated by only $1^\circ$ in polar angle!
These high-angular-resolution annealed azimuthal data were also analyzed by comparing them to theory with the summed R-factor ($R_1$) discussed earlier. SSC calculations for a cluster of 20 Å in radius containing approximately 120 atoms per layer were done to determine the best structural fit, and such large clusters were found to be necessary to predict all the diffraction features present. Based on a preliminary XPD analysis of this system [13] which showed that the best visual fit for the annealed oxide was with 2-ML of NiO(001), a number of calculations were done to both check this and to see whether clusters having an expanded $a_L$ lattice constant might better describe the data. In Figure 5.12, several theory curves are compared to experiment for $\theta = 43^\circ$, 45°, and 47°, and in Figure 5.13, the summed $R_1$ results for a variety of structures are shown. The curves for 2-, 3-, and 4-ML of cubic oxide (no vertical expansion) all predict the locations and relative intensities of the experimental diffraction features very well, with the summed $R_1$ results in Figure 5.13 (shown as the open circles connected by the line) yielding a better fit for 3-ML of oxide. The prior XPD analysis [13] only looked at the azimuthal results at $\theta = 35^\circ$ and 45°, with both polar angles including emission directly along low index directions, and so was not as sensitive as the present data set to minor differences with thickness.

The structural parameters for the annealed oxide were also further adjusted by allowing various expansions in both the $a_{L2}$- and $a_{23}$-spacings. An expansion of the 2-ML NiO(001) model so as to increase $a_{L2}$ by 0.1 Å (shown in Figure 5.13 as the solid circle) results in a significantly higher R-factor, and other larger expansions are off scale and give rise to noticeably poorer fits. After a number of trials, we determined that the best summed $R_1$ fit was for a cluster having an unequal $a_L$-expansion; that is, the $a_{L2}$ distance was found to be increased by 0.1 Å, with no expansion in the $a_{23}$ separation over the reference cubic structure where $a_L = a_{LL} = 4.11$ Å (point denoted by a filled diamond). For this structure, the comparison between experiment and theory shown in Figure 5.12 is excellent.
throughout the lower θ-range, with some minor discrepancies in the mid-φ range arising by
the maximum θ = 47°.

For the annealed oxide data, the polar and azimuthal results are again consistent,
both indicating 2–3 ML of highly ordered oxide with domains at least 20 Å in radius and an
a_{12} expansion by about 0.1–0.2 Å. Beyond this, we note that our XPS intensity analysis of
the unannealed oxide indicates a total of 4–5 ML of oxide, whereas the XPD results are best
fit for 2–3 ML. Thus, if we assume the total thickness of the annealed oxide to be at least
4–5 ML thick also, the bottom 1–2 layers of it may be much more strained, with stacking
faults and defects that could wash out diffraction features.

We turn now to low-θ (grazing-emission) azimuthal data for the unannealed oxide
to see what further they can tell us about the structures involved. The contrast between the
diffraction patterns of c(2×2)O and of the unannealed oxide are readily apparent in a series
of O 1s azimuthal scans taken at θ = 8°, 11°, 14°, and 17°, as shown by the solid curves in
Figures 5.14 and 5.15. These experimental data were taken for the onset of the sharpest
c(2×2) LEED spots (30 L) and for the fully saturated oxide (1200 L). The anisotropies
remained fairly constant over this angle range, varying between 19% and 22% for c(2×2)
and between 17% and 21% for the unannealed oxide. The experimental oxide curves were
compared to single-scattering cluster calculations for two layers of NiO(O01) having an
intermediate-sized cluster of 35-atoms with an expansion of a_{12} + 0.2 Å and for a cubic
cluster about 10 Å in radius, with the former being the structure determined from the
analysis of the data at higher θ values. The data for the c(2×2) structure at 30 L is
compared with calculations for a c(2×2) overlayer occupying the fourfold hollow site at a z-
value of 0.75 Å. (This will be seen below as our final structure from this study, in excellent
agreement with other recent experimental and theoretical work [15]).
The experiment/theory comparison for the oxide in Figure 5.14 at \( \theta = 8^\circ \) and \( 11^\circ \) is very good to excellent, with all of the peak positions and most of the relative intensities very well described for either cluster. In Figure 5.15 at \( \theta = 14^\circ \), theory predicts too small a peak along \( \phi = 0^\circ \) and \( 90^\circ \) and also incorrectly predicts the central peak at \( \phi = 45^\circ \) to be a doublet. At \( \theta = 17^\circ \), theory once again describes the experiment very well, especially the doublet centered at \( \phi = 45^\circ \), but while the 35-atom cluster fails to predict a major peak centered at \( \phi = 0^\circ \) and \( 90^\circ \), this feature is very well described using the slightly larger 10 Å cluster. The difference could be due to a larger effective scattering region for the photoelectrons along the surface due to the lower takeoff angles involved here. Thus, these data may be sensitive to scatterers further out along the chains of O and Ni scatterers than expected. As one reason for the observed inadequacy of the 35-atom cluster of Figure 5.5(b) in describing such low-\( \theta \) emission, it possesses only a single forward scattering atom along the \( \phi = 0^\circ \) and \( 90^\circ \), which is insufficient to provide the additional intensity to form the required diffraction peak along this direction for the experimental data at \( \theta = 14^\circ \) and \( 17^\circ \).

We have also analyzed these low-\( \theta \) unannealed oxide data via R-factors for different structures (see Figure 5.16) and we find that SSC calculations using the larger 2-ML, 20 Å-radius clusters yield summed R$_1$'s (shown as the open diamonds) that are lower than those from the 35-atom cluster (open squares). This analysis clearly rules out the minimal five-atom cluster (downward pointing triangle) and it also leads to the conclusion that a modest increase in the cluster size to 10 Å (shaded circles) gives a somewhat better fit for all vertical expansion values. The optimal structure is a 2-ML,10 Å cluster, with no expansion in the \( a_{12} \)-spacing. This lack of an \( a_{12} \) increase for these grazing-emission data is thus at first sight in disagreement with the analysis of the polar- and azimuthal-data for higher takeoff angles considered previously. This difference between the low- and high-angle data is not however very large, and it may be due to an effectively longer range along the surface that is
seem for grazing emission. High takeoff angles should be more sensitive to the local environment around an oxygen emitter, and we thus believe that these data overall provide evidence for an expansion in $a_{1/2}$, even if this is not evident in Figure 5.16.

It is also worth noting in concluding our discussion of the annealed oxide that our annealing temperature of approximately 523 K is, according to a recent XPS study by Hall et al. [30] probably not high enough to produce significant oxide layer thickening that can, for temperatures of 100 K or more above this, lead to oxide islands of as much as 50 Å in thickness.

5.5.4. STRUCTURE OF c(2×2)O ON Ni(001)-

A series of four O 1s azimuthal scans were performed at 30 L oxygen exposure and for the polar angles of 8°, 11°, 14° and 17°, as shown already in Figures 5.14 and 5.15. As mentioned earlier, even at this low oxygen exposure, we estimate that between 10 and 15% of the O atoms are in the form of small oxide islands. We expect such oxide/subsurface species to be more important for higher $\Theta$ values due to the enhanced electron emission from deeper layers and/or the influence of subsurface oxygen that is responsible for certain forward scattering peaks. We have thus tried to estimate the relative contributions of c(2×2)O and oxide nuclei of 2-ML and 3-ML thickness, as normalized to unit surface area. If we neglect the effect of diffraction on the XPS intensities, the intensity ratios (O 1s, c(2×2)O)/(O 1s, 2-ML NiO) per unit area are 1.1 at $\theta = 8^\circ$, 1.4 at $11^\circ$, 1.6 at $14^\circ$, and 1.8 at $17^\circ$. The corresponding numbers for 3-ML of NiO are 1.2, 1.6, 1.9, and 2.2, respectively. Therefore, in order to minimize the effect of this oxide interference, we have carried out our c(2×2) structural analysis only for the lowest two grazing angles of $\theta = 8^\circ$ and $11^\circ$. The R-factor analysis of these low-$\Theta$ azimuthal data was done for a wide range of $z$-distances, but
only the region between 0.60 Å and 0.90 Å is shown in Figure 5.17(a). These SSC calculations used a large clusters of 20 Å in radius to insure full convergence of all the diffraction features, and they were done for the oxygen residing in both the fourfold hollow sites (shown as the solid curve) and in various pseudobridge sites having offsets of 0.1 Å (long dash curve), 0.3 Å (short dash curve) and 0.5 Å (dot-dash curve). The R1 result for the pseudobridge structure reported by Demuth et al. [10], is indicated by the filled circle.

In Figure 5.17(b), we also address the question of whether the five R-factors considered previously yield similar structural conclusions. For adsorption in the fourfold-hollow site, we here show curves for summed R1, R2, R3, R4, and R5 as a function of z. It is most encouraging that all of R1, R2, R4, and R5 yield the same z value to within about ±0.02 Å. R3, which is less analytical in being just a percentage of the interval over which the slopes disagree, shows less regular behavior, and the largest shift in position from the R1 reference, although even here, the difference in optimum z is only 0.04 Å. We have made similar checks for other cases, and have concluded that the use of R1 only is sufficiently accurate.

Overall, the best fit to the XPD data is thus found to be for the fourfold hollow site at z = 0.75 Å ± 0.05 Å, which is slightly better than for the best pseudobridge site at z = 0.74 Å and a very small offset of 0.1 Å, and is considerably better than the previously proposed pseudobridge structure with its uncertainty. Note that the pseudobridge site requires four separate domains, each offset along the <110>-equivalent directions, so the average emitter position is in this sense not much different from that for emission from the fourfold hollow site. Curves derived for our optimum fourfold site are compared to experiment in Figures 5.14 and 5.15. Agreement is excellent for the two lowest θ values, but not as good for θ = 14° and θ = 17°, probably due to interference from oxide or buried oxygen. Our final z value, while somewhat lower than some of those previously reported
is in excellent agreement with the most recent multilayer LEED and theoretical calculations [15] of this system. We summarize some of the prior structural parameters derived for this system in Table 5.1; included here are results from low energy electron diffraction (LEED) [15], total energy calculations [15], angle-resolved photoemission fine structure (ARPEFS) [6], surface extended x-ray adsorption fine structure (SEXAFS) [12], and ion scattering spectroscopy (ISS)[11].

Figure 5.18 compares experiment (solid curve) with theory for the optimum fourfold hollow geometry (long dash curve) and the pseudobridge site of Demuth et al. (short dash curve) [10]. The visual agreement is excellent for either structure at $\theta = 8^\circ$, with all of the major diffraction features and relative intensities being very well described, but the fourfold hollow is definitely better at $\theta = 11^\circ$. At $\theta = 8^\circ$, the fourfold hollow curve seems to better describe the depth of the valley at $\phi = 45^\circ$ and the relative intensity of the doublet centered there, but does a poorer job at determining the relative height of the weak doublet centered at $\phi = 0^\circ$ and $90^\circ$. This relatively minor misfit at this polar angle gives the pseudobridge site a marginally better R1 value (0.024 versus 0.030). At $\theta = 11^\circ$, the fourfold hollow site does a significantly better job in predicting the relative intensities of the doublet centered between $\phi = 15^\circ$ and $30^\circ$ and its mirror equivalent between $\phi = 60^\circ$ and $75^\circ$. In particular, the peaks at $\phi = 28^\circ$ and $62^\circ$ are much better predicted and this is reflected in the much lower R1 value for fourfold (0.011 versus 0.024 for the pseudobridge site).

As a final general aspect of using such low-$\theta$ data to determine the surface structures, we note a potentially confusing type of behavior that has been observed in the R-factors of individual azimuthal scans as the structural parameter $z$ is systematically varied. The tendency is to have a minimum R-factor near the optimum $z$-distance and then to have periodic local minima at somewhat higher $z$'s, as illustrated in Figures 5.19(a) and 5.19(c).
for fourfold comparisons to experiment at $\theta = 8^\circ$ and $11^\circ$, respectively. The most likely explanation for this quasi-periodicity is pathlength-related variations of the phase between the direct photoelectron wave and its components scattered off the dominant nearest-neighbor Ni scatterers. A schematic of a general scattering geometry is shown in Figure 5.19(a). These phase changes of the scattered wave are due to both changes in the geometric path length difference and the scattering phase shift, with the equation describing the locations of successive orders $n$ of constructive interference being:

$$n\lambda_e = r_j(1 - \cos \theta_j) + \frac{\lambda_e}{2\pi}[\psi_j(\theta_j)]$$  

(5-6)

where $r_j$ = the distance to the $j^{th}$ scatterer = $\sqrt{z^2 + d^2}$, $\theta_j$ = the associated scattering angle = $\theta + \gamma = \theta + \tan^{-1}(r/d)$, $\psi_j(\theta_j)$ = the scattering phase shift, and $\lambda_e$ = the electron De Broglie wavelength. Using $\psi_j(\theta_j)$ values from a plane-wave calculation, a nearest-neighbor Ni distance of $d = 1.762$ Å, $\lambda_e(954$ eV) = 0.40 Å, and an electron emission angle of $\theta = 8^\circ$, we find that $z = 0.65$ Å for $n = 1$. Other minima are calculated to be at $z = 1.20$ Å for $n = 2$ and at $z = 1.66$ Å for $n = 3$ before passing beyond the $z$-range of the available R-factor data. In the same way, $z$ values up to $n = 4$ have been calculated for $\theta = 11^\circ$. These values are indicated in both Figures 5.19(a) and 5.19(c) as vertical arrows, and they provide a good estimate of the rate at which the overall phase of the waves scattered from the nearest-neighbor Ni atoms changes by $2\pi$. The fact that the minima in R-factors calculated between experiment and a large-cluster calculation have essentially the same distances between them for both cases is strong evidence for our explanation of this periodicity.

To further test our hypothesis concerning the origin of these oscillations in R-factors, we have performed additional two-atom cluster calculations. In Figures 5.19(b) and 5.19(d), two-atom SS calculations involving only one oxygen emitter and one nearest-
neighbor nickel scatterer have been compared using the $R_1$ criterion. Based on the observation that the minimum in $R_1$ occurs in the experiment/theory for $z = 0.80$ Å at $\theta = 8^\circ$, and for $z = 0.70$ Å at $\theta = 11^\circ$, we have used these same two theory curves as references for comparison in the R-factor analysis; thus we have a two-atom theory-to-two-atom theory comparison resulting in an $R_1 = 0.00$ at these two $z$-distances. Any effects due to the scattering phase shift will thus automatically be included here. It is striking that we find in these two-atom calculations a series of local minima that exactly matches the periodicity observed in the analysis of the experimental data shown in Figures 5.19(a) and 5.19(c).

Summarizing this analysis, the primary contributor in producing these R-factor oscillations with $z$ is the nearest-neighbor Ni scatterer and we have been able predict the position of the local minima to within a few tenths of an angstrom using Equation (5-6). Although such oscillations are well known in LEED R-factor optimizations [39], this is the first time to our knowledge that they have been seen in XPD. Such oscillations are expected to be general effects in the analysis of such low-$\theta$ data from adsorbates, and considerable care should be exercised to be sure that a local minimum is not mistaken for the true minimum.

5.6. CONCLUDING REMARKS:

The interaction of oxygen with Ni(001) is quite complex and it fully deserves the extensive effort put forward to date in an attempt to identify the geometric structures of the various species that grow on this surface. In this study, XPD and LEED have been shown to be a powerful combination of techniques for monitoring the growth of these various surface species from submonolayer adsorption to the saturated oxide. All exposures were done at at ambient temperatures. From our data, we find that the c(2×2)O structure is
optimal at approximately 30 L and 0.38 ML coverage. LEED measurements indicate that this c(2×2)O pattern displays its sharpest and most intense spots for oxygen exposures between 30 and 70 L. At higher oxygen exposures, NiO island formation is first observed in LEED for a 150 L exposure and 0.85 ML coverage, with two orientations of the oxide being observed; these are the minority NiO(111) and the majority NiO(001). This oxide diffraction pattern is quite apparent well before the final disappearance of the c(2×2) spot pattern at 300 L. Saturation of the Ni(001) surface in this study was somewhat arbitrarily set at 1200 L, a point at which a significantly larger oxygen exposures did not appreciably increase the oxygen coverage. XPS intensities with proper allowance for inelastic attenuation in the overlayer yield a saturation cover of 4–5 ML of NiO that is larger than that derived in some prior studies; however, only 2–4 ML of this overlayer are found to be sufficiently ordered to lead to the well defined XPD patterns observed.

Using combined polar- and azimuthal-XPD data, we furthermore find clear evidence that oxygen burial and/or oxide nucleation occur well before the end of the c(2×2) "plateau". The presence of such subsurface oxygen is a likely factor in earlier reports of an in-plane phase for the c(2×2) structure that were done at higher coverages near 0.5 ML. Later studies done at coverages near 0.35–0.40 ML can also be affected by oxide nuclei if the technique is particularly sensitive to subsurface oxygen and no precautions have been undertaken to minimize the interference between the two types of oxygen.

The unannealed saturated oxide grown at ambient temperature forms a superlattice structure that is expanded in the parallel direction by very nearly 1/6 relative to Ni(001), as based on the dimensions of the LEED spot splitting that has been discussed in a prior paper by Saiki et al. [13]. A series of XPD data, some taken at a high angular resolution of ±1.5°, show a very strained unannealed NiO(001) overlayer of approximately 2–3 ML in thickness having a lattice parameter (a/2) in the vertical direction that is expanded by about 0.2 Å.
The size of the individual domains are rather small, averaging between 5 Å and 10 Å in radius. Annealing the surface very briefly to 523 K results in a noticeable increase in order in both the vertical and horizontal directions. Annealing is further found to increase the average thickness of the ordered oxide to between 2- and 4-ML, and the higher angular resolution data permits estimating relative vertical interplanar spacings. We find the $a_{23}$-spacing to have no expansion, while the two layers closest to the surface, as given by the $a_{12}$-spacing, have a slight expansion of 0.1 Å.

We have also determined the structure of the c(2×2) overlayer. Grazing emission angles were used to enhance surface sensitivity. Nonetheless, there will be some interference of the O signal from buried NiO due to the presence of in-plane chemisorption sites in oxide nuclei distributed over the more widely dispersed c(2×2) geometry. Comparing theoretical calculations of mixed c(2×2)O and vertically-expanded NiO with experiment yields an estimated 10–15% contribution of NiO to the c(2×2)O intensity at the optimal exposure of 30 L. By further restricting the azimuthal data analyzed to only the lowest two $\theta$ values of 8° and 11°, we further suppress this interference due to subsurface oxygen and we finally find the optimal geometry to be for oxygen residing in the fourfold hollow sites at a z-distance of 0.75 Å. The R-factor for this structure is lower than that for a previously proposed pseudobridge site.

More generally, the results presented here illustrate the utility of XPD, together with single scattering calculations and simple R-factor analysis, for determining structures present in an epitaxial-like overlayer that contains significant amounts of strain due to a misfit of the lattice parameters in the lateral directions. With the development of higher intensity x-ray sources such as those using synchrotron radiation, the routine use of higher-angular resolution studies should permit the study of even deeper lying structures, for example, for buried interfaces, clusters or islands on the surface.
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Table 5.1

Values of $z$ and $d_{12}$ from selected techniques. The multilayer LEED result changes to $z = 0.85$ Å if the $d_{12}$ spacing is fixed at the bulk value of 1.76 Å.

<table>
<thead>
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<th>Parameter</th>
<th>XPD&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Multilayer LEED</th>
<th>Total Energy</th>
<th>ARPEFS</th>
<th>SEXAFS</th>
<th>ISS</th>
</tr>
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<td>$z$</td>
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<td>0.75 ± 0.04 Å</td>
<td>0.84 ± 0.01 Å</td>
<td>0.90 ± 0.04 Å</td>
<td>0.88 ± 0.04 Å</td>
<td>0.86 ± 0.1 Å</td>
</tr>
<tr>
<td>$d_{12}$</td>
<td>1.86 ± 0.02 Å</td>
<td>1.76 Å (fixed)</td>
<td></td>
<td></td>
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<tr>
<td>Reference</td>
<td>[a]</td>
<td>[b]</td>
<td>[c]</td>
<td>[d]</td>
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</tbody>
</table>

[a] This work
[b] Reference 15
[c] Reference 6
[d] Reference 12
[e] Reference 11
Figure 5.1. A schematic of the principle surface structures that appear on Ni(001) under ambient-temperature oxygen exposures from approximately 30 L up the 1200 L. (a) Very rapid atomic O adsorption leading to a c(2×2) overlayer. The c(2×2) structure results in a temporary reduction of the oxygen uptake as all available dissociation/chemisorption sites are filled. (b) Formation of small oxide nuclei well before the ideal c(2×2) coverage of 0.50 ML is reached. At ambient temperatures, these islands are thought to be predominantly NiO in the [001] orientation and they have been estimated to be between 2- and 3-ML thick. (c) Continued lateral growth at the oxide perimeters on additional oxygen exposure in the range of 70 to 600 L and a corresponding reduction in the c(2×2) structure. (d) Saturation of the oxide overlayer is reached at ~1200 L and two, very distinct epitaxial orientations have been detected. The majority oxide is in the (001)-orientation, while a minority (111) species has also been observed. (e) Annealing briefly to 523 K for about five minutes results in a vertical thickening of the oxide islands and the appearance of oxygen-depleted regions indicated by the reappearance of the c(2×2) structure.
Figure 5.2. General geometry of our experiment, showing the directions of the polar ($\theta$) and azimuthal ($\phi$) specimen rotations. The angle $\alpha$ was fixed at 72° for the HP spectrometer and at 48° for the VG spectrometer. Al Kα radiation ($h\nu = 1486.6$ eV) was used in either case. The surface normal of the specimen is the [001] direction of nickel, and $\phi$ is measured with respect to [100].
Figure 5.3. (a) XPS oxygen coverage data (solid curve) as a function of oxygen exposure and associated LEED observations from the clean surface up to 1200 L. Also shown are the O/Ni Auger ratio data of Wang et al. (dashed curves) at substrate temperatures between 300 K and 400 K. The Auger curves have been normalized so that the result at 400 K crosses the XPS curve at 30 L. The XPS observation direction was chosen to represent an average Ni 2p3/2 intensity from the surface and thus to avoid the enhancement of photoemission intensity commonly found along low-index rows of atoms. The XPS coverages here do not allow for attenuation in the oxide overlayer, and thus represents lower bounds. (b) As in (a), but a close-up of the critical 0 L to 120 L region that spans the c(2x2) overlayer regime.
Two of the primary surface structures of interest here are: (a) the fourfold-hollow \( c(2\times2) \) structure occurring at submonolayer coverages of less than \( \sim 0.5 \) ML and (b) the saturated oxide in (001) orientation, which forms at coverages of 2-ML or more.

Grazing electron emission angles were used to obtain surface-sensitive diffraction information, while larger takeoff angles were used to probe the deeper subsurface structures, especially of the second and deeper lying oxygen emitters of the oxide.
Figure 5.5. (a) A schematic drawing of an ideal 2-ML of NiO(001) grown on Ni(001), with the oxide overlayer having a lattice constant parallel to the surface that is expanded by $\frac{1}{6}$ relative to the underlying Ni(001) substrate. The two bold arrows correspond to oxygen forward scattering along the [101] emission directions at a polar angle $\theta = 45^\circ$, and to nickel forward scattering along the [1\bar{1}1] directions at $\theta = 35.3^\circ$. (b) Two types of clusters used in our theoretical analysis: an intermediate-sized 35-atom cluster, 2-ML thick, that spans approximately two unit cells, and a minimal five-atom cluster (one emitter plus four scatterers) shown here as those atoms with the heavier outline.
Figure 5.6. Experimental O 1s azimuthal scans taken along $\theta = 36.3^\circ$ (very close to the $<\bar{1}11>$ direction at $35.3^\circ$), with a standard angular resolution of $\pm 3.0^\circ$ and for a series of oxygen exposures from c(2×2) at 30 L up to the saturated oxide at 1200 L. These curves are compared to SSC calculations for fourfold hollow c(2×2) oxygen at $z = 0.75$ Å and for saturated oxide made up of 2-ML of NiO(001) having various cluster sizes to explore the effect of domain size and strain on the diffraction patterns. Also shown is the calculated diffraction pattern for 2-ML of NiO(111) having long range order.
Figure 5.7. Same as Figure 5.6, but for $\theta = 46^\circ$, which is close to the \(<101\) direction at $\theta = 45^\circ$. 
Figure 5.8. (a) Experimental polar scans of the O 1s intensity along the <101> azimuth, obtained under high angular resolution of ±1.5° before and after a quick anneal of the saturated oxide to 523 K, are compared to theoretical diffraction calculations for a variety of clusters. The position of the forward scattering peak along the <101> direction is used to determine the interplanar separation of the oxide in the NiO(001) overlayer. (b) As (a) but along the <1\bar{1}1> azimuth.
Figure 5.9. Experimental fourfold-averaged O1s azimuthal scans of the unannealed saturated oxide at $\theta = 43^\circ$, $45^\circ$, and $47^\circ$ are compared to theoretical calculations for intermediate-size 35-atom clusters incorporating various structural distortions as described in the text, as well as for a minimal five-atom cluster.
Figure 5.10. Sums of $R_1$ R-factors comparing different theoretical calculations to the five azimuthal scans at $\theta = 43^\circ$, 44°, 45°, 46°, and 47° for the unannealed oxide data summarized in Figure 5.9.
Figure 5.11. High angular resolution O 1s azimuthal experimental data from an annealed oxide overlayer for five closely spaced polar angles near [101].
Figure 5.12. Similar to Figure 5.9, but after a quick anneal to 523 K and obtained with a high angular resolution of ±1.5°. Theoretical calculations are for fully converged clusters of 20 Å in radius that were found to be necessary in order to predict all of the diffraction features present.
Figure 5.13. Summed $R_1$ results similar to Figure 5.10, but this time for the high angular resolution annealed oxide azimuthal data of Figures 5.11 and 5.12.
Figure 5.14. Experimental azimuthal scans of the O 1s intensity for c(2×2) oxygen (30 L) and the unannealed saturated oxide (1200 L) at (a) $\theta = 8^\circ$ and (b) $\theta = 11^\circ$. These curves are compared to SSC calculations for the c(2×2) overlayer residing in the fourfold hollow at $z = 0.75$ Å and for the oxide to calculations for a 35-atom cluster having an $a_{12}$ expansion of +0.2 Å, as well as for a 2-ML NiO(001) cluster of 10 Å in radius.
Figure 5.15. As Figure 5.14, but for (a) $\theta = 14^\circ$ and (b) $\theta = 17^\circ$. 
Figure 5.16. Summed $R_1$ results for the unannealed oxide azimuthal data shown in Figures 5.14 and 5.15.
Figure 5.17. (a) Summed $R_1$ results comparing the c(2×2) azimuthal data taken at the grazing emission angles of $\theta = 8^\circ$ and $11^\circ$ to theoretical calculations comparing the fourfold hollow and the pseudobridge bonding site. (b) Comparison of all five summed R-factors for the fourfold hollow site. (See definitions of $R_1$, $R_2$, $R_3$, $R_4$, and $R_5$ in the text.)
Figure 5.18. Comparison of experimental and theoretical azimuthal curves for the c(2x2)O structure at θ = 8° and 11°. Theoretical curves are for the optimal geometry based on the R₁ analysis of the fourfold hollow (z = 0.75 Å) and for the pseudobridge site proposed by Demuth et al.
Figure 5.19. (a) and (c) Height-dependent R-factor analysis comparing experiment to the fully converged fourfold hollow theory at $\theta = 8^\circ$ and $11^\circ$, respectively. The downward pointing arrows indicate the expected positions of the different orders of constructive interference between the direct wave and a wave singly scattered from the nearest-neighbor Ni atom, as calculated from Equation (5-6). (b) and (d) Analogous R-factor comparisons of theory to theory in which only the nearest-neighbor Ni scatterer is present in a two-atom cluster. In (b), the two-atom curve at $z = 0.8$ Å is used as the reference, and in (d) the curve at $z = 0.7$ Å is used.
Figure 5.20. Geometry of the nearest-neighbor scattering interaction, illustrating the pathlength difference involved in producing the oscillations in Figure 5.19.