LBNL-38805
UC-401
Preprint

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Adsorption Site and Structure Determination of C(2×2) N_2/Ni(100) Using Angle-Resolved Photoemission Extended Fine Structure

E.J. Moler, S.A. Kellar, Z. Hussain, W.R.A. Huff, Y. Zheng, E.A. Hudson, Y. Chen, and D.A. Shirley
Accelerator and Fusion Research Division

May 1996
Submitted to
Chemical Physics Letters

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library.
LBNL-38805
Copy 1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBNL-38805
LSBL-324
UC-401

ADSORPTION SITE AND STRUCTURE DETERMINATION OF c(2X2) N_2/Ni(100) USING ANGLE-RESOLVED PHOTOEMISSION EXTENDED FINE STRUCTURE*

E.J. Moler, S. A. Kellar, Z. Hussain
Advanced Light Source, Lawrence Berkeley National Laboratory
University of California, Berkeley, CA 94720

W.R.A. Huff
Research Institute for Scientific Measurements, Tohoku University
Katahiria 2-1-1, Aoba-ku, Sendai 980, Japan

Y. Zheng
Qualop Systems Corp., 568 Weddell Dr., Suite 8, Sunnyvale, CA 94089

E.A. Hudson
Lawrence Livermore National Laboratory
Livermore, CA 94551

Y. Chen and D.A. Shirley
Departments of Chemistry and Physics, Pennsylvania State University
University Park, PA 16802

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Recycled Paper

ght Source Note:
uthor(s) Initials EJM 5-6-96
Date
Group Leader's initials 5-16-96
Date

Adsorption Site and Structure Determination of c(2x2) N_2/Ni(100) using Angle-Resolved Photoemission Extended Fine Structure

Edward J. Moler, Scot A. Kellar, Zahid Hussain

Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

W. R. A. Huff

Research Institute for Scientific Measurements, Tohoku University, Kkatahiria 2-1-1, Aoba-ku, Sendai 980, Japan

Yu Zheng

Qualop Systems Corp., 568 Weddell Drive, Suite 8, Sunnyvale, CA 94089

Eric A. Hudson

Lawrence Livermore National Laboratory, Livermore, CA 94551

Yufeng Chen, David A. Shirley

Departments of Chemistry and Physics, The Pennsylvania State University, University Park, PA 16802

Abstract

We have determined the atomic spatial structure of c(2x2) N2/Ni(100) with Angle-Resolved Photoemission Extended Fine Structure (ARPEFS) using the nitrogen 1s core level. The chemically shifted N 1s peak intensities were summed together to obtain ARPEFS curves for both nitrogen atoms in the molecule. We used a new, highly-optimized program based on the Rehr-Albers scattering matrix formalism to find the adsorption site and to quantitatively determine the bond-lengths. The nitrogen molecule stands upright at an atop site, with a N-Ni bond length of 2.25(1) Å, a N-N bond length of 1.10(7) Å, and a first layer Ni-Ni spacing of 1.76(4) Å. The shake-up peak shows an identical ARPEFS diffraction pattern, confirming its intrinsic nature and supporting a previous use of this feature to decompose the peak into contributions from the chemically

inequivalent nitrogen atoms. Comparison to a previously published theoretical treatment of N-N-Ni and experimental structures of analogous adsorbate systems demonstrates the importance of adsorbate-adsorbate interactions in weakly chemisorbed systems.

1. Introduction

Angle-Resolved Photoemission Extended Fine Structure (ARPEFS) is a well established technique for determining the spatial structure of atomic and molecular adsorbates on metal surfaces[1-3]. One of the advantages of the technique is its elemental selectivity due to the unique binding energies of core electrons. We have used ARPEFS to determine the adsorption site and bond lengths of C(2x2) molecular nitrogen on Ni(100).

This system has been the subject of several investigations, as it represents an analogue to the prototypical CO adsorbate on transition-metal surfaces. Stöhr and Jaeger determined that N_2 stands up normal to the surface on Ni(100)[4]. Grunze and Dowben established that molecular nitrogen forms a C(2x2) LEED pattern on Ni(100)[5]. Subsequent TPD studies indicated that only one adsorption site was occupied by N_2 at saturated coverages (≈0.5 monolayer) for well ordered overlayers, even those with somewhat diffuse LEED patterns[6]. Nilsson and Mårtensson found two sharp peaks in the photoemission spectrum of the N 1s core-level corresponding to the two chemically inequivalent nitrogen atoms in the molecular adsorbate[7]. They also investigated the broad satellite peak 6 eV below the main peaks and concluded that it was a shake-up peak associated with final-state molecular excitations. Their analysis of the shake-up satellite was based on the implicit assumption that the satellite peak showed identical scattering characteristics as the main peak. This assumption has not been previously established.

In this paper we report an experimental determination of the adsorption site, the the N-N and N-Ni bond lengths, and the first Ni-Ni layer spacing. We also show that the shake-up peak associated with the nitrogen 1s core level displays an identical diffraction pattern as the main peak. We found that it is not necessary to resolve the chemically shifted peaks to determine the adsorbate structure.

2. Experiment

The experiments were performed using the high resolution Spherical Grating Monochromator (SGM) on beam line 6-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). Photon energies from 480-700 eV were utilized. The UHV vacuum chamber was equipped with a 5 cm hemispherical electron energy analyzer, a liquid helium cooled sample manipulator, a LEED/Auger system, and an ion-sputtering gun. The bulk nickel substrate was cleaned by sputtering, annealing, and roasting in oxygen. The final surface cleaning was done by dosing O_2 at 3×10^{-9} torr for 20 seconds with the sample at 450° C. Sample cleanliness was monitored by XPS and sample order was checked by LEED. The nickel crystal was oriented by laser autocollimation, angular scanned photoemission along [110], and LEED. The C(2x2) N_2 overlayer was prepared by back-filling the chamber to 1×10^{-8} torr while cooling the sample from 140 K to 75 K at a rate of ~.12 K/s. The order of the overlayer was checked with LEED on trial preparations. LEED was not done on the overlayers used to take the ARPEFS curves, to avoid damage from electron bombardment. NEXAFS was used to confirm that the molecules were indeed standing up on the surface. The sample was free of measurable contamination, but we observed an accumulation of oxygen on the surface at a rate of approximately 3% monolayer/hour. Thus, we cleaned the surface and prepared a new overlayer after 1.5 hours with a single overlayer. The synchrotron radiation was incident on the sample at 25° between the electric vector and the sample normal and the photo-emission direction was 5° off the normal to the nickel(100) surface towards the [110] direction. The UHV chamber pressure was $<3 \times 10^{-10}$ torr. The sample temperature was 75 K as measured by a thermocouple spot-welded near the sample.

3. Surface Structure Determination

Figure 1 shows a typical photoemission spectrum and its deconvolution into three peaks. Nilsson and Mårtensson showed that the two lower binding energy peaks are due to the two chemically inequivalent nitrogen atoms[7]. The lowest binding energy peak is due to the nitrogen atom furthest from the nickel substrate. We call this nitrogen the "outer nitrogen" and the corresponding peak ,"peak 1." The next lowest binding energy peak is due to the nitrogen atom closest to the nickel surface. We call this nitrogen the "inner nitrogen" and the corresponding peak, "peak 2." Nilsson and Mårtensson measured the splitting between these peaks to be 1.33 eV. They also determined that the broad satellite peak approximately 6 eV below the two has contributions from both higher kinetic energy peaks using normal and off-normal emission. The peak intensities were extracted by fitting all three peaks with Voigt functions and normalized to the background the in the standard method[1]. We obtained the total ARPEFS diffraction curve by summing the intensities of peaks 1 and 2.

We have performed full Multiple Scattering Spherical Wave (MSSW) calculations using the formalism of Rehr and Albers[8] to determine the best match of adsorption site and bond lengths to the experimental ARPEFS χ-curve. The program, developed entirely within our group, is highly optimized for obtaining a best fit to experimental data including multiple emitters[9]. It uses second order matrices (6x6) and up to 8th order scattering, which produce a convergent calculation at these energies and inter-atomic distances. The best fit was defined by the conventional R-factor analysis[1]. We show the experimental chi-curve and the best fit for each of the three adsorption sites in figure 2. To obtain these fits we allowed the N-N and N-Ni distances and the spacing between the first two nickel layers to vary. We also allowed the inner potential, the Debye temperatures of the near surface layers, and the tilt of the N-N molecule to vary. Clearly the atop site is the best fit, with an R-factor of 0.34. The N-Ni bond length is found to be 2.25 Å and the N-N bond length is found to be the gas-phase nitrogen value of 1.10 Å. Interestingly, the spacing between the

first two nickel layers is found to be the bulk nickel value of 1.76 Å, in contrast to the contracted clean-metal layer spacing of 1.60 Å[10]. A surface debye temperature of 220 K and an inner potential of 15.1 eV were found to give the best fit.

To examine the sensitivity to the layer spacings and establish error bars we calculated the R-factor for various interlayer spacings and inner potentials. It has been shown that the inner potential may affect the derived layer spacings and must be included in the R-factor analysis[11]. The uncertainty is reported as one standard deviation, i.e. a confidence level of 0.68, and is written in parentheses following the last significant digit. Figures 3 and 4 show the R-factor contours for the N-Ni layer spacing and inner potential and the first layer Ni-Ni spacing, respectively. The R-factor result for the nitrogen-nitrogen bond length is shown in figure 5, with the inner potential was held constant at 15.1 eV. Extraction of the error bars from the R-factor analysis has been discussed previously[12]. We conclude from these analyses that the error in the N-Ni layer spacing is 0.01 Å , the Ni-Ni layer spacing is 0.04 Å, and the N-N bond length is 0.07 Å.

4. The Satellite Peak

An interesting feature of the photoemission spectra is the broad, intense peak at 6 eV below the main peaks. Nilsson and Mårtensson assigned this peak as an intrinsic satellite feature, and shows that it contains contributions from both of the main peaks by spectrum subtraction, making use of the variation in peak intensities with emission angle[7]. In figure 6 we compare the χ-curve of the sum of peaks 1 and 2 to the χ-curve of peak 3. These two curves are each plotted against the k-value of the corresponding (sum) peak. The peak 3 chi-curve follows the summed main peak chi-curves very closely, showing that it displays an identical ARPEFS diffraction pattern as the main peaks, including identical amplitudes. We infer that the 6 eV peak arises from intrinsic satellite structures, each having the same intensity ratio as its main peak.

5. Discussion

In this work we have shown that the nitrogen adsorbs on an atop site with a nitrogen-nickel bond length of 2.25 Å, with approximatedly the gas phase nitrogen-nitrogen bond length and bulk nickel-nickel layer spacing. We now examine the bonding characteristics in the context of theoretical predictions and in comparison to related adsorbate systems. The bonding is qualitatively described by the molecular nitrogen donating electrons to the nickel from its HOMO $3\sigma_g$ orbital and accepting electrons into the LUMO $1\pi_g^*$ orbital from the nickel 3d orbitals[13]. There is a repulsive interaction between the $3\sigma_g$ occupied level and the metal electrons. The electron accepted into the $1\pi_g^*$ is thought to stabilize the $3\sigma_g$ interaction by creating a partial positive charge on the metal atom. The induced dipole is then attractive to the $3\sigma_g$ electrons. The relative importance of molecular bonding and mutually induced dipole interactions remains to be clarified. This model also ignores adsorbate-adsorbate interactions, which may occur both directly and through the substrate.

There have been several ab-initio calculations published for the N-N-Ni system examining the bonding characteristics of the molecular nitrogen-metal system [14-16]. The investigations of Freund, et. al., found a minimum total energy at a N-Ni bond length of 1.64 Å for a $3d^{10}$ configuration nickel atom and 1.96 Å for a $3d^94s$ configuration. They found that the $3d^{10}$ configuration led to a better match to the calculated core-level splitting between the two inequivalent nitrogen atoms. These calculations clearly overestimate the molecule-metal interaction strengths for the saturated overlayer. The large discrepancy between our measured N-Ni bond lengths of 2.25 Å and the theoretical predictions of 1.96 Å underscores the importance of including the effects of other interactions with the surface layer metal atoms and other neighboring molecules. This is not surprising considering that Varma and Dowben have shown that there are strong lateral interactions between nitrogen molecules in the ordered c(2x2) overlayer[6].

It is useful to compare our results to the structure of the related systems, c(2x2) CO/Ni(100) and low-coverage NH_3/Ni(100). The CO molecule adsorbs on Ni(100) in an atop site with a C-Ni layer spacing of 1.80 Å[17]. The first-layer Ni-Ni spacing was assumed to be the bulk value in that analysis. The heat of adsorption of CO on Ni(100) is 122(2) kJ/mole at low coverage and drops to 100(2) kJ/mole at high coverage[17]. The heat of adsorption of N_2/Ni(100) is much lower, 45(4) kJ/mole to 25(2) kJ/mole[5], which is consistent with the longer N-Ni bond length. The bonding scheme for CO to Ni(100) is expected to be analogous to N_2. The relatively large N-Ni bond length is consistent with the molecular orbital interaction picture. The CO molecule has a stronger covalent interaction with the metal surface due to the concentration of the $2\pi^*$ antibonding orbital on the carbon and the greater oxygen character of the 5σ donor orbital. This enhances the orbital overlap relative to the N_2 MO's and results in a stronger bond with shorter bond length.

The NH_3/Ni(100) also adsorbs on an atop site with an N-Ni spacing of 2.01 Å and an Ni-Ni layer spacing of 1.81 Å[18]. The spacing for that system was determined at low coverage. The bonding scheme of the ammonia is understood to be a σ donation to the metal and a large electrostatic interaction between the ammonia dipole and the metal atoms[19]. Considering the electrostatic interactions, the larger N-Ni spacing for N_2 is expected, as there is no molecular dipole and the N_2 molecule has a low polarizability relative to the ammonia, 1.74×10^{-24} vs. 2.26×10^{-24} cm^3, respectively[20]. The expansion of the initially contracted clean metal surface has not been investigated theoretically for either the NH_3 or the N_2 adsorbate systems. We note that the more strongly interacting ammonia adsorbate leads to a greater expansion of the surface nickel layer than the molecular nitrogen from the clean metal 1st layer Ni-Ni spacing of 1.60 Å.

It is clear that the interaction of the molecular nitrogen overlayer with the surface is very weak. There is neither a strong covalent interaction nor an electrostatic one. The weak-chemisorption picture analogous to CO is supported by the analysis of the core-level

photoemission satellites[7,15] and valence level UPS[21]. The weak interaction with the metal substrate emphasizes the importance of lateral interactions among adsorbates. A quantitative theoretical treatment will need to include adsorbate-adsorbate interactions and possibly sub-surface nickel layers.

6. Conclusion

We have measured the nitrogen 1s ARPEFS oscillations from c(2x2) N_2/Ni(100). We find that the nitrogen molecule adsorbs in an atop site with the N-N bond normal to the surface with a N-N length of 1.10(7) Å. The N-Ni bond length is 2.25(1) Å and the first Ni-Ni layer spacing is 1.76(4) Å. The satellite peak intensity shows the same chi curve as the sum of the two main peaks, confirming that the component satellite peaks are intrinsic, and with the same intensity ratio as the main peaks. Comparison with theoretical treatments of the N-N-Ni system and experimental structures of analogous adsorbate systems suggests that a quantitative theoretical treatment of weakly adsorbed systems must include lateral interactions between adsorbates.

Acknowledgements

We would like to thank the staff and management of the Stanford Synchrotron Radiation Laboratory in Stanford, CA for their support and help with the experimental work. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under contract No. DE-AC03-76SF00098.

References

1 J. J. Barton, C. C. Bahr, C. C. Robey, Z. Hussain, E. Umbach, and D. A. Shirley, *Physical Review B* **15,** 3807 (1986).

2 C. C. Bahr, J. J. Barton, Z. Hussain, S. W. Robey, J. G. Tobin, and D. A. Shirley, *Physical Review B* **35,** 3773 (1987).

3 L. G. Terminello, X. S. Zhang, S. Kim, A. E. Schach von Wittenau, K. T. Leung, and D. A. Shirley, *Physical Review B* **38,** 3879 (1988).

4 J. Stöhr and R. Jaeger, *Physical Review B* **26,** 4111 (1982).

5 M. Grunze, P. A. Dowben, and R. G. Jones, *Surface Science* **141,** 455-472 (1984).

6 S. Varma and P. A. Dowben, *Journal of Vacuum Science and Technology A* **8,** 2605 (1990).

7 A. Nilsson, H. Tillborg, and N. Martensson, *Physical Review Letters* **67,** 1015 (1991).

8 J. Rehr and Albers, *Physical Review B* **41,** 8139 (1990).

9 to be published.

10 J. W. M. Frenken and J. F. van der Veen, *Physical Review Letters* **51,** 1876-1879 (1983).

11 W. R. A. Huff, Y. Zheng, Z. Hussain, and D. A. Shirley, *Journal of Physical Chemistry* **98,** 9182-9186 (1994).

12 Z. Huang, Ph. D. Thesis, in Chemistry, University of California, Berkeley, 1992.

13 C. N. R. Rao and G. R. Rao, *Surface Science Reports* **13** (1991).

14 C. R. Brundle, P. S. Bagus, D. Menzel, and K. Hermann, *Physical Review B* **24,** 7041-7056 (1981).

15 H. J. Freund, R. P. Messmer, C. M. Kao, and E. W. Plummer, *Physical Review B* **31,** 4848-4853 (1985).

16 C. M. Kao and R. P. Messmer, *Physical Review B* **31,** 4835-4847 (1985).

17 J. T. Stuckless, N. Al-Sarraf, C. Wartnaby, and D. A. King, *Journal of Chemical Physics* **99,** 2202-2212 (1993).

18 Y. Zheng, E. J. Moler, E. A. Hudson, and D. A. Shirley, *Physical Review B* **48,** 4760-4766 (1993).

19 C. W. Bauschlicher, *Journal of Chemical Physics* **83,** 3129-3133 (1985).

20 *CRC Handbook of Chemistry and Physics*, Vol. , edited by R. C. Weast, J. A. Melvin, and H. B. William (CRC Press, Inc., Boca Raton, Florida, 1988).

21 P. A. Dowben, Y. Sakisaka, and T. N. Rhodin, *Surface Science* **147,** 89-102 (1984).

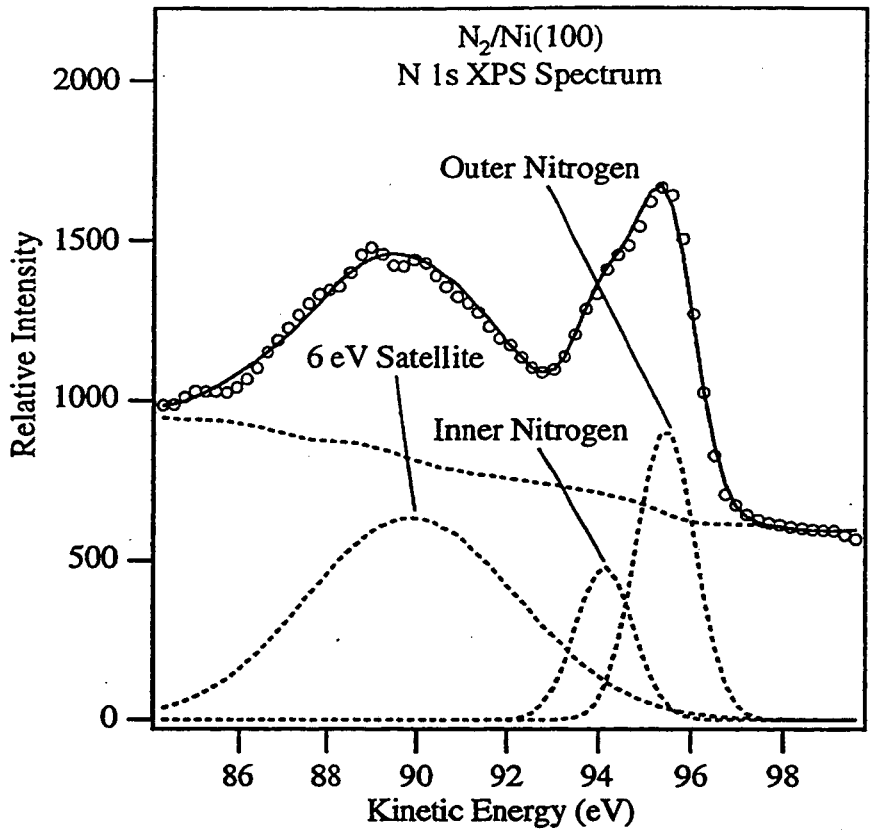

N2/Ni(100)
N 1s XPS Spectrum
Outer Nitrogen
6 eV Satellite
Inner Nitrogen
Relative Intensity
2000
1500
1000
500
0
86
88
90
92
94
96
98
Kinetic Energy (eV)

Figure 1.

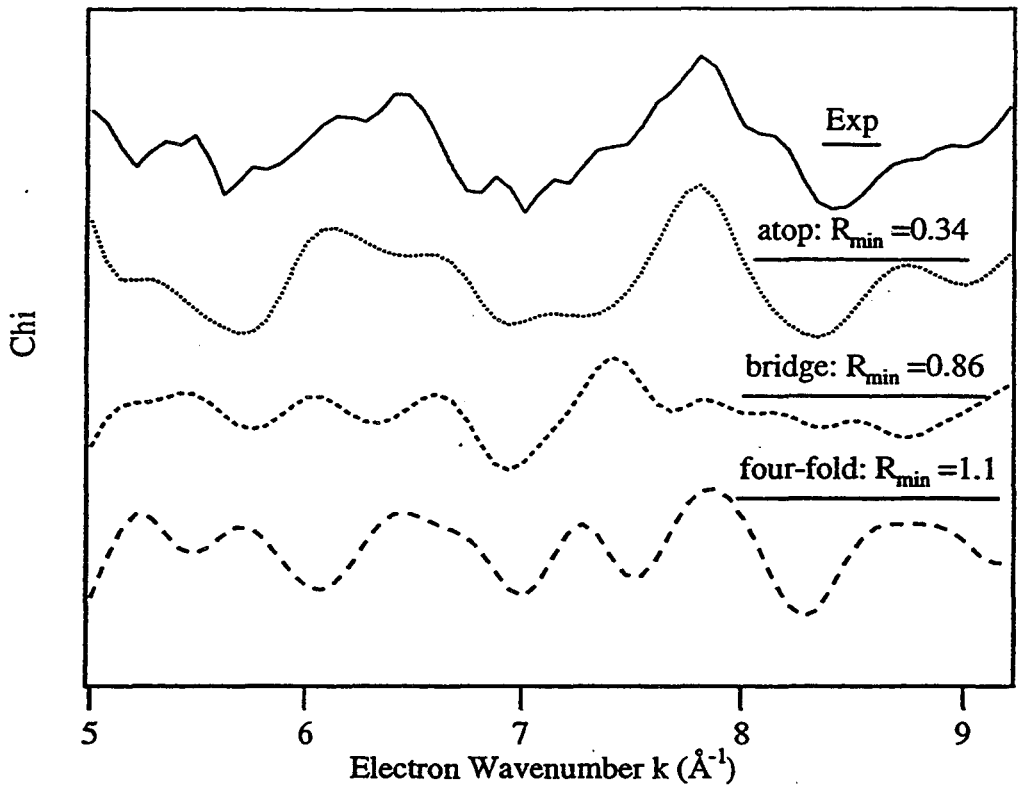
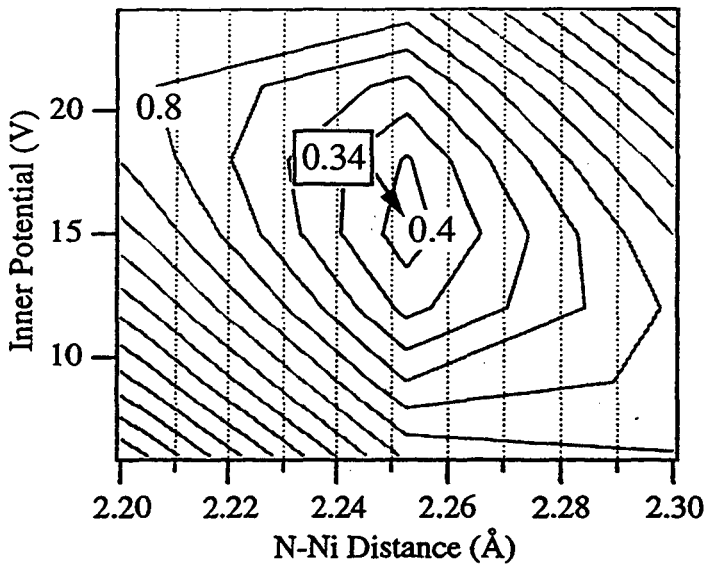

Exp
atop: R_{min} =0.34
bridge: R_{min} =0.86
four-fold: R_{min} =1.1
Chi
5
6
7
8
9
Electron Wavenumber k (Å^{-1})

Figure 2.

(a)


0.8
0.34
0.4
20
15
10
Inner Potential (V)
2.20
2.22
2.24
2.26
2.28
2.30
N-Ni Distance (Å)

(b)

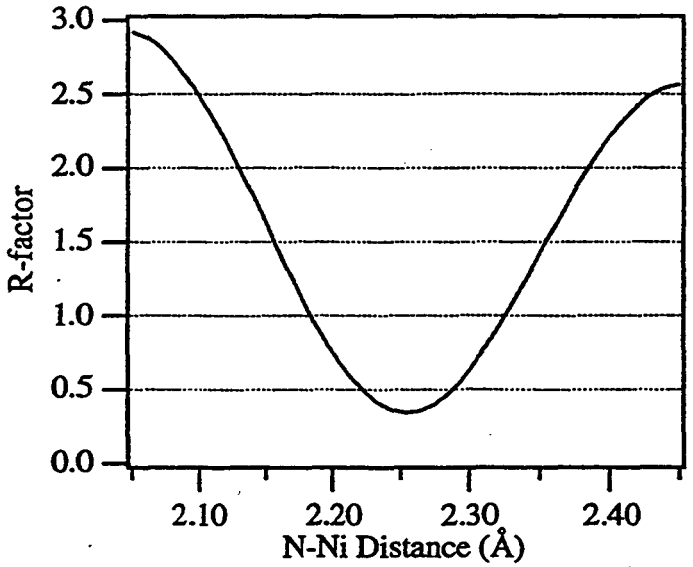

3.0
2.5
2.0
1.5
1.0
0.5
0.0
R-factor
2.10
2.20
2.30
2.40
N-Ni Distance (Å)

Figure 3.

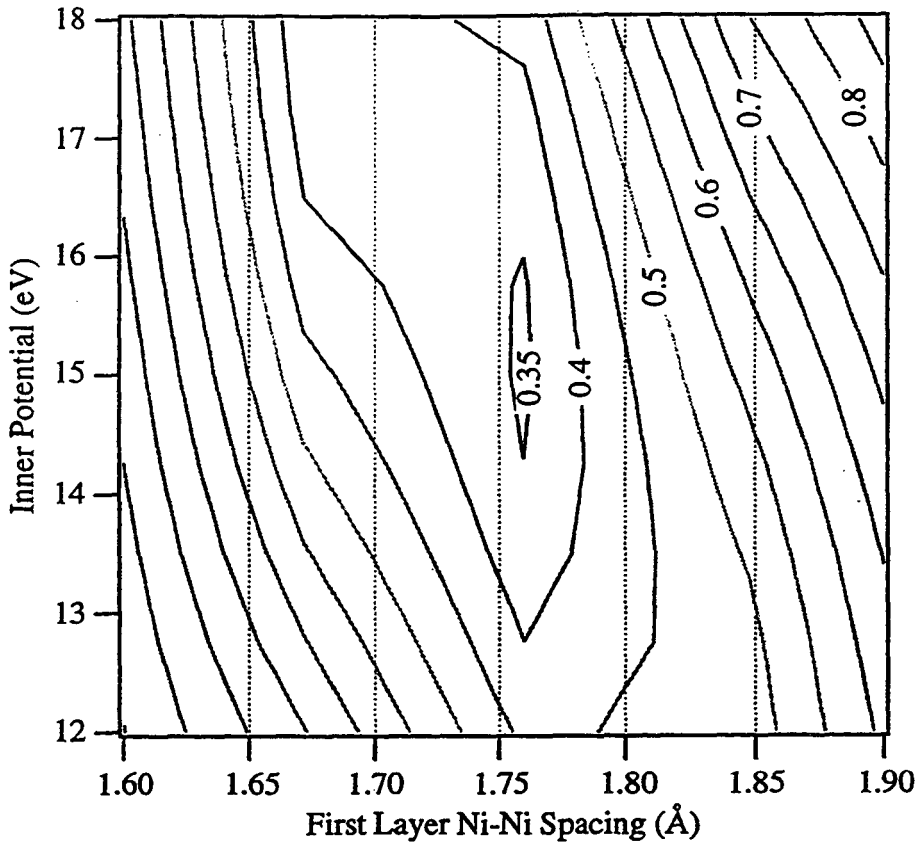

18
17
16
15
14
13
12
Inner Potential (eV)
1.60
1.65
1.70
1.75
1.80
1.85
1.90
First Layer Ni-Ni Spacing (Å)
0.35
0.4
0.5
0.6
0.7
0.8

Figure 4.

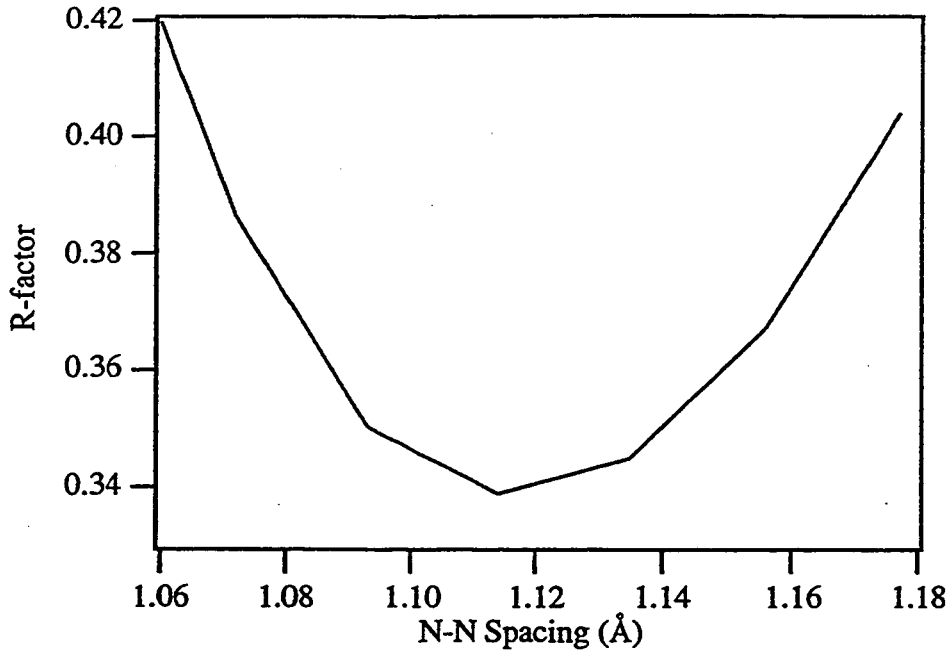

0.42
0.40
0.38
0.36
0.34
R-factor
1.06
1.08
1.10
1.12
1.14
1.16
1.18
N-N Spacing (Å)

Figure 5.

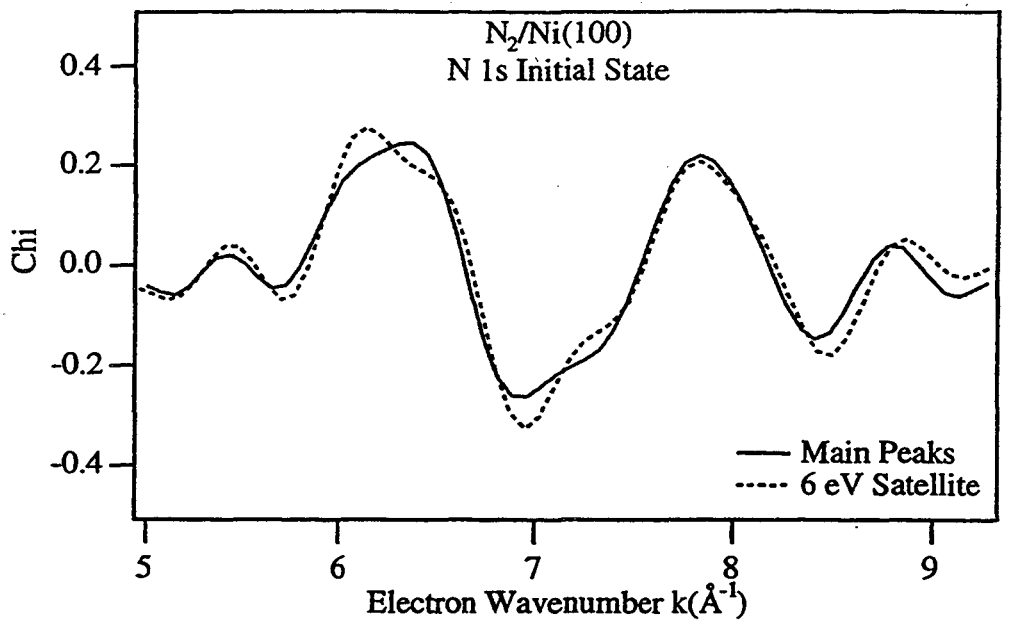

N2/Ni(100)
N 1s Initial State
0.4
0.2
0.0
-0.2
-0.4
Chi
Main Peaks
6 eV Satellite
5
6
7
8
9
Electron Wavenumber k(Å-1)

Figure 6.

Figure Captions

Figure 1.

Typical XPS spectrum of c(2x2) N2/Ni(100) for this work. The circles are the data points, the dashed lines are the deconvolved fit to the data, and the solid line is the total fit. See the text for explanation of "outer" and "inner" nitrogen peaks.

Figure 2.

Experimental ARPEFS curve and best fit calculation for each adsorption site. The experimental curve is derived from the sum of the intensities from the two main peaks in the XPS spectrum. Clearly the atop adsorption site gives the best fit with an R-factor of 0.34.

Figure 3.

(a) R-factor vs. inner potential and N-Ni layer spacing. The minimum is at a layer spacing of 2.255 Å. (b) R-factor vs. N-Ni layer spacing with inner potential fixed at 15.1 eV.

Figure 4.

R-factor vs. inner potential and spacing between the first and second nickel layers.

Figure 5.

R-factor vs. nitrogen-nitrogen bond length. The inner potential is fixed at 15.1 eV

Figure 6.

Comparison of ARPEFS chi-curves for the main peaks and the satellite peak. The curves have been Fourier smoothed to a 13 Å cutoff to facilitate comparison.

Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road | Berkeley, California 94720

Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098