type of step boundary ([$\bar{1}\bar{1}2$] steps). There is no agreement for 5-1, 5-2, or 3-2 models. Nor is there agreement for any model with the opposite type of step boundary ([$11\bar{2}$] steps).

LEED experiments as interpreted here cannot distinguish between an island model and the corresponding "trough" model where island and trough are interchanged. What is definitely established is that the islands (or troughs) are approximately triangular with [$\bar{1}\bar{1}2$] step boundaries, have area approximately half that of the 7 × 7 unit mesh, and have height close to the Si(111) double-layer spacing.

In discovering these unprecedented structures we have expanded the repertory of useful applications of kinematical LEED. The use of the shape transform is an extension of previous highly successful applications of kinematical LEED to parallel step arrays.[10] The same method should be applicable to any crystal surface made up of large repeating units that are individually of relatively simple structure.

Helpful discussions with M. J. Cardillo, Y. J. Chabal, H. D. Hagstrum, J. C. Phillips, T. M. Rice, and J. E. Rowe are acknowledged.

---

[a] Retired.

[1] J. J. Lander, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1965), Vol. II, p. 26; W. Mönch, Surf. Sci. 86, 672 (1979).

[2] J. C. Phillips, Phys. Rev. Lett. 45, 905 (1980).

[3] M. J. Cardillo, Phys. Rev. B 23, 4279 (1981).

[4] T. Sakurai and H. D. Hagstrum, Phys. Rev. B 12, 5349 (1975).

[5] Appreciable diffusion of Si atoms on Si(111) requires temperatures above 200 °C (Y. J. Chabal, J. E. Rowe, and S. B. Christman, to be published).

[6] D. J. Chadi, Surf. Sci. 99, 1 (1980).

[7] C. A. Taylor and H. Lipson, *Optical Transforms* (Cornell Univ. Press, Ithaca, 1964).

[8] The substrate crystal orientation, which must be known to index the pattern, was determined by comparing relative IO spot intensities for Si(111)-(7× 7) with published results for a crystal of known orientation [W. Mönch and P. P. Auer, J. Vac. Sci. Technol. 15, 1230 (1978)]. The (10) spot in Fig. 1 is the same as the (10) spot of Mönch and Auer.

[9] The main consequence of the assumption that the trough boundary is the mirror image of the island boundary is that the intensities of a given FO spot for any two values of $S_\perp d$ differing by π are complementary, i.e., the intensities add up to a constant times the intensity shape transform [cf. Eq. (1)]. An approximately complementary character is evident experimentally (e.g., *Y* and inverted-*Y* formations) but there are noticeable departures from strict complementarity and these departures could be due to moderate departures from the above assumption.

[10] M. Henzler, in *Electron Spectroscopy for Surface Analysis*, edited by H. Ibach (Springer-Verlag, Berlin, 1977), p. 117.

Evidence for Two States of Chemisorbed Oxygen on Ni(100)

Thomas H. Upton
Corporate Research–Science Laboratories, Exxon Research and Engineering Company,
Linden, New Jersey 07036

and

William A. Goddard, III
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

(Received 15 January 1981)

Generalized valence-bond calculations suggest that atomic oxygen chemisorbed on Ni(100) leads to two distinct low-lying states: (1) the *radical state* with $R_\perp = 0.88$ Å and $\omega_\perp = 55$ meV and (2) the *surface oxide state* with $R_\perp = 0.26$ Å and $\omega_\perp = 38$ meV. We suggest that the radical state dominates for $p(2\times 2)$ and that the oxide state dominates for $c(2\times 2)$. We find that atomic H, Cl, and S lead to only one low-lying state.

PACS numbers: 68.20.+t, 71.45.Nt

In experimental studies of chalcogen bonding on single-crystal nickel surfaces, oxygen has long been known to exhibit anomalous behavior. The results of high-resolution energy-loss spectroscopy (HRELS),[1,2] Auger-electron spectroscopy and low-energy electron diffraction (LEED),[3] ultraviolet photoelectron spectroscopy (UPS),[4] and reflection high-energy–electron diffraction

© 1981 The American Physical Society

(RHEED)[5] show behavior for oxygen that is different from the other chalcogens and not explained solely by its increased electronegativity or smaller size.

In this Letter we report the results of first-principles Hartree-Fock (HF) and generalized valence-bond (GVB) calculations, comparing the properties of atomic oxygen and sulfur bound to a cluster of 20 Ni atoms chosen to model the Ni(100) surface. For oxygen we find two distinct low-lying states that have quite different properties and suggest an interpretation of the anomalous experimental results in terms of these states. For S, Cl, and H we find only one low-lying state, implying that this anomalous behavior is special to oxygen. A two-state system has been observed experimentally for oxygen on Pt,[6] Ni,[6] and Pd,[7] but no direct identification has previously been presented for these states.

The calculations were carried out with use of the same procedures as reported previously.[8-10] For each geometrical configuration we obtained the GVB wave function including electron correlation in all electron pairs involved with bonding the adsorbate and metal (for O, S, and Cl, there are three such pairs; for H there is one). The total energy is calculated for several geometries, and the resulting potential curves lead to $R_\perp$ (bond distance), $\omega_\perp$ (vibrational frequency), and D_e (bond energy).

The bonding of oxygen and sulfur atoms was considered at both two-coordinate [denoted 2(001)] and four-coordinate sites [denoted 4(001)]. Considering first the bonding of sulfur at 4(001), we find from a projection of the $Ni_{20}S$ orbitals onto the original Ni_{20} ground-state orbitals[8] that a σ bond is formed between the sulfur $3p_z$ (a_1 symmetry) orbital and the highest occupied Ni_{20} orbital, an orbital with significant density in the bonding region. The bond is diffuse, but localized at the S atom. The three remaining sulfur $3p$ electrons are in $3p_x$ and $3p_y$ (e symmetry) orbitals that extend across the 4(001) site. In forming the bond to the cluster, the singly occupied e orbital of S becomes coupled to a high-lying cluster orbital having e symmetry across the site (analogous to a molecular π bond). Near the equilibrium geometry, this bond orbital and the remaining e orbital (which is doubly occupied in the isolated S atom) are equivalent in shape. The final state then is one in which the σ bond (a_1) is polarized towards the S atom, and the e (or π bonding) orbitals are polarized back towards the corners of the site. The redistribution of charge at the site is complex and serves to minimize charge transferred onto the sulfur atom.

The optimum position for the sulfur is found to be about 1.24 Å (Table I, part A) above the 4(001) site [LEED results[11] give 1.3 Å for $c(2\times2)$ and $p(2\times2)$] with a bond energy of 4.3 eV. Comparison with σ bond energies for H_2S (3.8 eV[12]) and NiS (3.5 eV[13]) suggests that the π bond strength here is about 1.0 eV. Only polycrystalline bond energies[14] are available for direct comparison with $Ni_{20}S$, and they range from 4.8 to 4.9 eV. The bond energy of S at the 2(001) site was far weaker (see Table I, part D), partly due to the weak π bond (less than 0.2 eV). Estimates of the position of the ion states from small-configuration-interaction calculations suggest that e and a_1 levels should appear in the UPS spectrum at 4.6 and 7.0 eV, respectively, and a reduction in state density near E_f should occur.

Qualitatively, the lowest state (referred to below as the surface oxide state) for oxygen chemisorption at each site strongly resembles that found for sulfur. At the 4(001) site, the σ bonding interaction was again with the highest occupied cluster orbital. The $2p_x$ and $2p_y$ orbitals are more diffuse than the $2p_z$ orbital, but the back donation here is less extensive than for sulfur, resulting in greater charge transfer to the oxygen. An (oversimplified) description of this state is in terms of three doubly occupied $2p$ orbitals on the oxygen (i.e., the closed-shell wave function, O^{--}), each delocalized back onto nearby Ni atoms. Thus we refer to this as the *surface oxide state.*

As mentioned at the outset, a key difference between oxygen and sulfur is the appearance of a second low-lying state for oxygen chemisorption at the 4(001) site, one with *no analog in the $Ni_{20}S$ system.* This new state (referred to as the *radical state*) can be viewed as having two doubly occupied e or π orbitals and a *singly occupied* σ (or a_1) orbital. The π orbitals are similar to the oxide state, but the σ orbital is only weakly coupled to the cluster.

Some insight into the nature of these states is provided by comparison with the low-lying states of the diatomic alkali oxides.[13] In each case the molecule is highly ionic (M^+O^-), leading to two states that are almost degenerate: a $^2\Sigma^+$ state (with a singly occupied $p\sigma$ orbital) and a $^2\Pi$ state (a singly occupied $p\pi$ orbital). The $^2\Sigma^+$ state represents a direct analog of the radical state described above for $Ni_{20}O$, while the $^2\Pi$ state is analogous to the oxide state (where the singly occupied oxygen e orbital is coupled to the cluster

TABLE I. Bond parameters for $Ni_{20}X$. (A) Comparison with experiment for O and S at 4(001) sites, (B) other results for 4(001), (C) results for 3(111), and (D) results for 2(001).

		D_e (eV)		$R_\perp$ (Å)		$\omega_\perp$ (meV)	
		Theor.	Expt.	Theor.	Expt.[a]	Theor.[f]	Expt.
(A)	$p(2\times 2)$-S	4.34		1.24	1.3 ± 0.1	(37) 44[f]	46[b]
	$c(2\times 2)$-S	4.34		1.24	1.3 ± 0.1	(37) 44[f]	44[b]
	$p(2\times 2)$-O[h]	3.29		0.88	0.9 ± 0.1	(46) 55[c]	53[b]
	$c(2\times 2)$–O[i]	3.85		0.26	(0.9 ± 0.1)	(33) 38[c]	39[b]
(B)	O [oxide (neutral)]	3.63		0.55		(27) 36[f]	
	O [radical (ion)]	2.78		0.83		(44) 52[f]	
	Cl	4.90		1.38		(30) 36[f]	
	H	3.04	2.87[d]	0.30		(73) 73[f]	74[e]
(C)	O [radical (neutral)]	2.59		1.31		(64) 70[f]	
	O [oxide (neutral)]	2.35		1.26	1.2 ± 0.1	(61) 67[f]	
	S	3.85		1.55	1.4 ± 0.1	(49) 57[f]	
	H	3.21	2.95[d]	0.78		(155) 155	139[g]
(D)	O	2.15		1.48		(68) 75[f]	
	S	2.47		1.81		(48)	

[a] Ref. 11.

[b] Ref. 1.

[c] Ref. 16.

[d] K. Christman, O. Schober, G. Ertl, and H. Neuman, J. Chem. Phys. 60, 4528 (1974); J. Lapujoulade and K. S. Neil, Surf. Sci. 35, 288 (1973), and J. Chem. Phys. 70, 798 (1973). We have included zero-point energies to obtain experimental D_e values.

[e] S. Andersson, Chem. Phys. Lett. 55, 185 (1978).

[f] The rigid-cluster value was modified using the effective-mass correction of J. E. Black (to be published).

[g] W. Ho, Ph.D. thesis, University of Pennsylvania, 1979 (unpublished).

[h] Theoretical calculations for radical state of $Ni_{20}O$.

[i] Theoretical calculations for surface oxide state of $Ni_{20}O^+$.

to form a weak π bond). Simple estimates of bond energies for forming O^- and S^- on the surface (obtained by comparing atomic electron affinities and bond distances) indicate that O^- would be 2 eV more favorable than S^-, suggesting that only O should form low-lying radical states (of course, charge redistribution from back donation makes the net charge transferred less than one in each case). Bonds to halogens could also be ionic; however, this would lead to only one state, in contrast to the two oxygen states.

The charge redistribution that occurs on bonding of O implies that at higher coverage, neighboring adsorbates would tend to withdraw charge from any particular surface site. To model this high-coverage situation, we used an $Ni_{20}{}^+$ cluster to which O was bonded. The radical state was found to be insensitive to charge with $\Delta R_\perp = -0.05$ Å, while the surface oxide ground state moves much closer to the surface ($\Delta R_\perp = -0.29$ Å to $R_\perp = 0.26$ Å. In these calculations all metal-atom positions were held fixed. We expect that if the metal-atom positions were relaxed this surface oxide state would move closer to the surface, perhaps penetrating the top layer. The qualitative picture that emerges is one in which it should be possible for oxygen to populate two distinct states. The surface oxide state may be identified as a precursor to formation of a bulk oxide, a state in which the O atom ultimately enters the surface as coverage increases. The oxygen radical state should be more easily formed from initial dissociation of O_2 and should be highly reactive but less sensitive to changes in the surface electron density. The strength and character of the bond found for this state indicates that a σ bond might form between it and an alkyl radical without great energetic penalty.[15]

While the splitting between the two low-lying oxygen states may be slightly different on the bulk surface, the implications of these findings on the current experimental picture of oxygen chemisorption on Ni(100) are considerable. The $p(2\times 2)$ and $c(2\times 2)$ HRELS spectra of Andersson[1] each show a feature (at 53 and 39 meV, respectively) that may be attributed to oxygen [a second low-energy feature in the $p(2\times2)$ spectrum has been shown to be due to phonons[2]]. The correspondence between these two frequencies and our calculated values[16] (55 meV for the radical and 38 meV for the oxide) suggests the following interpretation: For $p(2\times2)$ most of the chemisorbed oxygen is in the radical state, but at higher coverage the charge depletion due to other adsorbed oxygen atoms facilitates conversion to the surface oxide state so that for $c(2\times2)$ the surface oxide state dominates. By comparison, peaks at 46 and 44 meV are observed[1] for $p(2\times2)$-S and $c(2\times2)$-S, in agreement with our finding of a single state with a frequency of 44 meV. Angle-integrated photoemission may not be a good probe for the two oxygen states since their ionization features may overlap.

The two-state view of oxygen binding is also supported by other experimental studies. LEED studies have been interpreted in terms of oxygen positioned 0.9 Å above 4(001) sites for both $p(2\times2)$ and $c(2\times2)$ overlayers,[17] in excellent agreement with our result of 0.88 Å for the radical state. However, in the RHEED work[5] it was concluded that the kinetics of the initial stages of oxidation cannot be explained by a model in which oxide layers result from a "precipitation" of the $c(2\times2)$ overlayer. The formation of nucleation sites for oxidation was observed to become temperature independent above a critical coverage, leading to the conclusion that an equilibrium exists between oxide and nonoxide forming nucleation sites and shifts towards the former with increasing coverage. More recent x-ray photoemission spectroscopy (XPS) results[5] support this finding and further conclude that the oxide precursor is not identical to the species responsible for the $c(2\times2)$ and $p(2\times2)$ LEED patterns. de Bokx *et al.*[17] found that a surface oxidized beyond the $c(2\times2)$ phase layer would revert to $c(2\times2)$ and yield water after admission of hydrogen. As noted above, the radical species should be far more reactive than the surface oxide species and should be preferentially reduced by the hydrogen, thus shifting the equilibrium in its direction, as was observed.

The results presented here for sulfur and for the surface oxide form are in qualitative agreement with recent local-density studies that include surface periodicity.[18] Strictly speaking, our results may be compared only at Γ where similar splittings between a_1 and e levels are found in both studies. Observation of the "radical" state would require a spin-optimized local-density formalism along with some means of comparing total energies of the surface "oxide" and "radical" forms. As noted above, comparing calculated and observed UPS spectra is likely to produce ambiguous results.

Since submission of this manuscript there have been two reports providing support for our two-state model of O chemisorption on Ni(100). Rahman, Black, and Mills[16] showed that coupling of our parameters (for a rigid Ni lattice) with surface phonon bands leads to a quantitative fit of the full electron-energy-loss spectrum (EELS) for both the $p(2\times2)$ and $c(2\times2)$ structures *if, and only if,* the radical state predominates for $p(2\times2)$ and the surface oxide state predominates for $c(2\times2)$. In addition, Fadley[19] has observed that the angle-resolved photoemission for $c(2\times2)$ can be understood only if the O is in or nearly in the Ni surface. In addition, we have learned (i) that the early LEED analysis for $c(2\times2)$-O was not carried out for distances as small as 0.26 Å,[20] and (ii) that the fit for the LEED spectrum of $c(2\times2)$-O (assuming 0.9 Å) is much poorer than for all other chalcogenides.[21]

This work was supported by the National Science Foundation under Grant No. DMR-79-19689.

---

[1] S. Andersson, Surf. Sci. 79, 385 (1979), and Solid State Commun. 20, 229 (1976).

[2] H. Ibach and D. Bruchmann, Phys. Rev. Lett. 44, 36 (1980).

[3] J. Demuth and T. Rhodin, Surf. Sci. 43, 249 (1974).

[4] C. Brundle and H. Hopster, to be published.

[5] D. Mitchell, P. Sewell, and M. Cohen, Surf. Sci. 61, 355 (1976).

[6] P. Norton, R. Topping, and J. Goddale, J. Vac. Sci. Technol. 14, 446 (1977), and Surf. Sci. 65, 14 (1977).

[7] D. Weissman, M. Shek, and W. Spicer, Surf. Sci. 92, L59 (1980).

[8] T. H. Upton and W. A. Goddard, III, Phys. Rev. Lett. 42, 472 (1979); T. H. Upton, W. A. Goddard, III, and C. F. Melius, J. Vac. Sci. Technol. 16, 531 (1979); C. F. Melius, T. H. Upton, and W. A. Goddard, III, Solid State Commun. 28, 501 (1978).

[9] Valence double zeta basis sets were used for all adsorbates. For S and Cl we used the Ne effective core potential (T. Smedley, A. Rappé, and W. A. Goddard, III, to be published). The Ni effective potential and basis were the same as in Ref. 8 [T. H. Upton and W. A. Goddard, III, *ISISS 1979, Surface Science: Recent Progress and Perspectives* (CRC Press, Boca Raton, Florida, 1980)].

[10] F. W. Bobrowicz and W. A. Goddard, III, in *Modern Theoretical Chemistry: Methods of Electronic Structure Theory,* edited by H. F. Schaefer, III (Plenum, New York, 1977), Vol. 3, Chap. 4.

[11] J. Demuth, D. Jepsen, and P. Marcus, Phys. Rev. Lett. 31, 540 (1973), and 32, 1182 (1979), and Solid State Commun. 13, 1311 (1973); P. Marcus, J. Demuth, and D. Jepsen, Surf. Sci. 53, 501 (1975).

[12] S. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).

[13] K. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[14] H. Windawi and J. Katzer, J. Vac. Sci. Technol. 16, 497 (1979); J. McCarty and H. Wise, J. Chem. Phys. 72, 6332 (1980).

[15] J. Demuth and H. Ibach, Chem. Phys. Lett. 60, 395 (1979).

[16] Starting with our calculated frequencies (values in parentheses) for fixed metal atoms, T. S. Rahman, J. E. Black, and D. L. Mills [Phys. Rev. Lett. 46, 1469 (1981)] included coupling with surface-phonon bands to obtain the quoted vibrational frequencies.

[17] P. de Bokx, F. Labohm, O. Gijzeman, G. Bootsma, and J. Geus, Appl. Surf. Sci. 5, 321 (1980).

[18] E. W. Plummer, B. Tonner, N. Holzwarth, and A. Liebsch, Phys. Rev. B 21, 4306 (1980); A. Liebsch, Phys. Rev. B 17, 1653 (1978).

[19] C. Fadley, private communication.

[20] J. Demuth, private communication.

[21] S. Y. Tong, private communication.