terials Sciences.

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[1]C. Probst and J. Wittig, in "Handbook of the Physics and Chemistry of Rare Earths," edited by K. A. Gschneidner, Jr., and L. Eyring (North-Holland, Amsterdam, to be published), Chap. 10.

[2]H. Capellmann, J. Low Temp. Phys. 3, 189 (1970).

[3]G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in Superconductivity, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, p. 665.

[4]F. P. Bundy, Rev. Sci. Instrum. 46, 1318 (1975).

[5]"Compax," registered trademark of the General Electric Co., Worthington, Ohio. Wire drawing die blanks No. 5535.

[6]J. Wittig, Z. Phys. 195, 223 (1966).

[7]J. Wittig and C. Probst, in Proceedings of the Conference on High-Pressure and Low-Temperature Physics, Cleveland, 1977, edited by C. W. Chu and J. A. Woollam (Plenum, New York, 1978), p. 433.

[8]F. A. Schmidt and O. N. Carlson, J. Less-Common Met. 50, 237 (1976).

[9]K. A. Gschneidner, Jr., T.-W. E. Tsang, J. Queen, S. Legvold, and F. A. Schmidt, in Rare Earths and Actinides—1977, The Institute of Physics Conference Series No. 37, edited by W. D. Corner and B. K. Tanner (The Institute of Physics, Bristol and London, 1978), p. 23; also see Solid State Commun. 20, 737 (1976).

[10]G. J. Piermarini and S. Block, Rev. Sci. Instrum. 46, 595 (1975).

[11]The metallic GaP became superconducting between 4.07 and 3.72 K with the midpoint at 3.85 K. This is lower by 2 K than recently reported by Vereshchagin et al. {L. F. Vereshchagin, E. N. Yakovlev, Yu. A. Timofeev, and B. V. Vinogradov, Pis'ma Zh. Eksp. Teor. Fiz. 26, 61 (1977) [JETP Lett. 26, 55 (1977)]}.

[12]A. Eichler and J. Wittig, Z. Angew. Phys. 25, 319 (1968).

[13]J. F. Cannon, J. Phys. Chem. Ref. Data 3, 781 (1974).

[14]L. G. Liu, J. Phys. Chem. Solids 36, 31 (1975).

[15]D. G. Pettifor, J. Phys. F 7, 1009 (1977).

[16]D. Glötzel and O. K. Andersen, private communication.

Chemisorption of Atomic Hydrogen on Large-Nickel-Cluster Surfaces

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First-principles Hartree-Fock calculations are reported for binding of a hydrogen atom at high-symmetry sites of low-index faces of Ni surfaces (using an Ni_{20} cluster as a model). Chemisorption energies increase with ligancy of the binding site, with bond energies of 1.6, 2.8, 3.2, and 3.0 eV for onefold, twofold, threefold, and fourfold sites, respectively. A reverse trend is found for ω_e with values of 275, 170, 150, and 73 meV for ligancies of 1, 2, 3, and 4, respectively.

Despite numerous experimental[1-3] and theoretical investigations,[4,5] there is currently great uncertainty concerning the qualitative and quantitative aspects of H-atom chemisorption on transition metals. Here we report first-principles Hartree-Fock calculations for the interaction of atomic hydrogen with a twenty-atom Ni cluster. This cluster possesses chemisorption sites corresponding to most of the important sites on the (100), (110), (111), and (112) surfaces of this metal.

From calculations on small clusters of Ni atoms (up to eight) we have found the following:

(i) The lowest states have a localized $3d^9$ configuration on each Ni atom with bonding that is dominated by delocalized $4s$-like orbitals.[6-8]

(ii) The use of delocalized Hartree-Fock orbitals (as in usual band calculations) leads to large errors in describing the d orbitals with an overemphasis of $3d$-$4s$ mixing.[9] Allowing these orbitals to be localized, we find lower total energies and reduced mixing of $4s$ and $3d$ orbitals, permitting a factorization of the electronic states into a set of conduction-band (delocalized $4s$) orbitals and the localized $3d$ orbitals consisting of five orbitals and nine electrons for each Ni atoms. In addition, we have found that the role of the $3d$ orbitals in determining the shape of the conduction-

band orbitals can be accurately represented by an effective potential obtained from fitting to a spherical average of the orbitals of the free atom (the $4s^1 3d^9$ state). This is equivalent to including the average $3d^9$ configuration explicitly in the calculation but without allowing readjustment of the $3d$ orbitals. Use of the average $3d^9$ potential reduces Ni_n to an n-electron problem for the delocalized conduction-band states, allowing enormous computational simplification. Although many-body effects are quite important in describing the states involving $3d$ orbitals,[10] for clusters larger than ~12 atoms the Hartree-Fock description of the s-band orbitals is quite accurate. For example, we find that inclusion of electron correlation and relaxation effects in larger clusters is of only minor importance (0.1 to 0.2 eV) in describing ionization processes, in marked contrast to more "molecular" systems. From studies of the conduction bands of clusters as large as 87 atoms, we have concluded[6] that the smallest cluster adequate for use in treating chemisorption in this manner is a twenty-atom cluster containing all twelve nearest neighbors to two adjacent Ni atoms (arranged with the experimental geometry of face-centered cubic Ni).[11,12] This cluster includes most chemisorption sites of importance on low-index faces, allowing reliable comparisons of bond energies and band effects between these various sites.

Although use of the $3d^9$ averaged potential was adequate for description of the conduction band, this need not imply that this potential would also be adequate for describing the bond of an H atom to the Ni. In order to test the use of d^9 averaged potential for Ni-H bonds, we examined $Ni_{20}H$ with H at a twofold site (later called site A). In one calculation, referred to as $Ni_{16}Ni_4H$, all ten valence electrons were allowed full variational freedom[11] for the four Ni atoms closest to the H (a tetrahedron of Ni atoms consisting of the two surface Ni bonding to the H and the two center atoms of the cluster), and the d^9 averaged potential was used on the remaining sixteen Ni atoms. In the second calculation, referred to as $Ni_{20}H$, the d^9 averaged potential was used for all twenty Ni atoms. As summarized in Table I, these calculations yield very similar results. Once again, the $3d$ orbitals remain localized and do not participate significantly in the NiH bond. Thus *the use of the d^9 averaged potential is adequate for describing the bonding of the H to Ni clusters.* Using the d^9 averaged potential, we have calculated geometric and bonding parameters for various chemisorption sites with the results in Table II. Values not in parentheses are believed to most closely represent parameters expected on the infinite surface (*vide infra*). Trends to note are the following:

(i) Bond energies tend to increase with the ligancy of the H atom (number of nearest neighbors to the hydrogen) with $D_e = 1.6$, 2.8, 3.2, and 3.0 eV for ligancies of 1, 2, 3, and 4. The best experimental numbers suggest[1] that $D_e = 2.74$ eV for the (100) and (111) surfaces, indicating that our bond energies may be high by 0.3 to 0.5 eV.

(ii) The Ni-H bond distance increases monotonically with ligancy of the H atom with R_e(Ni-H) = 1.50, 1.59, 1.63, and 1.78 Å for ligancies of 1, 2, 3, and 4. In comparison, for diatomic NiH the bond length is 1.47 Å.[13]

(iii) The vibrational frequency of the H atom relative to the surfaces changes markedly with H ligancy, with $\omega_e \approx 275$, 170, 150, and 73 meV for ligancies of 1, 2, 3, and 4, respectively. By comparison, $\omega_e = 237$ meV for diatomic NiH.[13]

To provide further characterization of the bonding, we also considered the modifications of the band spectrum resulting from chemisorption of an H atom at different sites. Spectra for representative sites are shown in Fig. 1, illustrating the following general trends:

TABLE I. $3d$ orbital effects in bonding H to Ni_{20}.

Description of cluster atoms		Bond energy		Vibrational frequency		Bond distance	
All ten[a] valence electrons	d^9 averaged potential	(eV)	(kcal)	(cm^{-1})	(meV)	R ($\perp$) (Å)	R (NiH) (Å)
4	16	2.86	66	1507	187	1.03	1.61
0	20	2.73	63	1428	177	0.99	1.59

[a] $3d$ orbitals allowed to readjust self-consistently.

TABLE II. Bond parameters for H binding sites.

Site	Surface	Ligancy of H^a	Bond length $R_\perp{}^b$ (Å)	Vibrational frequency (meV)	Chemisorption Energy (eV)
B	⟨001⟩	1(7)	1.50	283	1.56
F	⟨110⟩	1(5)	1.49	280	1.43
C	⟨112⟩	1(7)	1.49	(231)	(1.00)
A	⟨001⟩	2(7)	0.99	177	2.73
G	⟨001⟩	2(5)	0.99	(173)	(2.17)
E	⟨110⟩	2(6)	0.93	(161)	(1.56)
H	⟨112⟩	2(5)	0.96	176	2.34
I	⟨111⟩	3(6,7)	0.78	155	3.21
D	⟨111⟩	3(5,5)	0.79	(131)	(2.12)
J	⟨001⟩	4(7,5)	0.30	73	3.04

^{a}In parentheses is the number of nearest neighbors for the Ni atom(s) at the binding site. Where nonequivalent surface atoms are present, values are given for each type.

^{b}Optimum distance from H to the plane representing the surface.

(i) For each chemisorption site, one of the cluster orbitals originally occupied in Ni_{20} is destabilized above the Fermi energy (i.e., unoccupied). Analysis of orbital shape shows this orbital to be the highest Ni_{20} orbital having significant density at the bonding site.

(ii) The group of sites used in Fig. 1 represents a series of adjacent sites on the surface of the Ni_{20} cluster. Thus moving from Fig. 1(b) to 1(f) represents a traversal around the surface of the cluster. By taking the overlap of the $Ni_{20}H$ orbitals with the Ni_{20} orbitals [Fig. 1(a) or 1(g)], it was found that the band orbitals at different sites correlate quite well (in the figure, orbitals of similar character are connected by dashed lines).

(iii) A new H-like level appears at 3 to 10 eV below the Fermi level and is denoted as "H" in Fig. 1. In all cases, this level interacts most strongly with one of two Ni_{20} levels near 13.6 eV absolute ionization potential (the value for a free H atom).

(iv) Levels excluded by symmetry from direct interaction with the H atom are shown as dashed levels. Of the levels allowed to interact by symmetry, certain ones interact strongly and are marked with thick lines in the figure. Comparing these levels with the free cluster levels from which they originate shows them to be pushed away in energy from the new "H-binding" level.

(v) The occupied band orbitals of $Ni_{20}H$ are linear combinations of the original Ni_{20} occupied orbitals, with less than 1% incorporation of empty Ni_{20} band orbitals in almost all cases.

These results suggest the following qualitative model for the hydrogen chemisorptive bond. An electron is removed from a high-lying Ni_{20} orbital directed towards the H atom, allowing the H atom to adsorb effectively as an $H^{\delta-}$ species (i.e., with a small negative charge on the H). The orbital energies of the antisymmetric orbitals are insensitive to this change, indicating that the readjustments in electron density are too small to affect orbitals not directly involved in the bond.

The variation in heats of adsorption noted in Table II may be addressed using the results of Fig. 1. Two sites, D and E in Table II, show binding energies that are significantly lower than the other values at similar sites. In Fig. 1 we see that for sites D and E it is the third-highest Ni_{20} level that is ionized [Figs. 1(e)-1(f)], while for the remaining sites in the figure it is the highest Ni_{20} orbital that is removed. The energy difference between these two orbitals is ~0.8 eV, the same magnitude as the discrepancy in the binding energies for sites D and E. Binding at all other sites considered leads to ejection of the electron from the highest Ni_{20} orbital, resulting in internally consistent binding energies. Thus we conclude that in using clusters to obtain chemisorption energies, it is essential that the cluster be such that the ground-state wave function of the cluster possesses a conduction-band orbital near the Fermi energy with large amplitude at the chemisorption site. If, in solving for the ground state of the Ni_nH complex, it is found that the ejected electron is from a deeper orbital,
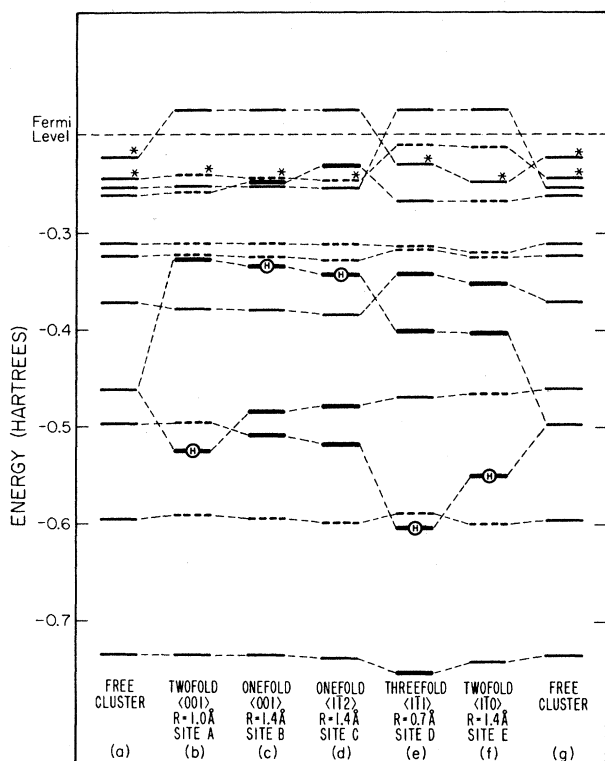
FIG. 1. Spectrum of states for Ni_{20} and $Ni_{20}H$ clusters. Levels connected by light dashed lines are of similar orbital character. Heavy lines indicate levels interacting significantly with the H atom. The H on a level indicates the orbital with maximum H character. Dashed levels are for orbitals unable to interact with the H atom by symmetry. Asterisks indicate singly occupied orbital levels. The d levels are spatially localized and have been replaced by an effective potential. The position of the Fermi level is approximate and is used primarily to distinguish between occupied and unoccupied levels.

then we expect the bond energy to be low.

In Table II we note that the bonding of an H directly on a single Ni is quite unfavorable. From Fig. 1 we note that the band spectra of the linear sites also fall into a class by themselves. Both linear sites in Fig. 1 (as well as site F, not shown) possess an "H-level" 5 to 7 eV higher in energy than any of the other sites. Apparently the presence of an Ni atom directly beneath the H atom produces a more "covalent" bond than is observed for the other sites, indicating that the cluster density at this site is not as polarizable.

The results obtained here compare favorably with the few experimental values currently available. Work function values are calculated to increase upon chemisorption of H to all Ni sites,

in agreement with available data.[1] Heats of adsorption on the two highest-density faces are predicted to be quite similar [i.e., ΔH(threefold) $\approx \Delta H$(fourfold)], also in agreement with experimental results.[1,14]

Photoemission studies for H on Ni(111) lead to a single level at 5.9 eV below E_F, with a width of 3 eV.[3] Very recent angle-resolved studies also indicate the presence of an sp surface state 0.25 eV below E_F on Ni(111) that is strongly attenuated on adsorption of H.[15] Our calculations predict the presence of this surface state and suggest the source of the attenuation (i.e., destabilization of the high-lying levels). In addition, a single broad level would be expected from our results at about 7–9 eV below E_F. We find that the width and position of this level are sensitive to $R_\perp$, but are nearly independent of site ligancy. The single exception is the unfavorable linear site.

The most sensitive experimental probe for determining the binding site is high-resolution energy-loss spectroscopy,[2] but results are presently available only for the (100) plane of Ni.[2] The observed value of 75 meV is in excellent agreement with the value (73 meV) we predict for fourfold binding on Ni(100).

[1]K. Christmann, O. Schober, G. Ertl, and M. Newman, J. Chem. Phys. **60**, 4528 (1974); J. Lapujoulade and K. S. Neil, J. Chem. Phys. **70**, 798 (1973), and references cited therein.

[2]S. Andersson, in *Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces, Vienna, 1977*, edited by R. Dobrozemsky *et al.* (F. Berger and Söhne, Vienna, Austria, 1977).

[3]H. Conrad, G. Ertl, J. Kuppers, and E. E. Latta, Surf. Sci. **58**, 578 (1976); J. E. Demuth, Surf. Sci. **65**, 369 (1977).

[4]D. J. M. Fassaert and A. van der Avoird, Surf. Sci. **55**, 313 (1976).

[5]C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baillie, and M. A. Ratner, Surf. Sci. **59**, 279 (1976); T. H. Upton and W. A. Goddard, III, unpublished results; D. E. Ellis, H. Adachi, and F. W. Averill, Surf. Sci. **58**, 497 (1976).

[6]C. F. Melius, T. H. Upton, and W. A. Goddard, III, to be published.

[7]W. A. Goddard, III, in Proceedings of the 176th National Meeting of the American Chemical Society, Anaheim, California, 12–17 March 1978 (unpublished),

Physical Chemistry Division Talk No. 30.

[8]T. H. Upton and W. A. Goddard, III, J. Am. Chem. Soc. 100, 5659 (1978).

[9]As the $3d$ orbitals of Ni are quite tightly bound, Coulomb and exchange integrals involving these orbitals are large ($J_{dd} \approx 1.0$ hartree = 27 eV). Thus, it is of utmost importance that the correct open-shell Hamiltonian be used in solving for these orbitals. Anomalously large amounts of $4s$-$3d$ mixing result when the $3d$ orbitals are forced to become delocalized through use of the incorrect or approximate Hamiltonians.

[10]T. H. Upton and W. A. Goddard, III, J. Am. Chem. Soc. 100, 321 (1978); S. P. Walch and W. A. Goddard, III, Solid State Commun. 23, 907 (1977); G. A. Ozin, W. J. Power, T. H. Upton, and W. A. Goddard, III, J. Am. Chem. Soc. 100, 4750 (1978).

[11]An effective potential was used to replace the Ar core initially [M. J. Sollenberger, M. S. thesis, California Institute of Technology, 1975 (unpublished)], and then further modified to replace the $3d^9$ core as well using the method of C. F. Melius, B. D. Olafson, and W. A. Goddard, III, Chem. Phys. Lett. 28, 457 (1974).

[12]Basis sets were those (4s) of S. P. Walch and W. A. Goddard, III, J. Am. Chem. Soc. 100, 1338 (1978). H-atom basis sets were DZ (unscaled) from S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).

[13]G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand–Reinhold, New York, 1950).

[14]Similar conclusions have been drawn from extended Hückel studies (Ref. 4); however, the predicted trend in binding energies is linear > bridge > fourfold, which is the reverse of that obtained here.

[15]F. J. Himpsel and D. E. Eastman, Phys. Rev. Lett. 41, 507 (1978).

Hydrogen on Pd(111): Self-Consistent Electronic Structure, Chemical Bonding, and Photoemission Spectra

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The electronic properties of H chemisorbed on the Pd(111) surface are studied using a self-consistent pseudopotential mixed-basis method. The H atoms are predicted to prefer a threefold hollow over the top site. Strong bonding between hydrogen and the substrate results in (a) dramatic changes in the surface electronic structure and (b) the formation of bonding and antibonding adsorbate states. The combined effects of both accurately reproduce and explain the salient features of recent photoemission measurements.

The interaction of hydrogen with group-VIII transition-metal surfaces (Ni, Pd, Pt, ...) is fundamental to the understanding of a number of physically interesting and technologically important processes. These include the dissociative chemisorption and reactivity of hydrogen on the surfaces of these metals and the solubility of atomic hydrogen (hydrogen-storage technology) in these metals. Our knowledge of H chemisorption on transition-metal surfaces is, however, quite limited. Previous theoretical (jellium-H, parametric tight-binding, and cluster) studies[1] have provided a partial picture but none of them is capable of properly describing all the known aspects of the problem. For example, a full understanding of the H-induced structures found in recent photoemission measurements and the answer to the simple, yet crucial, question of the adsorption site have been lacking.

In this Letter the results of a realistic, fully self-consistent calculation describing H chemisorption on a transition-metal surface are presented. The system observed experimentally is an ordered (1 × 1) monolayer of atomic hydrogen on the Pd(111) surface.[2] Since the adsorption site is unknown, calculations were performed for the three different high-symmetry structural geometries. Unlike previous theoretical approaches,[1] the full effects of the underlying band structure and of the various interactions (Pd-Pd, H-Pd, and H-H) at the surface are treated on an equal footing and in a self-consistent, parameter-free fashion.[3] Comparison of the calculated results with experimental spectra[4,5] shows that the H atoms prefer a threefold hollow over the top site. Strong bonding between the H $1s$ orbital and the Pd d electrons is observed which results in dramatic changes in the Pd surface electronic structure. In the preferred geometry, both an occupied H-Pd bonding surface band centered at 6.5 eV below E_F (in excellent agreement with experiment) and an unoccupied antibonding H-Pd surface band are found. Moreover, with only initial-state effects included, the theory repro-