

These experiments show that the LRO is 3-D at T_c although SRO above and below T_c has a 2-D character. The critical temperature $T_c = 122.9^\circ\text{K}$ is in reasonable agreement with earlier work.^{6, 7} No indication of a second phase transition at the lower resistivity anomaly at^{6, 7} 95°K or at the transition temperature of 98°K given by Nixon and Parry⁴ could be detected in the $hk0$ x-ray scans. Thus, the 98°K transition seems to result from additional interplane sequencing.⁶

The exponent $\beta = 0.18 \pm 0.01$ is certainly well removed from the Padé-approximant value of 0.312 for a 3-D Ising model.¹⁰ It is slightly closer to the exponent for the 2-D antiferromagnets of the class¹¹ K_2NiF_4 for which the most recent determinations by Ikeda, Suzuki, and Hutchings¹² show true 2-D Ising behavior with $\beta \approx 0.125$. Clearly a very anisotropic (essentially 2-D) interaction Hamiltonian is responsible for the intraplane ordering. Presumably a weak longer-range interaction between planes¹³ results in simultaneous interplane and intraplane ordering with no apparent transition regime from 2-D to 3-D behavior.

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Nature of the Bond in Hydrogen Chemisorption on Ni, Pd, and Pt

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We describe a model of H chemisorption on Ni, Pd, and Pt in which both extended sp bands and the more localized d bands are appropriately incorporated. It is found that interaction between the H $1s$ level and the substrate d levels plays an important role which increases in the order Ni > Pd > Pt. The results are in good accord with ultraviolet-photoelectron-spectroscopy data.

The chemisorption of hydrogen on such metals as Ni, Pd, and Pt has been extensively studied experimentally. Many theoretical calculations¹⁻⁵ exist on these systems but a clear insight into the nature of the bond still seems to be lacking.

Ultraviolet photoelectron spectroscopy (UPS)

studies⁶ on the Ni(111), Pd(111), and Pt(111) surfaces show a peak below the d band induced by H chemisorption, described in Anderson-model theories as a $1s-d$ bonding state. This contrasts clearly with the much simpler H-jellium system, where first-principles calculations⁷ reveal the

existence of a similar (but relatively broad) H-induced state considered to be largely a 1s resonance. Recent calculations for H on Pd(111) (Ref. 5) are apparently consistent with the Anderson-model picture, while in contrast results for H on Ni(111) (Ref. 4) suggest little involvement of the d band.

The parameter-free model presented here starts out from the H-on-jellium system, then adds the d band, the effect of which is seen to get partly back to the Anderson-type result. We are able to explain the observed variation in width of the H-induced peak with substrate,⁶ and other features of the systems, and to cast our results in the form of a new type of Anderson model.

A remarkably simple model able to reproduce one-electron features of the H-on-jellium calculations has been put forward by the present authors.⁸ The model simply takes a square barrier for the jellium surface and adds a muffin-tin contribution of 1-a.u. cutoff radius for the H atom. The potential inside the H muffin tin, $-2.7e^{-r}$ (in atomic units and with bottom of sp band as energy zero), is chosen to give correct results for H in bulk jellium.⁹

The Muscat-Newns (MN) model⁶ may be naturally extended to transition-metal (TM) substrates by adding muffin tins centered on the TM atoms. When the $l=0$ and $l=1$ logarithmic derivatives of these muffin tins are sufficiently free-electron-like, we need only take into account their $l=2$ logarithmic derivatives. But this 1s- d interaction should be largely local. This suggests that an embedded-cluster approximation, in which only muffin tins belonging to the hydrogen and its TM nearest neighbors are included in the calculation, should be rather good. Since the method depends essentially only on the $l=0$ and $l=1$ logarithmic derivatives being reasonably free-electron-like, it is inherently superior to the strictly localized clusters employed with the $X\alpha$ scattered-wave technique.³

By an extension of the methods of Ref. 8, we calculate the cluster density of states $N(\epsilon) = -(2/\pi)d \arg(\det A)/d\epsilon$ and the chemisorption-induced density of states $\Delta N(\epsilon) = -(2/\pi)d \arg(Z)/d\epsilon$ in terms of the matrix A , where

$$A_{ilm, j'l'm'} = \gamma_{jl'} \langle ilm | G^0(\vec{r}, \vec{r}') | j'l'm' \rangle - \frac{\partial}{\partial r'} \langle ilm | G^0(\vec{r}, \vec{r}') | j'l'm' \rangle, \quad (1)$$

$$Z = A_{H00, H00} - \sum_{\alpha, \beta} A_{H00, \alpha} A_{\alpha\beta}^{-1} A_{\beta, H00}. \quad (2)$$

Here $G^0(\vec{r}, \vec{r}')$ is the Green's function of the square barrier. In this work we are mainly interested in energies well below the top of the barrier, for which we have found that it causes very little error if G^0 is calculated using the eigenstates of an appropriately displaced infinite barrier. The position of the infinite barrier is obtainable relative to the nickel lattice by charge-neutrality arguments in terms of the number N_s of sp electrons per TM atom. In Eq. (1), i and j are TM sites and l, m and l', m' refer to angular momenta. $\langle ilm | G^0(\vec{r}, \vec{r}') | j'l'm' \rangle$ is defined by setting \vec{r} and \vec{r}' , respectively, on to the surfaces of spheres i, j and then integrating $Y_{lm}^*(\Omega_i) G^0(\Omega_i, \Omega_j) Y_{l'm'}(\Omega_j)$ over Ω_i, Ω_j . $\gamma_{jl'}$ are the logarithmic derivatives at energy ϵ of the wave functions of angular momentum l' inside the muffin tin j on the surface of the sphere at j .

H on Ni(111) is known from low-energy electron diffraction (LEED)¹⁰ to occupy equivalently the two possible threefold-coordinated hollow sites, for which the cluster of nearest-neighbor Ni atoms is, respectively, an equilateral triangle or a regular tetrahedron. Since our results are very similar for these two types of cluster, only the triangular cluster is considered in the following. For H on Ni the H-Ni distance is LEED determined,¹⁰ but on Pd and Pt we have had to make an estimate of the distance (see Table I). The potential of the H muffin tin is the same as that used in the previous jellium work (see above), while we have used best available band-structure potentials for the TM muffin tins.¹¹

The principal curves in Fig. 1 show $N(\epsilon)$ for the Ni₃H and Ni₃ clusters, the difference between these being, of course, $\Delta N(\epsilon)$. The Ni₃ cluster shows little density of states outside the " d band." The Ni₃H cluster shows a distinctive H-induced

TABLE I. Parameters and results. N_s is the number of s electrons per TM atom; d_H is the distance between proton and surface plane of TM atoms; n_T is the integral of adsorbate-induced density of states (DOS) up to ϵ_F ; n_{TM}^e is the integral of adsorbate-induced DOS up to $\Delta N = 0$; and $n_{jellium}^e$ is the jellium-substrate-induced DOS up to $\Delta N = 0$.

	N_s	d_H	n_T	n_{TM}^e	$n_{jellium}^e$
Ni	0.6	2.2	0.60	1.67	1.16
Ni	1	2.2	0.58	1.65	1.00
Pd	0.4	2.5	0.64	1.87	1.28
Pt	0.4	2.5	0.39	1.87	1.24

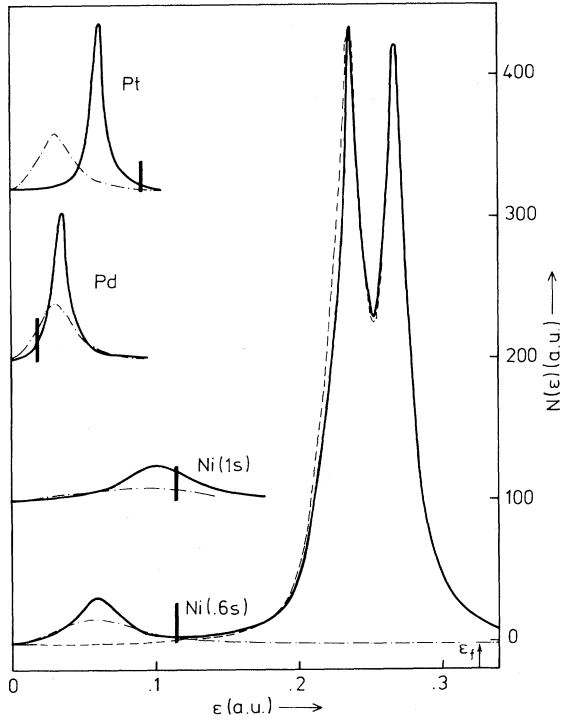


FIG. 1. Lower curves: $N(\epsilon)$ for Ni_3 (dashed curve), for Ni_3H (full curve), and for jellium-H (dash-dotted curve). Insets are $\Delta N(\epsilon)$ for Ni_3H , Pd_3H , and Pt_3H (full curves) and jellium-H (dash-dotted curves). Scales are uniform. Positions of ultraviolet-photoelectron-spectroscopy peaks are given by vertical bars.

resonance below the d band, and a depletion in density of states from the bottom of the d band. For Pd_3 and Pt_3 the d bands are wider in the order $Pt > Pd > Ni$ but the H-induced structures are qualitatively the same as for Ni. These findings for the chemisorption-induced $\Delta N(\epsilon)$ also seem to resemble the effects found on alloying H in Pd.¹²

For H on Ni, where the H position is accurately known, the energy of the resonance, taking no account of a relaxation shift, agrees better with UPS results on an assumption of 1 rather 0.6 sp electron per Ni atom; the former choice is based on an allowance for $sp-d$ hybridization. Comparison is made in Fig. 1 between the widths of the resonances and the H-on-jellium results obtained on removing the TM muffin tins. We see

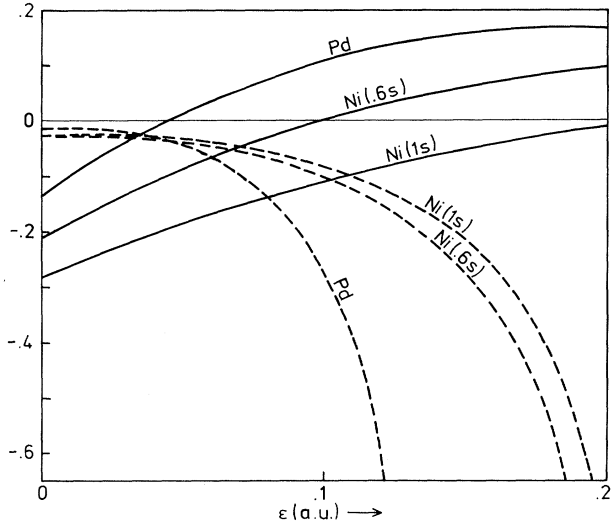


FIG. 2. Terms in Eq. (2): first term (full curves) and second term (broken curves).

that the H-on-TM resonances are narrower than the H-on-jellium resonances, and are narrower on Pd and on Pt than on Ni. The latter result is very distinctive—not varying, for example, with H position. It is also distinguishable in the ultraviolet-photoelectron-spectroscopy results⁶ that the Pd and Pt resonances are indeed narrower. This constitutes the first success of our model, though a similar result has been obtained in a model calculation by Schönhammer.¹

For self-consistency the integral of $\Delta N(\epsilon)$ up to ϵ_F would be $n_T = 1$ electron, but in practice n_T is found to be smaller (see Table I). The deficit means that, e.g., for Ni, 0.4 hole must come out of the d band per H atom—a result in fair agreement with that deduced (~ 0.6 hole) from the reduction in magnetic moment per H atom adsorbed.¹³

It is also useful to integrate ΔN up to $\Delta N = 0$, to give the number of electrons n^e bound by the resonance (see Table I). We see that n^e is greater for TM than jellium substrates, and approaches 2 for Pd and Pt. This is remarkably similar to the old Anderson model, in which the resonance would be a virtual $1s-d$ bound state containing two electrons.

In fact, our formula for ΔN resembles that in the Anderson model, which is reproduced on redefining Z as

$$Z = \epsilon - \epsilon_{\text{eff}} - \sum_{\alpha, \beta} \langle 1s | V | \alpha \rangle \langle \alpha | (\epsilon - H_0 + is)^{-1} | \beta \rangle \langle \beta | V | 1s \rangle. \quad (3)$$

In (3) ϵ_{eff} is an effective $1s$ level, α and β run over the neighboring d orbitals, and H_0 is the Hamiltonian of the free TM surface. If now we make the assumption of perfectly free-electron-like $l = 0$ and

$l=1$ logarithmic derivatives, the second term of (2) contains only $l=2$ α and β , there being now a compelling analogy between the two terms in (2) and those in (3). The terms in (2) are plotted in Fig. 2, where it is seen that their behavior is not dissimilar to their analogs in the regular Anderson model (3). However, while the second term in (3) describes the effect of the d orbitals on the unperturbed $1s$ level, that in (2) describes the effect of the d orbital on an H atom already adsorbed onto jellium. The two models seem to be different representations of the same problem.

In Fig. 2 the energy of the resonance is given by the intersection of the two curves. The broken curve is seen to be strongly negative going above the resonance; this acts to ensure the saturation of the resonance, i.e., large $n^e \sim 2$. The larger $d \operatorname{Re}(Z)/d\epsilon$, the sharper the resonance, and so we see that the steepness of the broken curve ensures the narrowness of the resonance even well above the bottom of the sp band in which region only broad resonances are found on jellium. The virtual $1s$ - d bound-state picture of the regular Anderson model proceeds from quite analogous considerations based on Eq. (3).

In conclusion, it is found that bonding between the H $1s$ level and the substrate d band plays an essential role in the chemisorption of H on Ni, Pd, and Pt.

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