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## A tight-binding study of hydrogen chemisorption on Pt<sub>7</sub>/Ni(111) and Pt/Ni(111) systems

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**Abstract.** We study the electronic structure of a Pt overlayer and Pt<sub>7</sub> adatom cluster, respectively, on the Ni(111) surface by using a self-consistent tight-binding model. Together with epitaxial geometries, a mean-field 'non-epitaxial' model is also employed. For these structures, calculations for hydrogen adsorption are performed. Correlation between the geometry, surface reactivity, core-level shifts and local surface electronic structure has been recently discussed for Pd and Pt ultrathin films on bcc substrates. Similar correlation is also found in the present study. Nevertheless, its origin is now traced to the change of the local d-band width due to overlayer compression rather than to a specific hybridization between orbitals on different atoms. An analogy with PtNi alloy surfaces and their catalytic properties is pointed out.

### 1. Introduction

Surface science of bimetallic systems is presently developing rapidly. Although a vast variety of bimetallic surfaces can be prepared, a number of characteristic features are often common to unlike surface structures. Thus, by studying a particular system, there is a hope of acquiring information that is of more general validity.

It is amazing how rich a set of phenomena is displayed by bimetallic systems with isoelectronic constituents. In the present paper we intend to study theoretically Pt<sub>7</sub> adatom cluster on Ni(111) surface and hydrogen chemisorption at this and some related systems. Experimentalists agree that Pt grows epitaxially (pseudomorphically) on Ni(111) in the submonolayer range and perhaps even an epitaxial Pt overlayer can be formed [1–3]. Yet one can wonder whether in the adatom islands numerous defects such as vacancies or buckling are not present that release to some extent the stress originating from the 11% misfit between the Pt and Ni atomic radii. Other arguments in favour of a departure from ideal pseudomorphism will be given later. The specific role of the Pt/Ni(111) system is accentuated by its close analogy to the case of the popular PtNi alloy. It has been established experimentally [4–7] that Pt segregates on the (111) face and at stoichiometry close to 1:1 forms a quasi-pure Pt layer, whereas the subsurface layer becomes Ni-rich. The effect is accompanied by a drop in chemisorption heats for CO and hydrocarbons; a large reduction of the hydrogen adsorption is evidence for the 1:1 composition—it seems that H adsorbs only at sites with a Ni atom at the surface [7]. For the (110) surface the segregation trend is just reversed with some reduction of the reactivity of the Ni-rich surface as well. The Pt overlayer compression as a possible source of this behaviour has been considered [4, 5]. It follows from the bond-length analysis in PtNi alloys [8, 9] that the Pt-rich (111) face is stressed, although less than the pseudomorphic Pt layer on Ni(111), whereas the Ni-rich

(110) surface gets strained. We note that the Pd/Ni(111) system has also been studied experimentally [10].

Recently, the present authors [11] employed semiempirical methods to calculate the local density of electronic states (LDOS) and the initial-state component of the core-level shift (CLS) for small Pt<sub>N</sub> ( $N \leq 7$ ) clusters grown on Ni(111). It appeared that the results were highly sensitive to the Pt–Pt distance. Further we have extended the study to a Pt overlayer on Ni(111), and to a single hydrogen atom on H(1 × 1) overlayer adsorbed on it. To this goal the tight-binding model [12] and the extended Hückel method [13] were used. Together with epitaxial Pt growth, also a ‘non-epitaxial’ mean-field Hamiltonian was constructed (see below). The results confirmed a reduced Pt-atom reactivity, which was again strongly sensitive to the Pt–Pt separation. Here, we consider hydrogen chemisorption on and near the Pt<sub>7</sub> adatom cluster. A few results obtained in papers [11, 12] are presented for comparison as well.

## 2. Model

We use the tight-binding s–d electron Hamiltonian described in detail for metallic systems in [14]. The hopping matrix elements are constructed from the most localized LMTO (linear muffin-tin orbitals) parameters by scaling with the tabulated [15]  $\bar{\Delta}_x$  factors ( $x = s, d$ ):  $h_{ij} \rightarrow \bar{\Delta}_x^{1/2} h_{ij} \bar{\Delta}_y^{1/2}$ . In analogy to the Shiba approximation known in alloy calculations, we apply the above formula also when the indices  $i, j$ , and hence also  $\bar{\Delta}_x, \bar{\Delta}_y$ , are associated with different kinds of atoms. Besides that we suppose  $R^{-1}$  ( $R^{-5}$ ) distance dependence of  $\bar{\Delta}_s$  ( $\bar{\Delta}_d$ ). As a consequence the d–d hopping elements for Pt in epitaxial structures, i.e. with the Ni first-nearest-neighbour (NN) interatomic distance, are enlarged by about 1.7 times. The M–H ( $M = \text{Ni, Pt}$ ) interactions are derived from the fit for palladium hydride [16]. Within the above simplifications, the Pd–H matrix elements are first brought to the appropriate interatomic distance  $R$  and then multiplied by the factor  $[\bar{\Delta}_x(M, R)/\bar{\Delta}_x(\text{Pd}, R)]^{1/2}$  with  $x = s$  (d) for ss (sd) interactions [17].

The interatomic distances we use conform with the respective atomic radii sums. For hydrogen the atomic radius  $r_H$  varies considerably throughout chemisorption systems [18]. In the previous study [17] for H chemisorption on Pd(111) and Pt(111) surfaces, respectively, we reproduced the position of the H-derived state seen in photoemission spectra by taking  $r_H \sim 0.5$  Å, and the same was checked for the Ni(111) substrate (see below). Since the H-derived peak represents a stringent test for model assumptions [19], the above results give us some confidence in our model. Because of a rather large change when scaling the matrix elements from PdH [16] to the chemisorption system, and the approximate nature of the scaling itself, the metal–H distance guess is only approximate, too. Ni atoms are treated as paramagnetic ones. We take  $N_d = 9$  for the d-electron count for both Ni and Pt bulk atoms, which ensures the correct position of the Fermi level  $E_F$  when compared with the literature LDOS. The model is not sensitive to s-electron parameters and we take the occupation  $N_s$  from [15]. It is likely that the usual model utilizing solely the metal d electrons would be able to describe the phenomena we are interested in. Nevertheless, in crystals containing late transition metals, low-density tails in LDOS are readily formed at the Fermi level and they are better described when a hybridization with s electrons is allowed [14]. We do not consider any charge transfer between Ni and Pt atoms, and  $N_s$  and  $N_d$  are fixed at bulk values for all metallic atoms. Small charge transfer onto H could take place, although it should be very limited owing to the high electronegativity of Ni and Pt. We have found previously, however, that the best results are obtained in the locally charge-neutral

model [17] (cf also [20, 21]). To respect the local charge neutrality we use a self-consistent procedure consisting of shifting the local diagonal matrix elements (Coulomb integrals) for *s* and *d* electrons, respectively. The charge values are calculated by the recursion method with 24 Hamiltonian moments evaluated for any orbital considered [14].

Let us give additional information on self-consistency. For the semi-infinite Ni(111) crystal we adjust Coulomb integrals on the first four atomic layers; it is supposed that on the fourth layer, the bulk situation is attained. The next system to study is the Pt<sub>7</sub> cluster with Pt adatoms above FCC-like sites on Ni(111) (see figure 1). We find the Coulomb integrals for the two non-equivalent kinds of Pt atoms, and also for their first and second nickel NN. On more distant atoms, values from the Ni(111) model are retained. When the hydrogen in a threefold site is chemisorbed we calculate Coulomb integrals on it and on its first and second (Pt or Ni) NN; the values from Pt<sub>7</sub>/Ni(111) and Ni(111) calculations are again ascribed to more distant atoms. A similar scheme has been applied also to geometries not considered here in detail [12, 17]. Particularly, it has been checked that Coulomb integral changes on third and more distant NN of H are very small [17].

We consider also a 'non-epitaxial' model [12] in which the Pt-Pt hopping elements are not scaled to the reduced separation but keep the Pt bulk values. Such an assumption represents a mean-field model reflecting the situation when the Pt-adatom coordination is reduced by vacancies or the full compression to the Ni first NN distance is not achieved. The mean-field models in alloy calculations can fail easily (cf the virtual-crystal approximation [22]) if the existence of different kinds of interactions is not respected. This is not the case here, and we believe that comparison of our epitaxial and non-epitaxial model results will allow us to understand better the role of the surface stress in PtNi systems.

We define the adsorption energy  $E_a$  per hydrogen atom as the hydrogen binding energy minus half the dissociation energy of H<sub>2</sub>. The binding energy is equal [20] to  $-(\Delta E_{\text{band}} + E_{\text{rep}})$  where [23]

$$\Delta E_{\text{band}} = \sum_j \left( \int^{E_F} E \Delta \rho_j dE - N_j \Delta \epsilon_j \right) \quad (1)$$

is the change of the band energy due to the chemisorption. In equation (1)  $\rho_j$  is the partial LDOS associated with an orbital  $\phi_j$ ,  $N_j$  is the corresponding electronic occupation and  $\Delta \epsilon_j$  is the change of Coulomb integral. In our calculation the sum in equation (1) extends always over the H adatom and its first and second NN.  $E_{\text{rep}} = \sum_j \Phi_j(R_j)$  is the sum of pairwise repulsive terms acting between hydrogen and its metallic first NN at distance  $R_j$ . We suppose that H-Pt (H-Ni) distance is always the same as at the Pt(111) (Ni(111)) surface. Since we are always most likely close to the equilibrium position the first derivatives of the total energy with respect to the hydrogen coordinates are small. Subsequently, the error we introduce by neglecting the bond-length optimization is also small. (In other words the errors in  $E_{\text{band}}$  and  $E_{\text{rep}}$  nearly cancel mutually.) On the other hand, owing to the above simplification we can express  $E_{\text{rep}}$  by using only two constants,  $\Phi(\text{H-Pt})$  and  $\Phi(\text{H-Ni})$ , that are readily fitted. It is convenient to write

$$E_a = E_a^0 + (\Delta E_{\text{band}} - \Delta E_{\text{band}}^0) + (E_{\text{rep}} - E_{\text{rep}}^0) \quad (2)$$

where the superscript '0' refers to the reference system Ni(111) or Pt(111), and  $E_a^0$  is the experimental value [18],  $E_a^0(\text{Ni}(111)) = 0.49$  eV/H atom,  $E_a^0(\text{Pt}(111)) = 0.28$  eV/H atom.  $E_{\text{rep}}$  can be fitted to the latter values. Moreover, in all the cases we study with the exception of the adsorption site C (figure 1), we have  $E_{\text{rep}} = E_{\text{rep}}^0$  because of the above

simplifications. By using the equation (2) containing the experimental value  $E_a^0$  we bypass dangerous problems such as the change of many-body contributions to energy when going from bare to chemisorbed H atom.

Core-level shifts (CLS) are of major interest in similar systems [3] since they can serve, more or less, as fingerprints of the local geometry. To get accurate values, demanding calculations are to be performed [24]. There are, nevertheless, many applications of simplified theories considering either initial-state or final-state effects only in the photoemission. The two approaches provide comparable results ranging from excellent agreement with experimental values to a rough CLS guess. The recent development in this field sheds some light on the elusive question of surface CLS origin. The calculations [25] suggest that the initial-state picture might be a fair approximation and the first principles study [26] of surface CLS in transition metals shows that the error introduced in this way is about 0.2 eV or less. Another theoretical paper [27] indicates that the use of Slater's transition state, situated formally halfway between the pure initial-state and final-state pictures, respectively, offers further improvement. In our method we can calculate the initial-state part of CLS (chemical shift) if we accept the idea that the outer-core electrons feel similar potential changes as the compact d electrons. Then CLS can be expressed as  $-\Delta(\epsilon_d - E_F)$  where  $\Delta\epsilon_d$  is the shift of the local d-electron Coulomb integral, which is identical to the shift of the d-electron LDOS centre of gravity. For the late transition metals the generally observed negative surface CLS are consistent with the picture [28, 29] in which the effective surface band narrowing caused by the reduced surface-atom coordination tends to increase the local d-electron count and must be opposed by a repulsive change of the potential ( $\epsilon_d > 0$ ). For the (111) face of (paramagnetic) Ni, Pd and Pt our model predicts [29] the surface CLS of  $-0.25$ ,  $-0.33$  and  $-0.43$  eV, respectively, close to the available data ( $-0.2$  to  $-0.3$  eV for Pd(111),  $-0.4$  eV for Pt(111) [26, 27] and about  $-0.2$  for nickel surfaces). In the compressed Pt structures that we study here, an opposite effect can take place: because of the Pt-Pt hopping elements enlargement an effective d-band widening can occur making CLS positive. In other words, the lower coordination and surface layer compression are two competing mechanisms deciding upon the CLS sign.

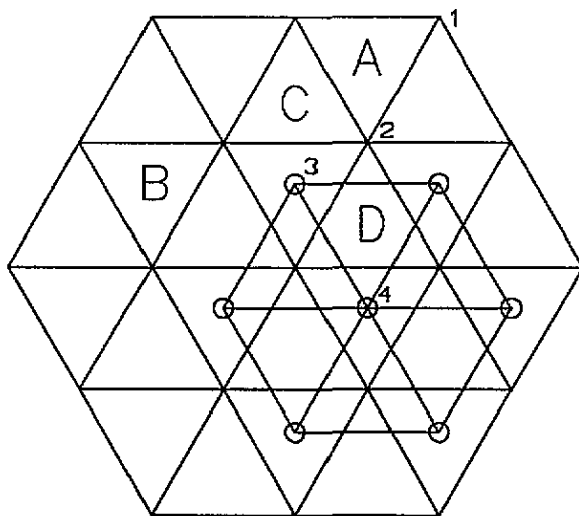


Figure 1. The Pt<sub>7</sub> adatom cluster (O) on the hexagonal Ni(111) surface. A–D label different hydrogen adsorption sites; numbers stand for selected Ni (1,2) and Pt (3,4) atoms.

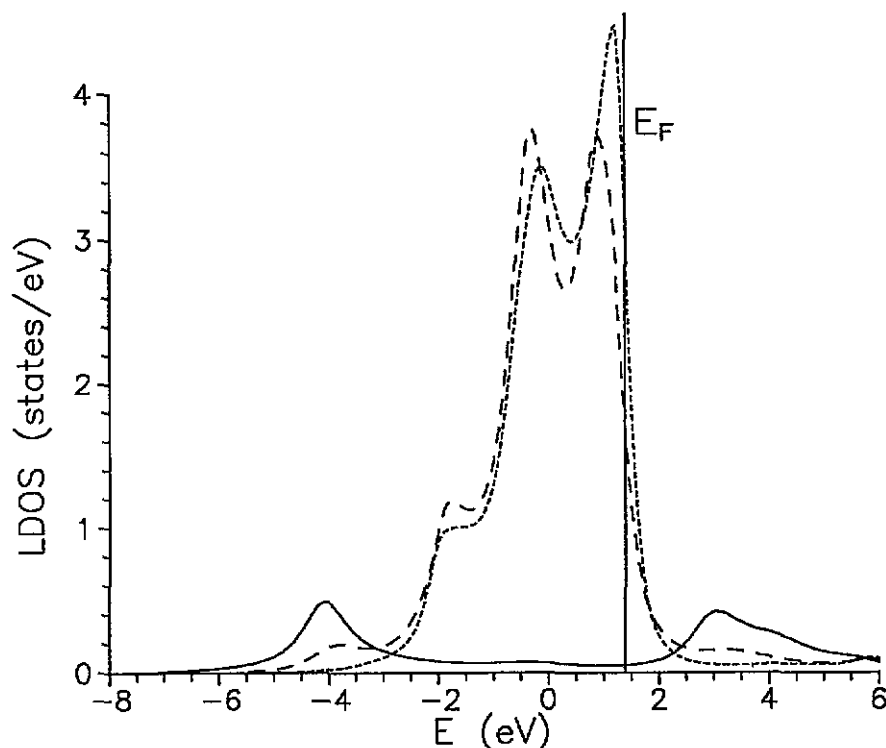


Figure 2. The local density of electronic states (LDOS) for a single H atom (—) adsorbed on Ni(111), and the *d*-electron LDOS at the hydrogen Ni nearest neighbour (---), and at a free Ni(111) surface atom (.....).

### 3. Results and discussion

Let us discuss the changes in the LDOS introduced by the chemisorption. The results could enable, in principle, comparison with photoemission spectra. Unfortunately, for surfaces of Pt–Ni systems we are aware only of unpublished results (see below) that provide limited information. We shall open the discussion by considering the Ni(111) surface. For the H(1 × 1) overlayer we get [12] agreement with the experimental position of the H-induced split-off state at 5.9 eV below  $E_F$  [18]. The LDOS is not shown here since it resembles in many respects the published results [17] for H(1 × 1)/Pd(111). In contrast to the latter system, however, the split-off feature on Ni(111) does not have the two-peak structure, which is most probably caused by a different interaction with Ni *s* electrons. In figure 2 we show LDOS for single H at the threefold site above Ni(111). At low H coverage the perturbation of substrate *d*-electron LDOS (which represents the main contribution to photoemission spectra) is not large [17] and this is especially true for the Ni(111) case. Hence, our LDOS corroborate the hypothesis [17, 30] that the lack of new features in photoemission spectra [31] from Ni, Pd and Pt(111) surfaces, respectively, at low hydrogen coverage, does not need special effects to be invoked for its explanation. In figure 3 we display results for the adsorption site A near the epitaxial Pt<sub>7</sub> adatom cluster. For the non-epitaxial cluster as well as for the adsorption site B the results are much alike.  $E_a$  is somewhat smaller (see below or [12]) than at the ideal Ni(111) surface but the corresponding LDOS presented in figure 3 are quite

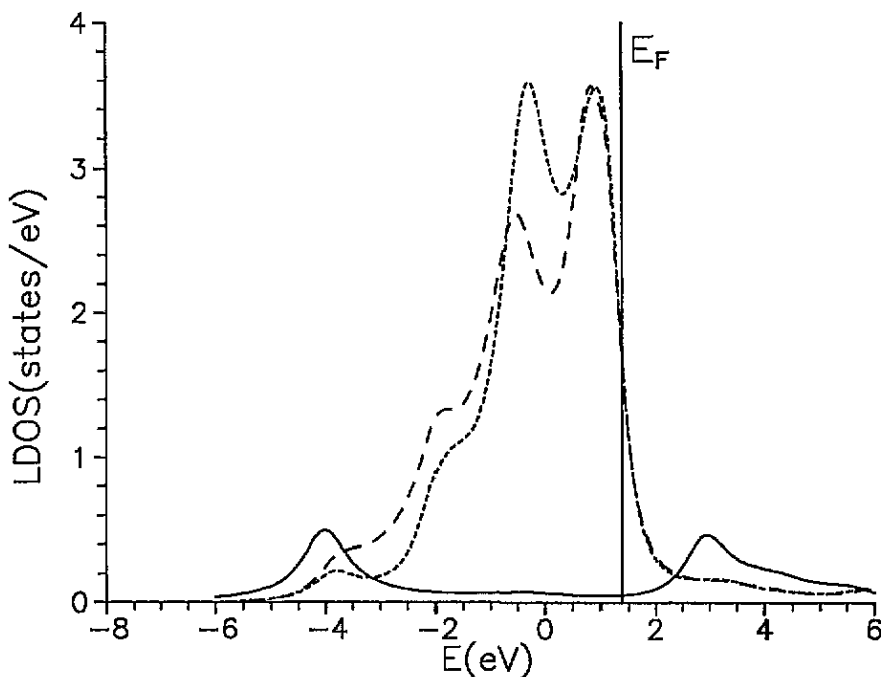


Figure 3. LDOS for H adsorbed at the site A near the epitaxial Pt<sub>7</sub> cluster (—), and the d-electron LDOS at Ni atoms 1 (---) and 2 (.....) (figure 1).

similar. We see that it is difficult to suggest a simple and at the same time accurate criteria relating the chemisorption bond strength and LDOS, although such a possibility exists in many important situations (see below).

The HCP-like site C is an analogue of a step site [20]. For a hydrogen atom at this site and for our choice of hydrogen atomic radius the separation between H and its first NN in the Pt<sub>7</sub> cluster (atom 3 in figure 1) is equal almost exactly to the corresponding atomic radii sum. However, the energy of the additional H–Pt bond is not large enough to outweigh the H–Pt repulsive term and  $E_a$  is again lower than on Ni(111). It is interesting that an analogous conclusion was reached for the hydrogen atom at the ledge site just below the step on a BCC metal (110) surface [20]. We conclude that the Pt cluster poisons partly adsorption sites in its very neighbourhood. The results are similar for the epitaxial and non-epitaxial clusters. Such a behaviour can be rationalized within the bond-order conservation picture [32] for sites A and B: if a Ni surface atom gets bonded to an additional Pt atom, its ability to form other bonds must be reduced.

Electronic properties of the Pt<sub>7</sub> cluster depend strongly on the postulated Pt–Pt separation. Let us consider first the LDOS without the H chemisorption (figures 4 and 5), which have been described only partly in [11]. One should realize that the d-band width of the elemental Pt is almost twice as large as that of Ni [15, 23] and, as a result, the adatom-cluster d-band spectrum is wide enough to produce some LDOS features outside the substrate d band. The effect is naturally much stronger for the epitaxial case. If there were no s–d hybridization these features would have the form of  $\delta$ -functions in LDOS and they would belong to the point spectrum. It is only because of the interaction with the wide s band that they acquire a finite width. In this process s electrons on both Pt atoms and Ni atoms close to the cluster participate. This kind of hybridization that we find for the cluster

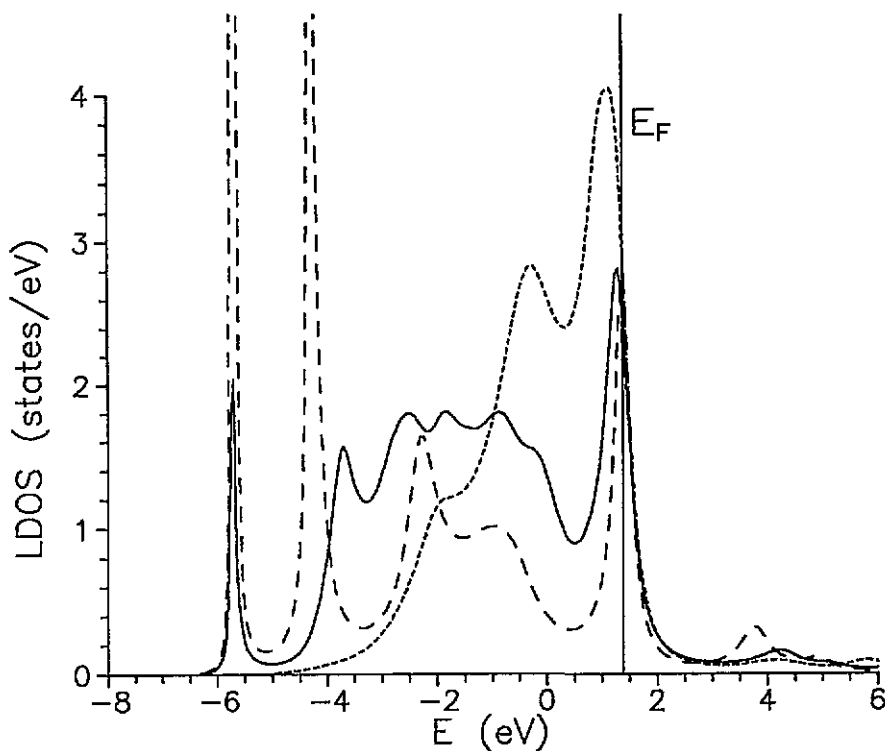


Figure 4. The d-electron LDOS at the epitaxial Pt<sub>7</sub> cluster for atom 3 (—), atom 4 (---) and Ni atom 2 (.....) (figure 1).

at the bottom of valence bands is quite remarkable since it is symmetry-forbidden at the point  $\Gamma$  of the Brillouin zone in bulk crystals of elemental metals and it is not strong at their high-symmetry surfaces. Such a hybridization has been documented, however, also for a Pd monolayer, be it free-standing or adsorbed [33]. Comparison with LDOS for the Pt(111) surface (see e.g. [12]) is difficult but some states are clearly transferred from the region just below  $E_F$  to higher binding energies. The LDOS at Pt atoms in the epitaxial cluster is depleted near  $E_F$  as compared with the non-epitaxial cluster; the effect is best visible at about 1 eV below  $E_F$  (see the large dip in LDOS for the central Pt atom in figure 4) and is related to the local d-band widening. The effect is yet more pronounced for the Pt overlayer on Ni(111) [11, 12]. The changes due to hydrogen adsorbed at the site D (figure 1) are depicted in figures 6 and 7. The perturbation of bonding d-electron states is clearly seen; the position of the obvious split-off state is rather different for the two geometries we consider. The geometry effect upon the chemisorption is drastic (figure 8): for the epitaxial cluster  $H_2$  dissociation is highly unfavourable, whereas in the non-epitaxial model the binding energy of H is higher than on Pt(111). The latter effect is caused by high reactivity of the cluster peripheral atoms. Similarly, on the epitaxial Pt/Ni(111) surface  $H_2$  should not dissociate (figure 8, see [11] for details). The results are again consistent with the bond-order conservation theory [32]. In the epitaxial geometry the short Pt–Pt bonds are too strong and prevent the Pt atoms from participating in other strong bonds; the peripheral atoms are more active because of their low coordination.

It is tempting to draw more general conclusions from results on particular systems. It



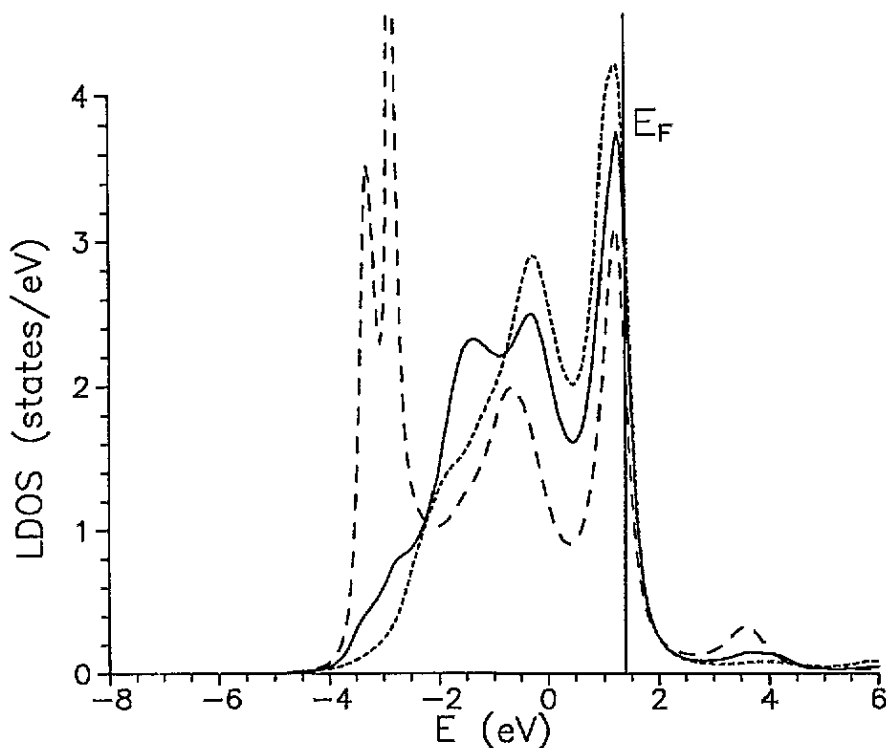


Figure 5. The same as figure 4 for the non-epitaxial Pt<sub>7</sub> model.

has been observed for ultrathin Pd films deposited on various unlike substrates that their smaller chemical activity towards CO and H chemisorption correlates with a depletion (before chemisorption) of LDOS below  $E_F$  [34,35]. An analogous situation is found [36] also for Fe/Rh(100). This is an appealing correlation since it is suitable for experimental study. It can be intuitively explained by simple formal models describing the interaction between empty and occupied effective levels (cf e.g. the HOMO-LUMO theory and [23]), since the stabilization decreases as the levels move away from  $E_F$ . A similar reasoning is often capable of coping with the observed chemisorption trends, but the definition of effective levels and interactions lacks a rigorous ground. We are going to show that in our case (isoelectronic metals) the chemical activity versus LDOS correlation is more or less right as well. For our purposes the metal d electrons are decisive. Although the chemisorption energy varies considerably from site to site, the contribution to  $\Delta E_{\text{band}}$  (1) coming from the metal s electrons is almost constant: for various sites it is 0.54–0.59 eV for H interacting with three Pt atoms and 0.68–0.73 eV for H above Ni atoms. As far as the d-electron LDOS is concerned, the peak around  $E_F$  lies at slightly lower energy for Ni surface atoms that are in direct contact with the Pt<sub>7</sub> cluster and which we have found to be less reactive. For the epitaxial Pt<sub>7</sub> cluster (figure 4) and the epitaxial Pt overlayer [11] LDOS is also transferred from  $E_F$  and a region below it to higher binding energies. Because of large differences between LDOS at the Pt(111) surface and Pt structures considered here, respectively, the depletion of LDOS has a non-uniform character and is best discerned at energies lying somewhat away from  $E_F$ . This picture should be compared with the systems reviewed in [34,35] where LDOS is subject to a rather uniform downward shift.

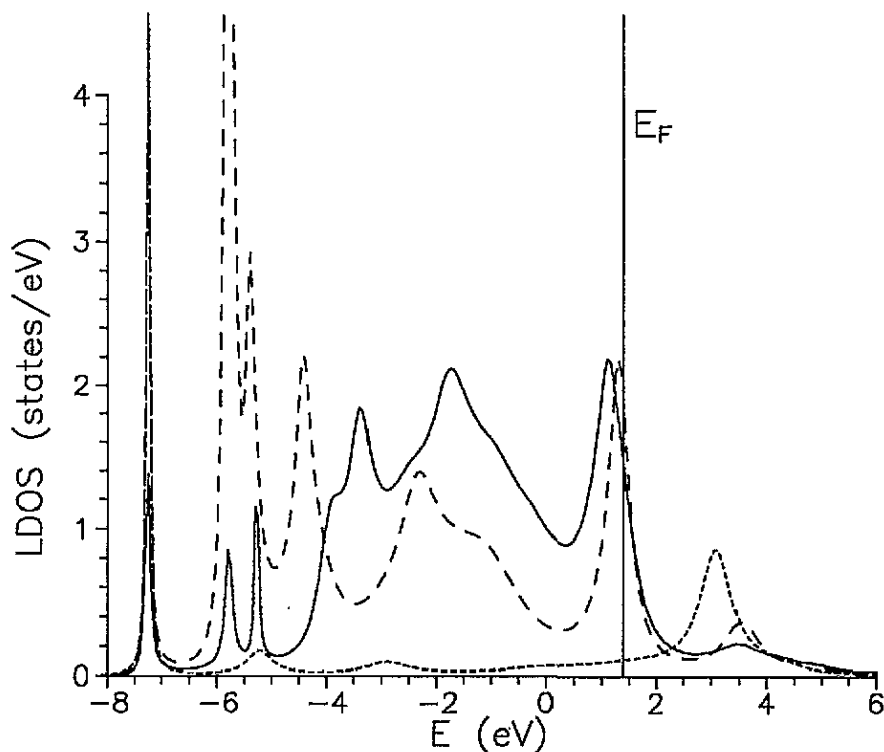


Figure 6. LDOS at the H atom (.....) adsorbed above the epitaxial Pt<sub>7</sub> cluster at the site D, and for Pt atoms 3 (—) and 4 (---).

The relation of CLS to other system properties is of considerable interest. For thin Ni, Pd, Pt and Cu films on a more electropositive BCC crystal substrate, the overlayer surface core level moves to a higher binding energy and, simultaneously, a decrease of the chemisorption energy of CO in these systems takes place [34, 35]. The likely link to the previous discussion of the role of LDOS is the fact that core levels and LDOS apparently move in the same direction. According to our opinion [17] the positive surface CLS in the just-mentioned systems result mainly from an 'asymmetric d-band widening': the hybridization of the surface d band with the substrate d band lying at higher energy produces a low-density tail in the surface-atom LDOS extending above  $E_F$ . To avoid a considerable departure from local charge neutrality the potential must get more attractive, thus making CLS positive. The overall downward shift of the surface LDOS is mainly due to the interaction between the surface and substrate d bands (cf the quantum-mechanical repulsion of two energy levels), although the potential change partly contributes, too. In any case, the magnitudes of the CLS and d-band shift, respectively, reflect (each in its own way) the strength of the surface-subsurface interaction, and it seems natural [32] that if this interaction is stronger the surface propensity for chemisorption is lowered. For Pt-Ni systems treated in our study the mechanism is somewhat different since Pt and Ni are isoelectronic, and CLS are controlled grossly by the surface d-band width (see below). The quantities under consideration thus reflect to a considerable degree the magnitude of the surface interatomic bond-length contraction. In figure 8, which is constructed in analogy to [34], we show that the correspondence between CLS and chemisorption energy changes is fulfilled rather well in

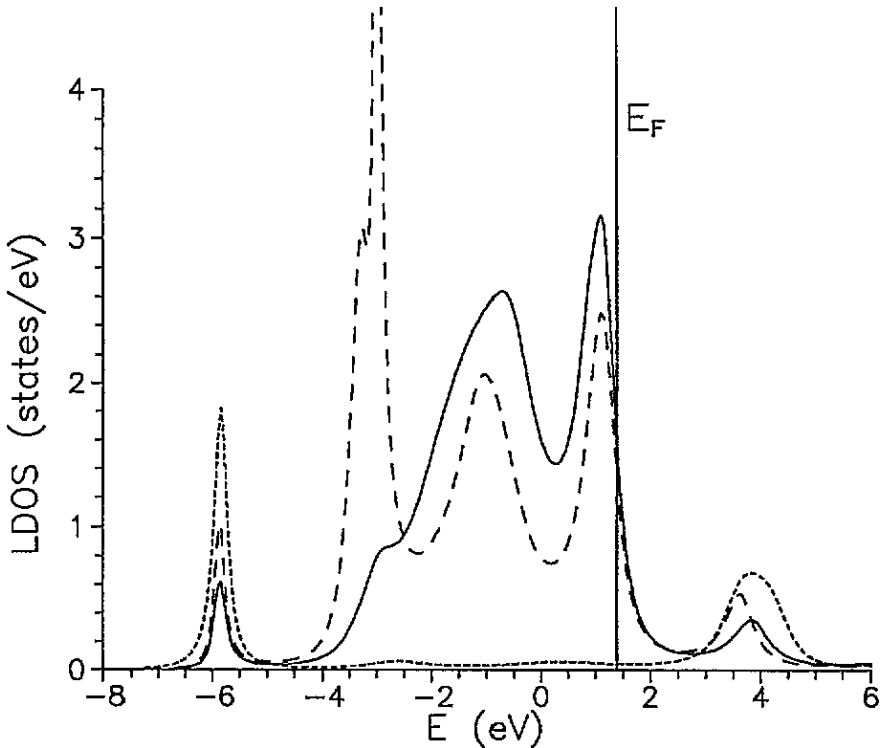
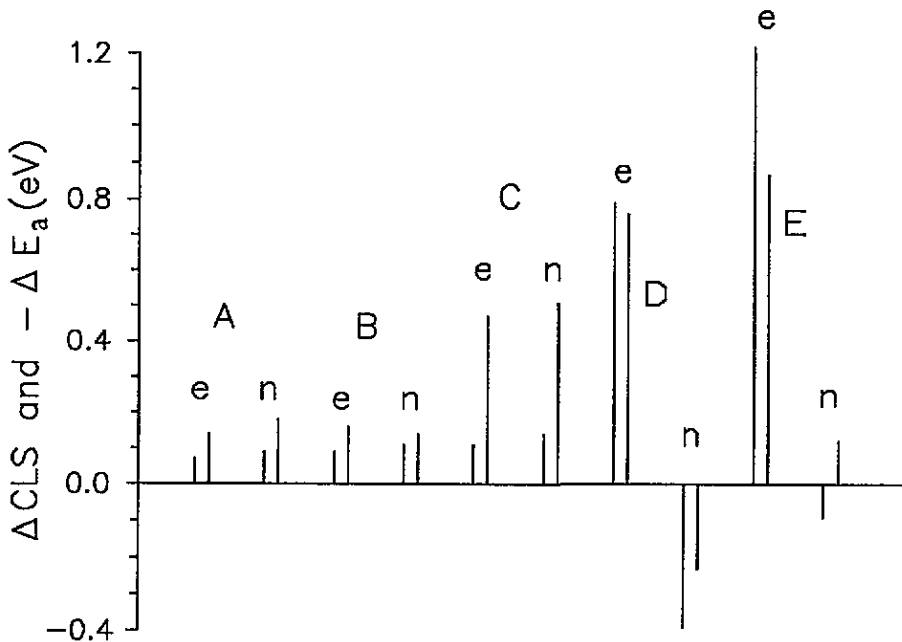


Figure 7. The same as in figure 6 for the non-epitaxial Pt<sub>7</sub> model.

our calculation, the only exception being the non-epitaxial Pt overlayer where the changes are small. In figure 8 we display the average change of CLS (before chemisorption) evaluated for the three Ni atoms determining a particular chemisorption site A–C together with the  $E_a$  change; the differences are taken with respect to the Ni(111) surface. Similar quantities for the Pt-coordinated sites D and E are related to Pt(111). The site C is included although it represents a partly different case because of the fourfold coordination of the chemisorbed H. The CLS trend obeys the band narrowing/widening idea [28]. For Ni atoms at the Pt adatom cluster the d band is effectively wider than on the Ni(111) surface owing to a higher coordination. On the epitaxial Pt overlayer the large positive CLS is caused again by the band widening introduced by large Pt–Pt hopping matrix elements, and the same is true for the central atom in the epitaxial Pt<sub>7</sub> cluster [11, 12]. The surface potentials are in most cases more attractive (positive contribution to CLS) than at the corresponding pure-metal surface and drag LDOS downwards, which, in turn, results in a lower reactivity. The experiment [3] finds a positive CLS of  $\sim 0.1$  eV with respect to the Pt bulk ( $\sim 0.5$  eV with respect to the Pt(111) surface) for Pt adatoms near monolayer coverage. Comparison with sites D and E in figure 8 reveals that this value is closer to CLS than we find for epitaxial structures although the real Pt/Ni(111) surface probably lies between our two extreme models. This is corroborated also by the photoemission data (P Légaré, private communication), which present the Pt states at platinum submonolayer and near-monolayer coverage as a band centred at 4.5 eV below  $E_F$ . For the non-epitaxial model only the band bottom lies in this energy region [12], but a compression shifts the d band downwards. Let us note that recent extended Hückel calculations [37] of very small Pt<sub>N</sub> ( $N = 1-4$ ) aggregates on Ni(111)



**Figure 8.** Change of the average core-level shift  $\Delta\text{CLS}$  (left bar of pair) and decrease of the hydrogen-adsorption energy  $-\Delta E_a$  (right bar of pair) for adsorption sites A–D (figure 1); E refers to the Pt overlayer on Ni(111); e and n denote the epitaxial and non-epitaxial model, respectively. The changes are taken with respect to the Ni(111) (sites A–C) and Pt(111) surface (sites D, E), respectively. See the text for details.

yield Pt–Pt bonds essentially expanded with respect to the substrate bond length but find virtually no LDOS at the above indicated energy. The difference between the LDOS of [37] and that obtained by the present method ([11] and unpublished results) consists essentially of scaling to the local platinum band width as expected. The quasi-pure Pt overlayer at the segregated (111) face of  $\text{Pt}_{0.5}\text{Ni}_{0.5}$  represents an intermediate case between the epitaxial and non-epitaxial models because of the crystal lattice parameter [8, 9] but we are not aware of any photoemission data.

From figure 8 and the previous discussion we conclude that compression of the Pt–Pt bond reduces the Pt adatom bonding ability. The latter statement offers a simple explanation [12] of the reactivity drop at the quasi-pure Pt(111) surface of the PtNi alloy (see section 1). The surface Pt atom is bonded to six, mainly Pt, surface neighbours but only to three, mainly Ni, subsurface atoms. Because of the atomic separation in the alloy the picture is dominated by compressed Pt–Pt bonds. Our explanation copes also with the reduced reactivity of the Ni-rich (110) surface in the alloy. Here, the surface bonds are less numerous (2) than the five (mainly Ni–Pt) bonds with the subsurface Pt-rich layer. Since the Ni–Pt hopping elements are essentially larger than the Ni–Ni ones, the surface Ni bandwidth is again effectively larger than at the Ni(111) surface.

Although CLS on various surface sites differ considerably, their changes due to hydrogen adsorption show up a regular trend. In all the cases we consider (sites A–D, Pt/Ni(111), in both epitaxial and non-epitaxial cases, respectively, Ni and Pt(111) surfaces), we find for the first nearest neighbours of a single H adatom a moderate positive additional contribution to CLS, which is  $\sim 0.1$ – $0.2$  eV for Ni atoms and  $\sim 0.2$ – $0.4$  eV at Pt ones. The sign and

magnitude agree with measurements for transition-metal surfaces [38–40]. For the H(1 × 1) overlayer the CLS changes are bigger and are of order 1 eV [17].

#### 4. Summary

To summarize, we have studied hydrogen chemisorption for a number of surface geometries in the late transition metal (Pt, Ni) bimetallic systems. By considering the epitaxial and non-epitaxial models, respectively, we can perform a ‘*gedankenexperiment*’, which helps us to find the relevant parameters. Similarly, as in earlier studies performed for somewhat different systems, it seems that for late transition metals the important experimentally well observable quantities are core-level shifts and/or the local density of electronic states near  $E_F$ . Namely, depletion of LDOS at  $E_F$  and a significant core-level shift to higher binding energy often occur simultaneously and indicate a drop in the chemical reactivity of the corresponding atom. The common underlying mechanism might be the local d-electron band widening or narrowing. The low-coordinated atoms at the cluster edge are more reactive because of the band narrowing. The low chemical activity of a strongly compressed Pt overlayer can be traced to the local band widening. Hence, the surface interatomic distance is an important parameter controlling the surface chemical properties. This fact can elucidate catalytic behaviour of systems such as various surfaces of the PtNi alloy.

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