Journal of Alloys and Compounds, 191 (1993) 173–178
JALCOM 521

A theoretical molecular orbital approach to the adsorption and absorption of atomic hydrogen on Ni(111)

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(Received June 22, 1992)

Abstract

A semiempirical molecular orbital approach to the H–Ni interaction for a hydrogen atom adsorbed on the (111) surface or immersed in the bulk of Ni is given.

The results show that the chemisorptive surface sites are more stable than the subsurface interstitials and that the bulk octahedral sites are more stable than the tetrahedral sites, in agreement with earlier models.

The repulsive influence on hydrogen atom adsorption due to other hydrogen atoms residing in the nearer subsurface interstitials is also considered and discussed in terms of electronic arguments.

1. Introduction

The interaction of hydrogen with transition metals is of considerable technological importance in relation to heterogeneous catalysis, passivated storage of hydrogen and the magnetic properties of hydrides [1]. The physicochemical phenomena which are involved, such as the dissociation of the H_2 molecule, the chemisorption of atomic hydrogen, its surface and bulk diffusion and the trapping of hydrogen at interstitials or defects, have been the subject of intensive experimental and theoretical work in recent years [2]. Atomic hydrogen can be viewed as a model for which theories are tested, particularly in the case of chemisorption.

In general, three different approaches have been considered for the investigation of the chemisorption of hydrogen on transition metal surfaces: the cluster approximation, the slab approximation and the embedding formalism. In the first, the chemisorption site and its neighbourhood are represented by a limited number of atoms. It has been used, for example, in *ab initio* [3], semiempirical [4] and density functional theory (DFT) [5] calculations. In the second case, periodic conditions are imposed along two independent directions of the substrate surface. This has been applied, for example, in DFT [6] and tight binding (TB) [7] calculations. Finally, in the embedding formalism, the interaction between the H atom and the rest of the solid is taken into account by means of a ground state functional which depends on the electronic density of the medium. This has been used in the effective medium method (EMM) of Nørskov and Besenbacher [8], which has been employed to describe the adsorption of H atoms on several transition metals, and the embedded atom method (EAM) of Daw and Foiles [9], a combined slab-embedding formalism developed to treat H atom adsorption on Pd.

The study of the interaction between hydrogen and a transition metal, when the H atom is an impurity in the bulk of the metal or in the case of hydrides, has been examined mainly using two different approaches: the cluster approximation and the embedding formalism. As for chemisorption calculations, the first approach intends to represent fundamentally the properties of more localized character. Approaches of this type include the intermediate neglect of differential overlap (INDO) calculations of Vargas *et al.* [10] and the extended Hückel theory (EHT) calculations of Companion *et al.* [11]. The second approach has been applied in recent EMM calculations of Nørskov and Besenbacher [8] and in the quantum mechanical calculations of Sugimoto and Fukai [12] for self-trapped hydrogen, both describing the ground state of hydrogen within the bulk of transition metals.

The evolution of an H atom from the adsorbed state on the (100) surface to the bulk of nickel has been studied by Nørskov and Besenbacher [8] using the EMM. The calculations show that an H atom in a subsurface site has greater (negative) binding energy than in a normal "hollow" site. Similar calculations

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0925-8388/93/$6.00

performed by Daw and Foiles [9] using the EAM for Pd(111) show that the subsurface site, compared with the surface site, has a slightly greater or a slightly lower binding energy, depending on the symmetry of the subsurface site.

In the present work we combine the cluster approximation and EHT calculations to study the chemisorption of atomic hydrogen on the (111) surface of nickel and its incorporation into the bulk of this metal, as an alternative methodology to the previous investigations. We also consider the repulsive influence of internal H atoms on the ground state potential energy curve. In the next section we describe the model used in the calculations. We then discuss the results of the model and, finally, draw conclusions.

2. Calculation method

The selection of the metallic clusters to be employed in our semiempirical molecular orbital calculations was based on structural arguments. The reported experimental information for the chemisorption geometry of hydrogen on Ni(111), obtained from low energy electron diffraction (LEED) [13], has shown that the H adatoms occupy the two hollow types of threefold symmetry in this surface. Moreover, according to the experimental data on the site occupancy for H isotopes in bulk nickel, the H atom prefers the octahedral (O) interstitial sites to the tetrahedral (T) interstitial sites, at low concentrations of H atoms [14]. In order to take into account the structural features mentioned above, two kinds of clusters, named I and II, have been considered in the present work.

Cluster I, to be used in calculations where the H atom moves perpendicularly to and goes across the Ni(111) surface, is shown in Fig. 1. It has 37 atoms distributed in four layers of 12, 6, 7 and 12 atoms, from the surface to the bulk of the metal. The site over the centre of the first layer corresponds to a threefold "hollow" site, or a bulk interstitial site of tetrahedral symmetry if the metal lattice is continued out of the surface. Between the first and the second layers we have a subsurface interstitial site of octahedral symmetry. Between the second and the third layers we have a tetrahedral interstitial site.

Cluster II, to be used in bulk calculations concerning the evolution of an H atom from a T site to an O site, is shown in Fig. 2. It has 38 atoms distributed in five layers of 6, 7, 12, 6 and 7 atoms. The sites between the first and the second, the second and the third, and the fourth and the fifth layers correspond to bulk interstitials of tetrahedral symmetry, whereas the site between the third and the fourth layers corresponds to an octahedral interstitial.

It is a well-established fact that hydrogen in transition metals produces relaxation in its neighbourhood. To take this effect into account, we have considered the empirical rule [14, 15] that the volume expansion per H atom is close to 2.8 Å^3. In our model, it was accomplished, at a first approximation, only for the nearest neighbours of the H atom.

The eigenvalues and eigenvectors of the valence electron hamiltonian have been calculated by the EHT. This is particularly suitable for making comparisons when 3d transition metal atoms are included, *e.g.* in the study of H–metal bonding in b.c.c. transition metals [16], or in the analysis of the relative binding energies for hydrogen trapped in interstitials of these metals [11]. Here a double basis set has been used for atomic d orbitals. The off-diagonal matrix elements of the hamiltonian have been obtained from the weighted formula of Ammeter *et al.* [17]. The atomic charges and bond orders were determined using Mülliken population analysis [18].

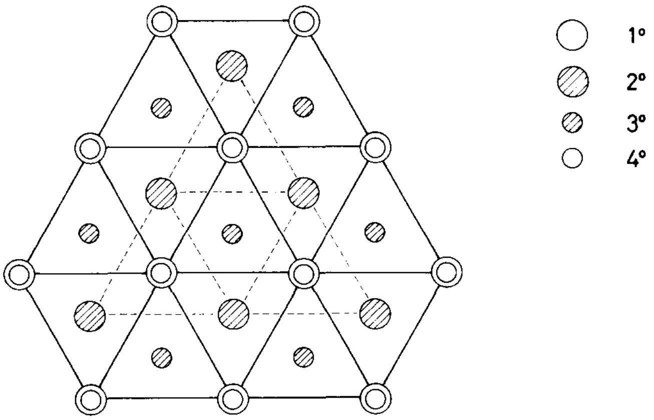

Fig. 1. Schematic diagram of the 37 metal atom cluster (cluster I) for Ni(111). The first layer corresponds to the (111) surface of nickel.

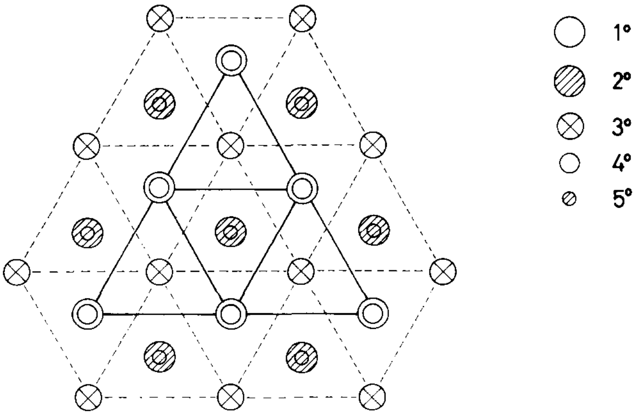

Fig. 2. Schematic diagram of the 38 metal atom cluster (cluster II) for Ni bulk. The central symmetry axis corresponds to the [111] direction.

TABLE 1. EHT parameters

Atom	Orbital	Ionization potential (eV)	Slater exponent (a.u.$^{-1}$)	Linear coefficient
H	1s	13.60	1	
Ni	3p	75[a]	4.330[c]	
	3d	10.03[b]	5.750[b]	0.5683[b]
			2.000[b]	0.6292[b]
	4s	7.63[a]	1.587[c]	
	4p	3.89[b]	0.968[c]	

[a] From ref. 21.
[b] See ref. 20.
[c] Calculated as in ref. 22.

The binding energy $E_B(z)$ of the H atom at position z was obtained from the following expression

$$E_B(z) = \Delta E_T(z) + \sum E_R(z) + E_{ee}(z) \qquad (1)$$

where the z coordinate refers to the position along the normal to the first layer in cluster I. This variable must be replaced by the position d_T along the axis connecting T and O interstitials for the cluster II calculations. $\Delta E_T(z)$ is the total valence electron energy difference with respect to $z=\infty$. $\Sigma E_R(z)$ is the sum of the repulsive interaction energies between the 1s level of hydrogen and the 4p core levels of nickel, calculated as in refs. 19 and 20. Each repulsive term is of the form $\beta \exp(-\alpha R)$, where α and β are parameters and R is the H–Ni interatomic distance. In our case $\alpha = 2.189$ Å^{-1} and $\beta = 17.634$ eV. The other parameters used in the EHT calculations are shown in Table 1.

$E_{ee}(z)$ is the repulsive electron–electron coulombic energy, which is not explicitly included in the first term. In the present work this energy is assumed to be

$$E_{ee}(z) = U\,\Delta Q(z) \qquad (2)$$

where $\Delta Q(z)$ is the excess electronic charge with respect to the $z=\infty$ limit, *i.e.* the free H atom, and U is a proportionality factor. Expression (2) can be viewed as the interaction between the electron of a neutral H atom and the excess negative charge residing on it. Or it can be interpreted as the remaining linear term (on ΔQ) when the repulsive electron–electron energy of the H atom is calculated as the difference between $z=z$ and $z=\infty$. This expression shows a close resemblance to the repulsive electron–electron term of the Newns–Anderson model [23]. For the U parameter we have adopted $U = 12.9$ eV electron^{-1}, from the difference between the ionization potential and electron affinity for free atomic hydrogen.

3. Results and discussion

The main objective of our calculations was to obtain the adiabatic potential energy curve corresponding to H–Ni interaction, which allows the determination of binding energy minima, activation energies, the equilibrium geometry and vibrational frequencies.

Three kinds of calculations were performed. In the first, for which cluster I was used, the H atom moves from the vacuum to the bulk of nickel, normally to the (111) surface and across a threefold hollow site of tetrahedral symmetry. In the second, carried out with cluster II, the H atom moves from a T interstitial to an O interstitial in the bulk of nickel. The calculations performed with clusters I and II, corresponding to regions of different topology, have been matched so that the binding energy for the T interstitial obtained with cluster I is the same as that obtained with cluster II, in order to ensure the continuity of the potential energy curve. Finally, in the third type of calculation, the H atom makes the same evolution as in the first case, but with consideration of the influence of three H atoms at the three nearest subsurface sites of tetrahedral symmetry, surrounding the central subsurface site which has octahedral symmetry. Therefore, in this case, the cluster representing the substrate has 40 atoms, with 10 atoms in the second layer.

The resulting adiabatic potential energy curves are shown in Fig. 3.

We consider firstly the situation with no H atoms trapped in the Ni lattice, *i.e.* Fig. 3, curves a and c. As can be seen, the E_B curve for atomic hydrogen has an absolute minimum at nearly 1.2 Å from the Ni surface and periodic minima towards the bulk of the substrate. They correspond respectively to a more stable chemisorbed species and to internal interstitial sites of alternate character: O, T, O.... This potential energy diagram for the entry of H atoms is in agreement with the model of endothermic solution, previously suggested by Comsa and David [24] and Chorkendorff *et al.* [2] in relation to their results of temperature programmed desorption (TPD) and time-of-flight experiments. It is also in agreement with the above-mentioned theoretical calculations of ref. 8 for H/Ni(111). The physical parameters obtained for the chemisorbed state (equilibrium position z_e, chemisorption energy E_c and perpendicular vibrational frequency ω) are shown in Table 2, where the values for z_e and ω are compared with the calculations of ref. 8 and the experimental results reported in ref. 25. The relative comparison between both calculation methods is within 17%, which is very good, taking into account the different approximations involved. The comparison between ref. 8 and the experiments is better, indicating that a repulsive component in our calculations could increase (decrease) and improve our value for z_e (for $\hbar\omega$).

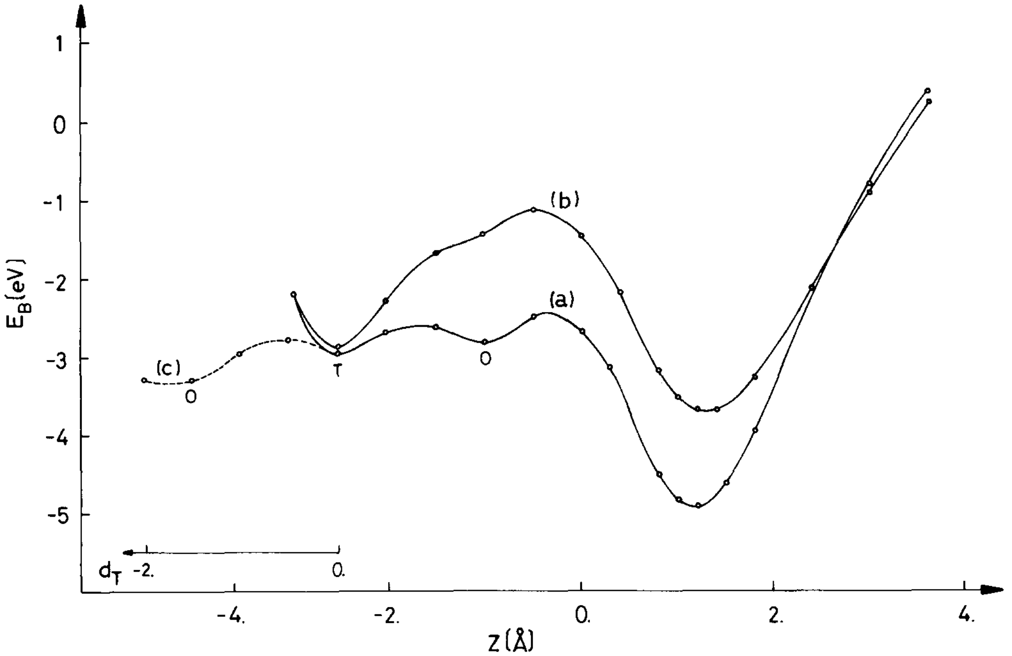

Fig. 3. Hydrogen binding energy as a function of the distance z to the (111) surface of nickel or as a function of the distance d_T to an interstitial of tetrahedral symmetry. O and T refer to the symmetry of the interstitial. Curve a, cluster I calculations. Curve b, cluster I+3H (second layer) calculations. Curve c, cluster II calculations.

TABLE 2. Equilibrium distance, binding energy and perpendicular vibrational frequency for the H atom adsorbed on Ni(111)

Cluster	z_e (Å)	E_B (eV)	$\hbar\omega$ (meV)
Cluster I	1.17	−1.46	109
	1.31[a]		131[a]
	1.36[b]		139[b]
Cluster I+3H (second layer)	1.29	−0.85	92

[a] Embedded atom method [8].
[b] Experiments [25].

TABLE 3. Hydrogen binding energy (in eV) for chemisorptive and subsurface sites, referred to the bulk interstitial of octahedral symmetry

Site	Cluster I	Ref. 8	Cluster I+3H (second layer)
Chemisorptive	−0.98	−0.66	−0.42
Subsurface	0.07	−0.01	0.71

The theoretical results corresponding to the H atom binding energy in subsurface and surface (chemisorptive) sites are compared in Table 3. Both calculations methods are in agreement in the sense that the subsurface interstitial is less stable than the surface site. This result is also in agreement with the picture suggested by Comsa and David [24] and Chorkendorff *et al.* [2], describing H atom adsorption–desorption experiments in Cu and Ni, but in contrast with the theoretical result of Daw and Foiles [9] for Pd(111), where the subsurface and surface sites have nearly the same binding energy. The binding energy values obtained in our calculations and those reported in ref. 8 show a relative discrepancy of 20%. The agreement is satisfactory if we recall that the results obtained by the linear augmented plane wave method and the generalized valence bond method for H/Ni(111) (hollow site), both reported in ref. 6., differ by 16% and 30% respectively from the effective medium result reported in the same reference.

Furthermore, the octahedral subsurface site has a binding energy very similar to that of the tetrahedral inner site. The activation energy for diffusion from the bulk to the surface is close to 0.3 eV, and from the surface to the bulk is close to 1.2 eV, *i.e.* much greater than in the opposite direction. The activation energy for diffusion between the subsurface O site and the inner T site is also close to 0.3 eV.

If a travelling H atom arrives from the surface to the bulk T site along a perpendicular direction, it will face a strong potential barrier originating from the Ni atom of the third layer of the substrate. This H atom cannot easily hop or tunnel the barrier and therefore it moves in the direction of a lateral O interstitial site. As the bonding energy shows, the bulk O site is 0.1 eV more stable than the bulk T site. This bulk site preference has been experimentally found for palladium by inelastic neutron scattering [26] and is a generally accepted rule for other transition metals at low hydrogen concentrations. Moreover, it has been theoretically predicted from potential field considerations [14] and electron density arguments in effective medium calculations [8]. In the present work an alternative explanation of this fact can be given from an analysis of each term of eqn. (1). Although the absolute value of the first contribution is greater for the T site than for the O site, the second contribution is smaller; the third term is independent of the interstitial symmetry. The corresponding H–Ni bond order for the T site, 0.25, is greater than that for the O site, 0.17. In other words, the O site preference can be ascribed to a smaller H1s–Ni3p repulsion.

The bulk diffusion activation energy from a T interstitial to an O interstitial is close to 0.3 eV, and in the opposite direction it is close to 0.1 eV. Both values are in acceptable agreement with the experimental value of 0.4 eV, reported in ref. 26.

In an Ni substrate with trapped H atoms, *i.e.* Fig. 3, curve b, a noticeable feature is the presence of an important repulsive component (*cf.* curves a and b of Fig. 3). As observed in Table 2, the equilibrium position is 10% greater and the perpendicular vibrational frequency 15% lower than in the case with no H–H repulsion. Furthermore, as shown in Tables 2 and 3, the binding energy (negative) exhibits an important increase of nearly 0.6 eV, owing to this repulsion. Moreover, there is no minimum at the subsurface interstitial site, which is by contrast energetically unstable. There is a large barrier between the chemisorptive site and the bulk O interstitial; the latter is almost at the same binding energy as in curve a. The activation energy for diffusion to the bulk is about 1.1 eV, whereas in the opposite direction it is about 0.9 eV. In other words, the diffusion to the bulk is not affected (in terms of activation energy) by the H–H repulsion, but the diffusion from the bulk is hindered by an activation energy which is 0.6 eV greater than in the case with no H–H repulsion.

The repulsive interaction between H atoms is also responsible for the occupancy of T sites at high H atom concentrations in the bulk of transition metals [14]. This short-range repulsive interaction can be explained in terms of electronic arguments. The incorporation of H atoms into nickel increases the population of antibonding H–Ni molecular orbital levels, and therefore the repulsive H–H interaction is mediated by the Ni matrix. Another way of showing this is to observe the variation in the H–Ni bond order in the following sequence: chemisorptive site, first Ni layer and subsurface site. When H–H repulsion is not present we have the values 0.29, 0.31 and 0.17. However, when this repulsion is present we have the values 0.26, 0.21 and 0.05 respectively.

Finally, we consider the electronic charge of the H atom. Recently, INDO calculations with the cluster approximation [10] have shown that a proton within nickel can be interpreted as an overscreened particle, with an excess of 0.45 of an electron. This value can be compared with the electronic charge excess obtained in our calculations, which is 0.27 of an electron for interstitial hydrogen and 0.37 of an electron for chemisorbed hydrogen. Although our approach is not self-consistent, these values show a non-negligible excess of electronic charge on the H atom. The presence of other competing H atoms in the neighbouring tetrahedral sites does not significantly change the value corresponding to chemisorbed hydrogen. Only at shorter H–H distances is the H atom charge smaller owing to other competing Ni to H charge transfers, and the repulsive term of eqn. (2) is lower.

4. Conclusions

The calculations performed here within the framework of the cluster approximation and the EHT formalism have allowed us to study at the local level the H–Ni interactions involved in the adsorption/absorption phenomena of atomic H on/in Ni(111).

Our results on the equilibrium position and perpendicular vibrational frequency of the chemisorbed state, the surface (chemisorbed), subsurface and bulk binding energies and the diffusion activation energies are in general good agreement with other calculations, mainly using the embedded atom approach.

The qualitative picture of the H atom potential energy diagram outlined by Comsa and David [24] and Chorkendorff *et al.* [2] to describe the entry of an H atom into an Ni matrix is also in agreement with the results obtained in the present work.

In the bulk of nickel the H atom prefers the interstitials of octahedral symmetry owing to a lower repulsion between the 1s level of hydrogen and the Ni cores.

The presence of H atoms trapped at the subsurface interstitials of nickel has an important repulsive effect which can be ascribed to a greater anti-bonding character between hydrogen and nickel.

Acknowledgment

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). R. F. would like to thank CONICET for financial support.

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