

phys. stat. sol. (b) 114, 439 (1982)

Subject classification: 4; 10.1; 13.4; 21.1

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Cluster Model for Interstitial Hydrogen Bonding in Nickel

By

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The CNDO, EHT, and SW- $X\alpha$ methods are used to investigate tetrahedral and octahedral Ni clusters with and without the interstitial hydrogen in the center. Optimized distances between atoms, one-electron energy levels, and the bonding mechanism of hydrogen in the nickel clusters are given and discussed in detail.

Unter Benutzung der CNDO-, EHT- und SW- $X\alpha$ -Methode wird der Einbau eines Wasserstoffatoms in das Zentrum eines tetraedrischen bzw. oktaedrischen Nickelclusters untersucht. Dabei wird der Abstand der Atome der Cluster mit und ohne H jeweils optimiert. Die berechneten MO-Niveaus und der Bindungsmechanismus des Wasserstoffs im Nickelcluster werden ausführlich diskutiert.

1. Introduction

It is well known that transition metals form, especially under high pressure (see also Appendix), hydrides which can be considered as the interstitial solid solution of hydrogen in the metal lattice. Such metal-hydrogen systems are important in many respects — they can serve as hydrogen containers, they are used in powder metallurgy, surface coating, and in many other applications [1, 2]. It is therefore of great interest to investigate their electronic structure and the nature of the metal-hydrogen bonding. In this paper we confine ourselves to the investigation of the nickel-hydrogen system. The experimental results show that hydrogen atoms occupy the octahedral interstitial sites in nickel [3, 4]. Therefore, as a problem of greatest interest, we consider octahedral clusters here. Further, we investigate clusters in form of the tetrahedron, which can be used as a model of the second interstitial site available in the f.c.c. lattice.

Dissolving hydrogen in a transition metal, the lattice constant of the host lattice increases. In case of Ni the experimental data show that this increase amounts to 5.7% [3]. The same effect appears in some transition metal atom clusters [5]. The theoretical calculation of this change of the lattice constant is the main purpose of this paper. Similar calculations were performed by means of the LCAO-SCF method [6], however, the calculated equilibrium geometries do not agree very well with the experimental data.

We also discuss here the mechanism of the hydrogen-nickel bonding. Our results are in qualitative agreement with those given in [7, 8]. However, we discuss in this paper the mechanism of bonding from the point of view of different methods and in more detail. Concerning the bonding mechanism of interstitial H in metal atom clusters see also our investigations in case of Nb_6I_{11} and HNb_6I_{11} [9].

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2. Models and Methods of Calculation

The clusters investigated in this paper are tetrahedral and octahedral Ni clusters with and without hydrogen in their centre. We denote these clusters as Ni_n and HNi_n ($n = 4, 6$). During the calculations, we optimized the distances between adjacent Ni atoms in order to get the minimum of the total energy. This is done in the framework of the CNDO and EHT methods. The CNDO parameters for Ni were given by Blyholder [10]. For hydrogen, standard parameters were used [11]. The EHT parameters were taken from [12].

The clusters Ni_6 and HNi_6 were also investigated by the SW- $X\alpha$ method, however, for fixed interatomic distances only. In both cases we use the lattice constant of Ni metal ($a = 3.517 \text{ \AA}$), i.e. the Ni-Ni bond lengths do not change as a result of H-Ni interaction. We do not perform the geometry optimization here since we do not expect any qualitative change of the main results. The muffin-tin radii of four touching atomic spheres are equal to $b(Ni) = \sqrt{2}a/4$ and $b(H) = (2 - \sqrt{2})a/4$. The following α -parameters were taken: $\alpha(Ni) = 0.70896$ and $\alpha(H) = 0.97804$ [13]. For the inter-sphere region we used their mean value 0.74740, for the outer sphere the same value as for the neighbouring Ni atoms was used.

3. Results and Discussion

3.1 Equilibrium geometries

The optimized distances between adjacent Ni atoms in the clusters Ni_4 , Ni_6 , HNi_4 , and HNi_6 following from the CNDO and EHT calculations and the corresponding experimental distances for Ni metal are given in Table 1.

The CNDO results are in excellent agreement with the experimental data. The distance between adjacent Ni atoms depends on the cluster size. It is greater in case of the tetrahedra, and for the octahedra it approaches the experimental value. Its relative change resulting from the installation of the interstitial hydrogen (5.1%) agrees quite well with the experimental result (5.7%). The distances between adjacent Ni atoms in our clusters are larger than those in the metal. It is the same result as in the case of nickel-carbonyl clusters (see experimental work [5]).

The binding energy $\Delta E = E_{HNi_n} - E_{Ni_n} - E_H$ for the equilibrium geometries are equal to -6.2 and -4.06 eV for the octahedral ($n = 6$) and tetrahedral ($n = 4$) clusters, respectively. The greater binding energy of the octahedral configuration agrees with the existence of the octahedral interstitial hydrogen known from the experiment.

Table 1

Calculated distances between adjacent Ni atoms (in \AA), their change in case of interstitial hydrogen, and the corresponding binding energies (in eV). The experimental values are from [5], the LCAO-SCF values are from [6]

	Ni-Ni distance		relative change (%)	ΔE	Ni-Ni distance		relative change (%)	ΔE
	Ni_4	HNi_4			Ni_6	HNi_6		
CNDO	2.63	2.81	6.8	-4.06	2.54	2.67	5.1	-6.2
EHT	1.76	3.13	78	-3.4	1.87	2.88	54	-2.7
LCAO-SCF	2.33	2.51	7.7	-3.3	2.28	2.31	1	-3.6
experimental values for the metal					2.49	2.63	5.7	

and octahedral Ni clusters these clusters as Ni_n and HNi_n distances between adjacent Ni atoms is done in the framework of the EHT method. The EHT parameters for Ni were given by Blyden [11]. The EHT parameters

of the SW- $X\alpha$ method, however, use the lattice constant of Ni which changes as a result of H-Ni interaction here since we do not expect the radii of four touching atoms to be $(\sqrt{2})a/4$. The following $\alpha = 0.97804$ [13]. For the inter-outer sphere the same value

for clusters Ni_4 , Ni_6 , HNi_4 , and HNi_6 and the corresponding ex-

perimental data. The inter-outer sphere size. It is greater in case of the experimental value. Its change of interstitial hydrogen (5.1%) and the distances between adjacent atoms. It is the same result as in the experiment [5].

The equilibrium geometries are calculated for tetrahedral ($n = 4$) clusters, and the configuration agrees with the experiment.

), their change in case of interstitial hydrogen (in eV). The experimental values

In contrast to the very good CNDO results the EHT results are not so favourable. The increase of the distance of the adjacent Ni atoms resulting from the installation of hydrogen is too great. Further, the binding energy ΔE of the octahedron (-2.7 eV) is less than the binding energy of the tetrahedron (-3.4 eV), i.e., we get an opposite result compared with the CNDO method. On increasing the size of the clusters from $n = 4$ to 6 the Ni-Ni distance increases in case of Ni_n and decreases in case of HNi_n . Since the convergence of the properties of the clusters is relatively slow in the EHT method [14], the calculation of bigger clusters can give better results.

In contrast to the CNDO method, the LCAO-SCF approach [6] does not give so good results. The calculated Ni-Ni distances for $n = 4$ are smaller than the experimental ones, and from $n = 4$ to 6 they change to still smaller values. From Ni_6 to HNi_6 the relative increase of the lattice constant is about six times smaller than it should be according to the experiment.

3.2 Mechanism of bonding from the CNDO point of view

The bond orders by Wiberg following from the CNDO calculations are given in Table 2. In favour of new H-Ni bonds in HNi_n clusters all total and partial bond orders between Ni atoms are lower than the corresponding bond orders for Ni_n ($n = 4, 6$). Due to the greater number of H-Ni bonds, H-Ni bond orders are lower in the case of HNi_6 clusters. The bond order between s(H) and sp(Ni) functions is greater than the bond order between s(H) and d(Ni). This means that H-Ni bond is essentially an s-sp bond.

In order to investigate the mechanism of H-Ni bonding in more detail, let us discuss the MO energy levels of Ni_6 and HNi_6 clusters (see Fig. 1a). In case of tetrahedron, the results are similar to those given in Fig. 1a. First we see that the absolute values of one-electron energies are very large in the CNDO calculation. However, the well-known shortening of the CNDO method is that it usually overestimates the absolute values of one-electron energies.

As the clusters Ni_6 and HNi_6 have O_h symmetry and the basis function of hydrogen is 1s orbital, the interstitial hydrogen directly influences A_{1g} energy levels only. The shifts of levels corresponding to different representations are relatively small so that they form a so-called "rigid band". Within the framework of the CNDO method, they do not influence the electron transfer H-Ni. The lowest valence level $1A_{1g}$ of HNi_6 is the hydrogen bonding level resulting from a strong interaction between 1s(H) and $1A_{1g}(Ni_6)$ levels. As a consequence of the interaction the $1A_{1g}(HNi_6)$ level has less energy than $1A_{1g}(Ni_6)$ one. The interaction is also accompanied by the decrease of sp(Ni) coefficients of the wave function in favour of the 1s(H) coefficient. This means that part of the sp(Ni) electrons is transferred from Ni to H. The $2A_{1g}$ level has non-

Table 2

Atomic bond orders by Wiberg for the considered clusters. The nearest neighbours are denoted by NN, the next nearest neighbours by NNN

distance	relative change (%)	ΔE
HNi_6		
2.67	5.1	-6.2
2.88	54	-2.7
2.31	1	-3.6
2.63	5.7	

cluster	atomic bond orders by Wiberg										
	Ni-Ni (NN)				Ni-Ni (NNN)				H-Ni		
	total	sp-sp	sp-d	d-d	total	sp-sp	sp-d	d-d	total	s-sp	s-d
Ni_4	0.33	0.11	0.06	0.10							
HNi_4	0.16	0.06	0.02	0.06					0.25	0.22	0.03
Ni_6	0.34	0.09	0.08	0.09	0.17	0.05	0.01	0.10			
HNi_6	0.17	0.04	0.05	0.03	0.06	0.02	0.01	0.02	0.17	0.15	0.02

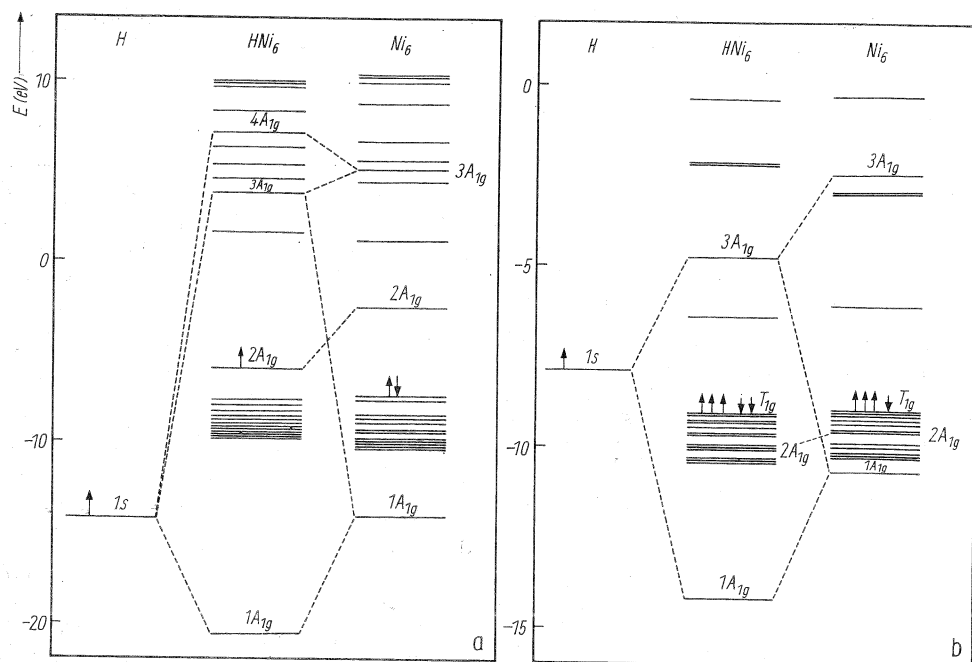


Fig. 1. The MO energy levels of HNi_6 and Ni_6 clusters following from the a) CNDO and b) SW-X α calculations

bonding character. It is shifted downwards without a substantial admixture of the $1s(\text{H})$ function. The corresponding wave function has $d(\text{Ni})$ character. The additional electron from the hydrogen atom occupies this level (in Ni_6 unoccupied) and shifts the upper d-band edge upwards. The $3A_{1g}$ and $4A_{1g}$ levels have antibonding character.

The charge transfer resulting from the existence of the interstitial hydrogen can be discussed in terms of the orbital populations given in Table 3.

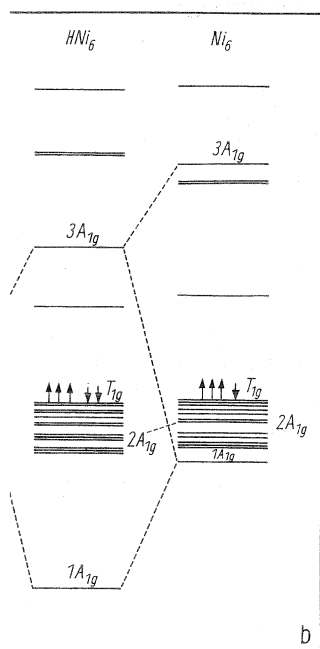
We observe a weak electron transfer from H to Ni d-band. In HNi_6 every Ni atom has ≈ 0.03 electron from hydrogen. Because of this weak electron transfer the interstitial hydrogen has not proton-like character. According to our result and in agreement with [7, 15], the hydrogen-metal bond has covalent character. In contrast to our result, however, hydrogen is in [7, 15] a weak electron acceptor, accumulating ≈ 0.2 electron.

Furthermore, we observe an electron transfer from $sp(\text{Ni})$ band to $d(\text{Ni})$ band. In

Table 3

The CNDO orbital populations in the clusters Ni_n and HNi_n ($n = 4, 6$)

	Ni_4	HNi_4	Ni_6	HNi_6
$Q_{sp}(\text{Ni})$	0.47	0.33	0.48	0.38
$Q_d(\text{Ni})$	9.53	9.68	9.52	9.65
$Q_s(\text{H})$		0.96		0.84

from the a) CNDO and b) SW-X α

substantial admixture of the (Ni) character. The additional (Ni₆ unoccupied) and shifts have antibonding character. Interstitial hydrogen can be able 3.

and. In HNi₆ every Ni atom α electron transfer the inter- to our result and in agree- ment character. In contrast to iron acceptor, accumulating

(Ni) band to d(Ni) band. In

HNi₆ cluster this transfer amounts to 0.1 electron per Ni atom. Summarizing, the occupation of an additional 2A_{1g} level of the Ni d-band occurs at the expense of Ni sp-band and the hydrogen atom.

3.3 Mechanism of bonding from the SW-X α point of view

The SW-X α method describes the physical properties of clusters in a somewhat different way than the CNDO method. Since both methods use a different basis, the interpretation of the results is in terms of different quantities. Finally, however, one should get the same physical picture. Our aim is to discuss the SW-X α results, too, and thus achieve a more complex and reliable picture of the H-Ni bonding mechanism.

The SW-X α one-electron energies of the clusters Ni₆ and HNi₆ and the atomic 1s Hartree-Fock-Slater energy of hydrogen are shown in Fig. 1 b. The SW-X α energy spectra are similar to those obtained from the CNDO method. Hydrogen mainly interacts with the lowest energy level 1A_{1g} of Ni₆ cluster forming the doubly occupied bonding orbital 1A_{1g} and the non-occupied antibonding orbital 3A_{1g} of HNi₆.

Therefore, Messmer et al. [8] discussed the metal-hydrogen interaction as an effect of the deepest orbital 1A_{1g} only. They concluded that in the case of nickel the metal-hydrogen bonding has mainly s-character of this orbital. However, according to our opinion, the bonding mechanism is not so simple.

To discuss this point we plotted the orbitals of Ni clusters with and without hydrogen in the centre in plane containing four metal atoms and the centre of the cluster (Fig. 2 a, b). The nodes of orbitals are illustrated by a high density of non-equidistant selected isolines. Comparing Fig. 2 a and b to each other it is obvious that 1) the charge from the Ni spheres is transferred into the H sphere forming the Ni-H bonds, and 2) the installation of hydrogen is accompanied by weakening the bond between Ni atoms. It will be shown below, however, that the remaining orbitals contribute to the metal-hydrogen bond, especially to the corresponding charge transfer, as well.

The charge transfer resulting from the hydrogen-nickel interaction can be characterized by the quantities

$$\Delta Q = \begin{cases} Q(\text{HNi}_6) - Q(\text{Ni}_6) & \text{for the six Ni spheres,} \\ Q(\text{HNi}_6) - Q(\text{H}) & \text{for the H sphere,} \\ Q(\text{HNi}_6) - Q(\text{Ni}_6) - Q(\text{H}) & \text{for the interatomic region and the outer sphere.} \end{cases}$$

Here, $Q(\text{H})$ is the charge of the isolated hydrogen atom inside (the second formula) or outside (the third formula) the sphere around the proton with the same radius as in HNi₆.

Table 4

The SW-X α charge transfer. SW-X α charge differences $\Delta Q = Q(\text{HNi}_6) - Q(\text{Ni}_6) - Q(\text{H})$

	6 Ni spheres	H sphere	interatomic region + + outer sphere
1s(H)		-0.31	-0.69
1A _{1g}	-0.65	0.43	0.22
2A _{1g}	0.30	0.01	-0.31
T _{1g}	0.96		0.04
bonding orbitals	0.61	0.13	-0.74
rigid band orbitals	-0.17	0.01	0.15
total	0.45	0.14	-0.59

HNi_n (n = 4, 6)

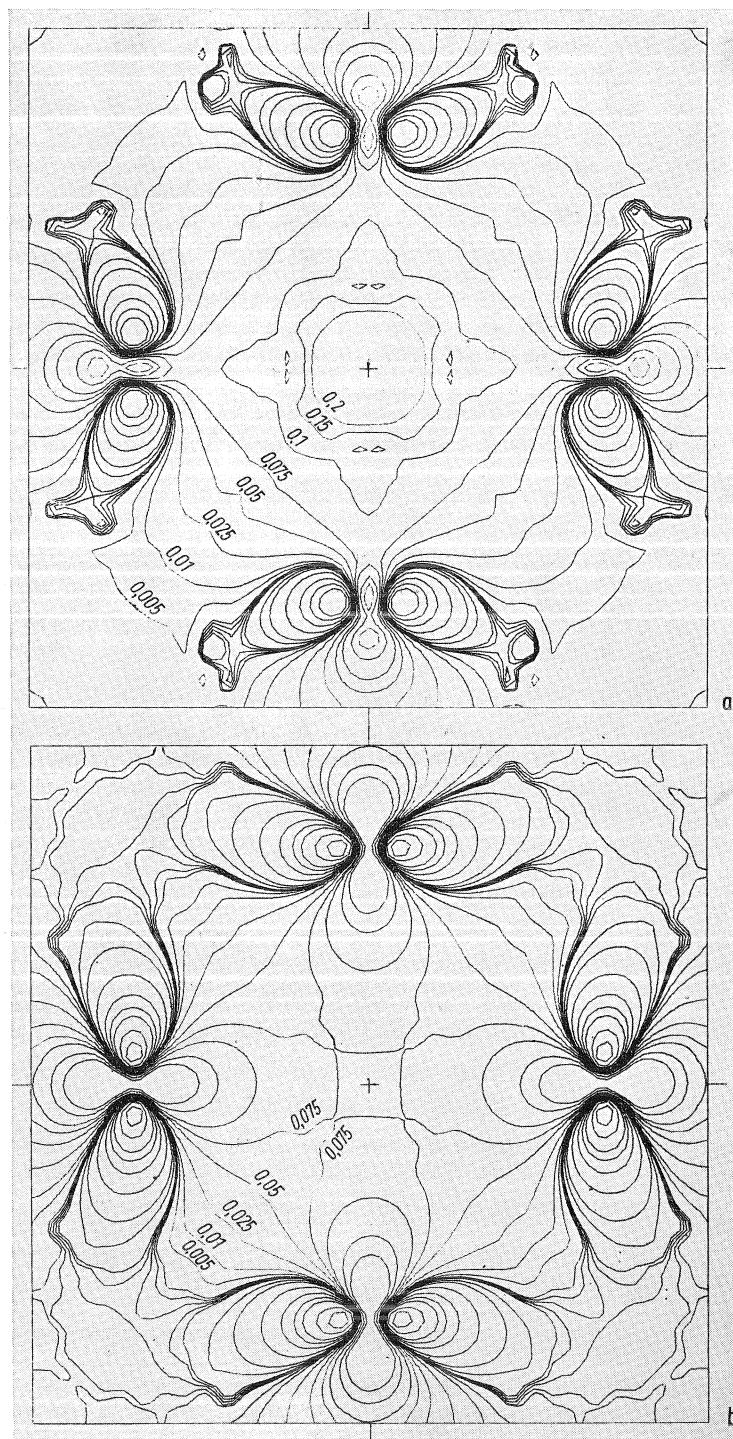


Fig. 2. The plot of the $1A_{1g}$ wave function for a) Ni_6 and b) HNi_6 clusters in the plane $z = 0$

Such a charge transfer refers to three selected geometrical regions of HNi_6 and cannot directly be compared with the CNDO charge transfer (Table 3) which refers to the charges in orbital spaces of Ni and H.

As seen from Table 4, the orbital $2A_{1g}$ does not contribute substantially to the charge in the H sphere. The transfer of 0.3 electron from the interatomic region and the outer sphere into the six Ni spheres lowers the energy of the orbital by 0.5 eV (see Fig. 1b). All other levels forming the "rigid band" are almost the same in Ni_6 and HNi_6 . The additional electron in HNi_6 occupies the pure d(Ni) orbital T_{1g} (HOMO) which is strongly localized at Ni atoms.

It is obvious from Table 4 that four main bonding orbitals ($1s(\text{H})$, $1A_{1g}$, $2A_{1g}$, and T_{1g}) undergo the greatest charge transfer. The orbital $1A_{1g}$ (see Fig. 2) transfers 0.65 electron from the six Ni spheres into the H sphere (0.43 electron) and into the interatomic region (0.22 electron). However, this charge transfer is overcompensated by the charge transfer of the $2A_{1g}$ and T_{1g} orbitals so that the resulting charge transfer from the main bonding orbitals amounts to 0.61 electron in the Ni spheres.

Each orbital of the "rigid band" transfers a smaller amount of charge, however, in the opposite direction, namely from the Ni spheres into the interatomic region and, to a smaller extent, into the H sphere.

The total charge transfer from the interatomic region and the outer sphere into the six Ni spheres and the H sphere amounts to 0.45 and 0.14 electron, respectively. However, due to the very small volume of the H sphere in comparison with the volume of the other spheres, the average change of the electronic density is greatest in this sphere (in electrons/ \AA^3): $\Delta\rho$ (H sphere) = 0.253, $\Delta\rho$ (Ni sphere) = 0.009, and $\Delta\rho$ (interatomic region) = -0.009.

In Table 5, the total charge transfer is subdivided into the partial charge transfers corresponding to $l = 0, 1$, and 2. The charge transfer to the H sphere consists of a large s-contribution from the bonding orbitals and the smaller p-contribution from the "rigid band" orbitals. It follows from Tables 4 and 5 that the charge transfer into the H sphere results from the interaction of $1s(\text{H})$ and $1A_{1g}$ orbitals with the same s-like character with respect to the proton.

The charge transfer into the Ni spheres consists of a large increase of the d-charge, a smaller one of the p-charge, and a decrease of the s-charge. This redistribution of the charge is essentially caused by the bonding orbitals $1A_{1g}$, $2A_{1g}$, and T_{1g} . The "rigid band" states have smaller influence of the opposite sign.

The only possibility of a comparison of the bonding mechanism as seen from the point of view of the CNDO and SW-X α methods is a direct comparison of the densities of charge. At the same time, the same basis (atomic orbitals or atomic spheres) must be used for their subdivision into atomic and orbital contributions.

Table 5

The SW-X α partial charge transfer. SW-X α partial charge differences $\Delta Q^l = Q^l(\text{HNi}_6) - Q^l(\text{Ni}_6) - Q^l(\text{H})$

		$l = 0$	$l = 1$	$l = 2$	total
H sphere	bonding orbitals	0.13			0.13
	rigid band orbitals		0.01		0.01
	total	0.13	0.01		0.14
6 Ni spheres	bonding orbitals	-0.24	0.11	0.74	0.61
	rigid band orbitals	0.4	0.02	-0.23	-0.17
	total	-0.20	0.13	0.51	0.44

6 clusters in the plane $z = 0$

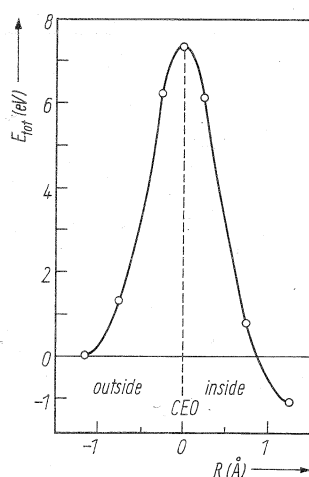


Fig. 3. The CNDO activation barrier of the penetration of H into Ni_6 octahedron along the path going through the centre of the edge of the octahedron (CEO). Chemisorbed state is used as reference state

3.4 Mechanism of penetration of H into Ni crystal

The next logical step of calculations should be the investigation of the penetration of H into Ni crystal and its diffusion inside. When hydrogen enters from the chemisorbed state into the crystal it has to overcome an activation barrier. The formation of Ni hydride is possible at room temperature under a hydrogen pressure of ≈ 7 kbar [16]. The activation energy of the hydrogen diffusion within the Ni crystal amounts to about 42 kJ/mol [16]. The barrier of the entrance into the crystal should be of the same order.

The preliminary estimation of the activation barrier of entering of H into the Ni_6 octahedron was performed by [17]. In this CNDO calculation the hydrogen atom is assumed to go into octahedron through the centre or an edge of the octahedron (CEO). The distance between Ni atoms was fixed in this calculation. The calculated activation barrier of about 700 kJ/mol (Fig. 3) is many times greater than the estimated experimental barrier. In order to obtain more accurate results, it is obviously necessary to consider also further possible paths of H into the cluster and optimize the Ni-Ni distances.

Detailed discussion of the origin of the activation barrier in terms of various components of the total energy is given in [17].

4. Conclusions

The main conclusions following from our calculations can be summarized as follows:

1) The equilibrium geometries and their change after the hydrogenation following from the CNDO calculations are in a good agreement with the experimental results. As far as the geometries are concerned, the CNDO method gives better results than the LCAO-SCF method [6].

2) The energy spectra following from the CNDO and SW- $X\alpha$ method are qualitatively the same. The three levels $1A_{1g}$, $2A_{1g}$, and $3A_{1g}$ of Ni responsible for the interaction with hydrogen go down. Other levels form with a good accuracy the "rigid band". In contrast to the CNDO method, however, the SW- $X\alpha$ method predicts a relatively small charge transfer from the "rigid band". It should be noted, however, that the concept of the charge transfer has somewhat different meaning in both methods. Further difference of the results regards the symmetry of the highest occupied level. According to the CNDO method it should have the symmetry A_{1g} whereby the

barrier of the penetration of H path going through the centre of EO). Chemisorbed state is used as

SW-X α method predicts T_{1g} representation. This difference, however, is not very important, since the order of the occupied levels can easily change from one method to another.

3) The CNDO method predicts for Ni₆ and HNi₆ a slight charge transfer from hydrogen to d-states of Ni atoms so that the number of electrons on hydrogen changes from 1 to 0.84. This value cannot be directly compared with the charge in the H sphere in the SW-X α method, nevertheless, this method gives opposite charge transfer (0.31 to 0.45). The LCAO-X α calculation [7] gives the same direction of the charge transfer as our SW-X α calculation. In all three cases, however, the hydrogen in HNi₆ has not proton-like character.

4) As far as the charge transfer on Ni atoms is concerned, both methods give the same result: The electrons transfer from sp-states to d-states.

5) Because of an other subdivision of the charge, the SW-X α method gives also the transfer of electrons from the interatomic region to atomic ones. The greatest change of the density of electrons appears in the H sphere.

6) The results of our work indicate that d-electrons of Ni play an important role in the creation of the H-Ni bond. It seems therefore that d-electrons of Ni cannot be included into the core as done by [6].

Appendix

Metallic modification of hydrogen

Especially with the support of high-pressure technique a lot of transition metal hydrides had been prepared. Concerning the metallic character of these compounds, very early hydrogen was regarded as a metallic alloying constituent and the question was asked whether hydrogen itself could be transformed into a metallic modification.

At present, there exists a lot of theoretical investigation in this field. Some years ago Müller developed an analytic cell model in order to describe this pressure induced phase transition of hydrogen [18].

Our model calculations on a metallic modification of hydrogen [18] allows to calculate the pressure $p_{v,j}$, which leads to the breakdown of the electronic structure (chemical bonding) within the hydrogen molecule in a given state (v, j):

$$p_{v,j} = -\frac{1}{4\pi r_0^2} \left(\frac{dE_{v,j}}{dr_0} \right), \quad v = 0, 1, 2, \dots; \quad j = 0, 1, 2, \dots, \quad (A1)$$

$$(r_0)_{v,j;n=\infty} = \frac{1}{8\gamma^2} \alpha_{2\kappa-1, v+1}^2, \quad (A2)$$

$$\left(\frac{dE_{v,j}}{dr_0} \right)_{n=\infty} = \frac{384\gamma^6}{\alpha_{2\kappa-1, v+1}^2 [\alpha_{2\kappa-1, v+1}^2 + 8\kappa(\kappa-1)]} \quad (A3)$$

(cf. equations (10), (8), (9) in [18]).

In calculating the compression pressure $p_{0,0}$ (from (1) to (3)) which causes the pressure induced dissociation of the ground state ($v = j = 0$) of H₂, there was a deplorable error in equation (11) in [18] which should be corrected here. The correct equation (11) of [18] reads as follows:

$$p_{\text{H}_2}^{\text{Koll}} \equiv p_{0,0} = \frac{6(2\gamma)^{10}}{\pi \alpha_{2\kappa-1,1}^6 [\alpha_{2\kappa-1,1}^2 + 8\kappa(\kappa-1)]}; \quad \left. \begin{array}{l} \gamma^2 = 625, \\ \kappa = 25.5, \\ \alpha_{50,1} \approx 57.12. \end{array} \right\} \quad (A4)$$

As a consequence, the pressure concerning this phase transition amounts to $p_{\text{H}_2}^{\text{Koll}} = 19.5$ Mbar.

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(Received June 22, 1982)