

# Interaction of hydrogen with a nickel surface in the low-temperature field evaporation

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## Abstract

The process of field evaporation of nickel in hydrogen atmosphere under pressure  $10^{-6}$  Pa at 20 K was investigated using a high resolution pulsed-laser time-of-flight atom-probe field ion microscope. Under these conditions, the ions of  $H^+$ ,  $H_2^+$  and  $H_3^+$  were detected as well as those of  $Ni^{2+}$ ,  $Ni^+$  and  $NiH_x^+$  ( $x = 1-3$ ). On the basis of both: experimentally determined energy distribution of ions and ab initio calculations in the density-functional theory (DFT) for Ni–H, including external homogeneous electrostatic fields, we can state that hydrogen atoms are bound to the nickel surface in the presence of the electrostatic field of strength about 30 V/nm. These complex ions are formed within two topmost layers at the nickel surface in the high electric field applied.

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## 1. Introduction

Surface-chemical reactions, in particular those of hydrogen with d-transition metals, are of increasing importance and stimulate interest in research methods which enable investigation in an atomic scale [1]. Such useful methods are STM and FIM. These methods are connected with the presence of high electric field at the metal surface. Electrostatic field of the strength of several volt per nanometer, used in the field emission desorption process [2], is of the same order as fields inside the atoms or molecule. Therefore, it is not surprising that such a field influences considerably atomic or molecular orbitals, which in turn leads to phenomena, which are described by a new speciality called field induced chemistry [3]. One of the most interesting phenomenon in this field is the synthesis of the metal–hydrogen complexes by means of low-temperature field-evaporation of a metal at hydrogen gas phase [4]. For example, such complexes as  $NiH_x^+$  ( $x = 1-3$ ) created during field evaporation of nickel are of special importance. These complex ions are detected right

at the metal surface. There is the question: does the nickel–hydrogen complex can be formed only on the outer surface or is created within the “surface region”, that means within several monolayers of the metal as hydride interstitial compound? This work was undertaken in an attempt to elucidate the reaction mechanism between hydrogen and nickel surface at the presence of high electric field.

## 2. Experimental and calculations

The instrument [5] used in this investigation was a high-resolution pulsed-laser time-of-flight atom-probe field ion microscope (PLTFAP). The ultrahigh vacuum experimental conditions and the measurement procedure were those described in Ref. [4]. The field emitter tip was obtained by means of electropolishing of nickel wire of 99.99% purity. The nickel tip was kept at a temperature of 20 K. The applied electric field strength was 30.3 V/nm. The partial pressure of hydrogen was  $10^{-6}$  Pa. Before each experiment, the emitter surface was processed to obtain an atomically smooth end-form by low-temperature field evaporation in the presence of neon. The emission occurred from (1 1 1)Ni steps.

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Table 1  
The relevant abundances of nickel and nickel–hydrogen ions

Ni <sup>+</sup>	23%
NiH <sup>+</sup>	29%
NiH <sub>2</sub> <sup>+</sup>	23%
NiH <sub>3</sub> <sup>+</sup>	25%

The quantum chemical calculations have been performed in order to interpret the results. For numerical computations, the GAUSSIAN 98 program package [6] was employed. The DFT theory was used to calculate the energy of the hydrogen–nickel complex by using a hybrid functional (B3LYP). The basis set taken for nickel atom was 6-31G.

### 3. Results and discussion

During the process of field desorption of nickel at a hydrogen gas phase the ions H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> were detected as well as nickel ions and nickel–hydrogen ions. The original mass spectrum obtained from a nickel specimen at hydrogen gas phase is shown in Fig. 1.

As each metal usually contains several isotopes, the mass-to-charge-ratios of metal–hydrogen ion species with a different number of hydrogen atoms can overlap with isotope mass lines of the metal. Fortunately accurate isotope abundances of elements are well known from isotope tables, thus using numerical fitting method, the relative abundance of various molecular ions can be derived. The relative abundances of nickel and nickel–hydrogen ions are listed in Table 1.

In the present investigation also, the field ion appearance energy was measured by using the time-of-flight method [7]. Contrary to expectations, the appearance energy of all ions was similar within the experimental error. Energy distributions of all ions Ni and NiH<sub>x</sub> show a very narrow distribution width, or practically there is no energy spread. This feature indicates that the detected ions are formed in the strictly specified place just at the metal outer surface [8].

The appearance energy of *n*-fold charged field-desorbed ions can be expressed from a thermionic cycle by [9]:

$$A_n^{hkl} = \sum_{i=1}^n I_i + \Lambda^{hkl}(F) - Q(F) \quad (1)$$

where  $I_i$  is the *i*th ionization energy of an atom,  $\Lambda^{hkl}(F)$  the binding energy of the atom (or the adsorption energy) in the high electric field at the (*hkl*) plane of the tip surface and  $Q(F)$  is the activation energy for field evaporation of the atom. Neglecting temperature effects (in our case  $T = 20$  K) and relatively small activation energy, the binding energy can be calculated from Eq. (1). Also in the case of nickel–hydrogen complex the binding energy can be evaluated based on these relations, where the respective values of the ionization potential and other quantities for a nickel–hydrogen molecule should be put in Eq. (1) instead of such data for nickel. These quantities, however, cannot be determined by means of the experiment. We have calculated the total binding energy  $E_b$  and ionization potential  $I_n$  of the nickel–hydrogen molecule using a quantum chemistry method. The geometry of a molecule in the equilibrium state was calculated by minimization of the total energy with respect to all its independent inner coordinates, i.e. the bond length, valence angles and dihedral angles. In Table 2 are collected results of these calculations.

On the basis of these data and calculations in an external electric field we can state that the NiH<sub>x</sub> molecules are stable as long as the field strength is not higher than 20–25 V/nm and (NiH<sub>x</sub>)<sup>+</sup> to 35–40 V/nm. Putting calculated values into Eq. (1) we were able to predict the value of adsorption energy of the measurement species, which is also shown in Table 2.

As a next step towards the understanding of the interaction between hydrogen and nickel surface we determined for the system of a hydrogen atom and a four-atom (like the tetrahedral void) and a six-atom (like the octahedral void) nickel cluster. Diagram of the binding energy as a function of the distance is shown in Figs. 2 and 3.

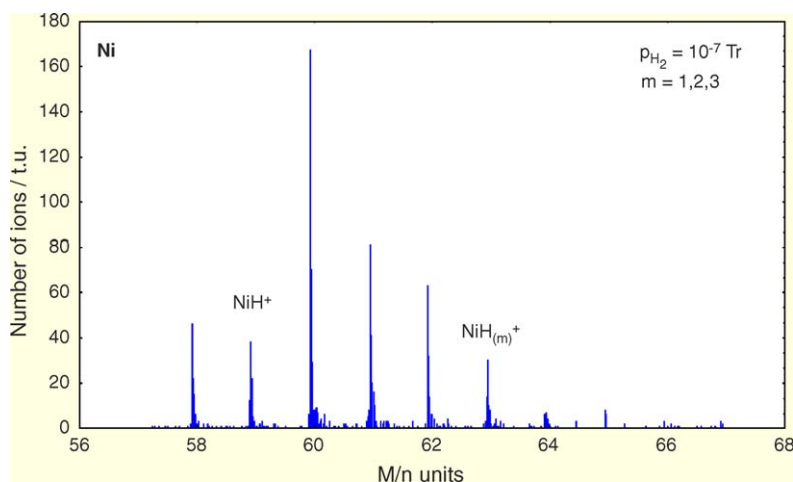


Fig. 1. Pulsed-laser field-evaporation mass spectrum of Ni taken in hydrogen atmosphere.

Table 2  
The binding characteristics of nickel hydrides in the equilibrium states

Molecule	Binding energy, per H atom [eV]	Ionization potential, $I_1$ [eV]	Adsorption energy, $A^{hkl}(F)$ [eV]
NiH	4.62	9.14	2.93
NiH <sub>2</sub>	3.32	6.60	5.47
NiH <sub>3</sub>	3.02	7.79	4.28

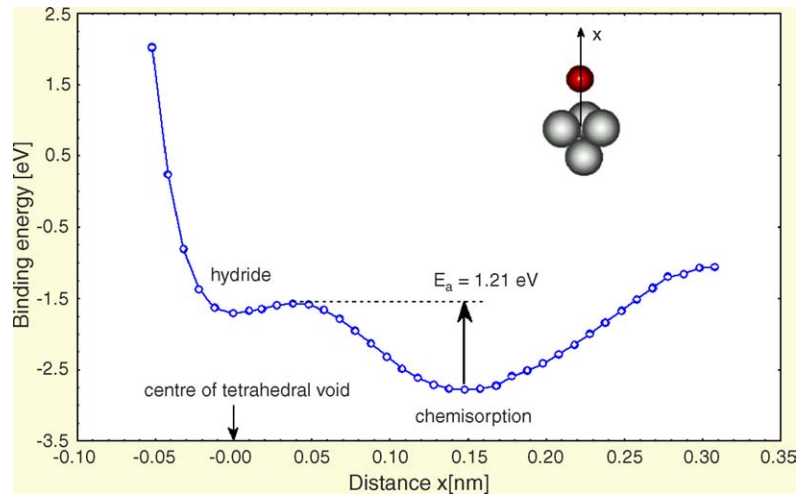


Fig. 2. Calculated binding energy changes in dependence on the distance  $x$  between hydrogen atom and four-atom nickel cluster. The distance between nickel atoms within the cluster is 248.9 pm.

As can be seen in these figures, the binding energy of hydrogen in the threefold hollow in both cases is the same and is equal to 2.78 eV. The results of this calculation are in accordance with the experimental value 2.74 eV [10]. Hydrogen forms ordered chemisorbed H-phases without reconstruction of the nickel surface. To diffuse into a tetrahedral or an octahedral void to create hydride, the hydrogen atom should pass over the barrier of activation energy of 1.21 eV and 1.61 eV, respectively. The binding energy of hydrogen with the tetrahedral void is 1.71 eV instead, and with the octahedral void is

1.64 eV. Due to the applied electric field, the field-free atomic interaction curve becomes bent down and shifted towards the low total energies. This indicates the occurrence of an effect in which the binding energy of the H–Ni complex reveals increase and the activation energy diminishes or disappears. On the other hand, the activation energies for the inverse process are 0.14 eV and 0.47 eV, respectively, and after withdrawal of the applied electric field the hydrogen may remain in the surface monolayer of nickel. Particularly in the octahedral void, this may lead to the appearance of NiH in NaCl-like

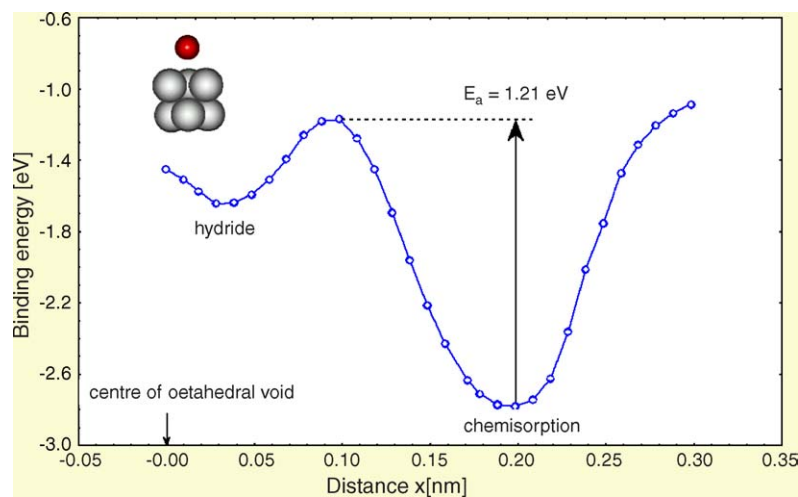


Fig. 3. Calculated binding energy changes in dependence on the distance  $x$  between hydrogen atom and six-atom nickel cluster. The distance between nickel atoms within the cluster is 248.9 pm.

structure. Nickel hydride was first prepared as a thin film on a Ni surface by electrolysis, with a maximum H:Ni ratio of approximately 0.6. Ni hydrides may have an fcc structure (defect NaCl structure), and this assumption agrees with the neutron diffraction studies [11,12]. NiH was obtained also at a room temperature in  $p_H = 600$  MPa.

In view of the presented results, we believe that nickel hydride interstitial compound is formed in the high electric field in the sites within two topmost monolayers (of the (1 1 1)Ni plane) and during the low-temperature field evaporation process it is desorbed and detected as NiH<sub>x</sub> molecules.

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