

# Excitation of Hydrogen Subsystem in Metals by External Influence

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## ABSTRACT

Experimental results which point to the existence of a hydrogen subsystem in solids and the possibility of its excitation by external influence are described. Occupying the equivalent positions inside host metal, hydrogen forms its own subsystem inside a crystal lattice and has vibration frequencies lying outside the phonon spectrum of a crystal. Under external energy input (for instance by means of radiation) an excitation of vibrations occurs in the hydrogen subsystem. The following facts point to this: intensive migration, diffusion and release of hydrogen isotopes from metals at low temperature; superlinear dependence of H, D release from metals on the electron current density and H, D concentration; H and D release from the whole volume of samples during the irradiation process by focused electron beam; H and D release in both molecular and atomic forms.

## Introduction

Hydrogen in metals is a very important technical and scientific problem. The technical problem is related to the negative influence of hydrogen on the mechanical properties of metals. Hydrogen produces various types of defects, cracks, and embrittlement. Hydrogen is the lightest element and possesses high mobility in solids; hence metal-hydrogen systems present special scientific interest. Pons and Fleischmann initiated great interest in the problem of hydrogen in metals in connection with so-called “cold nuclear fusion.” Numerous investigations have demonstrated that saturation of metals by hydrogen under electrolysis or in a glow discharge can lead to excess heat, X-ray emission, and change of isotopic and mass composition of metals. However all these processes, as a rule, are uncontrolled, realized spontaneously, and their mechanism is unknown. One of the reasons for this is insufficient knowledge about the influence of an electrolytic medium and glow discharge on the behavior of hydrogen dissolved in solids.

In the present report we discuss a new phenomenon: “excitation of hydrogen subsystems in metals by external influence,” which aids in the understanding of the processes enumerated above.

## Experimental results

Systematic investigations of the influence of hydrogen and radiation (accelerated ions and electrons, X-rays, gamma- quantum) on metal properties have shown [1-4] the following: hydrogen atoms occupy regular positions in the crystal lattice, forming their own hydrogen subsystem; the hydrogen subsystem is able to accumulate the external energy; the absorbed energy is distributed inside the hydrogen subsystem and, as a result, the hydrogen atoms' kinetic energy is much higher than that of the matrix atoms.

The following experimental findings point out the existence of the hydrogen subsystem in solids, and the possibility of its excitation by external radiation.

### 1. Intensive migration, diffusion and release of hydrogen isotopes from metals at low temperatures.

The hydrogen migration and release from metals caused by the accelerated ions was explored by the elastic recoil detection method. This method allows us to study the hydrogen migration in the sample irradiated by accelerated ions. Fig. 1 shows the change of hydrogen concentration in 12Cr18Ni10Ti stainless steel versus the radiation flux of the 12 MeV  $N^{14}$  ions for three depths  $x=50, 100,$  and  $200$  nm. In all layers the hydrogen concentration decreases in the process of irradiation. Similar results were obtained on other metals. A large yield of H atoms cannot be explained by the nuclear collision of H with nitrogen nuclei since the number of collisions calculated from the Rutherford cross-section is  $10^8$  times less than the corresponding experimental value.

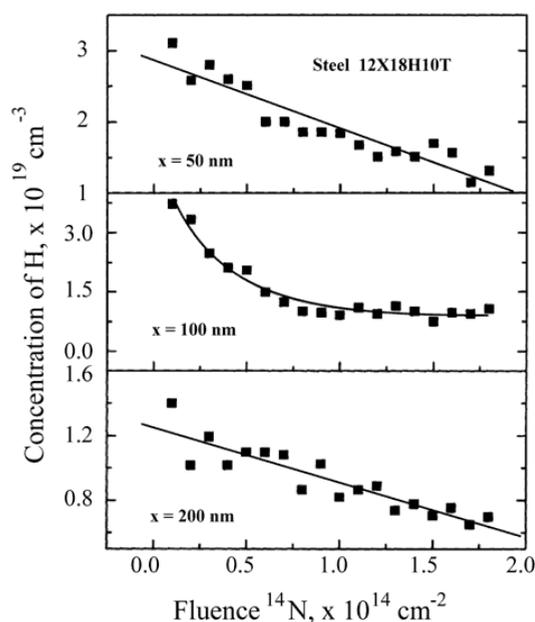


Figure 1. Hydrogen concentration dependence at different depths  $x$  on the  $N^{14}$  dose.

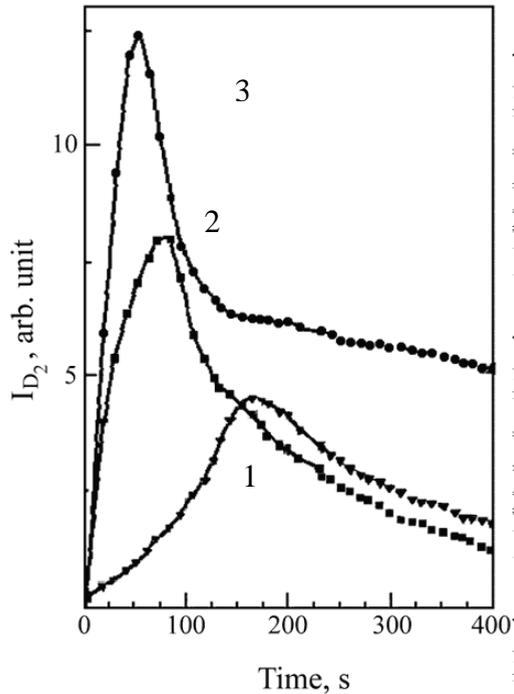


Figure 2. Intensity of deuterium release from stainless steel under the electron beam irradiation ( $U=20\text{keV}$ ). 1:  $I=50\ \mu\text{A}$ ; 2:  $I=100\ \mu\text{A}$ ; 3:  $I=150\ \mu\text{A}$ .

Hydrogen migration and release under irradiation by accelerated electrons and X-rays were studied in a high vacuum installation. This installation includes a programmed heating unit, a vacuum cell connected to a mass-spectrometer and an electron gun with energy of 10-100 keV. Metal samples were saturated with deuterium electrolytically. Loading with deuterium made it possible to study the gas release alone, separating it from uncontrollable hydrogen presence in the vacuum system. During radiation exposure the sample temperature was measured by a thermocouple. Under the electron beam influence  $U$  of 20 keV energy and the current  $I=50\ \mu\text{A}$ ,  $100\ \mu\text{A}$ , and  $150\ \mu\text{A}$ , the intensive release of deuterium from the stainless steel takes place (Fig. 2). The maximum deuterium release rates under accelerated electrons irradiation are observed at the times of 150s, 60s, and 45s for  $I=50\ \mu\text{A}$ ,  $I=100\ \mu\text{A}$ ,  $I=150\ \mu\text{A}$ , respectively. During these measurements, the temperature of the external side of samples in the electron beam area did not rise more than  $60^\circ\text{C}$ , and on the rear side, it did not rise more than  $40^\circ\text{C}$ . In the absence of an electron beam the equilibrium release of hydrogen was not observed at these temperatures.

## 2. Superlinear dependence of H, D release from metals on the electron current density and H, D concentration.

The dependence of H, D release from stainless steel and niobium on electron current density is shown on Figs. 3a and 3b. This dependence reveals that a collective interaction between the radiation and the hydrogen subsystem exists.

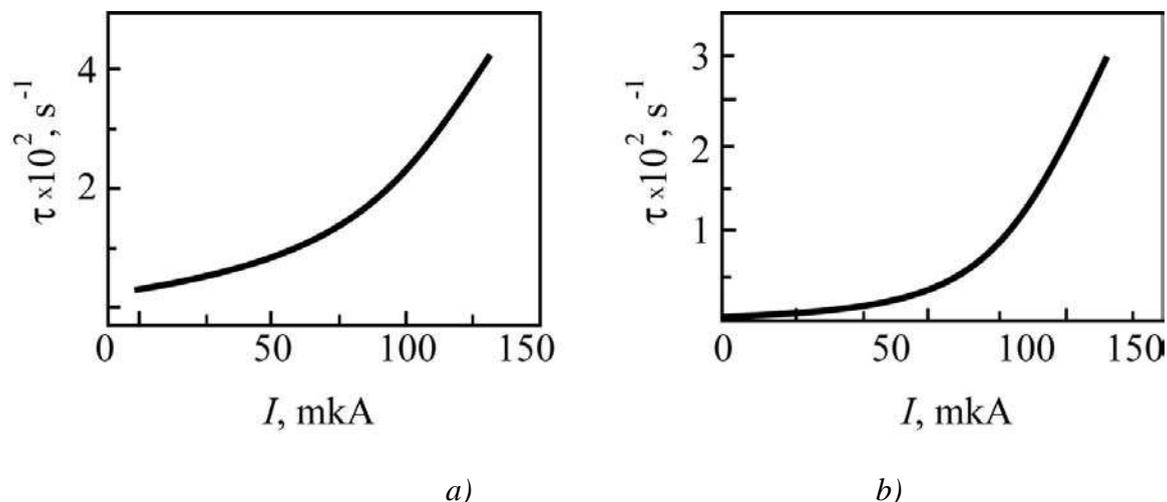


Figure 3. Dependence of D release from *a)* stainless steel and *b)* niobium on the electron current density,  $I$ .

## 3. Hydrogen isotopes release from the whole volume of samples during the irradiation process by focused electron beam.

Hydrogen isotope release from the metals was studied under the simultaneous application of an electron beam and linear heating. The area of the sample irradiated by the electron beam is  $0.20 \text{ cm}^2$ , which is much smaller than the total sample area ( $2\text{-}4 \text{ cm}^2$ ).

The linear heating along with the electron beam effect was accompanied by the maximum hydrogen release shift into the low temperature region (Fig. 4). This shift is  $80^\circ\text{C}$  in stainless steel;  $125^\circ\text{C}$  in niobium, and  $65^\circ\text{C}$  in palladium.

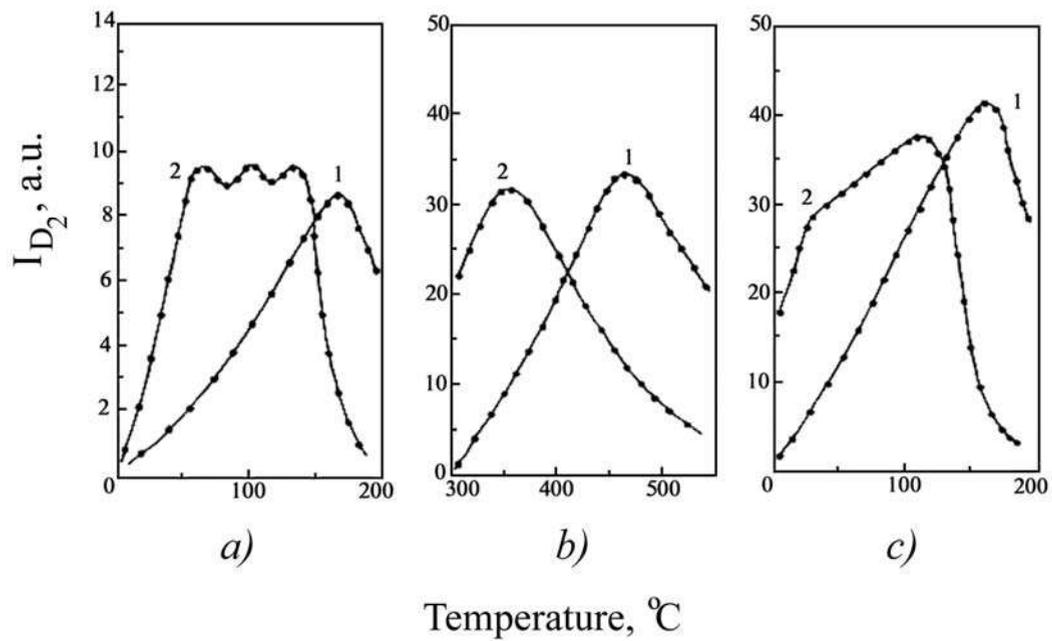


Figure 4. Deuterium release from stainless steel (a), Nb (b) and Pd (c) versus the linear heating at the rate of  $0.4^{\circ}C/s$ : 1 – without electron beam; 2 – with electron beam;  $E = 20$  keV. The current  $I$  is a)  $100 \mu A$ , b)  $50 \mu A$ , and c)  $20 \mu A$ .

#### 4. Hydrogen isotopes released in both atomic and molecular forms.

The presence of released atomic hydrogen was measured by a special dye, which is sensitive to hydrogen in atomic form. The measuring method is based on the bleach effect of organic pigments placed on a catalytic substrate. Atomic hydrogen bleaches the dye, changing its color from red to white, while molecular hydrogen does not affect the dye color. The bleach of the dye is more effective the longer it is exposed to hydrogen and the greater the hydrogen concentration is. The bleach of the pigment by D and H atoms allows us to estimate the intensity distribution of atom release along the surface. The experimental scheme is presented in Fig. 5.

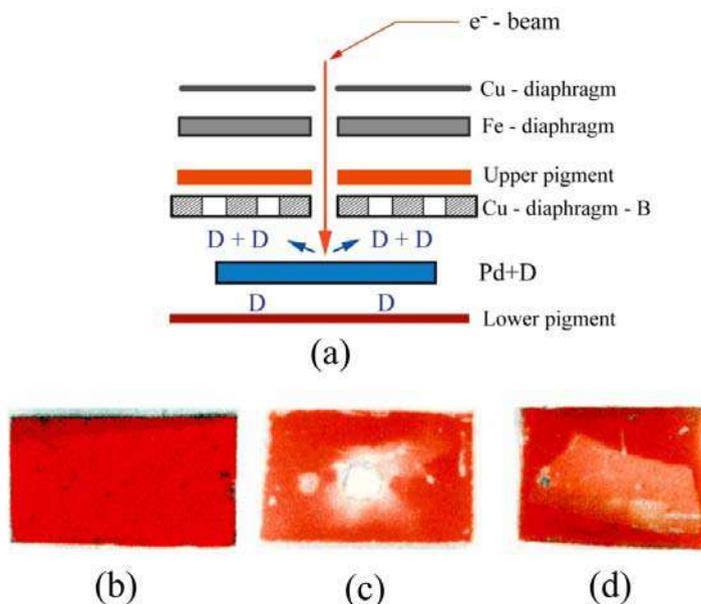


Figure 5. The arrangement of the diagram and pigments at the Pd film irradiated by an electron beam: (a) the scheme of the experiment; (b) initial pigment; (c) a state of the upper pigment after irradiation; (d) a state of the lower pigment after irradiation.

In this experimental setup the copper and iron diaphragms form an e-beam. A second copper plate with holes was placed between Pd and the dye. The whole "sandwich" was tightly pressed together in order to avoid a lateral clearance between the Pd film and the plates.

Measurements have shown that atomic hydrogen is released most intensively under the direct effect of the electron beam (Fig. 5c). In addition, a weak release of D and H atoms was observed from the opposite side which was not exposed to the electron beam. This resulted in the appearance of the bleach region in the dye in the shape of the Pd sample (Fig. 5d). The bleach area in the dye on the rear side of the Pd sample was uniform throughout the whole surface in its contact with Pd and had no peculiarities at the point

opposite to the electron beam entrance. The uniform bleach of the dye on the rear (not irradiated) side showed that D and H atom release is not correlated with the thermal heating of Pd at the point of electron beam effect. The temperature on both the lower and upper sides of the irradiated thin Pd sample ( $d \sim 0.15\text{mm}$ ) was practically the same. It was measured by thermocouples placed on the upper and lower sides of the sample. In our experiments it did not exceed 60-100°C.

The most important finding is that the hydrogen releases from metal not only in a molecular but also in an atomic form. Moreover, the electron beam directly affects the sample only locally, while it excites the entire internal hydrogen subsystem.

### **Electron structure of the palladium hydrogen system**

An unexpected observation here is that hydrogen diffusion is stimulated by ionizing radiation (accelerated electrons and ions, and X-rays). It is known that ionizing radiation loses its energy in the process of collision with sample electrons producing an excited electron subsystem. The lifetime of these processes in metal is very small ( $10^{-15} - 10^{-16}$  s) and it is not clear how the energy from the electron subsystem is transferred to the hydrogen subsystem.

To answer these questions it is necessary to study the modification of the host electronic structure of metals by the presence of hydrogen. With this purpose the electronic structure of a pure Pd crystal in the FCC lattice and the Pd-H system in which the hydrogen atoms occupy octahedral sites have been calculated using the self-consistent linearized augmented-plane wave method. The *ab initio* calculations were performed within the local-density-functional approximation, using the Hedin-Lundqvist exchange-correlation potential. The valence states were treated in a scalar-relativistic approximation, while the core states were treated fully relativistically. Using thus obtained band structure the imaginary part of the dielectric function  $\epsilon_2$  in the energy range  $\hbar\omega < 18$  eV has been calculated within the constant matrix element approximation.

Figure 6 shows the calculated electronic densities of states for pure Pd and PdH. From a comparison of the band structures of the pure Pd and Pd-H systems one can note the following characteristic modification of the pure Pd electronic structure upon hydrogen absorption:

- the filling of the *s* - band of palladium by the electrons of dissolved hydrogen;
- the lowering of the bottom of the conduction band due to hybridization of *s* states of hydrogen with *s*, *p*, and *d* states of Pd atoms;
- an upward shift of the Fermi level relative to the top of the *d* Pd band which results in a decrease of the electronic density of states of the system at the Fermi level.

It can be also seen from Fig. 6 that the presence of hydrogen in a Pd lattice results in a pseudogap in the electronic spectrum of the Pd-H system having energy of around  $\sim 4$  eV. The presence of this pseudogap in the electronic spectra of the Pd-H systems indicates the appearance of a covalent component of the bond between palladium and hydrogen atoms in addition to the metallic bond characteristic of the pure palladium. It is known that in crystals with a covalent bonding the lifetime of electronic excitations is longer than in pure metals. Hence, during this longer time, hydrogen is capable of starting to migrate.

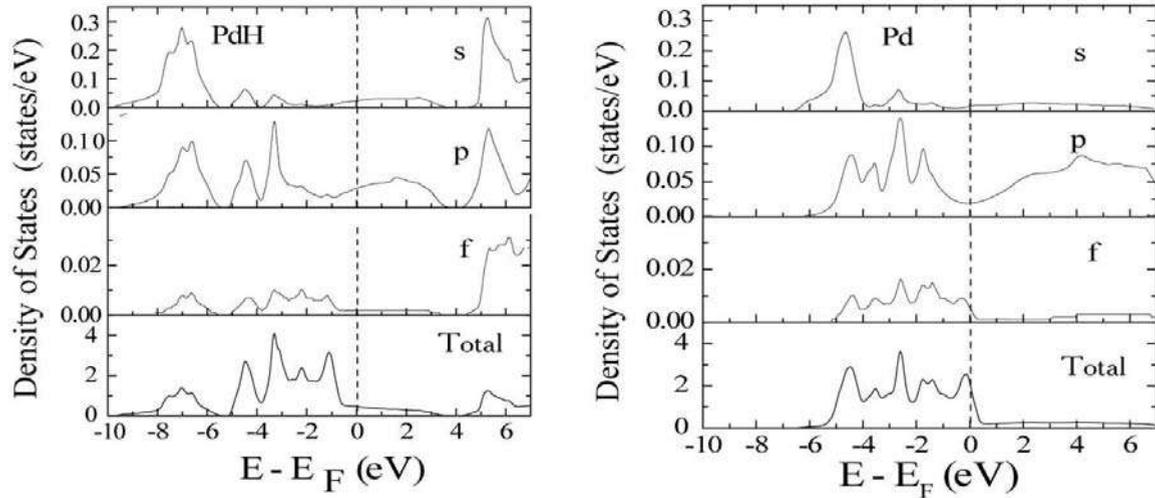


Figure 6. Calculated partial and total electron densities of state for Pd and PdH.

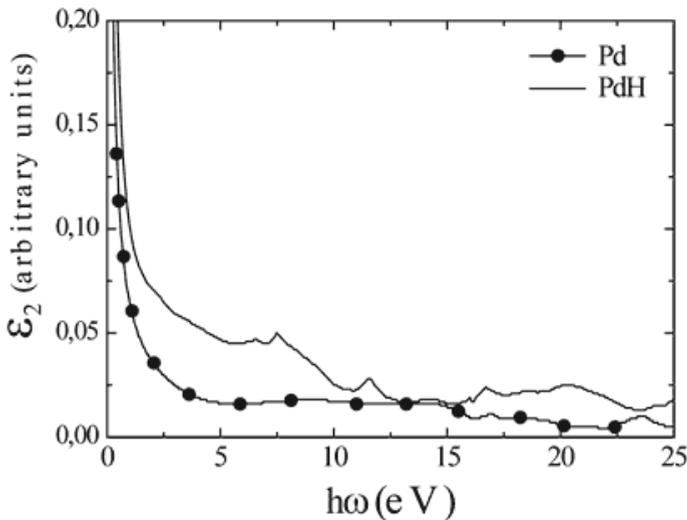


Figure 7. Imaginary part of dielectric function  $\epsilon$ .

Figure 7 shows the calculated imaginary part of the dielectric function,  $\varepsilon_2(\hbar\omega)$ . From this figure it is seen that the presence of hydrogen in the palladium significantly enhances the value of the dielectric function  $\varepsilon_2(\hbar\omega)$  in the energy range from  $\sim 1.5$  eV up to  $\sim 7$  eV. This fact leads to the increase in absorption by the metal-hydrogen system under the influence of external energy. Thus, one can conclude that the features of the electronic structure of the metal-hydrogen system can lead under the influence of irradiation to the following effects:

- increase of lifetimes of the one-electron excitations due to the local character of the metal-hydrogen bonds;
- increase in absorption of the irradiation energy by the crystal due to the appearance of an additional electronic density localized in the vicinity of the hydrogen atoms.

In the next stage of our research, we studied the characteristics of collective electronic excitations in metal-hydrides, taking as an example the Pd-H system. Our calculations show that in both pure Pd and PdH a large number of peaks are observed in the excitation spectra in agreement with existing energy-loss experiments. Fig. 8 shows the dominant plasmon peak dispersions in the pure Pd and Pd-H systems. One can see that dominant plasmon energy in the Pd-H system is lower than in the pure Pd case.

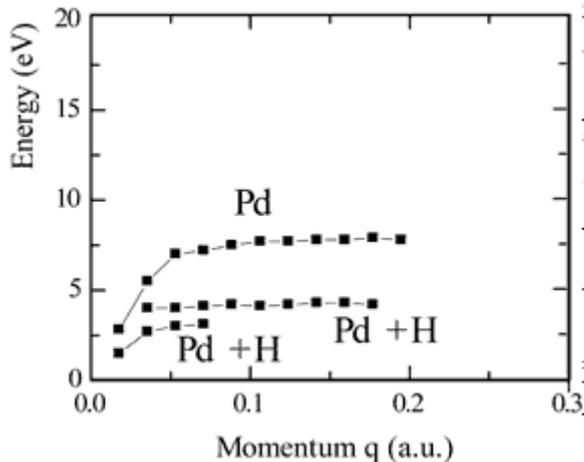


Figure 8. Dispersions of the low energy dominant collective electronic excitations in Pd and PdH.

This fact indicates that the probability of excitation of plasmons in Pd-H system increases in comparison with the pure Pd case. Hence one can suggest that in the process of ionizing irradiation large-scale oscillations of the electronic density are possible in the Pd-H system at lower energy. As a result, strong local electric fields can appear inside the crystals (Fig. 9) in which hydrogen atoms could be accelerated.

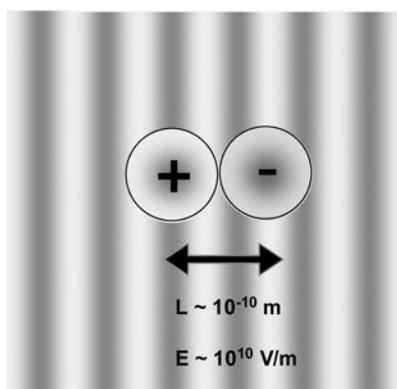


Figure 9. Possible local electric fields inside a crystal due to plasmon excitation.

The hydrogen subsystem can be excited under a glow discharge. Hydrogen atoms in plasma have energy sufficient to excite plasmons in metal. The excitation of the hydrogen subsystem during electrolysis process takes place as the result of impact of hydrogen babbles. The impact of babbles is accompanied by the emission of the low energy photons. The excitation probability can be increased by drawing the hydrogen bubbles to the cathode. This can be done, for instance, by using of porous films (such as nuclear filters).

## Conclusion

During occupation of the regular positions inside a metal, hydrogen forms its own subsystem inside a crystallographic lattice of a host metal. This subsystem has vibration frequencies lying above the phonon spectrum of a crystal. Under the input of energy, for instance, by means of radiation, electrolysis process, and glow discharge, the hydrogen subsystem can be excited. Non-equilibrium vibrations of the hydrogen subsystem are long-lived on the time scale of electronic relaxations in metals. Therefore, the diffusion of hydrogen can be stimulated by absorption not only of the energy of thermal vibrations  $kT$ , but also by the energy of non-equilibrium vibrations of hydrogen  $\hbar\omega$  which exceeds  $kT$ . In the process of ionizing irradiation, large-scale oscillations of the electronic density are possible in the Pd-H system at lower energy. As a result, strong local electric fields can appear inside the crystals in which hydrogen atoms could be accelerated. Excited hydrogen subsystem in metals is a specific medium, a high density and low temperature plasma, in which some exothermal chemical and nuclear processes can occur.

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