Excitation of Hydrogen Subsystem in Metals by External Influence

I.Chernov[1], Yu.Koroteev[2], V. M. Silkin[3], Yu.Tyurin[1]

Thermal and Isotope Effects during Metal Electrolytic Charging by Hydrogen with Divided Volume

I.Chernov[1], Yu Cherdantsev[1], A. Lider[1], N. Nikitenkov[1], Garanin[1], Khandorin[4]

[1]Tomsk Polytechnic University, Tomsk, Russia
[2]Institute of Strength Physics and Materials Science, Tomsk,
[3]Donostia International Physics Center, San Sebastian, Spain
[4]Tomsk Atomic Centre, Tomsk, Russia

Plan of Report

- Introduction
- Excitation of the hydrogen subsystem by irradiation
- Excitation of the hydrogen subsystem in electrolysis process
- Isotopic effects in process of the loading of metal by hydrogen
- Conclusion

Introduction

- Hydrogen in metals is very important technical and scientific problem.

- Technical problem is related with negative influence hydrogen on mechanical properties of metals. Hydrogen initiates different types of defects, cracks, hydrogen embrittlement.

- Hydrogen problem is central for construction materials in petroleum and chemical industries, nuclear, thermonuclear, hydrogen energy, medicine.

- Scientific problem is connected with searching for the ways of the reduction of the negative influence of the hydrogen on materials properties.
- Pons and Fleshman initiated great interest to problem of hydrogen in metals in connection of “cold nuclear fusion ”.
- Numerous investigations show, that loading of metals by hydrogen at electrolysis or in a glow discharge can stimulate excess heat, X-rays and alpha – particle emission, change of isotopic and mass composition of metals.
- However these processes, as a rule, are uncontrolled, realized spontaneously and their mechanism is unknown.

- One of reason - it is insufficient knowledge about influence of electrolytic medium and glow discharge plasma on the behavior of the hydrogen dissolved in a solid.

- Main subject of our group research - a study of the influence of the hydrogen and radiation on properties of construction materials for nuclear and thermonuclear reactors. We discovered new phenomena “Excitation of hydrogen subsystem in metals by external influence”

- In present report we are planning to discuss this phenomena which help us to understand the above enumerated processes.

Experimental procedure

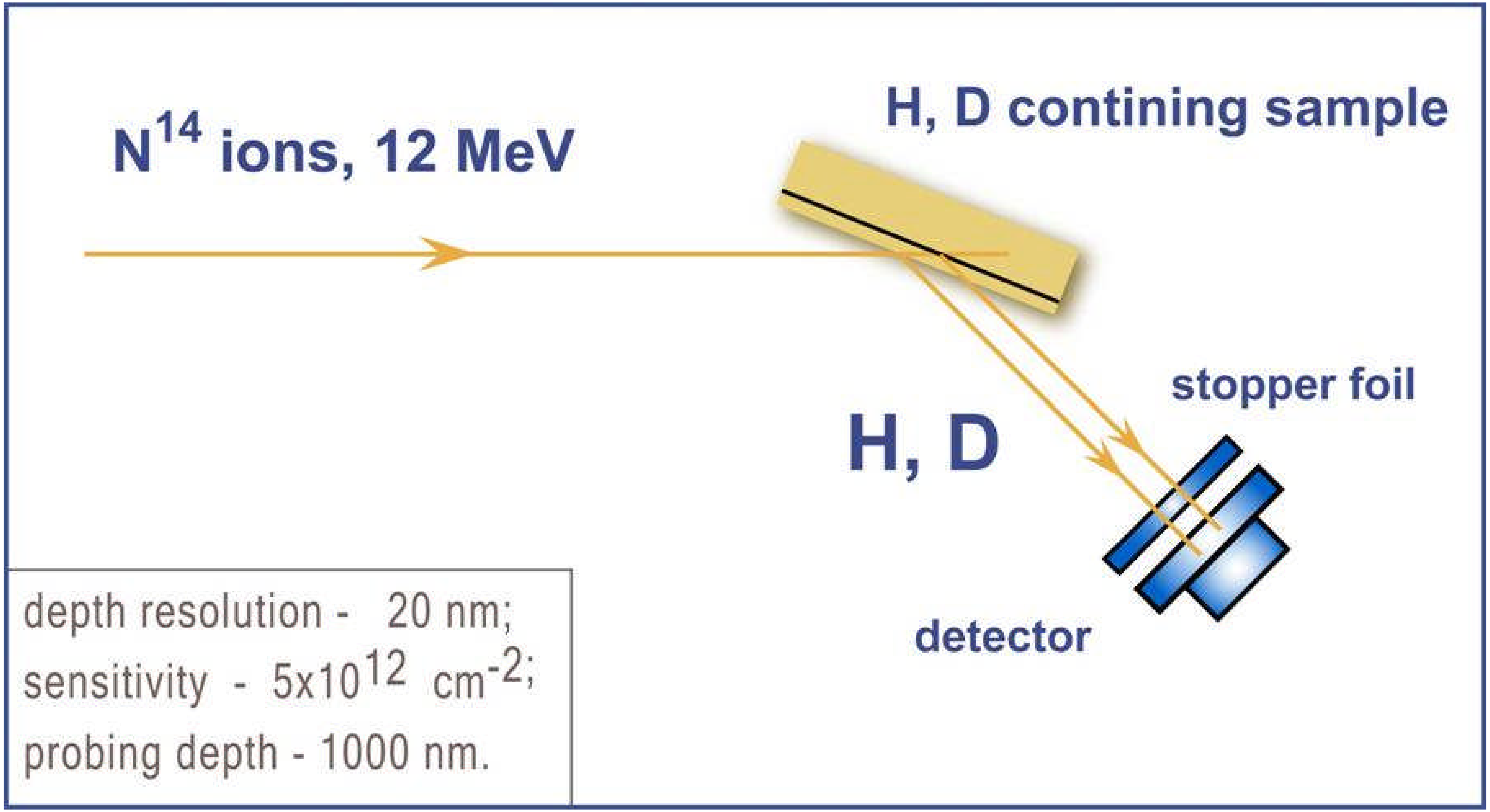
- ❖ High vacuum installation;
- ❖ SIMS - secondary ion mass spectrometer;
- ❖ Mass-spectrometer;
- ❖ Electron accelerator 10-100 KeV;
- ❖ X-ray sources 20-200 KeV;
- ❖ Microscopes;
- ❖ Cyclotron;
- ❖ Electron - Positron annihilation Installation.

- Metal samples were saturated by deuterium.

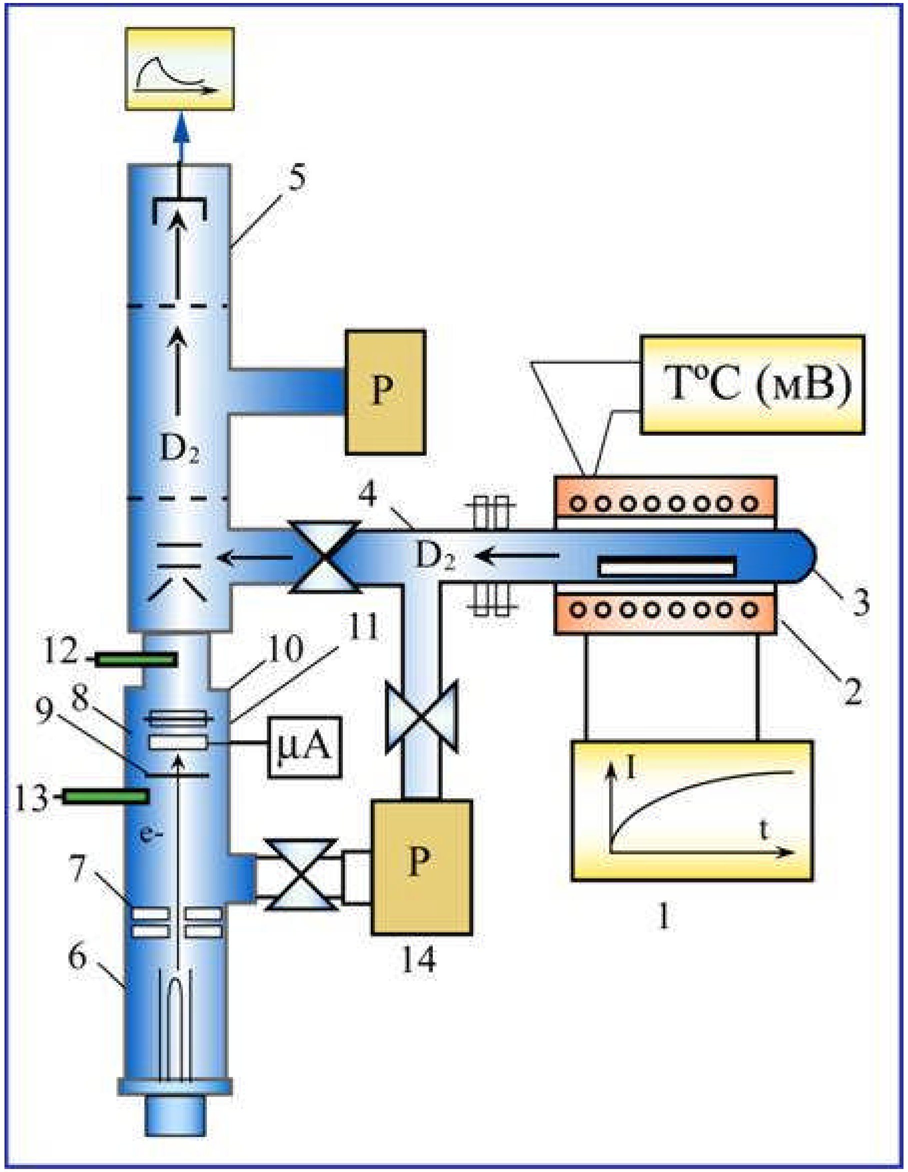
- It allows us to study the deuterium release alone, separating it from hydrogen which always presents in the vacuum system and samples.

- During the irradiation process the sample temperature was measured by a thermocouple.

- Hydrogen behaviour under effect of accelerate heavy ions we study by means of elastic recoil detection method which allows **in situ** to observe migration, diffusion and release of hydrogen.



Geometry of the Elastic recoil detection method



1,2 – programmed heating unit

3 – samples heating cell

4 – vacuum conductor

5 – mass-spectrometer

6,7 – electron gun

8-13 – cell for radiation effect on materials

14 – magnetic discharge pumps

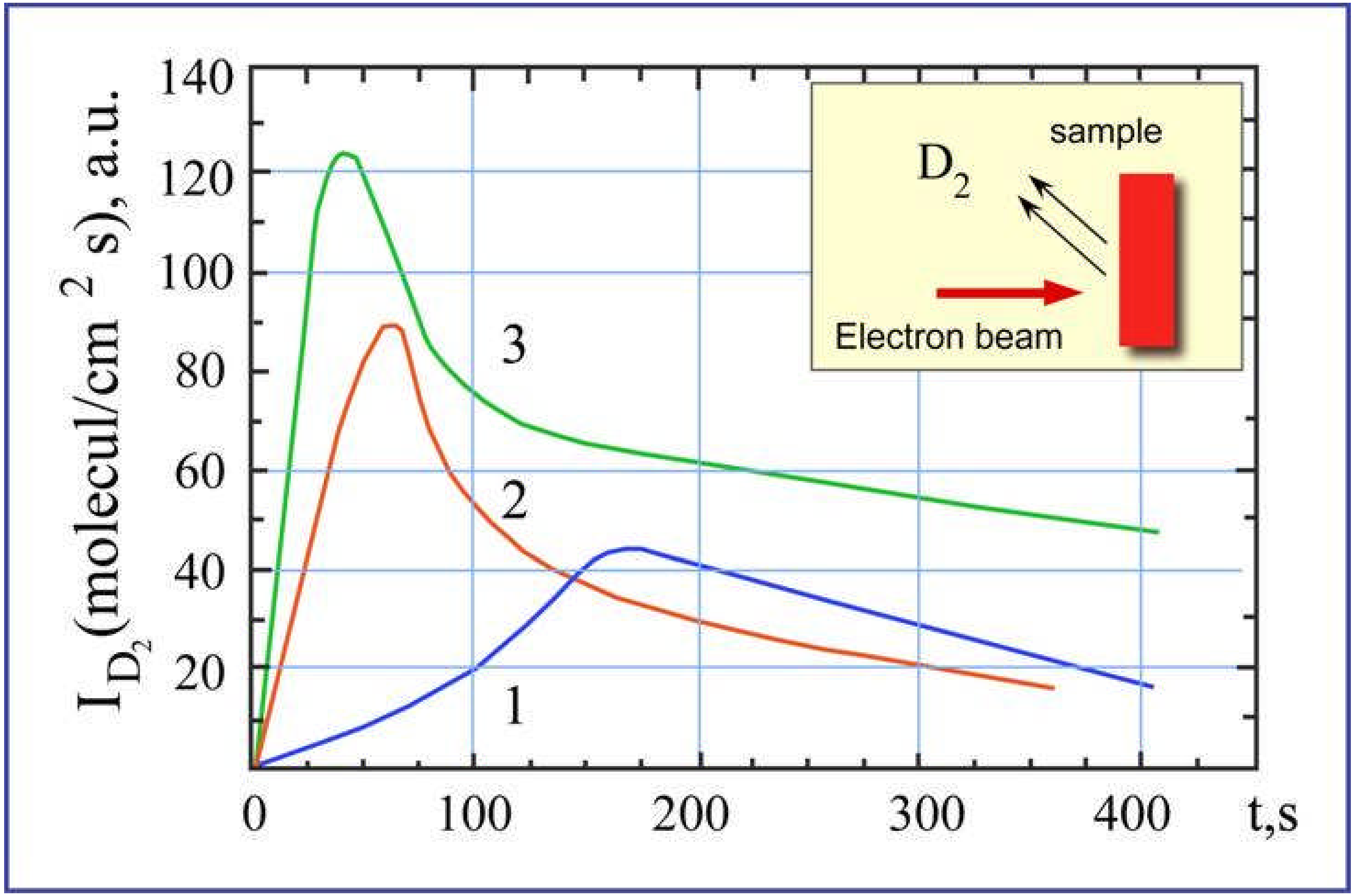
Experimental equipment for research of thermo- and radiation-stimulated hydrogen release

The experimental results testify

- H atoms occupy regular positions in the crystal lattice forming their own H subsystem
- The H-subsystem is able to accumulate the external energy
- Absorbed energy is distributed inside the H-subsystem and, as a result, the H-atoms kinetic energy is much higher compare witch matrix atoms.

The following facts point out to:

Migration, diffusion, and release of hydrogen isotopes from metals are stimulated by radiation at a low temperature of samples.

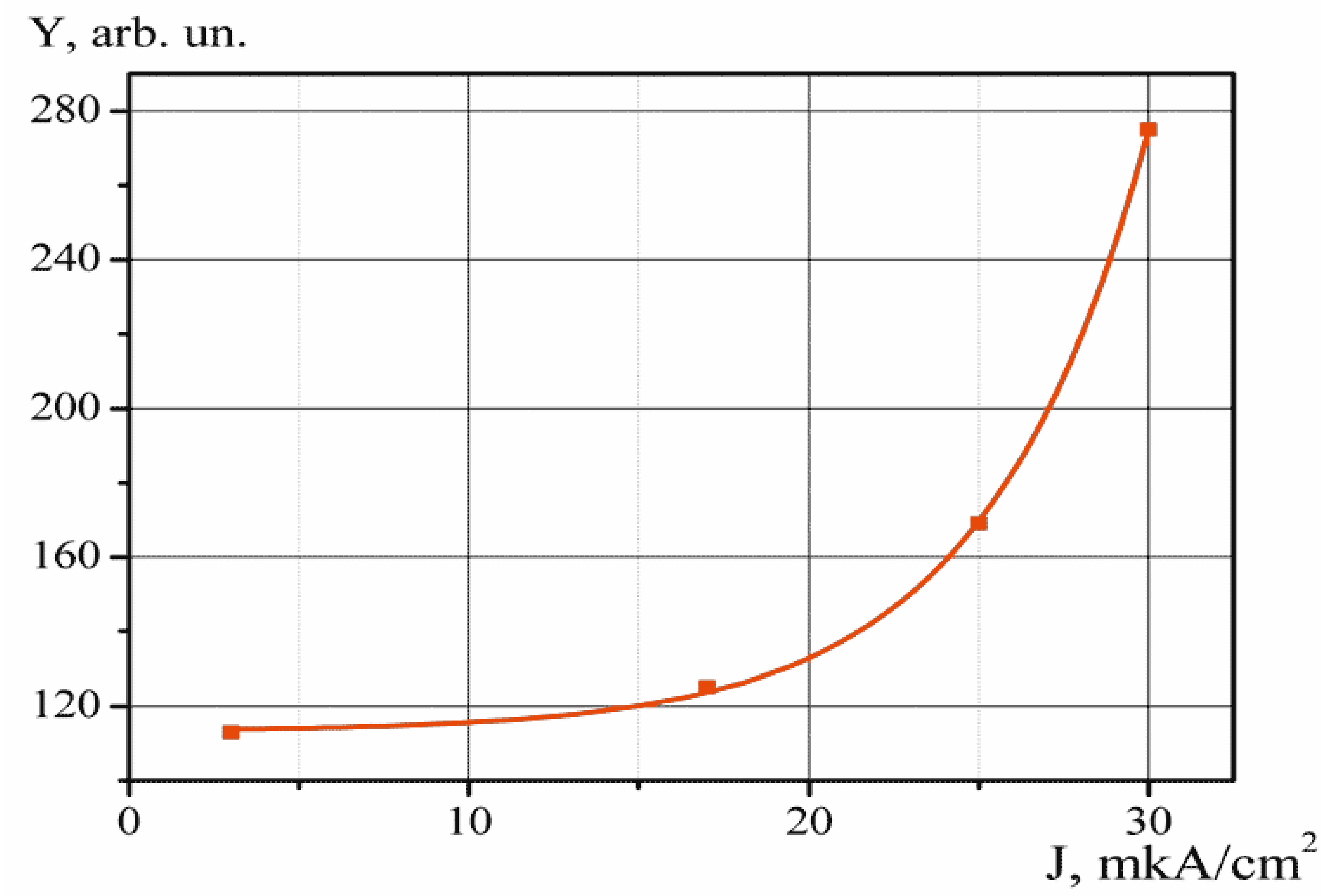


Intensity of deuterium release from stainless steel under electron beam effect (U=20 keV)

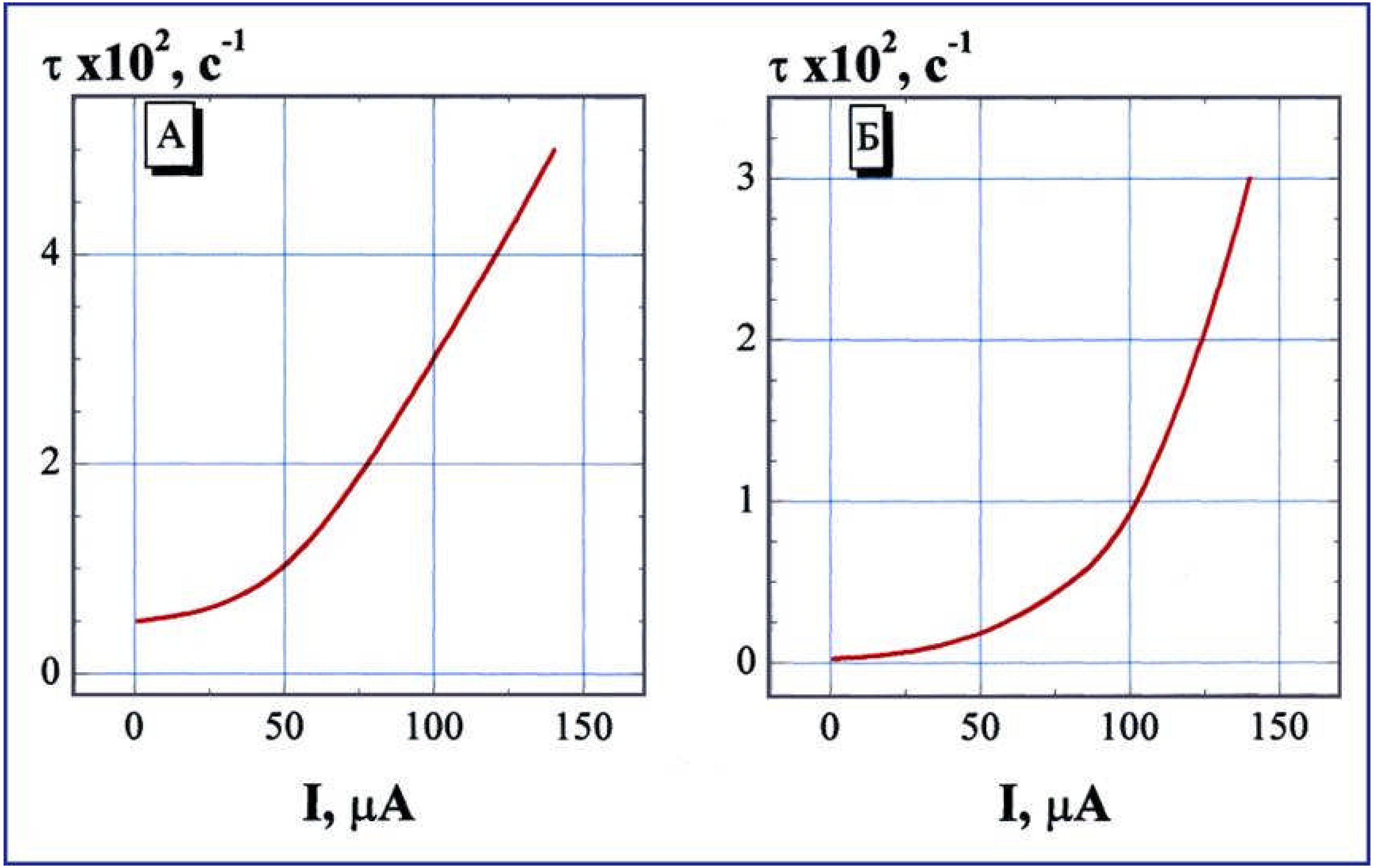
1) 50μA, τ^{-1} < 0.01 s^{-1}; 2) 100 μA, τ^{-1} < 0.03 s^{-1};

3) 150 μA, τ-1 < 0.03 s^{-1};

Super linear dependence of H, D release from metals on the electron current density and H, D concentration

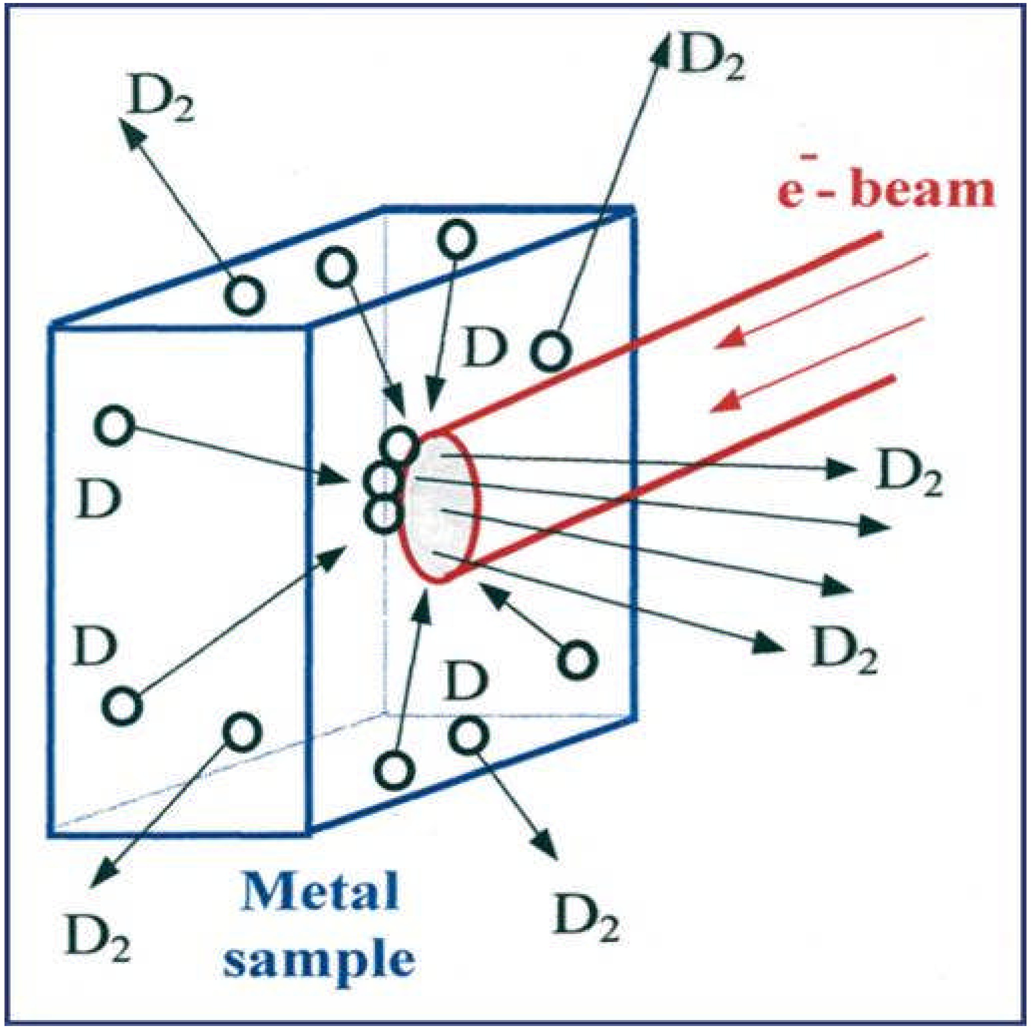


Dependence of deuterium release rate from Pd on electron beam current density. Electrons energy – 40 кэВ.

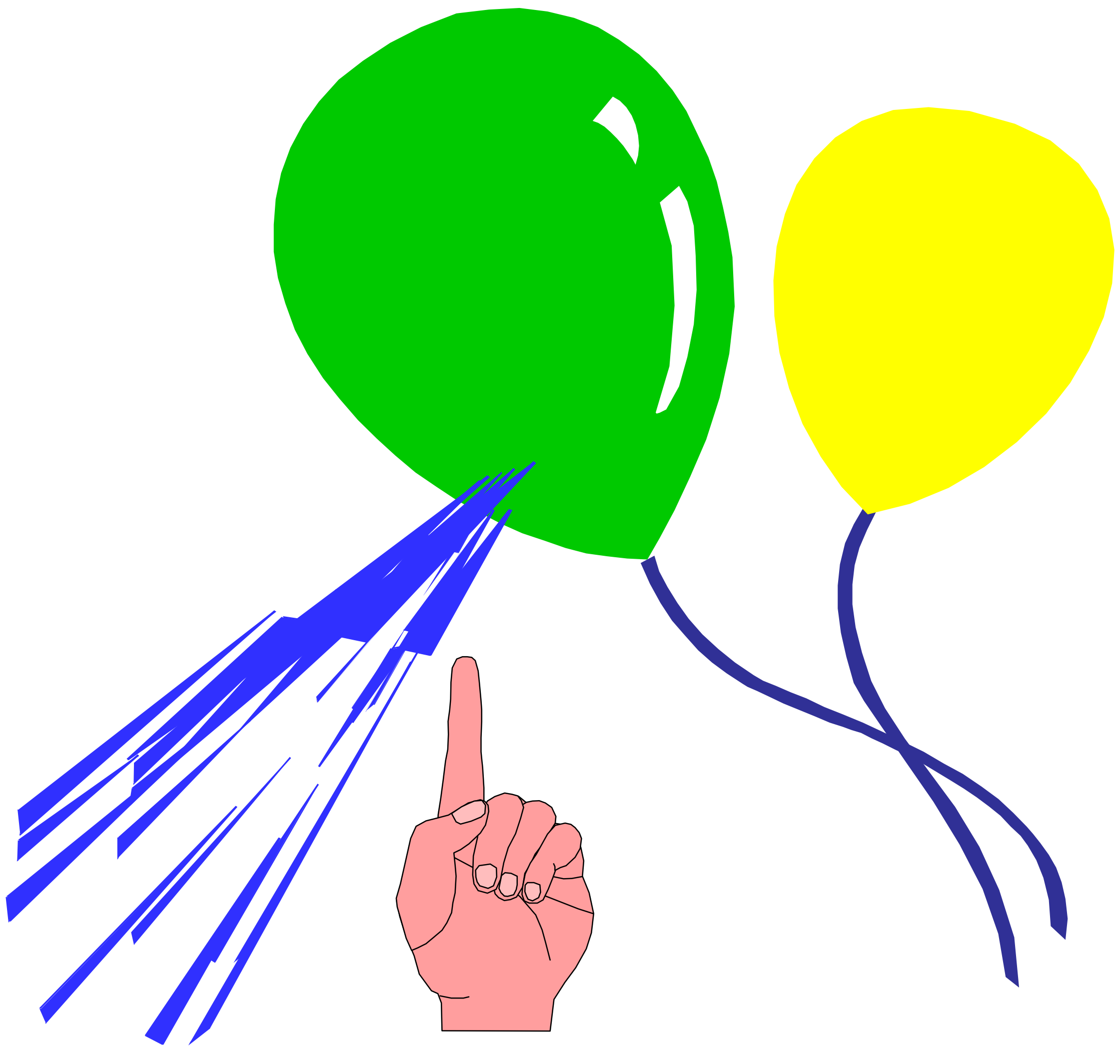


Dependence of deuterium release rate on electron beam current: a-stainless steel, b-Nb.

Hydrogen releases from a whole volume of samples under of external irradiation by focused electron beam



Focused electron beam stimulates H release from the whole sample. It testifies that H atoms are connected with each other and the energy interchange takes place.



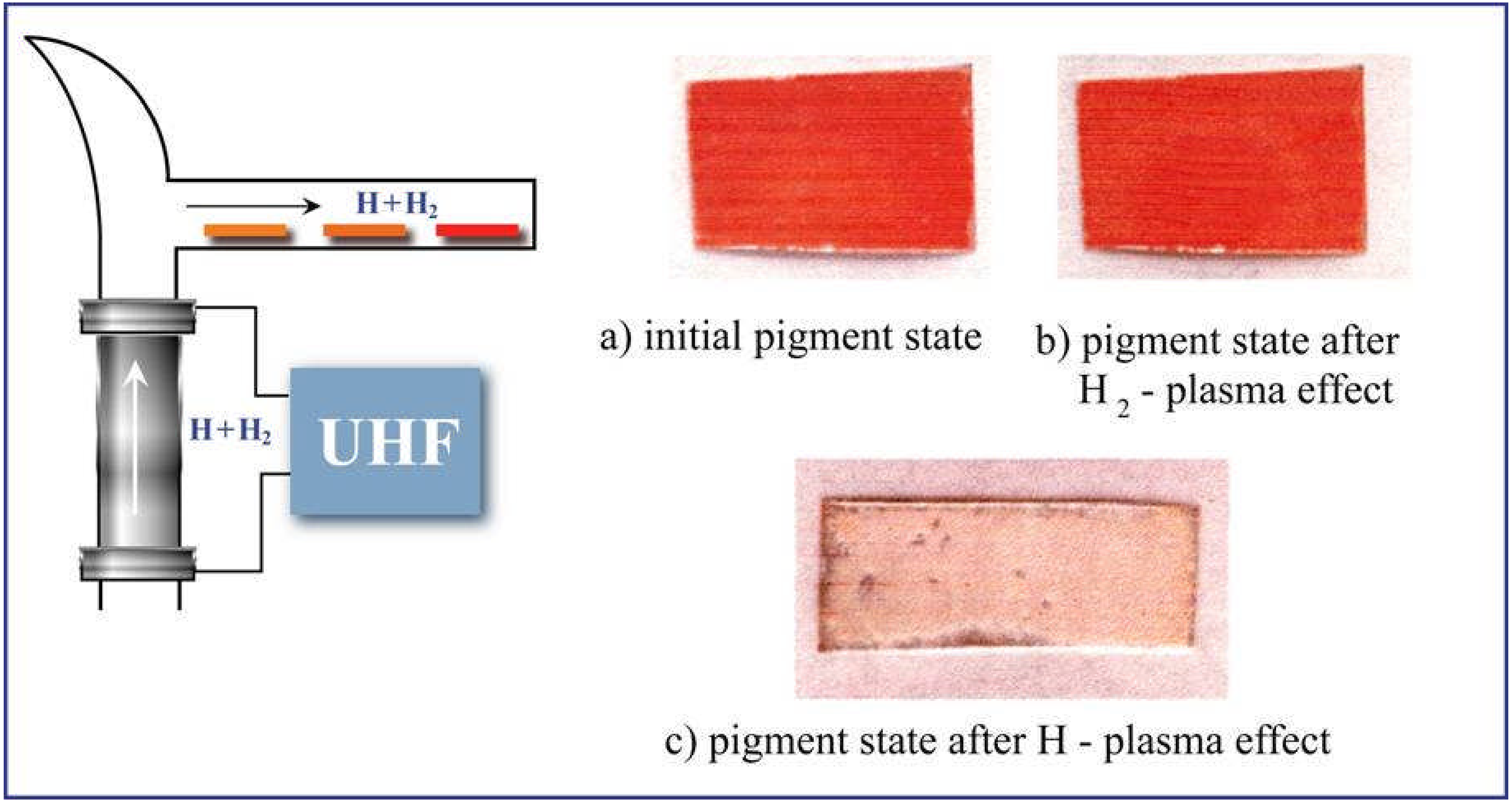
Balloon pricked by needle
Air is pushed out
A Balloon filled by air

Hydrogen isotopes release both in the molecular and atomic forms.

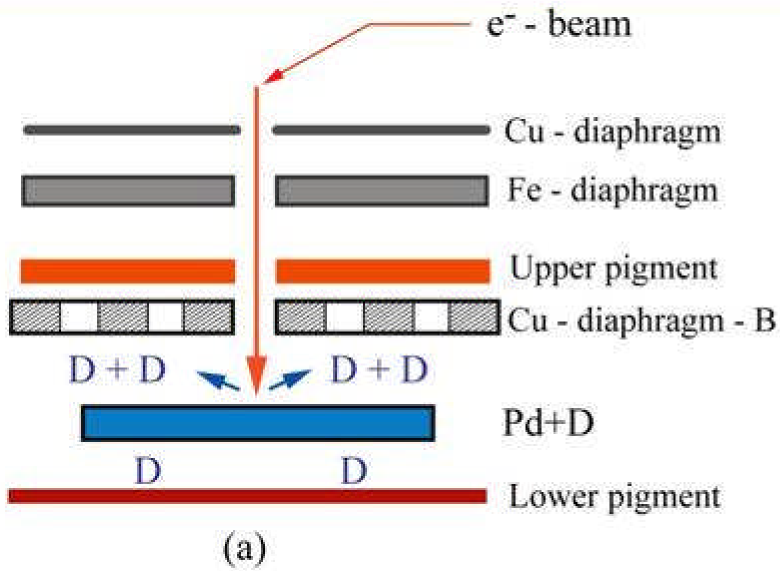
❖ Atomic hydrogen was measured by a special pigment (dye-staff), which is sensitive to the hydrogen in an atomic form.

❖ Atomic hydrogen changes the pigment color from red to white, while molecular hydrogen does not change it.

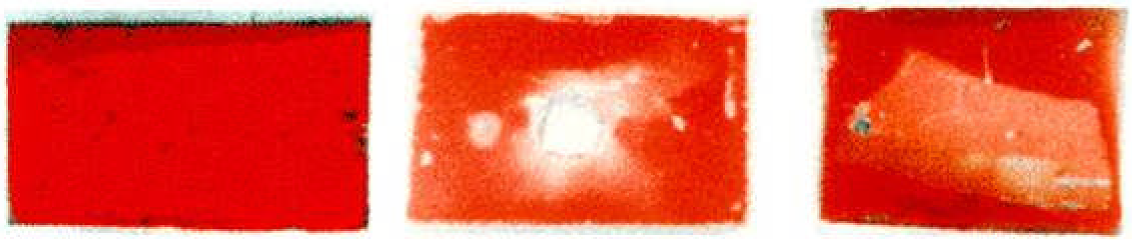
❖ The bleach of the pigment by D and H atoms allows us "to observe" the intensity distribution of atom release on the sample surface.



Pigment state, H_2 – plasma effect and UFH plasma $H+H_2$



Sandwich structure of sample with copper diaphragm between deuterated Pd and pigment



(b) - initial pigment (c) - upper pigment state after irradiation (d) - lower pigment state after irradiation

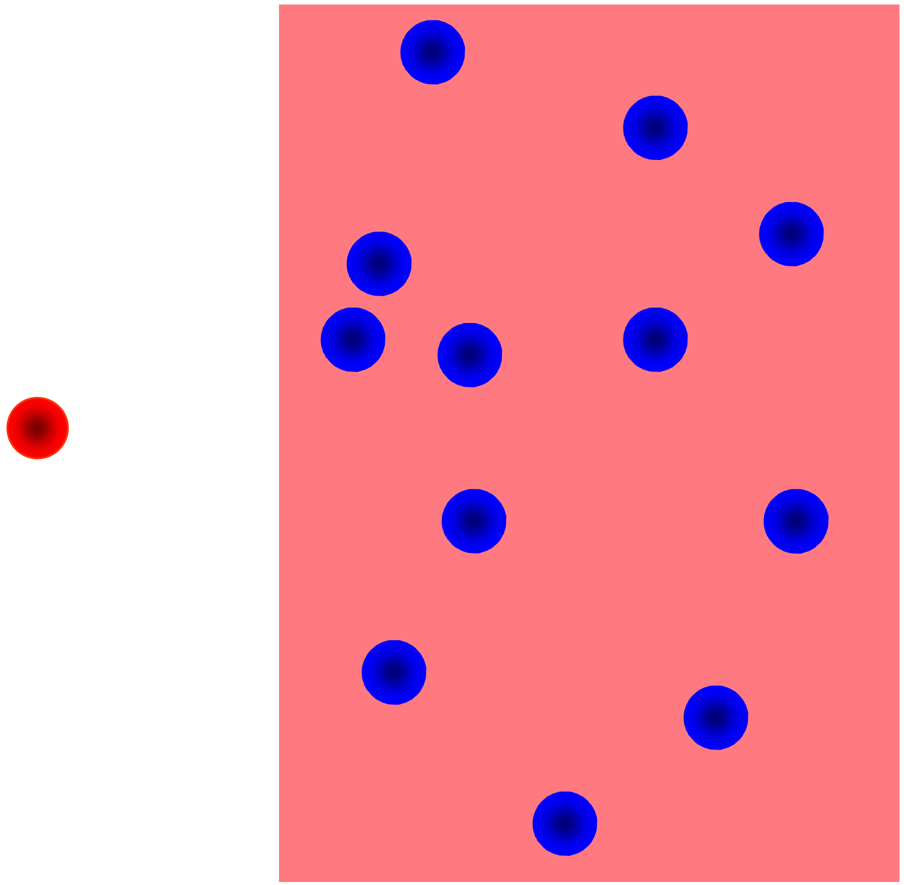
Experiment result of deuterium release in atomic from Pd, induced by e^- – beam

Thus, experimental results are shown:

- hydrogen forms in crystal lattice own subsystem.

- H-subsystem is able to accumulate the external energy.

- Hydrogen energy significantly increases and hydrogen is able to release from samples.



Electron

Electron subsystem

Hydrogen subsystem

Migration

Dessorbtion

- It is known that accelerated electrons lose its energy in the process of collision with sample electrons producing exciting electron subsystem

- Lifetime of these processes in metal is very small (10^{-15-16} s) and it is not clear:

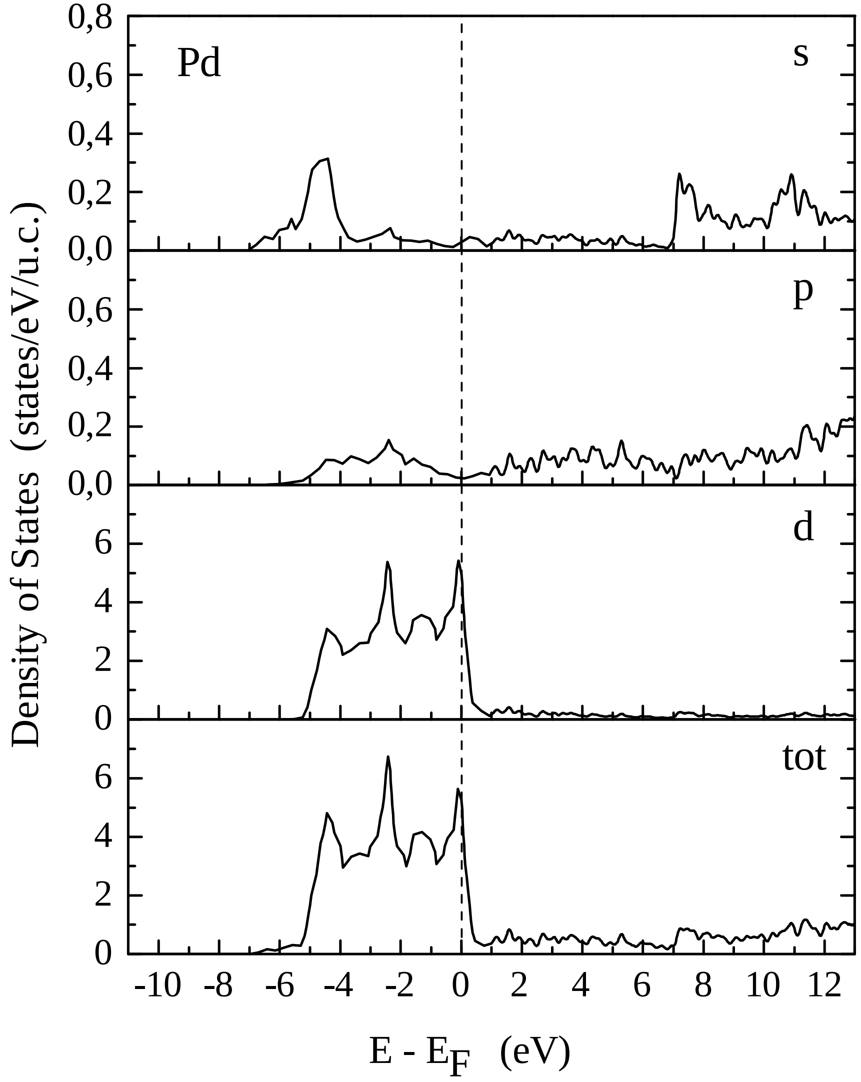
How the energy from the electron subsystem is transferred to the hydrogen subsystem?

- To answer these questions we have performed *ab initio* calculations of modification of the host electronic structure of metals by the presence of hydrogen for the systems: Pd and Pd-H.

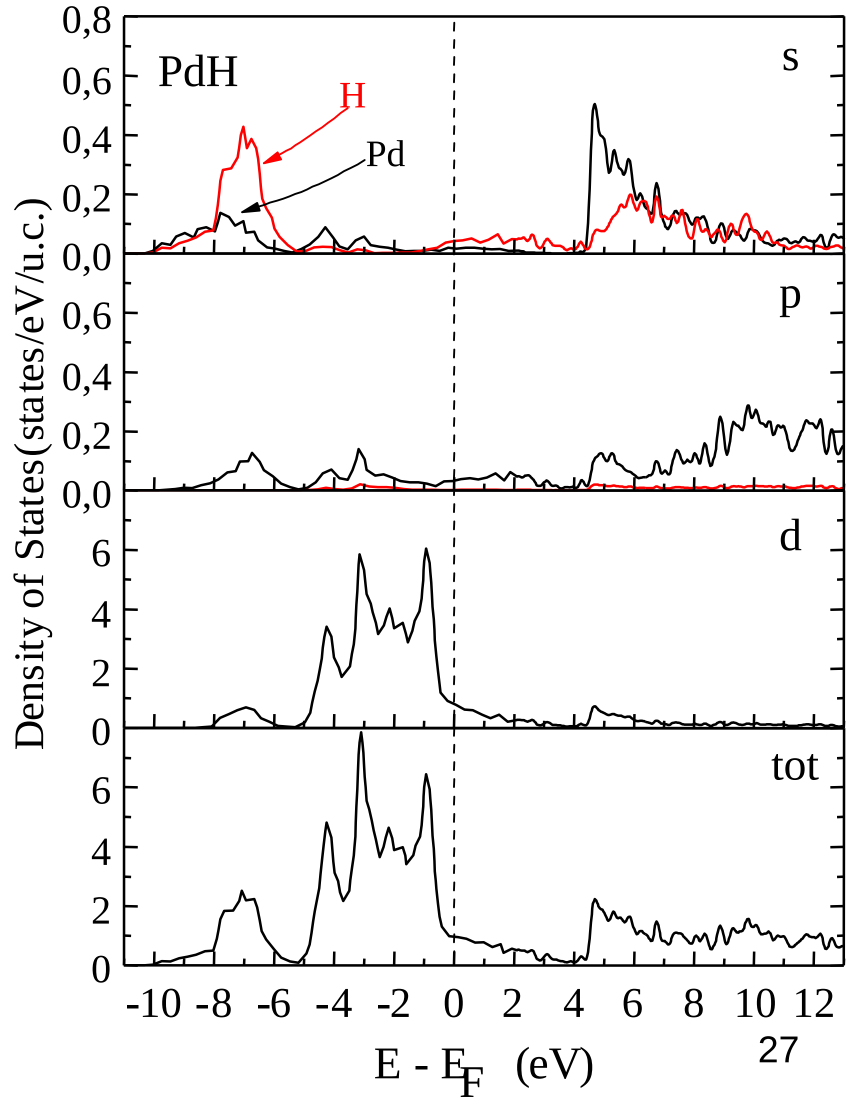
- In calculations we have used the self-consistent linearized augmented-plane wave method.

Density of electron states

in Pd



in Pd-H



In the electronic spectrum a pseudo-gap appears.

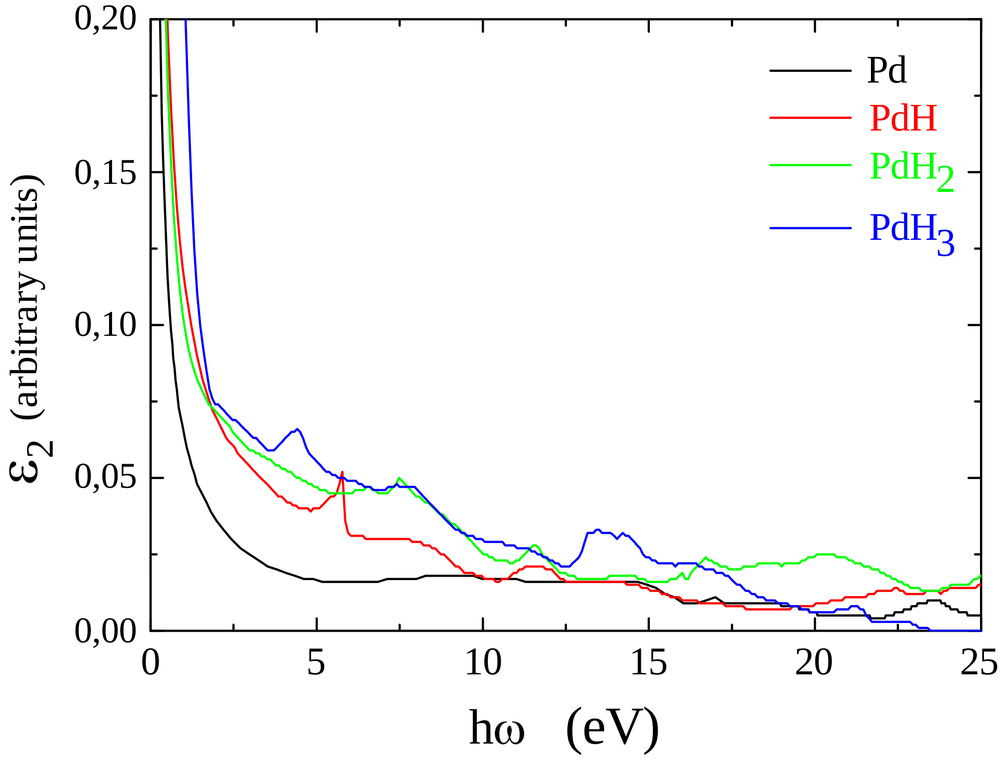
- The presence of pseudo-gap indicates on a covalent character of bonding between palladium and hydrogen atoms.

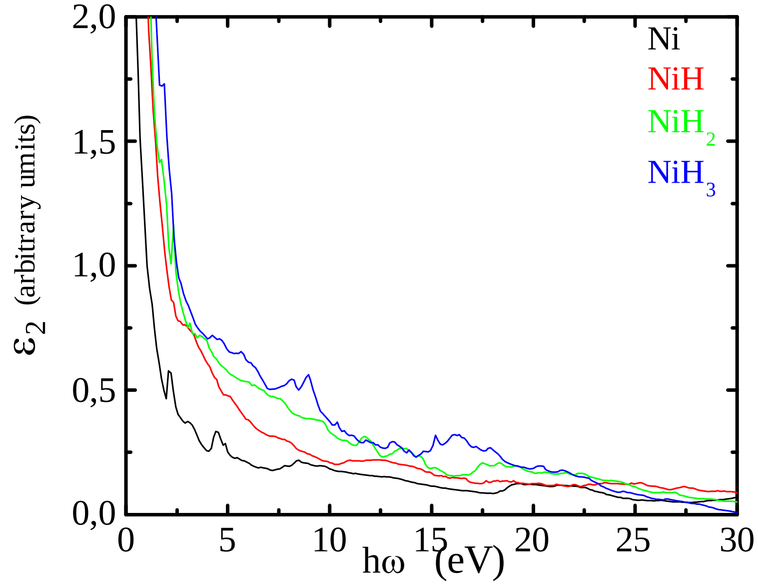
- It is known that in crystals with a covalent bonding a lifetime of electronic excitations is longer then in pure metals.

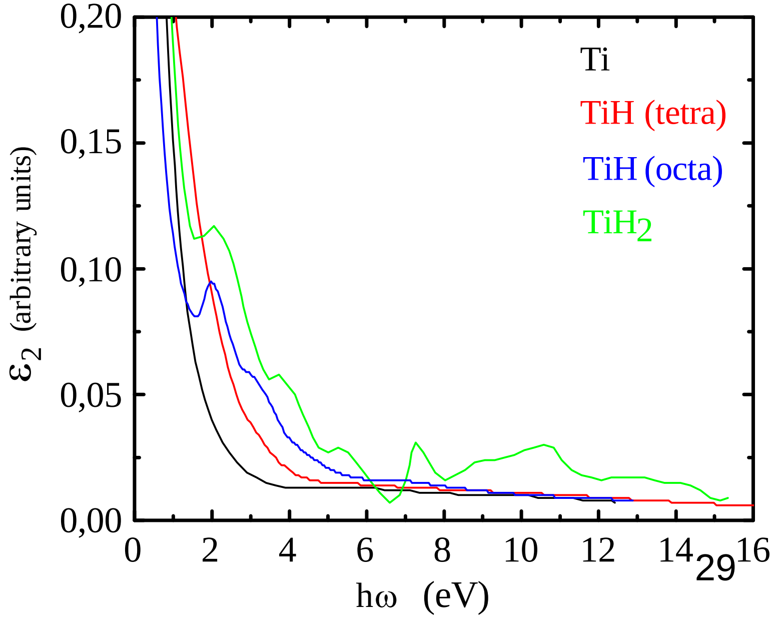
- During this time proton able to start to move.

Imaginary part of dielectric function ε

$$\varepsilon(\hbar\omega) = \varepsilon_1 + i\,\varepsilon_2$$







- Imaginary part of the dielectric function describes a capacity of the crystal to absorb an energy of the electromagnetic radiation.

- From figure we see that the dissolution of hydrogen in metal lead to increase of the dielectric function.

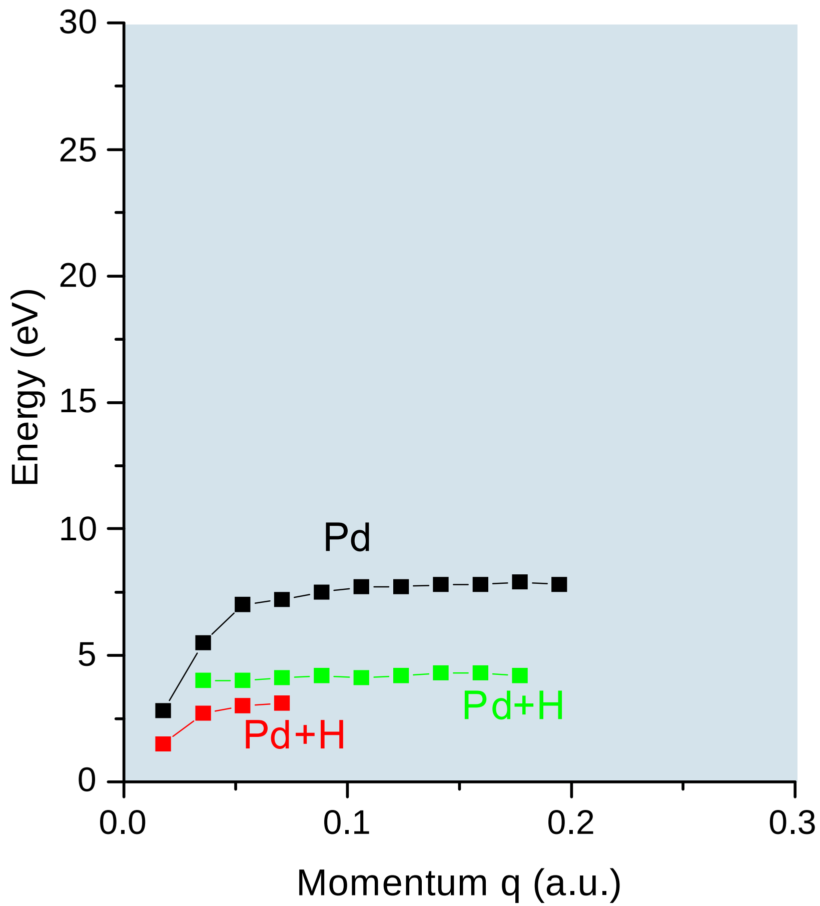
- That indicates on the increasing of the capacity of metal-hydrogen system to absorb an energy of electromagnetic radiation.

- On the next step we have studied the peculiarities of collective electronic excitations in metal–hydride systems on the example of Pd–H.

- Plasmon energy in the Pd–H system is much lower than in pure Pd. It means that probability of plasmon excitation in Pd–H system is higher than the pure Pd.

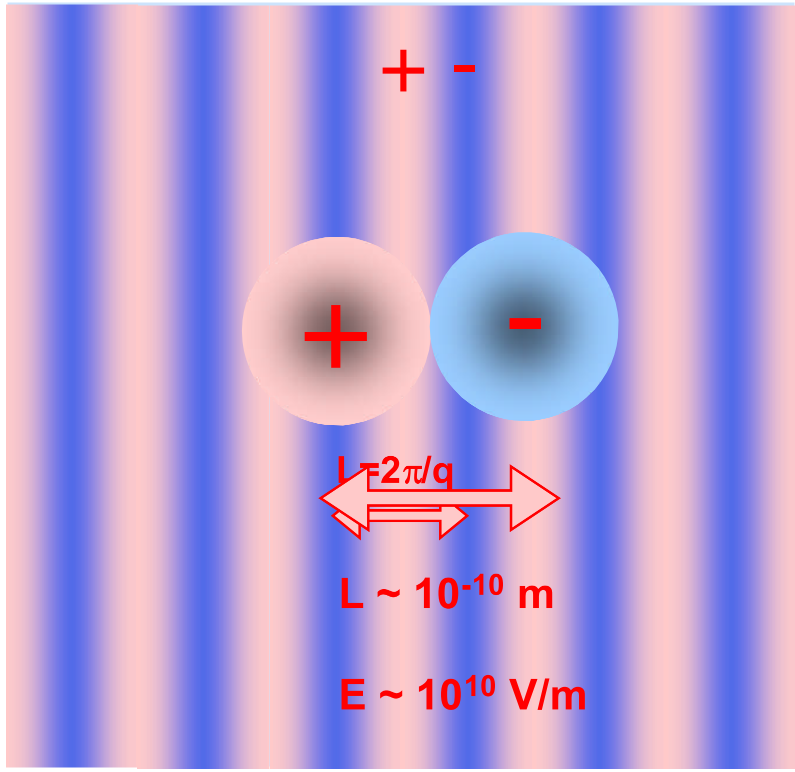
- Large oscillations of the electronic density are possible in the Pd–H system.

- As a result – a strong local electric field can appear in the crystal.



The low energy collective electronic excitations

Hypothesis



Large oscillations of the electronic density

High local electric fields in the whole crystal

- The calculation are shown that dissolved hydrogen in Pd has a charge equal 0.8 from charge of the proton.

- In this electric field charge hydrogen atoms and proton which appear in results excitations electronic system able to be accelerated to energy 1 eB.

Next important question:

Why practically all energy of accelerate electrons is accumulated by hydrogen atoms?

To answer this question we consider particularities of the interaction of accelerated electrons with matrix atoms and with hydrogen atoms dissolved in the metal.

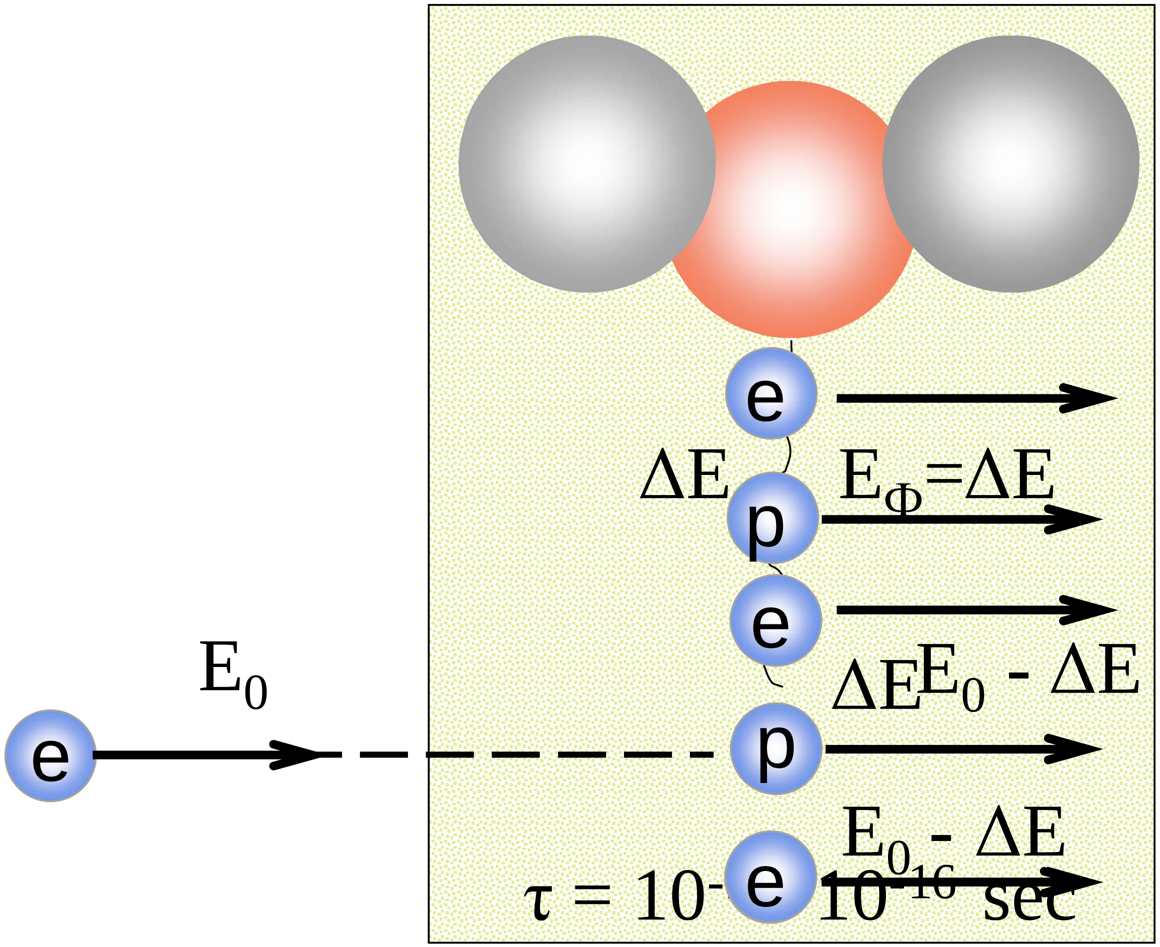
- In the process of interaction of accelerated electrons with matrix atoms the electrons transfer the part of its energy ΔE to matrix atoms exciting or ionizing them.

- Lifetime of these processes is of the order of 10^{-15}-10^{-16} s, during this time atoms go back into ground state.

- As result of interactions of electron with matrix atoms: atoms are in ground state plus a lot of low-energy photons and electrons.

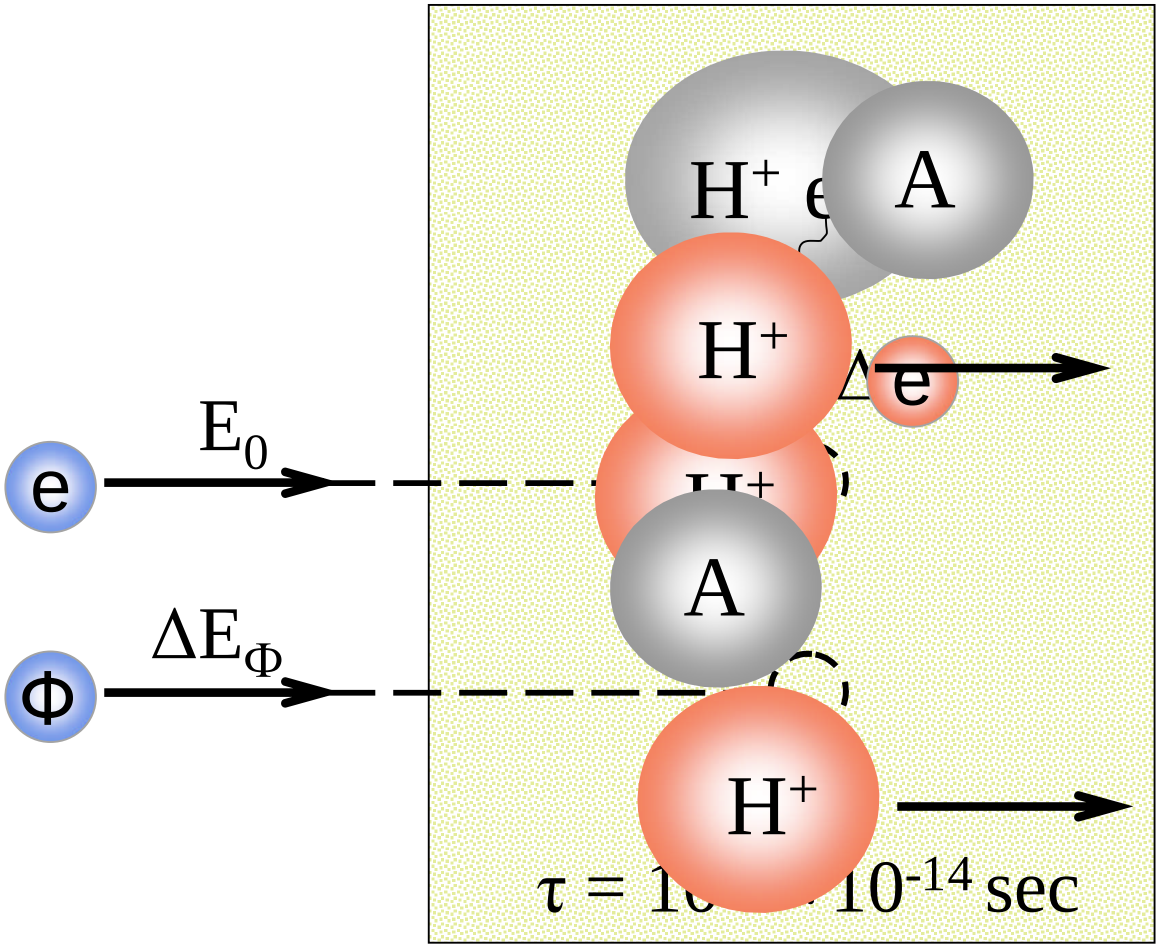
- Lifetime of exciting states of dissolved hydrogen atoms in metal much longer (10^{-13-14})s than excitations of matrix atoms and hydrogen during this time is able to leave initial location and to start to migrate.

- Low energy photons and electrons appeared as a results of interaction with matrix atoms are able to initiate hydrogen atoms migration as well.



$$N_{p,e} = \frac{E_0}{\Delta N_{p,e}}$$

Dynamic of interaction electron with atoms of the matrix



Dynamic of interaction electrons with hydrogen atoms

Excitation of the hydrogen subsystem under glow discharge

- ❖ Hydrogen subsystem is excited under a glow discharge. Hydrogen atoms have energy sufficient to excite plasmons in metal.

- ❖ High hydrogen atoms concentration in plasma greatly increase probability of excitation in comparison with excitation under electrolysis process.

- ❖ As a result the processes such as excess heat, X-rays emission, change of isotopic and mass composition of metals are more intensive under glow discharge than under electrolysis process.

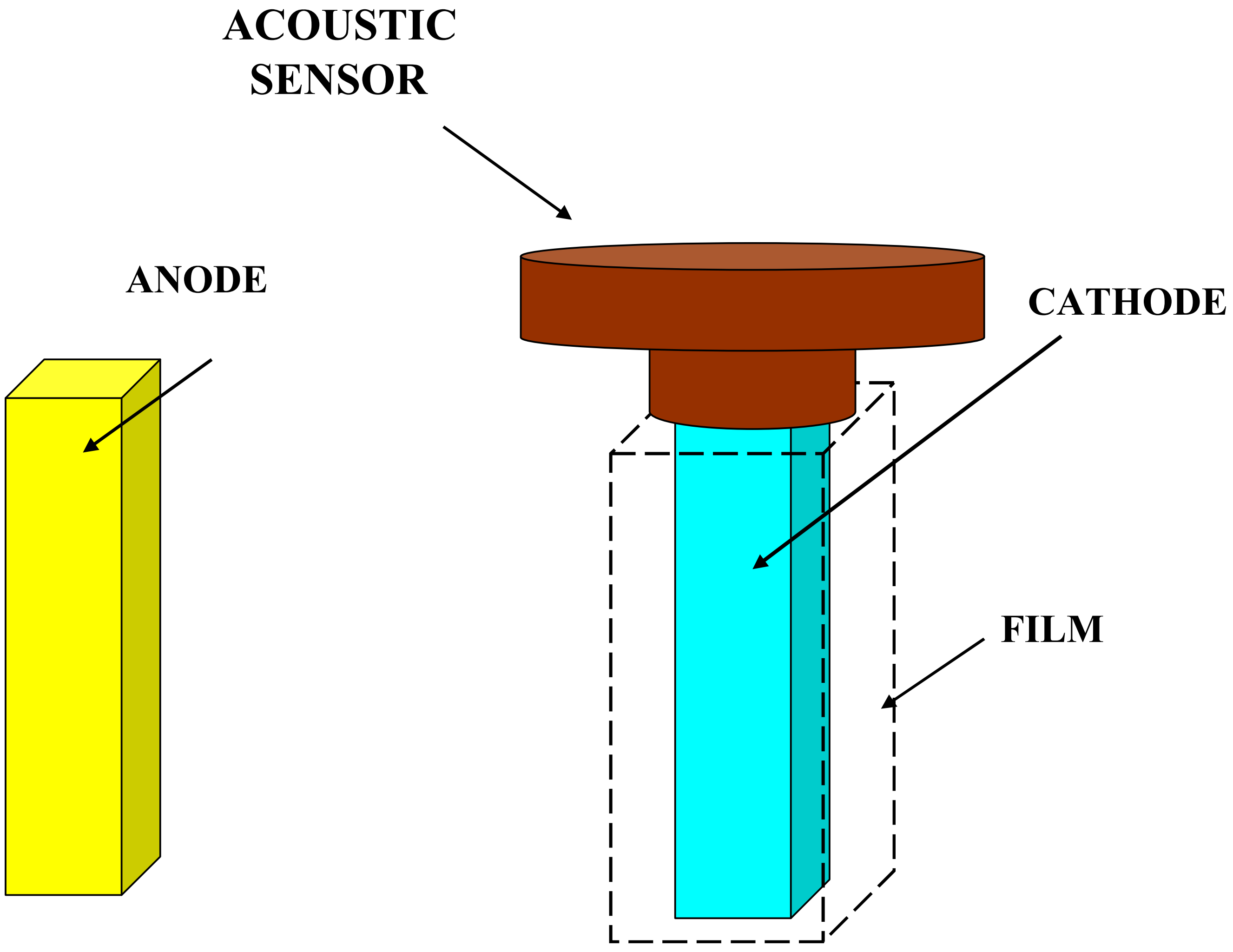
Excitation of the hydrogen subsystem at electrolysis process

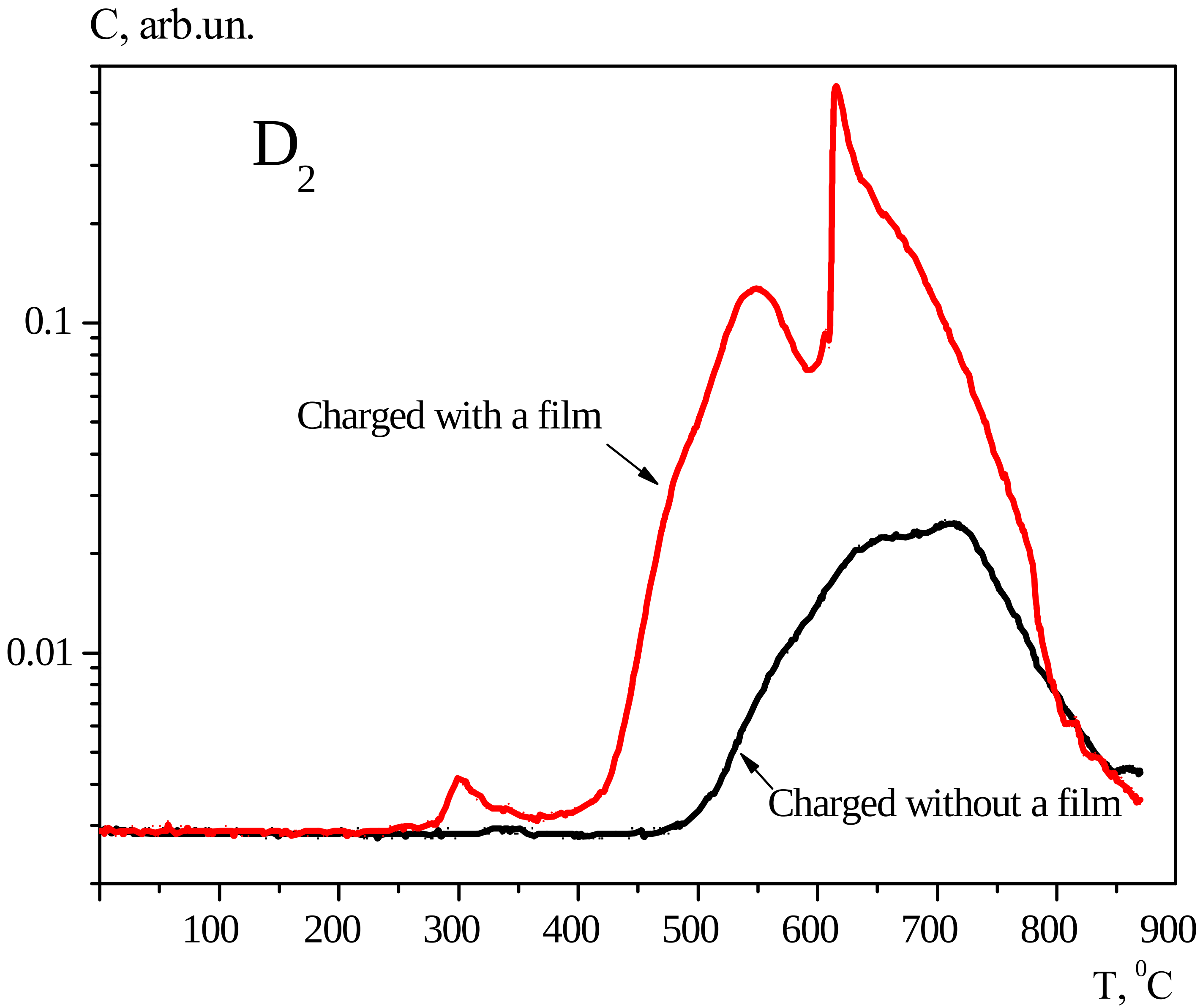
- Excitation of the hydrogen subsystem at electrolysis process takes place in a result of slam of hydrogen babbles. Slam of babbles is accompanied by emission of the low energy photons.

- Excitation probability can be increased in the case of draw of hydrogen babbles to a cathode.

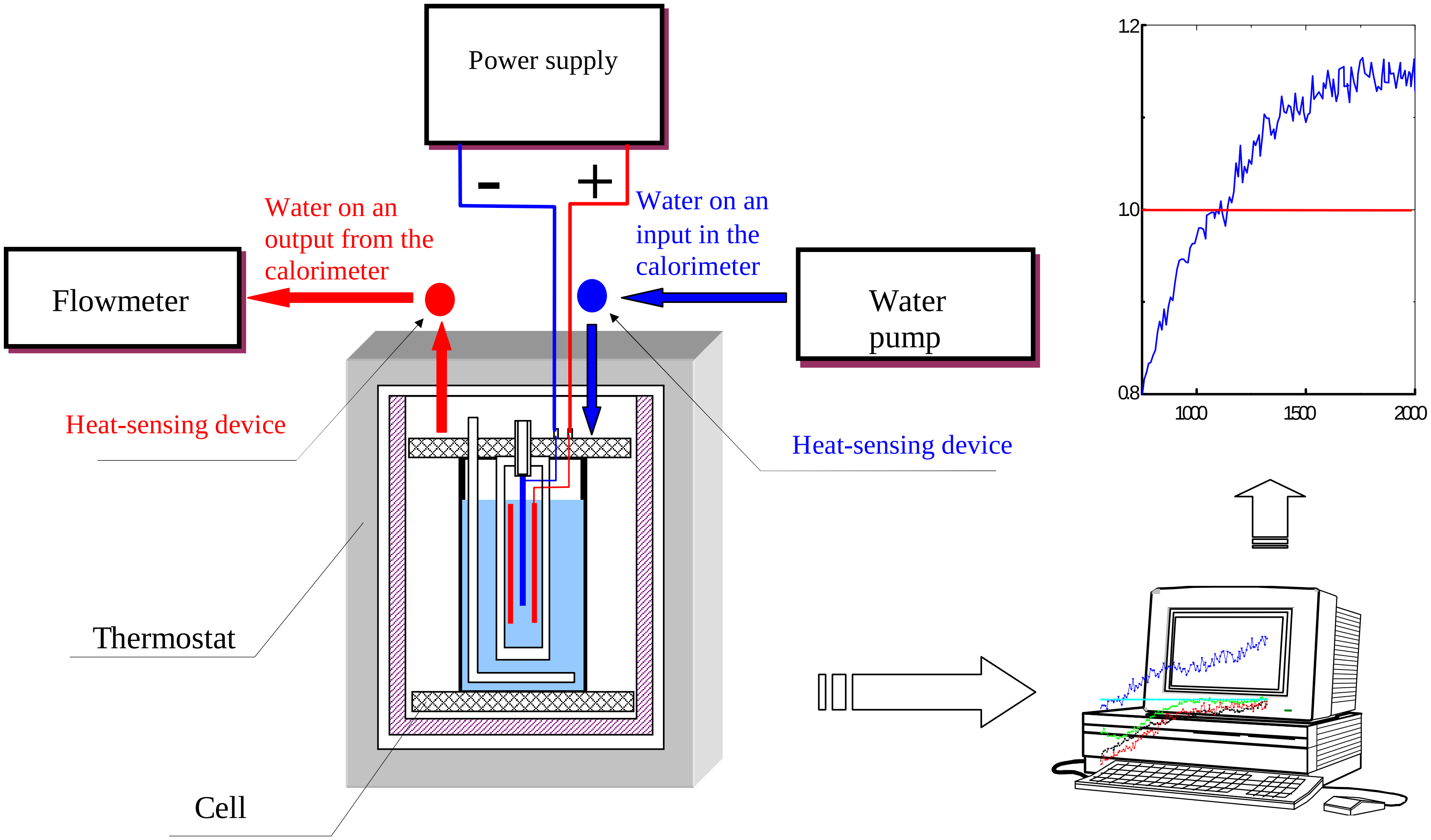
- It can realised for instance by using of the porous films (nucleus filter).

- With the use of porous films we observe the stable excess of heat.

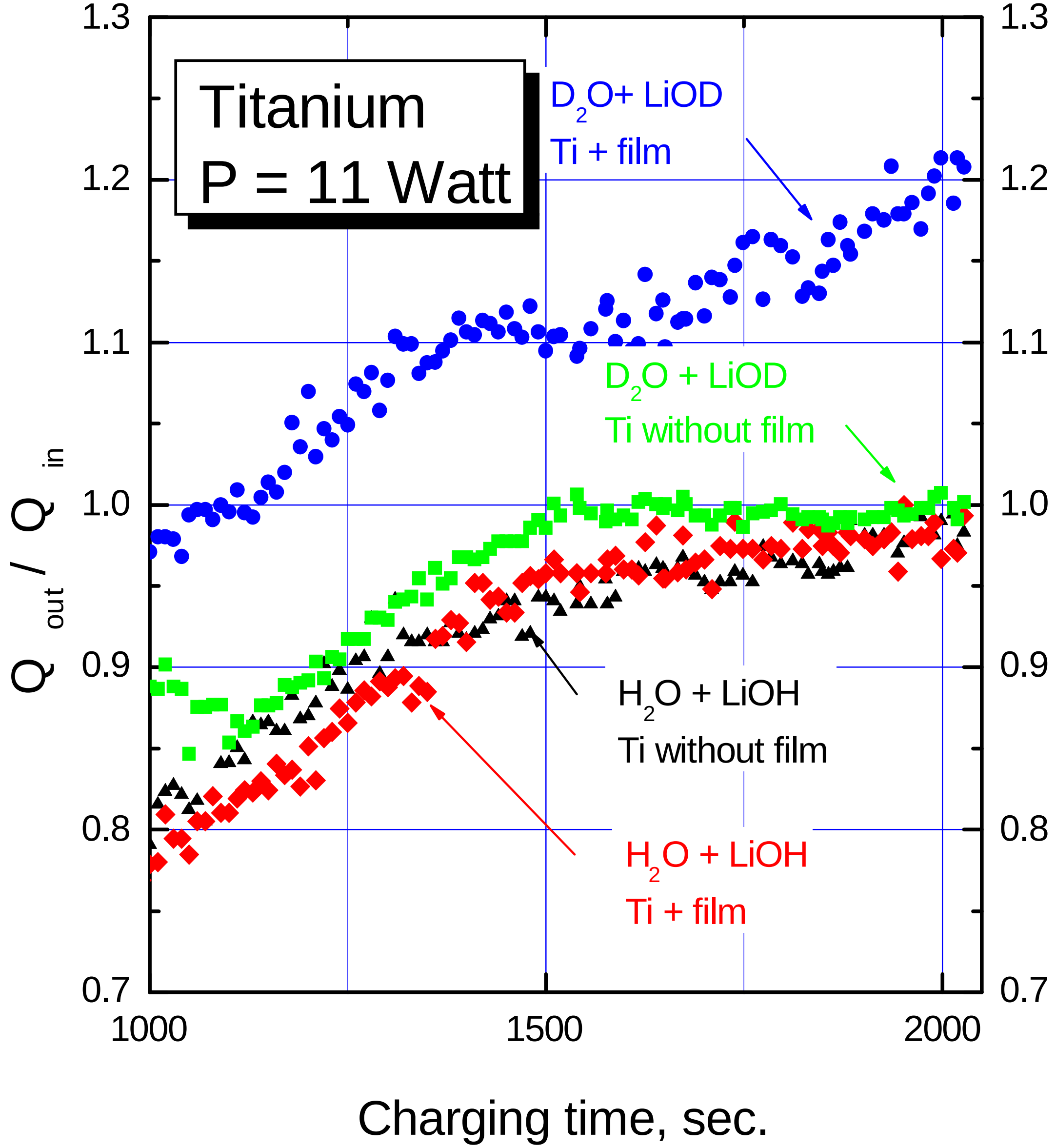

ACOUSTIC
SENSOR
ANODE
CATHODE
FILM



Thermostimulated deuterium release



The block diagram of excess heat measurement



Excess heat generation.
Titanium cathode.

- Now there are lot of information about excess heat at process loading Pd by deuterium.

- It is installed safely concentration of the hydrogen in Pd, under which excess heat are observed (H/Pd =0.97).

- First time about this <magic numeral> i have heard in report of prof. McKubre.

- To understand physical sense of <magic numeral> we have performed ***ab initio*** calculation of density of the electronic states in system Pd - H for different concentration H in Pd.

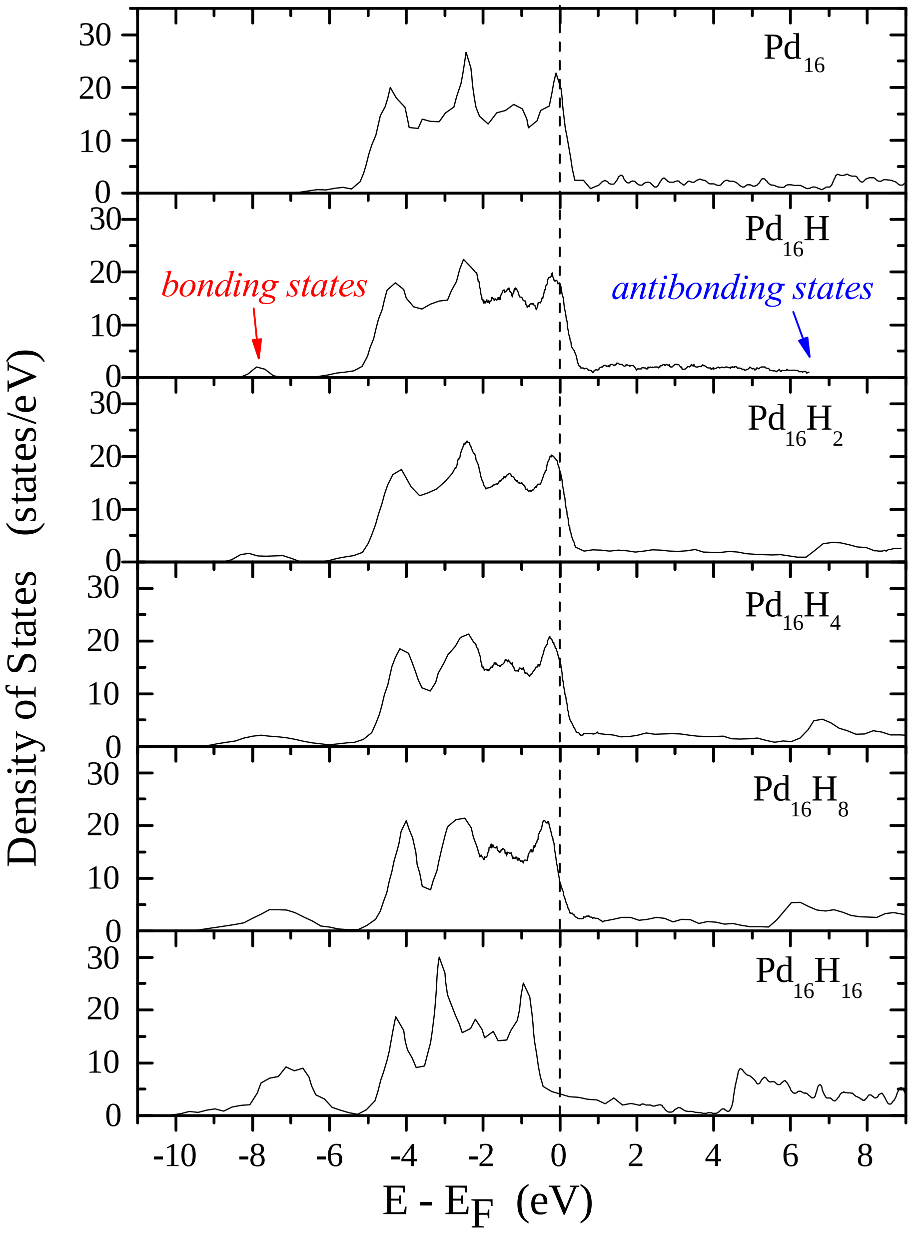
- In electronic spectrum of the systems Pd - H we observe states of electrons binding hydrogen atoms with Pd (below Fermi level, binding states) and anti binding states (above Fermi level).

- At systems Pd - H with concentration of the hydrogen H/Pd below 1 only binding states are separated by gap from rest states. As far as life time of these states is enough long (10^{-13} - 10^{-14} s) protons able to start to migrate.

- In this case probability of excitation H - subsystem is defined only electrons binding hydrogen with Pd (these electrons in system Pd - H less 2%).

- It means probability of excitation H - subsystem will be low.

Density of electronic states



- Situation absolutely other at system Pd - H with concentrations close to 1.

- In this case binding and anti binding electronic states are separated by gap from rest states.

- It means that electrons of hydrogen and Pd take part in excitation H - subsystem.

- Probability of excitation H - subsystems increases in nearly in 50 once.

- So <magic numeral> has a real physical sense.

- So to get the excess heat under loading Pd by deuterium necessary to saturate Pd by deuterium before concentration - 0.97 and excite D - subsystem.
- However very important questions remain opened: what exothermal chemical, atomic and nuclear processes provide excess heat.
- To understand the nature of the excess heat necessary to study the processes which take place in excite D - subsystem and interface D - subsystems - electrolyte.
- Excite D - subsystem it is a special medium – very high density plasma with temperature order eV.

Change of isotopic composition of metals at hydrogen loading

- This interesting and imported problem. To understand mechanism of this phenomena we researched the change of isotopic composition at process loading metal by deuterium, heating sample with load and without, under implantation ion and spraying metal accelerated ions.

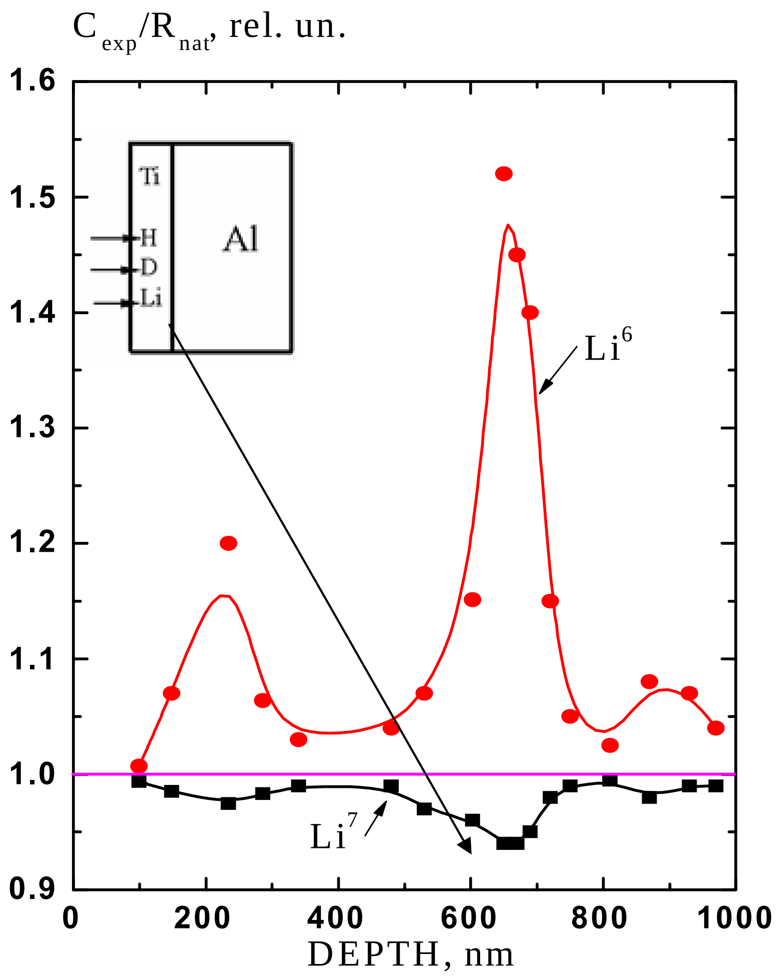
- Review article of our studies was published in journal VACUUM 81 (2006) 2002 – 210 <SIMS investigation of isotope effects at processed solid surface>.

- Our conclusion: mechanism of the change of isotopic composition at process loading metal by hydrogen is diffusion mechanism.
- The hydrogen plays the twofold role at change isotope composition in solid:
- First, migrating hydrogen stimulated migration of atoms matrixes and admixtures. Light atoms have a rate more than heavy atoms and, as result, isotope division are taked place.
- Second, at loading process hydrogen create stress in solid. Stress increase probability isotope effect.

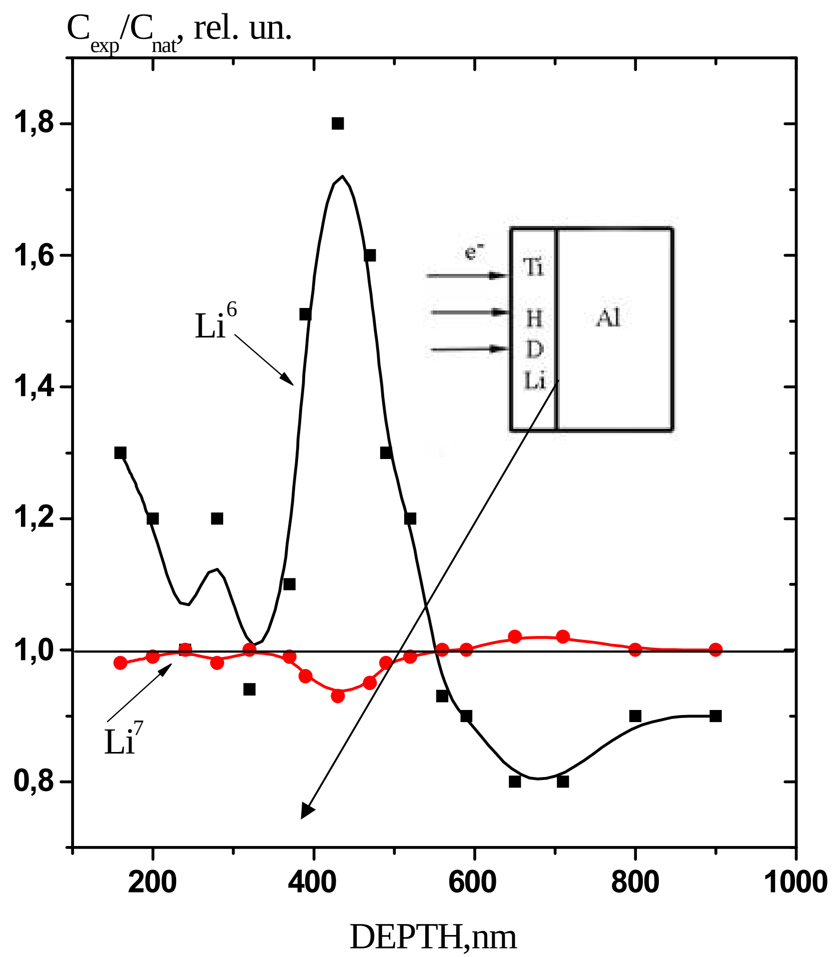
- At electrolysis process hydrogen moves inside sample and stimulate motion of isotopes Li. We observe isotope Li^6 in sample much deeper than Li^7.

- During irradiation hydrogen moves from sample and we observe isotope Li^6 closer to surface than Li^7.

Change of Li isotopic composition in Ti/Al thin-film system at hydrogen loading and electron irradiation

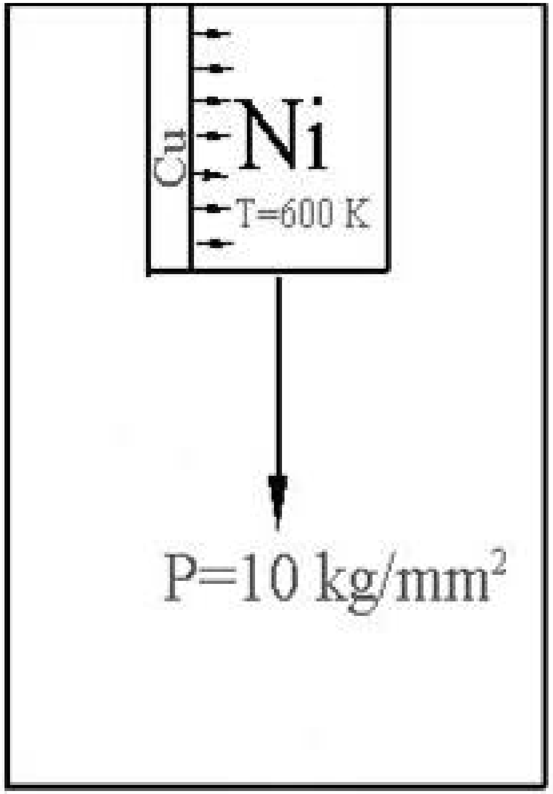


The relation of lithium isotopic concentrations to natural abundance depending on depth in structure Ti/Al after loading by hydrogen

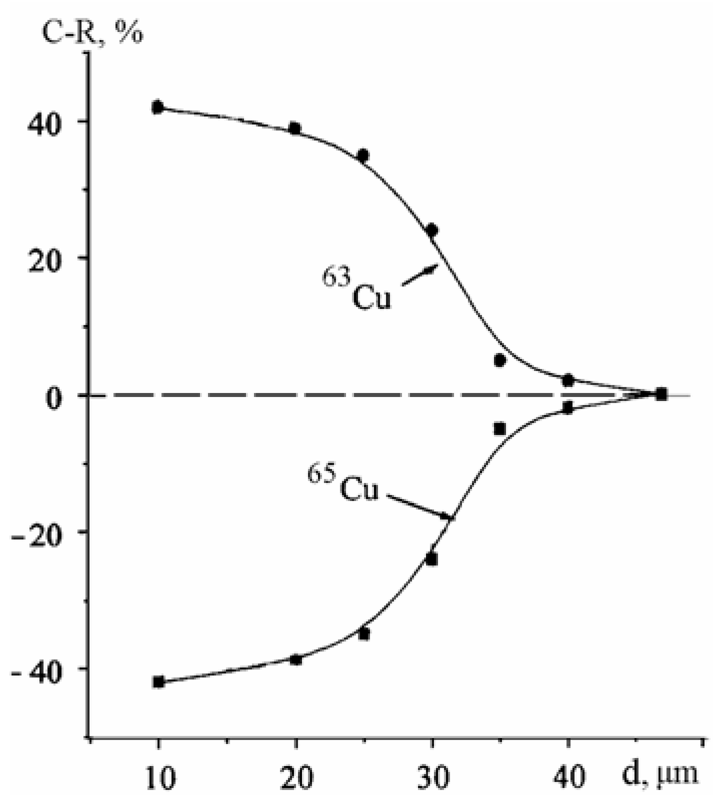


The relation of lithium isotopic concentrations to natural abundance of the same isotopes depending on depth in structure Ti/Al after hydrogen isotopes charging and electron irradiation.

Change of Cu isotopic composition at thermal diffusion of copper in nickel



The scheme of experiment



Isotopes distribution of cupper on depth of nickel after thermal diffusion of copper in nickel

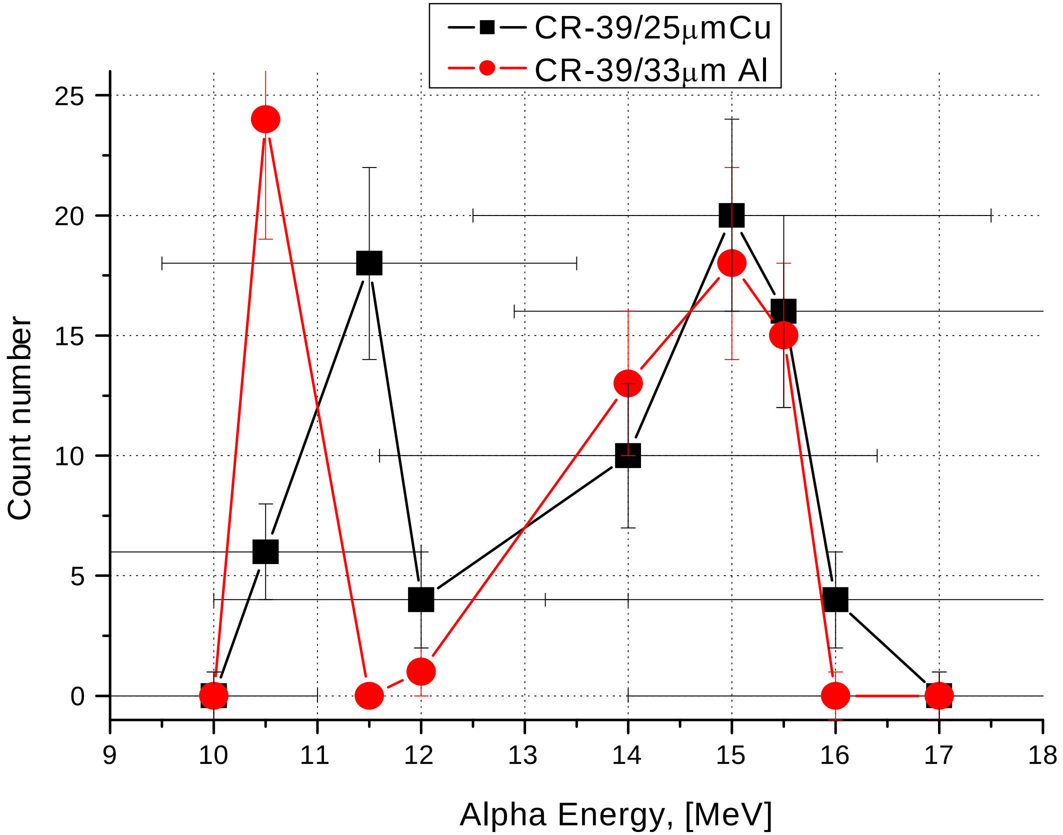
Low energy nuclear reaction

- It is very interesting problem but today very few experimental date about product nuclear reaction, their energy.

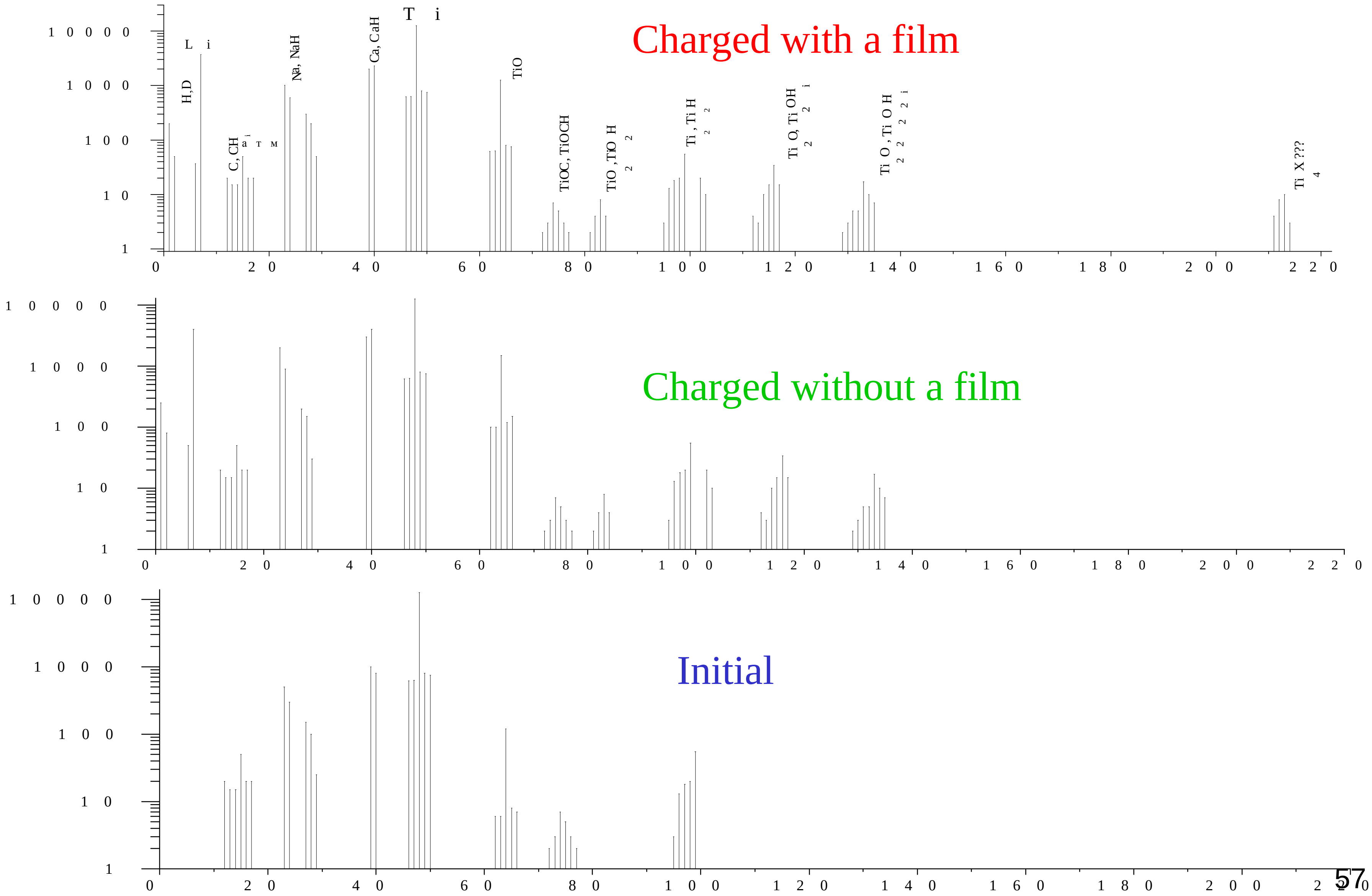
- In our view the most interesting results have Lipson group. They observe the alpha - particles with energy 11 and 15 Mev. It point on proceed nuclear reaction with very high Q-value.

- It is very important to continue such research.

Reconstruction of alpha spectra for the CR-39 detectors with 25μm Cu and 33 μm Al filters

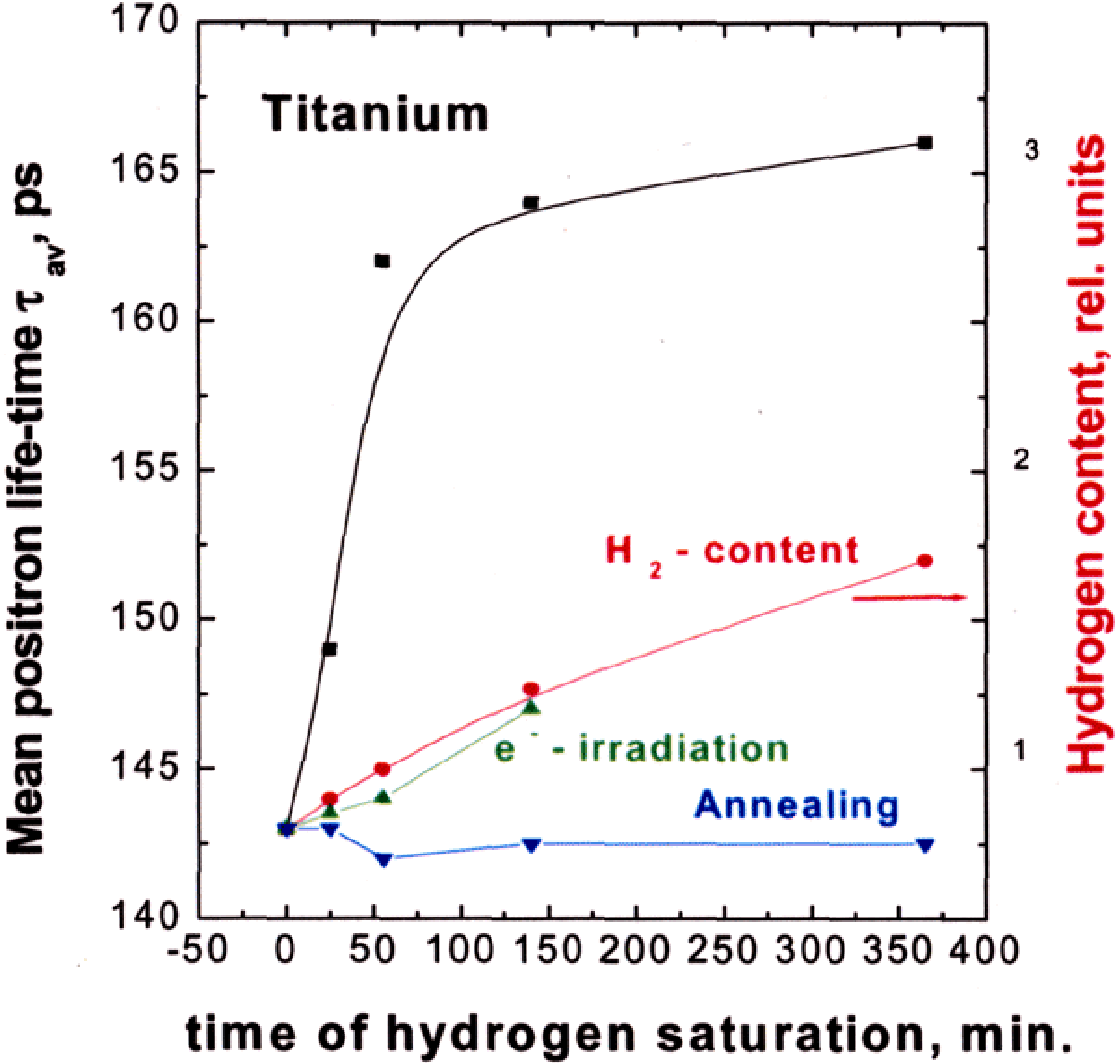


Change of SIMS mass spectrum after hydrogen charged of titanium with and without a film



Conclusions

- ❖Hydrogen forms in crystal lattice own subsystem
- ❖The H-subsystem is able to accumulate the external energy
- ❖Hydrogen subsystem is excited at electrolysis process and glow discharge
- ❖Excited hydrogen in metals is a special medium – a high density low temperature plasma where some exothermal chemical and nuclear processes can take place



Titanium
H_2 - content
e^- - irradiation
Annealing
Mean positron life-time τ_{av}, ps
Hydrogen content, rel. units
time of hydrogen saturation, min.
170
165
160
155
150
145
140
-50
0
50
100
150
200
250
300
350
400
3
2
1