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and F.W. Poulsen

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# **Experiments on Palladium- and Titanium-Deuterium Systems with Reference to Studies on »Cold Fusion«**

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**Abstract.** The work performed at Risø in connection with the claims of »cold fusion« is summarised in this report. The main purpose of the whole experiment was to analyse if structural anomalies of deuterated metals could support the occurrence of fusion processes in such systems by x-ray and neutron powder diffraction methods. Two types of systems were investigated. The first one was an electrolytic cell with palladium as electrode. No anomalous properties in the composition and positions of deuterium were found in this case. The other one was a titanium- deuterium-gas system which was studied in order to reproduce the »Frascati experiment«. However, no neutrons above the background level were observed in spite of the very sensitive detector system. By neutron diffraction of this system a 70% titanium-dideuterium phase was found.

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# 1. Introduction

Recently, several groups<sup>1,2,3</sup> have reported on observation of nuclear fusion processes in systems where deuterium is absorbed in a metal (palladium or titanium). In the first report<sup>1</sup>, the significance for cold fusion was mainly related to the large amount of heat generated after electrolytic deuteration of palladium. However, Ref.3 in which titanium shells are kept in a container under high deuterium pressure seems to give more convincing results, since neutron count rates up to 500 times the background level were reported. We have studied both systems.

For the palladium-hydride a literature survey in monographs on hydrides<sup>4</sup> and in Gmelin Handbuch<sup>5</sup> revealed that higher deuterium contents in palladium than found by gas equilibration can be obtained by electrolysis. Strong (usually acid) electrolytes, low temperatures (down to  $-40^{\circ}\text{C}$ ) and high current densities have been used (several amps/cm<sup>2</sup>). This knowledge dates back to the 1920-40-ies, and is a consequence of the chemical potential variations being linear with voltage and logarithmic in pressure. The purpose of the experiment to be described below was to determine if structural anomalies like close-lying deuterium-sites or large-amplitude deuterium vibrations could result and support occurrence of fusion in such »supersaturated« palladium systems. Both x-ray and neutron powder diffraction ex-

periments were carried out, the latter by on-line measurements with palladium as electrode in an electrolytic cell.

For the titanium-deuterium system we decided to reproduce the experiment reported in Ref.3 with the specific purpose to study structural phase properties by neutron powder diffraction, if fusion processes were observed. The experimental procedure, to be described more closely below, deviates significantly from that reported in Ref.3 in the detection system. We use He<sup>3</sup> detectors combined with paraffin blocks for thermalisation of neutrons and a multi-channel-analyser to analyse the spectrum, whereas BF<sub>3</sub> detectors were used in Ref.3, apparently without energy analysis. Further, in Ref.3 there was no indication of the sample composition and structure. Our sample has been characterised after the experiment by neutron powder diffraction studies.

The experimental conditions for sample preparation, and the set-up for on-line neutron diffraction studies on the palladium-deuterium system and for neutron detection on the titanium-deuterium system are given in Sec. 2. Results of neutron detection on the titanium-deuterium system and structural studies by x-ray and neutron powder diffraction are reported in Sec. 3. A discussion and conclusion can be found in Sec. 4.

## 2. Experiment

### 2.1 Palladium-deuterium

The diffraction experiments to be carried out, would only be meaningful if there were no (or as small as possible) concentration gradients in the Pd-sample. This working idea led us to select thin Pd, in order to reduce diffusion lengths. We chose to use the same dilute electrolyte as prescribed by Fleischmann and Pons<sup>1</sup>. A known amount of pure Li-metal was added to heavy water in a glass vessel. Deuterium gas evolved and LiOD was thus obtained. Pd-foil of 25 micron thickness was used as electrode material. Foils were annealed overnight in vacuum at  $1000^{\circ}\text{C}$ . The foil for x-ray investigation was approx. 1 cm<sup>2</sup>

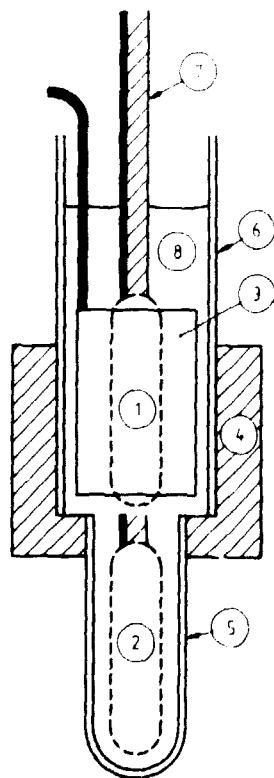
welded to a platinum wire. The neutron diffraction sample was 7 grams of foil welded together along one edge and then rolled up in a cigar-like manner. The package was 10 mm diameter and 40 mm high. A platinum wire (0.5 mm) was spot-welded to the top part of the Pd. Platinum foil electrodes (cylindrical geometry, 25 cm<sup>2</sup>), or 2 planar Pt electrodes (2 × 20 cm<sup>2</sup>) were used as counter electrodes. The cell for neutron diffraction contained approx. 100 ml solution, had an upper part of pyrex glass housing the cylindrical Pt electrode, and a lower part consisting of a quartz tube (12.5 mm o.d., 10 mm i.d.). The pyrex

tube (12.5 mm o.d., 10 mm i.d.). The pyrex and quartz part were joined by a machine piece of teflon. The 7 g Pd electrode could be transferred from the top electrolysis part to the lower »diffraction« part by means of a pyrex push rod, to which also a Ni/CrNi thermocouple was attached. The cell is shown in Fig. 1.

In the second phase of the »on site« neutron diffraction experiment the heavy water solution was pumped out into a cooling loop with a peristaltic pump. On the secondary side of the cooling system a conventional refrigerator cooled glycol bath was used. The heat exchanger between heavy water and glycol was made of pyrex.

Finally, for comparison the structural properties of pressure deuterated Pd were studied. The partially deuterated sample was transferred to a thermobalance system, the deuterium was desorbed under vacuum at 75°C, and the sample was redeuterated at room temperature under a deuterium

Fig. 1. The electrochemical cell. 1: Pd-cathode, position during heavy electrolysis, 2: Pd-cathode during neutron diffraction, 3: Platinum-anode, 4: Teflon block, 5: Quartz tube, 6: Pyrex tube, 7: Pushrod with thermocouple, 8: LiOD-D<sub>2</sub>O electrolyte.



pressure of 7.5 bar for 10 hours to PdD<sub>x</sub> with x = 0.7 (90% deuterium was absorbed during the first 3 hours). After deuteration and during the experiment the sample was contained in a small sealed Al-container.

## 2.2. Titanium-deuterium

It is well known that titanium can absorb large quantities of hydrogen to form either a solid solution or titanium-hydride. However, because of a surface oxide layer, the metal has to be prepared by a heating process in advance to the hydrogenation or deuteration. No information on the use of such a heating process is given in Ref.3. The exact procedure used in our experiment is described in the following. The titanium we used was in the form of shavings produced by a milling machine from a pile of plates. 85 g of shavings were placed in a stainless steel container welded to a long thin tube connected to a valve. The steel container was placed in an oven and heated to about 800°C while the content was evacuated by a vacuum pump during this heating process. At 800°C the titanium was deuterated at approximately one bar, and then the system was left for slow cooling to room temperature.

After the heating process the procedure described in Ref.3 was followed as precisely as possible. The Ti-container was placed in the experimental set-up shown in Fig. 2 and then pressurised with deuterium to around 50 bar. After several hours the dewar with the titanium container was filled with liquid nitrogen and left at this temperature under a constant deuterium pressure of 50 bar for approximately 72 hours. Around 50 bar-liters of deuterium gas were absorbed during the whole process. The last phase of the experiment consisted in increasing the temperature to room temperature and to evacuate the system to a pressure of  $\approx 0.01$  mm Hg. This is a rather peculiar process since titanium-hydride should be extremely stable at room temperature, and it should not be possible to remove any deuterium by lowering the pressure.

Six He<sup>3</sup>-neutron-detectors (10 × 2 × 2 cm<sup>3</sup> sensitive volume filled with 5 atm He<sup>3</sup>) placed approximately 10 cm from the centre of the Ti-container were used for detection. A 5 cm thick paraffin block was placed between the dewar and the detectors in order to thermalise the neutrons,

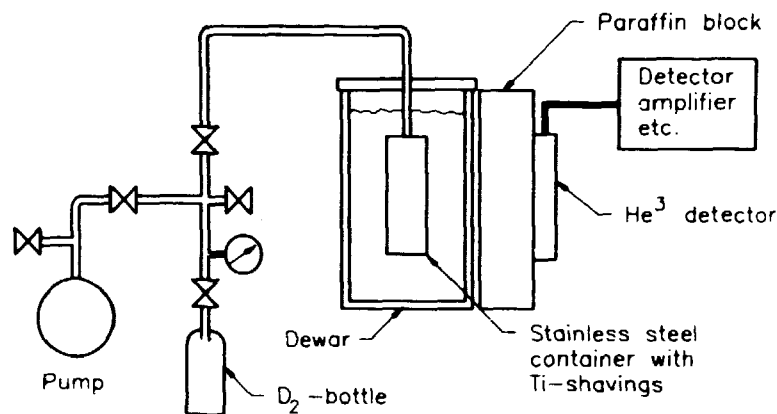
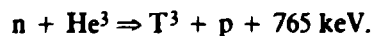


Fig. 2. Experimental set-up for neutron detection from  $TiO_2$ .

thereby increasing the detection efficiency. The detectors were connected in parallel with short wires to a preamplifier, and the signals were recorded on a multi-channel analyser. The whole set-up was shielded against neutrons with boron loaded polyester plates. The  $He^3$  neutron detector is based on the reaction:



The  $T^3$  and the proton ionise the  $He^3$  gas giving a signal to the counter. The observed spectrum is characterised by a peak at 765 keV and a smaller signal due to the termination of the ionisation tracks at the counter walls in the range from

$\approx 191 \text{ keV} (= 765/4)$  to 765 keV. If the neutrons are not completely thermalised there may be a signal from fast neutrons giving energies above 765 keV as well. However, the spectrum appearing from thermal neutrons is very characteristic and should be monitored in order to separate neutron signals from other signal (electrical noise etc.). The detection system was calibrated and tested by using a  $Cf^{252}$  neutron source with an intensity of  $1.5 \cdot 10^6$  neutrons/s. The best signal to noise ratio was found when only energies from 500-850 keV were taken into account. The average background measured during 16 hours was found to be 1.3 counts/min. The efficiency of the detector system was  $5 \cdot 10^{-3}$ .

## 3. Results

### 3.1. Neutron Detection on Titanium-deuterium

The energy spectrum integrated over 10 minutes measuring periods was recorded during the whole experiment. Each spectrum was saved for later analysis and the spectra from a certain time period could afterwards be added to a total spectrum. No significant deviation from the background was found in any of the 10 minutes measuring periods. In Ref. 3 the highest count rate was found during the phase where the system was heated to room temperature under eva-

uation. According to this work a maximum of 5000 neutrons/s with an average of  $\approx 3000$  neutrons/s in a 10 hours period were observed. To compare our measurements with this result we added all the spectra from the corresponding 10 hours period of our experiment. In Fig. 3 this spectrum is shown together with a background spectrum measured with the same set-up, but without the Ti-container. The neutron peak is seen at channel 108 which corresponds to



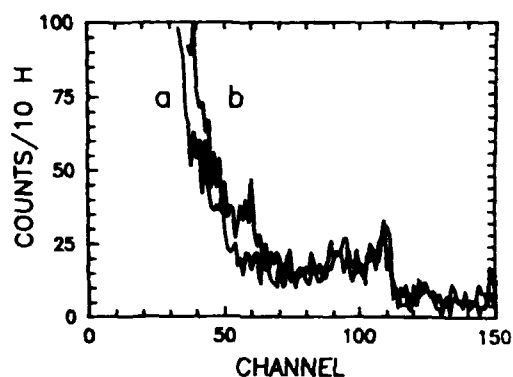


Fig. 3. Energy spectrum of  $\text{He}^3$  signal a: measured during the heating phase of the titanium system, and b: background measured without the titanium container. In both cases the time of measuring was around 10 hours. Channel 108 corresponds to an energy of 765 keV.

765 keV. The total amount of counts in channel 70-120 ( $\approx 500$ -850 keV) is 841 counts during the measurement and 815 for the background, i.e. the difference is within one st.dev. Let the level of a significant signal be 3-4 times the st.dev.  $\approx 100$  counts. This corresponds to 0.2 counts/min or 0.15 times the background. With the efficiency noted above we can conclude that although we can observe a signal from the Ti-container of the order of 40 counts/min or 0.7 counts/s we have not seen anything. In other words the neutron signal from our experiment, if any, is at least 4000 times smaller than the one observed in Ref. 3.

### 3.2. Neutron Diffraction Studies on Titanium-deuterium

The structural phase properties of the titanium-deuterium sample was examined at room temperature after the complete series of experiments by neutron powder diffraction using the TASI-triple-axes-spectrometer at the DR3-reactor, Risø National Laboratory. The spectrometer was operated in the elastic mode and a neutron wavelength of 2.020 Å was used, cf. Fig. 4. The sample was mounted in the stainless-steel container on the spectrometer and the diffraction pattern for scattering angles between 9 and 99 degrees was recorded. Analyses of the spectrum showed evidence for tetragonal  $\text{TiD}_x$  with  $x = 1.98$  ( $a = b = 4.46$  Å and  $c = 4.39$  Å) as reported by Yakel

Jr.<sup>6</sup>, hexagonal-closed-packed titanium metal ( $a = b = 2.950$  Å and  $c = 4.686$  Å), and some few additional peaks assigned to the stainless-steel container. Based on model structure calculations we evaluate the sample to consists of 30% titanium metal phase and 70% titanium-dideuterium phase. The existence of metallic phase most likely result from incomplete activation of the sample at elevated temperatures because titanium-dideuterium is very stable at room temperature or below even under reduced pressure<sup>7</sup>.

### 3.3. X-ray Results on Deuterated Palladium

Experiments were carried out on a standard x-ray powder diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.542$  Å). In a few test runs it was assured that the rolled foils had no texture. The Pd and  $\text{PdD}_x$  diffractogrammes were of high intensity and good resolution. Deuterium concentrations in the foil were evaluated from the lattice constants<sup>7</sup>. The major part of the charge passing the cell gives deuterium gas which leaves the cell as bubbles. Even after the solution has become saturated with  $\text{D}_2$  (and  $\text{O}_2$ , which bubbles from the Pt-anode) the rate of D-diffusion into Pd is very low compared to the parasitic gas-evolution. The temperature of the cell never exceeded 30°C.

Total rel. charge (DPd)	Current (A) average (pulse)	Remarks
0	0	pure metal
23	0.01, (0.1)	pure $\beta$ -phase
40	(0.4)	heavy electrolysis, pure $\beta$ -phase
40	(0.4)	after three days in ambient air, predominantly $\beta$ -phase

Table 1. X-ray diffraction of cathodically loaded Pd-deuteride foil (1 cm<sup>2</sup>, 25  $\mu\text{m}$ )

There was no sign of extra D going into the Pd at high current density. It could also be concluded that the 24 h electrolysis had produced a pure  $\text{PdD}_{0.67-0.70}$  phase. The lattice constants for the fcc-metal and fcc-deuteride were Pd-metal: 3.895 Å, Pd-D<sub>x</sub> ( $\beta$ -phase): 4.053 Å. After three days

in ambient air the sample still was predominantly PdD<sub>x</sub>-phase.

### 3.4. Neutron Diffraction on Deuterated Palladium

The experiment was carried out on the multi-detector powder neutron diffractometer (see Fig. 4) at the DR 3-reactor, Risø National Laboratory, using a neutron wavelength of 1.079 Å.

The idea behind the experiment was to use the ability of neutrons to penetrate matter and to be scattered by light atoms like deuterium. Hereby it should be possible to perform in-situ determinations of the structural properties of deuterium and study whether high concentrations of deuterium could be obtained and maintained in an electrochemical cell using palladium as a cathode.

The electrochemical cell is shown in Fig. 1. Prior to the diffraction experiment, the background from the cell (D<sub>2</sub>O and quartz-glass tube) was examined, and it was verified that the unactivated wrapped foil Pd-sample was texture free.

In the first experiment the sample was electrolysed for 6 hours with 8-10 V across the cell and a current of 0.5 A. During this process LiOD solution was added to compensate for losses by electrolysis, evaporation and violent foam formation

in the beginning. The temperature of the cell increased to 45-50°C due to Joule heating.

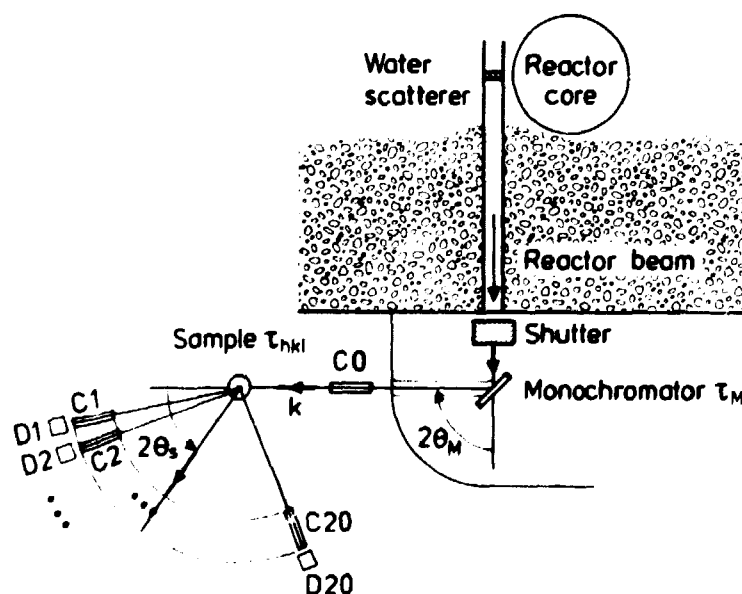
The total charge at this stage corresponded to a D/Pd ratio of 1.2. The current was then reduced to 0.1 A, the Pd sample was pushed down in the bottom of the cell and the first diffraction pattern was collected during the following 10 hours.

Analysis of the structural data based on peak positions and intensities reveal that the sample consists of mixed phase Pd-metal or α-phase PdD<sub>x</sub> ( $x \leq 0.08$ ) and β-phase PdD<sub>x</sub> with  $x = 0.66$ . Bragg-peak intensities for the β-phase structure are in good agreement with the structural model calculations involving only the octahedral sites. Evaluation of the ratio of α- to β-phase gives 80% α-phase and 20% β-phase.

In an attempt to increase the deuterium uptake, a cooling loop was established. The sample was then electrolysed in the upper part of the cell at 2 A for 14 hours with a stable cell temperature of 11-14°C. The total charge now corresponded to a D/Pd ratio of 15. The only structural change observed in the new powder pattern was a marginal increase in the amount of β-phase.

Subsequently the sample was removed from the electrolytic cell and three structure determinations carried out in time intervals of ten hours. During these experiments the amount of β-phase decayed to 15%, 9% and 5%, respectively. The

Fig. 4. The multi-detector powder diffractometer at DR 3, Risø. Twenty detectors D1...D20 with Soller collimators C1...C20 spans 100° of scattering angle so a 5° scan of the detector bank furnishes the complete powder pattern. CO defines the collimation of the incident beam.



The amount of deuterium in the  $\beta$ -phase stayed essentially constant at  $x = 0.66$ .

The cell was then taken apart and the Pd foil straightened out and placed between two planar Pd-electrodes so that »electrolytic pumping« could be done from two sides. The electrolysis continued overnight. The deuterated sample is however brittle, and during the process of reassembling the cell the Pt-wire/Pd-foil contact broke off. A new cell design would be required in

order to make in-situ measurements on a system with a more efficient contact between the electrolyte and the Pd-foil electrode.

Finally, a neutron powder diffraction study was carried out on the pressure deuterated PdD<sub>x</sub>-sample ( $x = 0.7$  from thermobalance measurements). The diffraction data showed that the sample was pure  $\beta$ -phase PdD<sub>x</sub> with approximately  $x = 0.61$ .

## 4. Conclusion

Structural studies of Pd-metal deuterated in-situ on a powder neutron diffractometer showed no anomalous properties in the composition and positions of the deuterium. It proved difficult to electrolyse the crumbled sample of Pd-foil, probably because the heat evolution during electrolysis evaporate the electrolyte inside the sample. Deuteration is therefore mainly taking place only from the exterior surface of the sample. However, it is observed that slightly higher deuterium concentrations are obtained in the  $\beta$ -phase of the electrolytic deuterated samples than in the pressure deuterated sample. A further study based on a massive palladium sample might be valuable in this respect.

In an experiment which was designed to reproduce the results of Ref.3 we have not seen any sign of neutron production above the measured background, even though our detection system was of the order of 100 times more efficient than the one used in Ref.3. One reason of this discre-

pancy could be that we have not prepared the titanium exactly the same way as it was done in Ref.3 or that we have missed some details in the experiment which have not been documented in the report. However, it is difficult to believe that the process should be that sensitive to the experimental details that we should not be able to measure any neutrons, especially taking into account our rather sensitive detection system. From our work we have learned that many possible misinterpretations of a neutron detection system are possible. For instance, cooling of detector wires can easily give some vapour condensation on the connectors which in turn may cause a higher counting rate. Also an increasing count rate from a defect amplifier and from noise from nearby electrical equipments were recognised, but in all these cases the energy spectrum was wrong. We therefore conclude that in order to believe this kind of measurements, it is very important to observe the energy spectrum of the signal from the He<sup>3</sup>-detector all the time.

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