Limits on Neutron Emission following Deuterium Absorption into Palladium and Titanium

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No evidence of neutron emission was observed following deuterium loading into palladium and titanium in both electrochemical and pressurization experiments. Upper limits obtained with a detector having a very clean neutron signature are at least 100 times lower than values reported in recent publications giving evidence of cold fusion. The deduced fusion rate limits were lower than 2×10^{-26} per second per pair of deuterons.

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Electrochemically induced nuclear fusion was first invoked by Fleischmann and Pons[1] to explain the heat excess observed in their electrolysis experiments. Dynamically induced fusion has been thought to be possibly at the origin of neutron events observed by Jones *et al.*[2] and De Ninno *et al.*[3] In both cases, monoenergetic neutrons of 2.45 MeV should have been produced if deuterium fusion had occurred.

For the purpose of a neutrino experiment, a new neutron detector based on lithium-6 loaded liquid scintillator has been developed by the Bugey Collaboration.[4] A neutron with a kinetic energy above 1 MeV is unambiguously identified by a recoil-proton signal followed within 30 μs by a signal of an α-triton pair produced in the thermal-neutron-capture reaction ($n+{}^6\mathrm{Li}\rightarrow\alpha+t+4.8$ MeV). The pulse-shape-discrimination method developed for our setup allows clean identification of the heavy charged particles with a discrimination factor better than 10^3 against the Compton electron background. The dead time per event, determined with fast electronics including 15-MHz flash analog-to-digital converters, was 1.5 μs.[4,5]

A cell of 6 liters with a detection efficiency of 2.3% was installed in the Laboratoire Souterrain de Modane. Because of the drastic suppression of the cosmic muon flux by the natural rock shielding ($4/\mathrm{m}^2\mathrm{day}$),[6] the neutron background is very low: $1.7^{+0.8}_{-0.5}$ neutron events per day at 95% confidence level, Poissonian statistics assumed. Both electrochemical and pressurization experiments were undertaken following closely the conditions of the original experiments.[1-3]

Electrochemical experiments.—Palladium electrodes of various sizes and shapes have been subjected to deuterium insertion using recipes similar to those described by Fleischmann and Pons.[1] The electrochemical cell was first cleaned with sulfo-chromic acid, then rinsed successively with high-resistivity water, and 99.84% pure heavy water. The LiOD electrolytic solution was obtained by direct reaction of 99.5% pure lithium metal with 99.84% pure heavy water. The palladium electrode was surrounded by a cylindrical platinum grid; separation between the two was maintained by a perforated glass cylinder. The reference electrode, when used, was a saturated calomel electrode (SCE) connected through a closed stopcock to a Luggin capillary which was set close to the palladium electrode. This arrangement ensured electrical contact through a thin film of electrolyte, and prevented interdiffusion of the cell solution with the reference electrode solution. Except in the first experiment, the cell temperature was maintained constant by a closed-circuit circulation of thermostated water.

Table I contains the details relative to electrode shapes, electrolytic solutions, and the various experimental conditions. A first set of three samples of palladium sheet of various sizes was subjected sequentially to electrochemical insertion of deuterium. For the first sample, the temperature of the electrochemical cell was allowed to increase resistively up to 80 °C. For the second sam-

TABLE I. Electrochemical experiments.

sample	1	2	3	4	5		6	7
origin	Johnson Mattey	Johnson Mattey	Lyon Allemand	Lyon Allemand	Lyon Allemand		Lyon Allemand	Lyon Allemand
preparation	annealed in an H_2O_2 flame anodic activation	annealed in an H_2O_2 flame anodic activation	cleaned with H_2O, ethanol, HNO_3, D_2O. anodic activation	annealed in an H_2O_2 flame anodic activation	fused in a graphite crucible annealed in an H_2O_2 flame		fused in a cold crucible annealed in an H_2O_2 flame	see text
shape	sheet	sheet	folded sheet	wire	cylindrical rod		sphere	
dimensions (cm)	2.6x1.8x0.01	2.6x1.6x0.01	4.0x3.0x0.005	Φ 0.1, L 6	Φ 0.4, L 6		Φ 0.8	
mass (g)	0.56	0.5	0.67	0.97	7.87		3.2	
surface (cm^2)	9.36	8.32	24	2.3	7.54		2.0	
electrolyte : LiOD	0.15 M	0.15 M	0.15 M	0.15 M	0.1 M		1 M	
cell current (A)	1, 0.75	1.65	1.5 (20 min) 3.0 (55 min) 4.0 (15 min)	0.5	0.38		0.13 (23 days) 0.5 (80 min) 1 0 (60 min) 2 0 (120 min) off (40 min) 0.5 (24 h)	
current density (mA/cm^2)	220, 160	200	63, 125, 167	220	50		65	
cell temperature (°C)	20 to 80	15, 30, 45	50	20	20		15	
loading (counting) time (h)	2 (1.9)	5 (4.9)	2 (2)	36 (36)	816 (457)	(92.5)[a]	552 (19)	(44.5)
total neutron events	0	0	0	1	42	19	2	3
upper limits of emission (n/h) at 90% C.L.	67.7	24.6	63.2	1.99	3.13	11.1	12.7	5.56

[a]Neutron counting during unloading.

ple, there were three steps of temperature of the same duration. For the third sample, the temperature was maintained stable at 50 °C and three steps of current densities were imposed. It was noticed that this last sample, a very thin sheet, was dramatically distorted after a 90-min loading time. No neutron event was detected during loading times of several hours. Sample 4 was a thin wire of 0.1 cm in diameter and 6 cm in length. One single neutron event was detected during 36 h of loading time.

To reproduce the Fleischmann and Pons neutron-detection experiment, a palladium cylindrical rod (sample 5) with the same diameter as the one used in Ref. 2, was mounted in the electrochemical cell. This rod was fabricated by fusing palladium in a graphite crucible immersed in an argon atmosphere. The surface was then machined to adjust the rod diameter to 0.4 cm. A microscopic porosity (open and/or closed) and a small concentration of carbon (0.01% in mass) were present. The working conditions of the electrochemical experiment were chosen as close as possible to those of Ref. 1. On the 30th day of loading, the potential of the electrode at null current, $E_I=0$, was measured using a freshly prepared saturated calomel reference electrode: $V_{SCE}(E_I=0)=-1.125\pm0.005$ V. The pH of the solution was 12.6 ± 0.1, which corresponds to an overpotential h with respect to the reversible hydrogen reference electrode $h(\mathrm{RHE})=-0.147\pm0.011$ V. This overpotential may be translated in terms of an equivalent fugacity P_{D_2} from the relation

$$\eta=-\tfrac{1}{2}\ln(10)(kT/e)\log_{10}(P_{D_2})a\,,$$

and thus

$$9.25\times10^4/2.35<P_{D_2}(\mathrm{atm})<9.25\times10^4\times2.35\,.$$

The amount of deuterium loaded in this rod was measured by unloading electrochemically at constant electrode potential and collecting gas in a water jar.

The collected gas was analyzed with gas-phase chromatography and was found to be isotropically pure with $Z=1$ (99.9%, water vapor excepted). The amount of deuterium collected (3.5 liters) was much larger than expected from the PdD formula and was probably due to the presence of microcavities mentioned above. 42 neutron events were detected during 457 h of loading time. Taking into account the total quantity of collected deuterium, the limit on the fusion rate was 0.92×10^{-26} per second per pair of deuterons. During the unloading time of 92.5 h, 19 neutron events were measured.

A test of possible dynamical effects was undertaken with sample 6, a 0.8-cm-diam palladium sphere, fused in a cold crucible. After loading with a current of 0.13 A for 23 days, the cell was placed in front of the neutron detector. In order to produce abrupt changes in the loading regime of the sphere, the cell current was set sequentially to 0.5, 1, and 2 A for more than 1 h each time, and then, after being switched off for 40 min, was set back to 0.5 A, and switched off again 24 h later. The

cell temperature was maintained at 15 °C. Two neutron events were detected during the 18.6-h loading time.

Finally, an experiment was made using an electrolyte recommended by Jones:[2,7] 0.2 g ($LiSO_4 \cdot H_2O$) + 0.1 g $PdCl_2$ diluted in 250 cm^3 of 99.84% purity D_2O ($pH = 3.5$) and, as an electrode, turnings of titanium metal (width 0.2 cm, thickness 0.01 cm, length 100 cm, surface 20 cm^2). The cell current was increased by abrupt steps of 1 A from 1 to 4 A every 30 min, and then abruptly switched off. Neutron counting was continued for an additional hour. Only three neutron events were measured for a total counting time of 44.5 h.

Gas-phase experiments.—The reversible absorption of deuterium in titanium has been studied under equilibrium and nonequilibrium conditions in order to create the dynamic conditions suggested by De Ninno *et al.*[3] for neutron emission associated with cold fusion. The experimental setup is presented in Fig. 1.

Titanium shavings were obtained from a high-purity titanium block (99.9% purity) and pressed into pellets in order to obtain a more compact rod of about 15 g with 30% density. The titanium charge was introduced in a stainless-steel vessel which could be either evacuated with a high-efficiency turbomolecular pump or subjected to deuterium high pressures (60 bars D_2, 99.5% purity) through a gas pressure regulator. Outside of the lead shielding containing the neutron detector, the pressure vessel could be heated up to 950 °C, with a resistance furnance. It could also be cooled down from room temperature to liquid-nitrogen temperature, inside the lead shielding, in front of the neutron detector. The warming up of the vessel was possible within 1 h by evaporating the liquid nitrogen quickly, but could also take about 10 h with natural evaporation. A thermocouple in close contact with the bottom of the pressure vessel measured the titanium temperature. Another thermocouple pasted on the neutron detector ensured that its temperature remained stable during the experiment.

The absorption of deuterium in titanium has been well known for a long time.[8] The solid hydride phase exists in equilibrium with the gas, the equilibrium pressure being a function of both the temperature and the concentration of deuterium in the metal. With increasing deuterium concentrations the hexagonal Ti metal phase transforms into a cubic-face-centered phase, with a final composition (around $TiD_{1.75}$) which is a function of the amount of impurities (O, N,. . .) and the mechanical history of the starting material.

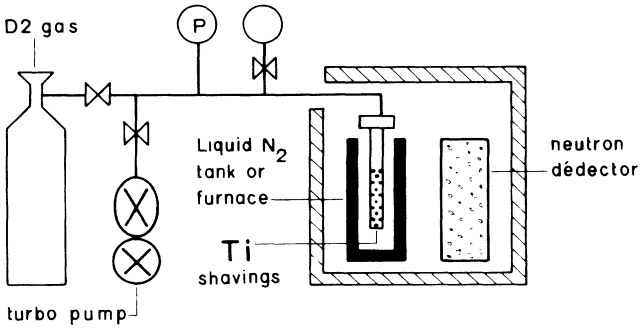

FIG. 1. Experimental setup for pressurization experiments.

In order to test the formation of Ti hydrides in different stages under varying pressure and temperature conditions, three typical runs have been made.

(a) In the first experiment the titanium rods were directly subjected to 2-bars D_2 pressure, without surface cleaning or outgassing. An increase of the temperature up to 550 °C activated the hydriding. The partially hydrided titanium was subjected to high pressure (50 bars) at room temperature and then cooled down to 77 K (three cycles of about 3 h each). During the third step, both temperature and pressure were changed between 77 and 300 K, and 1 and 50 bars, respectively (two cycles of 20 h).

(b) In a second experiment the Ti hydride was fully desorbed and reduced to pure Ti by pumping out the deuterium at a temperature as high as 930 °C without opening the vessel between the two experiments. Pressure was then admitted stepwise into the vessel to perform hydriding. The pressure indication which fell slowly at each pressure step showed that titanium was hydrided even at room temperature. The temperature was then lowered to 77 K and the pressure was monitored to 60 bars to ensure complete hydriding of the Ti shavings.

After two cycles between room temperature and 77 K with a slow warm-up (10 h), the TiD_x composition, calculated from the weight loss of TiD_x alloy heated up to 950 °C in another vessel, was estimated to be $x = 1.5$. Using this technique, the x value is underestimated. Four neutron events were measured during 36.3 h of counting time, which gives a deduced limit on the fusion rate of 1.8×10^{-26} per second per pair of deuterons.

(c) In the third experiment a new charge of 30 g of Ti was first outgassed and then hydrided under quickly changing pressure and temperature (cycles of a few hours).

(d) In a last run we decided to study the deuterium absorption of the oxide $Ti_4Ni_2O_x$ which is well known to react directly with D_2 at rather low pressure, with fast hydriding kinetics, and does not need any activation. 40 g of this material, roughly powdered, was put into the reaction vessel. The D_2 pressure was admitted stepwise in

TABLE II. Pressurization experiments.

	a	b	c	d
Counting time (h)	45.3	6.3	57	68
Total neutron events	5	4	10	5
Upper limits on neutron emission (n/h) at 90% C.L.	8.0	8.9	10.9	4.7

the vessel up to 60 bars but hydriding began immediately. Several runs of absorption-desorption have been made between room temperature and 77 K.

All the experimental ways to obtain the hydride starting from pure titanium (or $Ti_4Ni_2O_x$) have been explored within these four runs. The experimental setup was in front of the neutron detector during the whole time when the vessel was at room temperature or lower. The measured neutron counts and upper limits on neutron emissions at 90% C.L. are reported in Table II. These values are 100 times lower than those previously reported.[2,3]

Concerning neutron bursts as reported by Menlove *et al.*,[9] due to the 30-μs thermalization time, neutron events would not be simultaneous; i.e., our apparatus should have registered a few tenths of events from bursts of about 100-μs duration. No such series of events were observed. On the other hand, a random emission of 0.1 neutron per second would have resulted in a total number of events 1 to 2 orders of magnitude higher than we measured.

Extensive experiments were carried out in loading palladium samples with deuterium and in submitting titanium samples to abrupt changes in electrochemical conditions or to temperature and pressure variations, to approximate the conditions of previous experiments giving evidence of neutron emission.[1-3,9] Neutron events measured with a detector having a very clean signature for 2.45-MeV neutrons were compatible with the normally low background rates detected at the Laboratoire Souterrain de Modane. Upper limits on neutron emission deduced from present experiments are several orders of magnitude lower than reported in recent papers[1-3,9] on evidence for cold fusion. Upper limits on fusion rates (λ_f per second per pair of deuterons for the neutron production branch) deduced from our results are $<0.92\times10^{-26}$ for electrochemical experiments and $<1.8\times10^{-26}$ for pressurization experiments. These limits are much lower than recently published results.[10,11]

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