CLM-P864

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AEA TECHNOLOGY

EXPERIMENTAL SEARCH FOR "COLD FUSION" IN THE DEUTERIUM-TITANIUM SYSTEM

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Abstract

A series of experiments have been carried out to try and detect 'cold fusion' in titanium which has been loaded with deuterium at high pressure. No neutrons were detected using a range of counting systems, the most sensitive of which could detect 0.9 neutrons s^{-1} if sustained over 100 secs. Bursts of more than 30 neutrons occurring in a period of less than 0.1s could also have been detected using coincidence counting. Evidence for erratic behaviour of proportional counters, which could be mistaken for neutron emission is presented.

1. Introduction

The possibility of inducing nuclear fusion reactions at low temperatures in the solid state has recently been widely discussed (1). The evidence for such reactions occurring is based on two types of experiment. In the first type, electrolysis of an aqueous solution using heavy water was used to load palladium and titanium with deuterium. Heat generation and neutron emission were reported in ref 2 and a low emission rate of 2.5MeV neutrons was reported in ref 3. In the second type of experiment, the surface of titanium was loaded by subjecting it to a high pressure of deuterium (4). Neutron emission was reported when the temperature of the titanium was cooled below room temperature and, with a separate sample, when the titanium was warmed up from 77K to room temperature.

We have attempted to repeat the second type of experiment using high pressure deuterium to load a titanium surface. In these experiments we have followed the procedure used by De Ninno et al (4) as closely as possible. We have also varied their procedure by using a high temperature preparatory bake of the titanium in order to reduce the surface oxide layer. This procedure is well known to be necessary to get reproducible diffusion rates into bulk titanium. After preparation of the titanium the samples were taken to well characterised neutron counters at JET and at Harwell. Counting was carried out for periods of many hours while the samples were cooled below ambient temperature and warmed up from 77K. In no cases were any neutrons detected above the background level. In the following sections we discuss the details of our techniques.

2. Preparation of the titanium samples

There appear to be two notable features of the deuterium loading technique described by De Ninno et al; it is carried out at high pressure and at relatively low temperature. The equilibrium pressure over deuterated titanium as a function of temperature and concentration has been given by Morton and Stark (5). Although deuterium diffuses through titanium quite rapidly at temperatures above 300°C, at lower temperatures it takes inconveniently long times to reach equilibrium conditions. An additional problem is that titanium forms a strong surface oxide coating and this coating can seriously impede the absorption of hydrogen isotopes. For this reason our apparatus has been designed to be bakeable to high temperature, to be capable of obtaining ultra high vacuum and to be operable at pressures of up to 50 bar. The system is shown schematically in fig 1. It is evacuated with a turbomolecular pump and the residual gas pressure is measured with an ion gauge and analysed with a quadrupole mass spectrometer. Joints were made with all metal seals. The deuterium gas has a purity level >

99.9%, the main impurities being hydrogen (900ppm) and nitrogen (90 ppm). The gas inlet manifold consists of stainless steel pipe which goes through a liquid nitrogen cooled trap before entering the main system through valve 1. The gas pressure is measured by dial gauges on both the inlet system and the main system.

The titanium is prepared from commercially pure (99.5%) bar by milling under clean conditions without lubricant. The chips produced are typically 3 x 3 x 0.15mm. They are ultrasonically cleaned in Genklene and isopropyl alcohol, then weighed and put in the retort tube. The retort has an outer diameter of 30 mm with 3 mm thick walls. After pumping the vacuum system down to typically $< 10^{-6}$ mbar, the retort is heated up to outgas the titanium. A range of temperatures from 460K to 950K has been used for the different samples. The samples are then cooled down to near ambient temperature. The base pressure in the vacuum system is typically $< 1 \times 10^{-7}$ mbar at this stage, with the main residual gas species being water. The pumping system is valved off using valve 3, and deuterium is introduced via valve 1. The pressure is raised quickly to some predetermined value and the gas inlet valve resealed. The pressure is noted as a function of time. In most cases the temperature of the titanium increases during exposure to the high pressure deuterium. The reduction of pressure in the sealed off tube is a measure of the absorption rate, and is higher for higher diffusion rates. After a given time at high pressure the retort tube containing the titanium is sealed off using valve 2 and transferred to one of the two neutron detectors. The neutron emission rate has been measured over a range of conditions during which the samples were cooled to 77K and allowed to warm up to room temperature again.

2. Description of the neutron measurements carried out on a titanium cell

2.1 Three separate neutron counting systems have been used. The first is a single BF_3 counter mounted close to the titanium preparation tube. The counter is surrounded by 100 mm of parafin wax. This system was calibrated with a 9.1×10^4 neutrons s^{-1} ^{252}Cf source. It has an efficiency of 4×10^{-4} for neutrons emitted into a solid angle of 4π from the position of the titanium sample. The counter was connected to a ratemeter with a 30s time constant and used for routine monitoring of the titanium samples during preparation. It had a relatively high background rate varying from 1 to 3 counts s^{-1}. The titanium samples would thus have to emit between 2,500 and 7,500 neutrons s^{-1} to double this rate.

Two separate detector systems were used to detect neutrons after sample preparation. The first system is normally in use at JET for neutron activation studies and was used for the majority of the samples investigated. It is described in detail in the next section. The

second is the system set up at Harwell to investigate neutrons from electrolytic cells of the Fleischmann and Pons type (2). It is described in section 2.3.

2.2 The JET neutron detection system

For the present investigation, use was made of two identical neutron detection systems which are used to measure the delayed neutron activity of samples of fissile material. The two counting systems are located in a shielded counting room, separated from the JET tokamak by a 3 metre thick concrete wall. As both counting systems are in routine use, their efficiency and response are well known (6) and the counter assemblies are well suited for the measurement of neutron emission from titanium samples. Each assembly consists of a large polythene filled cadmium-clad vessel into which six proportional counters (350 mm long and 25 mm in diameter) are set in a compact regular hexagonal arrangement to form an approximately 4π geometry to samples which are placed in its centre. As the counters are most sensitive to thermal neutrons, polythene is used as a moderator. The sensitivity to neutrons originating outside the assembly is low and the background count rate for the assembly is approximately 0.2 cps. The detection efficiency for neutrons originating from within the assembly, on the other hand, is very high and accurately known to be 10%, ie 1 in 10 neutrons produced within the assembly will be detected. The counters are standard ^{3}He proportional counters (4 bar of ^{3}He and 2 bar of Krypton) and have been selected for matched sensitivity and gain. They operate at a bias voltage of 2.52kV and a gas multiplication of about 20. They are used in pulse-mode and each exhibits a 3% dead time at a count rate of 5 kHz. The output pulses are processed by charge sensitive pre-amplifier/ discriminator units which incorporate two separate leading edge discriminators to allow neutron events to be distinguished from events due to gamma radiation and other sources of low level noise. To monitor the detection systems over long periods, typically many hours, a computerised data-taking system was set up which performed the data collection in many batches of 40 seconds duration. At the start of each batch the data collection hardware was programmed to take 400 samples during which the counts from each of the two discriminator outputs

of each of the 12 individual counters were integrated over periods of 100ms and stored in local memory. After 40 seconds a program was triggered to read the memory, store its information on disk and start the next batch. The information stored for each event included: a) the absolute time of the event with 100 ms precision, b) a channel identifier specifying the counter and the discriminator of that counter which recorded the event and c) the number of counts that channel produced within the 100 ms integration period. During the experiments both assemblies were monitored this way; one contained the titanium sample while the other was used to monitor background.

The computer program also performed a real time analysis to bring out any granularity in the observed count rate which might be indicative of burst-like events like those claimed by De Ninno et al (4). Such bursts, when of moderate intensity, would be detected properly. Very intense bursts of neutrons could paralyse the counters, but such occurrences could not escape detection. With a burst intense enough to paralyse one counter, the remaining five counters in the assembly would also register counts, or possibly be paralysed. However, in these cases, the lower and upper leading edge discriminators of each of the six counters would fire at least once and, more importantly, on all six counters simultaneously, ie within 100ms. Such an event would then be detected as a six-fold coincidence. Given that the average count rate of each counter is low (approximately 0.035 counts/s), six-fold coincidences are extremely unlikely within a 100 ms period. Running both assemblies with no titanium sample present confirmed that single, double and triple coincidences follow a predictable pattern which is easily derived from Poisson statistics assuming a constant background. Four fold, five fold and six fold coincidences, although monitored, are too unlikely to be seen at all with any statistical significance.

2.3 Harwell Dual Cavity ^{3}He Neutron Detector

This detector was specifically constructed to provide a reasonable volume for continuously monitoring a number of electrolytic cells in recent measurements at Harwell attempting to reproduce the cold fusion results of Fleischmann and Pons (2). The detector consists of two cavities each 38cm x 42cm x 60cm and each furnished with sixteen 2.5cm diameter, 35cm active length ^{3}He proportional counters filled to 4 bar with ^{3}He. The counters are grouped into banks of 8, there being 4 banks in all. The counters are double bagged and sealed in polythene sheeting with silica gel desiccators. Behind the counters are 40mm of polythene moderater and 1mm of Cd sheet. The cavities are covered with 1mm of Cd sandwiched between two 10mm thick layers of polythene. The top and all four sides of the detector are shielded with 150mm thick interlocking borated resin blocks. The same thickness of borated resin also divides the two cavities and both cavities are continuously vented through pipes connected to extractor fans.

Signals from each of the 4 banks of detectors, which operate at a voltage of 1560V, are shaped and amplified by Harwell-type 0058 and 2151 preamplifiers and main amplifiers. Outputs from the amplifiers are passed to Harwell-type 2170 single channel analysers with gates set around the thermal peaks in the pulse height spectrum from the counters. Accepted events are counted along with clock pulses from a crystal oscillator by a LeCroy type 2551 CAMAC scaler which is read at fixed intervals by a PDP 11/45 computer.

For the present measurements, vessels containing the Ti chippings were surrounded by expanded polystyrene for thermal insulation and a third polythene sheeting seal was provided as an extra barrier between any condensation and the counters. Under normal operation the background rate in the banks of counters lay in the range 0.05 to 0.2 counts per second, with correlated changes in the rate in all four banks consistent with changes in the operational status of nearby neutron producing accelerators and reactors. Unexplained drifts in the count rate in one bank uncorrelated with the others have been observed (see for example bank 1 in figure 3 with time constants of the order of many hours. Such drifts can easily be distinguished from genuine neutron emission which would give correlated signals in the 2 banks viewing the cavity containing the source with any correlated rise in the other 2 banks being consistent with the known cross talk between the cavities.

The neutron detection efficiency of the detector was determined using a calibrated Am/Be source, which has a neutron energy spectrum with a mean energy of 2.7 MeV, positioned by or in place of the titanium sample tube. The average efficiency was 1% per bank of 8 detectors.

3. Results

A summary of the preparation of the different samples is given in Table I. The samples were exposed to deuterium over a range of temperature from 290 to 400K and pressures from 2 to 40bar. The preparatory baking temperature was also varied from 460K to 950K. In general when the samples are exposed to the deuterium in a sealed-off system the pressure p drops as the deuterium is absorbed into the metal lattice. The rate dp/dt depends on the sample temperature, due to the change of diffusion coefficient with temperature. At room temperature the initial dp/dt is $\sim 10^{-4}$ bar s^{-1} while at an initial temperature of 400K it is $\geq$ 1 bar s^{-1}. As the reaction is exothermic, with a heat of solution of 50 kJ/mole (5), the sample heats up as the deuterium is absorbed. At higher temperatures where the rate of absorption is more rapid the temperature rise is higher. The increase in sample temperature varies from ΔT = 10K with the sample at 290K to ΔT=290K with the sample initially at 400K. In one case, sample 4, where the initial bake was 460K, both the absorption rate and the temperature rise were undetectable. This was attributed to the presence of an oxide layer which had not been removed by the low temperature bake. The samples prepared by heating to the higher baking temperature had a hydrogen absorption rate and temperature rise which behaved reproducibly.

In the first few experiments an attempt was made to reproduce the conditions reported by De Ninno et al (4) and to detect the relatively high neutron flux reported when the titanium samples were warmed from 77K to room temperature. The samples were loaded at high pressure and temperatures in the range 300-340K. They were then cooled to 77K and

evacuated using the turbomolecular pump. No significant amount of gas was released at this stage. The valve 2 to the retort was then closed and the retort transferred to the high efficiency counter in a dewar. The retort was removed from the dewar and allowed to warm up in the counter. This typically took a period of 2 to 4 hours during which time the neutron rate was monitored both in the counter cavity in which the retort was contained and in the similar cavity without the retort (cf sections 2.2 and 2.3). Typical results are shown in fig 2 and 3. The structure in the bank 3 results of fig 3 is spurious as there is no corresponding structure in the results from bank 4 in the same cavity. No neutrons above background were observed in any case. The minimum neutron rate which can be detected with reasonable confidence (2 standard deviations above background) is given by $n_d = \sqrt{4R_b/E^2t}$ where R_b is the background counting rate, E is the counter efficiency and t is the period in seconds during which neutron emission is steadily sustained. For JET with $R_b = 0.2$ counts s^{-1} and $E = 0.1$ we could confidently detect an emission rate of 0.9 neutrons s^{-1} sustained for 100s or 0.14 neutrons s^{-1} sustained for 1 hour. Corresponding emission rate limits for the Harwell neutron detector system are 5 and 1 s^{-1} respectively. By virtue of the coincidence method the JET counters would also have detected a single burst $\geq$ 30 neutrons if such a burst had lasted for 100ms or less. Thus the 5000 neutrons s^{-1} reported by De Ninno et al would have been detected unequivocally.

It has been reported that in the Frascati experiment the titanium sample was baked to 470K (4). This is not the conventional procedure for loading hydrogen isotopes in titanium, as oxide layers tend to impede the rate of diffusion. One sample was prepared in this way in case such a procedure was important for some unsuspected reason: however, in this case no evidence of deuterium absorption was observed, ie no fall in deuterium pressure occurred nor was there any rise in the titanium temperature during exposure to the high pressure deuterium. No neutron flux above background level was detected when the samples were heated from 77 to 300 K. In the subsequent experiments a high temperature bake was used in order to remove the surface layer of oxygen and obtain reproducible absorption. In these cases, the samples were left at ambient temperatures and at loading pressure while they were sealed off and transferred to the high efficiency counters. They were then cooled and allowed to warm up again in situ in the counter cavity. In some cases they were cooled to $\sim$ 180 K using solid CO_2 and in other cases to 77K using liquid nitrogen. In a number of cases the same titanium samples were cooled and allowed to warm up again a number of times in succession. Two examples of the neutron counting rate as a function of time during the cooling and heating cycle are shown in figs 4 and 5. In no case was a significant neutron count rate above background detected. As in fig 3 the structure in the bank 3 results is spurious.

In all the runs up to this point the loading temperature was kept at ∿ 300K. This led to rather low average deuterium concentrations in the titanium ∿ 0.1-0.2 D/Ti, due to the low diffusion rates. However the concentration profile of deuterium in the solid is expected to be peaked at the surface as discussed in section 4. In the last two experiments the titanium chippings were deliberately heated to a higher temperature for loading. This results in a much larger quantity of deuterium absorbed and a consequently higher temperature excursion due to the exothermic reaction energy. In these cases the average deuterium concentration was ∿ 2.0 D/Ti. The concentration would be expected to be approximately uniform throughout the volume of the titanium. No neutrons above the background rate were observed when the titanium samples were cooled or heated.

4. Discussion

Electrochemical and high pressure, low temperature, gas charging, are in many ways similar approaches to inducing a high deuterium concentration in a metal surface. Both have high incident flux rates, and since they are carried out near ambient temperature the rate of diffusion into the bulk is low. The diffusion coefficient for deuterium in titanium can be written (7)

$$D = 0.013 \exp(-Q/RT)$$

where Q = 52kJ/mole, is the activation energy for diffusion, R is the gas constant and T is the absolute temperature. Although these data have been measured at temperatures above 770K they can be extrapolated to lower temperatures with reasonable confidence, obtaining a value of D = 2×10^{-11} $cm^2 s^{-1}$ at 300K. The characteristic diffusion length calculated on the basis of a one dimensional model is given approximately by $(4D\tau)^{\frac{1}{2}}$ where τ is the time for diffusion (8). Considering a loading time of 10^4 secs the diffusion depth will be ≈ 9μm. This is small compared to the typical sample thickness of 150μm and so only the surface of the sample will be loaded. Thus the surface concentration will be much higher than the average concentration quoted in samples 1 to 8 listed in Table I. Taking into account diffusion from both sides, the concentration in the surface layer will be ∿ 1.3 D/Ti ie not markedly below the concentration in samples 9 and 10.

During our attempts to produce neutrons from cold fusion with the ten samples listed in Table I we have not seen any significant evidence of neutron production. The upper limit of neutron emission, if present at all, is not higher than 0.14 neutrons s^{-1}. This is roughly four orders of magnitude lower than the emission rates reported by De Ninno et al. One interesting aspect of this work has been the observation of fluctuations in our counting systems, at Culham, JET and Harwell. In all cases the apparent signals have been shown to be due to counter

misbehaviour, as they usually occur only in one counter and continue even when the titanium sample is removed. In one case in JET the counting rate increased by a factor of 100 and gradually returned to its normal low level over a period of many hours. The reason for this counter behaviour is not fully understood but is presumably related to partial electrical breakdown in the insulating material of the HV connections. Such behaviour is particularly difficult to distinguish from neutron emission if only one counter is being used. If a number of independent counters are used the errant counter can be identified and its output rejected.

5. Conclusion

Ten separate titanium samples have been loaded with deuterium under high pressure in a way similar to that reported by other investigators (4). A number of variations in the procedure including a range of loading temperatures and pressures have been used. The prepared samples have then been transferred to well characterised neutron detectors and cycled in temperature. In no case has any evidence for neutron production been observed. In the case of our highest efficiency counter the neutron production rate, if present at all, was less than 0.14 neutrons s^{-1}, when averaged over a period of one hour. This is 4 orders of magnitude lower than the rates of neutron emission claimed to have been observed by other groups. In addition, if neutrons were to be emitted in brief bursts (lasting 0.1 sec or less) rather than continuously, then individual bursts would have to include less than 30 neutrons otherwise they would have been detected as triple coincidences in the JET experiments.

It is of course quite possible that we have not found the correct preparation procedure for loading titanium. There are a large number of possibly important parameters and it has not been possible to explore all combinations. It is evident from other reports that the statistical probability of observing neutrons is low. It seems likely that if neutron emission does occur then the preparation of the samples is critical. It is thus important that more emphasis is placed on the careful preparation and documentation of procedures in the reports of experiments.

Our experience of making measurements of low fluxes of neutrons has indicated that proportional counters of both the BF_3 and ^3He type are subject to random and unpredictable fluctuations in count rate. These fluctuations can in some cases exceed the average background count by two orders of magnitude. Thus, clearly, a number of independent counters are necessary to confirm that neutrons are really present. We suggest that in a number of reported cases where only single, low efficiency counters have been used that these random fluctuations may have been mistaken for neutrons.

References

(1) J S Cohen and J D Davies, Nature 338 (1989) 705

(2) M Fleischmann and S Pons, J of Electroanalytical Chemistry, 261 (1989) 301 + Errata 263 (1989) 187

(3) S E Jones, E P Palmer, J B Czirr, D L Deglaur, G L Jensen, J M Thorne, S F Taylor and J Rafelski, Nature 338 (1989) 737

(4) A De Ninno, A Frattolillo, G Lollobatista, L Martinis, M Martone, L Mori, S Podda and F Scaramuzzi, Europhys Lett, 9, (1989) 221

(5) J R Morton and D S Stark, Trans of the Faraday Soc, 56 (1960) 351

(6) P D'Hondt and S de Leeuw (private communication).

(7) R J Wasilewski and G L Kehl, Metallurgia, 50, (1954) 225

(8) H S Carslaw and J C Jaeger. Conduction of Heat in Solids, 2nd Edition, Oxford University Press, Oxford (1959)

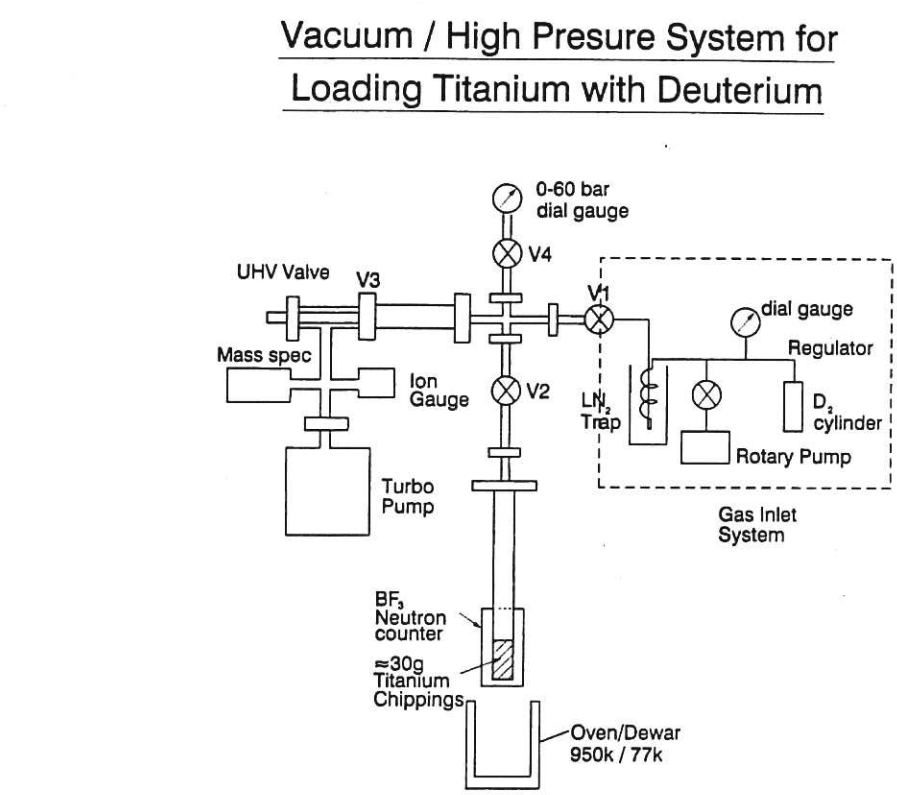

Figure 1. Schematic diagram of apparatus used to load titanium with deuterium.

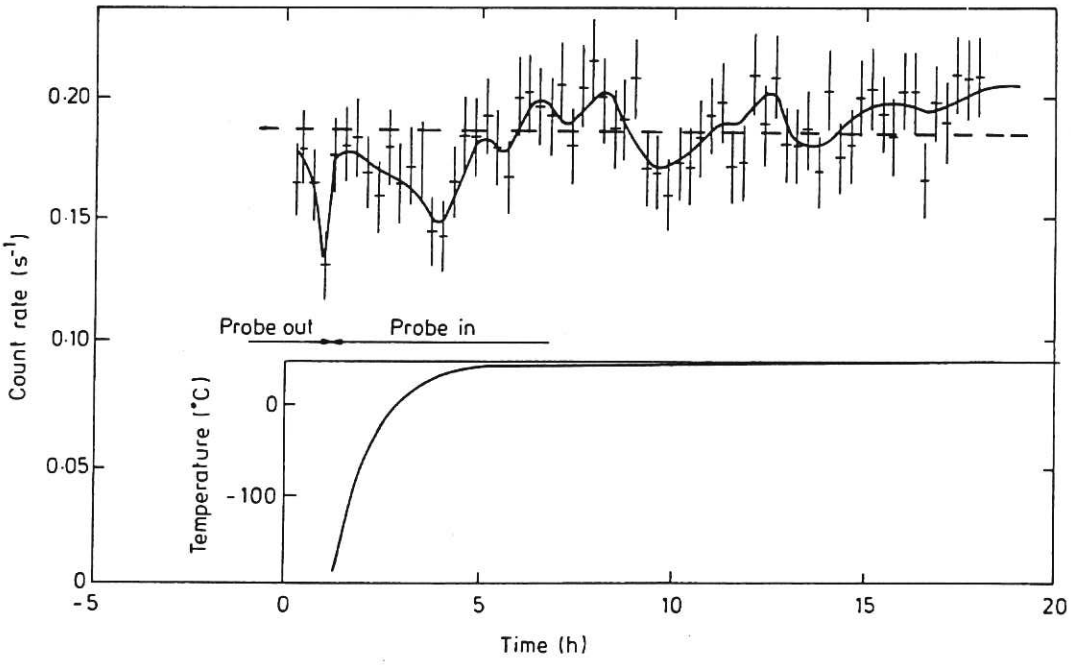

Figure 2 Neutron counting rate in the JET counter during the warm up of titanium from 77 to 300K. Sample No 1. Sum of 6 detectors. The thermocouple measurements were made on the outside of the retort.

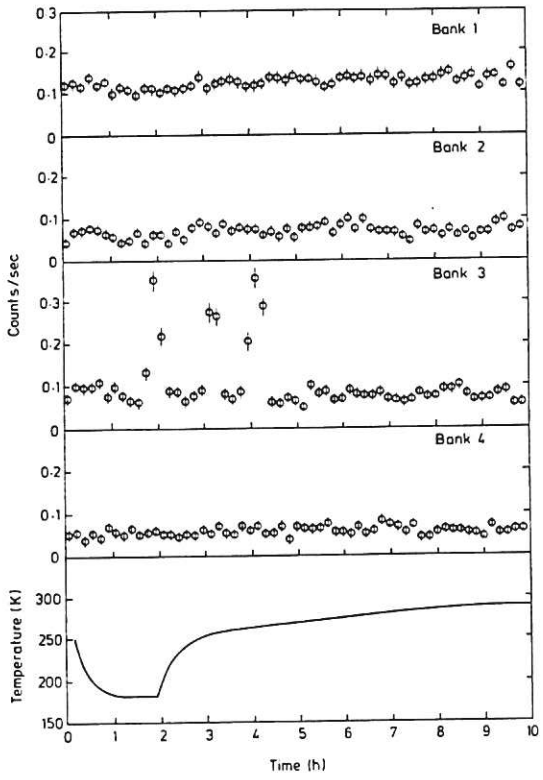

Figure 3 Neutron counting rate in the Harwell counter during the warm up of titanium from 77 to 300K. Sample No 2. The upper 4 plots show the mean count rate in each of the 4 counter banks. Banks 3 and 4 viewed the cavity containing the titanium sample, while banks 1 and 2 viewed the control cavity. Data was collected in 10 second intervals but have been summed into 10 minutes bins. The lower plot shows the temperature of the vessel as measured by a thermocouple in contact with the outside of the retort.

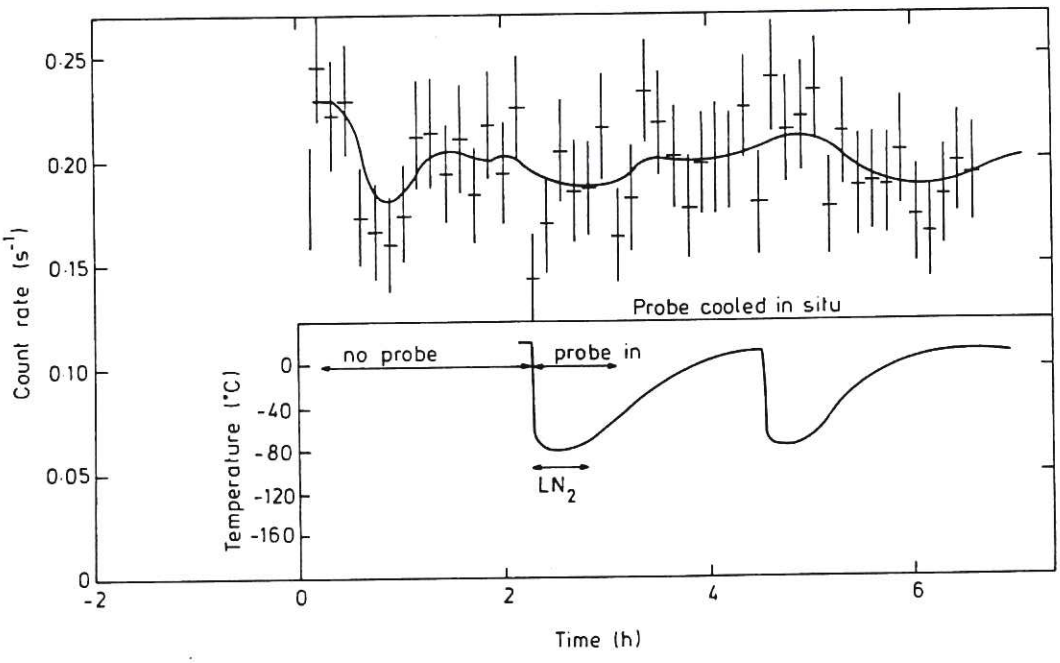

Figure 4 Neutron counting rate in the JET counter during temperature cycling from 300 to 180K. Sample No 5. Sum of 6 detectors.

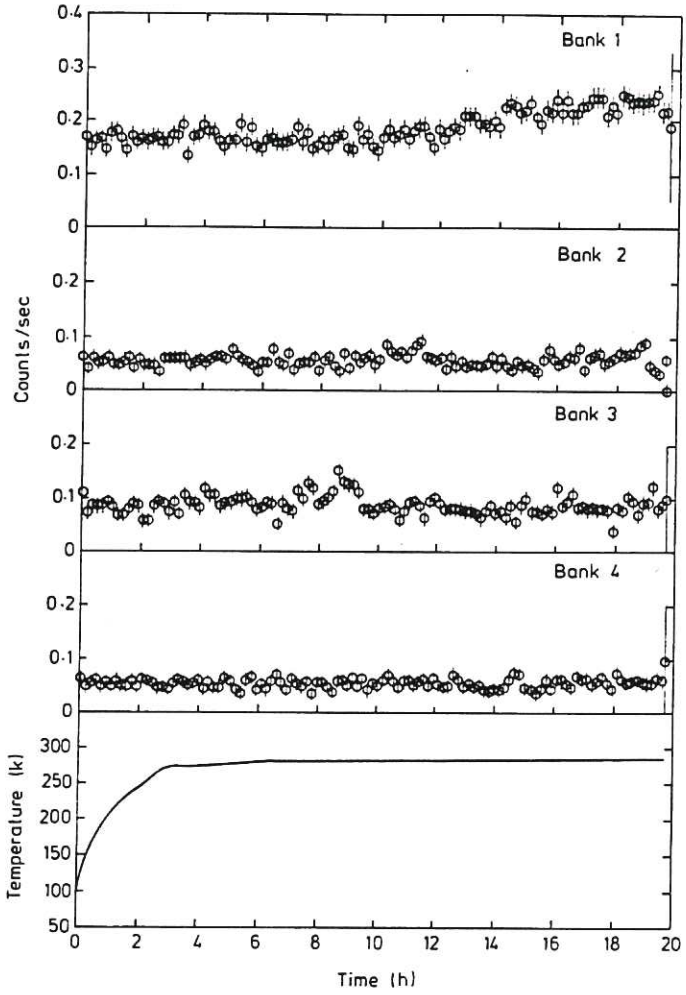

Figure 5 Neutron counting rate in the Harwell counter during temperature cycling from 300 to 180K. Sample No 6. The conditions are the same as for fig 4.