

SOME EXPERIMENTS ON THE DECREASE OF TRITIUM RADIOACTIVITY

NUCLEAR REACTIONS
IN SOLIDS

KEYWORDS: radioactivity, tritium, small particles

OTTO J. A. REIFENSCHWEILER* *Philips Research Laboratories
Eindhoven, The Netherlands*

Received April 13, 1995

Accepted for Publication April 19, 1996

Experiments claiming a sharp decrease in the radioactivity of tritium incorporated in small monocrystalline particles of titanium have been reported and are described here in more detail. Additional evaluation provides a high degree of evidence for the decrease in the radioactivity of tritium. A first attempt is made to explain this remarkable effect in terms of a "nuclear pair hypothesis."

I. INTRODUCTION

Since the discovery of radioactivity, many attempts have been made to change the radioactive decay constant λ by varying extranuclear conditions.^{1,2} Many half-life changes, e.g., of electron capture and of internal conversion, by altering the chemical environment have been reported. In this context, experiments with tritium to be used for technological applications³⁻⁶ performed at Philips Research Laboratories may be of interest. These experiments point to a sharp decrease in the radioactivity of tritium when tritium was incorporated into small particles of titanium.

In a recent letter,⁷ the author gave a short description and preliminary interpretation of the experiments as a first attempt to explain the effect in terms of a "nuclear pair hypothesis." This paper gives a more detailed description and interpretation of these and additional experiments, which results in a high degree of evidence for the strange effect of the decrease of tritium radioactivity.

This treatment seems to the author to be important because of the growing interest in the effect⁸⁻¹⁰ and because it facilitates repetition of the experiments and stimulates further exploration. Furthermore, understandable skepticism¹¹ requires this more comprehensive treatment.

II. EXPERIMENTAL

Figures 1 and 2 show the main setups used in the experiments. A mercury-diffusion pump with one or two liquid air traps was used in the vacuum installations. The temperature of the laboratory room was stabilized within 1°C. To ensure that as many impurities as possible were eliminated, we carefully degassed the vacuum installation, the tube, and the evaporator at the highest possible temperature. After this procedure, the pressure was $\sim 10^{-6}$ mm of mercury. The titanium preparation was made by evaporation of the metal in argon at a suitable pressure, e.g., 1 to 2 cm of mercury.^{3,4,12-15} Spectroscopically pure argon was always used. The titanium was deposited on the inner wall of the vessel as a kind of soot. Examination by electron microscopy showed that the preparation consisted of extremely small particles ~ 10 to 20 nm in diameter (dependent especially on the argon pressure and the evaporation rate) that were arranged in chains and occasionally exhibited ramification. Electron diffraction indicated *single crystallinity* of the particles. Figure 2 of Ref. 3 and Fig. 1 of Ref. 4 show electron micrographs of such preparations. After pumping out the argon, the tritium was added and was rapidly absorbed by the titanium preparation at room temperature. A typical time constant for the uptake of tritium into the alpha phase of titanium was ~ 10 s. This has been stated in thousands of experiments for technological applications. Our titanium preparations were very active for the uptake of tritium at room temperature because of their large surfaces. The ³He residue originating from the beta decay of the tritium was then removed by the vacuum pump.

*Current address: Jan Sluyterweg 13, 5645 JA Eindhoven, The Netherlands.

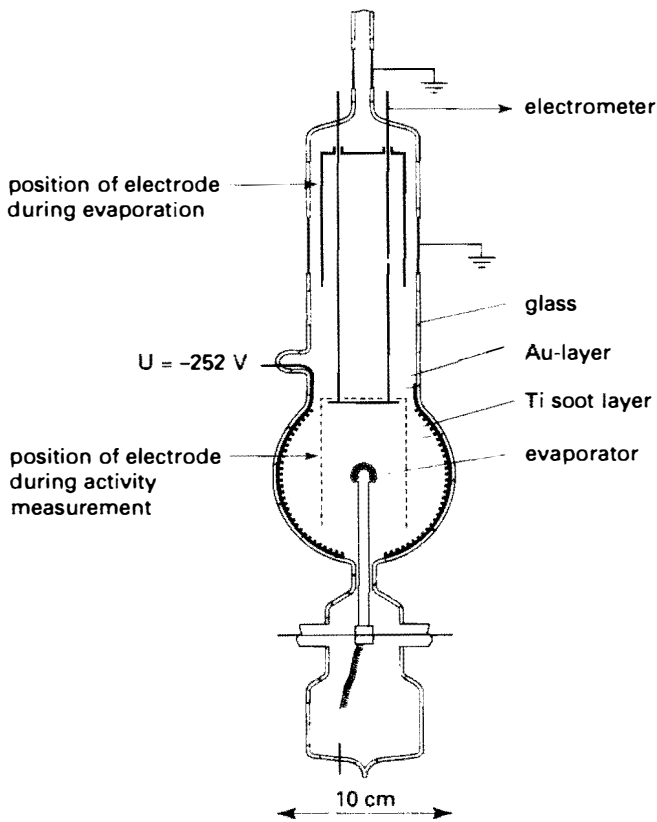


Fig. 1. Experimental arrangement for the (relative) measurement of the electron emission of a TiT_c layer.

In one part of the experiments, the beta electrons emitted from the TiT_c layer were measured via a cylindrical electrode by a vibrating reed electrometer (Fig. 1). The preamplifier containing the vibrating reed was connected to the TiT_c tube by a conductor held by sapphire supports. The negative voltage on the gold electrode where the titanium preparation was deposited was chosen in such a way that the $I = f(U)$ curve was nearly horizontal. In several other experiments, and especially in the heating experiments described in this paper, there was a thin nickel or steel window to enable measurement of the X radiation accompanying the beta decay of the tritium (internal and external bremsstrahlung and characteristic X rays) by a Geiger-Müller (GM) tube (Figs. 2 and 3; the specifications of the GM tube were as follows: a 19.8-mm-diam mica window, 2.5 to 3.5 mg/cm², and a 6.0- to 20-keV energy range). Of course, both experiments gave only a relative measure of the radioactivity, but we were especially interested in changes of the radioactive decay constant. Furthermore, we assumed in most experiments a "normal" emission at the beginning when the concentration of tritium in the TiT_x experiments was very small or when the temperature in the heating experiments was low.

The tube shown in Fig. 3 (placed in an oven⁷) had a

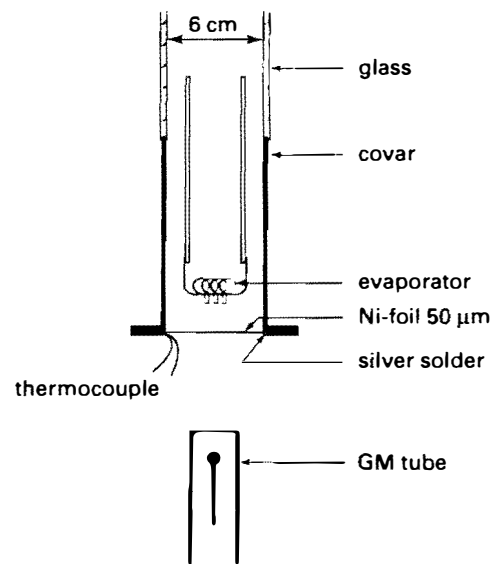


Fig. 2. Experimental arrangement for the (relative) measurement of the beta radioactivity of a TiT_c layer via the X radiation accompanying the beta decay. The tube has low heat capacity.

relatively large heat capacity because of the steel flanges by which a stainless steel foil was pressed vacuum tight between copper rings. In the tube of Fig. 2, a nickel foil was soldered to a covar pipe; this construction resulted in a relatively low heat capacity.

The generation of bremsstrahlung of tritium beta electrons was investigated by Budick et al.¹⁶ Furthermore, characteristic X radiation of titanium and of the walls of the tube was generated, but it was almost completely absorbed by the metal sheets between the preparation and the GM tube present during the experiments. If the geometry of the TiT_c preparation was unchanged, the radiation intensity measured by the GM tube was proportional to the total radioactivity of the tritium. The GM counting arrangement was checked before and after each experiment to ensure that the reading was proportional to the radiation intensity. For future experiments, it is recommended that modern detectors that enable determination of the detailed X-ray spectrum be used. This will give more information about the reliability of the measurements and facilitate interpretation.

An analysis of the methods used to measure the radioactivity is given in Ref. 7; this is omitted in the present paper.

In some experiments (the heating experiments), the evaporator consisted of a tungsten wire on which several pieces of titanium (each 7 mg) were fixed. The loss of titanium, mainly due to alloying with the tungsten wire, was ~15%. In other experiments (the TiT_x experiments), an improved evaporator was used, which Ref. 4 describes in detail. The evaporator consisted of a 0.3-mm-thick tungsten core wire on which a titanium and a

Hg-diffusion pump
 ↑
 liquid nitrogen trap

oven
 glass
 covar
 Ti soot layer
 evaporator
 stainless steel
 18 μm

metal
 asbestos
 1 2 3
 thermocouple

Fig. 3. Experimental arrangement for measuring the beta radioactivity as a function of temperature via the X radiation by a GM tube.

tungsten wire, both 0.2 mm thick, were tightly wound side by side. This evaporator design has the big advantage of allowing a check to be kept on the evaporation process; this is done by observing changes in the resistance of the evaporator. If the evaporation power is kept constant, one obtains an approximately constant evaporation rate, and $-d(I^2)/dt$ (I current through the evaporator) is proportional to this rate. Then a nearly uniform size of the titanium particles can be obtained if one uses only that part of the evaporation process where $d(I^2)/dt$ is constant. The loss of titanium due to alloying with the tungsten is higher with the improved evaporator than with the first described design because of the larger tungsten surface exposed to the molten titanium. It is ~25%.

In the heating experiments, the tritium was directly introduced into the titanium preparation from a small bottle that we obtained from the supplier. Table I gives the analysis of a typical batch of tritium.

In the TiT_c experiments, the tritium was first absorbed in a pressure regulator⁴ and then led into the tritium distribution system consisting of calibrated volumes. This procedure ensured that only hydrogen isotopes were added to the titanium preparation.

TABLE I

Typical Batch of Tritium*

Mass	Percent
2	0.01
3 (helium)	0.09
3 (hydrogen-deuterium)	Nondetectable
4 (helium)	Nondetectable
4 (hydrogen-tritium)	0.66
4 (D_2)	Nondetectable
5 (D-T)	0.44
6 (tritium)	98.74

*There were small quantities of additional atmospheric impurities in the shipment.

III. HEATING EXPERIMENTS

In one technical application, tritium was used as a priming agent for gas discharge tubes. To this end, tritium was absorbed in a finely divided titanium preparation, as described earlier, and then a suspension was made by ultrasonic treatment in a suitable suspension medium, e.g., butylacetate with 1% nitrocellulose. For the application as a priming agent, a small part of the suspension was painted at a suitable place in the gas discharge tube. For this application, the temperature stability of the TiT_c preparation was important because the gas discharge tubes had to be baked out at temperatures of several hundred degrees centigrade. Therefore, investigations were undertaken to see at what temperature tritium would be released from a TiT_c preparation with a certain concentration c of the tritium.¹⁷

III.A. A Remarkable Heating Experiment of a $TiT_{0.0035}$ Preparation (Heating Experiment of the First Kind)

The heating experiment presented in Ref. 7 is described and evaluated in more detail in this paper. In a preliminary experiment, the evaporation was accomplished in a glass bulb with a volume of ~500 cm³ at an argon pressure of 2 cm of mercury. The evaporator consisted of a tungsten coil on which eight pieces of 7 mg of titanium, totaling 56 mg, were fixed. This resulted in a finely divided titanium preparation of ~48 mg, taking into account the loss of titanium caused by alloying with the tungsten wire. By adding 100 mCi of tritium, a $TiT_{0.0035}$ preparation was obtained. The inaccuracy of the tritium concentration, which is estimated at 10%, is of no importance in the context of this and further heating experiments. After pumping out the ³He residue originating from the beta decay of tritium, the tube was sealed off. Then the system was heated in an oven twice up to

480°C, and the gas pressure was measured as a function of temperature by an ionization gauge. Extensive pumping was prevented by switching on the ionization gauge only during the measurements so that its effect could be neglected. The most important results are illustrated in Fig. 4. With the first increase of temperature, the tritium pressure (graph B) showed no increase at temperatures below ~350°C, and then the pressure increased. With the second rise of temperature, the tritium pressure (graph C) increased very much earlier at ~250°C. Obviously, at the first rise of temperature, tritium atoms, which were released from their bonds to the titanium lattice, could not leave the titanium particles, probably because of surface contamination (see, e.g., Peisl in Ref. 18, Vol. 1, p. 63). This contamination may especially have been caused during the introduction of the tritium, and it would have been dissolved in the metal during the heating up to 480°C at the first temperature cycle.

In a most important heating experiment, a $\text{TiT}_{0.0035}$ preparation was made by the procedure described earlier in the arrangement shown in Fig. 3 (Fig. 1 of Ref. 7). The mean thickness of the titanium layer was calculated as 0.54 mg/cm^2 . This is nearly the range of 18.6-keV electrons (the maximum energy of tritium beta particles).¹⁹ Then the system was heated in an oven, and the radioactivity was measured via the X radiation by a GM tube. It was completely impossible to distinguish between chemisorption at the surface and bulk absorption of the small titanium particles, as argued in Ref. 11, because ~80 titanium particles were piled up in the layer.²⁰ Because of the high heat capacity of the system, the rise of

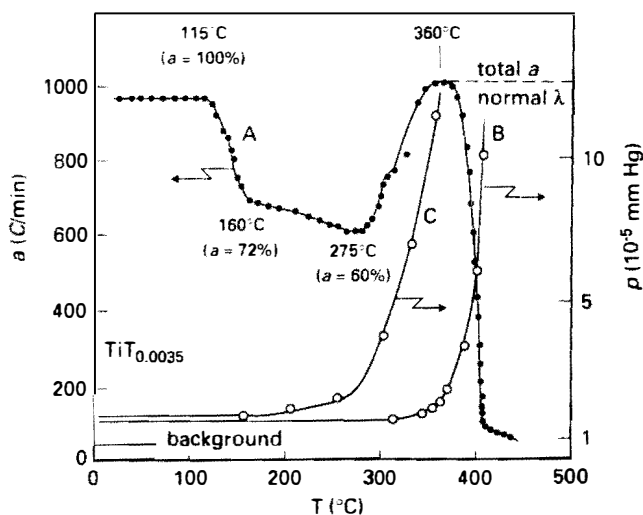


Fig. 4. As a function of temperature, $\text{TiT}_{0.0035}$ preparation, where graph A is the count rate, pumped system; graph B is the tritium pressure at the first rise of temperature, closed system; and graph C is the tritium pressure at the second rise of temperature, closed system.

temperature was accomplished slowly and took several (~10) hours. The temperature was measured by three thermocouples at different places of the arrangement, as shown in Fig. 3. The tritium that was released, if any, was pumped out continuously. The time constant of the decrease of tritium pressure was determined for such a vacuum system to be a few seconds (7 s for a similar system).

In Fig. 4, graph A gives the count rate as a function of temperature. It is very strange that the count rate decreased sharply between 115 and 160°C by 28% followed by a further slower decrease, reaching 60% of the initial value at 275°C and then rising to 105% of the initial value at ~360°C.

A constant temperature in this "valley region" corresponded to a constant count rate established at 150 and 300°C. With a further increase of the temperature above 360°C, the count rate decreased very fast because of the decomposition of the preparation.

The sharp decrease of the radioactivity especially between 115 and 160°C but also the further slower decrease between 160 and 275°C cannot be explained by decomposition of the $\text{TiT}_{0.0035}$ preparation. This is clearly shown by graph B, which represents the increase of the tritium pressure and hence the release of tritium at a first rise of temperature: In such a preparation, there is no measurable release of tritium below ~350°C. This statement is confirmed by many other experiments and also excludes the possibility of an alternative explanation that the course of $a = f(T)$ in Fig. 4 is simulated by the diffusion of tritium in the preparation from one place to another. But, the strongest argument against decrease of the radioactivity between 115 and 275°C being caused by a release of tritium from the $\text{TiT}_{0.0035}$ preparation is the fact that the radioactivity increases again between 275 and 360°C to approximately the initial value before decomposition of the preparation (the 5% higher count rate above the initial value is due to less absorption of the X radiation owing to heating of the air between the preparation and the GM tube, as observed in many experiments). This definitely shows that no tritium is lost during the first decrease of radioactivity.

Supported by the foregoing arguments, we conclude that something strange occurs in the $\text{TiT}_{0.0035}$ preparation during the decrease of the count rate especially between 115 and 160°C, during the further decrease up to 275°C, and during the renewed increase to approximately the initial value between 275 and 360°C. We argued earlier that during the whole temperature trajectory up to 360°C, no loss of tritium occurred. Therefore, we must conclude that the decrease of count rate was entirely due to a decrease of tritium radioactivity. Thus, we arrive at the following preliminary conclusion. In the temperature region between 115 and 275°C, a new compound of the tritium is formed in the $\text{TiT}_{0.0035}$ preparation with a lower radioactive decay constant, and upon a further increase of temperature and before the

decomposition of the preparation above 360°C, this lower emitting compound is destroyed.

A detailed discussion of Fig. 4 is especially interesting. The experiment where a $\text{TiT}_{0.035}$ preparation was heated and the pressure of tritium was measured shows that at the first rise of temperature, the release of tritium started seriously at $\sim 360^\circ\text{C}$ (graph B). This is precisely the temperature where according to graph A, the release of tritium began, demonstrated by the sharp decrease of the count rate. However, in a second temperature cycle, the release of tritium started seriously very much earlier, in fact, at $\sim 275^\circ\text{C}$ (graph C), where according to graph A, the re-increase of the radioactivity began. In the author's opinion, the rise of curve C is related to the release of the tritium atoms from their bonds to the titanium lattice; however, at the first rise of temperature, the liberated tritium could not leave the titanium particles, as shown by graph B. This release of the tritium atoms from their bonds to the titanium lattice coincided with the re-increase of the radioactivity between 275 and 360°C, as shown by graph A. Obviously, as stated earlier, the tritium atoms, liberated from their bonds to the titanium lattice, which exhibited normal radioactive decay, could not leave the small titanium particles at the first rise of temperature, as shown by graph B. This was probably caused by surface contamination that was removed during the heating to 480°C at the first temperature cycle. These observations suggest that the re-increase of the radioactivity between 275 and 360°C and, of course, also the decrease of the radioactivity between 115 and 275°C, and with it the destruction and formation of the hypothetical lower emitting compound, had something to do with the bonds of the tritium atoms to the titanium lattice. This remark may be important for a theoretical interpretation of the effect.

III.B. Evaluation of a Further Important Heating Experiment (Heating Experiment of the Second Kind)

In my recent letter⁷ a heating experiment is mentioned with a ten times higher concentration of the tritium and a faster increase of temperature, where the decrease and re-increase of the count rate did not occur. In the meantime, an interpretation of this experiment has been found that does show clearly the decrease and re-increase of radioactivity for this $\text{TiT}_{0.035}$ preparation during heating.

Figure 5 shows schematically the experimental arrangement. Two tubes with low heat capacity, according to Fig. 2, were used. In both tubes, a preparation of 48 mg of finely divided titanium was made by evaporation of the metal in argon of 2 cm of mercury. In tube S, 1 Ci of tritium was absorbed in the titanium. After removing the ^3He , which was left from the beta decay of the tritium, valve 2 was closed, and valves 1 and 3 were

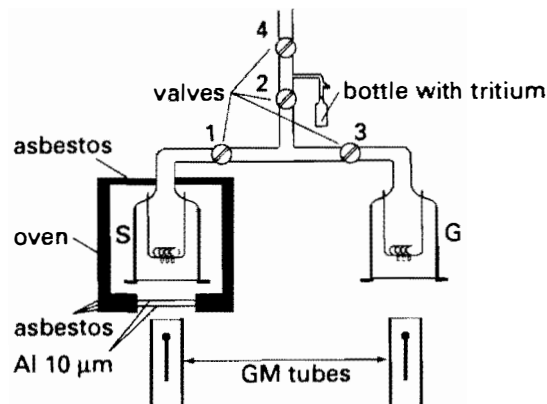


Fig. 5. Experimental arrangement with two tubes (Fig. 2). Tube S contains a $\text{TiT}_{0.035}$ preparation at the beginning of the experiment and is heated in an oven. Tube G contains a finely divided titanium preparation that absorbs the tritium released from preparation S.

opened. Then tube S was placed in an oven (see also Fig. 3) and was heated slowly but about five times faster than in the preceding experiment. The tritium, which was released from the preparation of tube S, was absorbed by the titanium preparation of tube G, which was left at room temperature. The radioactivity in both tubes was determined relatively via the X radiation by two GM tubes.

Graph S on Fig. 6a gives the count rate of tube S (solid), and graph g gives the count rate of tube G (gas). The count rate S is constant up to $\sim 210^\circ\text{C}$ and then decreases steeply. At the same temperature, the increase of the count rate g begins. This may lead to a preliminary conclusion that the tritium is desorbed from preparation S and that this tritium is absorbed by preparation G.

To proceed to a more complete evaluation of this experiment, we normalize the count rate of tube G to the same sensitivity as count rate S. Figure 6b gives the normalized count rate G together with the count rate S. The count rate G thus gives the radioactivity of the tritium gas released from tube S, and $S + G$ is a measure of the total radioactivity. This count rate $S + G$ is plotted in Fig. 6b. As one can see, a similar decrease and re-increase of the count rate takes place as in Fig. 4. The decrease starts at a higher temperature than in the experiment described in Sec. III.A, at $\sim 210^\circ\text{C}$, right at the beginning of the pure alpha phase.²¹ If we attribute the decrease of the radioactivity to only the solid preparation in tube S, we obtain graph S'.

Most interesting is the evaluation of the decrease of radioactivity S above 210°C. At 230°C, S has decreased by 10.6% ($[\Delta CR_S]_{230^\circ\text{C}}$); the increase of G, the tritium-gas released from S, is only 0.85% ($[\Delta CR_G]_{230^\circ\text{C}}$), thus, $(\Delta CR_S / \Delta CR_G)_{230^\circ\text{C}} = 12.5$. At 242°C, the corresponding values are $[\Delta CR_S]_{242^\circ\text{C}} = 20\%$, $[\Delta CR_G]_{242^\circ\text{C}} = 1.9\%$, and $(\Delta CR_S / \Delta CR_G)_{242^\circ\text{C}} = 10.5$. Thus, the strong decrease of the radioactivity S above 210°C cannot be caused

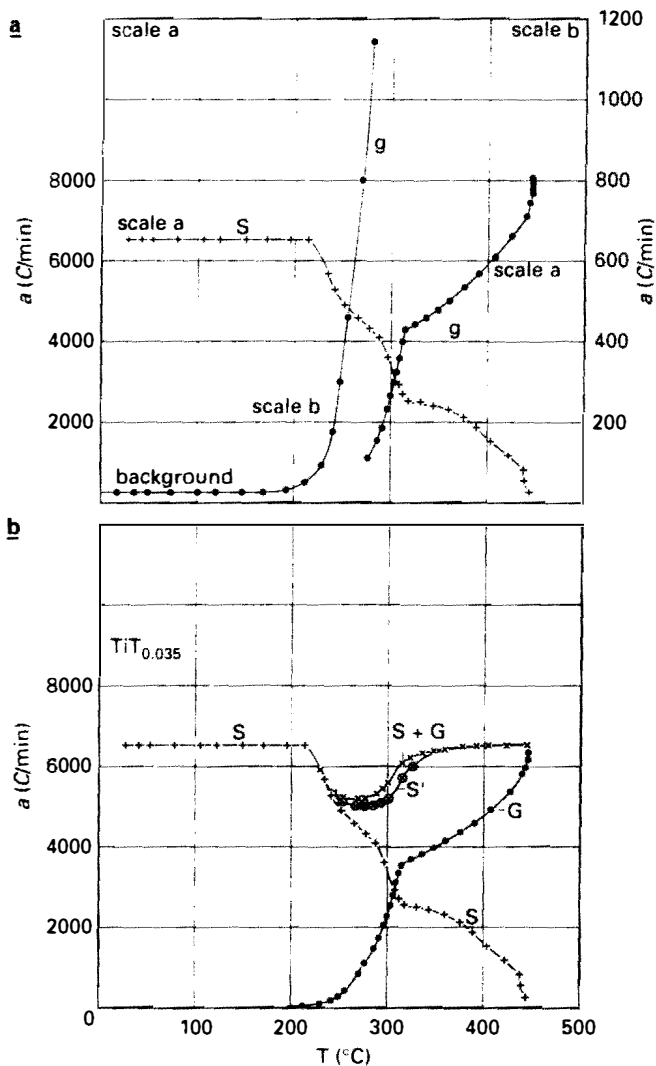


Fig. 6. (a) Count rate as a function of temperature, where S is for tube S and g is for tube G. (b) Radioactivity as a function of temperature, where S is for tube S, G is for tube G, S + G is the total radioactivity, and S' is the remaining radioactivity in the preparation of tube S.

by the release of tritium from the preparation. This is a further strong argument for the decrease of tritium radioactivity due to heating of our preparation above 210°C. Also very important is the fact that the re-increase of the total radioactivity S + G begins at the same temperature as in the experiment of Fig. 4 and ends also at ~360°C.

It is particularly interesting that this experiment was carried out under conditions quite different from those in the experiment of Fig. 4, with a 10 times higher and variable (decreasing) concentration. At a minimum radioactivity of 275°C (graph S') the concentration c is ~8.5 times higher than in the experiment of Fig. 4, and it decreases strongly during the re-increase of the radioactivity.

A possible error in the foregoing interpretation could be that the tritium released from preparation S is too

slowly absorbed by preparation G, so that a certain amount of tritium remains in the tubes as a gas. However, this is contradicted by the statement that the finely divided titanium preparation that is deposited in tube G absorbs the tritium fast at room temperature (Sec. II). Furthermore, a very strong contradiction to this objection is the measurement at 313°C where the temperature of tube S is kept constant during 15 min. If a measurable amount of tritium were left as a gas, this would show up as a measurable increase in the count rate G during the stay at 313°C. Such behavior was not observed. To be absolutely sure that no tritium is left as a gas in the tube, one should place a pressure gauge in the connecting tube between the two preparations.

III.C. Oxidized Preparations

Two other heating experiments using the experimental setup of Fig. 3 were carried out. After preparation of the titanium-tritium compounds, they were exposed to ambient air, a $TiT_{0.0035}$ preparation for 2 h, and a $TiT_{0.065}$ preparation for 3 days, both before heating. For both preparations, the count rate determined by a GM tube was decreased by this procedure by ~10%. This decrease of count rate must be due to a change in the efficiency of the external bremsstrahlung due to absorption of this gas. This result is important for estimating the influence of oxygen on the efficiency of external bremsstrahlung generation: The large changes in count rate given in graph A of Fig. 4 and in graph S of Fig. 6 can never be caused by the small oxygen contamination of the preparations. Furthermore, the observations have a bearing on the interpretation of the experiment described in Sec. IV, where the addition of tritium caused a decrease of the total beta emission of the preparation. With both (partially) oxidized preparations, a distinct decrease and re-increase of the count rate during heating was observed, as shown in Fig. 7. However, the decrease and re-increase of the radioactivity was not so clear, and the diminution was not so strong as with the preparations of Figs. 4 and 6b. Furthermore, it seems that for these oxidized preparations, the re-increase of the radioactivity began at a somewhat lower temperature than for the "pure" preparations. It is most interesting that with the $TiT_{0.065}O_2$ preparation where the tritium concentration was nearly two times higher than with the preparation of Fig. 6, no desorption of tritium occurred before the original radioactivity was recovered, obviously because of the strong oxide layer on the surface of the titanium particles. But, it seems from these experiments that oxidation of the preparation does not stimulate the decrease of radioactivity.

III.D. Conclusions from the Heating Experiments and Recommendations

With a more complete evaluation of our heating experiments than in Ref. 7, I have obtained a high degree

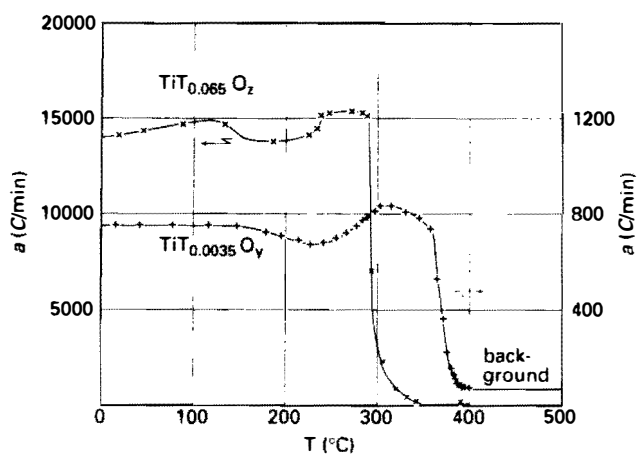


Fig. 7. Count rate as a function of temperature for oxidized preparations.

of evidence for the effect of the decrease of the radioactivity of tritium during heating of our TiT_c preparations. Two experiments carried out under quite different conditions showed that the maximum decrease of λ occurred at the same temperature, at 275°C, and with further increasing temperature, the lower emitting compound of tritium was destroyed (Figs. 4 and 6b). It appears that two processes are in competition as a function of increasing temperature: the formation of the lower emitting compound (Fig. 4, graph A, 115°C < T < 275°C) and the destruction of this compound by liberation of the tritium atoms (nuclei) from their bonds to the titanium lattice (Fig. 4, graphs C and A for $T > 160^\circ\text{C}$). Evidently, at 275°C, equilibrium of these two processes was attained, and with further increasing temperature, the second process predominated. It is particularly interesting that the relative contribution of these two processes appears to be independent of the concentration.

Two other experiments, where the TiT_c preparations ($c = 0.0035$ and $c = 0.065$) were strongly oxidized, also distinctly showed the decrease and re-increase of the radioactivity during heating (Fig. 7).

A most straightforward interpretation of our heating experiments was possible applying a preparation where the tritium was not released up to the temperature where the initial radioactivity was restored, indicated as a heating experiment of the first kind (Sec. III.A, Fig. 4: low concentration, barrier at the surface of the titanium particles that prevents desorption of the tritium). It may be a fortuitous and fortunate circumstance that at the time of the heating experiments, the ultrahigh vacuum (UHV) technique was not available. Without the surface layer preventing the release of tritium with the experiment of Fig. 4, only a decrease of count rate above 115°C and no re-increase would have been observed. In this case, the conclusion would have been that the tritium is desorbed when the temperature is increased above 115°C. The

change in radioactivity during heating would not have been noticed. Therefore, with experiments of this kind, it is most important to apply a surface barrier, e.g., an oxide layer, to prevent early desorption of tritium when working with the UHV technique. The thickness of such a layer can be precisely determined by the amount of added oxygen. Another means to prevent early desorption of the hydrogen isotope from the titanium would be embedding the TiT_c preparation in a nonoccluder with a low diffusion coefficient for hydrogen, e.g., gold. But, in any case, it is recommended that one apply a second tube G (Fig. 5) to determine a possible release of tritium from preparation S.

It is particularly interesting to compare the experiment of Fig. 4 with that of Fig. 6b, where tritium was released from the preparation during heating, indicated as a heating experiment of the second kind. According to our preliminary interpretation, graph C in Fig. 4 shows the release of the tritium atoms (nuclei) from their bonds to the titanium lattice, but the liberated tritium atoms could not leave the small titanium particles below $\sim 360^\circ\text{C}$ (graph B). They had normal λ , and the re-increase of the radioactivity above 275°C was due to these liberated tritium atoms remaining in the preparation. In Fig. 6b, graph G shows again the release of the tritium atoms from their bonds to the titanium lattice, but in this experiment, the tritium left the small titanium particles as a gas because of the ten times higher concentration. This gaseous tritium, too, has normal λ . If we add in Fig. 6b both radioactivities, the decreased radioactivity in the solid and the normal radioactivity in the gas, we get graphs S + G or S', respectively. In the experiment of Fig. 4, the addition of these two radioactivities is accomplished automatically in graph A because the liberated tritium atoms with normal radioactivity remained in the titanium particles. From this evaluation, we understand the analogous course of the radioactivities as a function of temperature in both experiments: first, a decrease of the radioactivities at a certain temperature, and then above 275°C, a re-increase to the normal radioactivity. In the experiment of Fig. 4, we again have in the temperature region above 360°C, a return to the normal radioactivity as in Fig. 6b because the gas released from the preparation had normal radioactivity (we could have measured it with a second tube G).

It is virtually impossible that the course of $a = f(T)$ is determined by a measurement artifact in the counting arrangements in the experiments of Figs. 3 and 4 and Figs. 5 and 6. If this were actually to be the case, then one would have to assume that the efficiency of the counting arrangement changes in such a way that the course of $a = f(T)$ results as observed in Fig. 4. In the experiment of Figs. 5 and 6, the efficiency of each of the two counting arrangements would then have to change in such a way that the observed course of S + G, which is equivalent to the course of $a = f(T)$ in Fig. 4, would be produced.

The decrease of the radioactivity begins in the experiment of Fig. 6 at a higher temperature ($\sim 210^\circ\text{C}$) than in the experiment of Fig. 4 (115°C). In Fig. 6, this indicates the beginning of the pure alpha phase.²¹ This observation suggests that monocrystallinity may be a necessary condition for the decrease of the radioactivity because monocrystallinity is destroyed when tritium is added at room temperature (by extremely small hydride particles) and is regained when the preparation enters the pure alpha phase. In the experiment of Fig. 4, the decrease of the radioactivity also occurred in the pure alpha phase.

Of particular interest will be experiments in which the temperature is decreased starting from the value where the radioactivity is recovered after the decrease as in Fig. 4 from 360°C . In our experiments, this was not done because the only question was the temperature stability of the preparations.

The release of tritium atoms (nuclei) from their bonds to the titanium lattice can be prevented by maintaining an equilibrium pressure of tritium above the preparation (Ref. 22, pp. 336–345), indicated as a heating experiment of the third kind. With this mode of operation, we may expect a further decrease of the radioactivity than was obtained in the experiments of Figs. 4 and 6. It may be somewhat difficult to measure directly the $a = f(T)_c$ graphs because one has to adjust continuously the equilibrium pressure during heating to maintain a constant concentration c . With a straightforward mode of operation, the tritium concentration has to be slowly increased at fixed temperatures T , and from the $a = f(C)_T$ graphs, the most interesting $a = f(T)_c$ graphs can be determined.

In the proposed isothermal experiments maintaining an equilibrium pressure, the radioactivity is advantageously determined by measuring the X-ray spectrum with modern detectors. The tritium pressure above the TiT_c preparation and the contribution of this tritium to the X-ray intensity has to be carefully measured.

Until now, in all heating experiments, the formation of the lower emitting compound occurred in the alpha phase of TiT_c (Ref. 21). It is extremely interesting to perform heating experiments also with a high tritium concentration, with hydride-phase TiT_c . Such experiments are advantageously accomplished applying an equilibrium pressure as described earlier.

For a theoretical interpretation of the effect, it may be important that the tritium atoms (nuclei) be bound as harmonic oscillators in the titanium lattice.^{23,24}

From the course of $a = f(T)$ (Fig. 4), we can determine the concentration of tritium with normal λ and that of the "compound" with decreased λ . These concentrations as a function of temperature follow the well-known laws of chemical equilibrium. A detailed discussion of the related thermodynamical functions that also presupposes careful determination of disturbing effects [e.g., release of the tritium atoms (nuclei) from their bonds to the titanium lattice] may lead to a deeper understanding of the decrease of tritium radioactivity.

IV. TiT_x EXPERIMENTS

Through our heating experiments, we arrived at the preliminary conclusion that under certain conditions—in our case, by heating TiT_c preparations (with $c = 0.0035$, 0.035 , and 0.065)—a new compound of the tritium in the small titanium particles with lower λ is formed. However, there is no physical effect known that accomplishes the observed decrease of radioactivity. Therefore, further experiments must be performed to search for an explanation of the observed effect.

It was speculated that the decrease of the tritium radioactivity in the small titanium particles may have something to do with the different phases of the TiT_c system, a suspicion that so far has not been confirmed. Therefore, experiments were undertaken to measure the radioactivity a as a function of the concentration c in such systems. The concentration c was taken as independent variable x , and the related experiments are therefore indicated as TiT_x experiments. It would be very interesting to do such experiments at different temperatures (see Sec. III.D), but until now, only TiT_x experiments at room temperature have been done. All TiT_x experiments are performed using the tube shown in Fig. 1.

In all TiT_x experiments, a substantial deviation from the expected proportionality between radioactivity and concentration x was observed. The $\Delta a/\Delta x$ is not constant with increasing concentration x but shows characteristic variations.

In the most important TiT_x experiment,⁷ 4.92 mg of titanium was evaporated in argon at a pressure of 1 cm mercury. After removal of the evaporator, the titanium left on it was determined quantitatively as 1.33 mg. Thus, the titanium soot layer contained 3.6 mg of titanium. The mean thickness of the titanium layer was calculated as 1.15×10^{-2} mg/cm² (25 nm). According to the energy-range relation of electrons,¹⁹ there could be no essential absorption effect of the beta electrons of tritium. The particle size was ~ 16 nm. After preparation of the titanium soot layer, the system was sealed off.

Small glass bottles with volumes of 2 and 4 cm³ were filled with tritium at a gas pressure of 7.5×10^{-3} mm mercury via a hydrogen pressure regulator.⁴ These little bottles were sealed to the vacuum system, and the tritium was introduced by opening a breaking seal. By addition of one bottle of 2 cm³, the increase of the concentration was $\Delta x = 2.2 \times 10^{-5}$. To exclude a possible influence of the sequence of the preparation of the bottles, we applied the bottles at random. The beta electrons emitted from the TiT_x layer were measured via a cylindrical electrode inside the vessel by a vibrating reed electrometer. This electrometer allowed the total current to be electronically compensated after each measurement to zero, so that the following $\Delta i \propto \Delta a$ could be determined accurately. By recording the tritium pressure using a special tube that measures the beta emission of the gaseous tritium, we ascertained that the tritium had been absorbed

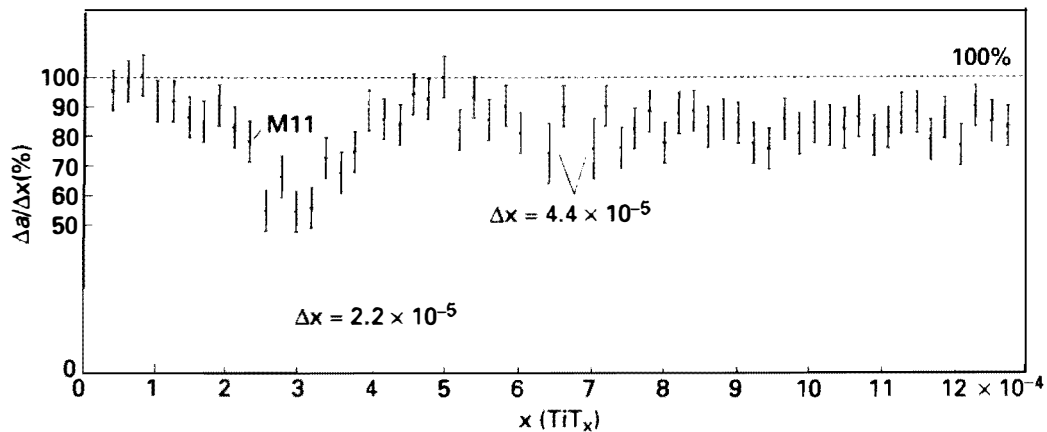


Fig. 8. The $\Delta a/\Delta x$ as a function of concentration x with a sealed-off system and with the evaporator removed.

completely after each addition. A time constant of ~ 10 s for the uptake of tritium ensured that the loading occurred uniformly.

Figure 8 gives the results of the experiment. The first value of $\Delta a/\Delta x$ was taken as 100%. The experiment took several weeks. The $\Delta a/\Delta x$ decreased first, reaching a minimum of $\sim 55\%$ of the initial value at $x \approx 3 \times 10^{-4}$. After reaching the minimum, $\Delta a/\Delta x$ increased again and reached the initial value at $x \approx 4.5 \times 10^{-4}$. Then $\Delta a/\Delta x$ decreases again and reached $\sim 85\%$ of the initial value at $x \approx 1.3 \times 10^{-3}$. This is the same value as was obtained in two other independent experiments.

From the course of $\Delta a/\Delta x = f(x)$ reaching a minimum and increasing again to the initial value, a nuclear pair hypothesis was derived as follows. Two tritium nuclei (identical nuclei with half integer spin) under certain conditions (in our case, by embedding in small monocrystalline particles of titanium) arrange themselves in a pair with nuclear spin zero. Such a nuclear pair acts for the decay to a certain extent as the parent nucleus, so that the radioactive decay changes to a certain extent into a higher forbidden one.

The author would like to emphasize that the nuclear pair hypothesis is a *hypothesis*. This implies that it is a first attempt to explain the strange effect of the decrease of tritium radioactivity. It is to be proved or disproved by further experiments, and if this hypothesis cannot be confirmed, we must search for another explanation of the effect. Furthermore, nothing has yet been said about the nature of the hypothetical nuclear pairs.^a

Pairing of atomic nuclei could be demonstrated by nuclear spin resonance. Also, scattering experiments with polarized neutrons might be interesting.

According to the theory of beta decay, the transformation of the decay to a higher forbidden one has remarkable consequences: The maximum of the energy spectrum and the mean energy must be shifted to higher energies. To be sure about this interesting fundamental effect, one must perform an ionization chamber, or better still, a proportional counter-type experiment.

The foregoing derivation of the nuclear pair hypothesis presupposed that the tritium nuclei are uniformly incorporated into the domains where pair formation takes place. If we assume random incorporation and that the nuclear pair hypothesis is true, we reach by elementary mathematics the following expression:

$$\frac{\Delta a}{\Delta x} \propto \frac{\Delta a}{\Delta n} = \lambda_2 + (\lambda_1 - \lambda_2) \exp\left(-2 \frac{n}{N}\right)$$

where

a = radioactivity

λ_1 = decay constant of unpaired nuclei

λ_2 = decay constant of paired nuclei

n = number of radioactive nuclei in the preparation

N = number of domains in the preparation where pair formation takes place.

With random incorporation, $\Delta a/\Delta x$ decreases exponentially with increasing concentration x to the lower value of the decay constant. This was indicated in our experiment where $\Delta a/\Delta x$ was decreased at $x = 13 \times 10^{-4}$ to $\sim 85\%$ of the initial value (not shown in Fig. 3 of Ref. 7). Random incorporation instead of uniform incorporation was probably caused by increasing impurities at the surface of the titanium particles during the course of the experiment so that thermodynamical equilibrium with an equal concentration of tritium in the titanium particles could not be attained.

There have been several other TiT_x experiments with interesting results. However, in these TiT_x experiments, which

^aThere is a well-known example for pair formation of elementary particles at a long distance: the Cooper pairs in superconductivity. A new entity is formed: The mass is experimentally determined as $2m_e$, the electrical charge as $2e$, and the spin as zero.

