region are in general considerably higher than any noncollective theory can conveniently explain, and in order to account for the moments of the scandium and the other titanium isotopes within the shell model it is necessary to assign to both neutrons and protons an effective charge of about $+2e$. With this assumption, the moments of Sc^{43}, Sc^{45}, Sc^{47}, Ti^{47}, and Ti^{49}, all of which are about 0.2–0.3 b in magnitude, can be reasonably well fit, but in a somewhat *ad hoc* fashion.[13] If, however, only protons are considered (as in Lawson's work), the moments are seriously underestimated.

The measured value for Q for Ti^{45} is very small, consistent, in fact, with zero. This is what one would expect by considering protons alone. Using Lawson's wave functions, we have calculated that the predicted values are -0.016 b for positive deformation, and -0.009 b for negative deformation.[14] This does not mean that the effective charge assumption is invalid, however, because with the wave functions of Ref. 10 the contributions from neutrons and protons nearly cancel, and the predicted moment with effective charges is $Q=-0.076$ b. This result seems to argue that the effective charge concept has utility in scaling the predicted moment so that it agrees with experiment. A perturbing of the core is surely responsible for the additional charge, but apparently the dominant effects are describable in shell-model terms. It is hard to imagine a collective theory which would lead to such a small Q, unless Ti^{45} is at the point where the static deformation changes sign. It may be that this is the case, because Ti^{47} and Ti^{49} both have positive Q, whereas the scandium isotopes have negative Q (including, however, Sc^{47}). But if it is, this should be the only such crossing point, whereas the shell theory predicts an equal Q for the cross-conjugate nucleus, in this case Mn^{51}. A measurement of the moment of Mn^{51} would help to resolve the question.

---

[13] L. Zamick and J. D. McCullen, Bull. Am. Phys. Soc. 10, 485 (1965).

[14] We wish to thank Dr. Lawson for making his wave functions available to us.

PHYSICAL REVIEW VOLUME 148, NUMBER 3 19 AUGUST 1966

Effect of Chemical State on the Decay Constant of U^{235m}

HIROMASA MAZAKI AND SAKAE SHIMIZU
Institute for Chemical Research, Kyoto University, Kyoto, Japan

(Received 9 February 1966)

Experimental investigation of the influence of chemical forms on the decay constant of U^{235m} has been performed. The U^{235m} atoms from a very thin Pu^{239} source were collected by the recoil method on platinum, carbon, and silicon plates in a pure argon atmosphere. Applying the differential method with two identical, specially designed 12-stage secondary electron multipliers, emission rates of the internal-conversion electrons of very weak energy from the isomer in different chemical states have been compared. Stability and sensitivity of the whole measuring system have been checked using C^{14} and metallic U^{235m} sources. We used metallic uranium (U) and uranium atoms slightly diffused into carbon (UC) or silicon (USi) base for the different chemical states. The results are: $\lambda(\mathrm{U})-\lambda(\mathrm{UC})=(3.18\pm0.50)\times10^{-3}\lambda(\mathrm{U})$, $\lambda(\mathrm{U})-\lambda(\mathrm{USi})=(2.21\pm0.36)\times10^{-3}\lambda(\mathrm{U})$, and $\lambda(\mathrm{USi})-\lambda(\mathrm{UC})=(0.97\pm0.43)\times10^{-3}\lambda(\mathrm{USi})$. Errors are standard deviations. We also determined the half-life of U^{235m} to be $T_{1/2}=26.05\pm0.05$ min by using a low-background 2π gas-flow counter. Furthermore, diffusion of the isomer into the base materials, carbon and silicon, was investigated in some detail.

I. INTRODUCTION

IN 1947, Segrè[1] and Daudel[2] first suggested that in the cases of an orbital electron capture decay and a partly converted isomeric transition of a nucleus, the decay constant might be changed by different chemical states. In the following years, experimental attempts to find chemical or other effect on the decay constants of Be^{7}, Tc^{99m}, and Te^{125m} have been made by some workers.[3–13] They found that the change of electronic environments of these elements by chemical means or otherwise apparently gives rise to an influence of the

---

[1] E. Segrè, Phys. Rev. 71, 274 (1947).

[2] R. Daudel, Rev. Sci. 85, 162 (1947).

[3] R. Bouchez, R. Daudel, P. Daudel, and R. Muxart, J. Phys. Radium 8, 336 (1947).

[4] R. Bouchez, P. Daudel, R. Daudel, and R. Muxart, Compt. Rend. 227, 525 (1948); J. Phys. Radium 10, 201 (1949); P. Benoist, R. Bouchez, P. Daudel, R. Daudel, and A. Rogozinski, Phys. Rev. 76, 1000 (1949).

[5] R. Bouchez, J. Tobailem, J. Robert, R. Muxart, R. Mellet, P. Daudel, and R. Daudel, J. Phys. Radium 17, 363 (1956).

[6] E. Segrè and C. E. Wiegand, Phys. Rev. 75, 39 (1949); Erratum, Phys. Rev. 81, 284 (1951).

[7] R. F. Leininger, E. Segrè, and C. Wiegand, Phys. Rev. 76, 897 (1949); *ibid.* 81, 280(E) (1951).

[8] K. T. Bainbridge, M. Goldhaber, and E. Wilson, Phys. Rev. 84, 1260 (1951).

[9] K. T. Bainbridge, Chem. Eng. News 30, 654 (1952).

[10] K. T. Bainbridge, M. Goldhaber, and E. Wilson, Phys. Rev. 90, 430 (1953).

[11] J. J. Kraushaar, E. D. Wilson, and K. T. Bainbridge, Phys. Rev. 90, 610 (1953).

[12] D. H. Byers and R. Stump, Phys. Rev. 112, 77 (1958).

[13] A. C. Malliaris, Ph.D. thesis, Harvard University, 1961 (unpublished).

order of 10^{-3}–10^{-4} on their decay rates. It is to be noted that Cooper *et al.*[14] have recently investigated the phenomenon with Nb^{90m} in metallic Nb and $KNbF_2$ and found a very large change in its disintegration rate, about 3.6%.

It seemed worthwhile to provide additional information on this effect for some other nuclei. The nuclear isomer U^{235m}, the first excited level of U^{235} undergoing an electric octopole transition to the ground state, seemed to be one of the most attractive nuclei for the detection of the chemical effect on its decay rate. The reason for this is that the transition energy of the level is so small, <70 eV reported by Michel *et al.*[15] or <23 eV by Freedman *et al.*,[16] that the internal conversion coefficient is about 10^{20}. All transitions from the first excited level of U^{235} to its ground state are converted without gamma rays. Besides, because of such a low transition energy, the whole contribution to the internal conversion comes from P- or Q-shell electrons, probably mainly the $6p$ and $6d$ levels. Advantageously, these electrons are the valence electrons of uranium, which may be affected by the chemical state of the atom involved. However, for the observation of any chemical effect with this isomer, there are three experimental difficulties: first, it is difficult to prepare a strong source because the most convenient way to get U^{235m} in a laboratory is by the so-called recoil method from a very thin Pu^{239} source; second, because of its rather short half-life ($T_{1/2}=26.05$ min), chemical treatment of such a microscopic amount of U^{235m} is troublesome; and third, the isomeric transition of U^{235m} is not accompanied by any gamma ray which can be conveniently measured by an ionization chamber. To overcome these difficulties, it is necessary to devise a method to detect and multiply the internal-conversion electrons of only a few tens of electron volts. It is also required that the electronic environment of the isomer be changed without treating it by an ordinary chemical method.

In the present paper, we wish to report details of our experimental work with U^{235m} as well as further results obtained since our preliminary short note.[17] The differences in λ of three kinds of U^{235m} samples (metallic U, UC, and USi) have been measured by the use of a pair of identical secondary-electron multipliers. In order to alter the electronic surroundings of the isomer, U^{235m} from a very thin Pu^{239} source is collected by the recoil method on thin carbon films and on silicon single crystals, and the samples are then heated in a pure argon atmosphere to ensure diffusion of the isomer into the base materials.

II. PRINCIPLE OF THE MEASUREMENT

The experimental method used in the present work is based on the so-called *differential method* first introduced by Rutherford.[18] The attractive features of using this method are that one can measure two sources at the same time with minimized systematic errors and it is not necessary to determine the exact amount of the background. Because of the absence of gamma rays from U^{235m}, the only way to observe the transition is the measurement of internal-conversion electrons. Therefore, a pair of identical secondary-electron multipliers M_1 and M_2 are used, and two U^{235m} sources 1 and 2, in different chemical states but with approximately the same intensities, are set on the first dynodes of M_1 and M_2, respectively. The output currents of the multipliers due to the conversion electrons of the sources 1 and 2 are mostly cancelled out and nearly balanced at time $t=0$ through a differential amplifier. The drift of the initially balanced output is recorded in volts by a digital voltmeter with a recorder, as a function of time. The procedure for analysis of the experimental data is similar to that pursued by Segrè *et al.*[6] and Bainbridge *el al.*[10]

In the first measurement, source 1 is inserted in the multiplier M_1, and source 2 in M_2. Thus the output from the differential amplifier at time t can be given as

$$E_{\mathrm{I}}(t)=G[G_1S_{\mathrm{I}-1}\exp(-\lambda t)-G_2S_{\mathrm{I}-2}\exp(-\lambda t-\Delta\lambda t)], \quad (1)$$

where G, G_1, and G_2 are the amplification factors of the differential amplifier and the multipliers M_1 and M_2, respectively. $S_{\mathrm{I}-1}$ and $S_{\mathrm{I}-2}$ denote the initial intensities of sources 1 (metallic U) and 2 (UC or USi) which are assumed to have the decay constants λ and $\lambda+\Delta\lambda$, respectively. A suffix I means the first measurement. When the sources are interchanged, the output is given by

$$E_{\mathrm{II}}(t)=G[G_1S_{\mathrm{II}-2}\exp(-\lambda t-\Delta\lambda t)-G_2S_{\mathrm{II}-1}\exp(-\lambda t)], \quad (2)$$

where $S_{\mathrm{II}-1}$ and $S_{\mathrm{II}-2}$ give the initial intensities of the sources 1 and 2 in the second measurement denoted by a suffix II. Thus the average value of the output $E(t)$ multiplied by $\exp(\lambda t)$ can be expressed as follows:

$$\begin{aligned} E(t)\exp(\lambda t) &= \tfrac{1}{2}[E_{\mathrm{I}}(t)-E_{\mathrm{II}}(t)]\exp(\lambda t) \\ &= \tfrac{1}{2}G[G_1(S_{\mathrm{I}-1}-S_{\mathrm{II}-2}) \\ &\quad -G_2(S_{\mathrm{I}-2}-S_{\mathrm{II}-1}) \\ &\quad +(G_2S_{\mathrm{I}-2}+G_1S_{\mathrm{II}-2})\Delta\lambda t]. \end{aligned} \quad (3)$$

The first and second measurements supply a set of data and this entire procedure is repeated. Since Eq. (3) has a linear form $y=a+bt$, the slope of a least-squares line of the observed values $E(t)\exp(\lambda t)$ is equal to b or $\frac{1}{2}G(G_2S_{\mathrm{I}-2}+G_1S_{\mathrm{II}-2})\Delta\lambda$. Therefore, in the calculation of $\Delta\lambda/\lambda$, the numerical values of G and $(G_2S_{\mathrm{I}-2}+G_1S_{\mathrm{II}-2})$

---

[14] J. A. Cooper, J. M. Hollander, and J. O. Rasmussen, Phys. Rev. Letters **15**, 680 (1965).

[15] M. C. Michel, F. Asaro, and I. Perlman, Bull. Am. Phys. Soc. **2**, 394 (1957).

[16] M. S. Freedman, F. T. Porter, F. Wagner, Jr., and P. P. Day, Phys. Rev. **108**, 836 (1957).

[17] S. Shimizu and H. Mazaki, Phys. Letters **17**, 275 (1965).

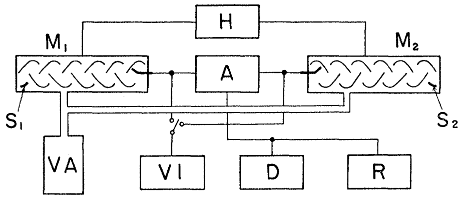
[18] E. Rutherford, Sitzber. Akad. Wiss. Wien. Math. naturw. Kl. **120**, 303 (1911).

must be known. The gain of the differential amplifier G can be determined experimentally as described in the following section. The value G_2S_{I-2} or G_1S_{II-2}, initial output current from M_2 or M_1, respectively, containing source 2 with $\lambda+\Delta\lambda$, can be obtained directly using a vibrating-reed electrometer (see Sec. III-C).

III. EXPERIMENTAL PROCEDURE

A. Apparatus

In Fig. 1 is shown the block diagram of the whole measuring system used in the present work.



M₁,M₂ : SECONDARY ELECTRON MULTIPLIER
A : DIFFERENTIAL AMPLIFIER
VI : VIBRATING REED ELECTROMETER
D : DIGITAL VOLTMETER
S₁,S₂ : SOURCE ; H : HIGH VOLTAGE
R : RECORDER ; VA : VACUUM PUMP

FIG. 1. Block diagram of the whole measuring system. The differential method is applied here using a pair of identical secondary-electron multipliers. Two kinds of sources are directly mounted on the first dynodes of these multipliers. The output currents are balanced through the differential amplifier.

The Nier-type secondary-electron multipliers (modified in some details) were used to multiply the internal-conversion electrons emitted from the U^{235m} sources. The essential construction is quite similar to that of a linear-type photomultiplier. The Be-Cu dynodes were specially treated by the oxidization process, in which the dynodes were heated in an oxygen atmosphere of appropriate pressure at 500°C for a few minutes. By this treatment, copper oxide decomposes and the dynode surface is covered only by beryllium oxide which has high secondary-electron emission efficiency and is stable even in air at room temperature.

At the beginning the over-all gains of the multipliers M_1 and M_2 were determined to be 2.0×10^5 and 1.1×10^5, respectively, at a pressure of 1.0×10^{-5} mm Hg with an applied voltage of -3600 V. The dark current under the same conditions was 2.5×10^{-18} A for M_1 and 1.2×10^{-18} A for M_2. But repeated exposures of the inside of the multipliers to the atmosphere gradually deteriorated the dynodes. To recover the gains, we had to re-treat the dynodes by the oxidization process.

To secure the maximum intensity of the source, U^{235m} was collected directly on the first dynodes, which were designed to be easily demountable from the multipliers. Therefore, M_1 and M_2 actually worked as 11-stage multipliers and the over-all gains were about one-half of the values given above.

The initial output currents from M_1 and M_2 were of the order of 10^{-11}–10^{-12} A. To measure the difference of the output currents, we manufactured a differential amplifier having a pair of sufficiently aged 5886 electrometer tubes, connected with input impedances of 0.980×10^{11} and 0.963×10^{11} ohms $\pm3\%$, respectively. Since the tubes have extremely delicate sensitivity, they were used with the following precautions: (a) The tubes were covered by a small brass box with a Lucite plate on the inner wall to eliminate electromagnetic induction and the noise due to photo-electrons; (b) for a power supply, dry and mercury batteries were used to avoid voltage fluctuations; (c) in order to obtain sufficiently good insulation and conduction, no socket was used, but all connections were directly soldered, and (d) room temperature was kept at 20±1°C and humidity less than 50% throughout the measurement. The gain of the differential amplifier G was obtained experimentally using standard inputs supplied from a mercury battery, and was found to be 2.92 ± 0.03. Since the output of the differential amplifier varies owing to the statistical fluctuations of conversion-electron emission from U^{235m} samples on the first dynodes and secondary-electron emission from other dynodes of the multipliers, a four-scale digital voltmeter was used to record the output of the amplifier continuously. A recorder was also used to monitor the performance of the whole measuring system. As mentioned in the preceding section, for the measurement of the factor $G_2S_{I-2}+G_1S_{II-2}$ in Eq. (3), a vibrating-reed electrometer was used.

The half-life of U^{235m} is only about 26 min and the sources are so weak that the measurements must be started as soon as possible after the preparation of the uranium samples. Using a powerful ion pump of 2400 liter/min connected with a subsidiary rotary pump of 250 liter/min, the inner pressure of the multipliers can be pumped out down to 1×10^{-6} mm Hg from 1 atm in less than 10 min. The advantages of using the ion pump instead of an oil diffusion pump are as follows: (a) perfect freedom from oil vapor, which may dirty the inside of the multipliers, (b) no mechanical vibration at all, and (c) the short time required to get a high vacuum.

B. Source Preparation

In the present work three different kinds of U^{235m} sources were investigated. These sources were prepared by collecting the recoiled uranium atoms from a plutonium source on different pure bases (platinum, carbon, and silicon) with a 600-V negative potential. These bases were then used as the first dynodes of the secondary electron multipliers. A very thin plutonium source of about 2 μg/cm² thickness supplied by the Centre d'Études Nucléaires in Saclay was prepared electrolytically on a pure copper plate 3 cm in diameter. To avoid the formation of uranium oxide in air during the collection, the U^{235m} atoms were collected on the base materials in an atmosphere of pure argon

(99.998%). The uranium sources thus prepared showed intensities of about 5×10^3 counts/cm^2 min at best, measured by a low-background 2π gas-flow counter.

The existence of a radioactive contaminant will introduce a critical error. To examine the purity of the source prepared by the recoil method, the measurements of the source intensity were extended through 5 mean lives. Furthermore, the collected uranium sources were covered by thin collodion films of about 6 μg/cm^2 thickness and counted by a low-background 2π gas-flow counter. It was found that the collodion film cut down the activity of the sources completely, and thus the uranium sources used were proved to be perfectly free from any radioactive contaminant. The alpha emission from U^{235} in the ground state is negligible because of its very long half-life.

For the comparison of the decay rates, we chose metallic uranium and uranium compounds with carbon and silicon. In general, the chemical bonding of U-C and U-Si is dominantly covalent but probably partially ionic. Unfortunately, it was not possible to determine the exact chemical forms of these compounds, because the ratio of the collected uranium atoms to the carbon or silicon atoms was extremely small, less than 10^{-12}. The only thing we can say in such circumstances is that the collected uranium atoms will diffuse slightly into the base materials when the sources are heated at an appropriate temperature, and the U^{235m} atoms will form a kind of solid solution with the surrounding carbon or silicon atoms. Even in this situation, it is hopefully assumed that the electronic combinations of these compounds are covalent bonding. In order to maintain the purity of these uranium samples, all procedures to prepare them were performed in a quartz tube 40 mm in diameter and 100 cm long, filled with flowing hydrogen or argon, and one section of which was heated in an electric furnace.

(*a*) *Metallic U:* A first dynode made of a platinum plate 0.25 thick, instead of Be-Cu, was used to make the metallic uranium source. First, the dynode surface was reduced in the flowing hydrogen atmosphere at 300°C for 5 h. Then, switching the flowing gas from hydrogen to argon, the dynode was shifted from the heated section to the end of the quartz tube where the U^{235m} atoms were collected on the dynode by the recoil method. After a 3-h collection in argon atmosphere at room temperature, the dynode was transferred into the multiplier.

(*b*) *U-C compound:* We prepared a Be-Cu dynode on which carbon was deposited in a vacuum. The thickness of this thin carbon layer was estimated to be about 500 Å. The surface of this carbon-deposited dynode was reduced in the quartz tube filled with flowing hydrogen at 300°C. After a 5-h reduction, the recoiled U^{235m} atoms were collected on the dynode in argon by the same procedure as was used for the metallic uranium source. When a 3-h collection of the isomer was completed, the source was returned into the electric furnace and heated again at 200°C (still in argon) for 5 min, on the expectation that the uranium atoms would diffuse slightly into the carbon layer and form a solid solution with the surrounding carbon atoms. Taking the source out of the furnace and letting it cool down to room temperature, we transferred it into the multiplier.

(*c*) *U-Si compound:* There are some difficulties in depositing silicon in vacuum on the Be-Cu dynode. As the vaporization rate of silicon is slow, oxygen is absorbed easily in the deposited silicon layer. Besides, at high temperature silicon reacts chemically with copper contained in the dynode, while at low temperature the deposited silicon surface becomes porous. Because of these difficulties, instead of using the silicon-deposited dynode, single-crystal silicon plates of 0.2 mm thickness were used as the collector.

Since the effective surface of the first dynode has a curvature, the silicon plate has to be curved to be attached to the dynode. For this purpose, an iron mold having the same curvature as that of the first dynode was first prepared and the silicon plate was pressed by it at 900°C. This procedure caused plastic deformation, giving the proper curvature to the silicon plate. The deformed silicon plate was etched by $HF(1)+HNO_3(3)$, $HF(1)+HNO_3(1)$, and then HF, to remove the SiO_2 film from its surface. Next it was washed in absolute alcohol and covered with a monolayer of silicon alcoholate. After this treatment, a very thin SiO_2 film covered the dynode surface again, but its thickness was only 10–20 Å. After the same procedures of reduction and collection as were used for metallic U and U-C compound, the silicon dynode with recoiled U^{235m} was heated at 500°C for 10 min in argon and then transferred into the multiplier. In this case the U^{235m} atoms are also expected to form a solid solution with the surrounding silicon atoms.

Diffusion of the isomer into the base materials is really essential in the procedures of source preparation. If the isomer diffuses deeply into the bases, the conversion electrons of very low energy will be absorbed in the bases. On the other hand, if the uranium atoms stay very near the dynode surface, the electronic environments of the U^{235m} will no longer be the same as those deep in the sample. It is advantageous to know how deep the isomer diffuses into the base materials by heat treatment. Some details on the diffusion effect of the uranium atoms will be described in Sec. IIIE.

C. Measurements of λ, G_2S_{I-2}, G_1S_{II-2}, $E_I(t)$, and $E_{II}(t)$

Prior to the measurement of $\Delta\lambda$, the absolute value of λ of metallic U^{235m} was measured. The source used for this purpose was prepared by the process described in the preceding section and its decay was measured by the use of a low-background 2π gas-flow counter. From this observation the decay constant of metallic U^{235m} was determined as $\lambda = 0.026\ 61 \pm 0.000\ 05\ \text{min}^{-1}$ or $T_{1/2} = 26.05 \pm 0.05$ min.

In the calculation of $\Delta\lambda/\lambda$ by Eq. (3), one must know the values of $G_2S_{\text{I}-2}$ and $G_1S_{\text{II}-2}$, which represent the products of the initial intensity of source 2 with $\lambda + \Delta\lambda$ and the gain of each secondary-electron multiplier containing the source in question. A vibrating-reed electrometer with an input impedance of 0.950×10^{10} ohms $\pm 3\%$ was used to measure these values. Just before we started each run, the electrometer was directly connected to the multiplier in which source 2 was mounted, and the value of $G_2S_{\text{I}-2}$ or $G_1S_{\text{II}-2}$ was obtained from the observed readings of the electrometer, corrected for decay and for the different input impedances of the differential amplifier and the vibrating-reed electrometer. All $G_2S_{\text{I}-2}$ and $G_1S_{\text{II}-2}$ thus obtained were summed up for each pair of sources. The numerical values of $G_2S_{\text{I}-2} + G_1S_{\text{II}-2}$ in Eq. (3) for estimation of $\Delta\lambda/\lambda$ are -22.02 ± 1.54 V for the U-UC pair, -20.69 ± 1.79 V for the U-USi pair, and -23.41 ± 1.80 V for the U-U pair.

A few minutes after the measurement of $G_2S_{\text{I}-2}$ or $G_1S_{\text{II}-2}$, we separated the electrometer from the multiplier and started to operate a digital voltmeter with a recorder to measure the output from the differential amplifier, $E_{\text{I}}(t)$ or $E_{\text{II}}(t)$, every second. To achieve good statistics, each measured value of $E_{\text{I}}(t)$ or $E_{\text{II}}(t)$ at time t was given by the average value of the outputs for the time period $t \pm 3$ min. A set of measurements of $E_{\text{I}}(t)$ and $E_{\text{II}}(t)$, each for 80 min, was repeated about 25 times for each pair of the uranium sources.

D. Stability of the Measuring System

The most important requirement was to maintain extremely good stability of the whole measuring system, especially of the two secondary-electron multipliers and the differential amplifier. To check the stability of the system over long periods, two C^{14} sources were used. They were prepared by depositing radioactive carbon on the first dynodes, which were aluminum plates of 0.25 mm thickness. Intensities of these sources were adjusted to be approximately the same as those of the uranium sources to be measured. After inserting these C^{14} sources into the multipliers, the output currents due to 158-keV beta rays of C^{14} were balanced through the differential amplifier. Then we carefully checked the drift of the initially balanced value for a couple of days.

After the stability checks on the measuring system with C^{14}, two metallic U^{235m} sources prepared by the method described in the preceding section were also used to ensure the performance of the system for the conversion electrons of the very weak energy. The results with these sources will be shown later by the lines designated (c) and (d) in Fig. 5. The lines are quite horizontal; this fact indicates that the stability of the whole measuring system was satisfactory. These stability checks were performed frequently during the work. By the procedures described here it was found that the measuring system used in the present work was able to detect the minute difference in the decay constants of two sources, $\Delta\lambda/\lambda$, down to 0.05%.

E. Diffusion of U^{235m} into Carbon and Silicon

It is interesting to observe some details of the diffusion of the U^{235m} atoms into the carbon and silicon bases. Owing to the self-absorption of very soft conversion electrons from the isomer in the base materials, the observable effect of diffusion is the decrease of source intensity as a function of heating temperature or of heating duration.

A linear decrease in the activity of the UC source was observed as heating temperature went up. The decrease of intensity of the USi source is slow compared with the UC source, as shown in Fig. 2. In addition, activities of these sources were observed for different heating durations at the same temperature. As shown in Figs. 3 and 4, the decrease of the source intensities is greater for UC sources than for USi. These differences in the rates of decrease of these two kinds of uranium sources may be due to the different constructions of the base materials.

One thing we worried about was the vaporization of the isomer from the dynode surface during heat treatment. To examine this possible vaporization, the uranium source on the carbon or silicon dynode was covered with a cap and heated at 500°C for 15 min so as to catch any vaporized isomer. The cap showed no activity greater than 0.2% of that of the uranium source used. From this observation, it can be concluded that the decrease of source intensity by heat treatment must be due to the diffusion effect.

Since it was not desirable to lose source intensities by this diffusion effect, in the actual measurements the

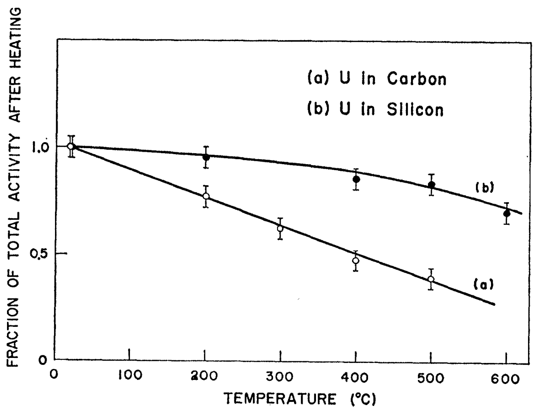


FIG. 2. Diffusion of U^{235m} into carbon or silicon base. Heating durations are 5 min for (a) and 10 min for (b). Observed values are corrected for decay and normalized to the initial activity at room temperature.

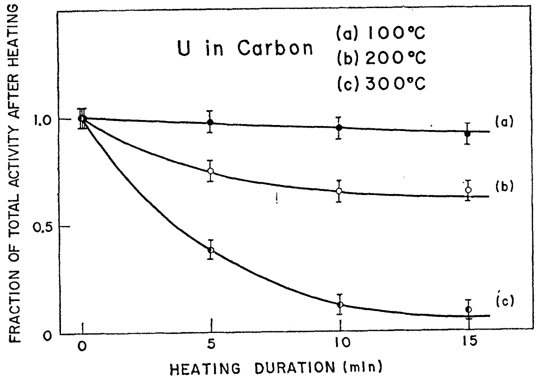


FIG. 3. Diffusion of U^{235m} into thin carbon layer deposited in vacuum. Observed values are corrected for decay and normalized to the initial activity at room temperature.

carbon dynodes were heated at 200°C for 5 min and the silicon dynodes at 500°C for 10 min. As the result of these heat treatments, the initial intensities of the UC and USi sources were reduced by factors of 0.75 and 0.84, respectively. Some discussion on this subject will be given in the following section.

IV. RESULTS AND DISCUSSION

The least-squares curves of $E(t)\exp(\lambda t)$ obtained for U-UC and U-USi pairs are shown in Fig. 5. The values of $\Delta\lambda/\lambda$ for these pairs can be obtained using the slopes of these lines. As a standard of comparison, the decay constant of metallic U^{235m}, $\lambda(U)=0.026\,61\pm0.000\,05$ min^{-1}, is used. The half-life $T_{1/2}=26.05\pm0.05$ min corresponding to this $\lambda(U)$ is slightly smaller than the previous results of 26.5±0.2 min, reported by Asaro and Perlman,[19] 26.6±0.3 min, by Huizenga *et al.*,[20] but it is in good agreement with the later value by Huizenga,[21] 26.16±0.03 min. The experimental results obtained for $\Delta\lambda/\lambda$ are listed in Table I. The third row of the table is derived from the results for U-UC and U-USi pairs. It can be ascertained that there are minute but apparent differences in λ of U^{235m} in the metallic state and embedded in a carbon or silicon base.

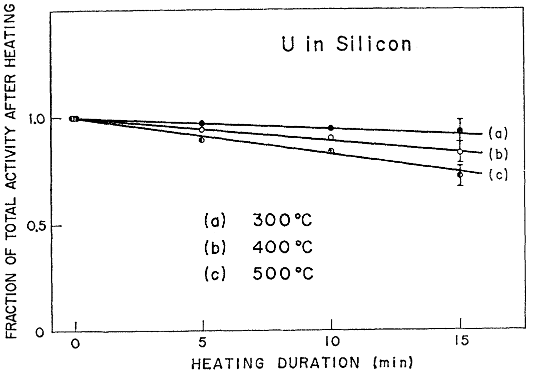


FIG. 4. Diffusion of U^{235m} into single-crystal silicon plate. Observed values are corrected for decay and normalized to the initial activity at room temperature.

There are some factors that could cause errors in the determination of $\Delta\lambda/\lambda$. These factors may be classified into two groups. The first group involves errors concerned with the measurements of $E_{\mathrm{I}}(t)$ and $E_{\mathrm{II}}(t)$. The magnitudes of the errors are given as fractions of the initial source intensity: (a) statistical fluctuations of conversion-electron emission from U^{235m} and secondary-electron emission in the secondary-electron multipliers, less than 0.1%; (b) errors introduced by the exponential decrease of source intensity when $E_{\mathrm{I}}(t)$ or $E_{\mathrm{II}}(t)$ was obtained as an average value for time duration $t\pm3$ min, about 0.11%; (c) zero drift of the digital voltmeter in 6 min, about 0.01%; (d) background of alpha particles from U^{235} in the ground state, negligible; (e) errors in time measurements, negligible; (f) gain drift of the secondary-electron multipliers; (g) gain drift and inaccuracy in setting of the base value of the differential amplifier; and (h) cosmic-ray background and wall-contamination effects. Errors due to the last three causes were determined experimentally to be 0.2%. In the second group, there are some sources of errors introduced in the calculation of $\Delta\lambda/\lambda$: (i) uncertainty in the decay constant $\lambda(U)$, (j) uncertainty in the measurements of $G_2S_{\mathrm{I}-2}+G_1S_{\mathrm{II}-2}$, and (k) uncertainty in the gain of the differential amplifier. Taking into account these factors of errors, the standard deviations of $\Delta\lambda/\lambda$ were determined as given in Table I.

The probability that a shell electron will be emitted by the mutual interaction with an excited nucleus depends on the wave function of the electron concerned at the nucleus. Accurate evaluation of the wave function is difficult because there are too many unknown factors involved. Only qualitative considerations on the electronic configurations changed by the different chemical combinations have been attempted. For the case of Tc^{99m}, rough theoretical estimation of the difference in λ of Tc^{99m} in metallic Tc and $KTcO_4$ has been made by Slater.[22] The most straightforward explanation mentioned in his note is the squeezing effect of Tc atoms in $KTcO_4$, resulting in alteration of electron density at the nucleus. In our case, however, the isomer may be considered to form a solid solution with the surrounding carbon or silicon atoms. The behavior of the outermost shell electrons in this solid solution is supposed to be mostly covalent bonding but probably partially ionic, as in ordinary uranium carbide or uranium silicide. In this situation, the most important factor in changing the electronic configurations of the isomer would be electronegativity of the atoms involved, as noted by Cooper *et al.*[14] Electronegativities of C, Si, and U (in

---

[19] F. Asaro and I. Perlman, Phys. Rev. **107**, 318 (1957).

[20] J. R. Huizenga, C. L. Rao, and D. W. Engelkemeir, Phys. Rev. **107**, 319 (1957).

[21] See Ref. 16, p. 836.

[22] J. C. Slater, Phys. Rev. 84, 1261 (1951).

TABLE I. Relative differences in the decay constant of U^{35m} in metallic state and embedded in carbon or silicon base.

Sources	Values from observed data
$[\lambda(U)-\lambda(UC)]/\lambda(U)$	$(3.18\pm0.50)\times10^{-3}$
$[\lambda(U)-\lambda(USi)]/\lambda(U)$	$(2.21\pm0.36)\times10^{-3}$
$[\lambda(USi)-\lambda(UC)]/\lambda(USi)$	$(0.97\pm0.43)\times10^{-3}$

the trivalent state) calculated by Allred[23] are 2.55, 1.90, and 1.38, respectively.

As a matter of fact, electronegativity has various values depending on the valence orbitals under consideration. In the present case, however, it seems to be pertinent to conclude that the electronegativity of the isomer is still smaller than those of carbon or silicon atoms. This may lead us to the conclusion that the outermost shell electrons of the isomer embedded in the carbon or silicon base spend most of their time in the vicinity of these base atoms, reducing the emission probability of internal-conversion electrons from the isomer. This qualitative consideration seems to be supported by the present experimental results.

Reflecting on this fact, we might suppose that λ of U^{235m} in uranium oxide or uranium fluoride would be affected more than in UC or USi, because the electronegativities of oxygen and fluorine are 3.44 and 3.98, respectively,[23] and the emission probability of the internal-conversion electrons from the isomer combined with these atoms would be smaller than that of uranium compounds used in the present work. Sources of uranium oxide or fluoride may be prepared by collecting the U^{235m} atoms in an atmosphere of oxygen or fluorine by the recoil method. However, since this procedure may damage the very thin Pu^{239} source during the collection, we have not attempted experiments with these compounds.

Of particular interest is diffusion of an isolated uranium atom into the base material. The electronic configurations of the isomer must depend on the conditions of heat treatment. The electronic environments of the isomer on the surface of the base materials and just below the surface may not be same, giving some changes in its disintegration rate. However, the isomer diffused as much as a few angstroms or more below the collector surface can be considered to be fully surrounded by the base atoms and consequently, in this case, the emission probability of the internal-conversion electrons from the isomer will not be changed any more. It is worth noting that the study of diffusion of an atom emitting soft internal-conversion electrons may suggest a new possibility for investigation of the problem of diffusion of an isolated atom, which promises to throw light on the structure of the uppermost layer of the base materials.

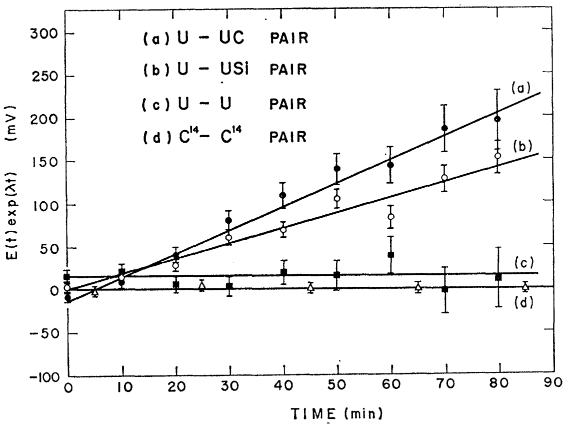


FIG. 5. Three U^{235m} sources are compared, i.e. metallic uranium (U) and uranium diffused into carbon (UC) or silicon (USi) base. For stability test of the measuring system, U-U and C^{14}-C^{14} pairs are measured.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor T. Takada and Dr. Y. Bando of our Institute for their helpful suggestions and discussions on the source preparation, and to Miss L. Cassin of Centre d'Études Nucléaires in Saclay for her kind cooperation in providing the very thin plutonium sources. Thanks are also due to R. Katano and Y. Nakayama for their kind help in setting up the measuring system. One of the authors (S. S.) gratefully acknowledges the stimulating discussions on this work with Professor K. T. Bainbridge of Harvard University, Dr. M. Goldhaber of Brookhaven National Laboratory, and Professor I. Perlman of Lawrence Radiation Laboratory, University of California. In addition, the valuable advice on the secondary-electron multipliers from Dr. M. Gotoh of Mitsubishi Electric Manufacturing Company, the kind present of silicon single crystals from Dr. Y. Sasaki of Nippon Electric Company, and the preparation of the carbon dynodes by S. Horii are greatly appreciated. This work was supported in part by a Scientific Research Grant from the Ministry of Education of Japan.

---

[23] A. L. Allred, J. Inorg. Nucl. Chem. **17**, 215 (1961).