Review

The discoveries of uranium 237 and symmetric fission —From the archival papers of Nishina and Kimura

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Abstract: Shortly before the Second World War time, Nishina reported on a series of prominent nuclear physical and radiochemical studies in collaboration with Kimura. They artificially produced ²³¹Th, a member of the natural actinium series of nuclides, by bombarding thorium with fast neutrons. This resulted in the discovery of ²³⁷U, a new isotope of uranium, by bombarding uranium with fast neutrons, and confirmed that ²³⁷U disintegrates into element 93 with a mass number of 237. They also identified the isotopes of several middle-weighted elements produced by the symmetric fission of uranium. In this review article, the highlights of their work are briefly summarized along with some explanatory commentaries.

Keywords: thorium, uranium, fast neutron, uranium 237, neptunium, symmetric fission

Introduction

At the beginning of the 1930's, epoch-making inventions or discoveries including the invention of the cyclotron by E.O. Lawrence (1931),¹⁾ the discovery of neutron by J. Chadwick (1932),²⁾ the discovery of deuterium by H.C. Urey $(1932)^{3)}$ and the discovery of artificial radioisotopes by J.F. and I. Joliot-Curie $(1934)^{4)}$ were successively reported. These important inventions and discoveries led to the rapid development of a new field of nuclear physical and radiochemical studies on artificial nuclear transformation.

At that time, Yoshio Nishina (Fig. 1a) had the opinion that a cyclotron is essentially necessary for Japan to develop experimental nuclear physics as well as to promote the production and application of radioisotopes. He intended to construct a 27 inch cyclotron on the campus of the Institute of Physical and Chemical Research (RIKEN) in Tokyo. The construction of the cyclotron started in 1935 and was completed in 1937 (Fig. 2). Thus, Japan became the second cyclotron-possessing country in the world after the United States. Nishina prepared such radioisotopes as ¹¹C, ¹³N, ²⁴Na and ³²P with his cyclotron, and applied them to biological tracer studies, obtaining many interesting results. He also started studies on the biological effects of radiations produced by the cyclotron.

In the physical and chemical fields, he carried out fast-neutron bombardment experiments on thorium or uranium in cooperation with Kenjiro Kimura (Fig. 1b) (Department of Chemistry, the University of Tokyo), and obtained several remarkable results, including the discovery of a new radioactive isotope of uranium, ²³⁷U, the discovery of symmetric nuclear fission and a trial to discover the missing element of atomic number 93.

This was carried out in a rather strained period of 1938–1940, shortly before the breakout of the Pacific War, and the papers were submitted to foreign journals and published in them. For these reasons, only a few Japanese physicists and chemists acquainted themselves with these prominent studies. The work of Nishina and Kimura was remarked and evaluated rather by foreign scientists.

In this paper, several main studies by Nishina and Kimura are reviewed along with some explanatory commentaries.

Artificial production of ²³¹Th from thorium⁵⁾

Thorium nitrate, carefully freed from any disintegration products except for 228 Th, was exposed

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Kenjiro Kimura

(1896 - 1988)

Yoshio Nishina (1890–1951)

Fig. 1.

to fast neutrons that were produced by bombarding lithium with 3 MeV deuterons in a cyclotron. The exposure duration ranged from 3 h to 15 h. The exposed sample was chemically purified for thorium, and the activity of the thorium fraction was measured with a Lauritsen electroscope.

It was revealed that two periods of β -activities were produced.

One showed a half-life of 26 m, and was identified with 233 Th, which was also observed by L. Meitner *et al.*⁶ by slow neutron irradiation of thorium.

The 24.5 h half-life of another one coincided with that of 231 Th, a member of the natural actinium series. 231 Th is the precursor of 231 Pa in the actinium series. (In the original paper, "²²⁸Th" and "²³¹Th" were denoted as "radiothorium (RdTh)" and "uranium Y (UY)", respectively, according to the conventional nomenclature and symbols used at that time.)

The formation of ²³¹Th from ²³²Th was surmised to be due to the loss of a neutron, and the reaction processes were considered to be as follows:

²³¹Th
$$\xrightarrow{\beta}$$
 ²³¹Pa (3.276 × 10⁴ y) [2]

Here, the figures in parentheses stand for the latest data⁷⁾ of the half-life of each corresponding nuclide.

The (n, 2n) reaction is a new type of nuclear reaction, and is called a "knock-out reaction", as compared with the (n, γ) reaction, which is called a "capture reaction". This work is also notable as the first example of an artificial transformation of the thorium series nuclide to the actinium series one.



Fig. 2. Nishina's 27 inch cyclotron constructed on the campus of the Institute of Physical and Chemical Research, Tokyo in 1937.

They also carried out radiochemical separations with respect to fractions other than the thorium one, and found several radioisotopes of silver (Ag), tin (Sn) and antimony (Sb) as fission products.⁸⁾

The discovery of a new uranium isotope, ${}^{237}\mathrm{U}^{9)}$

Uranium oxide (U_3O_8) was carefully purified and freed from its disintegration products in advance. A few grams of it was exposed to fast neutrons for more than 50 h. Fast neutrons were produced by bombarding lithium with 3 MeV deuterons in a cyclotron. After exposure, the exposed uranium oxide was again purified so as to eliminate any possible elements produced by fission as well as by its own disintegration. The activity of thus-obtained uranium oxide was measured with a Lauritsen electroscope, and compared with the activity of a non-irradiated uranium oxide sample of the same weight in order to subtract the growing β -activity due to the disintegration products of uranium. The difference, which corresponds to the net activity of exposed uranium oxide, showed a half-life of 6.5 d.

An uranium isotope having a half-life of 6.5 d was unknown at that time. Nishina and Kimura considered that this isotope would be produced by the (n, 2n) reaction, just as in the case of producing ²³¹Th from ²³²Th, shown in Eq. [1]. Thus, they came to the conclusion that the new uranium isotope is ²³⁷U. They confirmed that ²³⁷U is a β^{-} -emitter. Accordingly, they could suspect that the isotope of element 93 with a mass number 237 was produced by the β^{-} -decay of ²³⁷U. These nuclear reaction processes are represented as follows:

No. 7]

238
U (n, 2n) 237 U (6.75 d) [3]

$$^{237}U \xrightarrow{\beta} ^{237}[93]$$
 (probably very long) [4]

The element with the atomic number 93, which was later named neptunium (Np), was an unknown element at that time, and thus, the produced isotope of element 93 is denoted here as 237 [93] after Kimura.

In the decay series described by Eq. [4], ²³⁷U and ²³⁷[93] are both nuclides of the (4n + 1) family. At that time, three decay series, namely, the uranium series ((4n + 2) series), the thorium series (4n series) and the actinium series ((4n + 3) series) were known, while the (4n + 1) series was missing. It was thus revealed that Eq. [4] is the first example of the (4n + 1) series disintegration.

This work is also notable as being the first example of an artificial transformation of the nuclide in the uranium series to that in the (4n + 1) series.

The (4n+1) series was later named the neptunium series.

A trial to search for the missing element 93⁹⁾

As described above, Nishina and Kimura confirmed the production of β^- -emitting ²³⁷U. The decay product of ²³⁷U is consequently an isotope of element 93 with mass number 237, as shown in Eq. [4]. They tried to separate and discover the new element 93.

They suspected that element 93 would be homologous to rhenium in the 7th group of the periodic table, and its chemical properties would resemble those of rhenium. Therefore, they used rhenium as a carrier to collect element 93 along with it.

To separate element 93 from uranium, the exposed uranium oxide, which was freed from fission products as well as from its disintegration products, was left standing for about 7 days, and then dissolved in nitric acid. To the solution, perrhenic acid was added as a carrier. The solution was treated with ammonium sulfide, and then acidified with sulfuric acid to precipitate rhenium sulfide. The precipitate was washed with carbon disulfide to remove any sulfur contaminant. Thus-obtained rhenium sulfide was examined for β - and α -activities. However, neither of them could be observed within the error of their experiments. They considered that the halflife of element 93 in question is very long, as in the case of 231 Pa in Eq. [2], so that its activity would be too weak to be measured. They reported these results in the same paper as that reporting the discovery of $^{237}U.^{9)}$

At that time, the concept of "actinoids" was not yet proposed, and element 93 was considered to be the 7th group element, just below rhenium on the periodic table. Somewhat later, the concept of "actinoids" was proposed, and both uranium and neptunium were grouped as members of the actinoids, which come below the lanthanoids in the 3rd group on the revised periodic table. Then, the chemical behaviors of element 93 are considered to resemble those of uranium or lanthanoids, rather than those of rhenium. If so, the selection of rhenium as the carrier for element 93 would be inadequate for separation from uranium. However, if the best carrier had been chosen, and separation had been carried out quantitatively, the detection of ²³⁷[93] activity would have still been impossible because of its very long half-life. The fundamental reason why the trial for searching element 93 by Nishina and Kimura ended in vain could be attributed to its very long half-life.

The fact that the above-mentioned studies are highly evaluated by distinguished U.S. scientists is shown in a letter from Yasaki to Nishina.¹⁰⁾ T. Yasaki, a member of the Nishina group, together with other members visited Lawrence at the University of California and other Institutes in 1940. He was invited to a colloquium of the laboratory, and made a presentation on the above-mentioned subjects. Such eminent scientists as Lawrence, Oppenheimer, Segrè, Seaborg, McMillan and so on were present there, and they praised the outstanding achievements of the Nishina group. At this colloquium, McMillan said to Yasaki that he also observed a uranium isotope having a half-life of 7 d, produced by the fast neutron bombardment of uranium, which coincides with 6.5 d of ^{237}U obtained by the Japanese group. He also said that element 93 would not be coprecipitated with rhenium, but with cerium.

Missing element 93 was discovered by E.M. McMillan and P.H. Abelson¹¹⁾ of the California University group in 1940, and named neptunium (Np). In 1942, ²³⁷Np was synthesized in larger amounts, and its half-life was revealed to be 3×10^{6} y (2.144 $\times 10^{6}$ y, at present) by A.C. Wahl and G.T. Seaborg,¹²⁾ which is very long, as Nishina and Kimura had predicted.

In experiments by McMillan and Abelson, they irradiated uranium with slow neutrons. In this case, 239 U is produced by the (n, γ) reaction, which then disintegrates to 239 Np according to the following processes. They succeeded in separation of 239 Np by using cerium as the carrier:

²³⁸U (n,
$$\gamma$$
) ²³⁹U (23.45 m) [5]

$$^{239}\mathrm{U} \xrightarrow{\rho} ^{239}\mathrm{Np} \quad (2.356\,\mathrm{d})$$
 [6]

The half-lives of both 239 U and 239 Np are of convenient length for activity measurements. It is also advantageous that the produced 239 U decays out several hours after the end of neutron irradiation, and thereafter only 239 Np remains. Thus, the favorable half-life of 239 Np made McMillan and Abelson fortunate, while long-lived 237 Np made Nishina and Kimura unlucky.

The discovery of symmetric fission of $\operatorname{uranium}^{13)-17)}$

In the course of fast neutron exposure experiments on uranium, Nishina and Kimura also carried out the radiochemical separation and identification of various kinds of induced radioactive species other than uranium.

Uranium oxide (U_3O_8) , carefully purified and freed from its disintegration products just before the experiments, was exposed to fast neutrons produced by bombarding lithium with 3 MeV deuterons from their cyclotron. The exposure times ranged from a few hours to some fifty hours according to the object of the experiments. As results, they found that radioisotopes of such elements as ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), cadmium (Cd), indium (In) and tin (Sn) were produced. Nishina and Kimura were at first annoyed in understanding the nuclear reaction processes of concern. Soon, these elements were explained as the fission products when O. Hahn, F. Strassmann and L. Meitner^{18),19)} reported the discovery of nuclear fission.

It is thought to be helpful for a better understanding to take the atomic numbers into consideration. The atomic numbers of the above-mentioned elements are: Ru = 44, Rh = 45, Pd = 46, Ag = 47, Cd = 48, In = 49 and Sn = 50, respectively. By noticing that the atomic number 46 of palladium is just half that of 92 of uranium, it is supposed that one uranium atom splits into two palladium isotopes. When rhodium (atomic number 45) is produced with some probability (cross section), silver (atomic number 47) is the counter fragment. In the same way, ruthenium (atomic number 44) and cadmium (atomic number 48) are the pairing fragments. Thus, the nuclear fission observed by Nishina and Kimura is highly symmetric.

Meanwhile, G.T. Seaborg and E. Segrè²⁰⁾ of the Californian group carried out similar experiments using the cyclotron at the University of California, and observed a similar fission phenomenon somewhat later than Nishina and Kimura in 1940. In this connection, Seaborg himself stated as follows, when he visited Japan in 1989 and gave an invited lecture in Tokyo: "The symmetric fission which we observed in our fast neutron bombardment experiments on uranium in 1940 was already discovered by the Japanese group of Nishina and Kimura at the earlier time of the same year."²¹⁾ It is also to be noted that J. Wheeler,²²⁾ who had just published a comprehensive paper on nuclear fission together with N. Bohr, showed great interest in this Japanese result when Yasaki's group visited him at Princeton in 1940.²³⁾

This type of the fission caused by fast neutron bombardment is mainly composed of the 50%-50%splitting of a uranium atom, and is called symmetric fission. On the other hand, in slow neutron fission discovered by Hahn's group, it is mainly composed of the 40%-60% splitting of a uranium atom, showing two peaks at atomic numbers of around 36 and 56 on the fission yield *vs.* atomic number curve, and is called asymmetric fission.

Before the Second World War, 24 elements in all (Today, total 37 elements⁷) were known as fission products of uranium. Among them, the abovementioned 7 elements were found by the Nishina and Kimura group.

Conclusion

During the early stage of artificial nuclear transformation studies, more than 70 years ago, Nishina and Kimura obtained such remarkable results of world top level, as described above.

These results are largely attributable to the close collaboration between a physicist and a chemist, and their groups. Kimura, in his young days, studied about the chemical application of X-ray spectroscopy at Bohr's Laboratory in Copenhagen, where Nishina was also staying and working. During those days, Nishina and Kimura studied jointly about the relation between chemical bonds and X-ray absorption spectra, and published a coauthored paper.²⁴⁾ Ever since, they contracted an intimate friendship with each other. They were really the best and most superb combination for achieving the above-mentioned excellent and brilliant work at the world top level.

At the end of this review article, the author would like to pay his hearty respect and high tribute to Prof. Nishina and Prof. Kimura as well as the members of their groups.

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Profile

Nagao Ikeda was born in Tokyo in 1925. He graduated from the Department of Chemistry, Faculty of Science, the University of Tokyo in 1948, and obtained the degree of Doctor of Science from the University of Tokyo in 1953. He was appointed as assistant professor of the Tokyo Kyoiku University in 1954. In 1961–1963, he studied at the Max Planck Institute for Chemistry (in Mainz, Germany) as an overseas research fellow of the Nishina Memorial Foundation. He was appointed as professor of the Tokyo Kyoiku University in 1964. With the movement of his University to Tsukuba, he became professor of University of Tsukuba in 1977. His fields are mainly radioanalytical chemistry and environmental radioactivity. In connection with this review article, Ikeda was a member of Kimura Laboratory, and was concerned with radiochemical analyses of



the so-called "Bikini Ashes", in which relatively high amounts of 237 U were detected. In later years, he developed the radioactivation method as well as the ICP mass spectrometric method for the determination of 237 Np in the environment, and was able to first detect and determine 237 Np in some soil samples collected from several locations in Japan.