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Half-life estimation of the first excited state of ^{229}Th by using α-particle spectrometry

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To search for a direct-decay signal from the isomer ^{229}Th^m, α-particle spectra of ^{229}Th^{m,g} produced from 93 mg of ^{233}U have been measured by using a rapid and high-resolution α-particle spectrometry, which can distinguish α lines of ^{229}Th^m from those of its ground state. Although α events were not obtained in the expected energy region for ^{229}Th^m with the exception of those derived from ^{229}Th^g, we can estimate that the half-life of ^{229}Th^m is shorter than 2 h at 3σ confidence level under the chemical condition of chloride or hydroxide.

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I. INTRODUCTION

The first excited state of ^{229}Th (^{229}Th^m) is a very interesting nuclear isomer. A number of decay studies of ^{233}U have shown that ^{229}Th^m has the excitation energy of several electron volts [1–4]. Because of its extremely low energy comparable with the binding energy of valence electrons, the half-life of ^{229}Th^m is expected to vary with the interaction between the nucleus and its orbital electron [5]. Therefore, the half-life reflects not only the nuclear structure but also its chemical environments.

The values of the half-lives of ^{229}Th^m obtained in previous researches [6,7] appeared to be inconsistent. The first experimental data of the half-life was reported by Browne *et al.* [6] in 2001. Based on γ-ray spectrometry, they searched for the growth components on the ground state of ^{229}Th (^{229}Th^g) from ^{229}Th^m using approximately 25 g of ^{233}U. From unsuccessful observation of such growth, they concluded that the ^{229}Th^m half-life should be <6 h or >20 d in 2 M HCl. In our previous works [7,8], we attempted to produce ^{229}Th^m in nuclear reactions and to measure its half-life by α-particle spectrometry. Although a sufficient quantity of counting statistics was not obtained, the half-life of ^{229}Th^m in fluoride was estimated to be 13.9 ± 3 h [7]. More accurate determination of the half-life of ^{229}Th^m would improve the experimental design for measuring its nuclear processes including direct photon emission from ^{229}Th^m [9].

The previous studies indicate that the half-life of ^{229}Th^m is around several hours or less and hence we have optimized our experiment to measure the half-life below one day. In this study, we used α-particle spectrometry to estimate the half-life of ^{229}Th^m produced from the α decay of ^{233}U whereas ^{229}Th^m was produced in nuclear reactions in our previous works. The detailed characteristics of the α decay of ^{233}U are well known and the data up to 1996 are summarized in Ref. [10]. More recent data have been presented by Barci *et al.* [2], who investigated the nuclear level scheme of ^{229}Th in detail by γ-ray spectrometry. These data indicate that the ground state of ^{233}U, assigned as the $5/2^+[633]$ Nilsson state, decays to the ground state of ^{229}Th, $5/2^+[633]$, with the branching ratio of about 87%. All the rest decay to the excited states of ^{229}Th, so that higher than 2.1% [11] of the total decay of ^{233}U is expected to decay via the level of ^{229}Th^m, $3/2^+[631]$. Therefore, the initial α-particle spectrum of ^{229}Th separated from ^{233}U is expected on the assumption that the sample consists of 98% of ^{229}Th^g and 2% of ^{229}Th^m as shown in Fig. 1. The solid line shows the spectrum of ^{229}Th^g estimated from Ref. [10] and the dashed line shows the ^{229}Th^g spectrum with the component of ^{229}Th^m estimated by Dykhne and Tkalya [11] on the assumption that the transition from ^{229}Th^m to ^{229}Th^g is negligible. The transition from ^{229}Th^m to the 149.96-keV level, $3/2^+[631]$, of ^{225}Ra is expected to be the favored α decay, whereas ^{229}Th^g decays mainly to the 236.25-keV level, $5/2^+[633]$, and has α branching of 0.16% [10] to the 149.96-keV level of ^{225}Ra. There is a large difference between those spectra in the energy region around 4930 keV. Note that the difference would be detected even if ^{229}Th^m has such a long life as not to distinguish the signal from ^{229}Th^m by a radioactive decay or growth [6,7]. Moreover, it is possible to estimate the half-life even if the difference is not observed because of a short life, because the initial amount of ^{229}Th^m is able to be estimated from that of ^{233}U. Therefore, comparing the high-resolution spectrum of "freshly" isolated ^{229}Th^{m,g} from ^{233}U with the spectrum of ^{229}Th^g is efficient for estimation of the half-life of ^{229}Th^m. The method of rapid source preparation for high-resolution α-particle spectrometry [12] has been applied to the present study.

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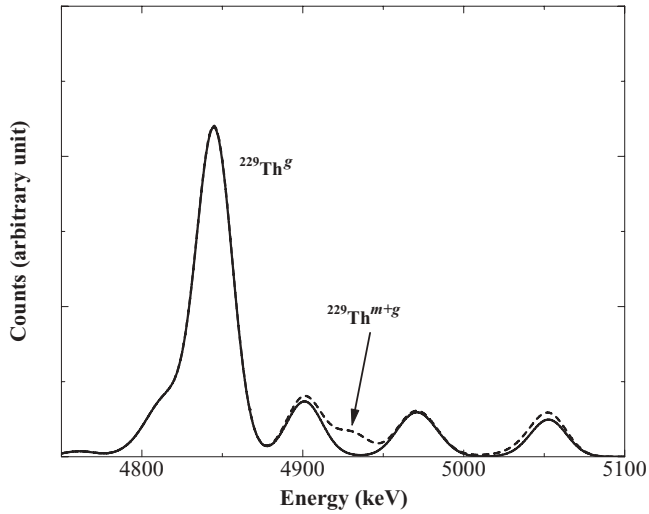

FIG. 1. Expected spectrum for fresh ^{229}Th produced from α decay of ^{233}U.

II. EXPERIMENTAL PROCEDURES

For the purification of the ^{233}U sample, we carried out an anion-exchange procedure. The U_3O_8 sample containing 93 mg of ^{233}U was supplied from the International Research Center for Nuclear Materials Science, Tohoku University. Generally, a ^{233}U sample contains ^{232}U produced in subnuclear reactions as an impurity. The ^{233}U sample used in this experiment contains 3.17 ppm of ^{232}U. The oxide sample of ^{233}U was dissolved in 12 M HCl and then precipitated by adding 15 M NH_4OH as ammonium diuranate. After a centrifugal separation, the precipitate was dissolved in 10 mL of 12 M HCl and the solution was passed through an anion-exchange column [Muromac(R) 1 × 8, 200–400 mesh, 8 mmϕ × 50 mm], which adsorbed uranium. The resin adsorbing uranium was washed with 25 mL of 9 M HCl to eliminate thorium. The uranium was eluted from the column with 10 mL of 2 M HCl and precipitated by adding 15 M NH_4OH as ammonium diuranate. The precipitate was separated from the supernatant by centrifugation. This purification was repeated three times.

The precipitate of ammonium diuranate was dissolved in 10 mL of 12 M HCl and then the solution was passed through an anion-exchange column [Muromac(R) 1 × 8, 200–400 mesh, 8 mmϕ × 50 mm] to adsorb uranium. The resin was washed with 15 mL of 9 M HCl to eliminate thorium, and then the column was left to stand for 1 h to allow the growth of ^{229}Th^{m,g}. These fresh thorium isotopes were eluted from the column with 5 mL of 9 M HCl and the eluate was passed through another anion-exchange column [Muromac(R) 1 × 8, 200–400 mesh, 8 mmϕ × 50 mm] to eliminate traces of ^{233}U from the thorium fraction. The thorium isotopes were coprecipitated with samarium hydroxide by adding 20 μg of samarium and 15 M NH_4OH in this order. The precipitate was collected on a 0.02-μm alumina filter (Whatman, ANODISC membrane) 18 mm in diameter to prepare a counting source [12]. The filter was fixed on a stainless-steel supporting ring and dried on a hot plate at 150°C. The sample was subjected to α-particle spectrometry as described below.

The accumulation for an α-particle spectrum for 600 s was repeated 20 times. The elapsed time from the elution of thorium to the start of measurement was about 15 min. After the above procedure for elution of ^{229}Th^{m,g} was performed 3 times, the ^{233}U atoms were eluted from the column with 20 mL of 2 M HCl, and again absorbed to a new column to avoid the leak of ^{233}U. The whole procedure was performed 9 times, so that a total of 27 α sources were measured.

The α-particle spectrometry was performed by using a SILENA Model 7937/B α-particle spectrometer and a 2048-channel pulse-height analyzer system assisted by a personal computer. The α-particle spectrometer was equipped with an ion-implanted planar silicon detector (Canberra, PD450-17-100AM). A counting source was placed at a distance of 3 cm from the detector and the counting efficiency was 3.4%.

III. RESULTS AND DISCUSSIONS

An α-particle spectrum obtained as the sum of the 27-sample spectra measured for the first 6000 s is shown in Fig. 2. The α peaks of ^{229}Th, ^{228}Th, and the daughters of ^{228}Th are seen in the spectrum. The ^{228}Th peak at 5423 keV has a full width at half maximum (FWHM) of about 25 keV. This resolution is sufficient to distinguish between α lines of ^{229}Th^{m} and those of ^{229}Th^{g}.

A magnification of the α-particle spectrum in Fig. 2 for the region related to ^{229}Th is shown in Fig. 3. The solid circles show a spectrum measured for the first 6000 s, and the open circles show a spectrum measured for the next 6000 s. The solid line shows a ^{229}Th^{g} spectrum estimated from the region of the main peak of ^{229}Th^{g}, which does not contain the component of ^{229}Th^{m}, and the linear background continuum. The component in the low-energy side of ^{229}Th is due to ^{233}U that passed through the anion-exchange column. From 1 h growth of ^{229}Th in a 93 mg sample of ^{233}U and using 27 such samples, we estimate 1800 counts due to ^{229}Th^{g} in an α spectrum measured with 3.4% efficiency for 6000 s.

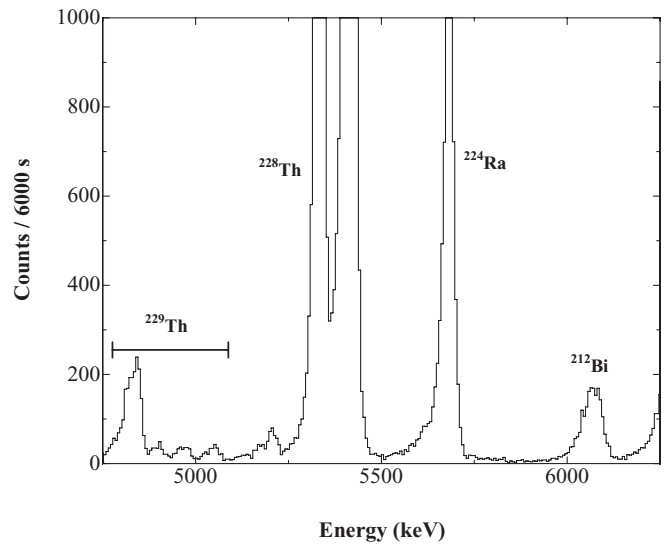

FIG. 2. An α-particle spectrum obtained as the sum of 27 spectra measured during the initial 6000 s.

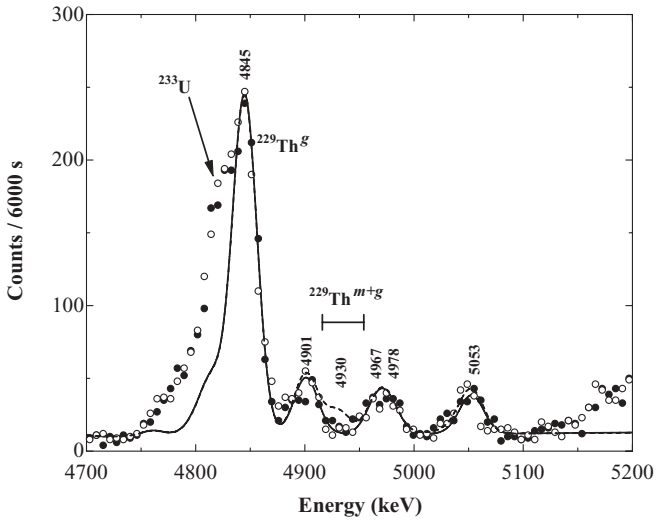

FIG. 3. A magnification of the α-particle spectrum for the region related to ^{229}Th. The solid circles show counts per channel for the initial 6000 s and the open circles show counts per channel for the following 6000 s. The lines drawn in the figures are the same as those in Fig. 1 (see text for detail).

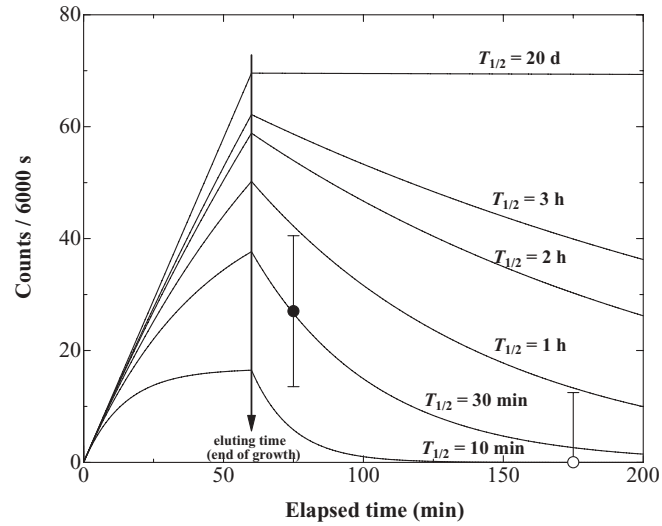

FIG. 4. Estimated growth curves in α counts in the energy region of the ^{229}Th^m α particle. Each of the six solid curves represents the expected counts of ^{229}Th^m with a half-life between 10 min and 20 d. The solid and open circles indicate the ^{229}Th^m α counts of the spectrum measured for the initial 6000 s and those for the following 6000 s, respectively.

By contrast, obtained counts of ^{229}Th^g were 1700 counts per 6000 s. The obtained counts are compatible with the expected counts considering the chemical yield in purification procedures. The ratio of the α counts of ^{229}Th^g/^{228}Th was about 1/30, which is consistent with the ratio of the α counts of ^{229}Th^g ($T_{1/2} = 7880$ y [13]) and ^{228}Th ($T_{1/2} = 1.9116$ y [10]) estimated from the ^{233}U ($T_{1/2} = 1.592 \times 10^5$ y [10]) atoms containing the ^{232}U ($T_{1/2} = 68.9$ y [10]) atoms at 3.17 ppm. The dashed line shows a spectrum that is the sum of the solid line and 2% of ^{229}Th^m as well as Fig. 1. Assuming that ^{229}Th^m is stable for isomeric transition or that it has a half-life longer than a few days, one expects to obtain a spectrum corresponding with the dashed line. However, the obtained spectrum is close to the solid line, which indicates that ^{229}Th^m scarcely remained at the measurement.

To estimate the half-life of ^{229}Th^m, in Fig. 4 we show the α counts in the region of 4915–4955 keV (hereinafter called the ROI, region of interest), where the main peak of ^{229}Th^m is expected to appear, as a function of elapsed time. As with Fig. 3, the solid and open circles indicate the ROI counts of the spectrum measured for the first 6000 s and for the next 6000 s, respectively. The solid lines show the growth curves of the ROI counts with various half-life values expected as described below. Thorium isotopes were eluted from the anion-exchange column adsorbing ^{233}U at the time when the curves turn off. Until this time, ^{229}Th^{m,g} increase because of the decay of ^{233}U, and the number of atoms is given by the following equations:

$$N_m(t) = \frac{\lambda_{233}}{\lambda_m - \lambda_{233}} N_{233} \mathrm{br}_m (e^{-\lambda_{233} t} - e^{-\lambda_m t}), \quad (1)$$

$$N_g(t) = \frac{\lambda_{233}}{\lambda_g - \lambda_{233}} N_{233}(1 - \mathrm{br}_m)(e^{-\lambda_{233} t} - e^{-\lambda_g t}) + \frac{\lambda_m}{\lambda_g - \lambda_m} N_m (e^{-\lambda_m t} - e^{-\lambda_g t}), \quad (2)$$

where N_m, N_g, and N_{233} are the numbers of ^{229}Th^m, ^{229}Th^g, and ^{233}U atoms, respectively, λ_m, λ_g, and λ_{233} are the decay constants of ^{229}Th^m, ^{229}Th^g, and ^{233}U, respectively, and br$_m$ is the branching ratio of the decay of ^{233}U via ^{229}Th^m. And then the ^{229}Th^m component disintegrates to ^{229}Th^g according to its half-life. Here, the ROI counts are given by

$$\text{ROI counts} = \text{eff}\left\{I_m \lambda_{m\alpha} N_m(t) + I_g \lambda_g N_g(t)\right\} + \text{BKG}, \quad (3)$$

where eff is the total efficiency, which is 3.4% in this case, I_m and I_g are the intensities of ^{229}Th^m and ^{229}Th^g in the ROI region, respectively, $\lambda_{m\alpha}$ is the partial α-decay constant of ^{229}Th^m, and BKG is the constant-background counts in the ROI region. The partial half-life of α decay of ^{229}Th^m is estimated to be 2000 y from Refs. [7,11]. According to Refs. [10,11], the ratio of I_m to I_g is 22.8 : 1. The value of eff$\{\lambda_g N_g(t)\}$ + BKG is fitted to the solid line in Fig. 3. Although the first observed value is reproduced most likely with the curve for a half-life of 30 min, no influence of ^{229}Th^m is observed on the second value. The 3σ confidence level of both values gives an upper limit of 2 h for the half-life of ^{229}Th^m. The result is consistent with the upper limit of the short-lived case in Ref. [6], namely, 6 h.

We note that the half-life of ^{229}Th^m may change depending on its chemical form. In this study, the ^{229}Th atoms formed chloride complexes before the α-source preparation and then hydroxides for α-particle spectrum accumulation. Therefore, the present results show the half-life of ^{229}Th^m is less than 2 h under the chemical condition of at least either chloride or hydroxide.

In the framework of a single-particle transition model, the radioactive transition probability via direct photon emission is

given by the following equation:

$$\lambda = \frac{\ln 2}{T_{1/2}} = \frac{8\pi(L+1)}{L[(2L+1)!!]^2} E_\gamma^{2L+1} B(ML), \qquad (4)$$

where $T_{1/2}$ is the half-life of a nuclear transition, L is the multipolarity, E_γ is an excited energy of a level, and $B(ML)$ is the reduced transition probability of the nucleus. The excitation energies of $^{229}\mathrm{Th}^m$ were reported to be 3.5 ± 1.0 eV [1], 3.4 ± 1.8 eV [2], 5.5 ± 1.0 eV [3], and 7.6 ± 0.5 eV [4]. However, the reduced transition probability of $^{229}\mathrm{Th}^m$ to $^{229}\mathrm{Th}^g$, $B(M1; +3/2 \rightarrow +5/2)$, was estimated to be 0.043 μ_N^2 [2]. Hence, the partial half-life of $^{229}\mathrm{Th}^m$ for direct photon emission is estimated to be between 29 min and 16 h in the energy range from 2.5 to 8.1 eV in a vacuum in the framework of a single-particle transition model.

The partial half-life of less than 2 h corresponds to the excitation energy of higher than 5 eV. Therefore, if the excitation energy of $^{229}\mathrm{Th}^m$ is lower than 5 eV, for example, 3.5 eV as reported in Ref. [1], the present results suggest that $^{229}\mathrm{Th}^m$ should decay via not only the direct photon emission but also other decay channels, such as an electron bridge mechanism [14] and a medium effect [5]. In contrast, assuming that the excitation energy of $^{229}\mathrm{Th}^m$ is larger than 5 eV, the obtained limit of the half-life of $^{229}\mathrm{Th}^m$ can be explained even if the decay occurs only via the direct photon emission. In other words, the half-life of $^{229}\mathrm{Th}^m$ should be shorter than 2 h regardless of the chemical forms of Th for this excitation energy. In particular, if the excitation energy is larger than an electron-binding energy of the outer valence molecular orbital of Th and its compounds, the internal conversion process is possible and the half-life is not to be significantly changed by the variation of chemical form; therefore, the half-live of shorter than 6 h [6] gives agreement with the present results whereas those of longer than 20 d [6] and 13.9 ± 3 h [7] fall outside of the limits of the results.

In conclusion, we have searched for the α events from $^{229}\mathrm{Th}^m$ produced from 93 mg of $^{233}\mathrm{U}$ by α-particle spectrometry with rapid source preparation. From the upper limit of such events, it was concluded that the half-life of $^{229}\mathrm{Th}^m$ may be less than 2 h. The excitation energy is strongly expected to be determined more accurately by direct photon emission. If one attempts to detect the photon of isomeric transition from $^{229}\mathrm{Th}^m$ with excitation energy higher than the electron-binding energy of Th compounds, as the most recent value 7.6 ± 0.5 eV [4], the experimental design for it should be based on the assumption that $^{229}\mathrm{Th}^m$ has a half-life shorter than a few hours.

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