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Existence of long-lived isomeric states in naturally-occurring neutron-deficient Th isotopes

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Four long-lived neutron-deficient Th isotopes with atomic mass numbers 211 to 218 and abundances of $(1–10)\times10^{-11}$ relative to ^{232}Th have been found in a study of naturally-occurring Th using inductively coupled plasma-sector field mass spectrometry. It is deduced that long-lived isomeric states exist in these isotopes. The hypothesis that they might belong to a new class of long-lived high spin super- and hyperdeformed isomeric states is discussed.

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Long-lived high spin isomeric states have been found in recent years [1–4] in the second minimum [the superdeformed (SD) minimum] [5–8] and in the the third minimum [the hyperdeformed (HD) minimum] [9,10] of the potential energy of nuclei when displayed as a function of deformation. These isomeric states have unusual radioactive decay properties. A SD isomeric state in the parent nucleus can decay by emitting low energy (relative to the g.s. to g.s. transition) and enhanced α-particles (as compared to the predictions of barrier penetration calculations [11,12]) to a SD state of the daughter nucleus [1], or by strongly retarded α-particles to a normally deformed or to the g.s. of the daughter. In some cases it can also decay by retarded proton radioactivity [2]. Similarly, a HD isomeric state can decay by high energy retarded α-particles to SD states [3], or by low energy [13] enhanced α-particles to HD states of the daughter nucleus [4].

It was found that the lifetimes of these isomeric states are much longer than those of their corresponding g.s. [14]. This is also true for the strongly enhanced SD to SD and HD to HD α-transitions, where the influence of the relatively low energy of these transitions overcomes the strong enhancements. The long lifetimes of the observed isomeric states against fission decay are probably due to their high spins. It was shown [15] that for high spin states produced by alignment [16], the barrier against fission increases significantly due to specialization energy [17].

These new radioactive decay properties enabled Marinov *et al.* [18] to propose coherent descriptions for previously unexplained radioactive decays seen in natural materials [18].

These developments motivated us to search for naturally-occurring long-lived isomeric states. (There is only one such state known, the 75.3 keV level in ^{180}Ta with a half-life of $>1.2\times10^{15}$ y [19].) The binding energy per nucleon (BE/u) of stable nuclei has a broad maximum near $A \simeq 60$ with a value of BE/u $\simeq$ 8.7 MeV/nucleon and falls monotonically to about 7.6 MeV/nucleon at around Th and U [20,21]. Hence, the masses of the isotopes of Th and U are higher than, and resolvable from, the masses of all molecules of the same mass number, except for multihydrogen-containing molecules. Therefore, accurate mass measurements on pure Th and U substances, where the Z-value is determined by the chemical properties of the element, can in principle provide unique isotope identification. These measurements are necessarily limited to radioactive nuclei, where no stable or long-lived isobars exist. Data are presented in the present work that argue for the existence of isomeric states in neutron-deficient Th isotopes.

Commercially available pure Th and U standard solutions were studied using an inductively coupled plasma-sector field mass spectrometer (ICP-SFMS). In such an instrument a solution of the material to be studied is introduced into a high temperature (6000 K–8000 K) plasma source. At these temperatures, predominantly atomic species are present. Molecular ions are produced after the source, mainly by interaction with oxygen and hydrogen ions from the solution. The instrument was an Element2 (Finnigan, Thermo-Electron, Bremen, Germany). The predefined medium resolution mode of $m/\Delta m = 4000$ (10% valley definition) was used throughout the experiments to separate atomic ions from interfering molecular ions with the same mass number. The sensitivity-enhanced setup of the instrument was similar to that described in Ref. [22]. It provided sensitivity for ^{232}Th in this resolution mode of up to 2×10^8 counts $s^{-1}mg^{-1}l^{-1}$. The sample uptake rate was approximately 60–80 μl min^{-1}. Methane gas was added to the plasma to reduce the formation of molecular ions [23]. Oxide and hydride formation (monitored as UO^+/U^+ and UH^+/U^+ intensity ratios) were approximately 0.04 and 1×10^{-5}, respectively. Accurate mass calibration was performed using the $^{209}Bi^+$, $^{232}Th^+$, $^{235}U^+$, $^{238}U^+$, and $^{238}U^{16}O^+$ peaks. Two 1000 mg l^{-1} Th solutions "A" and "B" from two manufacturers, Inorganic Venture and Customer

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Grade (obtained from LGC Promochem AB, Borås, Sweden) were purchased. Complete elemental screening was performed on both solutions to assess the impurity concentration levels.[1] The following concentrations, expressed as ppm of the Th concentration, of certain trace elements that can potentially give rise to spectrally interfering molecular species were measured:

A: U 80, Bi 0.01, Pb 0.2, Hg 0.03, Au 0.0004, Os 0.005, Hf 0.02, Dy 7, Ce 0.7, La 0.4, Ba 0.2, Cs 0.2, I 1.0, Te 0.5 B 3, Be 0.03.

B: U 2200, Bi 14, Pb 300, Hg 0.2, Au 0.006, Os 0.000, Hf 0.02, Dy 0.7, Ce 8, La 14, Ba 14, Cs 0.2, I 35, Te 0.5 B 3, Be 0.4.

The solutions were analyzed during three separate sessions: May 25 (run I), October 5 (run II), and November 6 (run III), 2005. A range of about 0.2 u, divided to 60 channels, was scanned in each measured spectrum. During the first session, masses from 210 to 269 were analyzed with an integration time of 0.6 s per channel. During the second and third sessions, selected mass regions, where some indication of unidentified signals had been detected, were measured using an integration time of 3 and 12 s per channel, respectively. Instrumental sensitivity varied significantly among runs as a result of matrix effects caused by the introduction of highly concentrated solutions into the ICP source. During the first session, solution A, diluted to 20 mg Th l^{-1}, was scanned once. During the second session, solutions A and B at 20 mg l^{-1} of Th, spiked with 2 μg l^{-1} Bi, were studied and each solution was measured three times. In the last session, the Th concentration was increased to 50 mg l^{-1}, and each solution was measured twice. Altogether, eleven spectra were taken with the Th solutions for each mass number studied. Replicate analyses of blank solution (0.14 M HNO_3) were performed. Very few events appeared in the blank measurements and no event appeared at masses corresponding to atomic species. An example of such a spectrum is given below in Fig. 3(a).

Figure 1 shows summed spectra of six measurements performed during the second session in the regions of the $^{209}Bi^+$, $^{230}Th^+$, and $^{238}U^{16}O^+$ peaks. The results show an accuracy of the mass calibration of approximately 0.002 u, using the $^{209}Bi^+$ peak for on-line adjustment of the mass calibration. However, shifts of up to about 0.025 u were sometimes seen in the measurements. These shifts were sometimes corrected by using known peaks in the spectra. The maximum correction that was applied to the data presented in this paper was 0.013 u. The full width at half maximum (FWHM) of the peaks is about 0.030 u.

The results for masses 211, 213, 217, and 218 are given below. Two spectra are given for each mass number. The first is the "best" of the individual measured spectra and the second is the sum of several spectra with events that fit, within experimental uncertainty, the known mass of the corresponding Th isotopes [21] (which were deduced from nuclear reactions and radioactive decay measurements). All

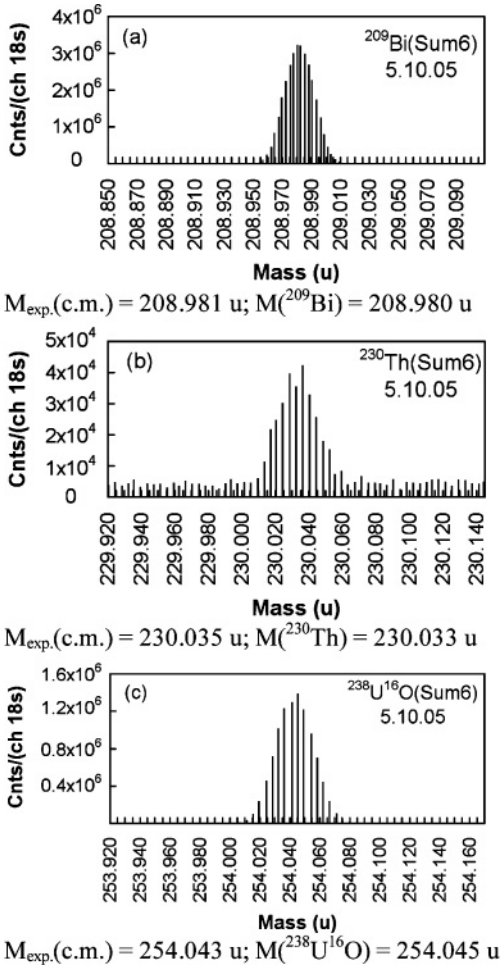

FIG. 1. Results of mass measurements on ^{209}Bi, ^{230}Th, and $^{238}U^{16}O$ obtained in run II. The sum of six measurements, three with solution A and three with solution B, are displayed. $M_{exp.}$—observed mass position; $M(^AZ)$, $M(^{A1}Z1^{A2}Z2)$—known mass of the atom or molecule taken from Ref. [21].

the individual spectra with events that fit the masses of the various Th isotopes are given in [24].

Figure 2 shows the results for mass 211. In Fig. 2(a), three (or potentially four) events are seen at a mass that corresponds to the known mass of ^{211}Th. The sum of two spectra is shown in Fig. 2(b). In addition to the peaks of $^{179}Hf^{16}O_2$ and $^{207}Pb^4He$,[2] a group of five (or six) events is seen at a mass that fits the known mass of ^{211}Th.

In Fig. 3, the results for mass 213 are given. Figure 3(a) shows a spectrum obtained with a blank solution. Only one event is seen in this spectrum. In Fig. 3(b), a group of four events is seen at a mass that fits the known mass of ^{213}Th. The sum of five spectra is seen in Fig. 3(c). In addition to $^{197}Au^{16}O$, a group of nine events is seen at the mass of ^{213}Th.

Figure 4 shows the results for mass 217. In Fig. 4(a), a group of six events is seen at a mass that fits the known mass of ^{217}Th. The sum of eight spectra is given in Fig. 4(b). A cluster of 15 events is seen at the mass of ^{217}Th. In addition

[1]The concentration level of various impurities might be different in different batches from the same manufacturer.

[2]The carrier gas was Ar which may contain traces of He.

to this group, six counts were seen at a higher mass around 217.060 u. However, they appeared in only one of the six spectra measured in run II [24]. We assume that they may be due to accidental ion scattering.

Figure 5 presents the results obtained for mass 218. A group of five events at the known mass of ^{218}Th is seen in Fig. 5(a). The sum of four spectra is given in Fig. 5(b). Two groups due to molecular ions and one group of 13 events at the mass of ^{218}Th are seen in this spectrum.

Altogether 42 events were seen in 19 measured spectra at masses of ^{211}Th, ^{213}Th, ^{217}Th, and ^{218}Th. The statistical significance of the newly detected peaks, that fit the known masses of the corresponding Th isotopes, was calculated as follows: The probability $P'_{\text{acc.}}$ that n out of a total number of N randomly distributed counts will occur accidentally in a small mass region r out of a total mass region R is given by [25]

$$P'_{\text{acc.}} = \binom{N}{n}(r/R)^n(1-(r/R))^{(N-n)}. \quad (1)$$

The total probability that such a group will occur accidentally in a predefined region r out of a total region R is given by

$$P_{\text{acc.}} = P'_{\text{acc.}}(r/R) \quad (2)$$

The values of $P_{\text{acc.}}$ were calculated for the data presented in the individual spectra in Figs. 2–5. The value of R was chosen as the whole measured region. Some of the events in R (outside of r) might be due to known molecular ions. We conservatively included them in these estimates.

The results are summarized in Table I. Column 2 gives the number of events that fit within the experimental uncertainties the known masses of the corresponding Th isotopes. Column 3 gives the number of measurements where these events were seen. $P_{\text{acc.}}$ values are given in column 4. In column 5, the average of the measured masses of the observed events is given. In making these averages, some corrections of up to 0.013 u, deduced from known masses of identified molecular ions, were applied. These corrections were made separately for each spectrum [24]. Column 6 gives the experimentally known g.s. masses [21] of the Th isotopes with the same mass numbers. It should be mentioned that the events assigned to a particular mass in the different experiments always occurred within the measured FWHM of 0.030 u.

TABLE I. Summary of results of mass measurements and comparison with the known masses of the various Th isotopes.

Mass number	No. of events	No. of meas.	$P_{\text{acc.}}$	$M_{\text{exp.}}$[a] (average)	$M_{\text{g.s.}}$ of Th isotope[b]
211	5	2	5×10^{-4}	211.021	211.015
213	9	5	6×10^{-7}	213.012	213.013
217	15	8	9×10^{-7}	217.018	217.013
218	13	4	6×10^{-6}	218.021	218.013

[a]The uncertainties in mass are estimated to be ±0.015 u.
[b]Reference [21].

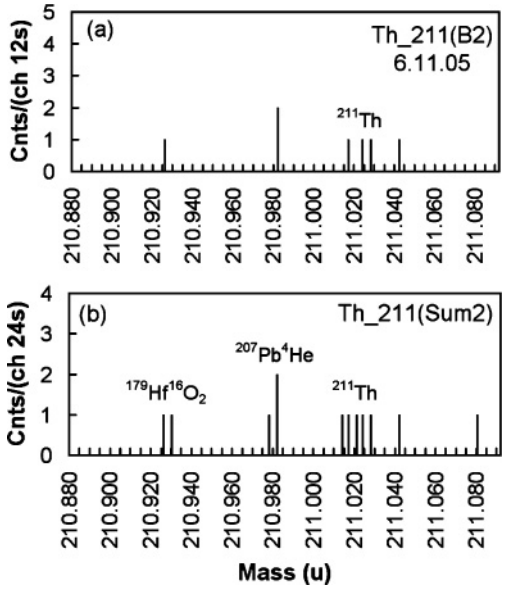

FIG. 2. Results of measurements for mass region 211. (a) shows the results obtained in run III, solution B, second measurement. The sum of two spectra is displayed in (b): run III, solution B, first measurement; run III, solution B, second measurement.

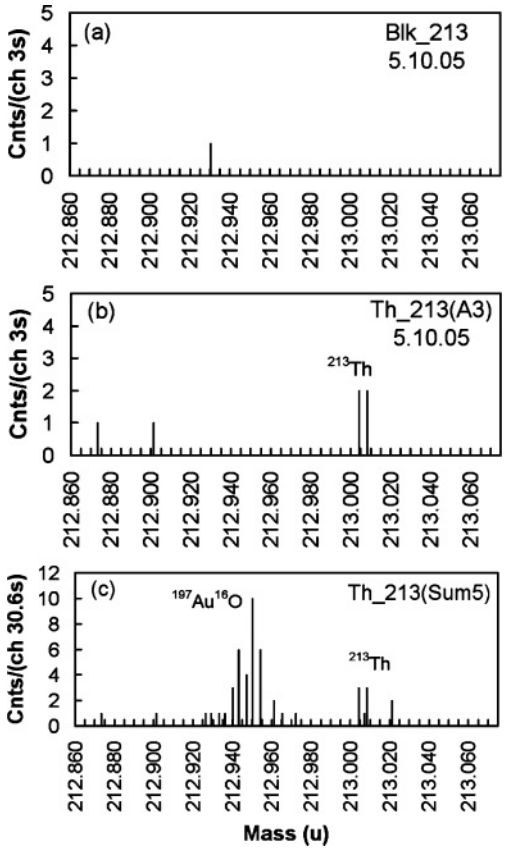

FIG. 3. Results of measurements for mass region 213. (a) shows the results with a blank solution. (b) gives the results obtained in run II, solution A, third measurement. The sum of five spectra is displayed in (c): run I, solution A; run II, solution A, third measurement; run II, solution B, second measurement; run III, solution A, first measurement; run III, solution A, second measurement.

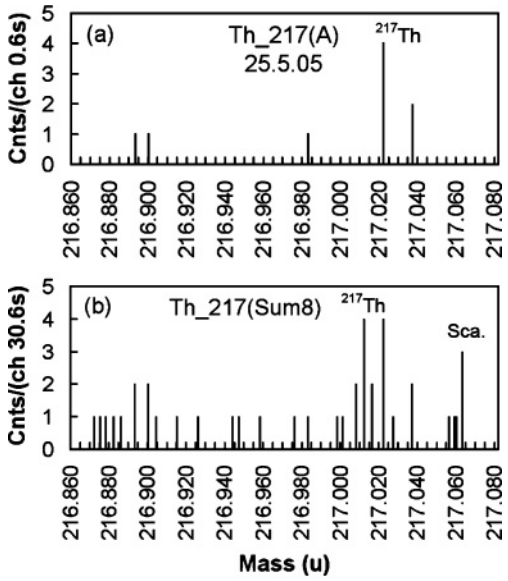

FIG. 4. Results of measurements for mass region 217. (a) gives the spectrum obtained in run I, solution A. The sum of eight spectra is displayed in (b): run I, solution A; run II, solution A, three measurements; run II, solution B, three measurements; run III, solution A, second measurement. Sca—scattering peak.

As can be seen in column 4 of Table I, the $P_{acc.}$ values are very small. In particular, one should remember that these values were calculated for just one individual spectrum in each case. Since the observed groups repeated themselves several times, the probabilities that they are accidental are even smaller.

We were unable to match the new mass peaks with the masses of any known molecular ions. Usually, as mentioned above and seen in some of the plots, because of the binding energies of the nuclei, the masses of the molecular ions are lower than the masses of the new peaks reported here. One exception is the peak at mass 213.012 u in Fig. 3. This peak could be due to $^{209}Bi^{1}H_4$ which has the same mass. However, based on the $^{209}Bi^{1}H$ peak at 209.975 u seen in Fig. 2(c) of Ref. [24], the expected intensity of the BiH_4^+ peak is on the order of 1×10^{-14} counts. This cannot account for the nine events detected at mass 213.012 u. Another possibility that should be considered is the potential presence of hydrocarbon-based molecular ions from pump oils. Their typical masses are higher than and well separated from the masses of the new peaks seen here. For instance, the mass of $CH_3(CH_2)_{14}^+$ is 211.243 u [21], compared with the average mass of 211.021 u of the new peak in Fig. 2.

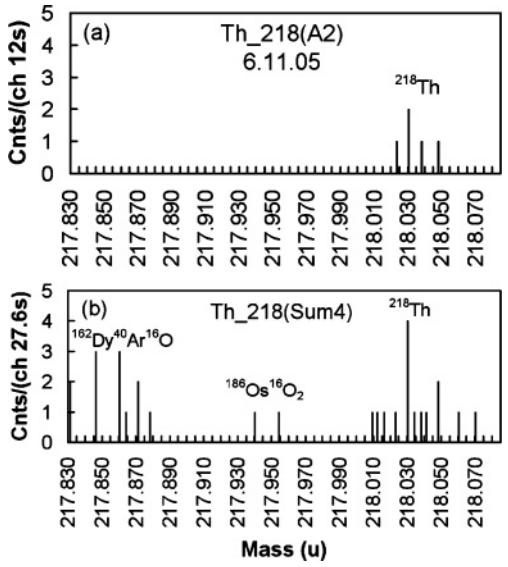

FIG. 5. Results of measurements for mass region 218. (a) shows the spectrum obtained in run III, solution A, second measurement. The sum of four spectra is displayed in (b): run I, solution A; run II, solution B, second measurement; run III, solution A, first measurement; run III, solution A, second measurement.

It is evident from the data in Table I that the average masses of all the measured peaks fit the known g.s. masses [21] of the Th isotopes to within 0.010 u. The observed masses could also fit the g.s. masses of corresponding (short-lived) isobars from U down to Pb. However, since the measured amounts of the various trace elements in the Th solutions, including those of U, Bi, Pb, and La-Te (the chemical homologues of Ac-Po), are very small, such correspondence would lead to unreasonably high abundances of the newly observed species.

As seen in Table I, some of the spectra (out of the 11 measured for each mass number) did not yield events for certain Th masses. This could be due to the extremely low counting rates and variations in the instrumental sensitivity as already mentioned. It is estimated that the concentration of these minor Th isotopes is $(1–10)\times10^{-11}$ of ^{232}Th (or about $(2–20)\times10^{-16}$ of the solutions).

The g.s. half-lives of these Th isotopes are very short, of the order of tens of ms to less than 1 μs [19]. This suggests that the observed events are due to previously unknown long-lived isomers of the Th isotopes. (The mass accuracy of the present experiment is not sufficient to determine the excitation energies of the isomeric states.) If their terrestrial concentration was initially similar to that of ^{232}Th, then the lower limit on their half-lives would be about 1×10^{8} y.

The character of the proposed isomeric states has not been directly measured. They cannot be high spin isomers that occur near doubly closed shells, like for instance the 9^- isomeric state in ^{210}Bi with a half-life of 3.0×10^{6} y, or the (18^+) 45.1 s state in ^{212}Po [19], since they are far from doubly closed shells. (The half-life of the isomeric state in the neutron closed shell nucleus ^{216}Th is 180 μs [19].) Nor are they related to the fission isomers found in actinides [5,7], since the lifetimes of the latter are in the region of ns to ms. They could be high spin K-type isomers [16], of which hundreds are known. However, the lifetimes of almost all K-type isomers, except for the isomer of ^{180}Ta mentioned earlier, are short compared to 1×10^{8} y. (The lifetimes of all known isomeric states in neutron-deficient nuclei with $Z \geqslant 84$ are not longer than several minutes.) One can hypothesize that the proposed isomeric states are aligned high spin SD and/or HD isomeric states like those mentioned above [1–4], where the high spin, the barriers between the various minima of the potential-energy surfaces and the unusual radioactive decay properties contribute to their long lifetimes.

High spin states in general and these kinds of states in the SD and HD minima in particular are preferentially produced by heavy ion reactions [4,14]. If the observed states turn out to be of the high spin SD and/or HD type, then heavy ion reactions could be involved in their nucleosynthesis.

In summary, data were presented that suggest the existence of long-lived isomeric states with $t_{1/2} \geqslant 1 \times 10^8$ y in the neutron-deficient isotopes ^{211}Th, ^{213}Th, ^{217}Th, and ^{218}Th. The hypothesis that they are high spin SD and HD isomeric states is discussed. The discovery of such nuclides in natural (nonirradiated) Th would lend independent support for the recently proposed coherent description of previously unexplained radioactivities [18] by such isomeric states.

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