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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE New Reprint	3. DATES COVERED (From - To) -
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4. TITLE AND SUBTITLE Optical spectroscopy of an atomic nucleus: Progress toward direct observation of the 229Th isomer transition	5a. CONTRACT NUMBER W911NF-11-1-0369
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 1D10BP

6. AUTHORS Wade G. Rellergert, Scott T. Sullivan, David DeMille, Robert A. Jackson, Eric R. Hudson, Justin R. Torgerson, Richard R. Greco, Markus P. Hehlen	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of California - Los Angeles Office of Contract and Grant Administration 11000 Kinross Avenue, Suite 211 Los Angeles, CA 90095 -1406	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 60694-PH.1

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
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15. SUBJECT TERMS
nuclear clock, crystal growth, crystal doping, thorium

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Eric Hudson
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 310-825-5224

Report Title

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REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 60694.1-PH

Optical spectroscopy of an atomic nucleus: Proç..

Block 13: Supplementary Note

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Optical spectroscopy of an atomic nucleus: Progress toward direct observation of the ^{229}Th isomer transition

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ARTICLE INFO

Available online 28 September 2011

Keywords:

Vacuum ultraviolet luminescence spectroscopy
Nuclear isomer
Nuclear clock
Thorium isomer transition
Fluoride crystal

ABSTRACT

The nucleus of the thorium 229 isotope possesses a first excited nuclear state ($^{229\text{m}}\text{Th}$) at an exceptionally low energy of 7.8 ± 0.5 eV above the nuclear ground state ($^{229\text{g}}\text{Th}$), as determined by earlier indirect measurements. This is the only nuclear excited state known that is within the range of optical spectroscopy. This paper reports progress toward detecting the $^{229\text{m}}\text{Th}$ state directly by luminescence spectroscopy in the vacuum ultraviolet spectral region. The estimated natural linewidth of the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ isomer transition of $2\pi \times 0.1$ to $2\pi \times 10$ mHz is expected to broaden to ~ 10 kHz for $^{229}\text{Th}^{4+}$ doped into a suitable crystal. The factors governing the choice of crystal system and the substantial challenges in acquiring a sufficiently large quantity of ^{229}Th are discussed. We show that the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition energy can be identified to within 0.1 nm by luminescence excitation and luminescence spectroscopy using the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. This would open the door for subsequent laser based measurements of the isomer transition and future applications of ^{229}Th in nuclear clocks. We also show that ^{233}U doped materials should produce an intrinsic, continuous, and sufficiently high rate of $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence and could be a useful aid in the initial direct search of the isomer transition.

Published by Elsevier B.V.

1. Introduction

Optical absorption and emission phenomena are commonly associated with excitation and relaxation processes of the electronic and/or vibrational systems of a material. The respective electromagnetic radiation is non ionizing and involves the ultraviolet, visible, and infrared spectral regions. In contrast, excitation and relaxation processes in atomic nuclei occur at much higher energies and involve ionizing radiation in the X ray and gamma ray regions. Nuclear energy levels are spaced by many keV, and even the lowest nuclear excited state energy is usually much greater than 1 keV [1]. There are only two known exceptions: the first nuclear excited state of ^{235}U is at 76.5 eV ($\lambda = 16.2$ nm) and that of ^{229}Th is at 7.8 eV ($\lambda = 159$ nm) [1]. This makes ^{229}Th special among all isotopes, as its first nuclear excited state is within the reach of optical spectroscopy [2,3]. The natural spectral linewidth, Γ_n , of the transition between the nuclear ground state ($^{229\text{g}}\text{Th}$) and first excited state ($^{229\text{m}}\text{Th}$) has been predicted to be between

$2\pi \times 0.1$ and $2\pi \times 10$ mHz [2–4] and to broaden to ~ 10 kHz when ^{229}Th is doped into a suitable crystal [5]. The prospect of having such a narrow nuclear transition within the reach of modern laser technology has spurred substantial interest from both fundamental and applied research communities in recent years. One exciting potential application is the use of ^{229}Th to create a time standard by locking a femtosecond laser comb to the $^{229\text{g}}\text{Th} \rightarrow ^{229\text{m}}\text{Th}$ transition. Such a highly stable oscillator could enable a “nuclear clock” with a precision far exceeding that of the current best atomic clocks and allowing, for example, tests of general relativity and measurements of the variability of fundamental constants [6].

The 7.8 eV energy of the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition has been inferred only indirectly by high resolution gamma ray spectroscopy [7,16]. The next necessary step is to observe the transition directly by optical spectroscopy and to determine the transition energy with high precision. This however proves to be challenging because of the rarity of the ^{229}Th isotope, the short optical wavelength involved, and the low transition oscillator strength. This paper reviews the properties of ^{229}Th and reports on our experiments toward observing the ^{229}Th isomer transition directly by luminescence spectroscopy.

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2. The ^{229}Th isomer state a brief review

Nuclear excited states typically decay within sub nanoseconds to lower energy states. States with a decay constant greater than 10^{-9} s are considered metastable. They are referred to as nuclear isomers and the associated transitions to the ground state as isomer transitions. $^{229\text{m}}\text{Th}$ has a lifetime on the order of hours and falls in this class of metastable nuclear excited states. Fig. 1 illustrates the lowest few nuclear energy levels of ^{229}Th and, in particular, the $^{229\text{g}}\text{Th}$ ground state ($J^\pi=5/2^+$) and $^{229\text{m}}\text{Th}$ first excited state ($J^\pi=3/2^+$) that are of interest here [7]. Kroger and Reich first proposed a low energy nuclear excited state in ^{229}Th 35 years ago [8]. An indirect measurement by Helmer and Reich in 1994 estimated the $^{229\text{m}}\text{Th}$ energy to be 3.5 ± 1.0 eV [9]. The corresponding emission around 354 nm however could not be detected by several subsequent studies [10–13]. Beck et al. reported a more precise indirect measurement in 2007 [7]. They used a 254 μm thick electroplated film of ^{233}U to populate the ^{229}Th nuclear energy levels via $^{233}\text{U} \rightarrow ^{229}\text{Th} + ^4\text{He}$. The resulting gammas (see Fig. 1) were analyzed using the high resolution X ray spectrometer at the National Aeronautics and Space Administration (NASA), which consists of a 6×6 microcalorimeter array and offers a spectral resolution of ~ 26 eV (FWHM) at a 90 mK operating temperature [14,15]. A differencing technique was applied to place the $^{229\text{m}}\text{Th}$ energy at 7.6 ± 0.5 eV [7]. This value was updated to the currently accepted 7.8 ± 0.5 eV as a result of including the $42.43 \rightarrow ^{229\text{m}}\text{Th}$ branching ratio in the analysis [16]. This energy may also explain the failure of earlier studies to detect the emission from $^{229\text{m}}\text{Th}$ because of the unique and difficult experimental challenges with seeing the corresponding 159 nm light in the vacuum ultraviolet, a spectral range where many optical window materials absorb strongly and detectors may not be sensitive.

The natural linewidth, Γ_n , of the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition is estimated to be between $2\pi \times 0.1$ and $2\pi \times 10$ mHz [2–4]. Additional interactions have to be considered when doping ^{229}Th into a solid. The Hamiltonian for the ^{229}Th nucleus consists of a single particle term (\hat{H}_0), a fine structure term (\hat{H}_{FS}), and a hyperfine term (\hat{H}_{HFS}) [5]. In the absence of unpaired electrons, such as when doping $^{229}\text{Th}^{4+}$ into an ionic crystal, the fine structure term vanishes and we are concerned only with \hat{H}_{HFS} . We have carefully analyzed the first three terms of the multipole expansion of $\hat{H}_{HFS} = \hat{H}_{E0} + \hat{H}_{M1} + \hat{H}_{E2} + \dots$ [5]. They are an electric monopole term (\hat{H}_{E0}), a magnetic dipole term (\hat{H}_{M1}), and an electric

quadrupole term (\hat{H}_{E2}). The combined effects of these interactions in a solid manifest as both shifts in and spectral broadening of the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition. We estimate that \hat{H}_{E0} dominates the temperature dependent shift and \hat{H}_{E2} dominates the broadening of the transition. The magnitude of the \hat{H}_{E0} interaction depends on the temperature gradient across the sample, and it will contribute ~ 1 Hz to the linewidth for temperature gradients of < 0.1 mK. The \hat{H}_{E2} interaction is sensitive to the crystal structure, and its magnitude is minimized for host crystals with cubic or icosahedral symmetry [17]. It is further minimized if all $^{229}\text{Th}^{4+}$ ions substitute for the same crystallographic site in a crystal, i.e. inhomogeneous broadening is minimized. \hat{H}_{E2} is expected to cause $1-10$ kHz of broadening. Nevertheless, even when doped into a solid, the Q factor ($f/\Delta f$) of the ^{229}Th isomer transition is still large compared to any electronic transition.

3. Discussion of ongoing experiments

3.1. Acquisition of ^{229}Th

Thorium is an actinide element, and the most abundant isotope is ^{232}Th with a half life of 1.4×10^{10} years [1]. In contrast, the $A=229$ isotope of thorium has no natural abundance and is produced almost exclusively by the α decay of ^{233}U (1.592×10^5 years half life [1]), which is in itself rare and highly controlled as a Special Nuclear Material. The ^{229}Th isotope has a half life of 7880 years and decays exclusively by α decay to ^{225}Ra [1]. ^{229}Th is therefore extraordinarily difficult to acquire in any useful quantity. This represents the single greatest obstacle for advancing any studies and applications of the ^{229}Th isomer. A viable yet highly complex route is the chemical extraction of ^{229}Th from decades old ^{233}U samples, in which the α decay has produced a worthwhile quantity of ^{229}Th . A 50 year old ^{233}U sample, for example, will have acquired ~ 300 ppm of ^{229}Th by α decay of ^{233}U . Processing 1 kg of such old ^{233}U would yield ~ 300 mg of ^{229}Th , enough to dope almost 100 crystals of 1 cm^3 volume with an ion density of 10^{19} ^{229}Th nuclei/ cm^3 (assuming 100% yield). The process would involve dissolving the ^{233}U in acid, performing ion exchange to extract the ^{229}Th from the solution, recovering and reconvert the excess ^{233}U for storage, eluting the ^{229}Th from the ion exchange column, and converting it to $^{229}\text{ThF}_4$ for use in subsequent fluoride crystal growth.

3.2. ^{229}Th doped crystals

We have shown in Section 2 that the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition retains much of its “free atom” properties even when ^{229}Th is exposed to the various interactions present in a crystalline solid. This gives us confidence that a ^{229}Th doped crystal can be used for the direct measurement of the isomer transition. This is critical, because a doped crystal can offer ^{229}Th densities on the order of 10^{19} ^{229}Th nuclei/ cm^3 , which is much greater than the $< 10^8$ ^{229}Th nuclei that can be trapped by laser cooling of ^{229}Th atoms [6,18]. As a result, absorption and emission rates for the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition can be much higher in a ^{229}Th doped crystal and thus greatly facilitate the direct observation of the transition.

Several factors guide the choice of crystalline host for ^{229}Th . First, the crystal has to be sufficiently transparent in the vacuum ultraviolet spectral region so that the ^{229}Th ions can be excited by an external light source and the $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence can emerge from the crystal. The band gap energy is to a large extent determined by ΔEN , the difference in the Pauling electronegativity of the cation and anion. Fig. 2 shows the band gap energy as a function of ΔEN for a wide range of binary metal oxides, metal

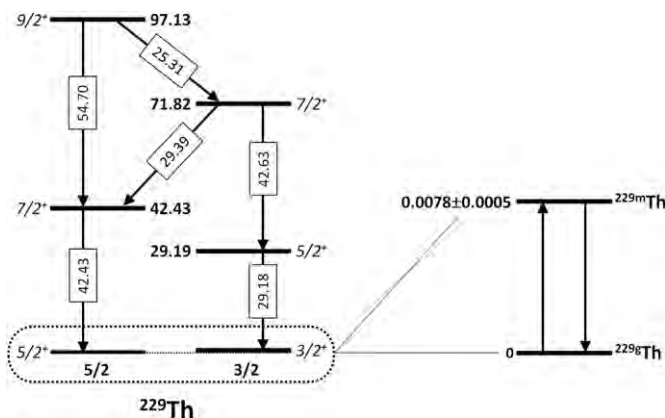


Fig. 1. Partial energy level scheme of the nuclear states of ^{229}Th , adapted from Beck et al. [7] in units of keV. Beck et al. measured the transition energies indicated in the left scheme and derived an energy of 7.8 ± 0.5 eV for the nuclear isomer state [7,16]. The scheme on the right shows the nuclear ground state ($^{229\text{g}}\text{Th}$) and the isomer state ($^{229\text{m}}\text{Th}$) along with the associated isomer transitions in absorption and luminescence relevant to the present discussion.

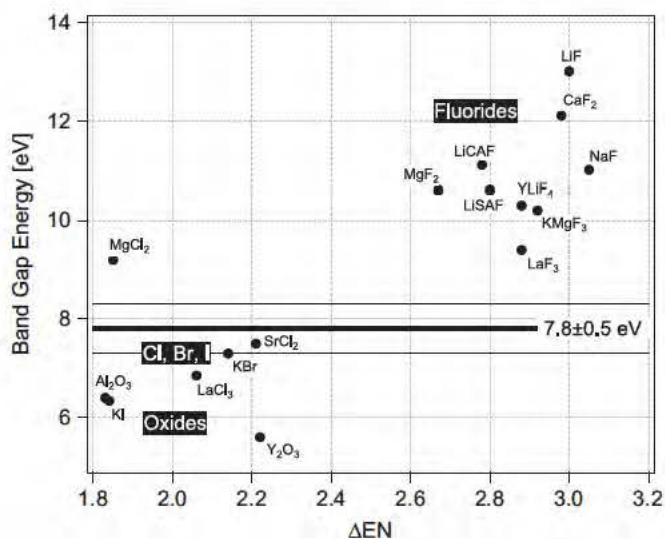


Fig. 2. Band gap energies of a range of oxide and halide materials as a function of the difference in the Pauling electronegativity between the respective cation and the anion. The 7.8 ± 0.5 eV energy of the ^{229}Th isomer transition is indicated. The family of fluorides is most likely to offer crystalline hosts with a band gap energy greater than the isomer transition energy.

chlorides, and metal fluorides. The large electronegativity of the fluoride ion causes the band gap energies of metal fluorides to be well above 8 eV, while the band gap energy for oxides and chlorides is typically < 8 eV. Crystal hosts that are transparent to the 7.8 eV light of the $^{229}\text{mTh} \rightarrow ^{229}\text{gTh}$ emission are therefore most likely to be found in the extensive family of fluoride crystals.

A second consideration is that the crystal has to accept Th^{4+} ions into a single well defined crystallographic site in order to minimize inhomogeneous broadening. Candidate crystal systems include Na_2ThF_6 , LiCaAlF_6 (LiCAF), LiSrAlF_6 (LiSAF), YLiF_4 (YLF), and CaF_2 . LiCAF is emerging as the leading candidate in our recent studies [19]. All spins in LiCAF are paired, and the crystal has good transparency for wavelengths down to 110 nm. Th^{4+} can enter the LiCAF crystal by substituting on the Li^+ , Ca^{2+} , or Al^{3+} site with a range of possible charge compensation arrangements. Jackson et al. have calculated the solution energies of 24 different charge compensated Th^{4+} sites and found that the energetically most favored arrangement involves placing Th^{4+} on the Ca^{2+} site with accompanying F interstitial vacancy compensation [20]. The LiCAF and LiSAF structures are isomorphous and belong to the trigonal space group $P\bar{3}1c$. All metal ions have an octahedral coordination with six fluoride ions, which in the case of the Ca^{2+} is trigonally elongated along the c axis to give the Ca^{2+} site a D_{3d} symmetry [21]. The near octahedral coordination of Th^{4+} on the Ca^{2+} site tends to minimize undesired electric field gradient effects on the $^{229}\text{mTh} \leftrightarrow ^{229}\text{gTh}$ linewidth. We have achieved a ^{232}Th (natural thorium isotope) doping of 0.1% in LiCAF and have measured a < 30 kHz background fluorescence rate from the crystal under excitation in the 6–9 eV range at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory [19]. The background fluorescence rate in LiCAF is sufficiently low and is expected to enable a future observation of the $^{229}\text{mTh} \rightarrow ^{229}\text{gTh}$ emission with a signal to noise ratio of 30:1 during an 8 h shift at the ALS.

A third consideration is the ability to grow a ^{229}Th doped crystal with high quality and purity. Transition metal ions such as V, Cr, Mn, Fe, Co, and Ni as well as oxygen based impurities such as oxides, hydroxides, and oxyfluorides have spectrally broad absorptions in the VUV and can lead to absorption coefficients of up to 0.1 cm^{-1} at ppm impurity levels [22].

These impurities could interfere with the VUV excitation and emission and have to be minimized during crystal growth. LiCAF can be grown by both the Bridgman and Czochralski methods [23,24], the latter being the more common approach. The Bridgman method contains the melt inside a crucible which is slowly lowered through a temperature gradient to induce crystal growth from the bottom up. The Czochralski method contains the melt in a stationary crucible from which a crystal is grown by slowly pulling up an initial seed crystal under rotation. The Bridgman method appears to be more favorable in view of the extreme rarity of the ^{229}Th isotope because it makes optimal use of the available melt.

Na_2ThF_6 is another crystal host that is currently under consideration. It belongs to the extensive family of hexafluoro metallates, A_2MF_6 , which typically contain MF_6^{2-} octahedral units. In some Hf^{4+} and Zr^{4+} [25,26], but more commonly with Th^{4+} and U^{4+} [27–29], the metal ion acquires a 9 fold coordination in a trigonal tri capped prism geometry, such as in the case of Na_2ThF_6 . The usual β Na_2ThF_6 phase, which is twinned in space group $P321$ ($Z=1$) [30], has a single site for Th^{4+} and, in contrast to LiCAF, LiSAF, YLF, and CaF_2 , does not require charge compensation when doping $^{229}\text{Th}^{4+}$. This would allow even higher ion densities because ^{229}Th could be doped stoichiometrically into a crystal of the natural isotope, $\text{Na}_2^{232}\text{ThF}_6$. Crystals can be grown in several cm^3 size by the Czochralski method [31]. We observed background fluorescence rates of up to 300 kHz for a $\text{Na}_2^{232}\text{ThF}_6$ crystal under VUV excitation at the ALS, a rate that may still be sufficiently low for detecting $^{229}\text{mTh} \rightarrow ^{229}\text{gTh}$ emission in a future ^{229}Th doped crystal [19]. The $\text{Na}_2^{232}\text{ThF}_6$ crystal also showed some VUV induced radiation damage, which may have been in part due to residual impurities.

3.3. Isomer luminescence spectroscopy

The present uncertainty in the isomer energy corresponds to finding a ~ 10 kHz wide spectral line in a $\sim 2 \times 10^{14}$ Hz frequency range. The direct search of the isomer transition, therefore, has to proceed in several steps of increasing spectral resolution. Once a ^{229}Th doped crystal is available, the first experiment will be luminescence excitation spectroscopy of the $^{229}\text{gTh} \rightarrow ^{229}\text{mTh}$ absorption using the VUV beam available at the ALS. It has a spectral linewidth of 0.175 eV and delivers a flux of 10^{16} photons/s in a $170 \times 50 \mu\text{m}^2$ cross sectional area. The ALS center frequency will be scanned across the 7.8 ± 0.5 eV range in steps of 0.05 eV. At each ALS frequency, the sample will be illuminated for 200 s followed by the collection of the total VUV luminescence for 100 s. The long ^{229}mTh lifetime may lead to accumulation of population in the isomer state during the experiment and distort the pure Lorentzian lineshape of the transition. The magnitude of this saturation effect depends on the exact value of the ^{229}mTh lifetime and the ALS scan rate, and it will have to be established by experimentation.

We estimate a fluorescence rate of ~ 1 MHz when the ALS beam is in resonance with the $^{229}\text{gTh} \rightarrow ^{229}\text{mTh}$ absorption. Compared to the measured < 30 kHz background luminescence of LiCAF, this will enable measurement of the $^{229}\text{gTh} \rightarrow ^{229}\text{mTh}$ luminescence excitation spectrum with a signal to noise ratio of at least 30:1. This measurement would narrow the current energy uncertainty by ~ 6 fold and identify the isomer transition wavelength within ~ 3.5 nm. A subsequent experiment will use the ALS beam to excite the sample on resonance and measure the $^{229}\text{mTh} \rightarrow ^{229}\text{gTh}$ luminescence spectrum with a VUV spectrometer. We expect to narrow the isomer transition wavelength to within 0.1 nm, a precision that is sufficiently high for subsequent laser based experiments to begin.

3.4. ^{233}U doping an alternative approach

The difficulty in acquiring useful quantities of ^{229}Th led us to explore a parallel approach to directly observing the $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence. The α decay of ^{233}U produces excited ^{229}Th nuclei that subsequently relax by emission of gamma rays. While this gamma decay sequence ultimately leaves the nucleus in the $^{229\text{g}}\text{Th}$ ground state, a portion of the gamma decay sequence branches into the $^{229\text{m}}\text{Th}$ isomer state. Therefore, a ^{233}U doped crystal should provide a continuous source of excited $^{229\text{m}}\text{Th}$ nuclei and thereby produce a continuous rate of $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence. A 1 cm^3 crystal doped with 10^{19} ^{233}U nuclei will produce an initial $^{233}\text{U} \rightarrow ^{229}\text{Th}$ decay rate of $\sim 2 \times 10^6\text{ s}^{-1}$, of which $\sim 2\%$ will populate the $^{229\text{m}}\text{Th}$ isomer state [32]. Assuming an optical capture efficiency of 0.5% this would yield a measured $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence rate of $\sim 10^2\text{ s}^{-1}$.

This approach has two main advantages. First, it does not require any ^{229}Th starting material for the initial growth of the crystal. Second, because excited $^{229\text{m}}\text{Th}$ nuclei are being produced by the intrinsic gamma decay sequence, no external VUV excitation source is required. This would allow luminescence measurement times to be significantly extended beyond the 8 h shifts typical for a facility like the ALS, allowing more accurate measurement of the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition energy with a VUV spectrometer. This potential advantage may be offset by the estimated $\times 10^4$ times lower luminescence rate ($\sim 10^2\text{ s}^{-1}$) compared to using the ALS beam on resonance in a ^{229}Th doped crystal (10^6 s^{-1} , see Section 3.3).

There are however a number of disadvantages with this approach. First, uranium can occur in different oxidation states such as U^{3+} , U^{4+} , and U^{6+} when doped into a solid. U^{3+} and U^{4+} have partially filled 5f shells and exhibit strong absorption in the visible and UV spectral regions due to allowed $5f^3 \rightarrow 5f^26d$ and $5f^2 \rightarrow 5f6d$ transitions, respectively [33]. These transitions may cause excessive reabsorption of the VUV photon emitted by the $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ isomer transition and reduce the observable luminescence rate. The closed shell U^{6+} would not suffer from this issue, and crystalline $^{233}\text{UF}_6$ may be a candidate for such an experiment. Second, the $^{233}\text{U} \rightarrow ^{229}\text{Th}$ decay produces an α particle with an energy of 5.168 MeV. This has two consequences. The α particle will cause excitation as it dissipates its kinetic energy, resulting in scintillation light that may lead to an excessive background signal [12]. The scintillation however will be spectrally broad and can be distinguished from the isomer transition in a VUV fluorescence spectrum. The other, potentially more problematic effect is that the ^{229}Th nucleus recoils upon α decay and will be physically displaced within the crystal. The recoil energy of the ^{229}Th nucleus is 90.3 keV and, from Monte Carlo simulations, we expect the ^{229}Th nucleus to travel $\sim 34\text{ nm}$ through LiCAF. This will likely produce different final sites for the $^{229\text{m}}\text{Th}$ nuclei, each site having an individual shift and broadening of the $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ isomer transition. As a result, ^{229}Th recoil is expected to cause inhomogeneous broadening of the isomer transition and thereby limit the level of precision to which the transition energy can be determined in a ^{233}U doped crystal. Third, the ^{233}U approach is not amenable to luminescence excitation spectroscopy or locking a femtosecond laser comb to the $^{229\text{g}}\text{Th} \rightarrow ^{229\text{m}}\text{Th}$ absorption because essentially no thorium atoms are available in the ^{233}U doped crystal. Therefore, any future studies geared toward using the $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ transition in a “nuclear clock” application will still require a ^{229}Th doped crystal.

4. Conclusions

The $^{229\text{g}}\text{Th} \leftrightarrow ^{229\text{m}}\text{Th}$ isomer transition is highly decoupled from the local environment around ^{229}Th , and its linewidth is

expected to broaden to only $\sim 10\text{ kHz}$ even when ^{229}Th is doped into a solid. The respective Q factor significantly exceeds that of any electronic transition and is poised to enable a new class of nuclear clocks with unprecedented precision. A ^{229}Th doped crystal offers ion densities of $\sim 10^{19}$ ^{229}Th nuclei/ cm^3 and can produce sufficiently high $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence rates under excitation with a VUV source such as the ALS. Our preliminary studies find LiCAF to be an attractive crystalline host for ^{229}Th . It has a high band gap energy, can incorporate ^{229}Th into a well defined charge compensated site with near octahedral symmetry, and shows relatively low intrinsic background fluorescence under VUV illumination. We estimate that the isomer transition can be identified to within 3.5 nm from a first luminescence excitation spectrum and to 0.1 nm from a subsequent VUV luminescence spectrum using a ^{229}Th doped LiCAF crystal on the ALS. The substantial challenges in acquiring a useful quantity of ^{229}Th are currently the single greatest obstacle for advancing any studies and applications of the ^{229}Th isomer. We also showed that ^{233}U doped materials should produce an intrinsic, continuous, and sufficiently high rate of $^{229\text{m}}\text{Th} \rightarrow ^{229\text{g}}\text{Th}$ luminescence and could be a useful aid in the initial direct search of the isomer transition.

Acknowledgments

The ALS is supported by the US DOE under Contract no. DE AC0205CH11231. This work was supported by UCLRP Grant no. 09 LR 04 120497 HUDE and the Los Alamos National Laboratory LDRD program. UCLA also acknowledges support from DARPA and the ARO under grant no. W911NF 11 1 0369. UCLA also acknowledges support from DARPA and the ARO under grant no. W911NF 11 1 0369.

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