X-ray pumping of the $^{229}$Th nuclear clock isomer

Takahiko Masuda, Akihiro Yoshimi, Akira Fujieda, Hiroyuki Fujimoto, Hiromitsu Haba, Hideaki Hara, Takahiro Hiraki, Hiroyuki Kaino, Yoshitaka Kasamatsu, Shinji Kitao, Kenji Konashi, Yuki Miyamoto, Koichi Okaï, Sho Okubo, Noboru Sasao, Makoto Seto, Thorsten Schumm, Yudai Shigekawa, Kenta Suzuki, Simon Stellmer, Kenji Tamasaku, Satoshi Uetake, Makoto Watanabe, Tsukasa Watanabe, Yuki Yasuda, Atsushi Yamaguchi, Yoshitaka Yoda, Takuya Yokokita, Motohiko Yoshimura & Koji Yoshimura

The metastable first excited state of thorium-$^{229}$, $^{229}$mTh, is just a few electronvolts above the nuclear ground state and is accessible by vacuum ultraviolet lasers. The ability to manipulate the $^{229}$Th nuclear states with the precision of atomic laser spectroscopy opens up several prospects, from studies of fundamental interactions in physics to applications such as a compact and robust nuclear clock. However, direct optical excitation of the isomer and its radiative decay to the ground state have not yet been observed, and several key nuclear structure parameters—such as the exact energies and half-lives of the low-lying nuclear levels of $^{229}$Th—remain unknown. Here we present active optical pumping into $^{229}$mTh, achieved using narrow-band 29-kiloelectronvolt synchrotron radiation to resonantly excite the second excited state of $^{229}$Th, which then decays predominantly into the isomer. We determine the resonance energy with an accuracy of 0.07 electronvolts, measure a half-life of 82.2 picoseconds and an excitation linewidth of 1.70 nanoelectronvolts, and extract the branching ratio of the second excited state into the ground and isomeric state. These measurements allow us to constrain the $^{229}$mTh isomer energy by combining them with $\gamma$-spectroscopy data collected over the past 40 years.

The isomeric state $^{229}$mTh has fascinated the scientific community for decades because its energy is expected to be only a few electronvolts away from the nuclear ground state, making it laser-accessible and the lowest-energy nuclear excited state reported so far. Although the optical excitation from the ground state to $^{229}$mTh has not yet been achieved experimentally, it is expected to be used as a new platform for a variety of investigations. One important application is an ultra-precise clock; such a ‘nuclear clock’ may reach a fractional uncertainty of about $10^{-17}$, which is accurately enough to enable direct excitation by a narrow-band laser. Recent experiments, however, have gradually constrained the possible value of $E_{\gamma}$. A $\gamma$-ray spectroscopy measurement using a high-resolution crystal calorimeter reported $E_{\gamma} = 7.8 \pm 0.5$ eV (the uncertainty indicates one standard deviation), which was obtained as a difference of $\gamma$-ray energies from excited states of $^{229}$Th (including the second excited state). More recently, an electronic decay channel of the isomeric state was observed by detecting electrons produced through an internal conversion process, producing the result $12.6$ eV $< E_{\gamma} < 18.3$ eV. An improved value of $8.28 \pm 0.17$ eV was reported recently. All these investigations used the $\alpha$ decay of $^{233}$U to produce $^{229}$mTh. Several experiments attempted a direct optical excitation with broadband synchrotron radiation of about 7.8 eV, but all gave null results, suggesting that $E_{\gamma}$ or the half-life of the isomeric state might lie outside the expected range.

In this Letter, we report the direct optical X-ray excitation of $^{229}$Th to the second excited state (29-keV level; Fig. 1) and determine its key nuclear parameters, such as its excitation energy $E_{2nd}$, half-life $T_{1/2}$, and the excitation linewidth of the cross-band transition, $\Gamma_{ee}$. A large fraction (about 58%; see Methods) of the 29-keV-level population decays quickly (in about 100 ps) into the isomeric state, thus realizing active pumping into the isomeric state.

Prior to this work, the energy of the 29-keV level was known only to within a few electronvolts $^{8,9}$. To excite the $^{229}$Th nucleus to that level using a narrow-band X-ray source, the resonance energy must be determined more accurately; thus, the energy of the X-ray source is scanned for the nuclear resonance. Once the nucleus is excited to the 29-keV level, it decays either to the isomeric state or to the ground state, predominantly via an internal conversion process, on the timescale of the half-life. Subsequently, various characteristic X-rays are emitted, among which the L-shell lines are detected as the signal. Enhancement of this signal indicates that the incident X-ray energy is at the resonance.

Conceptually, this approach is identical to nuclear resonant scattering (NRS) $^{22}$. The present experiment, however, requires several refinements to account for the short half-life (about 100 ps; the shortest half-life ever measured in NRS experiments) and the extremely small signal-to-background ratio (about $10^{-6}$) due to the narrow excitation linewidth of the 29-keV level. A state-of-the-art detector system specifically developed for this experiment and an enhanced luminosity, achieved by using a small beam spot and a small target, were crucial for the success of the measurement.

The experiment was carried out at the BL19LXU beamline of SPring-8 $^{23}$. Schematic drawings of the beamline and setup are shown in Fig. 2. The high-brilliance X-ray beamline starts with a 27-m-long undulator. The X-ray photons produced are monochromatized with two pairs of Si crystals, Si(111) and Si(440), inserted in series into the beamline. The intensity and full-width-at-half-maximum (FWHM) bandwidth after Si(440) are approximately 4 $\times 10^{12}$ photons per second and 0.26 eV, respectively. After identifying the resonance, the second monochromator is replaced by Si(660), which reduces the bandwidth to 0.10 eV. A system of compound refractive X-ray lenses $^{24}$ is used to focus the beam to a spot size of 0.15 $\times$ 0.065 mm$^2$ at the focal point, which is about 14 m downstream from the device, with a transmission of about 67%. The X-ray beam is a pulse train, with pulses separated by 23.6 ns and pulse duration of 40 ps. Typical properties of the monochromators and the 29-keV target are summarized in Table 1.

---

1Research Institute for Interdisciplinary Science, Okayama University, Okayama, Japan. 2National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan. 3RIKEN, Wake, Japan. 4Graduate School of Science, Osaka University, Toyonaka, Japan. 5Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori-cho, Japan. 6Institute for Materials Research, Tohoku University, Higashiibaraki-gun, Japan. 7Institute for Atomic and Subatomic Physics, TU Wien, Vienna, Austria. 8RIKEN SPring-8 Center, Sayo-cho, Japan. 9Japan Synchrotron Radiation Research Institute, Sayo-cho, Japan. 10Present address: Physikalisches Institut, Universität Bonn, Bonn, Germany. *e-mail: sasao@okayama-u.ac.jp; yosimura@okayama-u.ac.jp
A $^{229}$Th target with a small diameter (0.4 mm) is prepared by a dry-up method. A $^{229}$Th solution (0.1 mol l$^{-1}$ HNO$_3$) is poured into a groove machined into a thin graphite plate and dried up by heating, forming thorium oxide. A total of 0.24 $\mu$g $^{229}$Th (1.8 kBq, 6.3 $\times$ 10$^{14}$ nuclei) is deposited and hermetically sealed with Be cover plates. The target is placed at the focal point of the beam at an angle of 22°, as shown in Fig. 2b.

The X-ray fluorescence emitted by the target after exposure is detected by silicon avalanche photodiode (Si-APD) sensors (Fig. 2b). The detector, consisting of nine Si-APD chips (diameter of 0.5 mm; S12053-05, Hamamatsu Photonics) arranged in a 3 $\times$ 3 array, is placed at a distance of 3.5 mm from the target centre, covering 0.95% of the solid angle. The output signals are amplified by on-board preamplifiers and then sent to the subsequent signal-processing circuits, where the energy and arrival time of each photon is recorded with resolutions of $\Delta E/E \approx 1\%$ (FWHM)$^{25}$ and $\Delta t \approx 120$ ps (FWHM)$^{26}$, respectively, at 13 keV (the energy of the dominant $^{229}$Th characteristic X-ray line that is relevant for detecting the NRS signals; see Methods).

The energy of the incident beam is regularly monitored by an absolute energy monitor placed downstream of the $^{229}$Th target (Fig. 2a). This device measures the pair of Bragg angles formed on the left and right sides of the incident beam, using a Si(440) reference crystal mounted on a high-precision rotary table. With this method, developed originally by Bond$^{25}$, the energy can be determined with an accuracy of 0.07 eV (see Methods).

To isolate the NRS signal from the overwhelming background, it is essential to understand their properties, in particular their energy spectra and temporal behaviour. Figure 2c illustrates a temporal profile of the NRS signal and various backgrounds, along with the corresponding physical processes.

The decay of the 29-keV level occurs predominantly through the internal conversion process, followed by emission of characteristic X-ray detection system. Table 1 | Incident X-ray beam and $^{229}$Th target

| Monochromator   | Si(111) | Si(440) | Si(660) |
|-----------------|---------|---------|---------|
| Intensity ($\times$ 10$^{12}$ photons per second) | 80      | 4       | 1       |
| Energy bandwidth (eV) | 3.4     | 0.26    | 0.10    |
| Beam size without lens; horizontal $\times$ vertical (mm) | 1.5 $\times$ 0.8 | 0.15 $\times$ 0.065 |
| Beam size with lens; horizontal $\times$ vertical (mm) | 0.2 $\times$ 0.4 |
| Target size; thickness $\times$ diameter (mm) | 0.24 |
| Target total amount (μg) | |

Typical intensity and energy bandwidth of the 29-keV incident X-ray beam after the monochromators, and beam size with and without the lens system. The bottom two rows give the size and weight of the $^{229}$Th target.
X-rays, primarily Lα and Lβ3 lines with energies of 13 keV and 16 keV, respectively, are used in this study. The energy of the incident beam is determined by the well-known photoelectric absorption cross-section. In this study, the energy of the incident beam is determined by the photoelectric absorption cross-section.

Although weaker, other types of background, with different timing properties, also exist: one is caused by the radioactivity of 229Th and its daughter nuclei (random in time) and another by stray photons scattered off surrounding materials (specific time, depending on the distance between the material and the detector). The energies of these types of background are generally different from that of the signal, except for the photoelectric absorption process, which has an energy spectrum similar to that of the signal. See Extended Data Fig. 4 for more information.

The data presented below were taken in July (Campaign 1) and November (Campaign 2) 2018. Initially Si(440) was used to search for the 29-keV level. After identifying the level's resonance energy, Si(440) was replaced by Si(660), which has a smaller bandwidth (see Table 1). All physical quantities reported—such as the energy, half-life and excitation linewidth of the 29-keV level—are derived from the data obtained with Si(660) unless stated otherwise.

Successful excitation to the 29-keV level is signalled by an enhancement in the number of Si-APD signals within a specified energy–time window of 12–18 keV in energy and 0.40–0.90 ns in time after the prompt signal, considering the properties of the signal and background. The resonance curve obtained with eqn (440) monochromator was shown in Fig. 3a. A clear NRS peak is observed on a constant background. Figure 3b shows the resonance curve taken with Si(660) in Campaign 1. The resonance energy $E_{2nd}$ is obtained by fitting a Gaussian function plus a constant. We obtain $E_{2nd} = 29.189.961 \pm 0.006$ eV (Campaign 1) and $E_{2nd} = 29.189.908 \pm 0.005$ eV (Campaign 2), where the indicated uncertainties are statistical. By taking the weighted average and including all systematic uncertainties, the final value is determined as

$$E_{2nd} = 29.189.93 \pm 0.07 \text{ eV}$$

where the error is dominated by the uncertainty in determining the absolute energy of the incident beam (see Methods).

The width of the resonance curve is fully determined through the monochromator bandwidth; the actual root-mean-square (r.m.s.) width is found to be $\sigma_{Xray} = 0.112 \pm 0.014$ eV for Si(440) and $\sigma_{Xray} = 0.041 \pm 0.006$ eV for Si(660). We note that in Table 1 the energy bandwidth is listed as FWHM, which is $2 \sqrt{\log_2} \sigma_{Xray}$. The half-life of the second excited state of the 229Th nucleus is obtained with on- and off-resonance data taken with the Si(660) monochromator. The inset of Fig. 4 shows the on-resonance (red) and off-resonance (blue) temporal profiles, normalized to a 3,600-s run of Campaign 1 (which contains 12 on- and 8 off-resonance runs). The NRS time signal is obtained by subtracting the off-resonance data from the on-resonance data. As seen in Fig. 4, the signal exhibits a clear exponential decay. A least-squares fit with an exponentially decaying function to the region from 0.4 ns to 1.4 ns yields a half-life of $T_{1/2} = 84.2 \pm 6.3$ ps (red solid curve in Fig. 4). The resultant $\chi^2$ per number of degrees of freedom (ndf) and $p$ value are $\chi^2/\text{ndf} = 1.168$ and $p = 0.20$, respectively. Similarly, the data obtained with Si(660) from Campaign 2 (23 on-resonance and 14 off-resonance runs) yield $T_{1/2} = 80.9 \pm 5.1$ ps with $\chi^2/\text{ndf} = 1.30$ and $p = 0.10$. By taking the weighted average of these results, the half-life is

$$T_{1/2} = 82.2 \pm 4.0 \text{ ps}$$

This present result considerably improves the shortest half-life measured so far by NRS spectroscopy (about 630 ps in $^{201}$Hg)\(^\text{(10)}\).

Another key quantity of the 29-keV level is the excitation linewidth, that is, the radiative transition width between the ground state and the second excited state (cross-band transition, $\Gamma^{\text{rel}}$). This quantity may in principle be derived from the obtained NRS count rates and from known experimental parameters such as the beam intensity, target density and Si-APD detection efficiency. In reality, however, reliable values for all of these parameters are difficult to obtain. Fortunately, $\Gamma^{\text{rel}}$ can be expressed by the ratio of the NRS and prompt count rates, multiplied by the well-known photoelectric absorption cross-section\(^\text{(11)}\). In this ratio, several experimental parameters drop out, and the calculation...
of the $^{233}\text{U}$ $\alpha$-decay chain. First, the $^{229}\text{Th}$ production rate is high (25 kHz in the present experiment; see Methods). Obtaining this rate with the $\alpha$ decay of $^{233}\text{U}$ requires an activity about 700 times larger than that of our target.

Another advantage is experimental control. In the $\alpha$ decay of $^{233}\text{U}$, about 5 MeV of energy is released, generating a large stochastic background. A recoil energy of 84 eV is transferred to the nucleus, leaving it in a largely uncontrolled state concerning its kinetics and ionization level. These are challenging conditions for a direct optical excitation or detection of the isomeric state, let alone the construction of a nuclear clock. So far, only one group has reported the production of a controlled ion beam of $^{229}\text{Th}$ (refs. 12,35).

By contrast, optical X-ray pumping via the second excited state transfers a negligible recoil energy of 1.8 MeV to the nucleus, which does not affect its charge or motional state. It is hence compatible with $^{229}\text{Th}$ production in optically transparent samples. Any isomer-related signals can be unambiguously identified by switching the excitation on and off. Furthermore, when $^{229}\text{Th}$ targets are prepared usingionic states ($^{229}\text{Th}^{+}$ with $\gamma \geq 2$), the half-life of the isomeric state is expected to be long, so that any background generated by the incident X-ray beam can be almost entirely eliminated.

Direct optical detection and precision spectroscopy of the $^{229}\text{Th}$ isomer is the next important step towards the realization of the nuclear clock. Using the pumping scheme presented here, we are currently preparing an experiment to detect the vacuum ultraviolet transition using a $^{229}\text{Th}$-doped vacuum-ultraviolet-transparent crystal.

Online content
Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-019-1542-3.

Received: 8 February 2019; Accepted: 23 July 2019; Published online 11 September 2019.

1. Beck, B. R. et al. Energy splitting of the ground-state doublet in the nucleus $^{229}\text{Th}$. Phys. Rev. Lett. 98, 142501 (2007).
2. Beck, B. R. et al. Improved Value for the Energy Splitting of the Ground-State Doublet in the Nucleus $^{229}\text{Th}$. Report No. LLNL-PROC-415170 (Lawrence Livermore National Laboratory, 2009).
3. Kroger, L. A. & Reich, C. W. Features of the low-energy level scheme of $^{229}\text{Th}$ as observed in the $\alpha$ decay of $^{229}\text{U}$. Nucl. Phys. A 259, 29–60 (1976).
4. Helmer, R. G. & Reich, C. W. An excited state of $^{229}\text{Th}$ at 3.5 eV. Phys. Rev. C 49, 1845–1858 (1994).
5. Peik, E. & Tamm, C. Nuclear laser spectroscopy of the 3.5 eV transition in $^{229}\text{Th}$. Europhys. Lett. 61, 181–186 (2003).
6. Matinyan, S. Lasers as a bridge between atomic and nuclear physics. Phys. Rep. 298, 199–249 (1998).
7. Flambaum, V. V. Enhanced effect of temporal variation of the fine structure constant and the strong interaction in $^{229}\text{Th}$. Phys. Rev. Lett. 97, 092502 (2006).
8. Flambaum, V. V. Enhancing the effect of Lorentz invariance and Einstein’s equivalence principle violation in nuclei and atoms. Phys. Rev. Lett. 117, 072501 (2016).
9. Campbell, C. J. et al. Single-ion nuclear clock for metrology at the 19th decimal place. Phys. Rev. Lett. 108, 120820 (2012).
10. Kazakev, G. A. et al. Performance of a $^{229}\text{Th}$ doublet solid-state nuclear clock. New J. Phys. 14, 083019 (2012).
11. Peik, E. & Okhapkin, M. Nuclear clocks based on resonant excitation of $\gamma$-transitions. C. R. Phys. 16, 516–523 (2015).
12. von der Weisa, L. et al. Direct detection of the $^{229}\text{Th}$ nuclear clock transition. Nature 533, 47–51 (2016).
13. Takano, T. et al. Geopotential measurements with synchronously linked optical lattice clocks. Nat. Photon. 10, 662–666 (2016).
14. Hayes, A. C. & Friar, J. L. Sensitivity of nuclear transition frequencies to temporal variation of the fine structure constant or the strong interaction. Phys. Lett. B 650, 229 (2007).
15. Berengut, J. C. et al. Proposed experimental method to determine $\alpha$ sensitivity of splitting between ground and 7.6 eV isomeric states in $^{229}\text{Th}$. Phys. Rev. Lett. 102, 210801 (2009).
16. Thielking, J. et al. Laser spectroscopic characterization of the nuclear-clock isomer $^{229}\text{Th}$. Nature 556, 321–325 (2018).
17. Saefke, B. et al. Energy of the $^{229}\text{Th}$ nuclear clock transition. Nature https://doi.org/10.1038/s41586-019-1533-4 (2019).
18. Jeet, J. et al. Results of a direct search using synchrotron radiation for the low-energy $^{229}$Th nuclear isomeric transition. *Phys. Rev. Lett.* **114**, 253001 (2015).

19. Yamaguchi, A. et al. Experimental search for the low-energy nuclear transition in $^{229}$Th with undulator radiation. *New J. Phys.* **17**, 053053 (2015).

20. Stellmer, S. et al. Attempt to optically excite the nuclear isomer in $^{229}$Th. *Phys. Rev. A* **97**, 062506 (2018).

21. Browne, E. & Tuli, J. K. Nuclear data sheets for $A = 229$. *Nucl. Data Sheets* **11**, 2657–2724 (2008).

22. Seto, M. Condensed matter physics using nuclear resonant scattering. *J. Phys. Soc. Jpn.* **82**, 021016 (2013).

23. Yabashi, M. et al. Design of a beamline for the SPring-8 long undulator source 1. *Nucl. Instrum. Methods Phys. Res. A* **467–468**, 678–681 (2001).

24. Krywka, C. et al. Polymer compound refractive lenses for hard X-ray nanofocusing. *AIP Conf. Proc.* **1764**, 020001 (2016).

25. Masuda, T. et al. Energy response of X-rays under high flux conditions using a thin APD for the energy range of 6–33 keV. *Nucl. Instrum. Methods Phys. Res. A* **913**, 72–77 (2019).

26. Bond, W. L. Precision lattice constant determination. *Acta Crystallogr.* **13**, 814–818 (1960).

27. Barci, V. et al. Nuclear structure of $^{229}$Th from $\gamma$-ray spectroscopy study of $^{233}$U $\alpha$-particle decay. *Phys. Rev. C* **68**, 034329 (2003).

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2019
METHODS

Si-APD detector and readout system. The Si-APD detector was developed in cooperation with Hamamatsu Photonics K.K. on the basis of our custom design. It consists of nine Si-APD chips and is arranged in a 3 × 3 array with a 1.14-mm pitch between adjacent chips. Combined with a 0.5-mm-diameter photocathode placed 3.5 mm away from the target, the total geometrical acceptance of the detector amounts to 0.95%.

The signal processing diagram is shown in Extended Data Fig. 1. Each Si-APD output is amplified by a fast amplifier (RAM-8A+, Mini-circuits) located directly behind the Si-APDs. The amplified output is processed in several ways to obtain the event characteristics15,24,25,26. First, it is converted to a logic signal by a custom-built constant-fracton discriminator (CFD), yielding the event occurrence time. Second, the signal is converted to a logic signal with a delay time proportional to the amplitude of the Si-APD output (ATC), which provides the event energy. Third, the trailing-edge (TE) timing of the analogue signal is used to reject events with abnormal waveforms caused by, for example, multiple hits. These logic signals (CFD, ATC, TE) are sent to multiple-event time digitizers (MCS6, FAST ComTeC) with a time bin width of 100 ps, together with the accelerator clock signal, which provides a reference timing for the revolution of the electron bunch in the accelerator ring (every 4.7898.9 ns). Finally, the digitized signals are all stored in PCs for off-line analysis.

Absolute X-ray energy monitor. Our absolute X-ray energy monitor utilizes a method developed by Bond22. As shown in Extended Data Fig. 2, the monitor consists of a Si crystal plate and two X-ray sensors (p–i–n photodiodes). To control its orientation, the crystal is mounted on a swivel stage, which is in turn placed on a rotary table and another swivel stage. The monitor locates the two Bragg diffraction peaks formed on the left and right of the beam by rotating the table. The rotation angle of the crystal between these two peaks is measured with a rotary encoder attached to the table. The wavelength λ of the incident X-ray is derived using the relation

\[ \lambda = 2d(T, P)\sin\theta \cos\theta \]  

(5)

where \( d(T, P) \) is the smallest spacing between the crystal lattice planes at temperature \( T \) and pressure \( P \), and \( \theta \) are the deviations from the right angle defined by the incident beam and crystal’s rotation axis (the crystal’s reciprocal lattice vector). We note that \( \theta \) can be controlled by the swivel stages. The crystal used in this experiment is cut from the ingot of a standard reference crystal; the (220) crystal spacing, \( d_{220} \), has been measured at \( T = 22.5 \) °C and \( P = 0 \) atm (vacuum)24,25, and we conservatively quote \( d_{220} = 192.01559 \pm 0.00002 \) pm, considering the inhomogeneity of the crystal18. Because the monitor uses the (440) plane, \( d_{440} = \frac{d}{\sqrt{2}} \) is used in equation (5) with appropriate corrections for \( T \) and \( P \) (refs. 39, 41).

The heart of the monitor is a high-precision, self-calibrating rotary encoder (called SelfA)42. It has 12 optical sensors that ‘read’ gratings grooved along the circumference of a rotating disk attached to the table. The encoder generates its response function—the relation between the true rotation angle and the rotary encoder readings—using self-acquired data; namely, it analyses all the outputs from all sensors and gratings using Fourier analysis and corrects nonlinearity caused by, for example, eccentricity/inclination of the grating disk from the true rotation axis and non-uniformity of the grating intervals. One important feature of the monitor is that the 12 sensors are distributed at every 1/3, 1/4 and 1/7 of the disk periphery to maximize the order of Fourier components. The swivel angles are adjusted in situ by adjusting for the setting that yields the largest \( \lambda \) in equation (5); thus the procedure ensures that \( \theta \) is negligible.

In this monitor system, the largest uncertainty arises from the angle determination by the rotary encoder; this is found to be 0.044 arcsec, which translates to a fractional uncertainty of 0.67 ppm in \( \lambda \). The second-largest uncertainty stems from \( d_{220} \), which is 0.1 ppm. All other uncertainties, such as corrections due to \( T \) or \( P \), as well as non-zero \( \theta \), are found to be negligible (≪0.1 ppm). The combined uncertainty is 0.67 ppm or 0.02 eV for the ≈29-keV beam.

As an overall check, the stability or reproducibility of the energy measurement is tested by monitoring the 40K NRS resonance energy41. A typical temporal profile from a 40K target is shown in Extended Data Fig. 3, together with the resonance curve in the inset. The resonance energy was monitored 15 times in Campaign 1 and 2, with various angles between the Si crystal and the rotary table. The largest deviation from the average is found to be 0.07 eV. The error quoted in our absolute energy measurement is extracted from this deviation.

Data-taking procedure. The data presented in this Letter were taken in two separate campaigns, each lasting about one week, in July (Campaign 1) and November (Campaign 2) 2018. During the resonance search in Campaign 1, the energy range 29,189.6–29,198.0 eV was scanned using the Si(440) monochromator. A typical data-taking procedure during the energy scan is as follows. First, for each energy setting, the absolute value is measured with the absolute energy monitor; this measurement takes about 180 s. Then, data are collected for 1,800 s (one standard run). Finally, the energy is changed by a step of 0.08–0.12 eV, corresponding to less than half of the Si(440) bandwidth.

After finding the resonance, Si(440) is replaced with Si(660) to take advantage of its better energy resolution (see Table 1). The data-taking procedure using Si(660) is similar to that in the Si(440) runs; however, the beam energy is varied in the immediate vicinity of the resonance, and the acquisition time is increased to 3,600 s to compensate for the decrease in signal events (due to the reduced beam intensity) in each run.

Radiative width \( \Gamma_{\gamma\gamma}^{\text{cr}} \). To obtain the cross-band radiative width \( \Gamma_{\gamma\gamma}^{\text{cr}} \), the count rates of the photoelectric absorption process, \( \eta_{\text{pe}} \), and the NRS process, \( \eta_{\text{NRS}} \), are compared. As mentioned, the prompt signal consists predominantly of events caused by the photoelectric process (see below for the extraction procedure of \( \eta_{\text{pe}} \) from the prompt signal). The rate \( \eta_{\text{NRS}} \) is a product of three factors: the photoelectric absorption rate, the probability of yielding detectable X-ray photons and various detection efficiencies. Specifically, it is expressed by

\[ \eta_{\text{NRS}} = \gamma_{\text{pe}} \Phi \eta_{\text{X-ray}} \frac{\Delta \Omega}{4\pi} \]  

(6)

where \( \gamma_{\text{pe}} \) represents the total photoelectric cross-section, \( \Phi \) the incident beam intensity (the number of X-rays per unit time) and \( \eta_{\text{X-ray}} \) the column density of 220Th nuclei in the target. The factor \( \eta_{\text{pe}} \) represents the probability that the photoelectric process produces X-ray fluorescence with energy within our energy window (12–18 keV). The last two factors are efficiencies of the detectors: the Si-APD efficiency \( \gamma_{\text{NRS}} \) and the geometrical acceptance \( \Delta \Omega(4\pi) \). The notation \( \gamma_{\text{NRS}} \) indicates that, because the Si-APD efficiency depends on the X-ray energy, the energy average of \( \eta_{\text{pe}} \) is taken with a weight of \( \epsilon_{\text{APD}} \).

Similarly, the NRS rate is given by

\[ \eta_{\text{NRS}} = \int dE \int_{\text{peak}} dE_{\text{APD}} \Phi \eta_{\text{X-ray}} \frac{\Delta \Omega}{4\pi} \Delta E_{\text{APD}} \]  

(7)

where \( \gamma_{\text{NRS}}(E) \) is the NRS cross-section (given below) at the incident beam energy \( E \), \( dE/dE_{\text{APD}} \) is the beam intensity per unit energy, \( \eta_{\text{pe}} \) is equivalent to \( \eta_{\text{pe}} \) for the NRS internal conversion process and \( \Delta E_{\text{APD}} \) is the efficiency due to the time window (0.4–0.9 ns). We note that for the photoelectric process, the energy dependence of \( \gamma_{\text{pe}} \) can be ignored; for the NRS process, however, it is not possible to do so because \( \gamma_{\text{NRS}} \) is expected to have a much narrower width than the incident beam energy. The integration in equation (7) is carried out as follows. In the present experiment, \( dE/dE_{\text{APD}} \) is expressed well by a Gaussian-shape function

\[ \int_{\text{peak}} dE_{\text{APD}} = \Phi \int_{\text{peak}} dE \]  

(8)

where \( E_{\text{peak}} \) and \( \sigma \) are the centre energy and the r.m.s. energy width of the beam, respectively. The NRS cross-section is given by the Breit–Wigner formula (see section 49 in ref. 4)

\[ \gamma_{\text{NRS}} = \frac{1}{\pi \sigma} \exp \left[ \frac{-(E - E_{\text{peak}})^2}{2\sigma^2} \right] \]  

(9)

where \( E_{\text{peak}} \) and \( \sigma \) are the centre energy and the r.m.s. energy width of the beam, respectively. The NRS cross-section is given by the Breit–Wigner formula (see section 49 in ref. 4).
Among the quantities in equation (13), $V_{Sil}$/fo, $\omega_{Sil}$, $\sigma_{Sil}$ and $\tau_{Sil}$ can be determined from our measurements, whereas $\sigma_{Sil}$ is tabulated\(^{25}\). The ratio $\eta_{Sil}/\eta_{APD}$ is expected to be $\sim$1 because the processes are similar; this fact can be confirmed by theoretical estimates as well as by the experimental prompt and NRS spectra; details are provided below, together with the description of the procedure used to extract $V_{Sil}$ from the prompt signal. The efficiency $\eta_{Sil}$ is essentially given by the integral of the exponential decay probability in the time range 0.4–0.9 ns, in the actual calculation, however, a subtle effect due to the time resolution of the Si-APD is taken into account. All relevant values and their errors are listed in Extended Data Table 1. By inserting these values into equation (13), $\Gamma_{\gamma}$ is found to be $1.70 \pm 0.40$ keV is obtained, where the error is a quadrature sum of the individual errors listed in Extended Data Table 1. The main errors stem from $\tau_{Sil}$ which is sensitive to the half-life of the 29-keV level, and from $\sigma_{Sil}$, which is determined by the Gaussian fit to the resonance curve. The next-largest error comes from $\eta_{NRS}$, the accuracy of which is determined by the error on $\eta_{Sil}$. All the other errors are negligible compared to the three outlined above.

The ratio $\eta_{Sil}/\eta_{APD}$ is determined from both the photoelectric absorption and NRS scattering processes by X-ray fluorescence emitted during the corresponding relaxation processes. In the present experiment, X-rays of 12–18 keV are detected, which are produced only when vacancies are created in the L shell. There are three subshells: L$_1$, L$_2$, and L$_3$; each vacancy in a subshell emits characteristic X-rays ('emission lines') by filling the vacancy with electrons from the upper shells. Once a subshell is specified, then the energy distribution of the emission lines and their strengths (that is, the emission probability per vacancy) are determined, independent of the parent process. These data are compiled in Table 1. For each subshell, the X-ray emission spectra, which is necessary to calculate $(\eta_{Sil}/\eta_{APD})$, amounts to the determination of the subshell distribution for each process. For clarity, we denote by $\eta_{Sil}^{i}$ or $\eta_{Sil}^{j}$ the probability of creating a vacancy in the L$_i$ subshell, and by $\eta_{Sil}^{j}$ the strength of line $j$ from the L$_j$ subshell vacancy ($j$ runs over all possible emission lines, which are usually labelled as L$_3$, L$_2$, L$_1$, L$_2$, L$_1$, L$_3$, L$_2$, L$_1$, and so on). For the photoelectric process, the values of $\eta_{Sil}^{i}$ are well established\(^{20,25}\) to be (0.180, 0.257, 0.312, 0.749) for (L$_1$, L$_2$, L$_3$, L$_4$, respectively). On the other hand, the situation is more complicated for the internal conversion process because two all possible emission lines, which are usually labelled as L$_3$, L$_2$, L$_1$, L$_2$, L$_1$, L$_3$, L$_2$, L$_1$, and so on). For the photoelectric process, the values of $\eta_{Sil}^{i}$ are well established\(^{20,25}\) to be (0.180, 0.257, 0.312, 0.749) for (L$_1$, L$_2$, L$_3$, L$_4$, respectively). On the other hand, the situation is more complicated for the internal conversion process because two types of multipole, M1 and E2, play a role in this case, and they generally yield different $\eta_{Sil}^{i}$ values. At this stage, it is convenient to introduce a quantity called the internal conversion coefficient, $\alpha_{Sil}^{i}$, defined by the ratio of the internal conversion width to the corresponding radiative width. The merits of introducing $\alpha_{Sil}^{i}$ are as follows. First, the calculation of $\alpha_{Sil}^{i}$ is expected to be reliable because the nuclear matrix element cancels out in the ratio. Given $\alpha_{Sil}^{i}$ for a subshell L$_i$, $\eta_{Sil}^{i}$ is obtained by taking the ratio of $\alpha_{Sil}^{i}$ for that subshell to the total (for all shells and subshells) internal conversion coefficient. Second, because $\alpha_{Sil}^{i}$ in the present case is a linear mixture of the M1 and E2 components, it is bouded by two extremes, the pure M1 and pure E2 processes. $\alpha_{Sil}^{i}$ is evaluated at the energy of line $\Gamma_{\gamma}$.

$\eta_{Sil}^{i}/\eta_{Sil}^{j}$ is calculated for these extremes using the BrIcc v2.3S code\(^{46}\). The fit results may also be used to extract the photoelectric absorption rate from the prompt signal rate. The fraction of the Compton and background lines (such as Cu, Zn and Fe) with energies between 12–18 keV is found to be 0.097 $\pm$ 0.004. This value is used to obtain the ratio $V_{Sil}/V_{NRS}$ listed in Extended Data Table 1. Braching ratio. The branching ratio of the 29-keV level to the ground state by radiative transitions is defined by

$$B_{\gamma}^{i} = \frac{\Gamma_{\gamma}^{i}}{\Gamma_{\gamma}}$$

where $\Gamma_{\gamma}^{i}$ is the in-band transition width. Among the two widths, $\Gamma_{\gamma}^{i}$ is known (see equation (3)). The in-band transition width has been experimentally determined by two groups\(^{23,24}\), giving $\Gamma_{\gamma}^{i} = (2.161 \pm 0.240) \times 10^{-3}$ and $\Gamma_{\gamma}^{i} = (2.383 \pm 0.531) \times 10^{-3}$ (h, reduced Planck constant). Using a weighted average of these values ($\Gamma_{\gamma}^{i} = 1.43 \pm 1.4$ keV), $B_{\gamma}^{i}$ is found to be $10^{10}$ $\pm$ 0.027 or equivalently $B_{\gamma}^{i} = 10^{10}$ $\pm$ 0.027.

Isomer production rate. The isomer production rate is given by the product of the 29-keV level production rate and the branching ratio to the isomer state. In this case, the branching ratio should include not only the radiative transition but also the internal conversion processes, and is expressed by

$$B_{\gamma}^{ic} = \frac{\Gamma_{\gamma}^{ic}}{\Gamma_{\gamma}}$$

$$B_{\gamma}^{ic} = \frac{\Gamma_{\gamma}^{ic}}{\Gamma_{\gamma}}$$

and inserting the obtained values into the right-hand side, which gives $\alpha_{Sil}^{i} = 1.370 \pm 0.410$.

36. Cavagnero, G. et al. Measurement repetitions of the Si(220) lattice spacing. Metrologia 41, 56–64 (2004).
37. Cavagnero, G. et al. Erratum: measurement repetitions of the Si(220) lattice spacing. Metrologia 41, 445–446 (2004).
38. Fujimoto, H. et al. Homogeneity characterization of lattice spacing of silicon single crystals by a self-referenced lattice X-ray. Metrologia 48, 555–561 (2011).
39. Schoedel, R. & Boens, G. Precise interferometric measurements at single-crystal silicon yielding thermal expansion coefficients from 12°C to 28°C and compressibility. Proc. SPIE 4401, 54–62 (2001).
40. Lyon, K. G., Sailer, W. G., L. Simpson, C. A. & White, G. K. Linear thermal expansion measurements on silicon from 6 to 340 K. J. Appl. Phys. 48, 865–868 (1977).
41. Hall, J. J. Electronic effects in the elastic constants of the n-type silicon. Phys. Rev. 161, 756–761 (1967).
42. Watanabe, T., Kon, M., Nabethoma, N. & Taniguchi, K. n-Alpha encoder for super-high resolution and super-high accuracy using Self, Meas. Sci. Technol. 25, 06502 (2014).
43. Seto, M. et al. Nuclear resonance scattering of synchrotron radiation by $^{40}$K. Phys. Rev. Lett. 84, 566–569 (2000).
44. Kaneko, T. et al. Observation of a silicon Schottky barrier with a high field-effect mobility. Solid State Electron. 31, 79–84 (1988).
45. Tabanishi, M. et al. Review of Particle Physics. Phys. Rev. D 98, 030001 (2018).
46. Scofield, J. H. Theoretical Photoionization Cross Sections from 1 to 1500 keV. Theoretical Photoionization Cross Sections from 1 to 1500 keV. \footnote{Theoretical Photoionization Cross Sections from 1 to 1500 keV. \footnote{Theoretical Photoionization Cross Sections from 1 to 1500 keV.}}
20180045). We thank all members of the SPring-8 operation and supporting teams. The experiment received support from the KEK Photon Factory (proposal number 2017G085) and the Institute for Materials Research, Tohoku University (18F0014), where indispensable detector tests and target preparation were performed. We especially thank S. Kishimoto for support at KEK, T. Kobayashi for technical assistance at SPring-8 and K. Beeks for discussion during the preparation of the manuscript. This work was supported by JSPS KAKENHI grants JP15H03661, JP17K14291, JP18H01230 and JP18H04393. T.S. and S.S. gratefully acknowledge funding by the EU FET-Open project, grant number 664732 (nuClock). A. Yoshimi and A. Yamaguchi acknowledge the MATUSO foundation and Technology Pioneering Projects in RIKEN, respectively.

Author contributions The Okayama University group, S.K., M.S., K.T., A. Yamaguchi and Y. Yoda performed the synchrotron radiation experiments. T.M., A. Yoshimi, T.H., H.K., K.O., S.O., N.S., K.S., K.Y. and S.U. developed the detector system. The Osaka University, Tohoku University and RIKEN groups, together with A. Yoshimi, H.K. and K.Y. prepared the thorium-229 target. T.M., A. Yoshimi, T.H., N.S., K.S., K.Y., S.S. and T.S. analysed the data. H.F., T.W. and Y. Yoda developed the absolute energy monitor. T.M., A. Yoshimi, K.Y., T.S. and N.S. wrote the manuscript with input from all authors. All authors discussed the results.

Competing interests The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to N.S. or K.Y.
Peer review information Nature thanks Jason Burke, Fedor Karpeshin and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.
Reprints and permissions information is available at http://www.nature.com/reprints.
Extended Data Fig. 1 | Pulse-processing scheme. a, Timing diagram. Line (A) shows an analogue pulse from a Si-APD chip and line (B) represents the accelerator reference clock. The example shows two pulses with different photon energies within a cycle. 
b, Block diagram. For each pulse, three parameters are stored for the post-analysis: the timing of the pulse (CFD), the pulse height (ATC) and the TE timing. Preamp, preamplifier; Amp., amplifier; TDC, time-to-digital converter; USB, universal serial bus.
Extended Data Fig. 2 | Absolute energy measurement setup. The X-ray beam is diffracted by a single Si crystal. Two p–i–n (PIN) photodiodes monitor the diffracted beams. The rotary table (black disk) adjusts the angle between the Si crystal and the X-ray beam so that the diffraction condition is satisfied. The two swivel stages adjust the tilt angles between the X-ray beam, the reciprocal lattice vector of the crystal and the rotation axis of the rotary table.
Extended Data Fig. 3 | NRS spectrum of $^{40}$K. Temporal profiles measured at incident X-ray energy on resonance (blue histogram) and off resonance (black histogram). Inset, resonance curve (black dots) with a Gaussian fit (blue curve).
Extended Data Fig. 4 | Energy spectra of the prompt and NRS events.
a, Energy spectrum of the prompt signal (black line). The coloured lines show various X-ray emission lines convoluted with the Si-APD energy response function: the photoelectric absorption lines listed in Extended Data Table 2 (blue), Compton scattering (magenta) and the Kα and Kβ lines of Cu, Zn and Fe (green). The strengths of these lines are adjusted to give the best fit to the data. The sum of all lines (red) reproduces the data above 7 keV well. b, NRS energy spectrum, obtained by subtracting the off-resonance data from the on-resonance data. The coloured lines are fits of the X-ray emission lines. We note that there is no contribution from Compton scattering or the Cu, Zn and Fe lines. Both experimental datasets are normalized to a 3,600-s run. The error bars represent statistical uncertainty of one standard deviation.
### Physical quantities that are necessary to estimate $\Gamma_{\gamma}^{cr}$ (see equation (13)) and their errors (statistical errors of one standard deviation).

| Item | value and error | unit |
|------|-----------------|------|
| $Y_{nrs}/Y_{pe}$ | $(1.84\pm0.20)\times10^{-7}$ | |
| $\lambda_{2nd}$ | $42.5\pm0.00013$ | pm |
| $\sigma_{Xray}$ | $0.041\pm0.006$ | eV |
| $\varepsilon_{tw}$ | $0.039\pm0.006$ | |
| $\langle \eta_{ic} \varepsilon_{apd} \rangle / \langle \eta_{pe} \varepsilon_{apd} \rangle$ | $0.96\pm0.01$ | |
| $\sigma_{pe}$ | $15.4\pm0.8$ | kb |
Extended Data Table 2 | Comparison of energy-averaged line strengths

| Emission lines | Energy [keV] | Theoretical estimates | Experimental data |
|----------------|-------------|-----------------------|------------------|
|                |             | p.e. $\times 10^{-3}$ (%) | i.c. M1 $\times 10^{-3}$ (%) | i.c. E2 $\times 10^{-3}$ (%) | Prompt (%) | NRS (%) |
| $L_\alpha$     | 11.1        | 0.26 (5.3)            | 0.24 (5.0)       | 0.24 (5.0)       | (0.6±0.1)  | (1.5±0.6) |
| $L_{\alpha_1}, L_{\alpha_2}$ | 12.8-13.0   | 2.82 (56.9)           | 2.58 (54.1)      | 2.57 (53.6)      | (46.6±2.0) | (51.6±4.9) |
| $L_{\beta_1}, L_{\beta_4}, L_{\beta_5}, L_{\eta}$ | 14.5-15.6   | 0.55 (11.2)           | 0.81 (17.0)      | 0.42 (8.8)       | (11.9±3.5) | (13.7±5.3) |
| $L_{\beta_1}, L_{\beta_3}, L_{\beta_5}$ | 16.2-16.4   | 1.11 (22.5)           | 0.88 (18.6)      | 1.34 (28.0)      | (37.2±1.8) | (30.3±4.5) |
| $L_{\gamma_1}, L_{\gamma_2}, L_{\gamma_3}, L_{\gamma_4}$ | 19.0-19.6   | 0.22 (4.2)            | 0.25 (5.3)       | 0.22 (4.6)       | (3.7±0.4)  | (2.8±2.0)  |
| Sum            | 11.1-19.6   | 4.96 (100)            | 4.76 (100)       | 4.79 (100)       | (100)      | (100)     |

The left columns show the emission lines, with those with similar energies grouped together. The middle columns show theoretical estimates of energy-averaged line strengths corresponding to the cases in which the parent processes are assumed to be photoelectric absorption (p.e.) or internal conversion (i.c.) of pure M1 or E2 processes. The right columns show estimates obtained by fits to the experimental spectra of the prompt or NRS components.