Developments, features and prospects of crystal scintillators of the Cs_2MCl_6 family (M = Hf or Zr) to search for rare nuclear processes

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What we would consider as “rare nuclear processes”?

- **Effects unpredictable by Standard Model of elementary particles**

- **Violation of any conservation laws**
  (neutrinoless double decay, etc.)

- **Reactions with extremely low cross-section**
  (detection of neutrinos, dark matter particles, axions, etc.)

- **Decays with extremely large half-life value**
  (rare or forbidden alpha & beta decays with half-life values more than 10^{11} y)

- **Extremely tiny number of expected events**
  (less than 1 event/day)

- **Application of especially developed highly sensitive detection techniques**

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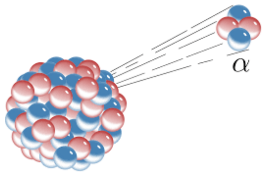
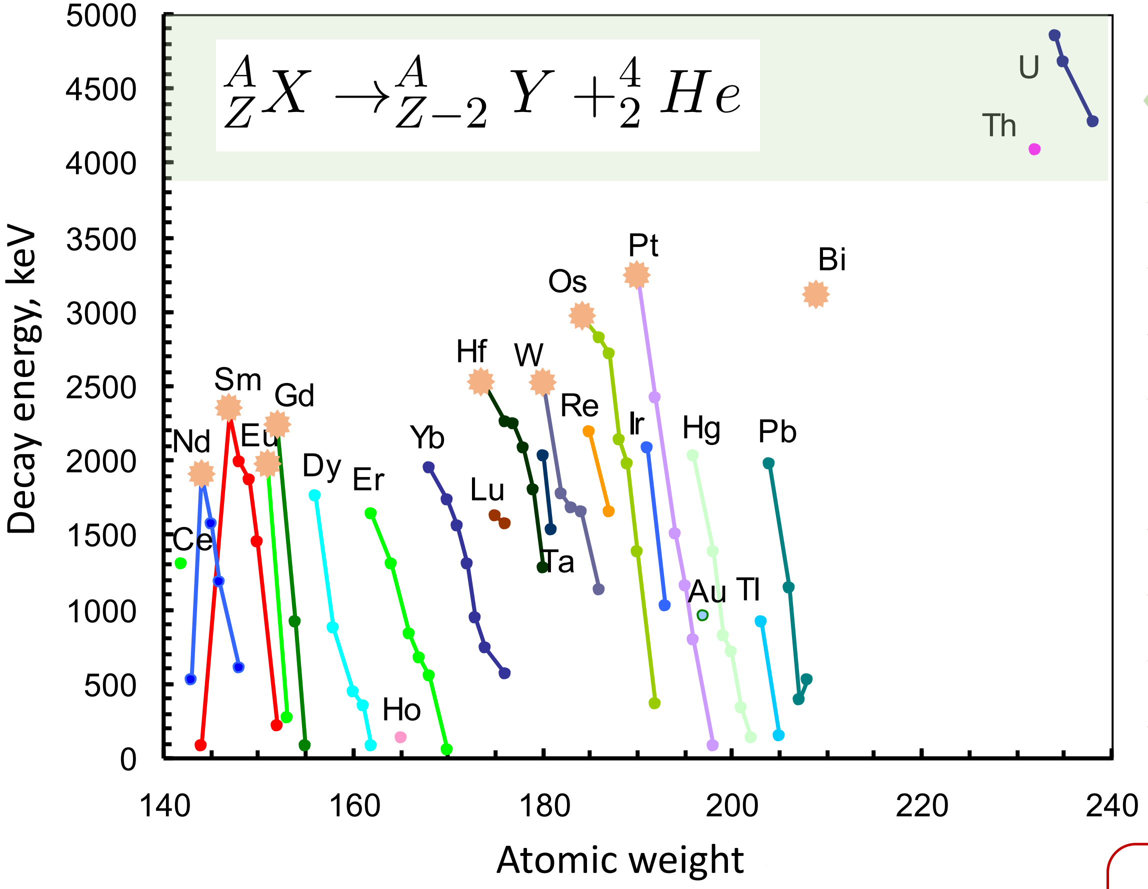


Natural alpha active isotopes



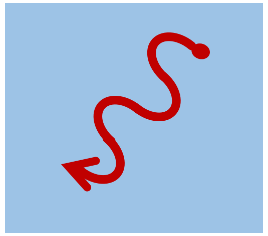
- ~ 10^{8} – 10^{10} y
- ^{190}Pt ~ 10^{11} y
- ^{209}Bi ~ 10^{19} y
- ^{184}Os ~ 10^{14} y
- ^{180}W ~ 10^{18} y
- ^{174}Hf ~ 10^{15} y
- ^{152}Gd ~ 10^{15} y
- ^{151}Eu ~ 10^{18} y
- ^{147}Sm ~ 10^{11} y
- ^{144}Nd ~ 10^{15} y

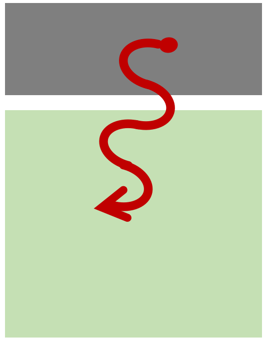
- **Details** on the **nuclear structure**, **nuclear levels** and the **properties of nuclei**
- Essential for **studies in nuclear and particle astrophysics** (α-capture reactions, β-delayed fission, nucleosynthesis)
- Essential for **background interpretation and models** in low-background long-term experiments
- **Geochronometry**

Highly sensitive experimental technique is required that is flexible towards isotope of interest

Two different experimental approaches

detector = source ***detector ≠ source***





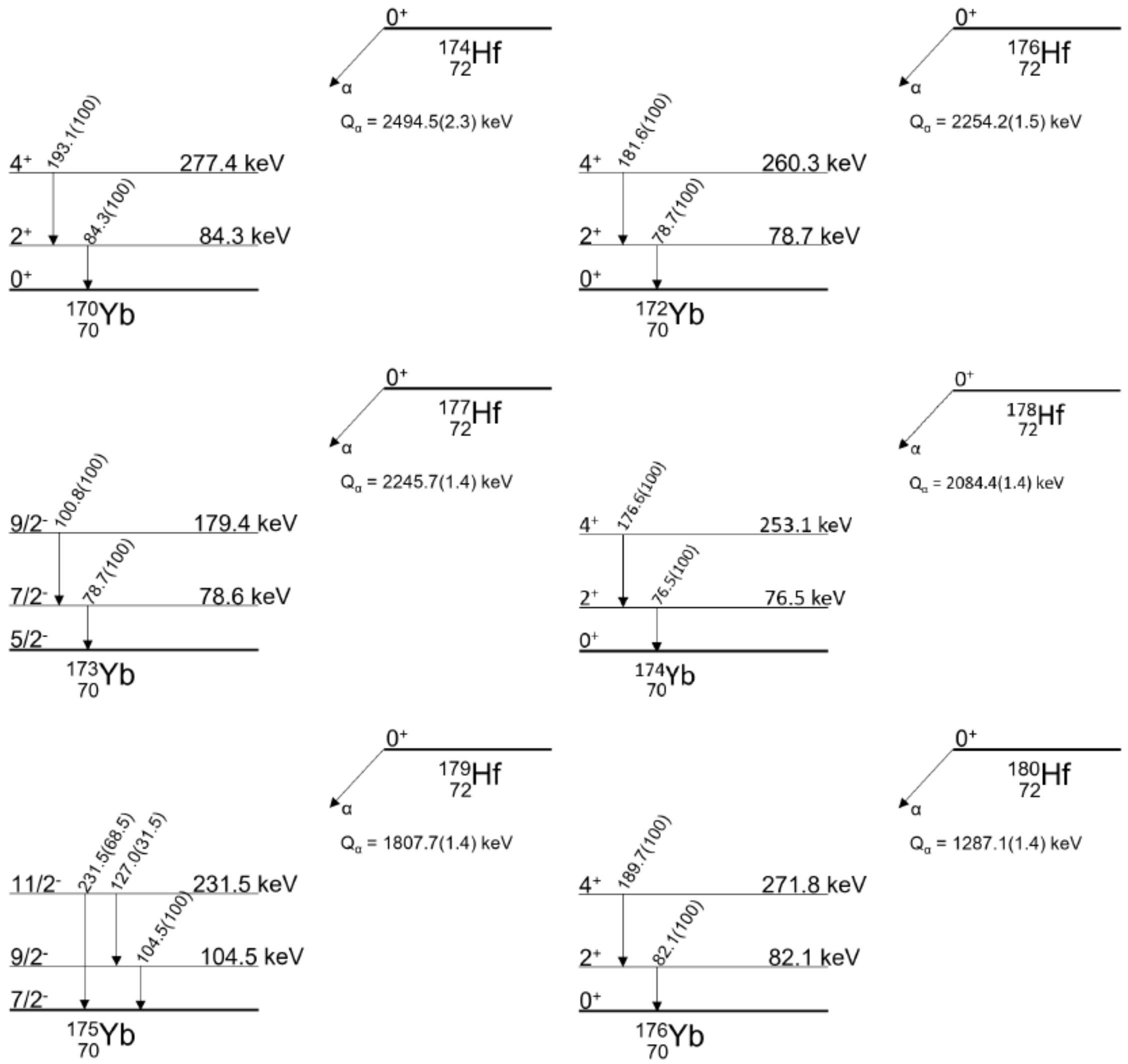
Light/Heat	*Possible channel/s*	Charge
Scintillator, Scintillating calorimeter	*Detector type*	HPGe, Ionization chamber
Partially	*Material flexibility*	Yes
No limitation	*Energy limitation*	> 300 keV (gamma)
High (up to 100%)	*Detection efficiency*	Low (few-dozen %)
High (1/1000)	*Energy resolution*	High (1/1000)
Yes	*Particle discrimination*	No
$\leq 10^{24}$ y	*Sensitivity*	$\leq 10^{22}$ y

Let's look at some successful examples of rare alpha decay detection

Material	Detector	Isotope	Process	Half-life, yr	Year
$Bi_4Ge_3O_{12}$	Scintillating bolometer	**^{209}Bi**	α	1.9×10^{19}	2003
$CdWO_4$	Scintillator	**^{180}W**	α	1.1×10^{18}	2003
$CaWO_4$	Scintillating bolometers	**^{180}W**	α	1.3×10^{18}	2004
$CaF_2(Eu)$	Scintillator	**^{151}Eu**	α	5.0×10^{18}	2007
$Li_6Eu(BO_3)_3$	Scintillating bolometers	**^{151}Eu**	α	4.6×10^{18}	2014
$PbWO_4$	Scintillating bolometers	**Pb isotopes**	α	$> 1.4\times10^{20}$	2012
Pt-metal	HPGe	**^{190}Pt**	α to exc. level	2.6×10^{14}	2011, 2021
Hf-metal	HPGe	**Hf isotopes**	α to exc. level	$> (10^{16} - 10^{18})$	2021
Os-metal	HPGe	**Os isotopes**	α to exc. level	$> (10^{16} - 10^{19})$	2020, 2024

Alpha decay of natural Hafnium isotopes

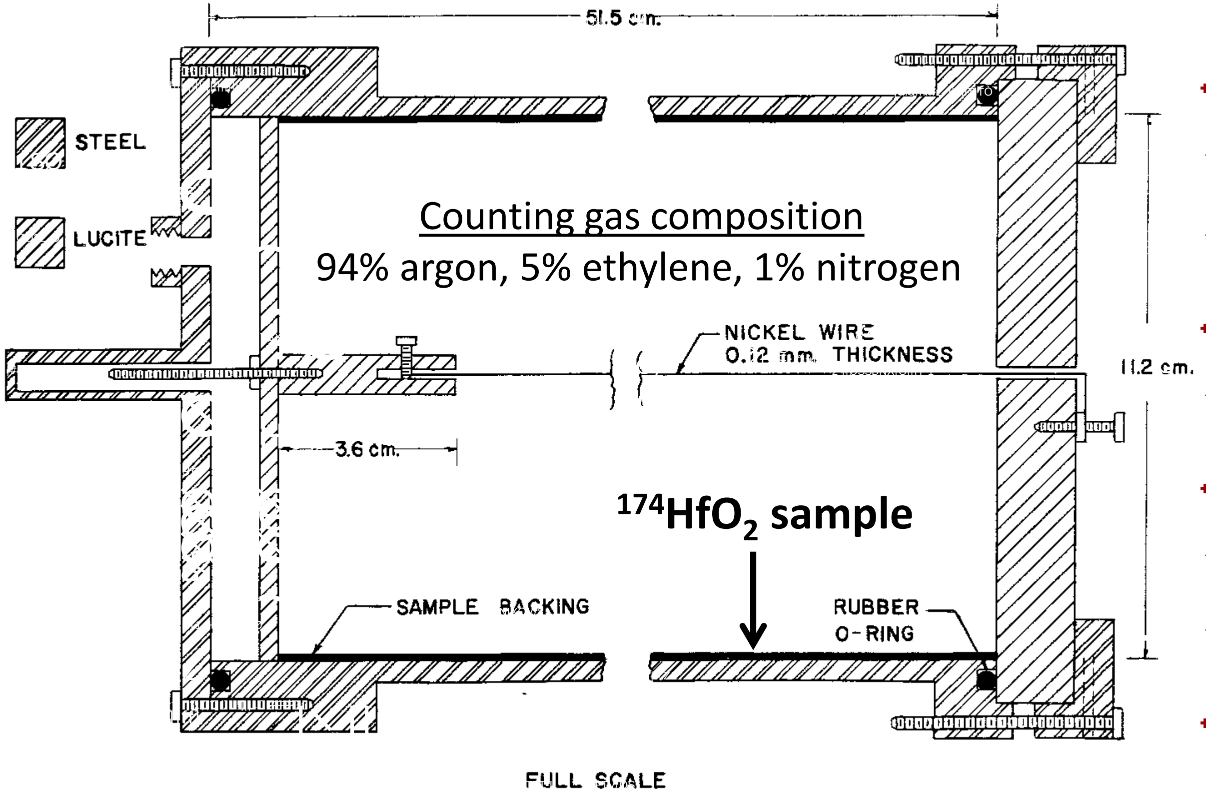
Isotope	I.a., % [1]	Q_{α}, keV [2]
^{174}Hf	0.16(1)	2493.2(2.4)
^{176}Hf	5.26(7)	2252.8(1.5)
^{177}Hf	18.60(9)	2244.3(1.5)
^{178}Hf	27.28(7)	2083.0(1.5)
^{179}Hf	13.62(2)	1806.3(1.5)
^{180}Hf	35.08(16)	1283.0(1.8)



[1] M. Wang, et al., Chinese Physics C 36 (2012) 1603

[2] M. Berglund and M.E. Wieser, Pure and Applied Chemistry 83 (2011) 397

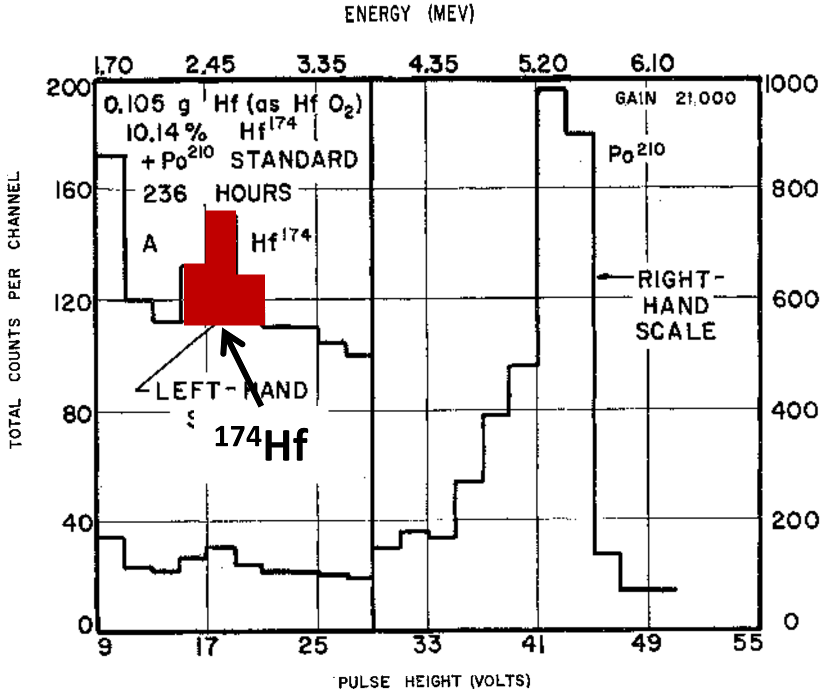
Early experiment: MacFarlane (1961)



- ✘ Surface lab
- ✓ Passive shield
- ✓ Active shield
- ✘ No PSD
- ✓ About 40 days of data taking
- ✘ 100-mg-scale sample
- ✓ Enriched in ^{174}Hf to 10.41%
- ✓ FWHM = 4% @ 2.3 MeV
- ✘ Bkg (1-3 MeV) = 9 counts/hour

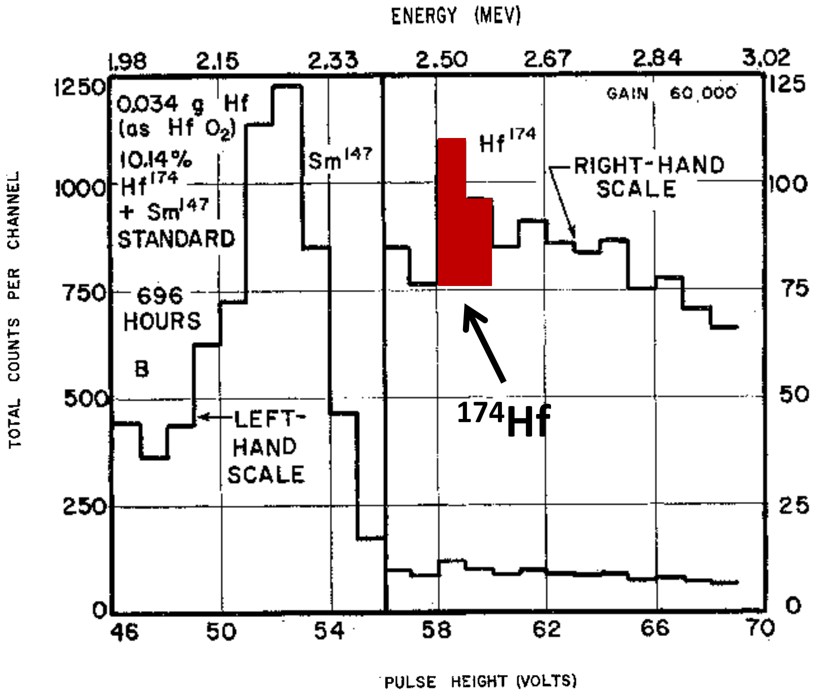
R.D. MacFarlane and T.P. Kohman, Phys. Rev. 121 (1961) 1758

Early experiment: MacFarlane (1961)



$^{174}HfO_2$ + ^{210}Po

alpha ^{210}Po @ 5.3 MeV



$^{174}HfO_2$ + Sm_2O_3

alpha ^{147}Sm @ 2.3 MeV

- **Low statistics**
- **Low signal-to-background ratio**

R.D. MacFarlane and T.P. Kohman, Phys. Rev. 121 (1961) 1758

Comparison of Theory predictions and early Experiment

Released energy Abundance	Level of daughter nucleus	Experimental $T_{1/2}$, yr	Theoretical estimation of $T_{1/2}$, yr
$^{174}Hf \rightarrow {}^{170}Yb$ 2497.4(24) keV [1] 0.16(1)% [2]	0^+, 0 keV g.s. $\rightarrow$ g.s.	2.0×10^{15} [3]	$(3.0 \text{ to } 7.0) \times 10^{16}$ [4,5,6]
	2^+, 84.3 keV g.s. $\rightarrow$ exc.l.	Not yet	$(0.9 \text{ to } 3.0) \times 10^{18}$ [4,5,6]

This one-order-of-magnitude discrepancy between theory and experiment has puzzled scientists for more than 70 years

[1] M. Wang, et al., Chinese Physics C 36 (2012) 1603
[2] M. Berglund and M.E. Wieser, Pure and Applied Chemistry 83 (2011) 397
[3] R.D. MacFarlane and T.P. Kohman, Phys. Rev. 121 (1961) 1758
[4] V.Y. Denisov and A. Khudenko, Atomic Data and Nuclear Data Tables 95 (2009) 815
[5] B. Buck et al., Journal of Physics G: Nuclear and Particle Physics 17 (1991) 1223; 18 (1993) 143
[6] D. Poenaru and M. Ivascu, Journal De Physique 44 (1983) 791

Cs_2HfCl_6 (CHC) and Cs_2ZrCl_6 (CZC) crystal scintillators

Some general properties	Cs_2HfCl_6	Cs_2ZrCl_6
Effective atomic number	58	46.6
Density (g/cm^3)	3.9	3.4
Melting point (°C)	820	850
Crystal structure	Cubic	Cubic
Emission maximum (nm)	430	460
Scintillation time constants (μs)	0.4; 5.1; 15.2 *	0.4; 2.7; 12.5*
Light Yield	up to 30000 photons/MeV**	up to 41000 photons/MeV**
Linearity of the energy response	Excellent, down to 100 keV	Excellent, down to 100 keV
Energy resolution (FWHM, %) @ 662 keV	3.2 - 3.7***	3.5 - 7.0***
Pulse-shape discrimination ability	Excellent	Excellent
Mass-fraction of element of interest (%)	27	16

* *for alpha events at room temperature (Dalton Trans. 2022, 51, 6944-6954)*

** *for gamma quanta at room temperature*

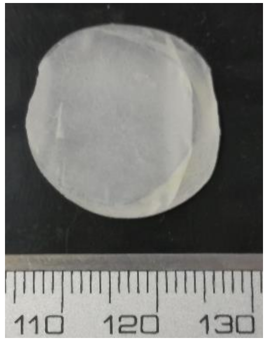
*** *depends on the crystal quality, surface treatment and readout system*

Production and growth of Cs_2HfCl_6 crystals

Produced at Queen's University, Canada

CHC-1 (6.90 g)

- ✓ **CsCl** (99.998%) + **$HfCl_4$** (99.8%) as starting materials
- ✓ $HfCl_4$ powder subjected to a three-fold purification process
- ✓ Grown by **Bridgman technique**: growth at 5°C/cm, at 10 mm/day)



CHC-2 (16.87 g)

- ✓ **CsCl** (99.9%) + **$HfCl_4$** (98%) as starting materials
- ✓ $HfCl_4$ powder subjected to a three-fold sublimation process
- ✓ Grown by **Bridgman technique**: «fast» (growth 25°C/cm, at 35 mm/day) + «slow» growth (20°C/cm, at 12 mm/day)

∅21.2×12.8 mm

Then polished with 1200 grit sandpaper, mineral oil as lubricant, cleaned by toluene

Chemical contamination of Cs_2HfCl_6 crystals

*HR-ICP-MS, concentrations are in **ppb** with 25% uncertainty*

Element	Concentration (ppb)	
	CHC-1, 6.90 g [1]	CHC-2, 16.87 g [2]
Nd	55	
Sm	36	2(1)
Eu	13	
Gd	18	
W	< 350	
Os	< 15	
Pt	< 1500	
Bi	< 2	
K		1900(570)
Pb	< 500	440(130)
Th		0.16(5)
U		0.7(2)

[1] V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941
[2] P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

Cs_2HfCl_6 crystal radiopurity

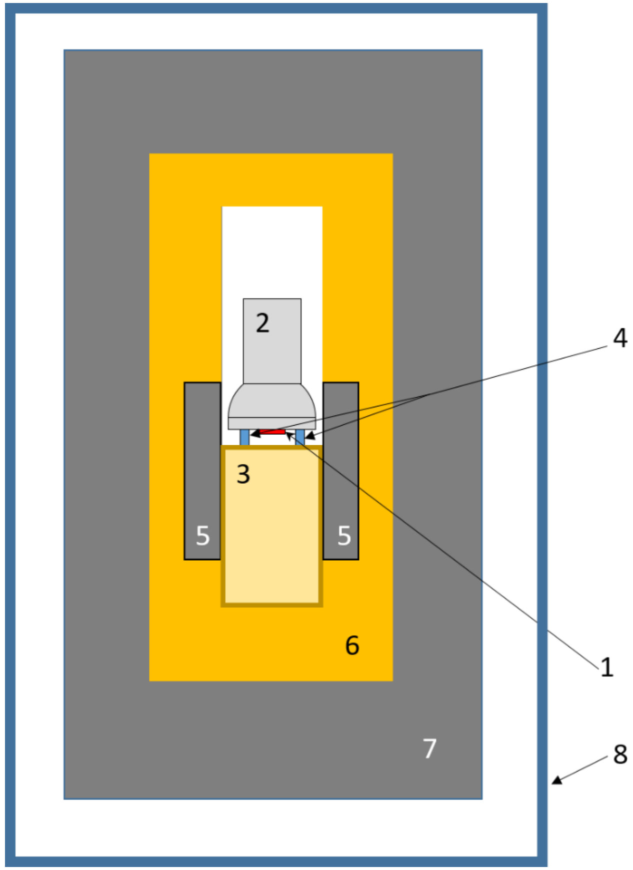
*measured with the ultra-low background **HPGe** γ spectrometers in the **STELLA** facility at LNGS, about 1000 hours*

Chain	Nuclide	Activity (mBq/kg)		
		6.90 g [1]	16.87 g [2]	
^{238}U	^{226}Ra	<23	<13	Natural
	^{234}Th	<0.80	<1200	Natural
	^{234m}Pa	<0.48	<18	Natural
^{235}U	^{235}U	<14	<18	Natural
^{232}Th	^{228}Ra	<12	<13	Natural
	^{228}Th	<3.6	<17	Natural
	^{210}Pb	<9.1	-	
	^{137}Cs	$0.78(8)\times10^3$	<10	→ Artificial
	^{134}Cs	79(8)	37(4)	Cosmogenic activation
	^{132}Cs	<15	-	Cosmogenic activation
	^{60}Co	<25	-	
	^{44}Ti	10(4)	-	→ Artificial
	^{40}K	$0.4(1)\times10^3$	<240	→ Natural

Only land transportation! $T_{1/2} \approx 2$ years (→ ^{134}Cs)

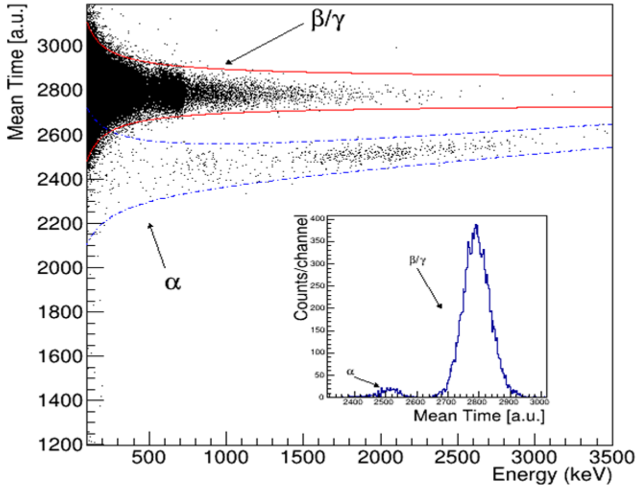
[1] V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941
[2] P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

First low-background measurements of Cs_2HfCl_6 at STELLA facility (LNGS)

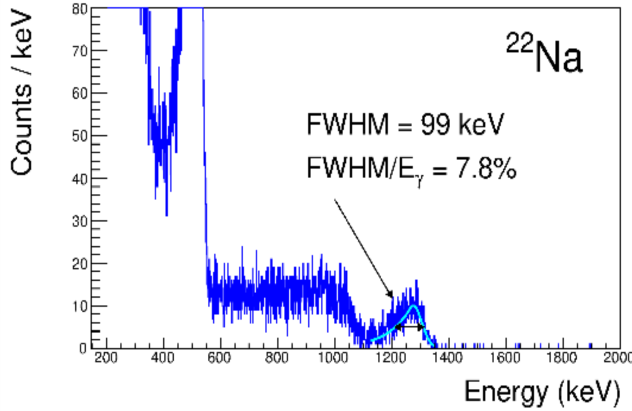


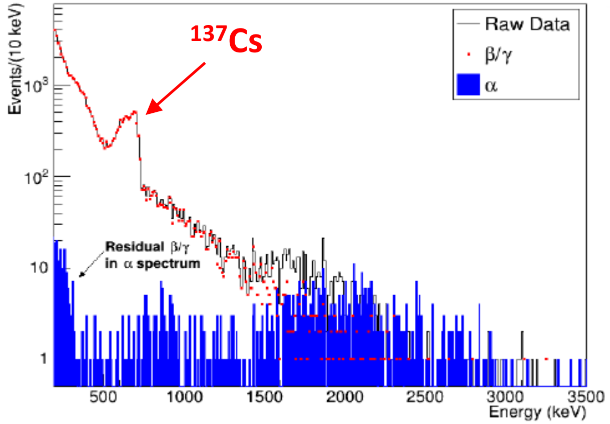
(1) CHC crystal scintillator
(2) PMT
(3) HP-Ge detector
(4) Teflon ring
(5) Pb, 2.5 cm
(6) HP Cu
(7) Pb, 25 cm
(8) Plexiglas box

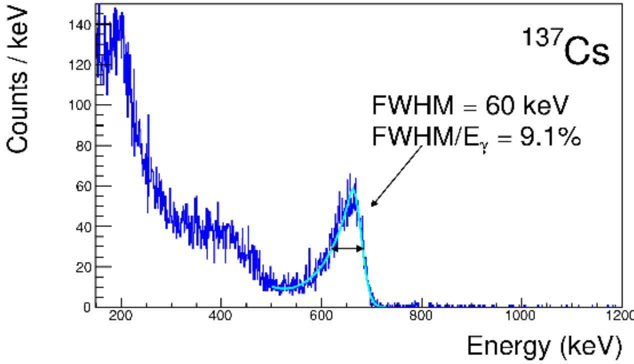
Selection efficiency is 99% in [0.4–3.0] MeV



FWHM = 9.1% @ 662 keV



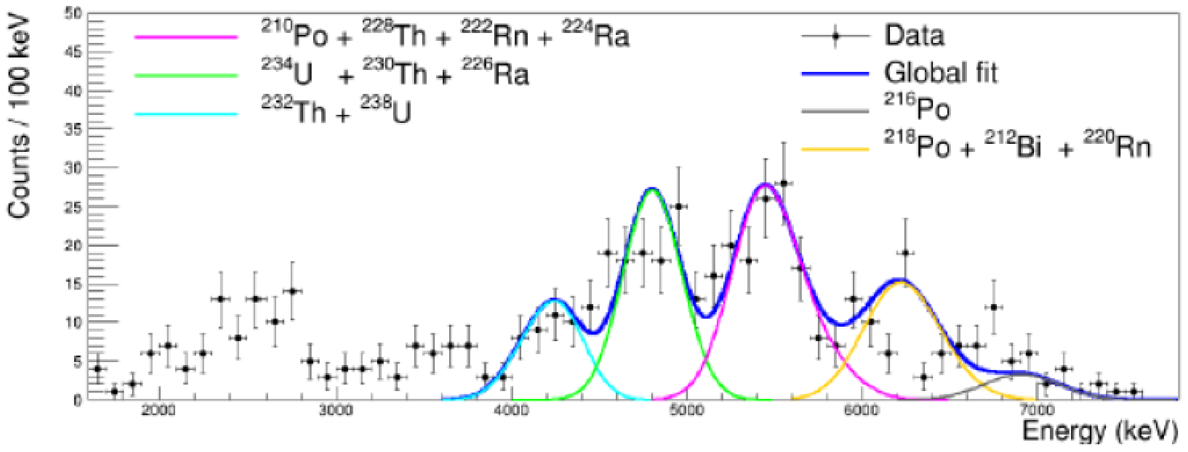




- ✓ CHC crystal coupled to low-radioactivity PMT (Hamamatsu R6233MOD) placed above the end-cap of the ultra-low background HPGe
- ✓ CAEN DT5720B digitizer 250 MSamples/s;
- ✓ 2848 h of data taking

V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941

Alpha spectrum and internal alpha activity



Total internal alpha activity = 7.8 mBq/kg

Chain	Nuclide	Internal contamination (mBq/kg)
		CHC-1 (6.9 g)
^{238}U	^{238}U	0.6(1)
	$^{234}U + ^{230}Th$	1.4(2)
	^{226}Ra	0.2(1)
	^{210}Pb	1.4(2)
^{232}Th	^{232}Th	0.2(1)
	^{228}Th	0.2(1)

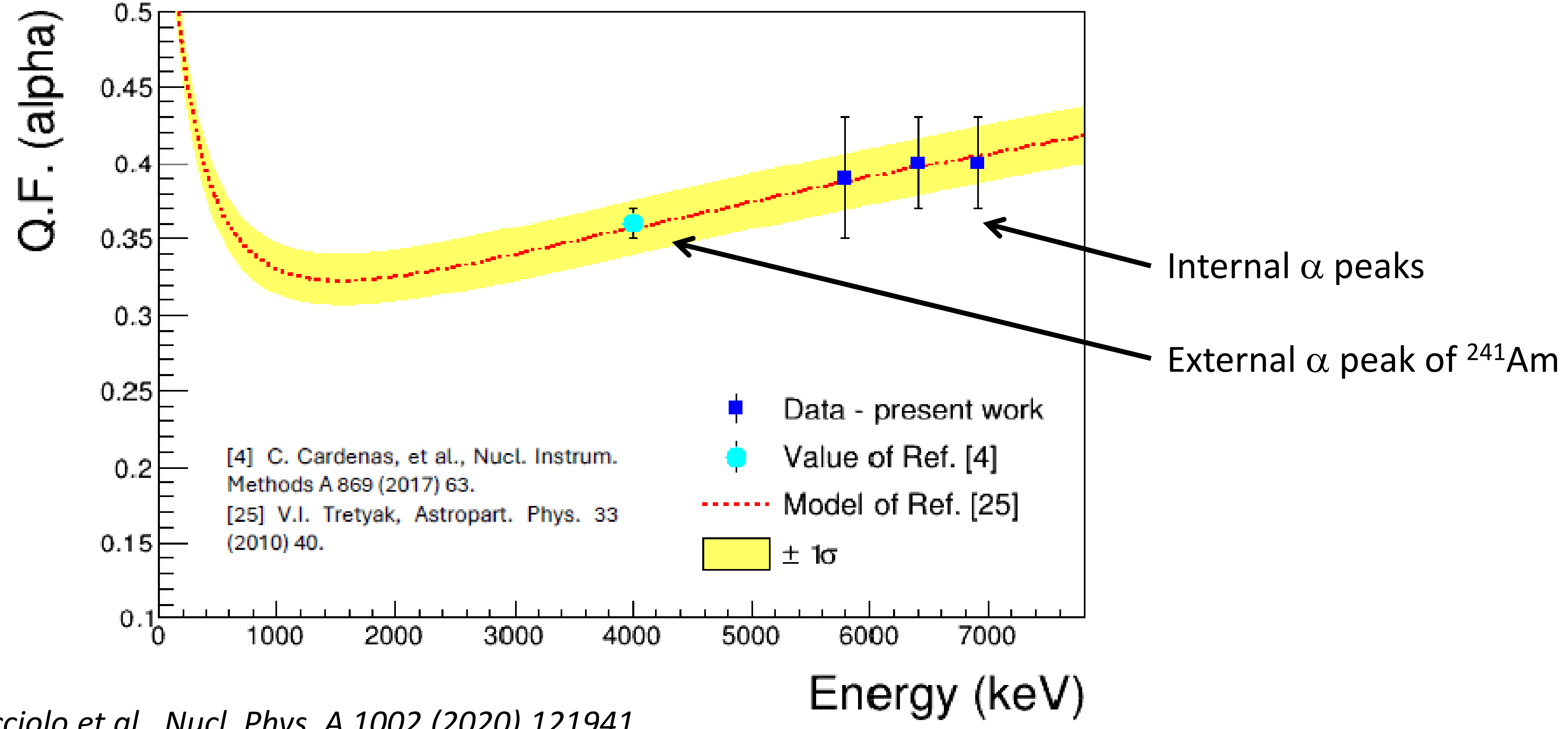
V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941

Quenching factor for alpha particles

- The time-amplitude analysis was used to select the events of the following decay sub-chain of the ^{232}**Th family**:

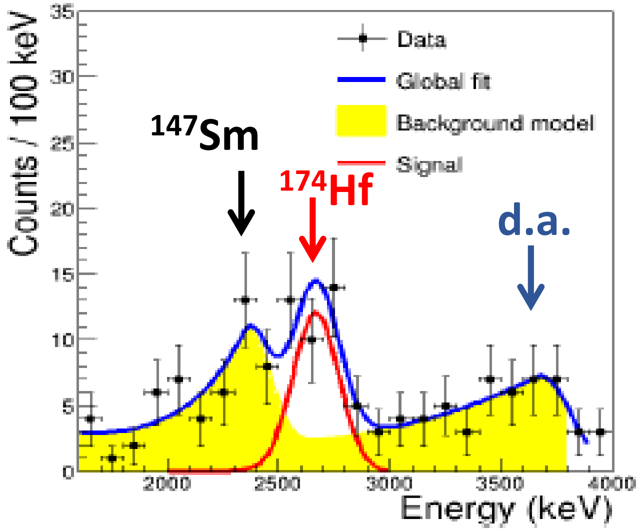
^{224}**Ra** (Q = 5789 keV; $T_{1/2}$ = 3.66 d) ⟶ ^{220}**Rn** (Q = 6405 keV; $T_{1/2}$ = 55.6 s) ⟶ ^{216}**Po** (Q = 6906 keV; $T_{1/2}$ = 0.145 s) ⟶ ^{212}**Pb**

- According to the result of the time-amplitude analysis, the Q.F. of the used CHC scintillator to α particles at the energies of ^{224}Ra, ^{220}Rn and ^{216}Po α decays is **0.39(4)**, **0.40(3)**, **0.40(3)**, respectively.



V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941

Alpha decay of ^{174}Hf



S = 31.7 ± 5.6 events

$T_{1/2}$ = (7.0 ± 1.2)×10^{16} y

Energy spectrum of α events in the region of interest selected by PSD over 2848 hours

<u>Background model:</u>

^{147}Sm + ^{174}Hf + degraded alphas + exp

Previous value should be discarded

$T_{1/2}$ = (2.0 ± 0.4)×10^{15} y

R.D. MacFarlane and T.P. Kohman, Phys. Rev. 121 (1961) 1758

High quality and radiopurity (especially on ^{147}Sm) CHC crystals are required for further studies of this process

V. Caracciolo et al., Nucl. Phys. A 1002 (2020) 121941

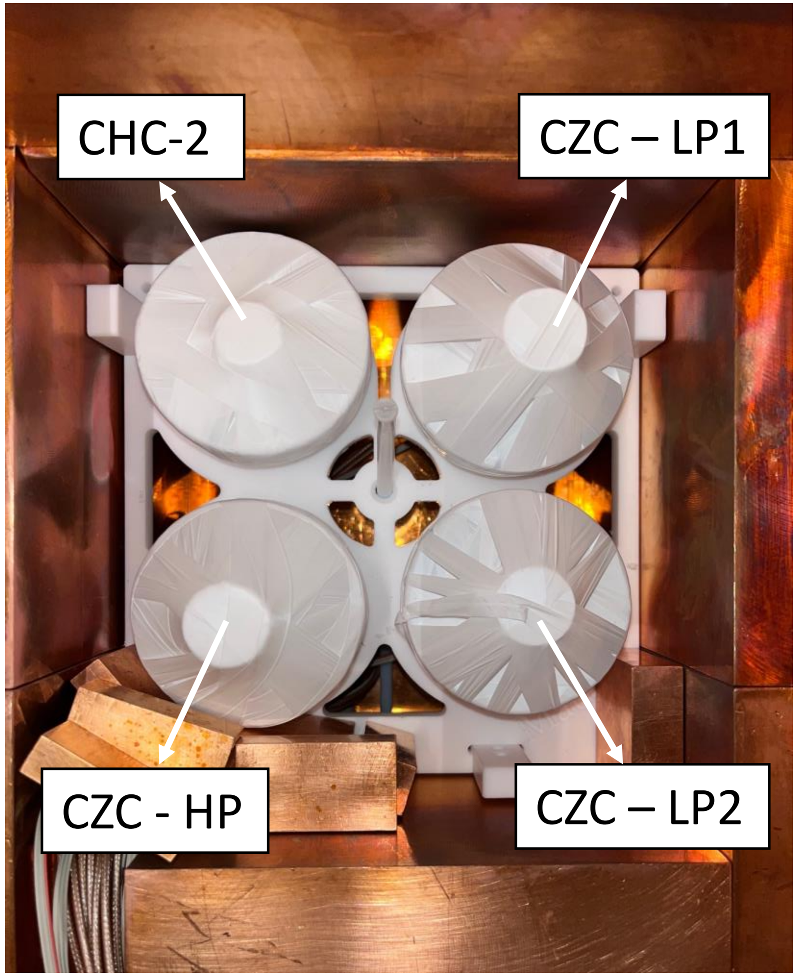
New experimental limits on various α decay modes in Hf isotopes

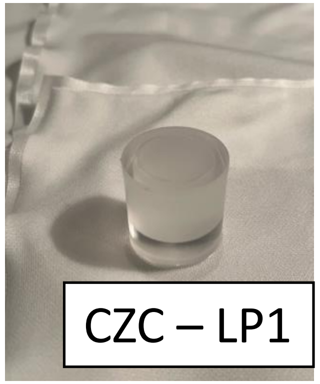
Transition	Parent/Daughter Levels, its Energy, keV	Experimental $T_{1/2}$, yr	Theoretical estimation of $T_{1/2}$ [1,2,3], yr
^{174}Hf → ^{170}Yb	$0^+ \to 0^+$, g.s.	$7.0(1.2)\times10^{16}$	$(3.0 \text{ to } 7.4)\times10^{16}$
	$0^+ \to 2^+$, 84.3	$> 1.1\times10^{15}$	$(0.7 \text{ to } 3.0)\times10^{18}$
^{176}Hf → ^{172}Yb	$0^+ \to 0^+$, g.s.	$> 9.3\times10^{19}$	$(2.0 \text{ to } 7.0)\times10^{20}$
	$0^+ \to 2^+$, 78.7	$> 1.8\times10^{16}$	$(0.5 \text{ to } 3.5)\times10^{22}$
^{177}Hf → ^{173}Yb	$7/2^- \to 5/2^-$, g.s.	$> 3.2\times10^{20}$	$(0.05 \text{ to } 5.2)\times10^{22}$
	$7/2^- \to 7/2^-$, 78.6	$> 7.5\times10^{16}$	$(0.01 \text{ to } 1.2)\times10^{24}$
^{178}Hf → ^{174}Yb	$0^+ \to 0^+$, g.s.	$> 5.8\times10^{19}$	$(0.2 \text{ to } 1.1)\times10^{24}$
	$0^+ \to 2^+$, 76.5	$> 6.9\times10^{16}$	$(0.7 \text{ to } 8.1)\times10^{25}$
^{177}Hf → ^{173}Yb	$9/2^+ \to 7/2^+$, g.s.	$> 2.5\times10^{20}$	$(0.01 \text{ to } 4.0)\times10^{32}$
	$9/2^+ \to 9/2^+$, 104.5	$> 5.5\times10^{17}$	$(0.01 \text{ to } 2.5)\times10^{35}$

[1] V.Y. Denisov and A. Khudenko, Atomic Data and Nuclear Data Tables 95 (2009) 815
[2] B. Buck et al., Journal of Physics G: Nuclear and Particle Physics 17 (1991) 1223; 18 (1993) 143
[3] D. Poenaru and M. Ivascu, Journal De Physique 44 (1983) 791

New low-background measurements of Cs_2HfCl_6 in DAMA/CRYS setup (LNGS)

DAMA/CRYS setup at LNGS

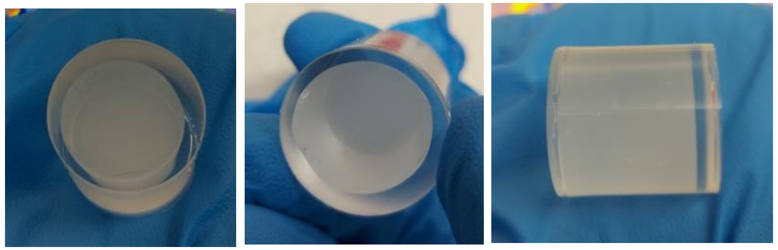




P. Belli et al., JINST 19 (2024) P05037

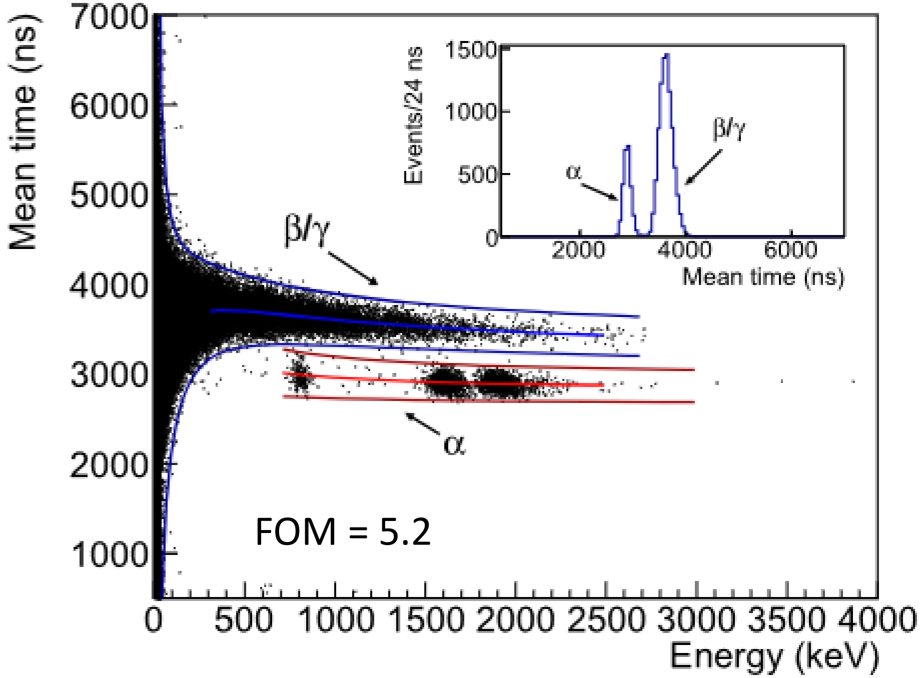
P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

- ✓ Three new Cs_2ZrCl_6 crystals + one Cs_2HfCl_6 (CHC-2)
- ✓ Total mass of Cs_2HfCl_6 = 16.87 g
- ✓ FWHM = 6-8% @ 662keV
- ✓ Produced from high purity and purified raw materials (> 99.99%)
- ✓ **CZC crystals are encapsulated in a silicon-based resin + quartz window**
- ✓ Modified experimental setup
- ✓ Measurements started on June 30th, 2023, for a total of 97.7 days live time

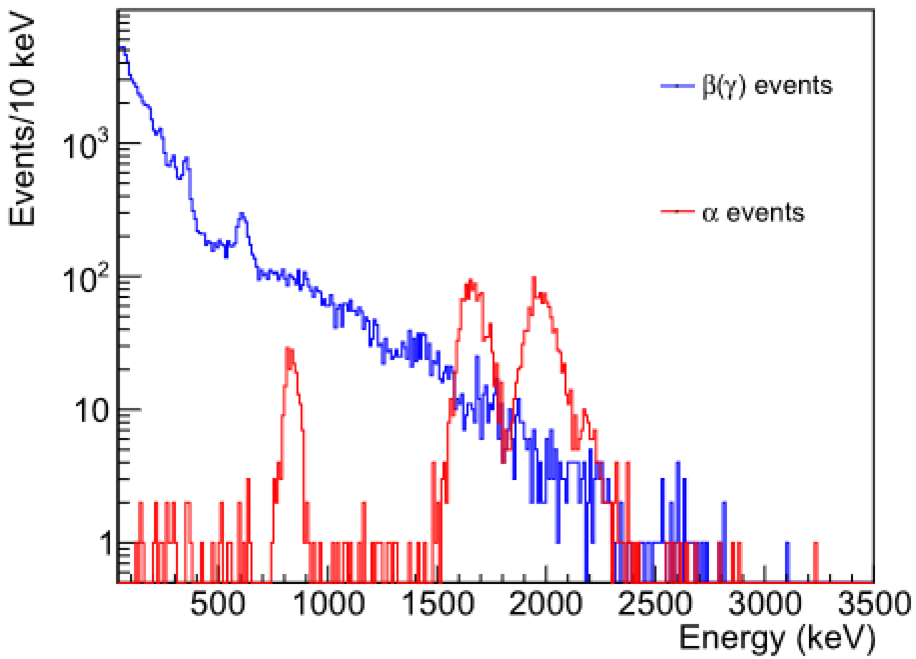


Data analysis of the new Cs_2HfCl_6 crystal

Selection efficiency is 99.7% in [0.6–3.0] MeV



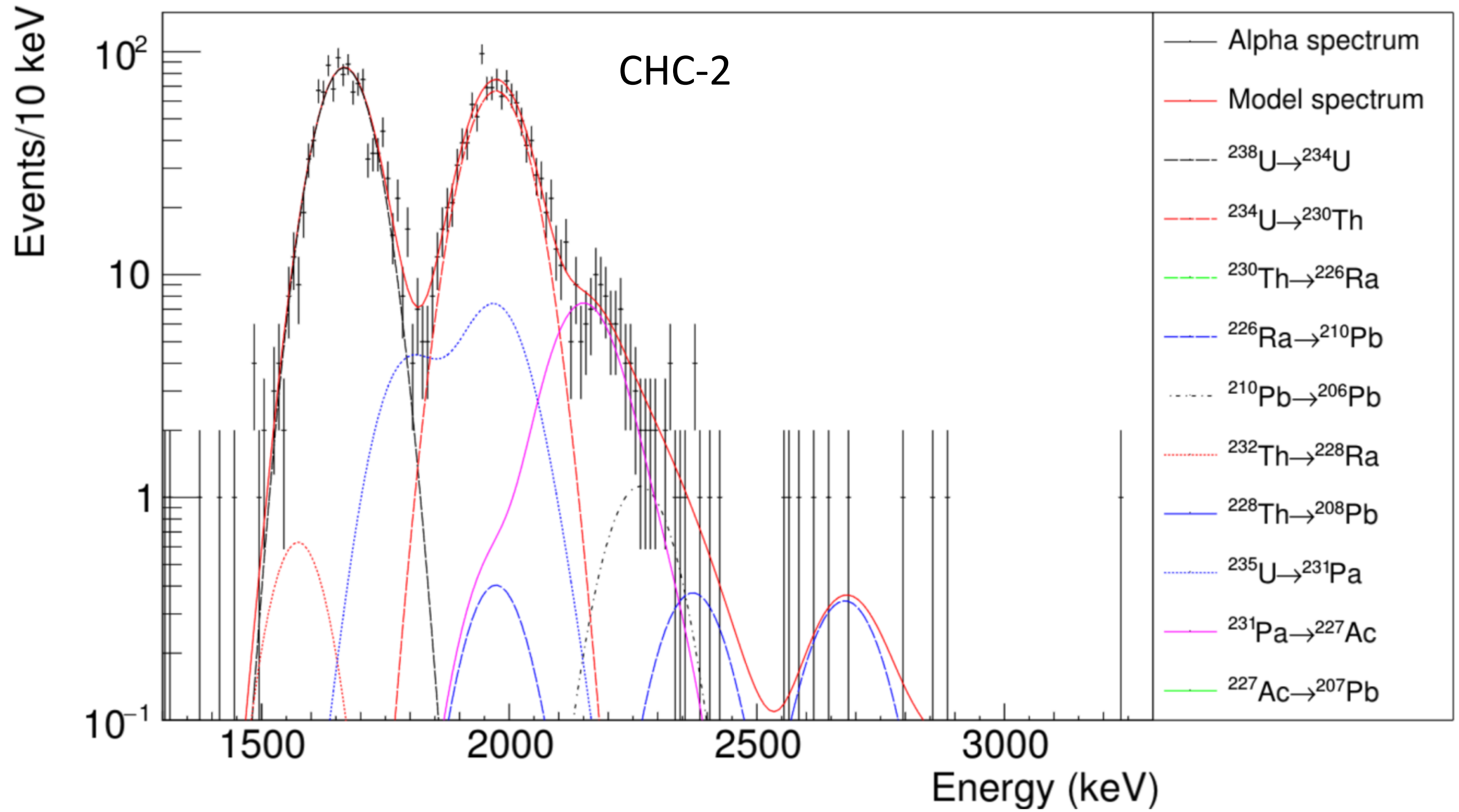
Measured energy spectra over 97.7 days of data taking



FWHM = 6.8% @ 662 keV

P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

Cs_2HfCl_6: alpha background model



Total internal alpha activity = 18.6 mBq/kg

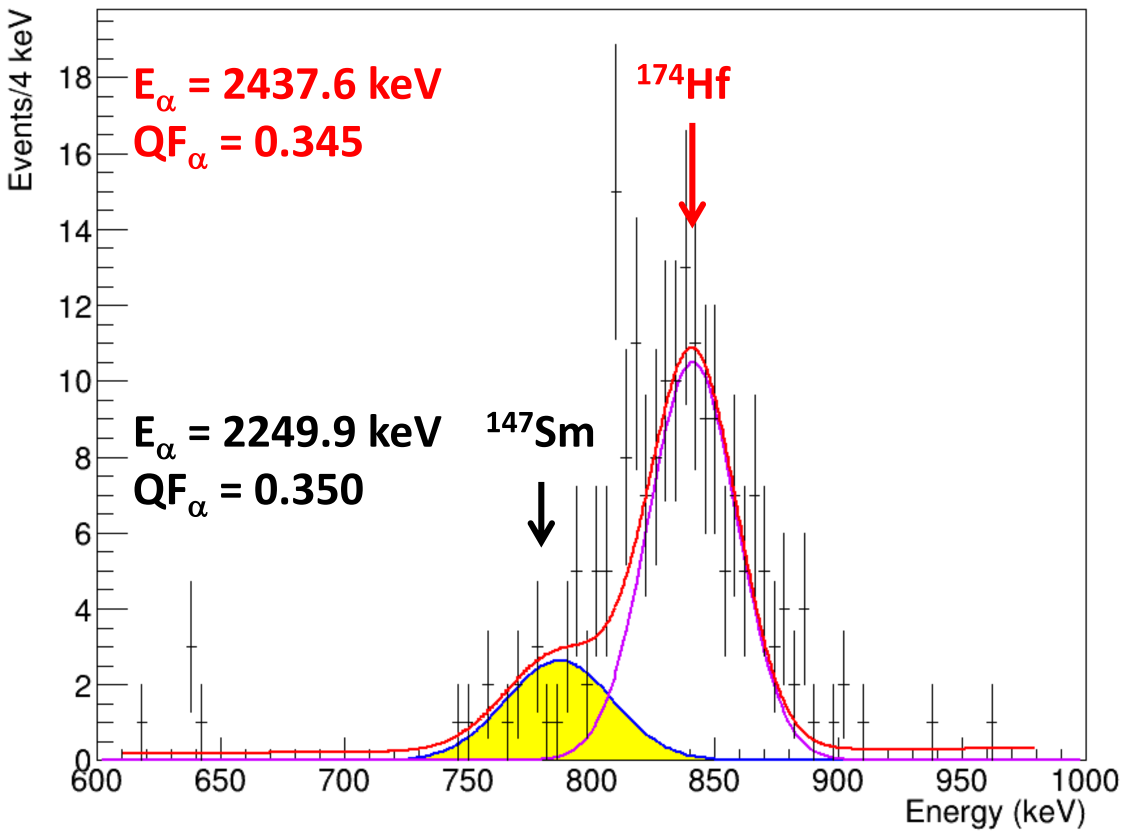
$\alpha/\beta = 0.2777(65) + 0.0278(14) \cdot E_\alpha[\text{MeV}]$

$\text{FWHM(keVee)} = \sqrt{5.97 * E[keVee] + 0.0014 \cdot E^2[keVee]}$

Chain	Nuclide	Internal contamination (mBq/kg)
		CHC-2 (16.87 g)
^{238}U	^{238}U	7.6(3)
	^{234}U	6.7(5)
	^{230}Th	< 0.5
	^{226}Ra	0.04(2)
	^{210}Pb	0.12(7)
^{235}U	^{235}U	1.3(5)
	^{231}Pa	0.92(13)
	^{227}Ac	<0.005
^{232}Th	^{232}Th	< 0.22
	^{228}Th	<0.02
	^{147}Sm	0.25(10)
	^{134}Cs	44(8)
	^{87}Rb	< 400
	^{40}K	< 2.3

P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

New measurement of ^{174}Hf alpha decay



(36 ± 15) counts (118 ± 37) counts

$T_{1/2} = (3.8^{+1.7}_{-0.9})\times10^{16}$ yr

Energy spectrum of α events in the region of interest selected by PSD over 2344.8 hours

Background model:

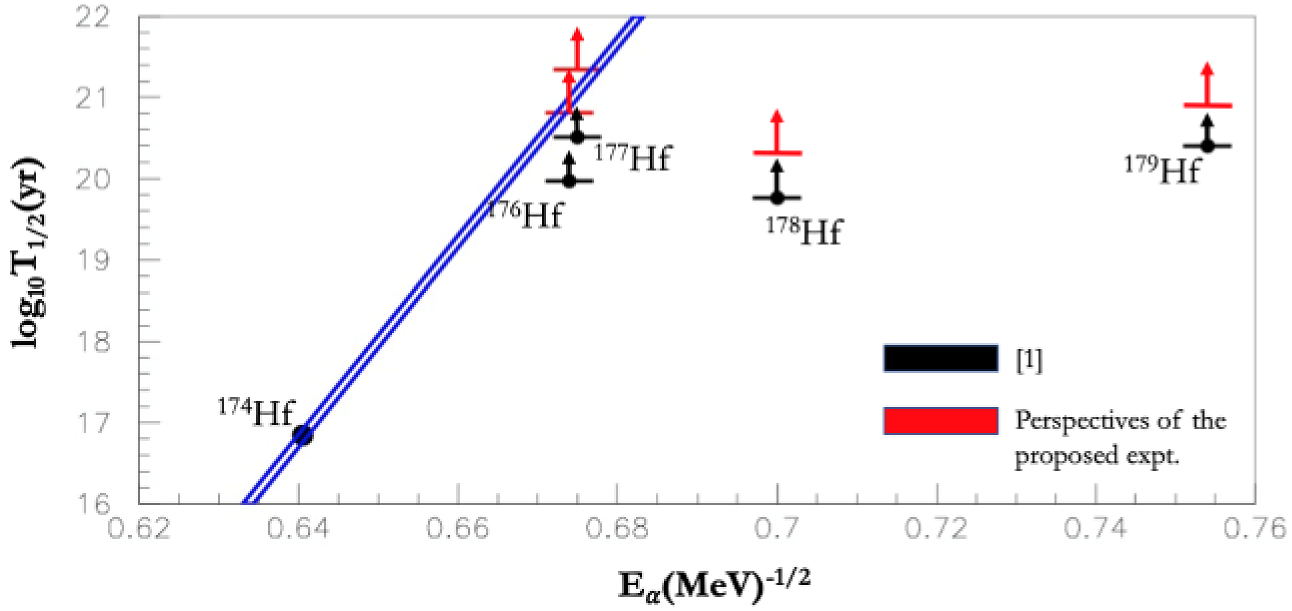
^{147}Sm + ^{174}Hf + polynomial

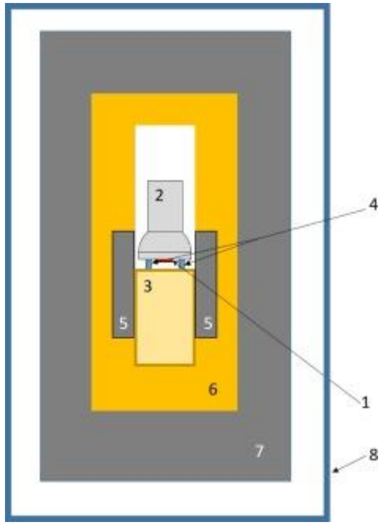
Activity of ^{147}Sm = **(0.25 ± 0.10) mBq/kg**, corresponding to a concentration of **(2.0 ± 0.8) ppb** of ^{nat}Sm, in agreement with ICP-MS measurements

P. Belli et al., Nucl. Phys. A 1053 (2025) 122976

Other rare alpha decays

- There are several undiscovered rare alpha decays yet
- $^{176,177}Hf$ rare alpha decays have an opportunity to be discovered in one year of measurements with 120 g of Cs_2HfCl_6 (CHC) scintillator



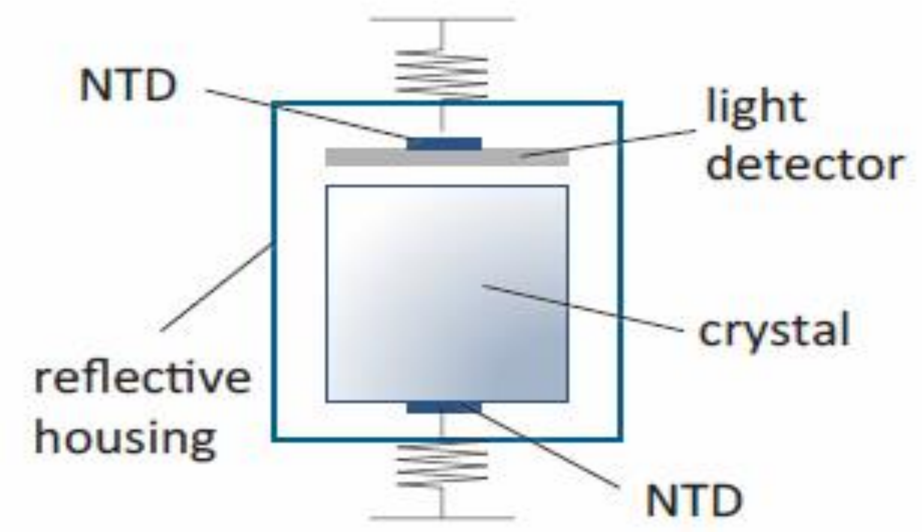


The red symbols represent the sensitivity that could be reached using a CHC crystal scintillators with 43.83 kg × day of exposure (120 g × year) in the current low-background setup at LNGS

The black symbols – current limits on rare alpha decays from measurements with CHC crystal with 7.12 kg × day exposure

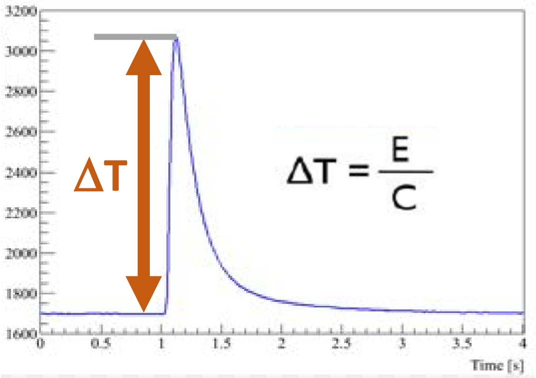
[1] Nucl. Phys. A 2020, 1002, 121941. https://doi.org/10.1016/j.nuclphysa.2020.121941
[2] Radiation 2022, 1, 1–14. https://doi.org/10.3390/radiation1010000

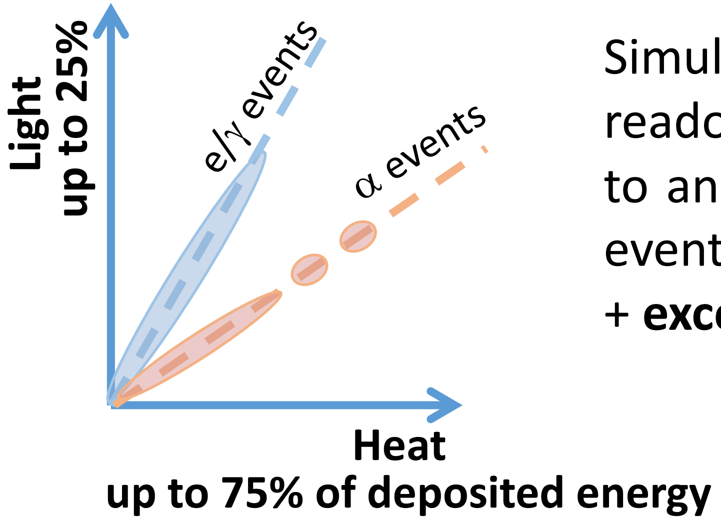
Cryogenic scintillating calorimeter



During particle interaction in the crystal a fraction of the deposited energy is converted into scintillation. Combining the crystal with cryogenic light detector allows to simultaneous measurement of the energy deposited in crystal (**H**) and produced scintillation (**L**)

Typical heat pulse

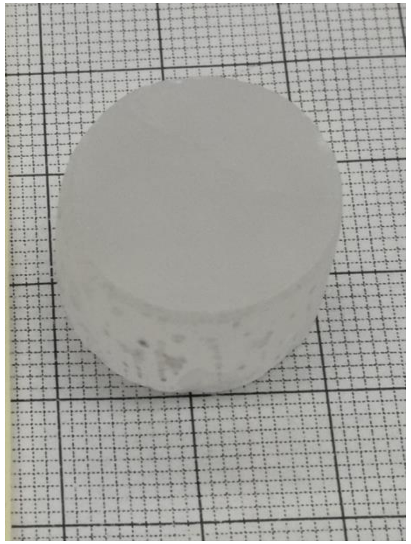




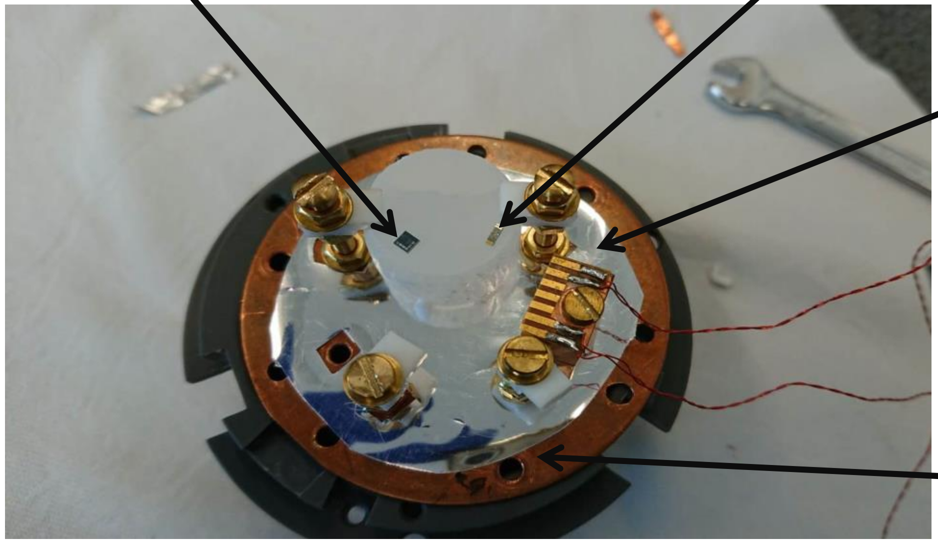
Simultaneous and independent, double readout of heat and scintillation light leads to an effective discrimination of e/γ from α events by the different **L/H ratio**

+ **excellent energy resolution**

Cs_2HfCl_6 as a scintillating calorimeter



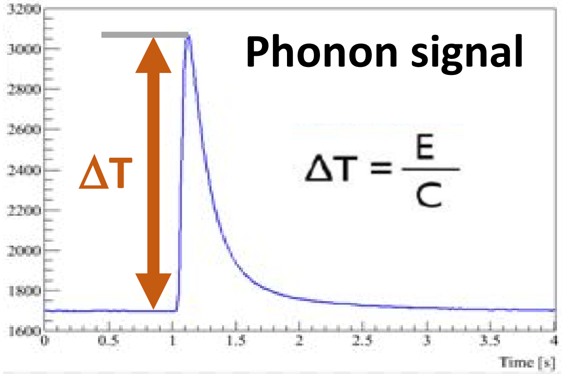
VN1031
16.2 g
∅20.8 × 13.2 mm
24,000 ph/MeV
10.5% @ 662 keV

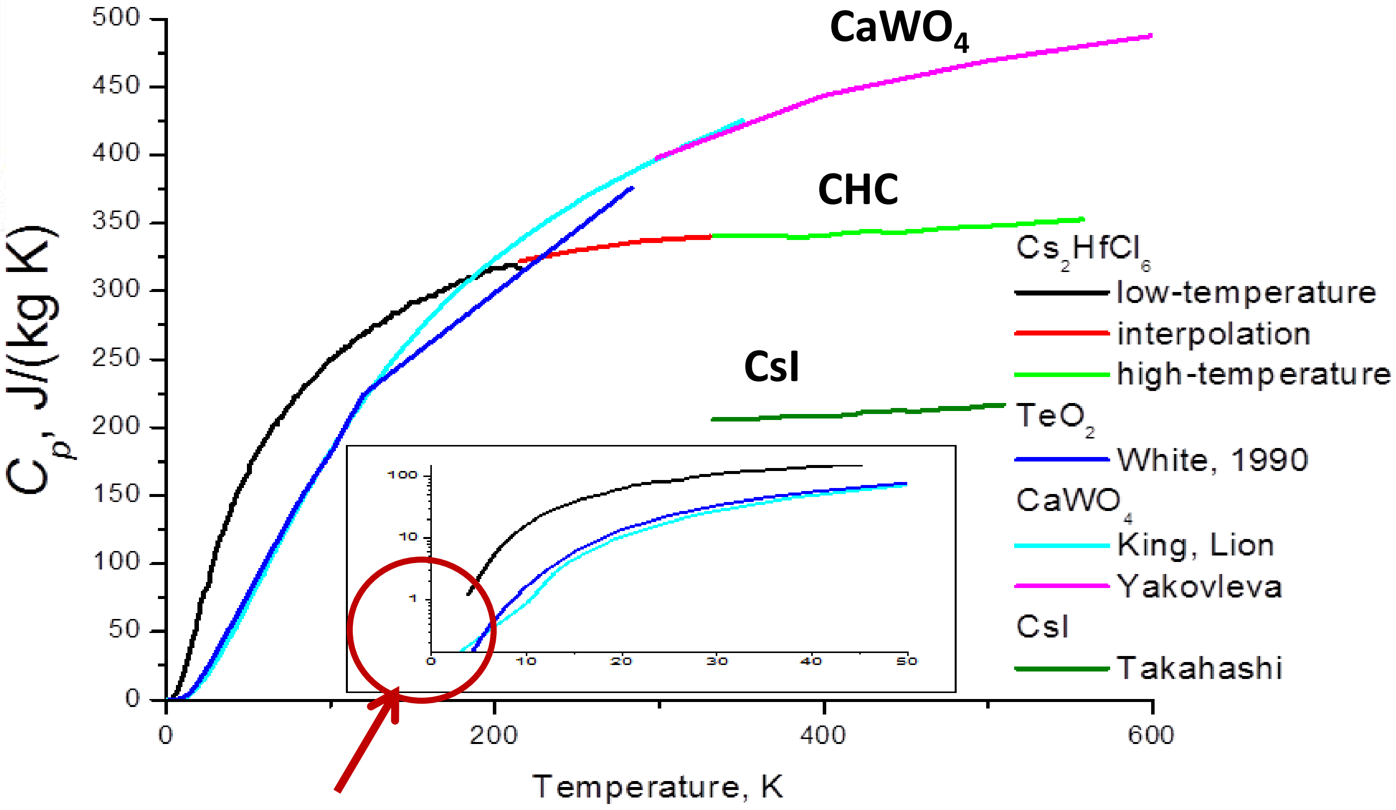


was tested at France, Orsay in 2020
Good scintillating signal at mK temperature,
but **NO phonon signal**

https://doi.org/10.1039/D1TC06166F

Cs_2HfCl_6: Heat capacity

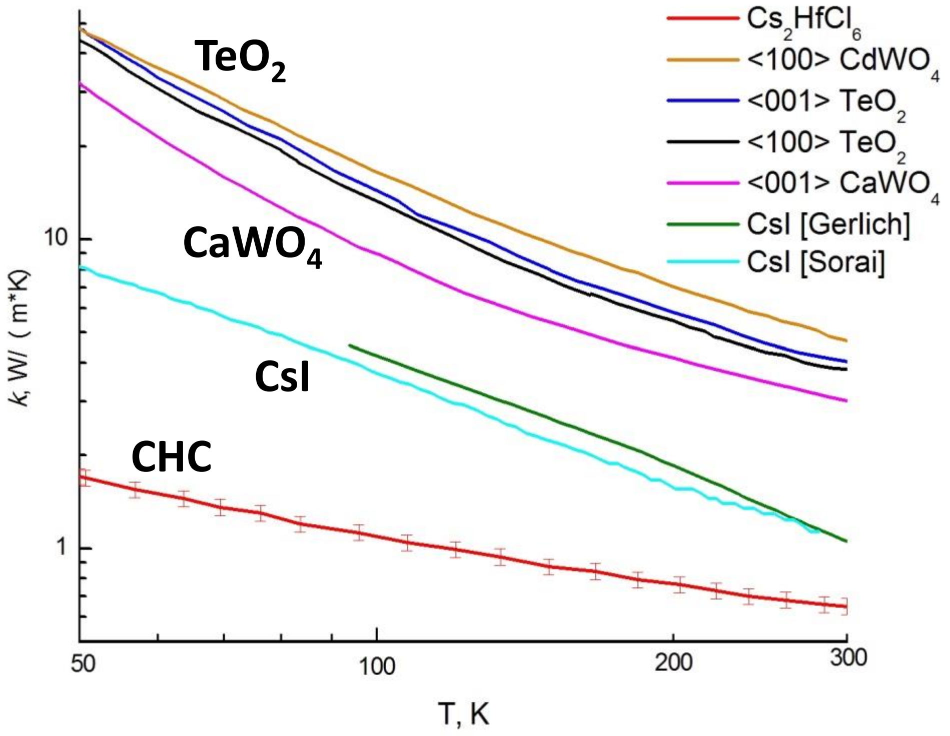


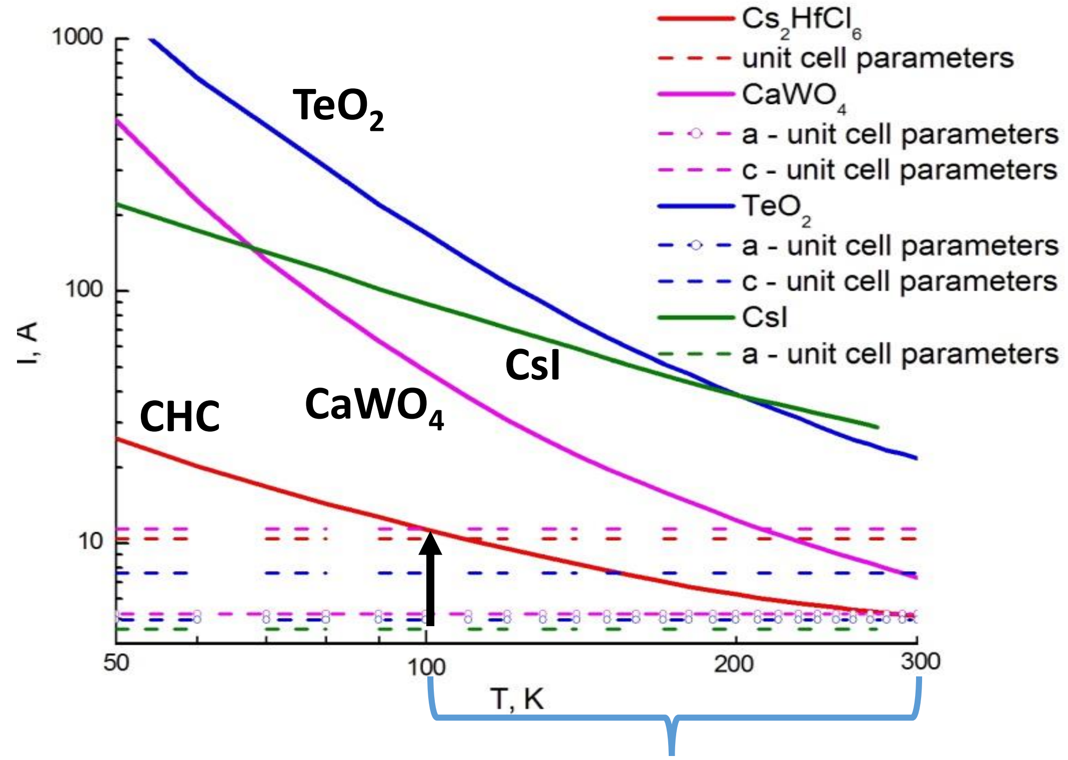


One could expect amplitude of the phonon signal of about 10 times less!

https://doi.org/10.1039/D1TC06166F

Cs_2HfCl_6: Heat conductivity and Phonon mean free path





Phonons captured in a single unit cell

Clear evidence
that Cs_2HfCl_6 cannot be a good calorimeter, but it is an excellent phonon insulator

https://doi.org/10.1039/D1TC06166F

Summary (1)

- The first experiment using a 6.9 g Cs_2HfCl_6 crystal scintillator in coincidence with a HPGe detector was successfully performed and α decay of ^{174}Hf was observed with $\mathbf{T_{1/2} = (7.0 \pm 1.2) \times 10^{16}}$ **yr**
- A new measurement using a new Cs_2HfCl_6 crystal (16.9 g) carried out in the DAMA/CRYS setup at LNGS confirmed previously obtained experimental value $\mathbf{T_{1/2} = (3.8^{+1.7}_{-0.9}) \times 10^{16}}$ **yr**
- A new experiment with four high-purity Cs_2HfCl_6 crystals (each about ∅21×20 mm and mass of about 20 g) in an optimized geometry and encapsulated in silicon-based sealant is ongoing aiming to improve sensitivity to ^{174}Hf alpha decay and to detect rare alpha decays of ^{176}Hf&^{177}Hf for the first time

Neutrinoless double beta ($0\nu\beta\beta$) decay of ^{94}Zr and ^{96}Zr

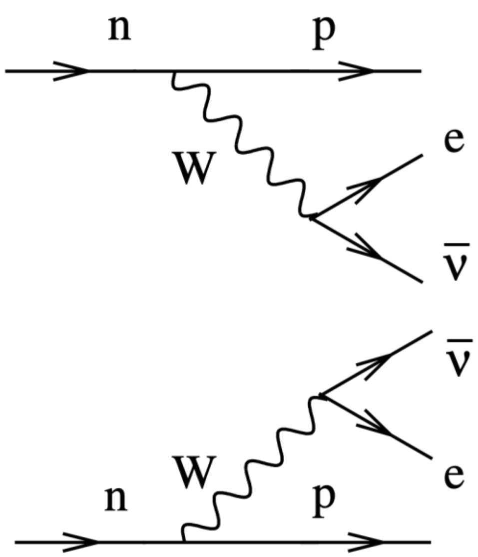
Neutrinoless double beta (0νββ) decay

$2\nu2\beta: (A,Z) \rightarrow (A,Z+2) + 2e^- + 2\bar{\nu}_e$

$0\nu2\beta : (A,Z) \rightarrow (A,Z+2) + 2e^-$

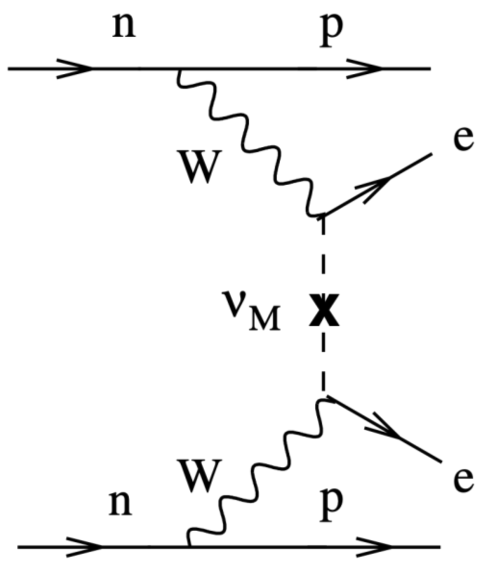
<ins>Why we need to search for 0ν2β decay?</ins>

- Lepton Number Violation process ($\Delta L = 2$), physics beyond the SM
- Determination of the neutrino nature (Majorana or Dirac particles)
- Majorana neutrino can help to explain the matter/antimatter asymmetry in Universe
- Constraints on neutrino mass hierarchy and mass scale



<ins>2ν mode:</ins>

- Allowed in SM
- Already observed for dozen nuclei
- Half-lives of the order 10^{18} - 10^{22} yr



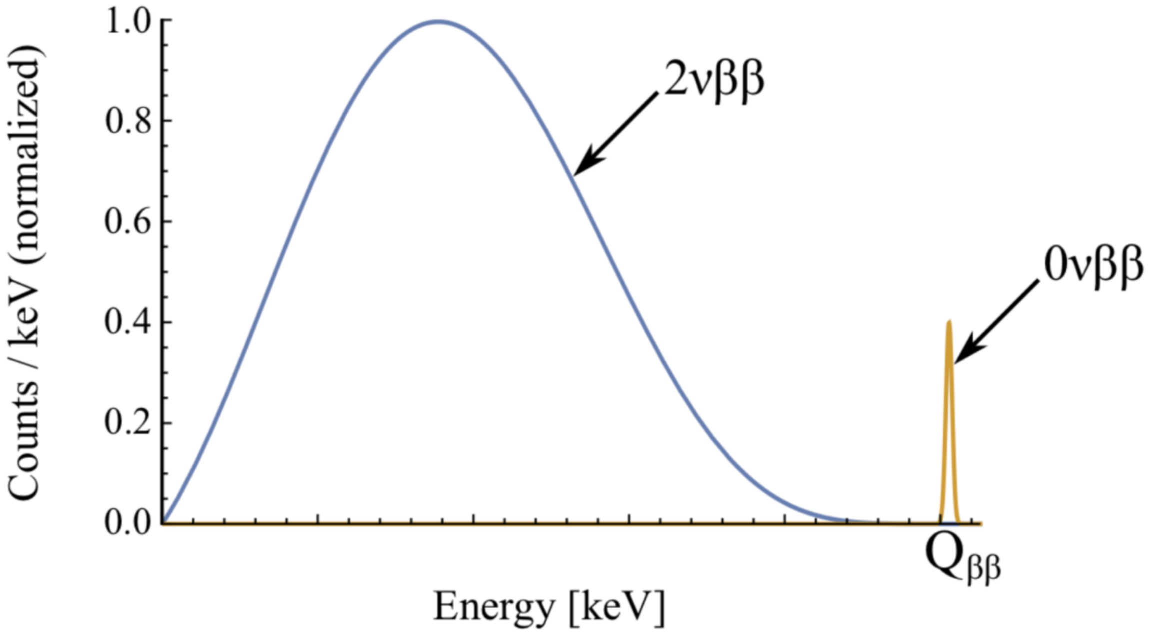
<ins>0ν mode:</ins>

- Not allowed in SM
- Never observed
- Limits on the half-life $T_{1/2} > 10^{24}$ - 10^{26} yr

Experimental search for 0νββ decay

The experimental signature in calorimetric experiments:

A monochromatic peak centered at $Q_{\beta\beta}$ over the 2νββ tail



Experimental sensitivity: $S_{0\nu} \propto \epsilon \sqrt{\frac{M \cdot T}{Bkg \cdot \Delta}}$

ϵ : detection efficiency;

M: source mass [kg];

T: measurement time [yr];

Bkg: background rate [counts/keV/kg/yr];

Δ: energy resolution [keV];

Phase space factor (computed)

Majorana mass (parameter of interest)

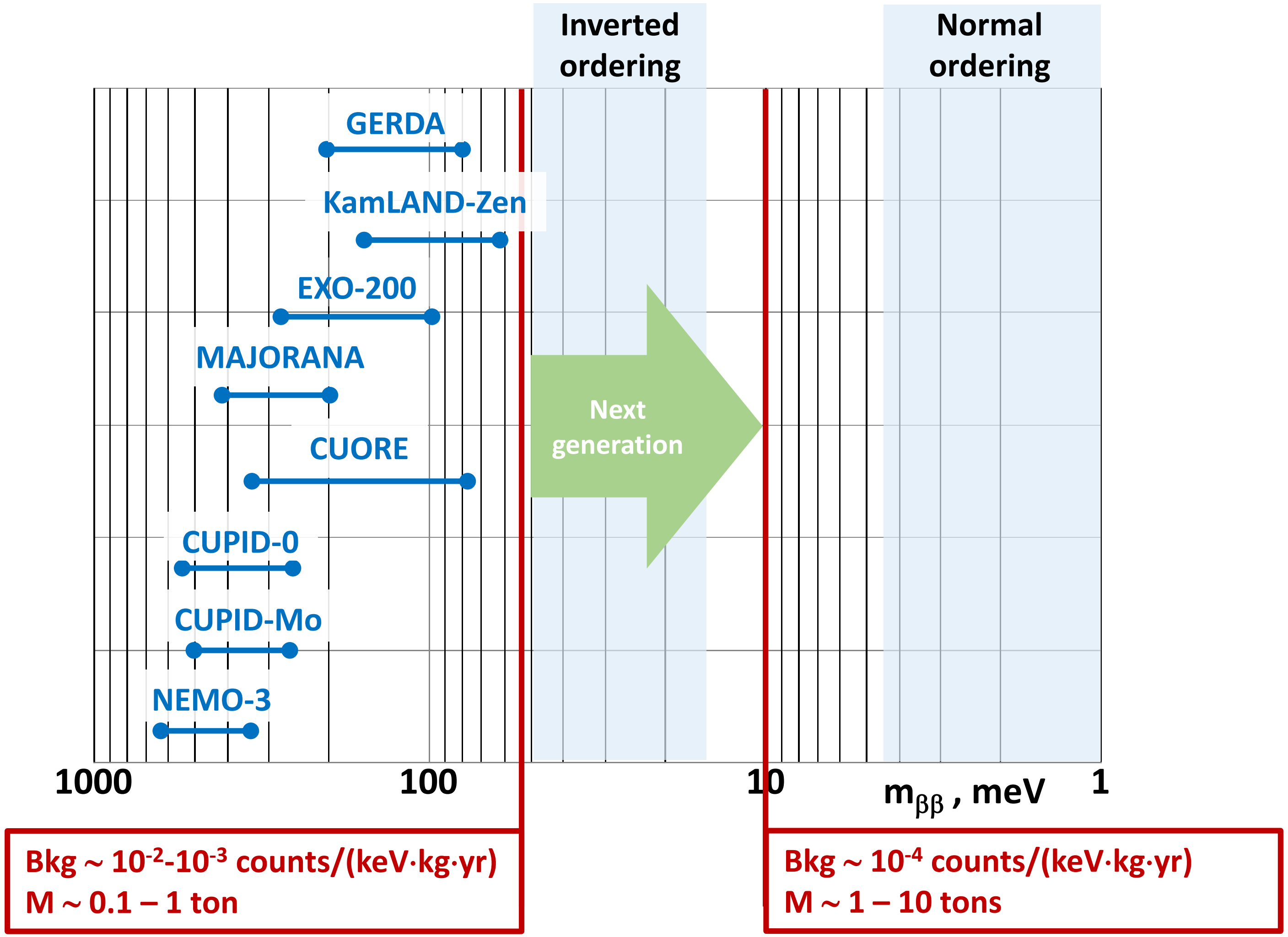
$$T_{1/2}^{0\nu} = \left[G_{0\nu} |\mathcal{M}_{0\nu}|^2 g_A^4 \left(\frac{m_{\beta\beta}^2}{m_e^2} \right) \right]^{-1}$$

Experimentally observable

Nuclear physics (models + experiments)

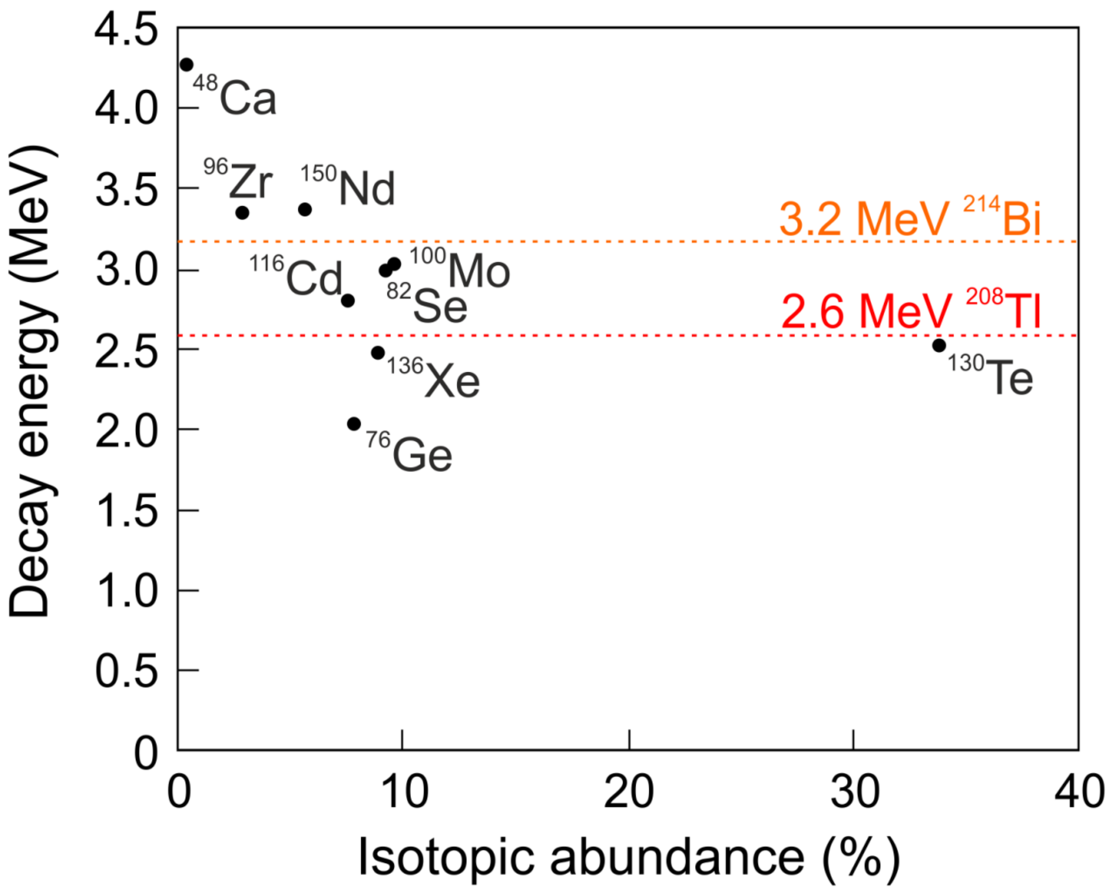
Impressive progress has been achieved in searches for 0ν2β decay

GERDA, ^{76}Ge *Phys. Rev. Lett. 125 (2020) 252502*	**$T_{1/2} > 1.8\times10^{26}$ yr**
KamLAND-Zen, ^{136}Xe *Phys. Rev. Lett. 117 (2016) 082503*	**$T_{1/2} > 1.1\times10^{26}$ yr**
EXO-200, ^{136}Xe *Phys. Rev. Lett. 123 (2019)161802*	**$T_{1/2} > 3.5\times10^{25}$ yr**
MAJORANA Dem., ^{76}Ge *Phys. Rev. C 100 (2019) 025501*	**$T_{1/2} > 2.7\times10^{25}$ yr**
CUORE, ^{130}Te *arXiv:2011.09295v2*	**$T_{1/2} > 3.2\times10^{25}$ yr**
CUPID-0, ^{82}Se *Phys. Rev. Lett. 129 (2022) 111801*	**$T_{1/2} > 4.6\times10^{24}$ yr**
CUPID-Mo, ^{100}Mo *Eur. Phys. J. C 82 (2022) 1033*	**$T_{1/2} > 1.8\times10^{24}$ yr**
NEMO-3, ^{100}Mo *Phys. Rev. D 92 (2015) 072011*	**$T_{1/2} > 1.1\times10^{24}$ yr**



0ν2β searches with non-trivial candidates

There are more than 60 potentially 2β-active isotopes, but only few of them are currently under consideration



^{76}Ge, ^{130}Te, ^{136}Xe are facing issues with an internal and environmental gamma background, while profiting from well-developed crystal production and material purification technologies

^{82}Se, ^{100}Mo, ^{116}Cd – only ^{100}Mo is under consideration due to a well-developed detector material and its high radiopurity

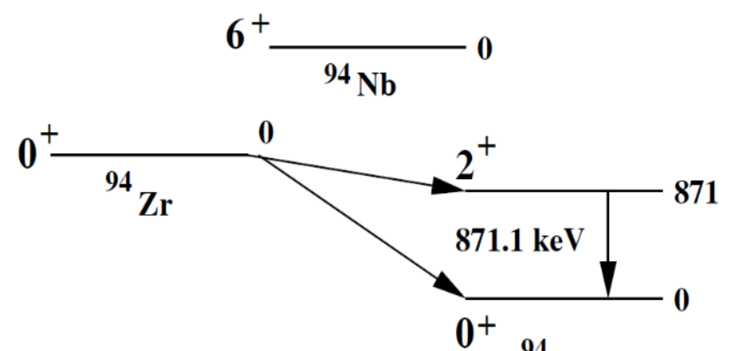
^{48}Ca, ^{96}Zr, ^{150}Nd are the less studied due to combination of unfavorable experimental conditions specific to each of them

Recent proposal: to study
0ν2β of **^{96}Zr** with novel Cs_2ZrCl_6 scintillators
via "source = detector" experimental approach

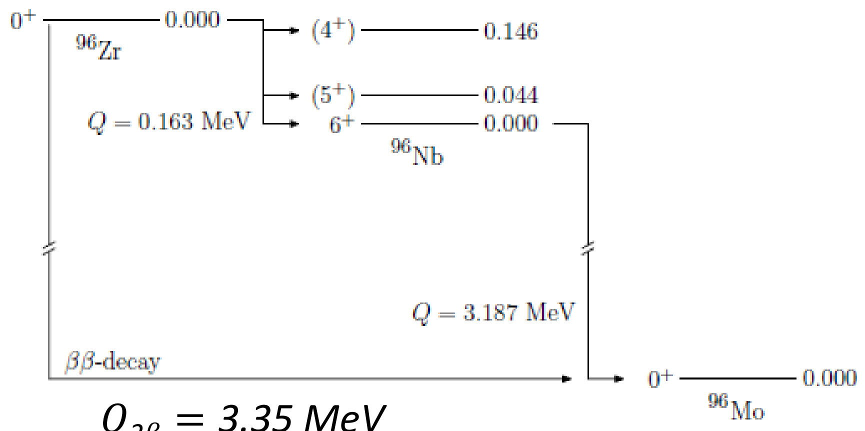
- *$Q_{ββ}$ (^{96}Zr) = 3.35 MeV*
- *Favorable from a theoretical point of view $T_{1/2}$ ~$(Q_{ββ})^{-5}$*
- *Reasonable natural i.a. (2.8%)*
- *New advanced detector material (Cs_2ZrCl_6)*
- *Crystal production under full control*
- *Extensive studies of the detector properties are ongoing*

Brief overview of rare decay search in $^{94,96}Zr$ isotopes

Experiment	Transition	$T_{1/2}$ @ 90% C.L. (yr)	Ref.	Technique
ZICOS (Kamioka Observatory, Japan)	$^{96}Zr \rightarrow ^{96}Mo$ (g.s.)	under construction	[1]	Liquid scintillator
NEMO-3 (Frejus, France)	$^{96}Zr \rightarrow ^{96}Mo$ (g.s.)	$> 9.2\times10^{21}$ $> 1.29\times10^{22}$	[2] [3]	Tracking detector
Kimballton Underground Research Facility, (USA)	$^{96}Zr \rightarrow ^{96}Mo$ (2^+_1)	$> 3.1\times10^{20}$	[4]	HPGe
Collaboration at Frejus, (France)	$^{96}Zr \rightarrow ^{96}Mo$ $(2^+_1, 0^+_1, 2^+_2, 2^+_3)$	$> (2.6 - 7.9)\times10^{19}$	[5]	HPGe
Collaboration at LNGS	$^{96}Zr \rightarrow ^{96}Mo$ (2^+_1)	$> 3.8\times10^{19}$	[6]	HPGe
Collaboration at LNGS	$^{94}Zr \rightarrow ^{94}Mo$ (2^+_1)	$> 2.1\times10^{20}$	[7]	HPGe
TILES (TIFR, Mumbai)	$^{94}Zr \rightarrow ^{94}Mo$ (2^+_1)	$> 5.2\times10^{19}$	[8]	HPGe
Kimballton Underground Research Facility (USA)	$^{96}Zr \rightarrow ^{96}Mo$ (6^+)	$> 2.4\times10^{19}$	[9]	HPGe



$Q_{2\beta} = 1.14$ MeV



$Q_{2\beta} = 3.35$ MeV

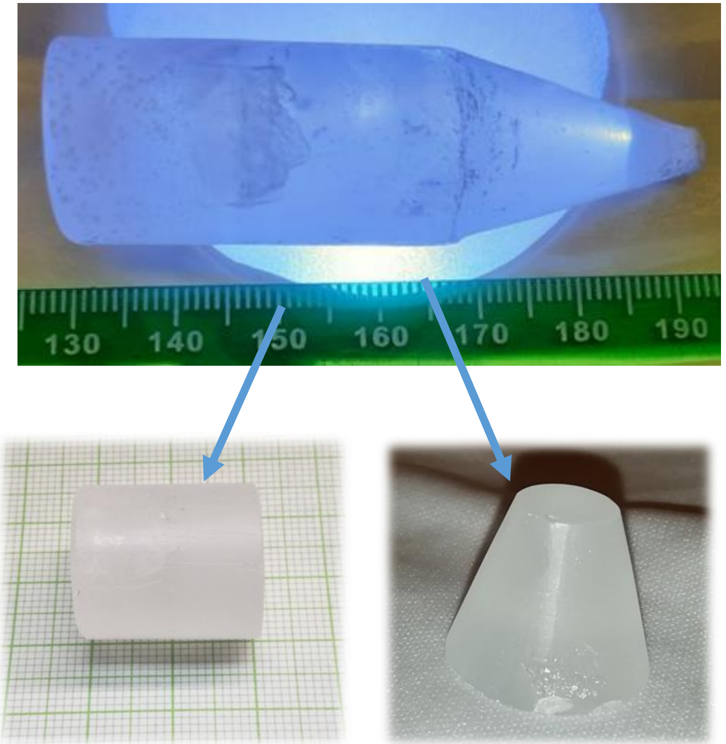
[1] EPS-HEP (2019) 437
[2] NPA 847 (2010) 168
[3] PhD U. Coll. London (2015)
[4] S.W. Finch et W. Tornow, Phys, Rev. C 92 (2015) 045501
[5] J. Phys. G: Nucl. Part. Phys. 22 (1996) 487
[6] C. Arpesella et al. Lett. 27 (l) (1994) 29
[7] E. Celi et al., Eur. Phys. J. C 83 (2023) 396
[8] N. Dokania et al. J. Phys. G: Nucl. Part. Phys. 45 (2018) 075104
[9] S.W. Finch, W. Tornow, Nucl. Inst. Meth. A 806 (2016) 70
[10] J. Heeck and W. Rodejohann, EPL 103 (2013) 32001

→ Possibility to study $0\nu4\beta$ decay of $^{96}Zr \rightarrow ^{96}Ru$

Production and growth of Cs_2ZrCl_6 crystals

Produced at Queen's University, Canada

∅21.5×60 mm, about 60 g



1st ingot of the Cs_2ZrCl_6 crystal

CZC cone (10.63 g) & cylinder (23.95 g)

Unencapsulated

- ✓ CsCl (99.9%) + **$ZrCl_4$** (99.9%) as starting materials
- ✓ $ZrCl_4$ powder subjected to a two-stage sublimation process
- ✓ Grown by **vertical Bridgman technique**: «fast» growth (28°C/cm, at 36 mm/day) + «slow» growth (25°C/cm, at 12 mm/day)

CZC – HP (19.21 g), CZC – LP1 (19.86 g), CZC – LP2 (20.43 g)

Encapsulated using SYLGARD 184™ Silicone Elastomer Kit

- ✓ CsCl (99.9%) + **$ZrCl_4$** (99.9%) [CZC-LP1 and CZC-LP2]
- ✓ CsCl (99.999%) + **$ZrCl_4$** (99.99%) as starting materials [CZC-HP]
- ✓ $ZrCl_4$ powders subjected to a two-fold sublimation process
- ✓ Grown by **vertical Bridgman technique**: «fast» growth (20°C/cm, at 24 mm/day) + «slow» growth (25°C/cm, at 12 mm/day)

Then polished with 1200 grit sandpaper, mineral oil as lubricant, cleaned by toluene

Chemical purity of reagents at the each production stage of Cs_2ZrCl_6

*HR-ICP-MS, concentrations are in **ppb** with 25% uncertainty*

	CsCl initial	$ZrCl_4$ initial	$ZrCl_4$ 1st sublimation	$ZrCl_4$ 2nd sublimation	CZC 1st growth, tail	CZC 1st growth, nose	CZC 2st growth, middle
K	300	15000	700	700	2500	200	500
La	0.7	1.5	1	1	1	0.6	0.6
Ce	1.5	2	1	1	2.5	3	2
Pr	0.1	4	6	6	1.5	1	1
Nd	<1	30	25	30	5	3	3
Sm	0.5	1	4	1	1	0.6	0.6
Eu-Lu	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Hf	35	6400	5200	5600	1200	1800	1600
Ta, W, Re, Os, Ir	<2	<2	<2	<2	<2	<2	<2
Pt	<1	<100	<100	<100	<25	<25	<25
Tl	0.4	<0.2	<0.2	0.2	1	<0.2	<0.2
Pb	<1	30	20	30	150	1	13
Bi	<0.5	<0.5	1.5	2.6	1.5	<0.5	1.6
Th	<0.05	70	0.5	0.2	<0.05	<0.05	<0.05
U	<0.05	1000	7	0.36	0.35	0.13	<0.05

Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9

Cs_2ZrCl_6 crystal radiopurity

over 700 hours of low-background measurements on HPGe detector (STELLA facility, LNGS)

Chain	Nuclide	Activity, mBq/kg	
		Cone	Cylinder
		10.63 g	23.95 g
^{232}Th	^{228}Ra	< 16	< 23
	^{228}Th	< 6.7	< 8.2
^{238}U	^{226}Ra	60(10)	< 8.7
	^{234}Th	< 180	< 260
	^{234m}Pa	< 630	< 160
^{235}U	^{235}U	< 16	< 12
	^{40}K	< 120	< 95
	^{137}Cs	< 7.1	< 1.6
	^{134}Cs	49(6)	42(5)
	^{132}CS	< 8.2	< 11

Surface cross-contamination during the sample preparation

Natural

Artificial

Cosmogenic activation

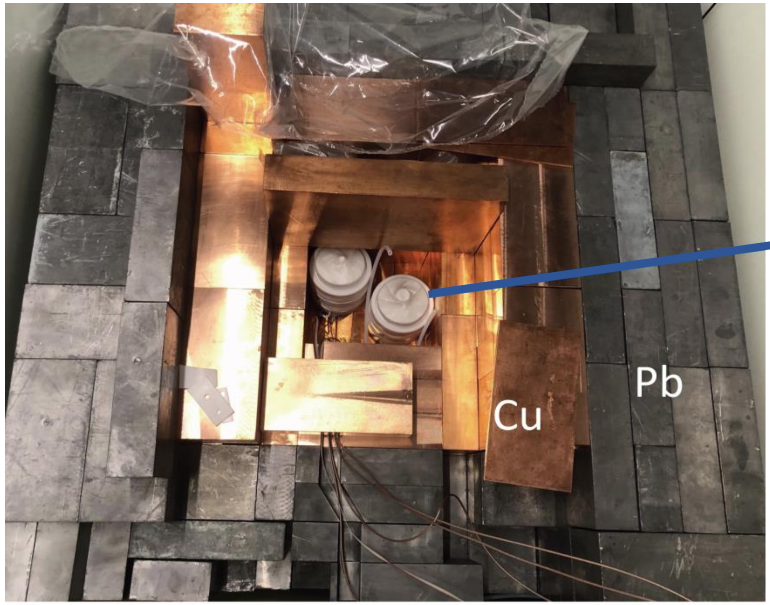
Only land transportation! $T_{1/2} \approx 2$ years

Our crystals are rather clean, even if they were grown from 99.9% purity grade raw materials

Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9

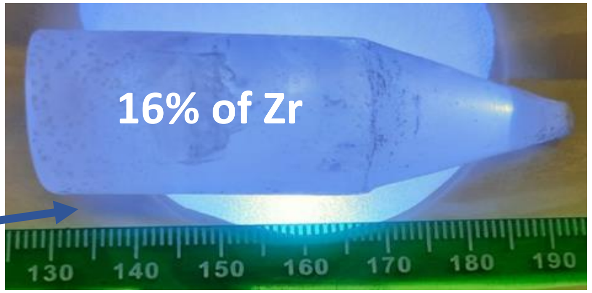
First low-background measurements of Cs_2ZrCl_6 at LNGS (Italy)

DAMA/CRYS setup (2021-2022)



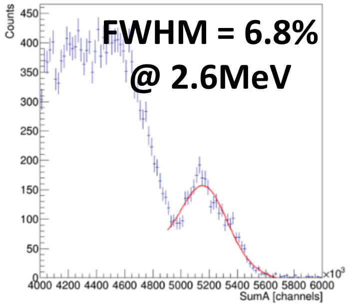
- OFHC Cu (15 cm)
- Low-activity Pb (20 cm)
- HDPE (5 cm)
- Borated HDPE (5cm)

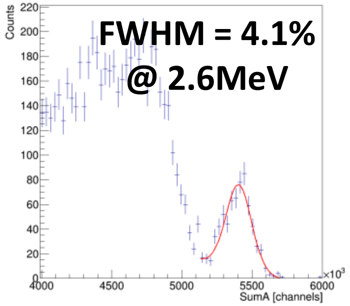
CsCl (99.9%) +
$ZrCl_4$ (99.9%) double sublimed
Bridgman growth technique



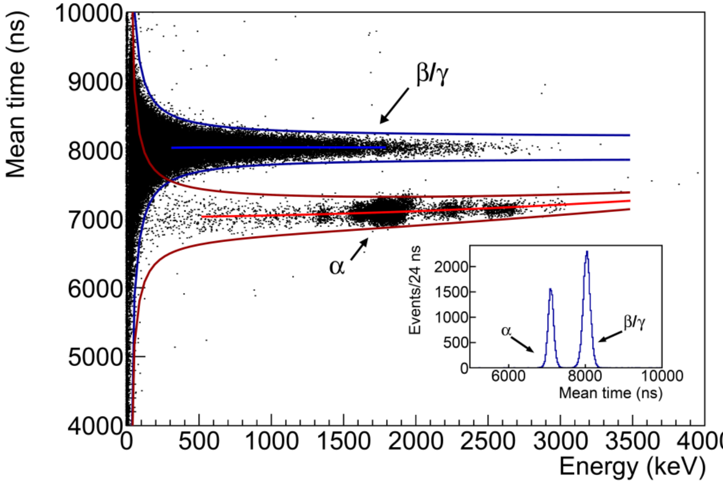
∅21.5×60 mm, about 60 g

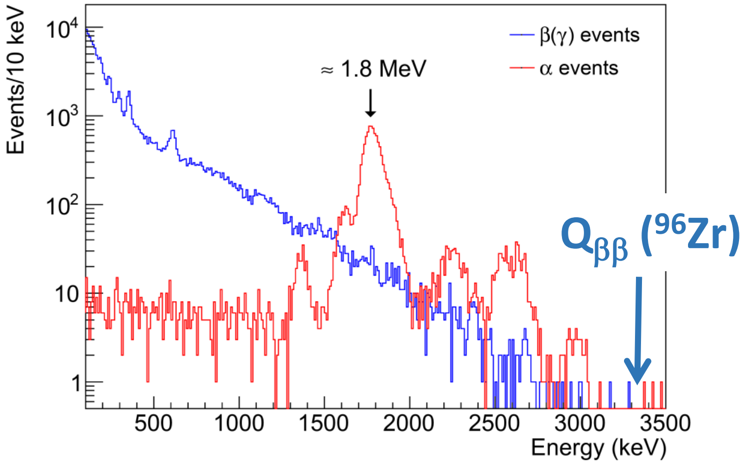
23.95 g ∅21.1×21.2 mm Cylindrical part	&	10.62 g ∅20.5×14 mm Conical part





Selection efficiency is 99.7% in [0.2–3.5] MeV

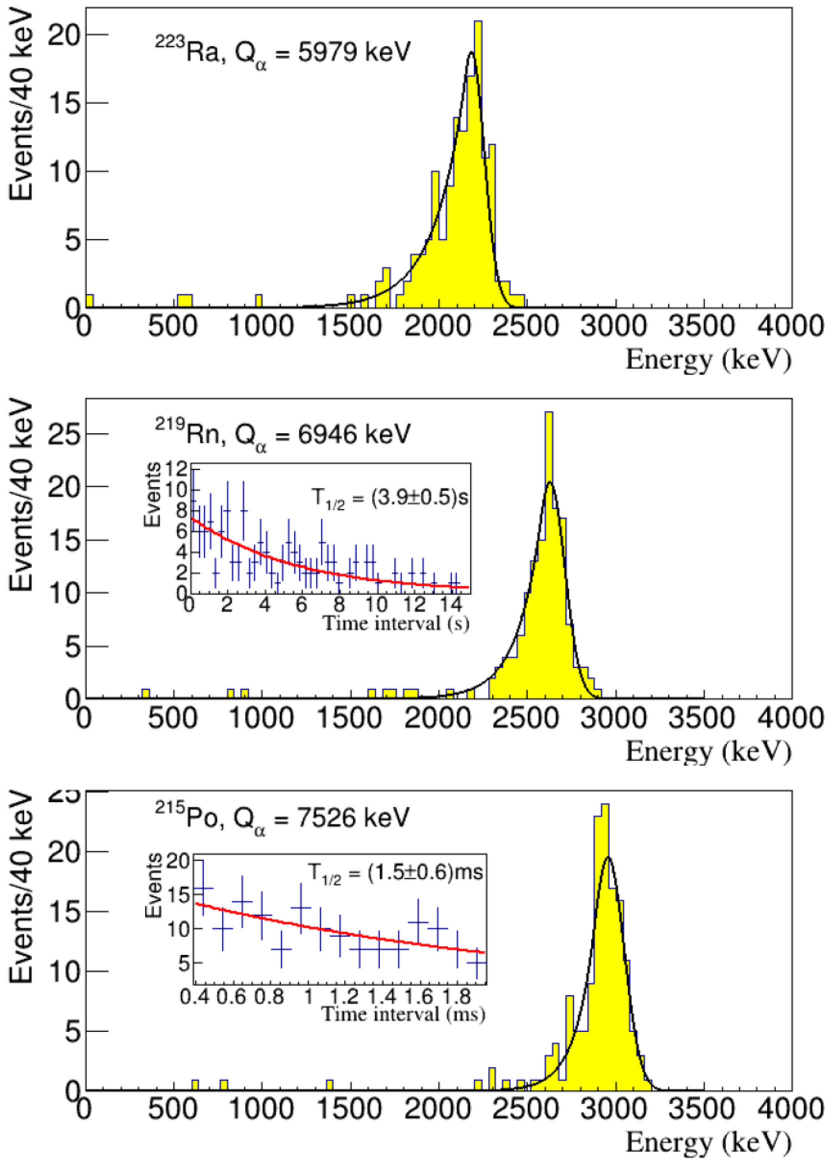




Counting rate at ROI is 0.09 counts/(kg·keV·yr)

More details in ***Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9***

Time-Amplitude analysis



<u>Run 2:</u> 65 days of data taking within Oct-Dec 2022 (extended time-window 2 ms)

To select the sequence of alpha events in ^{235}U sub-chain:

^{223}Ra (Q_α = 5979 keV, $T_{1/2}$ = 11.44 d) **39.28% selection eff.**

↓

^{219}Rn (Q_α = 6946 keV, $T_{1/2}$ = 3.96 s)

↓

^{215}Po (Q_α = 7526 keV, $T_{1/2}$ = 1.782 ms)

↓

^{211}Pb

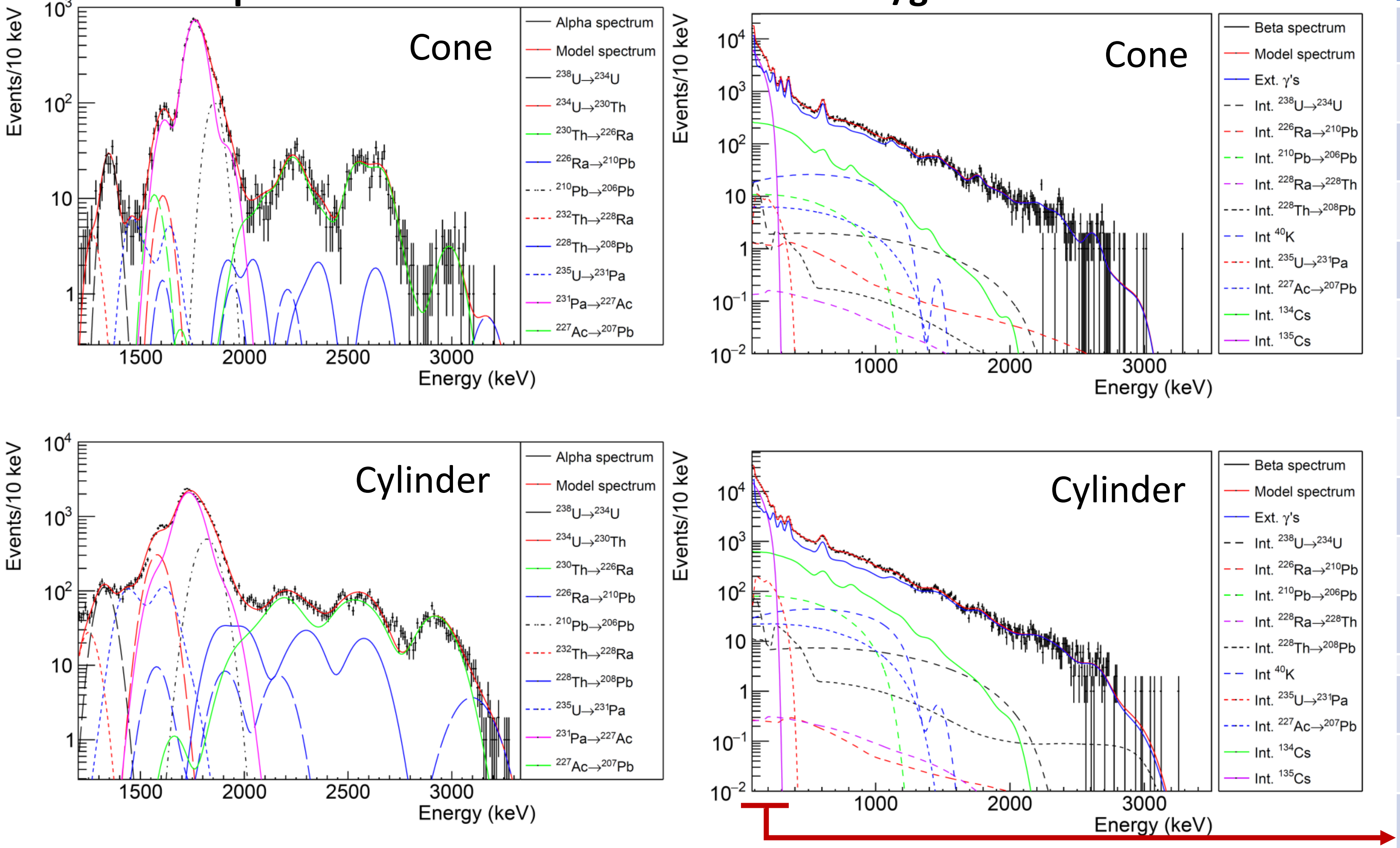
A(^{227}Ac) = 1.4(2) mBq/kg in cone
= 2.7(2) mBq/kg in cylinder

+ *Confirmation of ^{235}U decay chain presence*
+ *Alpha peaks to precisely determine α/β ratio*

Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9

Cs_2ZrCl_6: Comprehensive background model

Alpha events **Beta/gamma events**

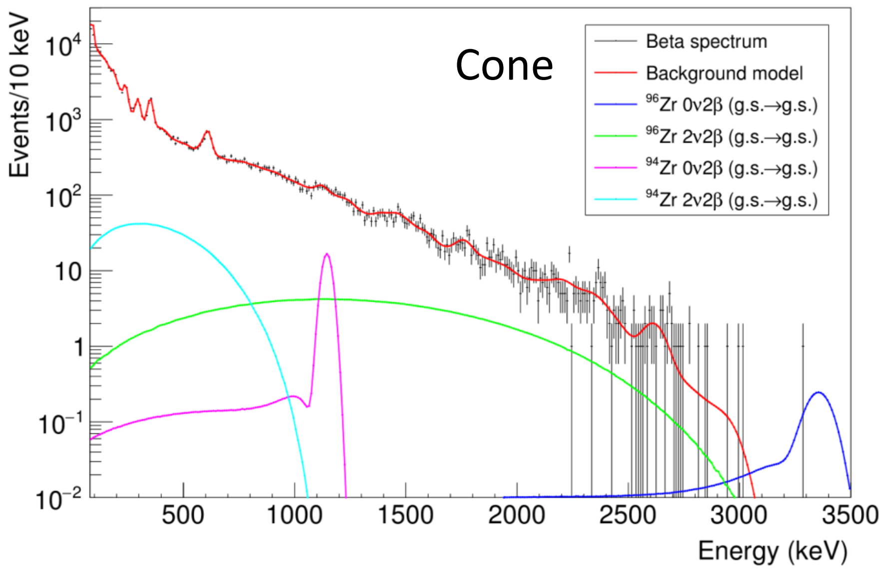


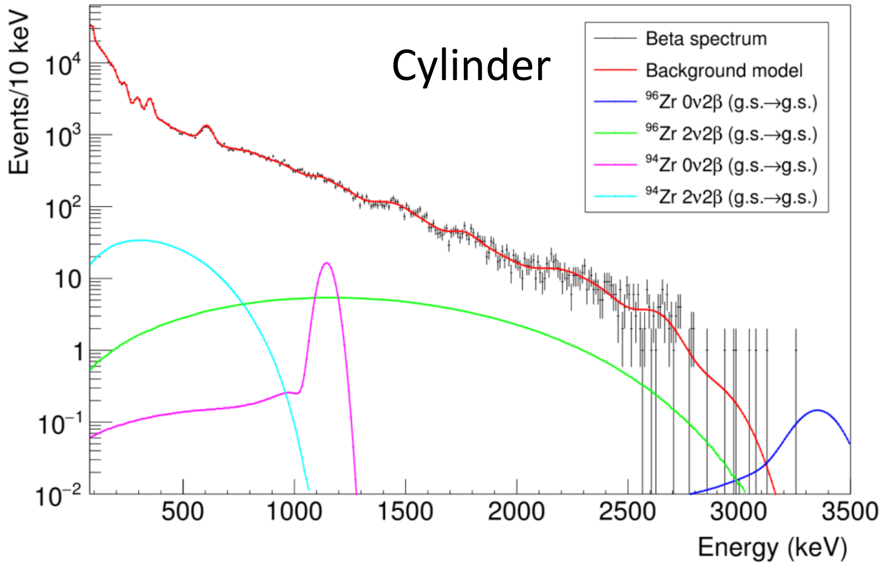
Chain	Nuclide	Internal contamination, mBq/kg	
		Cone	Cylinder
^{232}Th	^{232}Th	0.07(2)	0.28(7)
	^{228}Th	0.05(2)	0.44(4)
^{235}U	^{235}U	0.29(4)	3.0(1)
	^{231}Pa	**21.0(3)**	**33.9(3)**
	^{227}Ac	0.70(3)	1.08(3)
^{238}U	^{238}U	0.53(4)	1.17(5)
	^{234}U	0.2(1)	3.8(1)
	^{230}Th	0.23(7)	< 0.02
	^{226}Ra	0.03(3)	0.12(3)
	^{210}Pb	2.2(2)	6.7(3)
	^{40}K	6(1)	5(1)
	^{134}Cs	36(4)	42(2)
	^{87}Rb	**≈ 270**	**≈ 290**

- Comply with measurements on HPGe
- High contamination by ^{235}U daughters
- Segregation of impurities is observed

More details in ***Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9***

New experimental limits on various decay modes in $^{94,96}Zr$ isotopes



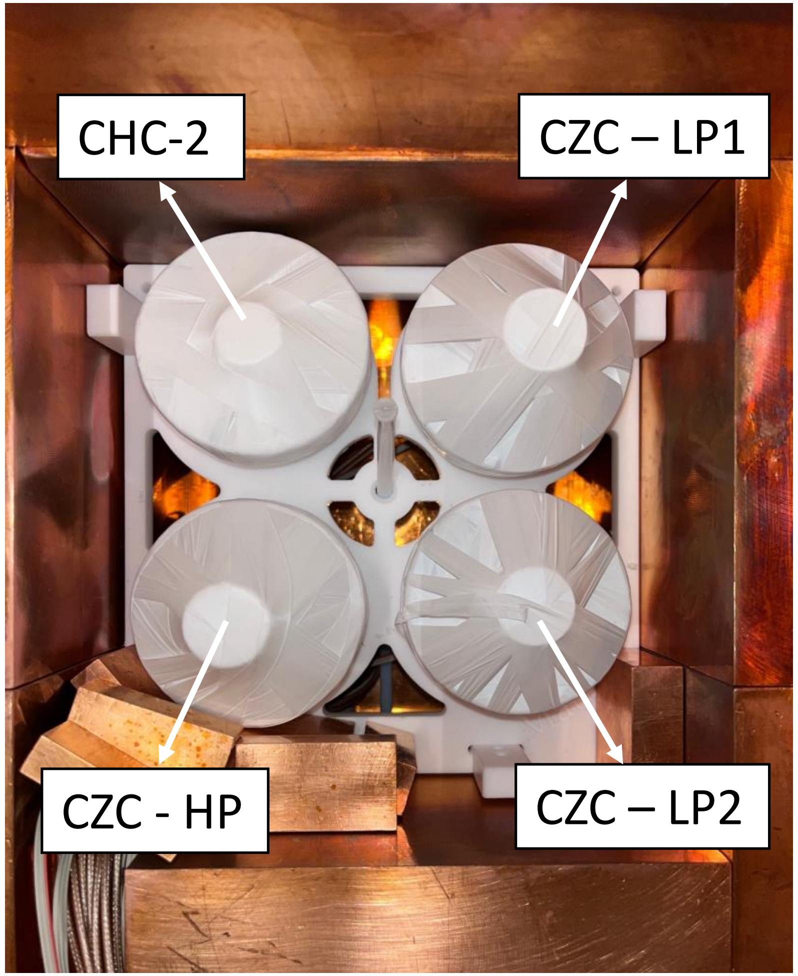


Transition	Decay mode	Final state of daughter nucleus, keV	Experimental limit on $T_{1/2}$ at 90%C.L., yr
$^{96}Zr \rightarrow {}^{96}Mo$	$2\beta0\nu$	g.s.	**$> 1.5\times10^{20}$**
		2_1^+, 778	$> 1.5\times10^{19}$
	$2\beta2\nu$	g.s.	**$> 7.4\times10^{17}$**
		2_1^+, 778	$> 3.8\times10^{17}$
	β	g.s.	**$> 1.0\times10^{17}$**
$^{94}Zr \rightarrow {}^{94}Mo$	$2\beta0\nu$	g.s.	**$> 2.6\times10^{19}$**
		2_1^+, 871	$> 3.8\times10^{18}$
	$2\beta2\nu$	g.s.	**$> 2.4\times10^{18}$**
		2_1^+, 871	$> 1.9\times10^{17}$

Eur. Phys. J. A 59 (2023) 176, https://doi.org/10.1140/epja/s10050-023-01090-9

New low-background measurements in DAMA/CRYS setup (LNGS)

DAMA/CRYS setup at LNGS



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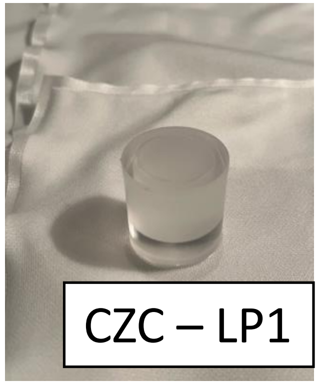
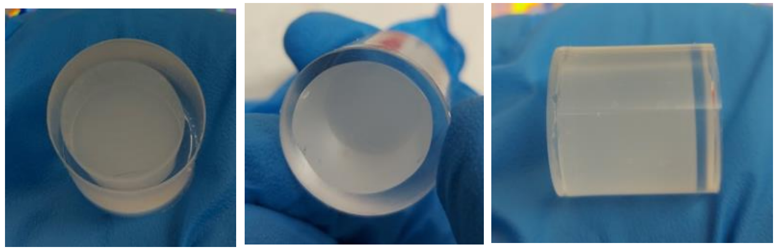
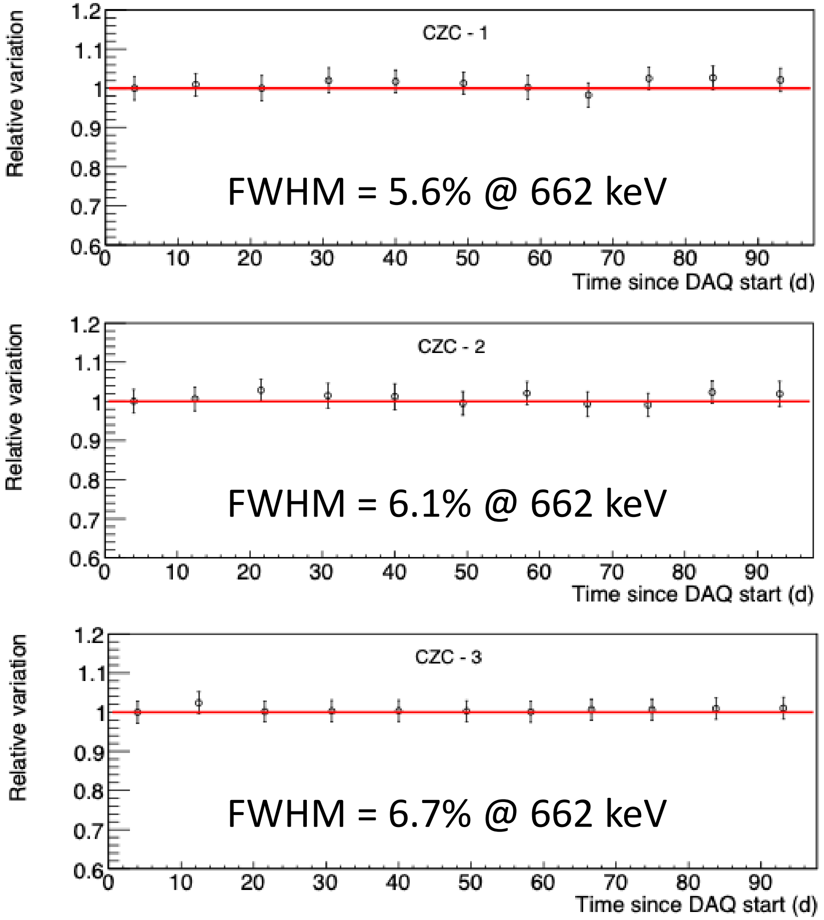


- ✓ Three new Cs_2ZrCl_6 crystals + one Cs_2HfCl_6
- ✓ Total mass of 3 CZC = 59.5 g
- ✓ FWHM = 6-8% @ 662keV
- ✓ Produced from high purity and purified raw materials (> 99.99%)
- ✓ **CZC crystals are encapsulated in a silicon-based resin + quartz window**
- ✓ Modified experimental setup
- ✓ Measurements started on June 30th, 2023, for a total of 97.7 days live time



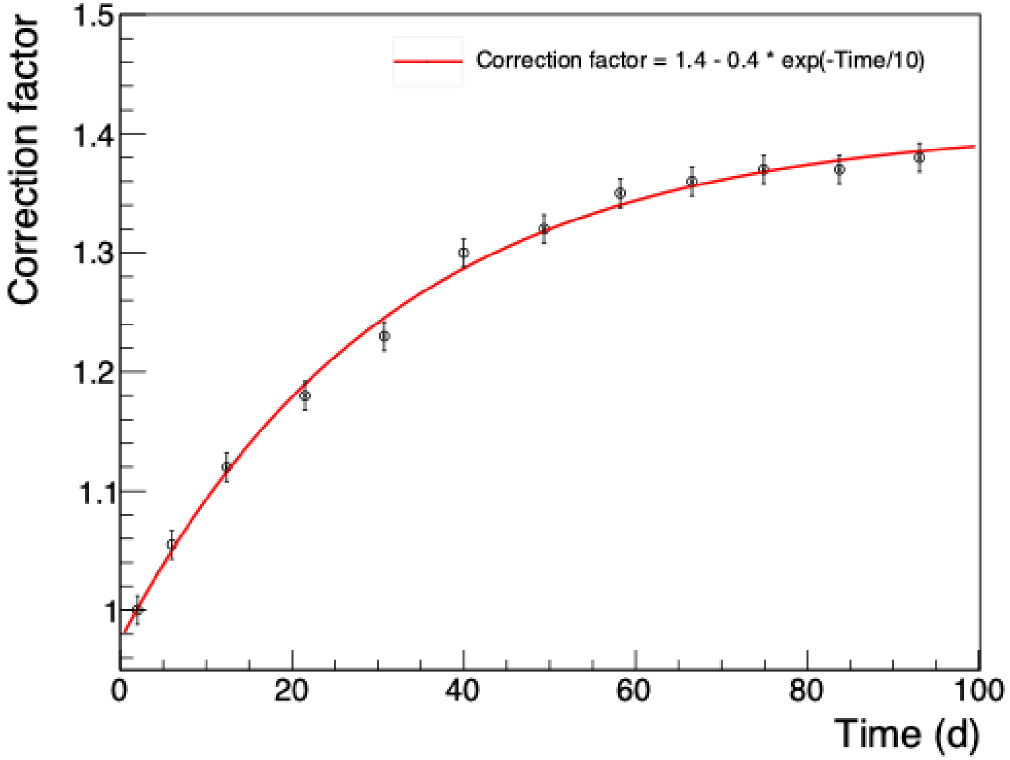
Detector time-stability

Variation of a reference peak position during the data taking



The reference peaks remain rather stable within the experimental errors, with a typical variation <1%.

Instead for the non-encapsulated **CHC-2** a **small shift in time** due to the hygroscopicity of thecrystal

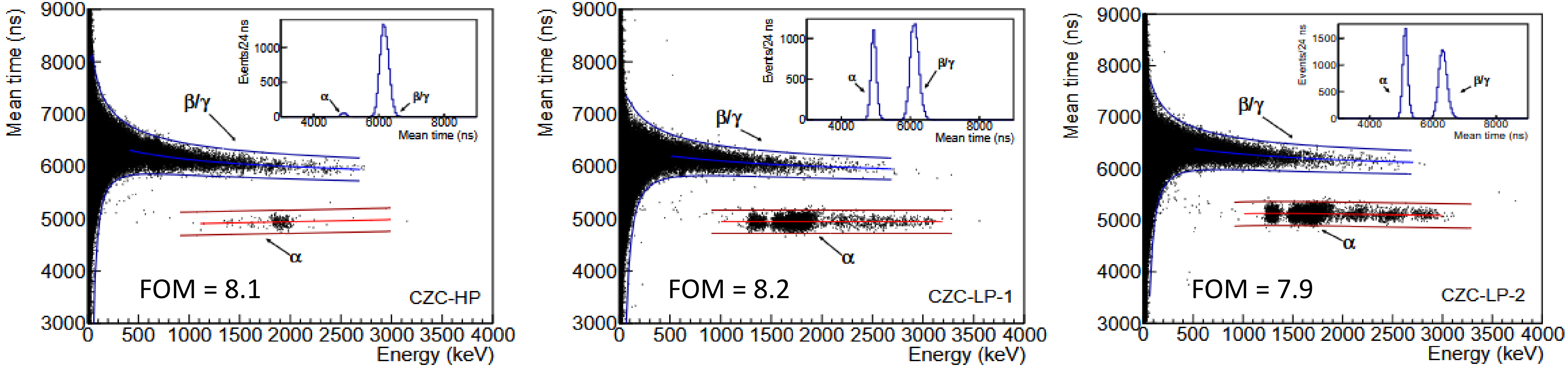


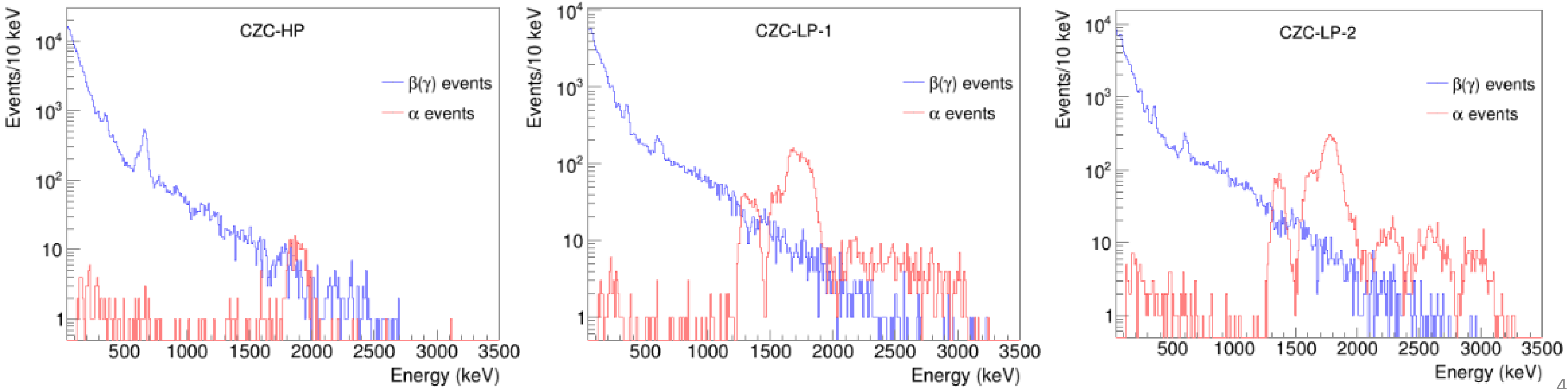
Correction factor to the calibration parameters as a function of time.

Data analysis of the Cs_2ZrCl_6 crystals

Selection efficiency is 99.7% in [0.5–3.5] MeV

Measured energy spectra over 97.7 days of data taking





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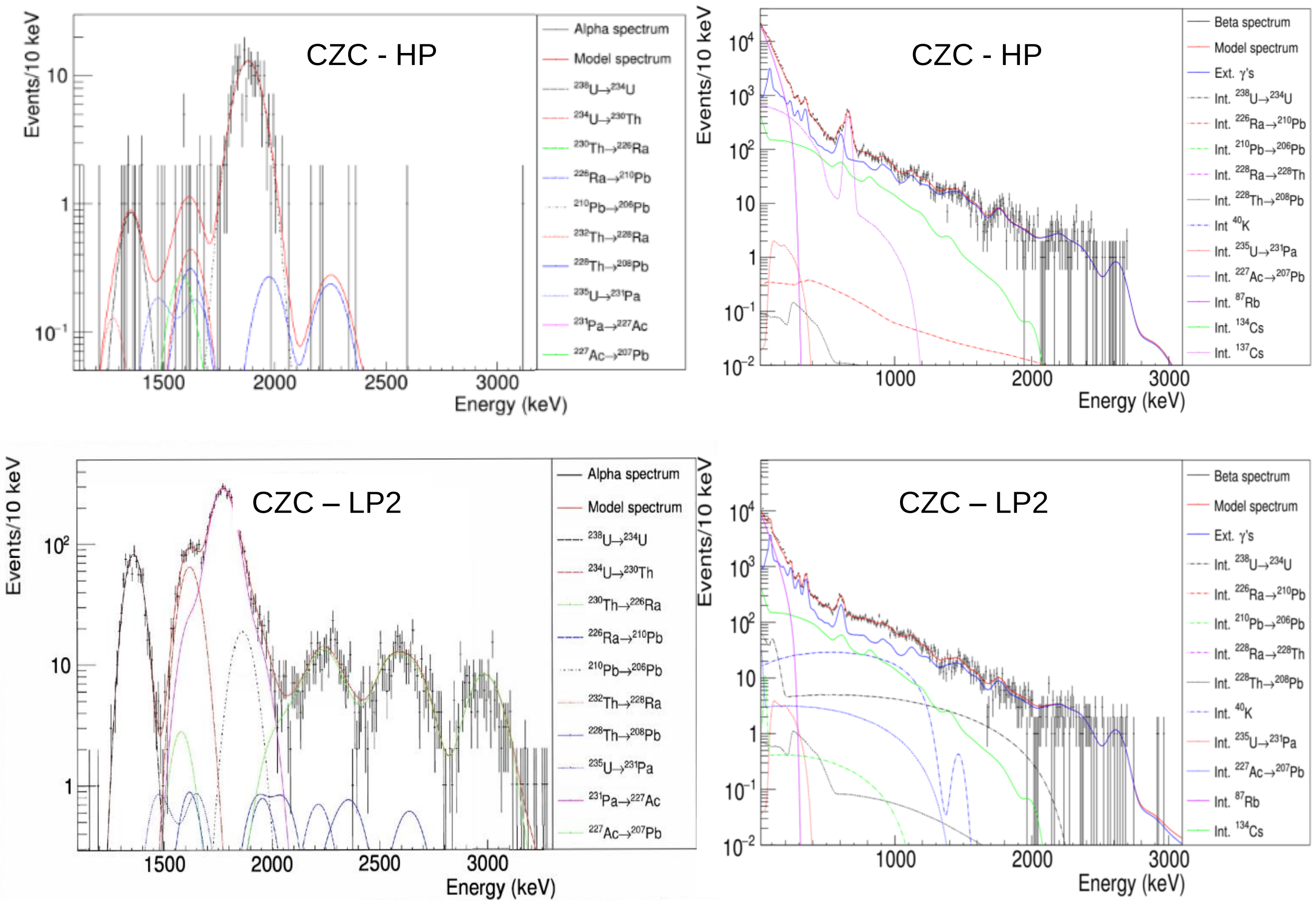
Cs_2ZrCl_6: Comprehensive background model

Alpha events / **Beta/gamma events**



Chain	Nuclide	Internal contamination (mBq/kg)		
		CZC - HP	CZC – LP1	CZC – LP2
^{238}U	^{238}U	< 0.08	3.2(1)	4.6(2)
	^{234}U	< 0.12	2.9(2)	4.2(3)
	^{230}Th	< 0.12	< 0.3	< 0.6
	^{226}Ra	< 0.05	< 0.06	< 0.2
	^{210}Pb	< 1.3	< 0.6	1.3(4)
^{235}U	^{235}U	< 0.14	< 0.2	< 0.4
	^{231}Pa	< 1.3	17.0(5)	24.7(6)
	^{227}Ac	< 0.013	0.62(3)	0.94(6)
^{232}Th	^{232}Th	< 0.10	< 0.12	< 0.12
	^{228}Th	< 0.01	< 0.04	< 0.16
	^{137}Cs	100(3)	-	-
	^{134}Cs	58(6)	42(7)	55(7)
	^{87}Rb	1067(5)	318(14)	441(9)
	^{40}K	< 1.1	11(2)	17(3)

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Can we enhance *Light Yield* of Cs_2ZrCl_6 crystals to improve

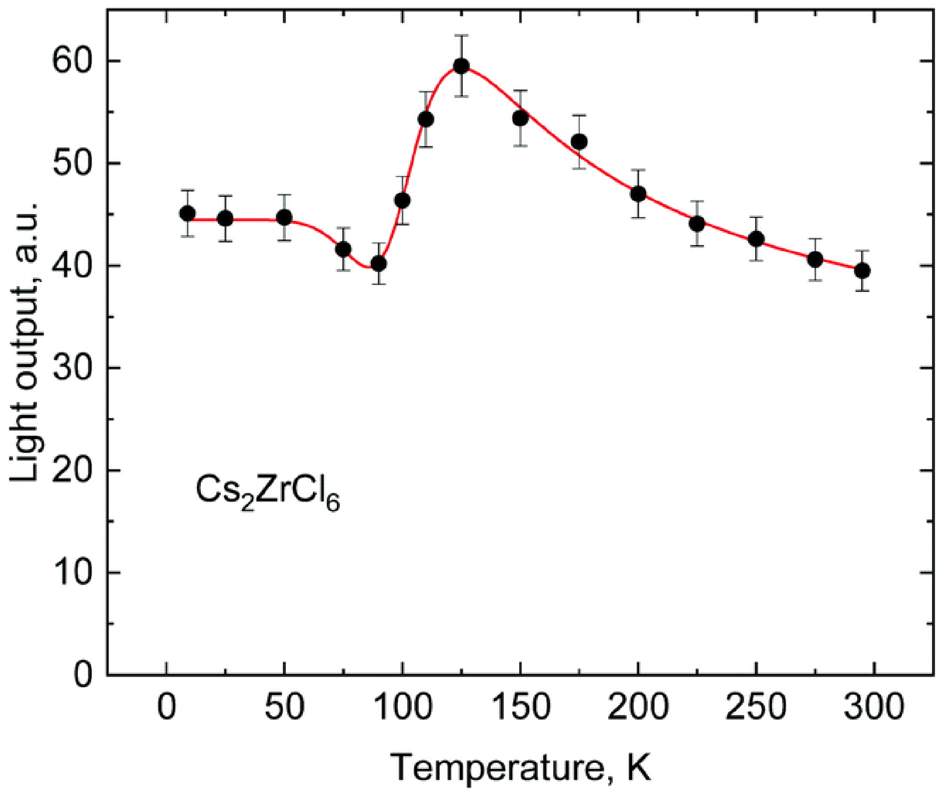
energy resolution and pulse-shape discrimination ability

that will result in a *higher experimental sensitivity*?

$$S_{0\nu} \propto \epsilon \sqrt{\frac{M \cdot T}{Bkg \cdot FWHM}}$$

First evidence of possible Light Yield enhancement

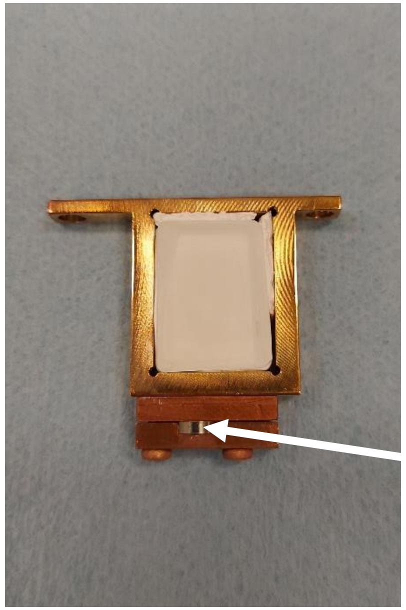
Dalton Transactions 51 (2022) 6944; DOI: 10.1039/D2DT00223J



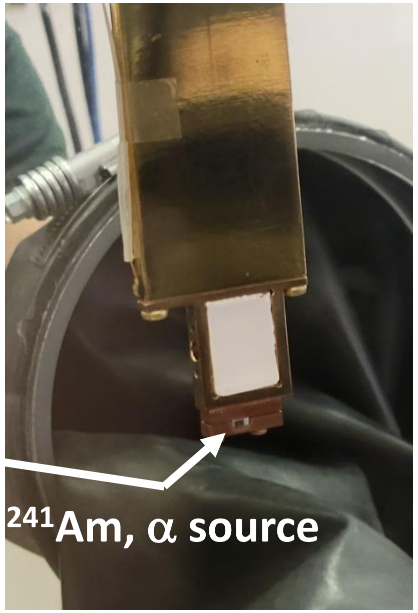
- Optical cryostat
- Tiny Cs_2ZrCl_6 sample 5×5×1 mm^3
- Under irradiation by ^{241}Am, α, 4.7 MeV
- No data with γ quanta
- The behavior of LY was explained by negative thermal quenching

Experimental data need to be extended

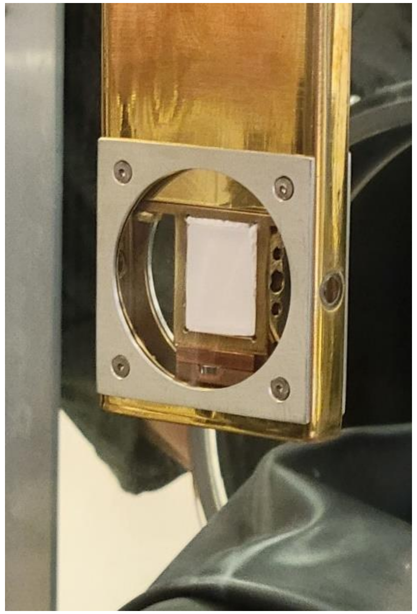
Measurement of a bulk Cs_2ZrCl_6 in optical cryostat



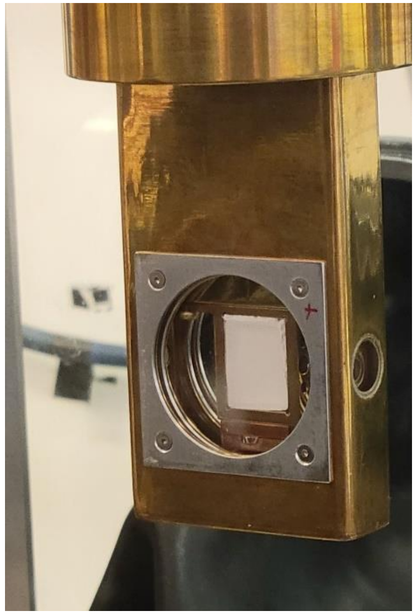
Cs_2ZrCl_6
20×14×6 mm



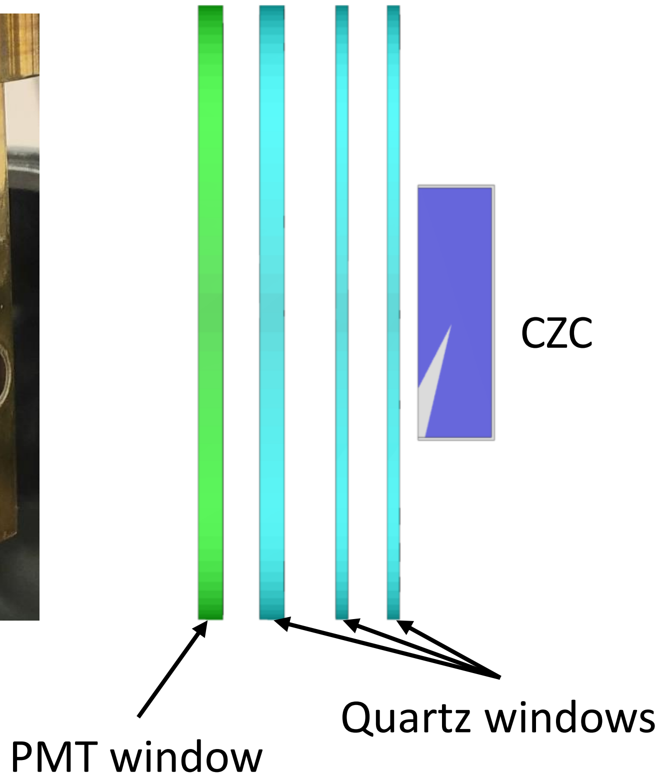
CZC crystal in
the sample holder



4K shroud



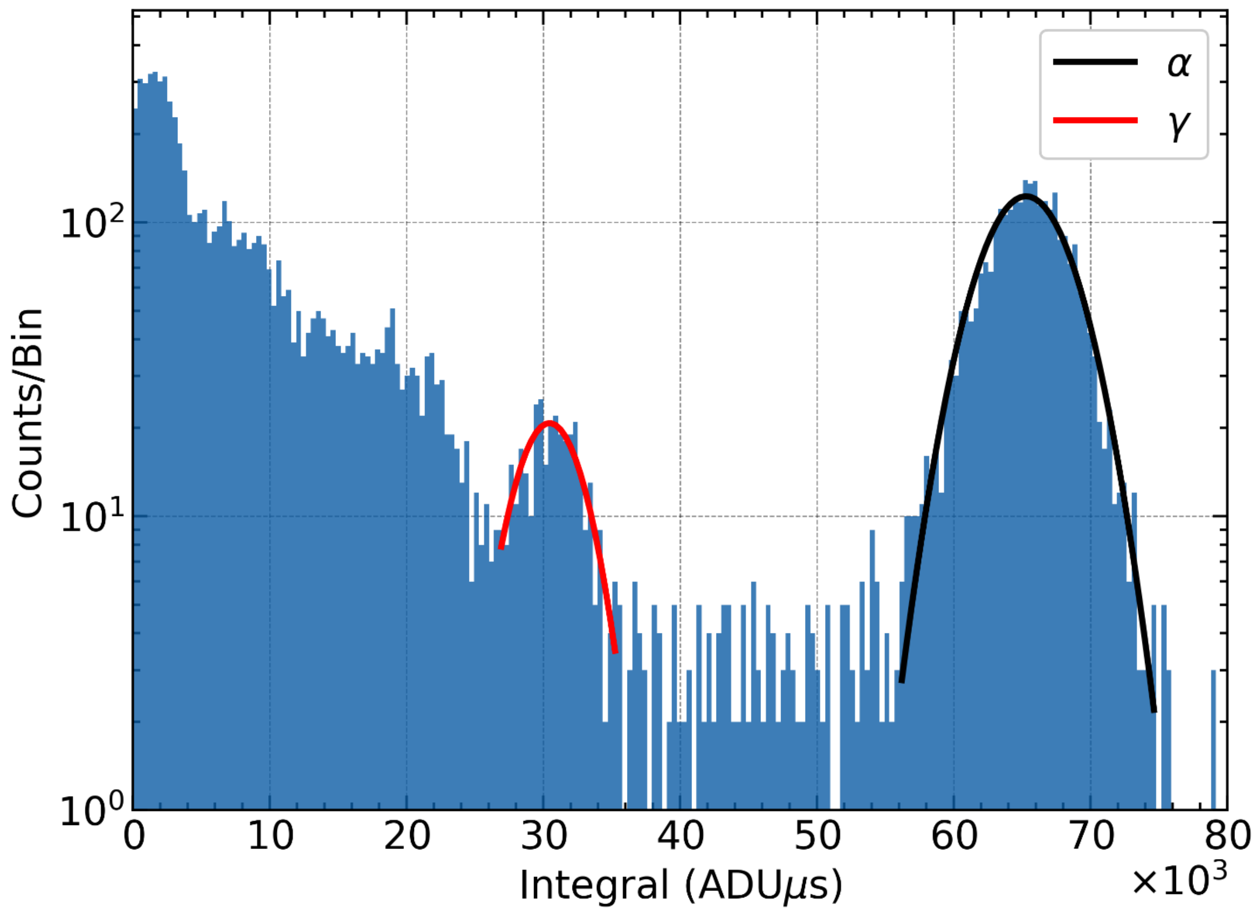
45K shroud



Geometry for GEANT4 simulation

Permanantly mounted α source
Removable external γ source

Energy spectrum at RT



^{137}Cs, γ, 662 keV

$FWHM_{\gamma}$ = 12%

^{241}Am, α, 4.7 MeV

$FWHM_{\alpha}$ = 11%

Event selection criteria:

- Starting point
- No pile-ups
- Fast-to-total charge ratio (noise reduction)
- Peak position
- Preliminary pulse-shape discrimination
- 10,000 events collected for each T-point

$$LY(photons/MeV) = \frac{N_{ph}}{E_{\gamma}}$$

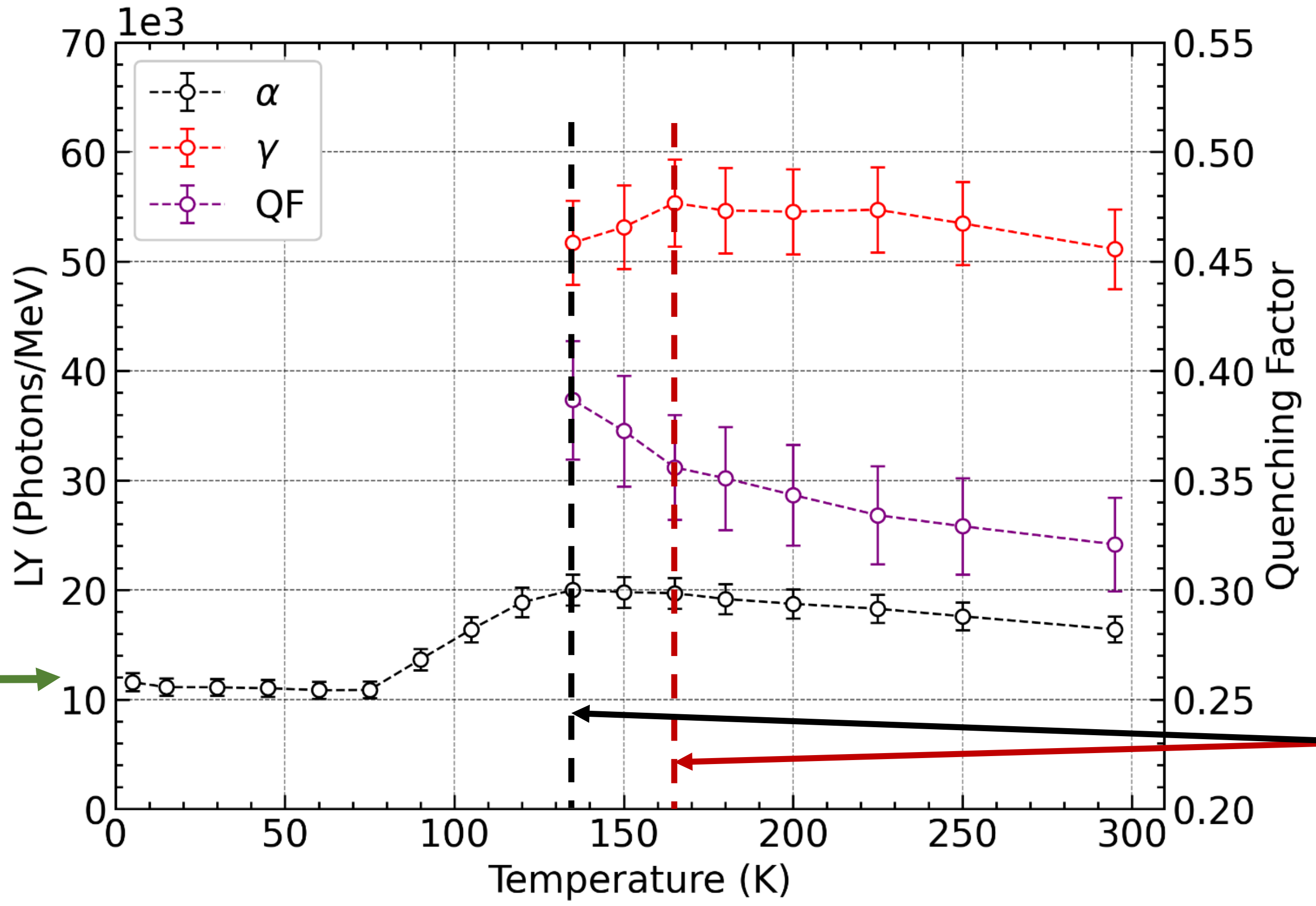
$$N_{ph} = \frac{integral_{peak}}{SPE} \frac{1}{QE \cdot LCE}$$

SPE: 29.3 ADUμs/phe

QE: 12%

LCE: α: 24.1%, γ: 25.6%

Light Yield & Quenching Factor temperature dependence



at room temperature

LY_γ = **51,200** ± 3,600 photons/MeV

LY_α = **16,400** ± 1,200 photons/MeV

QF_α = **0.32** ± 0.02

at optimum temperature

LY_γ = **55,000** ± 3,500 photons/MeV

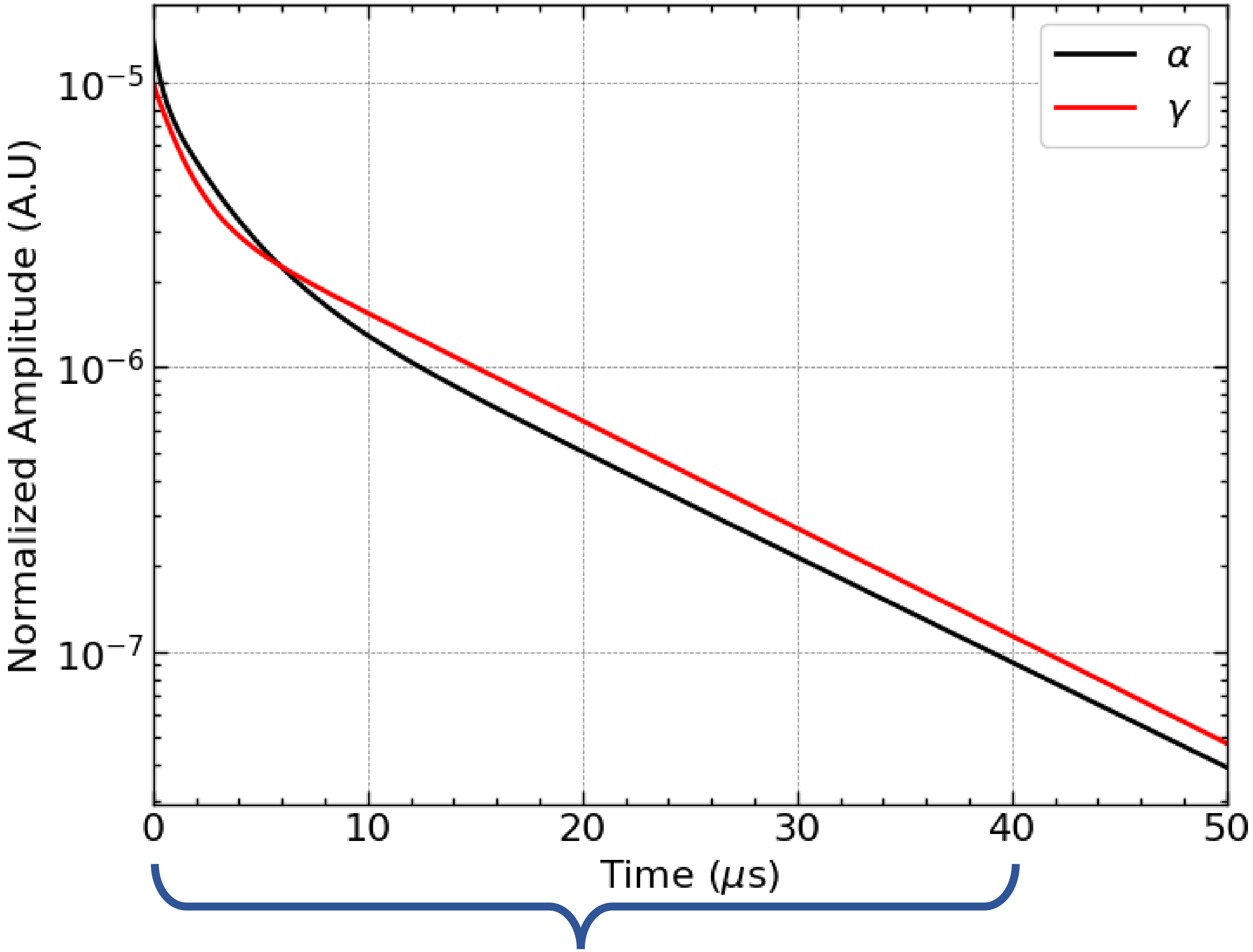
LY_α = **20,000** ± 1,200 photons/MeV

QF_α = **0.38** ± 0.03

Decrease of LY_γ and LY_α observed at different temperatures

Trend for LY_α confirming previous observation in ***Dalton Transactions 51 (2022) 6944***

Average scintillation pulses at RT



$$f(t) = \sum A_i(e^{-t/\tau_i})/\tau_i$$

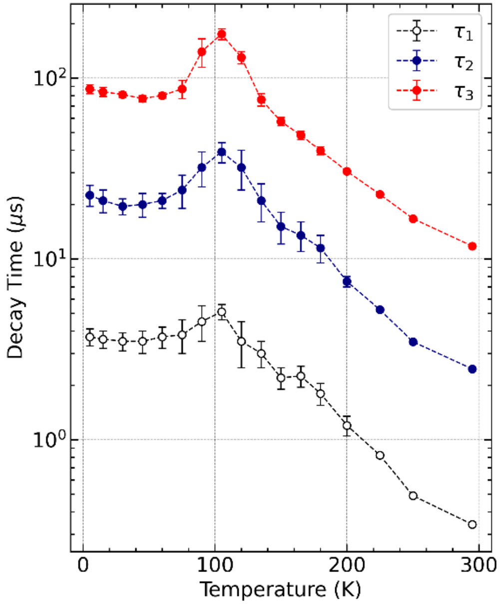
Pulse decay constants @ RT

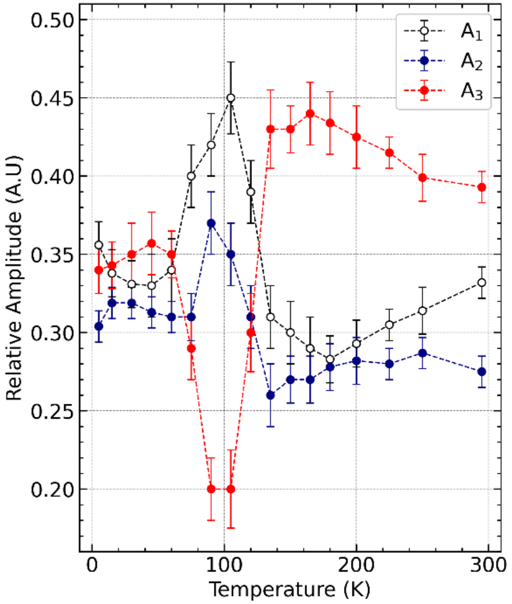
α: 0.3, 2.5, 11.8 μs (3 components)

γ: 1.3, 11.5 μs (2 components)

Time-interval used for further pulse-shape analysis (≈ 3 × longest decay constant)

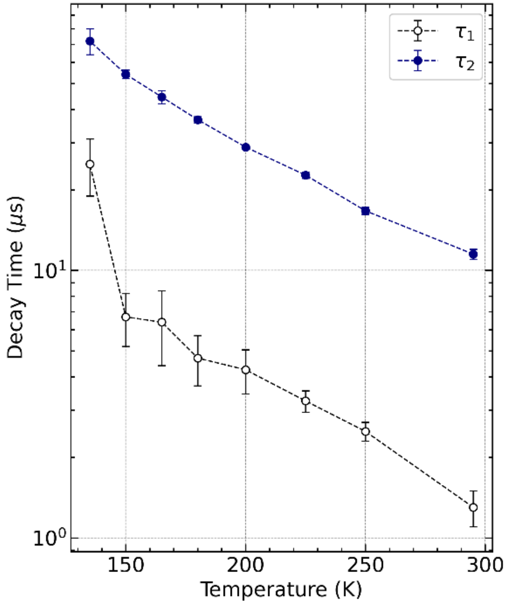
Temperature dependent pulse decay constants

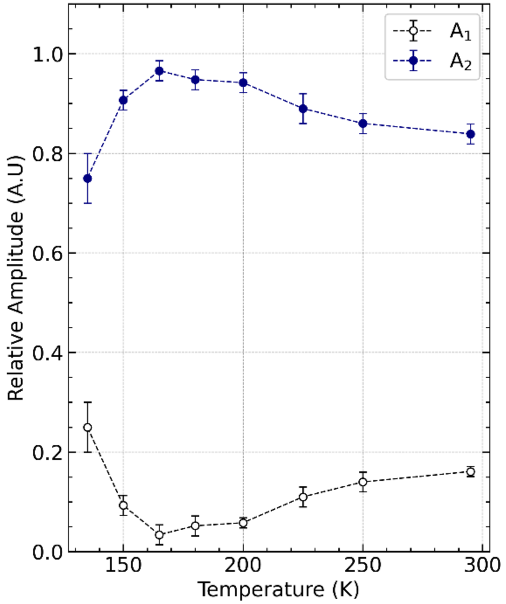




for α particles

T(K)	$\tau_1,\ \mu s$	A_1	$\tau_2,\ \mu s$	A_2	$\tau_3,\ \mu s$	A_3
295	0.34(1)	0.33(1)	2.46(2)	0.28(1)	11.76(2)	0.39(1)
250	0.49(1)	0.31(2)	3.84(2)	0.29(2)	16.69(2)	0.40(2)
200	1.3(2)	0.33(1)	8.5(5)	0.28(1)	30.5(5)	0.39(1)
165	2.3(3)	0.29(2)	14(3)	0.27(2)	48.3(2.5)	0.44(2)
135	3.0(5)	0.33(1)	21(5)	0.28(1)	76(6)	0.39(1)
105	5.1(5)	0.45(2)	39(5)	0.35(2)	175(12)	0.20(3)
15	3.6(4)	0.34(2)	21(3)	0.32(1)	84(5)	0.34(2)

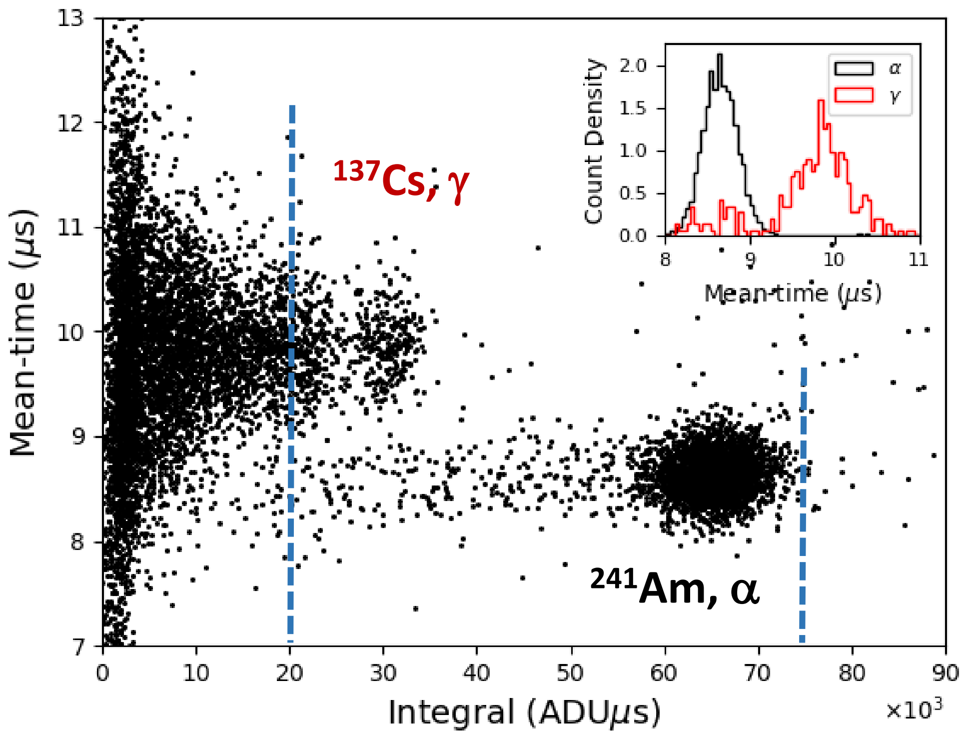


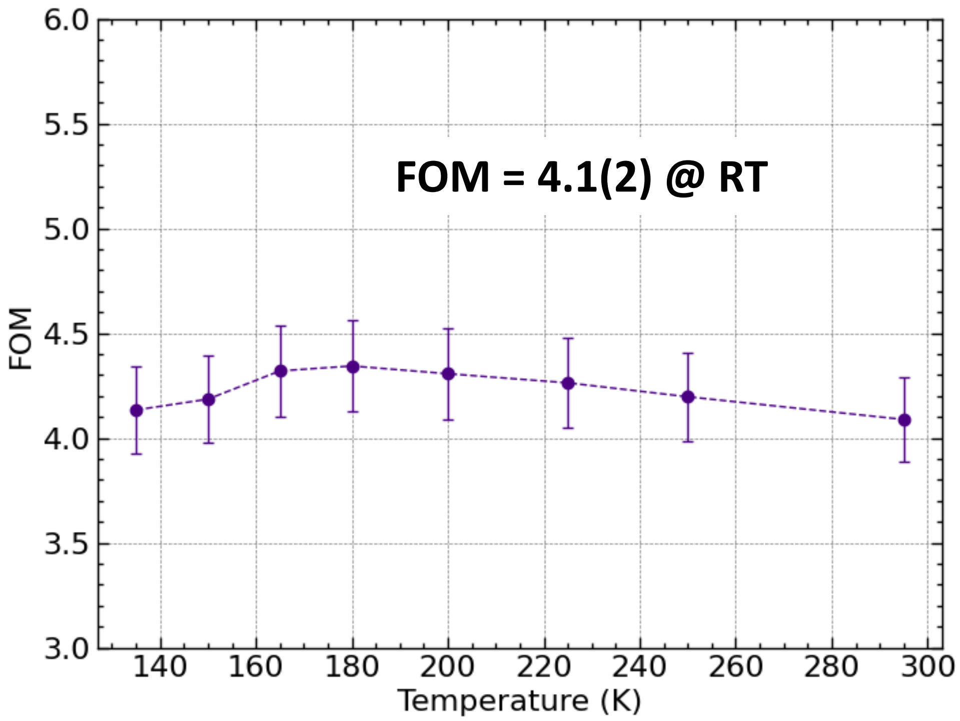


for γ quanta

T(K)	$\tau_1,\ \mu s$	A_1	$\tau_2,\ \mu s$	A_2
295	1.3(2)	0.16(2)	11.5(5)	0.84(2)
250	2.5(2)	0.14(2)	16.7(5)	0.86(2)
200	4.3(8)	0.06(1)	28.9(5)	0.94(2)
165	6.4(2.0)	0.034(20)	44.5(2.5)	0.966(20)
135	25(6)	0.25(5)	72(8)	0.75(5)

Pulse-shape discrimination





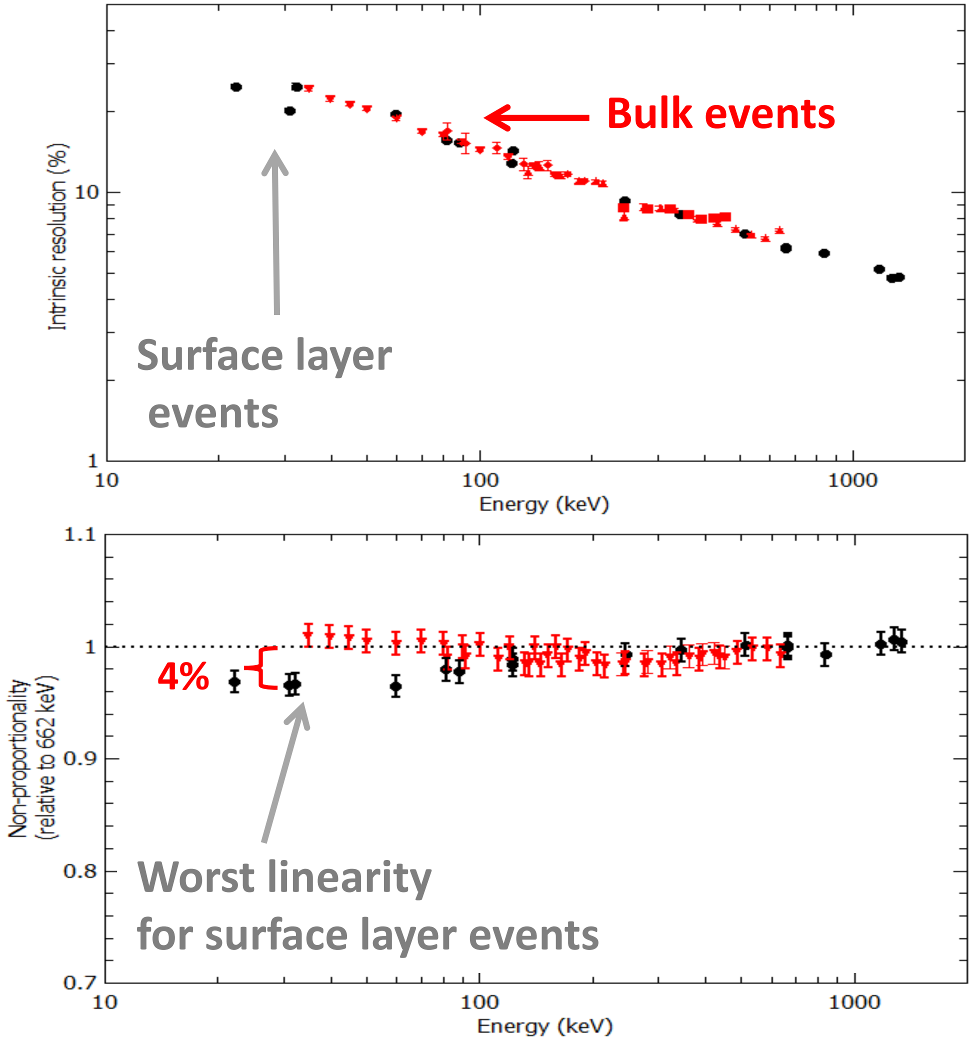
$$\langle t \rangle = \sum f(t_k)t_k \Big/ \sum f(t_k)$$

$$FOM = \frac{|\mu_\alpha - \mu_\beta|}{\sqrt{\sigma_\alpha^2 + \sigma_\beta^2}}$$

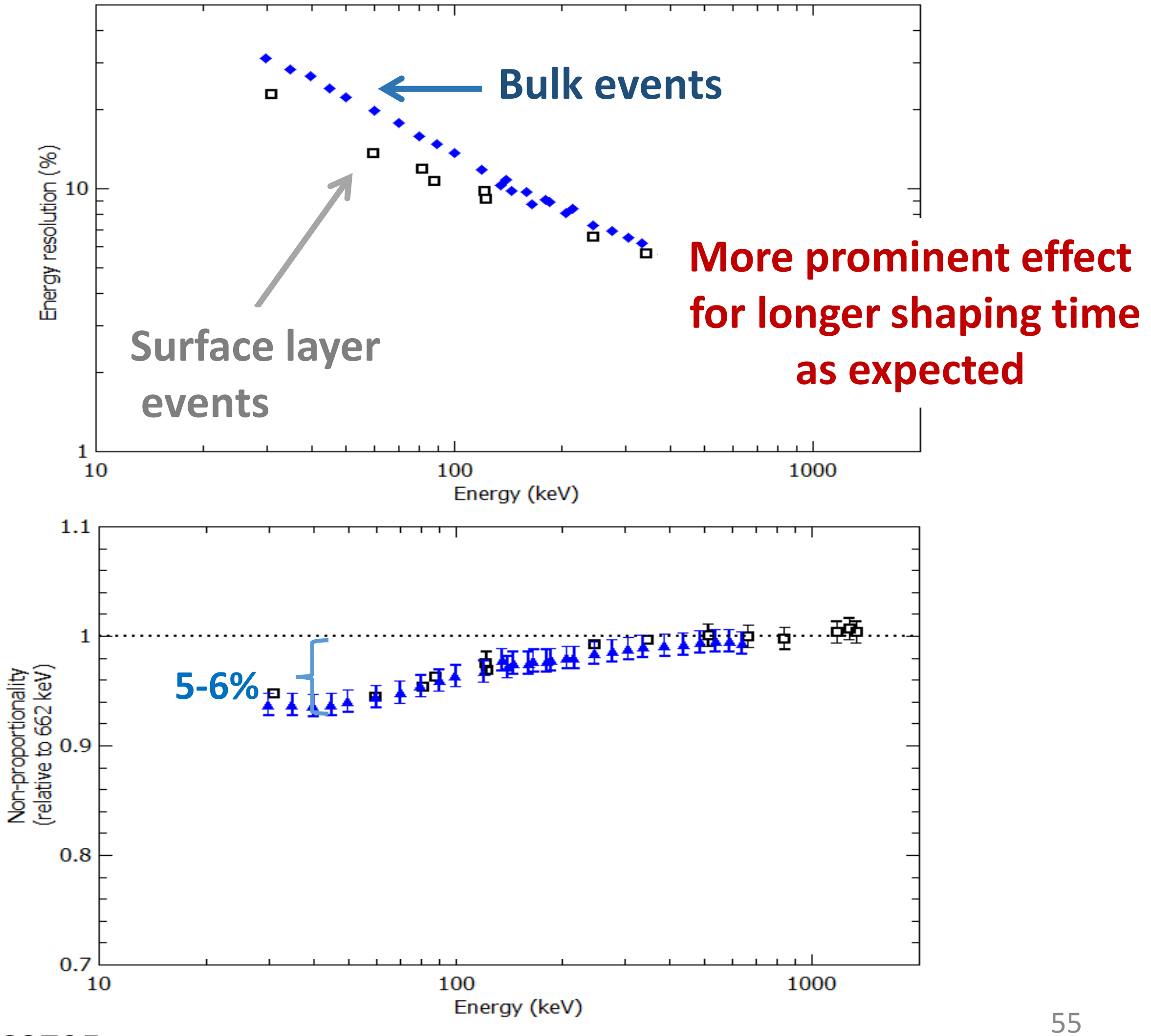
Cs_2ZrCl_6: Great linearity of scintillating response

Critical characteristic of detector to study the shape of $2\nu2\beta$ and single β energy spectrum of ^{96}Zr

1 μs shaping time



10 μs shaping time



L. Swiderski et al., Nucl. Instrum. Meth. A 1057 (2023) 168735

Summary (2)

- The first experiment based on Cs_2ZrCl_6 scintillating crystals aiming to study 2β decay processes of $^{94,96}Zr$ isotopes within the “source = detector” approach was successfully realized
- Despite a very limited mass of the Cs_2ZrCl_6 detector (about 35 g) the experimental limits were established at the level of 10^{17}–10^{20} yr, depending on the decay mode
- A new experiment, with new Cs_2ZrCl_6 crystals (59.5 g) in an optimized geometry, demonstrated the possibility of significantly improving crystals’ radiopurity
- Extensive studies of Cs_2ZrCl_6 scintillating performance, non-proportionality, internal and cosmogenically induced background, crystal lattice characteristics and phonon propagation properties, material handling and machining are on-going
- Cs_2ZrCl_6 crystals work better as RT scintillators or at moderate cooling
- Cs_2ZrCl_6 crystal scintillators provide an unique opportunity to study rare decays of Zr isotopes with an ultimate experimental sensitivity

Collaboration

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T. Leroy — Université de Lyon, Lyon, France