

CUPID-Mo inauguration

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History of lithium molybdate low-temperature detectors

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Outline

\Box ¹⁰⁰Mo as a $\beta\beta$ source

□ History of Li₂MoO₄ cryogenic detectors

- First low-temperature tests of small Li₂MoO₄ crystals
- Advanced Li₂MoO₄ scintillating bolometers: from LUMINEU to CUPID
- \circ Other CUPID oriented activities with Li₂MoO₄ crystals
- CUPID competitor: AMoRE path to Li₂MoO₄ bolometers

Summary

¹⁰⁰Mo as a $\beta\beta$ source





Alkali Meta	Alkaline Earth
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Noble Gas

Lanthanide 🛛 🛛 🗛

Actinide

Most promising isotopes for $0\nu 2\beta$ decay search



Scintillating bolometer approach



Further details: S. Pirro, talk @ CUPID-Mo inauguration

$\beta\beta$ source = bolometric detector

ββ Isotope	δ (%)	<i>Q</i> _{ββ} (keV)	Materials		
¹¹⁰ Pd	12	2018	None		
⁷⁶ Ge	7.7	2039	Ge (no scintillation, but ionization), BGO (good scintillator)		
¹²⁴ Sn	5.8	2287	Sn		
¹³⁶ Xe	8.9	2458	None		
¹³⁰ Te	34	2527	TeO ₂ (<i>extremely poor scintillator</i>)		
¹¹⁶ Cd	7.5	2813	CdWO ₄ , CdMoO ₄ (<i>both are good scintillators</i>)		
⁸² Se	8.7	2998	ZnSe, LiInSe ₂ (<i>both are good scintillators</i>)		
¹⁰⁰ Mo	9.8	3034	PbMoO ₄ , CaMoO ₄ , CdMoO ₄ , SrMoO ₄ , MgMoO ₄ , Na ₂ MoO ₄ , ZnMoO ₄ , Li ₂ MoO ₄ , Na ₂ Mo ₄ O ₁₃ , Li ₂ Mg ₂ (MoO ₄) ₃ (<i>most are good scintillators</i>)		
⁹⁶ Zr	2.8	3356	ZrO ₂ (<i>poor scintillator</i>)		
¹⁵⁰ Nd	5.6	3371	None (many attempts)		
⁴⁸ Ca	0.2	4268	CaF ₂ , CaWO ₄ , CaMoO ₄ (<i>all are good scintillators</i>)		
sotopic abundar Pure Appl. Chen 2 _{ββ} values: Pure Appl. Chen	nces: n. 88 (201 n. 88 (201	.6) 293] .6) 293]	Compilation is based on results of multiple bolometric tests performed by S. Pirro et al. @LNGS (Italy), A. Giuliani et al. @CSNSM & @LSM (France), H.J. Kim et al. @CUP & @Y2Y (South Korea) Scintillation of some materials was also studies by H. Kraus et al. @Oxford		

Bolometers can be used for studies of almost all most promising $\beta\beta$ **isotopes**!

History of Li₂MoO₄ cryogenic detectors

Lithium molybdate (Li₂MoO₄)

Compound: inorganic, soluble in water, slightly hygroscopic, not hazardous material.

Production: solid-phase synthesis from a stoichiometric mixture of MoO₃ and Li₂CO₃ powders followed by a recrystallization from acqueous solutions / a crystal growth from a melt



- Corrosion inhibitor (in LiBr absorption chiller) in some types of industrial air conditioning
- Electrode material in the fabrication of lithium-ion batteries

 Cryogenic particle detector for rare event searches (double beta decay, dark matter, solar axions) and neutron spectroscopy

First low-temperature tests of small Li₂MoO₄ crystals (grown by the Czochralski method)

2009: First bolometric test of a gram-scale Li₂MoO₄

Crystals production at Russian Chemistry-Technological University of D.I. Mendeleev (Moscow, Russia)

- **Solid-state synthesis** from MoO_3 and Li_2CO_3 powders (both of 99.5% purity) with subsequent recrystallization from water solutions

- **Czochralski growth** (4 mm/h) of transparent Li_2MoO_4 crystals up to $\emptyset 25 \times 35$ mm (Progress: up to $\emptyset 50 \times 60$ mm from the 99.98% purity mixture [J. Cryst. Growth 401 (2014) 853])

Radiopurity measurements @LNGS

- > Li_2MoO_4 crystal (34 g, \emptyset 22×33 mm)
- > **HPGe detector** at LNGS (Assergi, Italy)

Chain	Nuclide	Activity (mBq/kg)
²³² Th	²²⁸ Ac	≤ 32
	²⁰⁸ TI	≤ 12
²³⁸ U	²¹⁴ Bi	≤ 21
	⁴⁰ K	170(80)
	⁶⁰ Co	≤ 8
	¹³⁷ Cs	≤ 4

Bolometric test @LNGS

- $\blacktriangleright \text{ Li}_2\text{MoO}_4 \text{ crystal (1.3 g, } \emptyset 25 \times 0.9 \text{ mm)}$
- > **CUORE R&D set-up** at LNGS (Assergi, Italy)



Nucl. Instrum. Meth. A 607 (2009) 573

Nucl. Instrum. Meth. A 613 (2010) 54

2013: Further study of a larger Li₂MoO₄ (34 g)



Advanced Li₂MoO₄ scintillating bolometers: (based on crystals grown by the LTG Cz method) from LUMINEU to CUPID

Low-temperature-gradient Czochralski technique



LTG Czochralski method

Nikolaev Institute of Inorganic Chemistry (NIIC, Novosibirsk, Russia) J. Cryst. Growth 229 (2001) 305

- Low temperature gradients (~ 1.0 K/cm)
- Crystal inside a crucible during the process
- Weighing control at all the stages
- Closed crucible during the process
 - \Rightarrow losses < 1% of a charge
- Crystal's yield is up to 90% of a charge
- Crystal's diameter is up to 0.8x \varnothing of a crucible





LUMINEU: Zn¹⁰⁰MoO₄ scintillating bolometers





2014: Advanced Li₂MoO₄ scintillating bolometer

Crystal production @NIIC: highly purified MoO_3 + commercial Li₂CO₃ (4N purity grade) + LTG Cz growth



²¹⁴Bi

600

3000

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Bolometric test @CSNSM (Orsay, France)



2014: Advanced Li₂MoO₄ scint. bolometer test @LNGS







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Eur. Phys. J. C 77 (2017) 785

Pile-up problem due to high activity of ⁴⁰K

Random coincidences generation:

- > Li_2MoO_4 crystal (\emptyset 50×40 mm)
- > 10⁹ events of ⁴⁰K and $2v2\beta$ of ¹⁰⁰Mo



Bkg @ ROI: 40 K+2 ν 2 β ~ 2 ν 2 β pile-ups \Rightarrow 40 K ~ 57 mBq/kg in Li₂ 100 MoO₄ \varnothing 50×40 mm

Credit to V.I. Tretyak

2015: R&D of radiopure Li₂MoO₄ crystals







Li₂

	Harr	
MoO₄ ≺40 mm	LMO-2 241 g	LMO-3 242 g
M [keV] 15 keV	6 ± 1	5 ± 1

	9	
FWHM [keV] @ 2615 keV	6 ± 1	5±1
LY _{γ(β)} [keV/MeV]	1.0	0.12*
DP _{α/γ(β)}	9	11

- > Optimization of the LMO growth @NIIC J. Mat. Sci. Eng. 7 (2017) 63
- Li₂CO₃ powder screening @LNGS

Eur. Phys. J. C 77 (2017) 785

> Bolometric tests of large volume LMOs @LNGS

	Activity (mBq/kg)					
	Powder NRMP	LMO-1 Single cr.	LMO-2 Double cr.	Powder Alpha Aesar	LMO-3 Single cr.	Powder Sigma-Aldrich
²²⁸ Th	≤ 3.7	≤ 0.023	≤ 0.026	12(4)	≤ 0.024	13(4)
²²⁶ Ra	≤ 3.3	\leq 0.051	≤ 0.044	705(30)	0.13(2)	53(6)
⁴⁰ K	≤ 42	62(2)	≤ 12	≤ 42	≤ 3.3	210(70)



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LUMINEU protocol of the Li₂¹⁰⁰MoO₄ production

- Purification of ¹⁰⁰Mo-enriched MoO₃ sublimation in vacuum recrystallization from aqueous solutions
- Control of ⁴⁰K content in Li₂¹⁰⁰MoO₄ ultra-pure Li₂CO₃ powder (+ R&D of Li₂CO₃ purification) LMO growth by double crystallization
- Low-temperature-gradient Cz growth possible size: Ø6 cm; 14 cm length
- Cut of scintillation elements
- Extraction of ¹⁰⁰MoO₃ from residues

Eur. Phys. J. C 77 (2017) 785 J. Mat. Sci. Eng. 7 (2017) 63 AIP Conf. Proc. 1894 (2017) 020017





Batch production of large mass Li₂¹⁰⁰MoO₄ scintillation elements high optical quality crystal scintillators high crystal yield (~80-85% of charge) low irrecoverable losses of ¹⁰⁰Mo (~3%)



arXiv:1909.02994



2016-2017: Tests of Li₂¹⁰⁰MoO₄ scint. bolometers



Energy resolution of Li₂¹⁰⁰MoO₄ bolometers



Particle ID with Li₂¹⁰⁰MoO₄ scintillating bolometers



Light collection conditions	LD coating, M3 reflector	LD coating, no M3 reflector	no LD coating, no M3 reflector
LY (keV/MeV) @ γ(β)	0.73-0.77	0.38-0.41	~0.2
DP @ α+t/γ	14	9	n.a.

Eur. Phys. J. C 77 (2017) 785 AIP Conf. Proc. 1894 (2017) 020017

First background measurements with Li₂¹⁰⁰MoO₄



First measurements with 4-detectors Li₂¹⁰⁰MoO₄ array



Radiopurity of Li₂¹⁰⁰MoO₄ detectors



LUMINEU search for 2β decay of ¹⁰⁰Mo with Li₂MoO₄



Syst. error ~ few % (preliminary)

 $T_{1/2} \ge 1.1 \times 10^{24} \text{ yr PRD 92, 072011 (2015)}$

2 ν 2 β <i>T</i> _{1/2} [10 ¹⁸ yr]	¹⁰⁰ Mo exposure	Experiment	Ref.
7.11 \pm 0.02(stat) \pm 0.54(syst)	7.37 kg×yr	NEMO-3	PRL 95, 182302 (2005)
6.90 ± 0.15 (stat) ± 0.37 (syst)	0.02 kg×yr	LUMINEU	EPJC 77, 785 (2017)
$6.81\pm0.01(\text{stat})\pm0.46(\text{syst})$	34.7 kg×yr	NEMO-3	L. Simard @Neutrino 2018
6.90 ± 0.06(stat)	0.06 kg×yr	LUMINEU	D. Poda @Neutrino 2018

Follow ¹⁰⁰Mo $2\nu 2\beta$ updates: F.A. Danevich, talk @ CUPID-Mo inauguration

2018-present: CUPID-Mo experiment



232**Th**

< 1

CUPID: CUORE Upgrade with Particle IDentification

arXiv:1504.03599, arXiv:1907.09376 & M. Pavan, talk @ CUPID-Mo inauguration

$\frac{10^{9}\text{Mo-enriched Li}_{2}\text{MoO}_{4} \text{ scintillating bolometers}}{118 \text{ towers } 13 \text{ layers}}$





Other CUPID oriented activities with Li₂MoO₄ crystals (grown by Cz, LTG Cz, and Bridgman methods)

CRESST+LUMINEU: LMO water etching & DM search



2019: KID-instrumented Li₂¹⁰⁰MoO₄ scint. bolometer



CROSS: surface coated bolometers with particle ID



Cryogenic Rare-event Observatory with Surface Sensitivity

Core of the project (high risk / high gain):

- Background rejection through pulse shape discrimination
 - Surface sensitivity through superconductive AI film coating
 - Fast NbSi high-impedance TES to replace / complement NTDs
- > Complete crystallization of available 100 Mo (10 kg) in Li₂MoO₄ elements
- > Purchase / crystallize 130 Te (up to 10 kg) in TeO₂ elements
- Run demonstrator in a dedicated cryostat (LSC, Spain)

Tests of first prototypes of CROSS R&D @ CSNSM (Orsay France)



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CROSS: other Li₂MoO₄ tests in view of CUPID



Note: not optimal noise conditions and light collection

S. Dell'Oro @ CUPID meeting (Rome, 18/10/2019)

First test of Li₂MoO₄ (purified Li) @ LSC

- > Li_2MoO_4 crystal (0.21 kg, \emptyset 44×45 mm) developed from purified Li₂CO₃ powder
- CUPID-Mo like detector design







CLYMENE: R&D of Li₂MoO₄ crystals for CUPID

2012-2016

http://clymene.in2p3.fr

Agence Nationale de la Recherch-

• ICMCB (Bordeaux, France)

- Czochralski method
- Commercial compounds
- ➢ Li/Mo purification to 0.1/0.5 ppm K





Bolometric tests @CSNSM [in 2016]





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CLYMENE: R&D of Li₂MoO₄ crystals for CUPID



- > Ordinary Cz method
- Purified commercial compounds
- Numerically optimized furnace ⇒ Improved Cz growth of LMO's
 - J. Cryst. Growth 492 (2018) 6
 - J. Cryst. Growth 531 (2019) 125385

Bolometric test @CSNSM [in 2019]



A. Giuliani @ CUPID meeting (Rome, 18/10/2019)



Tests of Li₂MoO₄ crystals produced in China

- Ningbo University
- > Bridgman method
- Commercial compounds
 Mat. Lett. 215 (2018) 225
 J. Cryst. Growth 500 (2018) 80



Ningbo University

5 4 3 2 1 0 1cm 2



Nucl. Instrum. Meth. A 940 (2019) 320

Bolometric test @CSNSM [in 2018]



- SICCAS Corporation
- > Bridgman method
- Commercial compounds



A bolometric test of a large sample (4.5×4.5×4.5 cm) is foreseen soon



Tests of Li₂MoO₄ crystals produced in the U.S.

- Radiation Monitoring Devices
- Czochralski method
- Commercial compounds
- > Li_2MoO_4 samples up to $\sim \emptyset 5$ cm



J. Tower @ICCGE-2019

Fund

Seed

SBIR ·



Bolometric tests @CSNSM [in 2019]

×19 mm



CUPID competitor: AMoRE path to Li₂MoO₄ bolometers

AMORE: ¹⁰⁰Mo $0_V 2\beta$ search w/ CaMoO₄ & alternatives 2013-2022 Project fully funded by Korea (IBS CUNPA); after ~10-yr R&D http://amore.ibs.re.kr Baseline: MMC-instrumented ⁴⁰Ca¹⁰⁰MoO₄ (⁴⁰Ca = 99.964%, ⁴⁸Ca < 0.001%, ¹⁰⁰Mo = 96%) 2015-2019 ¹⁰⁰Mo delivery AMORE-II AMORE-I

Crystals

Crystals mass

Bkg @ROI goal

(c/keV/kg/yr)

 $\lim T_{1/2}$ (yr)

 $\lim \langle m_{\beta\beta} \rangle$ (eV)

Location

Schedule



Light detector 2 inch Ge wafer + MMC



2 inch Ge wafer + MMC

Main issues of CaMoO₄ detectors

- > $2\nu 2\beta \, {}^{48}Ca \ (Q_{\beta\beta} = 4.3 \text{ MeV}, \text{ i.a. } 0.2\%)$ \Rightarrow requires Ca depleted in ${}^{48}Ca$
- > **U/Th traces** (even after 2x crystallization)

AMoRE-Pilot 5x-6x CMO

Best [μ Bq/kg] ²²⁸Th = 50(15) ²²⁶Ra = 40(12)



AMoRE-I 13x CMO 5x LMO

Best [μ Bq/kg] ²²⁸Th = 10(3) ²²⁶Ra = 10(3)



AMoRE-II

⁴⁰Ca¹⁰⁰MoO₄

1.5-1.9 kg

0.01

~10²⁴

0.38 - 0.64

Yangyang

2016-2018

Technical Design Report arXiv:1512.05957



⁴⁰Ca¹⁰⁰MoO₄

+LMO,...

~6 ka

0.001

~1025

0.12 - 0.20

Yangyang

X¹⁰⁰MoO₄

X=Ca,Li,Zn,Na...

~200 kg

0.0001

~5×10²⁶

0.017-0.029

Yemilab (new)

AMoRE: R&D of Li₂MoO₄ crystal



Se Jin Ra @ICHEP 2018

LTG Cz using LUMINEU protocol

AMoRE: tests of MMC-instrumented Li₂MoO₄



Summary



> ¹⁰⁰Mo is among the most promising isotopes for 0v2 β decay search

- Over the last decade, natural and ¹⁰⁰Mo-enriched Li₂MoO₄ crystals have been extensively developed and tested as scintillating bolometers
- > Li_2MoO_4 is the best Mo-containing material ever developed for cryogenic $0\nu 2\beta$ experiments
- ➤ Li₂¹⁰⁰MoO₄ scintillating bolometers have been already used in LUMINEU, are operational in CUPID-Mo, will be used in AMoRE-I and CROSS, selected for CUPID & under consideration for AMoRE-II 0v2β experiments Stay tuned !

