Purification, growth and characterization of the first $ZnMoO_4$ LUMINEU crystals

Fedor Danevich

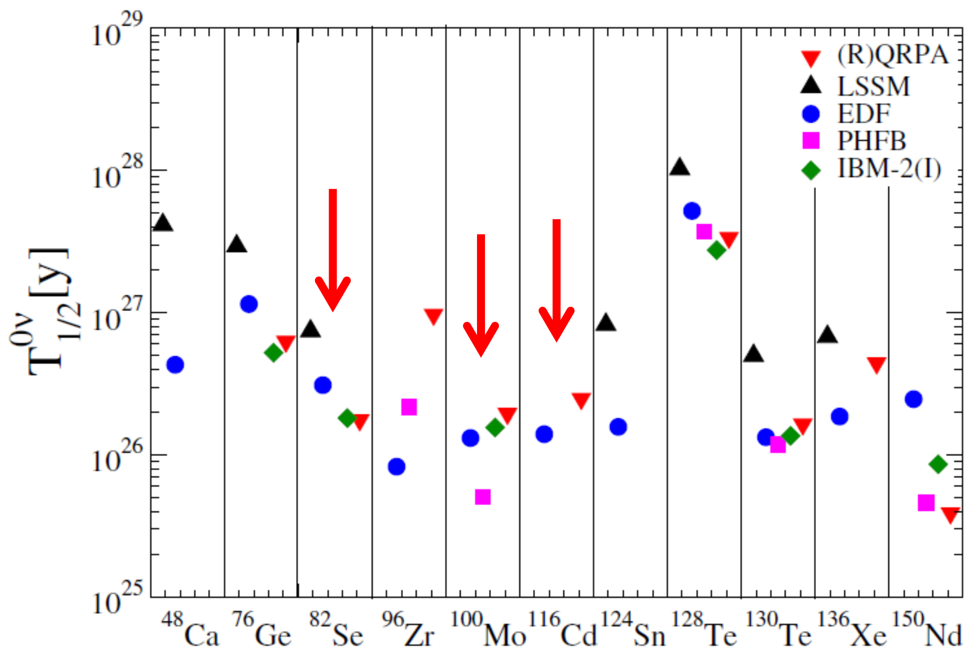
Institute for Nuclear Research, Kyiv, Ukraine

on behalf of LUMINEU collaboration

- Introduction
- Deep purification of Mo
- Crystal growth
- Tests of produced crystal samples
- Status of large size and enriched $ZnMoO_4$
- Conclusions and outlook

Test of the neutrino mass hierarchy

Theoretical calculations of $T_{1/2}$ for $\langle m_\nu \rangle$ = 0.05 eV [1]



To cover the inverted hierarchy region, one needs a sensitivity:
$\langle m_\nu \rangle$ ~ 0.02 eV $\rightarrow$ $T_{1/2}$ ~ 10^{27} – 10^{28} yr

[1] J.D.Vergados, H.Ejiri, F.Simkovic, Rep. Prog. Phys. 75 (2012) 106301

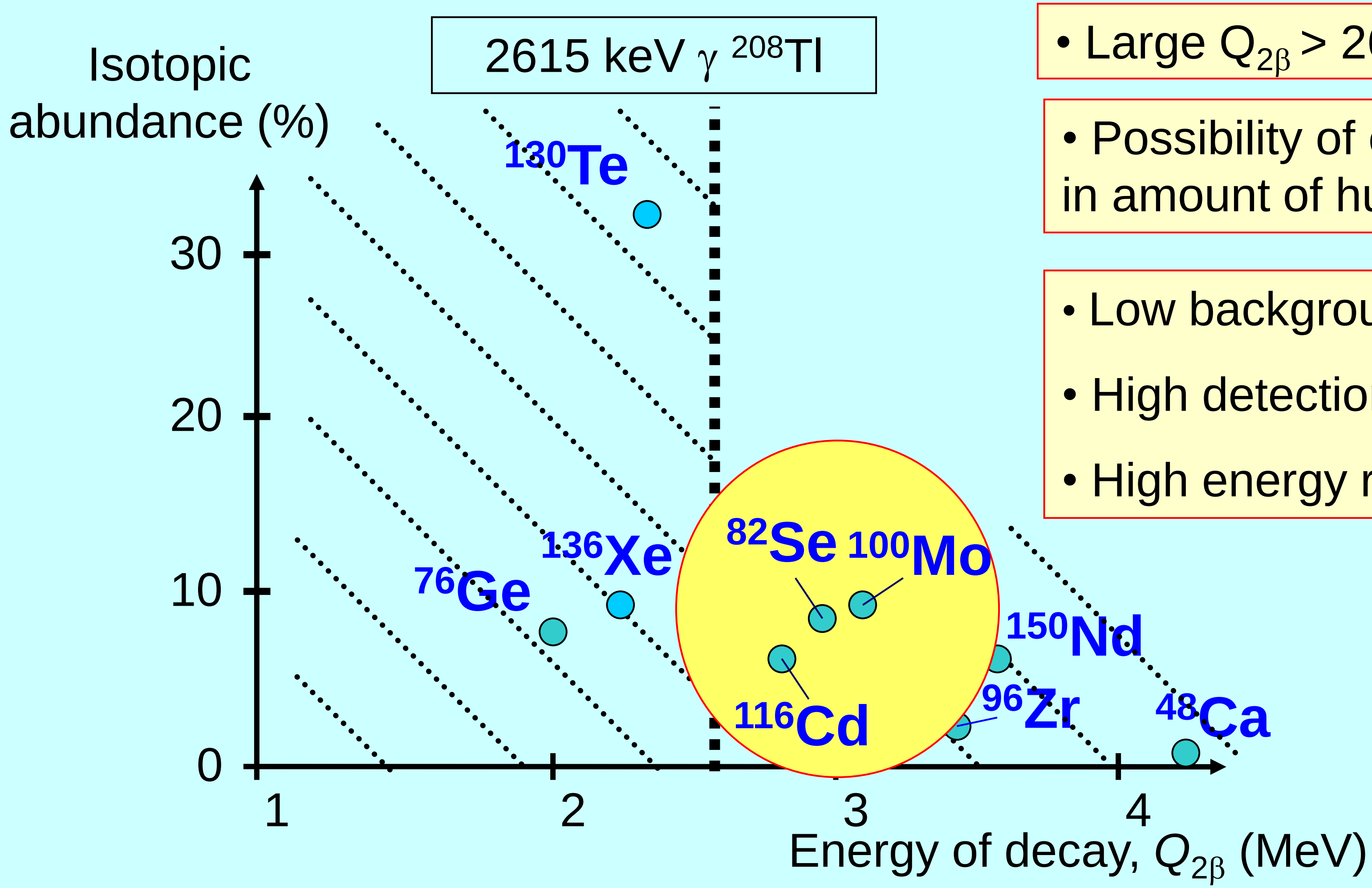
What does it mean $T_{1/2} \sim 10^{27} – 10^{28}$ yr ?

Nucleus	$T_{1/2}$ to reach $\langle m_\nu \rangle = 0.02$ eV [1]	Detector	Number of 2β nuclei in 1 ton detector	Number of decays over 5 yr
^{48}Ca	(3 – 28) ×10^{27} yr	$^{48}CaF_2$ (20%)	1.4 × 10^{27}	0.2 – 1.9
^{76}Ge	(3 – 17) ×10^{27} yr	HP ^{76}Ge	7.9 × 10^{27}	1.6 – 9
^{82}Se	(1 – 4) ×10^{27} yr	Zn^{82}Se	4.1 × 10^{27}	3 – 13
^{100}Mo	(0.3 – 1.5) ×10^{27} yr	$Zn^{100}MoO_4$	2.6 × 10^{27}	6 – 30
		$^{40}Ca^{100}MoO_4$	3.0 × 10^{27}	4 – 34
^{116}Cd	(0.8 – 1.3) ×10^{27} yr	$^{116}CdWO_4$	1.7 × 10^{27}	4 – 7
^{130}Te	(0.7 – 3) ×10^{27} yr	$^{130}TeO_2$	3.8 × 10^{27}	4 – 18
^{136}Xe	(1 – 4) ×10^{27} yr	^{136}Xe	4.4 × 10^{27}	4 – 14

[1] Table 3 in J.D.Vergados, H.Ejiri, F.Simkovic, Rep. Prog. Phys. 75 (2012) 106301

The most “promising” 2β nuclei

from the point of view of experiment



- Large $Q_{2\beta}$ > 2615 keV

- Possibility of enrichment in amount of hundreds kg

- Low background
- High detection efficiency
- High energy resolution *)

***) Pure energy resolution is still acceptable if one give a *limit* on 0ν2β decay, while it is not a case if one claim *detection* of the process**

LUMINEU

Luminescent Underground Molybdenum Investigation for NEUtrino mass and nature

A goal is to set the bases for a next-generation neutrinoless double-beta decay experiment with zinc molybdate ($ZnMoO_4$) scintillating bolometers

- It is foreseen to develop high quality radiopure $ZnMoO_4$ crystals (ideally of EDELWEISS size ∅6×4 cm, ~ 0.5 kg)
- ~1–1.5 kg $Zn^{100}MoO_4$ from enriched ^{100}Mo
    - Deep purification of Mo
    - Crystal growth & scintillation elements production
    - Recovery of Mo from $ZnMoO_4$
    - Test of radioactive contamination, bolometrical, diamagnetic, optical and luminescence properties, a pilot experiment

Sensitivity for 5 yr with 800 kg $Zn^{100}MoO_4$ (energy resolution 5−7 keV, background a few counts in ~ 1 ton per year):
$T_{1/2} \approx 10^{27}$ yr $\Rightarrow$ $\langle m_\nu \rangle$ **~ 0.013 − 0.05 eV** [1]

[1] J.W. Beeman *et al.*, PLB 710 (2012) 318

Purification of molybdenum is required

- There is no molybdenum of satisfactory quality on the market
- Furthermore, enriched ^{100}Mo surely will need purification

Material	Concentration of impurities (ppm)				
	Si	K	Ca	Fe	W
High purity MoO_3 (Russia)	60	50	60	8	200
5N5 grade MoO_3 used to produce $ZnMoO_4$ crystal studied in [1]	9	67	15	<18	96
Enriched ^{100}Mo (data of producer)	50–360	< 30	40-50	10-80	200

- Zinc of a good enough quality and radioactive contamination is available on the market (radiopurity tested with $ZnWO_4$ [2])

[1] L. Gironi et al., JINST 5 (2010) P11007
[2] P. Belli et al., NIMA 626&627 (2011) 31

Purification of MoO_3 by sublimation

- Sublimation of molybdenum oxide is widely used in the industry of molybdenum
- Nevertheless the concentration of impurities, particularly of W (up to 0.5wt% even in the high purity grade materials) still exceeds the $ZnMoO_4$ crystal growth requirements
- We have developed a technique of molybdenum purification by sublimation of MoO_3 in vacuum (with addition of zinc molybdate)

$$\mathbf{ZnMoO_4 + WO_3 = ZnWO_4 + MoO_3\uparrow}$$

Material	Concentration of impurities (ppm)			
	Si	**K**	**Fe**	**W**
Initial MoO_3	600	100 – 500	6	200 – 500
After 1st sublimation	100 – 500	10 – 50	2 – 6	100 – 200
After 2nd sublimation	70	1 – 8	< 1	30 – 40

The technique is expected to be efficient to remove Th and U

Purification by recrystallization from aqueous solutions

Additional purification by recrystallization from aqueous solutions of ammonium para-molybdate (using zinc molybdate as a collector)

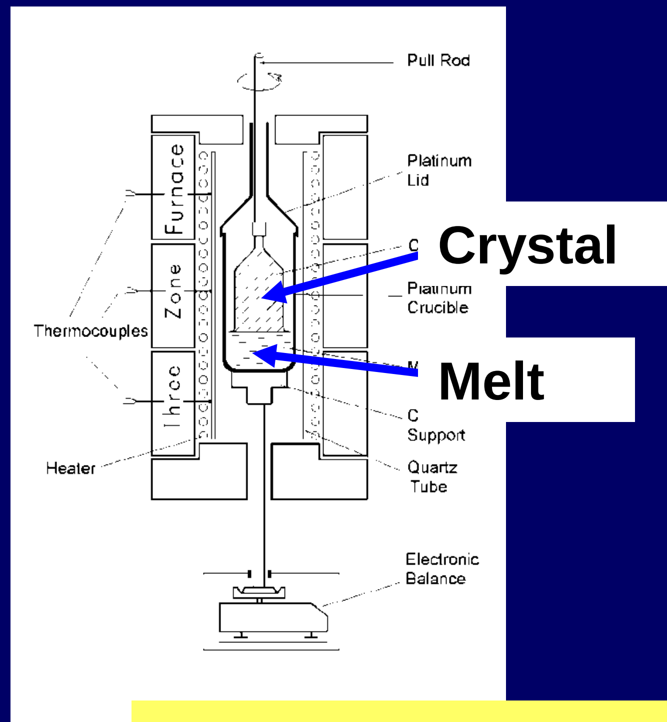
$$MoO_3 + 2NH_4OH = (NH_4)_2MoO_4 + H_2O$$

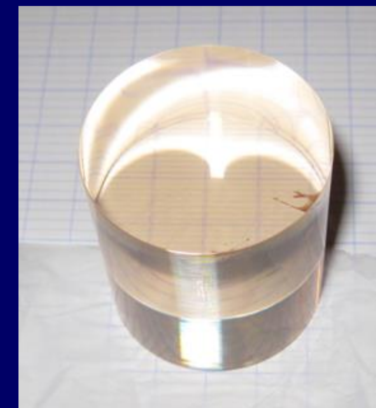
Material	Concentration of impurities (ppm)				
	Si	K	Ca	Fe	W
High purity MoO_3 (Russia)	60	50	60	8	200
Recrystallization from aqueous solutions	30	20	40	6	220
Double sublimation and recrystallization from aqueous solutions	<10	< 10	< 10	< 5	< 50

Low-Thermal-Gradient Czochralski technique

Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

Low-Thermal-Gradient Czochralski technique





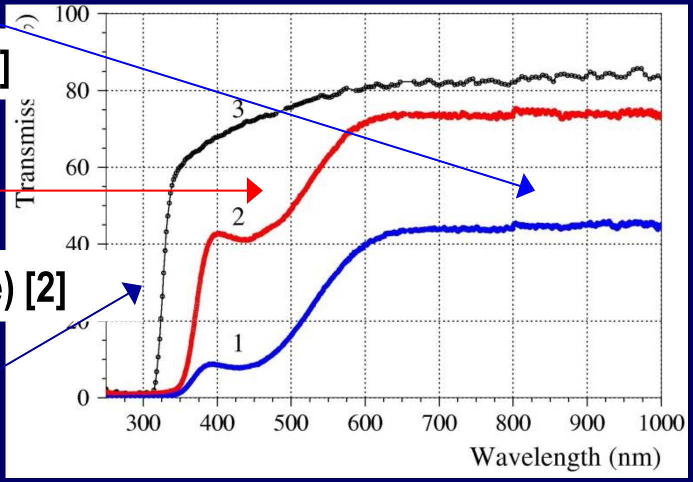
$ZnMoO_4$
∅35×40 (160 g) × 2
∅20×40 (55 g) × 2

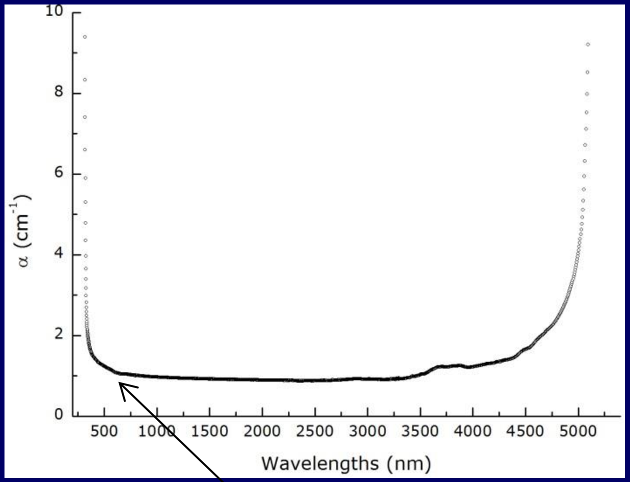
	standard	LTG-C
Output	25-30%	up to 90%
Quality		typically higher
Radiopurity		expected better
Loses of powder	2-3%	<0.3%

[1] A.A. Pavlyuk *et al.*, Proc. *APSAM*-92, April 26–29, Shanghai, China (1992)

Optical transmittance

2008 (IGP, Moscow, Russia) [1]





2009 (ISMA, Kharkov, Ukraine) [2]

2010 Low-Thermal-Gradient Czochralski (NIIC, Novosibirsk, Russia) [3-5]

[1] LI. Ivleva *et al.*, Crystallography Reports, 2008, Vol. 53, No. 6, pp. 1087

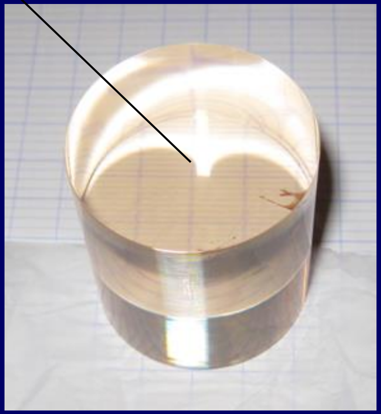
[2] L.L. Nagornaya, *et al.*, IEEE TNS 56 (2009) 2513

[3] J.W. Beeman *et al.*, J Low Temp Phys 167 (2012) 1021

[4] J.W. Beeman *et al.*, PLB 710 (2012) 318

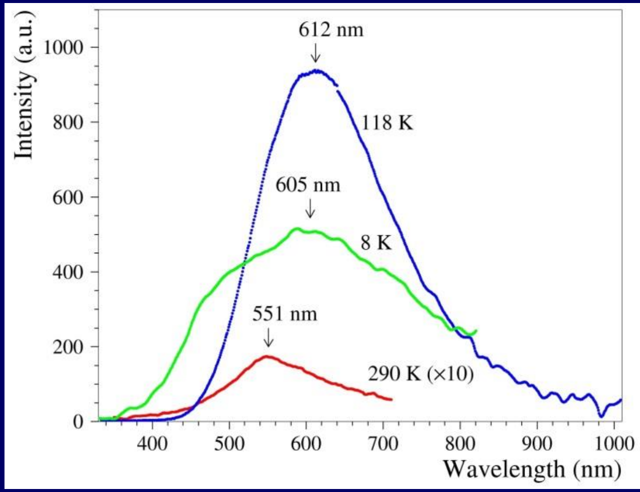
[5] D.M. Chernyak *et al.*, NIMA 729 (2013) 856

[6] V.N. Shlegel *et al.*, arXiv:1312.3515 [physics.ins-det]

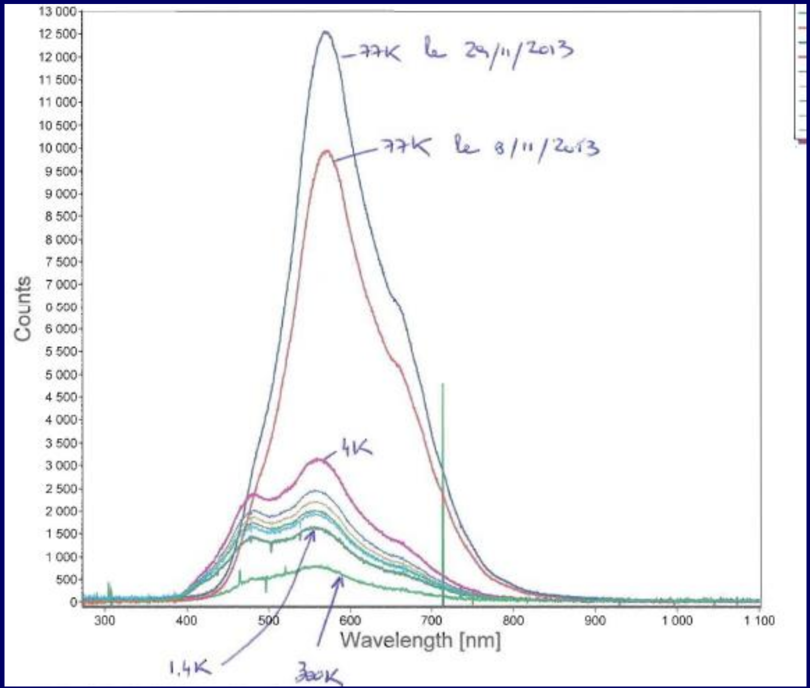


2013 Low-Thermal-Gradient Czochralski (NIIC, Novosibirsk, Russia) [6]

Luminescence under X-ray excitation



Measurements in the Kyiv Taras Shevchenko National University, Ukraine (corrected for the spectral sensitivity of PMT)



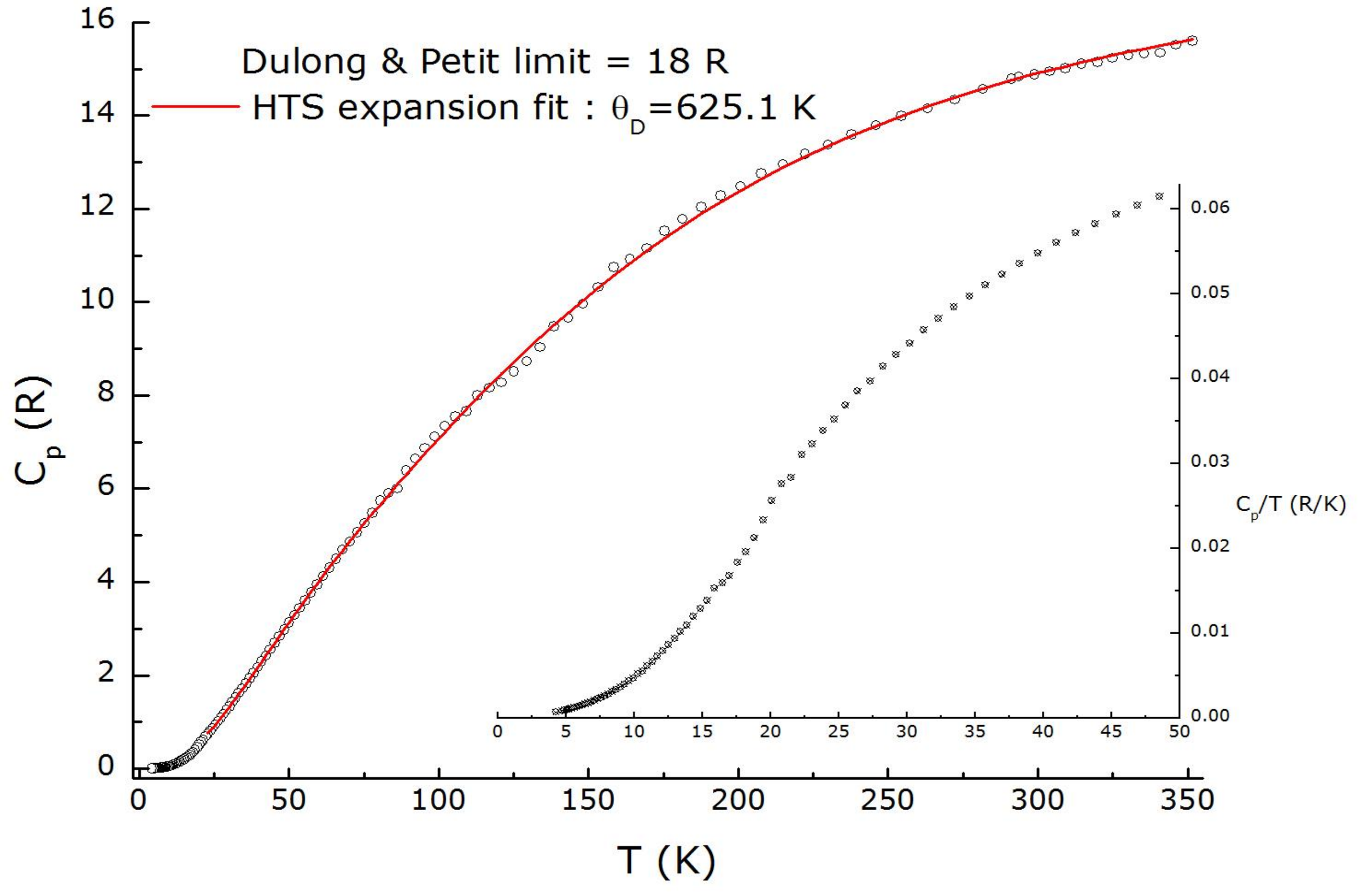
Data from the Institut d'Astrophysique Spatiale , Orsay, France
(no correction for the spectral sensitivity of photodetector)

- **How scintillation efficiency depends on W traces?**
- **Study of luminescence could allow to improve energy resolution**

Magnetic susceptibility

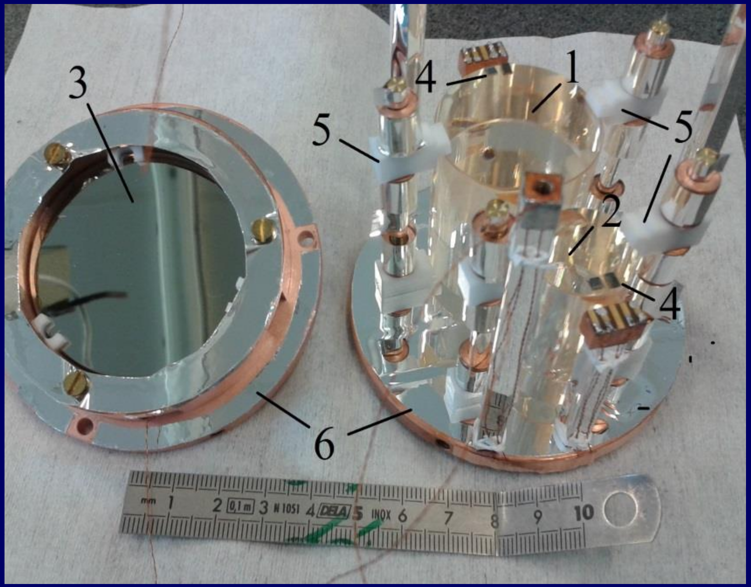
- Magnetic susceptibility was measured using a Quantum Design SQUID MPMS XL magnetometer operating in the 4.2 − 350 K temperature range and in the 0 − 5 T magnetic field range.
- $ZnMoO_4$ proved to be weakly diamagnetic with a MKSA $\chi = -(8.0 \pm 0.2) \times 10^{-6}$ over the whole temperature range investigated, from 20 to 320 K.
- Paramagnetic impurities such as Fe^{2+} or Fe^{3+} could not be evidenced even under higher applied magnetic fields up to 0.2 T

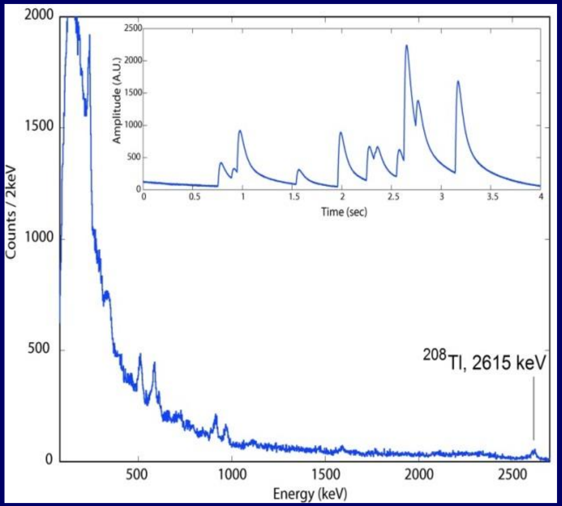
Specific heat measurements

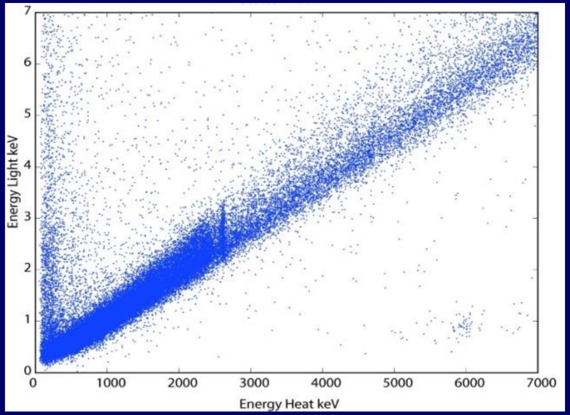


Debye temperature 625.1 K

Low temperature tests in Orsay

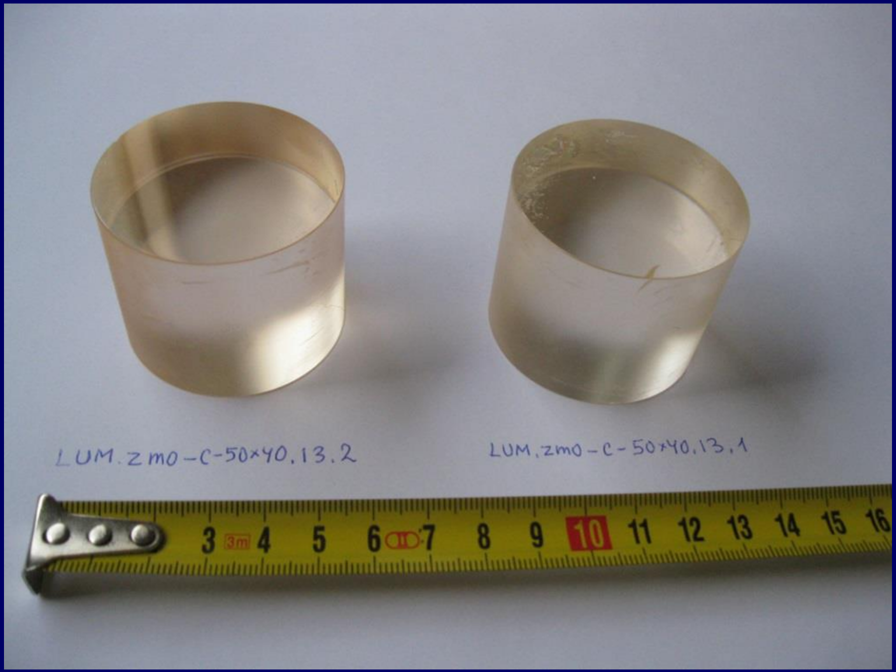






See the next report of **Michele MANCUSO**

Large $ZnMoO_4$ ∅50 × 40 mm



Possibility of re-crystallization from crystals is tested

Production of $Zn^{100}MoO_4$

- Production of "small" (≈ ∅ 2 cm) enriched $Zn^{100}MoO_4$ crystal(s) from ≈180 g of contaminated $^{100}MoO_3$ *) is in progress

*) rest after wet chemistry purification of $^{100}MoO_3$ for the ARMONIA experiment [1]:
a few mBq/kg of ^{228}Th and ^{226}Ra, 0.3 Bq/kg ^{40}K, 20 mBq/kg of ^{137}Cs)

[1] P.Belli *et al*., Nucl. Phys. A 846(2010)143

conclusions

- Method to purify molybdenum using sublimation (with addition of zinc molybdate) and recrystallization from aqueous solutions of ammonium para-molybdate (using zinc molybdate as a collector) for high quality $ZnMoO_4$ crystals growth were developed

- First LUMIENU crystals 55 g and 160 g were grown by low-thermal gradient Czochralski technique

- Tests of optical, luminescent and bolometric properties of the crystals confirem high quality of the samples

- Diamagnetic and thermal properties (Debye temperature) of $ZnMoO_4$ crystal were measured for the first time

- Large $\varnothing 5\times4$ cm high quality $ZnMoO_4$ crystals were produced by recrystallization; R&D of final $\varnothing 5\times4$ cm is in progress

- Production of ~0.1 kg $Zn^{100}MoO_4$ from ~ of enriched ^{100}Mo is in progress. Production of 1-1.5 kg $Zn^{100}MoO_4$ is foreseen in 2014

radiopurity of "small" $Zn^{100}MoO_4$

- Radioactive contamination of ~1 kg of $^{100}MoO_3$ was measured by low-background HPGe detector at LNGS [1]

$^{100}MoO_3$ (mBq/kg)	
^{40}K	36
^{226}Ra	2
^{228}Th	1

- Requirements of $0\nu2\beta$ experiment to $Zn^{100}MoO_4$ crystals:

$Zn^{100}MoO_3$ (mBq/kg)	
^{40}K	<10 *)
^{226}Ra	<0.1 – 1
^{228}Th	<0.01 – 0.1
Total α activity	< 1 mBq/kg

*) $2\nu2\beta$ activity of ^{100}Mo in $Zn^{100}MoO_4$ is 8 mBq/kg

[1] P.Belli et al., NPA 846 (2010) 143

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[1] Table 3 in J.D.Vergados, H.Ejiri, F.Simkovic, Rep. Prog. Phys. 75 (2012) 106301

Properties of $ZnMoO_4$ crystals

Property	Value	Measurements	Reference
Density (g/cm^3)	4.3		[1]
Melting point (° C)	1003 ± 5		[1]
Structural type	Triclinic, *P*1		[1, 2]
Cleavage plane	Weak (001)		[1]
Hardness Mohs scale	3.5		[3]
Index of refraction	1.89 – 1.96		[3]
Wavelength of emission maximum (nm)	605 585 625	SR 6.5 eV, 10 K X ray excitation, 8 K X ray excitation, 8 K	[1] [4] [3]
Scintillation decay time (μs)	1.3, 16, 150 3.9	SR 6.5 eV, 80 K SR 5.5 eV, 300 K	[5] [6]

[1] L.I.Ivleva *et al*., Crystallog. Rep. 53 (2008) 1087

[2] W.Reichelt *et al*., Z. Anorg. Allg. Chem. 626 (2000) 2020

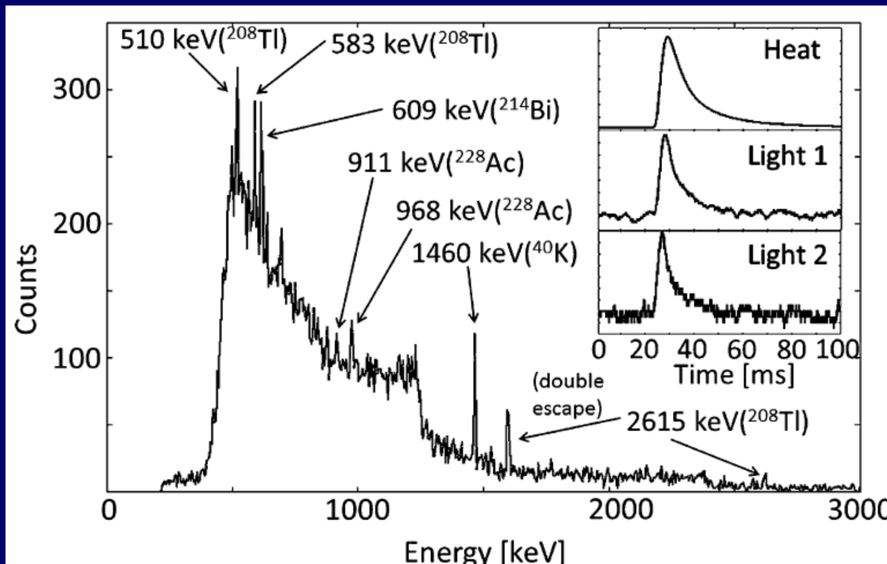
[3] D.M.Chernyak et al., in review in NIMA

[4] L.L.Nagornaya *et al*., IEEE Trans. Nucl. Sci. 56 (2009) 2513

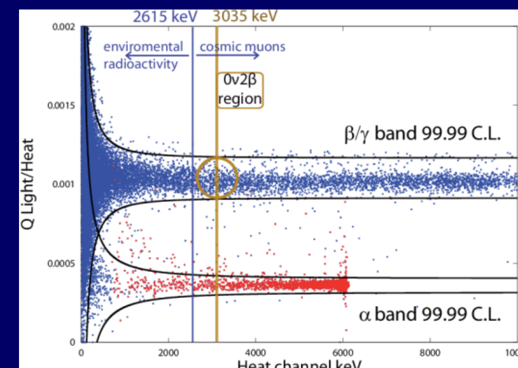
[5] V.B. Mikhailik et al., Nucl. Instr. Meth. A 562 (2006) 513

[6] D. Spassky et al., Phys. Status Solidi A 206 (2009) 1579

$ZnMoO_4$ scintillating bolometers



Chain	Activity (mBq/kg)	
	[1]	[2]
^{226}Ra	< 0.8	= 0.027(6)
^{228}Th	< 0.8	< 0.006



- **High energy resolution 3.8 keV at 2615 keV (0.15%)**
- **Estimated background is a few counts / yr at $Q_{2\beta}$ in 1 ton detector (the main background is expected to be from random coincidence of 2ν2β events [3])**

Sensitivity for 5 yr 800 kg $Zn^{100}MoO_4$: $T_{1/2} \approx 10^{27}$ yr → $\langle m_\nu \rangle \sim 0.013 - 0.05$ eV [4]

[1] D.M. Chernyak *et al*., submitted to NIMA; [2] J.W.Beeman *et al*., Eur. Phys. J. C 72 (2012) 2142
[3] D.M. Chernyak *et al*., Eur. Phys. J. C 72 (2012) 1989; [4] J.W. Beeman *et al*., PLB 710 (2012) 318