

# EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

## Investigation of doping influence on local structure and phase transitions in vanadium oxides by time-differential perturbed angular correlations at ISOLDE-CERN

Robinson A. dos Santos<sup>1,\*</sup>



A. W. Carbonari<sup>1</sup>, R. N. Saxena<sup>1</sup>, A. Burimova<sup>1</sup>, B. B. Santos<sup>1</sup>, L. F. D. Pereira<sup>1</sup>, G. A. C. Pasca<sup>2</sup>, R.S. Freitas<sup>3</sup>, D. Richard<sup>4</sup>, J. Schell<sup>5,6,\*,+</sup>, J.G.M. Correia<sup>5,7,+</sup>, D.C. Lupascu<sup>6</sup>, P. Schaaf<sup>8</sup>

\* Spokesperson

+ Local contact

1 Instituto de Pesquisas Energéticas e Nucleares, IPEN, São Paulo, Brazil

2 Universidade Federal do Pará, Campus de Abaetetuba, Pará, Brazil

3 Instituto de Física da Universidade de São Paulo (IFUSP), São Paulo, SP, Brazil

4 Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

5 EP Department, ISOLDE-CERN, CH-1211 Geneva 23, Switzerland

6 Institute for Materials Science and Center for Nanointegration, Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany

7 Centro de Ciências e Tecnologias Nucleares (CCTN), Instituto Superior Técnico, Universidade de Lisboa, Portugal

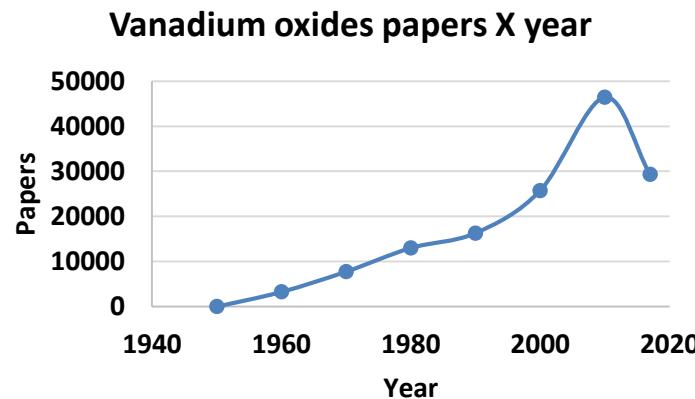
8 Chair of Department of Materials for Electronics, Technische Universität Ilmenau, Institute of Materials Science and Engineering, Gustav-Kirchhoff-Straße 5, 98693 Ilmenau, Germany

# OBJECTIVES

Studying the incorporation of selected dopants and phase transitions **in vanadium oxides ( $V_2O_5nH_2O$ ,  $V_2O_5$  and  $VO_2$ )** by ion implantation using TDPAC  
(dopant probe's lattice sites and local environment)

## SAMPLE PRODUCTION AND COMPLEMENTARY CHARACTERIZATION

- \*  $V_2O_5nH_2O$ ,  $V_2O_5$  and  $VO_2$ : sol-gel, spin coating and magnetron sputtering methods
- \* Crystal structures: X-ray diffraction (XRD)
- \* Morphology: transmission electron microscopy (TEM) and scanning electron microscopy (SEM)
- \* Chemical coordination and distances: extended X-ray absorption fine structure (EXAFS)
- \* First-principles calculations - full-potential linearized augmented plane waves method (FP-LAPW)



# VANADIUM OXIDES → “UNIVERSAL” MATERIALS

## $\text{V}_2\text{O}_5\text{nH}_2\text{O}$

- reversible cathode for lithium batteries
- storage of electrochemical energy through the intercalation of lithium ions
- electrochemical performance: a specific capacity of 438 mAh/g.  
(274 mAh/g for  $\text{LiCoO}_2$  and 170 mAh/g for  $\text{LiFePO}_4$ )

[Liu, Q., et al., Nature, 2015, DOI: 10.1038/ncomms7127; Wang, Y., et al., Adv. Func. Mat., 2006, DOI: 10.1002/adfm.200500662]

## $\text{V}_2\text{O}_5$

- storage of electrochemical energy through the intercalation of lithium ions
- Stable orthorhombic phase
- electrochromic devices, gas sensor, thermochromic windows, optical switching devices, solarcell and supercapacitor

[Pandit, B., et al., Nature, 2017, DOI: 10.1038/srep43430; Ma, W., et al., ACS Appl. Mater. Interf., 2016, DOI: 10.1021/acsami.6b06359; Gerling, L.G., et al., Ener. Proc., 2016, DOI: 10.1016/j.egypro.2016.07.029]

# VANADIUM OXIDES “UNIVERSAL” MATERIALS

## VO<sub>2</sub>

- metal – insulator transition at  $335.15\text{ K} < T_c < 341.15\text{ K}$

(tetragonal rutile for the monoclinic structure)

- change in the electrical resistivity ( $\Delta_{R\max} = 10^5\ \Omega$ )

- thermochromic windows, photochromic and electrochromic devices.

[Park, J.H., et al., Nature, 2013, DOI: 10.1038/nature12425; Wang, N., et al., T. Sol. F., 2013, DOI: 10.1016/j.tsf.2013.01.074; Jin, P. et al., J. Vac. Sci. Technol. A, 1997, DOI: 10.1116/1.580439; Wentzcovitch, R.M., Phys. Rev. Lett., 1994, DOI: 10.1103/PhysRevLett.72.3389; ]



[Wang, N., et al., T. Sol. F., 2013, DOI: 10.1016/j.tsf.2013.01.074; Ningyi, Y., et al., Ap. Surf. Sc., 2002, DOI: 10.1016/S0169-4332(02)00180-0;]

# WHY TDPAC SPECTROSCOPY AT ISOLDE-CERN?

Atomic resolution delivers information on

- Probe's lattice location & annealing of implantation defects
- Probes-host or probes-defects interactions
- Probing electronic structure and electron polarization
- Diffusion of probe atoms (dynamic interaction)
- Oxygen vacancy occurrence

## HOW?

As a function of

- sample **stoichiometry** with different impurities/**doping**
- annealing and measuring **temperature** from 333,15 – 873,15 K



## USING?

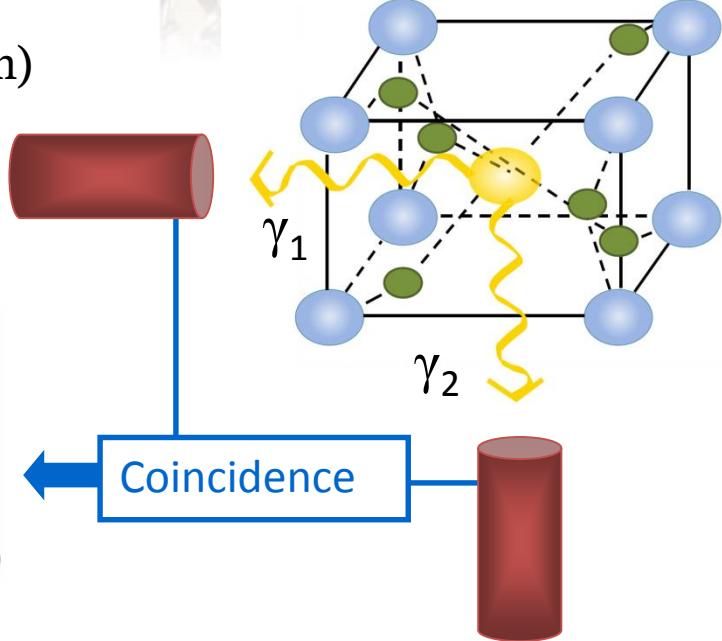
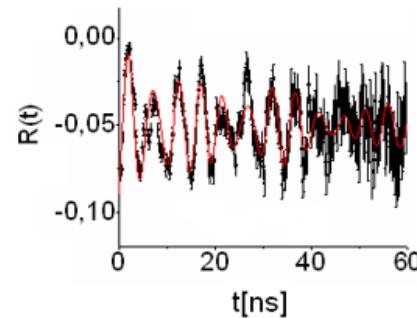
$^{111}\text{In}^{(111}\text{Cd}), ^{117}\text{Cd}^{(117}\text{In}), ^{111\text{m}}\text{Cd}^{(111}\text{Cd}), ^{119\text{m}}\text{Sn}^{(119}\text{Sn})$

Magnetic interaction:

$$\omega_L = -g \frac{\mu_N}{\hbar} B_{hf}$$

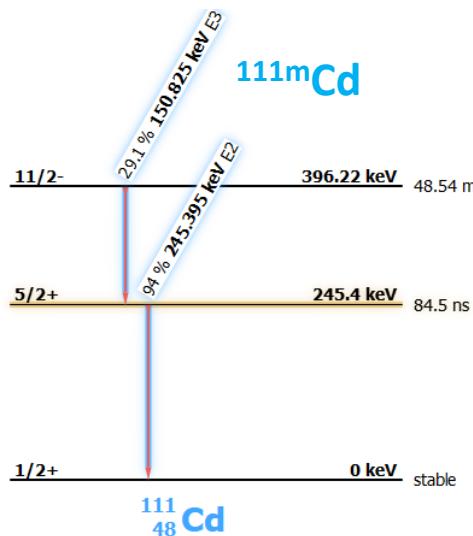
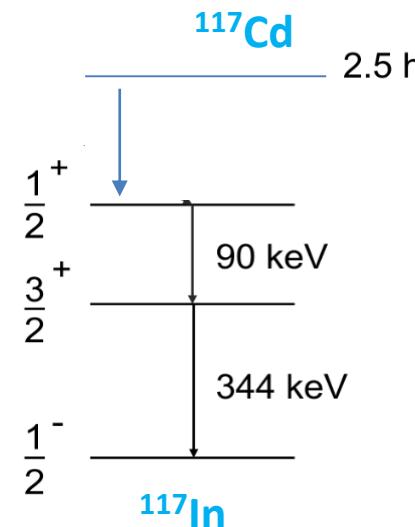
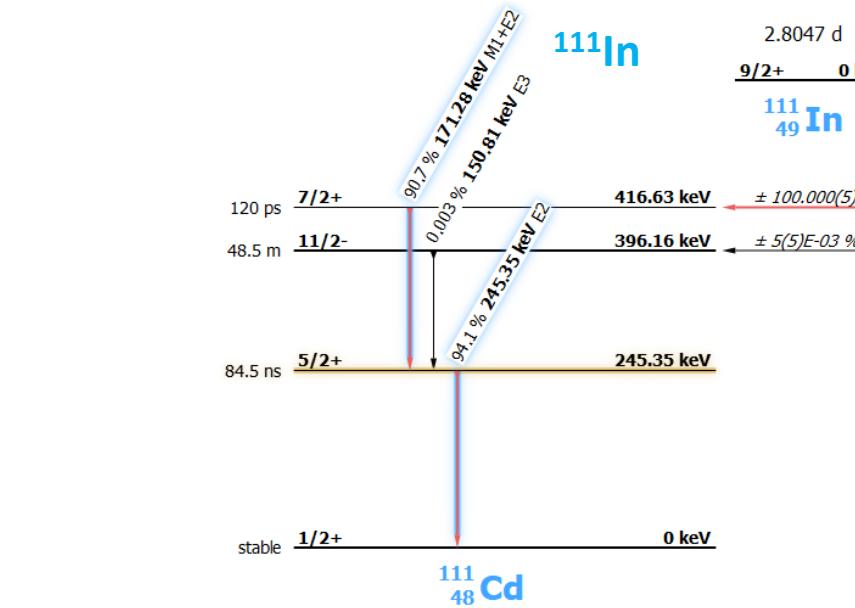
Quadrupole interaction:

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$



# WHY THESE TDPAC ISOTOPES?

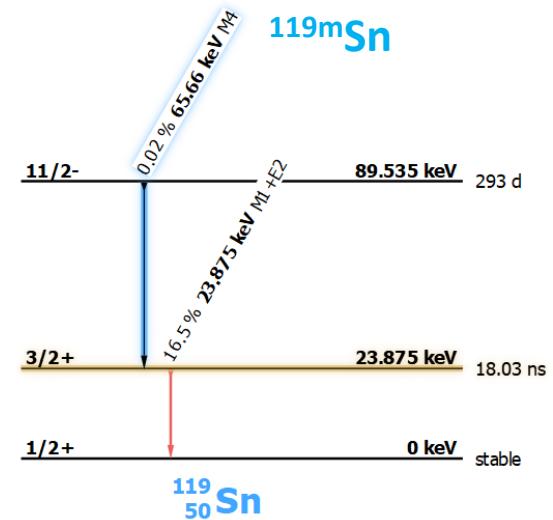
$^{111}\text{In}(\text{Cd})$ ,  $^{117}\text{Cd}(\text{In})$ ,  $^{111\text{m}}\text{Cd}(\text{Cd})$ ,  $^{119\text{m}}\text{Sn}(\text{Sn})$



## Physics behind the experiment:

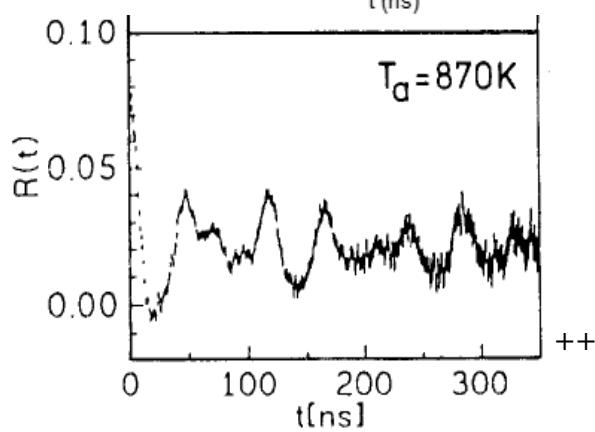
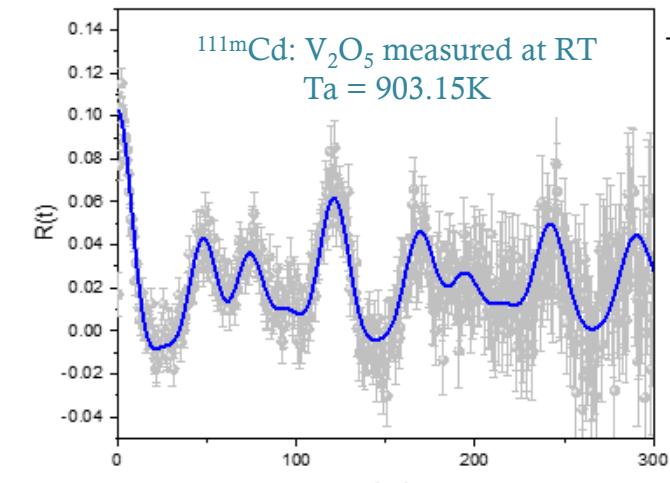
- Different probe ions/valences;
- Local effects of the probe elements on
  - a) Charge density
  - b) Electronic structure by measuring the EFG.

[Nagl, M. et al., NIM A 726, 2013, 17-30,  
DOI: 10.1016/j.nima.2013.05.045]



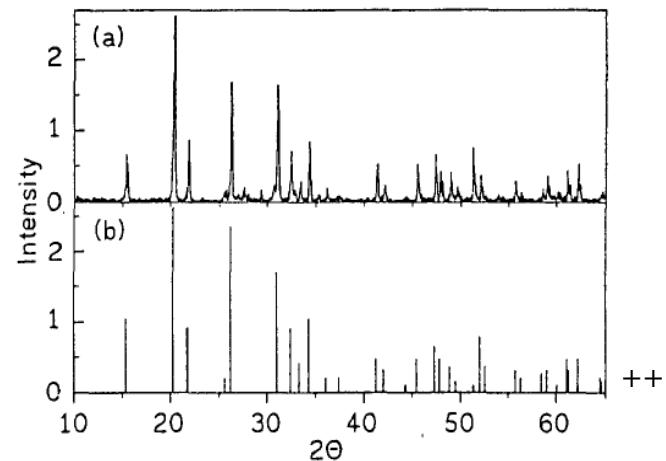
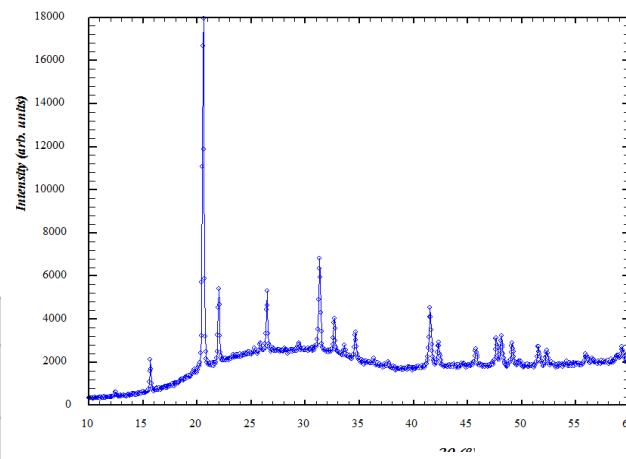
# FEASIBILITY OF CURRENT PROPOSAL

$^{111}\text{Cd}: \text{V}_2\text{O}_5 \gamma\text{-}\gamma$  (151-245 keV) - TDPAC from decay of  $^{111m}\text{Cd}$



+

	Exp.	Lit.
$\nu_{Q1}$ (MHz)	66.01	88.10
$\eta_1$	0.57	0.62
$\nu_{Q2}$ (MHz)	69.09	221.00
$\eta_1$	0	0.10



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[+ Vianden, G., Nightmare (MDI) Version RC3 (1.2.0.247), Universitat Bonn, 2005-2010; ++ Naicker, V., et al., Hyperf. Interact., 1993, DOI: 10.1007/BF00567448]

# SUMMARY OF REQUESTED SHIFTS



## Time-Differential Perturbed Angular Correlations Studies

Required isotope	Implanted beam	Probe element	Type of experiment	Approx. Intensity [at/ $\mu$ C]	Target / Ion source	Required atoms per sample	Comments	n° of shifts
$^{111m}\text{Cd}$ (48m)	$^{111}\text{Cd}$	$^{111}\text{Cd}$	$\gamma$ - $\gamma$ TDPAC	$10^8$	Sn target; VD5 ion source	$2 \times 10^{10}$		4
$^{117}\text{Cd}$ (2.49h)	$^{117}\text{Cd}$	$^{117}\text{In}$	$\gamma$ - $\gamma$ TDPAC	$10^8$	UC target; RILIS (Ag) ion source	$5 \times 10^{10}$		2
$^{111}\text{In}$ (2.8d)	$^{111}\text{In}$	$^{111}\text{Cd}$	$\gamma$ - $\gamma$ TDPAC	$10^8$	UC target; surface or RILIS ion source	$1 \times 10^{11}$		2
$^{119m}\text{Sn}$ (293d)	$^{119m}\text{Sn}$	$^{119}\text{Sn}$	e- $\gamma$ TDPAC	$10^8$	UC target; surface or RILIS ion source	$5 \times 10^{10}$		2
<b>TOTAL of requested shifts</b>								<b>10</b>

# FUNDING AGENCIES INVOLVED

## BMBF

Bundesministerium für Bildung und Forschung

Erforschung kondensierter Materie mit Großgeräten

Ausbau und Unterhalt der Einrichtungen an ISOLDE/CERN

Germany, contract: 05K16PGA

D. C. Lupascu, J. Schell



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## FCT

Fundaçao para a Ciéncia e a Tecnologia

Caracterização de Materiais com Técnicas Nucleares Radioativas - sinergia e complementaridade aplicadas ao treino e desenvolvimento. Portugal, Project: CERN-FIS-NUC-0004-2015

J.G. Correia

# FCT

Fundaçao para a Ciéncia e a Tecnologia  
MINISTÉRIO DA CIÉNCIA, TECNOLOGIA E ENSINO SUPERIOR

## CNPq

Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brasil



Conselho Nacional de Desenvolvimento  
Científico e Tecnológico

## CNEN

Comissão Nacional de Energia Nuclear – Brasil



Comissão Nacional  
de Energia Nuclear

**THANK YOU VERY MUCH FOR YOUR ATTENTION!**