EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

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

Influence of valence of doping element on local electronic and crystal structure in vanadium oxides: Time-Differential Perturbed Angular Correlations spectroscopy at ISOLDE
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A. W. Carbonari[1], R. A. dos Santos [1], R. N. Saxena[1], A. Burimova[1], B. Bosch-Santos[1], L. F. D. Pereira[1], G. A. Cabrera-Pasca[2], R. S. Freitas[3], D. Richard[4], J. Schell[5,6], J. G. Correa[5,7], D. C. Lupascu[6], P. Schaaf[8]

[1]Instituto de Pesquisas Energéticas e Nucleares. IPEN, São Paulo, SP, 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

Spokesperson(s): A. W. Carbonari, carbonar@ipen.br, J. Schell
Local contact: J. Schell juliana.schell@cern.ch, J. G. M. Correia joao@cern.ch

Abstract

Hyperfine interactions probed at different nuclei of implanted ions (acting as dopants) in vanadium oxides (VO_2 and V_2O_5) will be measured in order to understand, along with first-principles calculations, the doping phenomenology at the nanoscopic scale and its consequence on the electric and magnetic properties of the host oxides. Vanadium oxides are particularly attractive due to the phase transitions and to the capacity of the vanadium ion to change its oxidation state, being such properties well adequate for applications on, e.g., chemical sensors, electrochemical energy storage via the intercalation of Li-ions, catalytic and optoelectronic devices. At ISOLDE-CERN we will study the effects of the incorporation of selected dopants (Cd, In, Sn) using the radioactive nuclear technique Perturbed Angular Correlations (PAC). Measurements will be performed as a function of temperature to study the annealing of implantation defects and the dopant incorporation and stability, particularly probing its electronic configuration while interacting. This project is part of a larger and synergetic collaboration using a multitude of characterization techniques, where we specific aim unique local information that can be used to optimize doping device.
Requested shifts: 6 shifts in 2018, (split among different probe isotopes according to ISOLDE schedule)

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1. Introduction and motivation

The doping with other elements than the native cationic metal can enhance certain properties of oxides and turn them better materials for specific applications or make them suitable for new ones [1-3]. When a dopant atom replaces the cationic metal in an oxide host, even at very small concentrations, the properties of the host can be dramatically affected producing changes in electronic and transport properties, and altering phase transition temperatures [1,3]. These changes are essential for technological applications. The role of the dopant and its influence in the host oxide is desirable to be well understood so that a general model of the connection between dopant−oxide pairing and the functional performance must be developed. The lack of quantitative experimental data on the local neighbourhood of the dopant, which can give information about the local structure and the electronic structure in this region, has prevented the formulation of a general theoretical description of the doping phenomenon in oxides. Techniques sensitive enough to identify changes of specific quantities from different regions within samples on an atomic scale are welcome to produce new experimental data on the dopant effects in oxides.

Vanadium oxides (V_2O_5 and VO_2): The scope of already implemented and potential applications of vanadium oxides is, indeed, impressive [4,5]. The properties of each particular phase may be tuned by doping to satisfy specific requirements and/or improve the functional performance. Understanding the role of dopant and doping mechanism is, therefore, a key to control these features. Vanadium oxides appear in several different stoichiometries with a possibility of interphase transformations under certain conditions. Surface effects also have much impact in the case of nanoparticles and thin films, stoichiometry issue is even more evident for such systems. More specifically, desorption of vanadyl-oxygen from the surface leads to oxygen diffusion and creation of vacancies in the bulk[6]. Dopant implantation and impurities in general may be another reason for oxygen ions rearranging leading to phase transformations. Obviously, distinct phases have different properties, and thus suit for different applications. In this regard, the phenomenon that gained more attention is metal-to-insulator transition (MIT), whose parameters depend significantly on oxide stoichiometry. In what follows we consider separately the peculiarities of VO_2 and V_2O_5 phases with respect to this effect. MIT takes place at 341 K for vanadium dioxide (**VO_2**), the semiconductor to metal transition being accompanied by a monoclinic-rutile structural one. Its origin is not a consensus yet, and recently prevailing scenario suggests a Peierls assisted orbital selective Mott transition [7]. Various experiments revealing the role of doping and its effect on the transition temperature have been reported [8,9]. For example, tungsten-doped VO_2 has its MIT at 288 K, as shown by Jorgenson and Lee [9], who assumed it to be optimal for energy control in buildings. Vanadium pentoxide (**V_2O_5**) may be the most important compound of vanadium oxides since it is the most stable of vanadium oxides and the principal precursor to reduced oxides and vanadium alloys. Though it was believed that V_2O_5 experiences no MIT, there appeared several works where the possibility of the transition was discussed for thin films and V_2O_5 crystal surface [10,11]. The anisotropic surface re-structuring was reported and a transition similar to MIT was observed at 350-400 K (for surface) and at 533 K (for thin films).

The V_2O_5 crystallizes in an orthorhombic structure with layers of VO_5 of square pyramidal form sharing edges and corners. These layers are weakly linked along the c-axis and the space between them allows the accommodation of guest ions [12]. The Sol-Gel method can be used to obtain the $V_2O_5nH_2O$ and from this VO_2 [13], which presents semiconductor-metal phase transition at a critical temperature Tc = 341 K, changing the structure monoclinic for the tetragonal rutile structure. Due to this transition, a drastic change in the electrical

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resistivity and optical properties occurs [14-17]. All their properties allow V_2O_5 as well as VO_2 good candidates for several technological applications such as gas sensors [18,19] and storage of electrochemical energy through the intercalation of lithium ions [12], catalytic devices [20] and optoelectronic [21].

Doping can change some key properties of V_2O_5 and VO_2 which can make them better materials for technological applications. For example, Ag and Cu[22] as well as Sn[23] doping in V_2O_5 improves its electrochemical performance. The Sn-doped V_2O_5 film shows much enhanced lithium-ion storage capacity, faster kinetics, and improved cyclic stability in comparison with pure V_2O_5 film[23]. In these cases dopants have valence smaller than the valence of Vanadium (+5) in V_2O_5. The valence of the dopant is also important in electrical and optical properties of VO_2 as reported its influence in the temperature transition of VO_2 doped with elements of different valences [24]. In order to study the effect of dopant valence, which seems to be the most important factor in the doping mechanism, it is necessary to investigate how the dopant affects its neighborhood in the oxide host. Furthermore, the physics behind the properties of doping in Vanadium oxides is linked to the nanoscopic phenomenology, such as oxygen vacancies, point defects and the influence on the local structure. Taking all these points into account, perturbed angular correlation (PAC) spectroscopy allied to first-principles calculations (promising techniques to provide valuable information about doped systems[25-30]) will be used to study bulk and thin film samples of doped vanadium oxides to provide information on the atomic scale through the detection of the local electronic charge densities by measuring and calculating the electric field gradient (EFG) at the probe nuclei of dopants[31,32]. We, therefore, have chosen Cd, In, and Sn as dopant elements in V_2O_5 and VO_2 because their valence are, respectively, +2, +3, and +4, and because there are the PAC probe nuclei [111]Cd, [117]In and [119]Sn, which permits the experimental measurements of EFG.

Objectives: The doping mechanism in selected nanostructured vanadium oxides will be investigated by measuring the temperature dependence of hyperfine interactions at the nuclei of the implanted radioactive ions, which act as the dopants, using PAC spectroscopy as well as by first-principles calculations based on density functional theory (DFT). Our goal in the present project is to provide a description of the doping effects at an atomic level on the local crystal structure and the electronic structure around the impurity and the consequences on the properties of the host oxides. A description of the microscopic mechanisms that give origin to the properties of these oxides can also be investigated by tracking the hyperfine interactions at the probe nuclei using the data collected. It is important to emphasize that the results of this project can either contribute to the formulation of a general theory about the doping mechanism in semiconductor oxides as well they can contribute to the production of new materials for technological applications.

With [111m]Cd/Cd(48min) , ^{111}In/Cd(2.8d), [117]Cd/In (2.5h) and [119m]Sn/Sn (293d) PAC probes we study the incorporation of Cd, In and Sn dopants, annealing of point defects and the dopant's interaction with oxygen vacancies. The use of [117]Cd/In allows complementary measurements of ^{111}In/Cd since in both cases the "chemistry" of the incorporation is done on one element and the measurement of the other, after decay.

Description of the Proposed Work

Route to achieve the proposed objectives. The experiments at ISOLDE aim to use different probe ions having different valences and investigate the local effect of doping on the charge

density, oxygen vacancy occurrence, and electronic structure by measuring the major component of the electric field gradient tensor (Vzz) and the asymmetry parameter (η). These parameters are related to the density and symmetry of charges around the dopant and provide information on the local structure and presence of defects. Simulations will be performed by first-principles calculations with a supercell containing several vanadium oxide unit cells in which few vanadium atoms are replaced by the dopant. The hyperfine parameters (Vzz and η) are calculated and compared with the experimental values so that the charge state can be tuned. From results of calculations, the density of states (DOS) can be determined and information on the electronic structure, such as which electrons form the valence and conduction band and where is located the impurity band, can be obtained. This experimental plus calculations methodology has been used by our team to investigate doping in some oxides [25-30].

Preparation and characterization of samples at home institutions. Very pure samples of vanadium oxides will be prepared at the hyperfine interactions laboratory in IPEN, São Paulo. The IPEN's group is quite experienced in producing oxide samples by chemical routes. Sol-gel method will be used to prepare bulk samples as well as it is ideal to produce thin film samples deposited on substrates by spin-coating technique. Nanoparticles of vanadium oxides will be prepared by thermal decomposition, which produce small and monodisperse particles. Additional thin film samples of V_2O_5 and VO_2 will be prepared by magnetron sputtering in the Engineering College at São Paulo University. All samples will be characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Extended x-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES) will be carried out for thin film samples in the synchrotron accelerator in Campinas, SP, Brazil. EXAFS constitutes a powerful technique to extract direct information about type, number, and distances of neighbors of the absorber atom (dopant)[33]. XANES can provide the oxidation state of the element (dopant) and some eventual hybridization[34].

PAC probes to be implanted at ISOLDE-CERN (requested shifts)
$^{111}In(^{111}Cd)$, $^{117}Cd(^{117}In)$, $^{111m}Cd(^{111}Cd)$, ^{119m}Sn (Sn).
After implantation, prior to the TDPAC measurements, the samples will be submitted to different temperatures of annealing: 120 °C; between 210-270 °C and 350 °C, in which the samples suffer total dehydration and present the orthorhombic phase. The obtained V_2O_5 will be subjected to an anneling at 480 °C under 1-2 Pa for 20 minutes, obtaining VO_2. This VO_2 will be subjected to anneling above and below 68 °C, which is the semiconductor (monoclinic) - metal (tetragonal) transition temperature. This procedure will be done for thin films and V_2O_5 pellets. We intend choosing ions with different valences than that of the native cations and investigate the effect of the excess or lack of electrons on the crystal and electronic structure in the neighbourhood of the dopant.

PAC measurements at ISOLDE-CERN during the long shutdown (no shifts required)
$^{181}Hf(^{181}Ta)$ probe nuclei will be produced at IPEN, São Paulo, and exported to ISOLDE/CERN for measurements during the Long Shutdown. We aim optimized experiments during the long-shutdown, exploiting the parallel use of the four 6D-TDPAC instruments present at the ISOLDE-CERN off-line laboratory 508/R-008.

DFT simulations at home institutions. First-principles calculations, using full-potential augmented plane waves plus local orbital method (FP-APW+lo) based on the DFT will be performed in order to simulate the doping in the host oxides to interpret mainly the experimental hyperfine interactions results. Valuable information about the studied doped oxide (such as structural deformations, localization and charge state of defect centers and

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impurities, character of impurity levels, etc.) can be obtained by confronting experimental determination with very accurate theoretical predictions of the EFG using all-electron *ab initio* electronic structure calculations in the framework of the density functional theory (DFT)[25-29]. In the FP-APW+lo method, the wave functions are expanded in terms of spherical harmonics inside non-overlapping atom-centered spheres of radius R_{MT}, and in plane waves in the interstitial region. To determine the structural distortions induced by the impurity, when the self-consistency of the potential is achieved, the forces on the atoms are obtained, and they are displaced until the forces on them are below a given tolerance value in order to predict the final equilibrium structures. Since the substitutional dopant impurity has a nominal different character (donor or acceptor), the different charge states of the impurity can be simulated by removing or adding electrons[28,35]. For bulk samples the WIEN2k code will be used for the calculations. For thin films, two ab initio methods with different basis set (FP-APW+lo method and a linear combination of numerical localized atomic-orbitals basis set, implemented in WIEN2k and SIESTA packages, respectively) will be used [36]. In order to determine the electronic and hyperfine properties in the doped surfaces, we calculated the EFG using the FP-APW+lo method at the equilibrium atomic positions predicted by SIESTA since, for the pure surface, this method predicts final equilibrium structures with comparative lower energy than those predicted by the FP-APW+lo method.

PAC Spectroscopy technique and methodology justification. The PAC spectroscopy is based on the conservation of the angular momentum between the spin direction of the gamma emitting probe nucleus and the direction of the gamma radiation emission pattern. The hyperfine interaction consists of the coupling of the total angular momentum of the electrons with the nucleus spin. When the probe nucleus is inserted in the sample the hyperfine interaction induces a variation in the time of this emission pattern and the measurement of the time variation of this emission pattern in a plane at different angles it is possible to obtain the hyperfine electric field gradient and the magnetic hyperfine field. For all probe cores present in the sample to emit radiation in the
same direction generating an anisotropic pattern, PAC spectroscopy uses the coincidence measurement (W (θ)) between two gamma photons emitted successively in cascade. PAC spectroscopy is able to measure electrical, magnetic or combined electrical and magnetic hyperfine interactions. The number of radioactive nuclei, which are necessary to perform experiments, is generally less than 10^{12} radioactive atoms, at highly diluted concentrations generally, in the range between 0.01% and ppm. This number of atoms is still enough to produce an observable modulation of the decay curve, described by the so called anisotropy ratio, R(t). A fit to this curve allows identifying multiple fractions of probe atoms interacting with certain local environments. Phenomena related to the observation of lattice sites, defects, orbital ordering, electronic polarization, all being investigated as a function of parameters like temperature, electric field, and pressure are examples of the potentiality of the PAC technique. PAC is, therefore, suitable to a precise and detailed characterization of nanoscopic materials mainly because it can obtain information at different regions inside the whole sample. The method is complemented by first-principles calculations and this complementarity has been used with success by our team [25-30].

Resume of our earlier findings. An EFG study of [111]Cd in vanadium oxides were performed by implantation of ^{111}In nuclei at 400 keV with PAC results of ν_Q=88.1(3) MHz and η=0.62(2)[37]. In that study, samples were prepared by pressing the commercially obtained

oxide powders. However, TDPAC measurements considering the transition temperatures and V_2O_5 hydration stages in a systematic investigation, using the same experimental conditions are essential to know more details of the behavior and properties of this material as well as the effect of doping. Our initial early TDPAC measurements performed at ISOLDE-CERN during the test experiments resulted in promising spectra for V_2O_5 sample after annealing at 630 °C under

pressure of 2.10^{-4} mbar for 10 minutes (see Fig. 1) using [111m]Cd as radioactive probe. This sample will be submitted to complementary characterisation at the participating home institutions to check its structural conditions and the vanadium oxide phase present. Additional systematic measurements using different radioisotopes as probes under different temperatures are necessary to a complete investigation.
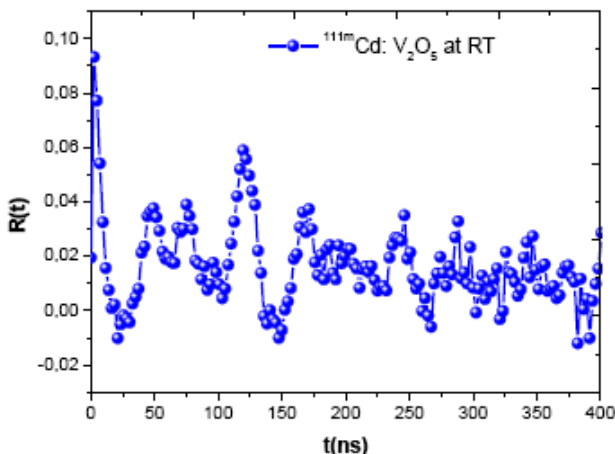

Figure 1. PAC spectrum for V_2O_5 sample synthesized by the Sol-Gel method at IPEN obtained at ISOLDE-CERN using [111m]Cd as probe nuclei.

Our collaboration includes the expertise of both material and nuclear applied physicists using these techniques at ISOLDE-CERN.

Summary of requested shifts:

We estimate the total amount of ISOLDE beam time needed to accomplish the above-described tasks to be 6 shifts, distributed according to table I:

Table I: Beam time request for PAC studies

Time-differential Perturbed Angular Correlations Studies								
Required isotope	Implanted beam	Probe element	Type of experiment	Approx. Intensity [at/μC]	Target / Ion source	Required atoms per sample	Comments	nº of shifts
[111m]Cd (48m)	[111]Cd	[111]Cd	$\gamma-\gamma$ PAC	10^8	Sn target; VD5 ion source	2×10^{10}		3
[117]Cd (2.49h)	[117]Ag	[117]In	$\gamma-\gamma$ PAC	10^8	UC target; RILIS (Ag) ion source	5×10^{10}		1
[111]In(2.8d)	[111]In	[111]Cd	$\gamma-\gamma$ PAC	10^8	UC target; surface or RILIS ion source	1×10^{11}		1
[119m]Sn (293d)	[119m]Sn	[119]Sn	$e-\gamma$ PAC	10^8	UC target; surface or RILIS ion source	5×10^{10}		1
TOTAL of requested shifts								**6**

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber, SSP-GHM chamber	☒ Existing	☒ To be used without any modification
Existing equipment on the solid state labs in building 508-r-002, r-004 and r-008 - 6 detector PAC standard setups - annealing furnaces - glove boxes art 1 of experiment/ equipment]	☒ Existing	☐ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
[Part 2 experiment/ equipment]	☐ Existing	☐ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed SSP-GLM chamber and building 508-r-002, r-004 and r-008 installations. Every experiment has its one written procedure file discussed with Radio Protection services, before every beam time.

Additional hazards:

Hazards	[Part 1 of the experiment/equipment]	[Part 2 of the experiment/equipment]	[Part 3 of the experiment/equipment]
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]	Vacuum	
Vacuum	10^{-6} mbar at SSP chamber 10 during collections	10^{-5} mbar	
Temperature	[temperature] [K]	Room temperature – 630 °C	
Heat transfer			
Thermal properties of materials			
Cryogenic fluid	[fluid], [pressure][Bar], [volume][l]		
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		

Ionizing radiation

Target material	[material]		
Beam particle type (e, p, ions, etc)	^{111m}Cd, ^{111}Cd, ^{117}In, ^{119}Sn		
Beam intensity			
Beam energy	50 keV		
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☐		
• Sealed source	☐ [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	☐ Removal from chamber, transport to TDPAC laboratory 508/R-002 in standard Pb castle shielding. Placed in PAC machine at 508/R-008 for measurement.		
• Dose rate on contact and in 10 cm distance	Max. 0.3 µSv/h (Nucleonica gamma dose rate)		
• Isotope	^{111m}Cd, ^{111}Cd, ^{117}In, ^{119}Sn		
• Activity	Max 6 MBq per sample		

Non-ionizing radiation

Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			

Chemical

Toxic	[chemical agent], [quantity]	$V_2O_5nH_2O$, V_2O_5, VO_2	
Harmful	[chemical agent], [quantity]	$V_2O_5nH_2O$, V_2O_5, VO_2	
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]	$V_2O_5nH_2O$, V_2O_5, VO_2	

Mechanical

Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		

Noise

Frequency	[frequency],[Hz]		
Intensity			

Physical

Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	SSP protocol		
Poor ergonomics	[location]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*