EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

Digital TDPAC with Rare Earth Isotope ^{169}Yb, ^{147}Gd, and ^{149}Gd in Yb and Gd Doped CeO_2 and ^{147}Gd in $GdBa_2Cu_3O_{7-\delta}$

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Abstract:
Digital PAC spectroscopy with ^{169}Yb/^{169}Tm, ^{147}Gd/^{147}Eu, and ^{149}Gd/^{149}Eu is used to investigate rare earth doped Ceria and a newer superconductor $GdBa_2Cu_3O_{7-\delta}$, which is only available yet as tiny single crystals. First principles theoretical calculations of hyperfine parameters will be performed with CRYSTAL code to support the understanding of the local structure.

Requested shifts: 4 shifts

1 Introduction

Perturbed Angular Correlation (PAC) is a technique currently used to study the local structure in materials. Two of the most commonly known and used isotopes for PAC are $^{111}In/^{111}Cd$ and $^{181}Hf/^{181}Ta$ probes, easily accessible for most laboratories. At ISOLDE a large number of exotic PAC isotopes can be produced to study materials choosing the probe according to the chemical environment. In a complex oxide this is clearly the only possibility to choose the site of the probe by selecting the appropriate isotope. Especially in doped materials, using PAC isotopes of the doping element provides the possibility to study the local structure around the dopant, particularly when this has a low concentration.

By developing a digital PAC setup we aim to simplify the measurements by reducing the calibration efforts and increase the analysis capabilities by recording all γ-events which allows one to reproduce and explore the PAC spectra at different energy windows and different channel time widths. Switching the isotopes does not need hardware re-adjustments for the recording procedure allowing viewer systematic errors and considerable freedom to optimize data analysis at a later stage. Two fully recording digital instruments exist now at ISOLDE. In the current experiment digital PAC will be used with exotic isotopes ^{169}Yb, ^{147}Gd, and ^{149}Gd in doped Ceria and $GdBa_2Cu_3O_{7-\delta}$. We also aim to test rarely used PAC isotopes with multiple complex cascades.

It is known that conductivity of Ceria can be improved by doping with rare earth elements. Samarium and Gadolinium provide the best conductivity improvements compared to other rare earth elements. Also the doping concentration follows a non-linear dependence. Measurements with two very different behaving dopants, together with theoretical calculations, shall investigate the local structure and give a better insight of the doping mechanism to the conductivity of Ceria. If proved with this letter of intent that PAC provides sufficient information for the Ceria system with the selected isotopes, concentration dependent measurements will follow in a later proposal.

The superconductor $GdBa_2Cu_2O_{7-\delta}$ (GBCO) has superior performing properties than $YBa_2Cu_2O_{7-\delta}$ (YBCO). However, only small whiskers-like single crystals have been grown yet. PAC is an excellent method for investigating especially very small samples. Using ^{147}Gd, PAC measurements can provide important information about the Electric Field Gradient (EFG) at the Gd site in GBCO to compare with theoretical calculations, which are currently in work with the CRYSTAL code. If successful, in a later proposal an experiment with ^{147}Gd, ^{133}Ba and ^{61}Cu will follow, looking for macroscopic phenomena at phase transitions and as function of doping.

2 CeO_2 Doped with Yb and Gd

Ceria is a ceramic used in a variety of applications. One of the challenging applications is solid oxide fuel cells (SOFCs), where Gadolinium or Samarium doped Ceria have reached high oxygen ion conductivity at ambient temperatures between 500-800°C. Depending on the dopant and its concentration, the conductivity can be varied. Comparing the rare earth elements as dopant, the optimum is found for Samarium and Gadolinium which appears to be related to their radii. However, the doping concentration follows a non-linear dependence. These effects are well known but yet not well understood in the local structure. Choosing Gadolinium and Ytterbium from the rare earths, which have very different doping effects, PAC may provide some information about the local structure and dopant coordination, respectively. So far PAC studies have mostly been performed using the $^{111}In/^{111}Cd$ or $^{181}Hf/^{111}Ta$ probe. However, in this study the parent isotopes ^{169}Yb and ^{147}Gd shall be used to probe the doping environment in Ceria directly. This measurement will be performed as a function of temperature. The aim is to use the EFG information obtained from the PAC data to compare with theoretical calculations of hyperfine parameters to the model the local dopant structure.

3 Superconductor $GdBa_2Cu_3O_{7-\delta}$

$YBa_2Cu_2O_{7-\delta}$ (YBCO) is among the most widely studied high-Tc superconductors, both from the point of view of basic science and from the one of applications. However, it has been recently found that the critical current density of the homologous compound $GdBa_2Cu_2O_{7-\delta}$ (GBCO) exhibits better performances. So far, there have been only a few attempts to grow whisker-like single crystals of such material , which has proven to be a difficult task. A breakthrough in the field has been achieved by our group by showing that the intentional addition of Al_2O_3 to the starting compounds greatly improves the yield of the growth process and the sizes of the resulting crystals. Moreover, there have been some hints that Al ions are partly incorporated in the crystal structure and may tune the doping level of the system. However, a clear determination of the substitution site and of the doping mechanism of Al-doped GBCO is still missing. Gd-based PAC could provide such information in a complementary way with XRD cell refinement.

4 *Ab initio* Prediction of Nuclear Response with the CRYSTAL Code

CRYSTAL is an *ab initio* quantum mechanical code mainly developed by the Theoretical Chemistry Group at the University of Torino, Italy, and distributed over almost 300 research groups all over the world [1].
It makes use of localized, all-electron, Gaussian-type basis sets to describe the electron wavefunction, and implements a wide variety of Hamiltonians, including Hartree-Fock, pure DFT (both LDA and GGA), hybrid HF-DFT (such as B3LYP and PBE0). Thanks to full exploitation of symmetry, both point- and translational, CRYSTAL permits to investigate systems with different dimensionality (from 3D to 0D), and with a large number of atoms in the unit cell (up to hundreds). The present public version of the code implements the calculation of quantities such as total energy, optimized geometry, vibrational frequencies, optical tensor, electronic bands, Density of states, Compton profiles.
A lot of features are currently under development, including the calculation of coupling constants related to nuclear response, which allow to interpret Mossbauer spectroscopies and related techniques. Within this framework, we plan to test this feature over a range

of case studies, including rare earth-containing compounds such as YBCO and GBCO.

5 Experimental

$GdBa_2Cu_3O_{7-\delta}$ single crystals have been grown yet only to a size of 500 μm. Implanting into such a small crystal requires sweeping the beam what is easily achieved at the GLM beam line at the SSP chamber. In order to improve the total efficiency of beam time, implantation in doped Ceria and $GdBa_2Cu_3O_{7-\delta}$ can be done simultaneously for the Gd beam. All can be mounted on standard sample holders at GLM. Beam energy can rate from 10 to 50 keV.
Measurements will be taken off-line in the solid state laboratory building 115 using the digital PAC spectrometer equipped with a high temperature furnace.
The measuring results will be used in theoretical calculations to develop models for the local structure of doped Ceria and $GdBa_2Cu_3O_{7-\delta}$ with the CRYSTAL code.

6 Isotopes ^{169}Yb, ^{147}Gd, and ^{149}Gd with Digital PAC

The current three rare earth isotopes have complex decay schemes which are a challenge for PAC spectroscopy. Fully recording digital PAC however provides the possibility to store all recorded γ-events on disc and research the saved data for coincidences with different energy and time window settings. Especially in complex cascades the population or depopulation of the PAC sensitive level can follow different branches. In conventional PAC the coincidences of alternative branches will be lost, but can be used in digital PAC to improve the efficiency particularly when using high energy resolving $LaBr_3$ detectors. Also in rare cases, some isotopes have more than one PAC sensitive level. Figure 1 shows the ^{169}Yb/^{169}Tm decay scheme: The 660 ns $\frac{7}{2}^{+}$ level depopulates on three important different routes with 10%, 22%, and 36% probability. However the populating decay has a low γ-ray with 63 keV which requires the use of $LaBr_3$ scintillator crystals. The second PAC sensitive level with a decay time of 52.6 ns is populated 2.6% by a 94 keV γ-emission and depopulated by 1.7% at 261 keV and 44% at 63 keV. The recorded data can be used to test, if the branch via the 52.6 ns PAC sensitive level can be separated.
For the Gd probe two different isotopes will be tested. The decay scheme of ^{147}Eu has a 765 ns $\frac{11}{2}^{-}$ PAC sensitive level, see Figure 2. The depopulation with 4.7% at 625 keV and 34% at 396 keV. The population is with 20% at 929 keV and 17% at 370 keV. It is to be tested to separate both narrow energies well or exclude them.
Figure 3 shows another challenging decay of ^{149}Eu with a for PAC very long sensitive level of 2.45 μs. Population and depopulation of the PAC sensitive level has branches of 28% and 24% at 298 keV and 347 keV, which are better to be separated.
Both PAC isotopes decay to other PAC isotopes on Sm. ^{147}Eu has a half life of 24 days and ^{149}Eu of 93 days. As the Gd isotopes have a shorter half life, after about four half lives, the probes will modify mainly to Eu probes and will become test samples for Eu/Sm PAC.
Figure 4 shows the decay scheme of ^{147}Sm, which has a PAC sensitive level with a $\frac{3}{2}^{-}$ state of 1.24 ns with good to separate energy levels while Figure 5 shows the decay scheme

of ^{149}Sm, which has a usable PAC sensitive $\frac{5}{2}^{-}$ level of 7.1 ns, however the challenge of a 22 keV decay. The samples are sufficient long lived to remain for testing purposes.

7 Perspectives

The following measurements using digital PAC spectroscopy with rare earth isotopes ^{169}Yb, ^{147}Gd, and ^{149}Gd will test the usability of these isotopes for exploring questions of doped Ceria and the newer superconductor GBCO. Rare earth doped Ceria is an important material for solid oxides fuel cells. PAC may contribute to the understanding of the relation between dopant, dopant concentration, and temperature by investigation of the local structure, especially the coordination of the dopant.
The superconductor GBCO has yet been grown as small single crystals of only about 500 μm. PAC is an excellent technique to also investigate very small samples. Theoretical calculations for GBCO with the CRYSTAL code by the group in Torino, also developer of CRYSTAL, are in progress to involve a better understanding of the different performing properties compared to YBCO. By measuring the EFG and magnetic field at a microscopic scale, PAC can contribute with important physical data to be compared first principles simulations, which model the systems under study.

Summary of requested shifts: 4 with a standard Ta-W unit.

References

[1] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, Ph. D'Arco, M. Llunell: CRYSTAL 2009 User's Manual **2009**, University of Torino, Torino

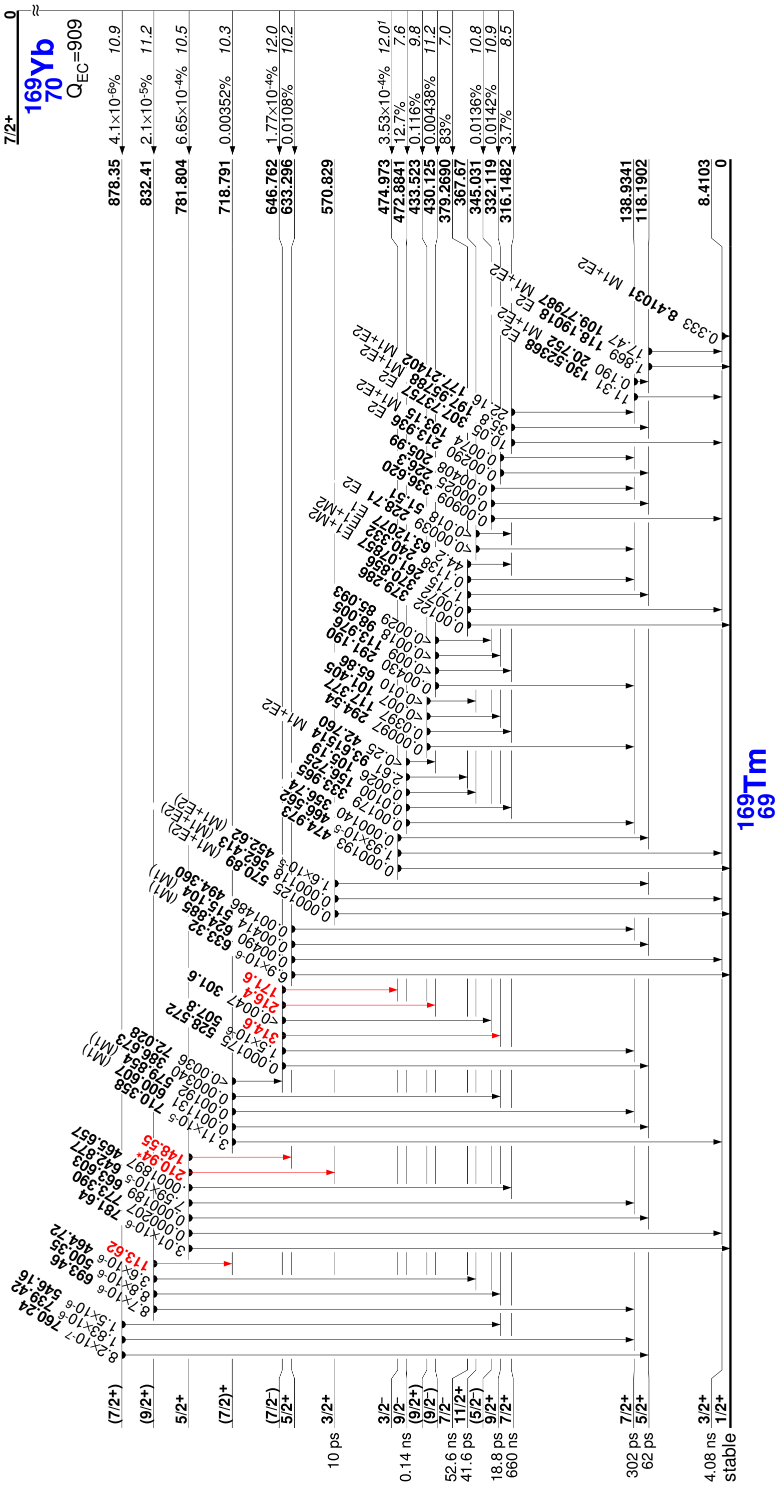

Figure 1: Decay Scheme of ^{169}Tm

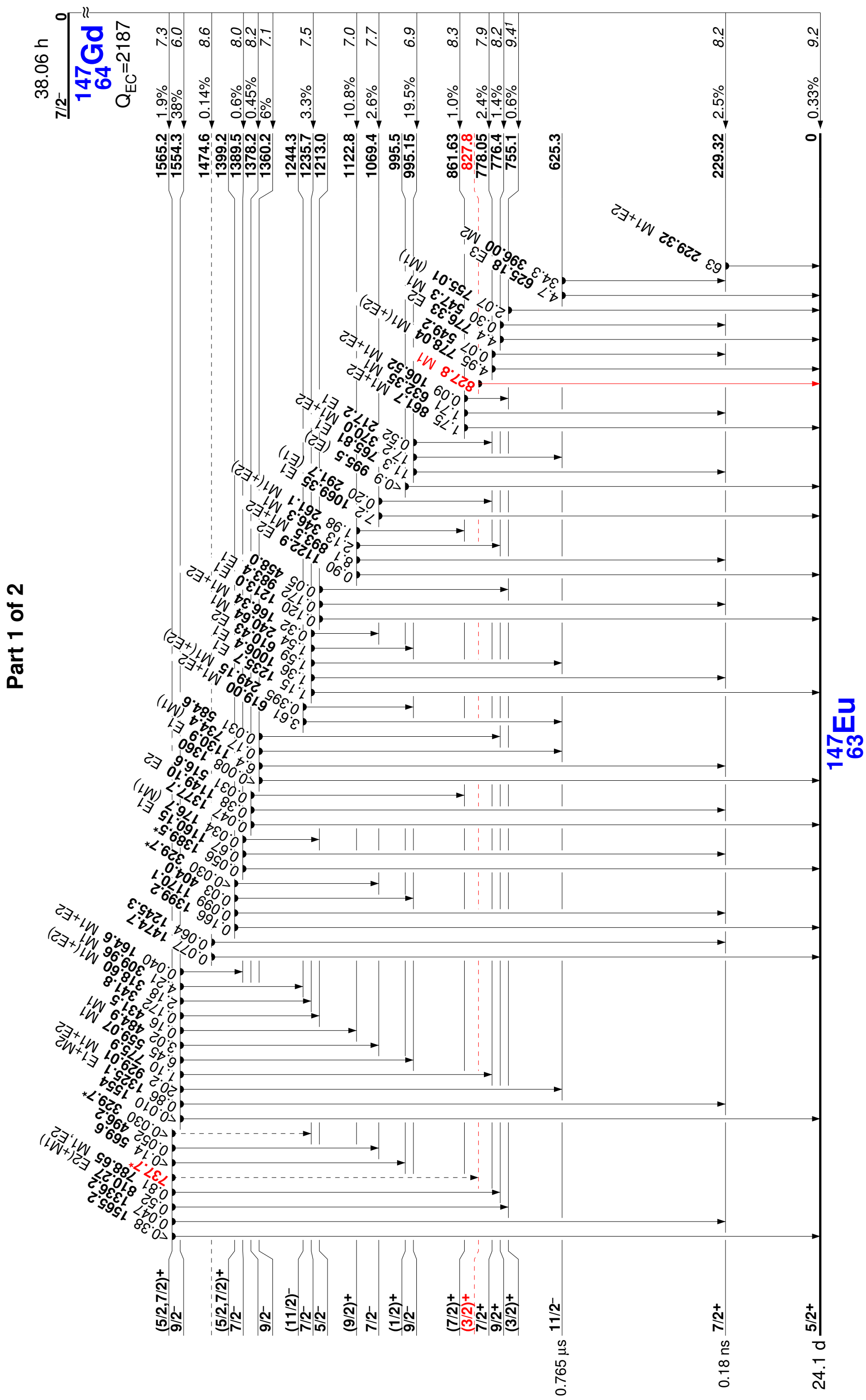

Figure 2: Decay Scheme of ^{147}Eu

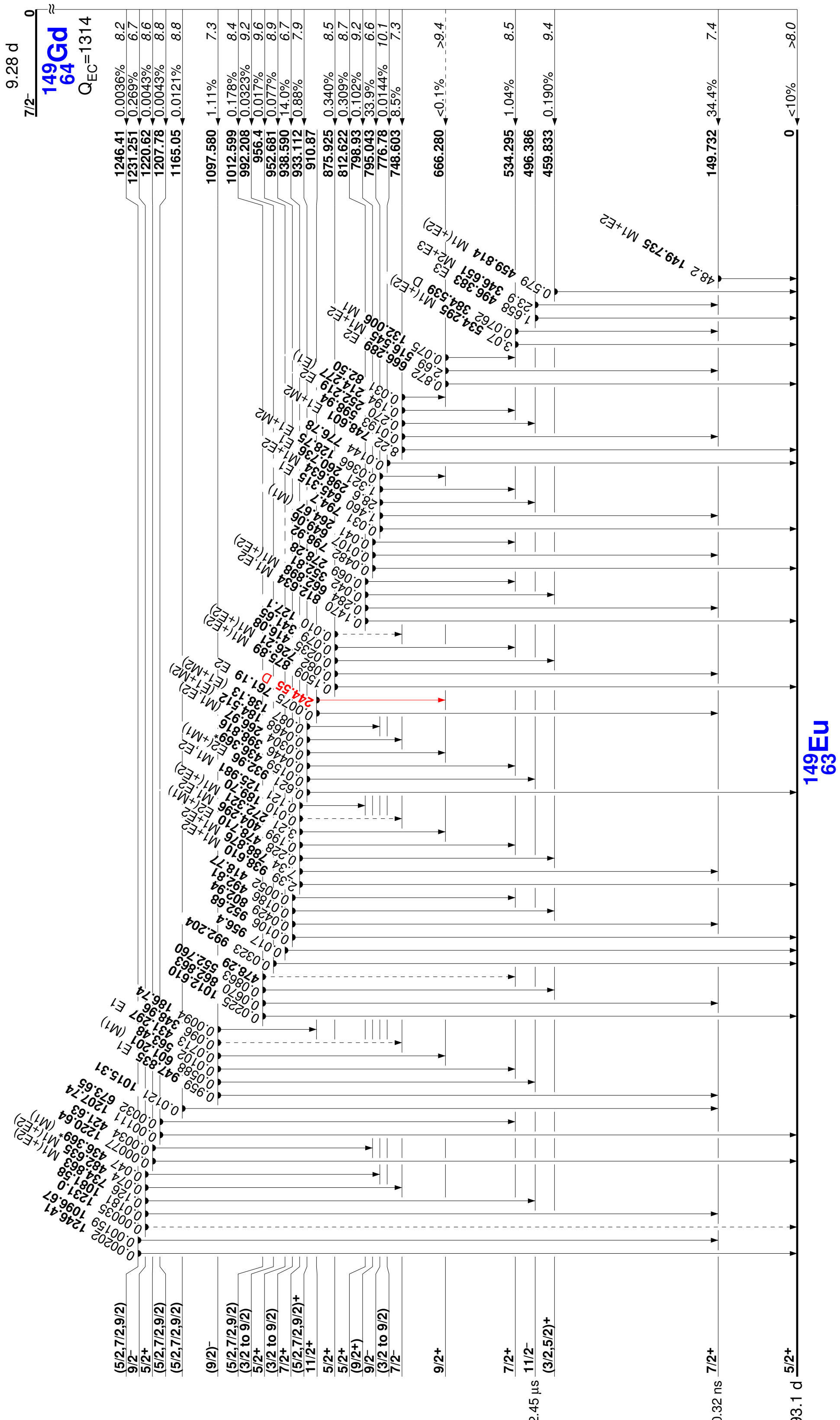

Figure 3: Decay Scheme of ^{149}Eu

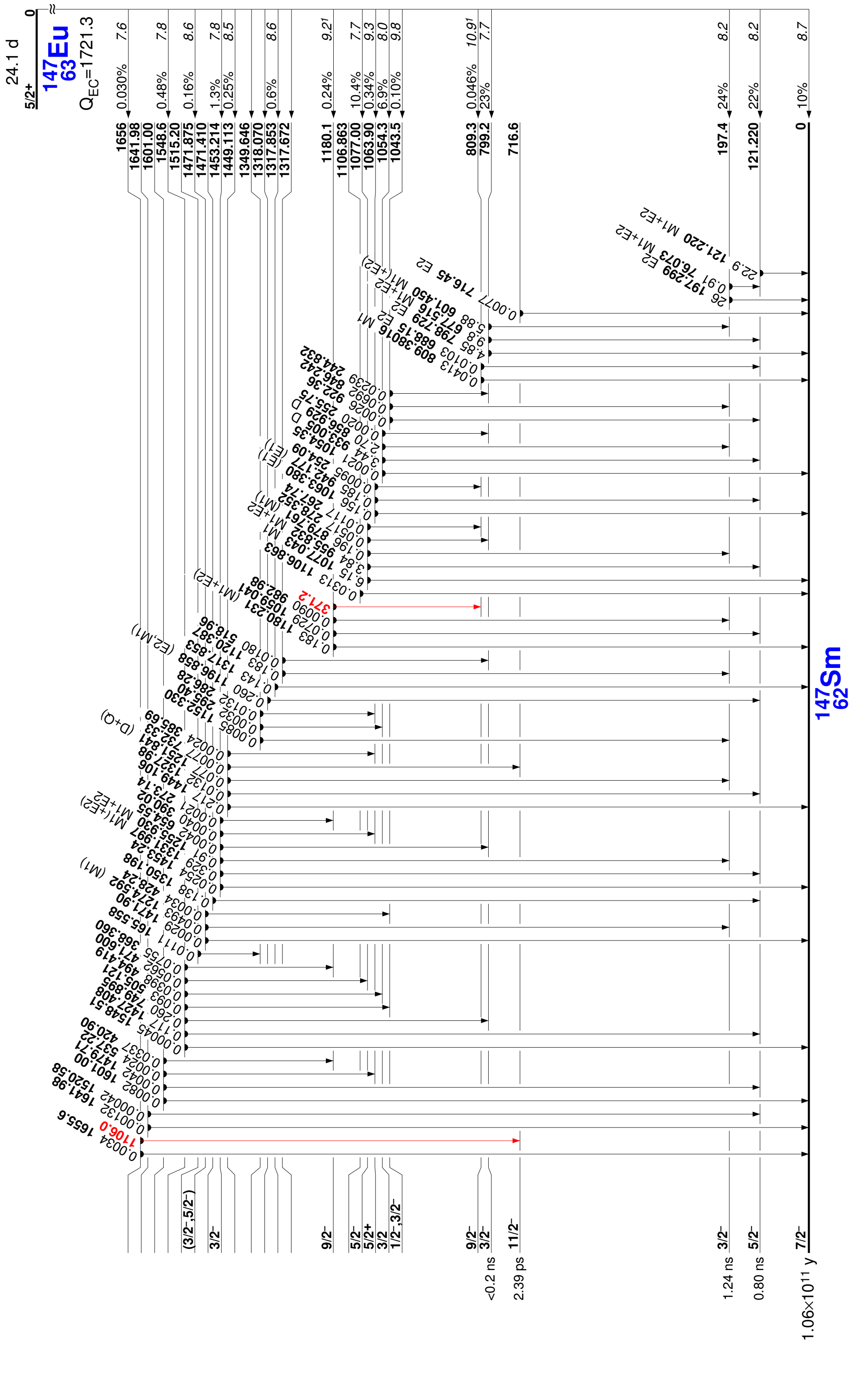

Figure 4: Decay Scheme of ^{147}Sm

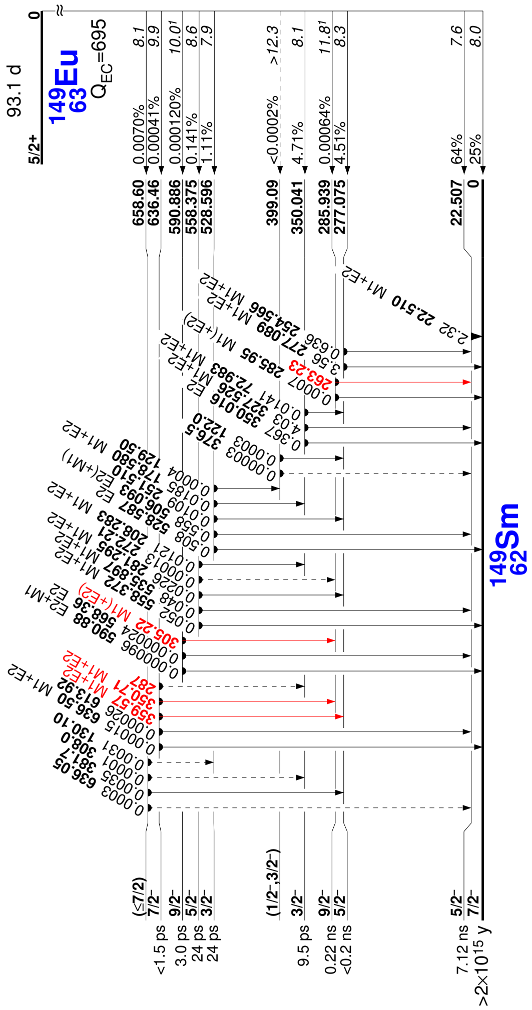

Figure 5: Decay Scheme of ^{149}Sm

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	Availability	Design and manufacturing
SSP-GLM , **SSP-GHM**	☒ Existing	☒ To be used without any modification
[Part 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 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
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT (if using fixed installation:) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards	[Part 1 of experiment/ equipment]	[Part 2 of experiment/ equipment]	[Part 3 of experiment/ equipment]
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]		
Vacuum			
Temperature	[temperature] [K]		
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)			
Beam intensity			
Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☒		
• Sealed source	☐ [ISO standard]		
• Isotope	^{147}Gd	^{149}Gd	^{169}Yb
• Number of atoms	$3{\cdot}10^{11}$	$1.74{\cdot}10^{12}$	$5.99{\cdot}10^{12}$
• Activity	1.52 MBq	1.5 MBq	1.5 MBq
Use of activated material:			
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300 MHz)			
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful	[chem. agent], [quant.]		
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chem. agent], [quant.]		
Corrosive	[chem. agent], [quant.]		
Irritant	[chem. agent], [quant.]		
Flammable	[chem. agent], [quant.]		
Oxidizing	[chem. agent], [quant.]		
Explosiveness	[chem. agent], [quant.]		
Asphyxiant	[chem. agent], [quant.]		

Dangerous for the environment	[chem. agent], [quant.]		
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	[location]		
Poor ergonomics	[location]		

Hazard identification:

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]