EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

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

MULTIPAC-Setup for Perturbed Angular Correlation Experiments in Multiferroic (and Magnetic) Materials: proof-of-concept

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Abstract

We propose three different time-differential perturbed angular correlation measurements in selected systems in order to test the MULTIPAC setup. Firstly, the measurement of a precision value of the magnetic dipole moment of the excited state of ^{111}Cd (5/2+) will be carried out. We also propose the measurement of the Knight shift for Cd in Pd as a function of temperature with much improved precision relative to an earlier experiment. Finally, the third experiment will be performed to test the feasibility of the MULTIPAC innovative idea, thus, by measuring a multiferroic system, $BiFeO_3$, with both probes ^{111}In and ^{111m}Cd.

Requested protons: 9 shifts of protons on target (split into at least 4 runs over 2 years)
Experimental Area: GLM area, ISOLDE hall or offline laboratories

Introduction to MULTIPAC

The MULTIPAC setup [1] consists of a unique cryogenic magnetic system that simultaneously allows to measure magnetic as well as ferroelectric properties by means of time-differential perturbed angular correlation (TDPAC) [2-4]. The cryogenic system includes the digital TDPAC equipment and software [5-6] with new Acqiris digitizers, $LaBr_3$ scintilation crystals and Multi-Pixel Photon Counter (MPPC). Preliminary tests review that the energy resolution of the system can achieve 3.30(2)% at 661.7 keV with FWHM 21.9(1) keV, while the time resolution can be slightly greater than 219.8(26) ps for ^{60}Co.

MULTIPAC setup being installed at ISOLDE in November 2022. Photo by Nicole Lima.

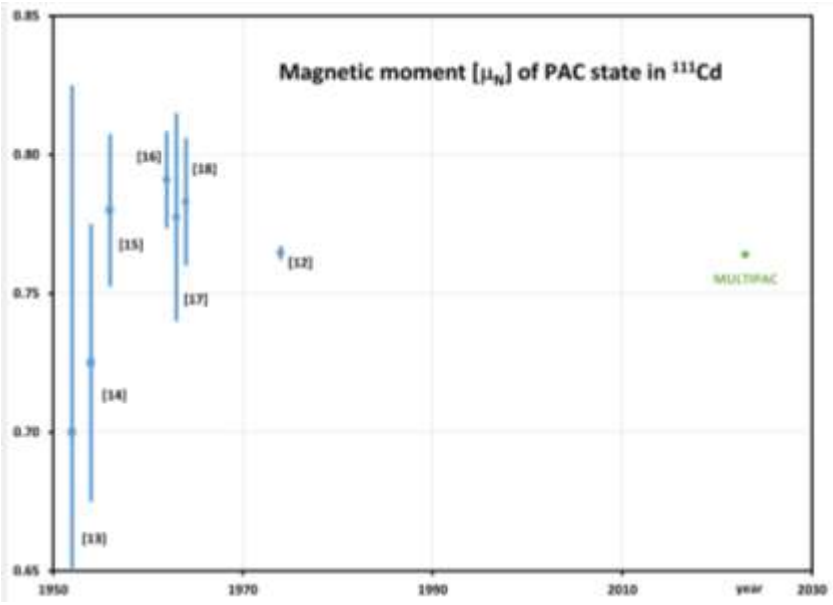
The first idea was to use this device to measure multiferroic materials [7], which present combined magnetic dipole and electric quadrupole interactions [8]. The device allows TDPAC measurements to be performed under applied magnetic fields up to 10 T and as a function of temperature. Alongside high voltage wiring to the sample will permit to apply electric fields and tune the multiferroic [7] structures electrically. Local structures on the scale of the unit cell and doping of intrinsic multiferroics will subsequently be accessible.

Due to the very low concentration of the nuclear probes using in a TDPAC experiment, the tracer ions represent only a weak dopant and do not influence the overall properties of the solid. A great advantage of TDPAC in comparison to other hyperfine techniques is that it can be performed in a wide temperature range, even at temperatures up to and beyond the melting point of materials without affecting the quality of the TDPAC signal. The technique has a high sensitivity to the local magnetic order, local crystallographic variations, and charge distributions around the lattice site where the probe nuclei are placed. Consequently, these probes can be used to detect the local magnetism [9], local symmetry changes as well as dynamic processes in a certain frequency window due to charge movement or spin fluctuations [10].

The MULTIPAC system was developed and assembled by Cryogenics and by the University Duisburg-Essen via the Federal Ministry of Education and Research (BMBF). It was presented for the first time during the 86th ISCC Meeting in 2019 and a letter of intent was then submitted to the 63rd meeting of the INTC [1]. Currently, the system is being installed and tested at ISOLDE by a team of postdocs and students. On the long run, the setup will be available to any group at ISOLDE working on magnetic materials and/or on the determination of nuclear magnetic dipole moments via TDPAC. It will thus serve many groups at very long term.

First physics case: Precise μ_N measurement for $5/2^+$, 247 keV state in ^{111}Cd

A precise value for the nuclear magnetic dipole moment (μ_N) for this state is necessary to normalize the multitude of existing PAC experiments. The currently accepted value, μ_N=−0.7656(25) [11], is based on a measurement performed some 50 years ago [12], using the then available experimental techniques. The impressive progress in precision achieved at this time is demonstrated in Figure 2 [13-18]. The MULTIPAC setup will undoubtedly allow to reduce the experimental error even further by at least a factor of three (possibly even ten), due to the higher magnetic field with better homogeneity, the precise digital timing, and the better detector energy resolution now available.



In order to eliminate any doubts about decay aftereffects in such a measurement and to demonstrate the advanced potential of the MULTIPAC setup, we propose to also make a precision measurement in liquid Cd, where the corresponding Knight shift is precisely known from NMR [19], using sources of ^{111m}Cd produced at ISOLDE.

Figure 2: Progress in accuracy of ^{111}Cd($5/2^+$) g-factor [13-18].

Obviously, our new facility will allow to obtain more precise magnetic moments for virtually all the excited nuclear states used in PAC experiments with long-lived sources ($t_{1/2}$ > 10 min). Representative cases would be ^{204}Pb(4^+), ^{197}Hg($5/2^-$), ^{181}Ta($5/2^+$), ^{77}Se($5/2^-$) and many more, but also states previously unstudied by PAC like ^{187}Ir($11/2^-$), ^{198}Au(5^+) or ^{118}Sn(5^-).

Second physics case: Measurement of the Knight shift for Cd in Pd as a function of temperature

The accurate value expected for the magnetic moment of the ^{111}Cd PAC state should allow to obtain much more precise data for the shift of the applied magnetic field observed at a nucleus in a condensed matter environment. The two effects that are present, the chemical shift in nonmagnetic solids and the Knight shift in condensed metallic systems, however, can be measured with even higher precision using the conventional NMR technique, that is particularly suitable for Cd. The chemical shifts measured for many compounds can actually be explained with high accuracy by modern theoretical methods [20]. In the theoretical understanding of the Knight shift in simple metals great progress in quantitative explanation have been made as well [21], though the observed solid-liquid changes for Cd [19] have

apparently not been accounted for. There is one system, however, the exchange-enhanced metal Pd, where even the most recent calculations [22] have completely failed to account for the very large Knight shifts measured for this material [23] a long time ago. In this context it appears reasonable to remeasure the early limited experimental data of the temperature dependent Cd Knight shift in this metal [12] with much improved precision.

For the proposed experiment samples of ^{111}In implanted into pure Pd at ISOLDE, after proper annealing, will be measured in the MULTIPAC setup at temperatures from 10 K. The old data, coming primarily from PAD experiments, predict a region of Knight shifts between -1.3 and -0.3 %, much larger than for metals without exchange-enhanced susceptibility. In addition, the unexplained large negative offset would need confirmation, particularly when compared with the equivalent data for Ag as impurity in Pd [24,25].

Third physics case: $BiFeO_3$ (or BFO)

For $BiFeO_3$, our work horse material so far [26-28], we found strong changes in the ionic order arising at the Néel temperature, so the coupling of magnetic and ionic order arises instantly. BFO is classified as type I multiferroics in which the hybridization between the two 6s electrons in Bi^{3+} with surrounding oxygen ions leads to a large displacement of the Bi^{3+} relative to the oxygen octahedral along [111] direction, producing spontaneous ferroelectric polarization [29,30]. Our TDPAC measurements were carried out at a wide range of temperatures up to 850°C, after the implantation of the ^{181}Hf [27], ^{111}In [28] and ^{111m}Cd [26]. The experimental results reflected the obedience to the Landau theory and the Brillouin-Weiss equation of local electric polarization and magnetization, respectively. Particularly, a huge coupling between local electric and magnetic fields has been investigated in anti-ferromagnetic order (see Figure B1). With the support of ab-initio DFT simulations, we could discuss the site-assignment for the probe nucleus, and concluded that under our experimental conditions, the ^{111m}Cd is located at the Bi-atom at the A-site, ^{181}Hf and ^{111}In probes substitute the Fe-atom at the B-site.

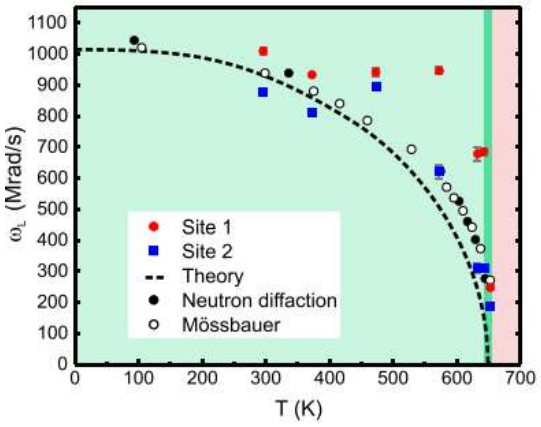


Figure B1. The magnetic Larmor frequency ω_L as a function of temperature [27]. TDPAC data are represented by site 1 and site 2.

In the figure B1, the antiferromagnetic order parameter is represented via the Larmor frequency. The Brillouin function curve characterizes the change of macroscopic and local magnetization at the Fe-site, as monitored by neutron diffraction data [31], Mössbauer spectroscopy [32] and TDPAC (for the site 2). On the other hand, site 1 is affected by the electric polarization of the lattice itself. Upon application of an external magnetic field (MULTIPAC), we expect to obtain a deeper knowledge of the magnetic behaviour at the probe-site and the general goal is to understand how multiferroic ordering will be reflected in the TDPAC spectra.

We aim to investigate how doping (among others by the probe isotope itself and its same chemical species or other species added intentionally) will alter the magnetic and electric structures of the materials as well as the defect structures.The magnetoelectric coupling coefficient, for certain probes, could be extremely large and be at least an order of magnitude larger than known values.

Future work: an infinite number of ideas

After demonstrating the functionality of our facility, we intend to submit a couple of proposals to the INTC. For instance, it is crucial that the involved students complete the preliminary studies proposed in this letter. Furthermore, within this big collaborative team, we expect to start the investigation of several materials and characterize the nuclear properties (such as magnetic dipole moment) of several isotopes with high accuracy. Concrete examples of materials to be investigated in the future are $CuInP_2Se_6$ [33], $CuCrP_2S_6$ [34], $Cu_xFe_{1-x}P_2S_6$ [35], $RMnO_3$ with R being a rare-earth element [36] such as Ho [37] or Tb [38], $Ca_3Mn_2O_7$ [39] and $Ca_{3-x}A_xMn_2O_7$ with A being a rare-earth cation [40].

Summary of requested protons

Beam	Min. intensity	Target material	Ion Source	Shifts	System
^{111}In	1.10^8	UC_x	Hot plasma	1	Ice
				2	Pd
				1	$BiFeO_3$
^{111m}Cd	1.10^8	Molten Sn	Vadis MK5	5	$BiFeO_3$

In this summary, we consider that the beam time can be shared with other active experiments.

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

Please describe here below the main parts of your experimental set-up:

Part of the experiment	Design and manufacturing
SSP implantation chamber and ice implantation chamber located at the GLM area	☒ To be used without any modification ☐ To be modified
Annealing furnaces located at 508/R-004	☒ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
MULTIPAC system located temporarily at b275. It includes a cryogenic system ordered from the company Cryogenics, London.	☒ Standard equipment supplied by a manufacturer ☒ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

Additional hazard from flexible or transported equipment to the CERN site:

Domain	Hazards/Hazardous Activities		Description
Mechanical Safety	Pressure	☒	Bottles of Helium compressed gas for compressors. Additional bottles of compressed gases for annealing such as Argon and Nitrogen may be required.
	Vacuum	☒	1.10^{-6} mbar
	Machine tools	☐	
	Mechanical energy (moving parts)	☐	
	Hot/Cold surfaces	☒	Quartz tube used for annealing at 508/R-004

Cryogenic Safety	Cryogenic fluid	☐	[fluid] [m^3]
Electrical Safety	Electrical equipment and installations	☒	Compressors and water system 16 A
	High Voltage equipment	☒	Up to 2 kV for TDPAC detectors
Chemical Safety	CMR (carcinogens, mutagens and toxic to reproduction)	☐	[fluid], [quantity]
	Toxic/Irritant	☐	[fluid], [quantity]
	Corrosive	☐	[fluid], [quantity]
	Oxidizing	☐	[fluid], [quantity]
	Flammable/Potentially explosive atmospheres	☒	He bottle with gas under pressure; may explode if heated. May displace oxygen and cause rapid suffocation.
	Dangerous for the environment	☐	[fluid], [quantity]
Non-ionizing radiation Safety	Laser	☐	[laser], [class]
	UV light	☐	
	Magnetic field	☒	Up to 10 T inside MULTIPAC magnet.
Workplace	Excessive noise	☐	
	Working outside normal working hours	☒	Yes, if beam time is scheduled 24 h per day.
	Working at height (climbing platforms, etc.)	☐	
	Outdoor activities	☐	
Fire Safety	Ignition sources	☐	
	Combustible Materials	☐	
	Hot Work (e.g. welding, grinding)	☐	
Other hazards	Ionizing radiation	☒	Measurements will be performed with ^{111}In or ^{111m}Cd, therefore a zone properly classified should be available for the equipment during the experiments.