EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

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

Testing ultra-low energy in new ion implantation chamber ASCII

11th of January 2023

K. van Stiphout[1], H. Hofsäss[1], J. H.-Schell[2,3], D. C. Lupascu[3], T. T. Dang[3], I. C. J. Yap[3], M. Escobar[3], P. Schaaf[4], K. Johnston[2], A. W. Carbonari[5], B. S. Correa[5], N. P. Lima[5], A. P. dos S. Souza[5], A. A. M. Filho[5], L. Scalise[5], A. M. Gerami[2,6], K. Glukhov[7], Y. Vysochanskii[7], O. Sipr[8], I. Efe[9], M. Trassin[9]

[1] II. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
[2] European Organization for Nuclear Research (CERN), CH-1211 Geneva, Switzerland
[3] Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany
[4] Department of Materials for Electronics, Institute of Materials Science and Engineering, TU Ilmenau, Gustav-Kirchhoff-Strasse 5, 98693 Ilmenau, Germany
[5] Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP, São Paulo 05508-000, Brazil
[6] School of Particles and Accelerators, Institute for Research in Fundamental, Sciences (IPM), Tehran P.O. Box 19395-5531, Iran
[7] Institute of Solid State Physics and Chemistry, Uzhgorod University, Uzhgorod, Ukraine
[8] Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, CZ-182 21 Praha 8, Czechia
[9] Department of Materials, ETH Zürich, Switzerland

Spokesperson(s): K. van Stiphout (koenkarlfrans.stiphout@uni-goettingen.de), Juliana H.-Schell (juliana.schell@cern.ch)
Technical coordinator: Juliana H-Schell (juliana.schell@cern.ch)

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Abstract

In this letter of intent, we propose a campaign of tests, to finalize the installation and streamline the operation of the brand-new setup *ASPIC's Ion Implantation* (ASCII) chamber in the ISOLDE experimental hall. This setup introduces the possibility of decelerating radioactive ions during implantation, including the capability of ultra-low energy (ULE) ion implantation (< 100 eV). By modifying the ion implantation energy, the ASCII enables the experimenter to choose the depth at which the probe isotopes come to rest, and consequently, granting them the choice of which part of the nanostructure is probed. This opens up many new and hitherto unavailable ways of conducting state-of-the-art solid-state research.

Requested protons: 8 shifts of protons on target, (split into 4 runs over 2 years)
Experimental Area: ISOLDE hall or offline laboratories

Introduction

The Apparatus for Surface Physics and Interfaces at CERN (ASPIC) was an experimental ultra-high vacuum (UHV, < 10^{-8} mbar) setup installed in the ISOLDE experimental hall for several decades since the 1980's [Ber2000]. It was dedicated to the study of (amongst other things) metallic surfaces, magnetic behavior of thin films and interface evolution, using radioactive isotopes and a myriad of surface and thin film preparation and modification techniques. Due to lack of dedicated personnel and financial support however, the use of the setup was discontinued. Thanks to the recent funding by the German *Bundesministerium für Bildung und Forschung* (BMBF) agency (grant 05K19 MG1) [Hof2020], the ASPIC has been refurbished and upgraded by the addition of a brand-new UHV chamber called the *ASPIC's Ion Implantation* chamber (ASCII) [Sti2022]. This new chamber provides users the ability to precisely decelerate radioactive isotopes, including the ability to perform ultra-low energy (ULE) ion implantations, opening up many new possibilities for solid-state research. The (re-)installation of these two chambers in the ISOLDE experimental hall is planned for Feb – April 2023 via BMBF grant 05K22PGA.

This letter of intent proposes a series of tests, conducted with the new ASCII setup. These tests, described below, have the following three aims: deliver a proof-of-concept of the implantation technique; show the reproducibility of published results; and break new scientific ground by applying the ULE ion implantation technique to highly relevant scientific systems, gaining previously unavailable information about their atomically local structure.

Perturbed angular correlation (TDPAC) spectroscopy, (ultra-low energy, ULE) ion deceleration and the new ASCII chamber

The solid-state physics group of ISOLDE [Joh2017] has long-standing experience with hyperfine techniques, such as time-differential perturbed angular correlation (TDPAC) spectroscopy [Fra1965] [Sch2017]. In this experimental technique, particular radioactive isotopes with well-known nuclear quadrupole moments and a short-lived, intermediate state in its decay branch (such as ^{111}In, ^{111m}Cd or ^{204}Pb) are introduced into a crystal structure. The radiation emitted by nuclei decaying via this branch (typically consisting of two gamma photons) is recorded along perpendicular or parallel angles. By examining the temporal delay between the detection of the first and second transition to and from the intermediate state along these angles, the influence (perturbation) of the atomic environment on the probe nuclei via hyperfine interactions can be inferred. In this way, the electric field gradient and magnetic field at the location of the probe nuclei is measured, providing highly accurate and unique information on the atomic structure of the nanostructures. Use of this technique and others, such as emission Mössbauer spectroscopy [Weyer2000], within the ISOLDE collaboration has led to new insights into phase transitions, magnetic properties or defect formation; in many, highly relevant systems, such as multiferroics [Mar2020][Sch2022][Dan2022].

Introducing the radioactive probes into the crystal structure is typically achieved using ion implantation at the general purpose separator (GPS), using kinetic energies of 30 – 60 keV. At these velocities, the ions come to rest many monolayers below the surface, up to several dozens of nanometer. While successfully used in research on bulk crystals, the ion energies available are too high for scientific systems that require more precise depth control of the probe nuclei, such as thin (< 10 nm) film systems. In the most extreme case, such as for 2D materials as graphene [Fen2021] or MoS_2 monolayers [Gon2014], the ions need to come to rest within the first nanometers. By introducing a new implantation chamber at ISOLDE,

these limitations can be overcome: a wider range of ion implantation energies (60 keV – 0.02 keV) allows precise control over the final location of the probe nuclei, vastly expanding the collaboration's ability to study nanostructures using hyperfine techniques, such as TDPAC spectroscopy. Moreover, the ability to decrease the ions kinetic energy down to only a few dozen eV is essential for experiments involving surfaces and atomically thin materials.
The new ASCII setup will serve as tool to accomplish ion implantations at different energies. The setup is based on the same design as the well-established *ADONIS* setup at the university of Göttingen, an ion implantation setup that has successfully applied ultra-low energy ion implantation (< 100 eV) of stable isotopes into many solid-state systems, resulting in several scientific achievements (Fig. 1) and publications in high-ranking journals [Lin2021][Vil2021][Lin2022]. In this design, the sample is centrally placed inside a cylindrical deceleration unit, consisting of a number of electrostatic lenses. By raising the sample to a well-regulated voltage, relative to the initial acceleration voltage, the impinging ions are decelerated to the appropriate kinetic energy. This system replaces the old, evaporation-based system of controlling the position of the radioactive probes used in the ASPIC, which was slow, cumbersome and, most importantly, could only be applied to a limited number of scientific cases. Indeed, it relied on the rapid (re)growth of the desired nanostructure in the ASPIC, excluding the study of systems that are difficult to grow, such as graphene or compound multiferroics with many different elements. By using ion implantation, these problems are circumvented: samples can be grown beforehand, and probe nuclei can be introduced without any additional layer growth.

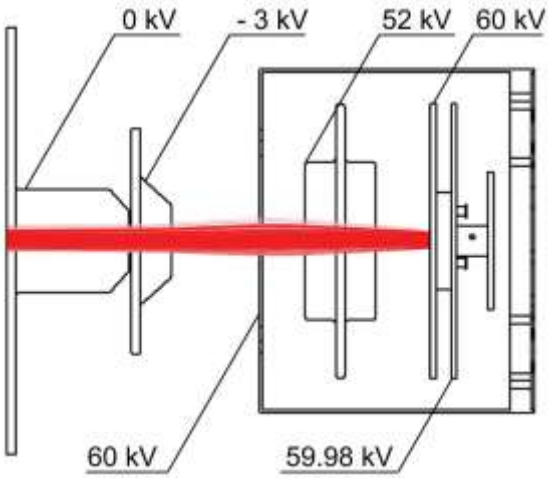

Fig.1: Schematic overview of the electrostatic lenses used in the ASCII, decelerating the ions to a certain kinetic energy upon implantation. In this specific case, 60 keV ^{111m}Cd ions (red lines) are focused onto the samples, impinging with an energy of 20 eV (= 60 kV – 59.98 kV)

Although the ASCII chamber was built with the experience and know-how of the successful ADNOIS setup, a series of tests to demonstrate its operation, troubleshoot initial problems and highlight its scientific potential must be conducted. To this end, we propose a series of experiments, divided into three aims: demonstrating the ASCII's ability to decelerate the ions selectively, down to 20 eV; reproduce old scientific achievements achieved in the old ASPIC system from the 1990's, in an easier and more time-efficient manner; conduct new research on highly relevant scientific systems.

Proof-of-principle experiments

The ability of the ASCII chamber to modify the depth at which the radioactive ions come to rest will be demonstrated by implanting such ions at various energies into a nanostructure that has multiple, highly distinct atomic environments within the first 10 nm of the surface. These different atomic environments the decelerated ions come to rest in will be reflected in the recorded TDPAC spectra of the samples. Such samples can be produced easily using the refurbished ASPIC chamber, which will be installed at the same time as the ASCII. One such example is shown in Fig. 2: a pure, 5 nm Ni layer is deposited onto a TiO_2 substrate in the ASPIC chamber, and subsequently brought into air, causing a small NiO layer of about 1.5 nm to grow at the surface of the Ni layer [Lam1996].

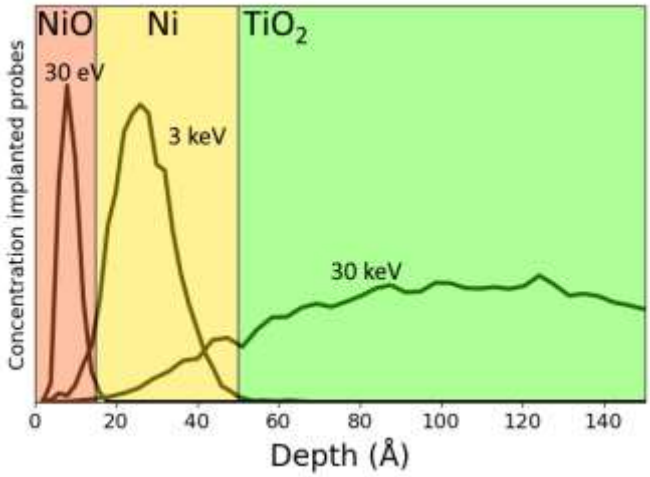

Fig. 2: By implanting ions at different implantation energies, the radioactive probe nuclei come to rest in vastly different atomic environments, with very different magnetic ordering and electric field gradients, shown here for arbitrary fluences of ^{111m}Cd ions, using SRIM [Bie1980] to simulated the implantation cascade. Using this sample structure, successfully decelerating radioactive isotopes will be reflected in the TDPAC spectra measured after implantation.

Impinging ions using the conventional implantation energy available at the GLM beamlines (≥ 30 keV) implants them into the TiO_2 substrate, by passing the upper layers completely. For this case, the TDPAC spectra will be dominated by the characteristic electric field gradients (EFG) of TiO_2 [Wen1994]. Slowing down ions to a few keV upon implantations, results in the probe ions coming to rest in the ferromagnetic Ni film. The successful deceleration of the ions will be proved by the observations of the Larmor frequency of the probe ions in the TDPAC spectra, as the probes are influenced by the well-known hyperfine field of pure Ni. Decreasing the implantation energy even lower, to the ULE regime (≤ 100 eV), causes the ions to come to rest in the first few Å, and hence be positioned in the NiO layer. Contrary to pure Ni, NiO is antiferromagnetic, and this different order of magnetic structuring will be reflected in the TDPAC spectra as well. Hence, in this way, a single sample structure can be used to prove the deceleration capabilities of the ASCII chamber, providing a set of proof-of-principle measurements.

Reproducing published results using the old ASPIC evaporation system

The ASCII aims to replace and improve upon the old system of controlling the location of the radioactive probes used in the ASPIC setup. In this 'catcher' system used in previous decades, ions were implanted at 30 keV into a metal foil, which was subsequently heated to high temperatures, allowing the probes diffuse to the surface. After the foil has been placed over a sample or substrate, a second heating period caused the radioactive ions to evaporate from the foil. This transfers the probes to the sample or substrate surface with 'thermal' energies (< 20 eV), after which new thin films can be grown. Despite the drawbacks of this system (slow,

difficult and limited by what can be grown post-evaporation), it offered the ability to carefully control the location of the probes, and several highly unique and valuable insights into metal surfaces and magnetic behaviour of thin films was published [Ber2000]. As the ASCII setup promises similar capabilities (only in a faster, easier and more versatile way), the replacement of the old by the new system is justified not only by breaking new scientific grounds, but also by reproducing some of the older, published scientific work.

One of the most remarkable results obtained using the old ASPIC system, was the investigation of how far magnetic fields of ferromagnetic substrates and films penetrate ultra-thin films, of only a few nm thick. An example of such results are shown in Fig. 3. By using the ASCII setup, we, too, will investigate the effect of ultrathin metal films on the vanishing magnetic fields on a sub-nm scale.

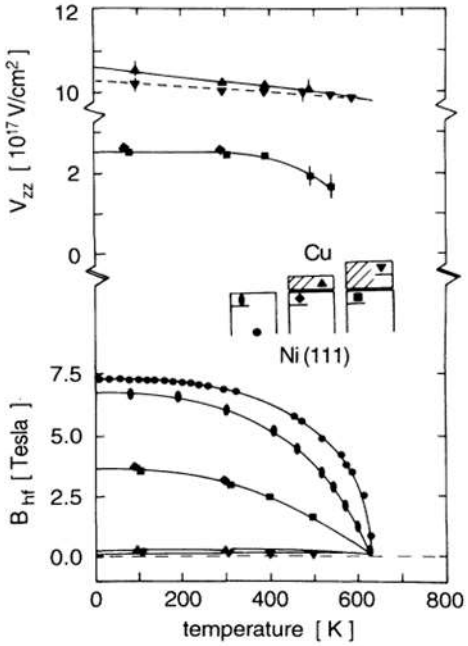

Fig. 3: Using the old, 'catcher' system of the ASPIC, radioactive probes could be placed at the interface of substrate and ultrathin metal films, granting insight into the reach of magnetic fields on the sub-nm scale. The new ASCII deceleration system will reproduce similar experiments, showing can achieved similar results as those published in [Voi991].

New directions: measuring bismuth ferrite nanoparticles and thin films

After demonstrating the functionality of the ASCII facility, we intend to start the tests in bismuth ferrite, $BiFeO_3$ or BFO, nanoparticles and thin films. BFO is one of the rare room-temperature multiferroics [Kad2006] with an unusually large spontaneous polarization. The symmetry in BFO can create weak ferromagnetism and linear magnetoelectric effect, but they have not been observed in BFO bulks [Kad2006]. This is related to the long-wave modulation of the spin structure, which forms a cycloidal structure with a period of around ~62 nm [Sos1982]. Moreover, this modulation results in a zero net magnetization value. The situation might be different in BFO nanoparticles (BFONPs) and BFO thin films. Particularly, enhanced magnetization has been reported for BFONPs [Par2007] [Maz2007] [Gos2011]. This was attributed to surface-induced magnetization related to the contribution of uncompensated surface spins [Par2007], an increase in spin canting due to lattice strain in the nanocrystals [Maz2007], ferromagnetism caused by an apparent oxygen deficiency [Maz2007], or an incomplete spiral of magnetic order in particles of size less than ~62 nm [Gos2011]. These hypotheses need to be experimentally proven by local techniques. Therefore, preliminary TDPAC measurements for BFONPs and BFO bulks using ^{111m}Cd as a tracer ion were carried out for the first time at ISOLDE and shown remarkable results (Figure 4). Particularly, no magnetic signal was locally detected by ^{111m}Cd in BFO bulks in

anti-ferromagnetic phase (below T_N ~ 370 °C) whereas magnetoelectric coupling was observed in BFONPs at the same measuring temperature. This can be reflected by undamped and damped R(t) spectra shown in Fig. 4. The absence of magnetic field at Cd-site in BFO bulks could be due to the cancellation of two opposite magnetic moments. Our former results show that ^{111m}Cd substitutes the Bi – site, which is a nonmagnetic ion [Mar2020]. In particular, two nearest Fe atoms have opposite magnetic moments, so net magnetic signals cancel out. Unlike BFO bulks, the internal magnetic signal was seen at Bi-site in BFONPs probably due to non-compensated surface spins. Particularly, BFONPs have a relative larger surface area when compared to the same volume of BFO bulks [Wan2020] [Dub2021]. Moreover, the average diameter of particle size (~ 50 nm [Esc2013]) is bigger than ionic implantation depth (~ 12 nm [Mar2020] or less). Therefore, ^{111m}Cd is probably trapped near the surface and experiences non-compensated surface spins.

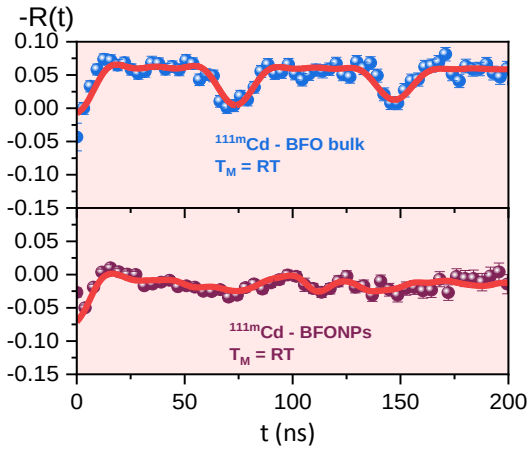

Fig. 4: TDPAC spectra for BFO bulk and BFONPs measured at room temperature.

The preliminary TDPAC results reported above show that the TDPAC technique can prove the existence of non-compensated surface spins in BFONPs. However, in order to confirm this, comprehensive TDPAC studies with ^{111m}Cd should be carried at ISOLDE in upcoming beam times using ASCII. TDPAC measurements using ^{111m}Cd have not been carried for BFO thin films elsewhere, and they are expected to give marvellous results about the enhancement of magnetization as BFONPs did. Furthermore, weak ferromagnetism has been also observed in BFO thin films and related to the destruction of the spiral modulated structure by epitaxial strain [Wan2003] [Bai2005].

Our former results show that after being implanted into BFO bulks, ^{111}In substitutes Fe-atom and detects magnetoelectric coupling at Fe-site [Dan2022]. Therefore, ^{111}In is the best probe that can locally measure the enhancement of magnetization at Fe – site in BFONPs and BFO thin films. The experimental results will be directly compared with those for BFO bulks [Dan2022] and are expected to give a huge magnetoelectric coupling at Fe-site. For BFO thin films, it is important to be implanted with ^{111}In at ISOLDE because ISOLDE has the unique ASPIC and ASCII equipment. Therefore, the functional ionic depth will be much smaller than the thickness of the prepared BFO thin films (23.5 - 100 nm). In particular, TDPAC measurements using ^{111}In have not been carried for BFONPs and BFO thin films elsewhere.

Summary of requested protons:

Beam	Min. intensity	Target material	Ion Source	Shifts	System
^{111}In	>1.10^7	UC_x	Surface or RILIS	1	Cu/Ni(111)
				1	NiO/Ni/TiO_2

			(RILIS is better)	1	$BiFeO_3$
^{111m}Cd	1.10^8	Molten Sn	VD7	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
ASCII	☐ Standard equipment supplied by a manufacturer ☒ CERN/collaboration responsible for the design and/or manufacturing
PAC spectrometer	☐ 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 compressed gases for annealing such as Argon, Helium and Nitrogen may be required.
	Vacuum	☒	At least 10^{-6} mbar
	Machine tools	☐	
	Mechanical energy (moving parts)	☐	
	Hot/Cold surfaces	☐	
Cryogenic Safety	Cryogenic fluid	☐	[fluid] [m^3]
Electrical Safety	Electrical equipment and installations	☒	16 A
	High Voltage equipment	☒	Up to 2 kV for PAC detectors
Chemical	CMR (carcinogens, mutagens and toxic to	☐	[fluid], [quantity]

Safety	reproduction)		
	Toxic/Irritant	☐	[fluid], [quantity]
	Corrosive	☐	[fluid], [quantity]
	Oxidizing	☐	[fluid], [quantity]
	Flammable/Potentially explosive atmospheres	☐	[fluid], [quantity]
	Dangerous for the environment	☐	[fluid], [quantity]
Non-ionizing radiation Safety	Laser	☐	[laser], [class]
	UV light	☐	
	Magnetic field	☐	[magnetic field] [T]
Workplace	Excessive noise	☐	
	Working outside normal working hours	☒	Possible, if the beam time is scheduled 24h 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.