EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

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

VITO – Versatile Ion-polarized Techniques On-line at ISOLDE (former ASPIC UHV beamline)

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Initial Remark

This letter of interest expresses the wide and general motivation of performing numerous experiments at a dedicated beamline for producing polarized beams at ISOLDE/CERN by modifying the former UHV beamline hosting the ASPIC apparatus. The usual letter of intents and full proposals for beamtimes at ISOLDE will be submitted to the INTC committee after the approval of the upgrade of the UHV beamline by the ISCC committee in July 2013. The presented scientific program in the near future will request approx. 70 shifts which will be spread over several runs for a period of 2 years, starting in 2014.

The planned upgrade of the UHV beamline is to be presented to the ISCC committee in July 2013. The major enhancement will be introducing the laser-based nuclear spin polarisation of the isotope beam at RB0 line, which will allow for establishing β-NMR and beta-asymmetry studies in a wide range of sample environments realized in all end-stations.

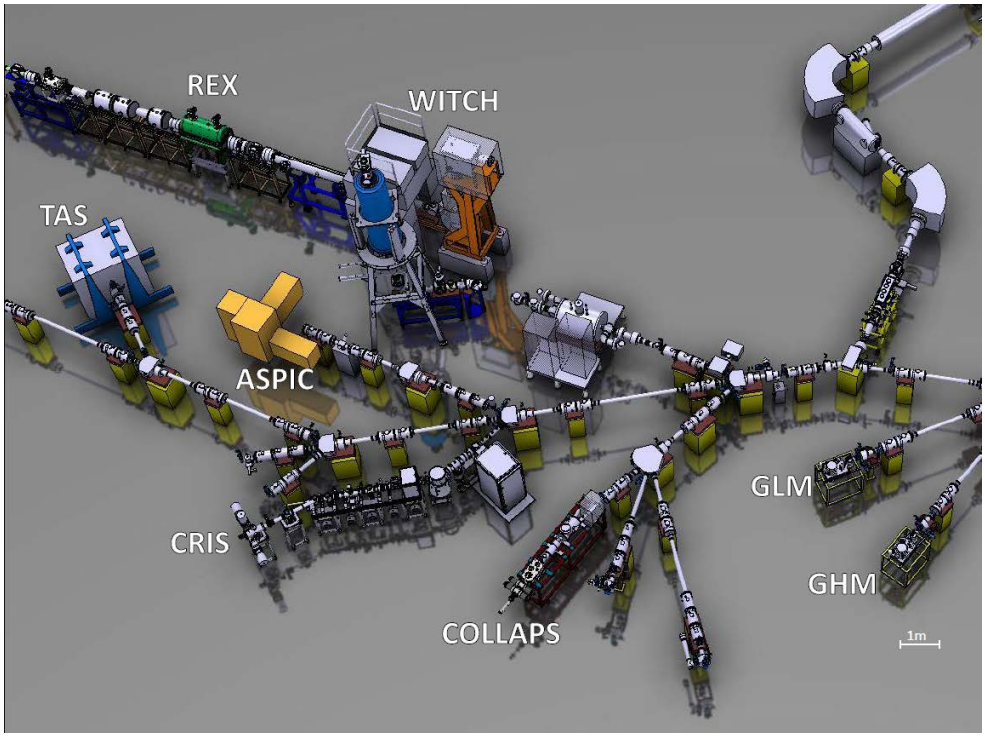

Figure 1. An overview of the beamline system at ISOLDE around RB0.

1 SCIENTIFIC MOTIVATION

The interest in using polarized beams for addressing various scientific phenomena has constantly increased over the past few years. Only at ISOLDE, there is one and frequently running experimental setup employing such beams (COLLAPS), besides other systems such as NICOLE or more recently the tilted foil setup using post-accelerated isotopic beams. However, neither of them provides the particular specifications needed for either of the following cases without major modification.

Therefore, we aim to establish a dedicated beamline for laser-induced nuclear orientation, which will open a wide range of possibilities for carrying out versatile and multidisciplinary experiments at ISOLDE by modifying the existing UHV beamline at the RB0 branch.

As shown in figure 2, the new beamline will provide three end stations after the intended upgrade: the ASPIC end station, the β-NMR spectroscopy end station and an open station for movable experiments requiring rare polarized ions e.g. for nuclear or fundamental physics studies. The UHV and low temperature ASPIC station will remain for PAC studies on sensitive surfaces and interfaces (see suggested experiments by **M. Deicher *et al.*, V. Amaral *et al.*,** and **J. Röder *et al.*, in section 2.1**) and shall later be extended for β-NMR spectroscopy (suggested experiment by **Z. Salman in section 2.1**). The second station will be open for movable experiments or UHV environment. The β-NMR spectroscopy station will be equipped with a strong differential pumping system allowing for online bio-β-NMR on liquid samples (suggested experiment by **L. Hemmingsen in the section 2.2**) and online PAC spectroscopy in volatile matter, such as biochemically relevant aqueous solution. Furthermore, after chamber exchange, this station will allow for other, non-biological experiments e.g. for weak interaction physics research (suggested experiment by **N. Severijns and G. Neyens,** and **D.T. Yordanov *et al.*, in section 2.2**). A short description of the two permanent end stations is presented below.

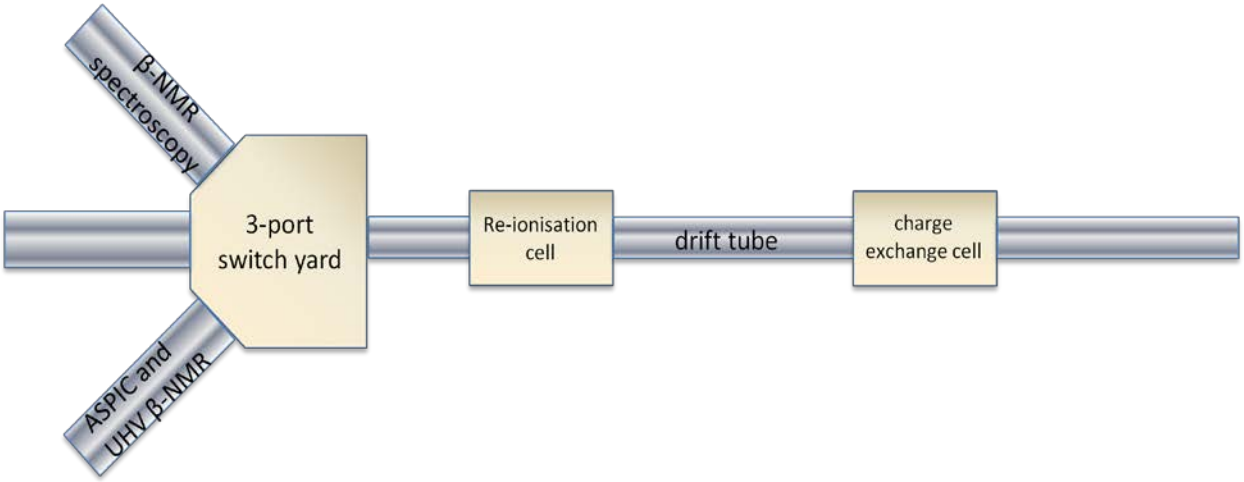

Figure 2. A schematic view of the three end stations.

1.1 The ASPIC end station

The Apparatus for Surface Physics and Interfaces at CERN (ASPIC) achieves high resolution of local electronic and magnetic properties and high surface sensitivity at the same time. Therefore it combines nuclear Perturbed Angular Correlation (PAC) spectroscopy with state-of-the-art sample preparation and manipulation hosted in a common ultra-high vacuum system. Samples can be prepared in-situ by molecular beam epitaxy (MBE), argon ion beam sputtering and heat treatment between 77K and 2800K. A low energy electron diffractometer (LEED) and an Auger spectrometer (AES) are in place

for chemical and structural characterisation. A base pressure of 10^{-10} mbar ensures the required high surface quality throughout the time required for detailed measurements.

Once the sample is prepared, suitable radioactive probe nuclei are collected from ISOLDE through a dedicated UHV beamline and transferred to the sample's surface by soft-landing, where the ions are deposited with thermal energy only on top of the first atomic layer. Additional preparation steps help to integrate the probes into defined crystalline sites on the surface or at an interface. Different detection geometries allow for PAC spectroscopy along and perpendicular to all surface directions at variable temperatures (4K to 500K) and variable magnetic field (0.01T to 0.8T).

The setup has been successfully used from 1990 until 2008, generating numerous results of relevance in the field of the interaction of single *add*-atoms with magnetic metallic surfaces. In 2009 it was left in a widely operating state under conserving conditions. In 2012 the UHV chamber was re-started and the individual connected elements were mostly commissioned, repaired or replaced by existing spares.

1.2 The β-NMR spectroscopy end station

Nuclear spin polarization induced by circular polarized laser light [1] appears to be the most appropriate technique for a β-NMR end station for applied research since it does not require stopping or extreme cooling of the ion, and it has provided very good and reproducible results for over a dozen of isotopes. After passing the polarization section, the ion beam is implanted into the NMR sample placed inside a strong magnetic field of some kG. Due to both, the high degree of nuclear polarization and the sensitive detection of asymmetry via the beta decay as little as 10^7 nuclei are required for observing a resonance, compared to 10^{17} for conventional NMR spectroscopy. Except for this difference, β-NMR spectroscopy provides the same information as conventional NMR: chemical shifts, line broadening or relaxation times providing information about energies and dynamics of chemical bonding.

The best polarization schemes are found by identifying strong transitions in atomic-transition databases, performing atomic calculations which involve coupled differential equations for light absorption and emission, and finally testing the schemes "online" with radioactive beam from ISOLDE. For ^{29,31}Mg such schemes have been already identified (see [2] for details on the calculations and their comparison to experimental data). For Cu strong excitation schemes have been already used online [3] (see figure 3), so calculations and "online" polarization tests have good starting points. For Zn, the candidate transitions have been identified and they will be tested on radioactive beams in 2014 [4].

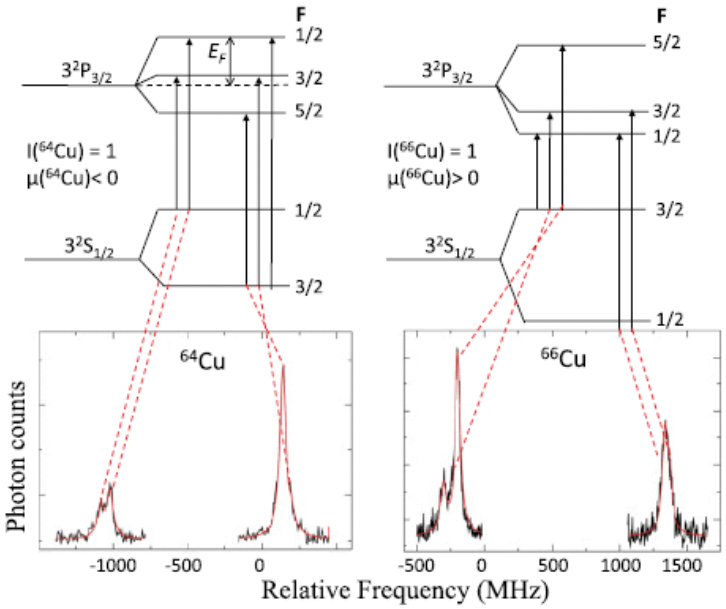

Figure 3. Top: Hyperfine splitting of the 2S1/2 and 2P3/2 levels for a Cu isotope nuclear spin I = 1. Bottom: Hyperfine spectra for 64Cu and 66Cu, observed in fluorescence (not β-asymmetry). Reprinted from [3].

A prototype spectrometer was successfully tested in August 2012, when the first β-NMR spectrum was recorded on a liquid sample. This spectrometer will be available for use at this end station.

2.1 The study cases at the ASPIC end station

2.1.1 Surface mediated magnetism in metal-oxide semiconductors

M. Deicher, K. Johnston, J. Lehnert, Th. Wichert, H. Wolf

Dilute magnetic semiconductors (DMS) are of great interest due to their potential applications in spintronics, which uses the electronic and magnetic properties of the semiconductor [5]. Especially, transition metal doped wide band gap metal oxide semiconductors, such as ZnO, are expected to exhibit ferromagnetism at room temperature [6]. A large number of studies on ZnO based DMS has been reported, but there is no clear agreement about the nature and origin of the ferromagnetism in this system. However, many studies, both experimental and theoretical, during the last years show strong evidence that defect-induced magnetism is a key mechanism for ferromagnetism in ZnO as well as in other non-magnetic oxides with a Curie temperature above room temperature. It seems that doping with magnetic elements is not the only and most promising way to achieve magnetic ordering in these oxides. The introduction of intrinsic defects of the order of a few percent, such as vacancies (with or without doping with magnetic or non-magnetic ions) plays a dominant role in triggering magnetic ordering.

It has been shown both for thin ZnO films [7] and nanostructured ZnO [8,9] that surface defects which can reach high concentrations play a critical role for achieving ferromagnetism in ZnO. There is also evidence that room-temperature ferromagnetism can be triggered by hydrogen adsorption at the surface of ZnO [10]. The ASPIC setup allowing the soft landing of radioactive isotopes on surfaces and nuclear spectroscopic techniques like PAC opens the possibilty to gain microscopic information both on the magnetic and structural properties of ZnO surfaces.

PAC studies using the probe atom ^{111m}Cd:

- Determine via magnetic hyperfine interaction the magnetic properties of surfaces of undoped ZnO with different native defects (O or Zn vacancies).
- Investigate the effect of native surface defects and hydrogen-related defect complex on ferromagnetism on undoped ZnO.
- PAC experiments on the ferromagnetic interplay between surface defects and transition metals in ZnO.

Estimated number of shifts: about 10 shifts for ^{111m}Cd.

2.1.2 Interaction and Dynamics of *add*-atoms with 2-Dimensional Structures

(PAC studies of mono- and low- number of stacking layers)

V.S. Amaral, A. Gottberg, J.G. Correia, K. Johnston

Y. Kadi, S-W Hong, D. Pribat, J. Röder, L. Hemmingsen, V.M. Pereira, K. Potzger, T. Trindade, J.P. Araújo, A.M.L. Lopes, C. Tenreiro, A.S. Fenta, S. Cottenier, S. Casassa

IDADS Collaboration

An international collaboration is being settled by grouping people and institutes from Belgium, Chile, Denmark, Italy, Korea, Portugal, Singapore and Spain to establish the (so far called) IDADS-Collaboration, aiming the study of interactions and dynamics of add-atoms with two-dimensional – single or few – atomic layers with the Perturbed Angular Correlation – PAC – technique. Graphene and derivate structures and new bi-dimensional materials like dicalcogenides (e.g. MoS_2, MgB_2) are the substrates where radioactive probe atoms will be deposited with the soft-landing technique under the UHV conditions proportionated by the ASPIC setup at ISOLDE. The hyperfine fields obtained under such clean environment are expected to reveal in detail the basic bricks of the 2D surface's unique phenomena.

1 Motivation in brief

Graphene presents unique physical and structural properties, and has captured the attention of a large number of researchers, as a strong candidate for a variety of electronic and energy-related devices and structures. It has recently been chosen as the subject of one of the two Europe's first 10-year FET flagship projects, and a R&D roadmap was elaborated. Among the properties of graphene outstands the tuneable electronic transport properties, with exceptional quantum characteristics associated to the massless Dirac fermions characteristics. Its stiffness, stretchability and impermeability, as well as optical absorption features are also distinctive. From a technological point of view, devices like ultrahigh frequency transistors, ultrafast photoactive structures, and transparent flexible electrodes for optoelectronics or photovoltaics were demonstrated and are being developed, combining also graphene with other 2D materials, such as atomically thin boron nitride or molybdenum disulfide. The growth of graphene (single or multiple) layers on metallic and semiconducting surfaces, which can then be transferred, goes already beyond wafer dimensions (several cm^2). Moreover, the low electronic noise in graphene makes its properties very sensitive to the presence of add-atoms or molecules (e.g. for sensors) and the manipulation of its properties by chemical functionalization is also focus of strong attention.

In the context of condensed-matter physics, radioactive ion beams and associated nuclear techniques available at ISOLDE-CERN have been applied to modify (dope) and probe materials with the exceptional possibility to "see and feel" at the nanoscale, to determine the positions and functions of atoms and electrons, of electric and magnetic fields, at a certain element/isotope with extreme sensitivity (doses of ppm or less). By using the soft-landing technique of add-atoms, ASPIC @ ISOLDE, allows doing all of this unique research under UHV conditions at surfaces and interfaces.

2 Case Studies

The opportunities for the application of radioactive ions in the study of graphene are numerous. The hyperfine properties of pure graphene were addressed theoretically, in the presence of a sea of 2D Dirac electrons, with a linear dispersion and the role of spin coherence relaxation mechanisms with nuclei for spintronics and quantum information processing applications was highlighted. The presence of a probe was not considered, although.

We propose to use Perturbed Angular Correlations (PAC) to study the interaction of the add-atom probe element, nucleus and the surrounding electrons with the surfaces, by assessing the Electric Field Gradient and the Hyperfine Magnetic Fields. Following the LOI132 first studies, drafted below, we will address the following topics of add-atoms physics that require the UHV ASPIC environment:

1- *Charge renormalization* in graphene was predicted to change considerably the electron motion in a strong Coulomb field of an ad-atom impurity, leading to quantum relativistic atomic collapse and the supercritical instability already at charges Z~1-2 in contrast to the heavy nuclei charge (Z>170) for free atoms. The crossover was very recently observed by Scanning Tunnel Microscopy in clusters of charged Ca dimers on electronically gated graphene on BN, thus, producing resonances in conductivity. *It is our intent to probe such catastrophic charge renormalization phenomena using hyperfine effects with radioactive ions of different valences soft-landed onto graphene.*

2- *The concept of topological insulator (TI), or Quantum spin-Hall state* was predicted initially to occur in graphene, but such new quantum state, with spin-filtered edge states (quantized conductance, with opposite spin electrons propagating in opposite directions), were first observed in HgTe quantum wells and in the surface states of Bi2Se3 and other materials with sufficiently strong spin-orbit coupling Recently, graphene as a viable candidate for TI was revived by predicting that a few % of heavy add-atoms (In, Os, Ir,..) can produce a robust gapped topological insulator state. However, the mechanism is still controversial, either involving electron tunnelling from graphene onto an add-atom or considering that despite their dilute character add-atoms form impurity states that hybridize with graphene. Further, it is found that the electronic structure of add-atoms (e.g. Co) deposited on back-gated devices, could be tuned by application of voltage and screening clouds around a single atom as large as 10 nm observed. Such tunability by external control and the emergence of extended screening effects are fundamental for electronic applications. *These issues highlight the need for locally and internally probing the add-atom physics on graphene, which we here propose now by using the PAC technique within the ASPIC environment.*

3- *Physics of add-atoms on other 2D materials, such as MoS_2, MgB_2* and similar dichalcogenides, is also poorly known in spite of its importance for understanding the catalytic properties, and for helping the designing of heterostructures with tuned properties, for which the first examples start to appear. *Again these are ideal subjects to be addressed with add-atoms probed by PAC under the UHV environment of ASPIC.*

4- *Addressing the preparation of isotopically pure graphene layers or their modifications.* Study of the growth on transition metal template coatings/ substrates. Graphene synthesis by ion implantation was demonstrated (carbon implanted at 30 keV on metal (Ni)

coatings/substrates, and subsequently segregated to the surface at lower temperature). *The use of add-atoms probes of PAC within the UHV ASPIC environment challenges our understanding of these processes and in-situ doping.*

5- *Studying of nucleation of nanostructures and clusters on graphene* and related phases requires the complementary use of ASPIC and wet chemical methods.

Graphene and graphene oxide have been investigated as new platforms for growing semiconductor nanostructures aiming diverse devices, such as quantum dots. Fundamental studies that address their nucleation are lacking. We intend to monitor the nucleation of CdS nanophases on graphene sheets. This task will involve the controlled generation of CdS seeds, in situ, using wet chemistry methods developed in our laboratories. Radioactive ^{111m}Cd will be implanted in the CdS precursors and then synthetic samples will be analysed for distinct reaction times to inquire the local environment of the CdS dots on the graphene surface. *Complementary studies in UHV will allow comparing the Cd local environment and the role of solvent (water).*

3 Short report on LOI I132: Radioactive Local Probing and Doping on Graphene

Experiments were performed using radioactive ^{111m}Cd/^{111}Cd and ^{199m}Hg/^{199}Hg on graphene laying into Si/SiO_2 wafers and PET polymer sheet substrates. Additional experiments on related materials, like graphite, graphene oxide and carbon nanotubes suspensions were done for comparison. On these preliminary studies two different methods were used to deliver the isotopes to the sample's surfaces. The first method consisted on implanting the ions on ice that, once melted, was used to wet the samples until some ions bind to graphene. In the second method, direct implantation of radioactive ions through graphene samples standing on a Si/SiO_2 wafer, was followed by subsequent annealing up to 800 º C and 1100 º C, in order to promote the diffusion of ions from the substrate to the graphene interface. The aim was to study the process of recovery of the substrate and graphene itself after suffering the 50kV ion beam bombarding. From these experiments we got amazing results regarding the determinant contribution of the *still surviving* graphene layer to the damage recovery of the implanted substrates (to be reported in detail elsewhere).

Hereby, are shown results obtained at different temperatures, after wetting with melted ice containing ^{111m}Cd and ^{199m}Hg, the graphene samples laying at PET and Si substrates: Figure 4 and Figure 5 show the experimental PAC observable, the R(t) function, as measured in graphene on Si and PET substrates with ^{111m}Cd ^{199m}Hg. The different spectra show multiple Electric Field Gradients, which reveal that the substrate is able to influence the binding of Hg and Cd ions to graphene. Due to the temperature dependence of the R(t) spectra, we further believe that water molecules are interfering with the bonding, and consequently, with the places where the Cd and Hg metal ions sit. DFT first principle simulations are in progress, which model atomic configurations containing metal ions and water molecules on graphene, aiming to reproduce the experimental data and help on explaining the interaction of metal ions with graphene in, e.g., catalytic processes.

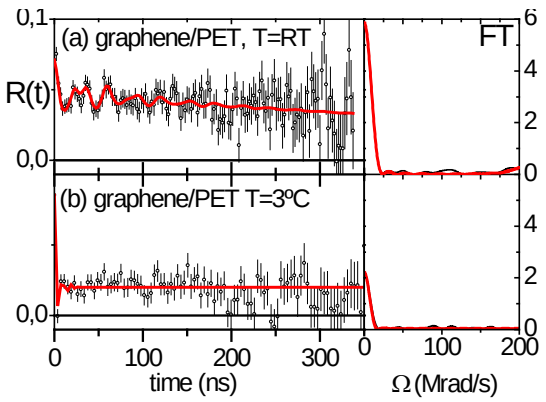

Figure 4. R (t) functions and respective Fourier Transforms (FT) obtained using PAC, with ^{111m}Cd isotope, measured at room temperature (RT) and 3 º C. The samples analyzed were graphene on PET - a) and b), and graphene on Si - c) and d).

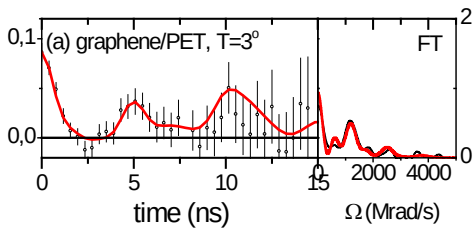

Figure 5. R (t) functions and respective Fourier Transforms (FT) obtained using PAC, with ^{199m}Hg isotope, measured at 3 ºC. The samples analyzed were graphene on PET - a), and graphene on Si - b).

Estimated number of shifts: 18 shifts, (over two years) regarding the following probes: ^{77}Br/^{77}Se, ^{73}Se/^{73}As$^{(M)}$, ^{80m}Br/^{80}Br, ^{111m}Cd/^{111}Cd, ^{111}In/^{111}Cd, ^{140}La/^{140}Ce$^{(M)}$ ^{147}Gd/^{147}Eu$^{(M)}$, ^{172}Lu/^{172}Yb, ^{199m}Hg/^{199}Hg. (M) accounts for magnetic probing only.

2.1.3 Surface and interface investigations of first, second, and third generation solar cells using ASPIC

J. Röder, A. Gottberg, T. Beckers, M. Martin

Solar cells of the third generation use multilayers of different semiconductors to overcome the Shockley-Queisser efficiency limit for conventional first generation solar cells. This limits the efficiency of converting the power of irradiated sun light to electrical power theoretically to about 34% up to about 87% for an infinite number of layers. Laboratory examples have already shown efficiencies of more than 43% while best examples one layer silicon cells may reach 25%. Understanding the behaviour of complex multilayer systems as shown in Figure 6 below is crucial for their implementation and in addition for addressing aging processes. At contact of interfaces additional phases may form at certain temperatures, or diffusion may take place, changing the designed properties. Due to the typical layer thicknesses in the range of nanometres to micrometres and the challenging conditions of interfaces, available methods to investigate the concerned material properties are challenging themselves.

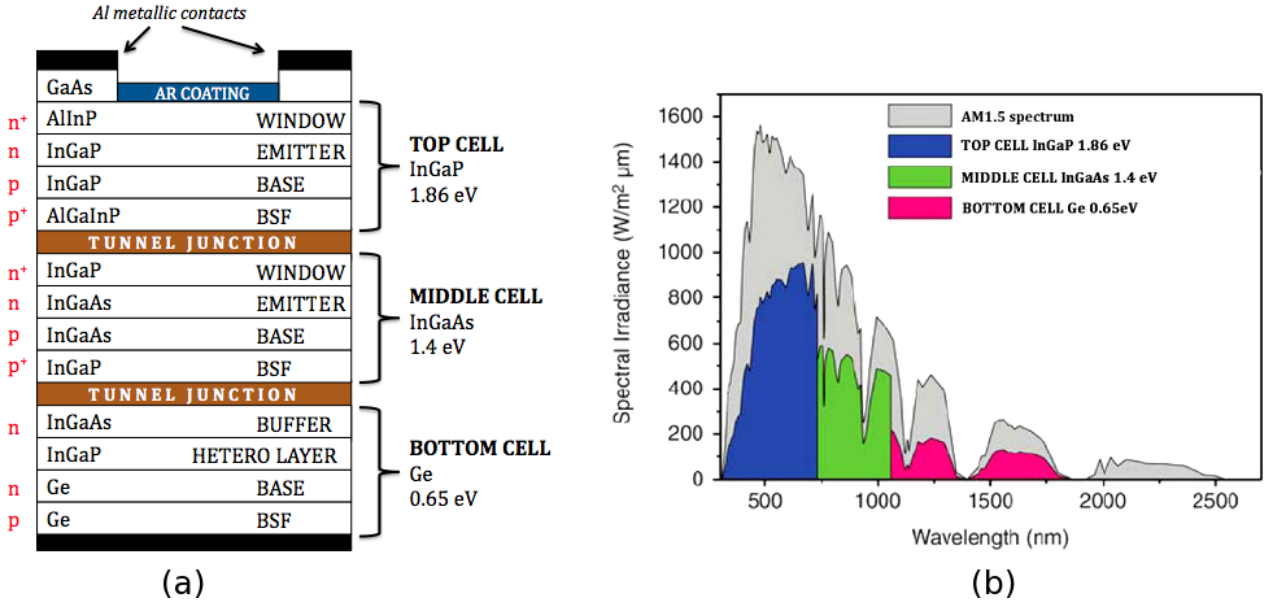

Figure 6. Typical solar cell multilayer (A) Coverage of the natural Sun spectrum for each of the layers (B)

Second generation solar cells are significantly simpler to implement with the advantage of requiring only a low amount of high purity semiconductor material as layer on a cheap and free to design carrier material, such as glass. Although a monolayer solar cell, the layer itself consists of several layers of different materials. One specific example is the question of sodium diffusion from the glass into the CIGS layers, which is crucial for a good performance and till now a poorly understood process.

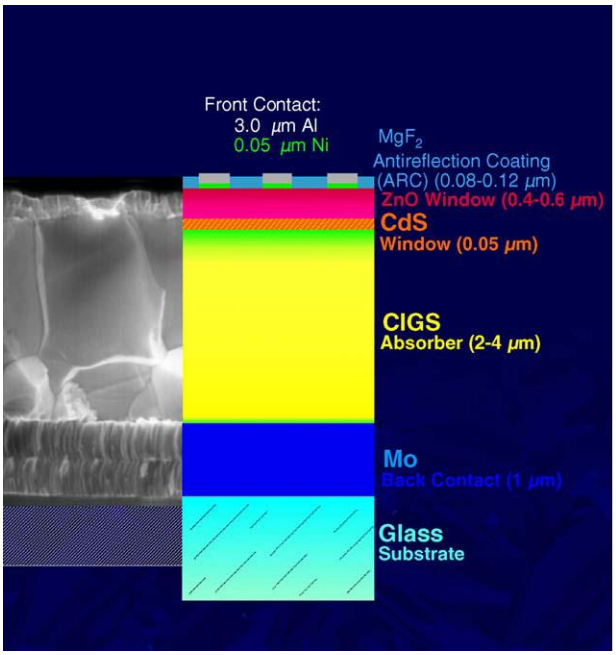

Figure 7. CIGS solar cell.

First generation solar cells with high efficiency are produced from wafers, mainly silicon, see Figure 8. The roughness of the surface is enlarged in order to increase the performance. Investigation of the defect structure of the surface and its influence of additional anti-reflexion coatings may result in better understanding of the involved processes. Furthermore, the contact conjunctions are produced of different layers, introducing various interfaces that are subject of aging and thermal changes, which are poorly understood.

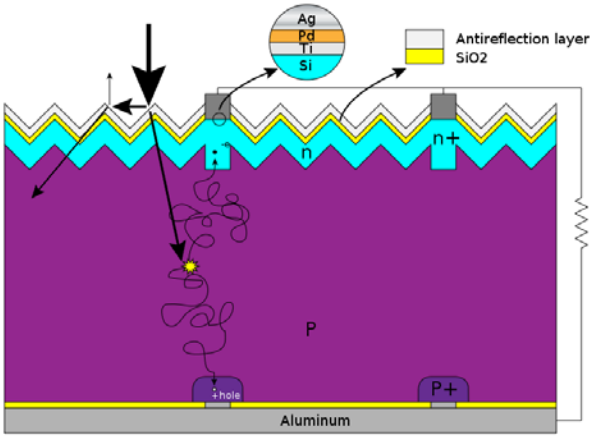

Figure 8. Typical single crystal solar cell.

PAC spectroscopy in combination with ASPIC can be a powerful tool to investigate the local structure in these materials as well as in the interfaces or surfaces. ASPIC is a decisive tool for preparing samples in ultra-high vacuum under controlled conditions in order to perform investigations in all fields described above.

As a first experiment Cu(In,Ga)Se semiconductor layers could be investigated temperature dependent, focussing on its properties in contact with the surrounding layers. Glass - molybdenum and Cu(In,Ga)Se will be studied, investigating the influence of sodium in the local structure.

In a second step, contact interfaces of silicon and common coatings for the solar cell production are planned to be studied. Finally multilayer systems of InGaP and AlInP and GaAs will be a challenging research interest.

Intermetallic conjunctions of aluminum and gold are used for contacts in space devices and on solar cells. Gold and aluminium have a complex phase diagram producing at contact different intermetalic phases. Phases causing mainly problems are Au_5Al_2, known as white plague, $AuAl_2$ as purple plague, and Au_2Al. These phases have different material properties, cause an increase of resistance and reduction in volume causing cavities. Solutions are using ultrasound welding or adding additional metals such as Ni and V as intermediate layer. To increase the understanding of the undergoing processes, intermetalic phase formations will be studied on Au-Al contact and with intermediate layers Ni:V/Ag as well as Ga as amalgam forming metal. Investigations will be performed in layers and temperature dependant. The preparation will be performed using ASPIC and phase changes will be studied by using PAC.

2.1.4 Low energy β-NMR for studies on condensed matter

Z. Salman

Nuclear magnetic resonance (NMR) and related nuclear methods are widely used in condensed matter physics. The magnetic moment of a nucleus acts as a sensitive probe of the local magnetic and electronic environment. All forms of magnetic resonance require generation of nuclear spin polarization out of equilibrium followed by a detection of how that polarization evolves in time. The spin precession rate or Larmor frequency is a measure of the local magnetic field at the nucleus, whereas the spin relaxation rate is determined by spin dynamics near the Larmor frequency. However, there are also significant differences which influence the specific applications. For example, in conventional magnetic resonance a relatively small nuclear polarization is generated by applying a large magnetic field after which it is tilted with a small RF magnetic field. An inductive pickup coil is used to detect the resulting precession of the nuclear magnetization. Typically one needs about 10^{18} nuclear spins to generate a good NMR signal with stable nuclei. Consequently conventional NMR is mostly a bulk probe of matter. On the other hand, in related nuclear methods such as muon spin rotation (mSR) or b-detected NMR (β-NMR) a beam of highly polarized radioactive nuclei (or muons) is generated and then implanted into the material. The polarization can be made much higher - between 50 and 100% . Most importantly, the time evolution of the spin polarization is monitored through the anisotropic decay properties of the nucleus or muon which requires about 10 orders of magnitude fewer spins. Furthermore one can control the depth of implantation of the probe on an interesting length scale (1-300~nm). Thus depth controlled low energy b-NMR [11-14] and mSR (LE-mSR) [15-17] are well suited to studies of dilute impurities, nano-structures or interfaces where there are few nuclear spins.

The low energy β-NMR technique used for condensed matter studies has the advantage of not being limited to a specific material or properties. It can be used to study any material whether they are conducting, insulating, magnetic or non-magnetic. This makes it extremely versatile and useful for different fields in condensed matter, and therefore has the potential of attracting many new users to ISOLDE. The low implantation energy of the spin probes in β-NMR, makes the technique useful mainly for studies of surfaces and interfaces. The electronic, magnetic and structural properties of an interface between two materials (or near the surface) are in general different from the bulk properties of both. In such systems the technique can provide depth resolved information of the properties of such systems. A dramatic example which was discovered recently [18–20], is the high mobility two-dimensional electron gas (2DEG) at the interface between two insulating perovskite oxides; TiO_2-terminated $SrTiO_3$ (STO) and $LaAlO_3$ (LAO). Surprisingly, there is evidence that this interface can be both magnetic and even superconducting below 300 mK [18-21]. In this example the high magnetic sensitivity of β-NMR was used (at TRIUMF) to detect weak magnetism at these interfaces and its dependence on the thickness of the LAO layers [22]. Another important example where β-NMR can provide unique information is the newly discovered class of materials called topological insulators (TIs) [23]. These are 3D insulating materials with a band gap in the bulk electronic structure but with metallic gapless surface states. The protected surface states are believed to be robust to disorder, interactions, and thermal fluctuations, potentially leading to room temperature device applications [24]. In this case we expect β-NMR to provide novel information regarding the depth dependence of

these surfaces states, and more importantly, study the properties of interfaces between TIs and other superconducting or magnetic materials. Such buried interfaces cannot be investigated using the commonly used techniques in TI studies such as angle resolved photo-emission spectroscopy and scanning tunneling microscopy.

Several isotopes have been identified as suitable for development as probes for condensed matter applications. ^{8}Li is the lightest and is relatively easy to polarize. There are, however, several other probes which could be very useful for β-NMR studies in the near future, including ^{15}O and ^{11}Be. Different nuclei offer complementary information since they have different nuclear dipole and quadrupole moments as well as a different decay lifetime. For example, since ^{8}Li has a nuclear moment of I=2 it experiences both the local magnetic field as well as electric field gradient. This may complicate the measured resonance results and makes it hard to disentangle the local magnetic and electronic information in the studied system. In contrast, ^{11}Be which has nuclear spin 1/2 will have a purely magnetic interaction with the system.

2.2 The study cases at the β-NMR spectroscopy end station

2.2.1 Bio-β-NMR spectroscopy on liquid samples

L. Hemmingsen, M. Stachura, A. Gottberg, M. Kowalska, P.W. Thulstrup

Metal ions are essential for life, and various functions have developed depending on the intrinsic properties of each metal ion. The current letter of interest is focused on establishing new spectroscopic possibilities for studies of the biologically highly important metal ions Mg^{2+}, Ca^{2+}, Cu^{+}, and Zn^{2+}. Mg^{2+} is involved in practically all phosphate metabolism as well as an integral component of chlorophyll in photosynthesis. Ca^{2+} is involved in a plethora of biochemical reactions, for example kinase reactions, muscle contraction, cell division, as well as biomineralization etc. Both of these ions also take part in the control of formation of negatively charged polymers, and thereby in the control of membrane stability and cell-cell interactions, a property that may be exploited in this project, vide infra [25]. $Cu^{+/2+}$ is essential in both various oxidases (enzymes) and in electron transfer processes, for example in photosynthesis, where so-called small blue copper-proteins play key roles as electron transporters. Finally Zn^{2+} is both an integral structural component of proteins, involved in many enzymes, and in biochemical control of the expression of genes. All these metal ions usually evade spectroscopic characterization, as they are invisible to most standard spectroscopic techniques. Thus, the application of radioactive ion beams and nuclear spectroscopic techniques would constitute an important, novel and most notably highly sensitive approach to the elucidation the biological chemistry of these elements.

The short term aim (1-3 years) of this project is to establish a proof-of-principle that on-line β-NMR and PAC spectroscopy on liquid samples using short lived radioisotopes of Mg, Ca, Cu, and Zn is feasible. The long term aim is to apply these spectroscopic techniques to elucidate both local structure and dynamics at the probe sites in biological systems. Only the short term aim is addressed in detail in the following. Once the short term aim is achieved, and the experimental setup has been optimized to allow for experiments on aqueous solutions (test experiments have indicated that this is within reach), a number of experiments elucidating the biological chemistry of the metal ions, vide supra, will be designed

In the following specific experiments on the different metal ions are described. They are all to be conducted using ionic liquid as solvent, as it displays very low vapor pressure, and thus is suitable for UHV beam lines:

- Mg^{2+}: ^{31}Mg β-NMR experiments have already been successfully carried out using ionic liquid as solvent [26]. Conventional ^{25}Mg NMR spectroscopy will be applied to validate the results.
    - The binding of $^{31}Mg^{2+}$ to a molecule in the ionic liquid solution would complete the experiment series, demonstrating that not only a signal from $^{31}Mg^{2+}$ in the solvent, but also the process of binding to high affinity site may be achieved within the lifetime of the radioisotope. As the chemical shift range for $^{31}Mg^{2+}$ in a variety of compounds is rather small (about 200 ppm), and this is close to the limit of what can be resolved (with the current setup), it will be very difficult directly to observe different chemical shifts. Thus we adopt a different strategy, and aim to bind Mg^{2+} to different sizes of

molecules, using anionic molecules exhibiting Mg^{2+} dependent polymerization, vide supra. The origin of this strategy is that for molecular species experiencing rotational diffusion on a time scale comparable to the inverse of the Larmor frequency, the spin-lattice relaxation time is minimal, and thus the signal is lost or reduced in intensity. That is, the binding of $^{31}Mg^{2+}$ to a certain size of polymer will give rise to loss of signal, and thus demonstrate that the metal ion is in fact bound.

In addition a number of test experiments are important:

- The resonance frequency in a reference (single crystal of MgO) must be recorded to calibrate the system
- A β-NMR experiment without any sample in the chamber, in order to test if the recently designed setup in itself gives rise to a signal (a fraction of the $^{31}Mg^{+}$ beam is deposited in the walls of the final pin-hole, and we suspect that the Knight shift of Mg in aluminum is consequently observed)
- Conventional ^{25}Mg NMR spectroscopic data indicate a strong temperature dependence of the signal, and we aim to carry out a similar series (20 °C – 100 °C) using β-NMR.

- For Ca^{2+}, Cu^{+} and Zn^{2+}: For these elements conventional NMR experiments are difficult, and we resort to other conventional techniques for validation of the results (electronic absorption and fluorescence spectroscopy), see the second bullet below.
  - The first experiments to be carried out will be simply implanting the spin-polarized radioisotope into ionic liquid, in analogy to the initial ^{31}Mg β-NMR experiments. The binding of the metal ions will most likely occur to the anion of the ionic liquid (acetate).
  - Next, a molecule with high affinity for each of the respective metal ions will be added to the solution. Fortunately, such metal ion specific chromophores and fluorophores exist, and additionally independently allow for spectroscopic characterization of the process of metal ion binding, using so-called stopped flow techniques (where the chromophore/fluorophore is mixed with the relevant metal ion, and then rapidly (with a dead time of ~1 ms) the time trace of the spectroscopic signal is followed.

Estimated number of shifts: ^{31}Mg, Ca, ^{58}Cu, ^{74}Cu or ^{75}Cu, ^{77m}Zn (10 shifts each element)

2.2.2 β-decay studies of laser-polarized radioactive beams

D.T. Yordanov for the proponents of INTC-I-090

Currently there is a strong interest in β-decay studies of laser-polarized radioactive beams. This technique has the capability of measuring spins of excited nuclear states and as such is expected to be an important tool for nuclear-structure studies. The basic principles, as well as a physics case were presented in a letter of intent [27] in the context of collinear laser spectroscopy at HIE-ISOLDE. The intention to establish a dedicated beam line for laser-induced nuclear orientations opens the possibility to employ an alternative geometry for optical-pumping, as shown in figure 9. The ion beam is deflected at 90° which is equivalent to, and therefore removes the need of, a 90° turn of the orientation axis. Under these conditions the nuclei will be delivered at the implantation point with a higher degree of polarization. Furthermore, the magnetic field needed to bend the orientation axis is obsolete in this configuration. In the absence of a large electromagnet the solid angle around the sample can be used instead for an efficient detection system.

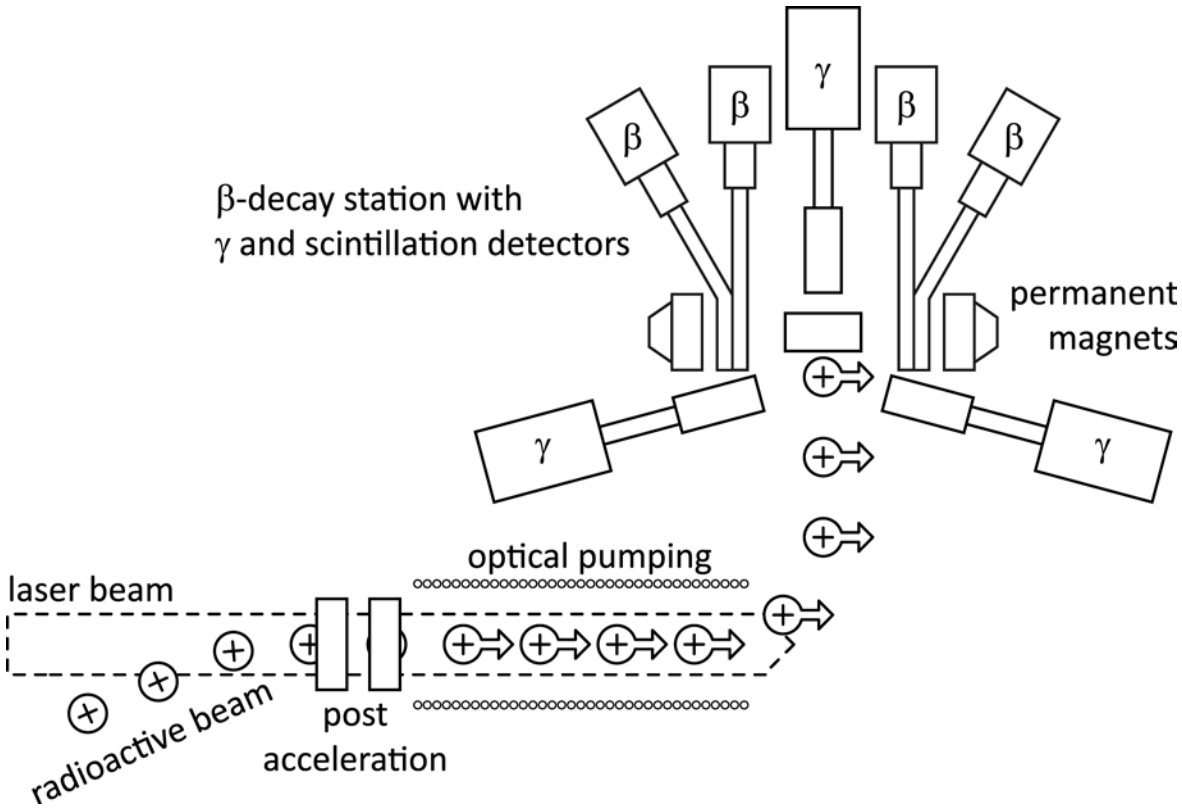

Figure 9. Geometry of β-delayed spectroscopy with optical pumping of ions.

2.2.3 Fundamental weak interaction physics using polarized beams: Precision measurements of the beta asymmetry parameter for mirror β transitions in ^{21}Na, ^{23}Mg and ^{35}Ar for determination of the V_{ud} element of the CKM quark mixing matrix

N. Severijns, G. Neyens, M. Bissell

Measurements of correlations in nuclear beta decay (e.g. the beta-neutrino correlation or the beta emission asymmetry) are a sensitive means to search for the presence of new charged gauge bosons mediating scalar or tensor type weak interactions not included in the Standard Model [28]. Moreover, when results of such measurements for mirror beta transitions are combined with the ft-value of the transition, then also the V_{ud} element of the Cabibbo-Kobayashi-Maskawa (CKM) quark mixing matrix is obtained. E.g the beta-asymmetry parameter A yields the Fermi-Gamow-Teller mixing ratio, ρ, $A = \frac{1}{1+\rho^2}\left[\frac{\rho^2}{J+1} - 2\sqrt{\frac{J}{J+1}}\rho\right]$, which in turn yields V_{ud} when combined with the corrected Ft-value $\Im t^{mirror} = 2\,\Im t^{0^+\to 0^+} / \left(1+\frac{f_A}{f_v}\rho^2\right)$. Via the unitarity requirement of the CKM matrix additional information on physics beyond the Standard Model is then obtained, such as e.g. on the existence of heavy Z bosons [29].

Recently, it was shown that existing results of correlation measurements in the beta decay of five mirror nuclei, originally not intended for this purpose, provide a value for V_{ud} of similar precision to that obtained in neutron decay [30]. Further, it was shown that the beta asymmetry parameter of the mirror beta decay of ^{35}Ar provides unrivaled sensitivity to V_{ud} [31] within the series of mirror nuclei. A measurement of the beta-asymmetry parameter with a relative precision of 0.5 %, would provide a value for V_{ud} that is only a factor of 3 less precise than the value for V_{ud} that is obtained from the entire set of superallowed pure Fermi beta transitions [32]. Furthermore, if the current ft-value [33]) can be improved by a factor of 5, the V_{ud} would be obtained with a precision that is half of the current precision as obtained from all data available till now. A measurement of the beta asymmetry parameter in the decay of ^{35}Ar would thus allow further improving the precision of the value of V_{ud} and thus the sensitivity to different types of new physics.

A measurement of the beta asymmetry parameter requires a polarized beam that is implanted in a suitable host material selected so as to maintain the nuclear polarization sufficiently long. Using optical pumping with a circularly polarized laser beam allows producing high degrees of polarization, as illustrated e.g. for Na and Mg isotopes [34, 35]. The polarization is maintained after implantation by placing the host crystal in a magnetic field of a few 1000 Gauss. The beta asymmetry will be observed with two ΔE-E telescopes (to reduce background counts) placed perpendicular to the polarization symmetry axis. As the measured asymmetry will provide the product of the nuclear polarization, P, and the beta asymmetry parameter, A, the nuclear polarization has to be determined with a precision better than 0.5%. Such methods have recently been developed at TRIUMF [36] and at Los Alamos Natl. Laboratory [37]. Alternatively, determining the polarization can be avoided by measuring simultaneously the asymmetry for the mirror beta transition and for the pure Gamow-Teller transition to the first excited state of ^{35}Ar (with a branching ratio of 1.2 %). The nuclear polarization then cancels in the ratio of both beta-asymmetries. This method has successfully been applied in the past already [38-40] and requires gamma

detectors to be installed as well, in order to select the two individual beta transitions via beta-gamma coincidences.

As polarizing of a noble gas such as ^{35}Ar requires some development, the method and setup will first be tested with ^{23}Mg and/or ^{21}Na which, apart from the dominant g.s. → g.s. mirror beta transition, also have a Gamow-Teller transition to the first excited state (branching ratio respectively 8.2 % and 4.8 %).

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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
Dedicated beamline for producing polarized beams at ISOLDE	☐ Existing	☐ To be used without any modification
	☒ New	☒ Standard equipment supplied by a manufacturer ☒ CERN/collaboration responsible for the design and/or manufacturing
ASPIC apparatus	☒ 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
β-NMR apparatus	☐ 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
bio-β-NMR apparatus	☒ New	☒ Standard equipment supplied by a manufacturer ☒ CERN/collaboration responsible for the design and/or manufacturing

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Datum: 28.05.2013

Letter of support for ASPIC

Together with the radioactive isotopes provided by ISOLDE, ASPIC opens world-wide unique possibilities to combine “classical” surface and interface experiments with nuclear solid state physic techniques like perturbed angular correlation spectroscopy (PAC) or spin polarization methods like β-NMR.

I hereby strongly support an upgraded ASPIC beamline at ISOLDE. Using ASPIC, we plan to perform PAC experiments in semiconductors, especially on surface and interface magnetism in spintronic systems.

Saarbrücken, May 28, 2013

Dr. Manfred Deicher

KU LEUVEN

DEPARTEMENT NATUURKUNDE EN STERRENKUNDE
INSTITUUT VOOR KERN- EN STRALINGSFYSICA
CELESTIJNENLAAN 200 D, BUS 2418
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ONS KENMERK
UW KENMERK
LEUVEN May 29, 2013

Support letter for a rebuilding of the ASPIC beam line for producing laser polarized beams

Production of polarized beams at ISOLDE is now possible in the COLLAPS beam line using the collinear interaction with a circularly polarized CW laser beam, inducing atomic and nuclear polarization through optical pumping. At present, polarized beams of Li, Na and Mg isotopes have been produced at COLLAPS with polarisations up to 30-40%. This is much larger that the polarisations that are achieved e.g. using the tilted foils technique, where typically a few % of polarization is achieved. Considering that scientists from different fields are interested in using polarized beams, it is not possible to perform all of these experiments at the COLLAPS beam line.

Furthermore, with a dedicated optical pumping beam line it is possible to achieve polarizations up to 80-90%, as illustrated at Triumf for Li isotopes. Most of the experiments that are intending to use polarized beams, would largely benefit from a maximum of polarization and thus from a dedicated polarization beam line (as the experimental sensitivity increases with the square of P).

At Leuven, we are interested to combine the expertise from the group of G. Neyens (strongly involved in COLLAPS) and Nathal Severijns (focusing on fundamental interaction studies) for using polarized beams for fundamental interaction studies. By performing high-precision beta-asymmetry measurements on some particular elements, very precise information on exotic currents (scalar, tensor) in weak interactions can be obtained. Such studies require regular short beam times for studying also possible systematic errors. Thus a dedicated beam line providing a maximum of polarization and with regular access would be needed for this project.

Therefore, we strongly support this initiative at ISOLDE. If approved, one of our post-docs currently working on COLLAPS (Mark Bissell) will help in designing the optical pumping and related sections of this new beam line.

Sincerely yours,

Gerda Neyens and Nathal Severijns

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Villigen PSI, 28 May 2013

Dear Monika

I am writing to support your plans for the ASPIC beamline upgrade for producing polarized beams at ISOLDE and the construction of beta-detected nuclear magnetic resonance (beta-NMR) spectrometers. The planned upgrade provides a great opportunity for multidisciplinary collaborations between scientists from nuclear physics, condensed matter, biology and chemistry. It will enhance the current capabilities of ISOLDE putting it at a leading position, not only in nuclear physics, but also in applications of nuclear methods for other branches of science. My colleagues and I at the laboratory for muon spin spectroscopy at the Paul Scherrer Institute will be delighted to contribute to such a project providing our technical experience and knowledge in the field. Moreover, the complementarity between the beta-NMR technique and muon spin spectroscopy will expand our research opportunities within Europe. Therefore, I will be extremely interested in using future beta-NMR facilities at ISOLDE, and believe that some of my colleagues and collaborators will also be.

Sincerely,

Zaher Salman

UNIVERSITY OF COPENHAGEN

Department of Chemistry

May 28, 2013

Letter of support for the "Letter of Interest" for a beam line at ISOLDE, for the production and application of spin polarized nuclei,

The possibility to carry out research in the fields of biochemistry and biophysics at ISOLDE, using ion beams with spin polarized nuclei represents a unique opportunity. It will allow us to conduct experiments that cannot be carried out elsewhere, and which are expected to significantly advance both basic and applied biochemistry, most notably concerning the role of metal ions in biological system, which is the core expertise of my group at the University of Copenhagen.

The group in Copenhagen has been fortunate enough to have had beam time grants for several years at ISOLDE, leading to publications in high ranking international chemistry and biochemistry journals, and expect to continue carrying out research for at this facility for many years to come. Similarly, the group has attracted funding for this research for several years, and hope and aim to attract future funding for biochemistry and biophysics projects to be carried out at this beam line at ISOLDE.

Thus, my group will greatly benefit from the facilities at proposed beam line, both on a short and on a longer time scale.

Sincerely,

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To whom it may concern

Having in mind research projects requiring the use of radioactive ion beams for hyperfine measurements in demanding conditions I hereby state my support to the *UHV RB0 beam line upgrade project*. This will allow the continuation of current activities and the enrichment of conditions to foster demanding experiments in solid-state, soft-matter and biophysics applications.

I will do my best to contribute to the progress of research in its multiple and interdisciplinary aspects, looking forward to the improvements well expressed, and justifiable, by the *UHV RB0 beam-line upgrade project*.

Aveiro, 28th May 2013

Vítor Amaral

(Vítor Brás de Sequeira Amaral)
Full Professor,
Physics Department University of Aveiro