Nuclear radioactive techniques applied to materials research

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Abstract

In this paper we review materials characterization techniques using radioactive isotopes at the ISOLDE/CERN facility. At ISOLDE intense beams of chemically clean radioactive isotopes are provided by selective ion-sources and high-resolution isotope separators, which are coupled on-line with particle accelerators. There, new experiments are performed by an increasing number of materials researchers, which use nuclear spectroscopic techniques such as Mössbauer, Perturbed Angular Correlations (PAC), β -NMR and Emission Channeling with short-lived isotopes not available elsewhere. Additionally, diffusion studies and traditionally non-radioactive techniques as Deep Level Transient Spectroscopy, Hall effect and Photoluminescence measurements are performed on radioactive doped samples, providing in this way the element signature upon correlation of the time dependence of the signal with the isotope transmutation half-life. Current developments, applications and perspectives of using radioactive ion beams and techniques in solid state and biophysics research are presented with a few examples.

Keywords: Materials characterization / Nanoscopic scale phenomena / Radioactive spectroscopic techniques / Radioactive tracer techniques / Radioactive ion beams,

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1. The ISOLDE facility at CERN

1.1 *The production of radioactive isotopes*

Radioactivity and Radioactive Isotopes (RI) are ordinarily present in daily life, contributing directly or indirectly to welfare as well as, more specifically, to both the applied science and research fields. Presently, three types of facilities produce the required excited and unstable nuclei, covering the full mass range, i.e., neutron-rich isotopes (reactors), proton-rich isotopes (cyclotrons) or both, when using high-energy proton induced reactions. Among the different and specific methods for delivery of RI, the production of radioactive ion beams (RIB) provides the most versatile and fastest delivery of the nuclei species, justifying the large investment in new RIB facilities, which are dedicated to a wide range of research and applications all-over the world [1].

Since its start in 1967, the ISOLDE facility at CERN has been successfully pioneering the *thick target* technologies for RIB production. There, an efficient and continuing R&D program has been constantly improving beam quality with high intensities and high elemental purity, diversifying element species and increasing the energy of delivered beams. This dynamic enables, on one hand, a steadily growing community of (young) users covering a wide range of research, which feeds back, and on the other, with resourced motivation for a continued development and coexistence of nuclear, atomic, solid state and biophysics research.

At ISOLDE the radioactive nuclei are produced through spallation, fission or fragmentation reactions in thick targets by the 1.4 GeV (1-2 μ A) proton beam from the CERN PS-Booster [2 - 5]. The target material and morphology are chosen to optimize production and release time of the desired isotope. The mass range mainly determines the target species (UC_2 , ThO, CaO, ZrO, YO, SiC, Ta, Nb, Sn, Pb) while the half-lives determine the morphology (solid discs, foils, powders, or liquid and nanostructured materials) aiming to optimize production and extraction of the desired isotopes. The target container is made of tantalum and heated to very high temperatures to allow the reaction products to diffuse within the target material and reach the surface. Then, by releasing from the target surface the radioactive elements are vaporized and conducted by a transfer line into several types of element-selective ion sources. In this way, the ISOLDE group develops different types of element-specific target-ion-source combinations that allow the use of more than 1000 radioactive isotopes and isobars of about 75 elements.

For two decades, efforts have been successful in improving the element selectivity at ISOLDE by developing state-of-the-art ion-sources consisting of tuneable multi-wave laser beams, which provide

clean radioactive beams of, e.g., Ag, Ni, Mn, Be, Cu, Zn and Cd [6 - 9]. The extracted ions are then accelerated to 60 keV and mass (M) separated by analyzing magnets.

Two independent mass separators are available at ISOLDE: - the General Purpose Separator (GPS) provides mass separation with a resolving power $M/\Delta M = 2400$ for 20 mm mrad beams. It is designed to provide up to three simultaneous beams, within a mass range of $\pm 15\%$, delivered to the beam lines in the experimental hall. The second mass separator, the High Resolution Separator (HRS), is equipped with two bending magnets achieving routinely $M/\Delta M > 6,000$.

To post-accelerate radioactive ion beams a low cost radio frequency quadrupole (RFQ) acceleration Linac [10 - 13] has been coupled to the low energy ISOLDE beam line. Before the Linac, the primary ISOLDE beam is continuously injected into a Penning trap which transforms a continuous ($1+$) beam to a bunch of cooled ions. These are then transferred to an Electron Beam Ion Source (EBIS) in order to achieve a charge to mass ratio larger than $1/4.5$. After selection of the desired charge to mass ratio by dipole magnets, the ions are gradually accelerated by a RFQ-structure, an interdigital H-type (IH) structure and three 7-gap resonators to a final energy of about 2.2 MeV/u. An efficiency of about 10% is achieved, essentially given by the EBIS ionization efficiency. For investigations in solid-state physics, lower energies between 1 and 10 MeV / A can be obtained. For energies below 1 MeV/A, a low charged ion beam ($4+$) coming out of the EBIS could be injected through an electrostatic high voltage 0-260 kV acceleration lens [14].

The post-acceleration of the ISOLDE beams opens new perspectives, particularly to produce polarized beams with the tilted foil technique. Presently, the feasibility of using polarized beams and β -NMR to study the binding of metal ions (Cu, Fe, Co, Zn, Mo, Ni) to biological macromolecules is being tested [15]. Since ever more energetic radioactive beams have a wide range of applications in nuclear and astrophysics research, CERN has recently approved the HIE-ISOLDE upgrade project [16], to be commissioned by 2016. This RIB upgrade contains three major issues: higher energies, improvements in beam quality and flexibility, and higher beam intensities, which require developments in radioisotope selection, improvements in charge breeding and target-ion source development. Most of the existing REX accelerating structure will be replaced by a superconducting linear accelerator with a maximum energy of 10 MeV/u. In this way all ISOLDE beams will be available within a large spectrum of energies, well below and significantly above the Coulomb barrier, boosting a large programme of nuclear structure and nuclear astrophysics studies using different classes of nuclear reactions.

1.2. Radioisotopes for materials and life sciences

The high intensity and wide range of radioactive isotopes has made ISOLDE a unique facility for solid-state and life science research. Such a scientific program was started in the late seventies with some pioneering experiments, e.g., by implanting the short-lived $^{111\text{m}}\text{Cd}$ and ^{119}Cd isotopes into non-cubic metals to study electric field gradients of impurities in metals [17]. Since then the work at ISOLDE has diversified, as previously reported in several reviews [18 - 28].

Figure 1 illustrates the panoply of elements which are produced at ISOLDE and have at least one radioactive isotope suitable for use as nanoscopic probes in solid-state and biophysics research. The whole spectrum of sophisticated techniques, which are being used at ISOLDE can essentially be divided into two groups:

1) TRACER TECHNIQUES where the half-life or simply the decay particles provide the element signature information and quantification.

2) NUCLEAR TECHNIQUES where the impurity/element position on lattice sites is directly measured, or where the probe element interaction with the host matrix is investigated via the measurement of the electronic charge density and symmetry, or of the magnetic fields, in the probe's neighbourhood.

H	H Available at ISOLDE																He	
Li	Be											B	C	N	O	F	Ne	
<i>C</i> <i>N</i>	<i>C</i>															→ <i>P</i>		
Na	Mg											Al	Si	P	S	Cl	Ar	
<i>C</i> <i>N</i>	<i>C</i> <i>N</i>																	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
<i>C</i>	<i>C</i>					<i>C</i> → <i>M</i>	<i>C</i>	<i>C</i>	<i>C</i>			<i>C</i>	<i>C</i> ← <i>P</i>	<i>C</i> ← <i>P</i>	<i>C</i> ← <i>P</i>	<i>P</i> ↔ <i>P</i>		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
<i>C</i>	<i>C</i>											<i>C</i> → <i>P</i>	<i>C</i> ↔ <i>P</i>	<i>P</i> → <i>PC</i>	<i>C</i> ← <i>M</i>	<i>M</i> ← <i>C</i>		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
<i>C</i> ← <i>P</i>	<i>C</i>							<i>P</i> ←	← <i>M</i>	← <i>C</i>	<i>P</i> ←				<i>C</i>	<i>C</i>	<i>C</i>	
Fr	Ra	Ac																
<i>C</i>	<i>C</i>																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			<i>C</i>	<i>C</i>	<i>C</i>	<i>C</i>	<i>C</i>	<i>M</i> ← <i>C</i>	<i>C</i> ←				<i>C</i> ←	<i>C</i> ←	<i>C</i> ←	<i>C</i> ←		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Figure 1: Periodic table of the elements produced as primary beams at ISOLDE. Shadowed frames show elements for which currently highly pure beams are produced with the laser ion-source. Elements that have isotopes, which are adequate for applied research at ISOLDE are also shown. Open N, M, P symbols assign probe elements with suitable cascades for β -NMR, Mössbauer or Perturbed Angular Correlations, respectively, when these are only obtained by β - decay (as indicated by the left arrow $\rightarrow$) or when obtained by electron capture and β -decay ($\leftarrow$). Closed symbols assign the existence of isotopes allowing the measurements to be done at the parent element without transmutation. Emission channeling, EC, studies and “tracer” techniques that only require charged particle emission and suitable decay half-lives are among the most versatile techniques, with almost all of the periodic table available for experiments. Underlined symbols indicate foreseen candidates for experiments.

2 – Tracer Techniques

2.1 Diffusion studies

Diffusion of impurity atoms in crystals can be studied by techniques like secondary ion mass spectroscopy (SIMS) or spreading resistance profiling (SRP), which have been developed to study diffusion profiles with depth resolutions of the order of nanometres. For specific applications such as highly diluted systems, self-diffusion and, in particular, studies of amorphous materials, radioactive tracers are particularly useful. The sensitivity is increased by orders of magnitude and, when combined with ion implantation, it avoids the deposition of thin transition-metal layer on the amorphous material which leads to significant modifications of the recrystallization temperatures. Back in the twenties, the first solid state physics experiment using radioisotopes was reported by G. v. Hevesy with the study of self-diffusion in solid lead (1921) by using the natural radioactive isotopes ^{210}Pb and ^{212}Pb [29]. An older example of such a kind of studies at ISOLDE is the finding of anomalous diffusion of low concentrations of gold in amorphous silicon, where it is shown that interstitial diffusion of Au in a-Si is significantly retarded by the presence of intrinsic defects, presumably immobile vacancy-type defects which trap the Au atoms [30].

An environment – such as at ISOLDE - where nuclear and solid-state physicists work side-by-side, provides a fertile ground for developing sensitive new methods. In a different type of experiment, α -particles emitted from the decay of implanted short-lived nuclei furnished a promising tool for diffusion profiling, due to the fact that the energy spectrum of the α -particles is particularly sensitive to the path length travelled within the sample. A test experiment using this method showed that the diffusion coefficient of ^{221}Fr implanted in potassium is several orders of magnitude larger than the potassium self diffusion coefficient [31].

In recent years tracer diffusion studies have dealt with transition metal diffusion in CdTe [32 - 37], diffusion of Be, Ga, and Sn in Ge and SiGe alloys [38], of Be in glassy carbon [39, 40] and of Mn in GaAs [41]. Of particular technological importance is the fact that the diffusion of charged dopant atoms is strongly affected by the presence of an internal electric field [42]. As a consequence, if an inhomogeneous distribution of charged defects is present, an internal electric field is generated acting on any charged particle present in the semiconductor. An internal electric field can also be generated exclusively by intrinsic defects if they act as donors and acceptors and are inhomogeneously distributed. One example of these phenomena is the diffusion of Ag, and, to a lesser extent also, of Cu in CdTe, which shows several very unusual properties depending on the sample conditions before diffusion and on the external conditions during diffusion.

Figure 2 shows a selected example of such type of diffusion behaviours where several concentration profiles are presented for the radiotracers ^{111}Ag , ^{67}Cu , ^{193}Au , and ^{24}Na measured in CdTe crystals after implantation and subsequent diffusion under external Cd vapour pressure.

All profiles are symmetrical with respect to the centre of the samples and exhibit 100–250 μm layers, below both surfaces, with low diffuser concentrations. Since the diffusion starts from a sharp, implanted profile on one surface as compared to the thickness of the crystal, the dopant atoms have to diffuse throughout the samples, from low to high concentration, in order to form this type of profile. Such unusual diffusion behaviour is called uphill diffusion and is due to the fact that these particular tracer elements are all fast interstitial diffusers, which are also electrically active interstitial donors, e.g. Ag_i^+ , Na_i^+ . The CdTe crystals are initially Te-rich but upon diffusion under a Cd atmosphere the surface regions become Cd-rich due to the in-diffusion of interstitial Cd_i . Since intrinsic CdTe point defects such as Cd_i and Cd vacancies, V_{Cd} , form shallow donor and acceptor levels in the band gap, upon diffusion under Cd atmosphere *pn*-junctions are established on both sides of the crystal. This is a consequence of the fact that *n*-type regions with Cd-excess develop near both surfaces while a *p*-type region with Te-excess remains in the center of the samples. When in thermal equilibrium with the host crystal, the fast interstitial donor impurities will mirror the profile of the electric potential across the crystal, in the present cases, by increasing the concentration in the Te rich region.

The extended research program envisaged on these subjects at ISOLDE can be found in ref. [43]. For this purpose a new setup is being commissioned at the University of Saarbrücken, which will allow implantation, annealing, sectioning of the sample by ion sputtering, and measurement of short-lived tracers (few minute half-lives) by detecting the decay-radiation, in situ.

Figure 2: Uphill diffusion profiles measured for the radiotracers ¹¹¹Ag, ⁶⁷Cu, ¹⁹³Au, and ²⁴Na in CdTe annealed under Cd atmosphere. The solid lines are simulations according to the model described in Ref. [33]. Note that the left and right end of the d-axis correspond to the two surfaces of the ~750 μm thick samples.

2.2 Non-standard tracer studies

About 25 years were needed from the first, unsuccessful attempts [44], to develop new “tracer” techniques combining standard electrical or optical measurements - commonly used in semiconductor physics, with the use of radioactive isotopes. It was first successfully demonstrated with the identification of the Deep Level Transient Spectroscopy (DLTS) signals from Au and Pt implanted Si, that when the radioactive decay involves the chemical transmutation of the dopant, the electrical properties of the semiconductors will change in time with the characteristic time constant of the radioactive decay [45]. Immediately after, techniques as Hall effect [46], DLTS, Capacitance-Voltage measurements [47, 48] and Photoluminescence Spectroscopy [49, 50] have proven to be quite useful when using radioactive isotopes to overcome the chemical “blindness” of non-radioactive methods, in studies of the electrical activation of impurities in intrinsic, III-V [51], and II-VI compound semiconductors [52].

Figure 3 shows one of the first – but illustrative - examples of PL spectra performed on samples doped with radioactive isotopes. In that work ^{111}In (2.83d) was implanted into MBE-grown GaAs and the PL spectra were measured as a function of time. The spectra show the increase with time of two PL peaks (at higher wavelengths, to the right of a peak identified as being due to the sample’s carbon contamination) which could be clearly assigned to $^{111}\text{Cd}_{\text{Ga}}$ acceptors generated from the decay of ^{111}In at Ga sites [51].

Figure 3: Examples of PL spectra of undoped and ^{111}In doped GaAs successively taken 4 h, 7 h, 12 h, 22 h, 2 d, 4 d, and 9 d after doping. All spectra are normalized to the intensity of the (e,C) peak. In the inset, the height $I_{\text{Cd}}/I_{\text{C}}$ of the (e,Cd) peak in these spectra is shown as a function of time after doping with ^{111}In . The solid line is a fit to the data, which includes the characteristic decay time constant of the $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ nuclear transmutation, as explained in Ref. [51]. Reprinted with permission from Ref. [51]. Copyright 1995, American Physical Society.

More recently, the properties of donor-related impurities in ZnO were studied using both stable atom implantations and radiotracer techniques [53]. Photoluminescence measurements were performed as a function of time, on ZnO implanted with radioactive isotopes ^{72}Zn and ^{73}Ga . The first of these isotopes decays to stable ^{72}Ge via ^{72}Ga , with half-lives of 46h and 14h, while the latter is a direct decay to stable ^{73}Ge with a half-life of 4.9 h. New data are presented that establish the association between the I_8 and I_1 bound exciton recombination with Ga, and luminescence attributed to Ge-related deep defects in ZnO. In detail, these experiments clearly identified a donor-related exciton feature I^8 at 3.3600 eV originating from bound exciton recombination at Ga donors. The I_1 line at 3.3718 eV is also likely to be due to Ga, and is attributed to ionized Ga donor bound exciton recombination. A feature at 3.3225 eV is observed following transmutation of radioactive Ga into stable Ge, and is attributed to Ge.

On a different but quite exciting new topic, it has been found that the use of highly enriched stable ^{28}Si samples could reveal many new features of well-resolved isotopic fingerprints, due to the reduction in the photoluminescence line-width of many deep luminescence centres [54]. This allows for a better characterization of a defect center, as not only the involvement of a specific element but also the number of atoms of that element within the complex can be determined. Using such type of

isotopically enriched material a consistent working program has been started with the aim to show that many well-known luminescence centers have a different composition than originally supposed. A large number of four- and five-atom luminescence centers involving the elements Cu, Au, and Li were already identified and a series of four- and five-atom deep luminescence centers involving a single Pt atom together with Cu and Li, similar to what has been seen previously for Au-containing luminescence centers has recently been measured [55]. Since there exists only one stable gold isotope in nature (^{197}Au), ISOLDE was used in order to provide a gold isotope of a different mass, with the same samples being useful for Pt studies after the decay.

3 – Nuclear Techniques

Emission Channeling (EC), Mössbauer Effect (ME), Perturbed Angular Correlations (PAC) and β -Nuclear Magnetic Resonance (β -NMR) represent the most common nuclear techniques using radioactive isotopes at ISOLDE. With these techniques, the radioactive nuclei are used as atomic scale *spies* in matter. They investigate impurity and dopant lattice sites in a single crystal, its local electronic environment in bulk solids, at surfaces and interfaces, and are used also to investigate the behaviour of single atoms attached to matter in molecular form.

All of these techniques depend critically on the availability of an appropriate radioactive isotope for a certain element. By emitting a specific decay particle or by just having excited states with the right spin and nuclear moments, radioactive isotopes overcome the limitations of ground states and stable nuclei. Hyperfine techniques (ME, PAC and β -NMR) rely on the interaction of the nuclear states, quadrupole and magnetic moments, with the electron density, electric field gradient (EFG) and magnetic hyperfine fields at the probe's location. By probing this information they provide nanoscopic scale information on defect structure, defect dynamics and electronic configuration. The EFG, in particular, provides information on the local charge density distribution and acts as a fingerprint of a specific defect trapped by the probe nuclei. These techniques are also used complementarily, e.g., while isomer and chemical shifts are only measured with ME, PAC is essentially temperature independent and a wider range of probe nuclei can be used.

3.1 Emission channeling

Since 1985 the emission channelling (EC) technique has been used at ISOLDE to determine with great accuracy the lattice site of dopant elements, by implanting their radioactive isotopes into single crystals. Upon decay, the nuclei emit charged particles, e.g., α , $\beta^{+/-}$, and conversion electrons, (e_c), which, emerge from the crystal, experience channeling or blocking effects along low-index crystal directions [56]. EC makes use of the fact that near the principal crystalline axes the particle emission yield from the crystal surface is anisotropic, depending in a characteristic way on the lattice sites occupied by the emitter atoms. A clear advantage of EC over Rutherford Backscattering/Channeling (RBS/C) is the fact that any element, lighter or heavier than the host matrix, can be used without sensitivity loss, since only the existence of a radioactive isotope decaying with charged particles is required. A very good report of such type of work is presented in ref. [57], where alpha particles

emitted from the decay of the short lived ^8Li are used to perform detailed lattice location studies of Li in elemental and compound semiconductors, to fluences even below 10^{12}cm^{-2} .

During 1997, as a result of a collaboration with detector groups at CERN currently developing new readout technologies for high-energy particle physics, a position-sensitive electron detector ($3\times 3\text{cm}^2$, 22×22 pixels) was successfully commissioned to perform EC experiments. Since then the EC technique has been boosted to high efficiency and improved angular resolution [58, 59]. In recent years, this technology got a further boost when much faster detectors - able to read up to 4 kHz events-rate - were developed. In 2007 one of these new detectors was implemented for EC experiments, opening up a panoply of new probing elements from where ^{56}Mn (2.6 h), ^{61}Co (1.6 h) and ^{27}Mg (9.5 min) are the most recent case studies [60].

During the last five years EC experiments focused on the lattice location of dopants and impurities in compound semiconductors ZnO [61 - 64], GaN [65, 66], AlN [67] and Si [68, 69], as well as on Ge. In the particular case of Ge, besides the preferred substitutional sites, the following impurities were found to occupy the so-called bond-center (BC) site: Er [70], In [71], the transition metals Fe, Cu and Ag [72], and Sn [73]. By investigating the formation energy of defect complexes with the help of density functional theory, the BC location was identified to be the preferred location for certain foreign substitutional atoms on interaction with a single vacancy. Hence, the impurity element relaxes to the BC site, opening an extra vacancy, and remaining in the mid-position of the two adjacent Ge vacancies, the so-called split-vacancy configuration.

Figure 4 shows a selected set of β - emission channeling patterns resulting from the decay of ^{111}Ag implanted into Ge. The experimental data can only be explained by assuming that they result from a superposition of emission channelling patterns originated from Ag on substitutional (Ag_S) and BC sites (Ag_BC), with the best fit results obtained for $\sim 20\%$ of $^{111}\text{Ag}_\text{S}$ and $\sim 37\%$ of $^{111}\text{Ag}_\text{BC}$ sites.

Figure 4: (a)–(d) Two-dimensional β -emission channeling patterns from ^{111}Ag in Ge around the $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 211 \rangle$ -axes, following 400 °C annealing in vacuum; simulated patterns for ^{111}Ag on the S site and on the BC site, respectively, are shown in panels (e), (f) for the $\langle 111 \rangle$, (g), (h) for $\langle 100 \rangle$, (i), (j) for $\langle 110 \rangle$ and (k), (l) for $\langle 211 \rangle$ -axes; (m)–(p) are the best fits to the experimental patterns, consisting of a superposition of $\sim 20\%$ S and $\sim 37\%$ BC patterns. From Ref. [72]. Copyright (2009) by the American Physical Society.

3.2 Hyperfine interactions techniques

3.2.1 - Perturbed Angular Correlations – Solid State Physics

In the late 1970s γ - γ Perturbed Angular Correlation (PAC) was introduced at ISOLDE [17]. γ - γ PAC is based on the observation of perturbations in the half-life time histogram of an intermediate state on a two – gamma quanta cascade. To extend the use of the technique to probe elements with highly converted electron cascades, e_c - γ PAC was later introduced in the 1990s [74]. PAC allows the measurement of the local electrical field gradient (EFG) and the magnetic field that a probe nucleus experiences when embedded in matter, independent of its physical state, i.e., solids, liquid, amorphous and molecules can be studied with PAC. Initially the bulk of the experiments at ISOLDE concentrated on semiconductors and on metal surfaces which has already been extensively reviewed in the past [20 - 25, 27, 28, 75]. During the last couple of years, the PAC work at ISOLDE in the field of semiconductors has concentrated on experiments using the probes ^{111}In , $^{111\text{m}}\text{Cd}$, ^{115}Cd , ^{117}Cd , and ^{111}Ag in the nitride semiconductors AlN, GaN, and InN. The general aim is to better characterize the properties of In, Cd and Ag impurities in nitrides, e.g., In is of relevance for understanding the technologically important ternary nitride $\text{In}_x\text{Ga}_{1-x}\text{N}$ [76]. Another experiment is exploring the feasibility of PAC experiments with several rare earth probes in nitride semiconductors, using for this purpose a new concept of PAC spectrometer with all-digital electronics and data acquisition, aiming to optimize gamma selection on complicated decay cascades [77].

The selected PAC examples shown here have been chosen from two very different fields which have gained increasing importance over recent years; e.g., a solid state physics case where electronic phase transitions in manganites are regarded at the microscopic level and a biophysics example where PAC assesses the function and toxicity of metal ions in biological systems.

The first example concerns manganese oxides of the manganite type, where several degrees of freedom coexist leading to a rich phenomenology at the microscopic level where charge, magnetism and lattice coordinates can be coupled and ruled by doping. The particular case of the mixed valence compound $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ has an orthorhombic distorted perovskite structure and belongs to the class of multiferroic oxides, i.e., it shows a combination of ferroelectric and magnetic behaviour, which in this case is associated with the occurrence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence charge order in the material. The PAC probe $^{111\text{m}}\text{Cd}$ (48.5 min) was implanted into different $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds, where it is incorporated on Ca sites [78, 79, 80, 81]. The electrical field gradient experienced by the probe atoms was then measured as a function of temperature [Figure 5 (d)-(f)] across the charge order (CO) phase transition that was established from the magnetic susceptibility [Figure 5 (a)-(c)]. At low temperatures,

in the CO regime, where the samples are ferroelectric or antiferroelectric, a slight temperature dependence of the main component V_{zz} of the EFG is observed, which decreases slowly with the increasing temperature until a prominent discontinuity is reached and a sharp increasing jump in V_{zz} occurs at a temperature T_{EDO} close to, but clearly below the charge order temperature T_{CO} , followed again by a less sharp decrease. The soft temperature dependence of the EFG below T_{EDO} was attributed to the onset of electrical dipole fluctuations at the probe site and T_{EDO} itself is hence interpreted as the temperature where electrical dipole order is lost completely, which surprisingly occurs clearly below the temperature T_{CO} where Mn^{3+}/Mn^{4+} valence charge order itself is disappearing. In conclusion, the PAC measurements gave clear evidence for a new phase transition occurring below the charge order transition in $Pr_{1-x}Ca_xMnO_3$ and it was interpreted in terms of a paraelectric to (anti)ferroelectric first-order phase transition related to electric dipole ordering.

Figure 5: Top row: temperature dependence of the inverse magnetic susceptibility $1/\chi$ for $Pr_{1-x}Ca_xMnO_3$ samples with $x = 0.35$ (a), $x = 0.40$ (b), and $x = 0.85$ (c). Bottom row: temperature dependence of the electrical field gradient V_{zz} seen by the radioactive ^{111m}Cd nucleus and corresponding fits below the charge order transition using the Landau theory of phase transitions for $x = 0.35$ (d), $x = 0.40$ (e), and $x = 0.85$ (f). Reprinted with permission from Ref. [79]. Copyright 2008, American Physical Society.

3.2.2 - Perturbed Angular Correlations – Biophysics

Since the beginning of the 1990s both biophysics and medical applications have embraced the ISOLDE research program. But, while biophysics has remained steadily active, medical applications – mainly concerning the production of radioisotopes for small-scale clinical studies [82], e.g., in cancer therapy - have declined in the past few years. This tendency seems now to have been reversed, with the submission of a new proposal to resume this activity at the upgraded HIE-ISOLDE facility [83].

Biophysics studies using the PAC technique with the probe nuclei $^{199\text{m}}\text{Hg}$ (43 min) and $^{111\text{m}}\text{Cd}$ (48 min) generally aim to identify the binding sites, ligands, and dynamic interactions of probe atoms attached to large biomolecules under specific conditions such as temperature, ambient solution, pH, etc, as partially reviewed by Hemmingsen [84] and Chain [85]. For that purpose, the radioisotopes are implanted in ice held at liquid nitrogen temperature so that, after removing the beam catcher from the vacuum chamber, the radioactive probes are directly available for biochemical processing in aqueous solution using a small chemistry lab located on-site. PAC spectra are then typically recorded by 6-detector setups [86] that are shared with the materials science community. Initially, in the work of Butz and Tröger [87 - 89], the main subjects were blue copper proteins doped with radioactive $^{199\text{m}}\text{Hg}$, while more recently the study of Hg-binding peptides and Zn-binding proteins emerged [90 - 92], both with the general aim to assess the function and toxicity of metal ions in biological systems.

Figure 6 shows the Fourier transforms of the $^{199\text{m}}\text{Hg}$ PAC spectra corresponding to the pH titration of a solution containing the peptide TRI L9C and Hg(II) ions (stable Hg carriers plus $^{199\text{m}}\text{Hg}$) at a peptide/ Hg(II) ratio of 12:1. While only one nuclear quadrupole interaction type (characterized by one single frequency triplet) is found for the experiment at pH 6.5, upon increasing the pH of the solution another set of signals appears in the PAC spectra, which then remains responsible for the major part (90%) of the signal at pH 8.7. At this pH value, the fitted PAC parameters indicate the formation of a complex with a trigonal-planar $[\text{Hg}(\text{TRI L9C})_3]$ coordination geometry, while the fitted PAC parameters for the species at low pH compare reasonably well with published data for linear $[\text{Hg}(\text{TRI L9C})_2]$ coordination geometry, supporting the formation of a dithiolate– Hg(II). The results support the existence of a dithiolate– Hg(II) complex encapsulated within a three-stranded coiled coil and a stepwise aggregation– deprotonation mechanism. For the future, it is planned to extend the ISOLDE biophysics experiments to in vivo studies, i.e., by introducing the PAC probes into living plants.

Figure 6: $^{199\text{m}}\text{Hg}$ PAC spectra of solutions containing TRI L9C (125–130 nm) and HgCl_2 (10.8 mM) at different pH values. The thin lines represent the Fourier transform ($F(\omega)$ in arbitrary units) of the experimental data and the bold lines represent the fit. Reprinted with permission from Ref. [90]. Copyright 2008, Wiley VCH Verlag.

3.2.3 - Mössbauer Effect

By yielding information on the charge state of probe atoms and on the materials electrical field gradients and magnetic fields interacting in their neighbourhood, Mössbauer spectroscopy is the oldest and the only worldwide-known hyperfine technique using radioisotopes in Materials Science. This is mainly due to the well-known ^{57}Fe (14.4 keV, 98 ns) isomeric state, i.e., an optimum case to be resonantly excited from decay of the long-lived ^{57}Co (271 d) gamma-ray source. The fact that 2.2% of the isotopic composition of natural iron is made of ^{57}Fe , further guarantees that $^{57}\text{Fe}/^{57}\text{Co}$ Mössbauer experiments remain preponderant in applied materials research.

To extend applications and the number of available probe elements for Mössbauer spectroscopy, two independent and complementary ways are investigated, both requiring the use of large-scale facilities, which aim to work with *no radioactive sources* or with *short-lived isotopes*. In

the case of no use of radioactive isotopes, the excitation gamma quanta are produced by proper wavelength filtering of synchrotron radiation to induce the nuclear resonant excitation, as had been proposed in the late 1950s and pointed out in ref. [93]. The advent of powerful synchrotron facilities for multipurpose use in materials, chemical and biophysics research, provides today a fertile ground for developing such techniques with great potential [94]. In the alternative and complementary case, highly pure beams of short-lived isotopes, produced on-line at radioactive ion beam facilities, are used to increase the number of available probe elements. For this reason, Mössbauer spectroscopy was introduced at ISOLDE in the late 1970s and is today being applied to new and exotic ME experiments as was recently reviewed by Weyer [95]. Studies of the structure and electronic states of impurity-vacancy complexes in III-V semiconductors and of Sb doping of Si-based semiconductors such as SiGe alloys have been performed at ISOLDE, by using the first excited state at 24 keV in ^{119}Sn , which is obtained either by the decay of the long-lived ^{119}Sb (38.2 h) or by decay of the short-lived ^{119}In (18 min) isotopes [96]. Such studies have been particularly extended to the wide band gap GaN semiconductor, by implanting ^{119}Cs which decays through the $^{119}\text{Xe} \rightarrow ^{119}\text{I} \rightarrow ^{119}\text{Te} \rightarrow ^{119}\text{Sb}$ isobaric chain to the Mössbauer ^{119}Sn nucleus. Since the recoil energies (>50 eV) are large enough to place, at the end of the decay chain, ^{119}Sb in Ga and N sites, this technique enables the measurement of isomer shifts, i.e., the electron densities, for Sn donors and acceptors on Ga and N sites, respectively [97].

In 1996, the technique received a considerable boost with the introduction of Mn laser ionisation sources at ISOLDE which made it possible to obtain high-intensity isotopically clean beams of the short-lived (1.5 min) ^{57}Mn that decays into the well-known $^{57*}\text{Fe}$ (98 ns) level. In comparison to $^{57*}\text{Fe}$ Mössbauer studies which use long-lived ^{57}Co sources, both in absorption and emission mode, the short half-life of ^{57}Mn in combination with the high purity- high - intensity beam available at ISOLDE (up to 2×10^8 at/s corresponding to ~ 30 pA) allows for several orders of magnitude faster data acquisition, making it possible to record hundreds of Mössbauer spectra per day. This is a particularly revealing example of the uniqueness and versatility of ISOLDE, far in the forefront of worldwide radioactive ion beam facilities. Since then, $^{57}\text{Mn} \rightarrow ^{57}\text{Fe}$ Mössbauer experiments have been undertaken in a large variety of semiconductors and oxides, with a focus on Si, $\text{Si}_x\text{Ge}_{1-x}$ [98], diamond [99] and especially ZnO [100 - 103] in recent years.

The example that will be briefly presented here relates to the long standing problematic of local magnetism at dilute Fe atoms in ion-implanted ZnO [100].

Figure 7 shows $^{57}\text{Mn} \rightarrow ^{57}\text{Fe}$ Mössbauer spectra, which were recorded during the implantation of low fluences ($< 10^{12} \text{ cm}^{-2}$) of ^{57}Mn at various temperatures. Below 600 K the Mössbauer spectra clearly show a pronounced sextet resulting from magnetic interaction of Fe^{3+} , on which two doublets D2 and

D3 are superimposed, resulting from quadrupole-split $\text{Fe}^{2+}(\text{Zn})$ and interstitial Fe_i , respectively. In addition two distributions (Dist. II and Dist. III) of magnetic signals were seen. For higher implantation temperatures the magnetic interaction gradually disappears until 770 K when only the weakly split D2 quadrupole doublet remains, which was interpreted as substitutional $\text{Fe}^{2+}(\text{Zn})$ on Zn sites. However, from these data alone, it was not possible to determine whether ferromagnetism or paramagnetism was responsible for the observed magnetic sextet [100]. The same group has recently shown, by means of measuring the angular dependence of the Mössbauer spectra in an external magnetic field, that the coupling is clearly paramagnetic and ferromagnetism could be ruled out [103], which obviously reduces the perspectives for ZnO:Fe acting as a true dilute magnetic semiconductor.

Figure 7: On-line Mössbauer spectra from the $^{57}\text{Mn} \rightarrow ^{57}\text{Fe}$ decay obtained in ZnO as a function of implantation temperature. The solid black lines are fits to the data points resulting from the superimposition of the various contributions shown in colour, as is explained in the text. Reprinted with permission from Ref. [100]. Copyright 2007, American Institute of Physics.

4 – Conclusions and Perspectives

The interface between nuclear and solid state physics has always been a fertile ground for discovering new phenomena and attractive applications. ISOLDE is a place of dynamic interaction between Solid State and Biophysics researchers on one side and Nuclear and Atomic physicists and their state-of-the-art techniques on the other. The permanent R&D program on beam variety, purity and energies guarantees that ISOLDE remains in the forefront of thick target technologies for the production of radioactive isotopes. The combination of these factors assures a bright future for ISOLDE's "exotic", still unique, physics in materials research as well as encouraging the development of complementary facilities, which could increase the availability of beam time, quite tight today due to the great demand by many different groups from all branches of physics.

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