Materials Characterization with Radioactive Nuclear Techniques

João Guilherme Martins Correia

A **laboratory infrastructure** dedicated to advanced materials research is maintained and developed at ISOLDE-CERN by the Nuclear Solid State Physics group of ITN and CFNUL. ISOLDE is a European Large Scale Facility that produces highly pure elemental and isotopic ion beams of more than 1000 isotopes and isobars of 80 elements, which is a unique feature in the world. In this context nuclear techniques such as Emission Channelling (EC) and Perturbed Angular Correlations (PAC) provide local- atomic-scale information complementing material analysis capabilities at ion beam, x-ray and microscopy laboratories. This infrastructure and related projects are refereed and evaluated each year within the scope of FCT - CERN projects. The scientific work in 2011 was centred in several research subjects approved by the ISOLDE-CERN (INTC) Scientific Committee:

1) IS453 (U.Wahl) "Emission Channelling Lattice Location Experiments with Short-Lived Isotopes". EC experiments study the lattice sites of dopants and impurities in scientifically and technologically relevant semiconductors (e.g., Si, Ge, ZnO, GaN and GaAs). Due to previous years efforts, elements having only suitable short-lived isotopes can now be studied on-line. In 2011, for the first time, Nickel sites were studied using the ^{65}Ni (2.5 h) isotope.

2) IS487 (V. Amaral) "Study of Local Correlations of Magnetic and Multiferroic Compounds". PAC studies a large variety os multiferroic manganites and cromites. By combining PAC data with first principle simulations of charge density distributions on these materials, local phenomena responsible for the coexistence of ferroelectricity, ferromagnetism and ferroelasticity are studied. 2011 was a year of concluding experiments, publications and of new discoveries, as the findings in $CdCr_2S_4$ that the puzzling relaxer behaviour in the paramagnetic (PM) regime is correlated to atomic displacements, where a new dynamic state caused by the presence of simultaneous polar and magnetic clusters is revealed.

3) IS481- addendum approved by INTC on Feb. 2011 (K. Lorenz) "The role of In in III-nitride ternary semiconductors", have combined γ-γ, e-γ and β-γ PAC using the ^{117}Cd/^{117}In, ^{111m}Cd/^{111}Cd, and the ^{115}Cd/^{115}In isotopes. The aim is to study the intrinsic nature of In/Cd defects in $Al_xGa_{1-x}N$ alloys, in order to understand the role of In, in the extraordinary luminescence performance of III-nitride semiconductors and to investigate Cd as a possible p-type dopant.

In early spring two new research proposals have been approved (V.Amaral): *"Radioactive probe studies of coordination modes of heavy metal ions from natural waters to functionalized magnetic nanoparticles"*, and a letter of intent, *"Radioactive Local Probing and Doping on Graphene"*.

2011 will further stay as a reference year due to the donation by the Leipzig University to ITN of their full PAC laboratory, just matching the essential needs of our groups and projects at ISOLDE to run multiple experiments in parallel during beam times. From the three highly efficient 6- detector arrays delivered, we point the new and unique digital spectrometer equipped with 6- $LaBr_3$ detectors and FPGA data acquisition and processing technology. Thanks to this setup, with outstanding energy and time resolution, we report the first ever done PAC measurement onto decay of ^{61}Cu/^{61}Ni, a probe element adequate for nanoscopic scale studies on solid-state and bio-physics materials.

In parallel, the new high-resolution Panmure goniometer, dedicated to on-line experiments with short-lived isotopes, was commissioned on-line at the GHM beam-line, a new arc-furnace has been tested for synthesising and study special compounds *in situ*, and new fast PAD detectors were tested for EC experiments.

Of interdisciplinary nature, these activities integrate and initiate students from different backgrounds and universities, in applied nuclear physics,with shared work between the different environments of ITN and ISOLDE. The work is carried out by students and senior researchers from the universities of Lisbon, Aveiro, Porto, Braga, ISEL as well as from Leuven in Belgium and Bonn in Germany. During 2011 three Ph.D. students defended their thesis; five other Ph.D., two M.Sc. and one Diploma students are performing their work using this infrastructure within the scientific proposals and R&D projects.

Research Team

Researchers

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U. WAHL, Princ.(75%)
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K. LORENZ, Aux., FCT (15%)

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IS453 experiment: Emission channelling lattice location studies

U. Wahl, J.G. Correia, E. Alves, L. Pereira[1,2], S. Decoster[1], L. Amorim[1], A. Vantomme[1], D.J. Silva[2], J.P. Araújo[2], M.R. da Silva[3,4], E. Bosne[5] and the ISOLDE collaboration

Objectives

Lattice location of diluted impurity-dopant elements on relevant materials.

Results

1. Mixed Zn and O substitution of Co and Mn in ZnO

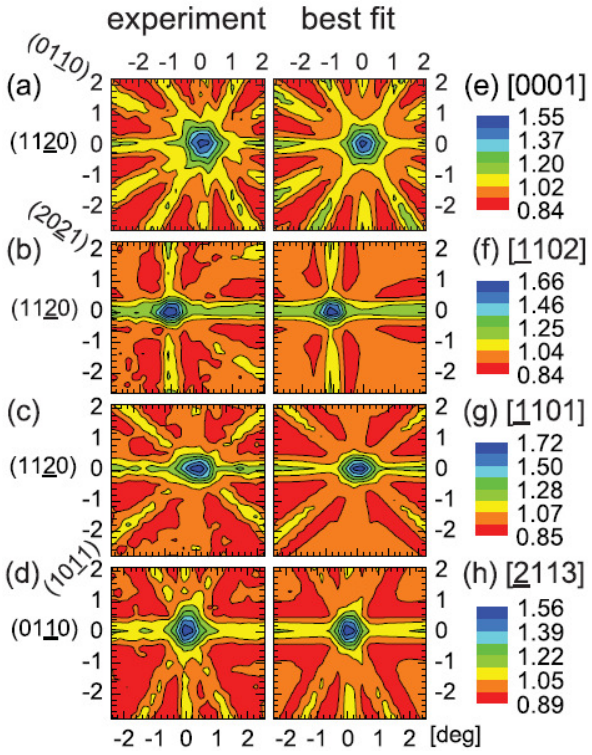

Fig. 1: (a–d) Normalized β^- emission channeling patterns from ^{61}Co in ZnO in the vicinity of the [0001], [-1102], [-1101], and [-2113] directions. (e–h) Corresponding best fits with 82% and 18% of the ^{61}Co atoms on S_{Zn} and S_O sites, respectively.

The physical properties of an impurity atom in a semiconductor are primarily determined by the lattice site it occupies. In general, this occupancy can be correctly predicted based on chemical intuition, but not always. We report on one such exception in the dilute magnetic semiconductors Co- and Mn-doped ZnO, experimentally determining the lattice location of Co and Mn using β^- emission channelling from the decay of radioactive ^{61}Co and ^{56}Mn implanted at the ISOLDE facility at CERN. Surprisingly, in addition to the majority of doping ions substituting for Zn, we found up to 18% (27%) of the Co (Mn) atoms in O sites, which is virtually unaffected by thermal annealing up to 900 °C. As possible reason for the anion site occupancy we tentatively propose that the incorporation might be due to these transition metals assuming 4+ charge states when replacing O atoms under vacancy rich conditions such as those resulting from ion implantation. However, since an anion site configuration had never been considered before for any transition metal in any metal oxide material our experimental results suggest a change in paradigm regarding transition-metal incorporation in ZnO and possibly other oxides and wide-gap semiconductors.

2. Emission channelling with short-lived isotopes

In 2011 we performed three beam times with short-lived radioactive isotopes using our emission channelling on-line setup at the ISOLDE GHM beamline. During the Mg beam time we determined the lattice location of the potential acceptor ^{27}Mg (9.5 min) in GaN and AlN for implantation temperatures from RT to 800 °C. While the majority of Mg was found on substitutional Ga and Al sites, for the first time also a minority fraction on hexagonal interstitial sites could be clearly identified. In both cases the interstitial Mg was converted to substitutional Ga or Al sites at temperatures between 600 °C and 800 °C. During the Mn beam time we used the decay chain ^{61}Mn (4.6 s)→^{61}Fe (6 min)→^{61}Co (1.6 h) to determine the lattice location of Co in n-Si and p^+-Si, where the co-existence of Co on substitutional and tetrahedral interstitial sites was found. As a new radioactive probe we used for the first time ^{65}Ni (2.5 h) to determine the lattice location of Ni in *p*-Si, p^+-Si, n^+-Si, Ge, 3C-SiC, 6H-SiC, diamond, ZnO, GaN, *si*-GaAs, and n^+-GaAs. While the preliminary results show similarities to the previously investigated transition metals Fe, Mn and Co, also clear differences were observed, e.g. in Si the emission channelling effects disappeared already around 600-700 °C, most likely due to long-range diffusion of the Ni probes, which therefore seems to occur, similarly to Mn, at lower temperatures than for Fe or Co. Also Ni in Si showed a greater tendency to occupy bond-centered sites in Si, most likely related to more prominent reactions with double vacancies.

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IS487 – Local distortions in multiferroic AgCrO2 triangular spin lattice (IS487)

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The study of the electric-field gradients and magnetic hyperfine fields of the multiferroic $AgCrO_2$ triangular spin lattice is presented (*A.M.L. Lopes et al. PRB84, 014434, 2011).* Perturbed angular correlation measurements performed with $^{111}In/^{111}Cd$ (at the Ag site) at different temperatures, revealed the coexistence of two electric-field gradients, i.e., two distinct local environments (EFGu) and (EFGd) at temperatures below 100 K. The emerging second local environment (d) appears as a distortion of the Cr surroundings resulting in a local symmetry lowering, which emerges much above T_N and concomitantly with the onset of short-range magnetic correlations. The data was correlated with complementary magnetization and complex dielectric permittivity measurements. We give evidence that at $T \approx 100$ K and, concomitantly with the onset of short-range magnetic correlations, a local distortion of the Cr surrounding emerges. We show that when lowering the temperature below 100 K, and still above TN, part of the system loses the local rhomboedral symmetry. Hence, this effect is associated to the coupling of elastic and magnetic degrees of freedom that provide a channel for magnetic frustration release through a lattice distortion. Though we cannot ascertain the detailed nature of the new structure, we argue that the distortions in the $AgCrO_2$ system are not a simple deformation of the equilateral Cr lattice into an in-plane isosceles configuration. Complementary measurements and EFG simulations are still necessary to unveil the details of the distortion aiming the full understanding of these exquisite systems.

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IS481 – Cd doping of $Al_xGa_{1-x}N$ alloys via ion implantation studied with perturbed angular correlation

K. Lorenz, S.M. C. Miranda, J.G. Correia, P. Kessler[1], R. Simon[1], R. Vianden[1], K. Johnston[2]

$Al_xGa_{1-x}N$ ternary compound semiconductors, with wide bandgaps ranging from 3.4 eV (GaN) to 6.2 eV (AlN), are promising candidates for ultraviolet light-emitting diodes and laser diodes. However, the production of the required p-type material is still challenging in particular for alloys with high AlN content. As a possible dopant Cd was suggested among other Group II atoms (Be, Mg, and Zn). In this study the incorporation of implanted Cd in $Al_xGa_{1-x}N$ was investigated with the method of the perturbed angular correlation (PAC). Radioactive ^{117}Cd or ^{111m}Cd ions were implanted into thin $Al_xGa_{1-x}N$ films (with $0 \leq x \leq 1$) on sapphire substrate with an energy of 30 keV and fluencies in the range of 10^{11} ions/cm^2. After thermal annealing most of the Cd-probes occupy substitutional lattice sites and almost all implantation damage can be annealed. This results in a distinct frequency in the PAC spectra, which increases almost linearly when the AlN content in the layers increases. The frequency distribution is slightly increased for the ternary compounds compared to the binary alloys due to alloy disorder. In contrast to the formation of an indium nitrogen-vacancy complex observed with the probe ^{111}In on substitutional cation-sites no defects are bound to substitutional Cd impurities.

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LOI132 – Radioactive local probing and doping on graphene

V.S. Amaral[1], T. Trindade[1], J.G. Correia, S-W Hong[2], D. Pribat[2], C. Tenreiro[2], Y. Kadi[3], A. Gottberg[3], K. Johnston[3]

Perturbed Angular Correlations is used to study graphene and graphene-derived structures, to locally investigate properties associated with electron density and interactions, by using a selection of pure isotopes, dopant elements and adatoms at the graphene surface. In 2011 we did specific trial experiments on graphene and pyrolytic graphite standing on water as the carrier support media for the radio-isotope. The aim was to compare different data obtained from different C samples and methods to organize and optimize procedures and to develop dedicated handling equipment. Experiments using the UHV-setup at ISOLDE, ASPIC, looking forward to investigate graphene in ultra clean environments, impurity free, are foreseen for 2012-2013.

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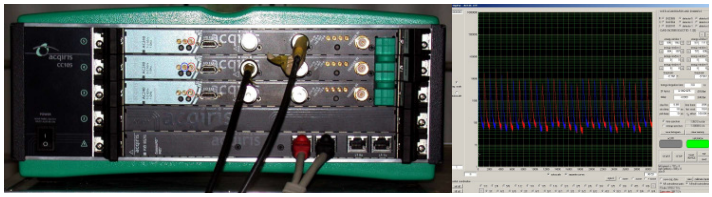
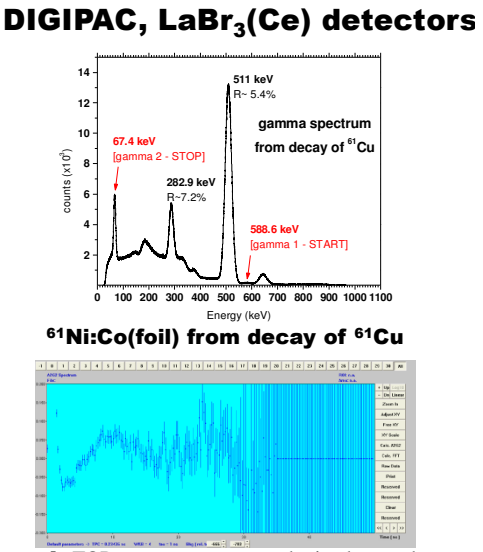
R&D - DIGIPAC and the ^{61}Cu/^{61}Ni New PAC probe isotope

J.G. Correia, M. B. Barbosa, K. Lorenz, T. Butz [1] and M.R. Silva[2]

In Spring 2011 our Laboratory - ITN @ ISOLDE received a donation from the University of Leipzig of three 6-D PAC spectrometers. Two of the traditional type equipped with BaF_2 detectors and one new digital machine (DIGIPAC) equipped with six $LaBr_3$ detectors. The excellent energy resolution of the detectors and the easiness of the data processing and human interface of this machine made possible the first ever done PAC spectrum onto the decay of ^{61}Cu/^{61}Ni. So far only the magnetic interaction has been measured for ^{61}Ni on a Ni foil. We expect having beam by 2012 to measure the quadrupole interaction of ^{61}Ni on materials.



Legend: LEFT DIGIPAC main core, consisting of 3 dual cards integrating each one, two digitizer Aquiris and two FPGAs for digitalizing data and processing
RIGHT data acquisition of 30 time spectra / combinations for each pair of detectors in coincidences γ_1 - γ_2, produced during the ^{61}Cu/^{61}Ni PAC experiment.



Legend: TOP gamma spectrum obtained onto decay of ^{61}Cu ($T_{1/2}$ = 3.3h) with $LaBr_3$ detectors.
BOT - R(t) experimental function where is clearly seen the larmor frequency due to the interaction of the 5/2 spin of the 67.4 keV state on ^{61}Ni with the Ni-host magnetic field.

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R&D data analysis - TDFIT- Dynamic Interactions in Perturbed Angular Correlations

M.B. Barbosa, J.G. Correia, K. Lorenz, M.R. Silva[1]

Hamiltonians for dynamic quadrupole and magnetic, hyperfine interactions have been implemented on a numeric generator of the perturbed angular correlation (PAC) observable. It rules the change of the population of the m states of the intermediate spin state of the PAC cascade, as due by time dependent operators (transient fields) on the so called "Stochastic Hamiltonean formalism". Systems to study are many, from dynamic correlation's on multiferroic compounds, to the so called “after-effects” in semiconductors and insulators. At the time of this report there are on-going experiments that combine e-γ and γ-γ PAC onto decay of ^{181}Hf/^{181}Ta, implanted and annealed on well characterized samples of (Si) n-GaN, (Mg) p-GaN, (Zn) p-GaN and AlN. The use of e-γ PAC allows to create deep level excitations and ionized states on these materials, which can be further studied as a function of temperature, learning about *point-like* electron dynamics on these materials.

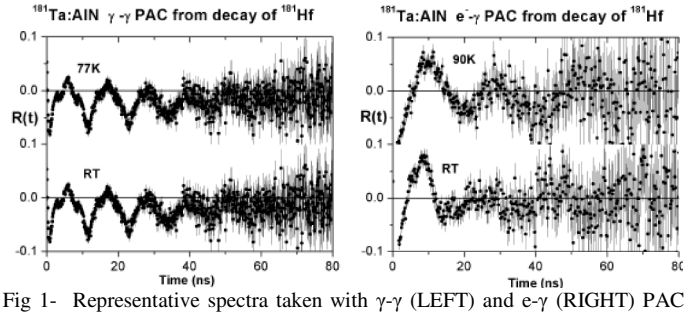

Fig 1- Representative spectra taken with γ-γ (LEFT) and e-γ (RIGHT) PAC where are clearly seen different EFGs and attenuations due to the slow electronic recombination after conversion electron emission. No such effect is observable with γ-γ PAC.

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