

Electronic structure, lattice location and stability of dopants in wide band gap semiconductors

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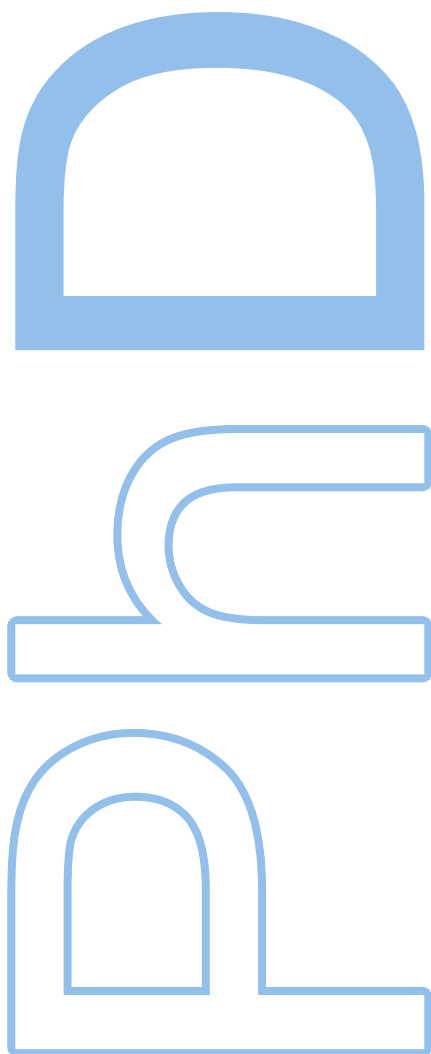
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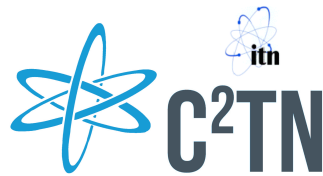
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Resumo

A importância de materiais funcionais, tais como nano-fios e filmes finos, na ciência e tecnologia tem crescido exponencialmente nos últimos anos. Devido ao seu pequeno tamanho e crescente ratio superfície/volume, novas propriedades (previsíveis ou insuspeitas) aparecem, com potenciais aplicações na indústria. No entanto, quanto mais pequenos os dispositivos ficam, mais as suas propriedades dependem nos factores de escala, geometria, simetria e localização de interacções de defeitos e impurezas, os quais não estão mais diluídos nos materiais constituintes^[1,2]. Para além disso, é sabido que as posições atómicas e as cargas de valência influenciam as propriedades dos nano-materiais de forma severa, devido ao facto de dependerem no carácter local da densidade electrónica. No caso particular dos nano-fios, a sua integração em dispositivos requer o controlo das propriedades eléctricas e da homogeneidade óptica, as quais não se conseguem atingir de forma sistemática^[3,4]. Devido ao facto da dopagem durante o crescimento ser principalmente governada por reacções em equilíbrio termodinâmico, é possível ocorrerem mudanças dramáticas na morfologia, densidade, alinhamento e homogeneidade durante esse processo (por exemplo, a concentração de dopantes é normalmente maior nas regiões próximas da superfície^[4,5]). Por outro lado, a implantação iónica tem mostrado ser uma técnica de dopagem bastante versátil. No entanto, tem algumas características inerentes e pouco desejadas no que toca aos defeitos de implantação, os quais precisam ser removidos, normalmente através de recozimento, de forma a ativar os dopantes. A técnica de Correlações Angulares Perturbadas (PAC) é particularmente adequada para se seguirem estes processos à escala atómica enquanto se estudam as interacções das sondas implantadas com defeitos pontuais e impurezas/dopantes introduzidos por implantação iónica, difusão ou quando depositadas por evaporação em superfícies de filmes finos. Depois de se realizar o recozimento adequado, podem-se combinar as técnicas de PAC $e^- - \gamma$ e $\gamma - \gamma$ para se obter uma imagem dinâmica das excitações electrónicas induzidas localmente e subsequentes fenómenos de recombinação na vizinhança das sondas.

No presente trabalho, esta metodologia foi utilizada para investigar a estrutura eletrónica, estabilidade e posição de átomos dopantes em pastilhas de pó, filmes finos e nano-fios dos semicondutores de grande hiato Ga_2O_3 , GaN and ZnO, para os quais é fácil crescer filmes finos e nano-fios com bom controlo nos comprimentos, diâmetros e ratio de proporcionalidade. Estes materiais têm grande potencial para aplicações em nano- e microelectrónica, optoelectrónica e nano-sensores^[1,3-6].

Contudo, anteriormente a este trabalho não existia nenhuma ferramenta disponível para analisar dados experimentais onde o campo hiperfino na vizinhança das son-

das fosse dependente do tempo, tal como no caso de sondas com decaimento por captura de eletrões (ex., $^{111}\text{In}/^{111}\text{Cd}$) ou por emissão de eletrões de conversão (ex., $^{181}\text{Hf}/^{181}\text{Ta}$). Assim sendo, a primeira parte deste trabalho foi o desenvolvimento de PACme, um programa em C++ que permite a simulação, análise e visualização do observável experimental de PAC para campos hiperfinos estáticos e dinâmicos (dependentes do tempo), considerando um conjunto de diferentes estados estocásticos possíveis e das transições entre eles. É completamente generalizado em relação ao número de diferentes frações (ambientes da sonda) e diferentes estados de cada fração, spin nuclear das sondas e estrutura cristalina (monocristal ou policristal) do material em estudo. Além disso, é o primeiro software, que tenhamos conhecimento, a integrar de forma analítica uma distribuição estática da frequência para cada estado individual em casos dinâmicos, onde a frequência que caracteriza um único estado deixa de ser um valor preciso e passa a ser representada por uma curva de distribuição normalizada centrada nesse valor. Distribuições estáticas são cruciais na análise dos espectros de PAC porque pequenos desvios no gradiente de campo elétrico e/ou no campo magnético à volta de sondas em posições equivalentes da rede cristalina (ex., devido a defeitos distantes das sondas) são muito frequentes e alteram o espectro de forma significativa.

As primeiras medidas de PAC foram realizadas em função da temperatura de recozimento após a implantação de sondas de ^{111m}Cd em amostras de ZnO/CdZnO e Ga_2O_3 . Em ZnO , foi observada a substituição de sondas de Cd nos sítios de Zn, assim como a formação de complexos sonda-defeito. A estrutura ternária $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.16$) apresentou boa qualidade macroscópica do cristal mas revelou algum aglomerado de defeitos locais à volta das sondas de Cd, os quais não desapareceram com o recozimento. Nas amostras de Ga_2O_3 , foi observada a substituição de sondas Cd nos sítios octaédricos do Ga, demonstrando o potencial da implantação iónica para a dopagem de nano-fios^[2].

Utilizando o conhecimento adquirido nas primeiras experiências, novas medidas de PAC foram feitas após a implantação de sondas de ^{111m}Cd e difusão de sondas de ^{111}In , ambas decaindo para o isótopo estável ^{111}Cd , em amostras de Ga_2O_3 . A localização na rede e estado de carga dos átomos de Cd foram determinados ao comparar os resultados de PAC com as simulações realizadas através da teoria da densidade funcional (DFT). Uma análise abrangente sobre o impacto da introdução de átomos dopantes de Cd na rede Ga_2O_3 foi realizada; a densidade de estados, a estrutura de bandas e a densidade de eletrões em redor dos átomos de Cd e dos seus primeiros vizinhos foram estudados. Foi demonstrado que o Cd induz uma banda de impurezas localizada 0,42 eV acima da banda de valência, a qual é completamente preenchida por um eletrão extra no seu estado mais estável, confirmando o seu carácter aceitador. Foi obtida uma energia de ativação de 0,54(1) eV relacionada com a mobilidade de carga eletrónica no material. Foi portanto possível confirmar que o Cd se torna num dopante aceitador no local octaédrico do Ga em Ga_2O_3 , sendo assim um muito bom candidato para dopagem

de tipo-p neste material.

Finalmente, foram realizadas medidas de PAC após a implantação de sondas de $^{181}\text{Hf}/^{181}\text{Ta}$ em amostras de GaN dopadas com Si (dopante tipo-n) e com Zn (dopante tipo-p) com o objetivo de estudar o local na rede dos iões implantados. A combinação das técnicas de $e^- - \gamma$ PAC e $\gamma - \gamma$ PAC foi utilizada para estudar a recombinação de estados eletrónicos ionizados e excitados da impureza/dopante em função da temperatura e do dopante. Isto demonstra o potencial uso de PAC para o estudo das propriedades elétricas de materiais onde, por exemplo, medidas do efeito Hall são difíceis/impossíveis de obter. Todos os resultados foram depois comparados a simulações DFT através da implementação de diferentes modelos atómicos locais, onde o gradiente de campo eléctrico e a densidade de estados de cada configuração foram calculados.

Abstract

The importance of functional nanomaterials, such as nanowires (NW) and thin films, in science and technology has been increasing exponentially over the years. Due to their small size and increasing surface-to-volume ratio, new (predictable or unsuspected) properties arise with potential applications in industry. However, the smaller the devices get, the more their properties depend on the scale factor, geometry, symmetry and localized interactions of defects and impurities, which are no longer diluted in the constituent materials^[1,2]. Moreover, it is known that the atomic positions and charge valences severely influence the properties of nanomaterials, since they depend on the local character of the electron density. In particular for NW, their integration in devices requires the control of electrical properties and optical homogeneity, which is not systemically achieved^[3,4]. Since doping during growth is mainly ruled by equilibrium thermodynamic reactions, a dramatical change of morphology, density, alignment and homogeneity can occur during the process (e.g., the dopant concentrations are generally higher in near-surface regions^[4,5]). Alternatively, ion implantation proves to be a versatile doping technique. However, it has some inherent and undesirable features regarding the effects of the implantation damage, which need to be removed, generally by thermal annealing, in order to activate the dopants. The Perturbed Angular Correlation (PAC) technique is particularly suitable for the follow-up of these processes at the atomic scale while studying the interactions of the implanted probe with point-like defects and impurities / dopants introduced by ion implantation, diffusion or when deposited by evaporation (soft-landing) on surfaces and build-up interfaces of thin films. After achieving proper annealing, the combination of the $e^- - \gamma$ and $\gamma - \gamma$ PAC techniques can be used to provide a dynamic picture of locally induced electronic excitations and subsequent recombination phenomena into the probe's neighborhood.

In this work, this methodology was used to investigate the electronic structure, stability and lattice location of single dopant atoms in samples of powder pellets, thin films and nanowires (NW) of the wide band gap semiconductors Ga_2O_3 , GaN and ZnO, for which growing thin-films and NWs is well achievable, the latter with good control of lengths, diameters and "aspect ratio". These materials have great potential for applications in nano- and microelectronics, optoelectronics and nano-sensors^[1,3-6]. However, before this work there was no available tool to analyze experimental data in cases where the hyperfine field around the probes is time-dependent, such as in the case of probes which decay by electron-capture (e.g., $^{111}\text{In}/^{111}\text{Cd}$) or by conversion electron emission (e.g., $^{181}\text{Hf}/^{181}\text{Ta}$). Therefore, the first part of this work was the development of PACme, a C++ program that allows the simulation, analysis and visualization of the experimental

PAC observable for static and dynamic (time-dependent) hyperfine fields considering a stochastic set of different possible states and the transitions between them. It is completely generalized in terms of the number of different fractions (probe environments) and different states of each fraction, nuclear spin of the probes and crystal structure (single crystal or polycrystal) of the material under study. Moreover, it is the first software, to our knowledge, to analytically integrate a static frequency distribution for each individual state in dynamic cases, where the frequency characterizing a single state is no longer a sharp value but is instead represented by a normalized distribution curve centered at that value. Static distributions are crucial in the analysis of PAC spectra since small deviations in the electric field gradient and/or magnetic field around probes in equivalent lattice sites (e.g. due to distant defects from the probes) are very frequent and change the spectra in a very strong way. The first PAC measurements were performed as a function of annealing temperature after implantation of ^{111m}Cd probes in samples of $\text{ZnO}/\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and Ga_2O_3 . For ZnO , the substitution of Cd probes at Zn sites was observed, as well as the formation of a probe-defect complex. The ternary $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.16$) showed good macroscopic crystal quality but revealed some clustering of local defects around the probe Cd atoms, which could not be annealed. In the Ga_2O_3 samples, the substitution of the Cd probes in the octahedral Ga-site was observed, demonstrating the potential of ion-implantation for the doping of nanowires^[2]. Using the knowledge gained from the first experiments, new PAC measurements were performed after implantation of ^{111m}Cd probes and diffusion of ^{111}In probes, both decaying to stable ^{111}Cd , in samples of Ga_2O_3 . The location and charge state of the Cd probe atoms were determined by comparing the PAC results to density functional theory (DFT) simulations. A comprehensive analysis regarding the impact of introducing Cd dopant atoms into the Ga_2O_3 lattice was performed; the density of states, band structure and the electron density around the Cd atoms and their first neighbors were studied. It was shown that Cd induces an impurity band located 0.42 eV above the valence band which is completely filled by an extra electron in its most stable state, confirming its acceptor character. An activation energy of 0.54(1) eV related with the electronic charge carrier mobility in the material was obtained. It was therefore possible to confirm that Cd becomes an acceptor dopant in the octahedral Ga-site of Ga_2O_3 , thus being a very good candidate for p-type doping in this material. Finally, PAC measurements were performed after implantation of $^{181}\text{Hf}/^{181}\text{Ta}$ probes into Si-doped (n-type dopant) and Zn-doped (p-type dopant) samples of GaN in order to study the lattice site of the implanted ions and the combination of the $e^- - \gamma$ and $\gamma - \gamma$ PAC techniques was used to study the recombination of ionized and excited electronic states of the impurity/dopant as a function of temperature and dopant. This demonstrates the potential use of PAC for the study of electrical properties of materials where, for instance, Hall effect measurements are difficult / impossible to perform. All the results were later compared to DFT simulations via the implementation of different atomic local models, where the electric field gradient and density of states of each configuration was calculated.

Contents

Acknowledgements	vii
Resumo	ix
Abstract	xiii
Contents	xvii
List of Figures	xx
List of Tables	xxi
List of Abbreviations	xxiii
Thesis Outline	1
1 Wide Band Gap Semiconductors	3
1.1 Ga ₂ O ₃	4
1.2 GaN	4
1.3 ZnO & Cd _x Zn _{1-x} O	5
2 Methods and Techniques	7
2.1 PAC – Perturbed Angular Correlations Spectroscopy	7
2.1.1 Electric Quadrupole Interaction	7
2.1.2 Magnetic Interaction	11
2.1.3 Angular Correlation	12
2.1.4 Perturbed Angular Correlation	13
2.1.5 The Experimental Perturbation Function	15
2.1.6 The Experimental Set-up	17
2.1.6.1 $\gamma - \gamma$ PAC	17
2.1.6.2 $e^- - \gamma$ PAC	18
2.2 Density Functional Theory	19
2.2.1 The Born-Oppenheimer approximation	20
2.2.2 The Hohenberg and Kohn theorems	21
2.2.3 The Kohn-Sham method	22

2.2.4	The exchange-correlation functional	23
2.2.5	The L/APW+lo method	24
2.2.6	Calculating the Electric Field Gradient	27
3	PACme: a generalized program for the simulation, analysis and visualization of PAC data	29
3.1	Introduction	29
3.2	Theoretical Overview	30
3.2.1	Hyperfine Interactions	30
3.2.2	Perturbed Angular Correlations for Fluctuating Hyperfine Fields . .	31
3.3	Breakthrough Implementation of Static Frequency Distributions	35
3.4	Test Cases and Examples	37
3.4.1	Unidirectional Transition	38
3.4.1.1	Simple Unidirectional Transition	38
3.4.1.2	Unidirectional Transition with Static Frequency Distributions	40
3.4.2	XYZ model	41
3.4.3	Fluctuating EFG strength in Thermal Equilibrium	42
3.5	Software Overview	43
3.6	Internal Algorithms	44
3.6.1	χ^2 -function and Minuit2	45
3.6.2	Fourier transforms class	46
3.7	Conclusion	48
4	Cd probes location in ZnO and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ as a function of annealing temperature	51
4.1	Introduction	51
4.1.1	Case studies: ZnO & $\text{Cd}_x\text{Zn}_{1-x}\text{O}$	52
4.2	Technical details	52
4.3	Results and discussion	53
4.3.1	ZnO	53
4.3.2	$\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$	55
4.4	Conclusion	59
5	Charge state and lattice location of Cd dopants in Ga_2O_3	61
5.1	Introduction	61
5.2	Perturbed Angular Correlation experiments	63
5.2.1	Experimental Details	63
5.2.2	Results	63
5.3	Density Functional Theory simulations	66
5.3.1	Simulation details	66
5.3.2	Results	68

5.4	Temperature dependence of the transition rates in PAC	73
5.5	Discussion of Results and Conclusions	79
6	Detailing the electronic mobility as a function of dopants in GaN	81
6.1	Introduction	81
6.2	Perturbed Angular Correlation experiments	82
6.2.1	Experimental Details	82
6.2.2	Results	83
6.3	Density Functional Theory simulations	87
6.3.1	Simulation details	87
6.3.2	Results	87
6.4	Temperature dependence of the transition rates in $e^- - \gamma$ PAC	93
6.5	Conclusions	97
7	General Discussion and Future Perspectives	99
	List of Publications and Awards	101
	Bibliography	103
	APPENDICES	112
A	PACme – Software Documentation	113
A.1	Software Installation	113
A.2	Usage Instructions	114
A.2.1	Input Parameters File	115
A.2.2	Output Files	121
A.3	Program Structure	122
A.4	External Libraries	128
B	Publication’s Inside Back Cover	129

List of Figures

1.1	Conventional unit cell of monoclinic β -Ga ₂ O ₃	4
1.2	Crystal structure of wurtzite-GaN.	5
1.3	Crystal structure of ZnO and CdO	6
2.1	Energy splitting of a $I = 5/2$ intermediate nuclear level depending on η .	11
2.2	Nuclear level splitting in a B magnetic field	12
2.3	A two-gamma nuclear cascade	13
2.4	Experimental $R(t)$ function and corresponding Fourier transform for spin 5/2	16
2.5	Schemes of the $\gamma - \gamma$ PAC spectrometer	17
2.6	Scheme of the $e^- - \gamma$ PAC spectrometer	18
2.7	Flow chart for the n^{th} iteration in the self-consistent procedure to solve the Khon-Sham equations	23
3.1	Gaussian function fitted to a sum of Lorentzian basis functions	37
3.2	Unidirectional transition for spin-3/2 in a polycrystal	39
3.3	Unidirectional transition for spin-5/2 in a single crystal	39
3.4	Analytical integration versus a numerical integration	40
3.5	Unidirectional transition from an initial state with broad static frequency distribution to a well-defined state	41
3.6	XYZ model for spin-5/2 in a polycrystal	41
3.7	Fluctuating EFG strength in Thermal Equilibrium	42
3.8	Kaiser-Bessel window for $\alpha = 0, 2, 4, 6$ and 8	49
4.1	¹¹¹ Cd:ZnO γ - γ PAC spectra	54
4.2	¹¹¹ Cd:Cd _{0.16} Zn _{0.84} O γ - γ PAC spectra	56
4.3	γ - γ PAC data of ZnO and Cd _{0.16} Zn _{0.84} O	57
4.4	RBS/C spectra of Cd _{0.16} Zn _{0.84} O	58
5.1	Decay scheme for ¹¹¹ In and ^{111m} Cd	63
5.2	PAC spectra from β -Ga ₂ O ₃ powder pellet, nanowires and single crystal .	64
5.3	Total DOS of Ga ₂ O ₃ and supercells with Cd ⁰ and Cd ¹⁻ in the octahedral Ga site	68
5.4	Partial DOS of Ga ₂ O ₃ and supercells with Cd ⁰ and Cd ¹⁻ in the octahedral Ga site	69

5.5	Band structure of Ga_2O_3 and supercell with Cd^{1-} in an octahedral Ga site	70
5.6	Electron density in pure Ga_2O_3 and in Cd^{1-} in an octahedral Ga	70
5.7	Simulated Cd sites in supercells of Ga_2O_3	71
5.8	Ga_2O_3 Arrhenius plot	73
5.9	(Biased) Double-Well Potential.	75
5.10	Illustrative curves for equations 5.1, 5.2 and 5.3 considering $\alpha = 0.3$, $\epsilon = 0.02$ and $\Delta_r = 10^{13}$.	77
6.1	Cascade decay and spectra of $^{181}\text{Hf}/^{181}\text{Ta}$	83
6.2	$\gamma - \gamma$ and $e^- - \gamma$ PAC spectra from GaN:Si	84
6.3	$\gamma - \gamma$ and $e^- - \gamma$ PAC spectra from GaN:Zn	84
6.4	GaN Density of States	88
6.5	GaN Band Structure	89
6.6	GaN lattice parameters optimization	89
6.7	Calculated EFG at the Ta_{Ga}^0 , $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$ sites as a function of the supercell's lattice parameters a' and c'	91
6.8	Density of States for GaN: $\text{Ta}_{\text{Ga}}^0/\text{Ta}_{\text{Ga}}^{1+}/\text{Ta}_{\text{Ga}}^{2+}$	92
6.9	GaN Arrhenius plot	93
6.10	GaN Band Diagram	95
B.1	M. B. Barbosa <i>et al.</i> , "Inside Back Cover"	129

List of Tables

1.1	Properties of the wide band gap semiconductors β -Ga ₂ O ₃ , GaN and ZnO	3
4.1	¹¹¹ Cd:ZnO γ - γ PAC fitting parameters	54
4.2	¹¹¹ Cd:Cd _{0.16} Zn _{0.84} O γ - γ PAC fitting parameters	56
5.1	¹¹¹ In:Ga ₂ O ₃ γ - γ PAC fitting parameters	64
5.2	Experimental and simulated EFG at the Ga and Cd sites in samples of Ga ₂ O ₃	71
5.3	p , d and s - d valence contributions to the EFG for the Cd probe in Ga ₂ O ₃	72
6.1	γ - γ PAC fitting parameters from GaN:Si and GaN:Zn	85
6.2	e^- - γ PAC fitting parameters from GaN:Si and GaN:Zn	85
6.3	Simulated and experimental EFG at the Ta probe's site	91
A.1	Available option flags to run the program.	115

List of Abbreviations

A

- **GGA**, Generalized Gradient Approximation
- **AFM**, Atomic-Force Microscope
- **C2TN**, Centro de Ciências e Tecnologias Nucleares
- **CBM**, Conduction Band Minimum
- **CERN**, European Organization for Nuclear Research
- **DFT**, Density Functional Theory
- **DLTS**, Deep Level Transient Spectroscopy
- **DOS**, Density of States
- **E**, Electric Field
- **EFG**, Electric Field Gradient
- **FCUP**, Faculdade Ciências da Universidade do Porto
- **FWHM**, Full Width at Half Maximum
- **HI**, Hyperfine Interactions
- **IFIMUP-IN**, Instituto de Física dos Materiais da Universidade do Porto
- **ISOLDE**, On-line Isotope Mass Separator
- **J**, Atom total angular momentum
- **L**, Lattice
- **LDA**, Local Density Approximation
- **LE**, Local Environment
- **LED**, Light-Emitting Diode
- **M**, Magnetization
- **MBE**, Molecular Beam Epitaxy
- **MES**, Mössbauer Effect Spectroscopy
- **MHF**, Magnetic Hyperfine Field
- **MOCVD**, Metal-Organic Chemical Vapor Deposition
- **MES**, Nuclear Magnetic Resonance
- **NW**, Nanowire
- **PAC**, Perturbed Angular Correlations
- **PL**, Photoluminescence Spectroscopy
- **RBS**, Rutherford Backscattering Spectrometry
- **STM**, Scanning-Tunneling Microscope
- **TCO**, Transparent Conducting Oxide
- **VBM**, Valence Band Maximum
- **VRH**, Variable Range Hopping
- **WBGs**, Wide Band Gap Semiconductor
- **XRD**, X-ray Diffraction
- N_A , Avogadro's number
- k_B , Boltzmann constant
- μ_B , Bohr magneton
- $\mu_0 H$, Magnetic Induction
- **RT**, Room Temperature
- **T**, Temperature
- **TA**, Annealing Temperature
- **TM**, Measuring Temperature
- **V**, Volume

Thesis Outline

In an ever changing world, an invariant is emerging: our dependence on smaller, faster and more efficient electronics. Semiconductors are the foundation of modern electronics, but as current technology reaches its limits, where do we go next? The answer: we advance the technology we already have by using better and improved materials, such as wide band gap semiconductors (WBGS). WBGS are able to operate at very high temperatures, handle higher voltages and are much more efficient in terms of power losses in electricity transfer compared to current technology. They are already revolutionizing our day-to-day life by enabling the production of more efficient LEDs with wavelengths that almost cover the entire visible spectra. The applicability of WBGS depends on the ability to correctly modulate their electronic properties, which is usually done by doping. This is even more important for low-dimensional samples, like thin films and nanowires. Therefore, the ability to study the impact of dopants and the environment around them in such samples at the lowest possible scale is paramount.

Having this in mind, this thesis is the culmination of several years of research done primarily on the development of methods to study the lattice location, stability and electronic properties of dopants at the nanoscale and, secondly, apply such methods to study the doping of Cd and Ta in the wide band gap semiconductors such as Ga_2O_3 , GaN and ZnO.

The experimental technique that was used is called Perturbed Angular Correlation (PAC) and it works by implanting radioactive isotopes in a sample which decay in a double cascade, therefore existing an angular correlation between the direction of emission of both photons (or conversion electron, depending on the isotope), which is dependent on the hyperfine fields around the probe. This enables the measurement (at the atomic scale) of the position of the probes within the crystal lattice and their charged state as a function of time and temperature, as well as the mobility of charges in the material itself. These experiments were performed at ISOLDE-CERN, the best place to get a clean beam of 'any' chosen isotope, and at CFNUL, in Lisbon. Then, by doing Density Functional Theory (DFT) simulations, it was possible to confirm the lattice location and charged state of the dopants in the materials as well as the resulting density of states, band structure, electron density, etc.

This thesis is outlined as follows:

Chapter 1: Brief review on the main characteristics of Wide Band Gap Semiconductors, specifically on the materials under study in this work: Ga_2O_3 , GaN and ZnO.

Chapter 2: Overview of the experimental technique used in the experiments, Perturbed Angular Correlation, explaining the possibility and the advantage of doing both $\gamma - \gamma$ and $e^- - \gamma$ PAC, as well as of Density Functional Theory (DFT), the method used for the several simulations performed regarding the different materials and probes.

Chapter 3: Explanation about the development of PACme, a C++ program that allows the simulation, analysis and visualization of the experimental PAC observable for static and dynamic (time-dependent) hyperfine fields. It includes several test cases and examples to showcase the potentialities of the program.

Chapter 4: Location of $^{111m}\text{Cd}/^{111}\text{Cd}$ probes as a function of annealing temperature in thin films of ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$.

Chapter 5: Location and charge state of Cd dopants in Ga_2O_3 after diffusion of $^{111}\text{In}/^{111}\text{Cd}$ probes, revealing that Cd is a good candidate for p-type doping in this material.

Chapter 6: $\gamma - \gamma$ and $e^- - \gamma$ PAC measurements in Si- and Zn-doped samples of GaN to study the location and charged states of Ta in the material as well as the impact of the different dopants in the electronic properties of GaN (alternative to Hall measurements in samples where electronic contacts are difficult).

Chapter 7: General discussion and the overall conclusions. An outlook is additionally contained in this chapter, exploring the future prospects of the work presented.

Appendix A: Software documentation regarding PACme, including instructions to install and use it.

Appendix B: M. B. Barbosa *et al.*, "Inside Back Cover: Nanostructures and thin films of transparent conductive oxides studied by perturbed angular correlations (Phys. Status Solidi B 4/2013)", Phys. Status Solidi B 250, No. 4 (2013).

CHAPTER 1

Wide Band Gap Semiconductors

Wide band gap semiconductors (WBGs) are semiconducting materials which have larger band gaps when compared to typical semiconductors (such as silicon), the latter having band gaps in the range of 1 eV to 1.5 eV, whereas WBGs have band gaps in the range of 2 eV to 5 eV. They are key components for the manufacturing of blue LEDs and lasers and can operate at much higher voltages, frequencies and temperatures than conventional semiconductors like silicon and gallium arsenide. Due to their promising technological applications, research regarding WBGs has been increasing at a high rate over the past few years.

In this work, three different WBGs were studied: gallium oxide (Ga_2O_3), gallium nitride (GaN) and zinc oxide (ZnO). Some of their more important parameters are summarized in Table 1.1.

Table 1.1 – Properties of the wide band gap semiconductors β - Ga_2O_3 , GaN and ZnO lattice structures.

	Ga_2O_3	GaN	ZnO
Crystal structure:	monoclinic (β)	wurtzite	wurtzite
Space group:	$C2/m$	$P6_3mc$	$P6_3mc$
Lattice param.: a[Å]	12.214 ^[7]	3.189 ^[8]	3.2489 ^[9]
b[Å]	3.0371 ^[7]		
c[Å]	5.7981 ^[7]	5.185 ^[8]	5.2053 ^[9]
Lattice angles: $\alpha = \beta$	90°	90°	90°
γ	120°	103.83° ^[7]	120°
Band gap [eV]:	4.85 ^[10]	3.50 ^[11]	3.4 ^[12]
Effective electron mass [m_e]:	0.28 ^[10]	0.20 ^[13]	0.24 ^[12]
Electron mobility, μ [$\text{cm}^2/(\text{Vs})$]:	300 ^[14]	1250 ^[14]	200 ^[12]
Density [g/cm^3]:	5.85 ^[10]	6.15 ^[15]	5.606 ^[12]
Melting point [°C]:	1800 ^[10]	2500 ^[15]	1975 ^[12]
Thermal expansion coefficient: a [$10^{-6}/\text{K}$]	1.54 ^[16]	5.59 ^[17]	6.5 ^[12]
b [$10^{-6}/\text{K}$]	3.37 ^[16]		
c [$10^{-6}/\text{K}$]	3.15 ^[16]	3.17 ^[17]	3.0 ^[12]

1.1 Ga₂O₃

Ga₂O₃ belongs to the family of transparent conducting oxides and has been gaining interest in recent years due to its potential application in power and high-voltage electronic devices^[10,18]. It is transparent in the ultraviolet (UV) range, thus being also very promising for solar cells and UV optoelectronic devices^[2,19,20]. Having a band gap of 4.8 eV^[21], Ga₂O₃ is intrinsically an insulator, but its conductivity actually depends on doping and growth conditions. N-type doping in this material is easily achieved but p-type doping has not been reliably proved yet, being, however, Cd a strong candidate^[2]. It is usually reported that there are five different polymorphs of Ga₂O₃, namely, the monoclinic (β -Ga₂O₃), rhombohedral (α), defective spinel (γ), cubic (δ), or orthorhombic (η) structures^[14]. Of these, the β -polymorph is the stable form under normal conditions and has been the most widely studied, including in this work. Thus from now on, Ga₂O₃ will refer exclusively to β -Ga₂O₃ unless otherwise stated. The crystal structure of β -Ga₂O₃ is base-centered monoclinic with space group 12 (C2/m), having the Ga ions occupying distorted tetrahedral (Ga_I) and octahedral (Ga_{II}) sites, and the O ions in a distorted cubic packing with three inequivalent sites^[7,22], with two threefold and one fourfold coordinated O (see Figure 1.1). It is usually described in a conventional unit cell (Fig. 1.1) with the lattice parameters a , b , c and β , the angle between the a and c axis.

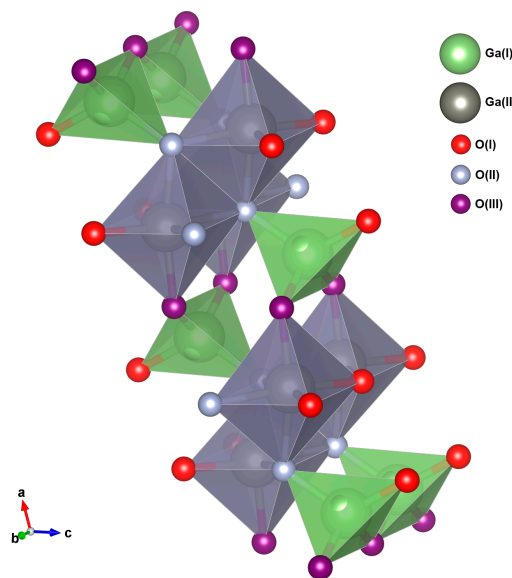


Figure 1.1 – Conventional unit cell of monoclinic β -Ga₂O₃

1.2 GaN

GaN belongs to the group III nitrides, a group of very useful systems used in semiconductor devices, especially in the development of blue- and UV-LEDs^[23,24]. It has a wide band-gap of 3.503(5) eV^[11] and exhibits piezoelectricity, high thermal conductivity, me-

chanical strength, and low electron affinity, making it an excellent material for optoelectronic device applications such as light-emitting diodes in the UV range, field emitters for flat displays, and high-speed transistors^[25]. At ambient pressure, GaN crystallizes in a hexagonal (wurtzite) structure with the space group 186 ($P6_3mc$) and is usually grown on sapphire or SiC substrates by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD)^[13,17]. It can also be grown in the meta-stable zincblende (cubic) structure by epitaxial growth on a GaAs or SiC substrate, but in this work only the wurtzite structure is considered.

In the wurtzite structure, it contains two Ga cations and two N anions per unit cell, with all Ga cations tetrahedrally coordinated by N ions (see Figure 1.4).

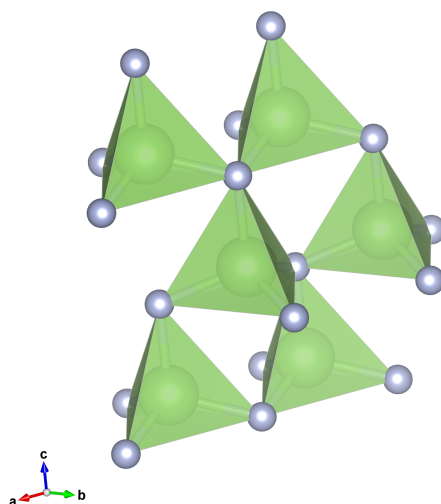


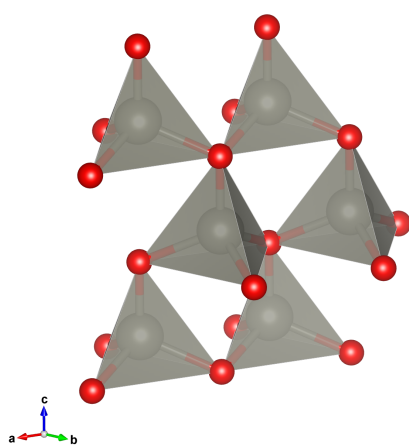
Figure 1.2 – Crystal structure of wurtzite-GaN.

The acceptor electrical doping is of utmost relevance, because the nitrides have an n-type (negative) characteristic background, and most of these applications require both a p-type (positive) and an n-type doping in order to obtain a p-n junction to produce diodes^[26]. Nowadays, Mg-doped p-type GaN is a core component of many optoelectronic devices which we find in our homes, e.g., LEDs for solid state white lighting or blue lasers^[27]. N-type doping has also been achieved by introducing Si at Ga sites^[28], whilst introducing Zn at Ga sites induces a deep acceptor level that compensates unintentional donor defects^[29], thus having p-type dopant character.

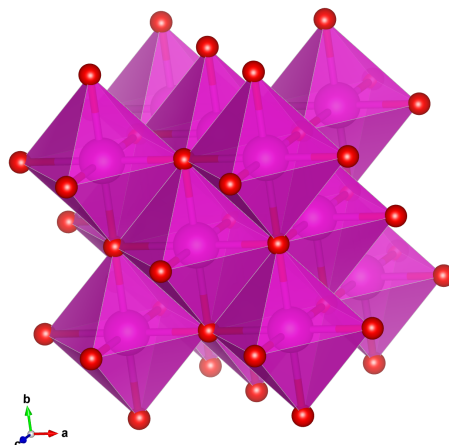
1.3 ZnO & Cd_xZn_{1-x}O

ZnO also belongs to the family of transparent conductive oxides and has been attracting attention for its application to UV light-emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas-sensing and

as a window material for display and solar cells^[12]. It is available in both bulk and single crystal forms^[12]. Furthermore, the possibility of growing pseudobinary compounds, for instance using CdO, allows band gap tuning and heterostructure growth^[2]. ZnO has a band gap of 3.4 eV whilst CdO has a band gap of 2.1 eV. Therefore, the ternary CdZnO can cover a spectral range extending from the ultraviolet to the yellow wavelengths^[30]. However, the binary components have different crystalline structures, namely wurtzite for ZnO (Zn cations tetrahedrally coordinated by N ions) and rock salt for CdO (Cd cations octahedrally coordinated by O ions) as can be seen in Figure 1.3. As a consequence, the equilibrium solubility limit of CdO in ZnO is of only about 2%. Phase separation is thus an obstacle that has to be overcome when aiming at devices emitting visible light^[30]. In this way, a complete understanding on the implantation site of Cd in samples of ZnO is paramount.



(a) ZnO



(b) CdO

Figure 1.3 – Crystal structure of ZnO and CdO

CHAPTER 2

Methods and Techniques

2.1 PAC – Perturbed Angular Correlations Spectroscopy

Perturbed Angular Correlations spectroscopy (PAC) originated in the field of nuclear physics but has since had widespread application in solid state systems, being a powerful technique for the microscopic investigation of solid state local phenomena. The application of PAC in the study of materials involves the (time differential) angular correlation between pairs of gamma rays emitted by radioactive nuclei, which work as probes of the local electric charge distributions and magnetic fields^[31]. This angular correlation depends on the interaction between the nucleus magnetic dipole or the electric quadrupole moment and the magnetic hyperfine field or electric field gradient produced at the nucleus. The hyperfine interactions are short-ranged, therefore PAC provides information on the local surroundings of particular atoms, being very sensitive to changes at their vicinity and offering unique possibilities for investigation of the structure and dynamics of the nearest neighborhood of the probes^[32].

Since the general theory of Perturbed Angular Correlations is mathematically complex and has been well explained in several textbooks^[33,34] and previous thesis^[35], here only the basic physics and phenomenology of this nuclear technique are discussed.

This section starts by revisiting the electric quadrupole and magnetic interactions, which are responsible for the time differential component of the angular correlation. Then, the (perturbed) angular correlation function is motivated and the experimental perturbation function is explained. In the end, the experimental set-ups for both gamma-gamma ($\gamma - \gamma$) and electron-gamma ($e^- - \gamma$) PAC experiments are shown.

2.1.1 Electric Quadrupole Interaction

The electrostatic energy for a nuclear charge density $\rho(\mathbf{r})$ in an external electrostatic potential $\Phi(\mathbf{r})$ is given by^[34,36]

$$E = \int \rho(\mathbf{r})\Phi(\mathbf{r})d^3r. \quad (2.1)$$

By expanding the potential in a Taylor series around $\mathbf{r} = 0$

$$\Phi(\mathbf{r}) = \Phi(0) + \sum_{i=1}^3 \left(\frac{\partial \Phi}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \Phi}{\partial x_i \partial x_j} \right)_0 x_i x_j + \dots \quad (2.2)$$

the electrostatic energy can be written as

$$E = q\Phi_0 + \mathbf{p} \cdot \nabla \Phi(0) + \frac{q}{6} \langle r^2 \rangle \nabla^2 \Phi(0) + \frac{e}{6} \sum_{i,j} \Phi_{ij} Q_{ij} \quad (2.3)$$

where $\Phi_{ij} = \left(\frac{\partial^2 \Phi}{\partial x_i \partial x_j} \right)_0$, ∇ is the gradient, ∇^2 is the laplacian, $\langle r^2 \rangle$ is the mean square nuclear radius and the following definitions for the total charge (q), electric dipole moment ($\mathbf{p}$) and electric quadrupole moment tensor (Q_{ij}) were used:

$$q = \int \rho(\mathbf{r}) d^3r \quad (2.4)$$

$$p_i = \int x_i \rho(\mathbf{r}) d^3r \quad (2.5)$$

$$Q_{ij} = \frac{1}{e} \int \rho(\mathbf{r}) (3x_i x_j - r^2 \delta_{ij}) d^3r \quad (2.6)$$

The first term in equation 2.3 (zero-order term) is the Coulomb energy of a point charge in an external potential. This term only contributes to the potential energy of the crystal lattice, being the same for every isotope of the same element and thus do not contribute to energy splitting. The second term (first-order) represents the electric dipole interaction, but due to well defined parity of the nuclear wave function, this term is zero. The third and fourth terms are both contributions from the the second-order term. The first one is the monopolar term and describes the electrostatic interaction of an expanded nucleus with electrons in the nuclear zone ($\nabla^2 \Phi(0) \propto |\psi(0)|^2$, where $-e|\psi(0)|^2$ is the electronic charge density at the nucleus, only non-negligible for s electrons). It contributes to the isotope shift of nuclear levels but not to their splitting, therefore it is not observed in a Perturbed Angular Correlation experiment where only the relative energy splitting of the measuring nuclear state is observed¹.

The last term is the electric quadrupole interaction energy and it is responsible for the nuclear level splitting for nuclei with non-negligible electric quadrupole moment. Since Q_{ij} is a traceless matrix, it is possible to introduce the electric field gradient tensor $V_{ij} = \frac{1}{3} \text{Tr}(\Phi_{ij})$, which is the traceless component of the Q_{ij} tensor. The electric quadrupole interaction energy is then invariant by substituting Q_{ij} for V_{ij} , so it can be written as

$$E_Q = \frac{e}{6} \sum_{i,j} V_{ij} Q_{ij} \quad (2.7)$$

Because the electric field gradient is a symmetric tensor, it is always possible to find

¹The monopolar term is responsible for the so called isomer shift in Mössbauer spectroscopy.

an eigenvectors basis where V_{ij} is diagonal. Moreover, since V_{ij} is a traceless matrix, it can then be completely described by only two of its components. The referential axis can be chosen such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Therefore, the electric field gradient is commonly described by its largest component, V_{zz} , and the so called asymmetry parameter η , defined as $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$. The asymmetry parameter only takes values between 0 and 1, and measures the deviation of the local charge distribution from axial symmetry.

Using the asymmetry parameter and the principal component of the EFG explicitly in the electric quadrupole energy yields

$$E_Q = \frac{eV_{zz}}{12} [3Q_{zz} + \eta(Q_{xx} - Q_{yy})] \quad (2.8)$$

To calculate the effect of the quadrupole interaction on a nuclear state characterized by its angular momentum $\hbar I$, the quantum formulation has to be used. The expression 2.8 remains valid for the interaction Hamiltonian $\hat{H}_Q$ with the quadrupole moment tensor components, Q_{ii} , substituted by the correspondent quantum operators, $\hat{Q}_{ii}$. The matrix elements of any operator in the space of states defined by $|I, m\rangle$ must be reproduced by an analogous operator formed from the angular momentum operator $\hat{I}_i$. The quadrupole operator is a rank 2, symmetric, traceless tensor and hence the operator given in terms of the I_i must also have these properties. Therefore we find that the general form for $\hat{Q}_{ij}$ must be^[35,37]

$$\langle I, m | \hat{Q}_{ij} | I, m \rangle = \alpha(I) \langle I, m | \frac{3}{2} (\hat{I}_i \hat{I}_j + \hat{I}_j \hat{I}_i) - \delta_{ij} \hat{I}^2 | I, m \rangle \quad (2.9)$$

where α is a yet to be determined constant. It is convenient to examine the matrix element $\hat{Q}_{zz}$ between states of $|I, m = I\rangle$

$$\begin{aligned} \langle I, I | \hat{Q}_{zz} | I, I \rangle &= \alpha(I) \langle I, I | \frac{3}{2} (\hat{I}_z \hat{I}_z + \hat{I}_z \hat{I}_z) - \hat{I}^2 | I, I \rangle \\ &= \alpha(I) (3I^2 - I(I+1)) \\ &= \alpha(I) I(2I-1) = Q \end{aligned} \quad (2.10)$$

where Q is the quadrupole moment and hence

$$\alpha(I) = \frac{Q}{I(2I-1)}. \quad (2.11)$$

so the quadrupole moment operator is

$$\hat{Q}_{ij} = \frac{Q}{I(2I-1)} \left[\frac{3}{2} (\hat{I}_i \hat{I}_j + \hat{I}_j \hat{I}_i) - \delta_{ij} \hat{I}^2 \right]. \quad (2.12)$$

Using equation 2.12 in equation 2.8, the quadrupole interaction Hamiltonian can be written as

$$\hat{H}_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[3\hat{I}_z^2 - \hat{I}^2 + \eta \left(\hat{I}_x^2 - \hat{I}_y^2 \right) \right] \quad (2.13)$$

and taking advantage of ladder operators - the raising operator $\hat{I}_+$ and the lowering operator $\hat{I}_-$,

$$\begin{aligned} \hat{I}_+ &= \hat{I}_x + i\hat{I}_y \\ \hat{I}_- &= \hat{I}_x - i\hat{I}_y \end{aligned} \quad (2.14)$$

the final expression is

$$\hat{H}_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2} \left(\hat{I}_+^2 + \hat{I}_-^2 \right) \right]. \quad (2.15)$$

Calculating $\langle I, m | \hat{H}_Q | I, m' \rangle$, the only non-zero matrix elements of $\hat{H}_Q$ are

$$H_{m,m} = \hbar\omega_Q (3m^2 - I(I+1)) \quad (2.16)$$

$$H_{m,m\pm 2} = \hbar\omega_Q \frac{1}{2} \eta \sqrt{(I \mp m - 1)(I \mp m)(I \pm m + 1)(I \pm m + 2)} \quad (2.17)$$

where the quadrupole frequency is defined as

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (2.18)$$

and gives the energy scale for the nuclear quadrupole interaction.

For the particular case of an axially symmetric interaction ($\eta = 0$), the eigenvalues of the hamiltonian are

$$E_Q = \hbar\omega_Q [3m^2 - I(I+1)] \quad (2.19)$$

The transition energy between two sublevels m and m' is given by

$$\Delta E_Q = \hbar\omega_Q |m^2 - m'^2| \quad (2.20)$$

$|m^2 - m'^2|$ is always integer so all transition frequencies are multiples of ω_Q and the fundamental observable frequency ω_0 , the lowest transition frequency is:

$$\omega_0 = 6\omega_Q, \text{ for } I \text{ half-integer}$$

$$\omega_0 = 3\omega_Q, \text{ for } I \text{ integer}$$

Is also usual to define another quantity, the fundamental frequency:

$$\nu_Q = \frac{eQV_{zz}}{\hbar} = \omega_0 \frac{4I(2I-1)}{2\pi k} \quad (2.21)$$

where $k = 3$ (for I integer) and $k = 6$ (for I half-integer).

Figure 2.1 shows the electric quadrupole splitting of a nuclear level with spin $I = 5/2$ depending on the asymmetry parameter η . The energy splitting between the sub-levels

is given by a frequency triplet ω_1 , ω_2 and ω_3 . In the particular case of an axially symmetric EFG ($\eta = 0.0$), we have $\omega_2 = 2\omega_1$ and $\omega_3 = 3\omega_1$.

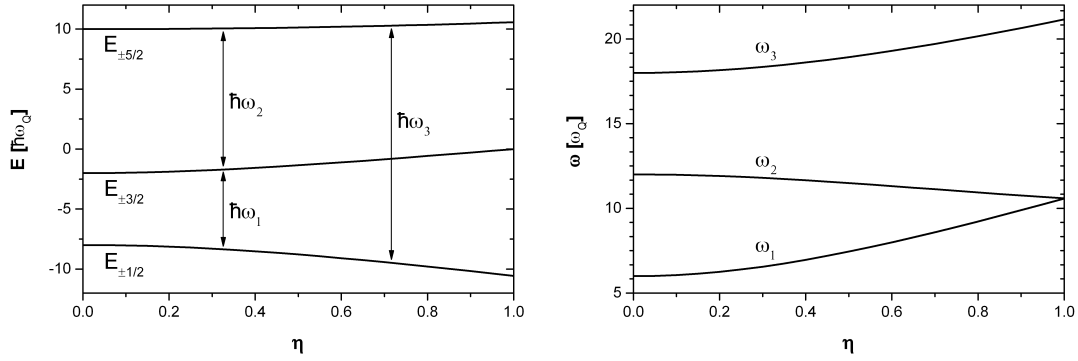


Figure 2.1 – Energy splitting of a $I = 5/2$ intermediate nuclear level depending on the asymmetry parameter η . **(left)** Dependence of the energy eigenvalues. **(right)** Splitting of the associated interaction frequencies.

2.1.2 Magnetic Interaction

The interaction energy between the nuclear magnetic dipole moment μ and a magnetic flux density $\mathbf{B}$ at the position of the nucleus is

$$E_m = -\mu \cdot \mathbf{B} \quad (2.22)$$

This interaction splits the degenerate nuclear levels into m sub-levels.

Considering a magnetic field along the z axis and the z -component of the magnetic moment, $\mu_z = \frac{g\mu_N}{\hbar} I_z$, the interaction energy in the state $|I, m\rangle$ is given by

$$E_m = \langle I, m | -\mu_z B_z | I, m \rangle = -\frac{g\mu_N}{\hbar} B_z \langle I, m | \hat{I}_z | I, m \rangle = -g\mu_N B_z m. \quad (2.23)$$

The energy difference between adjacent m sub-levels is

$$E_m(m+1) - E_m(m) = -g\mu_N B_z = \hbar\omega_L. \quad (2.24)$$

where ω_L is the Larmor frequency and so the splitting is the same between all consecutive m sub-levels (see Figure 2.2).

When both magnetic and electric interactions are present, the Hamiltonian of such combined interaction, in the proper reference frame of the EFG tensor, is given by

$$H_{comb} = \frac{eQV_{zz}}{4I(2I-1)} [3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)] + \mu \cdot \mathbf{B} \quad (2.25)$$

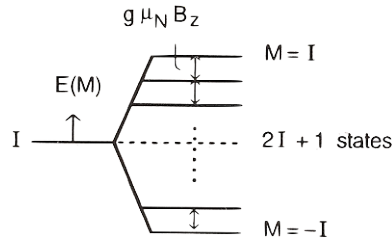


Figure 2.2 – Nuclear level splitting in a B magnetic field (nuclear Zeeman effect)^[34].

2.1.3 Angular Correlation

The probability of emission of a photon by a radioactive nucleus depends on the angle between the nuclear spin axis and the direction of emission. Under ordinary circumstances, the total radiation of a radioactive sample is isotropic since the nuclei are randomly oriented. However, anisotropy is verified when a nuclear state is well oriented. Such anisotropic γ angular distribution can be obtained if the $2I + 1$ degenerate m sub-levels cannot be equally populated, i.e., if the state from which the radiation is emitted is polarized or aligned. By definition, a state is said to be polarized when the density of states $\rho(m)$ depends on m with $\rho(m) \neq \rho(-m)$, and is said to be aligned if the density of states $\rho(m)$ of the sub-levels depends only on its absolute value, i.e., $\rho(m) = \rho(-m) \neq \rho(m')$ ^[33,38]. In the case of angular correlations, the oriented set of nuclei is obtained by choosing only those nuclei whose spins happen to lie in a preferred direction. Consider the case of a radioactive probe nucleus which decays in a double-cascade by emitting two consecutive γ -rays. The initial state $|I_i, m_i\rangle$ is randomly oriented and so all the different m_i states are equally occupied. The observation of γ_1 in a fixed direction $\mathbf{k}_1$ (which is defined as the z axis) selects an ensemble of nuclei in the intermediate state whose m magnetic sub-levels are no longer equally populated due to angular momentum conservation and the angular distribution of the electromagnetic radiation with respect to its angular momentum, L (see ref.^[34] for more details). The direction of emission of γ_2 will then be anisotropic and so it is possible to define the probability of measuring γ_2 in a certain direction $\mathbf{k}_2$ at an angle θ in coincidence with γ_1 , where θ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ (see Figure 2.3). This angular correlation is given by^[33]:

$$W(\mathbf{k}_1, \mathbf{k}_2) = \sum_{m, m'} \langle m | \hat{\rho}(\mathbf{k}_1) | m' \rangle \langle m' | \hat{\rho}(\mathbf{k}_2) | m \rangle \quad (2.26)$$

$$W(\mathbf{k}_1, \mathbf{k}_2) = W(\theta) = \sum_{k=0}^{k_{max}} A_k(\gamma_1) A_k(\gamma_2) P_k(\cos(\theta)). \quad (2.27)$$

$P_k(x)$ are the Legendre polynomialsⁱⁱ and reflect the spacial angular distributions

ⁱⁱA Legendre polynomial of degree n is given by $P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} [(x^2 - 1)^n]$

of the emitted particles. $A_k(\gamma_1)$ and $A_k(\gamma_2)$ are the anisotropy terms and describe the deviation of the coincidence probability from the isotropic case where $W(\theta) = 1$. The latter depend on the correspondent angular momentum of the involved levels, on the type (γ , e^- , β^+ , β^-) and multipolarity of the emitted radiation and on the mixing ratios in the case of non-pure transitions. The sum is only over even k because the odd $A_k(\gamma)$ vanish as a consequence of parity conservation and the fact that the polarization of the γ photons is not measured. Also, the summation is finite due to conservation of angular momentum^[31]. Moreover, it is usual to consider $k_{max} = 4$ because the contributions from higher values of k are negligible. The values of the $A_{kk} = A_k(\gamma_1)A_k(\gamma_2)$ coefficients for each double-cascade decay can be found in the program *Nuclei*^[39] which uses a library developed in collaboration with the author of this thesis to calculate them (following the theoretical work on refs. 33 and 40).

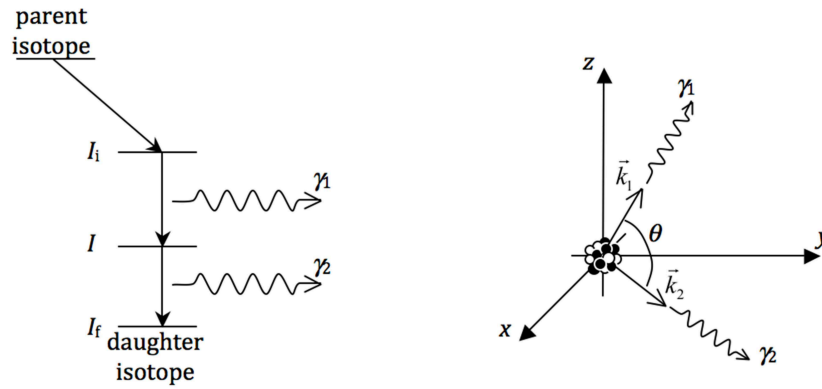


Figure 2.3 – A two-gamma nuclear cascade (from ref.^[31]).

Instead of measuring the directional correlation between successive γ photons, it is also possible to detect the corresponding conversion electrons and measure their correlation, thus enabling the following combinations: $\gamma - e^-$, $e^- - \gamma$, $e^- - e^-$. This procedure becomes feasible if at least one of the γ photons is moderately converted. In such cases, the equation 2.27 is still valid but with different anisotropy terms $A_k(e^-) = b_k(e^-)A_k(\gamma)$ ^[33], where the values for particle parameter $b_k(e^-)$ can be found in tables^[41].

2.1.4 Perturbed Angular Correlation

Note that in equation 2.27 it was used the state of the system immediately after the emission of γ_1 . However, this is only appropriate if the nuclei are not under the influence of external fields. Otherwise, hyperfine interactions may cause repopulations or state transitions before the second photon is emitted. This can be represented by replacing $\hat{\rho}(\mathbf{k}_1, 0)$ with $\hat{\rho}(\mathbf{k}_1, t)$, where

$$\hat{\rho}(\mathbf{k}_1, t) = \hat{\Lambda}(t)\hat{\rho}(\mathbf{k}_1)\hat{\Lambda}^\dagger(t) \quad (2.28)$$

and $\hat{\Lambda}(t)$ is the time-evolution operator. Inserting 2.28 into 2.26, it can be shown that the angular correlation function becomes^[33,35]

$$W(\mathbf{k}_1, \mathbf{k}_2, t) = \sum_{k_1, k_2, N_1, N_2} A_{k_1}(\gamma_1) A_{k_2}(\gamma_2) G_{k_1 k_2}^{N_1 N_2}(t) \frac{Y_{k_1}^{N_1*}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2)}{\sqrt{(2k_1 + 1)(2k_2 + 1)}} \quad (2.29)$$

where the angles θ_i and γ_i in the spherical harmonics refer to the direction of γ_i with respect to the z-axis and $G_{k_1 k_2}^{N_1 N_2}(t)$, the so-called perturbation factor, is given by

$$G_{k_1 k_2}^{N_1 N_2}(t) = \sum_{m_a, m_b} (-1)^{2I+m_a+m_b} \sqrt{(2k_1 + 1)(2k_2 + 1)} \begin{pmatrix} I & I & k_1 \\ m'_a & -m_a & N_1 \end{pmatrix} \times \\ \times \begin{pmatrix} I & I & k_2 \\ m'_b & -m_b & N_2 \end{pmatrix} \langle m_b | \hat{\Lambda}(t) | m_a \rangle \langle m'_b | \hat{\Lambda}(t) | m'_a \rangle^* \quad (2.30)$$

$m_{a,b}$ and $m'_{a,b}$ are the m quantum numbers of the intermediate state, the summation runs over $|m_{a,b}| \leq I$ and $m'_{a,b} = m_{a,b} - N_{1,2}$. Also, indices $N_{1,2}$ are restricted to $N_{1,2} \leq k_{1,2}$. It should be noted that all time dependence and effects of the perturbation due to the interaction of the nucleus with external electric or magnetic fields are contained in the perturbation factor.

The time-evolution operator $\hat{\Lambda}(t)$ obeys to Schrödinger equation

$$\frac{\partial}{\partial t} \hat{\Lambda}(t) = -\frac{i}{\hbar} \hat{H} \hat{\Lambda}(t) \quad (2.31)$$

so, if the Hamiltonian $\hat{H}$ is time-independent, the operator is given by

$$\hat{\Lambda}(t) = e^{-\frac{i}{\hbar} \hat{H} t}. \quad (2.32)$$

In the special case of magnetic interactions or axially symmetric electric quadrupole interactions ($\eta = 0$), by choosing the z-axis in the direction of the axial field, the matrix elements of the time-evolution operator are

$$\langle m_b | \hat{\Lambda}(t) | m_a \rangle = \langle m_b | e^{-\frac{i}{\hbar} \hat{H} t} | m_a \rangle = e^{-\frac{i}{\hbar} E(m)t} \delta_{m, m_a} \delta_{m, m_b} \quad (2.33)$$

where $m_a = m_b = m$, and a similar relation is valid for $\langle m'_b | \hat{\Lambda}(t) | m'_a \rangle$. Substituting eq.(2.33) in eq.(2.30) results in the perturbation factor for static axial interactions

$$G_{k_1 k_2}^{N N}(t) = \sum_m \sqrt{(2k_1 + 1)(2k_2 + 1)} \begin{pmatrix} I & I & k_1 \\ m' & -m & N \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m' & -m & N \end{pmatrix} \times \\ \times \exp \left\{ -\frac{i}{\hbar} [E(m) - E(m')] t \right\} \quad (2.34)$$

It can be seen that only the energy differences between m sub-levels appear in the perturbation factor, so a measurement of this factor allows one to determine these energy differences, and consequently the hyperfine interaction.

In the case of polycrystalline samples, the orientation of the hyperfine fields relative to the experimental frame of reference is not the same for all nuclei, hence the average of all possible orientations must be considered, which is done by integrating the Euler angles in the angular correlation function. The angular correlation function (eq. 2.29) then becomes

$$W(\theta, t) = \sum_k A_k(\gamma_1) A_k(\gamma_2) G_{kk}(t) P_k(\cos \theta) \quad , \theta = \angle(\mathbf{k}_1, \mathbf{k}_2) \quad (2.35)$$

where P_k are, once again, the Legendre polynomials and $G_{kk}(t)$ is given by

$$G_{kk}(t) = \frac{1}{2k+1} \sum_{N=-k}^{+k} G_{kk}^{NN}(t). \quad (2.36)$$

2.1.5 The Experimental Perturbation Function

A PAC experimental setup consists in a set of detectors whose apparatus is usually done in such a way that each pair of detectors has an angle of 90° or 180° between them. If a γ photon is detected by a detector i with energy $E_{\gamma 1}$, a clock is started. Then, after a certain amount of time, if a second γ photon is detected by another detector j with energy $E_{\gamma 2}$, the clock is stopped and the time and detector pair are stored in the coincidence counting rate of the pair of detectors i, j , given by:

$$N_{ij}(\theta, t) = N_0 e^{-\lambda t} W(\theta, t) + B \quad (2.37)$$

where N_0 is proportional to the number of radioactive nuclei present in the sample, $\lambda = 1/\tau$ for the intermediate state half-life time τ , θ is the angle between the direction of emission of each γ photon, $t = t_{\gamma 2} - t_{\gamma 1}$, $W(\theta, t)$ is the angular correlation function and B is proportional to the background random coincidence count rate, which is assumed to be time independent for simplicity.

After subtracting the background, B , an appropriate average of all the coincidence counting rate coming from the N_θ pairs of detectors with the same angle θ is made to minimize the effect of different detector efficiencies^[42]:

$$N(\theta, t) = N_\theta \sqrt{\prod_{ij} N_{ij}(\theta, t)} \quad (2.38)$$

To isolate the quantity providing all the relevant information (which is the angular correlation function, $W(\theta, t)$) and eliminate the undesired exponential terms, the experimental perturbation function $R(t)$ can be constructed as:

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)} = 2 \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)}. \quad (2.39)$$

since N_0 and $e^{-\lambda t}$ are the same for every $N(\theta, t)$.

The $R(t)$ function is the best way to get the information about the hyperfine interaction since it gives relevance to the perturbation factor $G(t)$ inside the angular correlation function. In Fig.(2.4) an example of the $R(t)$ function and its Fourier transform is shown for several values of η of a single EFG in a spin 5/2 intermediate nuclear level.

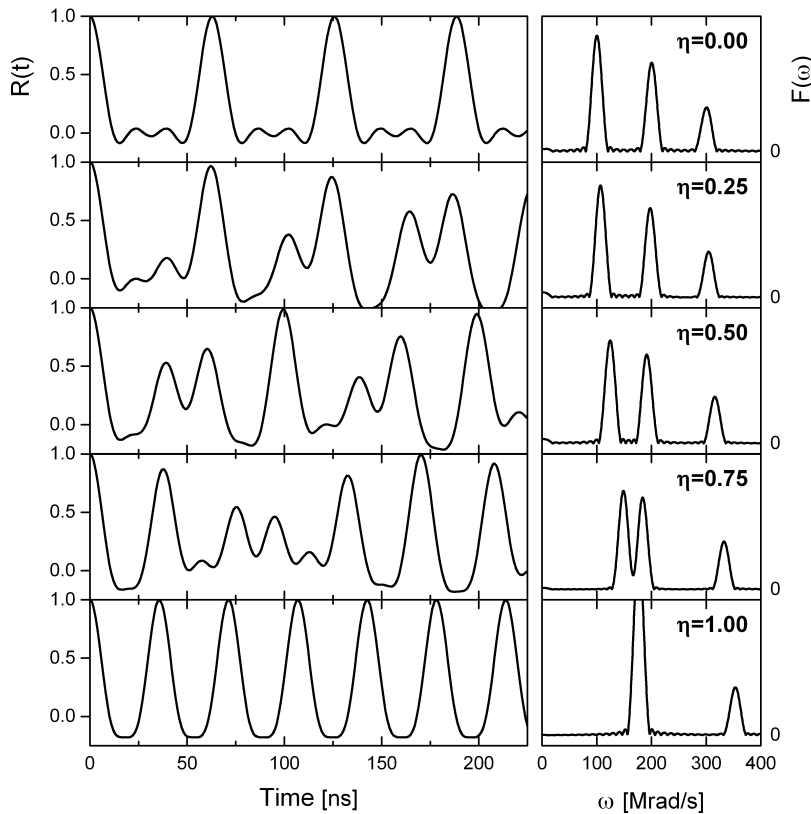


Figure 2.4 – Example of the experimental $R(t)$ function and the corresponding Fourier transform for different values of η in a spin 5/2 intermediate nuclear level, where the three characteristic frequencies ($\omega_1, \omega_2, \omega_3$) that fully characterize the EFG's parameters V_{zz} and η can be seen.

EFG Distribution

The existence of lattice defects near the probes (e.g. implantation defects) can produce slightly different hyperfine fields for probes that are in equivalent lattice sites. This means that instead of observing a well-defined hyperfine field, a distribution of hyperfine fields will be measured. For low concentration of defects, such distribution in the frequency space can be approximated to a Gaussian or Lorentzian distribution and it induces an attenuation in the PAC time spectrum amplitude. For static hyperfine fields (not time-dependent), such frequency (EFG) distributions are considered in time space

by multiplying each term of the $R(t)$ perturbation function by the adequate attenuation function.

For a Gaussian frequency distribution with standard deviation $\sigma = \frac{FWHM}{\sqrt{8 \ln 2}}$, the attenuation function (in time space) is given by:

$$D_{\text{gaussian}}(FWHM, t) = e^{-\frac{FWHM^2}{16 \ln 2} t^2} \quad (2.40)$$

whereas for a Lorentzian distribution it is given by:

$$D_{\text{lorentzian}}(FWHM, t) = e^{-\frac{FWHM}{2} t^2} \quad (2.41)$$

where FWHM is the distribution's Full Width at Half Maximum.

Time resolution

In order to take into account the finite time resolution (prompt) function of the spectrometer (which is assumed to be Gaussian-like), the coefficient of each observed frequency (ω_i) is multiplied by the term $P(FWHM^*, \omega_i)$, which has the form:

$$P(FWHM^*, \omega_i) = e^{-\frac{FWHM^{*2}}{16 \ln 2} \omega_i^2} \quad (2.42)$$

2.1.6 The Experimental Set-up

2.1.6.1 $\gamma - \gamma$ PAC

The $\gamma - \gamma$ PAC experiments reported in this work were performed in highly efficient 4- and 6-detector PAC machines equipped with BaF_2 or LaBr_3 scintillators^[43] (Fig. 2.5).

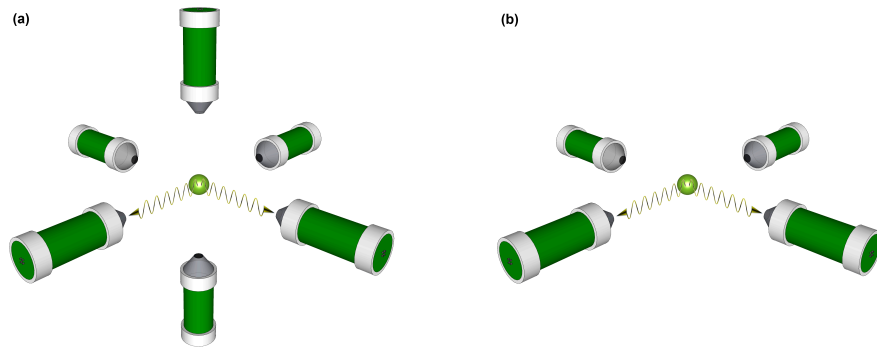


Figure 2.5 – Schemes of (a) 6-detector and (b) 4-detector assembly of the $\gamma - \gamma$ PAC spectrometer.

In the 6-detector setup, 6 $\gamma_1 - \gamma_2$ coincidence time spectra from detector pairs at $\theta = 180^\circ$ and 24 coincidence time spectra from detector pairs at $\theta = 90^\circ$ are simultaneously recorded, in a total of 30 spectra. In the 4-detector setup, only 12 spectra are recorded: 4 from detector pairs at $\theta = 180^\circ$ and 8 from detector pairs at $\theta = 90^\circ$. Using equations 2.38 and 2.39, the experimental $R(t)$ function is given by:

$$\begin{aligned}
 R(t) &= 2 \frac{\sqrt[6]{\prod_j N_j(180^\circ, t)} - \sqrt[24]{\prod_i N_i(90^\circ, t)}}{\sqrt[6]{\prod_j N_j(180^\circ, t)} + 2 \sqrt[24]{\prod_i N_i(90^\circ, t)}} && \text{for 6-detector set-up,} \\
 R(t) &= 2 \frac{\sqrt[4]{\prod_j N_j(180^\circ, t)} - \sqrt[8]{\prod_i N_i(90^\circ, t)}}{\sqrt[4]{\prod_j N_j(180^\circ, t)} + 2 \sqrt[8]{\prod_i N_i(90^\circ, t)}} && \text{for 4-detector set-up.}
 \end{aligned} \tag{2.43}$$

The measurements can be performed in a wide range of temperatures by using a temperature-controlled furnace for the high temperatures (up to 1100 °C) and a closed-cycle helium refrigerator equipped with a proportional-integral-derivative temperature controller (PID controller) and with the sample attached to the cold finger for the low temperatures (down to 10 K). In the cryostat case, a fast load-lock sample transfer system was developed to enable the presetting of the desired temperature in the cold finger to allow low temperature measurements in short-lived isotopes.

2.1.6.2 $e^- - \gamma$ PAC

The $e^- - \gamma$ PAC spectrometer used in this work has two magnetic lenses of the Siegbahn type^[44–46] for detection of conversion electrons and two BaF₂ scintillators for γ detection. Their arrangement is similar to the 4-detector PAC spectrometer set-up mentioned above, with each electron lens having a γ detector at an angle of 90° and 180° (Fig. 2.6). For measurements using a single crystalline sample, the sample surface normal usually makes 45° with both magnetic lenses.

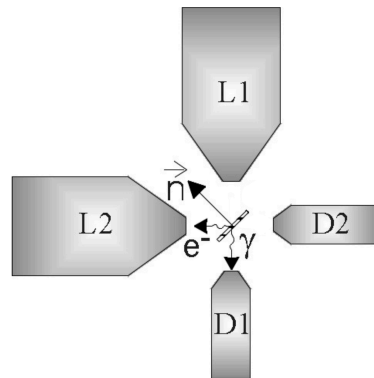


Figure 2.6 – Scheme of the $e^- - \gamma$ PAC spectrometer, composed by electron (L_1 , L_2) and gamma (D_1 , D_2) detectors. The sample surface normal $\vec{n}$ makes 45° with both electron detectors (adapted from ref.^[47]).

The sample is placed inside a vacuum chamber, where the sample holder is mounted on a feed-through system that allows sample changing without breaking the vacuum in

the chamber^[47,48]. Additionally, the sample holder is directly connected to the heating equipment for high temperature measurements (300 K to 1000 K) and a closed-cycle refrigerator with molecular shields allows the low temperature measurements (down to 10 K)^[47].

The energy resolution of the magnetic lenses mainly depends on the lens aperture. For a specific magnetic field only electrons with the right momentum will hit the plastic scintillators and trigger a signal. Since we use isotopes with simple decay schemes, the electron lines K, L and M are well separated for wide apertures leading to ~ 1 keV energy resolution, thus improving the selection of conversion electrons from the desired transition without admixtures from other ones. Moreover, since energy selection takes place before detection, the coincidence in the detectors is significantly reduced, allowing the selection of weaker peaks in the presence of intense transitions, as well as the use of samples with stronger activity without overloading the detectors. Finally, the time resolution is also enhanced by the detection of electrons in the magnetic lenses being optimized using plastic scintillators^[47].

In this set-up, 4 coincidence time spectra between a conversion electron and the γ radiation from the first and second transitions of the cascade, respectively, are recorder. There are electron-gamma detector pairs at relative angles of $\theta = 180^\circ$ and $\theta = 90^\circ$, whose respective counting rates are $N_j(180^\circ, t)$ and $N_i(90^\circ, t)$ (for $i, j = 1, 2$). Therefore, the experimental $R(t)$ function is given by:

$$R(t) = 2 \frac{\sqrt{\prod_j^2 N_j(180^\circ, t)} - \sqrt{\prod_i^2 N_i(90^\circ, t)}}{\sqrt{\prod_j^2 N_j(180^\circ, t)} + 2\sqrt{\prod_i^2 N_i(90^\circ, t)}}. \quad (2.44)$$

2.2 Density Functional Theory

An atom consists of a positively charged nucleus, which has most of the mass in it, with negatively charged electrons in well-defined orbitals. It is the motion of the electrons and their behavior that determines the chemical properties of the atom, how it reacts with other atoms, which molecules it can form and, in final instance, the structure of the materials formed by them and their physical properties. All these properties are dependent on the motion of electrons, which is well-described by Quantum Mechanics, namely by the Schrödinger equation. Nonetheless, the idea of calculating the properties of a given material is a many-body problem not possible to completely solve analytically, since the Schrödinger equation cannot be solved exactly for more than a few electrons due to each electron not only interacting with the nucleus but also interacting with all the other electrons. Moreover, even trying to solve the equation using a computer, the more electrons are added to the system, the larger the system gets and the problem becomes exponentially difficult to compute, including for sizes much lower than the typical size of

materials with physical, chemical or biological interest. A huge leap in the prospects of calculating such systems was given in 1964, when it was proven that all the properties of such interacting systems can be simply described by the electron density, where the electron density is basically the probability of finding one of the electrons somewhere in space. This is the basic premise of Density Functional Theory (DFT), which reduced a $3 \times N$ degrees of freedom problem (N electrons in 3 dimensions) to a 3 degrees of freedom problem (only the dimensions). In this section we will explore the most important characteristics of DFT in a summarized version, including the methods used specifically in this work.

2.2.1 The Born-Oppenheimer approximation

A solid composed of N atoms is basically a collection of N positively charged particles (nuclei) and $Z.N$ lighter, negatively charged particles (electrons) interacting electromagnetically (Z being the atomic number). This quantum many-body problem is exactly described by the following Hamiltonian:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} \\ & + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \end{aligned} \quad (2.45)$$

where M_i is the mass of a nucleus at $\vec{R}_i$, the electrons have mass m_e and are at $\vec{r}_i$, and Z_i is the atomic number^[49]. The first term is the kinetic energy operator for the nuclei, the second for electrons. The remaining terms correspond to the Coulomb interaction between electrons and nuclei, between electrons and other electrons and between nuclei and other nuclei, respectively. As said previously, it is impossible to solve the Schrödinger equation for such Hamiltonian. Therefore, one of the first approximations applied to simplify the equation is the Born-Oppenheimer approximation. This approximation states that, since the nuclei are much heavier (hence slower) than the electrons, they can be considered as having fixed positions with the electrons being in instantaneous equilibrium with them. Such approximation reduces the system to a collection of NZ electrons in an external field (whose source is the positive charge of the nuclei). Therefore, the first term in equation 2.45 disappears and the last term is a constant. The new Hamiltonian can now be written as

$$\hat{H} = \hat{T} + \hat{V} + V_{ext} \quad (2.46)$$

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}$ is the potential energy due to electron-electron interaction and V_{ext} is the potential energy of the electrons in the (external) potential of the nuclei^[49]. It is worth noting that the first two terms only depend

on the electrons and not on the nuclei, which means that all the information about the system (such as which nuclei and their positions) is only due to $\hat{V}_{ext}$.

For any eigenstate, Ψ , from the Hamiltonian, the correspondent energy E must verify:

$$E[\Psi] \geq E_0 \quad (2.47)$$

that is, the energy of state Ψ is always higher than the ground-state energy, $E_0 = E[\Psi_0]$. This means that the ground-state might be found by minimizing the ground-state functional or, using the Variational Principle, by:

$$\delta E[\Psi] = 0 \quad (2.48)$$

Although there are solutions to solve this problem, such as using Slater determinants, this is a very complex and expensive calculation due to the amount of degrees of freedom involved ($3 \times N$, as stated previously).

2.2.2 The Hohenberg and Kohn theorems

In 1964, Hohenberg and Kohn published two groundbreaking theorems that were the roots leading to the development of what was later designated Density Functional Theory^[50,51].

The first theorem states that the energy, E , of a system of interacting electrons in an external potential (in this case the potential due to the nuclei in a solid) is given exactly as a functional of the ground-state electronic density, ρ :

$$E = E[\rho] = T[\rho] + V[\rho] + V_{ext}[\rho] = F_{HK}[\rho] + \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \quad (2.49)$$

where the Hohenberg-Kohn functional $F_{HK}[\rho]$, defined as

$$F_{HK}[\rho] = T[\rho] + V[\rho] \quad (2.50)$$

is universal for any many-electron system^[49] and $V[\rho] = J[\rho] + \zeta[\rho]$ is the electron-electron interaction, where $J[\rho]$ is the classical repulsion

$$J[\rho] = \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2.51)$$

and $\zeta[\rho]$ is the non-classical term corresponding to the major part of the exchange-correlation energy^[52,53]. The exchange-correlation energy includes the interacting part of the electronic kinetic energy and the non-classical term from the electron-electron interaction:

$$E_{xc}[\rho] = T[\rho] + T_S[\rho] + V[\rho] - J[\rho] \quad (2.52)$$

where $T_S[\rho]$ is the non-interacting part of the electronic kinetic energy.

The second theorem states that the true ground-state density ρ is the density that minimizes $E[\rho]$ and that all the ground-state properties are also functionals of the ground-state density, existing a one-to-one correspondence between the ground-state density of the many-electron system and the external potential V_{ext} . $E[\rho]$ then reaches its minimum value E_0 (correspondent to the ground-state energy) for the ground-state density corresponding to V_{ext} :

$$E_0 \leq E[\tilde{\rho}] \quad (2.53)$$

such that $\tilde{\rho}(\vec{r}) \geq 0$ and $\int \tilde{\rho}(\vec{r}) d(\vec{r}) = N$. This is analogous to the variational principle in equation 2.47.

2.2.3 The Kohn-Sham method

Based on the Hohenberg and Kohn theorems, Kohn and Sham developed a model to find the ground-state of a many-electron system by introducing a fictitious system of non-interaction particles that generate the same ground-state density of the interacting particles system^[54]. The Hamiltonian for the non-interacting system is given by:

$$\hat{H}_S = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v_S(\vec{r}_i) \quad (2.54)$$

where there are no electron-electron interaction terms. The ground-state wave function of such system is given by $\Psi_S = \frac{1}{\sqrt{N!}} \det[\psi_1 \psi_2 \dots \psi_N]$, where ψ_i are the lowest eigenstates of the one-electron Hamiltonian $\hat{h}_S$

$$\hat{h}_S \psi_i = \left[-\frac{1}{2} \nabla^2 + v_S(\vec{r}) \right] \psi_i = \epsilon_i \psi_i. \quad (2.55)$$

and the electronic density for the N -particle system is $\rho = \sum_i^N |\psi_i|^2$.

By using the set of eigenstates ψ_i in the variational principle of Hohenberg and Kohn, the Kohn-Sham equations are obtained:

$$\left[-\frac{1}{2} \nabla^2 + V_{eff} \right] \psi_i = \epsilon_i \psi_i \quad (2.56)$$

with

$$V_{eff} = V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad (2.57)$$

and the exchange-correlation term given by $V_{xc}(\vec{r}) = \delta E_{xc} / \delta \rho(\vec{r})$.

The ground-state electronic density can then be found by solving these equations in a self-consistent way, starting by guessing an initial density which is used to calculate V_{eff} and then solve the Kohn-Sham equations to find the orbital functions ψ_i . These

orbital functions are used to calculate the new electronic density and the cycle starts again until convergence is reached, as illustrated in Figure 2.7.

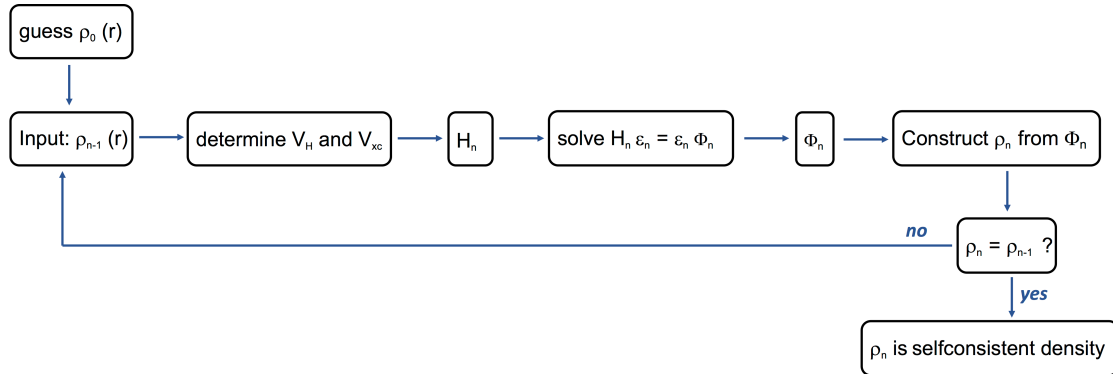


Figure 2.7 – Flow chart for the n^{th} iteration in the self-consistent procedure to solve the Kohn-Sham equations (adapted from ref.^[49]).

2.2.4 The exchange-correlation functional

Although the Kohn-Sham equations can be used to find the exact electronic density of a many-electron system (apart from the Born-Oppenheimer approximation), there is no known exact form for the exchange-correlation functional $E_{xc}[\rho]$. However, there are very good approximations that can be used to very accurately calculate physical quantities. The simplest and most widely used approximation is called the *Local Density Approximation* (LDA). It postulates that the exchange-correlation functional is given by

$$E_{xc}^{LDA} = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) d\vec{r} \quad (2.58)$$

considering that the exchange-correlation energy $\epsilon_{xc}(\rho(\vec{r}))$ due to a particular density $\rho(\vec{r})$ can be found by dividing the material in infinitesimally small volumes with constant density and each volume contributes to the total exchange-correlation energy by an amount equal to the exchange-correlation energy of an identical volume filled with a homogeneous electron gas that has the same overall density as the original material has in this volume^[49]. Despite the fact of LDA to be expected to perform well for systems with slow varying densities, it is verified that it works reasonably well for other cases too. To properly calculate the electronic density for magnetic systems, the *Local Spin Density Approximation* (LSDA) can be used, which generalizes the LDA method by using the spin-dependent densities in the calculation of the exchange-correlation function ($\rho = \rho_{\uparrow} + \rho_{\downarrow}$)^[51].

In order to improve on LDA, it is only logical for the contribution to the exchange-correlation of each infinitesimal volume to not only depend on the local density in that volume but also on the density in the neighboring volumes. This can be accomplished by

including gradient terms of the electron density into the exchange-correlation energy, i.e. $\epsilon_{xc}(\rho)$ is replaced by $\epsilon_{xc}(\rho, |\nabla\rho|)$ [49,51]. This approximation is called the *Generalized Gradient Approximation* (GGA). In LDA there is a unique definition of exchange-correlation functional, whereas in GGA there are several ways to incorporate the density gradient. Therefore, several versions of GGA exist. One such version was developed by Perdew, Burke and Ernzerhof (PBE) in 1996 [55] and it has been proven to be the best one for most cases. For this reason, it is the approximation used in the simulations performed in this work.

The use of GGA for the exchange-correlation energy and potential has been proven very successful on the calculation of structural properties of materials, whose accuracy is good enough to help interpret experimental data and even to have some predictive power. Unfortunately, GGA is known to underestimate the band gap of semiconductors and insulators, giving result to band structures that badly agree with experimental ones, whereas other methods such as hybrid functionals or the GW method can yield very accurate band gaps but lead to very expensive calculations. With this in mind, the modified Becke-Johnson potential (mBJ) was developed, yielding band gaps and band structures in very good agreement with experiment and with an accuracy comparable to approaches which are orders of magnitude more expensive, but being as cheap as LDA or GGA [56]. However, it is a potential and not a functional, so forces cannot be determined when using mBJ. The recommended approach is to use first a GGA functional for the structural properties and then use the mBJ potential for the calculation of the band structure and density of states. Consequently, this is was the approach applied in this work.

2.2.5 The L/APW+lo method

To solve the Kohn-Scham equations, a suitable basis set for the single-particle orbitals ψ_i must be chosen. In fact, solving the equations is basically to find the coefficients c_p^i needed to express ψ_i in a given basis set ϕ_p :

$$\psi_i = \sum_{p=1}^P c_p^i \phi_p \quad (2.59)$$

The wave functions ϕ_p belong to a function space which has infinite dimension, so P should be infinite. However, in practice a limited set of functions must be used. This limited set will never exactly describe ψ_i , but a basis set may be found that gives a solution very close to ψ_i . Evidently, the bigger the basis set, the more accurate the solution. On the other hand, the bigger the basis set, the bigger the matrices that have to be diagonalized to solve the Kohn-Scham equations. There are more efficient basis sets which are able to provide good convergence for smaller matrix sizes. However, such basis sets usually perform very well for some specific cases and very poorly for

the remaining cases, thus being called biased. The goal here is to find a basis set that is simultaneously efficient and unbiased^[49].

The description for a suitable basis set here discussed is called the *Augmented Plane Wave* (APW) method. In this method, the unit cell is divided in two regions: the region far away from the nuclei (interstitial space, I), where the electrons behave almost like free-electrons and are thus described by plane waves, and the region close to the nuclei (so-called muffin tin spheres, S_α) where the electrons behave quite as if they were in a free atom, so they can be described by atomic-like functions. For each atom is then defined a sphere with radius R_α that separates both regions. The basis functions $\phi_{\vec{K}}^{\vec{k}}$ for the expansion of $\psi_{\vec{k}}^n$ are

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{l,m} A_{lm}^{\alpha,\vec{k}+\vec{K}} u_l^\alpha(r', E) Y_m^l(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \quad (2.60)$$

Note that the basis set depends on $\vec{k}$, so different $\vec{k}$ corresponds to a different basis. Since it is not possible to have an infinite basis set, the set is limited to all $\vec{K}$ with $K \leq K_{max}$, corresponding to a sphere with radius K_{max} centered at the origin of the reciprocal space. A cut-off energy can then be defined as $E_{cut} = \frac{\hbar^2 K_{max}^2}{2m_e}$. V is the volume of the unit cell. α is the index of the muffin-tin spheres and $\vec{r}' = \vec{r} - \vec{r}_\alpha$ is the position given with respect to the center of each sphere. $\hat{r}'$ indicates the spherical coordinates θ' and ϕ' specifying the direction of $\vec{r}'$. Y_m^l are spherical harmonics. The $u_l^\alpha(r', E)$ are solutions for the radial part of the Schrödinger equation for a free atom α at the energy E . The atoms are not free, hence u_l^α are only working as parts of the basis functions, do not correspond to something physical themselves. $A_{lm}^{\alpha,\vec{k}+\vec{K}}$ are defined such that both functions are equal over the complete surface of the sphere. To do so, the plane wave can be expanded in spherical harmonics:

$$\frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} = \frac{4\pi}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}_\alpha} \sum_{l,m} i^l j_l(|\vec{k}+\vec{K}| |\vec{r}'|) Y_m^{l*}(\vec{k}+\vec{K}) Y_m^l(\hat{r}') \quad (2.61)$$

where $j_l(x)$ is the Bessel function of order l . The number of $A_{lm}^{\alpha,\vec{k}+\vec{K}}$ required to solve the equation is infinite, but in practice that number is truncated at some value l_{max} , which is defined by the condition $R_\alpha K_{max} = l_{max}$ since both values are comparable quantities. The APW method seems to be a good solution but there is an important drawback: in order to accurately describe an eigenstate, E needs to be equal to the eigenvalue of that state. However, the eigenvalues are exactly what it is supposed to be calculated! Therefore, one is forced to start with a guessed value for the eigenvalues and take this as E . The APW's are then possible to be constructed and the characteristic equation of the Hamiltonian can be determined, but one diagonalization is needed for every eigenvalue, thus making the APW method inherently slow^[49]. Such an issue would be solved

if the quantities $u_l^\alpha(r', E)$ could be known on the fly. For this reason, the LAPW method was developed on top of APW, enabling the calculation of $u_l^\alpha(r', E)$ from known quantities.

The *Linearized Augmented Plane Wave* (LAPW) method considers a Taylor expansion of $u_l^\alpha(r', E)$ around some energy E_0 [49]:

$$u_l^\alpha(r', \epsilon_k^n) = u_l^\alpha(r', E_0) + (E_0 - \epsilon_k^n) \frac{\partial u_l^\alpha(r', E)}{\partial E} \Big|_{E=E_0} + \mathcal{O}((E_0 - \epsilon_k^n)^2) \quad (2.62)$$

Substituting in equation 2.60, the basis functions become

$$\phi_K^k(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{l,m} \left(A_{lm}^{\alpha, \vec{k}+\vec{K}} u_l^\alpha(r', E_0) + B_{lm}^{\alpha, \vec{k}+\vec{K}} \dot{u}_l^\alpha(r', E_0) \right) Y_m^l(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \quad (2.63)$$

The A and B coefficients are determined by requiring that the function in the sphere matches the plane wave both in value and in slope at the sphere boundary. The value of E_0 must be approximately the energy at the center of the band corresponding to the eigenstate ψ_k^n which is being determined, thus resulting in a set of several E_0 : $E_{1,l}^\alpha$. For example, if ψ_k^n is predominantly composed by a superposition of p orbitals ($l = 1$), E_0 should be close to the center of the p band. The basis functions in the LAPW method are then given by:

$$\phi_K^k(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{l,m} \left(A_{lm}^{\alpha, \vec{k}+\vec{K}} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha, \vec{k}+\vec{K}} \dot{u}_l^\alpha(r', E_{1,l}^\alpha) \right) Y_m^l(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \quad (2.64)$$

Similar to the APW method, the cut-off parameter that determines the accuracy of the basis set is the product $R_\alpha^{\min} K_{\max}$ between the smallest muffin tin radius and $K_{\max}$. A bigger radius allows a smaller $K_{\max}$ without the loss of precision, thus fewer plane waves being needed. On the other hand, $R_\alpha^{\min}$ cannot be too large, as the spherical harmonics are not suited to describe the wave functions in the region far away from the nuclei [49].

The LAPW basis set is appropriate to describe electron states but not for all the electrons in a material. Electrons in lower orbits are extremely well bound to the nucleus and thus behave almost exactly as if they were in a free atom. These states are called *core states*. Core states do not participate directly in chemical bonding with other atoms, so they must be entirely contained in the muffin tin sphere. States that participate in the chemical bonds are the ones that leak out of the muffin tin sphere, called *valence states*. Only valence states are treated by LAPW, whereas core states are treated as in free atoms but subject to the potential due to the valence states. Nonetheless, this

binary definition allows states with the same l but different quantum number n to both be valence states, where the electrons with lower n are very close to the nucleus but not entirely confined in the core (e.g., bcc-Fe electrons in $3p$ - and $4p$ -states^[49]). These low-lying valence states are called *semi-core states*. This brings the question of where to set $E_{1,l}^\alpha$: close to the semi-core state, close to the valence state or at an intermediate level? This problem is solved by adding another type of basis function to the LAPW basis set, called a *local orbital* (LO), defined as:

$$\phi_{\alpha,LO}^{lm}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_\alpha \\ \left(A_{lm}^{\alpha,LO} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha,LO} \dot{u}_l^\alpha(r', E_{1,l}^\alpha) + C_{lm}^{\alpha,LO} u_l^\alpha(r', E_{2,l}^\alpha) \right) Y_m^l(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \quad (2.65)$$

A local orbital is defined for each atom independently and for a particular l and m , being zero in the muffin tin sphere of any other atom and in the interstitial region. The three coefficients A , B and C are determined by requiring that the local orbital is normalized and has zero value and slope at the sphere boundary. Increasing the basis set by adding local orbitals increases the computational time but the improvement in precision is more than compensatory.

The concept of local orbital can also be used to improve the APW method directly, resulting in the APW+lo method. This has the advantage of having a basis set of the same size as the regular APW. The local orbitals however are not the same type of local orbitals used with LAPW, being defined for a fixed set of energies $E_{1,l}^\alpha$ as^[49]

$$\phi_{\vec{K},\vec{k}}^{lm}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\vec{r}} & \vec{r} \in I \\ \sum_{l,m} A_{lm}^{\alpha,\vec{k}+\vec{K}} u_l^\alpha(r', E_{1,l}^\alpha) Y_m^l(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \quad (2.66)$$

For some particular states (e.g., states in atoms that have a muffin tin sphere that is much smaller than others spheres in the unit cell) to be described correctly, the use of LAPW would require a large number of basis functions, hence requiring a larger K_{max} than APW+lo. Therefore, a mixed basis set can be used, where those states are treated with APW+lo and the other states are still treated with LAPW. In this way, it is possible to achieve accurate results whilst keeping the value of $R_{min} K_{max}$ low^[49,51]. This method is usually referred to as L/APW+lo and it is the recommended choice in the WIEN2k package^[57], which was used for the DFT simulations in this work.

2.2.6 Calculating the Electric Field Gradient

One of the most important aspects of the DFT simulations in this work is the ability to calculate the electric field gradient at some impurity site in a given material in order to compare it to the PAC experiments. This way, we can reliably tell the position of the radioactive probes inside the material, as well as their charged state.

The principal component of the electric field gradient, V_{zz} , can be obtained from the

charge density $\rho(\vec{r})$ by^[58]

$$V_{zz} = \int \rho(r) \frac{2P_2(\cos \vartheta)}{r^3} dr \quad (2.67)$$

where P_2 is the second-order Legendre Polynomial given by

$$P_2(x) = \frac{1}{2^2 2!} \frac{d^2}{dx^2} [(x^2 - 1)^2] = \frac{1}{2} (3x^2 - 1). \quad (2.68)$$

The V_{xx} and V_{yy} components (and consequently the asymmetry parameter η) can be obtained in a similar fashion^[58,59].

CHAPTER 3

PACme: a generalized program for the simulation, analysis and visualization of PAC data

3.1 Introduction

As already introduced in Chapter 2, Perturbed Angular Correlations (PAC) is a nuclear hyperfine technique that has been widely used in the last decades to study a multitude of phenomena such as point defect structure, electronic excitation, local deformations, etc. By accurately measuring the electromagnetic field around a probe atom, which is very sensitive to the nearest neighbor atoms and charge distribution at the probe's site, it allows the characterization of the probes environment at the nanoscale. However, dynamic phenomena originating transient fields at the probes site are scarcely understood due to the complexity of the analysis. Meanwhile, electronic dynamic interactions are revealed in quite different research areas, often when using PAC as experimental method, e.g., (i) the existence of phenomena like polaron formation and dynamic distortions in manganite systems^[60], (ii) the locally restricted motion of hydrogen and deuterium trapped at Cd acceptors in silicon, with special interest in the ability of hydrogen to passivate the electrical activity of levels related to impurities by hydrogen-impurity pair formation^[61] and, besides research in Physics, (iii) very interesting applications of PAC to dynamic interactions systems are also being done in biochemistry due to the possibility of experiments to be carried out under physiological conditions as well as the capability of being applied to many physical states (in solution, frozen samples, crystals, in vivo, etc.), as can be seen in the work of L. Hemmingsen *et al.*^[62,63] relating to metal ions and their interaction with biomolecules with a particular focus on metalloproteins, describing the function of metal ions in biological systems at the atomic level.

In order to analyze time-dependent interactions in PAC, H. Winkler and E. Gerdau developed a theory based on stochastic fluctuating fields, where the underlying stochastic process which causes the fluctuations of the hyperfine interaction is by definition a stationary Markoff process^[64]. Despite having the knowledge about the theory, for one to be able to analyze experimental data showing the presence of this kind of dynamic phenomena, computational routines that include time-dependent interactions in PAC

are required, hence the development of PACme, the software we are herein reporting.

Zacate *et al.* ^[65,66] have developed a library containing a set of routines to assist on the design of applications using stochastic models of hyperfine interactions, providing an example code to illustrate the use of the library to generate PAC spectra for the special case of polycrystalline samples when anisotropy terms of higher order than A_{22} can be neglected. Nonetheless, the motivations driving us to make PACme are two-fold: First, we believe that there was the need for a program specifically tailored for PAC that should be able to handle any conceivable configuration from a PAC experiment right "out-of-the-box" (without requiring the user to program any line of code) and it should do it in a user-friendly way, enabling the simulation, analysis and visualization of PAC experimental data with dynamic hyperfine fields in such way that the user only had to provide the minimum parameters as possible. The program should then work for electric quadrupole and magnetic interactions with anisotropy coefficients up to A_{44} in polycrystalline and single-crystalline samples with any nuclear spin and being able to consider any number of different probe's sites with a different number of possible states for each site, including dynamic transitions between those states. Second, it is known that small imperfections in the crystal lattice or the existence of non-periodic defects might induce a distribution of frequencies around a central value for probes at the same lattice site, which is crucial to be considered for a correct analysis of experimental data in PAC. However, there was no known way to analytically integrate such static frequency distributions for different states in the presence of dynamic interactions.

As such, the purpose of this chapter is to report PACme, its construction, functionality and show how it implements all of the characteristics mentioned above. It starts with a theoretical overview about dynamic interactions (time-dependent interactions) in PAC. Then, an implementation of EFG distributions is explained, followed by some general test cases and examples to show the potential applications of the program.

3.2 Theoretical Overview

A more detailed overview regarding the theory of Perturbed Angular Correlations was already done on section 2.1, but here the most important remarks are reinforced for a better understanding on the introduction of dynamic interactions in PAC, followed by the development of the general expression for the perturbation function in such cases.

3.2.1 Hyperfine Interactions

Recalling the theory introduced in section 2.1, the interaction between a nucleus and its surrounding environment is called hyperfine interaction. The Hamiltonian describing this interaction is composed of a series of terms but in a PAC experiment the only two contributions come from the electric quadrupole interaction and the magnetic dipole interaction.

The electric quadrupole interaction corresponds to the hyperfine interaction between the electric quadrupole moment of a nucleus and the electric field gradient (EFG) at its site. The existence of a non-null quadrupole moment indicates a deformation in the spherical shape of the nucleus, however still existing a symmetry axis (thus, a spherically symmetric charge distribution has a null quadrupole moment) and the EFG is a tensor corresponding to the second-derivative of the electric potential at the nuclear site (therefore having information about the charge distribution around the nucleus). It is always possible to find a coordinate system where the EFG is a diagonal traceless matrix, so it can be completely described by two terms: the V_{zz} component and the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$, with $0 \leq \eta \leq 1$ ^[34]. The strength of this interaction is characterized by the observable quadrupole frequency ω_0 :

$$\omega_0 = k\omega_Q, \quad \omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (3.1)$$

where I and Q are the spin and electric quadrupole moment of the nuclear state, respectively, and $k=3$ (or 6) for integer (or half-integer) spin^[34].

The magnetic dipole interaction corresponds to the hyperfine interaction between the magnetic nuclear dipole moment and the magnetic field at the nuclear site. The strength of this interaction is characterized by the Larmor frequency ω_L :

$$\omega_L = -g \frac{\mu_N}{\hbar} B \quad (3.2)$$

where g is the g-factor, μ_N is the nuclear magneton and B is the magnitude of the magnetic field at the nuclear site. The origin of the magnetic field can come from an external applied field or from internal magnetic moments in the case of ferromagnetic and antiferromagnetic materials^[34].

3.2.2 Perturbed Angular Correlations for Fluctuating Hyperfine Fields

In section 2.1, it was explained that when a radioactive isotope decays in a double-cascade, there is an angular correlation between the direction of emission of γ_1 and γ_2 , which is described by the angular correlation function (see eq. 2.26):

$$W(\mathbf{k}_1, \mathbf{k}_2) = \sum_{m, m'} \langle m | \hat{\rho}(\mathbf{k}_2) | m' \rangle \langle m' | \hat{\rho}(\mathbf{k}_1) | m \rangle = \text{Tr} \{ \hat{\rho}(\mathbf{k}_2) \hat{\rho}(\mathbf{k}_1) \} \quad (3.3)$$

where the vector $\mathbf{k}_i$ defines the direction of emission of γ_i , $\hat{\rho}(\mathbf{k}_i)$ is the density operator representing the state of the system after the emission of γ_i and "Tr" is the trace of the matrix.

However, if during the time the isotope remains in the intermediate level before the emission of γ_2 the nucleus is subject to hyperfine interactions, the degeneracy of this level will be lifted and a change in the occupation of the different sub-levels will be promoted, therefore occurring a time modulation in the angular correlation. Considering

then the initial density operator $\hat{\rho}(\mathbf{k}_1, 0)$ describing the nuclear system after the emission of γ_1 , the nuclear state at the moment t when γ_2 is emitted is given by

$$\hat{\rho}(\mathbf{k}_1, t) = \hat{\Lambda}(t)\hat{\rho}(\mathbf{k}_1, 0)\hat{\Lambda}^\dagger(t) = \hat{\Omega}(t)\hat{\rho}(\mathbf{k}_1, 0) \quad (3.4)$$

where $\hat{\Lambda}(t)$ is the usual time-evolution operator and $\hat{\Omega}(t)$ is the time-evolution super-operator, represented in the Liouville formalism as

$$\hat{\Omega} = \exp \left\{ -\frac{i}{\hbar} \int_0^t H^\times(t) dt \right\} \quad (3.5)$$

such that $H^\times$ is the Liouville operator for the Hamiltonian H of the system, having the property of its action on any operator A being equal to the commutator of H and A : $H^\times A = [H, A]$ ^[67].

In this case, the angular correlation function is then given by

$$W(\mathbf{k}_1, \mathbf{k}_2, t) = \text{Tr} \left\{ \hat{\rho}(\mathbf{k}_2) \hat{\Omega}(t) \hat{\rho}(\mathbf{k}_1, 0) \right\} \quad (3.6)$$

To calculate the angular correlation function in the case of fluctuating hyperfine fields, H. Winkler and E. Gerdau^[64] considered a system described by a time-dependent Hamiltonian in which the interaction is jumping randomly between a finite number of N states:

$$\hat{H}(t) = \sum_{j=1}^N \hat{V}_j f_j(t) \quad (3.7)$$

being $\hat{V}_j$ the interaction Hamiltonian of state j and the set of functions $f_j(t)$, satisfying the condition $f_{k \neq j}(t_1) = 0$ if $f_j(t_1) = 1$, for any time t_1 , defining the state in which the system is at a given instant of time.

Also, they considered the dynamic of the system to be ruled as a Markov process, meaning that the probability $P_{a \rightarrow b}(\tau_1, \tau_2)$ of finding the system in the state b at a moment τ_2 when it was in the state a at $\tau_1 \leq \tau_2$ is independent of the "history", i.e., of the states which were passed by the system before τ_1 , and depends only on the time interval $t = \tau_2 - \tau_1$.

Then, to determine the time-evolution operator, one considers the vector space of the system to be a direct product of the angular momentum eigenstates $|Im\rangle$ and the states $|a\rangle$ of the nuclear environment, being the complete orthonormal set of base operators in the Liouville space represented by the ket-bra products $|a\rangle|Im\rangle\langle Im'|\langle a| \equiv |amm'\rangle$ and, assuming that the stochastic process is not influenced by the particular orientation of the nucleus, the time interval t is divided in $n + 1$ subintervals $\Delta t = t/(n + 1)$, resulting in

$$\begin{aligned} \langle c | \hat{\Omega}(t) | a \rangle &= \lim_{n \rightarrow \infty} \sum_{i_1, \dots, i_n} P_{a \rightarrow i_1}(\Delta t) \dots P_{i_n \rightarrow c}(\Delta t) \\ &\quad \cdot \exp\left(-\frac{i}{\hbar} V_c^\times \Delta t\right) \dots \exp\left(-\frac{i}{\hbar} V_{i_2}^\times \Delta t\right) \cdot \exp\left(-\frac{i}{\hbar} V_{i_1}^\times \Delta t\right) \end{aligned} \quad (3.8)$$

with $\exp(-i/\hbar V_i^\times \Delta t)$ representing the time-evolution when the system is on state i . For small time intervals Δt , the following relations are postulated:

$$P_{a \rightarrow a}(\Delta t) \approx 1 - \gamma_a \Delta t \quad (3.9)$$

$$P_{a \rightarrow b}(\Delta t) \approx \omega_{a \rightarrow b} \Delta t \quad (3.10)$$

being $\omega_{a \rightarrow b}$ the transition probabilities per time unit and, as a consequence of normalization (with $\omega_{a \rightarrow a} = 0$), $\gamma_a = \sum_b \omega_{a \rightarrow b}$.

After some calculations, the final expression for the time-evolution operator is obtained:

$$\hat{\Omega}(t) = \exp \left[\left(-\frac{i}{\hbar} H_{st}^\times + \hat{R} \right) \right] \quad (3.11)$$

with the elements of the argument matrix, the so-called Blume matrix, being given by:

$$(bm_2 m'_2 | \hat{R} | am_1 m'_1) = \delta_{m_1 m_2} \delta_{m'_1 m'_2} \omega_{a \rightarrow b} \quad (3.12)$$

$$(am_2 m'_2 | \hat{R} | am_1 m'_1) = -\delta_{m_1 m_2} \delta_{m'_1 m'_2} \sum_b \omega_{a \rightarrow b} \quad (3.13)$$

$$(bm_2 m'_2 | H_{st}^\times | am_1 m'_1) = \delta_{ab} (m_2 m'_2 | V_a^\times | m_1 m'_1) \quad (3.14)$$

$$(m_2 m'_2 | V_a^\times | m_1 m'_1) = \delta_{m'_1 m'_2} \langle m_2 | \hat{V}_a | m_1 \rangle - \delta_{m_1 m_2} \langle m'_1 | \hat{V}_a | m'_2 \rangle \quad (3.15)$$

$H_{st}^\times$ is the "super-Hamiltonian" constructed from the Hamiltonians $\hat{V}_j$ of the different stochastic states and the transition matrix $\hat{R}$ contains the transition probability rates $\omega_{a \rightarrow b}$ from $|a\rangle$ to $|b\rangle$ environment. Considering the eigenvalues and eigenvectors of the Blume matrix

$$\left(-\frac{i}{\hbar} H_{st}^\times + \hat{R} \right) |M_q\rangle = (-\lambda_q + i\omega_q) |M_q\rangle \quad (3.16)$$

$$(N_q | \left(-\frac{i}{\hbar} H_{st}^\times + \hat{R} \right) = (-\lambda_q + i\omega_q) (N_q | \quad (3.17)$$

it can be shown that the angular correlation function takes the form

$$W(\mathbf{k}_1, \mathbf{k}_2, t) = \sum_{k_1, k_2, N_1, N_2} A_{k_1}(\gamma_1) A_{k_2}(\gamma_2) \cdot \frac{Y_{k_1}^{N_1*}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2)}{\sqrt{(2k_1 + 1)(2k_2 + 1)}} G_{k_1 k_2}^{N_1 N_2}(t) \quad (3.18)$$

where A_k are the anisotropy coefficients, $Y_k^N(\theta, \phi)$ are the spherical harmonics (with θ and ϕ being the angles in spherical coordinates for the emission directions $\mathbf{k}$) and the perturbation factor being given by

$$G_{k_1 k_2}^{N_1 N_2}(t) = \sum_{m_1, m_2} (-1)^{2I+m_1+m_2} \sqrt{(2k_1 + 1)(2k_2 + 1)} \cdot \begin{pmatrix} I & I & k_1 \\ m'_1 & -m_1 & N_1 \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m'_2 & -m_2 & N_2 \end{pmatrix} \cdot \sum_{a, b, q} p_a(bm_2 m'_2 | M_q)(N_q | am_1 m'_1) e^{(-\lambda_q + i\omega_q)t} \quad (3.19)$$

The frequencies ω_q represent a set of oscillations in the angular correlation function and the terms $-\lambda_q$ were proven by Winkler and Gerdau to always be negative, thus representing a damping in the function. Without any kind of transitions between different states the latter term disappears, so the existence of a damping might be seen as the signature of the presence of dynamic processes.

In the case of polycrystalline samples, by averaging over the Euler angles, the angular correlation function for polycrystalline sources is

$$W(\theta, t) = \sum_k A_k(\gamma_1) A_k(\gamma_2) G_{kk}(t) P_k(\cos \theta) \quad , \theta = \angle(\mathbf{k}_1, \mathbf{k}_2) \quad (3.20)$$

where P_k are Legendre polynomials and $G_{kk}(t)$ is given by^[64]

$$G_{kk}(t) = \sum_{m_1, m_2} (-1)^{2I+m_1+m_2} \begin{pmatrix} I & I & k \\ m'_1 & -m_1 & N \end{pmatrix} \begin{pmatrix} I & I & k \\ m'_2 & -m_2 & N \end{pmatrix} \cdot \sum_{a, b, q} p_a(bm_2 m'_2 | M_q)(N_q | am_1 m'_1) e^{(-\lambda_q + i\omega_q)t}. \quad (3.21)$$

When more than one possible site exists for the probes, the observed angular correlation function will be given by

$$W(\theta, t) = \sum_i f_i W_i(\theta, t) \quad (3.22)$$

where f_i is the relative intensity of each angular correlation function $W_i(\theta, t)$ representing the i^{th} fraction of probes interacting with a particular EFG and/or magnetic field (with $\sum f_i = 1$) and θ is the angle between the direction of emission of the two photons.

3.3 Breakthrough Implementation of Static Frequency Distributions

PAC measurements in imperfect crystal lattices, where the hyperfine field responsible for the nuclear interactions is not exactly the same for all the probes, gives rise to the existence of a distribution of frequencies around a measured central value^[68]. Gaussian and Lorentzian distributions are often used to describe the effect of static fields distributions in the $R(t)$ perturbation function, being integrated in the angular correlation function for a proper analysis of the experimental spectra. The real shape of a static distribution depends very much on the origin of the distributions and most of the times these are not discussed in detail. Hereby we will concentrate on the implementation of Lorentzian distributions, further knowing that different shapes could be approximated by a linear combination of several Lorentzian terms, as will be demonstrated further ahead.

The time-evolution operator is the only component which depends on the observable frequencies, so it is the only component which has to be integrated over the distribution of each frequency. Considering a static frequency distribution $D(\omega)$ for each possible state in eq.3.8, we get

$$(c|\hat{\Omega}(t)|a) = \lim_{n \rightarrow \infty} \int_{i_1} \dots \int_{i_n} D(\omega_{i_1}) \dots D(\omega_{i_n}) d\omega_{i_1} \dots d\omega_{i_n} \cdot \sum_{i_1, \dots, i_n} P_{a \rightarrow i_1}(\Delta t) \dots P_{i_n \rightarrow c}(\Delta t) \exp\left(-\frac{i}{\hbar} V_c^\times \Delta t\right) \dots \exp\left(-\frac{i}{\hbar} V_{i_1}^\times \Delta t\right) \quad (3.23)$$

where $D(\omega_{i_1}) \equiv D(\omega_{i_1}; \omega_{0_i}, \Gamma_i) \equiv \frac{1}{\pi\Gamma} \left[\frac{\Gamma^2}{(\omega_i - \omega_{0_i})^2 + \Gamma^2} \right]$ is a Lorentzian distribution with central frequency ω_{0_i} and full width at half maximum (FWHM) equal to 2Γ that verifies $\int_{-\infty}^{+\infty} D(\omega_{i_1}) d\omega_{i_1} = 1$.

Since each exponential depends only on one frequency, we get

$$(c|\hat{\Omega}(t)|a) = \lim_{n \rightarrow \infty} \sum_{i_1, \dots, i_n} P_{a \rightarrow i_1}(\Delta t) \dots P_{i_n \rightarrow c}(\Delta t) \cdot \int_{i_1} D(\omega_{i_1}) \exp\left(-\frac{i}{\hbar} V_{i_1}^\times \Delta t\right) d\omega_{i_1} \dots \int_{i_n} D(\omega_{i_n}) \exp\left(-\frac{i}{\hbar} V_c^\times \Delta t\right) d\omega_{i_n} \quad (3.24)$$

By using the characteristic function of the Cauchy distribution

$$\phi(t; \omega_i, \Gamma) = \int_{-\infty}^{+\infty} D(\omega; \omega_i, \Gamma) e^{i\omega t} d\omega = e^{i\omega_i t - \Gamma|t|} \quad (3.25)$$

and considering that $t \geq 0$ and $\Gamma \geq 0$, it can be shown that

$$\begin{aligned}
\int_{-\infty}^{+\infty} D(\omega_i; \omega_{0_i}, \Gamma_i) e^{-\frac{i}{\hbar} V_i^{\times} t} d\omega_i &= \int_{-\infty}^{+\infty} D(\omega_i; \omega_{0_i}, \Gamma_i) e^{-\frac{i}{\hbar} \omega_i V_i^{\times'} t} d\omega_i = \exp \left(-\frac{i}{\hbar} \omega_{0_i} V_i^{\times'} t - \frac{\Gamma_i}{\hbar} |V_i^{\times'} t| \right) = \\
&= \exp \left[-\frac{i}{\hbar} \left(\omega_{0_i} V_i^{\times'} - |\Gamma_i V_i^{\times'}| \right) t \right] = \exp \left[-\frac{i}{\hbar} \left(V_i^{\times} - |V d_i^{\times}| \right) t \right]
\end{aligned} \tag{3.26}$$

where the substitution $V_i^{\times} = \omega_i V_i^{\times'}$ can be done due to the fact of the interaction Hamiltonian being always proportional to the frequency. $V d_i^{\times}$ is then equal to $V_i^{\times}$ but changing ω_{0_i} to Γ_i .

It is true that $|V d_i^{\times}| = P |W_i^{\times}| P^{-1}$ for a matrix P containing the eigenvectors of $V d_i^{\times}$ as columns and $|W_i^{\times}|$ being a diagonal matrix containing the norm of the eigenvalues of $V d_i^{\times}$, so

$$\exp \left[-\frac{i}{\hbar} \left(V_i^{\times} - |V d_i^{\times}| \right) t \right] = \exp \left[-\frac{i}{\hbar} \left(V_i^{\times} - P |W_i^{\times}| P^{-1} \right) t \right] = \exp \left(-\frac{i}{\hbar} H_i^{\times} t \right) \tag{3.27}$$

for $H_i^{\times} = (V_i^{\times} - P |W_i^{\times}| P^{-1})$. Therefore, eq.3.23 transforms into

$$\begin{aligned}
(c|\hat{\Omega}(t)|a) &= \lim_{n \rightarrow \infty} \sum_{i_1, \dots, i_n} P_{a \rightarrow i_1}(\Delta t) \dots P_{i_n \rightarrow c}(\Delta t) \\
&\cdot \exp \left(-\frac{i}{\hbar} H_c^{\times} \Delta t \right) \dots \exp \left(-\frac{i}{\hbar} H_{i_2}^{\times} \Delta t \right) \exp \left(-\frac{i}{\hbar} H_{i_1}^{\times} \Delta t \right)
\end{aligned} \tag{3.28}$$

This is equal to eq.3.8 only changing V to H , which means that the remaining calculation done by Winkler and Gerdau is still valid. Therefore, to include the static distributions for each state, the operators $H_a^{\times}$ must be used in equation 3.15 instead of the operators $V_a^{\times}$.

Lorentzian Basis Function for Generalized Distributions

It can be verified that for the majority of situations (if not all) where a distribution of frequencies (hyperfine fields) in PAC is needed, a Lorentzian distribution is very accurate to within the experimental errors. Nonetheless, some users might prefer to use other distribution functions, such as a Gaussian distribution. However, only a Lorentzian function can be analytically integrated in the perturbation function (for dynamic interactions) using the previously described method. Therefore, the use of Gaussian distributions requires numerical integration, which would be computationally very heavy (for a system with transitions between s different states, each one described by a Gaussian distribution function divided in N points, we would have N^s times more calculations).

Fortunately, there is a better solution by using a Lorentzian basis function, i.e., by constructing the desired distribution as a sum of several Lorentzian curves. This hy-

pothesis was tested for a Gaussian distribution $\left(f(\omega) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{(\omega-\omega_0)^2}{2\sigma^2}}\right)$ considering $\omega_0 = 100$ and $\sigma^2 = 10$, and fitting a Lorentzian basis function composed by: one, three, five and seven Lorentzian curves. The results can be seen on Figure 3.1 and it is clear that even a small-sized Lorentzian basis function gives a curve very close to the Gaussian curve. In fact, even using only 3 basis functions, the curves are already very similar.

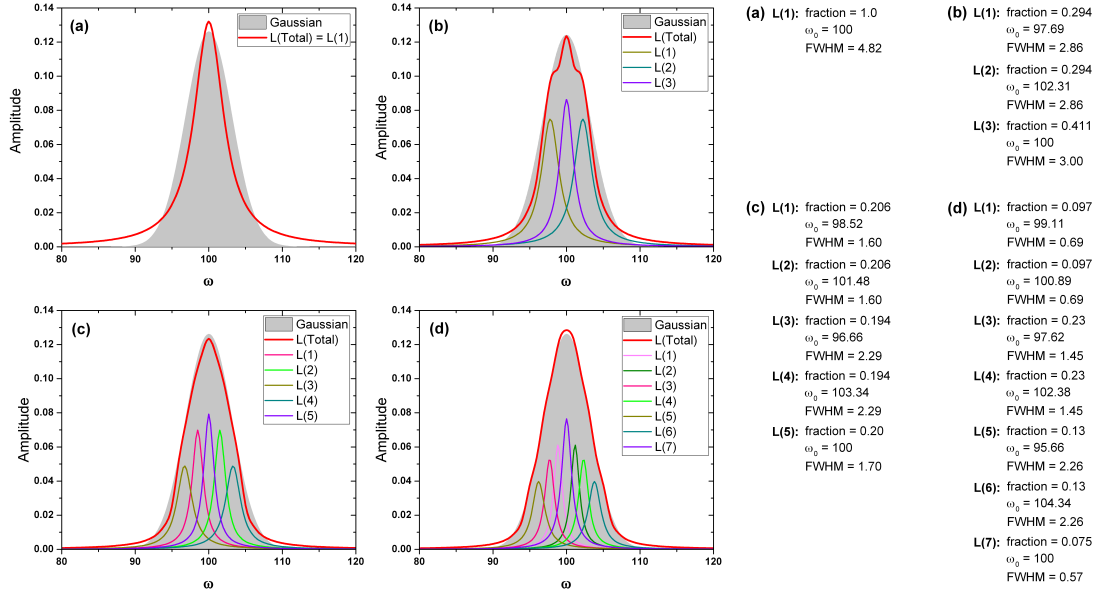


Figure 3.1 – Gaussian function fitted to a sum of Lorentzian basis functions, considering (a) one, (b) three, (c) five and (d) seven Lorentzian basis functions. The fitted fraction, central frequency (ω_0) and full width at half maximum (FWHM) of each Lorentzian base function ($L(i)$) are also shown, where $L(\text{total}) = \sum_i L(i)$.

In conclusion, if a more complex distribution must be used, a linear combination of Lorentzians can be found and easily implemented on PACme. The calculation will be more expensive than using a single Lorentzian-distributed state but it will be much cheaper than considering numerical integration for, e.g., a Gaussian distribution.

3.4 Test Cases and Examples

So far, we have only approached the theory of fluctuating hyperfine fields in PAC in its most general mathematical form. This is exactly as implemented in the PACme algorithm, where there are no limitations regarding the number of different states (hence hyperfine fields) under consideration and the corresponding transitions between them, as well as the initial probabilities of each one. However, in order to get a better sense of what kind of phenomena might be simulated or analyzed using PACme, here are demonstrated several practical examples. Moreover, in section 3.4.1.2, an ad-hoc comparison is made between the analytical solution implemented in PACme for the static frequency distributions of dynamic fields (see Section 3.3) and an implementation considering the

substitution of the integral by a direct sum of N different frequencies with the same distribution (numerical integration).

This is not an exhaustive study of all the specific cases and phenomena that can be analyzed using the program but rather a limited set of the more usual ones, often observed experimentally.

All the examples are simulations generated using PACme, but analytical solutions (or close approximations) for some of the most simple cases can be found for instance in refs. 64, 69 and 70, whose conclusions are in great accordance to our observations.

3.4.1 Unidirectional Transition

One of the most basic examples of fluctuating fields in PAC is described by an unidirectional transition from an initial state to a final state. This can be observed, e.g., for measurements performed with the ^{111}In isotope which decays to ^{111}Cd by electron-capture, thus being submitted to drastic changes in its electronic shells and its neighbors^[71]. After losing quite a number of electrons due to Auger emission, the system relaxes into thermal equilibrium by recovering the lost charges until a stable configuration is achieved. For slow recoveries (in the nanoseconds scale) such charge fluctuations are visible in a PAC experiment. Examples of such transitions have been observed in PAC measurements of La_2O_3 samples^[71] and Ga_2O_3 samples (Section 5 of this work) using ^{111}In probes.

3.4.1.1 Simple Unidirectional Transition

In Figure 3.2 it is shown the perturbation function and correspondent Fourier transform from a simple simulation of a probe with spin 3/2 in a polycrystal considering two axially symmetric EFGs having $\omega_0(1) = 100 \text{ Mrad/s}$ and $\omega_0(2) = 200 \text{ Mrad/s}$, respectively. At the instant $t = 0$ all probes are in state 1 and then transition to state 2 as a function of the transition rate $\Gamma_{1 \rightarrow 2}$ (where $\Gamma_{a \rightarrow b}$ corresponds to $\omega_{a \rightarrow b}$ in equations 3.12 and 3.13).

For slow rates, the initial state dominates and it is the only one being observed in the $R(t)$, having a single peak in the Fourier transform (due to the spin 3/2). As the transition rate increases, the final state starts to appear and at intermediate rates (around 20 MHz) the mixture of both states is at its highest, therefore the biggest damping in the $R(t)$ is observed. For fast rates, the final state becomes the only one being observed, due to transition times shorter than measurement times.

Another example of unidirectional transition can be seen in Figure 3.3 from a probe with spin 5/2 in a single crystal and considering two axially symmetric EFGs with the same $\omega_0 = 100 \text{ Mrad/s}$ but different orientations, as a function of the transition rate $\Gamma_{1 \rightarrow 2}$. The orientation of each EFG in the single crystal is given by the Euler angles, which are $\alpha(1) = 45^\circ$ and $\beta(1) = 90^\circ$ for EFG(1) (corresponding to a V_{zz} in the detectors' plane with 45° between them) and $\alpha(2) = \beta(2) = 0^\circ$ for EFG(2) (V_{zz} perpendicular to the detectors' plane).

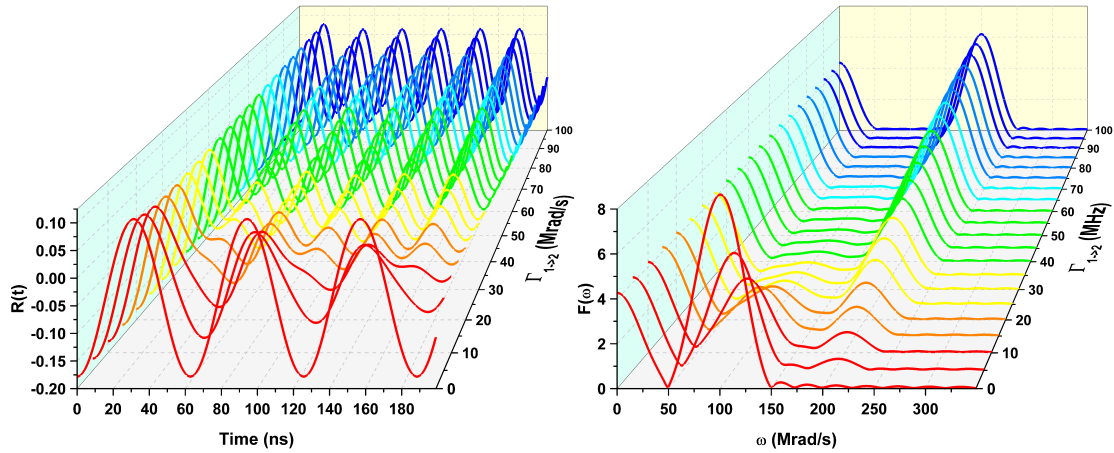


Figure 3.2 – Unidirectional transition from an initial state with $\omega_0(1) = 100$ Mrad/s to a final state with $\omega_0(2) = 200$ Mrad/s for spin-3/2 in a polycrystal as a function of the transition rate $\Gamma_{1 \rightarrow 2}$. Perturbation function $R(t)$ on the left and correspondent Fourier transform on the right.

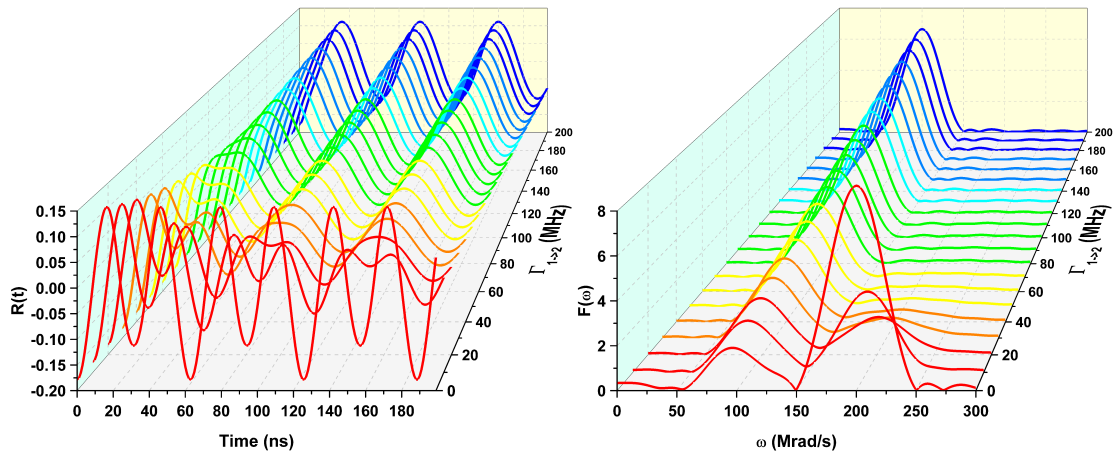


Figure 3.3 – Unidirectional transition from an initial state with $V_{zz}(1)$ having a 45° angle between the detectors to a final state with $V_{zz}(2)$ perpendicular to the detectors' plane for spin-5/2 in a single crystal as a function of the transition rate $\Gamma_{1 \rightarrow 2}$. Perturbation function $R(t)$ on the left and correspondent Fourier transform on the right.

In this case, the used anisotropy coefficients correspond to the double cascade of $^{111}\text{In}/^{111}\text{Cd}$: $A_{22} = -0.1782$, $A_{24} = -0.206$, $A_{42} = -0.00128$ and $A_{44} = -0.00147$. For such a probe, a unique EFG in a single crystal has only one peak at $\omega = \omega_0$ in the Fourier transform for a V_{zz} perpendicular to the detectors' plane and two peaks for a V_{zz} having a 45° angle between the detectors, one at $\omega = \omega_0$ and the other at $\omega = 2\omega_0$ (with the second peak much higher than the first). Similar to the previous example, for slow rates the initial state dominates and for faster rates the final state dominates, with the biggest mixture (hence bigger damping) at the intermediate rates.

3.4.1.2 Unidirectional Transition with Static Frequency Distributions

Although the previous examples are good enough to get a feeling on what to expect from an unidirectional transition between two EFGs in PAC, real-world experimental data require the implementation of static frequency distributions to be well analyzed, as explained in section 3.3.

To confirm that our analytical implementation for the integration of static frequency distributions is giving the correct results, a comparison can be done to a "brute-force" integration by substituting the integral by a sum of N different frequencies from the same frequency distribution curve and increase N until no changes are observed. Using once again the first example, fixing the transition rate at $\Gamma_{1 \rightarrow 2} = 20$ MHz and considering a Lorentzian frequency distribution for both states with $\text{FWHM}(1) = 20$ Mrad/s and $\text{FWHM}(2) = 25$ Mrad/s, a comparison between our analytical integration and a "brute-force" integration can be seen in Figure 3.4 for several values of N . For $N \geq 70$ the two curves are indistinguishable, thus showing that our analytical solution is indeed implementing the static frequency distributions for each state correctly, even for dynamic transitions.

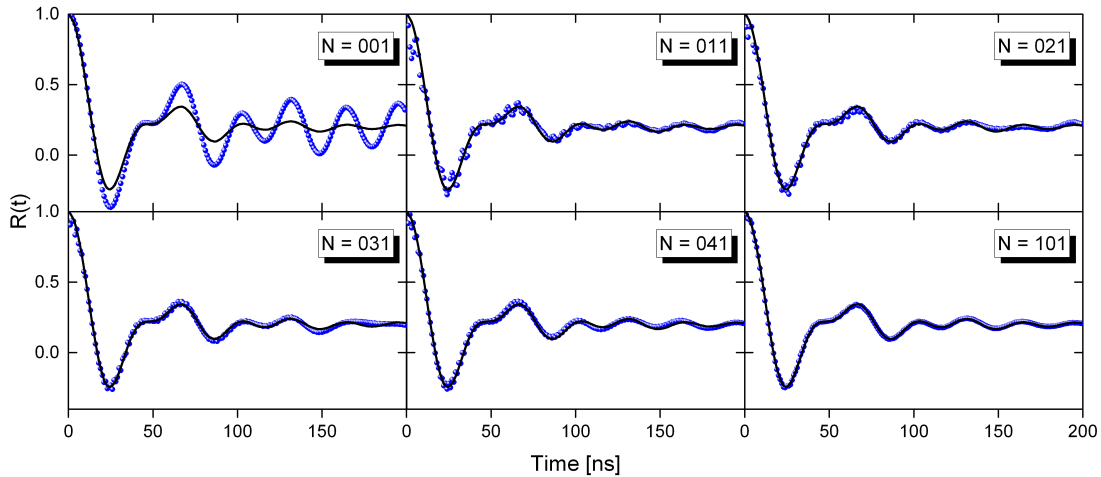


Figure 3.4 – Analytical integration of static frequency distributions (black curve) versus a numerical integration for different values of N summed frequencies (blue dotted curve).

For the experiments with ^{111}In ($I=5/2$) mentioned before, the recovery of the lost inner-shell electrons during the decay from higher orbit electrons is very fast (within about 10^{-14} s^[71]) but they leave holes in the valence band which are later compensated by electrons from the host material. The chaotic initial state of a probe before recovering the missing electrons in the valence band can be described by a single central quadrupole frequency with a broad distribution. After recovering the electrons, the probes are in a stable configuration with a well defined quadrupole frequency. Figure 3.5 represents such configuration as a function of the transition rate $\Gamma_{1 \rightarrow 2}$ with spin-5/2 in a polycrystal for $\omega_0(1) = 150$ Mrad/s, $\text{FWHM}(1) = 70$ Mrad/s, $\omega_0(2) = 100$ Mrad/s and $\text{FWHM}(2) = 0$ Mrad/s.

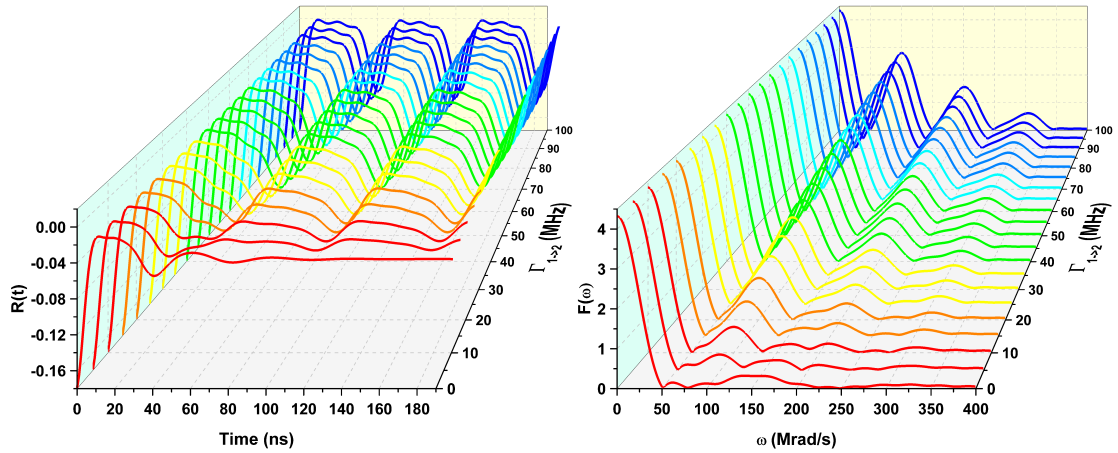


Figure 3.5 – Unidirectional transition for spin-5/2 in a polycrystal considering an initial state with broad static frequency distribution (FWHM = 70 Mrad/s) and a final well-defined state (FWHM = 0 Mrad/s).

3.4.2 XYZ model

The XYZ model describes the fluctuation in the orientation of the symmetry axis of an axially symmetric EFG along the x, y and z axis^[64,65,72]. It is a simple model for some Jahn-Teller distortions and jump diffusion of vacancies^[64]. In Figure 3.6 it is shown the perturbation function and correspondent Fourier transform from a simulation of such model for a probe of spin 5/2 in a polycrystal considering 3 states with the same $\omega_0 = 100$ Mrad/s and $\eta = 0$ as a function of the transition rates between two different orientations, Γ_r .

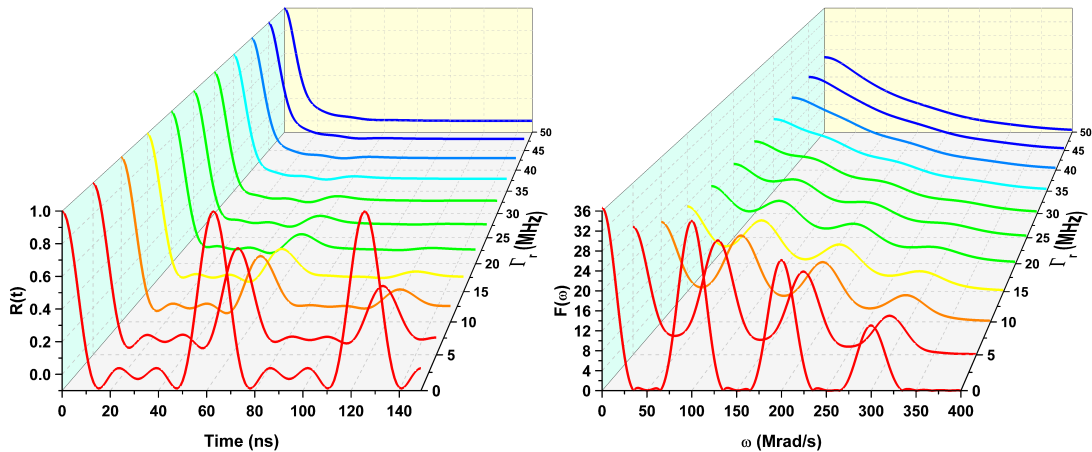


Figure 3.6 – XYZ model for spin-5/2 in a polycrystal as a function of the transition rate Γ_r . Perturbation function $R(t)$ on the left and correspondent Fourier transform on the right.

In a polycrystal with static hyperfine fields, the observable frequencies are independent of the direction of the field. Therefore, it can be seen that for $\Gamma_r = 0.0$ the $R(t)$ is equal to the one corresponding to a single EFG, which is composed of a series of oscillations described by three frequencies, ω_0 , $2\omega_0$ and $3\omega_0$ (for spin 5/2), even in the presence of more than one EFG as in this case, as long as they only differ in direction and not in ω_0 and η . However, as soon as Γ_r increases, the oscillations start to be

damped and for fast rates the $R(t)$ is approximately described by an exponential whose decay rate is inversely proportional to Γ_r , in accordance with Winkler and Gerdau^[64]. It must also be noted that the so-called "hard-core", which is preserved in damped spectra corresponding to strongly damaged environments, vanishes in this case.

3.4.3 Fluctuating EFG strength in Thermal Equilibrium

Let us consider a dynamic model where there are two possible states $|1\rangle$ and $|2\rangle$ for the charge distribution around a probe atom described by axially symmetric EFG's ($\eta = 0$) with the same principal axes system but different strengths ($\omega_0(1) \neq \omega_0(2)$). If $\Gamma_{1 \rightarrow 2}$ is the transition rate for $|1\rangle \rightarrow |2\rangle$ and $\Gamma_{2 \rightarrow 1}$ is the transition rate for $|2\rangle \rightarrow |1\rangle$, the equilibrium probability for the system to be in state $|1\rangle$ is $p_1 = \Gamma_{1 \rightarrow 2}/\Gamma$, with $\Gamma = (\Gamma_{1 \rightarrow 2} + \Gamma_{2 \rightarrow 1})$, and the system shows an exponential relaxation to this value with time constant $1/\Gamma$ ^[70]. The case of thermal equilibrium is then defined by $p_1 = p_{10}$, where p_{10} is the probability of state $|1\rangle$ at the instant $t = t_0$, and in this case the system only depends on the two dynamic parameters p_1 and Γ .

In Figure 3.7 we can see the perturbation function and corresponding Fourier transform for such a system as a function of Γ , considering spin 5/2, $\omega_0(1) = 120$ Mrad/s, $\omega_0(2) = 100$ Mrad/s and $p_1 = 50\%$.

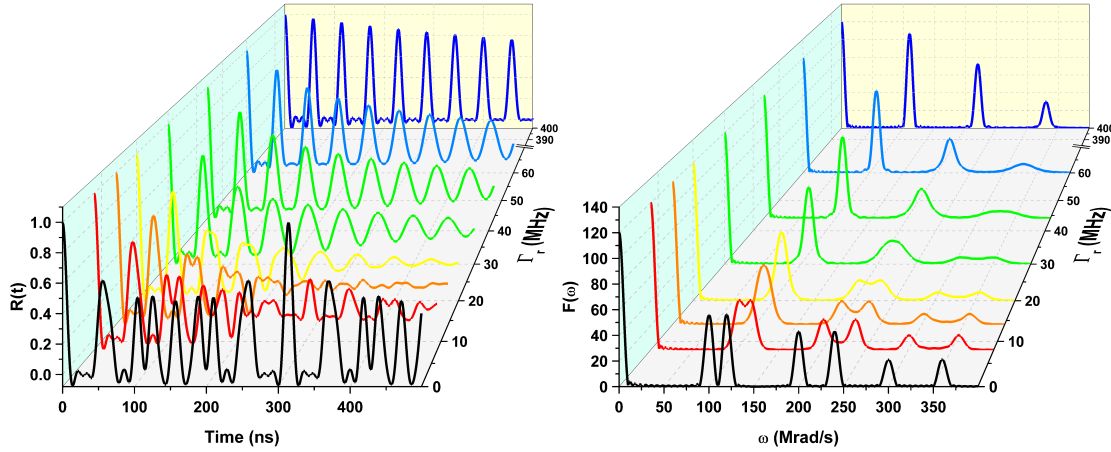


Figure 3.7 – Fluctuating EFG strength in Thermal Equilibrium for spin-5/2 as a function of the transition rate Γ . Perturbation function $R(t)$ on the left and correspondent Fourier transform on the right.

For $\Gamma = 0$, the perturbation function consists of two static fractions, each one corresponding to the EFG of one state. As soon as the transition rate increases, the three harmonics of each fraction start to be damped and the frequencies of both fractions slightly shift towards each other.

For fast rates ($\Gamma \rightarrow \infty$), the damping disappears and the perturbation function is described by a single static EFG whose strength is the average of the two single EFG's, weighted by the probabilities p_1 and $p_2 = 1 - p_1$, that is: $\omega_0 = p_1 * \omega_0(1) + p_2 * \omega_0(2)$. In the example presented in Figure 3.7 we have $p_1 = p_2 = 0.5$, $\omega_0(1) = 120$ Mrad/s

and $\omega_0(2) = 100 \text{ Mrad/s}$, so it can be seen that for the highest rate considered the perturbation function is already very close to the one corresponding to a single EFG characterized by $\omega_0 = 110 \text{ Mrad/s}$.

In the intermediate regime between the nearly static behavior and the fast fluctuations, the strongest phase shifts and damping occur when $\Gamma \sim \omega_0(1) - \omega_0(2)$ (considering $\omega_0(1) > \omega_0(2)$), as predicted by Achtziger and Witthuhn^[70].

As a final note, going from equilibrium to non-equilibrium conditions ($p_1 \neq p_{10}$) would make the initial probabilities to be the percentage of each fraction for $\Gamma = 0$ whilst the equilibrium probabilities would still be the weights of each EFG in the faster rates regime.

This simple model was analytically explored in ref. 70 and used to interpret PAC measurements regarding Cd-donor pairs in silicon.

3.5 Software Overview

PACme is a program that allows the simulation, analysis and visualization of the experimental PAC observable considering not only static hyperfine fields but also dynamic (time-dependent) hyperfine fields. The PAC spectra is determined using the theory developed by Winkler and Gerdau (see section 3.2), thus being possible to consider a set of different possible states and the transitions between them. Its main characteristics are:

- The possibility of simulation and fitting data obtained for both single-crystalline and polycrystalline samples;
- Any nuclear spin value for the intermediate state can be used;
- Unlimited number of fractions (see equation 3.22 for the definition of fraction), each one having different number of states and including dynamic transitions between those states;
- Static distributions implemented analytically for each state individually, even in dynamic interactions.

Such a program is the first, to our knowledge, to properly simulate and fit PAC experimental data for single crystals (in addition to polycrystals) considering dynamic interactions and, more importantly, to implement different static distributions for each state separately in such time-dependent interactions (see section 3.3).

It is completely written in C++ in order to make it cross-platform and computationally fast. The entire source code will be open-sourced and there are 4 external libraries being used, all of them open source as well: CLAPACK, GSL, Minuit2 and Gnuplot (see Appendix A.4 for more information). The program was written considering object-oriented programming (OOP) in order to provide a cleaner structure and a more easily

maintained source code, including the improvement of current features and even the inclusion of new ones (see Appendix A.3 for more information).

The operation of the program can be divided in two sections: the simulation routine and the fitting routine. The simulation routine aims the calculation of the perturbation function $R(t)$ for a set of input parameters and the fitting routine uses the simulation routine to find the best set of parameters that describe a given experimental data set. Therefore, when PACme is called, the following sequence occurs:

- Read and treatment of the input data (including parameters file and experimental data file);
- If the simulation routine is called
 - Construction of the Blume matrix $\left(-\frac{i}{\hbar}H_{st}^{\times} + \hat{R}\right)$ and calculation of its eigenvalues $(-\lambda_q + i\omega_q)$ and eigenvectors $|M_q\rangle$ and $|N_q\rangle$;
 - Construction of the perturbation function $R(t)$ and its Fourier transform;
 - Print the the perturbation function $R(t)$ and correspondent Fourier transform to external files and show the respective plots;
- If the fitting routine is called
 - The simulation routine is called for every new set of parameters until the χ^2 -function gets to its minimum;
 - The parameters corresponding to the minimum χ^2 are displayed;
 - Print the perturbation function $R(t)$ from the best fit and correspondent Fourier transform to external files and show the respective plots;

The software documentation of PACme is in Appendix A. It includes the software installation and usage instructions with full description of the input parameters file and the output files. It also includes the computational program structure with a description of the main functions inside each C++ class, as well as a description of all used external libraries.

For more details on the diagonalization of the Blume matrix, see Appendix A.4. For a comprehensive description of the minimization routine developed to find the set of parameters that minimizes the χ^2 -function, see section 3.6.1.

3.6 Internal Algorithms

From the several algorithms working inside of PACme, two of them are worth a detailed description: the minimization routine developed to find the set of parameters that minimizes the χ^2 -function and the routine used to calculate the Fourier transforms of the simulated and experimental data.

3.6.1 χ^2 -function and Minuit2

In order to find the best curve that fits the experimental data, the program searches for the set of parameters that minimize the following χ^2 (chi-squared) function:

$$\chi^2 = \frac{1}{N} \sum_{i=0}^N \left[\frac{(y_i - f(x_i))^2}{(\Delta y_i)^2} \right] \quad 0 < \chi^2 < \infty \quad (3.29)$$

where N is the number of data points, y is the independent variable, x is the dependent variable, f is the relationship between x and y , y_i is the "observed mean", $f(x_i)$ is the "predicted mean" and Δy_i is the error in the experimental measurements of y_i . Of course f might have several variables (parameters), being represented as $f((x_1)_i, (x_2)_i, \dots)$. In summary, the χ^2 -function will compare the difference between our experimental data points y_i and the fitting curve $f(x_i)$ (in our case, the simulated $R(t)$ function) with experimental error Δy_i . It is obvious that a better fit yields a smaller χ^2 . However, attention must be paid to the fact that $\chi^2 \ll 1$ might be achieved for small $(y_i - f(x_i))^2$ but it also might be due to big $(\Delta y_i)^2$. This means that $\chi^2 \ll 1$ might indicate a very good fit or indicate that the experimental errors are so high that no credible curve can be found for the data points, since several different curves might fit the data to within those errors. Therefore, the best scenario is to have $(y_i - f(x_i))^2 \approx (\Delta y_i)^2$ (considering reasonable experimental errors) which would mean a predictive curve whose difference from the experimental data is similar to the experimental error. In this situation, $\chi^2 \approx 1$. During a fit, the program always tries to find the minimum χ^2 , but if $\chi^2 \ll 1$, the magnitude of the experimental errors must be taken into consideration before accepting the fitting results as the correct ones.

For the minimization of the χ^2 -function, the Minuit2 package is used^[73]. It requires a dedicated class inherited from its *FCNBase* class, which implements the function to be minimized (the χ^2 -function, in this case). In PACme, the dedicated class is called *PMinimizer*. Several minimization methods are available in Minuit2, but in this case the MIGRAD method is used since it is the most efficient and complete single method, recommended for general functions^[73]. The parameters to be fitted are chosen by the user in the parameters' file and given to *PMinimizer* as input. Then, MIGRAD will be called internally and the parameters will be varied until the χ^2 -function minimum is found (to within a certain tolerance). The final parameters are considered to be the best fit to the experimental data.

Minuit2 treats all the parameters as independent variables. However, the weight of the fractions and the initial probabilities of all states in a single fraction are not completely independent, since their sum must be equal to 1 (required by equations 3.19 and 3.22). Therefore, if N fractions are considered, only $f_{i>1}$ will be varied by Minuit2 and f_1 is automatically set to $1 - \sum_{i=2}^N f_i$. In case $f_1 < 0$ is obtained, a huge value is automatically considered for the χ^2 to inform Minuit2 that this set of fractions is not physically valid. Moreover, if any fractions are fixed, 1 minus the sum of all fixed values is considered as

the maximum value that any other fraction might have. The same method is considered for the initial probabilities of the states of each fraction.

The “best” values of a set of parameters are defined as those values which minimize the χ^2 -function. The shape (or the width) of the function in the vicinity of the minimum gives information about the uncertainty of the parameters. In this case, the definition of “error” is given in terms of the change in the χ^2 value caused by changing one parameter by one “error”. It is known that for the usual χ^2 -function, if the user wants the usual one-standard-deviation errors, the “error” definition should be 1^[73]. Since in this case the χ^2 is being normalized by the number of points N (see equation 3.29), the definition of “error” is $1/N$ and the errors of each parameter correspond to one-standard-deviation. The minimization routine will run until the estimated vertical distance to minimum (EDM)^[74] is less than $0.002 * \text{tolerance} / N$ or a maximum number of calls is (approximately) reached. The default tolerance is set to 0.1 to ensure a value of EDM more than three orders of magnitude smaller than the “error”. The maximum number of calls and the tolerance might be set by the user (see section A.2).

3.6.2 Fourier transforms class

The method used to calculate the Fourier transform is based on the Fast Fourier Transform (FFT) routine from NNFit^[75], a Fortran 77 program that was developed to fit PAC data but only for static hyperfine fields. The routine is then a translation to C++ from the original Fortran 77 routine. Besides performing a regular FFT calculation of the given data, it includes extra options to manipulate the data and improve the resulting output. This options can be controlled in the parameters file:

Average Removal:

It is possible to calculate and remove the average from all data points to reduce the size of the zero-frequency peak in the Fourier transform.

Data Mirroring:

In a data set $\{f_k\}$ that starts at $f_0 = 0$ or at f_0 with zero slope, data mirroring can be used which will force the input to be an odd or an even series, doubling the size of the data set^[76]. In such cases:

$$f_{-k} = f_k \quad \text{for even series}$$

$$f_{-k} = -f_k \quad \text{for odd series}$$

Doubling the data set improves the resolution of the Fourier transform by a factor of two.

Attention must be paid to the fact that in the case of even/odd mirroring, the imagi-

nary/real component of the Fourier transform vanishes. Therefore, even (or odd) mirroring must only be applied to data sets which verify zero slope at f_0 (or $f_0 = 0$), at least approximately. Otherwise, information can be lost or fictitious peaks can appear.

Usually, the perturbation function $R(t)$ is approximately equal to a series of cosine terms, thus being an even series. Consequently, doing an even mirroring usually improves the Fourier transform of the PAC experimental data. Nonetheless, a throughout analysis of the real and imaginary components of the Fourier transform (and not only of its full amplitude) must be done to ensure that such mirroring can be performed without data damaging.

Kaiser-Bessel window:

The perturbation function $R(t)$ is defined between $t = 0$ and $t = +\infty$. However, in an experimental measurement we have a finite time interval. This is equivalent to multiplying $R(t)$ by a rectangular window (step function) $f(t)$:

$$f(t) = \begin{cases} 1 & \text{for } -T/2 \leq t \leq T/2 \\ 0 & \text{else} \end{cases} \quad (3.30)$$

where T is the experimental time interval. The resulting Fourier transform of such a product is given by the Convolution Theorem, which states that^[76]:

$$f(t) \leftrightarrow F(\omega) \quad (3.31)$$

$$g(t) \leftrightarrow G(\omega) \quad (3.32)$$

$$h(t) = f(t) \cdot g(t) \leftrightarrow H(\omega) = \frac{1}{2\pi} F(\omega) \otimes G(\omega) \quad (3.33)$$

$$(3.34)$$

where $F(\omega)$, $G(\omega)$ and $H(\omega)$ are the Fourier transforms and $F(\omega) \otimes G(\omega)$ is the convolution of $F(\omega)$ with $G(\omega)$:

$$F(\omega) \otimes G(\omega) = \int F(\omega') G(\omega - \omega') d\omega' \quad (3.35)$$

The Fourier transform of the rectangular window (eq. 3.30) is described by a bigger main-lobe centered at $\omega = 0$ and smaller side-lobes (top result in Figure 3.8). Therefore, the convolution of both functions means that the width of the main-lobe will be the frequency resolution of the Fourier transform of $R(t)$ and the side-lobes will add the different periodic components to the Fourier transform weighted by their amplitudes.

Instead of considering the natural rectangular window from the experimental measurements, a better Fourier transform can be obtained if the Kaiser-Bessel window function is used.

The Kaiser-Bessel window function is defined by the formula^[76]:

$$f(t) = \begin{cases} \frac{I_0(\alpha\sqrt{1-(2t/T)^2})}{I_0(\alpha)} & \text{for } -T/2 \leq t \leq T/2 \\ 0 & \text{else} \end{cases} \quad (3.36)$$

where $I_0(x)$ is the zeroth-order modified Bessel function of the first kind and α is an arbitrary, non-negative real number that determines the shape of the window. For $\alpha = 0$, the Kaiser-Bessel window is equal to the rectangular window (Figure 3.8). By increasing α , the dominance of the main-lobe in the Fourier transform increases and the amplitudes of the side-lobes decrease, but the width of the main-lobe increases as well, lowering the frequency resolution. A compromise between a better frequency resolution and lower side-lobe amplitudes is then needed. It is observed that $\alpha = 4$ results in a good compromise for the calculation of the Fourier transform of experimental $R(t)$, so this is the chosen default value.

Another consequence of the use of the Kaiser-Bessel window is the fact of reducing the contribution for the Fourier transform of the data points for higher t , which have higher experimental error.

For the calculation of $I_0(x)$, the following polynomial approximation is used^[77] Equations 9.8.1, 9.8.2 :

$$I_0(x) = 1 + 3.5156229t^2 + 3.0899424t^4 + 1.2067492t^6 + 0.2659732t^8 + 0.0360768t^{10} + 0.0045813t^{12} + \epsilon \quad (3.37)$$

with $|\epsilon| < 1.6 \times 10^{-7}$ and $t = x/3.75$, for the interval $-3.75 < x < 3.75$, or:

$$\begin{aligned} x^{1/2}e^{-x}I_0(x) = & 0.39894228 + 0.01328592t^{-1} + 0.00225319t^{-2} - 0.00157565t^{-3} + 0.00916281t^{-4} - \\ & 0.02057706t^{-5} + 0.02635537t^{-6} - 0.01647633t^{-7} + 0.00392377t^{-8} + \epsilon \end{aligned} \quad (3.38)$$

with $|\epsilon| < 1.9 \times 10^{-7}$ and $t = x/3.75$, for the interval $3.75 < x < +\infty$.

3.7 Conclusion

The development of PACme is herein justified and reported. It is a C++ program that allows the simulation, analysis and visualization of the experimental PAC observable for static and dynamic (time-dependent) hyperfine fields. The PAC observable is calculated considering the theory of stochastic fluctuating fields as developed by Winkler & Gerdaud^[64]. The data fitting is performed by minimization of a χ^2 -function with recourse to the Minuit2 framework. The entire code will be open-sourced, like all the used external libraries are.

Detailed software documentation is present (Appendix A), explaining all the needed

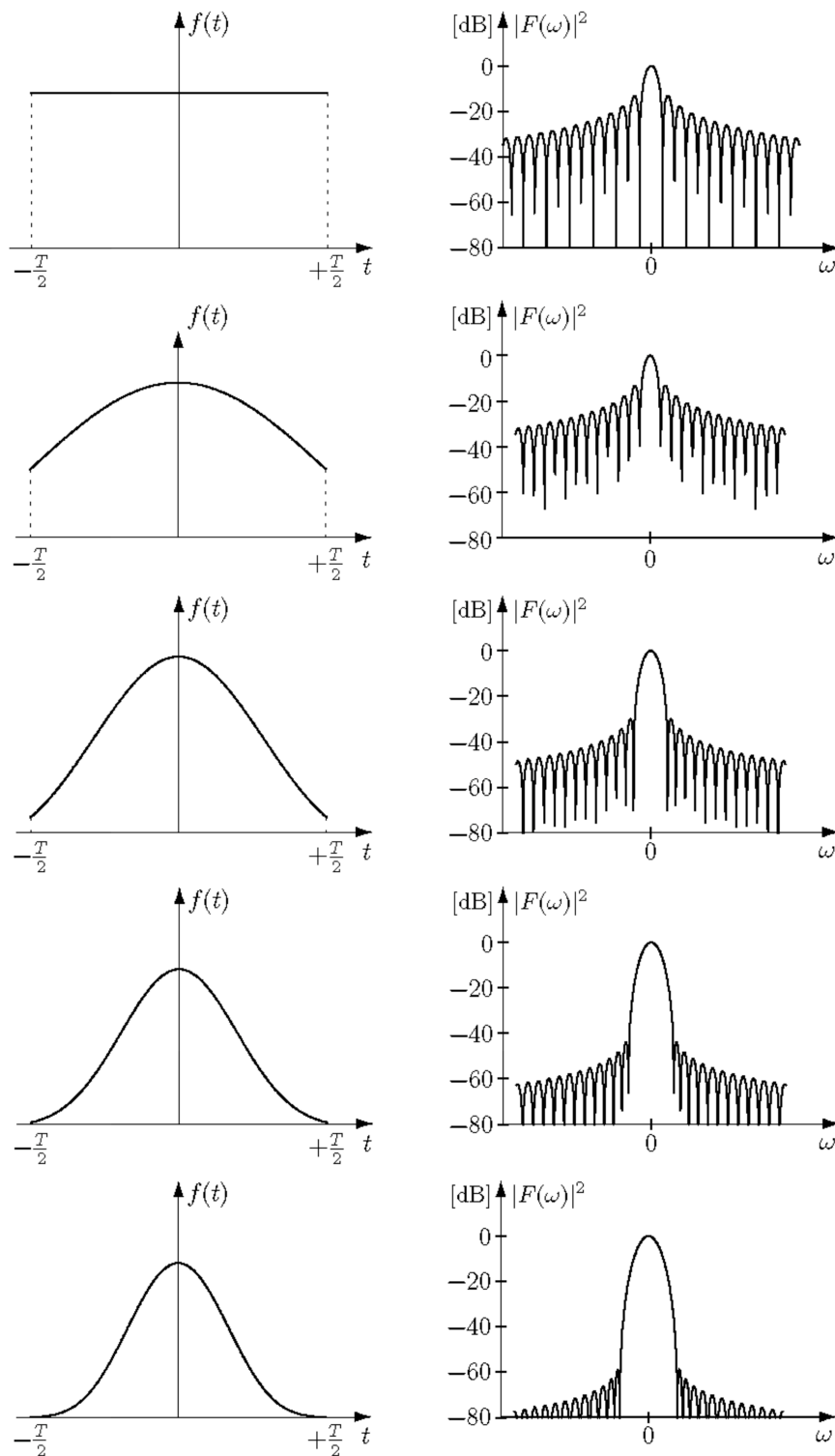


Figure 3.8 – Kaiser-Bessel window for $\alpha = 0, 2, 4, 6$ and 8 (left) and the respective power representation of the Fourier transform (right)^[76].

steps to install the program and use it properly, followed by a description of the code structure and its most important functions, in case the user wants to get deeper insight in the way it functions.

An innovative method for the analytical implementation of static Lorentzian frequency distributions in dynamic cases is proposed and applied in the program's calculations. It is also shown how to use a Lorentzian basis function to generate other distribution functions, such as Gaussian distributions, in case of user's need, to avoid computationally heavy solutions such as numerical integration.

Some test cases and examples are shown to demonstrate the proper function of the program according to the underlying theory and to get a better sense of the kind of phenomena that might be simulated and/or analyzed using the program.

CHAPTER 4

Cd probes location in ZnO and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ as a function of annealing temperature

4.1 Introduction

In the past decades, the development of integrated circuits has been responsible for a true revolution in electronics and photonics applications. However, with increasing miniaturization following Moore's law and the integration of nanotechnology in device applications, new and unpredicted properties are revealed, with potential applications to industry. Moreover, the modelling of these properties faces the fact that the smaller the devices get, the more they depend on the scale factor, geometry, symmetry and localized interactions of defects and impurities that can no longer be considered diluted and treated like "perturbations". Therefore, in this highly integrated new world the small scale rules both new properties and new problems. The future of potentially relevant nano-materials relies on both tunable properties and on large-scale integration feasibility^[1].

Nanostructures and thin film technologies might merge together where ion implantation is still envisaged as an integrated part of the processes. Still, ion implantation carries along with the benefits - universal dopant and profile tuning - intrinsic nuisances, i.e., defect generation. Willing to contribute to the better understanding of doping and processing by ion beams, we present here a study performed with the nanoscopic Perturbed Angular Correlation technique (PAC). We have chosen to study ZnO and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films, which are aimed to cover luminescence wavelengths from UV to yellow^[30]. These materials belong to the family of transparent conductive oxides and the used PAC probe, $^{111\text{m}}\text{Cd}/^{111}\text{Cd}$, is well suited to study their microscopic physical properties by being an isoelectronic impurity in ZnO.

For each case, we show how and to which extent the local environment of the implanted Cd is reconstructed to the one of the host crystalline matrix as a function of annealing temperature. We further attempt to identify local defects and the probes lattice site by comparing the experimental results with first principle simulations.

4.1.1 Case studies: ZnO & $\text{Cd}_x\text{Zn}_{1-x}\text{O}$

Zinc Oxide is subject of intense research due to its remarkable properties for optoelectronics, mainly for devices in the blue and UV range^[78]. Its wide band-gap (3.37 eV at room temperature) makes it desirable to adjust its electrical, optical and magnetic properties through doping with selective elements^[79]. Furthermore, the possibility of growing pseudobinary compounds with MgO and CdO allows bandgap tuning and heterostructure growth. In particular, ternary $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ alloys allow band-gap engineering in a wide range that covers the UV-yellow spectral region^[30]. However, ZnO and CdO have different crystalline structures, wurtzite and rock salt, respectively, being difficult to stabilize a wurtzite phase of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, which frequently results in phase separation^[80,81]. The solubility of CdO in ZnO, besides being low, depends strongly on the growth conditions and technique that is used. Concerning PAC studies, ZnO bulk crystals have been studied using different probes^[82] but, for technological purposes, thin films must be used. Thus, in this study, thin films of ZnO and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.16$) were investigated.

4.2 Technical details

The ZnO thin film (500 nm thick) was grown by molecular beam epitaxy (MBE) on an a-plane sapphire substrate at $T_s = 380^\circ\text{C}$ and subsequently annealed at $T_A = 650^\circ\text{C}$ for 5 minutes. The $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ thin film (200 nm thick) was grown at $T_s = 130^\circ\text{C}$ and annealed at $T_A = 400^\circ\text{C}$ for 4 hours. The film was grown on a 500 nm thick MgZnO buffer layer at $T_s = 380^\circ\text{C}$ on a-plane sapphire, the former serves to reduce the lattice mismatch and prevent the propagation of defects from the sapphire to the $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ layer^[30]. The structural characterization of these samples has been reported previously^[83].

Implantations were performed at ISOLDE/CERN with a 30 keV energy beam of radioactive $^{111m}\text{Cd}/^{111}\text{Cd}$ ($T_{1/2} = 48$ min to low fluences of $\sim 5 \times 10^{11}$ at/cm², at room temperature (RT). γ - γ PAC experiments were done onto decay of ^{111m}Cd ($\gamma_1 = 150$ keV, $\gamma_2 = 245$ keV) to ^{111}Cd ^[84], whose intermediate state has an electric quadrupole moment of $Q = 0.83(13)$ b and spin $I = 5/2$ ^[85]. A BaF₂ 6-detector PAC setup was used^[43], but since the samples were single crystalline only one 4-detector plane of this setup was selected, where the sample's c-axis was oriented within the detector plane at 45° with two 90° detectors (M45 setup). In the case of $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$, a complementary orientation was measured with the c-axis perpendicular to the 4-detector plane (M90 setup). The samples were annealed under air atmosphere during 10 minutes in a conventional tube furnace and the measurements were performed at $T_M = \text{RT}$.

X-ray diffraction (XRD) was used to determine the lattice parameters of the ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ thin films yielding $a = 3.2405 \text{ \AA}$ and $c = 5.2152 \text{ \AA}$ for the ZnO and $a = 3.283 \text{ \AA}$ and $c = 5.303 \text{ \AA}$ for the $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$.

Additional characterization of the as-grown and as-implanted (and annealed) samples was carried out by Rutherford Backscattering Spectrometry in the channelling mode (RBS/C) using a 2 MeV He^+ beam with 4 nA of current and a PIN diode detector at a backscattering angle of 165° .

To simulate the EFG at the probe's site, a $3 \times 3 \times 2$ supercell of the wurtzite crystalline structure of ZnO was considered (72 atoms) with a Cd probe located at one of the equivalent Zn sites, using first the lattice parameters measured by XRD on the film and second the lattice parameters of bulk ZnO, $a = 3.2489 \text{ \AA}$ and $c = 5.2053 \text{ \AA}$, reported on ref.^[9]. The simulations were performed *via* the L/APW+lo implementation of density functional theory (DFT), using the WIEN2k code^[57]. The GGA-PBE exchange-correlation functionals and a cut-off value for the plane wave expansion of $R_{mt}K_{max} = 7.0$ were considered, where R_{mt} is the muffin-tin sphere radius and K_{max} is the largest K-vector of the plane wave expansion of the wave function. Moreover, 24 k -points in the irreducible Brillouin zone were used. The convergence of the calculations was examined with respect to $R_{mt}K_{max}$ and to the number of k -points until the chosen values resulted in a convergence of the total energy of the crystal of less than 1 mRy. Relaxation of the atomic positions was done in a self-consistent way by minimizing the atomic forces to a maximum limit of 1 mRy/bohr. Smaller super-cells were attempted but the actual sizes were found to be the minimum required for achieving proper dilution of Cd at the DFT simulations.

4.3 Results and discussion

4.3.1 ZnO

Figure 4.1 shows (left) the PAC experimental functions, the fits and (right) the corresponding cosine Fourier transform components from ZnO after implantation and as a function of the annealing temperature up to 900°C . The obtained fitting parameters are presented in Table 4.1.

The data clearly shows the existence of a main position/situation for the probes revealed by one EFG_1 distribution that is characterized by the central frequency $\omega_{01} \approx 26 \text{ Mrad/s}$ and $\eta = 0$. In the plot of the Fourier transform there are two dashed lines, corresponding to the observables $\omega_0 = 26 \text{ Mrad/s}$ and $2\omega_0 = 52 \text{ Mrad/s}$, to mark the two main frequency components of EFG_1 for all measurements, as expected for a probe with spin $5/2$ and V_{zz} collinear with the sample's c -axis.

The existence of implantation defects is revealed by the important static distribution observed in the "as-implanted" sample that attenuates the frequency pattern at the $R(t)$ experimental function. In the absence of a second well-defined EFG signature, we conclude that most of these implantation defects are not correlated with the probe nuclei but are randomly dispersed in the sample within the implantation and defect profiles. Upon increasing the annealing temperature to 800°C , in addition to the first fraction

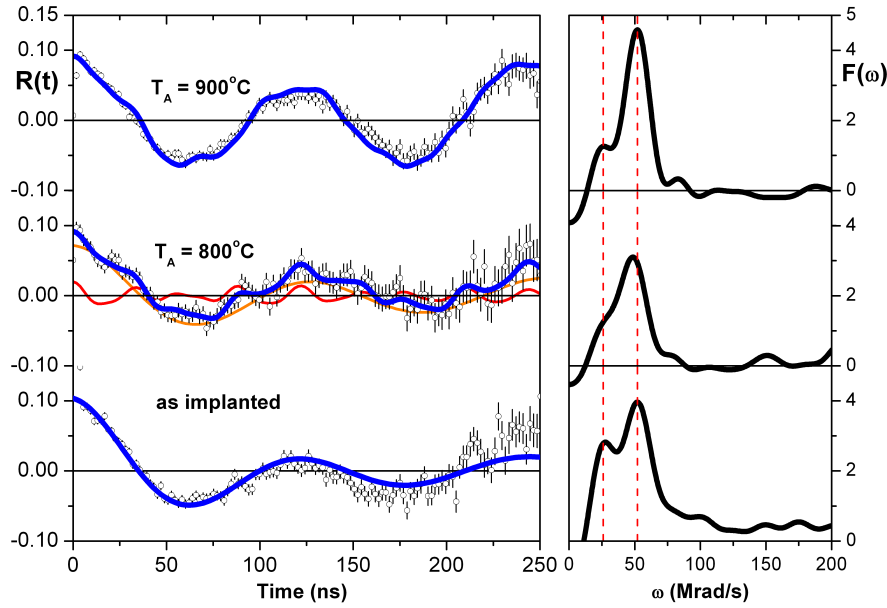


Figure 4.1 – $^{111}\text{Cd}:\text{ZnO}$ $\gamma\text{-}\gamma$ PAC from decay of ^{111m}Cd . Study as a function of annealing temperature under air. $T_M = \text{RT}$, Geometry: M45. **(left)** Counting rate ratio, $R(t)$. For $T_A = 800^\circ\text{C}$, besides $R(t)$, fraction 1 is represented in orange and fraction 2 in red, **(right)** Frequencies extracted from $R(t)$ after Fourier analysis.

Table 4.1 – $^{111}\text{Cd}:\text{ZnO}$ fitting parameters, related to Fig.4.1. ω_0 and FWHM are given in Mrad/s and V_{zz} is given in 10^{21} V/m^2 .

Annealing	Fraction 1					Fraction 2				
	Perc.	ω_0	V_{zz}	η	FWHM	Perc.	ω_0	V_{zz}	η	FWHM
900 °C	88%	26(-)			0.0(-)	12%	108(5)	5.7(1)	0.8(2)	0.0(-)
800 °C	78%	26(2)	1.37(5)	0.0(-)	4.5(7)	22%	111(1)	5.86(6)	0.6(3)	2.4(8)
As implanted	100%	26(1)			7.2(4)			-		

of probe nuclei with observable frequency ω_{01} , a second fraction starts to be observed indicating that defects are now present in more localized sites. On the one hand the width of the static distribution of the main fraction is reduced indicating a greater dilution of uncorrelated defects. On the other hand, some of the defects could come closer to the probes and eventually be trapped by the impurity Cd atom to originate EFG_2 , for a certain fraction of probe atoms. The results are in good agreement with previous works in ZnO implanted with ^{111}In and measured at the same ^{111}Cd state^[86–88], where M. E. Mercurio *et al.*^[86] obtained a main fraction with $\omega_{01} = 29.9(1) \text{ Mrad/s}$ and a second fraction with $\omega_{02} = 142(5) \text{ Mrad/s}$ in ZnO powders, assigning the last to interstitial sites or vacancy-related sites. H. Wolf *et al.*^[87] obtained a main fraction with $\omega_{01} = 29.4(1) \text{ Mrad/s}$ and a second fraction with $\omega_{02} = 174(1) \text{ Mrad/s}$ in ZnO single crystals, assigning the last to trapped oxygen-vacancies. P. Kessler^[88] confirmed the assigning of the larger frequency EFG to next-neighbour oxygen vacancies, based on the fact that PAC measurements performed in several different orientations gave simi-

lar results, which can be justified by the existence of 4 (almost) equivalent positions for oxygen near the Zn atoms. In our case, due to the small fraction for EFG₂, we have not implemented a multi-EFG orientation fitting regarding this fraction. After annealing at 900 °C the fraction of probes experiencing EFG₂ is decreasing suggesting that the probe-defect complex starts to dissociate at this temperature.

The smaller EFG₁ obtained for the thin film, compared to the one reported for bulk ZnO, can be explained by biaxial strain present in the epitaxial film. This assumption is confirmed by the DFT calculations, where the simulations carried out using the measured lattice parameters of the thin film resulted in a $V_{zz} = 1.374 \times 10^{21} \text{ V/m}^2$ for the Cd probe in the Zn site, which is in perfect agreement with $V_{zz} = 1.37(5) \times 10^{21} \text{ V/m}^2$ corresponding to the experimental frequency $\omega_{01} \approx 26 \text{ Mrad/s}$. Simulations using a variety of lattice parameters attributed for bulk ZnO were done in order to compare with the experimental results obtained by M. E. Mercurio *et al.*^[86] ($V_{zz} = 1.58(2) \times 10^{21} \text{ V/m}^2$ corresponding to the frequency $\omega_0 = 29.9(1) \text{ Mrad/s}$) and by H. Wolf *et al.*^[87] ($V_{zz} = 1.55(2) \times 10^{21} \text{ V/m}^2$ corresponding to the frequency $\omega_{01} = 29.4(1) \text{ Mrad/s}$). However, the lattice parameters of the samples used in these works were not reported and quite an amount of different lattice parameters for bulk ZnO can be found^[9,78,82]. Simulations were then performed with the parameters reported by H. Sowa and H. Ahsbahs^[9], $a = 3.2489 \text{ Å}$ and $c = 5.2053 \text{ Å}$, resulting in a $V_{zz} = 1.428 \times 10^{21} \text{ V/m}^2$. In the same article, a study of those parameters as a function of pressure was done, so using the parameters found for a pressure of 6.92 GPa, $a = 3.2049 \text{ Å}$ and $c = 5.1216 \text{ Å}$, resulted in a $V_{zz} = 1.672 \times 10^{21} \text{ V/m}^2$. Hence, due to the fact that the V_{zz} is very sensitive to small variations of the lattice parameters and that V_{zz} increases, for Cd at the Zn site, with the decrease of the ratio c/a , the measured V_{zz} 's in ref.^[86] and ref.^[87] were probably done in samples with lattice parameters slightly different from the values used in the simulation.

The simulations confirm that the probes are incorporated on substitutional Zn-sites.

4.3.2 Cd_{0.16}Zn_{0.84}O

Figure 4.2 shows the PAC results obtained for Cd_{0.16}Zn_{0.84}O, which could be described by using a single fraction of probe nuclei interacting with a large static EFG distribution around a central value for all annealing temperatures.

This indicates that, although the majority of the ¹¹¹Cd probes interact with a similar main EFG, implantation defects and intrinsic distortions due to crystal quality issues and the random distribution of Cd in the Cd_{0.16}Zn_{0.84}O lattice are present, even after annealing at 900 °C. We point out that in such kind of ternary compounds both Cd and Zn atomic distributions do not follow a regular super-cell-like pattern. The Cd concentration is big enough to clearly change the mean lattice parameters, but at the same time it will contribute to the non-unique EFGs that originate the large EFG distribution. The situation is clearly different from when implanting a small number of ^{111m}Cd atoms

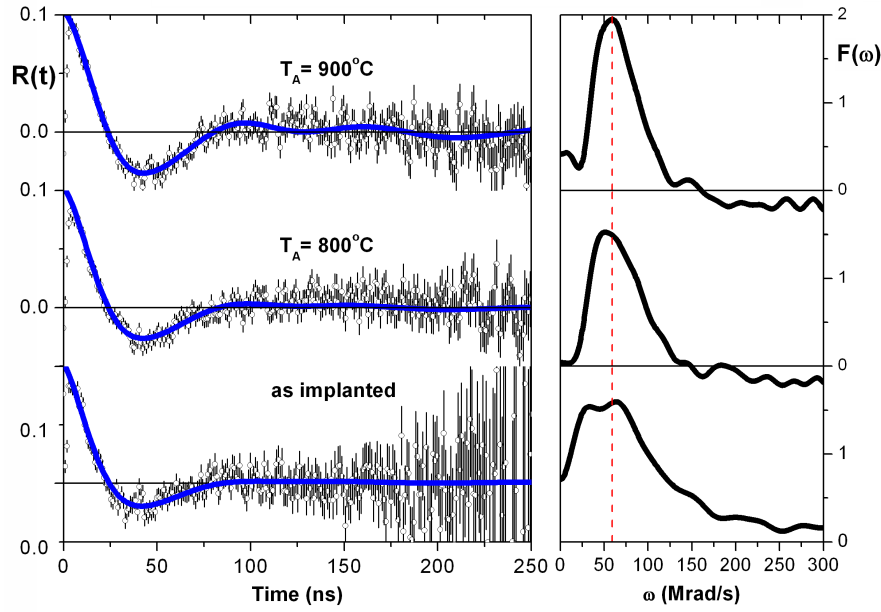


Figure 4.2 – $^{111}\text{Cd}:\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ γ - γ PAC from decay of ^{111m}Cd . Study as a function of annealing temperature under air. $T_M = \text{RT}$, Geometry: M45. **(left)** Counting rate ratio, $R(t)$. **(right)** Frequencies extracted from $R(t)$ after Fourier analysis.

Table 4.2 – $^{111}\text{Cd}:\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ fitting parameters, related to Fig.4.2. ω_0 and FWHM are given in Mrad/s and V_{zz} is given in 10^{21} V/m^2 .

Annealing	ω_0	V_{zz}	η	FWHM
900 °C				16.6(3)
800 °C				24.6(1)
600 °C	37(1)	1.96(6)	0.5(1)	27.8(2)
400 °C				33.3(1)
As implanted				32.6(7)

at the ppm concentration into the ZnO thin film. There, only implantation defects play a role and the Cd atoms themselves do not cause significant changes to the main ZnO EFG. Nevertheless, as can be seen by the fitting parameters in Table 4.2, the implantation defects contribution to the EFG distribution tend to be reduced as revealed by the decrease of the EFG distribution FWHM, with increasing annealing temperature. However, the attenuation of the curves remains high and little changes are observed in the PAC curves upon annealing.

The measurements indicate a higher central quadrupole frequency for the EFG distribution in $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ compared to ZnO, which has the same crystalline structure (wurtzite), and the existence of a non-zero axial asymmetry parameter. A different magnitude of the quadrupole interaction frequency could be expected since the lattice parameters expand with increasing Cd content in the ternary film but the latter does not explain the observed asymmetry of the EFG. Since it is difficult to determine frequencies and asymmetry parameters on such attenuated spectra, two different sample orienta-

tion experiments have been performed regarding the PAC setup detectors, previously referred as the M45 and M90 measurement geometries. If a main orientation of a central EFG persists within the EFG distribution, different amplitudes for each of the three harmonic components that characterise the EFG should be observed in a consistent way. Therefore, the obtained results and correspondent Fourier transforms for ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ measured with the M45 setup and for $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ measured with the M90 setup, all of them after annealing at 900 °C, are shown in Figure 4.3.

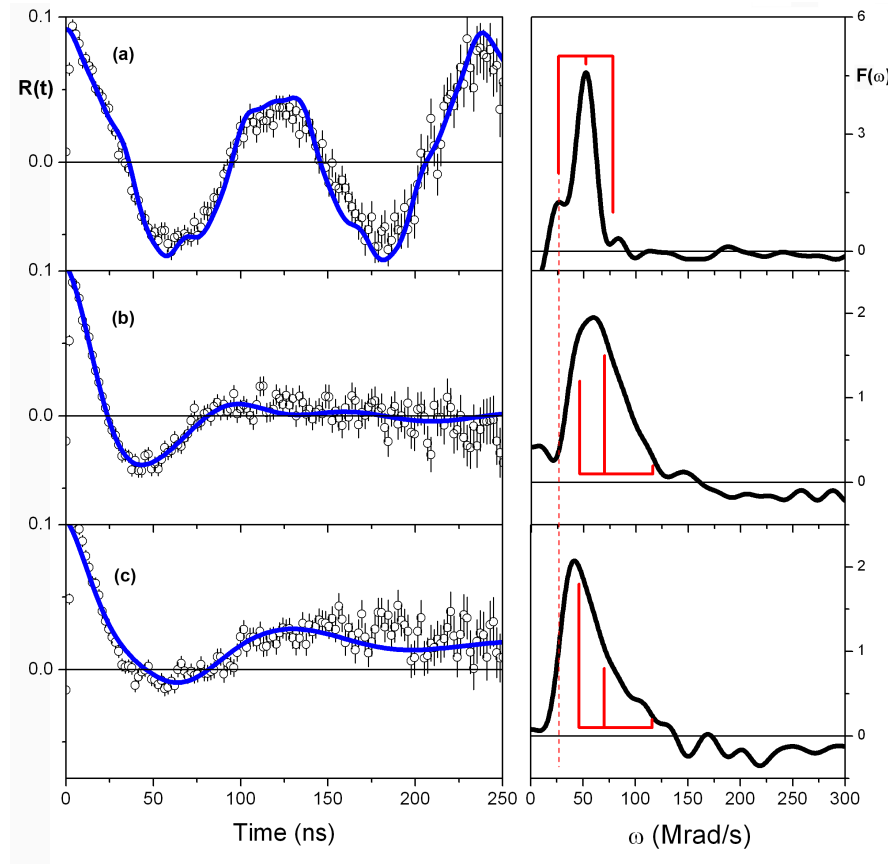


Figure 4.3 – γ - γ PAC data of ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ annealed at 900 °C, from decay of ^{111m}Cd . (a) ZnO, M45 setup. (b) $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$, M45 setup. (c) $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$, M90 setup.

By only changing the orientation angles, both fits of the M45 and M90 measurements give consistent results concerning quadrupole frequency and asymmetry parameter in the $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$, thus confirming that the central quadrupole frequency is higher than that obtained for ZnO. Still the observed non-zero axial asymmetry parameter reveals that from the local point of view of the ^{111m}Cd atoms the observed EFG does not reflect the expected axial lattice symmetry. This is most likely due to the incorporation of the implanted Cd probes in lattice environments which were strongly distorted by the implantation defects and/or imperfections in the original lattice structure, or due to different coordination in the next nearest shell, i.e., Cd probes with 4 oxygens as near neighbors but a mixture of Zn and Cd ions as next near neighbors. These distortions around the probes are thermally very stable and annealing up to 900 °C provides only

minor changes in the PAC curves.

In order to get additional information on the macroscopic crystal quality, before and after implantation and annealing, RBS/C measurements were performed.

Figure 4.4 shows RBS/C random and aligned spectra for the as-grown sample and after implantation and annealing at 400 °C and 900 °C.

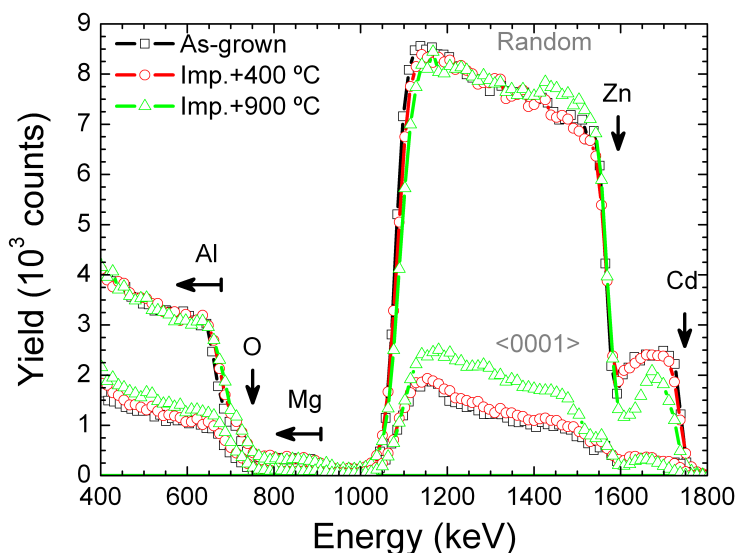


Figure 4.4 – RBS/C random and $\langle 0001 \rangle$ aligned spectra of as-grown $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ and after implantation and annealing at 400 °C and 900 °C.

The as-grown sample shows a minimum yield of 10.9(2)% in the Cd-signal revealing a good crystal quality for a ternary compound. However the crystal quality is significantly worse than that expected for a perfect crystal, or even for the ZnO film which has a minimum yield of 2.7(1)% (not shown). After implantation and 400 °C annealing the minimum yield is slightly increased to 12.3(3)%. Annealing at 900 °C removes implantation damage and a minimum yield similar to the as-grown sample is recovered. However, the random spectrum shows that some Cd is lost during this thermal treatment. Nevertheless, it is worth mentioning that the MBE material studied shows a significantly better thermal stability than reported for $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ with similar composition grown by metal organic chemical vapour deposition which showed an almost complete loss of Cd for annealing at 900 °C^[89].

In general, the RBS/C measurements show that the overall crystal symmetry and single crystalline character of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ is preserved after implantation and annealing and no indications of phase separation due to the transformation of wurtzite to rocksalt phase are observed. PAC, on the other hand, reveals that very stable local distortions or defect complexes are formed in the implanted Cd probe's neighborhood and that thermal annealing does not improve this situation. The Cd-loss evidenced by RBS at the highest annealing temperature does not seem to influence the PAC results measured at the

remaining $^{111m}\text{Cd}/^{111}\text{Cd}$ probe atoms, what further emphasizes the existence of highly stable defect complexes. Nonetheless, both RBS/C and PAC reveal the inefficiency of post-implant annealing treatments for $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ defect removal.

4.4 Conclusion

The usefulness of PAC in the study of thin films was demonstrated, allowing the observation of the local atomic environment around the probe and thus giving information about the lattice structure and probe's site. Two different samples were analyzed, ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ thin films, both measured after implantation of $^{111m}\text{Cd}/^{111}\text{Cd}$ ($T_{1/2} = 48$ min).

In the ZnO case, two different fractions were observed, as have been previously found for bulk samples. The smaller EFG was attributed to Cd probes on undisturbed substitutional sites. A smaller quadrupole interaction frequency was obtained in the studied films compared to the results found on the literature for bulk samples, but XRD measurements showed different lattice parameters ($a = 3.2405 \text{ \AA}$, $c = 5.2152 \text{ \AA}$) than the values for bulk samples ($a = 3.2489 \text{ \AA}$, $c = 5.2053 \text{ \AA}$)^[9], revealing a different strain state in the thin film and justifying this difference in the frequencies. DFT calculations performed with the measured lattice parameters showed excellent agreement with the experimental results and confirmed the high sensitivity to small changes in the lattice geometry of the EFG probed by the radioactive Cd atoms incorporated at Zn-sites in the thin films. The larger EFG only appeared after annealing and was attributed to the trapping of a defect, possibly an oxygen vacancy, in the vicinity of the probe.

The ternary alloy $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$, although having a wurtzite structure similar to ZnO, showed higher quadrupole frequencies, possibly due to the expansion of the lattice parameters with the Cd content, as well as a non-zero asymmetry parameter and large static distributions in the EFG, which were attributed to the clustering of defects close to the probe, even after annealing. The nontrivial differences observed at the nanoscopic scale between high-quality epitaxial thin films of ZnO, where ^{111m}Cd appears as a highly diluted probe, and on $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ alloy where the Cd is at the % range, encourage a systematic study for different Cd concentrations, from highly diluted to the % range, in fine increasing steps, aiming the observation and identification of defects forming and segregating with increasing x .

CHAPTER 5

Charge state and lattice location of Cd dopants in Ga₂O₃

5.1 Introduction

Ga₂O₃ is a wide band gap semiconductor which has been gaining interest in recent years due to its potential application in power and high-voltage electronic devices^[10,14,18]. It is transparent in the ultraviolet (UV) range, thus being also very promising for solar blind UV optoelectronic devices^[2,14,19,20,90] or, in the specific case of nanowires, to be used as effective waveguides^[6,91].

Having a band gap of 4.8 eV^[21], β -Ga₂O₃, the most stable of its polymorphic forms, is intrinsically an insulator, but its conductivity actually depends on doping and growth conditions^[10,14]. For instance, n-type semiconductivity is often observed and commonly attributed to ionized oxygen vacancies which act as donors^[10,92]. Differently, Varley *et al.*^[20,90] have questioned this assumption and attributed it to background impurities such as hydrogen, silicon and germanium, after first-principles calculations have revealed that oxygen vacancies act as deep donors in Ga₂O₃ and thus cannot be responsible for electron conductivity. Si is a common impurity in Ga₂O₃ powders and probably the reason for n-type doping in most materials. In fact, Si doping seems to be most promising to control conductivity and was achieved by in-situ doping^[93,94] and ion implantation^[95], where the former resulted in free-carrier concentrations as high as $1.74 \times 10^{20} \text{ cm}^{-3}$ ^[94]. Concerning p-type doping, several potential candidates have been proposed, such as Cd^[2], Ti^[96] and Mg^[97]. In some cases, p-type conductivity has even been reported, but the carrier mobility and concentration have not been analyzed or revealed themselves too low for practical applications^[96,98]. On the other hand, theorists pointed out fundamental issues for p-type doping as potentially due to strong hole localization in Ga₂O₃, which strongly limits hole mobility^[99]. The ability to p-type dope Ga₂O₃ would revolutionize the applicability of such promising material so, consequently, the search for the right p-type dopant is a very active subject of research.

Previous reports have shown evidence of Cd probes going into substitutional Ga sites in β -Ga₂O₃^[2,100]. Moreover, the difference in oxidation states (Ga³⁺ versus Cd²⁺) makes Cd a possible acceptor candidate and thus a suitable p-type dopant.

Since two main factors are in play regarding a dopant – location and charge state – this work is focused on the study of the location of implanted/diffused Cd probes in β -Ga₂O₃ as well as their charge state.

To address this problem, the Time Differential Perturbed Angular Correlation technique (TDPAC, or simply PAC) was used. PAC has been extensively applied in condensed matter physics to study structural, electronic and magnetic properties at the atomic scale^[31,101]. It accurately measures the hyperfine interaction between the nuclear quadrupole moment (Q) of a radioactive probe and the electric field gradient (EFG) at the probe's site. It is then very sensitive to the charge distribution close to the probe's nucleus, thus being a perfect tool to study phenomena such as the location of impurities or dopants, as well as their charge state and interaction with defects^[101–103]. Advantages of PAC rely on the use of adequate excited nuclear states in radioactive isotopes, where suitable spins and nuclear moments can be found which are different from those of the ground state of their respective stable isotopes.

The experiments were performed using two different kinds of radioactive probes, ^{111m}Cd/¹¹¹Cd and ¹¹¹In/¹¹¹Cd. Both decay to stable ¹¹¹Cd by gamma-gamma ($\gamma - \gamma$) emission through the spin 5/2, 245 keV level of ¹¹¹Cd^[39] (Fig. 5.1), so the measurements are done in the same nuclear level in both situations. However, ¹¹¹In decays to ¹¹¹Cd by electron capture before the $\gamma - \gamma$ emission, where an electron from the inner atomic K- or L- shell is absorbed by the proton-rich nucleus, thereby changing a proton to a neutron. The hole created at the atomic shell of the new-born Cd nucleus is very rapidly recovered (within about 10^{-14} s^[71]) by electrons in higher orbits of the same atom with consequent emission of characteristic X-ray photons and/or ejection of electrons (Auger effect) leading to ionization of the atom (the number of lost electrons for Cd is estimated to be between 3 and 8, on average^[71,104]). In the event of Auger electron emission, the lost electrons have to be recovered by electrons from the Ga₂O₃ host. During this entire process, the charge distribution around the probe is changing until the full recovery of the lost electrons is achieved and the probe reaches a stable charge state, hence the EFG around the probe is also changing. If the final electron recovery after decay is in the nanoseconds scale, the fluctuating EFG can be observed in a PAC experiment. Since the charge carrier mobility in a material is severely influenced by temperature, this process can be used to study the electronic properties of the host material by doing PAC experiments using ¹¹¹In probes at different measuring temperatures. The ^{111m}Cd/¹¹¹Cd isotope, where no element transmutation nor ionization state occur, can then be used to directly locate the Cd probes inside the lattice and the ¹¹¹In isotope can be further used to study the recombination of ionized and excited electronic states of Cd in order to draw conclusions on the electronic properties of the host material – Ga₂O₃, in this case.

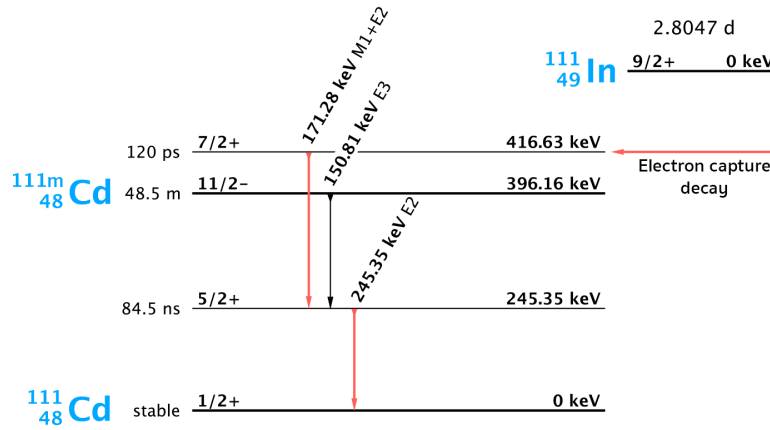


Figure 5.1 – Decay scheme for ^{111}In and $^{111\text{m}}\text{Cd}$

5.2 Perturbed Angular Correlation experiments

5.2.1 Experimental Details

99.999% purity Ga_2O_3 powder was pressed into pellets of about 7 mm diameter and 2 mm thickness and subsequently annealed at 1500 °C for 8 h. Single crystals were grown by the floating zone technique using 4N purity powder, as described elsewhere^[105]. Nanowires were grown from metallic gallium in a tube furnace using a vapour-solid growth mechanism reported elsewhere^[6], whose length and thickness was up to tens of microns and between tens to hundreds of nanometers, respectively.

^{111}In [$^{111}\text{In} \rightarrow ^{111}\text{Cd}$, $t_{1/2} = 2.8$ days] probes were introduced by wetting the powder pellet in a ^{111}In activated solution. Afterwards, the sample was annealed for 48 hours at 1100 °C in air. The PAC measurements were performed in a 4-BaF₂ detector spectrometer^[43] at CFNUL, in Lisbon. $^{111\text{m}}\text{Cd}$ [$^{111\text{m}}\text{Cd} \rightarrow ^{111}\text{Cd}$, $t_{1/2} = 48$ minutes] probes were implanted in the powder pellet (polycrystalline) sample, in the single crystalline sample and in the nanowires of Ga_2O_3 at ISOLDE/CERN to low fluences of 10^{11} atoms/cm² at room temperature. Then, the samples were annealed for 10 minutes at 1200 °C, at 1000 °C and at 800 °C in air, respectively, in order to remove implantation defects. The PAC measurements were carried out on a 6-BaF₂ detector spectrometer^[43].

5.2.2 Results

PAC experiments were performed as a function of the measurement temperature (between 20 °C and 750 °C) in the β - Ga_2O_3 powder pellets after diffusion of ^{111}In probes and annealing at 1100 °C for 48 hours in air. Figure 5.2(a) shows the resulting PAC $R(t)$ spectra and respective Fourier transforms.

Room temperature (20 °C) measurements were performed before and after the higher temperature measurements and no changes were observed in the spectra, thus ensuring that no extra annealing effects occurred while measuring at higher temperatures and all observed changes in the spectra are reversible. Also, there are no structural

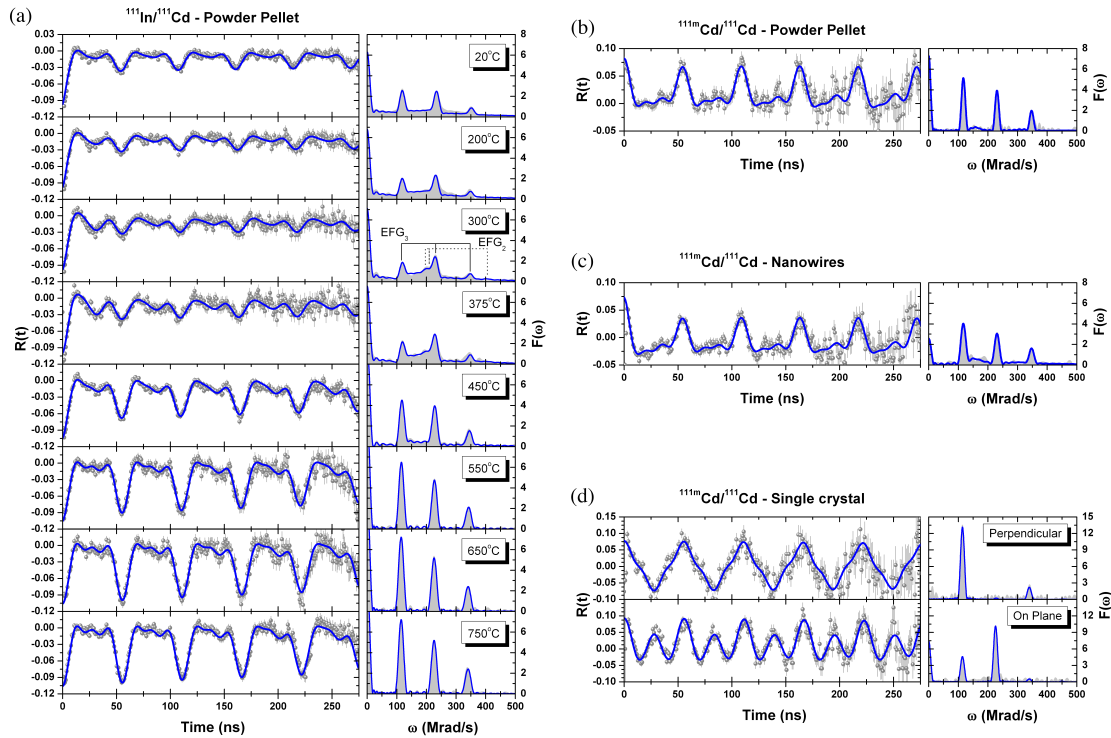


Figure 5.2 – PAC spectra (and their Fourier transforms) **(a)** as a function of temperature after diffusion of ^{111}In in the $\beta\text{-Ga}_2\text{O}_3$ powder pellet annealed at 1100°C for 48 hours; after implantation of ^{111m}Cd in the $\beta\text{-Ga}_2\text{O}_3$ **(b)** powder pellet annealed at 1200°C for 10 minutes, **(c)** nanowires annealed at 800°C for 10 minutes and **(d)** single crystal annealed at 1000°C for 10 minutes, all measured at room temperature. In the Fourier transform from 300°C , it is possible to see the triplet of frequencies associated with the EFG of states 2 and 3. Since the first two frequencies of EFG_2 are so close, they form a single broader peak. Note that the anisotropy sign changes from ^{111}In to ^{111m}Cd [39].

Table 5.1 – $^{111}\text{In}:\text{Ga}_2\text{O}_3$ PAC fitting parameters. Three different states described by a single electric quadrupole interaction each were considered. The transition rates between them are expressed in MHz. The quadrupole frequency ω_0 and the full width at half maximum for the Lorentzian, static-like, distribution (FWHM) are expressed in Mrad/s and the asymmetry parameter η is dimensionless. At 650°C , the transition is so fast that only the final state is observed. Therefore, two equal curves are obtained when considering a transition between states 1 and 3 with a high transition rate or when considering a single state 3 (last two lines of the table, respectively).

T ($^\circ\text{C}$)	State 1 (initial)			State 2 (intermediate)			State 3 (final)			Transition Rates		
	ω_0	η	FWHM	ω_0	η	FWHM	ω_0	η	FWHM	1 $\rightarrow$ 2	1 $\rightarrow$ 3	2 $\rightarrow$ 3
20			79(2)	-	-	-	117.8(1)	0.000(1)		-	59(2)	-
200			66(2)	-	-	-	116.4(2)	0.000(2)		-	41(2)	-
300			47(8)				116.1(1)	0.000(1)		3(1)	35(5)	0.5(1)
375	111(1)	1.0(1)	34(2)	117(2)	0.92(3)	0(2)	115.7(2)	0.000(5)	1.4(3)	3(2)	43(2)	8(4)
450			20(2)	-	-	-	114.6(1)	0.000(3)		-	112(3)	-
550			25(6)	-	-	-	113.7(1)	0.09(1)		-	344(26)	-
650			0(2)	-	-	-	113.1(1)	0.10(1)		-	761(216)	-
650	-	-	-	-	-	-	113.1(1)	0.10(1)	1.4(3)	-	-	-

phase transitions in $\beta\text{-Ga}_2\text{O}_3$ in this range of temperatures [10], so any differences in the spectra must be due to the temperature dependence of the electronic recovery after the electron capture decay from ^{111}In to ^{111}Cd . The spectra at 650°C and at 750°C are indistinguishable, which means that at these temperatures the electronic recovery

is faster than the experimentally observable timescale, so only the final stable configuration is observed. This stable configuration (State 3 on Table 5.1) shows a single EFG characterized by $\omega_0 = 113$ Mrad/s and $\eta = 0.10$, thus all probes are in a single location and the low damping (FWHM = 1.4 Mrad/s) suggests that surrounding defects in the next-nearest lattice neighborhood are negligible. Note that, for a decay with an intermediate level of spin 5/2, a single EFG will correspond to three observable frequencies, therefore three peaks appear in the Fourier transform. In the remaining measurements, that same EFG is visible but the amplitude of the oscillations in the $R(t)$ function varies, which means that the electronic environment around the probes is changing as a function of temperature. Also, it is clear in the Fourier transform that there is an additional component at 300 °C and 375 °C with the main peak of the triplet around 200 Mrad/s that corresponds to a different EFG.

To fully analyze this data, the theory of stochastic processes applied to dynamic transitions in PAC, as described by Winkler and Gerdau^[64], was used. This theory (which was introduced in Section 3.2.2) assumes that the environment around a probe might change with time in such way that allowed transitions between different states occur in a "Markov chain"-like fashion. Therefore, the system is described by the EFGs that characterize each possible state and the transition rates to go from one state to the other. The results obtained after analyzing the spectra are listed in Table 5.1 (only the non-zero transition rates are listed). Directly after the electron capture decay and before sufficient electronic recovery is achieved, the charge distribution around a probe is chaotic, hence the initial observable state describing all probes (State 1) is characterized by a distribution of EFGs which can be approximately represented by a single central EFG ($\omega_0 = 111$ Mrad/s, $\eta = 1.0$) with a very broad distribution (FWHM > 30 Mrad/s) to account for the dispersion in the initial EFGs of the different probe nuclei. Then, a transition occurs to the final stable state (State 3, as described above, with $\omega_0 = 113$ Mrad/s and $\eta = 0.10$), with no possibility of return to the initial state (unidirectional transition). Interestingly, at 300 °C and 375 °C a metastable Cd state was observed (State 2) ($\omega_0 = 117$ Mrad/s, $\eta = 0.92$ and very low FWHM < 2 Mrad/s) in addition to the final stable state, with a probe having a $\sim 7\%$ probability of going through this metastable state before achieving the final state at this temperature. It was then possible to obtain the EFG corresponding to each state and the transition rates between them for each temperature, where attention must be paid to the fact that each EFG barely changes with temperature but the transition rates ($R_{i \rightarrow j}$) have strong variations, in particular, for the transition $R_{1 \rightarrow 3}$ between the initial ($i = 1$) and final ($j = 3$) states above 375 °C (see Figure 5.8). Also, due to the huge η of state 2, the first two frequencies of its triplet of observable frequencies are very close ($\omega_1 = 196.0$ Mrad/s, $\omega_2 = 209.4$ Mrad/s and $\omega_3 = 405.4$ Mrad/s), so they merge into a single broader peak around 200 Mrad/s in the Fourier transform (Fig. 5.2(a)).

Since the previous results are obtained after diffusion of ^{111}In probes but the measurements are performed in the ^{111}Cd isotope after the decay, PAC measurements were

also performed after implantation of ^{111m}Cd and annealing at 1200 °C for 10 minutes in air (Fig. 5.2(b)) to confirm the location of the probes (preliminary results for annealings until 800 °C have been published in Ref. [2]). They showed a dominant position for the Cd probes with an EFG ($\omega_0 = 115.5 \text{ Mrad/s}$ and $\eta = 0.11$) matching the EFG in the final state of the ^{111}In measurements presented here. This means that the probes are incorporated in the same position in both experiments. Nonetheless, even after annealing at 1200 °C for 10 minutes, 21% of the ^{111m}Cd probes were located in a damaged lattice environment. This could indicate an advantage for doping using diffusion instead of implantation, since no point defects were detected in the former case. However, a shorter annealing time had to be considered after implanting ^{111m}Cd (necessary due to its short lifetime) which might not be enough to eliminate all implantation defects. In fact, a 1 hour annealing after diffusion of ^{111}In also showed the presence of some defects not properly annealed (results not shown here) but they were completely eliminated with a longer annealing. Moreover, measurements done in single crystal samples implanted with ^{111m}Cd using the same conditions but annealed at 1000 °C in air (Fig. 5.2(d)) showed a similar EFG ($\omega_0 = 112.9 \text{ Mrad/s}$ and $\eta = 0.09$) with no presence of implantation defects, thus hinting to a higher difficulty of recovering implantation defects in polycrystalline samples in comparison to single crystals, possibly due to Cd probes in grain boundaries.

Finally, regarding the nanowires implanted with ^{111m}Cd probes and annealed for 10 minutes at 800 °C (Fig. 5.2(c)), they also revealed a dominant position for the Cd probes with an EFG matching the one in the pellet samples ($\omega_0 = 115.4 \text{ Mrad/s}$ and $\eta = 0.10$), albeit with 46% of the probes located in a damaged lattice environment (but notice the lower annealing temperature in this case). This demonstrates that even in such nanostructures, the Cd probes have a single preferential site in Ga₂O₃.

The temperature dependence of the transition rates using ^{111}In probes will be fully discussed further ahead.

5.3 Density Functional Theory simulations

To aid understanding the lattice location and the charge state of the Cd probes in the Ga₂O₃ samples during the PAC measurements, Density Functional Theory (DFT) simulations were performed.

5.3.1 Simulation details

The simulations were performed via the full-potential (linearized) augmented plane wave plus local orbitals [FP-(L)APW+lo] method as implemented in the WIEN2k code^[57]. For the structural optimization and calculation of the electric field gradients, the generalized gradient approximation in the Perdew, Burke and Ernzerhof parameterization (GGA-PBE)^[57] was considered as exchange-correlation functional. For the calculation of the density of states, band structure and band gap, the optimized structures were used

and the modified Becke-Johnson exchange potential (mBJ) was applied, since it has been proven to better estimate band gaps in semiconducting materials than simply using GGA^[56,106]. It also has levels of agreement with experimental results comparable to hybrid functionals or Green function (GW) methods (which are computationally heavier and more time consuming) whilst being barely more expensive than GGA calculations^[56,106]. Although hybrid functionals have been previously proven very successful to simulate Ga₂O₃ systems^[20,99], they take three to four orders of magnitude more time in a simulation than GGA, thus being impractical for the several big supercells required in the present study.

The structural parameters of Ga₂O₃ in the β -phase (β -Ga₂O₃) as found in the work of Åhman *et al.*^[7] were considered, i.e. $a = 12.214(3) \text{ Å}$, $b = 3.0371(9) \text{ Å}$, $c = 5.7981(9) \text{ Å}$, $\alpha = \gamma = 90^\circ$ and $\beta = 103.83(2)^\circ$, with the internal atomic positions being optimized by minimizing the atomic forces to a maximum limit of 2 mRy/bohr in a self-consistent way. Optimization of the lattice parameters using the very precise HSE06 hybrid functional was previously reported elsewhere^[22] and the calculated lattice parameters are very close to the experimental ones (less than 0.5% variation), therefore no lattice optimization was performed in this work and the experimental values were used for the simulations.

To simulate an isolated Cd impurity, a $1 \times 4 \times 2$ supercell of Ga₂O₃ with dimensions $a' = a = 12.214 \text{ Å}$, $b' = 4b = 12.1484 \text{ Å}$, $c' = 2c = 11.5962 \text{ Å}$ and $\beta = 103.83^\circ$ was constructed. Its size was determined by increasing it until the variation of the EFG at the Cd site was in the same order of magnitude of the experimental error in the PAC measurements.

A cut-off value for the plane wave expansion of $R_{\text{mt}} \cdot K_{\text{max}} = 6.0$ was considered, where R_{mt} is the muffin-tin sphere radius and K_{max} is the largest K-vector of the plane wave expansion of the wave function.

90 and 20 k-points in the irreducible Brillouin zone were used for the Ga₂O₃ simple cell and for the $1 \times 4 \times 2$ supercell with the Cd impurity, respectively.

Different charge states for the Cd probes were considered, where additional charges were compensated by adding a homogeneous background of opposite charge to keep the entire cell in a neutral state^[57,107,108]. For instance, if an electron is added to the cell, the extra negative charge can be localized but a uniform positive charge will maintain the neutrality of the cell whilst not resulting in any extra interactions.

Spin-polarized calculations showed no magnetic moment for pure Ga₂O₃, therefore the results reported here were calculated using no spin-polarization. For the supercells with a Cd probe, the charged configuration showed no magnetic moment but the neutral configuration showed a very small one, hence the spin-polarized results are reported here.

5.3.2 Results

Starting by the pure system, a simple cell of Ga_2O_3 in the β -phase ($\beta\text{-Ga}_2\text{O}_3$) was considered. It has two non-equivalent Ga sites – a sixfold coordinated site (octahedral) and a fourfold coordinated site (tetrahedral) – and three non-equivalent O sites. After structural relaxation, the EFG in each of the two non-equivalent Ga atoms was found, as well as the distance to the nearest O atoms (Table 5.2). The distance between Ga and O neighbors is in excellent accordance with experimental results^[7] ($[1.83 \text{ \AA} - 1.85 \text{ \AA}]^{\text{sim.}}$ vs. $[1.83 \text{ \AA} - 1.86 \text{ \AA}]^{\text{exp.}}$ for Ga in the tetrahedral site and $[1.92 \text{ \AA} - 2.04 \text{ \AA}]^{\text{sim.}}$ vs. $[1.94 \text{ \AA} - 2.07 \text{ \AA}]^{\text{exp.}}$ for Ga in the octahedral site).

A band gap of 4.91 eV was obtained from the total density of states (DOS), which is in very good agreement with the experimental value of 4.85 eV^[10] (Fig. 5.3). Moreover, the atom-resolved partial density of states (PDOS) shows a very small contribution from the Ga-3d, Ga-4s and Ga-4p orbitals to the upper valence band but a valence band maximum (VBM) completely dominated by the O-2p orbitals, whereas the conduction band minimum (CBM) is mainly described by the Ga-4s orbitals (Fig. 5.4).

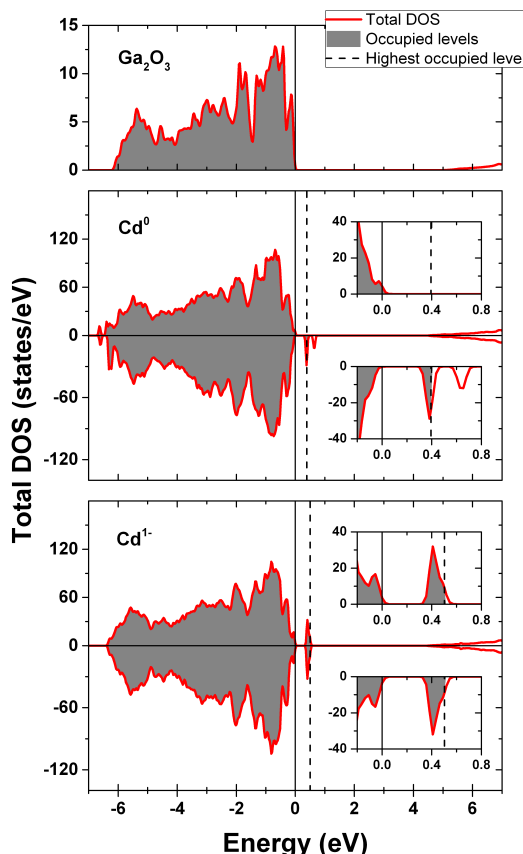


Figure 5.3 – Total density of states (DOS) of the Ga_2O_3 simple cell and the supercells with Cd^0 and Cd^{1-} in the octahedral Ga site. The top valence band of pure Ga_2O_3 is set at 0 eV (full line) and the energy of the highest occupied level is represented by the dotted line. For pure Ga_2O_3 , both lines are coincident. In the two bottom plots, the insets show a zoomed energy range focused on the impurity band.

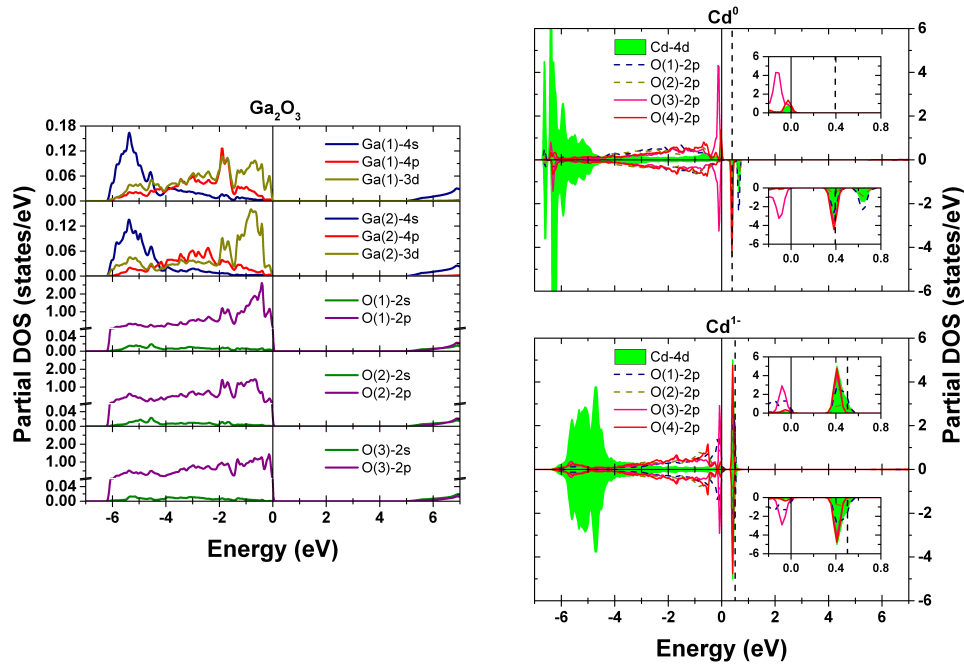


Figure 5.4 – Partial density of states (PDOS) of each orbital contribution from all non-equivalent atoms of the Ga_2O_3 simple cell, as well as the $4d$ contribution of Cd and the $2p$ contribution of its neighboring O atoms in the supercells with Cd^0 and Cd^{1-} in the octahedral Ga site (due to the break of symmetry by the Cd probe, it has 4 non-equivalent O neighbors instead of 3). The top valence band of Ga_2O_3 is set at 0 eV (full line) and the energy of the highest occupied level is represented by the dotted line. In the two bottom plots, the insets show a zoomed energy range focused on the impurity band.

The band structure (Fig. 5.5(a)) shows an indirect band gap between the VBM located on the I-L line and the free-electron-like CBM at the Gamma point. However, the valence band at the Gamma point is only 0.03 eV below that of the VBM, so there is an indirect band gap of 4.91 eV and a direct band gap of 4.94 eV, in good agreement with optical absorption measurements^[21] and with previous calculations^[18,22]. By fitting the energy dispersion of the CBM at the Γ point to a parabolic function, an electron effective mass (m_e^*) of $0.35 m_e$ was obtained. This is close to the experimental value of $0.28 m_e$ ^[109] but slightly higher, which is expected since the used mBJ exchange potential generally overestimates the effective masses^[110]. On the other hand, the top valence band is almost flat, indicating a rather large effective mass (m_h^*) for holes. This suggests that the electronic conductivity in Ga_2O_3 strongly depends on the mobility of the electrons that are thermally excited to the conduction band and less on the movement of holes created at the same time. These results are consistent with previous reports^[18,20,22,99,111].

The electron density (Fig. 5.6(a)) shows that the majority of the electron density is concentrated around the O atoms (similar picture is observed in any cut-plane direction) thus hinting ionic-like character for the Ga-O chemical bonds.

In order to simulate an isolated Cd impurity, a $1 \times 4 \times 2$ supercell of Ga_2O_3 was constructed. Since Cd usually has a cation-like oxidation state as Ga does, the following

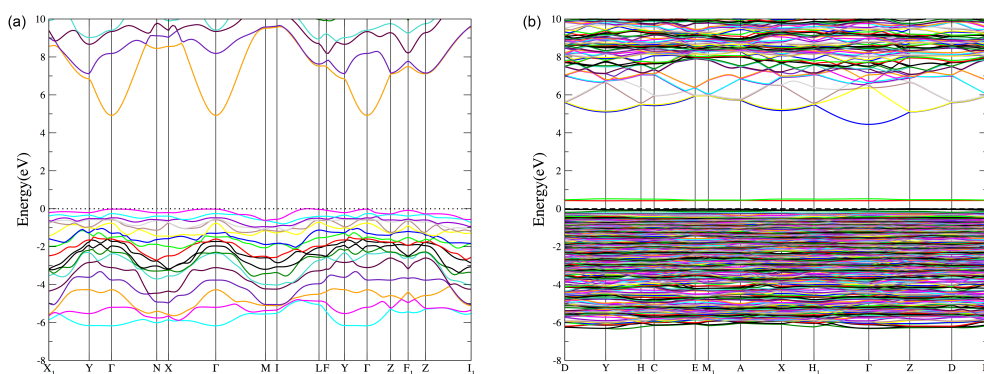


Figure 5.5 – Band structure of (a) pure Ga₂O₃ and (b) Cd¹⁻ in an octahedral Ga site of a $1 \times 4 \times 2$ supercell. The top valence band of pure Ga₂O₃ is set at 0 eV. The k-point labels are named as in Ref.^[22] for pure Ga₂O₃ and as in Ref.^[112] for the supercell containing Cd.

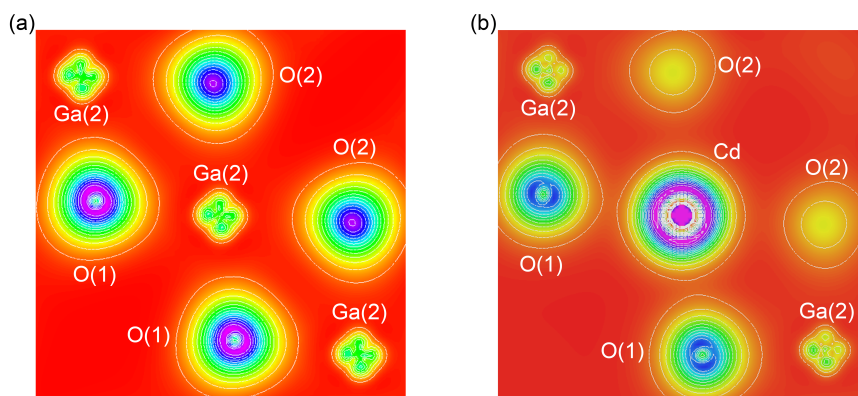


Figure 5.6 – Electron density considering the top of the valence band in a plane going through the centre of (a) Ga(2) and O(1) in pure Ga₂O₃ simple cell and of (b) O(1) and Cd¹⁻ in an octahedral Ga site within a $1 \times 4 \times 2$ supercell.

different sites were considered for the Cd atom: replacing a Ga atom in the octahedral and tetrahedral sites (corresponding to a cation dilution of 1:64) and in two possible interstitial positions (Fig. 5.7). Since Ga has 3 valence electrons whereas Cd has only 2 (thus the Ga atoms use one electron more than the Cd atoms for the chemical bonding), two different charge states were considered for the Cd probe replacing a Ga atom: neutral (Cd⁰) and adding an extra electron to the lattice (Cd¹⁻), which is compensated by an additional homogeneous positive background to keep the entire cell in a neutral state^[107,108]. For the interstitial sites, it would be expected for Cd to have donor character, so the following charge states were considered: neutral (Cd⁰) and removing two electrons from the lattice (Cd²⁺), also compensated by an additional homogeneous background.

The EFGs at the Cd probe calculated for each of the different sites and each of the charge states are presented in Table 5.2, together with the experimental EFGs observed in the PAC experiments.

It has been previously reported that InGaO₃ has the structure of β -Ga₂O₃ with In occupying the octahedral site and that the structure of In₂O₃ consists of two octahedrally

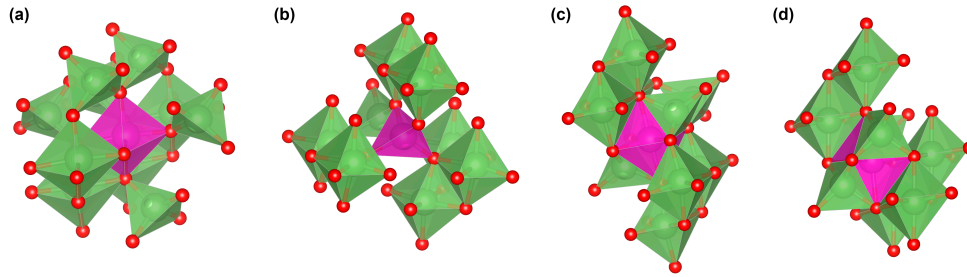


Figure 5.7 – Simulated Cd sites (in magenta) in supercells of Ga_2O_3 : **(a)** octahedral Ga site, **(b)** tetrahedral Ga site, **(c)** interstitial (I) and **(d)** interstitial (II). The figures do not show the entire supercells.

Table 5.2 – Calculated z-component of the EFG tensor in the principal component axis (in units of $\text{V}/\text{\AA}^2$) and asymmetry parameter for the Ga atoms in the simple cell and for each position and charge state of the Cd probe in the supercell, as well as the experimental values obtained in the PAC measurements (considering the electric quadrupole moment $Q = 0.765(15) \text{ b}^{[113]}$ and the fact of PAC not being sensitive to the sign of V_{zz} , so only the absolute values can be compared). The calculated distance to the oxygen nearest neighbors (ONN) is also shown.

	$V_{zz} (\text{V}/\text{\AA}^2)$	η	ONN ($\text{\AA}$)
Ga – octahedral	23.8	0.34	1.92 – 2.04
Ga – tetrahedral	-38.4	0.72	1.83 – 1.85
Cd^0 – octahedral	70.2	0.98	2.11 – 2.25
Cd^{1-} – octahedral	63.8	0.04	2.13 – 2.32
Cd^0 – tetrahedral	-44.0	0.75	2.04 – 2.08
Cd^{1-} – tetrahedral	-52.6	0.59	2.06 – 2.10
Cd^0 – interstitial (1)	38.7	0.45	2.17 – 2.20
Cd^{2+} – interstitial (1)	45.2	0.49	2.16 – 2.18
Cd^0 – interstitial (2)	-171.4	0.40	2.08 – 2.27
Cd^{2+} – interstitial (2)	-195.6	0.95	2.00 – 2.59
Exp. initial state	64(2)	1.0(1)	-
Exp. intermediate state	67(2)	0.92(3)	-
Exp. final state	65(1)	0.10(1)	-

coordinated cation (In) sites^[100], so a preference is expected for In probes incorporating in the octahedral Ga site in Ga_2O_3 . Since the PAC measurements were done in the ^{111}Cd probes but the diffused mother isotope was ^{111}In , it was expected for the Cd probes to be in the octahedral Ga site. Additionally, implanted ^{111m}Cd was also found on the octahedral site^[2]. As seen in Table 5.2, a very good agreement is found between the EFG for the Cd^{1-} charge state at the octahedral Ga site and the observed final state in the PAC experiments, as well as between the EFG for Cd in the neutral charge state in the same position and the intermediate state observed at 300 °C, thus showing that the Cd probes are indeed in substitutional octahedral Ga sites. Therefore, a more detailed analysis was performed only for the Cd probes at this position and considering both possible charge states.

It can be seen in the total DOS that by replacing a Ga atom by a Cd^0 probe, an

Table 5.3 – p , d and $s-d$ valence contributions to the EFG tensor in the principal components axes (in units of V/Å²) for the Cd probe at the octahedral Ga-site in the neutral and charged states (by definition, $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$).

	Ga ₂ O ₃ :Cd ⁰			Ga ₂ O ₃ :Cd ¹⁻		
	V_{xx}	V_{yy}	V_{zz}	V_{xx}	V_{yy}	V_{zz}
p	-19.6	-24.4	43.9	-23.1	-28.6	51.7
d	18.3	-46.0	27.7	-7.9	-5.0	12.9
s-d	0.5	0.8	-1.3	0.6	0.7	-1.4

impurity band appears in the band gap near the top of the valence band and is partially filled, while the basic electronic structure of Ga₂O₃ remains unaltered (Fig. 5.3). By integrating the unfilled region between the highest occupied state and the end of this peak, a value of 1.0002 electrons is obtained, in accordance with the expected behavior of a Cd dopant with single-acceptor character in this material. By looking at the atom-resolved partial DOS projected at the Cd and O atoms (Fig. 5.4), it is possible to see that the impurity band is composed of Cd-4*d* and O-2*p* orbitals. A similar behavior is observed for the charge state Cd¹⁻, but in this case the impurity band gets completely filled (Figs. 5.3 and 5.4). The top of the impurity band is ~ 4 eV from the conduction band, which is very close to the 4.3 eV reported for the band gap of amorphous Cd-Ga-O thin films^[114].

In the band structure (Fig. 5.5(b)) it is possible to see that the top of the impurity band is ~ 0.5 eV above the top of the valence band (the bottom is ~ 0.3 eV above). Nonetheless, the top of the valence band remains very flat as in pure Ga₂O₃, thus the effective mass for holes remains very large.

In terms of chemical bonding, it is possible to see in the electron density plot (Fig. 5.6(b)) that the charges are distributed among the Cd atom and its O atomic neighbors, indicating that the Cd-O bonds have a slightly more covalent character in contrast to the ionic character exhibited by the Ga-O bonds for the Ga atoms in the same position.

Finally, by comparing the p , d and $s-d$ valence contributions to the EFG tensor in the principal components (V_{xx} , V_{yy} , V_{zz}) for the Cd probe at the octahedral Ga-site in the neutral and charged states (Table 5.3), it is possible to see that the biggest variation occurs in the d valence contribution, mainly in the V_{xx} and V_{yy} components. This is in perfect agreement with the DOS results, since the impurity band is composed of Cd-4*d* states, which get filled when going from the Cd⁰ to the Cd¹⁻ charge state. Furthermore, since η depends not only on V_{zz} but also on V_{xx} and V_{yy} , this corresponds to a considerable change in η but little change in the value of V_{zz} , as can be seen in the EFG values obtained for Cd⁰ and Cd¹⁻ (Table 5.2). Again, experiment and calculations show very good agreement.

5.4 Temperature dependence of the transition rates in PAC

Regarding the temperature dependence of the transition rates between the initial (electronically unstable) and the final (stable) states in the PAC experiments using the ^{111}In probes, they have the unexpected behavior of slightly decreasing with rising temperature from 20 °C to 300 °C and then they exponentially rise for higher temperatures, so two different regimes are being observed.

To understand the higher temperatures regime, an Arrhenius plot was fitted to the data measured above 375 °C (Fig. 5.8), where a clear increase of the transition rates with the temperature is seen and the intermediate state is suppressed. The linear regime in log-scale is visible and an activation energy of 0.54(1) eV was obtained from the fitted curve.

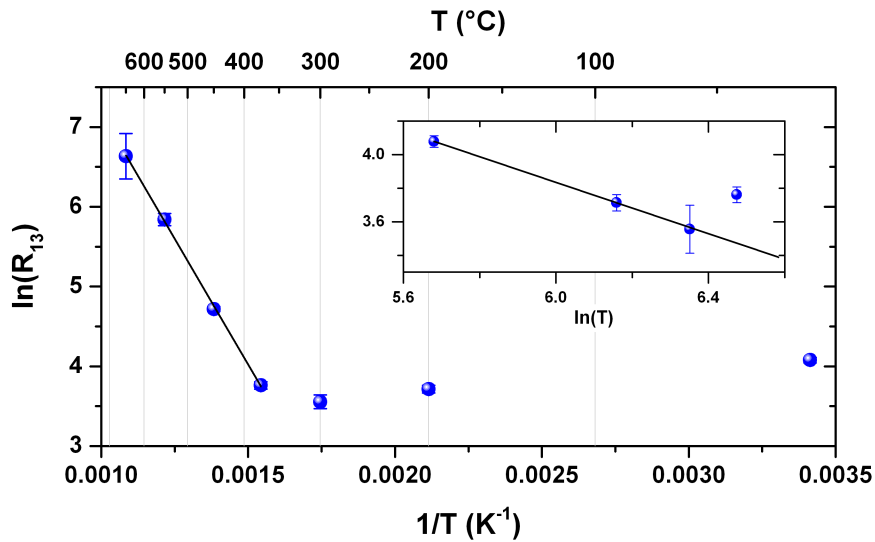


Figure 5.8 – Arrhenius plot of the transition rate $R_{1\rightarrow3}$ (MHz) as a function of temperature in logarithmic scale and the corresponding fit between 375 °C and 650 °C. The error bars were calculated considering $\Delta \ln(x) = \Delta x/x$. **(inset)** Logarithmic $R_{1\rightarrow3}$ plotted as a function of logarithmic temperatures between 20 °C and 300 °C. Two barely distinctive linear curves are present, corresponding to $T^{-3/4}$ and $T^{2\alpha-1}$ for $\alpha = 0.118$ (the slope of each curve is equal to the temperature's exponent).

Interestingly, an activation energy of 0.42 eV has been measured for the quenching of the typical blue luminescence band in Ga_2O_3 which is related with conductivity^[92]. Binet and Gourier^[92] interpreted this activation energy as the effect of hole detrapping from deep acceptor levels. On the other hand, Fleischer and Meixner^[115] reported a thermal activation energy of 0.6(1) eV for carrier mobility in Ga_2O_3 , and so the activation energy might be due to electron delocalization explaining an increase of the electron mobility with increasing temperature. Nonetheless, Ma *et al.*^[116] observed that ionized impurity scattering (which depends on donor concentration) decreases the electron mobility, hence charge carrier mobility and charge carrier density are interconnected. In addition, they identified polar optical phonon scattering as the dominant mechanism limiting electron mobility in $\beta\text{-Ga}_2\text{O}_3$ by observing a decrease in the electron mobility for

increasing temperature (in contradiction to the temperature dependence observed by Fleischer and Meixner^[115]). According to the DFT simulations, the Cd probes induce an impurity band ~ 0.3 eV above the top of the valence band of Ga₂O₃ (for the considered dopant concentration), so it is tempting to attribute this acceptor ionization energy to the activation energy of 0.54(1) eV measured in temperature dependent ¹¹¹In PAC measurements. However, ^{111m}Cd PAC measurements showed that in the present samples Cd is found in the Cd¹⁻ charge state already at room temperature, suggesting that the Fermi level lies above the acceptor level, as expected for n-type material. Finally, deep level transient spectroscopy (DLTS) measurements performed by Irmscher *et al.*^[117] showed the presence of several deep defect levels inside the band gap, including one 0.55 eV below the conduction band and another 0.74 eV below the conduction band (the second being dominant). Similar results were found by Zhang *et al.*^[118], also using DLTS, identifying defect levels 0.62 eV and 0.82 eV below the conduction band (the second being dominant as well). In summary, we can then conclude that the activation energy of 0.54(1) eV obtained by the electronic recovery as a function of temperature in the PAC experiments is most probably associated to electrons going from defect levels (observed in DLTS measurements^[117,118]) to the conduction band, but it might also be influenced by the electron mobility due to the interconnection between charge carrier mobility and donor concentration in the material^[116].

For the measurements below 300 °C, it is observed that lowering the temperature slightly increases $R_{1 \rightarrow 3}$. This counterintuitive phenomenon cannot be explained by low temperature conductive processes such as variable-range hopping (VRH). In the VRH regime, conduction is described as the result of many series of hops of charge carriers from some occupied states below the Fermi level to some unoccupied states above with very similar energies, due to thermal agitation. Its temperature dependence is proportional to $\exp(-1/T^{1/4})$ ^[119], therefore the transition rates should increase with temperature. A transition of Ga₂O₃ from insulator to metallic at these temperatures, even if possible, is also ruled out since the metallic conduction would result in an electronic recovery so fast that only the final state would be observed, which is not the case at room temperature. A promising solution to explain the observed behavior could be found based on the empirical model for enhanced tunneling probability at lower temperatures as previously discussed by Lupascu *et al.*^[71]. Following their arguments, in the picture of VRH the average tunnelling distance (R_m) between defect sites involved in the hopping of charges is proportional to $T^{-1/4}$ ^[119], thus rising with decreasing temperature. It is reasonable to consider that R_m is the average distance between a Cd probe and a defect that can tunnel an electron to the Cd site. Therefore, we can now roughly estimate that (for a fixed density of defect sites) the number of defects which can tunnel an electron to the Cd site will be proportional to $\frac{4\pi R_m^3}{3}$, hence proportional to $T^{-3/4}$, thus also rising with decreasing temperature. That same temperature dependence should then be observed for the transition rates. In fact, in the inset of Figure 5.8 it is possible to see that the transition rates between 20 °C and 300 °C follow this temperature de-

pendence within the experimental error, showing that the electronic recovery at these temperatures can be explained by direct electron tunnelling between defects and the Cd probes.

Although the $T^{-3/4}$ dependence fits the data at lower temperatures really well, the reasoning behind this empirical model is not fully proved. Therefore, we decided to explore on a deeper level the hypothesis of direct electron tunneling being responsible for the low temperature behavior.

The tunneling of an electron from a defect to the Cd probe raises the question on what is the shape of the potential barrier that the electron must cross. Let us suppose that the potential can be approximately described by a double-well potential, where the defect is in one of the wells and the Cd is in the other, as represented in Figure 5.9.

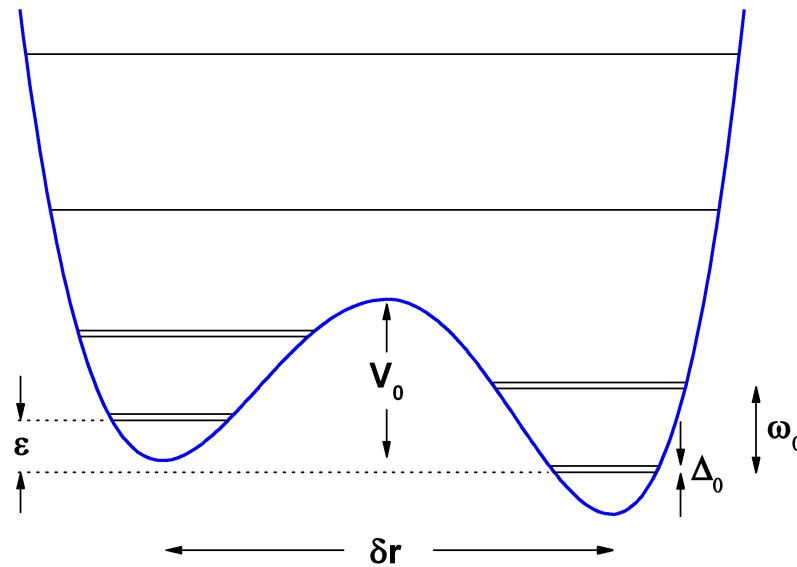


Figure 5.9 – (Biased) Double-Well Potential.

The Hamiltonian for a single electron moving in such a potential is $H_0 = (\epsilon/2)\sigma_z - (\hbar\Delta_0/2)\sigma_x$, where σ_i are Pauli spin matrices, ϵ is the energy asymmetry and Δ_0 is the bare tunneling matrix element, given in one dimension as $\Delta_0 = \omega_0 \exp \left[-\sqrt{(2mV_0/\hbar^2)}\delta r \right]$, where ω_0 is the undamped oscillation frequency in either well. The solution for the wavefunction of such system is very well known^[120]. For energies smaller than the middle barrier, the electron will be tunnelling from one well to the other and the wavefunction in this case is a linear combination of the wavefunctions in each well individually (which are approximated to harmonic potentials).

In 1984, Chakravarty *et al.*^[121] studied the effect of a dissipative field with ohmic dissipation in a double-well potential as a function of temperature and, in 1985, Fisher and Dorsey^[122] generalized the solution to a biased double-well potential (wells with different minimum energies, as in Figure 5.9). They observed that the tunneling rate from one well to the other is temperature-dependent due to the dissipative field and, in certain

conditions, it is possible to observe a decrease of the tunneling rate with increasing temperature.

In 1996, Chun and Birge^[123] used this theory to explain the dynamics of single bistable defects in disordered metals. They considered that the two stable positions for the defects were represented by a double-well potential (with the defects tunneling between them) and that the dissipative field was given by the electron bath in the metal. It was possible for them to observe the predicted behavior for a double-well potential coupled to a dissipative field and they summarized the different regimes predicted by the theory in a more comprehensive and resumed way, as follows:

Considering the operator $\sigma_z(t)$ (a Pauli matrix) which is 1 when the defect is in one well and -1 when it is in the other well, the occupation probability of the defect is given by $P(t) = \langle \sigma_z(t) \rangle = -\tanh(\epsilon/2k_B T) + [1 + \tanh(\epsilon/2k_B T)]e^{-\gamma t}$, with the tunneling rate given by:

$$\gamma = \frac{\Delta_r}{2} \left(\frac{2\pi k_B T}{\hbar \Delta_r} \right)^{2\alpha-1} \frac{\cosh\left(\frac{\epsilon}{2k_B T}\right)}{\Gamma(2\alpha)} \left| \Gamma\left(\alpha + i \frac{\epsilon}{2\pi k_B T}\right) \right|^2 \quad (5.1)$$

where ϵ is the bias energy between the two wells, Δ_r is given by $\Delta_r = \Delta_0 \left(\frac{\Delta_0}{\omega_0} \right)^{\frac{\alpha}{1-\alpha}}$ where Δ_0 is the bare tunneling matrix element mentioned before, $\Gamma(x)$ is the Gamma function and α is a dimensionless dissipation coefficient which is dependent on the material.

The tunneling rate also verifies $\gamma = \gamma_f + \gamma_s$, where γ_f and γ_s are called the fast and the slow rates respectively, which are nothing but the transitions from the well with the highest minimum to the well with the lowest minimum (γ_f) and vice versa (γ_s). These two transition rates must obey the principle of detailed balance, so $\gamma_f/\gamma_s = e^{\epsilon/k_B T}$. This results in:

$$\gamma_f = \frac{\Delta_r}{2} \left(\frac{2\pi k_B T}{\hbar \Delta_r} \right)^{2\alpha-1} \frac{e^{\epsilon/2k_B T}}{\Gamma(2\alpha)} \left| \Gamma\left(\alpha + i \frac{\epsilon}{2\pi k_B T}\right) \right|^2 \quad (5.2)$$

$$\gamma_s = \gamma_f e^{-\epsilon/k_B T} \quad (5.3)$$

When $k_B T < \epsilon$, the tunnelling rates follow a simple picture of stimulated absorption (determined by γ_s) and spontaneous emission (determined by γ_f), with γ_s almost null for really low temperatures. However, when $k_B T > \epsilon$, we have $\gamma \sim T^{2\alpha-1}$, so in the regimes where $0 < \alpha < 1/2$, the tunneling rate decreases with increasing temperature. In Figure 5.10 we can see the transition rates as a function of temperature as given by the previous equations with $0 < \alpha < 1/2$, including the regime of decreasing transition rates with increasing temperature.

In 1995, Louis *et al.*^[124] used this same theory to explain the tunnelling of a Xe atom between the tip of a scanning-tunneling microscope (STM) or an atomic-force microscope (AFM) and a Ni surface but, in this case, they considered that the system

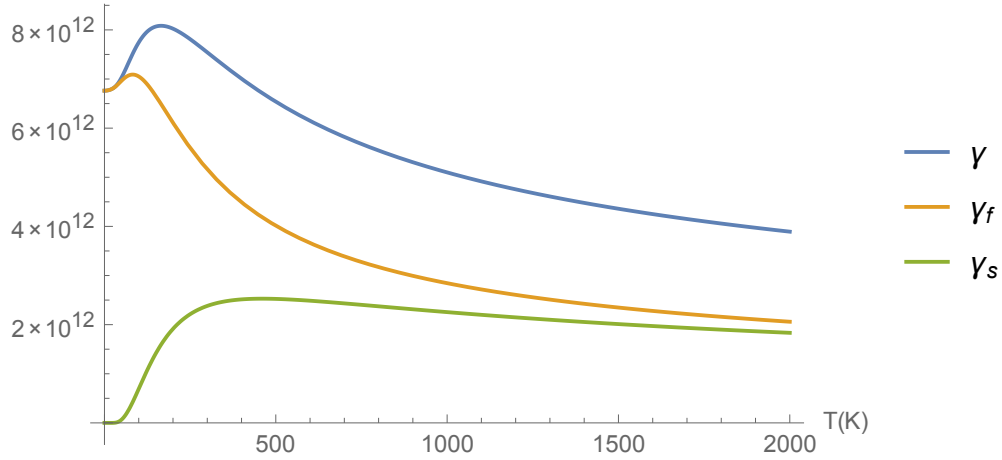


Figure 5.10 – Illustrative curves for equations 5.1, 5.2 and 5.3 considering $\alpha = 0.3$, $\epsilon = 0.02$ and $\Delta_r = 10^{13}$.

was coupled to phonons, so the phonons are the dissipative field with ohmic dissipation. The transition rates observed by them as a function of temperature showed the behavior predicted by the previous equations with $0 < \alpha < 1/2$, including a decrease of the rates with increasing temperature in a certain temperature range.

Attempting to apply such theory to our case, let us consider the equation for the tunneling rate (eq. 5.1) when $k_B T \gg \epsilon$:

$$\begin{aligned} \gamma &\approx \frac{\Delta_r}{2} \left(\frac{2\pi k_B T}{\hbar \Delta_r} \right)^{2\alpha-1} \frac{|\Gamma(\alpha)|^2}{\Gamma(2\alpha)} \iff \\ \iff \ln(\gamma) &\approx \ln(\theta) + (2\alpha - 1) \ln(T), \quad \theta = \frac{\Delta_r}{2} \left(\frac{2\pi k_B}{\hbar \Delta_r} \right)^{2\alpha-1} \frac{|\Gamma(\alpha)|^2}{\Gamma(2\alpha)} \end{aligned} \quad (5.4)$$

Fitting the logarithmic equation to the transition rates obtained between 20 °C and 300 °C yields $\alpha = 0.118(4)$ and $\Delta_r = 1.3(2) \times 10^{10} \text{ s}^{-1}$ (see inset of Figure 5.8), hence we are in fact in the regime of $0 < \alpha < 1/2$ and our transition rates behave as predicted by equation 5.4.

The theory is only valid for a specific set of values for each variable, so we can test them and set boundaries in our case:

First, since we are in the regime of $k_B T > \epsilon$, this means that $\epsilon < 25 \text{ meV}$.

Then, the theory requires that $\hbar \Delta_r \ll \alpha k_B T$, which is true even at room temperature ($8.53 \text{ } \mu\text{eV} \ll 2.98 \text{ meV}$).

The last requirement is that $\Delta_0 \ll \omega_0$. Considering as reference the frequency associated to the polar optical phonon energy reported in ref.^[116] ($\omega_0 = 6.7(6) \times 10^{13} \text{ s}^{-1}$) and using the definition of Δ_r , we have $\Delta_0 = 3.6(6) \times 10^{10} \text{ s}^{-1}$, therefore $\Delta_0 \ll \omega_0$ is verified.

A hypothesis for the observations at lower temperatures in this work can then be

formulated, stating that electrons are tunneling from some defects directly to the Cd probes and that such a system can be described by a double-well potential coupled to a dissipative field with ohmic dissipation. In this case, we believe that a phonon bath is the dissipative field, as observed in the example above from Louis and colleagues^[124].

One important comment must be made. Two different theories to explain the behavior of the transition rates at lower temperatures are mentioned here and both suggest the existence of direct electron tunnelling. However, at first sight they do not seem to be compatible. For instance, the empirical model for enhanced tunnelling probability based on the temperature dependence for the average distance of defects in VRH results in a temperature exponent ($T^{-3/4}$) which is the same for any sample or material. On the other hand, the theory regarding quantum tunnelling in a biased double-well potential with coupling to an ohmic dissipative field results in a temperature exponent which is a function of a dimensionless dissipation coefficient that depends on the material ($T^{2\alpha-1}$). Nonetheless, both models can be viewed as approximations for the same physical situation but in opposite regimes. By this, it is meant that the latter model (model 2) assumes that all defects are at the same site and at the same distance from the Cd probes, thus a single unique double-well potential is able to describe them all, whereas the first model (model 1) is based on VRH, so it depends on the existence of defects at different distances (and sites) from the Cd probes which can tunnel an electron to the probes, but in fact we can think of each of those defects as being described by a double-well potential similar to model 2, so model 1 can be viewed as a distribution of defects described by potentials similar to the potential described on model 2. If the defects' site and distance from the Cd probes are not much different from one another, it is reasonable to expect a similar temperature dependence from both models, at least in a first approximation.

Also, whilst model 2 has a much stronger foundation than model 1, it has some constraints that are not fully proved yet but instead postulated as true in our case since the model fits the data quite well. For instance, this theory is only valid for dissipative fields with ohmic dissipation, as previously mentioned. The coupling field has ohmic dissipation if its spectral density is proportional to the frequency: $J(\omega) \propto \omega$. This seems to be true if the coupling field is given by an electron bath in a metal^[123] as well as in the case of tunnelling between a microscope tip and the surface of Ni^[124], where the ohmic dissipation in the latter case is justified for occurring between two surfaces. However, Leggett *et al.*^[125,126] say that in the case of defect (or electron) tunnelling in a solid with coupling to a (three-dimensional) acoustic phonon bath, the dissipation is super-ohmic ($J(\omega) \propto \omega^s$, with $s > 1$). In our understanding, they are referring to the case of defects (or electrons) diffusing in a sample by quantum tunnelling, which is different from our case where there is solely tunnelling of an electron between a specific defect and a Cd probe, thus the possibility of ohmic dissipation remains true. This could be completely proved by performing lower temperature measurements to see if both regimes predicted by the theory are observed ($k_B T < \epsilon$ and $k_B T > \epsilon$), which is prone for future work. For this reason, both models are referred but firmly believing that this analysis is conclusive

enough to show that at the lower temperature regime observed in this work the electronic recovery is explained by direct electron tunnelling from defects to the Cd probes.

5.5 Discussion of Results and Conclusions

By connecting the PAC experimental results with the DFT simulations, it was possible to confirm that the Cd dopants occupy a single position in single crystalline and polycrystalline β -Ga₂O₃ (including nanowires), the octahedral Ga site, irrespective of the doping technique, i.e. diffusion or implantation. In the PAC experiments using ¹¹¹In, a very good agreement was found between the EFG in the final stable state (state 3) of the ¹¹¹Cd probes and the DFT simulations for the charge state Cd¹⁻ ($V_{zz}^{sim.} = 63.8 \text{ V/\AA}^2$, $\eta = 0.04$ versus $V_{zz}^{exp.} = 65(1) \text{ V/\AA}^2$, $\eta = 0.10(1)$) as well as between the intermediate state (state 2) and the neutral state Cd⁰ ($V_{zz}^{sim.} = 70.2 \text{ V/\AA}^2$, $\eta = 0.98$ versus $V_{zz}^{exp.} = 67(2) \text{ V/\AA}^2$, $\eta = 0.92(3)$).

The intermediate state is a metastable Cd state only clearly visible at 300 °C and 375 °C in the PAC experiments. Its mean life time can be estimated by the inverse of its transition rate to the final stable state^[64], being equal to $1/(0.5(1) \text{ MHz}) = 2.0(4) \mu\text{s}$ at 300 °C, where its presence is more pronounced. It is possible to see that the initial state ($V_{zz} = 64(2) \text{ V/\AA}^2$, $\eta = 1.00(1)$) is very similar to the intermediate state, apart from the broad Lorentzian distribution. From here we conclude that both of them correspond to the neutral state Cd⁰, which is achieved after recovering the lost electrons during the electron capture decay of ¹¹¹In, but due to the different Auger emissions and ionizations of different Cd probes, as well as the availability of electrons in their vicinity, initially some of the probes are not fully recovered electronically (i.e. there are still inner-shell transitions and Auger-processes in progress), hence the broad distribution in the initial state.

Regarding the temperature dependence of the transition rates, two different regimes were observed. For temperatures above 375 °C, an Arrhenius plot was fitted and the linear regime in log-scale is clearly visible, where an activation energy of 0.54(1) was obtained. On the other hand, below 300 °C it was shown that the electronic recovery can be explained by direct electron tunnelling between defects and the Cd probes. In summary, at lower temperatures the electronic recovery is accomplished by the tunnelling of electrons from defects and/or impurities to the Cd sites. Then, between 300 °C and 375 °C, the tunnelling is reduced and the thermal energy is still low, resulting in the lowest transition rates and longer mean life time for the neutral charge state Cd⁰. At higher temperatures, the thermal energy is able to increase the number of electrons going from defect levels inside the band gap to the conduction band and the Arrhenius plot behavior is observed. Independently of the measuring temperature, in the end all probes are in the charge state Cd¹⁻, proving the acceptor character of Cd in Ga₂O₃. This is also confirmed in the PAC measurements performed after implantation of ^{111m}Cd,

where no electronic changes occur during the decay but the single observed EFG also corresponds to the charge state Cd¹⁻.

It was also possible to conclude that the activation energy of 0.54(1) eV obtained by the electronic recovery as a function of temperature in the PAC experiments is associated to electrons going from defect levels previously observed in DLTS measurements^[117,118] to the conduction band, but it is not possible to completely rule out some kind of influence from the electron mobility due to the interconnection between charge carrier mobility and donor concentration in β -Ga₂O₃. Moreover, concerning the issue of strong hole localization in Ga₂O₃ referred before^[99], since no holes are present around the Cd probes, no polarons are formed. Besides, the Cd-O bonds showed a slight more covalent character, in contrast to the ionic character observed for the Ga-O bonds, so the probability of polaron formation in an adjacent O atom is reduced. Indeed, such polaron formation in the vicinity of the Cd-probe should be readily observable in the PAC measurements.

The measurement of the charge carrier density (and mobility) in a material is usually obtained by Hall effect experiments which are not always possible to perform, but the connection between PAC experiments and DFT simulations as performed in this work has been shown to be a good alternative to those kinds of experiments in samples for which electronic contacts are difficult to perform. Furthermore, it is possible to be done in smaller samples (e.g., nanowires) considering that PAC experiments have already been successfully performed in samples at those scales^[2].

The possibility of future experiments using insulating or p-type doped samples to measure the fraction of ionized Cd as a function of temperature, as well as the possible formation of polarons, seems to be very promising.

As a final note, it was shown that the use of very accessible ¹¹¹In activated solutions (currently used in hospitals as tracers, for instance) to dope a sample with Cd is a good option to take into consideration. Even though the use of radioactive materials for such a purpose seems risky, it must be noted that the radioactive isotope decays very rapidly. Also, transmutation doping is regularly used for commercial purposes in the production of silicon wafers doped with phosphorous by transforming the natural isotope ²⁸Si into ³¹Si by neutron activation, which decays by beta emission with a 2.62 hours half-life to the stable isotope ³¹P^[127].

CHAPTER 6

Detailing the electronic mobility as a function of dopants in GaN

6.1 Introduction

GaN is a wide band gap semiconductor (3.503(5) eV^[11]) especially useful in the development of blue- and UV-LEDs^[8,23,24]. Si is known to be a very good n-type dopant in GaN by substituting for Ga and introducing a shallow donor level into the band gap^[28]. On the other hand, Zn substitutes for Ga and introduces a deep acceptor level above the top of the valence band maximum, being responsible for the blue luminescence peaking at 2.9 eV that is often observed in PL spectroscopy^[128–130]. The deep acceptor is commonly used to compensate unintentional donor defects to manufacture semi-insulating GaN^[29]. Implantation studies of the double acceptor Ta in GaN have been done before^[24,131], but we provide now a new and detailed microscopic investigation enlightening both the Ta impurity states and its dependence from the properties of the pre-doped GaN host.

Hyperfine interactions techniques, such as $\gamma - \gamma$ Perturbed Angular Correlations (PAC), probe energy splittings below 10^{-7} eV, much lower than atomic binding energies, being particularly sensitive to the local electronic density and polarization at a nuclear probe's site. By measuring the electric quadrupole and magnetic interaction of the nuclear moments with the charge distribution in the surroundings of the probe nuclei, this is the way to find and further characterize point-like defects and the probe's electronic structure in the host matrix. Complementarily, the use of the $e^- - \gamma$ PAC technique, where the measurement starts after the ejection of a conversion electron from the deeper inner atomic K- or L- shells of the nuclear probe, forces the measurement to start in a perturbed and out-of-equilibrium (maybe) ionized environment. The electronic recombination ability depends on the affinity of the element's charge state in the specific matrix and on the host's electronic mobility. Since the observable of the PAC technique is time differential, the combined study using both $\gamma - \gamma$ and $e^- - \gamma$ techniques allows the local observation of the probe electronic recombination, which is a function, particularly, of charge diffusion and of the stability of localized excited electronic states during the recombination process. Although the combination of both techniques was suggested over 50 years ago by U. Baäverstam, A. Johansson and T.R. Gerholm, fa-

thers of magnetic electron spectroscopy^[132], this idea was not put into practice by the lack of isotopes of appropriate elements with enough purity and quantity (ppm), by poor experimental time resolution ($< \text{ns}$), and still not accessible modeling theory and computing power allowing to unambiguously analyze and interpret the experimental data. From the experimental point of view, the ISOLDE laboratory provides now short-lived radioactive probes with enough purity and quantity, and there are the most efficient $\gamma - \gamma$ and $e^- - \gamma$ PAC spectrometers ever built, including the only functional P. Kleinheinz and K. Siegbahn spectrometer with two magnetic lenses and two BaF_2 detectors^[44,45]. From the data analysis point of view, the development of PACme (see Chapter 3) was the turning point to analyze $\gamma - \gamma$ and $e^- - \gamma$ combined experiments in a truly informative manner.

One of the best suitable isotopes allowing to combine $\gamma - \gamma$ with $e^- - \gamma$ PAC is ^{181}Hf ($t_{1/2} = 42.4$ days) decaying by β^- to a first 615 keV long-lived metastable state ($t_{1/2} = 17.6 \mu\text{s}$) at ^{181}Ta . Stable ^{181}Ta is achieved following a double cascade whose intermediate level has spin 5/2 and $t_{1/2} = 10.8 \text{ ns}$ (Fig. 6.1). The first decay of this cascade may occur by emission of a photon or by emission of a conversion electron with a total internal-conversion coefficientⁱ of $\alpha = e^-/\gamma = 1.265$ ^[133]. This makes $^{181}\text{Hf}/^{181}\text{Ta}$ a good probe to combine $\gamma - \gamma$ PAC with $e^- - \gamma$ PAC by using γ_1 (133 keV) and γ_2 (482 keV) in the former and the conversion electron $< L >$ with average energy $133 \text{ keV} - 11 \text{ keV} = 122 \text{ keV}$ and γ_2 in the latter.

$\gamma - \gamma$ and $e^- - \gamma$ PAC measurements were then performed after implantation and annealing of $^{181}\text{Hf}/^{181}\text{Ta}$ probes into Si- and Zn-doped single crystalline samples of GaN in order to perform a detailed study of the lattice site of the implanted ions probing final and excited electronic states as a function of temperature and the electronic mobility of the hosts.

6.2 Perturbed Angular Correlation experiments

6.2.1 Experimental Details

The two commercially availableⁱⁱ $\sim 11 \mu\text{m}$ thick GaN samples were grown by hydride vapor phase epitaxy on sapphire substrates and doped with Si and Zn, respectively. $^{181}\text{Hf}/^{181}\text{Ta}$ probes were implanted at room temperature in each sample along the surface normal at the Bonn separator of the University of Bonn with 160 keV energy to typical fluences of $\sim 10^{13} \text{ atoms/cm}^2$. Then, the samples were annealed in a rapid thermal annealing apparatus between graphite strips under nitrogen flow with a holding time of 120 s at 950 °C and using a GaN proximity cap, as previously described to be optimal for GaN^[131]. The $\gamma - \gamma$ PAC measurements were carried out on a 6-LaBr₃ detector spec-

ⁱThe total internal-conversion coefficient is defined as $\alpha = \frac{\text{number of de-excitations via electron emission}}{\text{number of de-excitations via gamma emission}}$

ⁱⁱTechnologies and Devices International Inc., 12214 Plum Orchard Drive, Silver Spring, MD 20904, USA; GaN:Si concentration $N_d - N_a = (1-3) \times 10^{18} \text{ cm}^{-3}$ and GaN:Zn high resistivity $> 1 \times 10^5 \Omega \text{ cm}$.

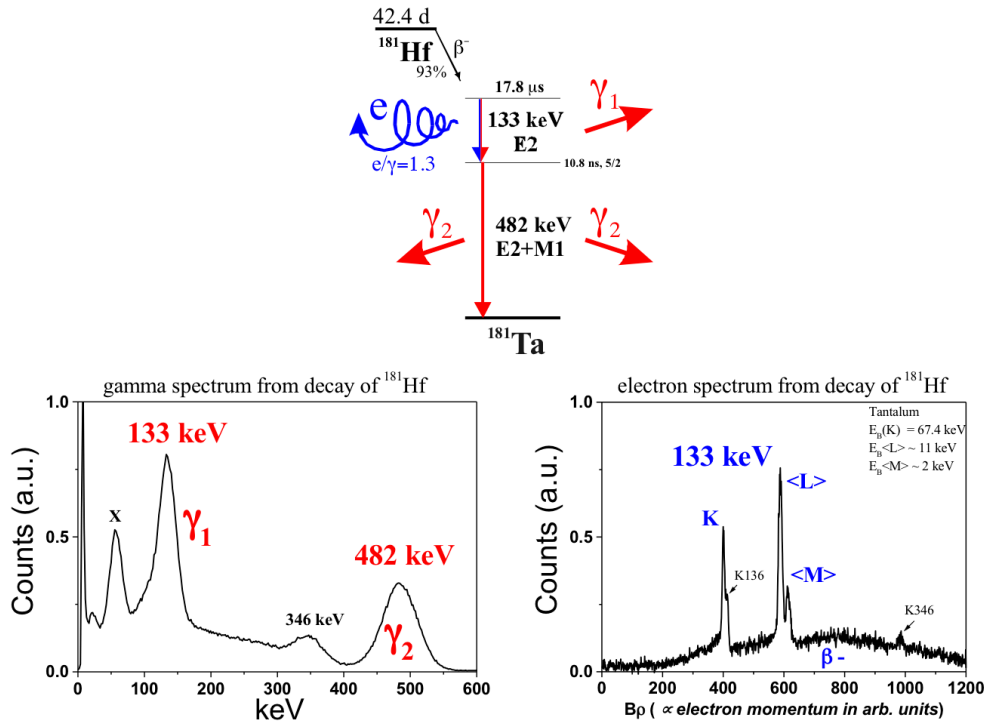


Figure 6.1 – Cascade decay of $^{181}\text{Hf}/^{181}\text{Ta}$ and corresponding gamma and electron spectra, where the first decay of the double cascade occurs by the emission of either a photon or of a conversion electron.

trometer^[43] and the $e^- - \gamma$ PAC measurements were carried out on a P. Kleinheinz and K. Siegbahn spectrometer with two magnetic lenses and two BaF_2 detectors^[44,45], both performed as a function of the measuring temperature, from room temperature down to lower temperatures using a cryostat (down to around 10 K). In the case of $e^- - \gamma$ PAC experiments, they were further performed (under vacuum) from room temperature up to ~ 500 K using a sample heating system. During the $e^- - \gamma$ measurements, the samples were oriented such that the perpendicular axis to their surface (corresponding to the c-axis of the wurtzite lattice) was in the detectors' plane with a 45° angle in between the detectors' axis. The $\gamma - \gamma$ measurements were performed in a 6-detector PAC spectrometer where the sample cannot be mounted keeping the same high symmetry orientation with all detector pairs, leading to an undetermined mixture of different orientations for different pairs of detectors. Still, that only affects the relative amplitudes of the triplet of frequencies characterizing the same EFG at the observable $R(t)$ function and do not affect the associated frequencies from where the hyperfine fields are determined.

6.2.2 Results

Figures 6.2 and 6.3 show the resulting PAC $R(t)$ observable spectra and respective Fourier transforms for each sample, including the $\gamma - \gamma$ and the $e^- - \gamma$ measurements, whilst Tables 6.1 and 6.2 summarize the fitting parameters.

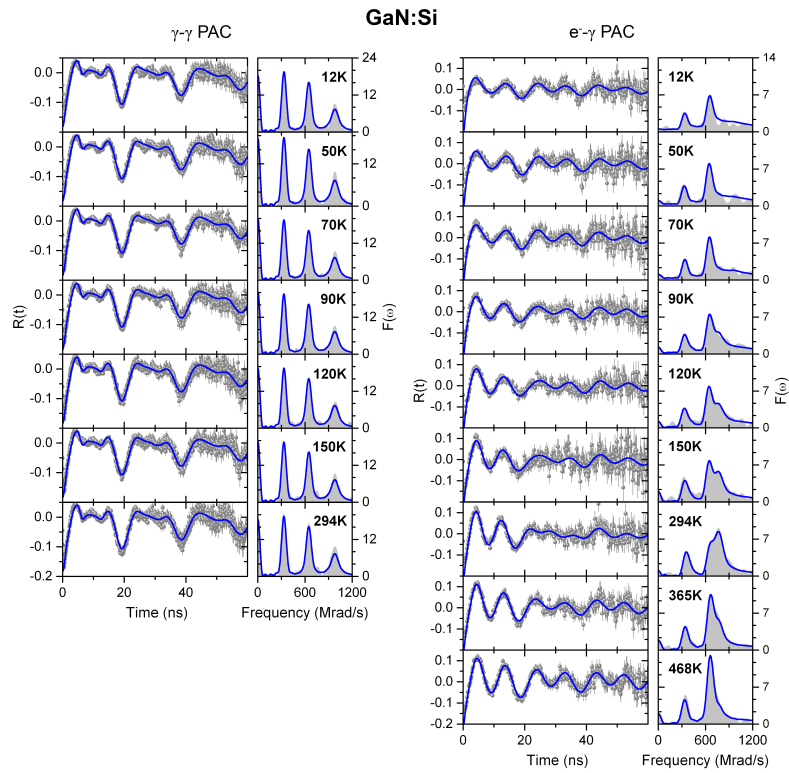


Figure 6.2 – (left) $\gamma - \gamma$ and (right) $e^- - \gamma$ PAC spectra (and corresponding Fourier transforms): as a function of measuring temperature after implantation of $^{181}\text{Hf}/^{181}\text{Ta}$ and annealing at 1000 °C for 10 minutes in a single crystalline sample of GaN(Si-doped).

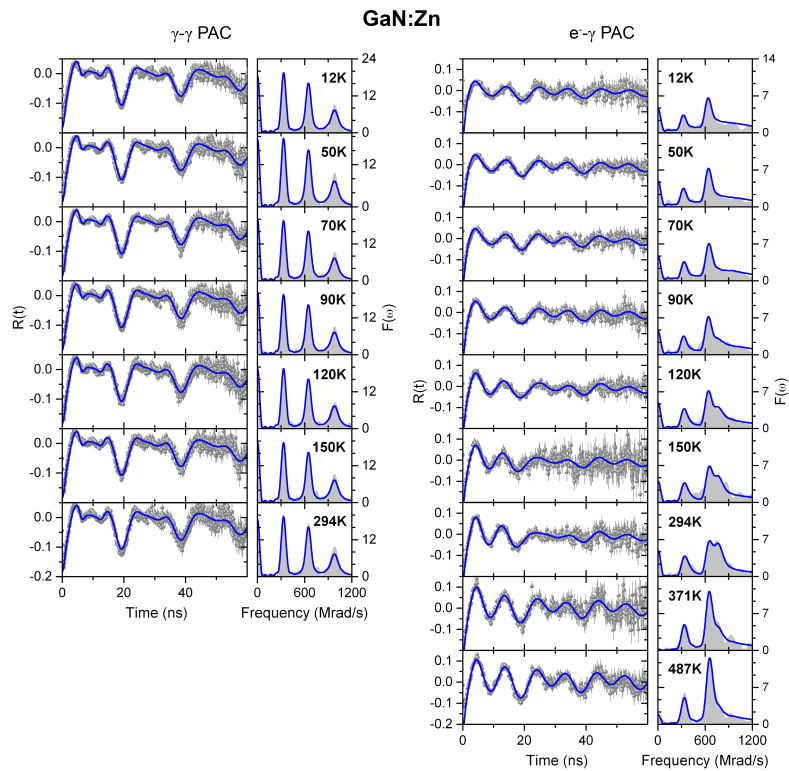


Figure 6.3 – (left) $\gamma - \gamma$ and (right) $e^- - \gamma$ PAC spectra (and corresponding Fourier transforms): as a function of measuring temperature after implantation of $^{181}\text{Hf}/^{181}\text{Ta}$ and annealing at 1000 °C for 10 minutes in a single crystalline sample of GaN(Zn-doped).

Table 6.1 – $\gamma - \gamma$ PAC fitting parameters obtained for the measurements as a function of temperature in GaN(Si-doped) and GaN(Zn-doped). Two different fractions were considered, each corresponding to a different probe's environment characterized by a single EFG. The first fraction corresponds to probes in a stable site whereas the second fraction corresponds to non-annealed probes and is treated as a polycrystalline environment. The quadrupole frequency ω_0 and the full width at half maximum for the Lorentzian distribution (FWHM) are expressed in Mrad/s and the asymmetry parameter η is dimensionless. α is the EFG's azimuth angle.

Sample	T (K)	Fraction 1					Fraction 2			
		%	ω_0	η	α	FWHM	%	ω_0	η	FWHM
GaN(Si)	12		325.1(4)	0.14(1)						
	50		325.1(4)	0.14(1)						
	70		324.4(3)	0.14(1)						
	90	95.7(1)	324.4(3)	0.14(1)	56.5(1)°	22.1(4)	4.3(1)	978(2)	0.0	146(4)
	120		324.7(5)	0.14(1)						
	150		324.8(2)	0.14(1)						
	294		324.7(2)	0.14(1)						
GaN(Zn)	12		323.2(6)	0.14(1)						
	50		322.2(5)	0.16(1)						
	70		322.6(7)	0.15(1)						
	90	95.9(2)	322.0(5)	0.16(1)	59.8(1)°	25.9(5)	4.1(2)	971(13)	0.0	536(37)
	120		322.0(7)	0.16(1)						
	150		322.4(5)	0.15(1)						
	294		322.6(2)	0.14(1)						

Table 6.2 – $e^- - \gamma$ PAC fitting parameters obtained for the measurements as a function of temperature in GaN(Si-doped) and GaN(Zn-doped). Three different states described by a single electric quadrupole interaction each were considered. The transition rates between them are expressed in MHz. The quadrupole frequency ω_0 and the full width at half maximum for the Lorentzian distribution (FWHM) are expressed in Mrad/s and the asymmetry parameter η is dimensionless.

Sample	T (K)	State 1			State 2			State 3			Transition Rates		
		ω_0	η	FWHM	ω_0	η	FWHM	ω_0	η	FWHM	1 → 2	1 → 3	2 → 3
GaN(Si)	12							322(2)	0.12(7)		0	221(18)	-
	50							319(2)	0.10(5)		0	317(27)	-
	70							322(2)	0.16(5)		0	342(33)	-
	90							319(2)	0.0(2)		194(33)	331(29)	
	120	423(19)	0.0(2)	400(56)	388(2)	0.00(2)	18(3)	315(2)	0.0(2)	22(4)	333(52)	439(46)	
	150							316(2)	0.10(6)		738(169)	614(122)	
	294							317(1)	0.18(5)		2074(356)	386(99)	38(3)
	365							327(1)	0.00(5)		1172(119)	1428(115)	
	468							328(1)	0.00(2)		617(107)	2293(358)	
GaN(Zn)	12							313(2)	0.0(1)		0	199(14)	-
	50							315(1)	0.0(1)		0	244(11)	-
	70							319(1)	0.13(5)		0	244(16)	-
	90							314(2)	0.0(1)		68(20)	265(18)	
	120	423(15)	0.0(4)	400(11)	388(3)	0.00(3)	18(5)	314(2)	0.1(1)	22(5)	226(32)	335(35)	
	150							317(4)	0.0(1)		345(91)	292(63)	
	294							315(3)	0.0(1)		730(101)	346(63)	42(5)
	371							322(1)	0.10(6)		341(92)	815(136)	
	487							325(1)	0.09(3)		230(52)	1033(106)	

E. Alves *et al.*^[24] showed that Hf is incorporated into substitutional Ga sites in GaN immediately after the implantation. In the $\gamma-\gamma$ PAC measurements of all samples it is indeed possible to see that a single environment is observed ($\omega_0 \sim 325$ Mrad/s, $\eta \sim 0.14$) – a unique electric field gradient (EFG) results in 3 observable frequencies for a spin-5/2 nuclear level – in concordance with the previous reports^[24,131]. Nonetheless, a small fraction ($\sim 5\%$) characterized by a very broad EFG (Lorentzian distribution with large FWHM) is also present, representing a small amount of implantation defects that were not properly annealed. More importantly, within the range of measured temperatures, it can be seen that no significant changes occur in the spectra, meaning that the electronic environment around the Ta probe stays particularly stable.

However, a different picture is seen in the $e^- - \gamma$ PAC measurements, where a clear dependence of the $R(t)$ function as a function of temperature is visible. Since both $\gamma-\gamma$ and $e^- - \gamma$ experiments are performed using the same probes in the same samples, this temperature dependence must be triggered by the emission of the internal conversion L-shell electron and the subsequent Ta electronic shells recombination process in the latter case.

To fit and analyze this data, the program PACme (Chapter 3) that incorporates the theory of stochastic processes applied to dynamic transitions in PAC, as described by Winkler and Gerdaul^[64], was used.

Table 6.2 shows the fitting parameters obtained after analyzing the spectra.

After the emission of the conversion electron, during the recombination of the atomic shells, it is possible that further Auger electrons are emitted, creating a distribution of charge states at the Ta probe. Consequently, before the electronic recovery is partially achieved / completed, the charge distribution around a probe nuclei is probabilistically different from probe atom to probe atom, depending on the initial distribution of charge states and on the possibility to rapidly recombine recovery electrons from its neighborhood. Therefore, the initial observable state describing all probes (State 1) is characterized by a distribution of EFGs which can be approximately described by a single central EFG ($\omega_0 = 423$ Mrad/s, $\eta = 0.0$) with a very broad distribution (large FWHM) to account for the differences in the initial EFGs of the different probe nuclei. Then, a transition occurs to the final stable state (State 3, $\omega_0 = 328$ Mrad/s, $\eta = 0.0$), with no possibility of return to the initial state (unidirectional transition). Interestingly, between 120 K and 294 K a metastable Ta state is observed (State 2) ($\omega_0 = 388$ Mrad/s, $\eta = 0.0$) in addition to the final stable state. In fact, at around 294 K this metastable state is inclusively more visible than the final stable state for the GaN:Si sample. It was then possible to obtain the EFG corresponding to each existing state and the transition rates between them for each temperature, where attention must be paid to the fact that each individual EFG barely changes with temperature but the transition rates have strong variations. Also, only the relevant transitions State 1 $\rightarrow$ State 2, State 1 $\rightarrow$ State 3 and State 2 $\rightarrow$ State 3 are listed, where the remaining possible transitions are null throughout the entire experiments.

6.3 Density Functional Theory simulations

In order to better understand the location and the charge state of the Ta probes in the GaN samples during the PAC measurements, DFT simulations were performed for pure GaN and for GaN supercells with Ta impurities.

6.3.1 Simulation details

The simulations were performed using the same approach as employed in the Ga₂O₃ simulations reported in Chapter 5, i.e., via the full-potential (linearized) augmented plane wave plus local orbitals [FP-(L)APW+lo] method as implemented in the WIEN2k code^[57]. The Perdew, Burke and Ernzerhof parameterization (GGA-PBE)^[57] was considered as exchange-correlation functional for the structural optimization and calculation of the electric field gradients, and the modified Becke-Johnson exchange potential (mBJ)^[56] was used for the calculation of the density of states, band structure and band gap.

The wurtzite structural parameters of GaN as found in the work of Miwa *et al.*^[8] were considered, $a = 3.146 \text{ \AA}$, $b = 3.146 \text{ \AA}$, $c = 5.125 \text{ \AA}$, with the internal atomic positions being optimized by minimizing the atomic forces to a maximum limit of 2 mRy/bohr in a self-consistent way.

To simulate an isolated Ta impurity, a $3 \times 3 \times 2$ supercell of GaN with dimensions $a' = 3a = 9.438 \text{ \AA}$, $b' = 3b = 9.438 \text{ \AA}$ and $c' = 2c = 10.25 \text{ \AA}$ was constructed. Its size was determined by increasing the supercell until the variation of the EFG at the Ta site was in the same order of magnitude of the experimental error in the PAC measurements.

A cut-off value for the plane wave expansion of $R_{\text{mt}} \cdot K_{\text{max}} = 7.0$ was considered, where R_{mt} is the muffin-tin sphere radius and K_{max} is the largest K-vector of the plane wave expansion of the wave function.

76 and 24 k-points in the irreducible Brillouin zone were used for the GaN simple cell and for the $3 \times 3 \times 2$ supercell with the Ta impurity, respectively.

Different charge states for the Ta probes were considered, where removed charges were compensated by adding a homogeneous background of opposite charge to keep the entire cell in a neutral state^[57,107,108]. For instance, if an electron is removed from the cell, the extra positive charge (the hole) can be localized but a uniform negative charge will maintain the neutrality of the cell whilst not resulting in any extra interactions.

All calculations were performed with spin-polarization, although the simple cell and one of the Ta charged states were observed to have no magnetic moment and thus produce the same results without spin-polarization.

6.3.2 Results

A simple cell of GaN in the wurtzite (hexagonal) structure was simulated considering the previously reported lattice parameters^[8] with the Ga cation tetrahedrally coordinated by

the N anions and vice versa. After structural relaxation, a value of $u = 0.377$ was obtained for the internal parameter, which corresponds to the value reported experimentally by Schulz and Thiermann^[134] and from previous simulations^[135].

The density of states (Fig.6.4) shows the top valence band dominated by N $2p$ states, as well as the chemical bond regions and hybridization of the Ga $4p$ and N $2p$ states between -1.0 and -2.0 eV and of the Ga $4s$ and N $2p$ states between -5.5 and -6.5 eV, in accordance with earlier works^[25]. The main contribution from the Ga $3d$ states occurs deeper into the valence band (between -11.3 eV and -13.3 eV, not shown here) but a small contribution is also present at the top valence band.

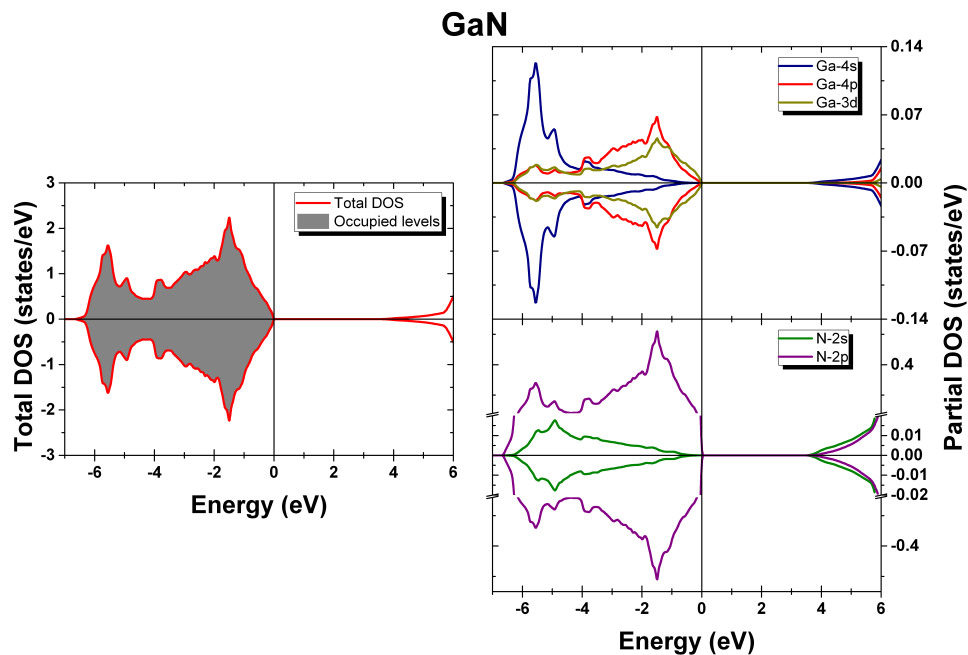


Figure 6.4 – Total and partial density of states (DOS) for spin-up and -down from the GaN simple cell. The top valence band is set at 0 eV.

A band gap of 3.46 eV was obtained, which is in very good agreement with the experimental value of 3.503(5) eV^[11], having an accuracy comparable to simulations using the OEPx(cLDA)+ G_0W_0 method (3.24 eV)^[135] and a much better estimation than previous simulations using the WC-GGA+U functional (2.40 eV)^[25]. It is a direct band gap at the Γ point, as expected for the wurtzite structure of GaN (Fig. 6.5). Since the bottom of the conduction band is well approximated by a parabolic dispersion relation (albeit a slight anisotropy due to the reduced lattice symmetry^[13]), an electron effective mass of $0.24 m_e$ was found by parabolic fitting the conduction band minimum (CBM), in good accordance with the experimental electron effective mass of $0.20 m_e$ ^[13].

Since the EFG is very sensitive to the structural parameters (specially in the case of impurity atoms in supercells), a volume optimization was performed to test the reported lattice parameters before calculating the supercells with the Ta atom. This was done by calculating the total energy of the system for a series of lattice parameters a and c

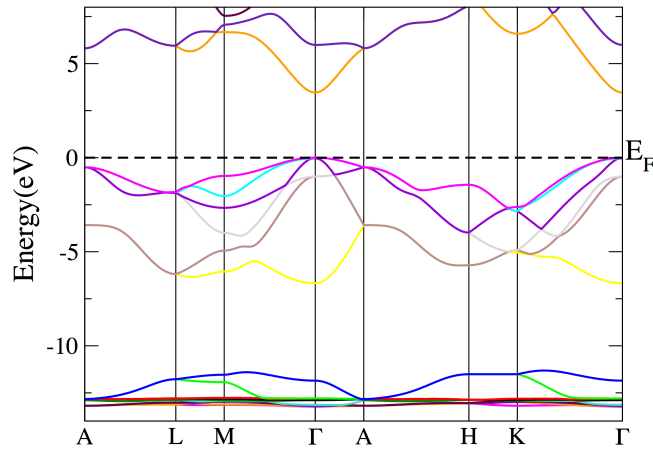


Figure 6.5 – Band structure of GaN in the wurtzite structure. The Fermi energy is set to 0 eV. The k-point labels are named as in Ref.^[112] for the hexagonal lattice and following the same path as in Ref.^[8].

(b is always equal to a in the wurtzite structure) around the reported values and then the results were fitted to a 2-dimensional parabolic curve in order to find the pair of values corresponding to the minimum energy. A first optimization was done considering a variation of -6% , -4% , -2% , 0% , 2% and 4% for each lattice parameter, resulting in 36 pairs of parameters. The optimal pair of parameters was used as the starting point for another optimization but this time considering a variation of -2% , -1% , 0% and 1% for each lattice parameter (16 pairs of parameters). Afterwards, one final optimization was performed using the latter conditions to ensure that the final parameters were in fact the ones corresponding to the lowest energy, which are $a = b = 3.2187 \text{ \AA}$ and $c = 5.2415 \text{ \AA}$. The results from all pairs of parameters considered in this optimization can be seen in Figure 6.6, where the blue sphere corresponds to the final optimized parameters.

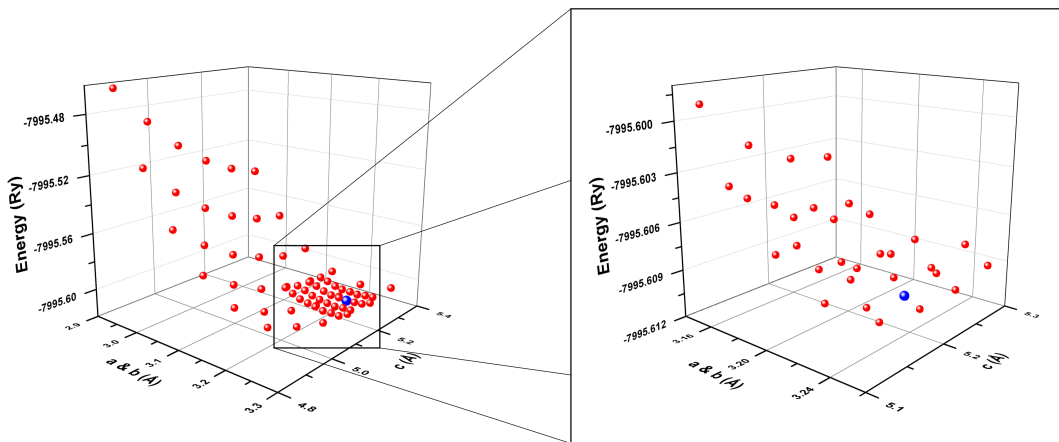


Figure 6.6 – Total energy of the system for several sets of lattice parameters. The blue dot corresponds to the lattice parameters with minimum total energy ($a = b = 3.2187 \text{ \AA}$ and $c = 5.2415 \text{ \AA}$).

The density of states and band structure obtained for the optimized lattice parameters are similar to the previous results (Figures 6.4 and 6.5) but the top valence band is 0.44 eV narrower and the band gap is 0.4 eV smaller.

However, the lattice parameters changed quite a bit, which could lead to considerable changes in the EFG at the Ta site in a supercell. Therefore, both sets of lattice parameters were considered to study the environment around the Ta impurity in GaN.

In order to simulate an isolated Ta impurity, a $3 \times 3 \times 2$ supercell of GaN was constructed. Since Ta usually has a cation-like oxidation state as Ga does but their usual oxidation states are different (+3 for Ga and +5 for Ta), i.e., Ta has 2 extra valence electrons, the following different positions and charge states were considered for the Ta in the supercell:

1. Ta at the Ga site with the following charge states:

- (a) Ta_{Ga}^0 : neutral,
- (b) $\text{Ta}_{\text{Ga}}^{2+}$: two electrons removed from the system,
- (c) $\text{Ta}_{\text{Ga}}^{1+}$: one electron removed from the system.

2. Ta at the interstitial position between the tetrahedra formed by a centered Ga atom with N atoms in the vertices, with the following charge states:

- (a) Ta_i^0 : neutral,
- (b) Ta_i^{5+} : five electrons removed from the system,
- (c) Ta_i^{4+} : four electrons removed from the system.

All charge states were compensated by an additional homogeneous positive background when needed.

Table 6.3 summarizes the EFGs at the Ta probe calculated for each of the positions and charge states, together with the experimental EFGs observed in the PAC experiments.

It can be seen that only the EFGs corresponding to the Ta atom at the Ga site are comparable to the experimental EFGs that were obtained from the PAC experiments (the remaining are much higher) but there is no exact match. Therefore, we tested other sets of parameters for the supercell considering a variation of -2% , -1% , 0% and 1% around the original lattice parameters. In Figure 6.7, the variation of the EFG for each charge state can be seen, where the most pronounced variation is the decrease of the EFGs for increasing c . More importantly, it can be seen that the EFG for the neutral state of Ta is always higher than any of the experimental EFGs, whilst the other two charge states have several crossovers with the experimental values. In fact, the EFGs from the charge states of one set of parameters match very well the experimental EFGs (see arrow in Figure 6.7). This enables us to conclude that Ta is indeed at the Ga site

Table 6.3 – Calculated z-component of the EFG tensor in the principal components axis (in units of $V/\text{\AA}^2$) for each position and charge state of the Ta probe using the reported^[8], optimized and best lattice parameters, as well as the experimental values obtained in the $e^- - \gamma$ PAC measurements (considering the electric quadrupole moment $Q = 2.35(6) \text{ b}^{[39,133]}$). The asymmetry parameter is zero for all cases.

		$V_{zz} (V/\text{\AA}^2)$		
		Reported lattice ^[8]	Optimized lattice	Best lattice
Simulated	Ta_{Ga}^0	113.3	65.4	114.2
	$\text{Ta}_{\text{Ga}}^{1+}$	63.3	45.4	73.0
	$\text{Ta}_{\text{Ga}}^{2+}$	47.2	37.1	62.0
	Ta_i^0	134.2	160.1	-
	Ta_i^{4+}	155.6	240.2	-
	Ta_i^{5+}	226.3	257.6	-
Exp.	State 2	72(2)		
	State 3	61(2)		

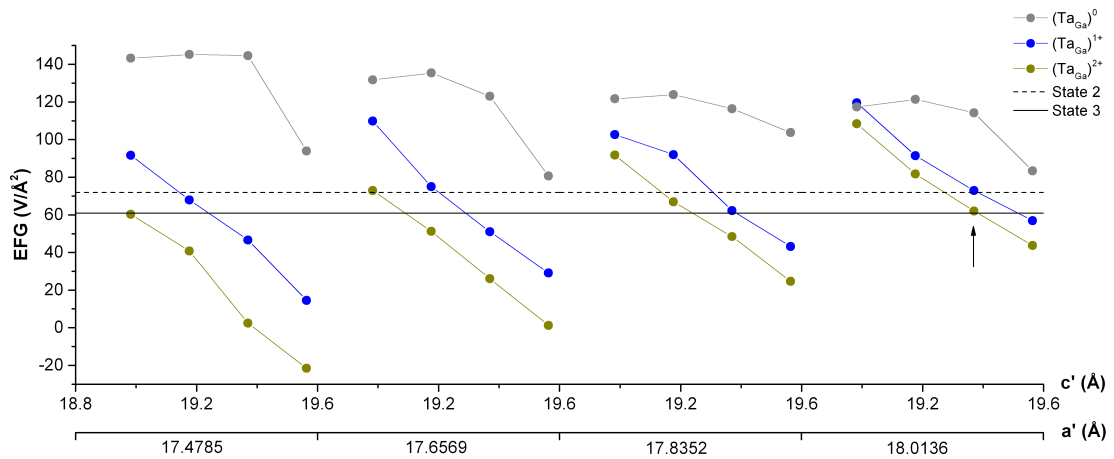


Figure 6.7 – Calculated EFG at the Ta_{Ga}^0 , $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$ sites as a function of the supercell's lattice parameters a' and c' . EFGs corresponding to State 2 and State 3 are from the $e^- - \gamma$ PAC experiments. The arrow shows the best fit between experimental and calculated EFGs.

with State 2 corresponding to Ta in the charge state $\text{Ta}_{\text{Ga}}^{1+}$ and State 3 corresponding to Ta in the charge state $\text{Ta}_{\text{Ga}}^{2+}$.

The density of states for all charge states of Ta at the Ga site was calculated using the lattice parameters whose EFGs best match the experimental EFGs (see Figure 6.8). Nonetheless, using the original parameters for the DOS calculation shows almost indistinguishable variations. It can be seen in the total DOS that replacing a Ga atom by a Ta^0 probe leaves the basic electronic structure of GaN unaltered but a partially filled impurity band appears in the bottom of the conduction band. By integrating the unfilled region between the beginning of this peak and the highest occupied state, a value of 1.9 electrons is obtained, revealing a double-donor character for Ta in this material.

The atom-resolved partial DOS projected at the Ta and neighboring N atoms (Fig. 6.8) shows that the impurity band is mainly composed of Ta-5d orbitals, with a very small contribution from N-2p orbitals. The Ta-4f orbitals are too deep in energy (≈ -20 eV) and therefore do not have a significant role in this case. A similar behavior is observed for the charge states $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$, but the integration of the impurity band in the former case gives 1.0 electron and it is completely empty in the latter case.

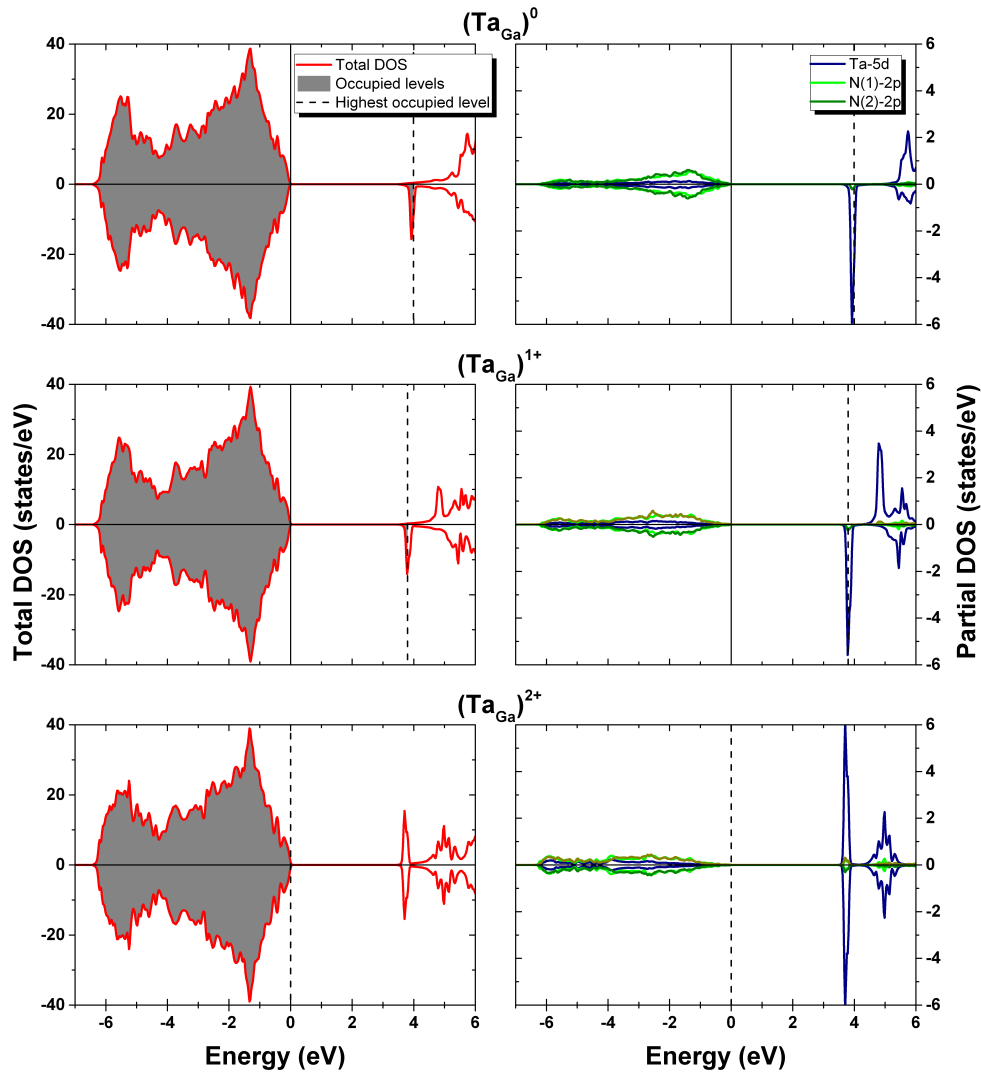


Figure 6.8 – Total and partial density of states (DOS) for spin-up and -down from the GaN supercells with Ta_{Ga}^0 , $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$. The top valence band of pure GaN is set at 0 eV (full line) and the energy of the highest occupied level is represented by a dotted line. For $\text{Ta}_{\text{Ga}}^{2+}$, both lines are coincident.

6.4 Temperature dependence of the transition rates in

$e^- - \gamma$ PAC

After identifying $\text{Ta}_{\text{Ga}}^{1+}$ as the intermediate state (State 2) and $\text{Ta}_{\text{Ga}}^{2+}$ as the final state (State 3) in the $e^- - \gamma$ PAC experiments ($\text{Ta}_{\text{Ga}}^{2+}$ is also the only stable state present in the $\gamma - \gamma$ PAC experiments), the temperature dependence of the transition rates must be understood.

Since the most pronounced observed phenomena is the electronic recovery from the highly ionized initial state to any of the stable/metastable states, we can look at this process as equivalent to the "decay" of State 1 and therefore analyze the sum of all transition rates from this state to all of the other states: $\Gamma_1 = \omega_{1 \rightarrow 2} + \omega_{1 \rightarrow 3}$, where $\omega_{i \rightarrow j}$ is the transition rate from state i to state j . In fact, the inverse of this sum ($\tau_1 = 1/\Gamma_1$) can be interpreted as the mean life time of State 1 [64].

In the reasonable attempt to try an Arrhenius temperature dependence for $\Gamma_1(T)$ (expected for a thermally activated process), it can be seen in Figure 6.9 that two different regimes are present in both samples, one for temperatures below 70 K and another for temperatures above. In the higher temperatures regime, a linear behavior is observed with associated activation energies of 15(2) meV and 12(1) meV for the GaN:Si and GaN:Zn samples, respectively.

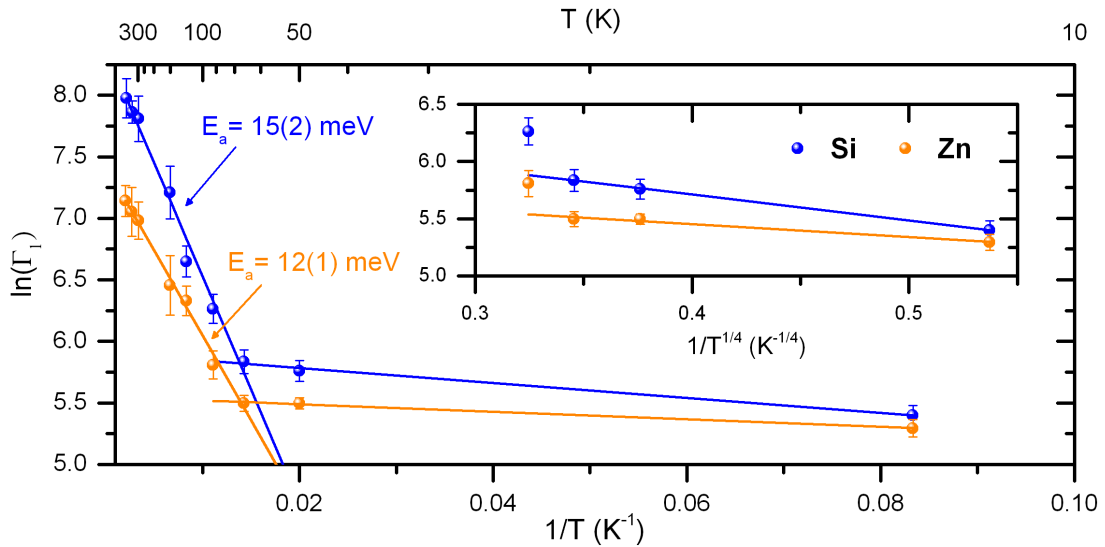


Figure 6.9 – Arrhenius plot of $\Gamma_1(T)$ in logarithmic scale and the corresponding fit for the two different temperature regimes. The error bars were calculated considering $\Delta \ln(x) = \Delta x/x$. In the inset, the transition rates between 12 K and 70 K are plotted as a function of $T^{-1/4}$, characteristic for Variable Range Hopping.

Götz *et al.* [28] performed variable temperature Hall effect measurements (from 80 K to 500 K) and low-temperature (2 K) photoluminescence spectroscopy (PL) in n-type GaN films which were either unintentionally doped or Si doped. They found that the n-type conductivity for both types of samples was dominated by a donor with an activation

energy between 12 meV and 17 meV. This is in very good agreement with our activation energies. They attributed this donor to Si atoms substituting for Ga in the GaN lattice (Si_{Ga}) and justified the range of activation energies to different levels of donor concentrations and acceptor compensation in the samples. Their PL measurements yielded the position of the optical Si donor level in the band gap at 22(4) meV below the conduction band. Another deeper donor level with an activation energy around 34 meV was also present and was assigned to oxygen donors substituting for nitrogen (O_{N}).

In earlier publications, the unintentional n-type conductivity that has often been observed in as-grown GaN has commonly been attributed to nitrogen vacancies (V_{N}) but first-principle calculations performed by Van De Walle *et al.*^[136] have shown that the high formation energy of nitrogen vacancies under n-type conditions makes it very unlikely that they would form spontaneously during growth of not-intentionally doped GaN, and hence they cannot be responsible for n-type conductivity. Their calculations together with experimental evidence that unintentionally doped n-type GaN samples contained concentrations of extrinsic donors high enough to explain the observed electron concentrations are enough to confirm that the unintentional n-type conductivity is due to unintentional incorporation of donor impurities (particularly oxygen), reinforcing the conclusions made by Götz and colleagues. Nonetheless, it must be noted that purposely created nitrogen vacancies (for instance during irradiation or ion implantation) will increase the electron concentration as well, which is probably the case in this work. Furthermore, contrary to n-type conditions, nitrogen vacancies have a low formation energy in p-type GaN, making them a likely compensating center in the case of acceptor doping^[136].

Regarding Zn-doped GaN, it has already been shown in several works that Zn substitutes for Ga (Zn_{Ga}) and introduces an acceptor level around 350 meV above the top of the valence band maximum^[128–130]. It is established that Zn_{Ga} is responsible for the blue luminescence peaking at 2.9 eV that is often observed in PL spectroscopy, not only on Zn-doped GaN samples but also in undoped and Si-doped^[129,130]. This blue band is attributed to transitions from the conduction band (or shallow donors at very low temperatures) to the Zn_{Ga} acceptor. Zn-doped GaN also shows the presence of unintentionally introduced O_{N} shallow donors with ionization energies in the range of 20 meV to 30 meV^[137] (similar to the n-type doped samples) but by adding a sufficient concentration of Zn, it is possible to closely compensate the donors and thus render the material insulating^[128].

In Figure 6.10 it is possible to see a band diagram including the impurity bands from the simulated DOS of $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$ and the bands from the previously mentioned defects in GaN.

We can now have a glimpse of what is being observed in the $e^- - \gamma$ PAC measurements, focusing primarily on the GaN:Si sample. The electron that is lost by the Ta probe during the internal conversion decay provokes a cascade of ejected Auger electrons that leaves the atom in a highly electron deficient/unstable state (it can be estimated that af-

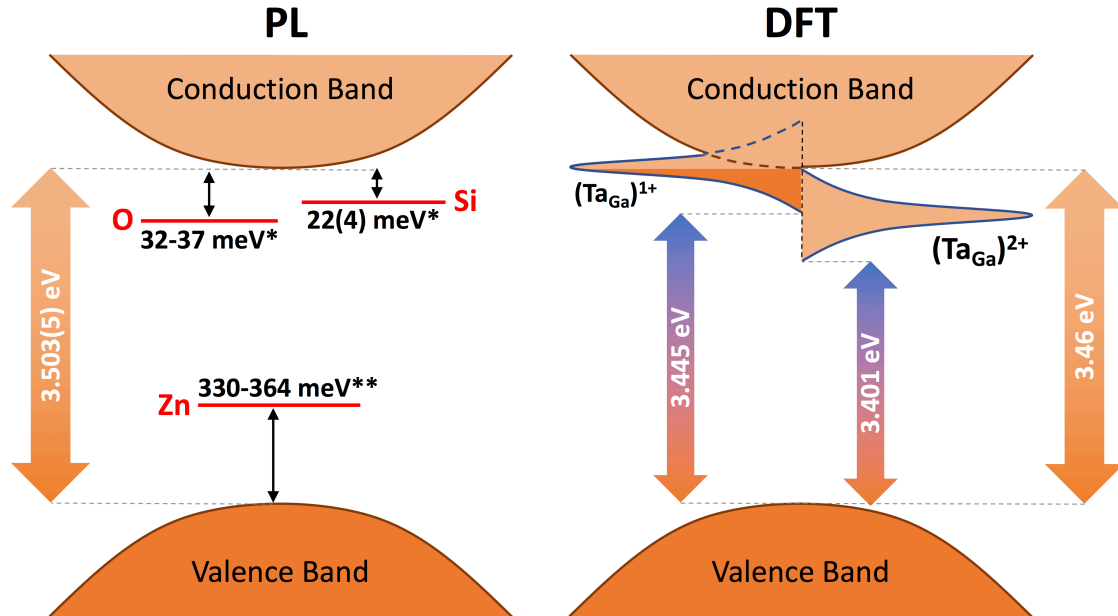


Figure 6.10 – GaN band diagram inside the band gap including the impurity bands from the simulated DOS of $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$ and the reported bands associated to Si, Zn, and O dopants/defects. For the $\text{Ta}_{\text{Ga}}^{1+}$ state, the band is partially filled. * from Ref. 28, ** from Refs. 128–130.

ter the emission of a L-shell electron, Ta loses on average around 9 electrons in the entire process^[104]). This disturbance takes place in the picoseconds scale, therefore when the PAC measurement starts, the holes left by the Auger electrons are usually already located in the valence band. However, this is a very unpredictable process due to the different Auger emissions and ionizations of different Ta probes, as well as the availability of electrons in their vicinity, therefore initially some of the probes are not fully recovered electronically (i.e. there are still inner-shell transitions and Auger-processes in progress) and thus the initial state (State 1) is a very chaotic state characterized by a very broad distribution. After fully recovered, all probes are in the final stable state, $\text{Ta}_{\text{Ga}}^{2+}$, with the Ta impurity band completely unfilled. The electrons needed for the electronic recovery come from the Si_{Ga} donors (and most probably from O_{N} and V_{N} as well), hence the obtained activation energy for this thermally activated process at higher temperatures is in great accordance with the activation energy previously associated to Si_{Ga} shallow donors from Hall effect measurements. For the measurements between 120 K and 294 K, the intermediate state corresponding to $\text{Ta}_{\text{Ga}}^{1+}$ is also visible before the full transition to $\text{Ta}_{\text{Ga}}^{2+}$. We suspect that this is due to the impurity band of $\text{Ta}_{\text{Ga}}^{1+}$ being slightly lower in energy than the Si_{Ga} impurity band (see Figures 6.8 and 6.10), therefore some of the donor electrons that are not yet thermally excited to the conduction band will tunnel to the Ta probes and hence both Ta charge states are visible. The extra electron in $\text{Ta}_{\text{Ga}}^{1+}$ will ultimately go to the conduction band and so only the $\text{Ta}_{\text{Ga}}^{2+}$ is seen as the final state. The higher the temperature, the faster the electronic recovery is and the faster all donor electrons are excited to the conduction band, therefore at higher temperatures

only the $\text{Ta}_{\text{Ga}}^{2+}$ state is visible. In the low temperature regime, not only the transition rates are much lower but also only the $\text{Ta}_{\text{Ga}}^{2+}$ state is visible. This is due to the fact of holes in the valence band being easily recovered by donor electrons even at low temperatures (hence the $\text{Ta}_{\text{Ga}}^{2+}$ state is easily achieved) but the energy is probably not enough for an extra electron to tunnel from a Si_{Ga} donor to a Ta probe to produce the $\text{Ta}_{\text{Ga}}^{1+}$ state. Also, the charge mobility in this regime is possibly not thermally activated but instead better described by a Variable Range Hopping (VRH) mechanism. This hypothesis is tested on the inset of Figure 6.9 and the characteristic $T^{-1/4}$ dependence of VRH for the transition rate is observed. With the reported experimental errors and few experimental data points, the exact model cannot be fully confirmed, but since the transition rates in this regime are much above the expected value from the linear curve related to the thermal activation process observed at higher temperatures, we expect that defects are predominantly contributing for the transition rates, which is typical of a Variable Range Hopping process (see Fig. 6.9).

Going from the GaN:Si sample to the GaN:Zn sample, the presence of unintended donor defects (including Si-donors) besides the intentionally introduced Zn dopants is expected, as previously mentioned, and since the results for both samples are very similar, the majority of the physical processes involved are expected to be the same. The activation energy obtained in the higher temperatures regime is very close to the GaN:Si sample but the biggest difference is the downshift to lower amplitudes in the Arrhenius plot. This can be understood by the fact that the Zn_{Ga} deep acceptor band compensates some of the electrons provided by the shallow donors. Therefore, in spite of the available electrons for the electronic recovery having the same origin as in the GaN:Si sample (therefore similar activation energy), the number of available electrons is much lower, hence the downshift in the Arrhenius plot. In fact, for GaN:Si at 294 K the $\text{Ta}_{\text{Ga}}^{1+}$ state is inclusively more visible than the $\text{Ta}_{\text{Ga}}^{2+}$ state due to the high number of Si_{Ga} donors with non-ionized electrons (thus available to tunnel to the Ta probes), but that same state is not so visible in GaN:Zn at the same temperature due to the high number of donors compensated by the Zn_{Ga} acceptors and lower donor concentration.

One final note must be made regarding the fact of the transition rate from the intermediate state ($\text{Ta}_{\text{Ga}}^{1+}$) to the final state ($\text{Ta}_{\text{Ga}}^{2+}$) (transition rate $2 \rightarrow 3$ in Table 6.2) to be constant as a function of temperature. Since the impurity band of $\text{Ta}_{\text{Ga}}^{1+}$ is in the conduction band minimum (Figures 6.8 and 6.10), the activation energy corresponding to this transition is very low when compared to the other transitions (in fact it should be very close (or equal) to 0 eV). This means that the variation of this transition rate with temperature is much smaller than the variation of the other transition rates, so the fitting can be done considering this transition to be constant in temperature to within the experimental error. The inverse of the transition rate can be used to estimate the mean life time of the $\text{Ta}_{\text{Ga}}^{1+}$ state^[64], which is equal to $1/(38(3) \text{ MHz}) \approx 26(2) \text{ ns}$ for GaN:Si and $1/(42(5) \text{ MHz}) \approx 24(3) \text{ ns}$ for GaN:Zn.

This entire process observed in $e^- - \gamma$ PAC does not occur in $\gamma - \gamma$ PAC because

there is no loss of inner orbit electrons during the decay in the latter case. After the decay of ^{181}Hf to ^{181}Ta there is a first state of $17.8\ \mu\text{s}$ (see Figure 6.1) long enough for the probes to fully recombine the electronic states and relax to their stable position with the electronic state $\text{Ta}_{\text{Ga}}^{2+}$ before the PAC cascade occurs. This means that during the $\gamma-\gamma$ PAC measurement only the most stable state $\text{Ta}_{\text{Ga}}^{2+}$ is observed (having no relevant variations with temperature), hence a single EFG is present. We suspect that the $\text{Ta}_{\text{Ga}}^{1+}$ state visible at some temperatures in $e^- - \gamma$ PAC is favored in that situation due to the avalanche of electrons that are lost in the internal conversion decay, thus turning the probes into very strong Coulomb attractors that increase the probability of one electron to go from a donor to a Ta probe even after all the needed electrons are recovered to achieve the $\text{Ta}_{\text{Ga}}^{2+}$ state, which is not the case in $\gamma-\gamma$ PAC. This premise is reinforced by the higher expression of the $\text{Ta}_{\text{Ga}}^{1+}$ state in the Si-doped sample when compared to the Zn-doped sample, where the former has more electron donors available than the latter.

6.5 Conclusions

The combination of the $e^- - \gamma$ and $\gamma-\gamma$ PAC techniques after implantation and annealing of $^{181}\text{Hf}/^{181}\text{Ta}$ probes into Si- and Zn-doped GaN samples allowed performing a detailed study of the Ta impurity dopant at a Ga site and the characterization of different localized electronic states, as a function of temperature and sample doping.

The $\gamma-\gamma$ PAC measurements showed a single stable state that was attributed to the probe state $\text{Ta}_{\text{Ga}}^{2+}$ with no relevant changes with temperature. On the other hand, the $e^- - \gamma$ PAC measurements showed not only the presence of the stable state $\text{Ta}_{\text{Ga}}^{2+}$ but also the presence of the metastable state $\text{Ta}_{\text{Ga}}^{1+}$ at some temperatures, including strong temperature-dependent variations. Such detailed observations are only possible due to the creation of a localized highly ionized Ta state after the loss of electrons triggered by the internal conversion decay and the underlying processes for their recovery.

A comparison of the density of states (DOS) for the simple cell of GaN to the super-cells with the different charged states of Ta (Ta_{Ga}^0 , $\text{Ta}_{\text{Ga}}^{1+}$ and $\text{Ta}_{\text{Ga}}^{2+}$) was also done. It was possible to see that Ta induces an impurity band adjacent to the conduction band that is semi-filled for Ta_{Ga}^0 and $\text{Ta}_{\text{Ga}}^{1+}$ but it is completely empty for $\text{Ta}_{\text{Ga}}^{2+}$. In fact, by integrating the filled part of the impurity band gives 1.9 electrons for Ta_{Ga}^0 and 1.0 electrons for $\text{Ta}_{\text{Ga}}^{1+}$. This is in accordance with the oxidation state of Ga at that site (3+) and to the preferred oxidation state of Ta (5+), therefore being expected that Ta at that position to have three valence electrons being used for the chemical bonding with the neighboring N atoms and to give away two valence electrons to the conduction band, which was indeed observed in this work.

Regarding the temperature dependence of the transition rates in the $e^- - \gamma$ PAC measurements, two different regimes were observed. At higher temperatures, a thermally activated process was observed for the electronic recombination with activation ener-

gies of 15(2) meV and 12(1) meV for the GaN:Si and GaN:Zn samples, respectively, which were associated to Si_{Ga} shallow donors in both samples (and probably having some contributions from unintended O_{N} and V_{N} defects). However, the Arrhenius plot of GaN:Zn is downshifted in comparison to GaN:Si due to donors compensated by the Zn acceptors, hence reducing the number of available electrons during the electronic recovery. At lower temperatures, it is suggested that the recombination process occurs via Variable Range Hopping instead of via a thermally activated process. Nonetheless, the experimental errors do not allow for a completely verified solution in this regime.

Given the amount and the quality of the information that was possible to obtain about the studied samples and, more importantly, how it was possible to distinguish the doping characteristics from one sample to another, we believe that this work demonstrates the potential use of $e^- - \gamma$ PAC in combination with $\gamma - \gamma$ PAC for the study of electronic properties of materials and/or samples where, for instance, Hall effect measurements are difficult/impossible to perform due to small dimensions or low-quality ohmic contacts.

CHAPTER 7

General Discussion and Future Perspectives

The Perturbed Angular Correlation technique, including the joint use of $\gamma - \gamma$ and $e^- - \gamma$ PAC, was used to study the lattice location of implanted dopants in several technologically relevant semiconductors and also to measure the mobility of charges in these materials.

Annealing tests in thin films of ZnO and $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ as well as in a powder pellet and nanowires of Ga_2O_3 after implantation of $^{111m}\text{Cd}/^{111}\text{Cd}$ probes were successfully done and the identification of the probes lattice location in all samples was possible by comparing the results to DFT simulations. In ZnO, it was observed the existence of two Cd environments, one in undisturbed substitutional Zn sites and another which was attributed to the trapping of a defect, possibly an oxygen vacancy, in the vicinity of the probe. $\text{Cd}_{0.16}\text{Zn}_{0.84}\text{O}$ showed higher electric field gradients as well as non-zero asymmetry parameter and large frequency distributions, attributed to the clustering of defects close to the probe, even after annealing. Both Ga_2O_3 samples gave similar results, showing also the existence of two Cd environments, the first one attributed to substitutional octahedral Ga sites and the second one to the existence of residual implantation defects that could not be annealed. Nonetheless, the most important result was the fact of demonstrating that efficient doping of nanowires through ion implantation is conceivable.

Improved results were obtained in Ga_2O_3 powder pellets by increasing the annealing temperature after implantation of $^{111m}\text{Cd}/^{111}\text{Cd}$ but the best results were obtained for single crystalline thin films, where a unique defect-less site was observed for the Cd probes. Also, by diffusion of $^{111}\text{In}/^{111}\text{Cd}$ probes into Ga_2O_3 , it was possible to observe the electronic recovery as a function of measuring temperature due to the electron-capture decay of ^{111}In . In this case, two different charged states of Cd were observed, Cd^0 and Cd^{1-} (the second one having an extra electron), being Cd^{1-} the more stable state. This was confirmed by DFT simulations, including the calculation of the density of states, band structure and electron density for both cases, in comparison to pure Ga_2O_3 . In this way, it was possible to confirm that Cd is indeed a very good candidate for p-type doping in Ga_2O_3 , a key component for the application of this material in technological devices.

The use of $\gamma - \gamma$ PAC and $e^- - \gamma$ PAC in Si-doped (n-type) and Zn-doped (p-type) GaN thin films after implantation of $^{181}\text{Hf}/^{181}\text{Ta}$ enabled the identification of the lattice location of the probes in the samples and also the observation of different charged states of Ta in the material. The temperature dependent measurements revealed a thermally activated process at higher temperatures and suggested a recombination process via Variable Range Hopping at lower temperatures. Moreover, they allowed the observation of the difference in terms of number of available electrons during the electronic recovery between the two different dopings. This experimental method revealed to be a good alternative to, e.g., Hall effect measurements in samples where ohmic contacts are very difficult to form.

Finally, none of this would be possible without the development of PACme, the program that allowed the analysis of the experimental data containing dynamic hyperfine fields, such as in the case of the electron-capture decay of ^{111}In as well as in the $e^- - \gamma$ PAC experiments using $^{181}\text{Hf}/^{181}\text{Ta}$. The breakthrough implementation of static Lorentzian frequency distributions was vital for the correct analysis of the data. More importantly, the program is completely general in terms of setup parameters such as the crystal type, nuclear spin and the number of possible fractions and states being considered in a single experiment, providing a very important tool for future PAC experiments in a wide range of subjects.

We are confident that the development of PACme and the experimental approach of using $^{111m}\text{Cd}/^{111}\text{Cd}$ versus $^{111}\text{In}/^{111}\text{Cd}$ and $\gamma - \gamma$ versus $e^- - \gamma$ to provide information about the lattice location of the probes together with information about the mobility of charges in a material can be a starting step for future proposals and ideas for the use of PAC.

List of Publications and Awards

Several contributions were made to the scientific community related to the work developed in the present thesis, including: 1 invited communication, 5 oral communications, 8 poster presentations, 12 (overall) publications and 1 award, including:

Publications

- M. B. Barbosa, J. G. Correia and J. P. Araújo, "PACme: A generalized program for the simulation, analysis and visualization of Perturbed Angular Correlations", *In Preparation*
- M. B. Barbosa, J. G. Correia, K. Lorenz and J. P. Araújo, "Characterization of electron mobility in GaN without electrical contacts", *In Preparation*
- M. B. Barbosa, J. G. Correia, K. Lorenz, J. Schell, R. Teixeira, A. S. Fenta, E. Nogales, B. Méndez and J. P. Araújo, "Lattice location and charge states of Cd acceptors in Ga_2O_3 ", *In Preparation*
- M. B. Barbosa, J. N. Gonçalves, A. Redondo-Cubero, S. M. C. Miranda, R. Simon, P. Kessler, M. Brandt, F. Henneberger, E. Nogales, M. Méndez, K. Johnston, E. Alves, R. Vianden, J. P. Araújo, K. Lorenz and J. G. Correia, "Nanostructures and thin films of transparent conductive oxides studied by perturbed angular correlations", *Phys. Status Solidi B* 250, No. 4, 801-808 (2013)
- M. B. Barbosa, J. N. Gonçalves, A. Redondo-Cubero, S. M. C. Miranda, R. Simon, P. Kessler, M. Brandt, F. Henneberger, E. Nogales, M. Méndez, K. Johnston, E. Alves, R. Vianden, J. P. Araújo, K. Lorenz and J. G. Correia, "Inside Back Cover: Nanostructures and thin films of transparent conductive oxides studied by perturbed angular correlations (*Phys. Status Solidi B* 4/2013)", *Phys. Status Solidi B* 250, No. 4 (2013)

Several collaborations also took place, resulting in the following publications:

- Rui M. Costa, João H. Belo, Marcelo B. Barbosa, Pedro A. Algarabel, César Magén, Luis Morellón, Manuel R. Ibarra, João N. Gonçalves, Nuno M. Fortunato, João S. Amaral, João P. Araújo, André M. Pereira, On the nature of the (de)coupling of the magnetostructural transition in Er_5Si_4 , *Phys. Status Solidi B*, 170014, (2017)

- J.H. Belo, M.B. Barbosa, A.L. Pires, R.M. Costa, J.G.V. Teixeira, J. Silva, P.A. Algarabel, C. Magen, L. Morellon, J.S. Amaral, U. Zeitler, G. Veerendra, A.M. dos Santos, Y. Ren, M.R. Ibarra, J.P. Araújo and A.M. Pereira, Insights on the origin of the Tb₅Ge₄ magnetocaloric effect, *Physica B* **513**, 72-76 (2017).
- J. Schell, D. C. Lupascu, J. G. Correia, A. W. Carbonari, M. Deicher, M. B. Barbosa, R. D. Mansano, K. Johnston, I. S. Ribeiro Jr., "In and Cd as defect traps in titanium dioxide", *Hyperfine Interactions*, 238:2 (2017)
- H. Haas, M. B. Barbosa, J. G. Correia, "The quadrupole moments of Cd and Zn isotopes - an apology", *Hyperfine Interactions*, 237:115 (2016)
- Satyendra K. Das, Rashmohan Guin, Debasish Banerjee, Karl Johnston, Parnika Das, Tilman Butz, Vitor S. Amaral, Joao G. Correia, Marcelo B. Barbosa, "Perturbed Angular Correlation Study of the Static and Dynamic Aspects of Cadmium and Mercury Atoms Inside and Attached to a C₆₀ Fullerene Cage", *Z. Naturforsch.* 69a, 611-618 (2014)
- K. Lorenz, M. Peres, M. Felizardo, J. G. Correia, L. C. Alves, E. Alves, I. Lopez, E. Nogales, B. Mendez, J. Piqueras, M. B. Barbosa, J. P. Araújo, J. N. Gonçalves, J. Rodrigues, L. Rino, T. Monteiro, E. G. Villora, K. Shimamura, "Doping of Ga₂O₃ bulk crystals and NWs by ion implantation", *Oxide-based Materials and Devices V*, vol. 8987 (2014)
- M. A. Nagl, M. B. Barbosa, U. Vetter, J. G. Correia, H. C. Hofsäss, "A new tool for the search of nuclides with properties suitable for nuclear solid state physics based on the Evaluated Nuclear Structure Data Files", *Nuclear Instruments and Methods in Physics Research A* 726, 17-30 (2013)

Awards

- **"Youngster of The Year 2015"**, "VerdadeiroOlhar.pt" newspaper, January 2016, Portugal
- **"Best Poster Award"**, given by CAEN – Tools for Discovery Workshop and Users Meeting 2014, 15th-17th December 2014, CERN, Geneva, Switzerland.
- **Individual Ph.D. Grant** from the Portuguese Foundation for Science and Technology (FCT) - Grant number SFRH/BD/97591/2013

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APPENDIX A

PACme – Software Documentation

A.1 Software Installation

The source code of the program is distributed in the archive file `PACme.tar`. To extract the files in a UNIX-like system (Linux or MacOS), use the command `tar -xvf PACme.tar`.

To install the software, first and foremost, a C++ compiler (such as `g++`) is required. Then, the used external libraries must be installed.

In a Linux system, `g++`, `GSL` and `Gnuplot` can be installed by using repositories such as `apt-get` (or `yum`):

```
$ sudo apt-get install g++
$ sudo apt-get install libgsl0-dev
$ sudo apt-get install gnuplot
$ sudo apt-get install gnuplot-x11
```

`CLAPACK` (<http://www.netlib.org/clapack/>) and `Minuit2` (<http://seal.web.cern.ch/seal/snapshot/work-packages/mathlibs/minuit/>) have to be compiled from source. The most recent versions available at the time of publishing are also distributed in `PACme.tar`. To install `CLAPACK`, the following commands must be used:

```
$ tar -xvf clapack.tgz
$ cd CLAPACK-***
$ cp make.inc.example make.inc
$ make f2clib
$ make blaslib
$ make
$ sudo cp blas_LINUX.a /usr/local/lib/libblas.a
$ sudo cp lapack_LINUX.a /usr/local/lib/liblapack.a
$ sudo cp tmglib_LINUX.a /usr/local/lib/libtmglib.a
$ sudo cp F2CLIBS/libf2c.a /usr/local/lib
$ sudo cp INCLUDE/clapack.h INCLUDE/f2c.h INCLUDE/blaswrap.h /usr/local/include
$ sudo chown -R $(whoami) /usr/local
$ sudo /sbin/ldconfig
```

If a path other than `/usr/local/` is desired for the installation, that path must be substituted in the previous commands.

To install Minuit2, the following commands must be used:

```
$ tar -xvf Minuit2-5.34.14.tar.gz/  
$ cd Minuit2-5.34.14/  
$ ./configure  
$ make  
$ sudo make install  
$ sudo /sbin/ldconfig
```

As in the previous case, the installation path by default is `/usr/local/`. If another destination is desired, the command `./configure --prefix=$<folder path>` has to be used instead, where `<folder path>` is the desired path for installation.

In a MacOS system, the installation of Xcode is recommended since it provides a C++ compiler as well as the Accelerate framework, the latter containing the CLAPACK library functions. For GSL and Gnuplot, the Homebrew package manager (<https://brew.sh>) is a suitable option. After installing Homebrew, type the following commands:

```
$ brew install gsl  
$ brew install gnuplot --with-x11
```

By default, the packages installed with `brew` are also located in `/usr/local/`. Gnuplot needs a X11 Window system, so XQuartz is recommended (<https://www.xquartz.org>). Finally, Minuit2 can be installed using the same commands as in a LINUX system, except the last command (`$ sudo /sbin/ldconfig`) which is not needed. However, there is a caveat. Minuit2 uses OpenMP to parallelize its execution but the C++ compiler from Xcode does not support it, so this option will be disabled. Nonetheless, another compiler can be installed which supports OpenMP (e.g., `brew install gcc --without-multilib --without-fortran`) and if this compiler is used to install Minuit2 and to compile PACme, the OpenMP parallelization will be enabled.

To compile PACme, three Makefiles are provided: `Makefile.linux`, `Makefile.macOS` and `Makefile.macOS_openMP`. The user must copy the appropriate file to a new file named `Makefile`, without the extension. If the external libraries being used were not installed in the default location (`/usr/local/`), the correct paths must be added in the `Makefile`. Then, just type the command `make` to compile the program. To be able to call PACme from any folder in the system, move it to the folder `/usr/local/bin` by typing the command `$ sudo mv PACme /usr/local/bin`.

A.2 Usage Instructions

To run the program, just type the command `PACme`, followed by any of the available option flags (see Table A.1). There are two kinds of flags: mandatory and optional. To

run the program, one of the mandatory flags has to be used and no two mandatory flags can be used at once. The optional flags are freely used or not by the user. There is no specific order for the flags when calling the the program, including the mandatory and the optional. Only the flags that require any kind of input variable (e.g., `-sim`, `-tol`, etc.) must have the variable written right after the flag. The `-help` flag can be used to display a table with all the available flags.

Table A.1 – Available option flags to run the program.

Mandatory flags	
<code>-sim <file(s)></code>	Simulates the $R(t)$ and the Fourier transform for the given parameters file(s).
<code>-fit <file(s)></code>	Calls the fitting routine for the given parameters file(s).
<code>-createTemplate (or -ct) <file></code>	Creates a new parameters file.
Optional flags	
<code>-tolerance (or -tol) X</code>	Set tolerance = X.
<code>-maxCall (or -mxc) X</code>	Set maximum number of iterations (calls) that the Minuit2 package calculates the χ^2 -function during a fit (this number might not be exactly ...).
<code>-png</code>	Export the plots as png files instead of displaying them.
<code>-printAll (or -pall)</code>	Set print level to maximum level during a fit.
<code>-newFile (or -nf)</code>	Create a new parameters file with "_NEW" appended to the original file name having the final fitting parameters after the fit.
<code>-go</code>	Skip initial plots before fitting.
<code>-help (or -h)</code>	Show the instructions menu.

For example, if the user wants to fit a data set using the parameters file `params1.txt`, export the plots to png files, set the maximum number of iterations to 100 and skip the initial plots before fitting, the following command can be used: `PACme -fit params1.txt -png -maxCall 100 -go`. Another example, if the user wants to fit two parameters files at onceⁱ and create new files with the final sets of parameters after the fit: `PACme -fit params1.txt params2.txt -nf`.

A.2.1 Input Parameters File

To create a new file of parameters, the command `PACme -ct <file>` has to be used (if no file's name is given, the program will ask for one). The user will then be asked for how many different fractions are needed and how many different states each fraction has. Here is an example of a parameters file with two different fractions, the first with two states and the second with only one state:

ⁱThe functionality of fitting several files at once is explained further ahead.

```

data.txt          ! File with data to be fitted #
output.txt        ! File with calculated output #
1                ! Calibration [ns/ch] #
200              ! number of channels #
0                ! ch initial for fit #
200              ! ch final for fit #
0.0              ! Fwhm [] #
2.5              ! Spin #
1.0              ! Q - electric quadrupole moment [barn] #
1.0              ! mu - magnetic moment #

! Fourier Transform options #
0                ! 0/1/2 = amplitude/real/imaginary #
0                ! Mirror (0/1/2 = even/odd/no) #
0                ! Average (0/1 = not_remove/remove) #
4.0              ! Kaiser-Bessel alpha #
1000.0           ! Maximum frequency displayed [Mrad/s] #

! Akk coefficients #
1.0              ! A22 #
0.0              ! A24 #
0.0              ! A42 #
0.0              ! A44 #

! Multip and add cte to R(t) (A*R(t)+B+C*t) #
1.0    0          ! A #
0.0    0          ! B #
0.0    0          ! C #

2                ! Number of Fractions (never change this value) #

*****
      Fraction 1
*****#

1                ! trigger (1/0, "use"/"not use") #
2                ! Number of States (never change this value) #
1                ! Static/Dynamic = 0/1 (if 0, only first state considered) #
1                ! 0/1 single crystal/polycrystal #

```



```

0.8      1      ! f1 #

----- State 1 -----#
0          ! Interaction type (0/1/2 = EQ/Mag/combined) #
100.0     1      ! w0(1) [Mrad/s] #
0.0       0      ! wb(1) [Mrad/s] #
0.0       0      ! eta(1) #

! Angles from Mag referential to EFG #
0.0       0      ! thetaMag(1) #
0.0       0      ! gammaMag(1) #

! Euler-angles of Vzz(1) relative to lattice #
0.0       0      ! alpha(1) #
0.0       0      ! beta(1) #
0.0       0      ! gamma(1) #

1.0       0      ! initial probability of w0(1) #
0.0       0      ! FWHM(1) [] #

----- State 2 -----#
0          ! Interaction type (0/1/2 = EQ/Mag/combined) #
150.0     0      ! w0(2) [Mrad/s] #
0.0       0      ! wb(2) [Mrad/s] #
0.1       0      ! eta(2) #

! Angles from Mag referential to EFG #
0.0       0      ! thetaMag(2) #
0.0       0      ! gammaMag(2) #

! Euler-angles of Vzz(2) relative to lattice #
0.0       0      ! alpha(2) #
0.0       0      ! beta(2) #
0.0       0      ! gamma(2) #

0.0       0      ! initial probability of w0(2) #
0.0       0      ! FWHM(2) [] #

---- Transition Prob. ---#
50.0     0      ! physical fluctuation rate 1->2 [MHz] #
0.0       0      ! physical fluctuation rate 2->1 [MHz] #

```

```

*****
Fraction 2
*****#

1          ! trigger (1/0, "use"/"not use") #
1          ! Number of States (never change this value) #
0          ! Static/Dynamic = 0/1 (if 0, only first state considered) #
1          ! 0/1 single crystal/polycrystal #

0.2      1      ! f2 #

----- State 1 -----#
0          ! Interaction type (0/1/2 = EQ/Mag/combined) #
50.0      2      ! w0(1) [Mrad/s] #
0.0       0      ! wb(1) [Mrad/s] #
0.0       0      ! eta(1) #

! Angles from Mag referential to EFG #
0.0       0      ! thetaMag(1) #
0.0       0      ! gammaMag(1) #

! Euler-angles of Vzz(1) relative to lattice #
0.0       0      ! alpha(1) #
0.0       0      ! beta(1) #
0.0       0      ! gamma(1) #

1.0       0      ! initial probability of w0(1) #
10.0      0      ! FWHM(1) [] #

```

All the phrases ending in # and (usually) starting in ! are comments that cannot be removed.

The description of each parameter line-by-line (ignoring the lines with comments and white spaces) is:

Lines 1-10:

- The name of the file with the experimental data to be fitted. It must have 3 columns separated by a space or a tab, with the first column having the time, the second column having the $R(t)$ and the third column having the experimental error.

- The name of the file for the output data. If `-sim` is used, only two columns (time and $R(t)$) are written. If `-fit` is used, the first three columns will have the experimental data and a fourth column will have the points from the fitting curve.
- Time calibration, which is only used for `-sim`. For `-fit`, the experimental time points are used.
- In a simulation, it is the number of points to be calculated. In a fit, it is the number of points to be plotted.
- Initial point to fit.
- Final point to fit.
- Full width at half maximum for the time resolution (prompt) function of the spectrometer, which is assumed to be gaussian-like: $P(Fwhm, \omega_q) = \exp\left(-\frac{Fwhm^2}{16 \ln 2} \omega_q^2\right)$.
- Nuclear spin of the intermediate level of the cascade.
- Electric quadrupole moment to get the V_{zz} from the quadrupole frequencies ω_0 (not mandatory).
- Magnetic moment to get the magnetic field from the magnetic frequencies ω_b (not mandatory).

Lines 11-15: Parameters to configure the Fourier transform (see Appendix 3.6.2 for more information about the calculation of the Fourier transform):

- 0 = returns the total amplitude of the Fourier transform $\left(\sqrt{\text{real}^2 + \text{imaginary}^2}\right)$, 1 = returns the real component, 2 = returns the imaginary component.
- Set the mirrored copy of data points to even (0), odd (1) or not at all (2).
- Remove (1) or not remove (0) the average of the data points.
- Set the value of α for the Kaiser-Bessel function.
- Set the maximum frequency to be displayed (if the value is bigger than the maximum frequency possible to calculate with the given data points, it will be automatically reduced and a warning is shown).

Lines 16-19: Anisotropy coefficients from eq.3.18, where $A_{22} = A_{k_1=2}(\gamma_1)A_{k_2=2}(\gamma_2)$, $A_{24} = A_{k_1=2}(\gamma_1)A_{k_2=4}(\gamma_2)$, $A_{42} = A_{k_1=4}(\gamma_1)A_{k_2=2}(\gamma_2)$ and $A_{44} = A_{k_1=4}(\gamma_1)A_{k_2=4}(\gamma_2)$. They should be effective values, including solid angle corrections.

From this point further, some parameters have a second value in the same line, which will be explained ahead.

Lines 20-22: The perturbation function $R(t)$ is calculated considering the formula $A \times R(t) + B + C \times t$. Therefore, A is a multiplicative constant, B is an additive constant and C is the slope.

Line 23: Number of fractions (Never change this value manually).

Lines 24-27:

- 0 = do not consider this fraction for the calculation, 1 = consider this fraction.
- Number of states in this fraction. (Never change this value manually).
- 0 = static hyperfine fields (only the first state is used if the fraction has more than one state), 1 = dynamic transitions between all the states.
- Crystal type. 0 = single crystal, 1 = polycrystal.

Line 28: Relative intensity (percentage) to be considered for this fraction according to eq.3.22.

Line 29: 0 = Electric Quadrupole interaction (EQI), 1 = Magnetic interaction (MI), 2 = Combined interaction (EQ + MI).

Lines 30-32:

- Observable quadrupole frequency ω_0 in Mrad/s for EQI or combined interactions.
- Larmor frequency ω_L in Mrad/s for MI or combined interactions.
- Asymmetry parameter η for EQI or combined interactions.

Lines 33-34: θ_m and ϕ_m are the polar angle and azimuthal angle for the magnetic field in relation to the electric field gradient (only needed in combined interactions).

Lines 35-37: α , β , γ are the Euler angles for the orientation of the interaction field (using the convention from ref.^[138]).

Lines 38-39:

- Initial probability of the correspondent state (between 0 and 1).
- Full width at half maximum for the Lorentzian static distribution of the interaction field (not possible for combined interactions).

Lines 40-50: Equal to lines 29-39 but for the second state.

Lines 40-50: Transition rates (in MHz) from state i to state j .

Lines 51-66: Equal to lines 24-39 for the second fraction but with only one state.

Regarding the intensity of fractions and the initial probability of states, the chosen values must respect the fact that both the sum of the intensity of the fractions and the sum of the initial probability of each state in a single fraction are normalized to 1.

The parameters which have a second value in their line are the parameters that can be fitted during the minimization of the χ^2 -function. This second value is the fitting flag and can be set to:

- 0 = constant parameter,
- 1 = fit the parameter,
- 2 = for a single file, it is equivalent to 1, but if several files are being fitted at once, the parameter value is equal to the value from the first file of parameters.

For example, if the user types the command `PACme -fit params1.txt params2.txt params3.txt`, the parameters with flag = 1 will be fitted independently as well as the parameters with flag = 2 in `params1.txt`, but the parameters with flag = 2 in `params2.txt` and `params3.txt` will have their value set to the value in `params1.txt`. This means that if the same parameter has flag = 2 in all three files, it will be fitted equally for all three. To better illustrate this functionality, let's suppose a situation where the user is expecting a temperature dependence of some parameter, e.g. the quadrupole frequency, but the remaining parameters to be temperature independent (at least to within the experimental error). The user can then call all the files of parameters from the several measured temperatures at once and then set all the parameters but the quadrupole frequency to be fitted equally for all files. Instead of the user having to fit one data set at a time and use the resulting parameters in the other data sets until the best values are found, the program can then find the best fit for all data sets at once, saving the user a lot of time.

When setting the name of the data file and output file, a path can be given as well if these files are not meant to be in the same folder as the parameters file. For example, the user can set the name of the data file to `./data/data.txt` and the name of the output file to `./results/output.txt` to read the data file from the folder `data` and export the output file to the folder `results`, with both folders in the same folder as the parameters file.

The file with the experimental data (`data.txt` in the example above) must have three columns of values with time, $R(t)$ and experimental error, respectively.

A.2.2 Output Files

After running the program, two output files are created.

The first one is named as set in the parameters file (`output.txt` in the example above). If `-sim` is used, it will have two columns of N values, the first column with time and the second one with the calculated $R(t)$, for N ="number of channels" set in the parameters file. If `-fit` is used, it will have four columns, the first three equal to the columns in the data file and the fourth column containing the values of the fitted $R(t)$ curve.

The second file will have the same name but with "FFT_" appended to the beginning of the name. With `-sim`, it has two columns: frequency (in Mrad/s) and the Fourier transform (amplitude, real component or imaginary component, depending of the option chosen in the parameters file). With `-fit`, it has three columns: frequency, Fourier transform of the experimental data, Fourier transform of the fitting curve.

If the flag `-nf` is used, a new file with the final set of fitting parameters is created and named with "_NEW" appended to the original file name. If the flag `-png` is used, a png file containing the $R(t)$ function will be named as the parameters file (but with the .png extension) and the file containing the Fourier transform will also have the same name but with "FFT_" appended to the beginning of the name. In both cases, all files are placed in the same folder as the output files with the calculated data.

A.3 Program Structure

PACme was written considering an object-oriented programming approach. All the class variables are encapsulated and every class has an overload constructor, destructor, copy constructor and assignment constructor. Here we have a description of all existing classes and their respective functions.

PState

An object from `PState` represents a single state characterized by an Hamiltonian H , considering the correspondent interactions. Therefore, their single purpose is the construction of the Hamiltonians. The main public functions of `PState` are:

```
void operator()(double w0, double wb, double eta, double thetaMag, double gammaMag,
               double alpha, double beta, double gamma, double Fw);
```

Called to set the new values for the `PState` object and calculate the correspondent Hamiltonian.

- Input
 - `w0`: Observable quadrupole frequency in Mrad/s
 - `wb`: Larmor frequency in Mrad/s
 - `eta`: asymmetry parameter

- `thetaMag`, `gammaMag`: polar and azimuthal angles for magnetic field
- `alpha`, `beta`, `gamma`: Euler angles for the interaction field
- `Fw`: Full width at half maximum for the Lorentzian distribution of the interaction field.

```
std::complex<double> hamiltonian(int row, int column);
```

Returns the value of the Hamiltonian matrix for indices `row` and `column`.

```
std::complex<double> hamiltonianDist(int row, int column);
```

Returns the value of the matrix V_d (to be used in equation 3.27) for indices `row` and `column`.

PFraction

An object from `PFraction` calculates the angular correlation function for a single fraction. It contains a vector of `PState` objects whose Hamiltonians are used to construct the Blume matrix. The Blume matrix is then diagonalized and two vectors are constructed, $A_q(\theta)$ and $(-\lambda_q + i\omega_q)$ in order for the angular correlation functions to be calculated as:

$$W(\mathbf{k}_1, \mathbf{k}_2, t) = W(\theta, t) = \sum_q A_q(\theta) e^{(-\lambda_q + i\omega_q)t} \quad (\text{A.1})$$

$$\begin{aligned} A_q(\theta) = & \sum_{k_1, k_2, N_1, N_2} A_{k_1}(\gamma_1) A_{k_2}(\gamma_2) \cdot \frac{Y_{k_1}^{N_1*}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2)}{\sqrt{(2k_1 + 1)(2k_2 + 1)}} \\ & \cdot \sum_{m_1, m_2} (-1)^{2I+m_1+m_2} \sqrt{(2k_1 + 1)(2k_2 + 1)} \cdot \begin{pmatrix} I & I & k_1 \\ m'_1 & -m_1 & N_1 \end{pmatrix} \begin{pmatrix} I & I & k_2 \\ m'_2 & -m_2 & N_2 \end{pmatrix} \\ & \cdot \sum_{a,b} p_a(bm_2m'_2|M_q)(N_q|am_1m'_1) \end{aligned} \quad (\text{A.2})$$

Equation A.1 makes the calculation of the angular correlation much easier and faster for all time points since the vectors $A_q(\theta)$ and $(-\lambda_q + i\omega_q)$ only need to be calculated once.

The main public functions of `PFraction` are:

```
void setAkk(double a22, double a24, double a42, double a44);
```

Set the anisotropy coefficients A_{22} , A_{24} , A_{42} and A_{44} .

```
void addState(int interactionType);
```

Add a new state to this fraction with `interactionType = 0` (electric quadrupole interaction) / `1` (magnetic interaction) / `2` (combined interaction). It creates a new `PState` object with the given interaction and adds it to the vector of `PFraction` containing all the `PState` objects.

```
void setStateVars(int stateIndex, double theInitialProbOfState, double w0, double wb,...);
```

Sets the initial probability of the `PState` object in vector index `stateIndex` and calls the function `operator()` of that state with the correspondent variables.

```
void setTransitionRate(int initialState, int finalState, double rate);
```

Sets the transition rate `rate` (in MHz) from state in index `initialState` to state in index `finalState`.

```
void calcAngularCorrelationAmplitudes();
```

Creates the Blume matrix using the Hamiltonians from all its states and transition rates between them, finds its eigenvalues and eigenvectors and then calculates the amplitudes $A_q(180^\circ)$ and $A_q(90^\circ)$ from equation A.2

```
std::complex<double> W180(double time, double resolFWHM);
```

Calculates and returns the value of $W(180^\circ, t)$ at the time point `time` and considering a time resolution FWHM of `resolFWHM`.

```
std::complex<double> W90(double time, double resolFWHM);
```

Calculates and returns the value of $W(90^\circ, t)$ at the time point `time` and considering a time resolution FWHM of `resolFWHM`.

PSetup

Each object of `PSetup` manages everything related to a single parameters file, including the experimental data to be fitted and the model used to simulate/fit the data.

```
void setCalibration(double calibration, double fwhm, int channelMax);
```

Sets the calibration (in nanoseconds) used to calculate the $R(t)$, sets the FWHM for the prompt and sets `channelMax` as the number of points of $R(t)$ to be calculated.

```
void setDataFiles(std::string &inFile, std::string &outFile);
```

Sets `inFile` as the file with experimental data to be fitted and `outFile` as the file with the fitted data (or simulated data).


```
void setParametersFileName(std::string &parFile);
```

Sets the name of the parameters file to be read and used as input.

```
void setFitRange(int initialChFit, int finalChFit);
```

Sets the fit range to be between the data point at index `initialChFit` and the data point at index `finalChFit`.

```
void setSpin(double spin);
```

Sets the spin of the nuclear level under consideration.

```
void addFraction(int transitionType, int crystalType);
```

Adds a new fraction (which is an object of `PFraction`) considering static (`transitionType=0`) or dynamic (`transitionType=1`) transitions in a single crystal (`crystalType=0`) or polycrystal (`crystalType=1`).

```
void addStateToFraction(int fractionIndex, int interactionType);
```

Adds a new state to fraction at index `fractionIndex` considering electric quadrupole interaction (`interactionType=0`), magnetic interaction (`interactionType=1`) or combined interaction (`interactionType=2`).

```
void setRtConstants(double multConstant, double addConstant, double slope);
```

Sets the multiplicative constant (`multConstant`), additive constant (`addConstant`) and slope (`slope`) to be used when calculating the perturbation function $R(t)$.

```
void setFractionValue(int fractionIndex, double fractionValue);
```

Sets the value of the fraction at index `fractionIndex` to be `fractionValue`. Later on, the routine checks if the sum of all fractions is equal to 1.

```
void calcPerturbationFunction();
```

Calculates everything that is needed to get the perturbation function $R(t)$.

```
double calcRt(double time);
```

Returns the value of the perturbation function $R(t)$ at instant `time` (in nanoseconds).

```
double chi2();
```

Returns the value of the χ^2 -function for the current set of parameters (it is called by `PMinimizer`, which is explained below).

PMinimizer

```
void fit(double tolerance, unsigned int maxCalls, int printLevel);
```

Calls the minimization routine which terminates either when the function has been called (approximately) `maxCalls` times, or when the estimated vertical distance to minimum (EDM) is less than $0.002 * \text{tolerance} / N$, where N is the number of data points. `fit()` can be called without any argument, hence running with default values. The default value of `tolerance` is 0.1. `printLevel` is an integer that should be 0 if the user wants less information to be printed during the fit or bigger (such as 3) if the user wants more information. The default value is 0.

PFFT

Class responsible for the calculation of the Fourier Transforms.

```
void setData(std::vector<double> &data);
```

Sets the vector with the data whose Fourier Transform must be calculated.

```
void calcFFT(double calibration, int mirrorType, int removeAverage,  
             double alphaKaiseBessel);
```

Calculates the Fourier Transform, where `calibration` is the time scale between two data points, `mirrorType` sets the mirroring option for even (0), odd(1) or not at all (2), `removeAverage` removes (1) or not (2) the average of the data points and `alphaKaiserBessel` is the value of α for the Kaiser-Bessel function used as window.

```
double amplitude(int i);
```

Returns the amplitude for point `i`.

```
double real(int i);
```

Returns the real component for point `i`.

```
double imag(int i);
```

Returns the imaginary component amplitude for point `i`.

```
double frequency(int i);
```

Returns the value of frequency for point `i`.

PLib

Library of mathematical functions needed along the calculations.

```
int factorial(int n);
```

Calculates the factorial $n!$

```
std::complex<double> legendrePolynom(int k, double x);
```

Calculates the Legendre Polynomial: $P_k(x)$

```
std::complex<double> sph(int l, int m, double theta, double phi);
```

Calculates the spherical harmonic $Y_l^m(\theta, \phi)$

```
double wigner_3j(int j1, int j2, int j3, int m1, int m2, int m3);
```

Calculates the Wigner 3j-symbol $\begin{pmatrix} j1 & j2 & j3 \\ m1 & m2 & m3 \end{pmatrix}$

```
void diagonalizeMatrix(std::complex<double> * matrix, std::complex<double>
    * eigValues, std::complex<double> * rightEigVectors,
    std::complex<double> * leftEigVectors, int NDIM);
```

Diagonalizes `matrix` with dimensions $\text{NDIM} \times \text{NDIM}$, returning the eigenvalues in the vector `eigValues`, as well as the right and left eigenvectors in `rightEigVectors` and `leftEigVectors`, respectively.

PMaster

Here are contained the functions that call the simulation or the fitting routines depending on the user input, the functions that handle the data reading and data writing to and from external files – including the parameters files, the experimental data files and the simulated/fitted data files – and the functions responsible for plotting the data.

PInterface

Routine responsible for reading the user inputs when the program is called and pass the appropriate options to PMaster. It also displays the program header when it starts and all the help menus when needed.

A.4 External Libraries

The external libraries being used in the program are:

CLAPACK: a linear algebra library which is used to diagonalize the Blume matrix and calculate its eigenvalues and eigenvectors. In specific, the function `zgeev()` is used to calculate the eigenvalues and the right eigenvectors. Although this function can also calculate the left eigenvectors, they are not guaranteed to be orthonormal to the right eigenvectors, so a matrix with the right eigenvectors as columns is inverted, first by computing a LU factorization using the function `zgetrf()` and then by inverting the result using `zgetri()`. The computed matrix will then contain the orthonormal left eigenvectors as its rows.

GSL: used to calculate the Legendre polynomials using the function `gsl_sf_legendre_Plm()`, the spherical harmonics using the function `gsl_sf_legendre_sphPlm()` and the 3-j symbols using `gsl_sf_coupling_3j()`.

Minuit2: a library developed by CERN which is used for the minimization of the χ^2 -function (details explained in section 3.6.1).

Gnuplot: used to create and display the plots of the perturbation function $R(t)$ and correspondent Fourier transform, as well as export them to png files.

APPENDIX B

Publication's Inside Back Cover

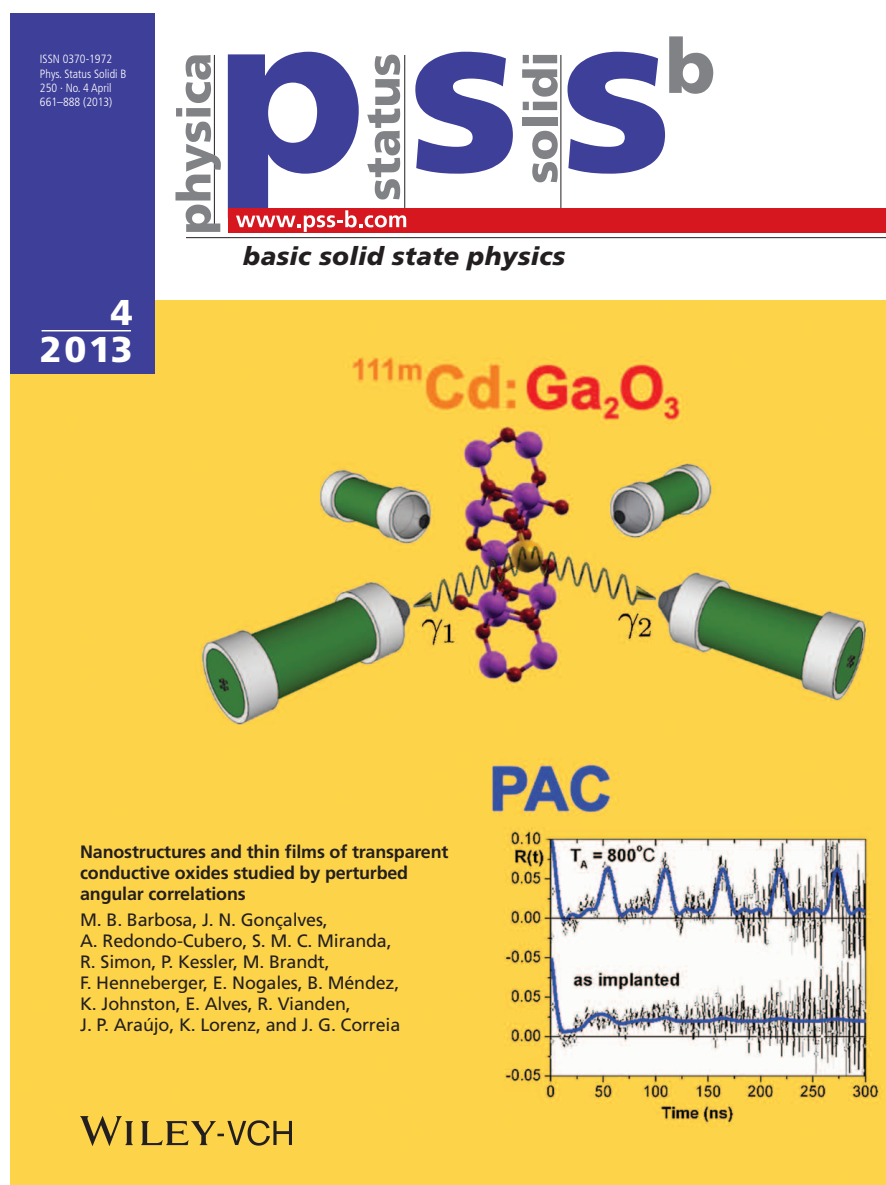


Figure B.1 – M. B. Barbosa *et al.*, "Inside Back Cover: Nanostructures and thin films of transparent conductive oxides studied by perturbed angular correlations (Phys. Status Solidi B 4/2013)", *Phys. Status Solidi B* 250, No. 4 (2013)

